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Part I: Mass spectrometry of organic azides and

diazocompounds. Part II: Transformations of

α-organosilyldiazoacetates. Part III: Solvolysis

of 2-ferrocenylcyclopropylcarbinyl esters

by

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PART I: MASS SPECTROMETRY OF

ORGANIC AZIDES AND DIAZOCOMPOUNDS

HISTORICAL

Mass Spectrometry of Diazocompounds

Mass spectrometry has been used to investigate many classes of organic

compounds. Diazocompounds constitute a class of compounds of synthetic and

mechanistic importance but, until recently, the mass spectral behavior of

these compounds received but little attention.

The first report (1), which appeared in 1963, discussed the mass spec-

tra of four simple compounds: diazoacetone, diazoacetophenone, monochloro-

diazoacetone and trichlorodiazoacetone. The fragmentation patterns of the

compounds were not discussed in any detail nor was any metastable ion data

presented. However it was shown that all four compounds exhibited a molec-

ular ion and that diazoacetone and diazoacetophenone showed ions corres-

ponding to their respective carbene structures.

The authors felt that the appearance of the latter ions was due to a

primary ionization process of the neutral carbene moieties formed by ther-

mal decomposition of the more thermally unstable diazoacetone and diazo-

acetophenone in the inlet system of their instrument rather than from frag-

mentation of the molecular ions since the appearance potentials of those

ions were a mean 0.6 eV higher than for the corresponding molecular ions.

The authors acknowledged the possibility that loss of nitrogen from

the molecular ions could also have occurred and that the absence of the

corresponding ions in the spectra of mono- and trichlorodiazoacetone could

have been due to rapid depletion of the ions by subsequent fragmentation.

Alternatively, owing to the inductive effect of the halogen substituents,

the consequent variation of the charge distribution on the molecular ions

could be of such an amount as to leave, after fragmentation, the charge on the nitrogen. In support of the latter argument they pointed out that the halogen substitution caused a decrease in the relative abundances of ions corresponding to CR_3CO^+ and an increase in the relative abundances of ions corresponding to $COCHN_2^+$. Additionally it must be pointed out that an ion corresponding to the carbene dimer was observed in the spectrum of diazoacetone, further substantiating their argument of thermal decomposition.

Based on appearance potential data the authors felt that the $M^{+\cdot}-28$ ions observed in the spectra of diazoacetone and diazoacetophenone would not have the ketene structure formed by a Wolff rearrangement since the appearance potentials of the respective ketenes should be lower than observed for the ions in question. The appearance potential of the $M^{+\cdot}-28$ ion for diazoacetone and diazoacetophenone were determined to be 9.86 ± 0.03 and 10.08 ± 0.11 eV respectively, whereas the literature value for the appearance potential of ketene is 9.4 eV (2) and alkyl substitution should lower the value (3). However, in all spectra but that of trichlorodiazoacetone an ion corresponding to loss of nitrogen and carbon monoxide from the molecular ion appeared indicating rearrangement had occurred at some point.

In 1969 Kinson and Trost (4) reported the mass spectra of 10-diazo-9-ketophenanthrene 1 and 10-diazo-9-keto-4,5-methylenephenanthrene 2.
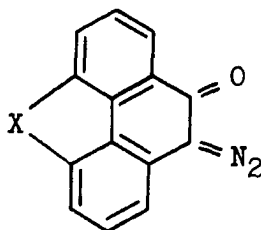
1 X = H, H
2 X = CH_2

The base peak in the spectra of both compounds resulted from the loss of 56 mass units from the molecular ion. This loss was interpreted to be the loss of nitrogen followed by the loss of carbon monoxide.

Other important ions in these spectra were the $M^{\ddagger}$-28 ions. The relative abundance of the $M^{\ddagger}$-28 ion in the spectrum of $\underline{1}$ was 21.5% and the relative abundance of the corresponding ion in the spectrum of $\underline{2}$ was 87.9%. The structures of the ions were of particular interest as to whether the Wolff rearrangement occurred under electron impact. To investigate the structures of the ions further, the corresponding ketene ion molecules were generated independently from the esters $\underline{3}$ and $\underline{4}$.

$$\underline{3} \quad X = H, H$$
$$\underline{4} \quad X = CH_2$$
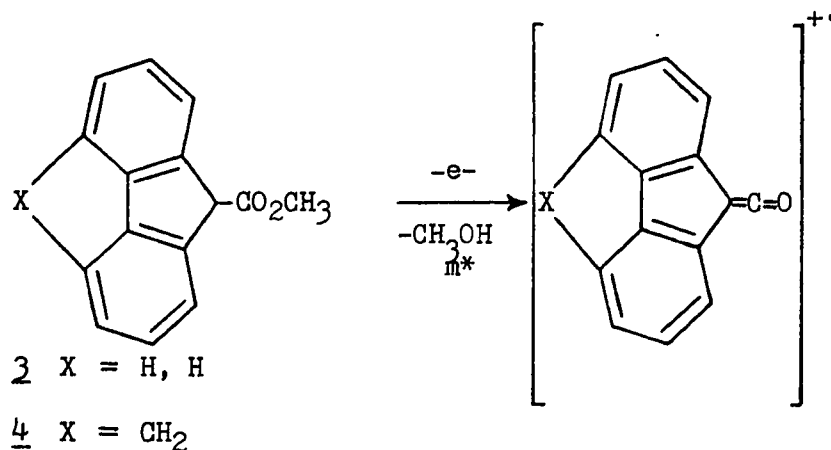
The ketene ions generated from the esters and the corresponding ions in the spectra of $\underline{1}$ and $\underline{2}$ all exhibit metastable ions for the subsequent loss of carbon monoxide. It has been shown (5) that metastable ion characteristics serve as a fingerprint for ions of identical structure and energy. Comparison of the appropriate metastable ion pairs strongly indicated that the ions derived from the diazoketones have the same structure as the corresponding ions derived from the esters. Furthermore, the

relative abundances of the metastable ions for the loss of nitrogen from the molecular ions of 1 and 2 suggest that the loss of nitrogen and rearrangement to ketenes is concerted under electron impact conditions (6).

DeJongh, Van Fossen, Dusold and Cava (7) have reported the mass spectra of eleven cyclic diazoketones 5-14.
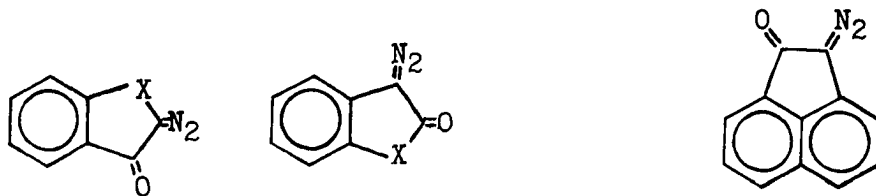
5	X	=	C=O		10	X	=	NH
6	X	=	CHPh		11	X	=	S
7	X	=	CH$_2$		12	X	=	SO$_2$
8	X	=	CHCH$_3$		13	X	=	CPh$_2$
9	X	=	CPh$_2$					
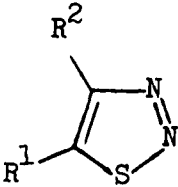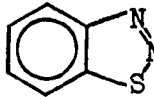
High resolution mass measurements showed that the initial fragmentation in the spectra was due solely to a metastable loss of nitrogen resulting in a ketocarbene or a rearranged ketoketene ion. This ion suffered, in most cases, loss of carbon monoxide, also usually in a metastable process. The low energy spectrum (about 13 eV) of 12 did not show any M^+-N_2 ion although the ion M^+-56 persisted. The authors concluded that both nitrogen and carbon monoxide could be simultaneously lost, in part, although no metastable peaks were present.

Zeller, Meier and Müller (8) reported the mass spectra of some alkyl-, aryl-, acyl- and aroyl-substituted 1,2,3-thiadiazoles 15 and of

	R^1	R^2
15a	CH_3	H
15b	CH_3	COOH
15c	CH_3	$COOC_2H_5$
15d	CH_3	$COCH_3$
15e	CH_3	COPh
15f	Ph	$COCH_3$
15g	Ph	Ph
15h	H	Ph

15

16

benzothiadiazole 16. Initial elimination of nitrogen occurred from the molecular ion. Some of the subsequent fragmentation processes demanded a rearrangement of the $M\cdot^+$-N_2 ion to a thioketenion-radical structure. Losses of S and ·SH were also observed to occur from the unrearranged $M\cdot^+$-N_2 ion.

In 1971 the same authors reported the mass spectra of some 2-diazo carbonyl compounds (9). The mass spectra of the diacyl diazomethanes 17-19 exhibited metastable losses of nitrogen followed by metastable losses of carbon monoxide indicating the occurrences of electron impact induced Wolff rearrangements.

$$R^1\text{-C-C-C-}R^2$$

17 $R^1 = CH_3$, $R^2 = CH_3$

18 $R^1 = CH_3$ $R^2 = Ph$

19 $R^1 = Ph$, $R^2 = Ph$
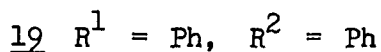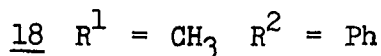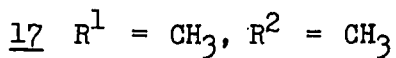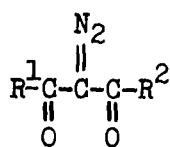
Since in 18 R^1 is not the same as R^2, the rearrangement following loss of nitrogen could proceed to produce two different ketoketenion-radical

structures. To measure the migration aptitudes of the methyl versus the phenyl group under electron impact [2-^{13}C]-2,4-dioxo-3-diazo-4-phenyl-butane $\underline{20}$ was synthesized. Mass spectral examination of the loss of ^{12}CO and ^{13}CO from $\underline{20}$ at electron energies between 12 and 70 eV indicated equal production of ^{12}CO and ^{13}CO and thus an equal migration aptitude for the methyl and phenyl groups.
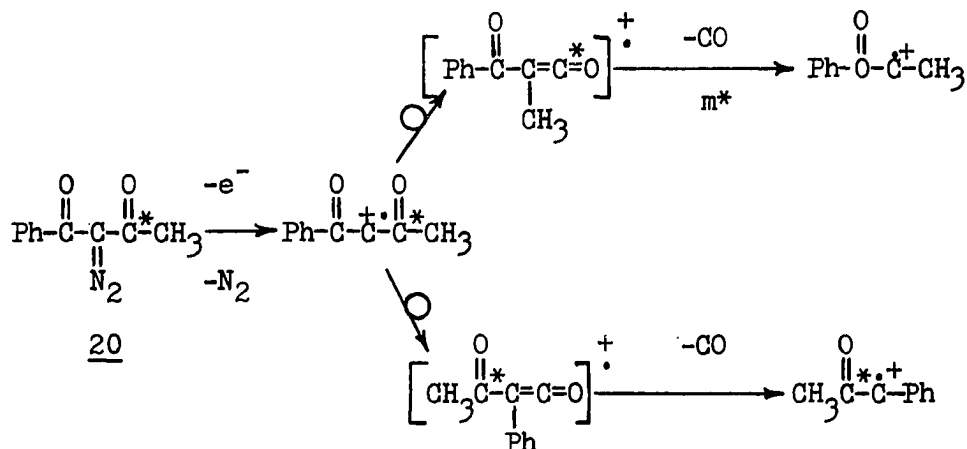
It is interesting to note here that in the photolysis of $\underline{18}$ the methyl group migrates (10) and in the thermolysis of $\underline{18}$ the phenyl group migrates (11).

In the mass spectrum of 5-methyl-4-benzoyl-1,2,3-thiadiazol $\underline{15}$, ($R^1 = CH_3$, $R^2 = COPh$) the $M^{\ddagger}$-N_2 ion could have similar rearrangement options as the $M^{\ddagger}$-N_2 ion of $\underline{20}$. In fact, however, only the phenyl group was found to migrate and hence only CO and no CS was lost from the $M^{\ddagger}$-N_2 ion (8).
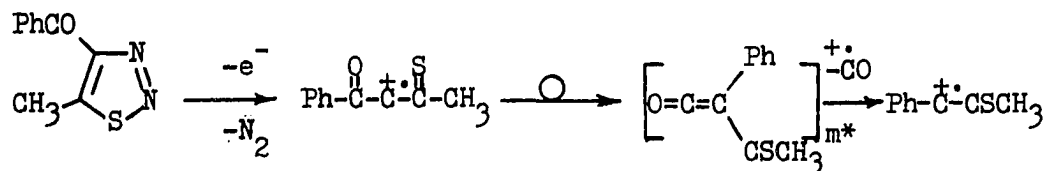
High resolution spectra of the ethyl esters of acetyl and benzoyl diazoacetic acid 21, 22 revealed that carbon monoxide was eliminated only after the ester function of the $M^+ \cdot - N_2$ ion underwent a McLafferty rearrangement to eliminate ethylene (9). Though it was not possible to distinguish between several different possible fragmentation paths for the subsequent elimination of carbon monoxide from the $M^+ \cdot - N_2 - C_2H_4$ ions, it was necessary that some rearrangement occur.

$$RCO-\underset{\underset{N_2}{\overset{\|}{C}}}{}-CO_2C_2H_5 \xrightarrow[-e^-, -N_2]{m^*} RCO-\overset{+\cdot}{C}-CO_2C_2H_5 \xrightarrow{O} \left[O=C=C \overset{R}{\underset{CO_2C_2H_5}{}} \right]^{+\cdot}$$

21 R = CH_3

22 R = Ph

$$m^* \downarrow -C_2H_4 \qquad m^* \downarrow -C_2H_4$$

$$\left[RCO-\underset{\underset{OH}{|}}{C}=C=O \right]^{+\cdot} \xleftarrow{O} RCO-\overset{+\cdot}{C}-CO_2H \xrightarrow{O} \left[O=C=C \overset{R}{\underset{CO_2H}{}} \right]^{+\cdot}$$

$$m^* \downarrow -CO \qquad\qquad\qquad\qquad\qquad m^* \downarrow -CO$$

$$RCO-\overset{+\cdot}{C}-OH \qquad\qquad\qquad\qquad R-\overset{+\cdot}{C}-CO_2H$$
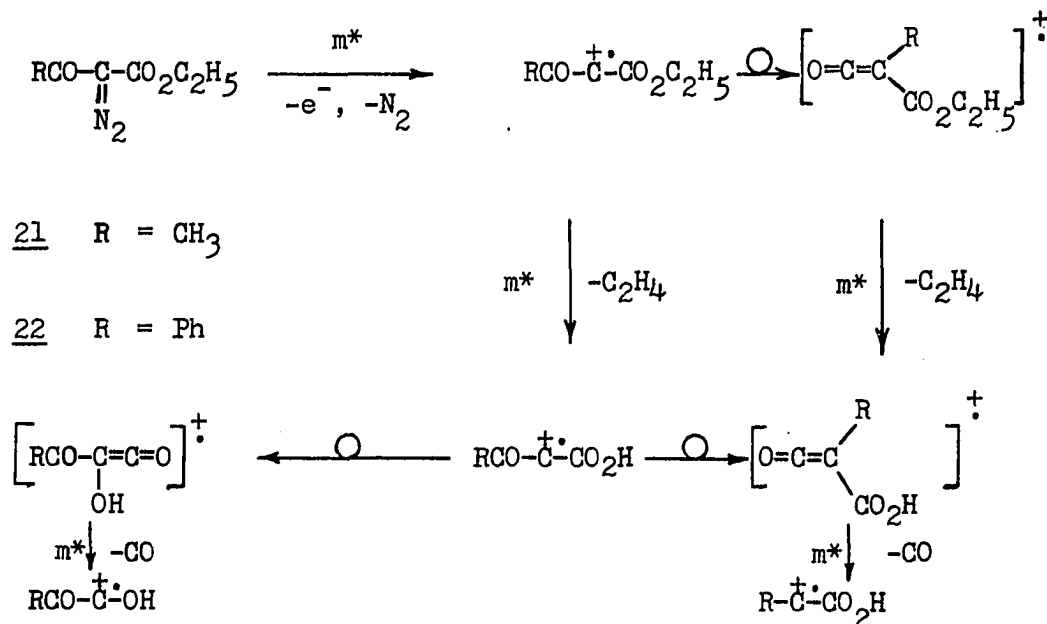
Since no rearrangement of the ethoxy group had been observed for 21 and 22, the question of whether it could occur under electron impact arose. Consequently the spectrum of dimethyl diazomalonate was obtained which showed no evidence for methoxy migration by the absence of the loss of carbon monoxide from the $M^+ \cdot - N_2$ ion.

In contrast to the absence of a Wolff rearrangement in the mass spectrum of dimethyl diazomalonate, the photolysis reaction (12) did, in part, proceed through a Wolff rearrangement to the corresponding ketene with

migration of a methoxy group by way of an oxirene intermediate.

Similarly the photolysis of [carbonyl-^{13}C]azilbenzil $\underline{23}$ proceeded with the formation of an oxirene intermediate, but the thermal and electron induced Wolff (13) rearrangement occurred without migration of the label and thus without the intermediacy of an oxirene or oxirenion-radical.
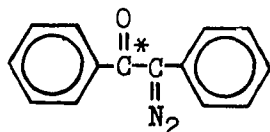
$\underline{23}$

Zeller, Meier and Müller (14) have also investigated the photochemically, thermally and electron impact induced Wolff rearrangements of some aroyl-acyl-diazomethanes $\underline{18}$, $\underline{24}$-$\underline{26}$.
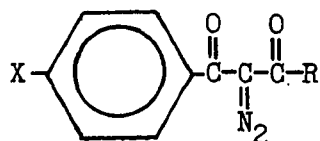
$\underline{24}$ X = H, R = H

$\underline{25}$ X = OCH$_3$, R = CH$_3$

$\underline{26}$ X = NO$_2$, R = CH$_3$

The thermal reactions proceeded with the following order in migration ability:

The photochemical reactions proceeded with the following migration aptitudes:
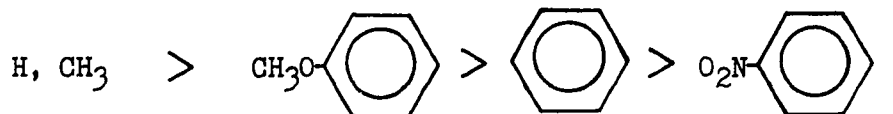
The order of the aryl groups remained the same in both cases indicating a stronger sensitivity to the aryl groups in the rearrangement. A previous

examination (9) of the spectrum of ^{13}C-labelled 20 indicated no preference in migration aptitude for the methyl or phenyl group in the electron impact induced Wolff rearrangement by contrast. To broaden the scope of the latter comparison, 24 was prepared with ^{18}O-labeling at the formyl carbon. The mass spectrum of the labelled compound likewise revealed no difference in migration aptitude of hydrogen or phenyl group (14).

The combined result of the two investigations, then, was to indicate no migration preference between methyl, phenyl or hydrogen in the electron impact induced Wolff rearrangements of these diazocompounds. The authors felt that the lack of preference for migration was due to the higher electron-deficiency present at the reactive center of the electron impact induced ketocarbenion-radical.

Mass Spectrometry of Organic Azides

The electron impact decompositions of three triarylmethyl azides 27-29 have been reported (15) to proceed with loss of •N$_3$ from the molecular ion to produce the base peak in the spectra which would correspond to the respective triarylmethyl carbonium ions. This process was in marked contrast to the paths of photolytic (16) and pyrolytic (17) decomposition in which the primary process was loss of molecular nitrogen and migration of an aryl group to yield the corresponding Schiff's bases.
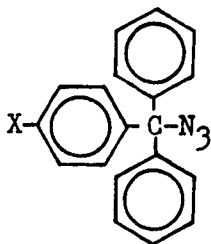
27 X = CH$_3$

28 X = Cl

29 X = NO$_2$

$M^+.-28$ ions were observed in the spectra which varied in intensity from 1 to 10% of the base peak and which were confirmed by high resolution mass measurements to be due to loss of nitrogen. Because lowering the ionizing voltage caused little change in the intensity of the $M^+.-N_2$ ion, it was thought that the ion was produced by primary ionization of the species produced by thermal loss of molecular nitrogen from the azides.

Whatever the source of the $M^+.-N_2$ ions, there were two different, but indistinguishable, structures possible: the positively charged nitrenes, $(Ar)_3C-\overset{+.}{N}$, or the rearranged arylimino positive ions, $(Ar)_2C \overset{+.}{N}-Ar$. There were two sets of fragmentation ions observed; one from the $M^+-N_3\cdot$ ions, and one from the $M^+.-N_2$ ions.

Since the $M^+-N_3\cdot$ ions appeared to be so highly stable and to be the determinative factor in the spectra, the spectrum of azidodiphenylacetic acid $\underline{30}$ was obtained in order to obtain data on the effect of having a less stable $M^+-N_3\cdot$ ion. The spectrum of $\underline{30}$ had as the base peak an ion corresponding to $M^+.-N_2-CO$ by contrast, a result in conformity with the mode of decomposition observed in the solution photolysis of $\underline{30}$ (18).

$$N_3-\underset{|}{\overset{|}{C}}-CO_2H$$

$$\underline{30}$$
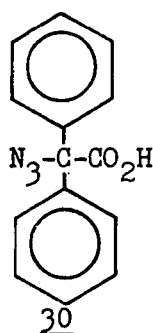
Crow and Wentrup (19) reported the mass spectrum of phenyl azide which exhibited a molecular ion and had as the base peak the $M^+.-N_2$ ion. The

$M^{+}\cdot$-N_2 ion subsequently lost, in a metastable process, hydrogen cyanide followed by the metastable loss of hydrogen.

Kingston and Henion (20) examined the mass spectrum of 2,4,6-d_3-phenyl azide and determined that the loss of HCN and C_2H_2 from the corresponding phenyl nitrenium cation radical was preceded by complete randomization of the hydrogen atoms.

Later Woodgate and Djerassi (21) examined the mass spectrum of phenyl azide-1-^{13}C and showed that randomization of C-1 occurred prior to expulsion of HCN. These data concerning phenyl azide support the processes illustrated in Scheme 1.
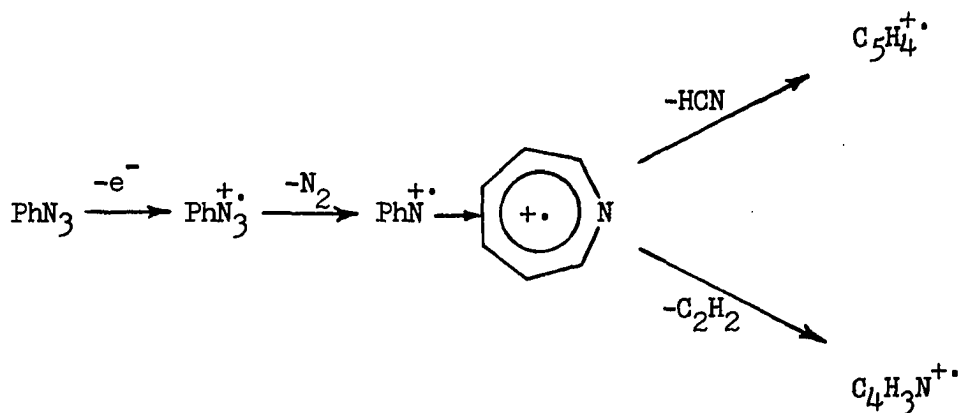
Scheme 1

Abramovitch, Kyba and Scriven (22) have reported the mass spectra of a number of mono- and disubstituted phenyl azides. It was found that for eight monosubstituted azides 31-38 the fragmentations observed could be adequately described by a pattern quite analogous to that of phenyl azide (Scheme 2).

$\underline{31}$ X = $\underline{o}$-Cl $\qquad$ $\underline{35}$ X = $\underline{p}$-NO$_2$

$\underline{32}$ X = $\underline{m}$-Cl $\qquad$ $\underline{36}$ X = $\underline{o}$-CN

$\underline{33}$ X = $\underline{p}$-Cl $\qquad$ $\underline{37}$ X = $\underline{m}$-CN

$\underline{34}$ X = $\underline{m}$-NO$_2$ $\qquad$ $\underline{38}$ X = $\underline{p}$-CN
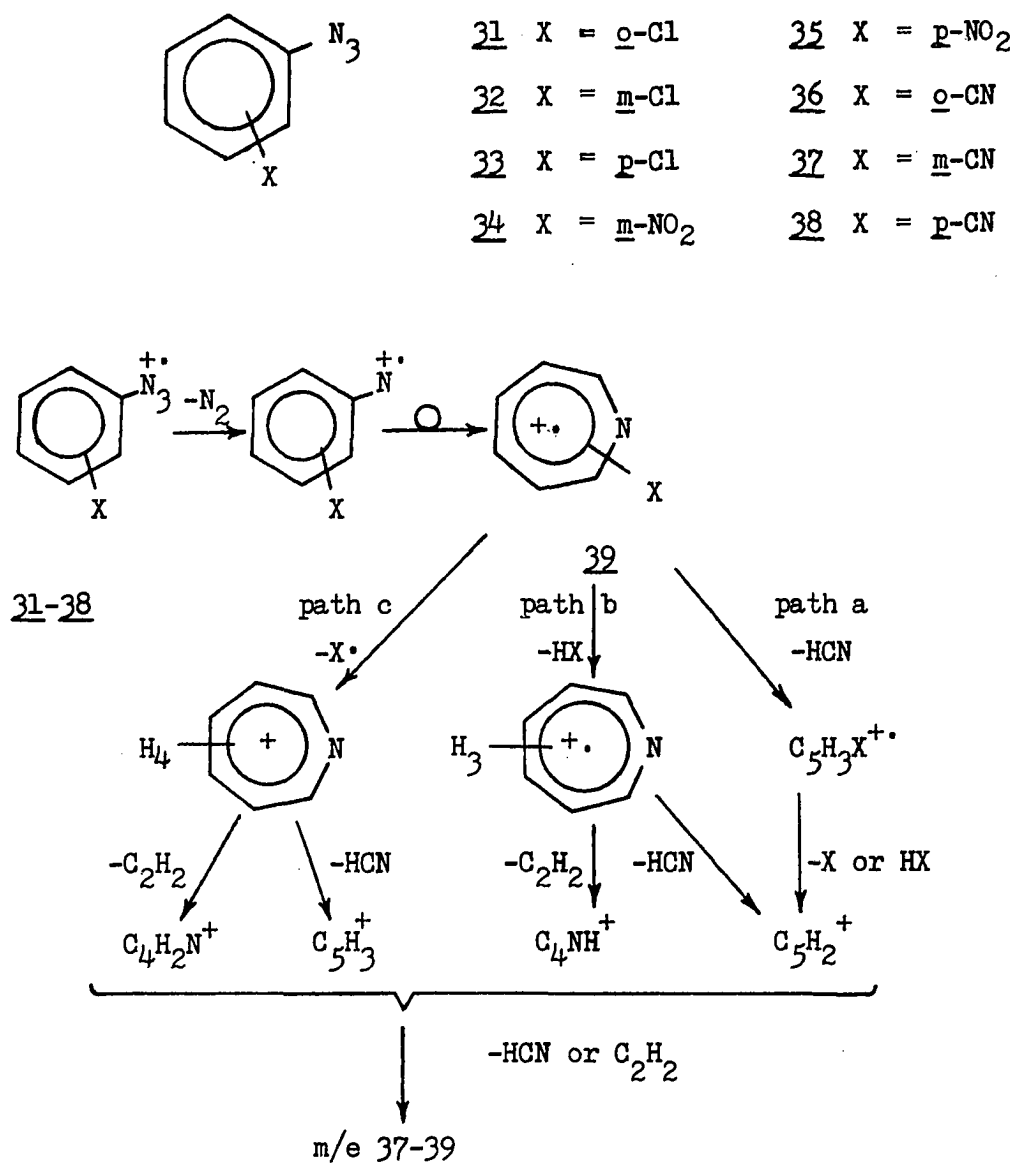
Scheme 2

Except for the chloro derivatives $\underline{31}$-$\underline{33}$, the loss of hydrogen cyanide from the substituted azepinium ion $\underline{39}$ was usually observed to be negligible (path a, Scheme 2). Path b (loss of HX) was followed predominantly by the cyano derivatives, $\underline{36}$-$\underline{38}$, path c (loss of ·X) mainly by the chloro- and $\underline{m}$-nitrophenyl azides, $\underline{31}$-$\underline{34}$, and an appreciable amount of path b was

was followed by p-nitrophenyl azide 35.

The mass spectra of the o-nitro-, the three methoxy-, the three phenyl- and the three methyl substituted phenyl azides were also obtained, but in each case exceptions to the fragmentation pattern shown in Scheme 2 were observed. The spectra of 2-azido-3-nitrotoluene and 4-azido-3-nitrotoluene were also presented.

Fraser, Paul and Bagley (23) also reported the mass spectra of some aromatic azides, some of which were reported previously (22). Spectra for the following eight azides were reported for the first time: 2,6-dimethylphenyl azide; 3-nitro-4-methylphenyl azide; 3-nitro-6-methylphenyl azide; o-, m-, and p-bromophenyl azide; benzoyl azide and p-nitrobenzoyl azide.

The bromophenyl azides provided the first examples of loss of the substituent from the molecular ion in a metastable process. However, a metastable loss of nitrogen from the molecular ion still produced the base peak.

Benzoyl azide 36 lost nitrogen but not carbon monoxide from the molecular ion. The authors concluded that rearrangement of the $M^{+\cdot}-N_2$ ion to the isocyanate ion was not occurring since the $M^{+\cdot}-N_2$ ion subsequently lost an oxygen radical, a nitrogen radical or carbon monoxide (Scheme 3).

$$Ph-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow{-e^-} Ph-\overset{O}{\overset{\|}{C}}-\overset{+\cdot}{N_3} \xrightarrow{-N_2} Ph-\overset{O}{\overset{\|}{C}}-\overset{+\cdot}{N}$$

$$\overset{O}{\overset{\|}{Ph-C+}} \xrightarrow{-CO} C_6H_5^+$$

$$\xrightarrow[\substack{-N\cdot \\ -O\cdot \\ m^*}]{} Ph-CN^+$$

$$\xrightarrow[\substack{-CO \\ m^*}]{} Ph-\overset{+\cdot}{N} \xrightarrow{-HCN} C_5H_4^{+\cdot}$$

36
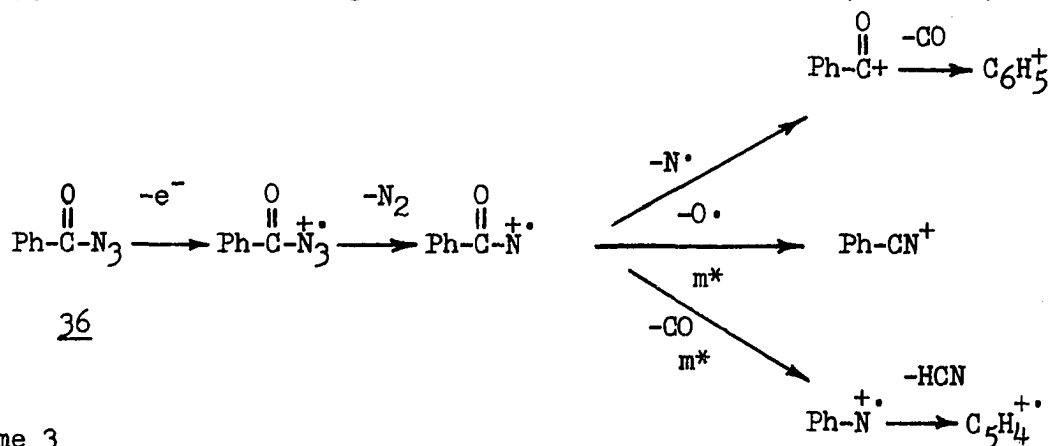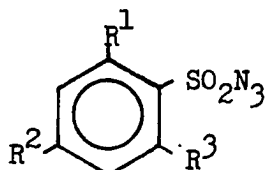
Scheme 3

However a rearrangement would be necessary in order for the loss of CO to occur from the nitrenium ion.

The spectrum of p-nitrobenzoyl azide was reported to be similar with loss of NO· from both the $M^{\ddagger}-N_2$ ion and M^+-N_2-N· ion in metastable processes.

Sulfonyl azides 37 - 41 have been reported to lose azide radical from the molecular ion upon electron impact (24) in marked contrast to the thermal and photochemical loss of molecular nitrogen for the compounds (25).

	R^1	R^2	R^3
37	H	H	H
38	H	CH_3	H
39	H	NO_2	H
40	CH_3	CH_3	CH_3
41	i-Pr	i-Pr	i-Pr

The loss of nitrogen under electron impact conditions was of minor importance (0-1%), instead the loss of N_3· was a dominant process except for 41. Metastable ions associated with the loss were observed for 37, 39 and 40. The authors noted the similarity of this loss with that of N_3· from the triarylmethyl azides (15) discussed above but did not attempt to account for the loss in their molecules. They noted that after losing N_3·, the ions produced fragmented as expected for sulphoxides and sulphonyl compounds.

RESULTS AND DISCUSSION

At the time that the following work was undertaken, there was only one mass spectral study of diazocompounds (1) reported in the literature and only two mass spectral studies of azides (18, 19) reported. Because of the lack of knowledge concerning the mass spectral behavior of these compounds and because of the current interest and synthetic usefulness of these compounds, it was decided to investigate their reactions under electron impact conditions. The initial interest was to do more than observe fragmentation patterns, hence para-substituted diazoacetophenones and substituted benzoyl azides were chosen for study because of their potential ability to rearrange concurrent with or subsequent to the elimination of molecular nitrogen and because they offered the possibility of observing substituent effects.

Mass Spectra of Para-substituted Diazoacetophenones

The mass spectra of seven para-substituted diazoacetophenones 42 - 48 were obtained and the 70 eV spectra are reproduced in Figures 1-6 for compounds 42 - 48 respectively.
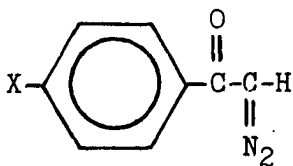
42   X = CH₃O
43   X = CH₃
44   X = H

45   X = Br
46   X = CN
47   X = Ph
48   X = NO₂

Figure 1. Mass spectrum p-methoxydiazoacetophenone 42 (top)

Figure 2. Mass spectrum p-methyldiazoacetophenone 43 (bottom)

R. I.

CH₃O—⟨benzene ring⟩—COCHN₂

42

50   100   150   200

R. I.

CH₃—⟨benzene ring⟩—COCHN₂

43

50   100   150   200

Figure 3. Mass spectrum diazoacetophenone 44 (top)

Figure 4. Mass spectrum p-bromodiazoacetophenone 45 (bottom)
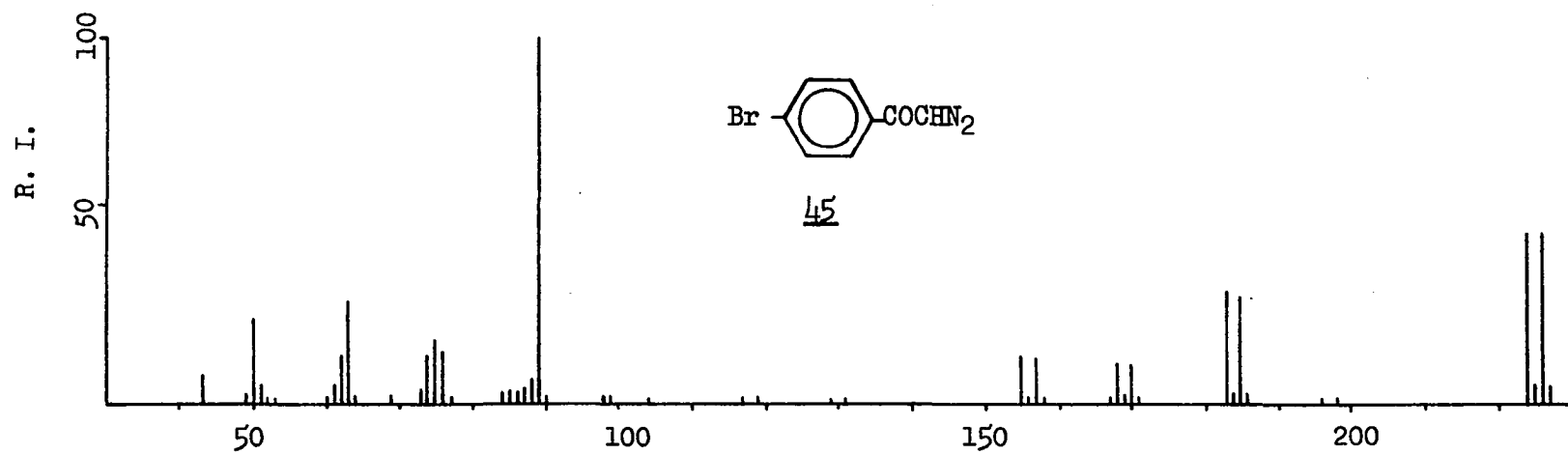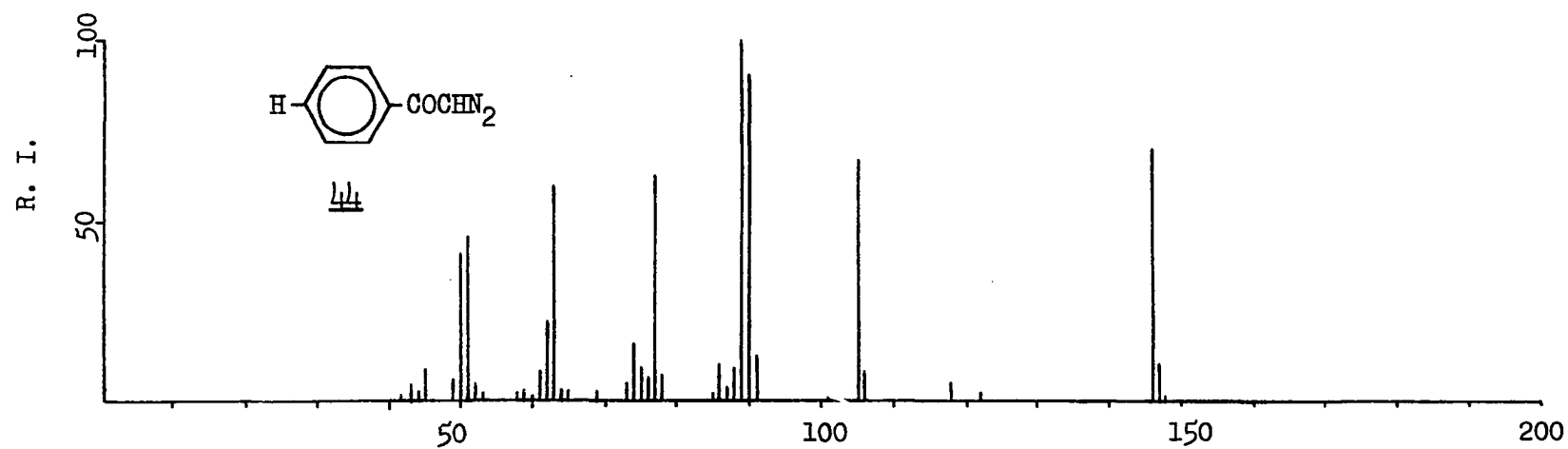
Figure 5. Mass spectrum p-cyanodiazoacetophenone 46 (top)

Figure 6. Mass spectrum p-phenyldiazoacetophenone 47 (bottom)

R. I.

100

50

CN—⬡—COCHN$_2$

46

imp

50 100 150 200

R. I.

100

50

Ph—⬡—COCHN$_2$

47

50 100 150 200
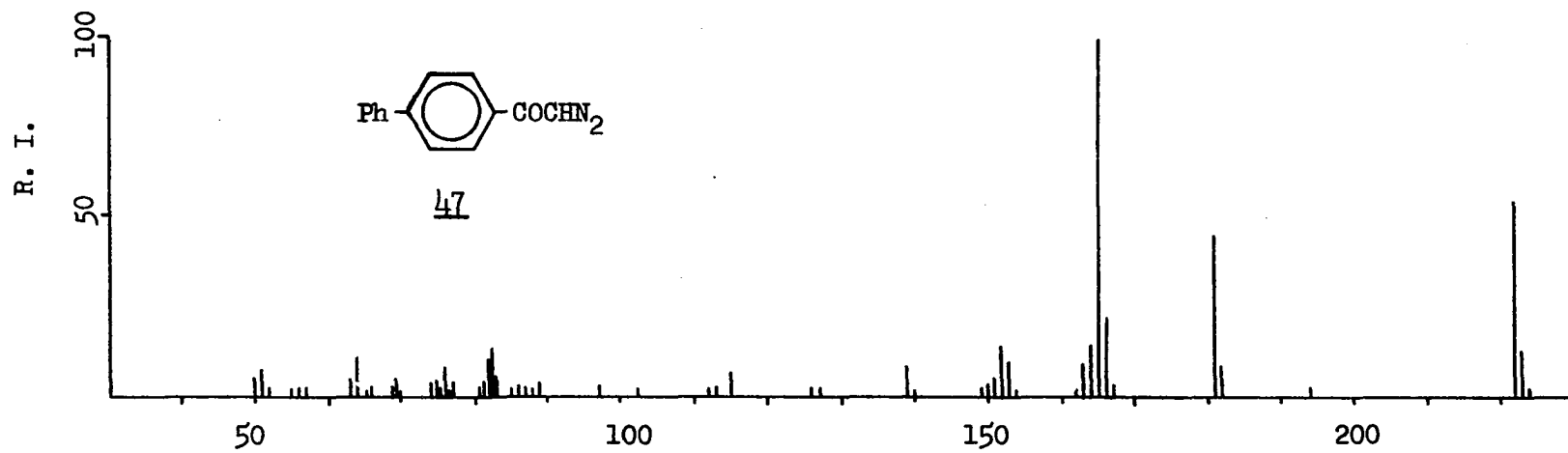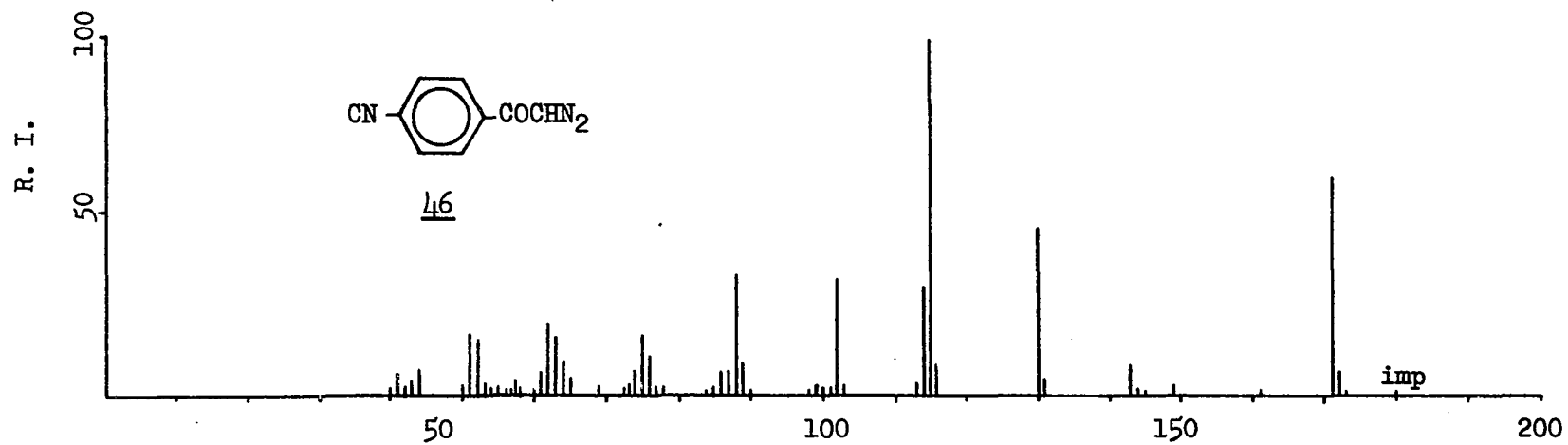
Compounds $\underline{37}$ - $\underline{42}$ exhibited a common fragmentation pattern which is illustrated in Scheme 4. The spectrum of $\underline{48}$, which differed markedly will be discussed separately.

Scheme 4 indicates a metastable loss of twenty-eight mass units from the molecular ion and a subsequent metastable loss of twenty-eight mass units from the M^+-28 ion $\underline{49}$ to yield ion $\underline{50}$ occurred generally. In analogy with the fragmentations observed for other diazoketones (4, 9, 13, 14) and in particular the high resolution mass measurements reported by DeJongh, Van Fossen, Dusold and Cava (7), the initial loss of twenty-eight mass units was elimination of nitrogen and the subsequent loss of twenty-eight mass units was elimination of carbon monoxide.
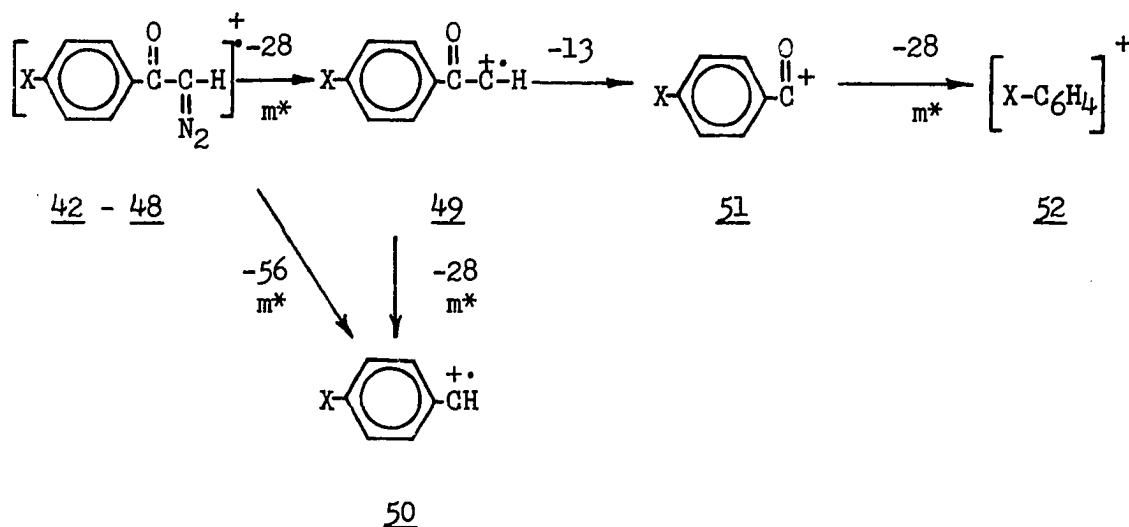
Scheme 4

$\underline{50}$ was also obtained through a metastable process directly from the molecular ion with a loss of 56 mass units. This result may mean that there are two processes occurring simultaneously: a concerted loss of nitrogen with carbon monoxide during rearrangement and a stepwise loss of

nitrogen followed by either loss of thirteen mass units to form ion 51 or

rearrangement and loss of carbon monoxide to form ion 50. There is also

the possibility that 49 does not lose CH· to form 51 but rearranges entire-

ly to a ketene like structure which eliminates carbon monoxide to yield 50.

If the latter process is occurring, then the observation of seemingly

both concerted and stepwise metastable processes leading to the same ion

50 may only reflect that both processes are occurring sequentially within

the field free region of the spectrometer and that the exact timing of the

processes within the flight tube determines which process is observed. The

observation of 51 could then reflect the direct loss of 41 mass units from

the molecular ion. However for 45 and 47 the loss of CH· from the 49 ion

is a metastable process.

The metastable loss of 56 mass units has not been reported before,

however the low energy spectra of 2-diazo-3-ketothianaphthane-1,1-dioxide

12 caused DeJongh, Van Fossen, Dusold and Cava (7) to suspect that concert-

ed loss of nitrogen and carbon monoxide was occurring as mentioned

previously.

In compounds 42-48, the loss of 28 mass units (probably carbon mon-

oxide) is observed from the arylonium ion 51 to give rise to ion 52. Ion

52 then undergoes further fragmentation, the exact nature of which depends

upon the nature of the para-substituent. The subsequent fragmentation of

ion 50 also follows distinctive lines depending upon the nature of the

para-substituent.

The large ion at m/e 133 (90%) in the spectrum of p-methoxydiazoace-

tophenone 42 corresponds to the loss of molecular nitrogen and methyl ra-

dical from the molecular ion. Such a fragmentation indicates that the

ion 44 does have existence at least in this case. The structure of the m/e
133 ion may be shown as the structure below which allows extensive delocal-
ization of the positive charge.
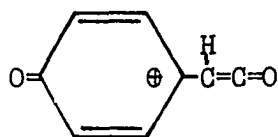
m/e 133

The presence of this ion suggests a non-mass spectral study in which the
following reaction of p-hydroxybenzoyl chloride with base might give rise
to an interesting conjugated ketene.
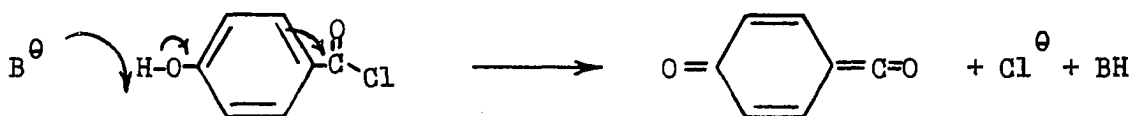
Similarly, a reaction might be observable with p-hydroxycinnamoyl chloride.
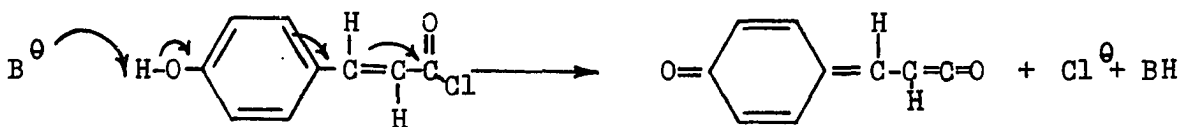
In the spectra of p-methyldiazoacetophenone 43 (Figure 3) and p-phenyl-
diazoacetophenone 47 (Figure 6) large ions were observed which correspond
to the loss of molecular nitrogen, carbon monoxide and hydrogen atom from
the molecular ions. The ions are base peaks in the 70 eV spectra of 39
and 42. Similar ions are frequently observed in mass spectra and could
correspond to apparently stable dehydrotopylium or substituted dehydro-
tropylium ion structures (26).

p-nitrodiazoacetophenone 38 exhibited an unusual spectrum (Scheme 5, Figure 7) compared to the fragmentation pattern found for 42 - 48 (Scheme 4).
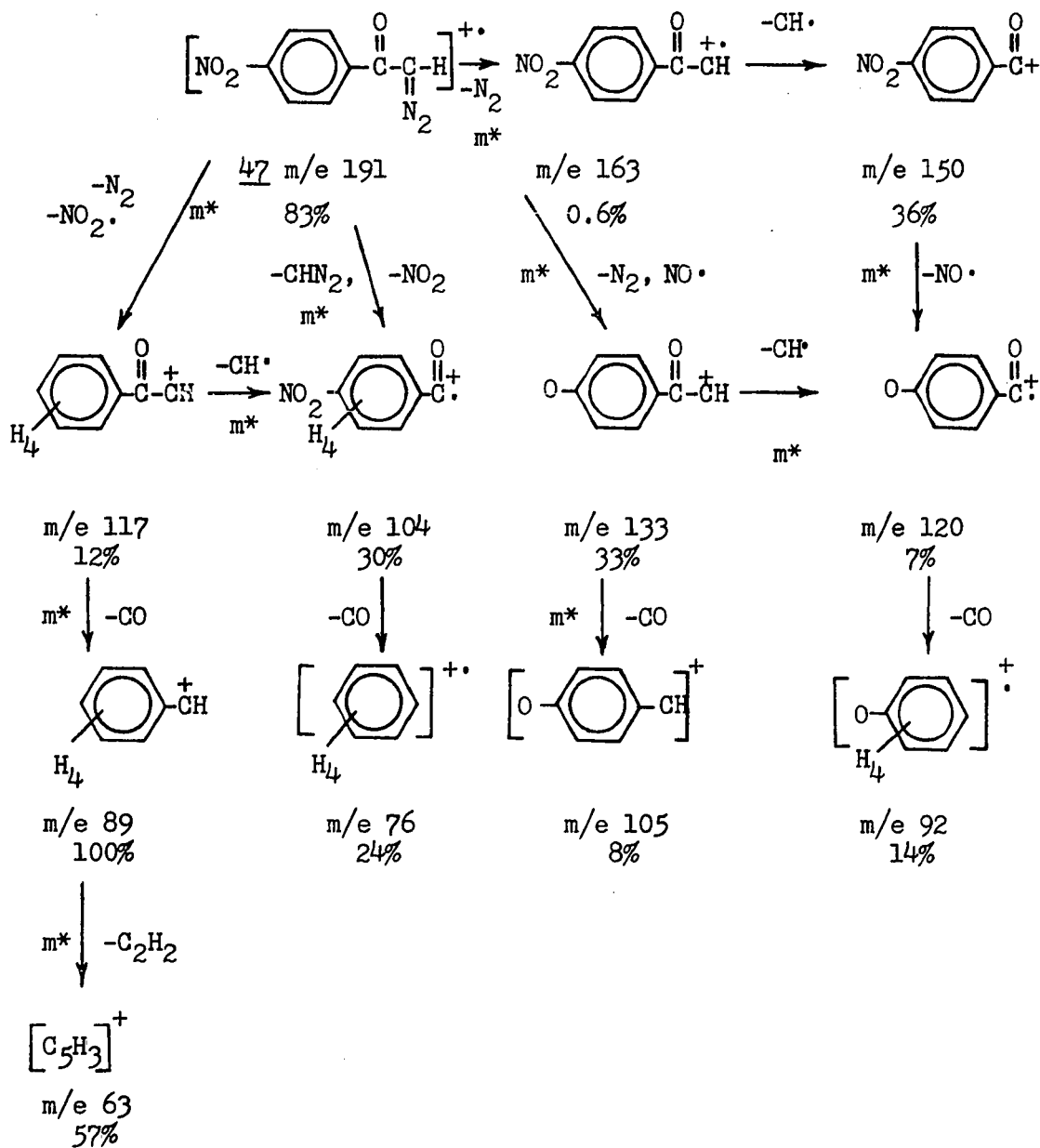
Scheme 5

Figure 7. Mass spectrum p-nitrodiazoacetophenone <u>48</u> (top)

Figure 8. Mass spectrum o-nitrodiazoacetophenone (bottom)

R. I.

NO₂ — ⬡ — COCHN₂

48

R. I.

⬡ — COCHN₂
NO₂
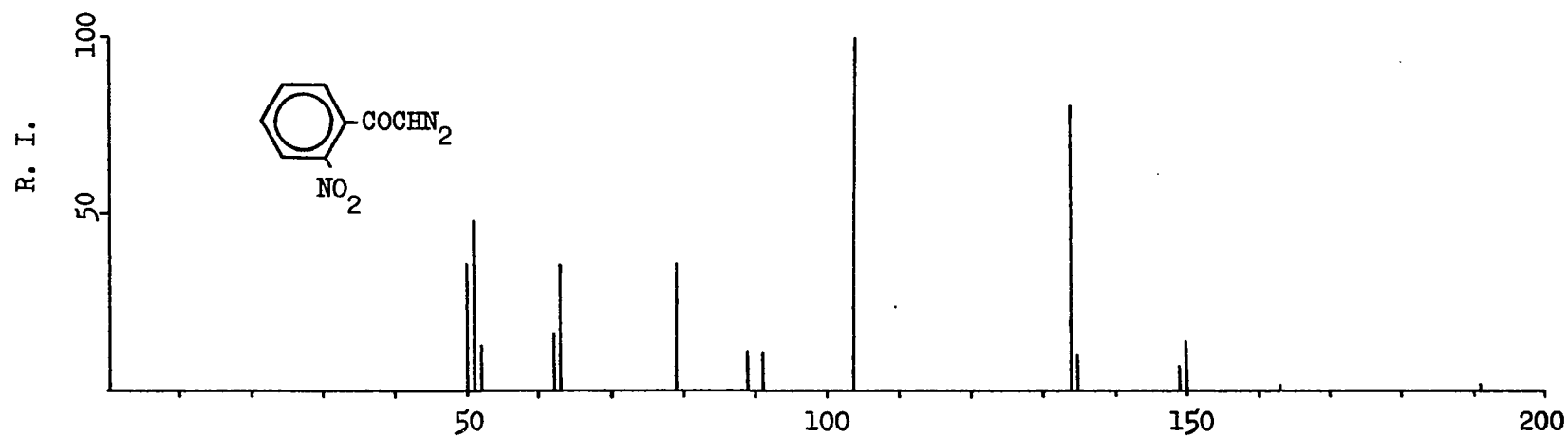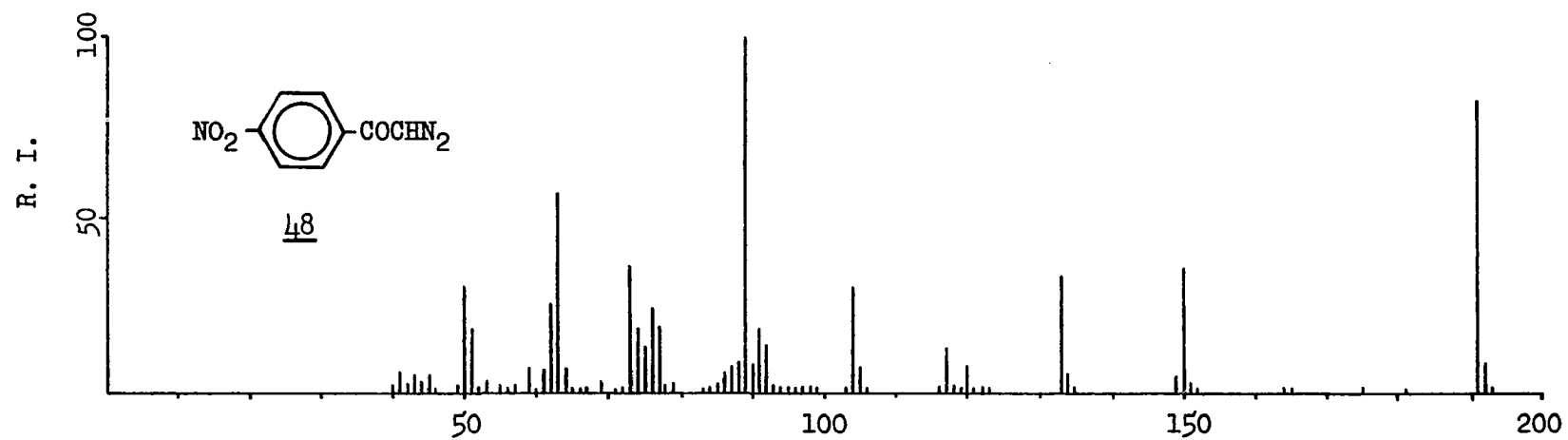
For **48** there was a metastable loss of 28 mass units from the molecular ion at m/e 191 to m/e 163, but there was no loss of 56 mass units, as observed for the other five compounds, either step-wise or concertedly. There were metastable losses of N_2 and NO_2 from the molecular ion to give m/e 117, of N_2 and NO from the molecular ion to give m/e 133, and of CH·, N_2 and NO_2 from the molecular ion to give the ion at m/e 104. The resulting ions above all subsequently suffered metastable losses of CO.

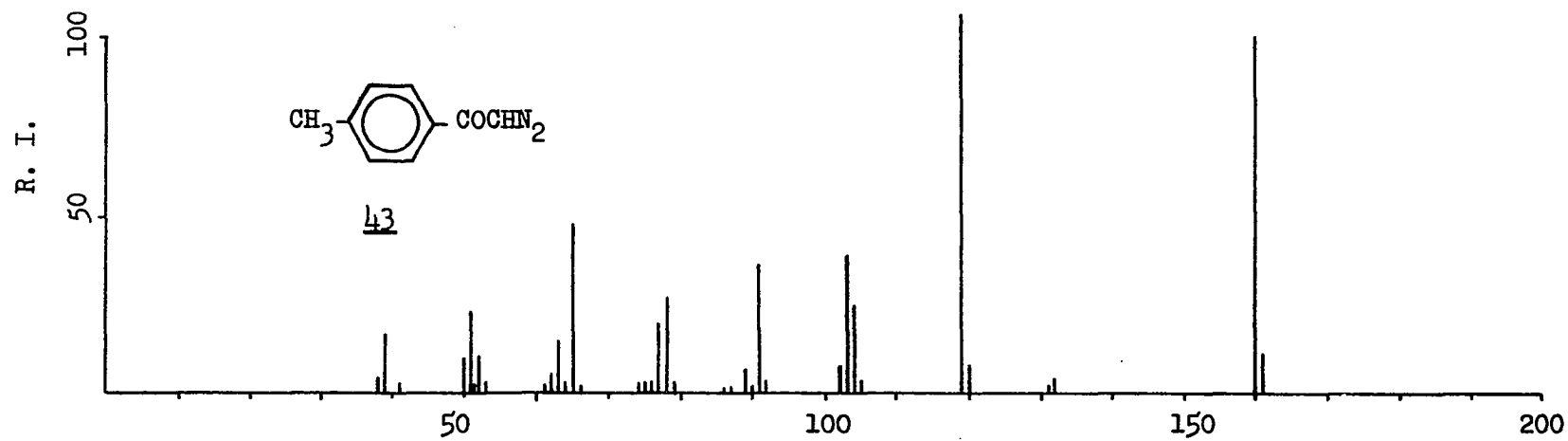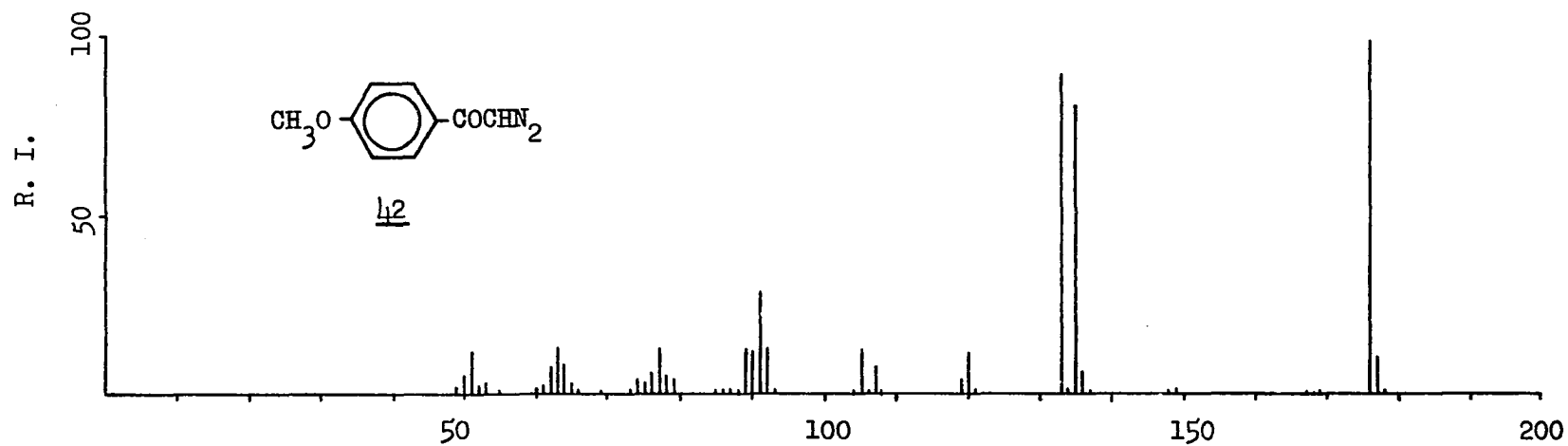The spectrum of **48** is strongly influenced by the presence of the p-nitro group. The absence of metastables for the loss of M^{+}-56 or for the loss of CO from m/e 163 to m/e 135 process (1.8%) could be due to the participation of the highly polar resonance structure **53** for the ion at m/e 163 (13).
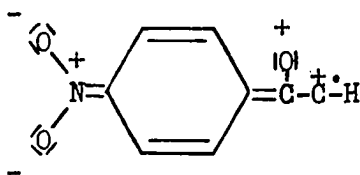
53

The development of double bond character between the aryl group and the carbonyl carbon would certainly curtail a rearrangement and emphasize fragmentations common to aromatic nitro compounds (26), M^{+}-NO_2 and M^{+}-NO, and fragmentations probable for simple diazocompounds, M^{+}-N_2. Significantly, the only obvious skeletal rearrangements indicated by loss of CO from m/e 117 to form m/e 89 and from m/e 133 to form m/e 105 both occur only after the destruction of the nitro group.

The mass spectrum of o-nitrodiazoacetophenone was also obtained

(Figure 8). In this case the resonance structure 54, analogous to 53,

should be less important because of steric crowding between the nitro group

ortho to the carbonyl group, which would prevent the ortho group from be-

coming coplanar and thus the necessary p orbital overlap between the group
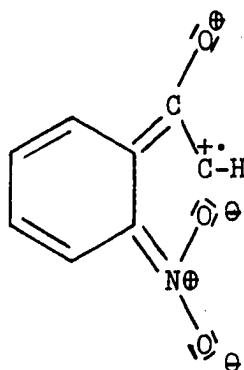
54

and the ring could not be entirely established.

In such a case the normal fragmentations of diazoacetophenones

(Scheme 4) would be expected to play a more dominant role, and that was

observed in the spectrum. Ions corresponding to the loss of N_2, N_2 and CO,

and N_2 and CH· from the molecular ion were observed, though none were meta-

stable fragmentations. Not unexpectedly, the more abundant ions in the

spectrum corresponded to fragmentations which could be derived from ions

involved in ortho interactions (Scheme 6).

Though the spectra reported here were not run under standardized con-

ditions, a qualitative trend was sought for any of the fragmentation and/or
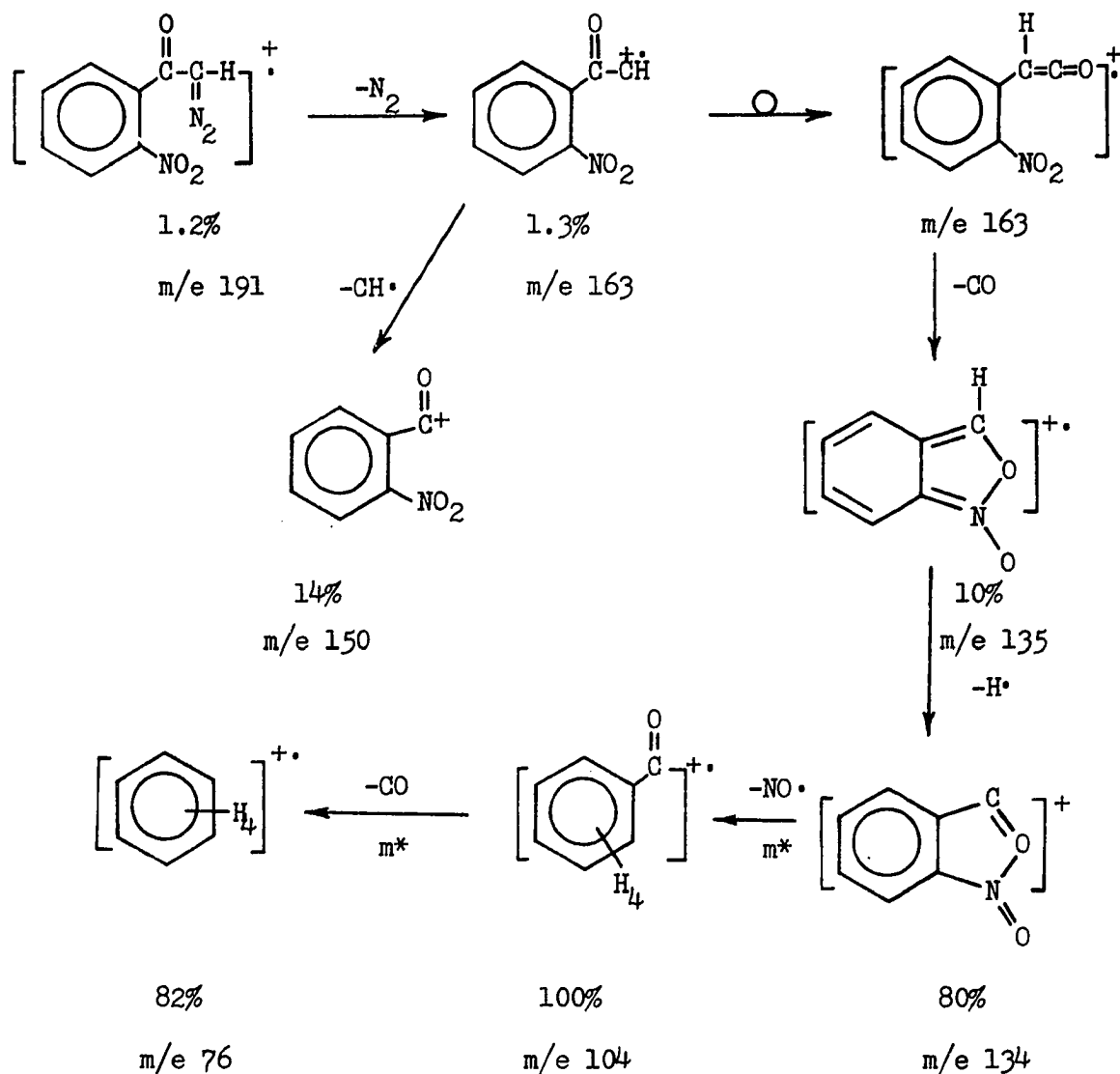
Scheme 6

rearrangement processes. The seeking (and finding) of substituent effects
in mass spectrometry is difficult due to the many interrelated factors
which can influence the energies of ions in the spectra (27). However,
that some trend might qualitatively be found was suggested by the work of
Ziffer and Sharpless (28) in 1962.

They studied quantum yields in the photolysis of substituted diazo-acetophenones and found, ϕ correlating with Hammett's equation, that the reaction had a ρ value of -0.26 and hence the reaction was favored by a high electron density at the reaction site. For the compounds of interest here they observed the following quantum yields: 42, 0.36; 43, 0.42; 44, 0.46; 45, 0.45; 46, not studied; 47, 0.27; and 48, 0.18.

Kirmse (29) has pointed out that the significance of the correlation above with the Hammett equation is not certain and, unfortunately, the significance of any correlation of data obtained here with the quantum yields may be more uncertain since for whatever ion or ratio of ions one chooses to correlate, the abundances of the ion or ions is greatly dependent upon the energies of fragmentation precursors, the availability of alternate fragmentation pathways for precursors, the rate or rates of fragmentation of the ion being investigated and the interrelation of these factors.

Despite these difficulties a tabulation of the relative abundance of the $M^{+}.-N_2-CO$ ions at 70, 20 and 16 eV is presented (Table 1) and it is seen that roughly the same pattern is followed as with the quantum yields. The $M^{+}.-N_2-CO$ ions were chosen because they should give the best measure of rearrangement which has occurred (realizing in doing so the uncertainties which are certain to be present).

Table 1. Correlation of quantum yields with relative intensities of $M^{\ddagger}-N_2-CO$ ions of para-substituted diazoacetophenones

Compound	p-substituent	Quantum Yield	Relative Intensity (%)[a]		
			70 eV	20 eV	16 eV
45	Br	0.45	22	42	22
46	CN	-	100	100	-
44	H	0.46	91	-	62
43	CH_3	0.42	25	52	-
42	CH_3O	0.36	12	16	16
47	Ph	0.27	22	24	12
48	NO_2	0.18	2	3	-

[a]Rounded to nearest unit.

While there is a rough consistency, the substituents exert a greater influence upon the fate of molecular species under electron impact conditions by way of their individual fragmentation patterns and this effect is reflected in Table 1.

Mass Spectra of para-substituted Benzoyl Azides

The mass spectra of seven para-substituted benzoyl azides 36 and 55 - 60 were obtained and the 70 eV spectra are reproduced in Figures 9 - 15.
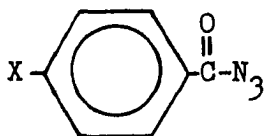
36 X = H
55 X = CH_3O 58 X = Br
56 X = CH_3 59 X = Ph
57 X = Cl   60 X = NO_2

A common fragmentation pattern was observed for the compounds with the exception of 60 (Scheme 7). 60 differed slightly and will be discussed separately.
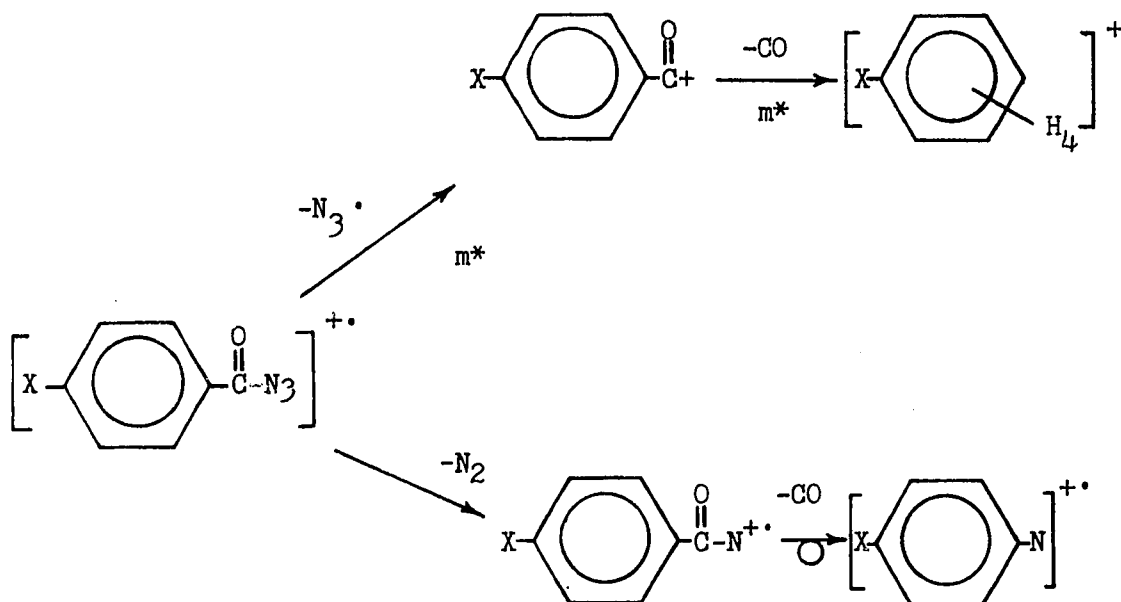
Scheme 7

The primary fragmentation process in each case (except for 59) was the metastable loss of 42 mass units corresponding to loss of the azido radical. Loss of 28 mass units followed by another loss of 28 was also an observed process and in some cases (55 and 59) was a metastable process.

p-nitrobenzoyl azide 60 differed somewhat in that it lost NO in a metastable process from the M^+-$N_3\cdot$ ion before losing CO.

In all cases the further fragmentation of the $M^{+\cdot}$-$N_3\cdot$-CO and M^+-N_2-CO ions depended upon the particular nature of the substituent.

The sample of p-methoxybenzoylazide 55 was contaminated and impurities were observed in the spectrum each time it was run. The very large $M^{+\cdot}$+1

Figure 9. Mass spectrum benzoyl azide <u>36</u> (top)

Figure 10. Mass spectrum p-methoxybenzoyl azide <u>55</u> (bottom)
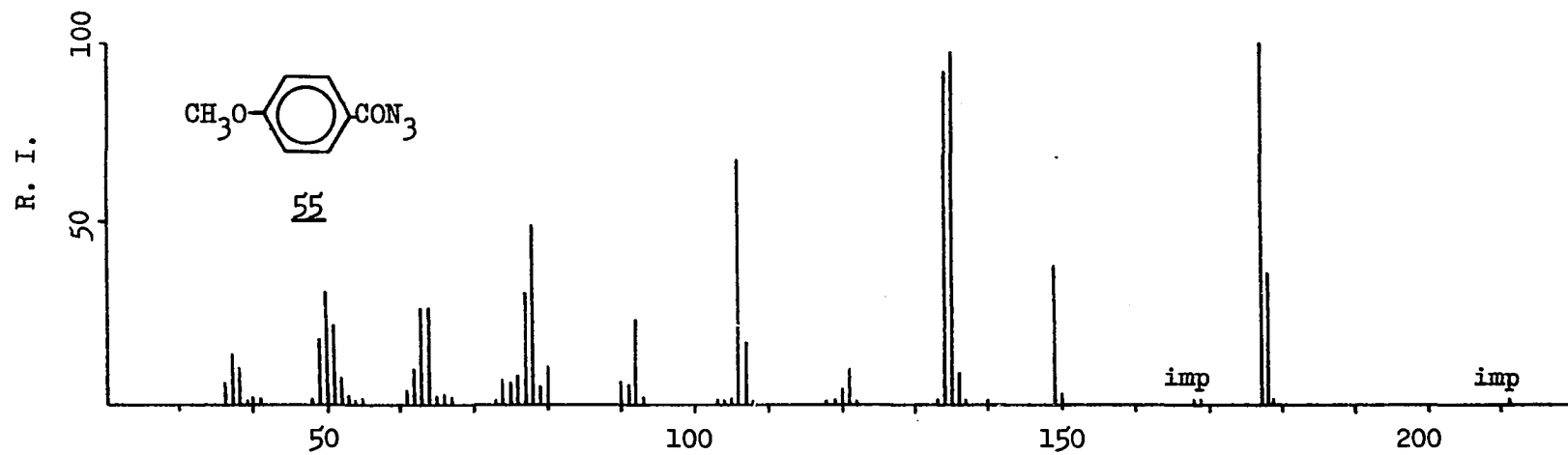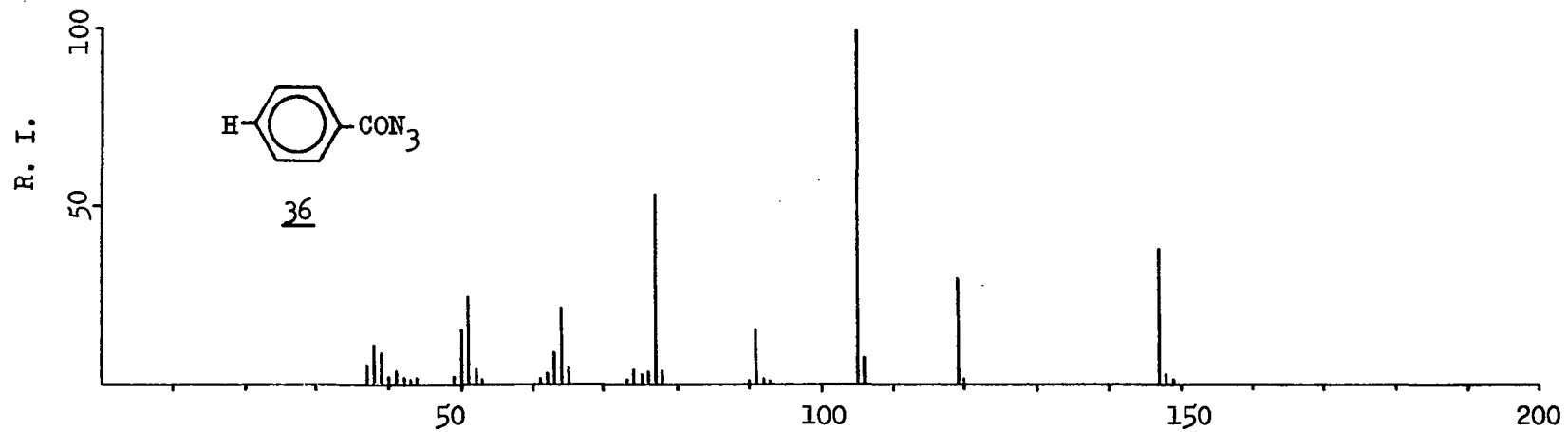
Figure 11. Mass spectrum p-methylbenzoyl azide 56 (top)

Figure 12. Mass spectrum p-chlorobenzoyl azide 57 (bottom)

R. I.

CH₃—⟨ring⟩—CON₃

56

R. I.

Cl—⟨ring⟩—CON₃

57

38
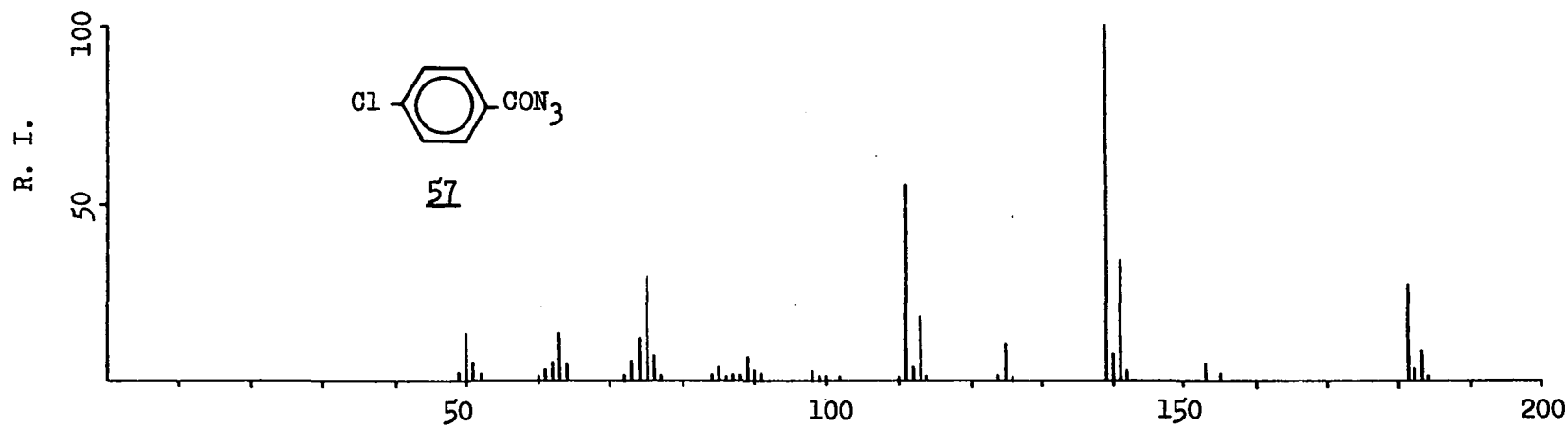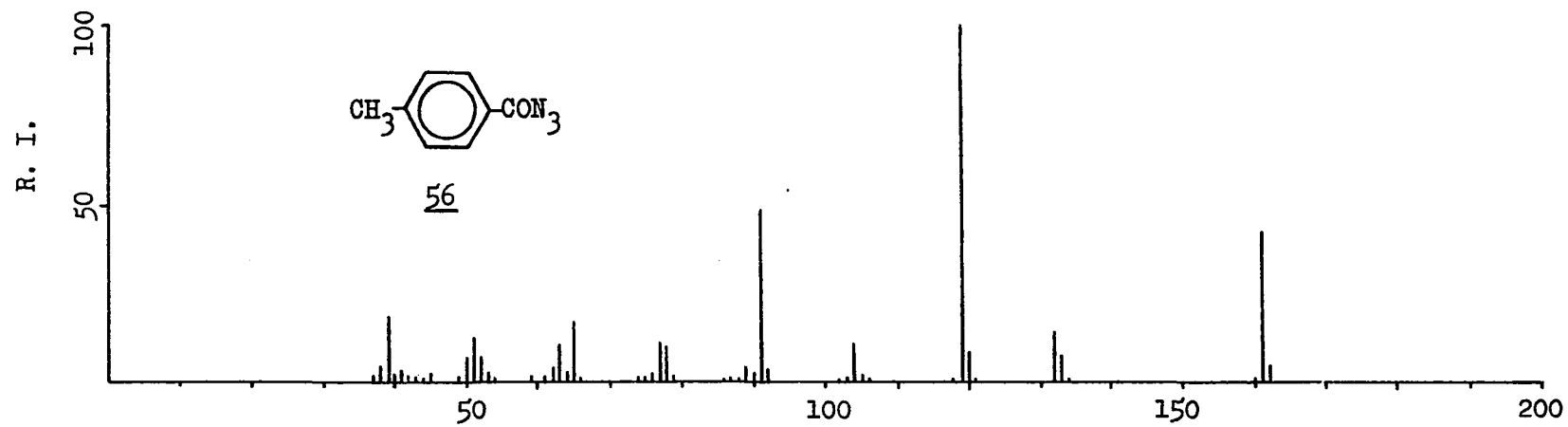
Figure 13. Mass spectrum p-bromobenzoyl azide 58 (top)

Figure 14. Mass spectrum p-phenylbenzoyl azide 59 (bottom)
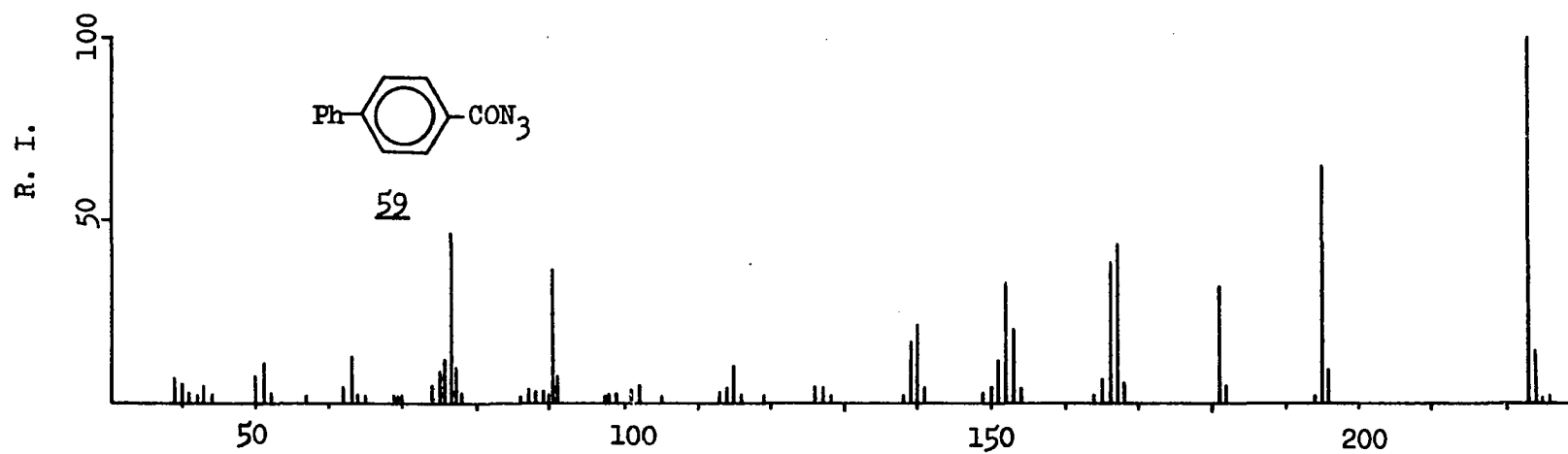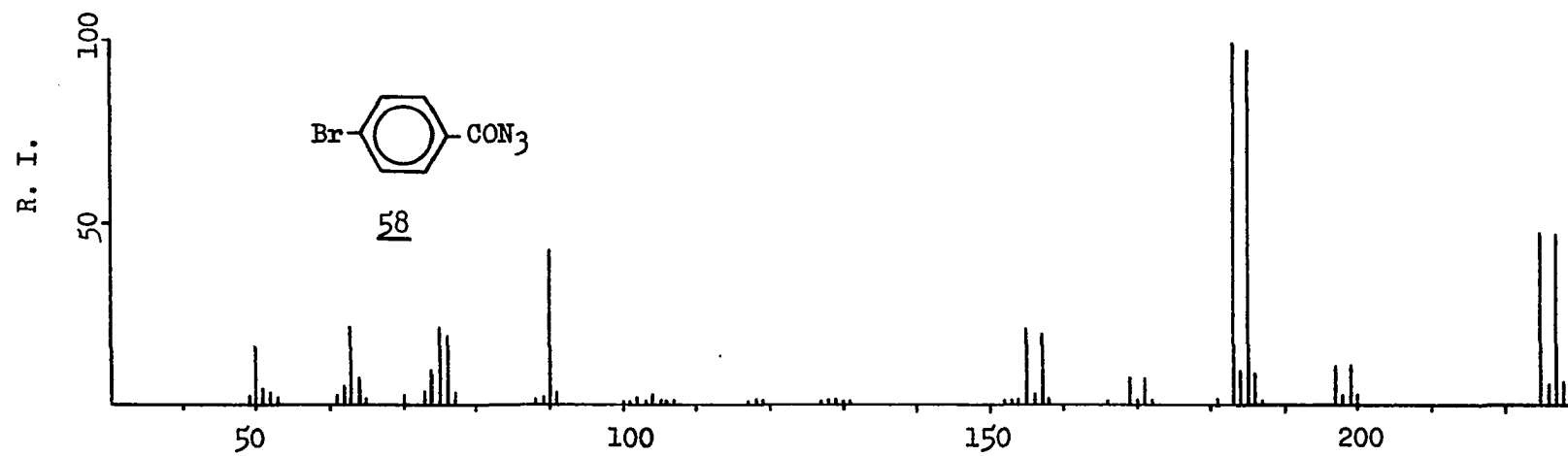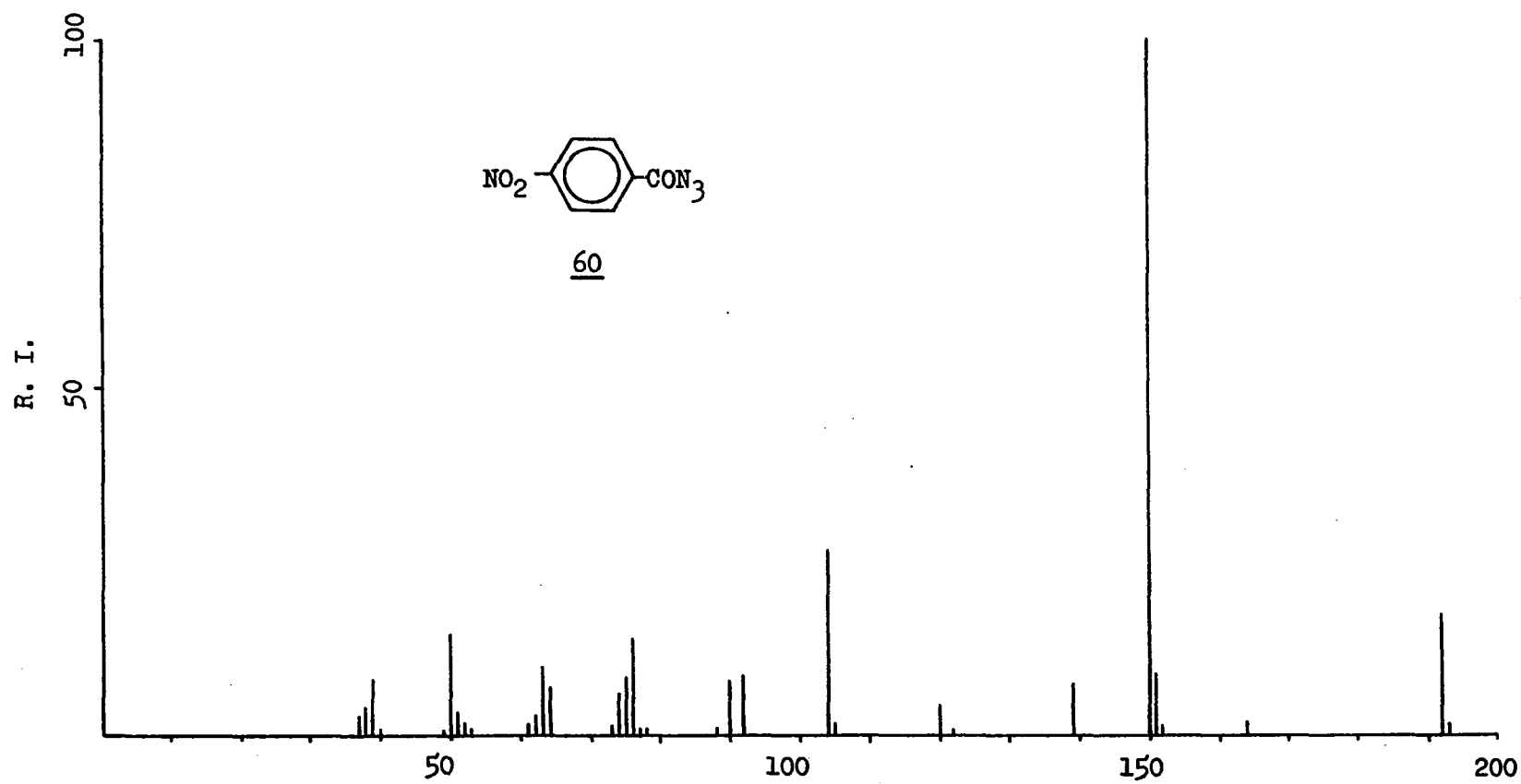
Figure 15. Mass spectrum p-nitrobenzoyl azide 60

ion at m/e 178 may be due to an impurity. A notable feature of the spectrum is the abundant ion at m/e 134 corresponding to loss of molecular nitrogen and methyl radical from the molecular ion. The ion is almost as abundant as the $M^{+\bullet}$-$N_3\bullet$ ion at m/e 135. The m/e 134 ion is formally similar to the ion at m/e 133 discussed earlier in the spectrum of p-methoxy-diazoacetophenone 42. A possible structure by analogy would be the following conjugated isocyanate ion.

$$O = \langle \text{ring} \oplus \rangle - N{=}C{=}O$$
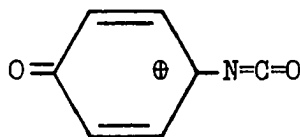
As in the case of p-phenyldiazoacetophenone 47 whose spectrum exhibited a large $M^{+\bullet}$-N_2-CO-H$\bullet$ ion at m/e 165, the fragmentation of p-phenylbenzoyl-azide 59 produced an ion at m/e 167 from the process $M^{+\bullet}$-N_2-CO at the expense of the $M^{+\bullet}$-$N_3\bullet$ process. The m/e 167 ions were also observed by Abramovitch, Kyba and Scriven (22) in the spectra of 2-azidobiphenyl and 3-azidobiphenyl, where they were the base peaks of the spectra.

There are differences in the spectra as reported here and as reported by Fraser, Paul and Bagley (23) for 36 and 60. These authors did not obtain metastables for the loss of $N_3\bullet$ from either compound and reported a loss of O$\bullet$ from the $M^{+\bullet}$-N_2 ion as a metastable process. The $M^{+\bullet}$-N_2-O$\bullet$ ion was not observed here however. For 60 they noted that NO$\bullet$ rather than NO_2 was lost from the $M^{+\bullet}$-N_2 or $M^{+\bullet}$-$N_3\bullet$ ions in metastable processes, however, here NO_2 was observed to be lost from both of these ions although the metastable formation of the $M^{+\bullet}$-$N_3\bullet$-NO$\bullet$ was also observed.

The reason for the differences observed is not known. Several factors

could play a part in causing the differences. Fraser, Paul and Bagley (23) used several different spectrometers none of which were the same as used here. The exact kind of inlet system used and temperature could have a bearing in particular since these compounds are thermally labile to varying degrees. Different inlet temperatures were on occasion employed here to determine the effect of heat upon the samples being run. The effect noted was one of changing abundances of ions rather than one of different fragmentations. Indeed these authors noted that large changes in spectra were not noted for aromatic azides due to temperature or instrument with the exception of 36 and the character of the spectrum changes in that case were not specified. Abramovitch, Kyba and Scriven (22) also noted no changes in the spectra of their compounds except for changes in intensities. There is the possibility also that surface reactions could cause some of the differences.

A search for trends due to substituent effects was made with the spectra of the azides. However because the base peak was due to the loss of N₃· in all but two cases (the base peak for 55 and 59 was the molecular ion), which did not involve any rearrangement process and because Yukawa and Tsuno (30) observed little substituent effect in the Curtius rearrangement of benzoyl azides the lack of any trend was not surprising.

The mass spectra of two other azides 61 and 62 were also examined (Figure 16 and 17).

$$X-C_6H_4-CH=CH-\overset{O}{\underset{\|}{C}}-N_3$$
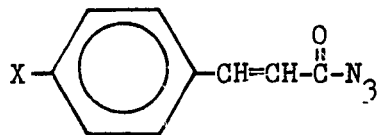
61 X = H   62 X = OCH₃

Figure 16. Mass spectrum cinnamoyl azide <u>61</u> (top)

Figure 17. Mass spectrum p-methoxycinnamoyl azide <u>62</u> (bottom)
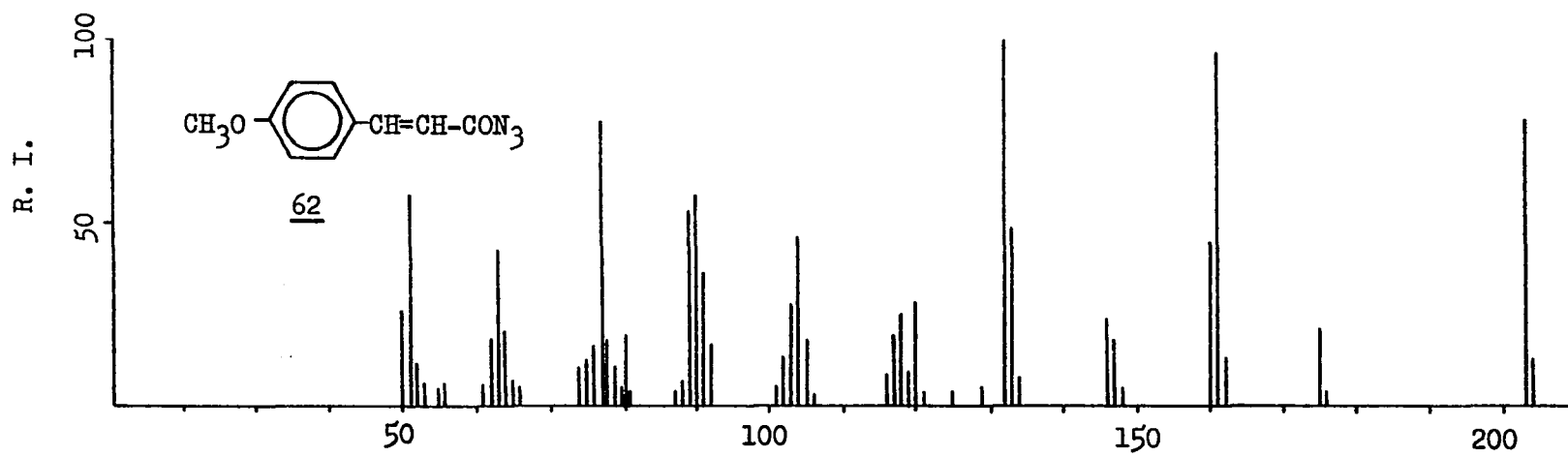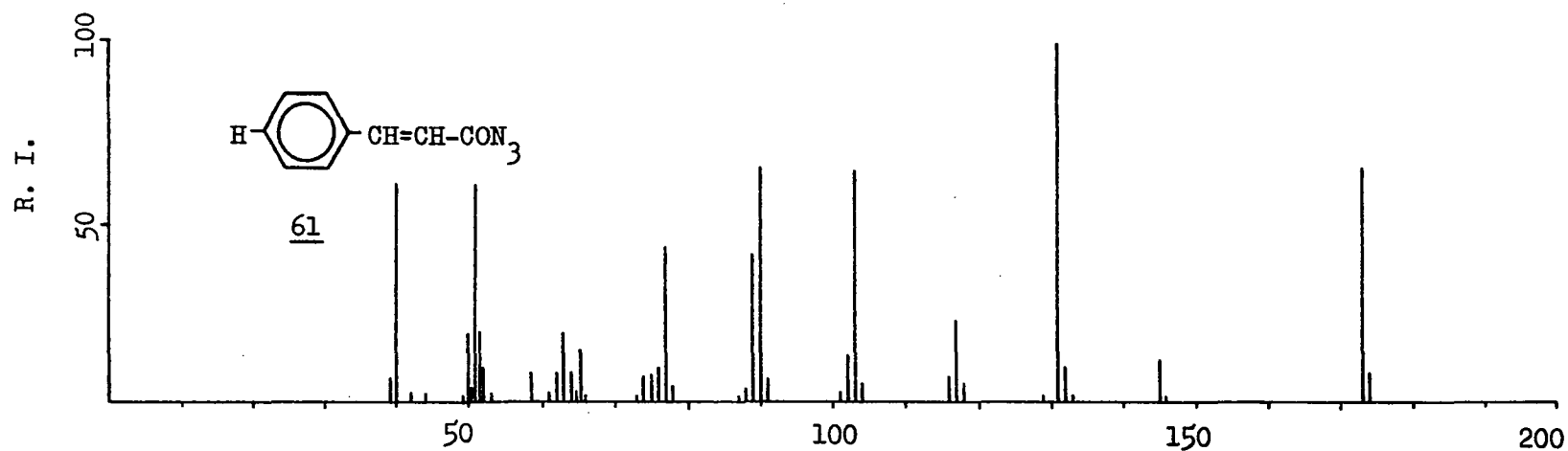
Both compounds fragmented in a manner analogous to that found for $\underline{36}$

and $\underline{55}$ - $\underline{59}$ (Scheme 7) by loss of $N_3\cdot$ followed by loss of CO as well as by

loss of N_2, rearrangement and subsequent loss of CO. Both also lost HCN

from the $M^{\overset{+}{\cdot}}$-N_2-CO ion and then suffered fragmentations from the resulting

ion and $M^{\overset{+}{\cdot}}$-N_2-CO ion particular for the presence of the substituent.

EXPERIMENTAL

All mass spectra were obtained on an Atlas MAT model CH 4 single focusing mass spectrometer operating at 70 electron volts ionizing potential and 3,000 volts accelerating potential. Mass spectra of most samples were also obtained at lower electron energies.

All of the diazoacetophenones studied, diazoacetophenone 44 (31), p-methyldiazoacetophenone 43 (31), p-methoxydiazoacetophenone 42 (31), p-bromodiazoacetophenone 45 (31), p-cyanodiazoacetophenone 46 (32), p-phenyldiazoacetophenone 47 (33) and p-nitrodiazoacetophenone 48 (31), have been reported previously in the literature. The diazoacetophenones were prepared by the established method of treating the appropriate acid chloride with an excess of ethereal diazomethane at 0°C. After removing the solvent and excess diazomethane under water pump pressure, the crude diazoacetophenone was recrystallized from an appropriate solvent.

Benzoyl azide 36 (34), p-methoxybenzoyl azide 55 (34), p-methylbenzoyl azide 56 (34), p-chlorobenzoyl azide 57 (34), p-bromobenzoyl azide 58 (34) and p-nitrobenzoyl azide 60 (34) have been reported previously in the literature. p-phenylbenzoyl azide 59 has not been reported in the literature. All of the benzoyl azides were prepared by the established method of treating the appropriate acid chloride with an excess of sodium azide. The benzoyl azides were generally unstable and were therefore purified prior to use by silica gel thin layer chromatography. A mass spectrum of the azide thus separated was quickly obtained as a solid sample adsorbed on silica gel.

PART II: TRANSFORMATIONS OF

α-ORGANOSILYLDIAZOACETATES

HISTORICAL

Organometallic and carbene chemistry are two rapidly expanding areas of current interest in chemical science. It is only natural that the two areas should interact to some extent. Diazocompounds represent a versatile, reliable and usually convenient source of carbenes. The presence of a hetero- or metallo-atom _alpha_ to the diazo group of a diazocompound can have a profound influence upon the stability and reactivity of the compounds and upon the stability and reactivity of the resultant electron-deficient carbene. The number of α-substituted diazocompounds which have been synthesized and studied has increased significantly (35) within the last decade. The nature of the influence of the α-substitutent depends, to a large extent, upon the possibility of electronic interaction existing between the electron-deficient carbene and non-bonding electrons or accessible empty orbitals of higher energy of the substituent. The lower electronegativity (relative to carbon) and ability of silicon to utilize the 3d-orbitals for bond formation (36) makes the study of α-silylcarbenes, and thus α-silyldiazocompounds, not only interesting, but also theoretically important in understanding the electronic nature of the species involved.

α-silyldiazocompounds

In 1965 Scherer and Schmidt (37) reported that the reaction of lithium diazomethane with trimethylchlorosilane produced a volatile, vile-smelling, colorless-to-light yellow liquid which on the basis of its total analysis and molecular weight, determined in freezing benzene, had the constitution $(CH_3Si)_2N_2C$. However, the available evidence suggested that the product was not bis(trimethylsilyl)diazomethane since its infra-red spectrum showed

no absorption in the 2900 to 1500 cm^{-1} region and it did not react with dilute acids with evolution of nitrogen. Rearrangement to bis(trimethylsilyl)carbodiimide was observed when the compound was heated at greater than 120°.

Lappert, Lorberth and Poland (38) reinvestigated the reaction and confirmed the results of Scherer and Schmidt. In addition, it was claimed that the compound produced was monomeric in benzene but dimeric in the vapor phase since a molecular ion for the dimer was observed in its mass spectrum. On this basis, these authors attempted to rationalize the apparent nonexistence of bis(trimethylsilyl)diazomethane in terms of a less important contribution of the canonical form 63 to the ground state of the molecule as compared to the equivalent canonical form for the isolable bis(trimethylstannyl)diazomethane, leading to a more ready dimerization of the silyl compound to give (presumed) 64.

$$(Me)_3Si \diagdown \atop (Me)_3Si \diagup C \overset{\delta-}{-}N\overset{\delta+}{=}N \qquad\qquad (Me)_2Si-C \overset{N=N}{\underset{N=N}{\diagup \diagdown}} C-Si(Me)_2$$
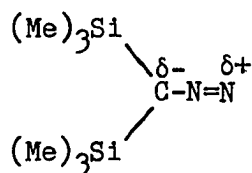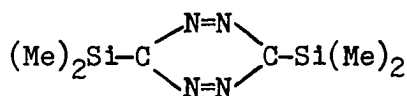
63   64

Lappert and Lorberth (39) did however report the isolation of trimethylsilyldiazomethane 65 from the reaction of trimethylsilyl chloride and lithiodiazomethane in 5% yield (38) although no experimental details were given.

In 1968, Seyferth, Dow, Menzel and Flood (40,41) reported an improved synthesis of 65 (56%) from N-nitroso-N-(trimethylsilylmethyl)urea in a manner analogous to the production of diazomethane from N-nitroso-N-methylurea. The method provided not only an improved yield but a far less

hazardous procedure because lithiodiazomethane, as the dry solid, is explosive (42). Unfortunately, the production of 65 was always accompanied by the production of hexamethyldisiloxane (23%), requiring that 65 be isolated in analytical purity by gas-liquid partition chromatography. The compound 65 was a greenish yellow liquid, was very stable thermally, and could be distilled at atmospheric pressure.

Treatment of 65 with dry acetic acid in benzene at room temperature yielded not only the expected trimethylsilylmethyl acetate but also equimolar quantities of methyl acetate and trimethylsilyl acetate indicating cleavage of the trimethylsilyl group. 65 in the presence of copper(I) chloride in benzene was found to have some promise as a useful Me$_3$SiCH transfer agent to olefins. Thus, such a reaction with cyclohexane gave anti-7-trimethylsilylnorcarane (65%), syn-7-trimethylsilylnorcarane (7%), cis- and trans-1,2-bis(trimethylsilyl)ethylene (9% and 13%, respectively), and an unidentified Me$_3$SiCH trimer (2.3%). Compound 65 also underwent 1,3-dipolar addition reactions with a number of olefins (40,41,43,44).

Compound 65 has also been synthesized by other methods. Seyferth, Menzel, Dow and Flood have also utilized ethyl N-nitroso-N-(trimethylsilylmethyl)urethane (41) but found the silyl-substituted urea to be the preferred precursor. Sheludyakov, Khatuntsev and Mironov (45) have synthesized 65 using methyl N-nitroso(trimethylsilylmethyl)carbamate. It has also been reported (41) that Schöllkopf, Reetz, Banhidai and Scholz (46) have developed an improved synthesis of 65 which should enhance its utility but no experimental details have been published.

Seyferth and Flood (47) have used 65 to prepare bis(trimethylsilyl) diazomethane 63 whose existence had previously been disputed (38). Thus 63

was produced by metalation of 65 with n-butyllithium at -90° to -100° and

reaction of the presumed intermediate, Me₃SiC(Li)N₂, with trimethylchloro-

silane. Compound 63 was a pale yellow-green liquid which had a very sweet

odor and was stable indefinitely in air. It was necessary, however, to

isolate 63 from some air-unstable by-products, which had a pungent odor, by

column chromatography on alumina.

The infra-red spectrum of 63 showed a very strong band at 2040 cm^{-1}

and its mass spectrum showed a molecular ion at m/e 186. Compound 63 was

recovered essentially undecomposed (98%) after heating for seven days at

about 151°; however, when heated with copper(II) sulfate or the by-products

(or by-product) of the original synthesis 63 rearranged to bis(trimethyl-

silyl)carbodiimide. Compound 63 underwent slow protonolysis on treatment

with acetic acid in benzene or with neat propionic acid and, as was the

case with 65, loss of trimethylsilyl groups occurred. Nucleophilic attack

at silicon was a more important process with 63 because the introduction of

a second trimethylsilyl group increases the probability of such an attack

occurring and at the same time decreases the accessibility of the diazo

carbon atom.

Seyferth and Flood were unable to account for the results of Scherer

and Schmidt (37) and Lappert, Lorberth and Poland (38), though it is clear

that they had isolated bis(trimethylsilyl)diazomethane, and the confusion

that thus exists in the literature concerning its chemistry has not, as yet,

been resolved.

Two groups have reported the production of α-silyldiazoalkanes by more

familiar methods. Kaufmann, Auräth, Träger and Rühlmann (48) made 66 by

HgO, Ag₂O or MnO₂ oxidation of the hydrazone of benzoyltriphenylsilane.

Brook and Jones (49) made 66 - 71 by treating the tosylhydrazones of the corresponding acylsilanes with n-butyllithium. The latter group found the conv-rsion to take place under milder conditions and the resulting compounds to be more stable than the corresponding carbon analogues.

$$Ph_3-Si-\overset{\overset{\displaystyle O}{\|}}{C}-R$$

66 R = Ph

67 R = Me

68 R = C_6H_4-p-Cl $(Me)_3-Si-\overset{\overset{\displaystyle O}{\|}}{C}-Ph$

69 R = C_6H_4-p-F   71

70 R = CH_2Ph
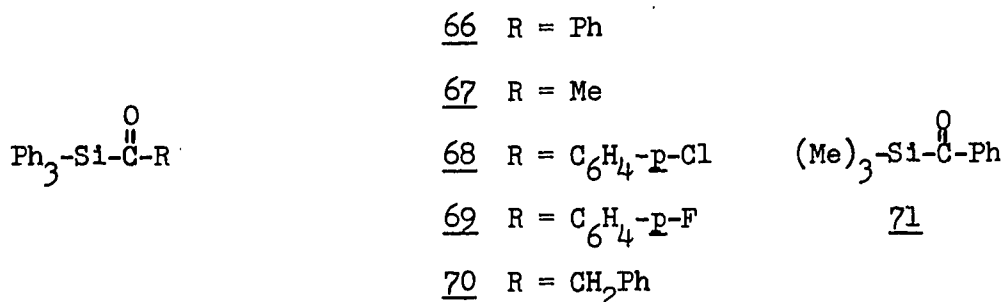
In 1967, Schöllkopf and Rieber (50) reported the synthesis of ethyl diazo(trimethylsilyl)acetate 72. It was prepared in 95% yield by treating diethyl mercuribis(diazoacetate) 73 with bis(trimethylsilyl)sulfide 74 in benzene at reflux (Scheme 8).

$$Hg\left[-\overset{\overset{\displaystyle N_2}{\|}}{C}-\overset{\overset{\displaystyle}{\underset{\underset{\displaystyle O}{\|}}{C}}}-OC_2H_5\right]_2 + Me_3Si-S-SiMe_3 \xrightarrow{-HgS} 2\ Me_3Si-\overset{\overset{\displaystyle N_2}{\|}}{C}-\overset{\overset{\displaystyle}{\underset{\underset{\displaystyle O}{\|}}{C}}}-OC_2H_5$$

   73   74   72
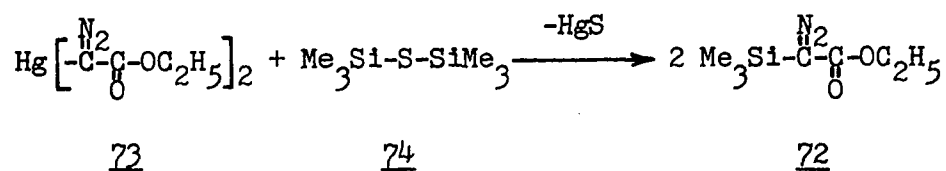
Scheme 8

In 1968, Kaufmann and Rühlmann (51) modified the synthesis by utilizing trimethylsilyliodide in place of 74 in ether at room temperature. By this method they made 72, ethyl diazo(triethylsilyl)acetate and ethyl diazo(triphenylsilyl)acetate in 80 - 90% yields. The synthesis was further modified by Schöllkopf and Frasnelli (52). They obtained 72 by treating trimethylsilyl chloride with ethyl lithiodiazoacetate at -110° in 52% yield.

Compound 72 (51, 53), as with other α-silyldiazocompounds (40, 41, 43,

44, 54) has been observed to undergo 1,3-dipolar addition reactions. As in the cases of the other α-silyldiazocompounds, rearrangement of the initially formed adduct was observed with dimethyl acetylenedicarboxylate (51) (Scheme 9) and diethyl fumarate (53).

$$\underline{72} + \text{MeO-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-C}\equiv\text{C-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-OMe} \longrightarrow \left[\begin{array}{c} \text{MeO-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-C}\!=\!\!\text{C-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-OMe} \\ \end{array} \right] \xrightarrow{\Delta} \text{MeO-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-C}\text{---}\text{C-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-OMe}$$
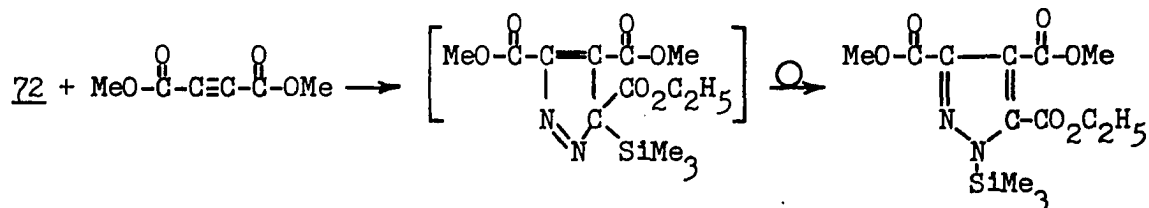
Scheme 9

When 72 was heated with ethyl acrylate at about 150° cycloaddition occurred, followed by elimination of N_2 to yield a mixture of cis- and trans-1-trimethylsilylcyclopropane-1,2-dicarboxylic acid ethyl esters (51). Brook and Jones (54) had also obtained silyl-substituted cyclopropanes upon photolysis of the pyrazolines formed by 67 and several olefins.

Schöllkopf, Hoppe, Rieber and Jacobi (53) found that direct photolysis of 72 produced trimethylsilylcarboethoxycarbene which was capable of inter-molecular carbon-hydrogen insertion and addition to olefins to yield in about 95% cis, stereospecific 1-trimethylsilyl-carboethoxycyclopropanes but not of intramolecular carbon-hydrogen insertions which would have produced silacyclopropanes. This is in contrast to the 1,3-intramolecular insertion observed for the analogous carbene formed from ethyl 2-diazo-3,3-dimethyl-butanoate. They felt that the absence of any silacyclopropane was due to the larger distance between the carbene center and the methyl carbon-hydrogen bond in the silyl carbene (about 3.0 Å) and the corresponding distance in the carbon carbene (about 2.5 Å).

Intramolecular 1,3-insertion is one approach to producing silacyclo-
propanes which is now possible because of the availability of these α-silyl-
diazocompounds. Until recently all other attempts to produce an isolable
silacyclopropane have been unsuccessful (55). Lambert and Seyferth were
able to prepare silacyclopropanes stabilized with bulky substituents.

Another reaction of diazocompounds which has thus far not been report-
ed for α-silyldiazocompounds is the Wolff rearrangement. Wolff rearrange-
ments have been reported for other α-heterodiazocompounds. Mulder,
van Leusen and Strating (56) have reported that a rearrangement analogous
to the Wolff rearrangement occurs with α-diazosulfones, although a compe-
tition experiment (57) showed the Wolff rearrangement to be the favored
process (Scheme 10).

p-X-Ph-SO₂CHN₂ $\xrightarrow[\text{MeOH}]{h\nu}$ p-X-Ph-SO₂C̈H $\underset{\text{O}}{\overset{\nearrow}{\searrow}}$

$\nearrow$ p-X-Ph-SO₂CH₂OMe

$\searrow$ p-X-Ph-CH=SO₂ $\longrightarrow$ p-X-Ph-CH₂SO₂OMe

X = MeO, Me, H, NO₂

10%

p-Me-Ph-SO₂CN₂COR $\xrightarrow[\text{C}_2\text{H}_5\text{OH}]{h\nu}$ p-Me-Ph-SO₂C̈COR $\underset{\text{O}}{\overset{/\!/}{\longrightarrow}}$

$\longrightarrow$ p-Me-Ph-$\overset{\text{SO}_2}{\underset{\text{}}{\text{C}}}$-COR

$\searrow$ p-Me-Ph-SO₂-$\overset{\text{R}}{\text{C}}$=C=O
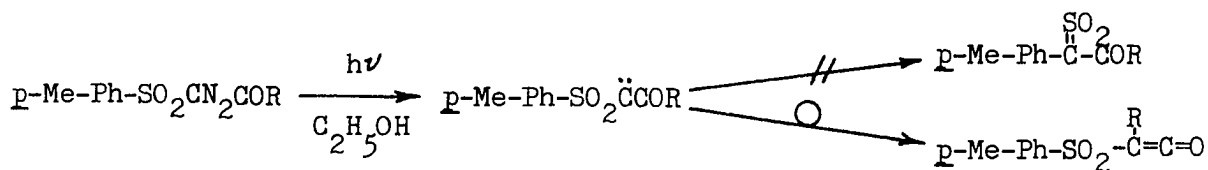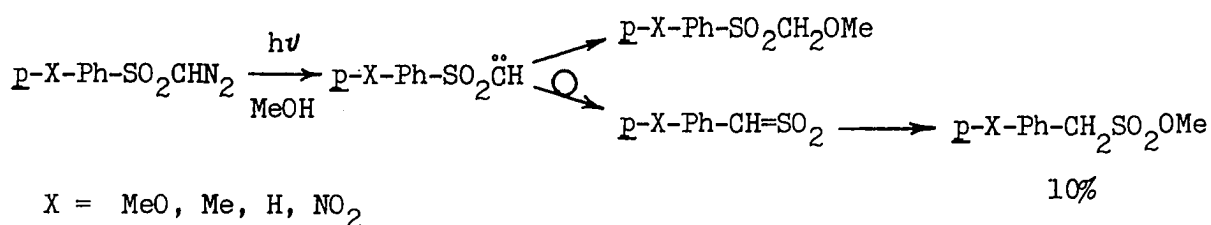
R = Me, Ph

Scheme 10

Diazocompounds containing an α-phosphorous have also been observed to
undergo an analogous Wolff Rearrangement (58) (Scheme 11).

$$\underset{\underset{N_2}{|}}{\overset{\overset{O}{\|}}{Ph_2P-C-R}} \xrightarrow[MeOH]{h\nu} \underset{}{\overset{\overset{O}{\|}\;\overset{OMe}{|}}{Ph_2P-CH-R}} + \underset{\overset{}{OMe}}{\overset{\overset{O}{\|}\;\overset{Ph}{|}}{Ph-P-CHR}}$$

$$R = Ph, \; CONH_2, \; CO_2C_2H_5$$
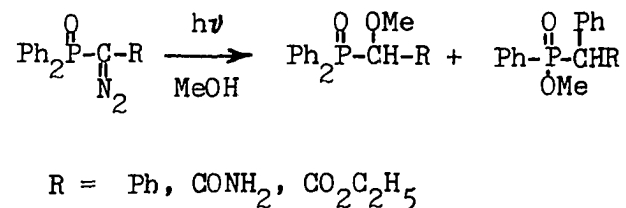
Scheme 11

Wolff Rearrangement

A notable feature of the Wolff rearrangement is that it can be brought about catalytically, thermally or photochemically (29*, 59, 60, 61). The rearrangement has proved to be of some synthetic value (62, 63). However, until recently no unified mechanistic picture of the reaction had emerged, in spite of over half a century of intensive research.

Fenwick, Frater, Ogi and Strausz (64) have shown that oxirenes can be detected as reactive transients in the photochemical Wolff rearrangement sequence of α-diazoketones and in the photolysis of ketenes, since ketenes have been isolated or trapped from photochemically induced rearrangements. On the basis of their work with the photolysis of several α-diazoketones labeled with carbon-13 in the carbonyl carbon, they were able to establish the mechanism shown in Scheme 12.

In an accompanying article (65) Csizmadia, Gunning, Gosavi and Strausz reported semi-empirical molecular orbital calculations on the α-diazoketones, oxirenes and other related reaction intermediates. They determined that concerted decomposition of the α-diazoketones (66) to ketenes was not feasible because of the large (computed) activation energies which would be involved. Thus, as shown, the ketocarbene would be the primary reaction

*Reference (29), pp. 118 - 127.
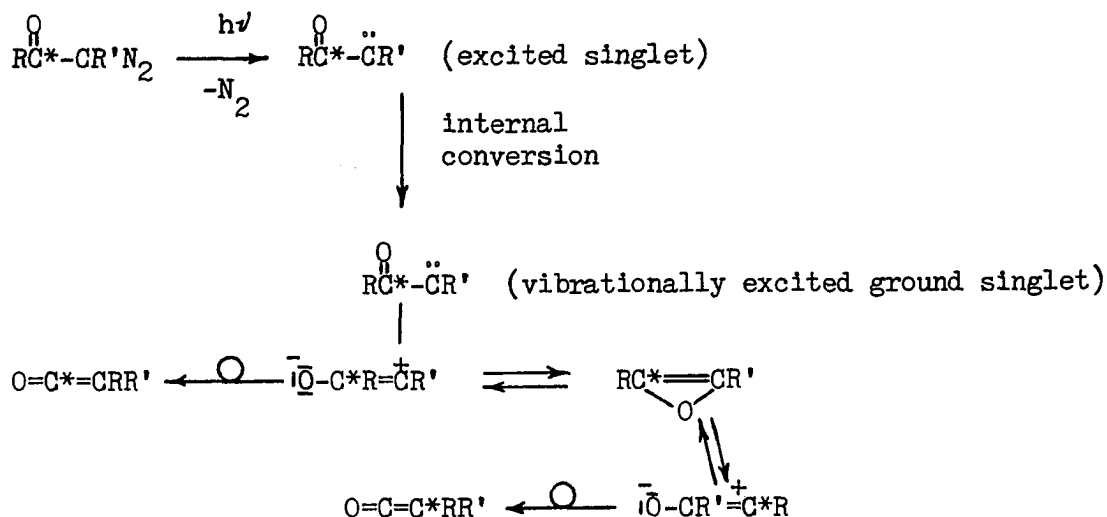
Scheme 12

product. This would, of course, also apply to thermally induced Wolff rearrangements.

Decomposition of the electronically excited diazoketones would give rise to the formation of electronically excited ketocarbenes which, in turn, would undergo rapid internal transition to yield vibrationally excited ground-state singlet carbenes. The calculated (65) state energy levels suggested that even in the pyrex filtered photoexcitation of the α-diazoketones, four different excited states could be reached. That a singlet is involved as intermediate in the rearrangement has been shown by several groups (64, 67, 68, 69, 70).

The carbenes can convert to a more stable tautomeric zwitterion (65) which can isomerize to ketene by way of a bridged cyclic intermediate, or in a simultaneous competing reaction to an oxirene. Oxirenes are inherently unstable with respect to C-O bond rupture, and therefore can revert to the zwitterion and ultimately to the ketene since the oxirene lies at a higher energy level than the transition state of the ketene forming step.

Since a moderately high-temperature, solution phase thermolysis should

lead to the lowest singlet state carbene and since the carbene would thus

not be vibrationally excited, the oxirene would not be attainable but the

energy level of the transition state of the ketene should be attainable.

Ketenes or secondary products derived from them have been isolated in

several cases of diazoketone thermolysis in aprotic solvents (59), but there

is no evidence of oxirene involvement in the reactions (64). Thus, the

difference in behavior between the thermal and photochemical rearrange-

ments can be ascribed to the difference in the excess vibrational energy of

the ground-state singlet ketocarbene intermediate.

The mechanism for the thermal rearrangement originally proposed by

Wolff (71, 72) would appear then to be correct (Scheme 13).

$$RC\overset{O}{\parallel}\text{-}CR'N_2 \xrightarrow{\Delta} RC\overset{O}{\parallel}\text{-}\overset{..}{C}R' \text{ (ground-state singlet)} + N_2$$

$$\downarrow$$

$$\bar{|\underline{O}}\text{-}CR\text{=}\overset{+}{C}R' \longrightarrow \bar{|\underline{O}}\text{-}C\text{≡}CR' \longrightarrow O\text{=}C\text{=}CRR'$$
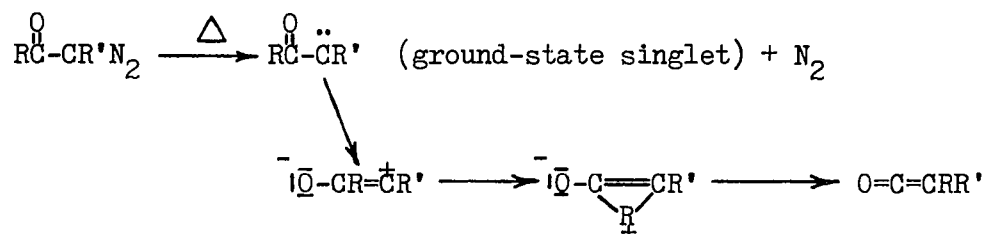
Scheme 13

Recently Matlin and Sammes (73, 74) presented evidence which was in

agreement with the conclusions of Strausz' work (64, 65) and they found, in

addition, no oxirene participation in either the silver or copper oxide

catalysed decomposition of diazoketones.

The Wolff rearrangement of carboalkoxycarbenes was, until rather

recently, a neglected reaction. Attention has now turned to this process,

however, and mechanistic information concerning the photochemical reaction

has been reported by several laboratories (70, 75, 76, 77, 78, 79, 80, 81

82, 83). The importance of oxirenes has been stressed (80, 81, 82), consistent with the discussion above, and intermediate alkoxyketenes have been trapped (70). The absence of the Wolff rearrangement in thermal reactions was noted in three reports (70, 81, 83), but in 1971, Richardson, Hendrick and Jones reported the rearrangement of biscarbomethoxycarbene in the gas-phase pyrolysis of methyl diazomalonate (84).

They obtained four products (methyl pyruvate, methyl acrylate, methyl acetate and methyl vinyl ether) between 330° and 540°, the exact yield of each depending upon the exact temperature, in about 65% overall yield based on carbene. (Below 330° only three products were obtained (methyl pyruvate was not), and below 420° the overall yield was somewhat lower). Scheme 14 accounts for the data, the yields indicated are for the 480° pyrolysis and varied little in a temperature range of $\pm 60°$.

The intramolecular reaction most favored is insertion into the carbon hydrogen bonds of the neighboring O-methyl groups followed by elimination of carbon dioxide to yield methyl vinyl ether and methyl acrylate. Thermal cleavage of β-lactones are known (85) and the isolation of stable lactones from irradiations of t-butyl and t-amyl diazoacetates and ethyl diazomalonate (86) have been reported (87). Lactams have also been made from diazo-amides (88, 89).

The Wolff rearrangement seemed to be slightly favored over carbon-oxygen insertion since methyl acetate was formed slightly faster than methyl pyruvate from the presumed (but not isolated or identified) methoxy-carbomethoxyketene.

Scheme 14

61
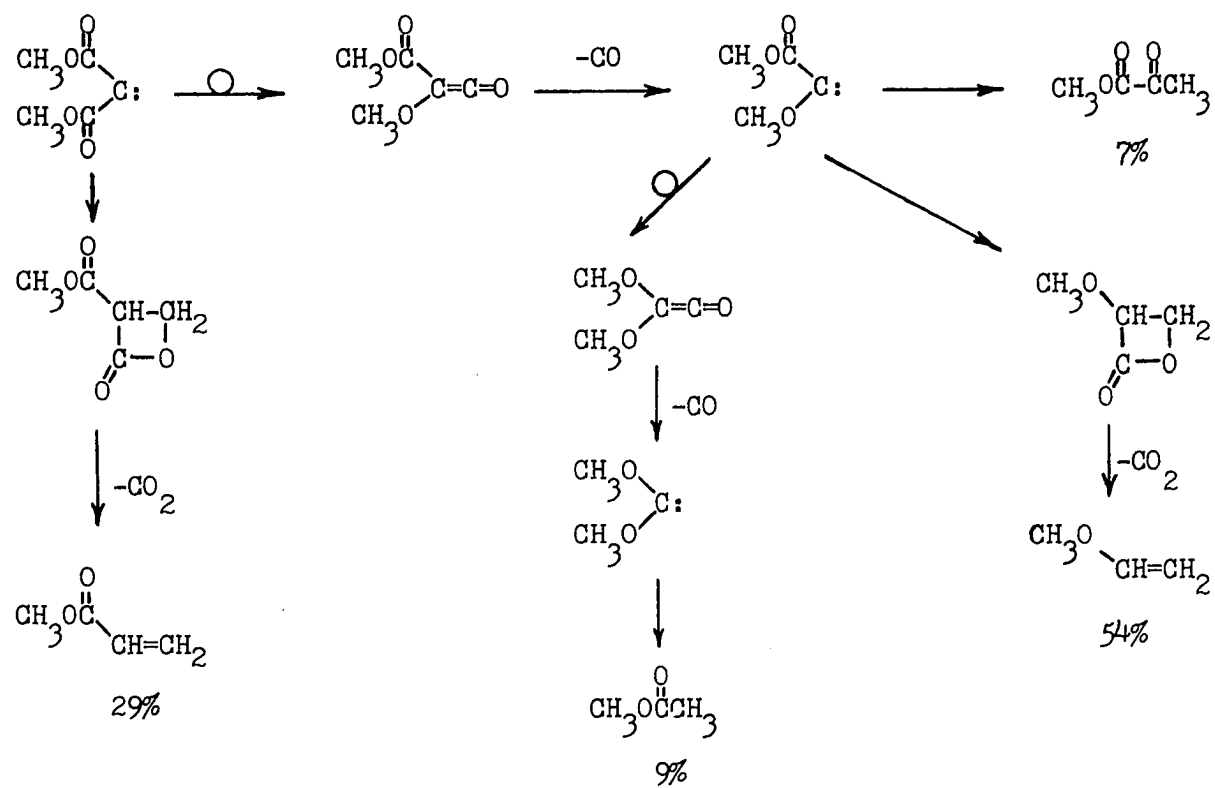
RESULTS AND DISCUSSION

When our work into the transformations of α-silyldiazocompounds was

begun, the known compounds were all symmetrically substituted at the sili-

con atom with methyl, ethyl or phenyl groups. It was felt, however, that

compounds substituted at the silicon with two methyl groups and one phenyl

would have several advantages: they would have physical properties inter-

mediate between the normally volatile trimethyl-derivatives and the non-

volatile triphenyl-derivatives making it a better laboratory system; they

would have a built in handle for spectroscopic analysis, particularly nmr;

and for transformations in which the possibility of 1,3-reaction between a

carbene center and silylmethyl was conceivable, the phenyl group could

make the methyl groups more accessible for steric reasons.

Several approaches to the synthesis of ethyl diazo(dimethylphenyl-

silyl)acetate 75 were used. The first approach was to utilize the method

of Schöllkopf and Rieber (50) (Scheme 8) which employed diethyl mercuribis-

(diazoacetate) 73 and disilthianes.

73 could be synthesized from ethyl diazoacetate and either yellow or

red HgO (35, 53, 90) (Scheme 15). There is no real problem in obtaining

this reagent except that the reaction is somewhat unpredictable. Very often

it would not start, but by separating the reactants by filtration and re-

combining them again, it would.

$$HgO + 2\ HC\underset{\underset{O}{\|}}{\overset{\overset{N_2}{\|}}{C}}-OC_2H_5 \xrightarrow[0°]{ether} 73 + HOH$$
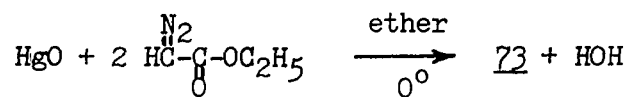
Scheme 15

The end of the react⁻ᵗ⁻ was usually indicated by the formation of bubbles, probably N_2. Compound 73 could be recrystallized from ether and stored at 0° or lower, but it was best to use it as quickly as possible since it did decompose even at 0°.

Dimethylphenylchlorosilane 76 could be purchased or it could be synthesized from dichlorodimethylsilane by a Grignard reaction with phenyl magnesium bromide (91). 76 was used to prepare the disilthiane.

1,3-diphenyl-1,1,3,3-tetramethyldisilthiane 77 was prepared by the method of Champetier, Etienne and Kullmann (92) from dimethylphenylsilyl chloride and hydrogen sulfide (Scheme 16).

$$\begin{array}{ccc}
& & \text{Me} \quad \text{Me} \\
& \text{pyridine} & \\
2 \text{ Ph-Si-Cl} + \text{H}_2\text{S} \xrightarrow{\text{pentane}} & \text{Ph-Si-S-Si-Ph} + \text{pyridinium chloride} \\
\text{Me} & & \text{Me} \quad \text{Me}
\end{array}$$

76   77 (54%)
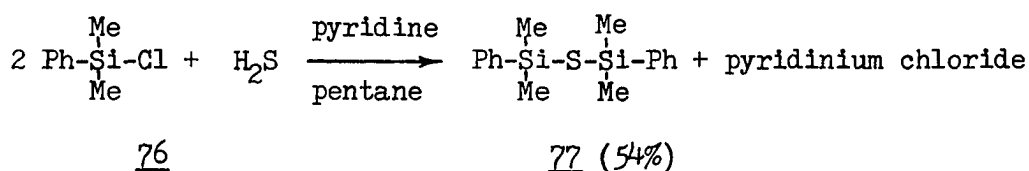
Scheme 16

The reaction of 77 with 73 proceeded smoothly as long as a slight excess of 77 was present, to yield 75 (84%) with a trace of the corresponding siloxane (1.5% by nmr) (Figure 18).

The stench and time involved in preparing and working with 77 however prompted efforts to find other means to 75. Attempts were made to use more readily available chlorosilanes and siloxanes in place of disilthianes to produce the silyldiazoacetates. Thus the reactions of trimethylsilyl chloride and hexamethyldisiloxane with 73 were attempted, but with no success. The compounds were just not reactive enough.

The report of activated carbon chlorides reacting with ethyl argentodiazoacetate 78 in situ (93) made an analogous chlorosilane reaction worth
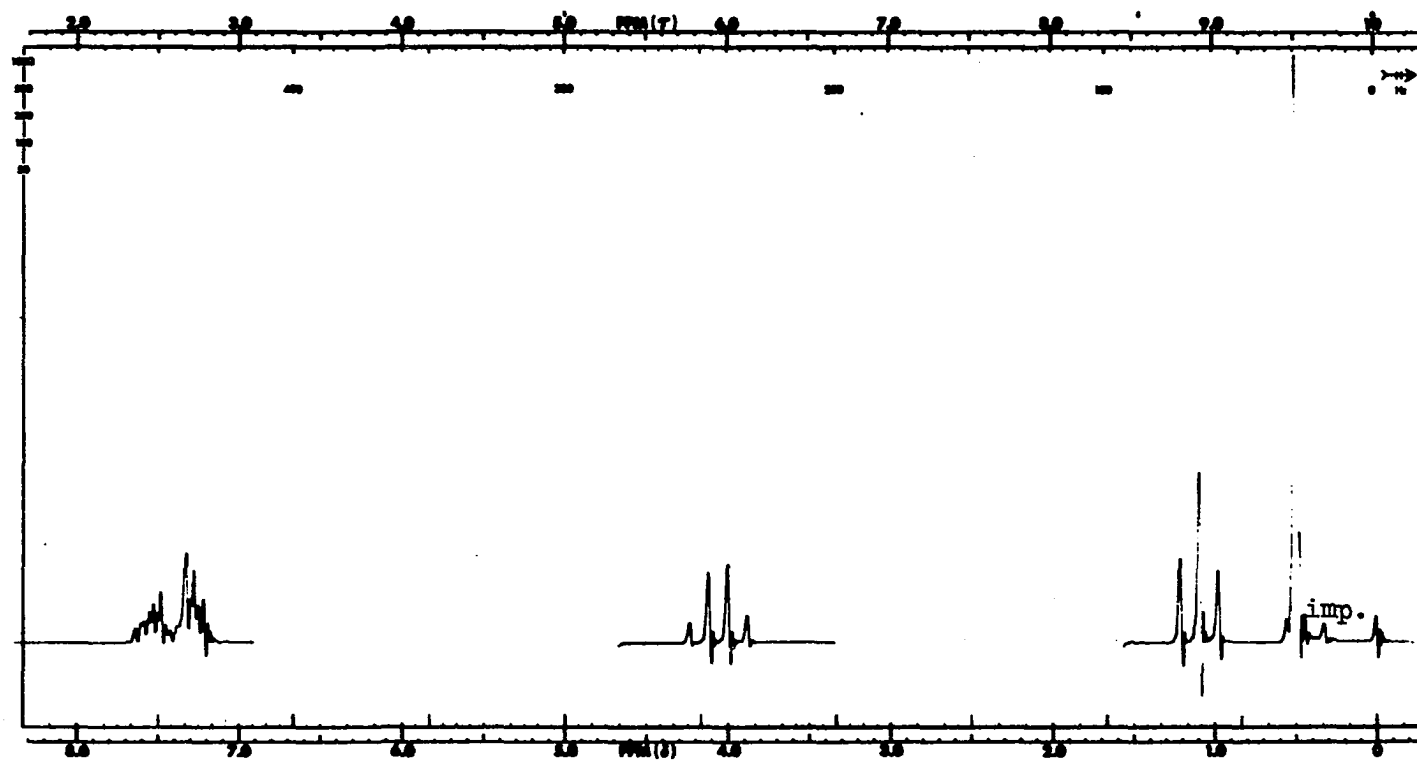
Figure 18. 60 MHz nmr spectrum of purified ethyl diazo(dimethylphenylsilyl)acetate 75

pursuing. There were several problems with the sequence, however. The argento compound was made in a manner similar to that of the mercuri compound 73 using silver oxide and ethyl diazoacetate, but it was thermally unstable and could not be isolated. The water produced as the by-product therefore had to be eliminated in situ. And like the preparation of 73, the reaction was unpredictable.

None-the-less 78 was prepared and anhydrous magnesium sulfate was was added to remove the water, but no reaction occurred with 76.

At about that time the report of Kaufmann and Rühlmann (51) appeared indicating silyl iodides were reactive with 73. Therefore, efforts were directed towards obtaining dimethylphenylsilyl iodide 79. Silyl iodides may be made from silyl hydrides in a number of ways (94). Dimethylphenyl-silane 80 was obtained by the lithium aluminum hydride reduction (91) of the chloride in an 89% yield. The presence of the aryl group presented problems, however, since aryl-silicon bonds can be cleaved by halogens. The reaction of iodine with 80 with no solvent proceeded quite vigorously with extensive cleavage of the phenyl-silicon bond. Since in other iodina-tions, carbon tetrachloride had moderated the reactions, using carbon tetrachloride as solvent was tried. The reaction was not as vigorous but yielded the same result. When the solvent was changed to ethyl iodide (95) the reaction proceeded quite smoothly and 79 was obtained in 38% yield.

The reaction of 79 with 73 also proceeded smoothly to yield 75 in 82% yield. For this compound this preparation seems to be the method of choice. But there was one other method reported in the literature, that of using ethyl lithiodiazoacetate with silyl chlorides (52). For completeness, this reaction was also tried with trimethylsilyl chloride. The reaction is

conducted at -110° and with small molar quantities since the reagents are quite reactive and potentially dangerous. The process proved to be less than satisfactory for several reasons: the reported yield, 50%, was only moderate; the side products of the reaction and unreacted starting materials were difficult to separate and finally, unless the reaction is practiced to gain optimum technique and performance the yields did not approach the literature value. Since the compounds appeared to be more readily obtainable by using iodosilanes and 73, time was not expended in perfecting the reaction using ethyl lithiodiazoacetate.

Vacuum Pyrolysis of α-silyldiazoacetates

Ethyl diazo(trimethylsilyl)acetate 72 had been reported to have remarkable thermal stability (53) since it could be distilled (55°/3.0 mm) easily and could be heated for several hours at 130° without decomposition. Ethyl diazo(dimethylphenylsilyl)acetate 75 also proved to be remarkably stable thermally. Compound 75 could be distilled (104°/0.5 torr) and was stable up to approximately 220° under vacuum pyrolysis conditions.

The increased stability of α-silyldiazocompounds has been attributed (40, 49) to increased importance of the resonance form 81 in the compounds.

$$\begin{array}{c} R' \\ \diagdown \\ \diagup \\ R \end{array} \bar{C}-N{\equiv}N$$

81
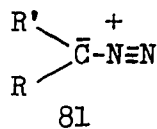
The presence of an α-silicon atom would be expected to destabilize 81 because of its positive inductive effect, but silicon can act also as a pi-acceptor since it possesses energetically available empty d orbitals capable of intereaction with, and stabilization of, the adjacent carbanion center. The presence of the phenyl group in 75 should also increase the

importance of <u>81</u> and thus increase, somewhat, the stability of <u>75</u> (94*).

The nmr spectrum of <u>75</u> in carbon tetrachloride consisted of a complex multiplet for 5 protons from δ 7.70-7.13, a quartet for 2 protons centered at δ 4.08, a triplet for 3 protons centered at δ 1.16, and a singlet for 6 protons at δ 0.50. When <u>75</u> was pyrolyzed at 245-260° and the products collected in a liquid nitrogen cooled trap, nmr showed that the multiplet broadened from δ 7.69-7.02, a new quartet appeared centered at δ 3.72 in addition to the one at δ 4.08, a new triplet appeared centered at δ 1.13 in addition to the one due to <u>75</u>, and a new singlet appeared at δ 0.32 in addition to the one at δ 0.50. The ratio of the new set of absorbances to the absorbances for <u>75</u> was approximately 1:3.6.

Some material could also be washed from the pyrolysis column and an nmr of the material produced complex multiplets from δ 7.7-6.85, from δ 1.45-0.75 and from δ 0.75 to above TMS. In addition, small singlets were observed at δ 0.23 and δ 0.07.

Some decomposition of <u>75</u> appeared to be occurring, and in the trap sample, the new product <u>82</u> appeared to be rather clean. When <u>75</u> was heated to 320-370° under vacuum and an nmr run on the trapped products, the spectrum indicated that no starting material remained. However, besides the new product <u>82</u> which was trapped in the 245-260° pyrolysis, there was significant evidence that other products were also being obtained and that the new product was only about 60% of the materials trapped. Notably in the aromatic multiplet of the products, a singlet had developed at δ 7.11.

As <u>75</u> was pyrolyzed at higher temperatures (to 700°) the amount of <u>82</u> obtained in the 245-260° pyrolysis decreased (to about 35% at 600° and to

*Reference (94), p. 101.

a very small amount at 695-705° while the other products increased in importance. As the amount of $\underline{82}$ decreased so did the intensity of the δ 7.11 singlet, but a new singlet began to appear at δ 0.54.

With the liquid nitrogen trapped products of pyrolyses was also obtained a white solid which rapidly sublimed when the liquid nitrogen trap was removed. The white solid was first noted in the 320-370° pyrolysis and was always obtained in the higher temperature runs. A sample of the sublimed gas was collected after the 700° run and was submitted for mass spectral analysis. The analysis indicated a significant increase in the m/e 44 ion compared to background and thus indicated that the gas could have been carbon dioxide.

The most obvious mode of decomposition for $\underline{75}$ would be to lose molecular nitrogen to form an intermediate carbene species $\underline{83}$. Table 2 summarizes the mass losses observed during the pyrolysis runs at different temperatures.

Table 2 indicated that weight loss began at about 250°. Since spectral evidence indicated no change in a sample pyrolyzed at $200^{\pm}15°$, it would appear that decomposition is concurrent with weight loss (at least at lower temperatures). The mass lost equals approximately the theoretical loss of nitrogen somewhere between 260° and 370°. At higher temperatures, the mass lost exceeded the theoretical nitrogen loss until it more than doubled it at 695-705°. The isolation of carbon dioxide could at least in part explain the additional mass difference. On the basis of the data presented, it is not possible to distinguish between the possibility that one major product $\underline{82}$ is being produced and then further decomposing at higher temperatures, or whether at higher temperatures additional reaction

Table 2. Mass losses observed during pyrolysis of ethyl diazo(dimethyl-phenylsilyl)acetate $\underline{75}$ at various temperatures

Column Temperature (°C)	Original Sample	Theoretical N_2 Loss	Mass Residue[a]	(mg) Column Wash[b]	Trap Sample[c]	Total Collected	Total Lost
200-220	169	18	-	-	169	169	-
245-260	967.1	109	0.4	46.3	899.2	945.9	21.2
320-370	1101.4	124	1.8	77.3	875.4	954.5	146.9
295-420	1053.5	119	6.0	136.1	742.9	885.0	168.5
495-505	1119.9	126	8.9	46.0	852.8	907.7	212.2
695-705	1180.5	133	10.0	17.5	832.7	860.2	320.3

[a]Residue remaining in sample holder at end of run.

[b]Material washed from pyrolysis column with methylene chloride.

[c]Material collected in liquid nitrogen cooled trap (not including CO_2 which sublimed away).

pathways are possible leading to other products at the expense of $\underline{82}$.

Assuming that the carbene intermediate $\underline{83}$ is a likely initial product of the pyrolysis, several intramolecular reactions are possible under high vacuum conditions.

Carboalkoxycarbenes have been observed to produce intramolecular insertion products (87, 89, 96-98) under photolytic conditions. Kirmse, Dietrich and Bücking (86) reported the formation of γ-lactones, in addition to intermolecular insertion products, when t-butyl diazoacetate or t-amyl diazoacetate were photolyzed in the presence of cyclohexane (Scheme 17).

69

Lowe and Parker (98) have reported the formation of a β-lactone in addition to a γ-lactone in the photolysis of N-[(ethoxycarbonyl)diazoacetyl]pyrrolidine and N-[(t-butoxycarbonyl)diazoacetyl]pyrrolidine in carbon tetrachloride in a pyrex vessel. Thus in the former case the following results were observed (Scheme 18).
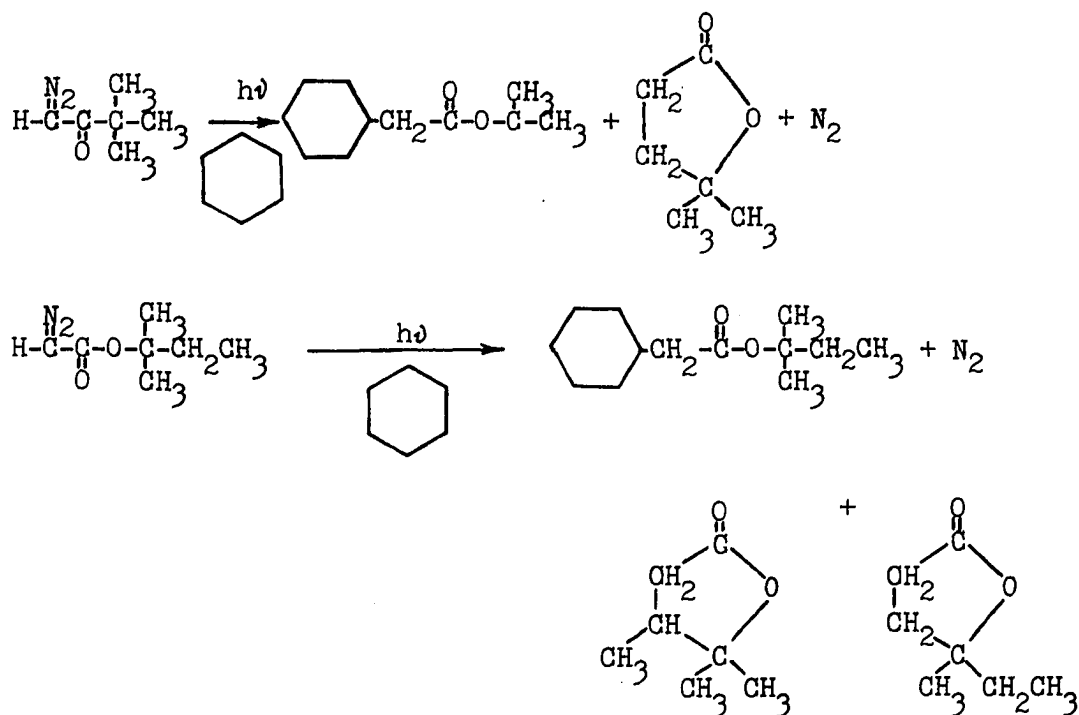
Scheme 17
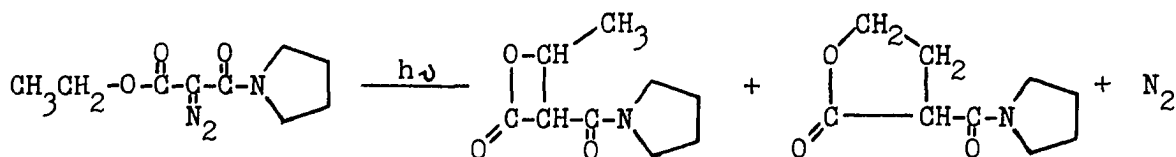
Scheme 18

By analogy two lactones 84 and 85 may be imagined in the pyrolysis of 75 even though the reactions discussed above were photolytic (Scheme 19).

$$Ph(Me)_2Si-CN_2-\overset{O}{\underset{}{C}}-O-CH_2CH_3 \xrightarrow[\triangle]{vacuum} Ph(Me)_2Si-CH\overset{CH_2-CH_2}{\underset{C-O}{\big|}} + Ph(Me)_2Si-CH\overset{CH_3}{\underset{C}{\big\langle}}O + N_2$$

75   **84**   **85**
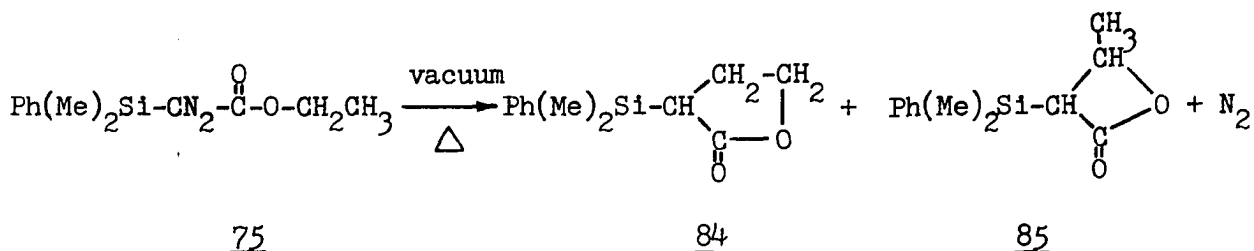
Scheme 19

Of the two lactones the γ-lactone **84** seems the more likely to be found and would be expected to be unstable under the reaction conditions since γ-lactones are known to extrude carbon dioxide under pyrolysis conditions to form olefins (99) and as seen earlier β-lactones also lose carbon dioxide (85).

1,3-intramolecular insertion into one of the silylmethyl carbon-hydrogen bonds to form a silacyclopropane **86** would be another reaction pathway for **82** (Scheme 20).

$$\mathbf{75} \xrightarrow[\triangle]{vacuum} \overset{Ph}{\underset{Me}{\diagdown}}Si\overset{CH_2}{\diagup\diagdown}CH-\overset{O}{\underset{}{C}}-O-CH_2CH_3 + N_2$$

86
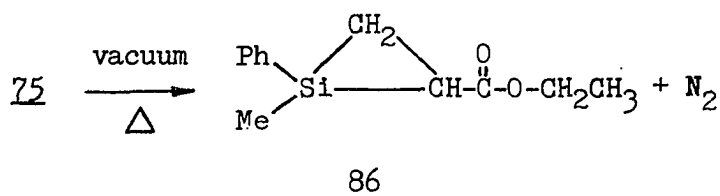
Scheme 20

Numerous attempts have been made to prepare silacyclopropanes but only one has been successful (55). Lambert and Seyferth were able to isolate highly substituted silacyclopropanes such as **87** by treating the correspondingly substituted 1,3-dibromosilapropane in THF with magnesium (Scheme 21).

The successful isolation of **87** and similar silacyclopropanes was attributed to the greater degree of substitution in the product compared to

71

the lightly substituted products expected in other attempts:

Me
  \
   Si————CHR   R = H or alkyl
  /   \   /
Me   CH₂
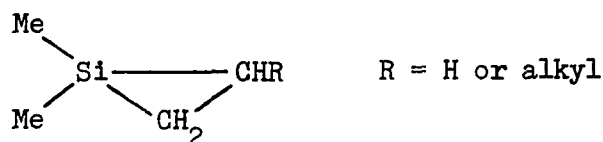
The higher degree of substitution of **87** was considered to give the molecule a higher degree of kinetic stability, but the molecule was still air sensitive and had to be handled under an inert atmosphere. A related silacyclopropane **88** was shown to be more reactive towards a number of reagents (i.e., water, phenol, diethylamine, acetic acid t-butyl mercaptan, etc.) than 1,1-dimethylsilacyclobutane. Ring opened products were formed (100) (Scheme 22). Even **87** reacted exothermally with methanol to produce a ring opened methoxysilane (55). The greater reactivity of **87** and **88** was attributed to greater ring strain and to greater "s" character in the silicon silacyclopropane ring bonding orbitals compared to the ring strain and silicon orbitals in the silacyclobutane (100).
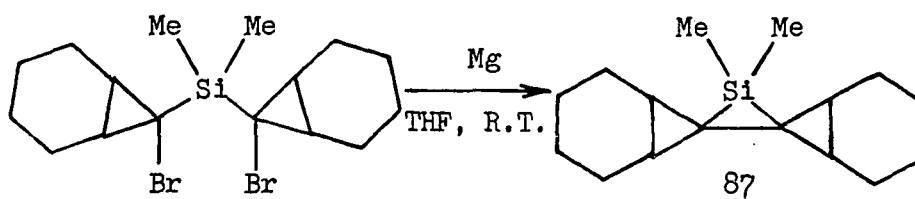
Scheme 21

It should be noted that both **87** and **88** possessed some thermal stability since both could be purified by distillation (95-97°/0.01 mm and 50-51°/3.5 mm respectively) (55).

The silacyclopropane **86** which could arise by 1,3-intramolecular insertion of the carbene intermediate **83** would not be as highly substituted as
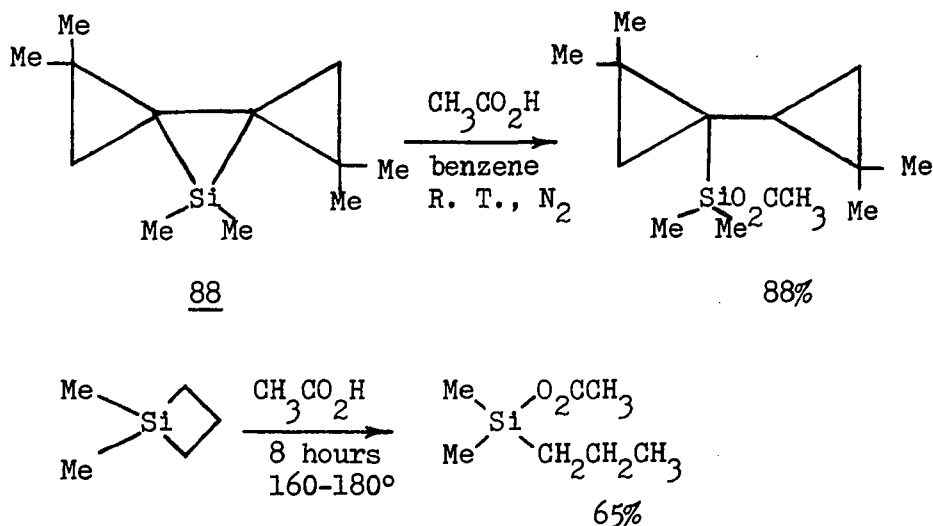
Scheme 22

Scheme 23

87 and if the arguments presented by Lambert and Seyferth (55) hold, would not be expected to be stable.

Another possible mode of reaction for 83 would be a Wolff rearrangement to form ketene 89 (Scheme 23).
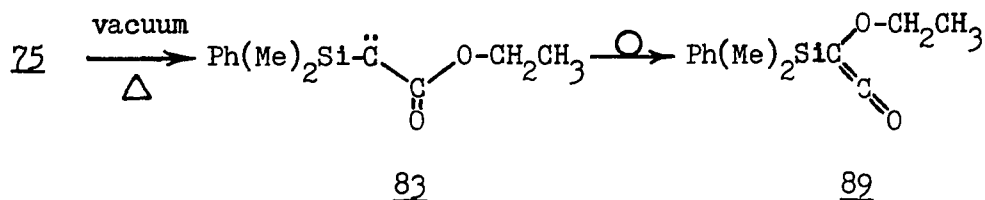
As discussed in the Historical Section, alkoxyketenes, obtained by the Wolff rearrangement of carboalkoxycarbenes, have been trapped but not isolated (70, 84). A number of silylketenes have been isolated by Russian workers (101-108).

In 1965, trimethylsilylketene 90 was reported as the product of the pyrolysis of ethoxy(trimethylsilyl)acetylene (101) (Scheme 24) in 90% yield.

$$(Me)_3Si\text{-}C\text{≡}C\text{-}OCH_2CH_3 \xrightarrow{120\text{-}130°} (Me)_3Si\text{-}\overset{H}{\underset{}{C}}\!\!\diagdown_{C}\diagdown_{O} \quad + \quad C_2H_4$$

$$\underline{90}$$
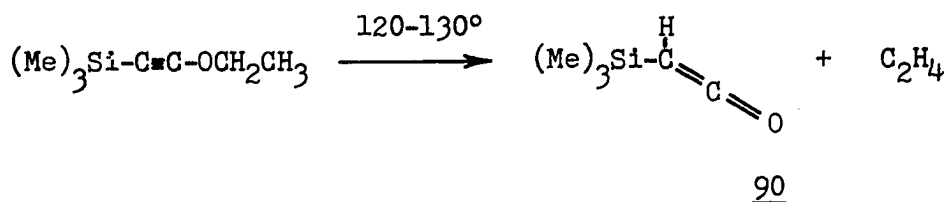
Scheme 24

The procedure appeared to be general and other silylketenes could be prepared in the same fashion (102, 105, 108). 90 and other silylketenes could also be prepared as illustrated in Scheme 25 (103, 106). When the

$$(Me)_3SiCH_2CO_2H \xrightarrow{H_2C=C=O} (Me)_3SiCH_2\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[-(CH_3CO)_2O]{80\text{-}90°, 1 mm} \left[(Me)_3SiCH_2\overset{O}{\overset{\|}{C}}\right]_2 O$$

$$\xrightarrow[30\text{-}40 mm]{140\text{-}150°} \underline{90}, 30\%$$
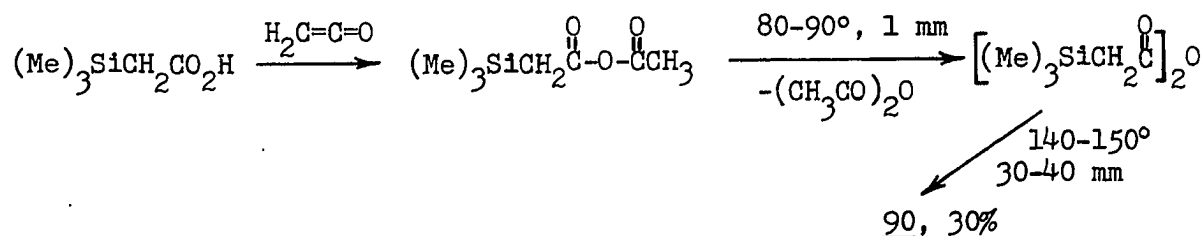
Scheme 25

triethyl analogue was used, the yield of triethylsilylketene was 83% and the loss of acetic anhydride was spontaneous. Silylketenes have also been prepared by dehydrohalogenation of silyl-substituted acid chlorides with tertiary amines (106).

90 and other silylketenes react with water, alcohols, halogens and other reagents to give the expected acids, esters, α-haloacid halides and other derivatives (101). The silylketenes exhibited notable stability with respect to dimerization as compared to ketene and alkylketenes (109). The increased stability was attributed to a decrease in importance of resonance form 91 for silylketenes based upon vibrational spectra data (109, 110) and dipole moment data (110). The data indicated that the substitution of a silyl group, with a positive inductive effect, for hydrogen increased the

C-C bond order and decreased the C-O bond order relative to ketene making

resonance form 92 more correctly the electronic structure for silylketenes

than for most ordinary ketenes (109).

$$\begin{array}{ccc}
\begin{array}{c} R' \\ \diagdown \\[-4pt] \diagup \\ R \end{array}\!\!\overset{-}{C}\!-\!\overset{+}{C}\!\!\equiv\!\!O & \longleftrightarrow & \begin{array}{c} R' \\ \diagdown \\[-4pt] \diagup \\ R \end{array}\!\!C\!=\!C\!=\!O \qquad R, R' = H, \text{trialkyl-silyl} \\[4pt]
\underline{91} & & \underline{92}
\end{array}$$
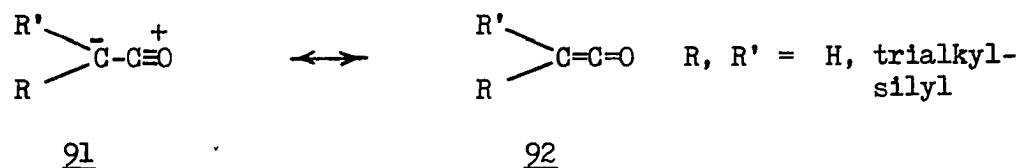
Richardson, Hendrick and Jones (84) observed the loss of carbon mon-
oxide from methoxycarbomethoxyketene obtained in the pyrolysis of methyl
diazomalonate (Scheme 14). An analogous process would be conceivable for
89 to produce the carbene 93 which by analogy could lead to a silylketone
and intramolecular insertion products (Scheme 26).

$$\underline{89} \xrightarrow[\Delta]{-CO} Ph(Me)_2Si\text{-}\overset{..}{\overset{\bullet}{C}}\text{-}OCH_2CH_3 \longrightarrow Ph(Me)_2Si\text{-}\overset{O}{\overset{\|}{C}}CH_2CH_2 + Ph(Me)_2Si\text{-}CH\text{-}O$$

(with $\underline{93}$ below the second structure, $H_2C\text{-}CH_2$ above the third structure, and below, a "+" and the structure:)

$$\begin{array}{c} Ph \\ \diagdown \\[-4pt] \diagup \\ Me \end{array}\!\!Si\overset{CH_2}{=\!\!=}CH\text{-}OCH_2CH_3$$
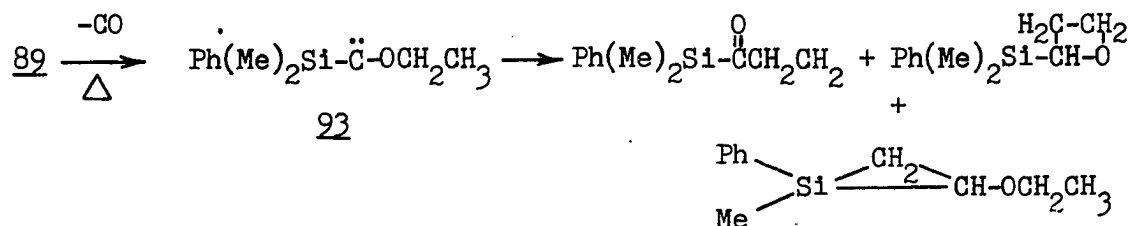
Scheme 26

The nmr spectrum obtained for the liquid nitrogen trapped products
in the 495-505° pyrolysis of 75 suggested that a variety of products
were being produced. The spectrum showed a complex multiplet in the
aromatic region which included a sharp singlet at δ 7.11, some small peaks
in the olefinic proton region at δ 6.02, δ 5.93 and δ 5.85, a quartet at
δ 3.68, a multiplet extending from δ 1.95 to 1.6, a small singlet at
δ 1.48, a triplet centered at δ 1.14, a moderate singlet at δ 0.54 and an
intense singlet at δ 0.30. In addition there were abundant small peaks

and/or multiplets obviously above noise level but of low intensity and difficult to classify (Figure 19).

The ratio of the intensities of the aromatic region to that of the silylmethyl proton region remained 5:6, but the intensity of the new quartet and triplet to the aromatic or silylmethyl protons dropped to about 40%. As mentioned before the drop in intensity of the quartet (and triplet) was reflected in a drop in intensity of the δ 7.11 and δ 0.30 singlets even though the latter two retained the same intensity ratio. The small olefinic resonances which had appeared even at low temperatures remained consistently small. The multiplet at δ 1.95-1.6 varied significantly at different temperatures as did the singlet at δ 0.54 which appeared only at higher temperatures, and increased in importance with increasing temperature.

When the trapped products of the 495-505° pyrolysis were separated using silica gel thin layer chromatography, at least five components could be detected. The separation was scaled up to thick layer proportions and five components were collected. When the least polar and largest fraction was checked for completeness of separation using thin layer chromatography, seven components were detected. The largest layer was chromatographed again and the least polar and largest component again indicated the presence of seven components. One of the smaller components separated in the last chromatography proved to be a solid which upon recrystallization was shown to be phenylacetic acid based on its melting point and nmr spectrum. The presence of the acid could not be seen in the nmr spectrum of the original mixture, hence it was concluded that at least one product of the pyrolysis was unstable and that therefore gas phase chromatography
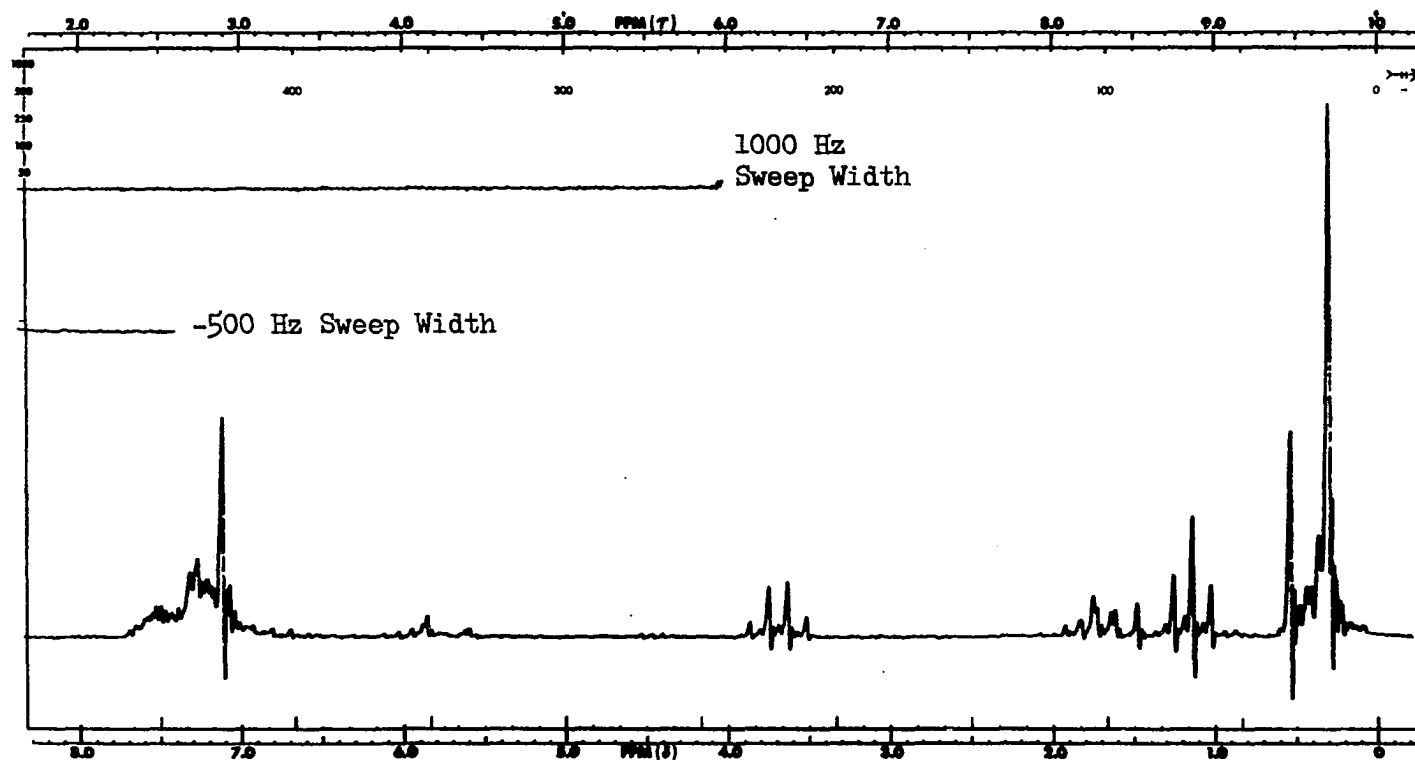
Figure 19.   60 MHz nmr spectrum of trapped products in the 495-505° vacuum pyrolysis of ethyl diazo(dimethylphenylsilyl)acetate 75

76

would probably be a better technique to use.

A pyrolysis at $600^{\pm}5°$ was carried out with five approximately one gram samples of $\underline{75}$. An nmr spectrum of the products obtained indicated that all of the components obtained in the 495-505° and 695-705° runs were present and that it was a representative mixture of the pyrolysis products.

Since the mixture obtained in the 495-505° pyrolysis had been reactive, separate samples were treated with deuterium oxide and methanol. An nmr spectrum of the deuterium oxide treated sample was taken and no change could be detected in the sample. An nmr spectrum of the methanol treated sample did show some change had occurred. The intensity of the singlets at δ 7.11 and δ 0.30 decreased, a small singlet appeared at δ 3.57 and a larger one at δ 3.33, three new small peaks appeared at δ 1.08, δ 0.12 and δ 0.08 and the δ 0.54 singlet essentially vanished. Since the methanol had been removed by using a water pump and some external heat, a sample of the product mixture was dissolved in carbon tetrachloride and then the solvent removed just as the methanol had been. Removal of the carbon tetrachloride caused no change in the nmr of the sample.

It was somewhat surprising that methanol had reacted rapidly with the mixture but that deuterium oxide had not. The difference was probably that the methanol reaction was in a homogeneous mixture but the deuterium oxide formed a heterogeneous mixture and hence any reaction would be slower.

It was determined that separation of the product mixture could be achieved using a butanediol succinate column run at 175°. Twelve distinct peaks could be detected with such a column. The relative areas and

possible resolution of the fractions seemed to depend upon the size of the sample being injected which seemed to suggest that not all of the products were stable under these separation conditions.

For a 1.0 μl sample the following relative areas and retention times were obtained for the separate peaks: a, b and c comprised about 3.4% of the mixture and were seen at 1.0, 1.32 and 1.52 minutes respectively; d, 19.5%, at 2.68 minutes; e, 0.05%, at 3.15 minutes; f, 9.7%, at 3.84 minutes; g, 1.1%, at 4.51 minutes; h, and i, 36.6%, at 5.26 and 5.6 minutes; j, 12.6%, and 6.49 minutes and k, 16.5%, at 11.0 minutes. With larger samples another peak could be seen at about 15.8 minutes.

Since some decomposition was suspected, the integrity of the collection process was checked by separating 50 μl samples and collecting peaks a–j in one fraction and k in a separate fraction. When nmr spectra for the two fractions were obtained, it was found that all of the resonances found in the nmr of the crude mixture were present with some differences in intensities. The spectrum of the second fraction (peak k), for the most part, consisted of those absorbances due to the initial pyrolysis product 82. In the spectrum of the first fraction, those peaks were essentially missing.

Better resolution was obtained using 25 μl injections. 35 samples were chromatographed and collected in 7 fractions consisting of the following peaks: fraction 1 consisting of a, b and c; fraction 2 consisting of d and e; fraction 3 consisting of f and g; fraction 4 consisting of h and i; fraction 5 consisting of j; fraction 6 consisting of k and fraction 7 consisting of l.

Fraction 1 was quite small and even though it consisted of three

components, one of the components could be identified from spectral data obtained. The nmr spectrum was weak but showed only a multiplet in the aromatic region and a singlet at δ 0.30. The mass spectrum gave a molecular ion at m/e 286 which would correspond to 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane. The disiloxane had been a minor impurity in the sample of 75 pyrolyzed.

Fraction 2 was a mixture of two components but one was quite small (peak e). The nmr of fraction 2 showed an aromatic multiplet, a heptet at δ 4.40 for one proton and a doublet at δ 0.32. The spectrum was essentially identical to one obtained for dimethylphenylsilane 80 prepared earlier. A molecular ion at m/e 136 in the mass spectrum of fraction 2 confirmed the structure. The heptet did appear in the nmr spectrum of the crude mixture, but was so small as to be unrecognizable and was generally ignored. 80 did not appear as a product below a pyrolysis temperature of 500°.

The formation of 80 was consistent with the known behavior of alkylsilanes at temperatures exceeding 500° (94*). Above 500° alkylsilanes decompose forming a great variety of products including hydrogen, carbon, silicon, silanes and hydrocarbons among other products.

Fraction 3 was a mixture of two components although one (f) was considerably more abundant than the other (g). An nmr spectrum of the fraction indicated that the ratio of aromatic to silylmethyl protons had remained fairly constant. It further indicated that there were at least two compounds present because of the lower intensity of the other peaks. The presence of dimethylethoxyphenylsilane was suggested by the appearance

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*Reference (94), pp. 122-123.

of a quartet at δ 3.63 proportionally equal to a triplet at δ 1.16. A

singlet at δ 0.32 was also roughly in the same magnitude for six protons.

A mass spectrum for the fractions showed a weak molecular ion at m/e 180

which lost 1 mass unit at higher energies, 15 mass units corresponding to

the loss of a methyl group, 45 mass units to give a dimethylphenylsilyl

ion at m/e 135 and overall the loss of 59 mass units to form an ion at

m/e 121. The latter ion could arise from the $\overset{+}{M}\cdot$-15 ion by the loss of the

elements of acetaldehyde with the concurrent transfer of a proton to a

positively charged silicon atom (Scheme 27) in a process analogous to one

observed by Ihrig for alkylsilanes (111).
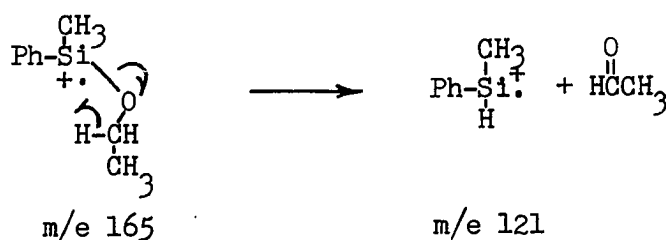
Scheme 27

The nmr spectrum indicated the presence of at least one other com-

pound since there was another methylsilyl proton singlet of slightly

greater intensity at δ 0.22. In addition part of the aromatic multiplet, a

multiplet at δ 2.05-1.74 (for about one proton) and a "set" of peaks at

δ 0.96, δ 0.95-0.80, δ 0.79 and δ 0.55 (accounting for about three protons

altogether) remained unaccounted for. The silylmethyl proton chemical

shift suggested that the fourth bond from the silicon was also to a carbon,

but the pattern of the rest of the peaks was not deciphered. The mass

spectrum of the fraction had not produced another molecular ion and the

structure of the remaining components remains unresolved.

The isolation of dimethylethoxyphenylsilane, which exhibited an nmr spectrum which corresponded closely to the resonances attributed to the initial pyrolysis product 82 and the spectrum attributed to peak k (and 82) earlier, initially cast some doubt on the degree of success in the separations.

That 82 and fraction 3 consisted of different compounds was quickly resolved. Both 82 and dimethylethoxyphenylsilane have almost, but not quite, identical chemical shifts for the quartets, triplets and silyl-methyl singlets but 82 exhibits a strong singlet in the aromatic regions as opposed to a multiplet for the ethoxysilane. In hindsight, the presence of a small additional quartet and triplet could be rationalized in the spectra of the crude pyrolyses products because of the slight shoulders which generally were associated with those peaks. Therefore the quantities of 82 which had been estimated using the intensity of the δ 3.72 triplet would be high and therefore can be taken only as rough approximations.

The ethoxysilane should be reasonably stable, whereas the other component of fraction 3 may not be. The δ 0.54 singlet in the crude product was of some importance but its intensity in the spectrum of fraction 3 was not very great. These data, when considered with the results obtained when the crude mixture was treated with methanol (rapid disappearance of the singlet), supports the notion that the unidentified product is un-stable (or at least quite reactive) and that the minor component (peak g) of fraction 3 is the silylether. The silylether is difficult to ratio-nalize as a primary product of the pyrolysis of 75 and was not one of the products considered earlier.

Fraction 4 consisted of the large peak h and its poorly resolved

shoulder (peak i). An nmr spectrum of the fraction showed that it contained the olefinic components. The aromatic region was a multiplet and the silylmethyl region consisted of two singlets at δ 0.36 and δ 0.29. The remainder of the spectrum showed a multiplet extending from δ 6.73 to δ 6.46 on the basis of the spectrum integration. Predominant in the multiplet were poorly resolved small peaks at approximately δ 6.66, δ 6.54, δ 6.42, δ 6.31, δ 6.23, δ 6.10, δ 5.73, and δ 5.53. Three much more intense peaks could also be differentiated at δ 6.02, δ 5.93 and δ 5.84. Upfield there were two doublets at δ 1.82 and δ 1.68 in the ratio of about 3:1. The upfield doublet was further slightly split. The ratio of the olefinic multiplet to doublets was 2:3.

As indicated earlier olefins could be expected as decarboxylation (Scheme 28) products from lactones 84 and 85 which in turn could be obtained by intramolecular insertion of the intermediate carbene 83 into the ethoxy chain.

$$Ph(Me)_2Si-CH\begin{matrix} \diagup CH_2-CH_2 \\ \diagdown C-O \\ O \end{matrix} \xrightarrow[\Delta]{-CO_2} Ph(Me)_2Si-CH=CH-CH_3 + Ph(CH_3)_2Si-CH_2-CH=CH_2$$

cis- and trans-94   95

84

$$Ph(Me)_2Si-CH\begin{matrix} \diagup \overset{CH_3}{CH} \\ \diagdown C \diagup O \\ O \end{matrix} \xrightarrow[\Delta]{-CO_2} Ph(Me)_2Si-CH=CH-CH_3$$

cis- and trans-94

85
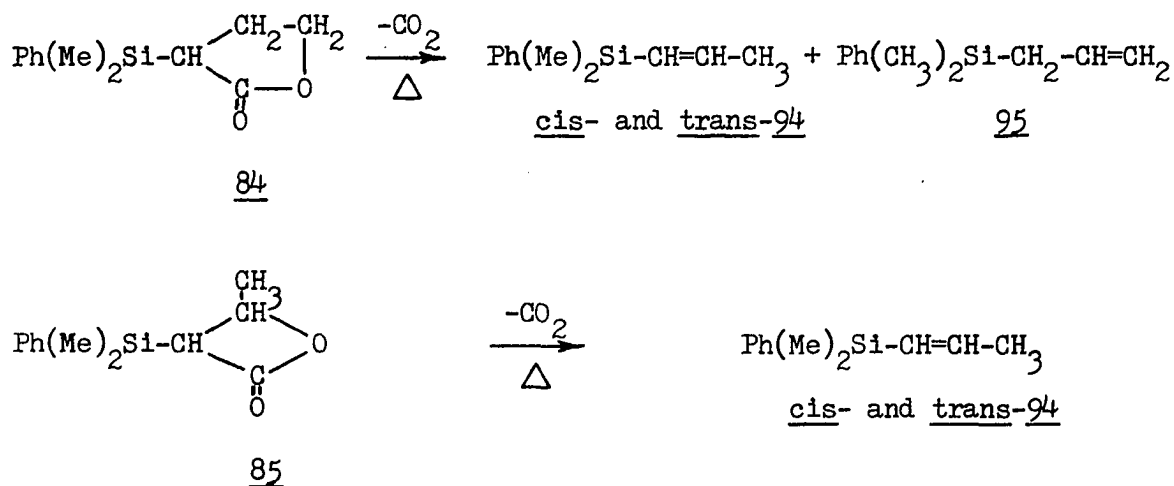
Scheme 28

Both lactones could produce the same olefins, cis- and trans-propenyl-

dimethylphenylsilane 94 if a 1,2-hydrogen transfer occurs from the decar-boxylation intermediate of 84. With a different hydrogen shift, 84 could also yield the allyl-product 95.

The allyl-product 95 would be expected to show terminal vinyl protons at about δ 4.95 (112) and there are no protons in that region of the spectrum taken for fraction 4.

Cis- and trans-propenylsilanes similar to cis- and trans-94 have been studied by Seyferth and Vaughan (113). They obtained the nmr spectra for cis- and trans-propenyltrimethylsilane 96. Trans-96 showed one olefinic proton as a pair of quartets (J = 18.6 cps) at δ 6.41 and δ 6.11, the second as a doublet (J = 18.6 cps) at δ 5.76 and the methyl group protons of the propenyl substituent as a doublet (J = 5.4 cps) at δ 1.95. Cis-96 showed one olefinic proton as a sextet (J = 7.2 cps) at δ 6.35, the second as a doublet (J = 14.4 cps) at δ 5.40 and the methyl group as a doublet (J = 7.2 cps) at δ 1.75.

By analogy the δ 5.84 and δ 5.53 peaks (J = 18 cps) in the spectrum of fraction 4 could be taken as the doublet of trans-94, the peaks at δ 6.02 and δ 5.93 (J = 5 cps) as part of the pair of quartets and the doublet at δ 1.82 (J = 5 cps) being the methyl group protons of the trans isomer.

The cis isomer then would be the minor component of the mixture with its methyl group protons at δ 1.68 (J = 7 cps) and the peak at δ 5.73 being part of the olefinic doublet. Some of the small downfield peaks could be part of the olefinic sextet but they were quite ill-defined.

Assuming the assignments above, the ratio of cis to trans isomers of 94 would be 1:3. The assignment of structure 94 to the material was

supported by the presence of a strong band at 1622 cm^{-1} and a moderate one at 985 cm^{-1}. Seyferth and Vaughan (113) had reported 1620 and 987 cm^{-1} for trans-96. Fraction 5 appeared to be essentially peak j but has not been characterized. The nmr spectrum of the material consisted of an aromatic multiplet for five protons, a multiplet from approximately δ 3.8 to 3.4 for about 0.5 proton, a multiplet at δ 2.0-1.65 for about 0.7 proton, a multiplet resembling a triplet at δ 1.33-1.02 for about 0.7 proton and a group of multiplets at δ 0.6-0.49, δ 0.49-0.18 and δ 0.18-0.0 for a total of about three protons. The integrity of the phenyl silylmethyl ratio had been lost and the spectrum resembled closely the spectra obtained for the column washings in other runs. It could then represent the more volatile components of a complex mixture.

Fraction 6 corresponded to peak k and the nmr spectrum of the fraction was consistent with that obtained earlier (Figure 20). There was considerable impurity present, however, which appeared to be and probably was carried over from fraction 5. Excluding the carry-over, the spectrum showed a singlet in the aromatic region, a quartet for an ether bonded ethyl group methylene, an ethyl group methyl triplet and a silylmethyl singlet. The ratio of intensity was 5:2:3:6. The data suggested a ketene derived from 83 by a Wolff rearrangement, a process which was considered earlier.

The ketene would have a molecular ion at m/e 220 and the mass spectrum of fraction 6 exhibited such an ion. A ketene would also be expected to have a band at about 2150 cm^{-1} (114) in the ir with no carbonyl band in the 1700 cm^{-1} frequency range. An ir spectrum of fraction 6 exhibited a ketene band at 2080 cm^{-1} but had no carbonyl band. The data strongly support the assignment of the dimethylphenylsilylethoxy ketene 82.

1000 Hz
Sweep Width
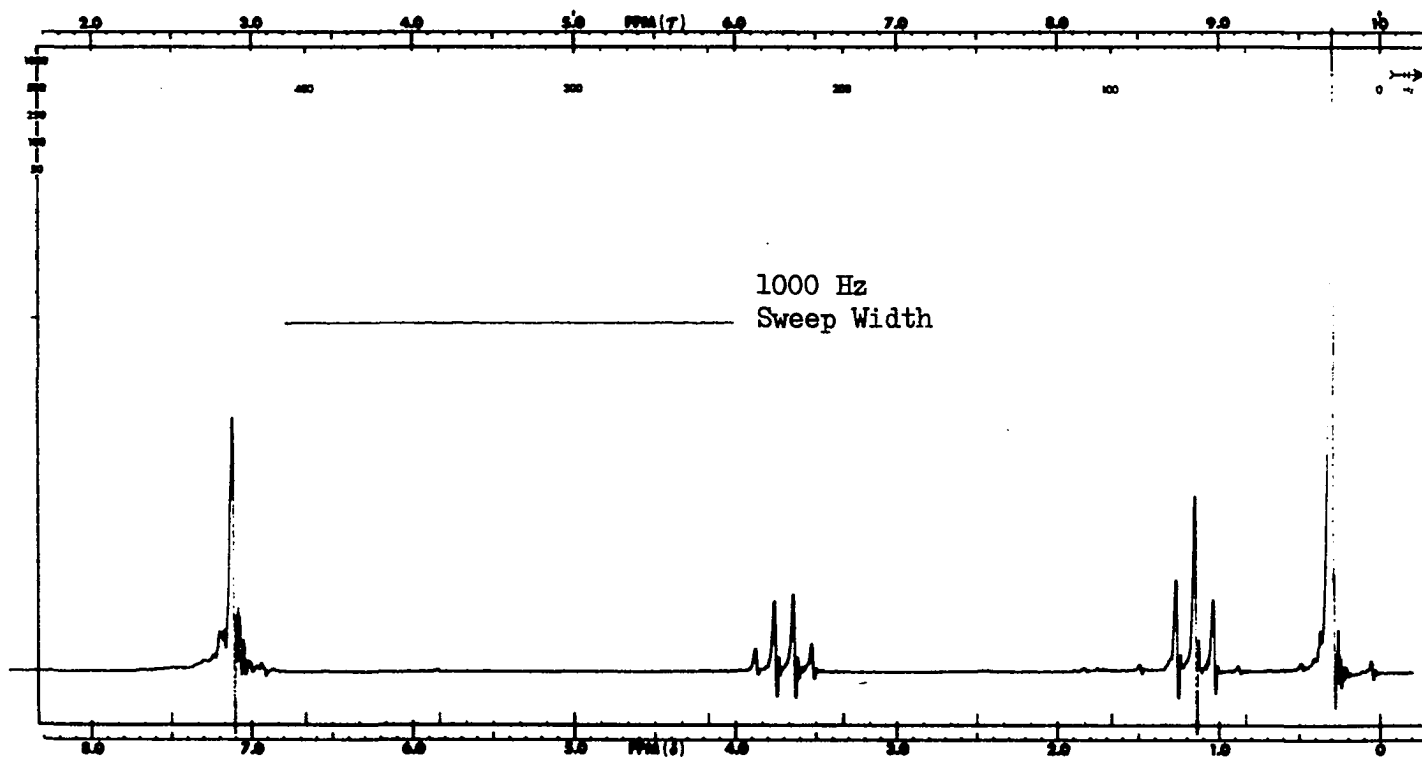
Figure 20. 60 MHz nmr spectrum of gc collected dimethylphenylsilylethoxyketene 82

The isolation of this ketene was of considerable interest. It represents the isolation of a ketene derived by a Wolff rearrangement of an alkoxy group. It was a silylketene which also had considerable stability despite the presence of the ethoxy group. Other alkoxyketenes had been observed only as reactive intermediates (70, 84).

The presence of the silylgroup apparently overcame the destabilizing effect of the alkoxy group since the structural integrity of the ketene was retained during the considerable period of time that it took to separate the mixture.

Peak 1 was also collected as fraction 7. An nmr spectrum of the material was essentially the same as the spectrum obtained for fraction 5 except for a large singlet at δ 0.30. The mass spectrum of the material produced a molecular ion at m/e 186 which again suggested the presence of 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane. It is not inconceivable that the disiloxane isolated in fraction one could have been tailings from fraction 7, since the latter fraction was quite broad.

Thus the pyrolysis of $\underline{75}$ at $600^{\pm}15°$ produced several compounds, and structures for some may be proposed on the basis of spectral data. Two of those products, the ketene $\underline{82}$ and the silylhydride $\underline{80}$, could be expected to be reactive and there was evidence that at least one other product produced at higher temperatures was reactive. The ketene $\underline{82}$ appears to be the major product (especially at lower temperatures) with the other materials being produced in amounts dependent upon the pyrolysis temperature. Some of the products identified can be rationalized on the basis of known reaction pathways. Overall the pyrolysis can be summarized by Scheme 29.

$$Ph(Me)_2Si\text{-}\overset{N_2}{\underset{O}{C}}\text{-}C\text{-}OCH_2CH_3 \xrightarrow[\Delta]{-N_2} Ph(Me)_2Si\text{-}\overset{..}{C}\text{-}\overset{}{\underset{O}{C}}\text{-}OCH_2CH_3$$

$$\underline{75} \qquad\qquad\qquad \underline{83}$$

$$Ph(Me)_2Si\text{-}CH\overset{\overset{CH_3}{\underset{}{CH}}}{\underset{\overset{C}{\underset{O}{}}}{}}O \qquad Ph(Me)_2Si\text{-}\overset{OCH_2CH_3}{\underset{C\overset{}{\diagdown}_0}{C}} \qquad Ph(Me)_2Si\text{-}H$$

$$\underline{85} \ (\text{and/or } \underline{84}) \qquad\qquad \underline{82} \qquad\qquad \underline{80}$$

$$\bigg\downarrow -CO_2 \qquad\qquad\qquad \bigg\downarrow ? \qquad\qquad +$$

$$Ph(Me)_2Si\text{-}CH\text{=}CH\text{-}CH_3 \qquad Ph(Me)_2Si\text{-}OCH_2CH_3 \quad Ph(Me)_2SiOSi(Me)_2Ph$$

$$\text{cis- and } \underline{\text{trans-}94} \qquad\qquad\qquad\qquad (\text{product ?})$$
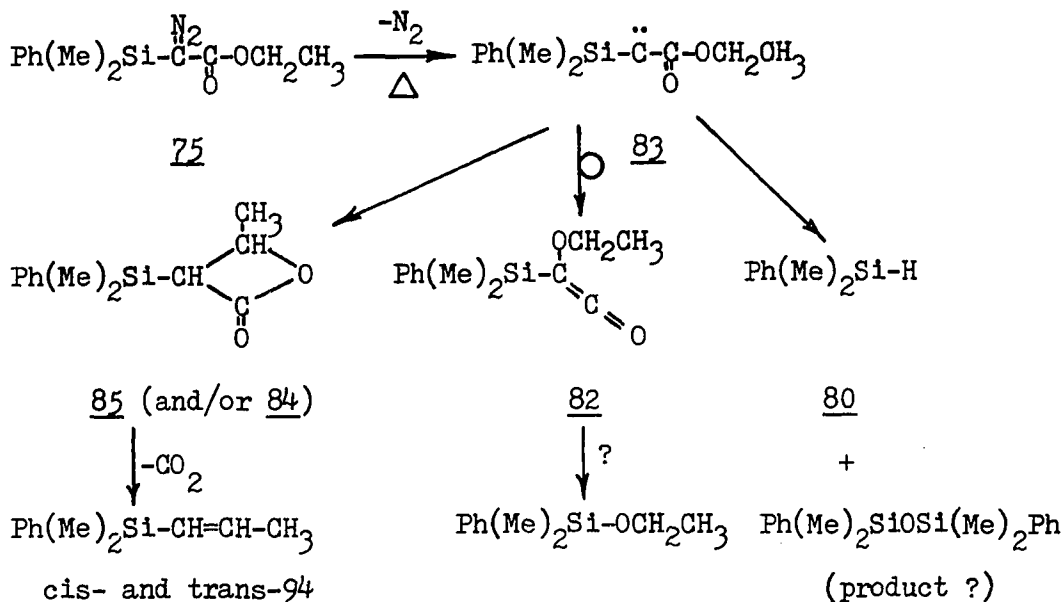
Scheme 29

The unexpected isolation of 82 prompted the investigation of its reactions and the remaining unidentified products of the pyrolysis were not investigated further.

It was found that pyrolysis of 75 at about 300° was the optimum temperature for maximum production of 82 unaccompanied by large amounts of recovered starting material. Below 300° starting material remained unconsumed and higher temperatures lead to more complex reaction mixtures.

Since 82 would be expected to be reactive, and indeed did react rapidly with methanol, it seemed best to continue to isolate it by gas chromatography. The process was slow and tedious and at best produced small amounts of ketene.

Seyferth, Dow, Menzel and Flood (40) had purified a sample of tri-methylsilyldiazomethane 65 for analysis by gas chromatography with success. When a sample of 75 was chromatographed higher temperatures were required

because of its decreased volatility. It became apparent that the purification of 75 was accompanied by decomposition at the higher column temperatures. Furthermore, the higher the temperature, the more the chromatogram pattern began to look like that obtained from pyrolysis mixtures.

By experimenting with different temperatures and column lengths it became obvious that the vacuum pyrolysis step could be avoided and that the pyrolysis, separation and collection could be accomplished in one step using the chromatograph as an oven. Several column packings worked equally well, but the length of needle used to inject the sample of 75 made a difference. Apparently for maximum decomposition of 75 to occur, the sample had to be injected onto the hot surface of the injection port. The optimum temperature for the injection port seemed to be about 200° which was at least 50° below that necessary to effect pyrolysis in vacuum. The longer residence time in the hot injection port as compared to the pyrolysis tube might account for the lower decomposition temperature.

About a 30% yield of 82 could be obtained by the gc pyrolysis-collection method. The purified ketene had a green-yellow color like most ketoketenes (115) which was almost indistinguishable from the appearance of 75. When the other products produced in the process were collected there was strong evidence for the presence of the olefins 94 and dimethyl-ethoxyphenylsilane among the products.

Even with the improved method of obtaining the ketene, large quantities were still not available. Therefore those reactions carried out with 82 were generally done in solution in an nmr sample tube. It was hoped that by conducting reactions in this manner, smaller quantities could be used and work-ups might be eliminated if the products were also

spectroscopically discernible. The technique also had the added advantage of allowing the reaction course to be followed spectroscopically.

Generally the samples of 82 collected were stored in a jar filled with desiccant in a freezer, but occasionally samples were left at room temperature in CCl_4 or $CDCl_3$ solution. The samples remained unchanged for several days when they were stored in either manner, attesting to the remarkable unreactivity of 82 towards dimerization.

82 could be expected to react with a variety of reagents (116). A reaction with methanol had been observed to occur earlier using the crude trap mixture obtained in the $600\pm5°$ pyrolysis, therefore a purified sample of ketene 82 dissolved in carbon tetrachloride was treated with a few drops of methanol in an nmr sample tube.

The sample was kept in a freezer except when a spectrum of the reaction was being recorded, but slight changes could be observed after one hour. A new peak began to appear at δ 3.53 and several new peaks at δ 0.13, δ 0.08 and δ 0.05. After 13 hours, the aromatic singlet was greatly reduced in area and was being replaced by a multiplet, the ethyl group methylene quartet had essentially vanished, the ethyl group triplet had diminished and was superimposed on a multiplet and the δ 0.30 methyl-silyl singlet had been diminished. The δ 3.53 peak had intensified as had the new upfield peaks. In addition a new broadened singlet began to appear at δ 3.61. The intensity ratios of the various regions had not changed however. After 21 hours, the aromatic protons were a multiplet, a new quartet appeared at δ 4.10, the δ 3.61 singlet had greatly intensi-fied. The triplet region appeared to be a triplet of triplets and the δ 0.13 and δ 0.08 peaks had become the most intense in the spectrum.

The sample was then left overnight in the freezer and allowed to stand for four hours at room temperature the next morning. An nmr spectrum at that point revealed that the ketene had been substantially consumed, and the excess methanol was removed under water pump pressure. The residue obtained was again dissolved in CCl_4 and an nmr spectrum recorded (Figure 21).

The new quartet now appeared in the region expected for the methylene of an ethyl ester and one triplet had been lost along with the δ 0.05 singlet. Integration showed that about 10% of the silylmethyl proton resonance had been lost and that about 20% of the ethyl group resonance had been lost. The new peak mentioned above at δ 3.53 now appeared as two singlets (or a doublet) at δ 3.52 and δ 3.49. The large singlet at δ 3.63 could be the methyl resonance of a methyl ester and the singlet at δ 3.33 could be unremoved methanol. The large chemical shift difference in the two remaining triplets suggested that there were two quite different ethyl groups present, but only the quartet at δ 4.13 was clearly discernible.

A mass spectrum obtained for the reaction mixture produced three intense molecular ions at m/e 266, 252 and 238. The expected product of the reaction, methyl (dimethylphenylsilyl)ethoxyacetate 96, would have a molecular weight of 252. An infrared spectrum of the reaction mixture gave a carbonyl stretch at 1726 cm^{-1} which was quite strong.

The other two molecular ions cited above have a mass difference of 14 units from m/e 252. They could be accounted for if instead of having a methyl ester and ethyl ether as in 97, a methyl ester-methyl ether (for m/e 238) and an ethyl ester-ethyl ether (for m/e 266) were also obtained.
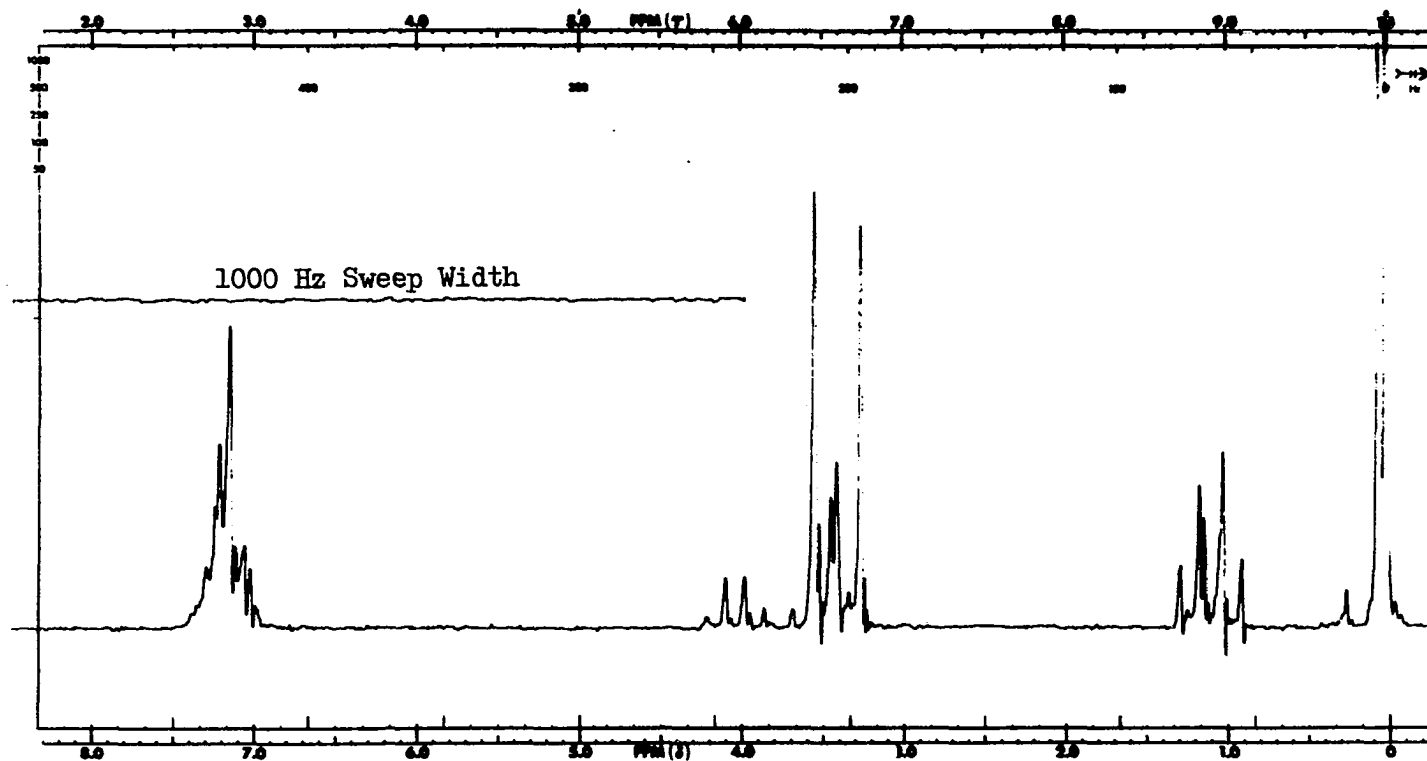
Figure 21.   60 MHz nmr spectrum of the products obtained from the reaction of dimethylphenyl-
silylethoxyketene 82 with methanol

To produce a methyl ether product would require a rearrangement during the addition of methanol to the ketene to yield ethyl (dimethyl-phenylsilyl)methoxyacetate $\underline{98}$. The ethyl ester then could undergo trans-esterification to yield methyl (dimethylphenylsilyl)methoxyacetate $\underline{99}$ with its molecular weight of 238. Compound $\underline{98}$, of course, would have a molecular weight of 252, like $\underline{97}$. Transesterification of the normal addition product $\underline{97}$ would produce ethyl (dimethylphenylsilyl)ethoxyacetate $\underline{100}$ with a molecular weight of 266.

$$OEt$$
$$Ph(Me)_2Si-\underset{\underset{H}{|}}{C}-CO_2Me$$

$$\underline{97}$$

$$OMe$$
$$Ph(Me)_2Si-\underset{\underset{H}{|}}{C}-CO_2Et$$

$$\underline{98}$$

$$OMe$$
$$Ph(Me)_2Si-\underset{\underset{H}{|}}{C}-CO_2Me$$

$$\underline{99}$$

$$OEt$$
$$Ph(Me)_2Si-\underset{\underset{H}{|}}{C}-CO_2Et$$
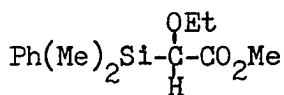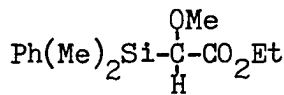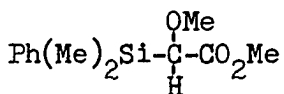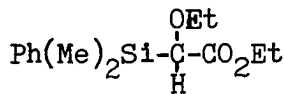
$$\underline{100}$$

Rearrangements of ketenes during the addition of nucleophiles have not previously been observed. The silyl ketenes produced by the Russian workers added a number of reagents in the normal fashion (101). Ethoxy-ketene has been trapped with a number of alcohols (77, 78, 80).

Chaimovich, Vaughan and Westheimer (77) trapped ethoxyketene generated by photolysis of ethyl diazoacetate with perdeuteriomethanol as solvent with the results shown in Scheme 30.

The methyl ethoxyacetate product was accounted for by addition of the solvent to the ketene, but the ethyl methoxy product was accounted for by insertion of the carbene into the O-D bond of the solvent. No evidence for

methyl methoxyacetate or ethyl ethoxyacetate was presented. They also photolyzed phenyl diazoacetate in methanol to obtain phenyl methoxyacetate and methyl phenoxyacetate among other minor products. Again, they reported no phenyl phenoxyacetate or methyl methoxyacetate.

$$CH_3CH_2O\overset{O}{\overset{\|}{C}}CHN_2 \underset{\longleftarrow}{\overset{CD_3OD}{\longrightarrow}} CH_3CH_2O\overset{O}{\overset{\|}{C}}CDN_2 \overset{h\nu}{\longrightarrow} CH_3CH_2O\overset{O}{\overset{\|}{C}}CD\colon + N_2$$

$$CH_3CH_2OCD{=}C{=}O$$

$$\downarrow CD_3OD$$

$$CH_3CH_2OCD_2\overset{O}{\overset{\|}{C}}OCD_3$$

$$\overset{CD_3OD}{\longrightarrow} CH_3CH_2O\overset{O}{\overset{\|}{C}}CD_2OCD_3$$
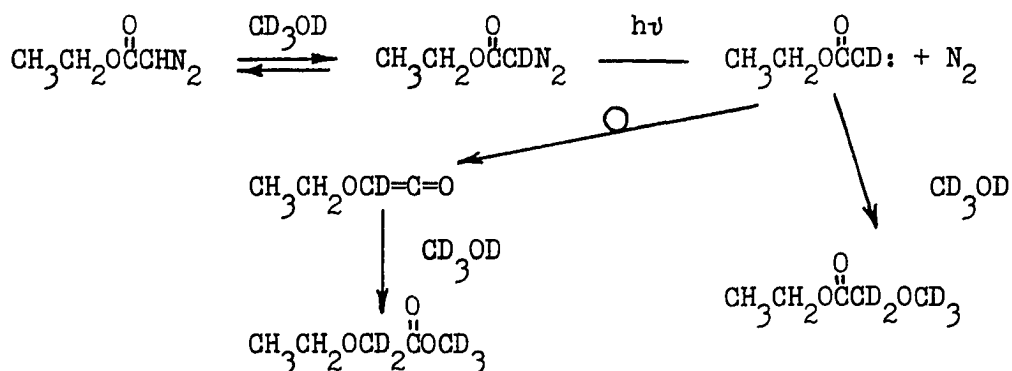
Scheme 30

Strausz, DoMinh and Gunning also investigated the reactions of ethoxy-ketene in alcohols (78, 80). When they photolyzed ethyl diazoacetate in isopropanol they isolated four products 101-104. The formation of 101 was accounted for by addition of solvent to ethoxyketene in the expected

$$CH_3CH_2OCH_2\overset{O}{\overset{\|}{C}}OCH{\overset{CH_3}{\underset{CH_3}{}}}$$

101 (29%)

$${\overset{CH_3}{\underset{CH_3}{}}}CHOCH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$$

102 (25%0

$${\overset{CH_3}{\underset{CH_3}{}}}CHOCH_2\overset{O}{\overset{\|}{C}}OCH{\overset{CH_3}{\underset{CH_3}{}}}$$

103 (12%)

$${\overset{CH_3}{\underset{CH_3}{}}}\overset{}{\underset{OH}{C}}CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$$

104 (9%)
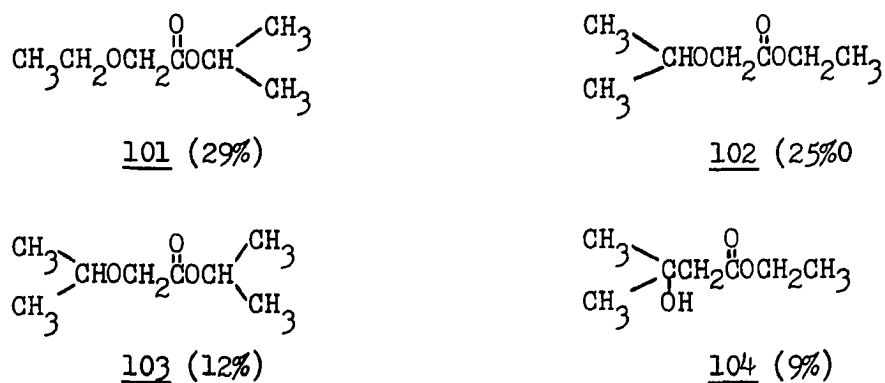
manner. 104 was considered to be the result of insertion of the carbene into the tertiary carbon-hydrogen bond of isopropanol.

102 which would be analogous to the methoxyacetate products reported by Westheimer's group (77) was considered to be the result of a polar addition of the intermediate carbene to isopropanol rather than insertion into the oxygen-hydrogen bond. In neither case, however, were those products considered to be derived from ketene intermediates.

The final product 103, which would be analogous to 99 was considered to be the result of a rather general exchange reaction (80) between ion pairs produced by photolysis. Significantly, when ethyl diazoacetate was photolyzed in the gas phase (with isopropanol present) only 101 and ketene degradation products were obtained.

The same group noted that thermolysis of ethyl diazoacetate produced 101-104 with 102 and 104 strongly predominating (80). They did not report any product analogous to 100.

As was noted above, the exchange reaction leading to 103 was considered to be general (80) and the authors noted that the efficiency of exchange varied with respect to substituents in the order PhO $\simeq$ MeO$>$EtO$>$ i-PrO $\simeq$ allylO $\simeq$ t-BuO, and with respect to the solvent, Me$<$Et$<$i-Pr$<$ t-Bu alcohol.

A similar reaction possibly involving a silylalkoxyketene has also been reported. Ando, Hagiwara and Migita (117) photolyzed ethyl diazo-(trimethylsilyl)acetate 72 in alcohols and found four products 105-108.

105 was considered the product of carbene reaction with solvent, 107 as the result of an intermediate ketene and 108 was accounted for by the intermediacy of an unstable silicon carbon double bonded species. Product 106 which would be analogous to 98 was again thought to be derived from an ion pair process.

$$(Me)_3Si-\overset{\overset{H}{|}}{\underset{\underset{OR}{|}}{C}}-CO_2Et$$

105

$$(Me)_3Si-\overset{\overset{H}{|}}{\underset{\underset{OR}{|}}{C}}-CO_2R$$

106

$$(Me)_2Si-\overset{\overset{H}{|}}{\underset{\underset{OEt}{|}}{C}}-CO_2R$$

107

$$(Me)_2Si-\overset{\overset{Me}{|}}{\underset{\underset{OR\ H}{|}}{C}}-CO_2Et$$
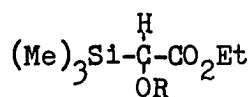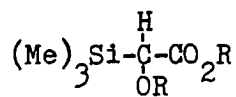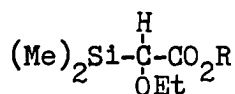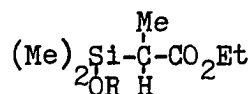
108

Hill, Senter and Hill (118) reported the preparation, isolation and reactions of phenoxyketene and six chlorine-substituted phenoxyketenes. They observed no unusual processes occurring.

The nmr spectrum of the reaction mixture (Figure 21) substantiated the presence of more than one product in the reaction of $\underline{82}$ with methanol. The quartet at δ 4.11 is indicative of a methylene in an ethyl ester and just upfield can be seen a small quartet at δ 4.09 suggesting the presence of a second, but less concentrated, ethyl ester. The ethyl esters could be $\underline{98}$ and $\underline{100}$ (or vise versa). The small peak at δ 3.77 could represent the most downfield portion of a quartet for the methylene of an ethyl ether. An ethyl ether group should be present in both $\underline{97}$ and $\underline{100}$. Two ethyl triplets might be expected since the triplets due to the ethyl esters should be found with little difference in chemical shift. The triplet due to the ethyl ethers should be in a very different molecular environment and would be expected to exhibit a chemical shift different from the ester triplet.

If there are both methyl esters and ethers present, two distinctly different methyl singlet resonances should be seen. The singlet at δ 3.62 would correspond to a methyl ester and the singlet at δ 3.33 would

correspond to a methyl ether. The downfield singlet appears to be larger but that may be due to the fact that one portion of the ethyl ether quartet should also absorb at that point.

The peaks at δ 3.52 and δ 3.49 could be interpreted as the methyne protons of these compounds. The analogous methylene protons in ethoxy-acetic acid appear at δ 4.13 (119) but the proton in the present compound would be shielded by silicon. The methyne proton for 97 and 100 could be expected to be slightly different than the corresponding proton in 98 and 99. If there are two types of ethers present, the ether carbon atoms bonded to the silyl groups would not only be asymmetric but crowded, therefore a change from ethyl to methyl could influence the chemical shifts of the silylmethyl protons. If that is the case, two silylmethyl proton peaks might be expected as found.

The nmr spectrum, then, does not refute the possibility of all four ester-ethers being present, but there are other interpretations of the spectrum.

In the nmr spectrum of triethoxymethylsilane, the ethyl protons absorb at δ 1.22 for the triplet and δ 3.80 for the quartet and the methyl protons are found at δ 0.12 (120). The spectrum is of interest because of the chemical shift of the silylmethyl protons found in Figure 21 and because of the chemical shift found for one of the triplets. The δ 0.12 singlet and δ 1.22 triplet could be interpreted as due to the methyl and ethoxy groups respectively in dimethyldiethoxysilane. There was no molecular ion found for such a compound in the mass spectrum of the reaction mixture. Similarly, the δ 3.62 singlet could be interpreted as a silyl-methoxy group since trimethoxymethylsilane produces a methoxy singlet at

δ 3.55 as well as a silylmethyl singlet at δ 0.12 (120*). Again, however,
no molecular ion for the compound could be found, nor could an ion be
found for any combination of ethoxy, methoxy or hydroxy groups on a
dimethylsilyl moiety.

The δ 3.33 singlet could also be interpreted as excess methanol,
however, as mentioned earlier, about 20% of the protons originally present
in the ethyl triplet region were lost as one of the triplets was lost.
The loss was thought to be due to the loss of ethanol produced in a trans-
esterification process, and if ethanol was removed under waterpump
pressure any methanol present should also have been eliminated as well.

97 may be accounted for by the normal addition of methanol to 82
(Scheme 31). The intermediate resonance form 109 for the addition process
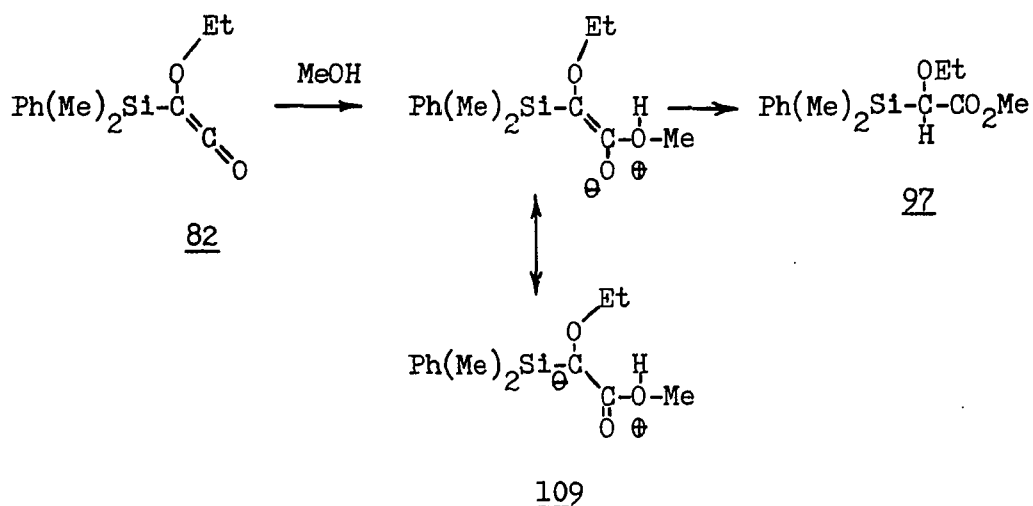
Scheme 31

would be destabilized by the resonance effect of the ethoxy group, but
stabilized by the resonance effect of the silyl group. Since the two

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*Reference (120), spectrum number 93.

effects are opposite and since normal addition occurs for alkylketenes in which the analogous resonance form is destabilized by an inductive effect, it could be expected that normal addition should occur.

In order to obtain 98 either an exchange of alkoxy groups or a rearrangement would have to occur during the addition process. Vinyl ethers are more reactive than simple ethers, particularly in the presence of acid catalysis, but the acid usually protonates in the β-alkene carbon and leads to the formation of a carbonyl compound (116*). In the case of ketenes the attack of strong electrophiles has been shown to occur, but at the terminal carbon of the ketene (70).

Exchange of alkoxy groups initiated by nucleophilic attack of methanol at the terminal ketene carbon can be imagined (Scheme 32). The terminal ketene carbon in 82 could have some electrophilic character because
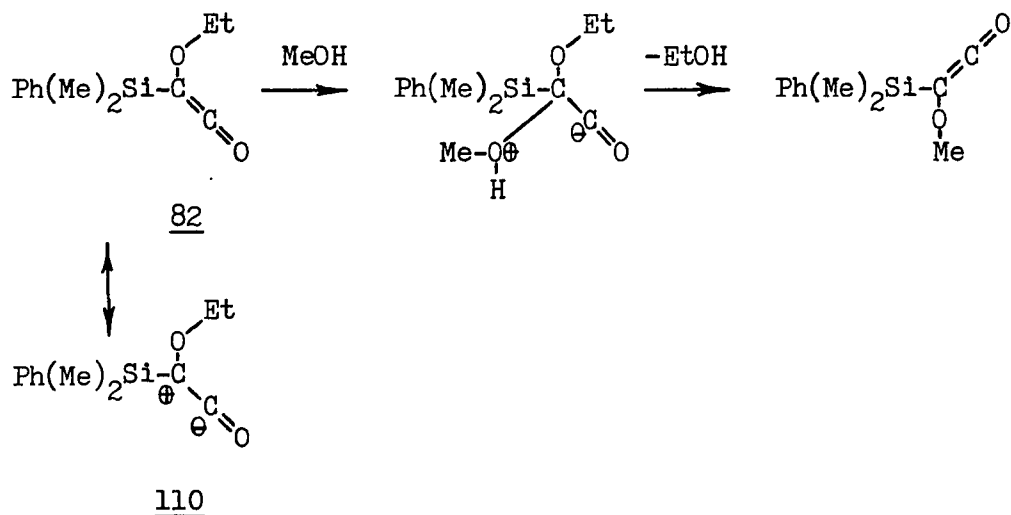
Scheme 32

the resonance form 110 could be expected to be stabilized due to the

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*Reference (116), p. 307.

positive resonance effect of the ethoxy group and positive inductive effect of the phenylsilyl group (121).

An alkoxy exchange might also be imagined as in Scheme 33 involving a ketene-carbene equilibrium in which the carbenic species could be stabilized by the same factors as 110.
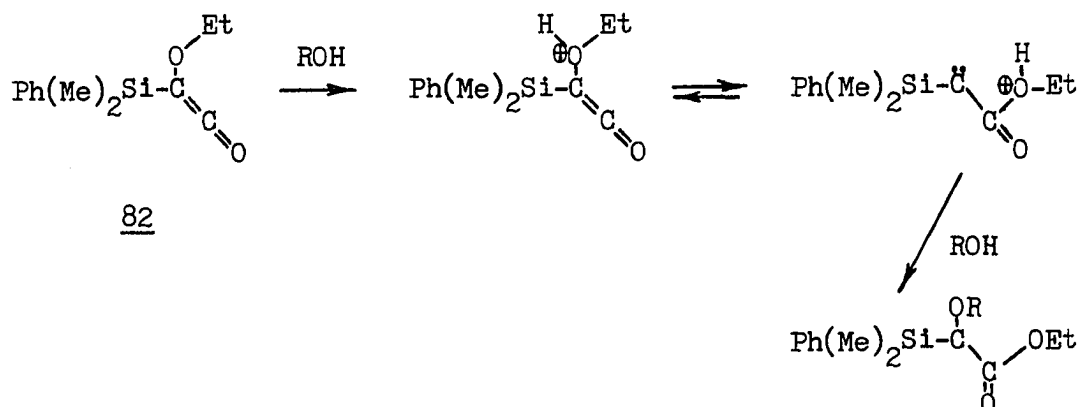
Scheme 33

If however the negative inductive effect of the ethoxy group and negative resonance effect of the phenylsilyl group are important, then the resonance form 111 ought to be important making the terminal ketene carbon somewhat nucleophilic, thus making 82 susceptible to attack by electrophiles (Scheme 34).

The process described in Schemes 32 and 33 would be considered to be less likely than that described in Scheme 34, but would be considered to emphasize a possible lessened electrophilicity of the middle ketene carbon in 82 relative to other ketenes. The relative increased importance of resonance form 111 would increase the probability of an electrophilic attack at the terminal carbon as has been observed with other ketenes (70). Whether nucleophilic or electrophilic attack would occur, then, would

depend upon the attacking species and its particular electronic characteristics.

The addition of hydrogen halides to vinylsilanes has been reported to proceed in an anti-Markownikoff direction which suggested that the negative resonance effect overshadowed the positive inductive effect of the silyl group (122). The reaction proceeded with Markownikoff addition when the α-hydrogen of the vinyl group was replaced with a methyl group with its positive inductive effect (123).
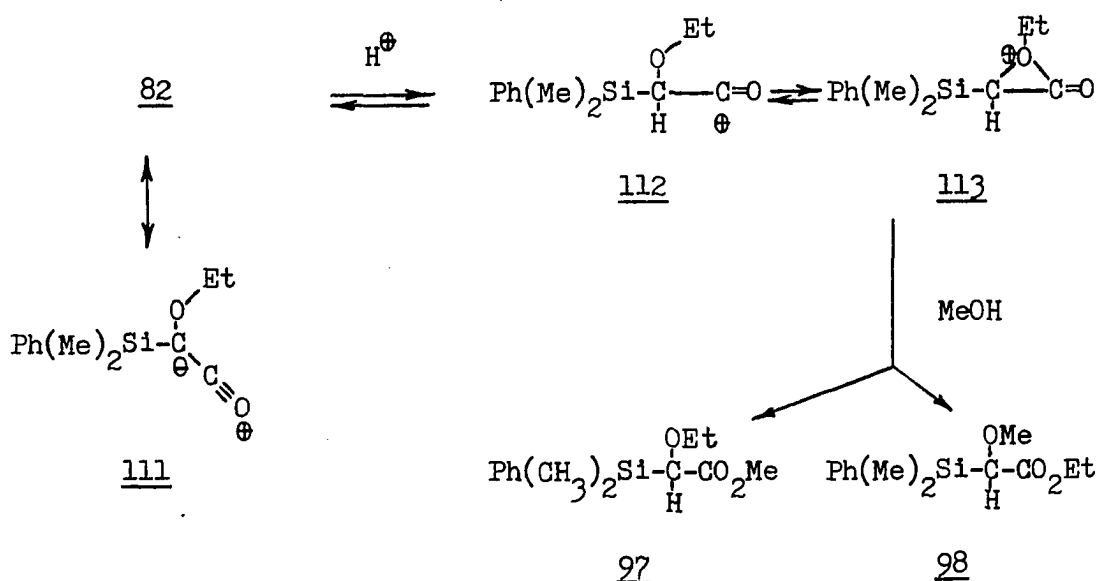
Scheme 34

If electrophilic attack on the ketene 82 were an available reaction pathway, some of the intermediate 112 could arise which might form a cyclic oxonium ion 113. The 113 ion could suffer nucleophilic attack at either the terminal or middle carbon of the original ketene structure to yield 98 or 97 respectively.

Transesterification would then account for the formation of 99 and

100. The production of <u>100</u> would be a reasonable process because methanol was present in less than 13% excess in the reaction. Thus any tranesterification leading to <u>99</u> would produce a competitive amount of ethanol.

The mass spectrum of the reaction mixture also produced molecular ions at m/e 150 and m/e 164 which could correspond to methyl phenylacetate and ethyl phenylacetate respectively. These products are of interest since phenylacetic acid had been isolated in the chromatographic work-up of the $500 \pm 5°$ pyrolysis. The presence of the esters in the nmr spectrum of the methanolysis reaction mixture can not be confirmed since all of the resonances due to the esters could be expected to come within a region of the spectrum where the esters <u>97-100</u> are found. The phenylacetate esters however would produce a singlet in the aromatic region at about δ 7.20 and an enlarged peak does appear at that point. It may, however, be only fortuitous.

The formation of phenylacetic acid esters would necessitate silicon-carbon aryl migration, silicon-carbon bond cleavage as well as loss of an alkoxy group. The loss of silicon product would be expected to occur, and indeed, it was noted that a peak at δ 0.05 in the nmr spectrum was eliminated when the excess methanol was removed, accounting for about 10% of the silylmethyl groups and implying a 10% yield of phenylacetates.

Molecular rearrangements in organosilane chemistry have long been known and have been observed to occur under a variety of conditions from a variety of compounds (94*, 124).

Brook and Jones (125) reported a novel thermal rearrangement involving migration of a substituent on carbon to silicon accompanied by shift of a

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*Reference (94), pp. 355, 362-363, 397-398, 434-441.

phenyl group from silicon to carbon in α-substituted benzyltriphenyl-silanes (Scheme 35). The rearrangement of the fluoro-compound took 14 hours at 110° but the other compounds were completely rearranged after 1 hour at 250-270°.

$$\underset{\underset{Y}{\overset{Ph}{|}}}{Ph_2Si\text{-}CHPh} \quad \xrightarrow{\;\;\Delta\;\;} \quad \underset{\overset{}{Y}}{\overset{Ph}{\underset{|}{Ph_2Si\text{-}CHPh}}}$$
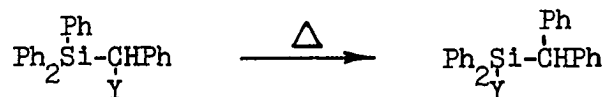
(Y = F, Cl, OAc, OTs)

Scheme 35

A silicon to carbon aryl migration also occurred when benzoyltri-phenylsilane was treated with ethoxide ion in ethanol (126) (Scheme 36) to produce ethoxybenzhydryloxydiphenylsilane which underwent alkoxide exchange to yield diethoxydiphenylsilane and benzyhydrol.

$$PH_3Si\overset{O}{\overset{||}{C}}\text{-}Ph \;\xrightarrow{\;EtO^{\ominus}\;}\; \underset{\underset{Ph}{}}{EtO\text{-}\underset{Ph}{Si}}\text{---}\overset{\ominus}{\underset{}{C}}\text{-}Ph \;\longrightarrow\; EtO\text{-}\underset{Ph}{Si}\text{---}\overset{O}{\underset{Ph}{C}}\text{-}Ph \;\xrightarrow{\;EtOH\;}\; EtO\text{-}\underset{Ph}{Si}\text{-}O\text{-}\underset{H}{\overset{Ph}{C}}\text{-}Ph$$
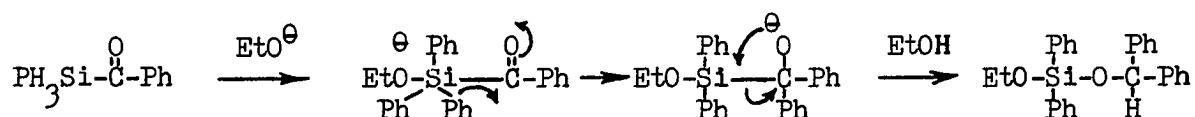
Scheme 36

Silylcarbinols in general have been shown to undergo the silyl carbon to oxygen migration (124) in the presence of small amounts of active metals, organometallic reagents or bases.

Migration of a phenyl group has been observed in the reaction of aqueous alcoholic solutions of hydrogen fluoride with ethoxymethylaryl-silanes (127) (Scheme 37).

When aryldimethylsilylmethyl chlorides were treated with sodium

Me OEt
Me-Si—CH₂   ——HF→   Me-Si—CH₂ ——→ Me-SiCH₂-⟨◯⟩-Cl
     | | |
    ◯   Me   Me
     | ◯
    Cl |
                         Cl
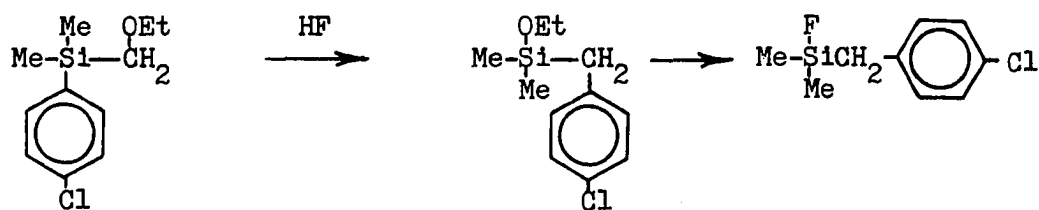
Scheme 37

ethoxide in ethanol migration of the aryl group from silicon to the carbon

of the chloromethyl group occurred (127) (Scheme 38).

Me Cl
Me-Si—CH₂   ——$^{\ominus}$OEt→   EtOSi-CH₂Ph
    | HOEt |
   Ph   Me
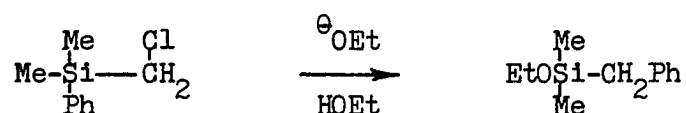
Scheme 38

O-silyl-O-alkylketene acetals have been observed to rearrange to silyl-

acetates (128) (Scheme 39).

$$CH_2=C\begin{smallmatrix}OSiR_3\\OR'\end{smallmatrix} \xrightarrow{\Delta} R_3SiCH_2\overset{O}{C}OR'$$
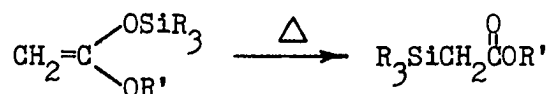
Scheme 39

The ketene acetals can be obtained by treating esters of stannylacetate

with chlorosilanes and are readily hydrolyzed to esters of acetic acid and

the corresponding silanol. The reaction is of interest because β-silyl-

ketones undergo a reaction which is to a certain extent the reverse

reaction (129) (Scheme 40).

$$R_3SiCH_2\overset{O}{C}CH_3 \xrightarrow{HgI_2} CH_2=C\begin{smallmatrix}OSiR_3\\CH_3\end{smallmatrix}$$
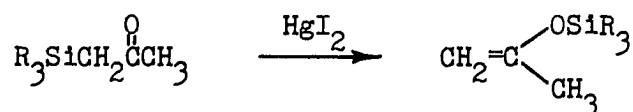
Scheme 40

The rearrangement of the α-substituted benzyltriphenylsilanes (125)

discussed above was of interest because it illustrated the migration of a

phenyl group and cleavage of an oxygen-carbon without the presence of base.

The rearrangement of silylacetic acids to the isomeric acyloxysilanes

under both thermal and basic conditions has been reported (130) (Scheme 41).

Base was shown not to be present in the thermal reaction suggesting that the

same reaction may proceed by two different mechanisms depending upon the

reaction conditions, as has been shown to be the case in other rearrange-

ments (124).

$$R_3Si-\overset{\overset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle R''}{|}}{C}}-CO_2H \quad \xrightarrow{\Delta} \quad H-\overset{\overset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle R''}{|}}{C}}-CO_2SiR_3$$
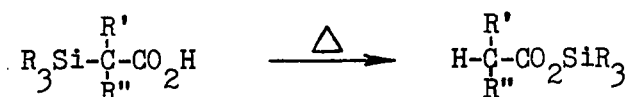
Scheme 41

Facile silicon-carbon bond cleavage under relatively mild conditions

has been reported by Kaufmann and Rühlmann (51). They reported that heat-

ing ethyl diazo(trimethylsilyl)acetate 72 with methanol yielded ethyl

diazoacetate and trimethylmethoxysilane. Similarly, heating 72 with water

in THF produced ethyl diazoacetate and hexamethyldisiloxane.

The formation of phenylacetate in the methanolysis of 82 might be

accounted for by the processes illustrated in Scheme 42 for 97. Pathway a

utilizes an initial attack at silicon with subsequent rearrangement and

silicon-carbon bond cleavage. Initial attack by methanol may not be

necessary (pathway b), in analogy with the α-substituted benzyltriphenyl-

silane rearrangement (125).

Since water was not rigorously excluded, the formation of some silyl-

acetic acid from 82 would be conceivable. Therefore the small amount of

$$
\begin{array}{c}
\underset{\underset{Ph}{|}}{\overset{\overset{Me}{|}}{Me\text{-}Si}}\overset{\overset{OEt}{|}}{\text{---}CHCO_2Me}
\end{array}
\xrightarrow[a]{MeOH}
\begin{array}{c}
\underset{\underset{\underset{H}{\overset{\bullet}{MeO\oplus}}}{|}}{\overset{\overset{Me}{|}}{Me\text{-}Si}\overset{\ominus}{}}\overset{\overset{OEt}{|}}{\text{---}CHCO_2Me}\quad Ph
\end{array}
\longrightarrow
\underset{\underset{Me\text{-}O}{|}}{\overset{\overset{OEt}{|}}{Me\text{-}Si\text{-}Me}} + PhCH_2CO_2Me
$$

$$
\underline{97}\quad b\searrow\;\Delta
$$

$$
\underset{\underset{Me}{|}\;\;\underset{Ph}{|}}{Me\text{-}Si\text{---}CHCO_2Me}
\xrightarrow{MeOH}
\underset{\underset{Me\text{-}O}{|}}{\overset{\overset{OEt}{|}}{Me\text{-}Si\text{-}Me}} + PhCH_2CO_2Me
$$
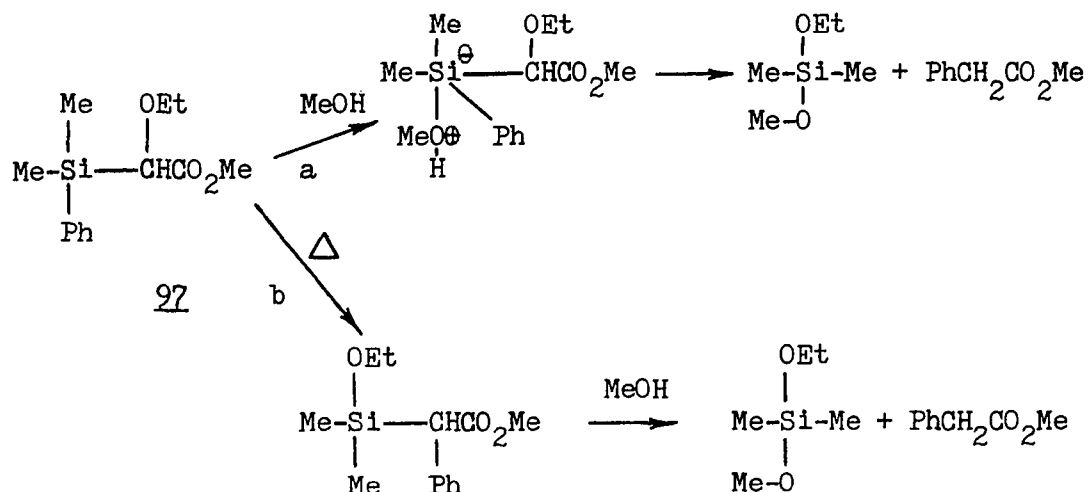
Scheme 42

rearrangement which occurred might be accounted for if rearrangement were dependent upon formation of the carboxylic acid in analogy with the rearrangement process cited earlier for silylacetic acids (130) (Scheme 43). Such a process would lead to the formation of 114 as a product which would have a molecular weight of 238. A corresponding molecular ion was found in the reaction mixture but has been ascribed to 100. If the m/e 238 ion were due, instead, to 114, the silylethoxy ethyl quartet in its nmr spectrum would be expected to appear at δ 3.8 (120), but no quartet appears in that region in Figure 21. However, acyloxysilanes are known to undergo facile solvolysis (36*).

$$
\underline{82}\xrightarrow{HOH}
\underset{\underset{Ph}{|}}{\overset{\overset{Me\;\;OEt}{|\;\;\;\;|}}{Me\text{-}Si\text{-}CHCO_2H}}
\longrightarrow
\underset{\underset{Me\;\;Ph}{|\quad|}}{\overset{\overset{OEt}{|}}{Me\text{-}Si\text{-}CHCO_2H}}
\longrightarrow
PhCH_2CO_2\underset{\underset{Me}{|}}{\overset{\overset{OEt}{|}}{OSi\text{-}Me}}
$$
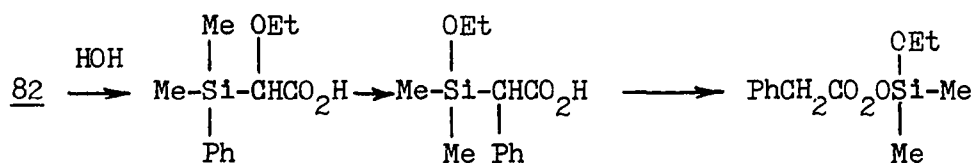
Scheme 43

*Reference (36), p. 63.

When a sample of 82 (obtained as the second gc fraction of the $600^{\pm}5°$ pyrolysis crude mixture) was refluxed with methanol for one hour and then the solvent removed under water pump pressure, evidence for more rearrangement and greater loss of silylmethyl groups was obtained. A mass spectrum of the resultant reaction mixture produced an intense molecular ion at m/e 150 corresponding to methyl phenylacetate. There were no significant ions at m/e 238, 252 or 266. The nmr spectrum (Figure 22) compared to the spectrum in Figure 21, also supported the greater production of methyl phenylacetate since the aromatic singlet, the methyl ester singlet and and δ 3.52 singlet were enhanced. The presence of a small peak at δ 10.92 which was eliminated upon addition of D_2O suggested the presence of an acid, possibly phenylacetic acid. The presence of two methyl ester singlets, the small δ 3.48 singlet and the two singlets at δ 0.12 and δ 0.08 suggested that some unrearranged product remained despite the lack of the corresponding molecular ions in the mass spectrum. In support of unrearranged products, evidence of a small ill-resolved ethyl ester quartet and triplet can be seen. The δ 3.33 singlet may again be unremoved methanol or a methyl ether. Since about 50% of the silylmethyl protons were lost, and if they were lost as dimethyldimethoxysilane whose boiling point has been reported as 82.2° (131), then the methanol should have been removed.

The results of the latter reaction suggested that the rearrangement process might be occurring from the esters formed from 82, but it must be acknowledged that moisture was not rigorously excluded from the reaction. Curious indeed, was the observation of an exchangeable proton at δ 10.93 in the nmr spectrum when the reaction was carried out in methanol.

1000 Hz Sweep Width
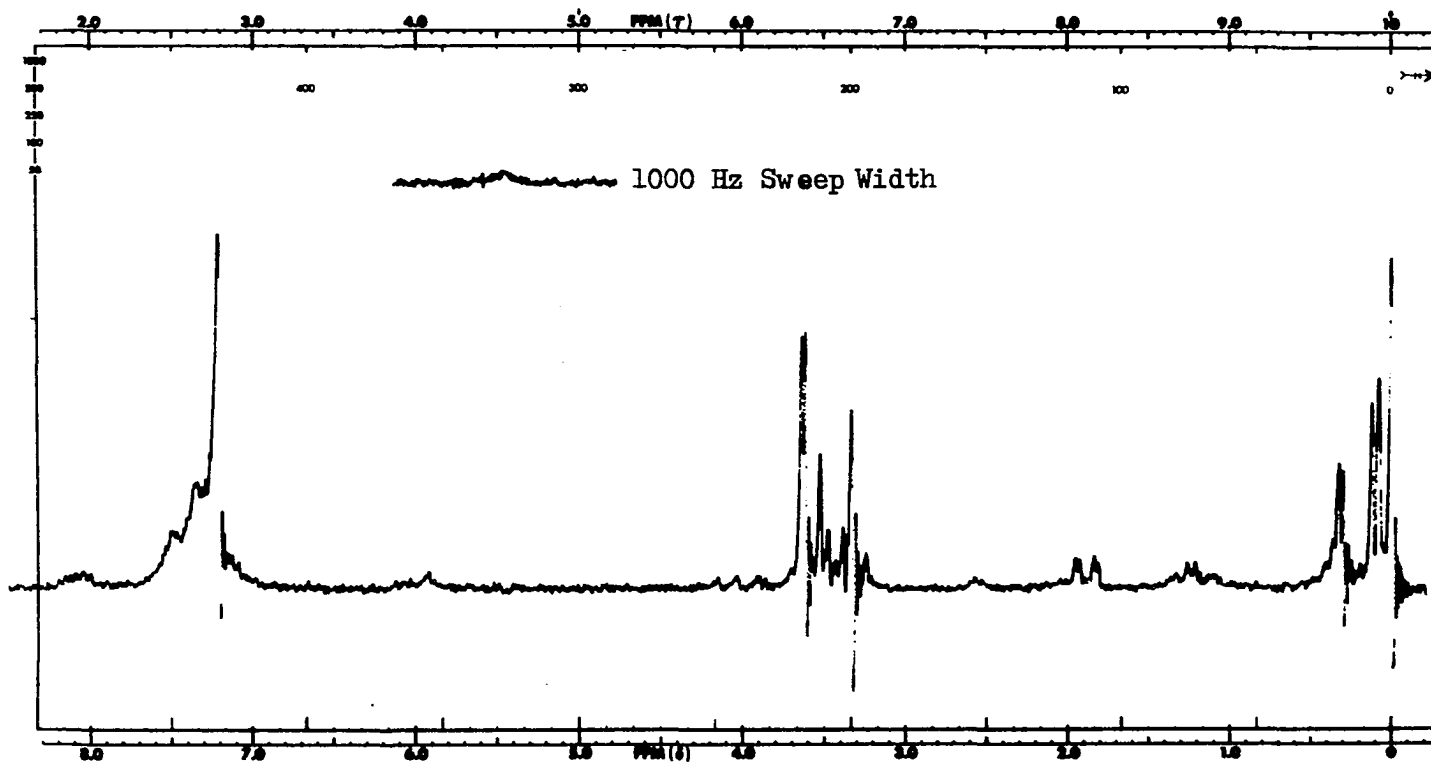
Figure 22.   60 MHz nmr spectrum of the products obtained from the reaction of dimethylphenylsilyl-
ethoxyketene 82 with methanol at reflux for one hour

Treatment of <u>82</u> in carbon tetrachloride with one drop of distilled water at room temperature resulted in complete reaction of <u>82</u> in less than 21 hours despite the fact that the reaction was heterogeneous. After 21 hours, an nmr spectrum of the reaction mixture showed a small aromatic multiplet underlying a large singlet at δ 7.19, a small multiplet at about δ 6.39, two quartets at δ 4.07 and δ 3.57 respectively, a singlet at δ 3.50, two triplets at δ 1.17 and δ 1.11 and a singlet at δ 0.08. When the sample was washed with D_2O, (Figure 23) the upfield quartet and triplet were eliminated suggesting that ethanol was being extracted. At the same time the multiplet at δ 6.39 was eliminated and the δ 3.50 singlet split into two peaks at δ 3.52 and δ 3.49.

The nmr spectrum could be interpreted as a mixture of phenylacetic acid (whose acid proton would be shifted upfield with ethanol and water present) and ethyl (dimethylphenylsilyl)hydroxyacetate <u>115</u>. <u>115</u> might be obtained by electrophilic attack on <u>82</u> just as <u>98</u> was in methanol. This interpretation again suggested that rearrangement might be occurring in the normal hydrolysis product dimethylphenylsilylethoxyacetic acid <u>116</u>.

$$\underset{\underline{115}}{\overset{\overset{\textstyle OH}{\textstyle |}}{Ph(Me)_2SiCHCO_2Et}} \qquad \underset{\underline{116}}{\overset{\overset{\textstyle OEt}{\textstyle |}}{Ph(Me)_2SiCHCO_2H}}$$
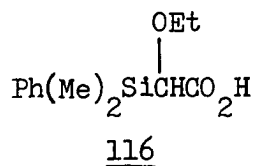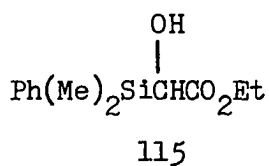
Alternatively the spectrum may be interpreted as a mixture of phenylacetic acid and ethyl phenylacetate. The silylmethyl protons would then be part of a siloxane or silanol structure or structures exclusively. Based on the integration of the aromatic to δ 3.51 region (5:1.5) the first interpretation would be valid if a 50:50 mixture were present. If
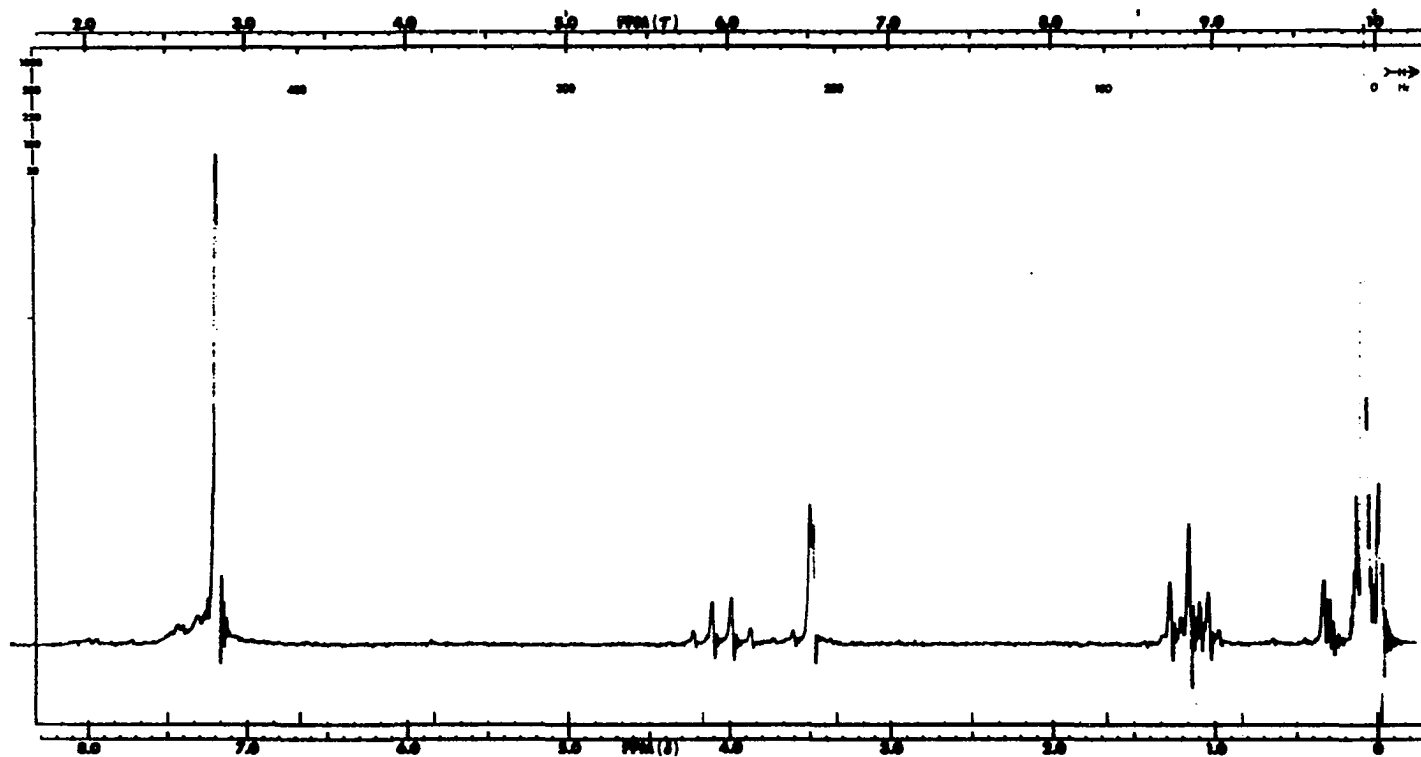
Figure 23. 60 MHz nmr spectrum of the products obtained from the reaction of dimethylphenylsilyl-ethoxyketene 82 at room temperature with water after washing with deuterium oxide

the multiplet in the phenyl region is discounted, however, the integration is 5:2.

The silylmethyl protons on the phenyl substituted atoms have been appearing further upfield than might be expected. Methyl protons of mono-phenyl substituted bonded only to carbons generally appear in the region of δ 0.3. The silylmethyl protons in Figure 21 and 22 attributed to dimethyl-phenylsilyl groups appeared at δ 0.12 and δ 0.08. If a phenyl group is present, the difference may lie in the ability of the alkoxy oxygen to coordinate with the silicon atom increasing the electron density at silicon and thus further shielding the methyl group protons causing a lower chemical shift. Such coordination might in part account for the ability of the rearrangement to occur and would predict some shift in configuration from tetrahedral to occur.

When an etheral solution of diazomethane in excess was added to the product mixture obtained with the reaction of 82 with water, some indication of the production of a methyl ester could be seen. The nmr spectrum of the reaction mixture exhibited a new singlet at δ 3.60.

Treatment of 82 dissolved in carbon tetrachloride with 2.3 M aqueous potassium hydroxide in an nmr sample tube resulted in complete reaction after 45 hours. An nmr spectrum of the CCl_4 layer showed only a small aromatic multiplet and a singlet at δ 0.05. The aqueous layer showed two singlets attributable to phenylacetate and a quartet and triplet attributable to ethanol. In addition there was a silylmethyl singlet at about δ 0.05 (estimated since there was no internal standard present). When the aqueous layer was acidified and extracted with CCl_4, the aqueous layer showed only a quartet and triplet left. The CCl_4 layer showed a singlet

at δ 7.87, at δ 7.18 and δ 3.49 for phenylacetic acid plus some ethanol and a silylmethyl multiplet at about δ 0.08. The ratio of aromatic singlet at δ 3.49 singlet was 5:2, indicating that the phenyl group was no longer associated with the silicon atom or that complete rearrangement had occurred.

The results of this last experiment could be accounted for by the processes in Scheme 42 or 43. Hydroxide ion would be a better nucleophile than either methanol or water, therefore if rearrangement occurred through nucleophilic attack at silicon (Scheme 42), the process should have been better under basic conditions as indeed it was.

If Scheme 43 were operable, hydroxide being a better mecleophile than methanol or water should have lead to greater production of the acid 116 by nucleophilic attack on ketene 82 at the expense of electrophilic attack. Therefore greater production of 116 should have yielded more phenylacetic acid as observed.

There appeared, then to be two unusual processes occurring when the ketene 82 reacted with nucleophiles (Scheme 44). To investigate the generality of both the unusual addition reaction (pathway a) and the aryl migration reaction (pathway b), two other α-silydiazoacetates were prepared: ethyl diazo(trimethylsilyl)acetate 72 and ethyl diazo(triphenyl-silyl)diazoacetate 117.

The preparation of 72 as a model for preparing 75 was discussed earlier. However the ease of preparing 75 by the reaction of dimethylphenyl-iodosilane 79 with diethyl mercuribis(diazoacetate) 73 prompted the use of that method. 72 had been prepared by that method by Kaufmann and Rühlmann (51).

Trimethyliodosilane was prepared by trimethylchlorosilane with magnesium iodide in xylene (132). The reaction of trimethyliodosilane with 73 to yield 72.

117 was also prepared by the iodosilane method. Triphenyliodosilane was prepared from triphenylsilane with iodine in ethyl iodide solution (133). The triphenylsilane was obtained from trichlorosilane with phenyl Grignard reagent (134). The reaction of triphenyliodosilane with 73 was difficult because of the extreme reactivity of the iodide toward hydrolysis. The product was very impure and purified with difficulty by repeated recrystallizations from pentane.

$$
\underset{\underset{82}{\text{Ph(Me)}_2\text{Si-C}}}{\overset{\text{OEt}}{\underset{\diagdown}{}}}\overset{}{\underset{\text{C}}{}}\diagup\text{O}
\begin{cases}
\xrightarrow[a]{\text{MeOH}} & \underset{\underset{97}{\overset{\text{H}}{}}}{\text{Ph(Me)}_2\text{Si-}\overset{\text{OEt}}{\underset{}{\text{C}}}\text{-CO}_2\text{Me}} + \underset{\underset{98}{\overset{\text{H}}{}}}{\text{Ph(Me)}_2\text{Si-}\overset{\text{OMe}}{\underset{}{\text{C}}}\text{-CH}_2\text{Et}} \\[4ex]
\xrightarrow[b]{\text{OH}^{\ominus},\ \text{HOH}} & \text{Ph(Me)}_2\text{Si-}\overset{\text{OEt}}{\underset{\text{H}}{\text{C}}}\text{-CO}_2\text{H} \longrightarrow \text{PhCH}_2\text{CO}_2\text{H}
\end{cases}
$$
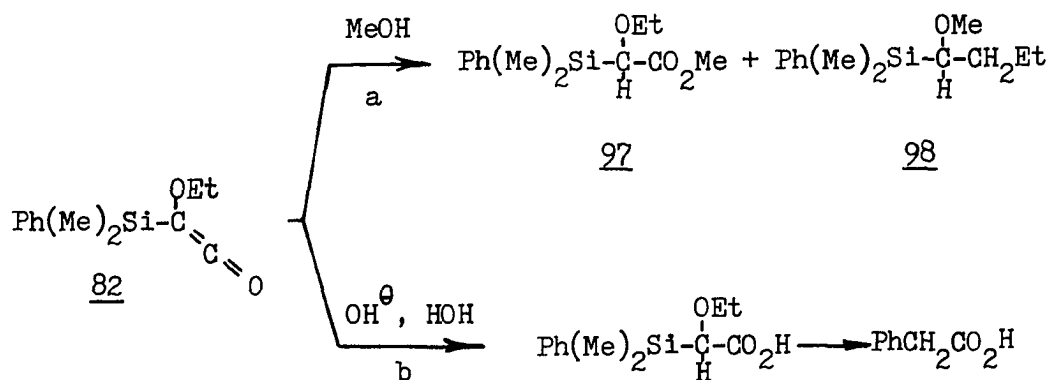
Scheme 44

Ethyl diazo(trimethylsilyl)acetate 72 was also found to be stable to 200° under vacuum pyrolysis conditions. At 260° decomposition had begun and only about 70% of 72 was recovered. An nmr spectrum of the trapped products showed evidence of some minor formation of olefinic products with a pattern very similar to that found with 75. Two quartets could be recognized at δ 6.37 and δ 5.95 (J = 5.5 cps), a doublet at δ 5.61 (J = 19 cps) and a doublet of doublets at δ 1.78 (J = 5.5 and 1.0 cps). Those

peaks would be consistent with the nmr spectrum reported by Seyferth and Vaughan (113) for trans-propenyltrimethylsilane (trans-96). There were other minor peaks in the olefinic region but they were too small to speculate about. The upfield region in which one would expect the olefinic methyl group resonance of cis-96 was obscured. The ethyl and methyl group protons unaccounted for by recovered 72 appeared to be parts of complex multiplets suggesting the presence of polymeric material.

When 72 was pyrolyzed at 300° the trapped products were initially orange but upon warming to room temperature they rapidly turned light yellow and some solid formed in the trap. The nmr spectrum of the trapped material which did not solidify showed the olefinic protons along with a small singlet at about δ 1.56. The ethyl and methyl group protons appeared only as complex unresolved multiplets. An nmr spectrum of the solid material which would dissolve in $CDCl_3$ also exhibited complex multiplets for the same protons. An ir spectrum of the liquid material showed a strong 1745 cm^{-1} band and a small band at 2110 cm^{-1} which decreased rapidly with time.

Pyrolysis of 72 at 340±5° resulted in a bright orange product which again lost color rapidly on warming with the formation of a gelatinous solid. A portion of the trapped material was kept at -78° until an ir spectrum could be taken, and again, a small 2110 cm^{-1} band was found which decreased with time. An nmr spectrum of the trapped material in $CDCl_3$ was essentially the same as found in the previous pyrolysis except that the olefinic resonances were somewhat more important and an ir band at 1630 cm^{-1} was now evident.

Even though the nmr spectra of the trapped materials were not very

different, subjection of the trapped materials to gc analysis showed that the mixtures obtained with increasing pyrolysis temperatures were becoming increasingly more complex.

The formation of the olefin trans-96 suggested that intramolecular insertion of the intermediate carbene into the alkoxy side chain to form lactones in a process similar to that shown in Scheme 19 was occurring. The lactones could then lose carbon dioxide in a process similar to that shown in Scheme 28. The rapid solidification of the trapped materials upon warming and the vanishing 2110 cm^{-1} ir band suggested that the ketene 118 was being formed but rapidly polymerizing.

In an attempt to trap any ketene formed, a sample of 72 was pyrolyzed at 300° as methanol was concurrently vaporized through the oven. The vaporization of the alcohol was kept at a low level to avoid intermolecular reactions, but trapped along with any ketene formed to maximize reaction when the trap was warmed to room temperature.

The trapped product was again red-orange and upon warming turned light yellow. Before removing the methanol from the sample, an nmr spectrum was taken which appeared to be much less complex than the sample pyrolyzed at 300° without methanol present and it indicated that about 12% of 72 remained unreacted.

The methanol was removed by vacuum distillation and an nmr spectrum taken of the residue. Except for the absence of the resonances due to methanol and a small singlet upfield, no difference in spectra was discernible. An ir spectrum of the residue showed a small band at 2095 cm^{-1} and an intense band at 1736 cm^{-1}.

The residue was then distilled under vacuum by cooling the material

in an ice water bath and trapping the distillate in a Dry Ice-acetone cooled trap.

The residue remaining after the pot to pot distillation exhibited an nmr spectrum which was remarkably similar to the polyerized materials obtained in prior pyrolyses. The distillate produced an nmr spectrum which appeared very simple at first glance but upon investigation showed four small quartets at δ 4.06, δ 3.66, δ 3.47 and δ 3.20. The first one was probably due to 72 since some remained in the mixture. There was, however, only one triplet (besides a small one due to 72). There also appeared two singlets in the ratio of 1:3 at δ 3.77 and δ 3.70 in addition to a silyl-methyl singlet at δ 0.0.

The nmr spectrum of the distillate strongly suggested the presence of only one ketene addition product, the one normally expected, methyl (tri-methylsilyl)ethoxyacetate 119. The presence of several ethyl group quartets was bothersome, particularly the quartet at δ 3.66 which accounted for 50% of the methylene protons. Its presence suggested that some of the rearranged ketene addition product, ethyl (trimethylsilyl)ethoxyacetate 120 could be present. However, if 120 were present, a sizable methyl ether singlet would be expected to appear, and none was observed.

The quartets might be accounted for if besides the chirality of the molecule, silicon-oxygen interaction were occurring producing some increased stability to certain conformations of the molecule.

The inductive effect of the phenyldimethylsilyl group would be less positive than that of the trimethylsilyl group (36*). The resonance effect of the phenyldimethylsilyl group would be more negative than that

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*Reference (36), p. 17

of the trimethylsilyl group however (94*). Since the two ketene molecules

thus far considered, 82 and 118, would be structurally the same except for

the substitution on the silyl groups, the difference in products upon

methanolysis might cast some light upon the mechanism of the reaction.

It was argued earlier that the phenyldimethylsilyl group in 82 stabi-

lized the resonance forms 109 and 111 in Schemes 31 and 34 respectively,

thus not destabilizing the normal ketene addition process (Scheme 31) but

making the terminal ketene carbon somewhat more nucleophilic by stabiliza-

tion of resonance form 111 (Scheme 34).

A trimethylsilyl group should also stabilize the analogous resonance

forms for 118 but with the form analogous to 109 somewhat more stabilized

relative to the form analogous to 111. Thus overall, the trimethylsilyl

group might be expected not to make either resonance form much more favor-

able than the analogous forms for any ketene and addition should proceed

normally for 118.

It would be expected then that a triphenylsilylethoxyketene 121 from

117 would produce just the opposite effect.

No alkyl migration from silicon to carbon was noted in the methan-

olysis of 118. Alkyl migrations from silicon to carbon have been observed

with strong acids like concentrated sulfuric acid (130) and Lewis acids

like $AlCl_3$ (131). Such a process, then, would not be expected under the

mild methanolysis conditions utilized for 118.

Finally no evidence for silicon carbon bond cleavage was noted. This

would agree with the fact silylacetate esters do not suffer migration of

the silyl group from carbon to oxygen whereas the silylacetic acids do (130).

*Reference (94), p. 101.

If the lack of rearrangement of the silyl group is due to the absence of acid, the appearance of some silicon-carbon bond cleavage in the methanolysis reaction of 82 could very well have been due to some accidental hydrolysis in that reaction.

The pyrolysis of a 0.75 g sample of 117 at 300° took 96 hours even with the sample being heated to about 130°. The high sample temperature resulted in decomposition of the starting material in the sample holder and it formed a red-brown glassy solid. It was expected that such harsh treatment would result in an unclean product mixture. The trapped materials were lighter in color than those obtained with either 72 or 75.

An nmr spectrum of the light green (to yellow) oil obtained exhibited a complex aromatic multiplet and only one ethyl group quartet and triplet (Figure 24) which were at distinctly different chemical shifts than those observed for 117 (Figure 25). Integration of the spectrum indicated that the compound contributing the ethyl group was present in about 83% yield. An ir spectrum of the material showed a strong band at 2105 cm^{-1} with none appearing at 1700 to 1750 cm^{-1}. Indications were then that the major product of the pyrolysis was triphenylsilylethoxyketene 121. No evidence for olefinic protons was observed. All unaccounted for materials showed only evidence of aromatic protons.

The result of this pyrolysis at 300° compared to the 300° pyrolyses of 72 and 75 suggested that decomposition of the diazocompounds was facilitated by electron withdrawing groups adjacent to the carbene developed on loss of nitrogen since starting material had been recovered in the cases of 72 and 75. This may be due instead to the fact that the pyrolysis of 111 proceeded over a much longer period due to its lack of volatility and

Figure 24. 60 MHz nmr spectrum of triphenylsilylethoxyketene 121 (top)

Figure 25. 60 MHz nmr spectrum of ethyl diazo(triphenylsilyl)-
            acetate 117 (bottom)
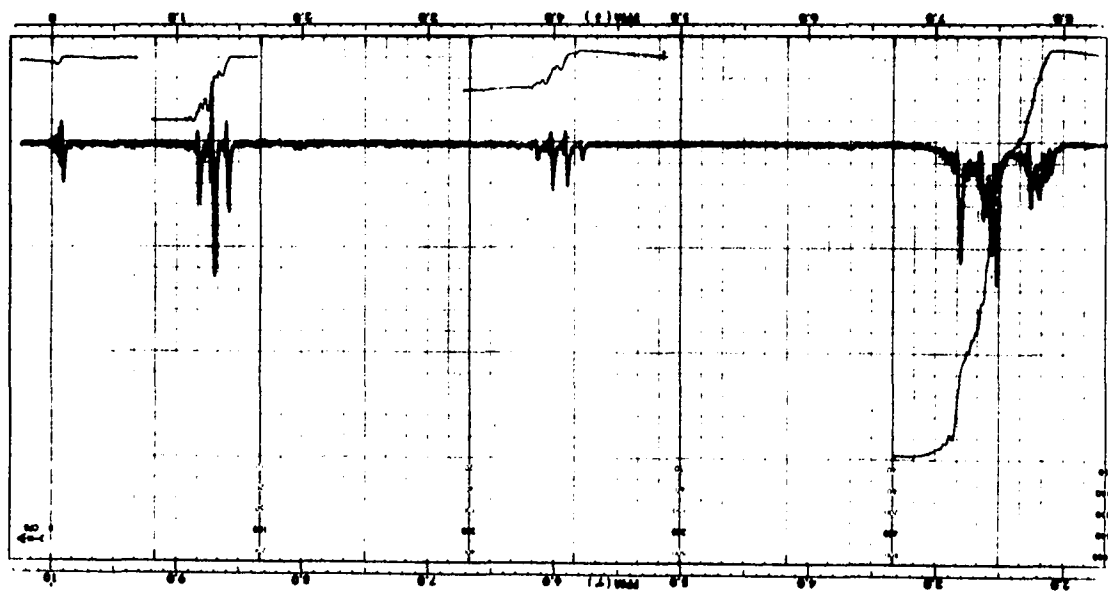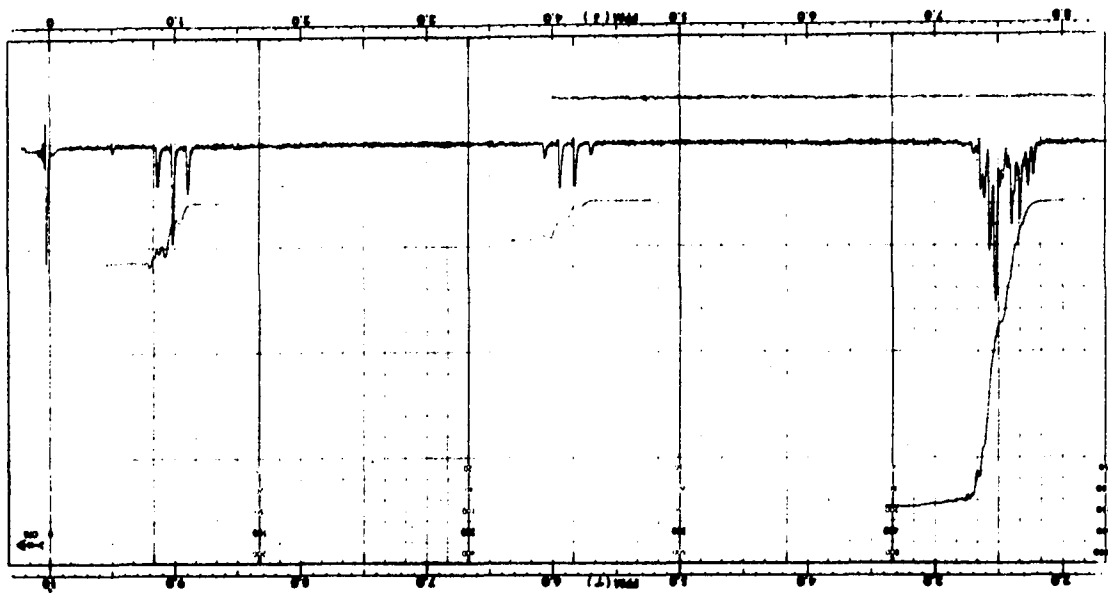
thus had a greater opportunity to react.

The yield of ketene in the three cases, though only qualitative, suggested that the presence of a strongly electronegative group adjacent to the carbenic center, made migration to electron deficient carbon a better process.

Addition of methanol to 121 also appeared to be a relatively clean process. After 21 hours at room temperature no further change could be observed in the nmr spectrum of the sample. To insure that reaction was complete, the sample was allowed to stand at room temperature 21 hours longer (no additional change was observed) and then the excess methanol removed. In one case the methanol was removed under water pump pressure and in another case by extracting with water. In both cases an nmr of the mixture appeared as in Figure 26. The water wash produced an nmr spectrum which showed the methanol methyl singlet and a small amount of ethanol.

Figure 26 could be interpreted as being the nmr spectrum of ethyl (triphenylsilyl)methoxyacetate 122 predominantly. The singlet at δ 4.07 accounts for one proton and appeared about where the methylene protons in ethoxyacetic acid appear (119). The analogous proton in the compounds 97-100 appeared at δ 3.52 and δ 3.49 and in 120 at δ 3.77. Shielding by the trimethylsilyl and dimethylphenylsilyl groups would cause them to appear at lower field whereas with the strongly electronegative triphenylsilyl group shielding would not be as important.

The ethyl group quartet at δ 4.74 would be satisfactory for an ethyl ester and the methyl singlet at δ 3.43 would be satisfactory for a methyl ether. Integration of the upfield triplet at δ 1.11 compared to the δ 4.07 singlet and δ 3.43 singlet indicated that 122 was probably present.
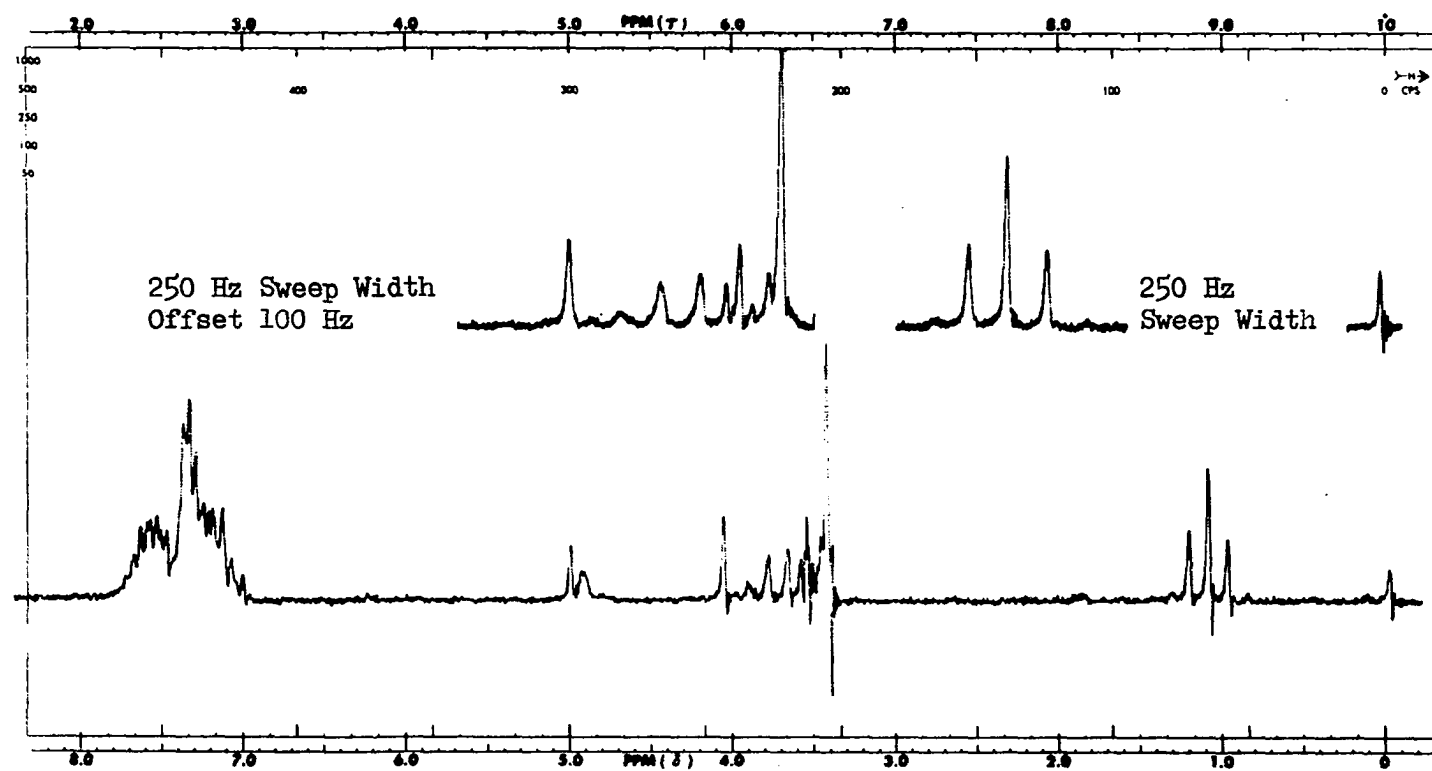
Figure 26. 60 MHz nmr spectrum of the products of triphenylsilylethoxyketene 117 with methanol

in about 93-100%.

Several small peaks can be seen in the expanded portion of Figure 26 at δ 3.59, δ 3.56, δ 3.53 and δ 3.48 which have not been accounted for and which were not exchangeable with D_2O.

An ir spectrum of the material confirmed the presence of an ester showing a strong band at 1737 cm^{-1}. A mass spectrum of the material produced a molecular ion at m/e 376. The fragmentation observed was not typical for esters (112*) and suggested the presence of 122 and the normal ketene addition product methyl (triphenylsilyl)ethoxyacetate 119 in lower yield (Scheme 45 and 46 respectively).
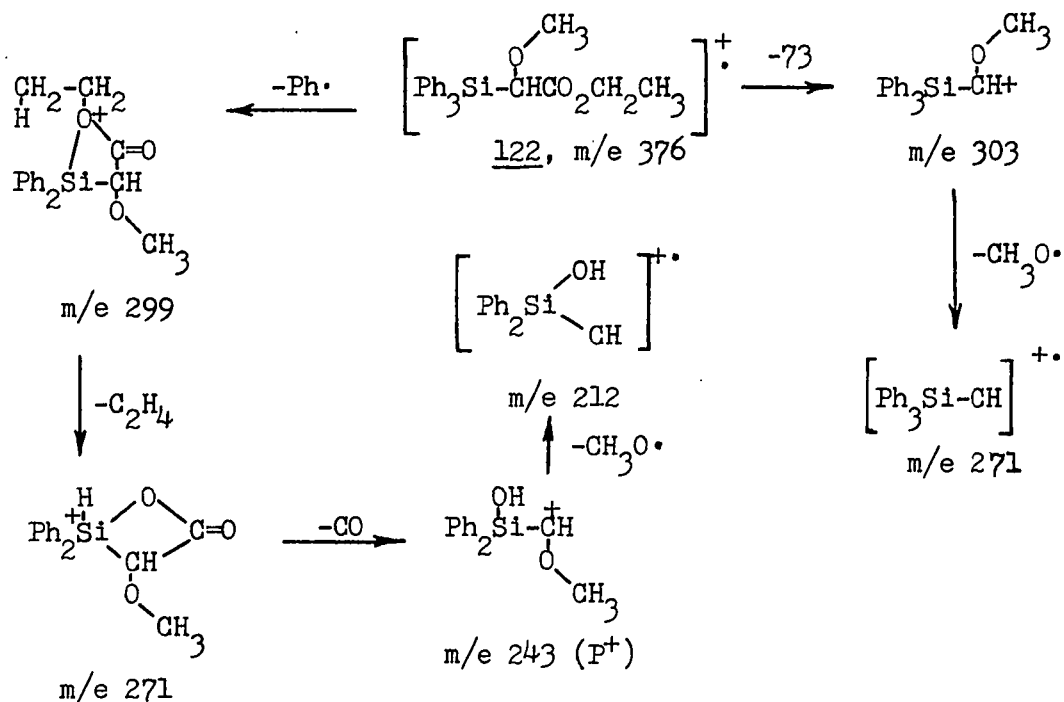
Scheme 45

The fragmentations emphasize the strong interactions between silicon

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*Reference (112), p. 14.

$$\left[Ph_3Si\text{-}\overset{O}{\underset{\mid}{C}}H\,\overset{O^{CH_2CH_3}}{}CO_2CH_3 \right]^{+\cdot}$$

123, m/e 376

-Ph·

-59 → $Ph_3Si\text{-}\overset{O^{CH_2CH_3}}{\underset{\mid}{C}}H^+$ m/e 317

$$Ph_2Si\text{-}\overset{+}{\underset{\mid}{C}}H \overset{\displaystyle O\text{-}CH}{\underset{\displaystyle O}{\big|}} \overset{C=O}{}$$
$$O\text{—}CH_2CH_3$$

m/e 299

$Ph_3Si\text{-}\overset{OH}{\underset{\mid}{C}}H^+$ m/e 289

$-C_2H_4$

$-CH_3CH_2O\cdot$

$Ph_3Si\text{-}CH^{+\cdot}$ m/e 271

-CH₂=C=O

$Ph_2Si\text{-}\overset{OH}{\underset{\mid}{C}}H^{\;OCH_2CH_3}$

$-CH_3CH_2O\cdot$ →

$Ph_2Si\diagdown_{CH}^{OH}{}^{+\cdot}$ m/e 212
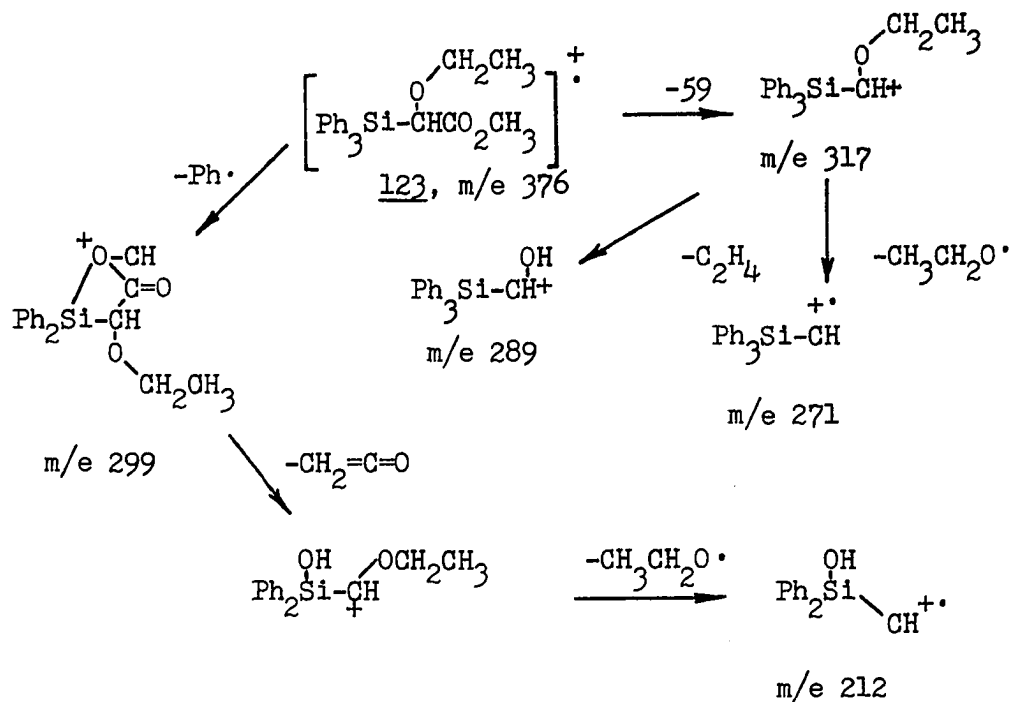
Scheme 46

and oxygen in these molecules. It is tempting to speculate concerning the unaccounted for resonances in the nmr spectrum in light of the mass spectrum.

If, indeed the fragmentations shown in Schemes 45 and 46 are correct, the δ 3.56 singlet could be due to a methyl ester and at least part of the other three peaks due to the ethyl ether portion of 123. The δ 3.59 and δ 3.48 resonances are approximately 7 cps apart and thus would place a quartet in the correct region for an ethyl ether methylene.

The almost exclusive rearrangement in addition in 121 as opposed to that found with the trimethylsilyl ketene 118 would be in agreement with the earlier discussion concerning the electronic effects of the silyl groups upon the reactivity of the ketenes.

The mass spectrum of 122 and 123 also produced an ion at m/e 150 but its intensity was not determined nor was it determined whether or not it was due to a molecular ion. There is no positive evidence for the presence (or absence) of methyl phenylacetate in the nmr spectrum of the mixture either. There could be no significant amount of methyl phenylacetate present however, again indicating that the esters do not rearrange.

To determine whether the carboxylic acids corresponding to 122 and 123 undergo rearrangement to phenylacetic acids, the esters were treated with 5% aqueous sodium hydroxide. The sample was shaken vigorously periodically, but after 83 hours no change could be determined. It was thought that stronger base and heat would lead to silicon-carbon bond cleavage (36*), therefore the basic layer was removed from the nmr tube and the reaction mixture washed with water. A drop of 1 N hydrochloric acid was then added which caused no change to occur in the nmr of the mixture. Additional acid was then added and the mixture was transferred to a flask and heated to about 100° overnight.

The organic portion of the hydrolysis mixture was taken up in CCl_4 and its spectrum determined. The results were not definitive, however, the nmr spectrum showed a complex aromatic multiplet with a significant singlet at δ 7.19. Upfield there were two small singlets at δ 3.52 and δ 3.44 respectively, the latter being twice as intense. When the CCl_4 layer was washed with aqueous base the aromatic singlet and a singlet at about δ 3.41 appeared (along with some aromatic multiplet). If the peaks were due to phenylacetate, acidification should cause them to become CCl_4 soluble again.

*Reference (36), pp. 213-216.

When the aqueous layer was acidified, an emulsion formed which was extremely difficult to break up. The CCl_4 extract eventually obtained was quite dilute and only indicated the presence of a peak at δ 7.16 and a smaller one at δ 3.53.

There would be other ways to interpret the results of that experiment, however, it would be very tempting to rationalize the material as phenylacetic acid produced when 122 and 123 were hydrolyzed.

Hydrolysis of a sample of the ketene 121 dissolved in CCl_4 was accomplished in 122.5 hours. The nmr of the reaction products strongly suggested the presence of phenylacetic acid with a large singlet at δ 7.19 and a smaller one at δ 3.43. The aromatic region in particular appeared very much like that obtained in the hydrolysis of 122 and 123. There also appeared an ethyl group quartet and triplet along with multiplets in both regions. When the sample was washed with additional water the quartet and triplet were lost.

When the CCl_4 layer was treated with concentrated aqueous potassium carbonate, the aromatic and upfield singlet were lost to the water layer. When the water layer was acidified and extracted with CCl_4, the nmr spectrum obtained was that of phenylacetic acid.

The material left in the CCl_4 layer of the reaction mixture still exhibited a small singlet at δ 3.43. Rewashing the sample with water or continued treatment with concentrated potassium carbonate did not remove the singlet or alter the spectrum. The singlet which remained accounted for about 20% of the original singlet and therefore phenylacetic acid accounted for about 80% of the product. The nmr spectrum of the material remaining consisted of an aromatic multiplet, a multiplet from δ 4.08-3.52,

the δ 3.43 singlet and a multiplet at δ 1.39-0.70. There were in addition two peaks at about δ 5.0 which varied both in size and location from run to run and were probably hydroxylic peaks. The upfield multiplet could be analyzed as a set of four triplets.

When the sample was treated with 5% aqueous base for 10 hours, no change could be determined although the aqueous portion showed a small amount of material having a triplet to be present at about δ 1.35. However when the basic strength was increased to 25% and left overnight, three layers were formed. The top layer was aqueous and produced only a trace of aromatic protons in its nmr spectrum. The middle layer was very viscous. When water was added to it a lower layer separated and the water layer became cloudy. The nmr spectrum of the aqueous layer showed an aromatic multiplet with a large singlet at about δ 7.20 (no internal standard except water) a quartet at about δ 3.50, a singlet at about δ 3.38 and a triplet at about δ 1.0. The spectrum suggested that a mixture of phenylacetate and ethanol were present (there were other interpretations). In strong base phenylacetate would probably oil out but not dissolve in CCl_4. On adding water the salt could dissolve in the diluted base and any associated CCl_4 would separate. The cloudiness could be explained by the results obtained with the bottom layer. The nmr of the bottom (CCl_4) layer showed only an aromatic multiplet and perhaps a singlet at about δ 3.5. The material was probably polymeric and some of it became associated with the oiled out phenylacetate. On adding water any polymer should have precipitated.

These results indicated that the material left when phenylacetic acid was extracted which had a singlet at δ 3.43 could have been ethyl phenyl-

acetate or ethyl (triphenylsilyl)hydroxyacetate 124. If the methyne proton in 122 appeared at δ 4.07, the methyne proton for 124 would be expected to be similar and therefore the minor product of the reaction would be more likely ethyl phenylacetate. If true, then the mixture obtained from the hydrolysis of 82 would be more likely phenylacetic acid and ethyl phenylacetate.

The addition of one drop of 50% aqueous sodium hydroxide to a CCl_4 solution of 121 produced an immediate precipitate. The precipitate was dissolved in water and on the basis of its nmr spectrum in that solution and in CCl_4 solution after acidification, it was shown to be phenylacetic acid. As final proof, the compound was isolated and after recrystallization had a melting point of 75.5-77° and mixed melting point with authentic phenylacetic acid of 76-77.5°.

The CCl_4 in which the reaction was originally carried out showed an nmr spectrum predominantly of phenyl protons. However there were complex unresolved multiplets in the ethyl group quartet and triplet regions which suggested that some polmerization had occurred in this reaction just as in the neutral hydrolysis.

In summary, two rather stable triorgansilylethoxyketenes have been prepared and evidence has been presented for the transient formation of a third. The formation of all three was due to facile Wolff rearrangement of ethoxy group in the pyrolysis of stabilized α-silyldiazoacetates. Not an unimportant factor in the reactions was the lack of opportunity for intermolecular reactions to occur under the high vacuum conditions.

Two novel rearrangements of the ketenes have been observed (Scheme 47). One involved what appeared to be a new reaction pathway for ketenes.

Factors which appeared to control the direction of reaction were the presence of strong resonance electron withdrawing groups at the terminal ketene carbon and reaction with a weak nucleophile. When stronger nucleophiles were present no strong evidence for abnormal addition was seen.

| $\underline{75}$ R = Me | $\underline{97}$ R = Me | $\underline{98}$ R = Me |
| $\underline{121}$ R = Ph | $\underline{123}$ R = Ph | $\underline{122}$ R = Ph |
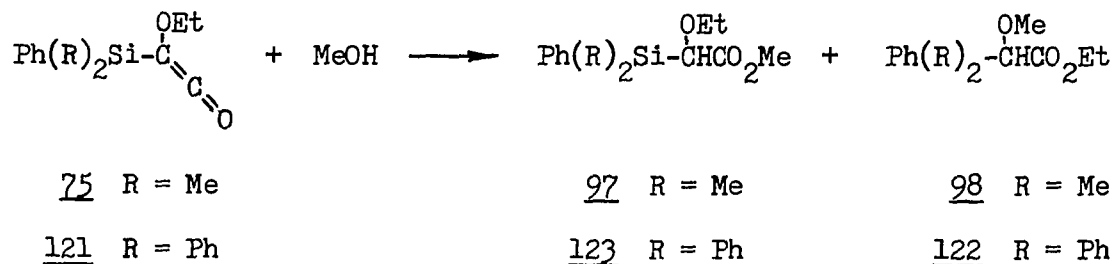
Scheme 47

A second rearrangement process occurred when the product of the ketene addition reaction was a carboxylic acid. The fact that phenyl migration occurred with silicon-carbon bond cleavage suggested that perhaps the one process assisted the other (Scheme 48). It has not been conclusively demonstrated that rearrangement only occurred from a carboxylic acid, nor has it been shown that rearrangement could not have occurred from the ketenes directly, but it seems difficult to imagine a process so facile that addition to the ketene was superseded.
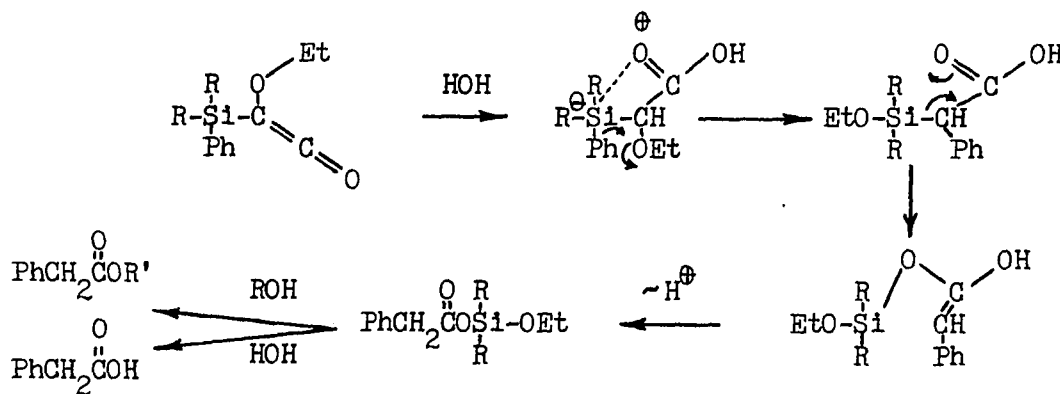
Scheme 48

Photolysis of Ethyl Diazo(dimethylphenylsilyl)acetate 75

When 75 was originally prepared, a photolysis was carried out under

conditions in which 72 had been shown to react (53). Photolysis through

pyrex of 75 dissolved in cyclohexane produced the expected intermolecular

insertion product 125 in conformity with the results obtained by others

with 72 (53). Besides siloxane (the sample of 75 used was contaminated with

25% disiloxane) and several minor products (unidentified), another product

of some interest was also obtained, namely ethyl phenylacetate 126.

Ph(Me)$_2$Si-CHCO$_2$Et

125
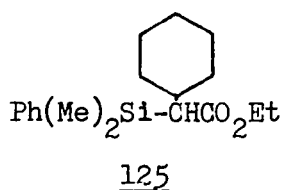
It was difficult to determine whether or not 126 was present in the

crude photolysis mixture by nmr or ir. The nmr was not useful in deter-

mining whether the ketene 82 or the diazocompound 75 were present either.

The ir of the crude exhibited a band at 2090 cm^{-1} which could be due to

the presence of either ketene or starting material. The carbonyl group of

the diazocompound, however, absorbed at 1685 cm^{-1} and there was no carbonyl

absorption at that wavelength in the crude product (it absorbed at 1720

cm^{-1}). Since the carbonyl absorption for 75 was somewhat stronger than

the diazo absorption, the 2090 cm^{-1} band which was strong in the crude

mixture points to the formation and initial isolation of the ketene.

126 was isolated from the reaction mixture by thick layer chromato-

graphy. The isolation of 126 was unexpected in light of the results of

the chromatographic work up of the pyrolysis products obtained in the 500$^{\pm}$

5° pyrolysis of 75. In that experiment, phenylacetic acid had been

isolated as a minor polar product presumably by hydrolysis of 82. Since the other fractions were not characterized, some 126 may also have been present and overlooked.

The formation of 126 could be accounted for by hydrolysis of 82, rearrangement and esterification on the chromatographic plate. 126 could then have been separated from any unesterified phenylacetic acid during the chromatographic process.

At the time the photolysis was carried out, the ketene 82 had not been characterized yet and it was thought that unreacted 75 was recovered. Therefore several reactions with 75 were carried out to determine whether decomposition of 75 during chromatographic work up would account for the formation of 126.

75 was treated with silica gel in CCl_4 solution in various concentrations. On prolonged standing, the mixture did show evidence of decomposition by nmr, but there was no evidence formation of 126. Since the silica gel was acidic, 75 was also treated with hydrochloric acid, rapid decomposition occurred with the formation of ethyl chloroacetic acid in agreement with the results of Kaufmann and Rühlmann (51) obtained on treating 72 with hydrogen chloride, but again no evidence for formation of 126 was obtained.

Schöllkopf, Hoppe, Rieber and Jacobi (53) had not observed formation of the ketene 118 or products derived from it in their photolysis of 72. This is not surprising since 126 is unstable at room temperature and due to its instability with respect to that of 82 (and 121) it may not have been formed, the carbene reacting instead by intermolecular insertion with the solvent. With alcohols as the solvent Ando, Hagiwara and Migita (117)

did report products arising from the intermediate ketene 118.

Other Studies with α-silyldiazocompounds

The presence of the silyl group α to a diazo group imparts stability to diazocompounds relative to their carbon analogues. The presence of a carboxy group also stabilizes diazocompounds. The presence of both groups apparently makes the compounds quite stable, to the extent that 1,3-intramolecular insertions of the corresponding carbenes does not occur, and other reactions are more favorable. Of course, as Schöllkopf, Hoppe, Rieber and Jacobi (53) pointed out, other factors such as bond distances also can influence such reactions.

The absence of the carboxy group, however, could make the carbenes reactive enough to overcome any other negating factors such as bond distances and, at least at lower temperatures, insert in a 1,3-intramolecular fashion. (See pages 285-286 for further related work.)

Thus far there have been only two reports of the direct photolysis of α-silyldiazocompounds. The work concerning 72 (53) has been mentioned. Brook and Jones (54) photolysed the diazoalkanes 66, 67 and 70. The results, shown below, (Scheme 49), were unexceptional. Mention was also made of work in progress in cyclopropane formation and they only noted that the reactions were very unclean.

For the reasons indicated at the beginning of this section, a phenyl-substituent on the silicon was desirable. The only compounds which have been synthesized to date which have substituents which would allow a 1,3-intramolecular insertion are trimethylsilyldiazomethane 65 and phenyltrimethylsilyldiazomethane 71. When this work was begun only 65 was known.

$$Ph_3Si-CN_2Me \quad \xrightarrow[\text{ether}]{h\nu} \quad Ph_3Si-CH=CH_2$$

$$Ph_3Si-CN_2-CH_2Ph \quad \xrightarrow[\text{ether}]{h\nu} \quad Ph_3Si-CH=CHPh$$

$$(54\% \text{ \underline{trans}}, \ 21\% \text{ \underline{cis}})$$

$$Ph_3Si-CN_2-Ph \quad \xrightarrow[\text{MeOH}]{h\nu} \quad Ph_3Si-\underset{\underset{OMe}{|}}{CH}-Ph$$

$$\underline{66}$$
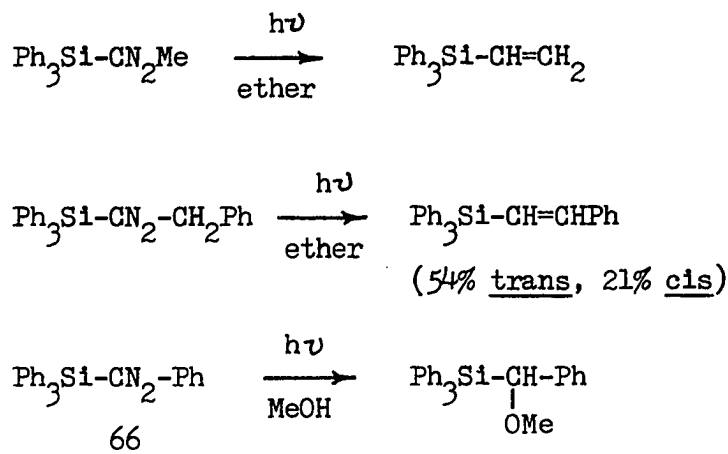
Scheme 49

Therefore the synthesis of dimethylphenylsilyldiazomethane $\underline{127}$ was begun utilizing a modification of the procedure used to synthesize $\underline{65}$ from N-nitroso-N-trimethylsilylurea (68, 69) (Scheme 50).

$$Me_3SiCH_2Cl \quad \xrightarrow{NH_3} \quad Me_3SiCH_2NH_2 \quad \xrightarrow{\text{urea, HCl}} \quad Me_3SiCH_2NHCONH_2$$

$$\Big\downarrow HNO_2$$

$$Me_3SiCHN_2 \quad \xleftarrow{20\% \text{ KOH}} \quad Me_3SiCH_2N(NO)CONH_2$$

$$\underline{65}$$
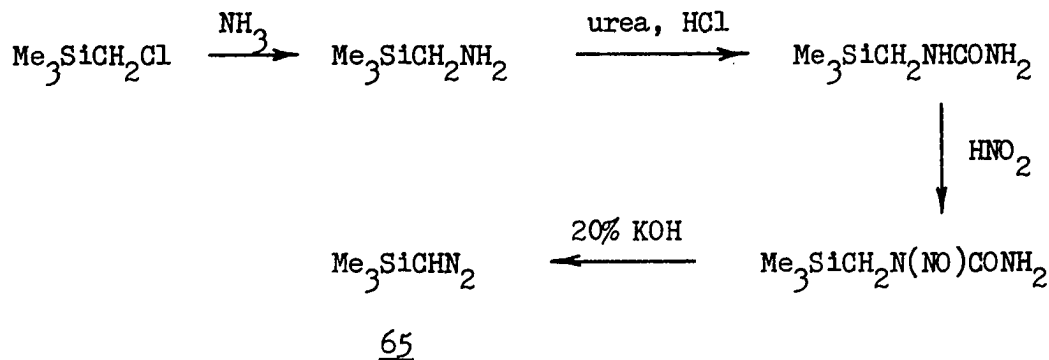
Scheme 50

The modification consisted of using a Gabriel synthesis to obtain the required primary amine. The entire sequence, including the substituted Gabriel reaction, was carried out for $\underline{65}$ as a trial with success.

The synthesis of $\underline{127}$ was then begun. Chloromethyldimethylphenyl-silane $\underline{128}$ was obtained (80%) by the reaction of phenyl magnesium bromide

with commercially available chloromethyldimethylsilylchloride. The

reaction of 128 with phthalimide gave the desired N-substituted phthal-

imide derivative (46%) but substantial amounts of N-methylphthalimide and

the disiloxane were also isolated (Scheme 51). The same reaction with the

trimethyl derivative had, by contrast, gone in 92%.

$$Ph(Me)_2Si-CH_2Cl \quad + \quad \overset{\displaystyle O}{\underset{\displaystyle O}{\bigcirc\!\!\!\bigcirc\overset{C}{\underset{C}{}}}}NH \quad \xrightarrow[\text{DMF}]{K_2CO_3} \quad \overset{\displaystyle O}{\underset{\displaystyle O}{\bigcirc\!\!\!\bigcirc\overset{C}{\underset{C}{}}}}N-CH_2-Si(Me)_2Ph$$

128

+

$$\overset{\displaystyle O}{\underset{\displaystyle O}{\bigcirc\!\!\!\bigcirc\overset{C}{\underset{C}{}}}}N-CH_3 \quad + \quad Ph(Me)_2Si-O-Si(Me)_2Ph$$
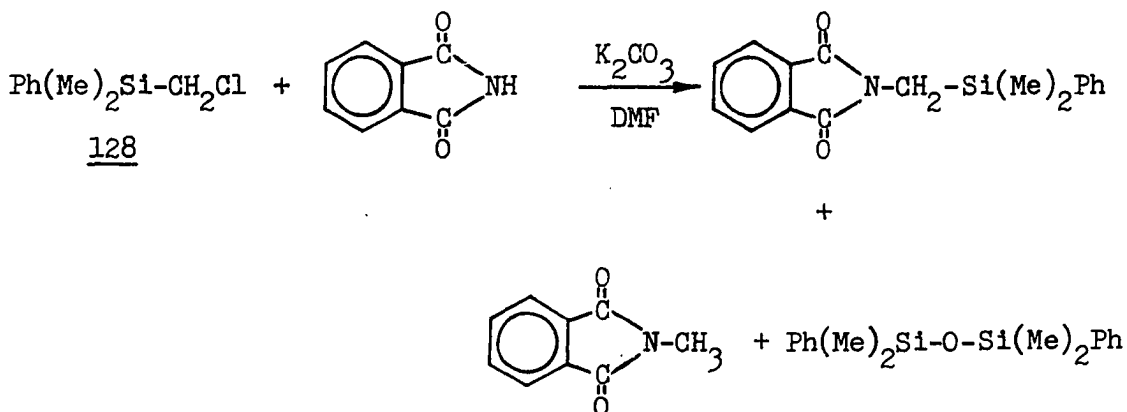
Scheme 51

The conversion of the N-substituted phthalimide to the amine hydro-

chloride also went in low yield (19%) (Scheme 52).

$$\overset{\displaystyle O}{\underset{\displaystyle O}{\bigcirc\!\!\!\bigcirc\overset{C}{\underset{C}{}}}}N-CH_2-Si(Me)_2Ph \quad \xrightarrow[\text{2) HCl}]{\text{1) } H_2NNH_2,\ C_2H_5OH} \quad Ph(Me)_2Si-CH_2NH_3\overset{\oplus}{}\overset{\ominus}{Cl}$$
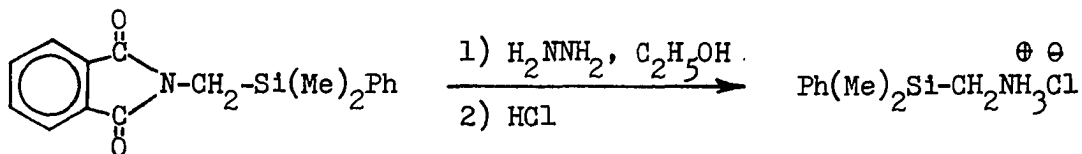
Scheme 52

The amine hydrochloride was then converted to N-nitroso-N-dimethyl-

phenylsilylurea in about 69% yield (Scheme 53) but before the conversion

to 127 was carried out, it decomposed thoroughly while stored in a vacuum

desiccator, under conditions in which the trimethylsilyl analogue was

stable.

$$\underset{Me}{\overset{Me}{Ph\overset{|}{S}iCH_2NH_3Cl}} \xrightarrow[\text{HOH}]{\text{urea}} \underset{Me}{\overset{Me}{Ph\overset{|}{S}iCH_2NHCONH_2}} \xrightarrow[KNO_2, \ H_2SO_4]{C_2H_5OH, \ HOH} \underset{Me}{\overset{Me \ \ \ NO}{Ph\overset{|}{S}iCH_2\overset{|}{N}CONH_2}}$$
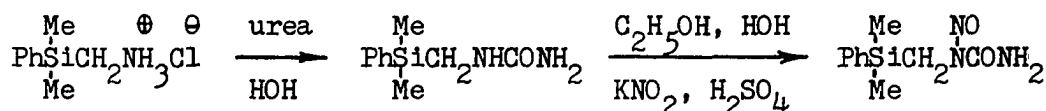
Scheme 53

The overall yield (up to the urea derivative) was then an unexceptional 4.7%. The next step would have been conversion of the urea derivative to 127 by means of 20% potassium hydroxide. Seyferth and his group (40, 41) had only obtained 56% of 65 contaminated with 23% disiloxane for the trimethylderivative. It should be noted that the source of the cleavage seems to be attack at the silicon in the urea derivative, since 65 in the presence of base is unaltered (41). The presence of the phenyl group in the desired compound would probably have then made the cleavage of the silicon-carbon bond an even more important process thereby making the yield of 127 quite low.

This approach to 127 was then abandoned in favor of the more hazardous approach reported by Lappert and Lorberth (39) for 65. Unfortunately they had given absolutely no experimental details and the work of Scherer and Schmidt (37) made the obvious approach seem unpromising. The situation was made even more confusing later, when Lappert, Lorberth and Poland (38) confirmed Scherer and Schmidt's report but still failed to give any indication as to how they had obtained 65 using the same reagents. They did report, at that time, that their yield of 65 was only 5%.

Lacking a distinct alternative, the first attempt to synthesize 127 followed the general procedure Scherer and Schmidt had used unsuccessfully. A slight excess of ethereal diazomethane was added to methyllithium at 0° and the resulting suspension of white lithiodiazomethane allowed to

stir at 0° for about 45 minutes. Then to the suspension was added an equivalent and a half of dimethylphenylchlorosilane dropwise. During the addition the reaction produced several different colors--from light green to orange. The mixture was allowed to stir, then at room temperature, for 24 hours before filtering the salt produced and removing the solvent. Distillation of the residual liquid afforded a fraction whose ir spectrum exhibited a band at 2190 cm^{-1}. The nmr spectrum showed only a multiplet in the phenyl region and two singlets at δ 0.32 and δ 0.27, the latter being a minor peak. Mass spectral analysis showed two molecular ions at m/e 286 and 310 respectively. The former ion corresponds to the molecular weight of the corresponding siloxane and the latter ion to a structure having the same molecular formula as bis(dimethylphenylsilyl)diazomethane 129. Considering the results of Scherer and Schmidt and noting that carbo-diimides absorb at 2140-2130 cm^{-1} (114*), the structure of the ion at m/e 310 could have the carbodiimide structure 130 (Scheme 54).

$$Ph(Me)_2Si\text{-}Cl + Li,CHN_2 \longrightarrow Ph(Me)_2Si\text{-}N\text{=}C\text{=}N\text{-}Si(Me)_2Ph + Li,Cl$$

130
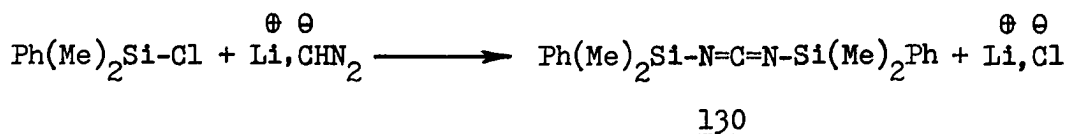
Scheme 54

Both Scherer and Schmidt, and Seyferth and Flood had noted formation of carbodiimide only after heating their respective compounds. In this case also the 2190 cm^{-1} peak did not appear in the crude reaction mixture, did appear in the distillate of the reaction mixture.

The possibility that something other than 127 could be formed by the

*Reference (114), p. 28.

reaction may be better appreciated when it is understood that lithiodiazo-methane is a tautomeric compound that reacts mainly as N-lithioisocyan-amine, H-N=N=CH,Li (135).

Before progressing any further, a few empirical observations should be made. The ir absorptions for the diazo-moiety in several selected diazo-compounds are: diazomethane 2074 cm^{-1} in solution and 2108 cm^{-1} in the gas phase (40); trimethylsilyldiazomethane 65, 2070 cm^{-1} (40, 41); bis-(trimethylsilyl)diazomethane 63, 2040 cm^{-1} (47); ethyl diazo(trimethyl-silyl)acetate 72, 2090 cm^{-1} (50, 51); ethyl diazo(dimethylphenylsilyl)-acetate 75, 2110 cm^{-1}; and ethyl diazo(triphenylsilyl)acetate, 2095 cm^{-1} (51). The silylmethyl protons appear at approximately the following δ values relative to TMS for the compounds indicated: trimethylsilyldiazo-methane 65, δ 0.20 (40, 41); hexamethyldisiloxane, δ 0.20; ethyl diazo-(trimethylsilyl)acetate 72, δ 0.24; trimethylchlorosilane, δ 0.30; bis-(trimethylsilyl)diazomethane 63, δ 0.20 (47); 1,3-diphenyl-1,1,3,3-tetra-methyldisiloxane, δ 0.30; ethyl diazo(dimethylphenylsilyl)acetate 75, δ 0.50 and dimethylphenylchlorosilane, δ 0.50.

From these data it can be seen that the probable ir absorption for the diazo-moiety in dimethylphenyldiazomethane 127 would be about 2070-2080 cm^{-1} and for bis(dimethylphenylsilyl)diazomethane 129 would be about 2040 cm^{-1}. The silylmethyl protons would probably appear at about δ 0.30.

We were not convinced that the reaction of lithiodiazomethane and di-methylphenylchlorosilane would not yield 127, the reaction was carried out under different conditions. To avoid desilation and gain more selec-tivity in the reaction, the reaction was carried out at lower temperature and with less than an equivalent of chlorosilane.

Thus lithiodiazomethane was generated at -78° and 0.8 equivalents of trimethylchlorosilane added. No visible reaction occurred at that temperature, hence it was allowed to warm slowly. At about -30° the lithiodiazomethane suspension dissolved to produce a light green solution, which then turned yellow and finally orange with the concurrent formation of a white precipitate. The reaction was then warmed to room temperature and upon work-up afforded an orange oil. An ir spectrum of the oil showed three bands between 2500 and 2000 cm^{-1}. A band at 2200 cm^{-1}, a very small band at 2130 cm^{-1} and a band at 2070 cm^{-1} which was sharper and more intense than the 2210 cm^{-1} absorption. An nmr spectrum showed, besides the phenyl multiplet, only a singlet at δ 0.32 (though there were small peaks about the base of the singlet).

An attempt was made to chromatograph the material, but upon adsorption upon silica gel vigorous bubbling commenced and only siloxane was eluted. Diazocompounds can be chromatographed (77), however the proper conditions must be worked out empirically.

The results of the last experiment were encouraging and suggested a further experiment. Lithiodiazomethane was again generated at -78° and to the suspension was added 0.5 equivalent of dimethylphenylchlorosilane. The resulting mixture was then kept at between -50° and -30° for two hours. At the end of the period an excess of aqueous potassium carbonate was added. Work-up of the reaction produced a yellow oil which had no absorption between 2500 and 2000 cm^{-1}. This suggested that the prior reaction had taken place above -30° (or that all of the products were unstable in water).

A final experiment was conducted in which 0.6 equivalent of dimethyl-

phenylchlorosilane at once at 0°. The resulting light green solution was stirred for four hours further at 0° and then worked-up. Only on warming to room temperature did the solution turn deep orange. The resulting yellow-orange liquid exhibited ir absorptions at 2200 and 2070 cm^{-1}. Thus limiting the amount of chlorosilane present did not preclude the formation of the species responsible for the 2200 cm^{-1} absorption, but keeping the temperature between -30° and 0° allowed the formation of the species absorbing at 2070 cm^{-1} which could have been the desired compound 127.

If the 2200 cm^{-1} absorption was due to carbodiimide, it was being formed at much lower temperatures with the substitution of a single phenyl for a methyl group on the silicon. In any case avoiding its formation did not seem easy, and just what was occurring at the time was even less certain because not all of the literature data presented here was available then. Therefore attention was diverted towards the promising work with the α-silyldiazacetates discussed earlier.

As was pointed out in the Historical Section, there is still confusion in the literature concerning these lithiodiazomethane reactions. The results outlined above tend to confirm the reports of Scherer and Schmidt (37) and Lappert, Lorberth and Poland (38). The apparent important difference seems to be that Seyferth and Flood (47) may have avoided the complications of the tautomeric form of lithiodiazomethane by using trimethylsilyldiazomethane as their starting material, and hence were able to obtain 63.

139

EXPERIMENTAL

General

All boiling points and melting points are uncorrected and reported in degrees Centigrade.

The 60 MHz nmr spectra were recorded on a Varian A-60 spectrometer. All chemical shifts are reported in parts per million (ppm), δ units, relative to tetramethylsilane as internal standard unless otherwise noted. The number in parentheses indicating the number of protons causing the signal and the letter following within the parentheses designating the multiplicity of the signal: s, singlet; d, doublet; t, triplet; q, quartet; m, unresolved multiplet.

Infrared spectra were recorded on a Perkin-Elmer model 21 or Beckman IR 12 spectrometer and are reported in wavenumbers.

Mass spectra were obtained on an Atlas CH-4 or an Atlas CH-7 spectrometer.

Vacuum pyrolyses were carried out with a Vycor tube packed with Vycor chips and heated with a Sola Basic Industries Linberg Hevi-Duty model 55035-A tube furnace. Temperatures are uncorrected and reported in degrees Centigrade. Vacuum was furnished by a Consolidated Vacuum Corporation Type VMF oil diffusion pump backed by a Welch Duo-Seal vacuum pump. A hollowed aluminum rod wrapped with heating tape and equipped with a thermometer provided the heat necessary to vaporize the samples into the furnace tube. The pyrolysis products were condensed in a U-tube cooled in liquid nitrogen, a Dry Ice-acetone slush, and were washed from the trap with an appropriate organic solvent after flushing the system with nitrogen

gas.

Photolysis was conducted using a 450 watt Hanovia type 673A high-pressure mercury arc lamp contained in a water cooled quartz immersion well.

Microanalytical data were obtained from Chemalytics, Inc., Tempe, Arizona.

Diethyl mercuribis(diazoacetate) 73

Diethyl mercuribis(diazoacetate) 73 was prepared by the method of Buchner (90) from ethyl diazoacetate, purchased from the Aldrich Chemical Company, Inc., and either red or yellow mercuric oxide. The ethyl diazoacetate was used both unpurified or purified by drying over anhydrous magnesium sulfate, filtering and trap to trap distillation under reduced pressure; mp 101.5-103° (lit. (90) mp 102-103°).

Dimethylphenylchlorosilane 76

Dimethylphenylchlorosilane 76 was either purchased from Pierce Chemical Company or prepared by the method of Maienthal, Hellmann, Haber, Hymo, Carpenter and Carr (91) from dichlorodimethylsilane purchased from Ventron Corp. The material prepared by the Grignard reaction was always contaminated with dimethylphenylbromosilane which was not separated.

1,3-Diphenyl-1,1,3,3-tetramethyldisilthiane 77

The title compound was prepared by the method Champetier, Etienne and Kullmann (92) for hexamethyldisilthiane; 54%, mp 38.5-40°; bp 149°/mm; nmr (CCl_4): 7.60-7.03 (m, 5H) and δ 0.38 (s, 6H).

Ethyl diazo(dimethylphenylsilyl)acetate <u>75</u>

Prepared by the method of Schöllkopf and Rieber (50), and Schöllkopf,

Hoppe, Rieber and Jacobi (53) for ethyl diazo(trimethylsilyl)acetate <u>72</u>,

84%; bp 104°/0.5 mm; nmr (CCl$_4$): 7.70-7.13 (m, 5H), 4.08 (q, 2H), 1.16

(t, 3H) and δ 0.50 (s, 6H) (see Figure 18); ir (film): 2100 (C=N$_2$) and

1700 cm^{-1} (C=O); uv (methanol): 254 mμ (ε = 10,900); molecular ion at

m/e 248; <u>Anal</u>. Calcd. for C$_{12}$H$_{16}$O$_2$N$_2$Si: C 58.03; H 6.49; Found: C 58.15,

H 6.58.

Attempted reaction of trimethylchlorosilane with diethyl mercuribis(diazo-

acetate <u>73</u>

To 150 ml of anhydrous ether under a nitrogen atmosphere at 0° was

added 3.93 g (0.0092 mole) of <u>73</u> with stirring. To the resulting solution

was added dropwise over 0.5 hr 3.0 g (0.0276 mole) of trimethylchloro-

silane dissolved in about 25 ml of anhydrous ether. The mixture was

stirred for one hr at 0° but no reaction seemed to occur. The reaction

was then warmed to room temperature and stirred for an additional 2.5 hr

with no apparent reaction. The solution was then filtered and the ether

removed under reduced pressure from the filtrate to afford a yellow-green

oil. Treatment of the oil with pentane and then ether produced a light

green precipitate and a viscous yellow-orange oil. An nmr of the material

showed no silylmethyl protons and resembled the spectrum of <u>73</u>. An ir of

the material was superimposable upon the spectrum of <u>73</u>.

Attempted reaction of hexamethyldisiloxane with diethyl mercuribis(diazo-

acetate) <u>73</u>

To 7.8 g (0.0183 mole) of unpurified <u>73</u> dissolved in benzene was

added about 3 g (about 0.0183 mole) of hexamethyldisiloxane. The solution was then heated at reflux for 7.5 hr. After 0.5 hr beads of metallic mercury were observed. The solution was then filtered and the benzene removed from the filtrate. An ir of the residue produced bands at 2070 and 1675 cm^{-1} for the diazo and carbonyl groups respectively identical to those of 73.

Attempted reaction of dimethylphenylchlorosilane 76 with ethyl argento-diazoacetate 78

A portion of 0.96 g (0.00812 mole) of silver oxide was added, with stirring, to 0.94 g (0.00825 mole) of ethyl diazoacetate at room temperature. The mixture was then cooled to 0° and stirred for four hr. To the resulting brown mixture was then added the remaining silver oxide over a 1.5 hr period while keeping the mixture at 0°. During the addition of the final portions of the silver oxide, ether was also added. After the final portion of silver oxide was added, the mixture was stirred an additional four hr at 0°. Then 0.99 g (0.00825 mole) of anhydrous magnesium sulfate was added and the mixture stirred for 0.5 hr. Then 1.55 g (0.009 mole) of 76 was added. No reaction was apparent and after 5.5 hr, during which time the reaction was allowed to warm to room temperature; ir and nmr spectra showed no evidence of 75 being present.

Dimethylphenylsilane 80

Dimethylphenylsilane was prepared by the method of Maienthal, Hellmann, Haber, Hymo, Carpenter and Carr (91) by reducing dimethylphenyl-chlorosilane 76 with lithium aluminum hydride; bp 156.5-157.5° (lit. (91) 158-164°).

Reaction of dimethylphenylsilane 80 with iodine

The procedure of Eaborn (136) for iodotriethylsilane was modified.

To 83.9 g (0.33 mole) of iodine crystals in a flame-dried reaction system

under a nitrogen atmosphere was added dropwise 44.9 g (0.33 mole) of di-

methylphenylsilane 80. An immediate reaction occurred producing clouds of

purple fumes. After about one-half of the silane had been added, the reac-

tion subsided. When it was then shaken, a violent reaction occurred. Ad-

dition of the rest of the silane was then added at such a rate as to main-

tain reflux. Once all of the silane had been added and the reaction had

again subsided, the iodine condensed on the condenser was washed into the

reaction vessel with ether. An immediate and violent reaction again

occurred. Once the reaction had settled, it was heated to reflux for one

hr. The reaction remained deep purple, however, hence 6 g (0.044 mole) of

80 was added. The addition caused violent bubbling to occur but the color

remained. After an additional 7 hr at reflux, the color of the solution

was light pink. A small amount of metallic magnesium was then added and

the solution distilled at atmospheric pressure using a short path distilla-

tion apparatus. A low boiling fraction was collected between 30-90°. A

fraction boiling at 150-185° was then collected which appeared to form to

layers; nmr (CCl_4): 7.7-7.0 (m), 1.53 (s), 1.01 (s), 0.9-0.8 (m), 0.32 (d),

δ 0.09 (d). The resonances at δ 1.53 and δ 0.09 were considerably larger

than any others in the spectrum, especially the aromatic multiplet. Hence

it was concluded that silicon-aryl cleavage had occurred (94*).

_____

*Reference (94), pp. 152-154.

Reaction of dimethylphenylsilane <u>80</u> with iodine in carbon tetrachloride

To 9.35 g (0.0367 mole) of iodine dissolved in 15 ml of carbon tetra-
chloride in a flame dried apparatus under nitrogen was added dropwise 5.0 g
(0.0367 mole) <u>80</u> dissolved in 5 ml of carbon tetrachloride. No reaction
seemed to occur after about one-third of the silane had been added, hence
the mixture was heated to reflux. The rest of the silane was then added
and the mixture kept at reflux for 12 hr. The mixture was still a deep
purple (it had been kept wrapped in aluminum foil), hence it was cooled to
room temperature and a sample taken directly for nmr. The spectrum showed
singlets at 7.22, 1.50, 0.98 and δ 0.62. The order of intensity was also
in the order given. There were several other resonances (multiplets and
singlets) but they were very small. The large singlet at δ 7.22 was taken
to be evidence of silicon-aryl cleavage to produce iodobenzene (94*).

Reaction of dimethylphenylsilane <u>80</u> with iodine in ethyl iodide

The procedure was adapted from that of Fritz and Kummer (133) for
phenyliodosilane. To 22 g (0.162 mole) dimethylphenylsilane dissolved in
30 ml of ethyl iodide was added 24.6 g (0.097 mole) of iodine dissolved in
30 ml of ethyl iodide dropwise. After all of the iodine had been added the
mixture was heated to reflux overnight. A small quantity of powdered
copper was then added and the ethyl iodide distilled out of the mixture.
Vacuum distillation of the residue afforded 18 g at 67-75°. Redistillation
at full vacuum yielded a liquid, 16.3 g (37.5%); bp 72-74°; nmr ($CDCl_3$):
7.8-7.18 (m, 5H) and δ 0.97 (s, 6H).

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*Reference, (94), pp. 152-154.

Reaction of dimethylphenyliodosilane 79 with diethyl mercuribis(diazo-

acetate) 73

To 13 g (0.03 mole) of 73 dissolved in ether was added 16.3 g (0.062

mole) of 79 in ether, dropwise. There was no rapid reaction, hence the

reaction was stirred overnight to produce a green-yellow solution and an

orange precipitate. The mixture was filtered and the solvent removed under

reduced pressure to yield a yellow-green oil and more precipitate. The

residue was filtered and the filtrate distilled to afford a yellow-green

liquid, 12.3 g (81.5%); bp 103-104° (full vacuum); spectral data identical

to that reported above for 75.

Reaction of ethyl lithiodiazoacetate with trimethylchlorosilane

The reaction was carried out according to the procedure of Schöllkopf

and Frasnelli (52) using 5 g of trimethylchlorosilane. Analysis of the

crude product by nmr showed a complex mixture present which included, at

least in part, the following compounds: ethyl diazoacetate, hexamethyldi-

siloxane, ethyl diazo(trimethylsilyl)acetate and an olefinic product(s).

Attempts to chromatograph the material on silica gel gave poor separation.

Distillation at atmospheric pressure was considered to be too dangerous

because of the ethyl diazoacetate still present and distillation at reduced

pressure gave no hope of separation. To make this synthesis work one would

need practice, standardized reagents and products whose physical properties

are significantly different from those of ethyl diazoacetate.

Pyrolysis of ethyl diazo(dimethylphenylsilyl)acetate 75 at various

temperatures

A. 0.169 g of 75 was pyrolyzed at 200-220°. Thin layer chromatography

of the trapped product showed it to be identical to the starting material.

B. A sample of 75 heated to about 100° was pyrolyzed at 200±15°. An nmr spectrum of the trapped material was identical to that of the starting material.

C. 0.9671 g of 75, heated to about 70°, was pyrolyzed at 245-260°. 0.4 mg of residue was left in the sample tube, 46.3 mg of material was washed from the pyrolysis column and 899.2 mg of material, yellow-green, was collected in the liquid nitrogen trap. An nmr spectrum of the trap material in CCl_4 showed 7.69-7.02 (m), 4.07 (q), 3.72 (q), 1.13 (t), 0.5 (s) and δ 0.32 (s). Integration gave for m:q:t:s, 5:2:3:6 with the ratio of singlets being 3.6:1. An nmr spectrum of the column wash in CCl_4 showed 7.7-6.85 (m), 1.45-0.75 (m) and δ 0.75-(-0.1) (m). Prominent were 0.23 (s) and δ 0.07 (s). The spectrum was too dilute to be integrated.

D. 1.1014 g of 75 was pyrolyzed at 320-370°. 1.8 mg of residue remained, 77.3 mg of material was washed from the column and 875.4 mg of yellow-orange material was trapped. The trapped material bubbled upon warming and a white solid material sublimed. An nmr (CCl_4) of the trap material showed a multiplet at 7.67-6.89 with a prominent singlet at 7.11, three small singlets at 6.02, 5.93 and 5.85, a small singlet at 4.39, a quartet at 3.68, small prominent peaks at 1.82, 1.75 and 1.48, a triplet at 1.14, a small peak at 0.9, and a multiplet at 0.69-0.3 with prominent singlets at 0.41, 0.35 and δ 0.30. The singlet at δ 0.30 dominated the methylsilyl-proton region. Integration showed the aromatic to methylsilyl regions to be 5:6 and the quartet to triplet regions to be 2:3. The quartet due to the starting material was no longer present, but the intensity of the new quartet ascribed to 82 indicated it to be about 60% of the

material present. An nmr (CCl_4) of the column wash showed multiplets at 7.74-7.04, 1.53-0.83 and 0.68-0.0 with prominent singlets at 0.39, 0.32 and δ 0.08. Integration of the multiplets gave a ratio of approximately 5:2:6.

E. 1.0535 g of 75 was pyrolyzed at 395-420° to afford 6.0 mg of residue, 136.1 g of column washings and 742.9 mg of trapped material. On warming the trap, a white solid sublimed. An nmr (CCl_4) of the trapped material was essentially similar to that of the trapped material obtained in the 320-370° run with the following exceptions: the singlet at 4.39 was less prominent, a small multiplet appeared to underlie the 1.82 and 1.75 peaks, the small peak at 0.9 was less prominent and a new singlet developed at δ 0.54. Integration gave approximately the same ratios for the aromatic to methylsilyl regions and quartet to triplet regions, but the intensity of the quartet decreased to suggest that 82 amounted to about 50% of the material. An nmr spectrum (CCl_4) of the column washings exhibited the same absorbances and intensities as the corresponding spectrum in run D, except that a small sharp singlet had developed at δ 5.2.

F. 1.1199 g of 75 was pyrolyzed at 495-505° to afford 852.8 mg of light red-orange trapped material, 46.0 mg of column washings and 8.9 mg of unpyrolyzed residue. On warming, a white solid in the trap sublimed. An nmr spectrum (CCl_4) (Figure 19) of the trapped material exhibited essentially the same absorptions as those obtained in run D and E with the following exceptions: the singlet at 7.11 appeared to be less intense, the region 1.95-1.6 appeared as a multiplet with prominent peaks at 1.93, 1.83 1.76, 1.74, 1.65, and 1.63, and the singlet at 0.54 increased significantly in intensity relative to the δ 0.30 singlet. Integration gave region intensity ratios essentially the same as found in runs D and E and indicated

that 82 was approximately 40% of the mixture. An nmr spectrum (CCl_4) of the column washings showed a broad complex multiplet from 7.83-6.85, a singlet at 5.25, a multiplet from 0.6 to about 0.2 above TMS with a large singlet at δ 0.7. An ill-resolved multiplet of low intensity was also present at 1.3-1.1. Integration showed the intensity of the aromatic region to the δ 5.25 singlet to the methylsilyl region to be about 58:5:94, which suggested that the integrity of the phenyl groups had been lost to some extent.

An attempt was made to separate the components of the trap mixture by thin layer chromatography. Using silica gel as the adsorbent and 5% ethyl acetate in Skelly B, separated the mixture into at least five components. When the separation was scaled up to thick layer chromatography with 666 mg of sample and using ultraviolet light as a detector, again five components could be identified. When the least polar and largest component (375 mg) was isolated and rechromatographed, using 3% ethyl acetate in pentane, seven components were detected. Again, the least polar component was by far the most abundant (241 mg). These results suggested that either the first separation was very poor or that the components were unstable or reactive (or both). An nmr spectrum (CCl_4) of the largest component obtained in the second separation showed those peaks associated with 82 along with some remaining multiplet in the aromatic region, the three small peaks at about δ 6 and the two small peaks at 1.82 and δ 1.75. Notably gone was the new singlet at 0.54 and the multiplet about δ 3.0.

Rechromatography of the component by double elution with hexane again produced seven components, the largest of which was again the least polar. One of the smaller components (29 mg) was found to be crystalline and was

recrystallized; mp 72-75°, nmr (CDCl$_3$): 10.8 (s, about 1H), 7.3 (s, 5H) and δ 3.65 (s, 2H). The spectrum was identical to that of an authentic sample of phenylacetic acid, literature mp 76-77° (137).

It was not possible to tell if phenylacetic acid had been a small component of the trap mixture or if it had been generated from the trap mixture as a result of the work-up.

G. 1.1805 g of 75 was pyrolyzed at 695-705° to afford 832.7 mg of trapped material, 17.5 mg of column washings and 10.0 mg of unpyrolyzed residue. An evacuated tube fitted with a stopcock was attached to the pyrolysis system before the trap was warmed to room temperature in order to trap the gas produced by the white solid as it sublimed.

Mass spectral analysis of the gas sample showed a significantly enhanced m/e 44 peak compared to background m/e 44 ion.

An nmr spectrum (CCl$_4$) of the trap sample showed a complex multiplet at 7.72-6.82 in which the 7.11 peak was obscured; somewhat enhanced peaks at 6.02, 5.93 and 5.85 compared to runs D, E and F; a heptet or quintet at 4.45; a low intensity multiplet at 3.97-3.39 underlying a less prominent quartet at 3.68 as compared to runs D, E and F; a multiplet at 2.181.5 with a significant new singlet at 1.89 and other prominent peaks at 1.7, 1.61 and 1.48; a multiplet at 1.45-0.7 underlying a less prominent triplet at 1.12 than in runs D, E and F; a singlet at 1.54 and a large multiplet at 0.5-0.05 with a prominent singlet at δ 0.30. The quartet at 3.68 was not intense enough to reliably estimate the amount of 82 by integration.

H. Five approximately 1 g samples of 75 were pyrolyzed in succession at 600° to obtain a large sample of trapped product. The quantity of column washings obtained was small and not retained. The usual white solid was

also produced but allowed to sublime. An nmr spectrum (CCl_4) of the

material was essentially similar to that obtained for the corresponding

material in run F at 495-505°. Some of the peaks obtained in the spectrum

of the corresponding material obtained in run G at 695-705° also appeared

in low intensity. These peaks would be the multiplet (quintet or heptet)

at 4.45 and the singlet at δ 1.89. Integration showed that the aromatic

to methylsilyl protons remained 5:6 and that the quartet to triplet protons

were still 2:3. Taking the quartet protons as an indication of the amount

of 82 present revealed it to be present in about 37%. A mass spectrum

gave molecular ions at m/e 58(?), 116, 136, 176, 220 and 344.

To determine whether volatile components might be present, a portion

was dissolved in carbon tetrachloride and then the solvent was removed

under water pump pressure with mild external heat applied. An nmr spectrum

(CCl_4) of the residue obtained was identical to the untreated mixture.

D_2O was added to an nmr sample of the mixture in carbon tetra-

chloride, but the only effect was to significantly enhance the resolution

of the spectrum.

A sample of the mixture was treated with methanol and the methanol

then removed under water pump pressure. An nmr spectrum (CCl_4) of the res-

idue showed a loss in the intensity of the singlet at 7.11, a new singlet

at 3.57, a new intense singlet at 3.33, a small new peak at 1.08, almost

complete loss of the 0.54 peak and two small new peaks at 0.12 and δ 0.08.

Separation of the mixture with a butanediol succinate column at 175°

produced eleven peaks with the following retention times: peak a, 1 min;

peak b, 1.32 min; peak c, 1.52 min; peak d, 2.68 min; peak e, 3.15 min;

peak f, 3.84 min; peak g, 4.51 min; peak h, 5.26 min; peak i, 5.6 min;

peak j, 6.49 min; peak k, 11 min and peak l, 15.8 min. Peaks d, f, h, j and k were the predominant peaks. Peak e was a small shoulder of d and i was a shoulder of h. Peak l was so small that it was initially overlooked. Peaks a, b and c comprised 3.4% of the mixture; d, 19.5%; e, 0.05%; f, 9.7%; g, 1.1%; h and i, 36.6%; j, 12.6% and k, 16.5%.

Peaks a-j and peak k were separated and collected by running 50 μl samples. An nmr spectrum of peaks a-j in CCl_4 showed a multiplet at 7.73-7.04; small peaks at 6.11, 6.02, 5.93 and 5.04; a singlet at 1.97; peaks at 1.85 and 1.77; small multiplets at 1.73 and 1.59; a multiplet at 1.34-0.72; a singlet at 0.53 and a large multiplet at 0.5-0.0 with prominent singlets at 0.31 and δ 0.28. An nmr spectrum (CCl_4) of peak k showed the absorbances due to 82 with a low intensity multiplet at 7.72-6.68; very low intensity multiplets at 1.98, 1.88 and 1.77 and a small singlet at δ 0.53. Integration of the peak a-j spectrum showed an aromatic to silylmethyl proton ratio of 158:165 and integration of the peak k spectrum showed a ratio of 5:6 with 82 being approximately 86% of the material as indicated by the intensity of the quartet protons.

An ir spectrum of peak k (capillary film) showed bands at 2941 (w), 2083 (s), 1786 (w), 1695 (m), 1592 (w), 1493 (w), 1253 (m), 1163 (w), 1099 (m), 1073 (m), 948 (w), 922 (w), 821 (s), 790 (m), 751 (w) and 693 cm^{-1} (w). The strong band at 4.80 would be consistent with a ketene structure. A mass spectrum of peak k produced a molecular ion at m/e 220 with losses of 15 and 59 mass units from the molecular ion. The data are consistent with peak k being predominantly 82, and 82 being dimethylphenylsilylethoxyketene.

The material from peak k was taken up in methanol and heated to reflux for 1 hr. The methanol was then removed under water pump pressure and

the residue taken up in CCl_4; nmr (CCl_4): see Figure 22; mass spectrum: molecular ions at m/e 150, 336(?), 344 and 416.

Using 25 μl samples better resolution was obtained in separating the mixture on the butanediol succinate column. Peaks a, b and c because of their size and proximity were collected together; nmr (CCl_4): 7.5-7.17 (m) and δ 0.3 (s) (the sample was too dilute to integrate); mass spec: molecular ion at m/e 286 with a large loss of 15 mass units. The data suggest that a major component could be 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane.

Peak e because of its size and proximity to d was collected with d; nmr (CCl_4): 7.6-7.1 (m, 5H), 4.4 (h, 1H) and δ 0.32 (d, 6H); mass spec: molecular ion at m/e 136. The data suggest dimethylphenylsilane 80 and the nmr is consistent with that obtained for 80.

Peak f and g were collected together; nmr (CCl_4): 7.67-7.13 (m, 5H), 3.63 (q, 0.6H), 2.05-1.74 (m, 0.5H), 1.16 (t, 1.25H), 0.96 (s, 0.5H), 0.95-0.80 (m, 1H), 0.78 (s, 0.3H), 0.55 (s, 0.4H), 0.32 (s, 2.75H) and δ 0.22 (s, 3H); mass spectrum: molecular ion at m/e 180 with losses of 15, 45 and 59 mass units. The mass spectrum and parts of the nmr spectrum (i.e., part of the aromatic multiplet, the quartet, the triplet and the δ 0.32 singlet) suggest dimethylethoxyphenylsilane. The siloxane, however, accounts for slightly less than half of the protons in the nmr spectrum. It should be recalled that this fraction was a mixture of at least two components. The mass spectrum showed no other distinguishable molecular ion and the other component (or components) have not been identified.

Since peak i was a shoulder of peak h, they were collected concurrently; nmr (CCl_4): 7.61-7.10 (m, 5H), 6.73-5.46 (m, 2H), 1.82 (d, 2H); 1.68 (doublet of doublets, 0.7H), 0.36 (s, 2.3H) and δ 0.29 (s, 3.7H); mass

spectrum: molecular ion at m/e 176 with a metastable loss of 15 mass units; ir (capillary film): 2965 (s), 1622 (s), 1420 (m), 1250 (s), 1111 (s), 1068 (w), 985 (m), 836 (s) and 819 cm^{-1}(s). The data suggest a 3:1 mixture of trans- and cis-propenyldimethylphenylsilane 94.

Peak j was collected separately; nmr (CCl_4): 7.68-7.05 (m, 5H), 2.01 (s, 2H), 2.0-1.65 (m, 0.7H), 1.33-1.02 (m, 0.7H) and δ 0.6-0.0 (m, 3H); mass spectrum appeared to exhibit a molecular ion at m/e 116 but there were odd mass ions at larger m/e values also present. The nmr singlet at δ 2.01 was probably acetone contamination since a strong ion in the mass spectrum appeared at m/e 58.

Peak k was collected separately and appeared to equal in volume all of the other components combined. This is in contrast to the area of peak calculated earlier, but is in agreement with the quantity of 82 calculated from its intensity in the nmr spectrum of the crude mixture. The areas of the various peaks were observed to vary from time to time in the collection process and may reflect the presence of unstable components. The spectral data for peak k collected here were essentially identical to those obtained for the same fraction in the earlier separation.

Peak 1 appeared as a low broad fraction; nmr (CCl_4): 7.72-7.2 (m, 5H), 4.21-3.48 (m, 1H), 2.2-1.65 (m, 1H), 1.4-0.92 (m, 1.5H), and δ 0.65-0.0 (m, 6H): mass spectrum: molecular ion appeared at m/e 186 with a loss of 15 mass units. The data suggest a mixture with 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane as one of the components.

I. A sample of 75 was pyrolyzed at 290±5° to yield a Dry Ice-acetone trapped product, whose nmr spectrum indicated the presence of unreacted 75, ketene 82 and small amounts of the olefins 94. The ratio of unreacted 75

to ketene was 1:2.3.

Pyrolysis of ethyl diazo(dimethylphenylsilyl)acetate 75 using a gas phase chromatography column

Gas phase chromatography of 75 using a butanediol succinate column with an injection port temperature of 200° produced a large gas peak at low retention time (probably corresponding to nitrogen) and several peaks which were collected in two fractions. The first fraction consisted of all peaks eluted before the ketene 82 peak; nmr (CCl$_4$): 7.6-7.1 (m), 6.01 (s), 5.92 (s), 5.83 (s), 3.62 (q), 1.83 (d), 1.13 (t), 0.34 (s), 0.30 (s), 0.28 (s) and δ 0.02 (m). The two major components appear to be the cis- and trans-olefin 94 and dimethylethoxyphenylsilane. 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane may also be present. The second fraction consisted of the peak considered to be the ketene 82, ir (capillary film): 2985 (m), 2088 (s), 2035 (w), 1602 (m), 1580 (w), 1502 (m), 1395 (w), 1323 (w), 1261 (m), 1173 (m), 1107 (m), 1080 (m), 1034 (w), 955 (m), 928 (m) and 825 (m). An nmr spectrum (see Figure 20) of the second fraction was identical to those obtained for 82 previously, with no impurities, including the siloxane discernible. A sample of the second fraction was submitted for analysis. Anal. Calcd. for C$_{12}$H$_{16}$O$_2$Si: C 65.41; H 7.32; N 0.0; Found: C 65.20; H 7.01; N less than 0.1%, if any.

Reaction of dimethylphenylsilylethoxyketene 82 with methanol

A gc prepared and collected sample of 82 dissolved in carbon tetrachloride was treated with three drops of methanol in an nmr sample tube. The sample was allowed to stand in a freezer for 33 hr and periodically nmr spectra were taken to follow the course of the reaction. The sample was

then allowed to stand at room temperature for about 15 hr. The methanol

and CCl_4 were removed under water pump pressure; nmr (CCl_4): see Figure

21; ir (capillary film): 2980 (m), 1726 (s), 1604 (w), 1500 (m), 1458 (m),

1437 (m), 1345 (w), 1370 (w), 1350 (m), 1308 (m), 1280 (s), 1257 (s), 1200

(s), 1152 (s), 1100 (s), 1032 (w), 953 (w), 827 (s) and 700 cm^{-1} (s): mass

spectrum: molecular ions appeared at m/e 118, 150, 164, 238, 252 and 266.

Reaction of dimethylphenylsilylethoxyketene 82 with water

A gc prepared and collected sample of 82 dissolved in carbon tetra-

chloride was treated with one drop of distilled water in an nmr sample

tube. The sample was kept at room temperature for 21 hr and vigorously

shaken periodically, nmr (CCl_4): 1.17 (m, 0.25H), 7.59-6.85 (m) and 7.19

(s) for 5H, 6.45-6.33 (s, broad, 1.3H), 4.07 (q, 0.76H), 3.57 (q) and 3.50

(s) for 2.26H, 1.17 (t) and 1.11 (t) for 3H, 0.34 (m, 0.6H) and δ 0.08

(s, 6H).

After 26 hr at room temperature, the water layer was removed and the

sample was washed with deuterium oxide twice; nmr (CCl_4): see Figure 23.

The spectra indicated that ethanol was being extracted from the sample and

that the broad singlet at δ 6.39 was either water soluble material or

exchangeable hydrogens.

The reaction mixture was then added to an ethereal diazomethane solu-

tion and allowed to stand at room temperature for several hours. The ex-

cess diazomethane and ether was then removed under water pump pressure and

the residue taken up in CCl_4; nmr (CCl_4): 8.15-7.80 (m, 0.1H); 7.80-7.02

(m) and 7.20 (s) for 6H; 4.89 (q?, 0.45H); 4.07 (q, 1H); 4.0-3.21 (m), 3.60

(s) and 3.52 (s) for 4H; 1.45-0.80 (m, 7H); 0.38-0.28 (m, 0.7H) and δ 8.08

(s, 6H).

The sample was redissolved in ethereal diazomethane and allowed to stand overnight at room temperature. The solvents were then removed under water pump pressure and the residue taken up in CCl_4, nmr (CCl_4): essentially the same as above except the δ 4.8 quartet was now a complex multiplet.

Reaction of dimethylphenylsilylethoxyketene 82 with aqueous base

0.261 g (0.0012 mole) of gc prepared and collected sample of 82 dissolved in CCl_4 was treated with about 0.6 ml 2.3 M aqueous KOH in an nmr sample tube. The sample was kept at R.T. for 45 hr and vigorously shaken periodically; nmr (CCl_4): 7.6-6.97 (m, 2.25H), 4.85-4.57 (m, 1.65H), 4.2-3.2 (m, 0.9H), 1.9-1.75 (m, 0.2H), 1.45-0.8 (m, 1.2H), 0.37-0.23 (m, 1.8) and δ 0.05 (s, 6H).

The CCl_4 layer was removed; nmr (H_2O): 7.23 (s, 5H); 3.57 (q) and 3.52 (s) for 4H, 1.10 (t, 3H) and 0.05 (s, 3.76H). There was no internal standard present and the chemical shift of the latter singlet was assumed to be δ 0.05.

The aqueous layer was then acidified with a few drops of concentrated HCl and extracted with CCl_4 and the two layers separated; nmr $(H_2O$ with no internal standard): approximately 3.59 (q) and approximately δ 1.10 (t); nmr (CCl_4): 7.87 (s, 1.9H), 7.18 (s, 5H), 4.46 (broad s, 1H), 3.55 (q) and 3.49 (s) for 2.65H, 1.10 (t, 1.16H) and δ 0.18-0.0 (m, 4H). The ratio of intensities for the singlet at 7.18 and the singlet at δ 3.49 was 5:2 suggesting phenylacetate. Ethyl phenylacetate; nmr (CCl_4): 7.18 (s, 5H), 4.08 (q, 2H), 3.48 (s, 2H) and δ 1.21 (t, 3H).

Preparation of trimethyliodosilane

Trimethyliodosilane was prepared from trimethylchlorosilane with
magnesium iodide in zylene by the method of Krüerke (132), bp 103-105°
(lit. (132) bp 108°).

Ethyl diazo(trimethylsilyl)acetate 72

Ethyl diazo(trimethylsilyl)acetate 72 was prepared by the method of
Kaufmann and Rühlmann (51) from trimethyliodosilane and diethyl mercuribis-
(diazoacetate) 73, bp 65-67°/4 mm (lit. (51) bp 70-71°/12 mm): ir (capil-
lary film): 2990 (m), 2110 (s), 1470 (w), 1370 (w), 1280 (s), 1220 (m),
1194 (m), 1085 (s), 1025 (w) and 857 cm^{-1} (s) (lit. (51) ir: 2090 and
1695 cm^{-1}).

Preparation of triphenylsilane

Triphenylsilane was prepared from trichlorosilane with phenyl
Grignard reagent by the method of Reynolds, Bigelow and Kraus (134), mp
35-37°, (lit. (134) mp 36-37°).

Preparation of triphenyliodosilane

The procedure was adapted from that of Fritz and Kummer (133) for
phenyliodosilane. To 20 g (0.077 mole) triphenylsilane dissolved in 30 ml
of ethyl iodide was added 10.8 g (0.0425 mole) of I_2 dissolved in 20 ml of
ethyl iodide dropwise. After all of the I_2 had been added the mixture was
heated to reflux overnight. A small quantity of powdered copper was then
added and the ethyl iodide distilled out of the mixture. The residue was
not distilled but dissolved in hot petroleum ether and filtered under a
nitrogen atmosphere. An attempt was made to recrystallize the iodide from

the petroleum ether but the compound was too reactive and continuously pro-duced a white insoluble solid. The solution was then refiltered and the petroleum ether removed by distillation to afford about 8.0 g of a solid.

Ethyl diazo(triphenylsilyl)acetate 117

Ethyl diazo(triphenylsilyl)acetate 117 was prepared according to the procedure of Kaufmann and Rühlmann (51) using the reactive solid obtained as triphenyliodosilane above and diethyl mercuribis(diazoacetate) 73; mp 72-73.5° (lit. (51) mp 73-74°); nmr (CCl$_4$): 8.0-7.23 (m, 15 H), 4.06 (q, 2H) and δ 0.99 (t, 3H) (Figure 25).

Pyrolysis of ethyl diazo(trimethylsilyl)acetate 72 at various temperatures

A. At 205$^{\pm}$5°. The vacuum pyrolysis of 72 at 200$^{\pm}$5° took about 30 min holding the sample at room temperature. During the pyrolysis no loss in vacuum was observed and the trapped product appeared to be unreacted 72, nmr (neat): identical to 72; ir (capillary film): identical to 72.

B. At 260°. The vacuum pyrolysis of 72 at 260° was conducted with the sample held at 0° and took approximately 3 hr: nmr (neat): 6.37-5.18 (m, 0.16H) with prominent peaks at 6.0, 5.92 and 5.77, 4.15 (q, 2H), 3.95-3.27 (m, 0.95H), 2.24 (m, 0.12H), 1.76 (doublet of doublets, 0.39H), 1.56 (s, 0.16), 1.21 (t, 4.2H), 0.24 (s, 9H) and δ 0.21-0.0 (m, 4.2); ir (capillary film): 2990 (m), 2110 (s), 1740 (shoulder), 1700 (s), 1750 (w), 1370 (w), 1280 (s), 1220 (m), 1194 (m), 1080 (m) and 855 cm^{-1} (s).

C. At 300°. The vacuum pyrolysis of 72 was carried out with the sample held at 0° and required 3 hr. The trapped product appeared orange and rapidly turned yellow as the temperature of the trap rose to room temperature. The product consisted of a liquid and a solid (transparent).

The liquid was drawn off and dissolved in CCl_4, nmr (CCl_4): 5.94 (s), 5.86 (s) and 5.71 (s) were to small to integrate; 4.47-3.04 (m, 2H); 1.86 (d, 0.3H); 1.56 (s, 0.20H); 1.47-0.95 (m, 3H) and δ 0.4-0.0 (m, 9H); ir (capillary film): 2990 (m), 2110 (w, decreasing with time), 1745 (s), 1258 (s), 1120 (m), 1085 (m), 1040 (m) and 853 cm^{-1}(s). The solid material was washed with $CDCl_3$ (a white residue was left); nmr $(CDCl_3$, no internal standard); 4.58-3.25 (m, 2H), 1.57-0.95 (m, 3H) and δ 0.42-0.0 (m, 7H).

D. At $340^{\pm}5°$. The vacuum pyrolysis of 72 was conducted with the sample at room temperature and required 45 min. The trapped products were bright orange at liquid nitrogen temperature but turned pale yellow upon warming to room temperature in the trap. As the temperature of the trap rose a gelatinous solid also formed. The liquid was drawn off; nmr (CCl_4): 6.25-5.30 (m, 0.17H) with prominent peaks at 5.97, 5.89 and 5.75; 4.42-3.25 (m, 2H); 1.79 (d, 0.5H); 1.58 (s, 0.17H); 1.50-0.96 (m, 3H) and δ 0.41-0.0 (m, 10.4H); ir (capillary film): 2990 (s), 2110 (w, decreasing with time), 1740 (s), 1720 (s), 1630 (m), 1450 (w) 1400 (w), 1255 (s), 1120 (m), 1180 (m), 1035 (w) and 850 cm^{-1} (s).

E. At 300°. 0.5 g of 72 was pyrolyzed concurrently with 1.0 ml of methanol from a separate sample holder. The pyrolysis required one hr and afforded a bright orange-red trapped product (oil) which turned light yellow upon reaching room temperature. The trapped material was withdrawn from the U-tube, nmr (CH_3OH): 6.0 (s), 5.92 (s) and 5.87 (s) were too small to integrate; 4.67 (methanol O-H); 4.20 (q, 0.18H); 3.84 (s, 0.65H); 3.70 (s, 1.8H); 3.59 (s, 0.09H); 3.37 (methanol CH_3-); 1.77 (doublet of doublets, 0.25H); 1.22 (t) and 1.15 (t) for 3H; 0.24 (s, 1H) and δ 0.08 (s, 9H).

The methanol was then distilled from the reaction mixture to afford greenish yellow residue with sweet odor; ir (capillary film): 2970 (m), 2095 (w), 1746 (s), 1635 (w), 1440 (w), 1330 (w), 1255 (m), 1195 (m) and 850 cm^{-1} (s).

The residue was distilled from a pot at $0°$ to a pot cooled to $-78°$ under vacuum. The distilled material exhibited the following nmr spectrum ($CDCl_3$, $CHCl_3$ as internal standard): 4.06 (q, 0.37H), 3.77 (s, 1H), 3.70 s, 3H), 3.66 (q, 1H), 3.47 (q) and 3.20 (q) for 2H, 1.23 (t) and 1.17 (t) for 3.35H, 0.24 (s, 0.66H) and δ 0.09 (m, 9H). The residue of the pot to pot distillation was taken up in $CDCl_3$; nmr ($CDCl_3$): 4.6-3.17 (m, 6.3H), 1.5-0.9 (m, 5.8H) and δ 0.35-0.0 (m, 9H).

Qualitative gas chromatograph treatment of pyrolysis products of 72

A qualitative analysis of the pyrolysis trap products was conducted using a 6 foot silicon DC 11 column run at $150°$ with an injection port temperature of $162°$. Injection of 72 on the column produced peaks at retention times of 1.2, 4.1, 8.2 and 9.6 min. The first peak was probably air (or nitrogen) and the last 72. The $200^{\pm}5°$ trap product produced the same pattern. The $260^{\pm}5°$ trap product showed a new peak at 3.2 min which was just visible, otherwise the pattern was the same with 4.1 min peak growing and the 9.6 min peak decreasing. The $300°$ trap product showed three new peaks just visible at 4.6, 5.4 and 15 min. The largest peak was the peak at 4.2 min. In the $340°$ pyrolysis product there were two new products of significance at retention times of 1.6 and 3.2 plus two new small ones at 6.3 and 12.2 min respectively. The more volatile components appeared to predominate above $340°$.

Pyrolysis of ethyl diazo(triphenylsilyl)acetate 117

The pyrolysis of 0.75 g 117 at 300° required 96 hr. The sample
holder was eventually heated to 130° to effect volatilization at a reason-
able rate. Some material decomposed in the sample holder leaving a red-
brown glassy residue. The trapped material in one run appeared light green
and in another yellow green, the color depended upon concentration; nmr
(CCl_4): 7.97 (m, 19H), 3.96 (q, 2H) and δ 1.22 (t, 3H) (see Figure 24): ir
(capillary film): 3075 (w), 2995 (w), 2105 (s), 1600 (m), 1502 (m), 1435
(m), 1396 (w), 1320 (m), 1265 (w), 1180 (m), 1120 (s), 1085 (s), 1035 (w),
1000 (w), 958 (m), 932 (m), 860 (w) and 840 cm^{-1} (w).

The compound remained unchanged for periods of in excess of one week
when kept in CCl_4 solution in a freezer.

Reaction of triphenylsilylethoxyketene 121 with methanol

To a CCl_4 solution of 121 in an nmr sample tube was added one drop of
methanol (35% excess). The sample was kept at room temperature and nmr
spectra run periodically. After 21 hr no further uptake of methanol could
be determined and all 121 was consumed. The sample was kept at room tem-
perature for 21 hr more but no change in the spectrum could be determined;
nmr (CCl_4): 7.82-6.97 (m, 18.5H), 4.08 (s, 0.9H), 3.75 (q, 2.2H), 3.57
(s, 0.5H), 3.44 (s, 2.7H), 3.27 (s, 1H) and δ 1.11 (t, 3H).

In one run the sample was washed with water and in another run the
solvents were removed under water pump pressure. In both cases the nmr
spectrum of the organic products was the same with the exception of the
δ 3.57 singlet which was not present in the spectrum (or was observed
since the solvent $CDCl_3$ caused some shifts in the spectrum) of the sample

in which the solvents had been removed under vacuum; nmr (CCl_4): 7.82-6.97 (m, 20H), 4.07 (s, 0.93H), 4.74 (q, 2H), 3.59 (s, 0.2H), 3.56 (s, 0.2H), 3.53 (s, 0.1H), 3.48 (shoulder) and 3.43 (s) for 2.5H and δ 1.11 (t, 3H) (see Figure 26); ir (capillary film): 3080 (m), 2990 (m), 2110 (w), 1737 (s), 1605 (m), 1500 (m), 1460 (m), 1438 (m), 1396 (w), 1352 (m), 1310 (m), 1280 (m), 1210 (m), 1155 (m), 1124 (s), 1090 (m), 1036 (m), 1002 (w), 960 (m), 902 (w) and 879 cm^{-1} (m).

The aqueous layer obtained upon washing the sample above exhibited a quartet at about 3.61, a singlet at about 3.33 and a triplet at about δ 1.12 (no internal standard).

Treatment of the CCl_4 layer with D_2O caused no change after 5 hr in its nmr spectrum.

A few drops of 5% aqueous NaOH was then added to the nmr tube containing the CCl_4 (after removing the D_2O and washing with H_2O) but no change in the nmr spectrum could be determined after 83 hr although the aqueous layer turned yellow-brown.

The aqueous base layer was then removed and the CCl_4 layer washed with water. To one half of the washed CCl_4 layer was added 1 N HCl which produced no observable change in the spectrum. The contents of the tube were then combined with about 1 ml of 1 N HCl and heated (about 100°) overnight. The organic layer was then taken up in CCl_4; nmr (CCl_4): 7.73-6.9 (m) with a singlet at 7.19, 5.82 (broad singlet), 3.52 (s) and δ 3.44 (s). The areas were in a ratio of 32.5:2.6:1:2. A drop of 10% aqueous NaOH was then added to the sample which caused a white solid to form and become suspended in the aqueous layer. An nmr spectrum of the material was run such that the tube could be raised or lowered in order to scan alternatively

mostly the aqueous base layer or the CCl_4 layer. When the tube was raised in the probe so as to see the aqueous layer, the 7.19 singlet was enhanced relative to the aromatic multiplet and only one upfield singlet remained at δ 3.41. When the sample tube was raised, the aromatic multiplet was dominant and the aromatic singlet was essentially gone. Upfield two singlets could be just seen at 3.58 and δ 3.49 respectively.

When the two layers were separated, essentially the same patterns were seen in their spectra. Acidification of the aqueous layer and extraction with CCl_4 gave an exceedingly weak spectrum for the CCl_4 which showed a very small singlet at 7.16 and a smaller singlet at δ 3.53.

The solvent was removed, under house vacuum, from the remaining half of the sample and submitted for mass spectral analysis: molecular ions were found at m/e 376 and possibly 150 with fragment ions at 317, 303, 299, 289 (large), 284, 271, 257 (large), 243 (probably base peak), 226, 221 and 212.

Reaction of triphenylsilylethoxyketene 121 with water

To a sample of 121 dissolved in CCl_4 in an nmr sample tube was added one drop of distilled water. The sample was kept at room temperature and shaken vigorously periodically. The reaction appeared to be complete after 122.5 hr; nmr (CCl_4): 7.9-7.0 (m, 19.7H) with a prominent singlet at 7.19; 6.44 (s, 2.8H); 4.22-3.65 (m), 3.42 (q) and 3.43 (s) for 3.22H and 1.10 (unresolved triplet) and δ 0.95 (t) for 3H.

Washing the sample with water caused the quartet and δ 0.95 triplet to be lost from the nmr spectrum of the CCl_4 layer and appear in the nmr of the aqueous layer.

When the CCl_4 layer was allowed to stand for 24 more hours with water no change could be observed in its nmr spectrum. Treatment of the organic layer with one drop of concentrated aqueous potassium carbonate caused the 7.19 and about 10% of the δ 3.43 singlet to be lost from the organic layer to the aqueous layer. When the aqueous layer was acidified with HCl and extracted with CCl_4, an nmr spectrum for the CCl_4 layer was obtained as: 10.42 (s, 1.3H), 7.18 (s, 5H), 5.2 (s, water) and δ 3.56 (s, 2H).

Further treatment of the organic layer of the reaction mixture for 18.4 hr with concentrated aqueous potassium carbonate produced no further change in the nmr spectrum of the mixture, nor did treatment of the mixture with 5% sodium hydroxide solution for 10 hr; nmr (CCl_4): 7.78-6.5 (m, 29.5H), 4.94 (s, 0.95H), 4.75 (s, 3.5H), 4.08-3.52 (m, 2.06H), 3.4 (s, 0.5H) and δ 1.39-0.70 (m, 3H). The 4.08-3.52 multiplet can be seen as the following major peaks: 4.04, 3.97, 3.93, 3.85, 3.80, 3.73, 3.68 and δ 3.57. The 1.39-0.70 multiplet can be seen as the following major peaks: 1.32, 1.22, 1.19, 1.11, 1.07, 0.98, 0.97, 0.85 and δ 0.79 and could be interpreted as a set of four triplets.

Treatment of the organic layer with 25% aqueous sodium hydroxide overnight caused the sample to settle into three layers. The top aqueous layer was slightly colored, nmr (H_2O, no internal standard): nothing but a slight aromatic region multiplet. The middle layer was brown and appeared very viscous, the addition of water caused a light yellow lower layer to form (CCl_4 ?) and the aqueous layer to become cloudy; nmr (H_2O, no internal standard): 7.71-7.42 (m, 1.4H), 7.42-6.98 (m, 8H) with a singlet at 7.20 (assumed), 3.50 (q), 3.38 (s) and δ 1.0 (t, 3H). The lower layer was light yellow, nmr (CCl_4): large aromatic multiplet at 7.8-6.7 and a small

singlet (?) at δ 3.5.

Reaction of triphenylsilylethoxyketene 121 with aqueous sodium hydroxide

To a CCl₄ solution of 121 in an nmr sample tube was added one drop of 50% aqueous sodium hydroxide. When the tube was shaken an immediate gelatinous precipitate formed with darkening of the solution. The large amount of solid formed prevented taking an nmr spectrum until an equal volume of distilled water was added to dissolve the mass. The two layers were then separated to afford a light yellow organic layer and a brown aqueous layer. The organic layer gave the following nmr spectrum which was unaltered after standing 10 hr longer with the basic layer present; nmr (CCl₄): 7.82-6.94 (m, 20.6); 4.05-3.36 (m, 2H) which appeared in part as two quartets at 3.84 and 3.78; and 1.38-0.82 (m, 3H) which appeared in part as three triplets at 1.25, 1.22 and δ 1.06. The aqueous base layer gave the following nmr spectrum: 7.20 (s, assumed), 3.5 (q), 3.4 (s) and δ 1.01 (t).

Addition of acid to the aqueous layer produced a white solid which was extracted into CCl₄; nmr (CCl₄, no internal standard): 9.0 (s, 1.4H), 7.2 (s, 5H), 4.95 (s, water) and δ 3.5 (s, 2H).

Evaporation of the CCl₄ from the latter layer afforded a yellow semisolid mass. The material was recrystallized from petroleum ether to afford white crystals with a trace of liquid which repeated recrystallizations would not eliminate, mp 75.5-77° (lit. for phenylacetic acid (137) mp 76-77°). Mixed melting point with authentic phenylacetic acid gave 76-77.5°.

Photolysis of ethyl diazo(dimethylphenylsilyl)acetate 75 in cyclohexane

5.25 g of 85% ethyl diazo(dimethylphenylsilyl)acetate 75 and 15% 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane was dissolved in about 250 ml of

cyclohexane and irradiated in pyrex for 2 hr. The excess cyclohexane was then removed under reduced pressure at room temperature to afford about 6 g of an orange liquid; ir (film): 2940, 2100 and 1715 cm^{-1}; nmr (CCl_4): 7.8-6.77 (m), 4.32-3.37 (m), 2.27-0.68 (m) and δ 0.60-(-0.23) (m). There were several major resonances recognizable however: 1.41 (s), 1.03 (t), 0.49 (s), 0.39 (s) and δ 0.30 (s).

Thin layer chromatography (silica gel) indicated the presence of at least four components. A portion (250-500 mg) of the mixture was chromatographed on a thick layer silica gel plate with carbon tetrachloride. The plate was developed three times to yield eight recognizable bands using ultra violet light. Only the leading two bands were separated however. The bands were scraped from the plate and the components washed from the gel with chloroform.

The top-most band (band eight) was found to be a liquid; nmr (CCl_4): 7.57-7.07 (m, 5H) and δ 0.31 (s, 6H); mass spectrum: molecular ion at m/e 286. The data is consistent with band eight being the siloxane.

Band seven was also a liquid; nmr (CCl_4): 7.65-7.13 (m, about 7H), 4.18-3.60 (2 t, about 2H), 2.23-0.63 (m, about 15H) and δ 0.36 (d, about 6H) (there were also several other very small peaks present); mass spectrum: molecular ion at m/e 304. The data is consistent with the structure being the insertion product of the carbene into the cyclohexane: ethyl 2-cyclo-hexyl-2-(dimethylphenylsilyl)acetate 125. Bands five and six were essentially identical to band seven but smaller.

Band four was a liquid; nmr (CCl_4): 7.18 (s, about 5H) (a small multiplet 7.65-7.02 was also present), 4.08 (q, about 2H), 3.49 (s, about 2H), 1.22 (t, about 3H), 0.35 (d, small) and δ 0.09 (d?, very small); mass

spectrum: molecular ion at m/e 164. The data is consistent with the

major component of the band being ethyl phenylacetate 126. An authentic

sample was prepared and its nmr was identical.

Bands three, two and one were very small.

An attempt was made to chromatograph the mixture on silica gel but

only the siloxane separated, the other components coming off together with

no separation.

While being stored in the freezer the color of the mixture changed

from the original orange to yellow.

Treatment of ethyl diazo(dimethylphenylsilyl)acetate 75 with silica gel in

carbon tetrachloride

To 0.75 g of a mixture of 75% ethyl diazo(dimethylphenylsilyl)acetate

75 and 25% 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane was added 0.5 g of

silica gel "G" for thin layer chromatography and 2.5 ml of carbon tetra-

chloride. The mixture was stirred for 2.5 hr and then filtered. An nmr

was obtained for the filtrate which showed no change except for a slight

drop in intensity for the δ 0.51 (of 75) resonance and a corresponding

increase in the δ 0.31 (of the siloxane) resonance indicating that perhaps

some silicon-carbon cleavage had occurred. The ir spectrum of the material

was identical to that of starting material except for a new absorption at

757 cm^{-1}. Apparently very little decomposition had occurred and there was

no indication of ethyl phenyl acetate being formed.

Treatment of ethyl diazo(dimethylphenylsilyl)acetate 75 in CCl_4 with

aqueous hydrochloric acid

To a sample of 75 (75% mixture with siloxane) dissolved in CCl_4 in an

nmr sample tube was added 8-10 drops of concentrated hydrochloric acid. The tube was shaken and the mixture then allowed to settle. When no further gas formation was observed the CCl_4 layer was colorless; nmr (CCl_4): 7.37 (m, 11H), 4.08 (q, 2H), 3.81 (s, 2H), 1.18 (t, 3H), 0.61 (s, 3H) and δ 0.30 (s, 14H). Treatment of the material with D_2O caused the 0.61 singlet to dissipate and the δ 0.30 singlet to grown correspondingly larger.

Chloromethyldimethylphenylsilane 128

Chloromethyldimethylphenylsilane 128 was prepared from chloromethyldimethylchlorosilane with phenylmagnesium bromide by the procedure of Noll, Speier and Daubert (138), 79.5%; bp 50-55°/0.25-0.50 mm (lit. (138) bp 121°/24 mm); nmr (neat): 7.50-7.0 (m, 5H), 2.73 (s, 2H) and δ 0.28 (s, 6H).

N-trimethylsilylmethylphthalimide

N-trimethylsilylmethylphthalimide was prepared according to the procedure of Sommer and Rockett (139), 91.7%; bp 115-116°/1-2 mm (lit. (138) bp 117°/2 mm); nmr ($CDCl_3$): 7.90-7.43 (m, 4H), 3.19 (s, 2H) and δ 0.13 (s, 9H).

N-Dimethylphenylsilylmethylphthalimide

N-Dimethylphenylsilylmethylphthalimide was prepared by the same procedure as used for N-trimethylsilylmethylphthalimide according to the method of Sommer and Rockett (139), 46.1%; mp 48-49°, nmr (CCl_4): 7.72-7.02 (m, 9H), 3.27 (s, 2H) and δ 0.38 (s, 6H). Anal. Calcd. for $C_{17}H_{17}NO_2Si$: C 69.11; H 5.79; Found: C 68.88; H 5.66.

In addition to the desired product above considerable amounts of

N-methylphthalimide; mp 133-133.5° (lit. (140) mp 134°); nmr $(CDCl_3)$:

7.97-7.54 (m, 4H) and δ 3.15 (s, 3H), and 1,1,3,3-tetramethyl-1,3-diphenyl-

disiloxane, nmr (neat): 7.70-7.10 (m, 10) and δ 0.30 (s, 12H).

Trimethylsilylmethylamine hydrochloride

Trimethylsilylmethylamine hydrochloride was prepared according to the

procedure of Sommer and Rockett (139), 42.4%; mp 245-246° (lit. (139) mp

242-243°).

Dimethylphenylsilylmethylamine hydrochloride

Dimethylphenylsilylmethylamine hydrochloride was prepared by the

same procedure as used for trimethylsilylmethylamine hydrochloride accord-

ing to the method of Sommer and Rockett (139), 19%; mp 196-200° (lit. (138)

mp 198-200°); nmr $(CDCl_3)$: 7.67-7.20 (m, 7H), 7.2-6.60 (m, broad, 1H),

3.06 (d, 2H) and δ 0.38 (s, 6H). Addition of D_2O caused the doublet to

collapse to a singlet.

N-Trimethylsilylmethyl-N-nitrosourea

The procedure for N-trimethylsilylmethyl-N-nitrosourea was adapted

from the procedure for N-methyl-N-nitrosourea (141).

To 16.2 g (0.116 mole) of trimethylsilylmethylamine hydrochloride was

added 17.5 g (0.348 mole) of urea in 75 ml of water and the mixture heated

at reflux for 8 hr. On cooling the mixture separated into two layers, the

upper one solidifying. Enough ethanol was then added to this mixture to

effect complete solution. 16.0 g (0.232 mole) of sodium nitrite was then

dissolved in the solution, and the resulting solution added slowly below

the surface of a solution of 6.45 ml (0.116 mole) of concentrated sulfuric

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acid, 50 ml of water and 50 ml of ethanol at 0°. A fluffy white precipitate rose to the surface upon mixing the solutions. Upon completion of the addition, the precipitate was filtered off affording a yellow solid which, after drying in a vacuum desiccator, weighed 14.6 g. The filtrate was kept below 0° and filtered again two days later affording, after drying, 2.7 g more. The total yield was then 17.3 g, 84.8%; mp 96-96.5° (lit. (40) mp 95.5-96°); nmr (CDCl$_3$): 7.0-5.92 (s, 2H), 3.53 (s, 2H) and δ 0.0 (s, 9H); ir (CHCl$_3$): 3520 (w), 1740 (s), 1567 (m), 1473 (m), 1398 (m), 1290 (w) and 1013 (m).

N-Dimethylphenylsilylmethyl-N-nitrosourea

N-Dimethylphenylsilylmethyl-N-nitrosourea was prepared by the same procedure as used for N-trimethylsilylmethyl-N-nitrosourea (141), 69%; mp 63-64°; nmr (CDCl$_3$): 7.70-7.15 9m, 5H), 7.0-6.25 (s, broad, 2H), 3.70 (s, 2H) and δ 0.30 (s, 6H); ir (CHCl$_3$): 3530 (m), 3420 (m), 1740 (s), 1570 (s), 1470 (s), 1400 (s), 1292 (m), 1210 (m, broad), 1111 (m), 1016 (s) and 863 cm^{-1} (s); mass spectrum: major ion at m/e 221 (M$^{+\cdot}$-16).

Storage of N-dimethylphenylsilylmethyl-N-nitrosourea in a vacuum desiccator resulted in complete decomposition.

In one preparation of N-dimethylphenylsilylmethyl-N-nitrosourea the intermediate N-dimethylphenylsilylmethylurea urea product was not completely consumed; 98-99°; nmr (CDCl$_3$): 7.7-7.1 (m, 5H), 5.33 and 4.78 (broad, 2H), 2.77 (d, 2H) and δ 0.31 (s, 6H); ir (CHCl$_3$/CDCl$_3$): 3430 (w), 2950 (w), 2250 (w), 1670 (s), 1588 (m), 1510 (w), 1420 (w), 1330 (w), 1215 (w, broad), 1111 (m) and 905 cm^{-1} (s).

Trimethylsilyldiazomethane 65

Trimethylsilyldiazomethane 65 was prepared according to the method of

Seyferth, Dow, Menzel and Flood (40); ir (C_6H_6): 2070 cm^{-1} (lit. (40) ir:

2070 cm^{-1}). An attempt was made to avoid the problem of purifying 65 en-

countered with benzene as solvent for the reaction, since both 65 (bp 96°/

775 mm (40)) and benzene had similar boiling points. The reaction did not

proceed well with ether as solvent however and benzene was eventually sub-

stituted as solvent.

Reaction of dimethylphenylchlorosilane 76 with lithiodiazomethane at 0°

To 24 ml of 2.1 M (0.05 mole) methyllithium in ether in a flame

dried three necked round bottom flask under nitrogen atmosphere at 0° was

added dropwise an ethereal solution of diazomethane (dried over potassium

hydroxide pellets and then metallic sodium) until a yellow solution per-

sisted for 30 min. The white crystalline lithiodiazomethane suspension was

then stirred for an additional 45 min at 0°. To the suspension was then

added 12.8 g (0.075 mole) of 76 dropwise with stirring. The mixture soon

took on a yellow color and when about one half of the silyl chloride had

been added the solid dissolved and the solution turned orange. When the

rest of the silyl chloride had been added, the mixture became cloudy yellow

and after about 15 min yellow-green with a white precipitate. At that

point the temperature of the reaction mixture was 8°. After 30 min as the

temperature rose to room temperature more of the solution turned orange and

more precipitate formed.

A portion of the solution was withdrawn by syringe and the ether re-

moved under water aspirator pressure; ir (capillary film): ill-resolved

spectrum but no absorptions between 2500-2000 cm^{-1}. A second portion was withdrawn and added to CCl$_4$ for an nmr sample, but the material fumed and formed a white precipitate which had to be filtered off before running the spectrum; nmr (CCl$_4$, TMS not found): 7.15 (s, 5H); 0.50 (assumed, s), 0.23 (s) and δ 0.14 (s) for 9H.

The reaction mixture was filtered under nitrogen but the filtrate formed a precipitate, hence the ether was removed by distillation and then all volatile materials below 200° collected by distillation at about 0.5mm. The orange distillate obtained was redistilled at 0.5 mm to afford 2.5 g of colorless material from 42-80° and 5.85 g of a yellow material from 80-200°.

The 42-80° fraction fumed when exposed to air and became cloudy on standing; nmr (neat): 7.8-7.17 (m, 5H); 3.30 (s, 0.29H); 0.67 (s) 0.51 (s) and δ 0.30 (m) for 6H: ir (capillary film): 2980 (w), 1430 (m), 1255 (m), 1120 (m), 1068 (broad), 1000 (w), 840 (s), 813 (s), 792 (s), 733 (m), 709 (m) and 697 cm^{-1} (m). The 0.51 singlet in the nmr spectrum could be 76 and at least part of the δ 0.30 singlet could be the corresponding siloxane.

Spectral data for the 80-200° fraction; nmr (neat): 7.70-7.03 (m, 5H), 0.32 (s, 4.75H) and δ 0.27 (s, 1.5H); ir (capillary film): 2980 (m), 2190 (s), 1430 (m), 1406 (w), 1203 (s), 1177 (w), 1118 (s), 1058 (broad), 1000 (w), 932 (m), 833 (s), 807 (s), 788 (s), 729 (s) and 698 cm^{-1} (s).

The 80-200° fraction was refractionated under vacuum to afford 0.15 g at 80°, 2.2 g of a light green material at 132° and 2.8 of yellow material from 132-155°. The nmr and ir spectra for the last two fractions were identical to that of the original 80-200° fraction except for slight differences in relative heights in the δ 0.32 and 0.27 singlets.

Mass spectra for the latter two fractions also showed the same two

molecular ions at m/e 286 and 310. The m/e 286 ion probably corresponds to

1,1,3,3-tetramethyl-1,3-diphenyldisiloxane and the δ 0.32 singlet. The

m/e 310 ion corresponds to a molecular formula $C_{17}H_{22}N_2Si$.

Reaction of dimethylphenylchlorosilane 76 with lithiodiazomethane at -78°

To 82 ml of 0.36 M (0.0294 mole) ethereal diazomethane (dried over

sodium), under a nitrogen atmosphere at -78° was added 14 ml of 2.1 M

(0.0294 mole) of methyllithium dropwise with stirring. A white precipi-

tate formed and at the end of the addition a slight yellow color was still

present. To the lithiodiazomethane suspension was added 4.0 g of 76 in

ether dropwise. No apparent reaction occurred and the mixture was stirred

at -78° for 5 hr. The mixture was then allowed to warm to 0° over a 2.5 hr

period. Upon reaching about -30° the lithiodiazomethane dissolved and

formed a light green solution which in turn turned yellow and then orange

with the formation of a white precipitate before reaching -20°. When the

mixture reached 0° it was held at about 0° for 2 hr and then allowed to

warm to room temperature. Water was then added to the mixture which pro-

duced no visible reaction.

Solvent and excess diazomethane was removed under water pump pressure

to afford a residue which was dissolved in ether and filtered. The ether

was removed under water pump pressure from the filtrate to afford an orange

liquid; ir (capillary film): 2210 (m, broad), 2135 (w), 2090 (shoulder)

and 2075 cm^{-1} (m); nmr (CCl$_4$): 7.73-7.08 (m, 5H), 3.32 (s, too small to

integrate) and δ 0.30 (s, 6H).

An attempt was made to chromatograph the material on silica gel with

pentane, but when the neat liquid was added to the adsorbant, vigorous bubbling commenced. It could not be determined whether a reaction was occurring or whether the heat of adsorption was too high for pentane. When the bubbling subsided only one band was eluted, nmr (CCl_4): same as above crude material.

The spectra in both cases were indicative of 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane.

Reaction of dimethylphenylchlorosilane 76 with lithiodiazomethane at -50° to -30°

The reaction was initiated as in the -78° experiment with 164 ml of 0.36 M (0.0588 mole) ethereal diazomethane, 28 ml of 2.1 M (0.0588 mole) of methyllithium and 5.0 g (0.0294 mole) of 76.

The temperature of the reaction mixture reached -50° from -78°, it was held to between -50° to -32° for 2 hr. After that period excess potassium carbonate solution was added dropwise to the mixture. The addition caused gas to be evolved and when the addition was complete, the mixture was warmed to room temperature while removing any unreacted diazomethane and the solvent under water pump pressure. The residue was filtered to afford a pale yellow liquid; nmr (CCl_4): 7.63-7.05 (m, 5H), 5.0-4.6 (m, 0.77H), 3.68-3.27 (m, 0.385H), 1.27-0.80 (m, 0.52H), and 0.32 (s) and δ 0.24 (s) for 6H; ir (capillary film): 3310 (m, broad), 3080 (w), 2970 (m), 1258 (s), 1122 (s), 1069 (m, broad), 870 (s), 832 (s), 786 (s), 742 (m), 730 (m) and 701 cm^{-1} (s); mass spectrum: molecular ion at m/e 286 and a small ion at 310. The 0.31 and 0.24 singlets are in the ratio 1:2 in the nmr spectrum whereas usually the δ 0.31 peak is larger.

Reaction of 0.6 equivalent dimethylphenylchlorosilane 76 with lithiodiazo-methane at 0°

Ethereal diazomethane (dried over sodium) was added dropwise to 23.2 ml of 2.1 M (0.0489 mole) methyllithium at 0° with stirring until the resulting mixture remained yellow. An excess of diazomethane was then added and the mixture allowed to set for 1 hr at 0°. After that period 5 g (0.0293 mole) of 76 was added at once to the mixture and the reaction stirred for 4 hr at 0°. After that period the temperature was allowed to rise while the solvents were being removed under water pump pressure through a drying tube. As the temperature of the reaction rose the mixture changed from light green-yellow to orange. When removal of the solvents had been completed the residue was washed with pentane.

The pentane was removed from the yellow wash after drying over anhydrous magnesium sulfate to afford an orange oil; ir (capillary film): 3420 (, broad), 3080 (w), 2970 (m), 2200 (m), 2070 (w), 1720 (m), 1690 (s), 1450 (w), 1432 (m), 1330 (m), 1255 (m), 1120 (m), 1090 (w), 875 (m) and 830 cm^{-1} (s).

PART III: SOLVOLYSIS OF 2-FERROCENYL-

CYCLOPROPYLCARBINYL ESTERS

HISTORICAL

In 1957 Weliky and Gould (142) reported that ferrocenylphenylcarbinol and diferrocenylphenylcarbinol were converted to their corresponding methyl ethers by merely boiling the carbinols in aqueous methanol. They suggested that the ease with which the ethers were obtained indicated that the energy barrier for conversion of the carbinols to the corresponding carbonium ions was lowered possibly by an unusual ability of the ferrocene system to stabilize the carbonium ion. They further suggested that the stability was manifested by delocalization of the positive charge through a partial shift of d-electron density from the iron atom into the ring.

Further indications of unusual stability for α-ferrocenylcarbonium ions was reported by Schlögl and Mahar (143, 144) when they reported that ferrocenylmethylcarbinol could be converted to vinylferrocene 131 merely by shaking a benzene solution of the carbinol with acidic alumina. Methyl-phenylcarbinol was found to be inert under the same conditions.

Vinylferrocene 131 was found to add weak acids, such as hydrogen azide and acetic acid, under conditions which olefins generally do not add (145). The contrasting results with ferrocene induced Buell, McKwen and Kleinberg (145) to postulate that the mechanism of addition proceeded by way of a facilely formed intermediate carbonium ion which had unusual stability.

Reinhart, Kittle and Ellis (146) reported that the Friedel-Crafts alkylation of ferrocene with 1,2-dichloroethane produced 1,1-diferrocenyl-ethane through the rearrangement of an initially formed carbonium ion 132 (Scheme 55). Even though the reaction may have been predicted on the

assumption that a secondary carbonium ion would be more stable than a pri-

mary ion, the analogous reaction with benzene proceeded to yield dibenzyl

without rearrangement (147).

$$Fer-H \xrightarrow[\text{AlCl}_3]{\text{ClCH}_2\text{CH}_2\text{Cl}} \underset{\underline{132}}{Fer-CH_2CH_2^{\oplus},AlCl_4^{\ominus}} \longrightarrow Fer-\overset{\oplus}{CH}-CH_3,AlCl_4^{\ominus}$$

$$(Fer = C_5H_5FeC_5H_4)$$

$$\begin{array}{c} CH_3 \\ | \\ Fer-CH-Fer \end{array}$$
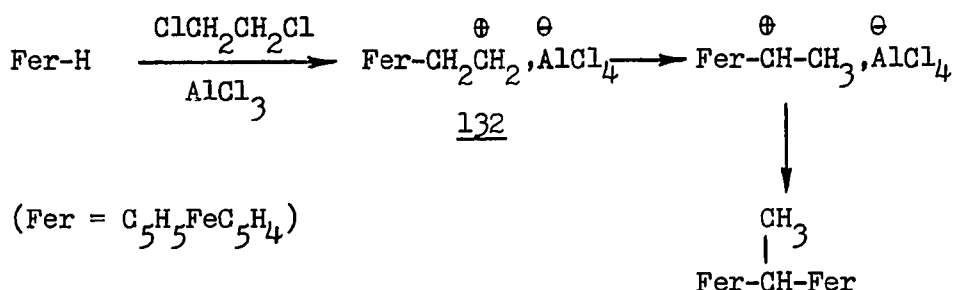
Scheme 55

The solvolysis of metallocenylcarbinyl acetates in 80% acetone-water

solution has been shown to proceed through a carbonium ion intermediate by

way of an uncatalyzed ionization of the carbon-oxygen bond (148, 149).

Table 3 summarizes the results of the reactions. The addition of acetate

ion to the reaction mixture of methylferrocenylcarbinyl acetate greatly

lowered the rate, but the addition of sodium perchlorate had only a negli-

gible effect on the rate. Similarly the addition of sodium hydroxide had

only a small influence on the rate suggesting that the main reaction was

not an S_N2 displacement of acetate by hydroxide. Of particular interest

was the observation that the metallocenyl acetates solvolyzed with rates

greater than those of triphenylmethyl acetate.

In 1963 Hill (150) reported the extremely rapid solvolysis of α-ferro-

cenylethyl chloride in 60% ether-40% ethanol. The compound was found to

solvolyze about 500 times faster than trityl chloride again indicating the

presence of a strongly stabilized α-ferrocenylcarbonium ion.

Other information concerning the relative stabilities of α-ferro-

179

Table 3. Relative rates of solvolysis of metallocenylcarbinyl acetates

Compound	Relative rate	Reference
methylferrocenylcarbinyl acetate	1.00	148, 149
methylferrocenylcarbinyl acetate	0.21^a	148
methylferrocenylcarbinyl acetate	0.98^b	148
methylferrocenylcarbinyl acetate	1.2^c	148
methylruthenocenylcarbinyl acetate	1.36	148
methylosmocenylcarbinyl acetate	5.37	148
phenylferrocenylcarbinyl acetate	3.8	149
p-tolyferrocenylcarbinyl acetate	6.9	149
p-anisylferrocenylcarbinyl acetate	36.1	149
p-carbomethoxyphenylferrocenylcarbinyl acetate	2.8	149
triphenylmethyl acetate	0.15, 0.24	148, 149

[a]Sodium acetate added.

[b]Sodium perchlorate added.

[c]Sodium hydroxide added.

cenylcarbonium ions and α-phenylcarbonium ions has recently been reported by Kaufman and Kupper (151). When 133 was treated with a catalytic amount of 25% sulfuric acid, ferrocenylbenzyl ketone was quantitatively produced but none of the ferrocenylmethyl phenyl ketone (Scheme 56).

They furthermore determined the rates of acid catalyzed hydration for the compounds shown in Table 4. The rates were found to be first order

$$\text{Fer-C} \equiv \text{C-Ph} \xrightarrow{\ \text{H}^{\oplus}\ } \text{Fer-}\overset{\oplus}{\text{C}}\text{=CHPh} \xrightarrow{\ \text{HOH}\ } \text{Fer-}\overset{\overset{\text{O}}{\parallel}}{\text{C}}\text{-CH}_2\text{Ph}$$

<u>133</u>
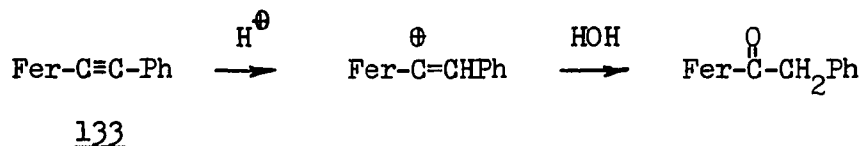
Scheme 56

and further confirmed that α-ferrocenylcarbonium ions were significantly more stable than the analogous α-phenylcarbonium ions.

Table 4. Relative rates of acid-catalyzed hydrations

Compound	Relative rate
Fer-C≡C-H	1.0
Ph-C≡C-H	10^{-5}
Fer-CH=CH$_2$	0.11
Ph-CH=CH$_2$	no perceptible reaction

A more direct study of the stabilities of some α-ferrocenylcarbonium ions has been reported (152, 153). The Hammett-Deno type indicator study (154) again demonstrated the high stability of α-ferrocenylcarbonium ions (Table 5). In all cases the carbinols were converted in acidic solution to a new species which absorbed in the visible and ultraviolet region and recovery experiments confirmed the reversibility of the conversions. Additionally, no further spectral changes occurred in acid solutions up to 96% sulfuric acid.

Habib and Watts have reported the immediate and quantitative formation of the cation <u>134</u> when <u>trans-3-ferrocenyl-1-phenylpropene</u> in methylene

Table 5. Acidities of some α-ferrocenylcarbonium ions

Carbonium ion	pK_R	Reference
ferrocenyl	-1.28^a	152
ferrocenylmethyl	-0.66^a	152
ferrocenyldimethyl	-0.01^a	153
ferrocenylphenyl	$+0.4^a$, $+0.1^b$	152
ferrocenyldiphenyl	$+0.75^b$	152
triphenyl	-6.63^a	154

^{a}In aqueous H_2SO_4.

^{b}In ethanol-water-H_2SO_4 by comparison with trianisylmethyl cation.

chloride was treated with an equimolar amount of triphenylmethyl tetrafluoroborate (155) (Scheme 57). An equivalent amount of triphenylmethane was formed and that indicated that the ion 134 possessed significantly greater thermodynamic stability than the triphenylmethyl cation.
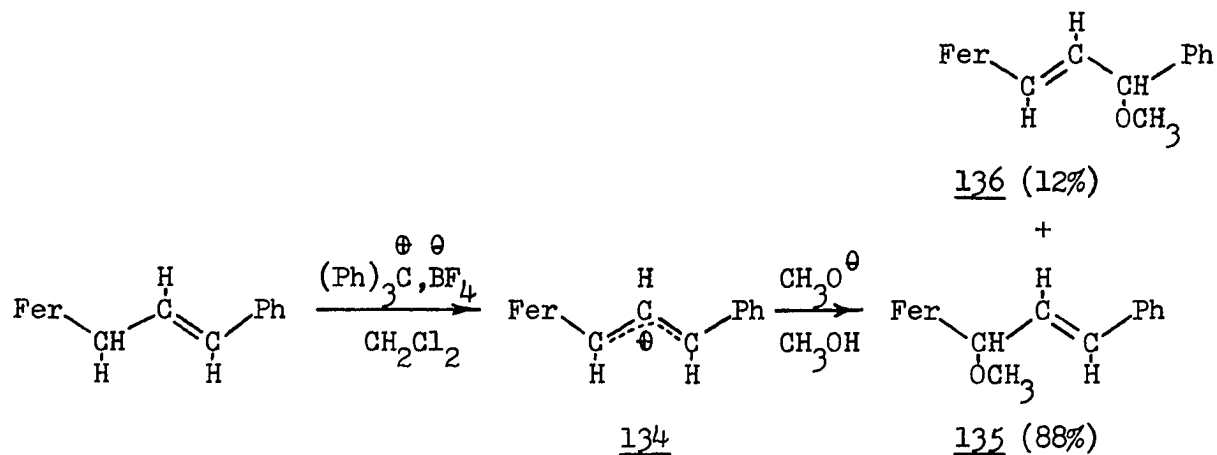
Scheme 57

Dilution of the solution with ether precipitated 134 as a brown air-sensitive tetrafluoroborate and treatment of the solution with sodium methoxide in methanol produced the methyl ether in about 88%, the remaining 12% being the isomeric ether 136 which indicated that the positive charge was localized mainly on the carbon adjacent to the ferrocenyl group.

A number of α-ferrocenylcarbonium ions have been isolated as stable salts (149, 156-163) and many others have been directly observed in concentrated sulfuric acid and other strong acid solutions (149, 164-176).

The mechanism for α-carbonium ion stabilization by a ferrocenyl group has been the subject of some diverse opinion.

Richards and Hill (148, 177, 178) and Trifan and Backsai (179) solvolyzed a number of ferrocenylcarbinyl acetates some of which were shown in Table 3. On the basis of their results with 137, 138 and 139 they ascribed the enhanced stability of the carbonium ions to the effect of neighboring group participation by the iron atom. They found that the acetate 137 solvolyzed about 4 times slower than trityl acetate but about 132 times slower than methylferrocenylcarbinyl acetate. The cationic center in 140 would be prevented from coplanarity with the cyclopentadienyl ring and thus its rate should have decreased if p orbital overlap were required, however its comparable rate with the solvolysis of the trityl acetate indicated that not only resonance with the ring was involved but also perhaps direct participation with the iron electrons (148).

The solvolysis of both 138 and 139 gave exclusively the exo alcohol 141. However the rate of solvolysis of the exo acetate 138 was 2200-2500 times greater than that of the endo isomer 139. In the case of 138, where the iron atom is located backside to the acetoxy group, the iron electrons
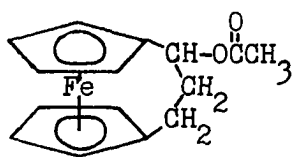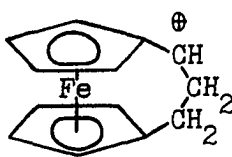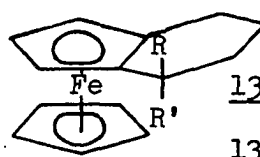
137   140   138 R = OAc, R' = H
139 R = H, R' = OAc
141 R = OH, R' = H

could participate in a backside displacement of the anion in such a way that the developing positive charge would be somewhat shared by the iron atom. Such a participation would stabilize the solvolysis transition state and thus enhance the reaction rate. In 139 such backside participation would not be attainable, since the leaving acetate group would sterically block donation of electrons by the iron atom, and consequently a slower reaction should occur. If there were participation by the iron electrons with the vacant p-orbital of the carbonium ion intermediate, attack by a nucleophile should be expected to occur exclusively from the exo direction since approach from the endo side would be sterically blocked by the participating iron electrons.

The entropy of activation of the exo acetate 138 ($\Delta S^{\dagger}$ = -12.0 e. u.) was found to be very similar to that of the endo isomer 139 ($\Delta S^{\dagger}$ = -11.0 e. u.) and therefore the possibility that the endo isomer was slowed down by some steric interaction can be ruled out. The enthalpy of activation of 138 ($\Delta H^{\dagger}$ = 18.5 kcal/mole) was 5 kcal/mole lower than that of 139 ($\Delta H^{\dagger}$ = 23.5 kcal/mole). The difference in enthalpy of activation was taken as evidence for participation of iron electrons and could account for the large difference in rates for 138 and 139.

Hon and Tidwell (180) found that $\underline{t}$-butylferrocenylcarbinyl acetate

solvolyzed at a rate 4900 times as slow as methylferrocenylcarbinyl acetate

in 60% acetone-water. It was felt that unfavorable steric interactions be-

tween the $\underline{t}$-butyl group and the ferrocenyl ring in the transition state for

$\underline{exo}$ departure of the acetate group accounted for the depressed rate.

The iron participation was originally (148, 177, 178, 179) visualized

as an interaction between the non-bonding E_{2g} ($3d_{xy}$ and $3d_{x^2-y^2}$) non-bonding

electrons with the vacant p-orbital of the carbonium ion $\underline{142}$. Hill and

Richards (177) also noted that by shifting the substituted ring relative to

the rest of the molecule $\underline{143}$ an increase in the total calculated overlap

integral resulted and that the increase could account for the stability of

the α-ferrocenylcarbonium ion. They pointed out however that the magnitude

of the increase was within the errors of calculation and they therefore

cautioned that $\underline{143}$ "is reasonable on the basis of these calculations, but

is not demanded by them".

$\underline{142}$ $\underline{143}$ $\underline{144}$
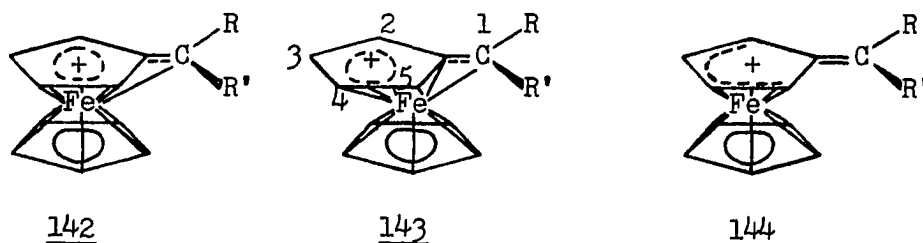
Kaufman and Kupper have reported that styrylferrocene $\underline{145}$ did not re-

act under the mild conditions used to effect hydration of ferrocenyl-

phenylethyne $\underline{133}$ (151). When the reaction was forced under more drastic

conditions, only polymeric addition products were obtained. The reaction was particularly surprising in view of the facile reactions of vinylferrocene with weak acids. The lack of reactivity for 145 may be ascribed to an unusual ground-state stability which may arise from the extended conjugation possible in the molecule (151). Thus reaction of 145 with acid would interrupt the extended conjugation. Of particular interest was the high reactivity of the acetylene 133. It was suggested that extended conjugation of that compound was not interrupted by formation of the carbonium ion 146. In 146 if the charge would be delocalized, it would apparently have to be through direct participation of iron, since resonance with the ring would be impossible.
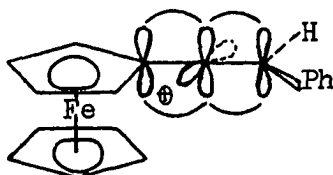
146

Studies by Ware and Traylor (181), Traylor and Ware (182) and Tidwell and Traylor (183) however suggested that ring resonance effects 144 were more important in stabilizing the α-ferrocenylcarbonium ion than direct participation by the iron atom. A linear correlation has been shown to exist between the log k for solvolysis of $ArCHClCH_3$ (Ar = α-Fer, p-anisyl, p-Fer-Ph, p-CH_3-Ph, m-Fer-Ph and Ph) and the carbonyl stretching frequencies of the corresponding ketones $ArCOCH_3$ (181, 182). Such a correlation has not been observed when any anchirmeric assistance occurred (184, 185). Traylor and Perrin (186) showed that neighboring group participation by carbon is eliminated by the substitution of

resonance stabilizing groups on a carbonium ion. The correlation of basic-

ities of aromatic aldehydes with ferrocenylaldehyde yielded σ^+_{-Fer} = -1.30

(187) and Traylor and Ware (182) found σ^+_{-Fer} = -1.4 in the solvolysis of

ArCHClCH$_3$. Since the protonation of the carbonyl group in the aldehyde

would produce the resonance stabilizing -OH group, and since the σ^+_{-Fer}

values observed were so close, it was concluded that if there were partici-

pation by iron, it was not like that of neighboring carbon.

Traylor and Ware also argued that if α-ferrocenylcarbonium ions were

stabilized by direct participation by iron electrons, the effect would not

be transmitted through a phenylene group since such transmission of such an

effect would destroy the aromaticity of the system. They showed that p-

ethylthiomethylbenzyl chloride was solvolyzed only 1.6 times as fast as

benzyl chloride whereas CH$_3$CH$_2$SCH$_2$CH$_2$Cl solvolyzed 10^7 times faster than

ethyl chloride (188). Both α-methoxyethyl chloride and α-ferrocenylethyl

chloride solvolyzed 10^{14} times faster than ethyl chloride and α-(p-anisyl)-

ethyl chloride and α-(p-ferrocenyl)ethyl chloride solvolyzed 5 x 10^4 and

2 x 10^4 times faster than benzyl chloride respectively (181, 182). Of in-

terest also was the observation that α-(anisyl)ethyl chloride and α-(ferro-

cenyl)ethyl chloride solvolyzed with relative rates of 0.5 and 1.0 with

respect to benzyl chloride (181, 182). These results indicated that where-

as the good neighboring group CH$_3$CH$_2$SCH$_2$- was ineffective as a para substit-

uent, the ferrocenyl and methoxy groups remained as effective in the para

position as in the alpha position and that their effects appeared to be

similar.

They also pointed out that comparison of σ^+_{-Fer} and σ^+_{-Fer} values ob-

tained from both solvolysis and carbonyl stretching frequency data showed

almost identical transmission coefficients ($\sigma^+_{-Fer}/\sigma^+_{-Fer}$) for phenylene as 2.1 for the carbonyl stretch and 2.0 for the solvolysis data. Such a correlation would not be expected if neighboring group effects were most important.

Tidwell and Traylor (183) reported that ferrocenylmethyl chloride reacted about eight times faster than methoxymethyl chloride toward either S_N1 ethanolysis or bimolecular reaction with ethoxide ion. Since ferrocenylmethyl chloride competed as well in both the uni- and bimolecular reactions and since neighboring group participation would not accelerate bimolecular reactions, they reasoned that no such interaction was involved.

Traylor and Ware rationalized the solvolysis of 138 and 139 by resonance with the substituted ring (182). Since resonance would be most facile when the leaving group was trans to the iron, by microscopic reversibility, the lowest energy pathway for the reverse process would take the trans geometry and give retention of configuration.

A structure 147 for the carbonium ion has been suggested by Fitzpatrick, Watts and Pettit (189) which is similar to 144 except that the top ring would be displaced relative to the iron atom and bottom ring. The model was based on their nmr study of the cyclobutadienyl-iron tricarbonyl carbinyl cation 148. The formulation of 148 was based upon its nmr spectrum which showed a deshielded singlet and two doublets at higher field and it was felt that the terminal (α) protons of an allylic system should come at higher field than the central (β) proton.

Recent evidence however has indicated that the central proton and the terminal syn (relative to the central proton) proton of various π-allyl tricarbonyl cations such as 149 have approximately the same chemical shift
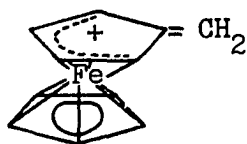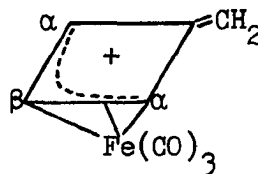
147   148

when the terminal carbon in question also carries a methyl substituent (173).

Moveover, the vinyl group with which the terminal carbons of the allylic

system 148 would be substituted should have a greater deshielding effect

than a methyl group (as in 149), suggesting that the α-protons of a struc-

ture such as 148 should be deshielded relative to the β-proton. Therefore

a preferable structure for the cyclobutadienyl iron tricarbonyl carbonium

ion would be 150 analogous to 142 for the α-ferrocenylcarbonium ion.
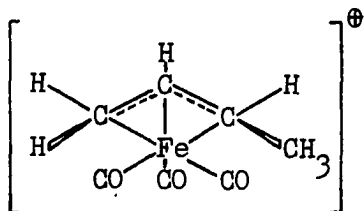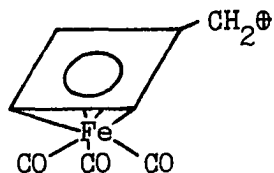
149   150

The structure 147 would coordinate iron with only 16 electrons instead

of 18 despite the availability of the two electrons in the vinyl group to

complete its valence shell. The Mossbauer spectrum of ferrocenylcarbonium

ion showed the same isomer shift as ferrocenylcarbinol (190) which has the

same isomer shift as ferrocene (191). Since the isomer shift would be a

sensitive measure of the relative density of s-electrons at the iron nu-

cleus, there would appear to be similar electronic environments about the

iron atom in the carbonium ion and ferrocene and 142 would better account

for the data.

Cais, Dannenberg, Eisenstadt, Levenberg and Richards (174) measured

the nmr spectra of a number of α-ferrocenylcarbonium ions 151 (Table 6) and

found that the four protons, H-2-H-5, of the substituted cyclopentadienyl

ring in 151 gave two pairs of absorptions, one of which was located at about

70-100 cps higher field than the other. Measurement of the nmr spectra of

the 2-deutero- and 2-methylferrocenylcarbonium ions 152 and 153, 154 led

to the assignment of the upfield absorptions to the H-2 and H-5 protons

(173, 174). That result would not be expected on the basis of a simple

model for the carbonium ion, but the apparently anomalous deshielding of

the β-protons with respect to the α-protons (H-2 and H-5) could be ratio-

nalized on the basis of structure 143 involving participation by the iron

atom. Movement of the iron atom closer to the carbinyl carbon would result

in greater overlap of the appropriate orbitals of the iron and C-2 and C-5

atoms and consequently an increase in electron density in the vicinity of

the α-protons and to a slight decrease in electron density in the regions

of the β-protons. Additionally the effect of the induced field caused by

the anisotropy of the iron atom should also shield the α-protons relative

to the β-protons.

151

152 Y = D, R = H

153 Y = CH₃, R = H

154 Y = CH₃, R = Ph

On the basis of a structure such as 143 for the carbonium ion the data

in Table 6 could be explained. Electron-releasing groups by supplying

electrons towards the positive charge would be expected to minimize the

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atoms and consequently an increase in electron density in the vicinity of

the α-protons and to a slight decrease in electron density in the regions

of the β-protons. Additionally the effect of the induced field caused by

the anisotropy of the iron atom should also shield the α-protons relative

to the β-protons.

151

152 Y = D, R = H

153 Y = CH_3, R = H

154 Y = CH_3, R = Ph

On the basis of a structure such as 143 for the carbonium ion the data

in Table 6 could be explained. Electron-releasing groups by supplying

electrons towards the positive charge would be expected to minimize the

Table 6. Nuclear magnetic resonance data for α-ferrocenylcarbonium ions __151__

Substituent R in __151__	Δv^a in cps	v^+_{CH} in ppm
H	118	5.75
CH_3	94	7.03
$CH(CH_3)_2$	93	6.98
$C(CH_3)_3$	90	7.07
Ph	66	7.92
p-CH_3Ph	71	7.94
p-CH_3OPh	76	7.96
p-CH_3O_2CPh	79	7.67
$C_6H_5\overset{\oplus}{C}HC_6H_5$	-	9.80
$C_6H_5\overset{\oplus}{C}HC_6H_5OCH_3$	-	9.06

[a]The separation $_H2,_H5-_H3,_H4$ between the centers of each pair of bands.

shift of the iron atom towards the charged center and such a reduction in shift would be reflected in a smaller degree of shielding of the α-protons with respect to the β-protons. The position of the carbinyl proton should also reflect the effects of the substituent and shift of the iron atom. Thus delocalization of the positive charge by the aryl groups would cause a smaller shift of the iron atom and the carbinyl hydrogen would experience less shielding from the magnetic anistropy of the iron and resonate at lower field.

Feinberg and Rosenblum (175) studied the nmr spectra of several

tertiary α-ferrocenylcarbonium ions 155-158 and confirmed that the α-protons appeared at higher field than the β-protons. They found that the geminal methyl proton chemical shifts in 156 and 157 were different by only 0.08 ppm with the latter further upfield. Similarly the substitution of a trimethylene bridge for the methyl groups in 157 did not appear to result in a significant change in positive charge at the tertiary cationic center since the geminal methyl protons appeared at an average of 0.08 ppm upfield from those in 156. The presence of the bridge in 158 however should preclude a distortion of the molecule in going to a structure such as 143 unless considerable valence angle distortion within the bridging element would be imposed. The near identity of geminal methyl resonances in those cations as well as those signals due to the cyclopentadienyl ring unsubstituted with the carbonium ion center suggested a close similarity both in charge distribution within the cations and in their structures. Furthermore the average signal for $H_{2,5}$ in 158 was shifted downfield by only 0.17 ppm compared to 157. They therefore concluded that the distortion depicted in 143 was not occurring in their cations.
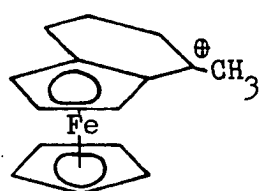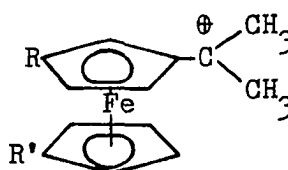
156   R = R' = H

157   R = R' = CH_3

158   R = R' = $(CH_2)_3$

155

Dannenberg, Levenberg and Richards (173) also noticed deshielding of the methylene protons of 153 relative to 151 (R = H) and 152. Consistent with their model of the carbonium ion, they rationalized that the methyl group at the α-ring position increased the amount of stabilization of the

positive character that was directly conducted through the cyclopentadienyl ring, the distance that the iron atom must move was decreased. They suggest then that similar substitution in 155-158 would also decrease the importance of displacement of the iron as suggested by Feinberg and Rosenblum (175).

Lillya and Sahatjian (192) have also disagreed with 143 being important in stabilizing the carbonium ion. They found that protonated ferrocenyl ketones were good models for the corresponding ferrocenylcarbinyl cations. Earlier it was noted that Traylor and Ware (182) found that σ^+ for α-ferrocenyl determined by comparing basicities of acetylferrocene and acetophenones agreed with σ^+ for α-ferrocenyl determined from solvolysis rates and from the Foote-Schleyer correlations with carbonyl stretching frequencies. Traylor and Ware discounted direct participation of iron on the basis of the latter correlations. Lillya and Sahatjian (192) considered direct participation to be less likely in their work also since the α-OH group would be expected to be a better conjugative stabilizing group than an α-ferrocenyl group ($\sigma^+_{p\text{-}OH}$ = -0.92 (193), $\sigma^+_{p\text{-}OCH_3}$ = -0.778 (193), $\sigma^+_{p\text{-}Fer}$ = -0.7 (182). Thus if an α-ferrocenyl group would not stabilize the carbonium ion by direct participation in the protonated acylferrocenes and since the protonated acylferrocenes correlated well with the corresponding carbonium ions, they concluded that the model of Traylor and Ware 144 better accounted for the data. The data may, however, be interpreted in terms of 143 in the same manner as that of Feinberg and Rosenblum earlier.

Hisatome and Yamakawa (170, 176) have reported the 100 MHz nmr spectra of a number of α-ferrocenylcarbonium ions 140, 159-166. In the spectra of 140 and 159-165 they noted a small coupling between the methyne proton and either the H-3 or H-2 proton (J = 0.8-0.6 cps) which suggested that the

methyne carbon was coplanar with the substituted cyclopentadienyl ring. They also noted that in 161 H-5 appeared further upfield than H-2 which suggested that the bonds between each of the carbons and the iron were non-equivalent. These data coupled with the fact that the H-3 and H-4 protons in 161 and 6-phenylfulvene appeared in almost the same region but that the H-2 and H-5 protons in 161 appeared at much higher field than in the 6-phenylfulvene caused them to suggest that some interaction between the cyclopentadienyl ring and the methyne carbon was occurring because of the coupling and coplanarity but that the iron was shifting toward the methyne carbon but so as to avoid steric interference with the R substituent. The same conclusions were arrived at in the cases of the bridged carbonium ions 140 and 163-165 despite the fact that coplanarity of the methyne carbon and the substituted ring would cause some ring tilting (176). Additionally, the carbonium ion 166 was found to be remarkably stable though less stable than the other ions which distinctly suggested that interaction with the ring was not the only factor influencing the ion but that direct interaction with the iron must play a role in stabilizing the ion (176).

162   166

159 R = H   163 R = R' = CH_3

160 R = CH_3 164 R = CH_3, R' = H

161 R = Ph   165 R = H, R' = CH_3
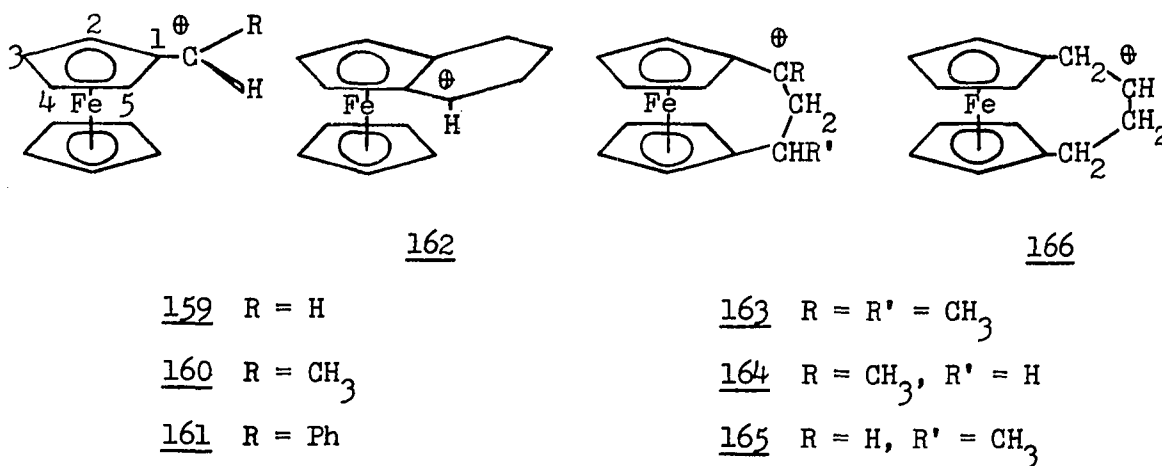
Sokolov, Petrovskii and Reutov (167) have investigated the ^{13}C nmr

spectrum of the 1-ferrocenyl-2-methylpropyl cation derived from the corres-

ponding alcohol in H_2SO_4. They concluded that the positive charge was

essentially absent from the carbinyl carbon but spread over the cyclopenta-

dienyl rings, especially the substituted one. They felt, however, that

ring resonance played an important role in stabilizing the ion and that

bending of the substituted ring was not necessary.

The coplanarity of the cyclopentadienyl ring and the carbinylcarbon

has been disputed however (149, 172, 194). Cais (149) has suggested that

tilting of the ring carbon bearing the carbonium ion center towards the

metal destroying the coplanarity and causing a slight change in the hybrid-

ization of C-2 and C-5 to sp^3 would allow for better iron participation in

bonding the carbinyl carbon and account for the higher field nmr of the

α-protons (structure 167).

Sutherland, Sutton and Horspool (168) have studied the nmr spectra of

several α-ferrocenylcarbonium ions derived from carbinols in which both

rings were alkyl substituted and analogous carbinols of [3] - and [4]

-ferrocenophanes. They reasoned that the carbonium ions derived from the

ferrocenophanes should be less stable if the structures of the ions were

similar to 143, but little effected if the ions had a structure similar to

167. They observed no difference in stability of the bridged and non-

bridged ions and found little difference in chemical shifts for the car-

binyl protons and little difference in Δν values for their α and β ring

protons. Therefore they concluded that 167 best accounted for their data.

Williams, Traficante and Seyferth (169) studied the ^{13}C nmr spectra

of the three carbonium ions 159-161 derived from the corresponding

carbinols in concentrated sulfuric acid and they concluded that their data
was best accounted for by a structure in which the position of the iron
atom with respect to the substituted ring had changed in going from the
carbinol to the carbonium ion. In addition they felt that the observed
chemical shifts and coupling constants of the carbonium ions were explicable
in terms of a structure which had the positive charge extensively delocal-
ized throughout the entire molecule.

Gleiter and Seeger (194) using self-consistent charge calculation
based on Extended Huckel Theory proposed 168 which would allow about equal
overlap between all iron-carbon bonds including the carbinyl carbon. The
carbinyl carbon would be bent towards the iron atom and both rings would be
tilted.

Recently Turbitt and Watts (172) reported the nmr spectra of 169 and
170 and several other compounds which also indicated that either 167 or
168 might be the structure of the carbonium ion. In the spectrum of 169
the C_5H_4R ring appeared to be unrestricted in its rotation since the ring
protons appeared as a broadened singlet. In compounds which have restrict-
ed rotation (such as 158) the corresponding ring protons appear as well
resolved multiplets. The ring protons of the methyl substituted ring in
170 however appeared as two well separated multiplets (approximate trip-
lets) indicating that rotation of the rings must be restricted, thus
indicating that the carbonium ion bearing ring might be non-planar in the
manner of 167 or 168.

Lupan, Kapon, Cais and Herbstein (195) have determined the structure
of α,α-diferrocenylmethylium tetrafluoroborate 171 by X-ray analysis of
the solid. They found that the rings in both ferrocenyl moieties were
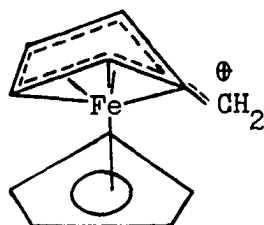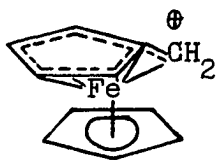
167 **168**
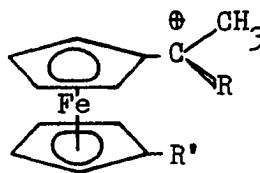
169 R = CH$_3$, R' = t-Bu

170 R = t-Bu, R' = CH$_3$

planar and almost parallel (angles between the pairs of rings were 3.1°

and 7.1° respectively). Significantly they found that the exocyclic carbon

atom deviated from the planes of the two cyclopentadienyl rings to which it

was attached by an angle of 17.7° toward the iron atom of one ferrocenyl

group and 19.9° away from the other ferrocenyl group. They thus found that

the exocyclic carbon was closer to one iron atom (2.71 Å) than the other

(2.85 Å). They felt, however, that the distances found were not indicative

of strong direct interaction between the iron atoms and the methyne carbon

atom.

An nmr spectrum of **171** showed that the rings bonded to the exocyclic

carbon rapidly flip at room temperature in solution (195) and measurements

of the Fe-2p$_{3/2}$ ionization energies indicated that the two iron atoms ex-

hibited the same charge density (162).
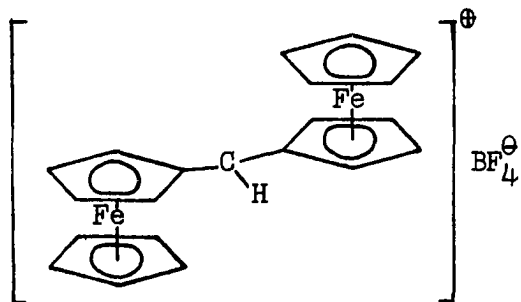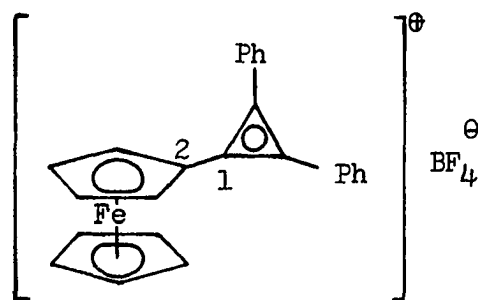
171 **172**

Sime and Sime (163) obtained the structure of ferrocenyldiphenylcyclo-propenium tetrafluoroborate 172 by X-ray diffraction studies. Their findings were also reasonably consistent with the structure calculated by Gleiter and Seeger (194). They found that the cyclopropenium ring was bent up towards the ferrocenyl group by an angle of 14.6°, a slight elongation of the ferrocenylcyclopropenyl bond distance (C-1 to C-2) to facilitate mixing of metal orbitals with empty orbital and bending of C-1 towards the iron. The C-2 to iron bond was the shortest iron carbon bond in the structure (1.99 $\overset{o}{A}$) and was thought to facilitate orbital overlap.

The molecular structure for bis(cyclobutadienyliron tricarbonyl)-phenylmethylium tetrafluoroborate has also been determined (196). The exo-cyclic carbon was coplanar with the butadienyl rings, no puckering of the rings was noted and the carbinyl carbon-ion bond distance was too large for direct metal interaction.

It would appear that the most data would support iron participation in stabilizing the α-ferrocenylcarbonium ion although the exact geometry of the ion has not been resolved. The data which was most in support of resonance stabilization for the ion came from solvolytic studies of ferro-cenylcarbinyl chloride and derivatives which had ferrocenyl groups insulated from the carbinyl carbon by phenyl groups, comparisons between ferro-cenylcarbinyl chloride and chloromethyl methyl ether, and the existence of linear relationships between those solvolytic data and carbonyl stretching frequencies of related ketones.

Work by Hill and Wiesner (152, 153) showed that pK_R data for α-ferro-cenyl carbonium ions did not correlate with rates of solvolysis for the ions, and that the pK_R data showed the ions to be more stable than the

kinetic studies indicated. The ferrocenylcarbinyl chlorides were shown to be very reactive in their solvolysis reactions and it would appear that factors which were influencing the transition state of the solvolysis reactions may have been more important in the ground state reactant than in the fully developed free carbonium ion. The solvolysis of the ferrocenylcarbinyl acetates which were less reactive may have been influenced by a transition state which had somewhat more of the character of the free carbonium ion. The nmr data which was presented may then have been dependent upon only those factors which were stabilizing the free carbonium ion (173, 194) and unaffected by the factors important in the ground state of the reactants. Hence the kinetic data and the thermodynamically controlled results need not have been contradictory but complementary and generated at different points on the energy surface from ground state reactant to free α-ferrocenylcarbonium ion (194).

The reported stability of the carbonium ion 166 (176) would indicate that the influence of the iron atom could extend beyond an alpha carbon in a substituent if the geometry of the system were appropriate. Nugent, Carter and Richards (197) and Nugent, Kummer and Richards (198) have reported the solvolysis of a number of α-ferrocenylalkyl tosylates 173-177 and have demonstrated that participation by the ferrocenyl group during the solvolysis occurred.

173 R = CH$_2$OTs,
     R' = H

174 R = H,
     R' = CH$_2$OTs

CH$_2$CRR'OTs

175 R = R' = H

176 R = R' = D

177 R = H,
     R' = CH$_3$
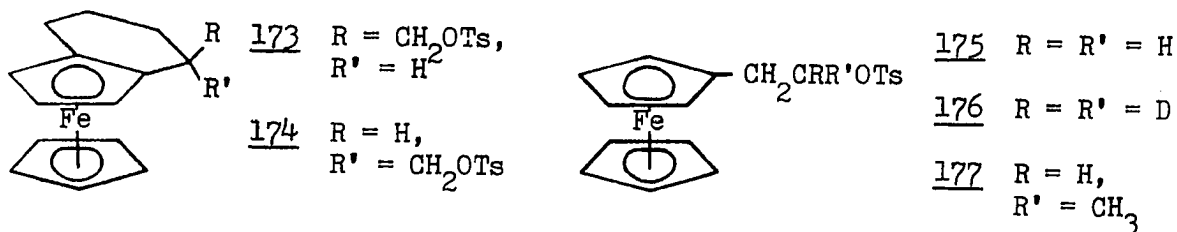
The entropy of activation for the solvolysis of 175 was found to be -8.9 e.u. in glacial acetic acid (197). The entropy of activation for the solvolysis of 175 in 80% aqueous acetone was estimated to be about -8 e.u. based on data of Trifan and Backsai (179). Winstein and Heck (199) concluded on the basis of rate comparisons for a number of primary tosylates that anchimerically assisted solvolyses tend to have $\Delta S^{\ddagger}$ of about -7 ± 2 e.u., while unassisted solvolyses tend to have $\Delta S^{\ddagger}$ of about -18 ± 2 e.u. Nugent, Carter and Richards concluded then that anchimeric assistance was involved in the solvolysis of 175.

Anchimeric assistance of the ferrocenyl group was also suggested by the observation that the solvolysis of 175 in 80% aqueous acetone was only 2.1 times faster than the solvolysis of 175 in glacial acetic acid. The ionizing power of acetic acid and aqueous acetone are not identical but they are similar, however, the nucleophilicity of aqueous acetone is significantly greater than that of acetic acid. The small rate increase in aqueous acetone then suggested that the solvolyses of 175 were nearly "limiting" and that moreover since the primary carbonium ion would not be expected to be very stable that the ferrocenylcarbonium ion was capable of obtaining an internal supply of electrons for stabilization (157).

That iron participation was involved in the solvolysis of 175 was also indicated by three other effects. The rate of solvolysis of 177 was found to be about 1.4 times greater than that of 175 in 80% aqueous acetone (157). The substitution of a methyl group for a hydrogen in a carbinyl carbon in a limiting solvolysis have given α-methyl effects of about 10^{4}. $S_{N}2$ process provide low α-methyl effects but low effects have been observed for processes in which anchimeric assistance existed (157). Thus since the

solvolysis of 175 appeared to be limiting, the low α-methyl effect may be attributed to participation.

The magnitude of the isotope effect for the solvolysis of 176 in 80% aqueous acetone $(k_H/k_D = 1.14)$ was found to be very similar to those for other systems in which ionization proceeded with little, if any, participation of the solvent, and quite unlike those found for $S_N 2$ processes. The observed isotope effect was also compatible with the presence of some neighboring group participation as evidenced by comparison with situations in which such participation was known to exist. For example, in the acetolysis and formolysis of 1,1-dideuterio-2-anisylethyl tosylate the observed effect was $k_H/k_D = 1.11$ per deuterium at 30° (200). The stereochemistry of participation in the solvolysis of 176 was also thought to be such that the two methylene groups did not become equivalent since no scrambling of the label was observed in the alcohol product isolated. The absence of scrambling and the lack of any bridged products such as 1,1'-dimethyleneferrocene made unlikely a type of participation in which the carbonium ion interacted with the heteroannular cyclopentadienyl ring. Cram and Singer presented a similar argument for lack of scrambling in the case of 4-(2-tosyloxyethyl-) 2,2-dideuterio)[2.2]-paracyclophane where the entropy of activation (-11.7 e.u.) for the acetolysis indicated significant aryl participation (201).

Lee, Sutherland and Thomson have recently reported that the solvolysis of 2-(p-ferrocenylphenyl)ethyl-1,1-d$_2$ tosylate did suffer scrambling of the label in 80% aqueous acetone at reflux and in glacial acetic acid and formic acid at 100° and 60° respectively (202). The extent of rearrangement from C-1 to C-2 was about 15-16 percent in aqueous acetone but complete in acetolysis and formolysis which was a similar result observed

for the acetolysis and formolysis of 2-(p-methoxyphenyl)ethyl tosylate (203).

The final evidence for participation of the ferrocenyl group in the solvolysis of 175-177 was the observation that solvolysis of 177 proceeded in glacial acetic acid and aqueous acetone to yield products with complete retention of configuration and no detectable rearrangement of the carbon skeleton (197). Overall the solvolysis of 175-177 indicated that the participation of the ferrocenyl group caused an increase in rate of about an order of magnitude over analogous 2-aryl systems such as phenyl, anisyl and [2,2] paracyclophane (197).

The rate of acetolysis of 174 at 25° proceeded 2780 times faster than the acetolysis of 173 (198). Furthermore the solvolysis of 174 produced unrearranged endo acetate as the sole product. The solvolysis of 173 produced only the rearranged acetate 178. Steric congestion in the endo-isomer was considered as one factor which might influence the higher rate of the endo compound by increasing the ground state energy of the compound. However the isolation of only the unrearranged endo acetate indicated that the congestion was not severe and probably not the most important factor in determining the rate of the reaction. Participation of interannular electrons was proposed as the factor leading to a higher rate for the endo isomer 174 and formation of unrearranged product (Scheme 58).
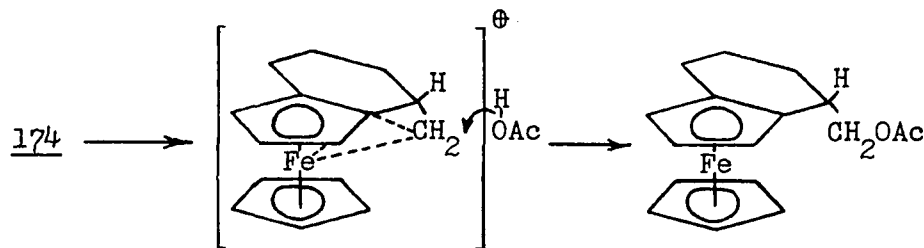
Scheme 8

In the exo isomer 173 the interannular electrons would not be available

for participation. The extraannular electrons would however be available.

They proposed that extraannular participation occurred during loss of the

tosylate anion, followed by rearrangement to allow for participation of

the interannular electrons, followed by attack of nucleophile from an exo

direction to account for the sole product (Scheme 59). They pointed out

that solvolysis of 1-tosyloxymethyltetralin involved participation by the

π electrons of the phenyl ring resulting in a partial rearrangement to a

secondary tosylate which then solvolyzed 200 times faster than cyclohexyl-

carbinyl tosylate and yielded only rearranged product (204). Since 173

solvolyzed only 1.6 times faster than the phenyl analog, it was considered

that the extraannular electrons of the ferrocene compound were about as

effective as the extraannular π electrons of the phenyl ring (198). There

was however an indication period noted in the solvolysis of the phenyl com-

pound and none noted with 173, however, the initial loss of tosylate

followed by rearrangement would account for the difference (Scheme 59).

The question of whether the participation by ferrocene was due to non-

bonding iron electrons or due to interaction of the d-π electrons involved

in iron-carbon bonding was not resolved.

173   178
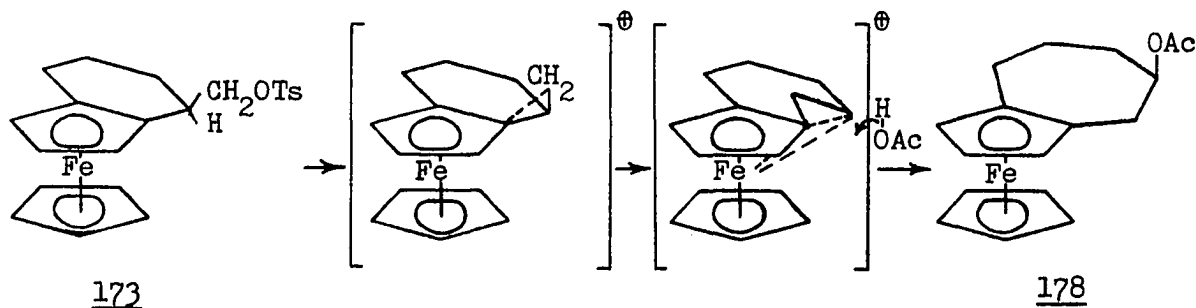
Scheme 59

The solvolyses of 2-arylcyclopropylcarbinyl 3,5-dinitrobenzoates have been shown to proceed to largely ring opened products through an intermediate in which the positive charge was delocalized to the 2 and 3 positions of the cyclopropane ring (205). The value of ρ (-1.48) obtained for the reactions however was lower than that expected for a benzylic cation and it was felt that that indicated that the conformation of the intermediate cation formed in the transition state of the solvolysis did not allow sufficient overlap for the π orbitals of the aryl groups and the p orbital of the carbonium ion for resonance stabilization by the aryl groups.

Substitution of a ferrocenyl group for the aryl group to produce 2-ferrocenylcyclopropylcarbinyl 3,5-dinitrobenzoate should not increase the stabilization of charge at the 2 position (relative to a p-anisyl group (142) since whether a ferrocenyl group would stabilize a carbinyl cation by resonance or by direct iron participation, the same geometry for overlap would be required.

The cis isomer of 2-phenylcyclopropylcarbinyl β-naphthalenesulfonate has been observed to solvolyze at a slower rate than the trans isomer (206). A rationale offered for that observation was that steric interaction between the cis-phenyl group and the 1-methylene group of the intermediate cation might transform the conformation of the cation into one that was unfavorable for the delocalization of the positive charge (205).

Molecular models of the cis isomer of the ferrocenyl ester however reveal that the carbinyl carbon would be able to assume a position in the plane of the substituted ring at a distance essentially identical to that of the carbinyl carbons in 173-177 relative to both cyclopentadienyl rings by rotation of the substituted cyclopentadienylcyclopropyl carbon-carbon

bond. Moreover the carbinyl carbon would be capable of being in the vicin-
ity of the non-bonded iron orbital in going from one ring to the other
during the rotation of the carbon-carbon bond.

If the stabilization of the intermediate carbonium ions formed from
173-177 were due to participation by electrons from an iron-carbon bond of
the substituted ring, the conformation of the ion might appear somewhat as
in 179. For either ring to overlap with the p orbital of the carbinyl car-
bon in an analogous process would lead to a conformation more like 180. A
conformation such as 180 would be dictated for the substituted ring inter-
action because of the constraints of bond lengths and in an interaction
with the non-substituted ring because of steric interactions between car-
binyl carbon protons with ring protons in attempting to bond "straight-on".
A conformation such as 180 would appear to be less favorable than 179 and
anchimeric assistance by ferrocene in a solvolysis of the cyclopropyl ester
would not seem reasonable from that mode.

179

substituted
ring

or

non-substituted
ring

180
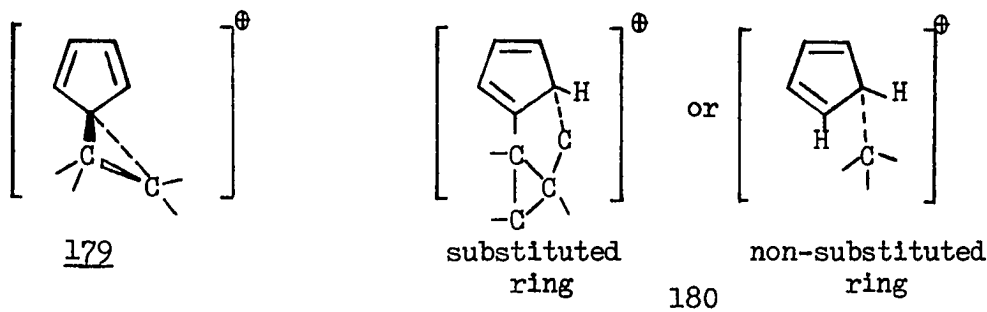
Additionally if stabilization of α-ferrocenyl carbonium ions occurred
by participation of iron-carbon bond electrons, positioning the carbinyl
carbon of the cyclopropylcarbinyl ester in an appropriate position for
interaction with the substituted ring causes significant steric interaction
to occur between the unsubstituted ring and the 3,5-dinitrobenzoate phenyl
ring.

Stabilization by interaction with non-bonding iron electrons may be equally possible in either the β-position or in a γ-position as in the cyclopropylcarbinyl ester. If such interaction occurred an increase in the rate of solvolysis of the <u>cis</u> isomer relative to the <u>trans</u> isomer might be observable.

RESULTS AND DISCUSSION

There were several procedures used in an attempt to synthesize the precursers, cis- and trans-1-carboethoxy-2-ferrocenylcyclopropane 181, for cis- and trans-2-ferrocenylcyclopropylcarbinyl esters. One route to 181 would be to utilize the addition of ferrocenylcarbene 182 to olefins, in particular ethyl acrylate. 182 would be of interest in its own right because like the α-ferrocenylcarbonium ion 183, it would be an electron deficient species in which the multiplicity might be influenced by the same bonding factors stabilizing the ion 183. Thus a determination of its multiplicity would be of some theoretical interest.

Attempts were then directed towards preparing ferrocenyldiazomethane 184 as a precurser to 182. Diazocompounds may be prepared by a variety of methods (35) but the availability of ferrocenylaldehyde made the tosyl-hydrazone method of Bamford and Stevens (207) particularly attractive. The tosylhydrazone of ferrocenylaldehyde 185 was readily prepared (73) from ferrocenylaldehyde 186 which may be prepared from ferrocene by a Vilsmeier-Haack reaction or purchased commercially.

When 185 was heated to about 60° with sodium methoxide in diethylene glycol a precipitate was obtained which was shown to be predominantly one product though thin layer chromatography indicated the presence of several minor products. When the same reaction was carried out in ethylene glycol between room temperature and about 100° a gas was evolved and collected commencing at about 40° and the reaction again produced a light brown precipitate. The volume of gas collected was equivalent to the number of moles of nitrogen to be expected by complete decomposition of 184 if

produced in the reaction. Mass spectral analysis of the gas gave a molecular ion at m/e 28 also indicating that the gas was molecular nitrogen. The production of nitrogen suggested that 184 was being produced but the evolution of gas at 40° suggested that the compound was more unstable than phenyldiazomethane which had been obtained by an essentially similar process at 60° (208).

The major product of the reaction was isolated and an nmr spectrum of the material was essentially the nmr spectrum of the crude reaction products, especially for the 60° pyrolysis. The spectrum consisted of a single proton downfield at δ 8.14, an AB pattern at δ 7.56 for four phenyl protons, twenty-one protons in the ferrocenyl region and a methyl group singlet at δ 2.45. The spectrum thus indicated that two ferrocene moieties and a tosyl group were present in the compound. A mass spectrum of the material gave a molecular ion at m/e 580. An ir spectrum of the material gave bands at 1600 cm^{-1} (-C=N-), 1342 cm^{-1} and 1159 cm^{-1} (-SO$_2$N-) (112*). The data suggested 187 shown below which may be accounted for by a reaction between ferrocenylcarbonium ion 183 and the anion of 185.

$$\text{Fer-CH=N-N} \diagup^{SO_2} \!\!\!\!\bigcirc\!\!\!\!- CH_3$$
$$\diagdown \underset{\underset{Fer}{CH_2}}{}$$
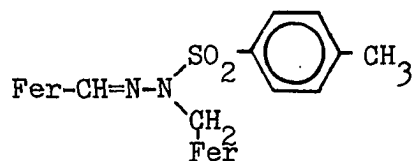
187

Base catalyzed thermal decompositions of tosylhydrazones in protic solvents have been observed to produce carbonium ions by transfer of a proton from solvent to the generated diazocompound followed by loss of nitrogen (207, 209, 210). The generation of the stabilized ferrocenylcarbonium

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*Reference (112), pp. 68-70

ion <u>183</u> would appear to be a particularly favorable process.

A similar product was observed by Lemal and Fry (211) in the photolysis of nortricyclanone tosylhydrazone sodium salt in THF, but it was attributed to alkylation of the weakly acidic sulfonamide function of unreacted nortricyclanone tosylhydrazone by diazonortricyclene. That their product arose by that route was supported by the observation that the compound was obtained (up to 52%) only when the tosylhydrazone was incompletely converted to the sodium salt by sodium hydride.

Mass spectral analysis of the crude reaction mixture obtained for the reaction carried out at 60° in diethylene glycol gave additional molecular ions at m/e 214, 304, 354, 396 and 424 presumably representing the minor products of the reaction. The ion at m/e 214 could correspond to <u>186</u> which might arise if any oxygen were present in the reaction (212). The ions at m/e 396 and 424 might also be the result of carbenic reactions to produce <u>188</u> and <u>189</u> respectively. Both azines and olefins have been observed as products of carbenic decompositions of diazocompounds (208, 211, 213, 214).

<div style="text-align:center">

Fer-CH=CH-Fer   Fer-CH=N-N=CH-Fer
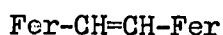
<u>188</u>   <u>189</u>

</div>

The ions observed at m/e 304 and 354 could be interpreted as minor products also derived from ionic pathways. The ion at m/e would correspond to <u>190</u> which could arise by reaction of <u>183</u> with diethylene glycol (or in the presence of excess sodium methoxide, diethylene glycolate (211, 215). The ion at m/e 354 would correspond to the sulfone <u>191</u> which could arise by reaction of <u>183</u> with the tosylate ion also produced in the reaction (207,

209, 210).

$$Fer-CH_2-O-CH_2CH_2OCH_2CH_2OH$$
$$\underline{190}$$

$$Fer-CH_2-SO_2\text{-}\langle\bigcirc\rangle\text{-}CH_3$$
$$\underline{191}$$
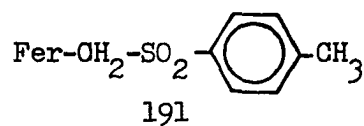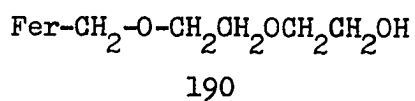
Applebaum, Fish and Rosenblum had decomposed the ferrocenyl tosylhy-drazone 192 under various conditions (216). When 192 was photolytically decomposed in the presence of sodium methoxide in DME the reaction did not produce any well defined products. When the decomposition was carried out thermally with sodium methoxide in DME both 193 and 194 were isolated indi-catiṇg that the reaction had followed a cationic pathway to some extent but when the thermal decomposition was conducted with sodium hydride or sodium methoxide in cyclohexane 193 and 195 were obtained (Scheme 60).
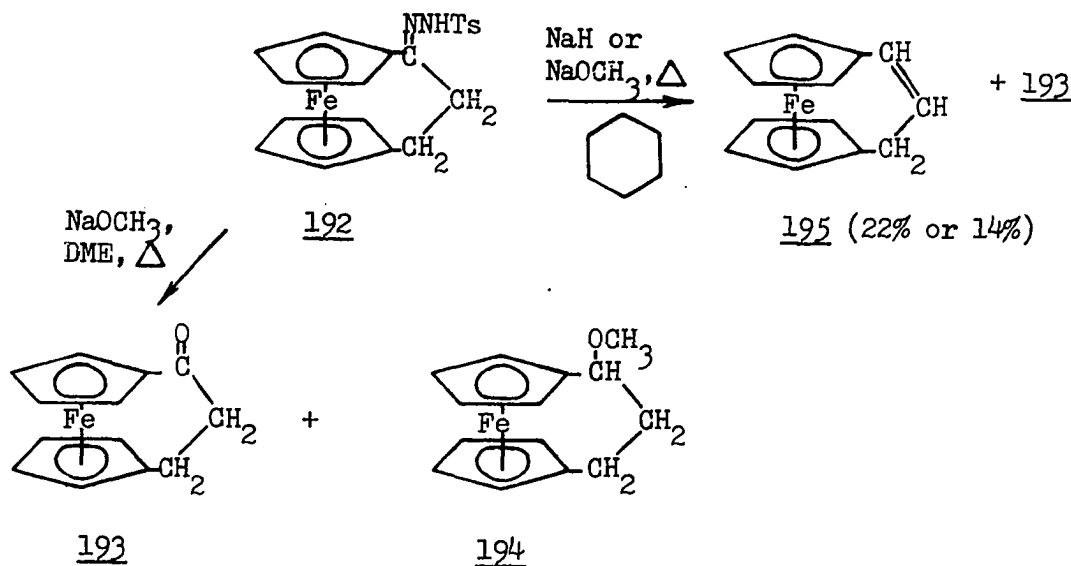
Scheme 60

It is of interest also that sulfones have been observed as products in the photolytic and pyrolytic decompositions of the sodium salts of

tosylhydrazones in aprotic solvents (211, 217). In these cases the sulfones were thought to arise by attack of tosylate ion on intermediate carbenes to form stabilized sulfone anions (211) or followed by elimination of anionic species (217).

Though the sulfone 191 was produced in quite small amounts, enough was eventually isolated by chromatography to obtain an nmr spectrum which exhibited an AB pattern in the aromatic region for four protons, resonances in the ferrocenyl region for eleven protons and a methyl group singlet at δ 2.38.

Indications were that a lower temperature and an aprotic solvent would constitute a better reaction system for isolating 184. Therefore a sample of 185 was treated with sodium methoxide in diglyme and pentane at a temperature of 30-40°. A precipitate again developed along with evolution of a gas as it initially developed. The solid was isolated and found to be soluble in water. The water soluble material could then be extracted into organic solvents and the organic soluble material was shown to be 185 by thin layer chromatography. The addition of acid to the water soluble material caused a purple color to develop initially and easier extraction to occur. The 185 was not soluble in water but treatment of 185 with acid caused a purple color to develop. Indications were then that the isolated material was the sodium salt of 185.

The lithium salt of 185 could also be prepared using organo-lithium reagents. When the lithium salt of 185 was pyrolyzed in ethylene glycol, no evidence for the formation of 187 was detected; but the products appeared to be 191 (about 11%) and 196 (about 78%) as a result of a protic reaction. These results may reflect the fact that the reaction was carried out with

a more dilute solution than the pyrolysis of the sodium salt of 185. The results also indicated that the pyrolysis of the lithium salt should be carried out in aprotic solvents also.

$$Fer-CH_2-O-CH_2CH_2OH$$
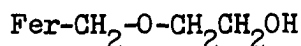
136

It was reported in 1965 that the vacuum pyrolysis of the sodium and lithium salts of the tosylhydrazones of aldehydes and some ketones would yield the corresponding diazocompounds (218). The temperatures required for the production of some secondary diazocompounds however was sufficient to decompose them at the same time.

When the sodium salt of 185 was heated in the mass spectrometer, a small ion at m/e 226 was detected which would correspond to the molecular ion of ferrocenyldiazomethane 184. As the temperature of the sample was increased, the m/e 226 ion remained but ions at m/e 211, 354, 396, 412 and 424 became more important.

When the lithium salt of 185 was pyrolyzed between 100° and 170° in a sublimation apparatus equipped with a Dry Ice-acetone cold finger, some material began to condense on the cold finger at about 100°. Mass spectral analysis of the material collected showed molecular ions at m/e 211, 276, 292 and 396. It was not clear whether the ion at m/e 276 contained iron. Initially the ion at m/e 211 was the most prominent, but as the sample was held in the spectrometer its importance decreased. There was no ion at m/e 226. The ion at m/e 211 could correspond to ferrocenylnitrile 197 and the ion at m/e 396 could correspond to 188. An ir spectrum of the material showed small bands at 2230 cm^{-1} and 1600 cm^{-1}. Thin layer chromatography

of the material indicated a gross mixture was present.

Pyrolysis of the sodium salt in a sublimation apparatus under vacuum also produced a mixture of products. The condensate was found to be partially soluble in pentane and to lighten from orange-red to yellow rapidly. Thin layer chromatographic separation of the mixture produced several fractions which were concentrated and submitted to mass spectral analysis. Molecular ions were found at m/e 396, 262 and 211. The m/e 396 ion could again correspond to the olefin 188. The ion at m/e 211 was found in all of the fractions but in one fraction it was the only molecular ion present. That fraction also produced an ion at m/e 184 with a metastable ion at m/e 160.5 corresponding to the loss of HCN from 211.

In an attempt to trap any 184 produced by pyrolysis of the salts of 185 under vacuum, the lithium salt of 185 was pyrolyzed up to about 145°. The system was connected to a flask containing dimethyl fumarate at -78°. A small drop of yellow-orange material condensed and dropped into the ester, but most material condensed just above the level of the oil bath in the apparatus. Three major fractions were detected in the condensate (exclusive of that in the ester) by thin layer chromatography and three major fractions were collected by column chromatography. Fraction one was a red solid which decomposed but did not melt below 280°. Mass spectral analysis showed a molecular ion at m/e 262. Its nmr spectrum was dilute but consisted of possibly a singlet at δ 6.4, multiplets at δ 4.38 and δ 4.26 and a singlet at δ 4.09. A small singlet may also have been present at δ 4.03. Fraction two was a yellow solid and melted at 102-104°. A molecular ion at m/e 211 was found and its nmr spectrum consisted of a triplet at δ 4.6 for 2 protons and a singlet at δ 4.3 for 7H. The data

again suggest ferrocenylnitrile 197. Fraction three was not cleanly sepa-
rated but appeared to be a mixture of 197 and 191 based upon its nmr spec-
trum. The absence of 188 may be accounted for if it were the material that
condensed into the ester.

The results of these reactions seemed to fairly clearly indicate that
thermolysis of the salts of 185 in protic solvents proceeded largely
through an ionic pathway and that thermolysis of the salts in aprotic sol-
vents or in vacuo probably lead to formation and carbenic decomposition of
184 at the temperatures required to effect elimination of the tosylate
group. The transient coloration noted in some vacuum pyrolyses indicated
that the compound might also be unstable at room temperature.

As noted before the thermal decomposition of salts of tosylhydrazones
of ketones also generally lead to decomposition of the diazocompounds under
vacuum pyrolysis conditions (218). The solution pyrolytic decomposition of
the salts of aliphatic aldehydes also lead to decomposition of the diazo-
compounds produced (29*). This was presumably due to the fact that the
diazocompounds were destabilized relative to the diazocompounds and hence
did not survive the reactions. That is that the resonance form 198 for
alkyl substituted diazocompounds would be destabilized by the inductive
effect of the alkyl groups whereas the same inductive effect would tend to
stabilize the corresponding electron deficient carbenes.

$$R \diagdown C-\overset{..}{N}=N: \diagup R'$$
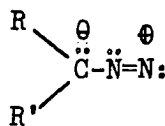
198

*Reference (29), p. 48.

The results of Traylor and Ware (182) had indicated that the electronic effect of a ferrocenyl group appeared to be similar to that of a p-anisyl group and therefore would also destabilize the analogous resonance form 198 for 184. It was found that p-anisyldiazomethane could not be prepared by the tosylhydrazone method and that further when it was prepared by mercuric oxide oxidation of the hydrazone that it was unstable and decomposed even at Dry Ice bath temperature (208).

The report by Jolly and Pettit (219) that methylene could act as an electron donor with organoiron complexes suggested that the presence of the iron in ferrocene might influence the course of reactions involving carbenes or carbene precursers. Therefore to demonstrate the compatibility of a diazo group and a ferrocenyl moiety in the same molecule, 199 was synthesized from the acid chloride of ferrocenylcarboxylic acid and diazomethane.

$$Fer-\overset{O}{\overset{\|}{C}}-CHN_2$$
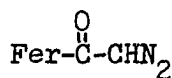
199

Since 199 could be synthesized and since p-anisyldiazomethane could be obtained at low temperatures, the oxidation of the hydrazone of ferrocenylaldehyde was undertaken.

The usual procedure for preparing hydrazones had been reported to yield the azine with 186 (220) and improvement in the result to produce only the hydrazone 200 could not be accomplished.

An alternative procedure for preparing difficult to prepare hydrazones was successful however (221). Treatment of 186 with unsymmetrical dimethylhydrazine yielded the corresponding dimethylhydrazone 201. The

dimethylhydrazone was then treated with an excess of anhydrous hydrazine to afford 200 was not isolated but reacted immediately.

Treatment of 200 with silver oxide at 0° produced vigorous gas evolution. Samples of the reaction mixture were periodically withdrawn and the 2100-2000 cm^{-1} region of the ir spectrum scanned, but no absorption in that region was noted even after the reaction mixture was warmed to room temperature. A similar reaction using manganese dioxide (222) as the oxidizing agent did result in the appearance of an absorption at 2070 cm^{-1} but the band rapidly decreased at room temperature producing evolution of a gas in the sample holder.

Thus it appeared that 184 could be produced and isolated although, as with p-anisyldiazomethane, it appeared to be somewhat unstable. The question of the multiplicity of the carbene 182 however was answered in a series of papers which began to appear in 1969 (223-226).

Sonoda and his group reported the preparation and reactions of four ferrocenylcarbenes 182 and 202-204. Generally they were prepared by thermal decomposition of the sodium salts of the respective tosylhydrazones but 203 was also prepared as a result of the mercuric oxide oxidation of the hydrazone of acetylferrocene. They were unable to isolate the precurser diazocompounds although they did observe the diazocompounds for 202 and 204 as transient species by ir as indicated by bands at 2060 cm^{-1} (223, 224).

Fer-C̈-R

202 R = Ph

203 R = CH_3
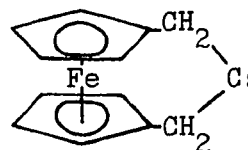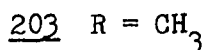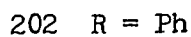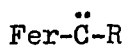
204

When <u>203</u> was generated by either thermal decomposition of the sodium
salt of the tosylhydrazone of acetylferrocene or by mercuric oxide oxidation
of the hydrazone of acetylferrocene in cyclohexene a complex mixture of prod-
ucts was obtained (Scheme 61 percent yields shown for the NaH reaction).

<u>205</u> (14%)

<u>206</u> (trace)

<u>207</u> (2.4%)

<u>208</u> (none)

<u>209</u> (0.5%)

<u>210</u> (0.2%)

<u>211</u> (1.5%)
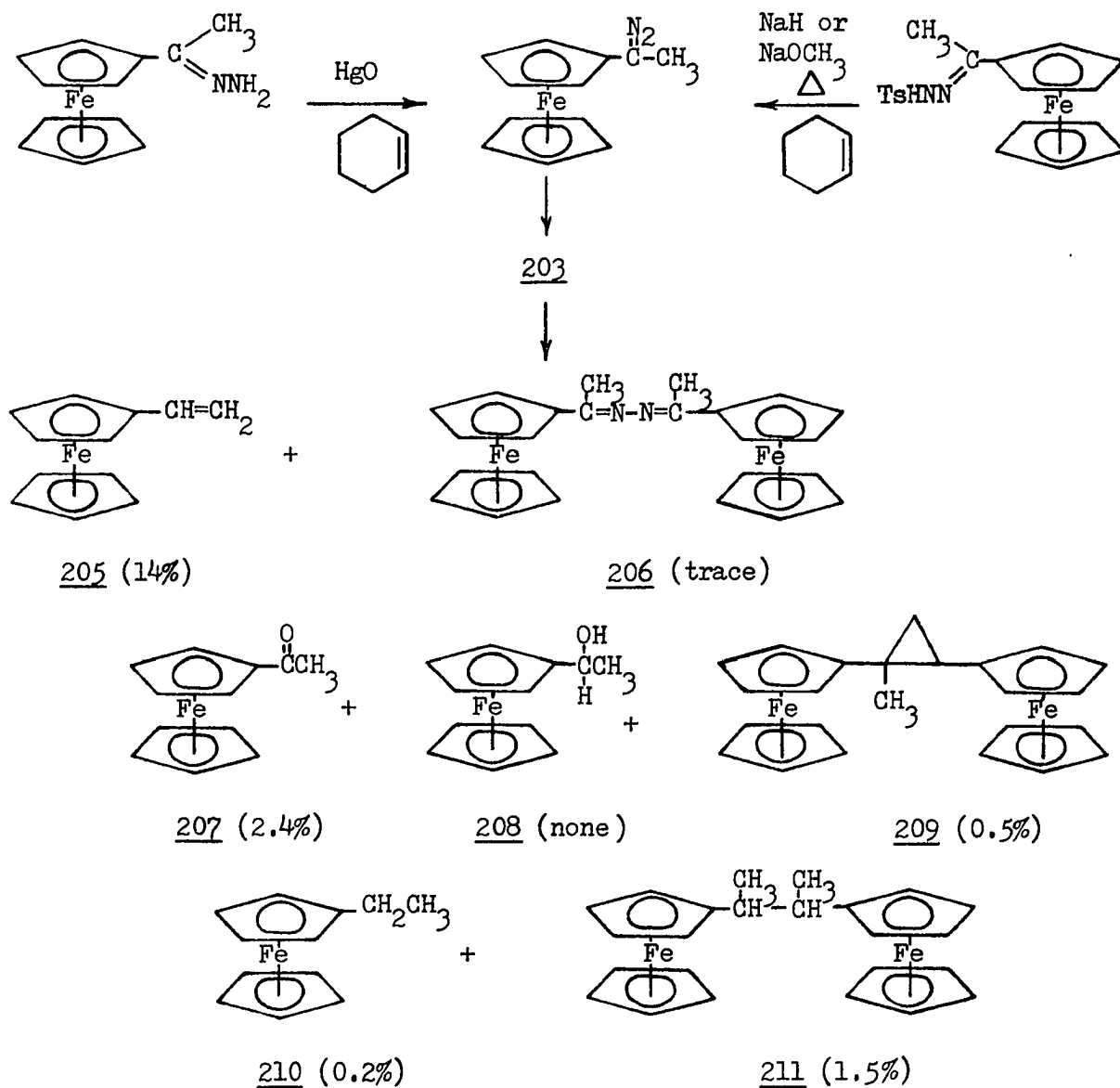
Scheme 61

The results of the reaction were explicable in terms of an intermediate triplet carbene species. The products 210 and 211 were accounted for by radical abstraction reactions which suggested that 203 existed as a triplet species. That a triplet was involved was also indicated by the fact that no cyclohexene addition products were found although 209 was obtained presumably as a result of addition of 203 to 205 obtained by a 1,2-intramolecular insertion reaction from 203. The isolation of 207 also indicated that a triplet carbene was involved since triplet carbenes were known to react with oxygen (29*).

The products derived from 202 in an analogous reaction were similar except that products like 205 and 209 were not obtained, of course, and again no addition product with cyclohexene was observed. The results suggested that 202 was also a triplet and further when 202 was generated in the presence of oxygen, benzoylferrocene was the major product (223).

The carbenes 182, 202 and 203 did add to 1,1-diphenylethylene which was known to be an efficient triplet carbene trapper (227), again indicating that they were triplet carbenes. It was also noted that neither 202 nor 203 afforded addition products with ethyl vinyl ether (223). Both 1,1-diphenylethylene and vinyl ferrocene 205 would be expected to produce stabilized radical intermediates with triplet carbenes but cyclohexene and ethyl vinyl ether would not be expected to afford a stabilized radical species (225).

Although 182, 202 and 203 acted as triplet species like phenylcarbene (225), it was found that the bulk of the ferrocenyl group caused those species to be somewhat less reactive in addition reactions with 1,1-

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*Reference (29), pp. 83-84.

diphenylcarbene. Since the electronic effect of the ferrocene group has been compared to that of the p-anisyl group (182) and p-anisylcarbene is more reactive than phenylcarbene in addition reactions to 1,1-diphenyleth-ylene (225), steric factors in the attack of 182, 202 and 203 appear to hinder the reaction. Further, the cyclopropyl compounds which were produced were observed to have restricted rotation about the ferrocenyl-cyclo-propyl bond as determined by nmr studies (225).

The ferrocenyl moiety thus appeared to act as other aromatic groups in producing stabilized triplet α-carbene species, however, the interaction appeared to be somewhat different in the ferrocenyl compounds. 204 was also found to act as a triplet even though the carbenic center was sepa-rated from the aromatic group by a methylene group in contrast to other aralkyl substituted carbenes (226). Thus 204 in the presence of oxygen produced [3]-ferrocenophan-2-one and was observed to react by addition with 1,1-diphenylethylene but not with 1-decene. Therefore it was concluded that there must have been an unspecified effect of the iron on the spin state of the compound (226).

Competition between a singlet and triplet spin state must have existed however since 203 and 204 also produced olefins by 1,2-intramolecular in-sertion reactions, presumably involving singlet species (214, 228).

The possibility of utilizing 182 as a means of generating cyclopropyl compounds by the addition to olefins still existed. When a thermal decom-position of the sodium salt of 185 was carried out in pyridine and cyclo-hexene at 80° in a manner similar to that described for the reactions of 202 and 203 (223), three major products and several minor products were obtained. Two of the products were identified as 188 (5%) and 189 (13%) on

the basis of mass spectra. The third product, a yellow oil, was of more interest. The mass spectrum of the material showed an intense molecular ion at m/e 280. Metastable losses of 68 and 81 mass units were observed from the molecular ion to m/e 212 and 199 respectively along with small losses of 28 and 29 mass units from the molecular ion. An ir spectrum of the material showed a strong band at 2910 and a moderate absorption at 1448 cm^{-1}. The nmr spectrum of the material showed small multiplets at 4.18 and 3.86 and a large singlet at 4.00 for 9 protons and an unresolved multiplet from δ 2.32 to 0.50 for about 13 protons. The data suggested that the structure might be 7-ferrocenylnorcarane (4.5%) but an analysis for the material was unsatisfactory. The mass spectrum of the material had substantial amounts of higher mass ions present and the small amount of material isolated (125 mg) was very soluble in the residues of Skelly B used to chromatographically isolate it. Furthermore the material decomposed upon storage as indicated by the observation of a colorless component and a residue spot being present when the material was thin layer chromatographed. The very intense ion observed at m/e 280 in the mass spectrum and the absence of olefinic protons in the nmr spectrum and the absence of any double bond absorption in the ir spectrum did suggest that some addition to cyclohexene did occur.

The addition of 182 to dimethylfumarate, methyl cinnamate and ethyl acrylate resulted in very poor yields of cyclopropyl compounds. Indeed if it were not for mass spectroscopic probing of the reaction mixtures, those products would have been difficult to detect.

The lithium salt of 185 was thermally decomposed with dimethyl fumarate between 75° and 145° both in diglyme and in the absence of solvent.

The tosylhydrazone of ferrocenylaldehyde 185 was recovered in substantial amounts from both reactions. The presence of addition product in the reaction carried out in diglyme was detected in the crude reaction mixture by mass spectroscopy by observing a molecular ion at m/e 342. In an attempt to concentrate the reactants, the reaction was carried out with no solvent since the ester would liquify at the thermolysis temperatures. In that reaction thin layer chromatography of the reaction mixture showed the separation of an orange fraction less polar than 185. A mass spectrum of the material adsorbed on alumina showed a molecular ion at m/e 342.

Photolysis of the lithium salt of 185 in THF with dimethyl fumarate gave comparable results, the isolation of 185 and detection of the addition product by mass spectroscopy in the small fractions afforded by chromatography of the crude product.

Pyrolysis of the lithium salt of 185 in DME with methyl cinnamate also produced a complex mixture but a molecular ion at m/e 360 was observed for the crude reaction mixture.

Of more interest was the pyrolysis of the sodium salt of 185 in ethyl acrylate since addition would yield 1-carboethoxy-2-ferrocenylcyclopropane 181. The product isolated was a viscous liquid from which a small amount of 181 could be extracted by pentane. The major product appeared to be a polymer of ethyl acrylate and ferrocene based both on its consistency and its nmr spectrum which exhibited large unresolved multiplets in the ferrocenyl and alkyl regions of the spectrum. The ir spectrum of the material did show a strong band at 1732 cm^{-1} and no evidence of double bonds.

The pentane extracts showed a very similar nmr spectrum with ferrocenyl ring protons at δ 4.06 and δ 3.95, small singlets at δ 4.29, δ 4.17

and δ 3.83, methyl ester singlets at δ 3.64 and δ 3.44 and a broad multiplet extending from about δ 2.8 to δ 0.5. The small singlets in the δ 4 region appeared, in part, to be part of a quartet, and the methyl ester singlets could be accounted for since methanol had been used several times in eluting the crude mixture from alumina columns in attempts to chromatograph the material and therefore ester exchange had apparently occurred. Since two ethyl esters could be expected by addition of 182 to ethyl acrylate, two methyl esters should have been produced. A mass spectrum of the pentane extracted material showed molecular ions at m/e 284 for the methyl ester and 298 for the ethyl ester. Thick layer chromatography separated the methyl and ethyl esters but the quantities were small and the following nmr spectra could not be integrated accurately. One methyl ester, the more abundant one, showed ferrocenyl singlets at δ 4.05 and δ 3.95, methyl ester singlet at δ 3.66 and a barely discernible multiplet upfield. The other methyl ester showed ferrocenyl ring proton s as a singlet at δ 4.02 and a multiplet form δ 4.25 to δ 3.84, the methyl ester singlet at δ 3.47 and an ill-defined multiplet upfield. The ethyl ester produced ferrocenyl protons at δ 4.16 and δ 4.06, with part of a quartet at δ 4.23 and δ 4.11, a triplet at δ 1.28 and evidence of a broad multiplet upfield also. The more abundant methyl ester and the ethyl ester appeared to be different esters of the same cyclopropyl isomer.

The material which had been extracted from the polymer accounted for only about a 6% yield and thus synthetically was not very practical. Therefore, other methods of synthesizing 181 were investigated.

The report by Johnson, Haake and Schroeck (229) that (dimethylamino)-phenyloxosulfonium methylide 212 could be added to electrophilic olefins to

yield cyclopropanes prompted the synthesis of 1-carboethoxy-2-ferrocenyl-ethene 213 to test the utility of the reaction to synthesize 181. The olefin 213 was synthesized by a Wittig reaction using the ylide generated from triethylphosphonoacetate with ferrocenylaldehyde (94%) (230, 231).

Reaction of 212 with methyl cinnamate had required 72 hours at 25° (72%) (229). When 213 was treated with 212 at room temperature for up to 7 days no reaction occurred although the olefin could be recovered unchanged. When the reaction was carried out overnight at room temperature and then heated to 50° for an hour and a half, no evidence for the formation of 181 was noted but the reaction did produce significant decomposition of the olefin 213.

It appeared that 213 was not sufficiently electrophilic to react with the stabilized ylide 212, therefore the reaction was attempted using the more reactive ylide dimethyloxosulfonium methylide 214 (232). Reaction of 214 with 213 in DMSO for 3 hours at room temperature resulted in no formation of cyclopropyl compound 181 and complete loss of 213. When the reaction of 214 with 213 was carried out in THF at room temperature overnight no 181 was detected in the reaction product but a small amount of 213 was recovered.

Horspool, Sutherland and Thomson (233) have reported the formation of ferrocenylcyclopropanes 215-218 in 80-90% yields by the addition of 214 to the corresponding olefins at room temperature.

An attempt was then made to prepare the pyrazoline 219 by the addition of diazomethane to 213. When 213 was allowed to react with excess diazomethane in ether at room temperature for several days, all of the olefin was consumed. An ir spectrum of the product mixture showed no band at

$$\underset{\text{Fer-C-CH}}{\overset{O}{\underset{\|}{}}}\overset{\diagup CH_2 \diagdown}{}C\overset{\diagup R}{\underset{\diagdown R'}{}}$$
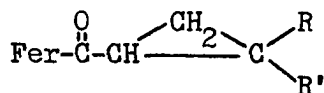
$\underline{215}$ R = Ph, R' = H

$\underline{216}$ R = p-anisyl, R' = H

$\underline{217}$ R = o-O$_2$N-Ph, R' = H

$\underline{218}$ R = R' = CH$_3$

1540 cm^{-1} (234) however there was a broad weak band at 1558 cm^{-1}. Therefore the material was irradiated but produced no evolution of nitrogen. An nmr spectrum of the photolyzed material was essentially identical to that of the original material. Further the 1558 cm^{-1} band remained in the ir spectrum. Thin layer chromatography also indicated that 181 was not present in the reaction mixture.

$$\underset{\substack{N \diagdown \diagup CH \\ N}}{Fer-\underset{|}{CH}-\underset{|}{CH}-CO_2CH_2CH_3}$$
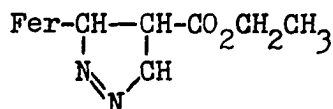
$\underline{219}$

No reaction appeared to occur when the simpler ferrocene olefins vinylferrocene 205 and 2-ferrocenylpropene 220 were treated with an excess of ethereal diazomethane, the starting materials were recovered. No formation of cyclopropylferrocenes occurred when the diazomethane was catalytically decomposed by cuprous chloride in the presence of 205.

When 205 and 220 were subjected to a Simmons-Smith reaction formation of cyclopropylferrocenes 221 and 222 respectively did result. An nmr spectrum of cyclopropylferrocene 221 showed two singlets at δ 4.02 and δ 3.91 for 5 and 4 protons respectively. Upfield two multiplets were observed at δ 1.7-1.2 and δ 1.05-0.32 for the five cyclopropyl protons. Thin layer chromatography of the material showed the presence of at least three

components even after repeated column chromatography and an impurity was evident in the nmr as evidenced by multiplets in the ferrocenyl region and a singlet at δ 1.26. The product of the addition to 220 was purified by vapor phase chromatography. The nmr spectrum of 1-ferrocenyl-1-methyl-cyclopropane 222 showed singlets at δ 4.00 and δ 3.88 for 5 and 4 protons respectively, a singlet at δ 1.34 for 3 protons and a multiplet at δ 0.64 for 4 protons. A mass spectrum of the material gave a molecular ion at m/e 240.

The comparative success with the Simmons-Smith addition encouraged the use of the same reaction with 213 to prepare 181. The reaction of 213 with methylene iodide and zinc/copper couple afforded 181 in about 33% yield. When the reaction mixture was separated from the spent couple and treated again with fresh couple the yield could be pushed to about 50%, moreover the unreacted olefin 213 could be recovered by chromatographing the product mixture. The 181 thus obtained exhibited singlets at δ 4.12 and δ 4.02 for 5 and 4 protons respectively, a quartet at δ 4.12 for 2 protons, a multiplet at δ 2.4-1.97 for 1 proton, a multiplet at δ 1.97-0.7 for 3 protons and a triplet at δ 1.22 for 3 protons. The compound appeared to be the same isomer as the most abundant methyl ester isomer and ethyl ester isomer isolated in the reaction of 182 with ethyl acrylate. The isolation of just the one isomer which was the same as the more abundant isomer synthesized previously suggested that perhaps it was the trans isomer of 181.

Since both isomers of 181 were desired, another approach to their synthesis was tried. Both isomers of 1-carboethoxy-2-phenylcyclopropane 223 had been prepared by the addition of carboethoxycarbene to styrene by thermally decomposing ethyl diazoacetate (235-237), therefore the analogous

reaction was carried out with vinylferrocene <u>205</u>.

When <u>205</u> was heated with a four molar excess of ethyl diazoacetate in toluene at reflux over about a 2.5 day period, the isomers of <u>181</u> were obtained in 72% yield and 56% of <u>205</u> was recovered. It was found that the isomers could be separated by column chromatography on alumina if done very carefully. The separation of the isomers was complicated somewhat by the apparent presence of products which were formed between carboethoxycarbene and toluene. Therefore other solvents were investigated and it was found that both decalin and isooctane worked as well without the formation of troublesome side-products. When the reaction was carried out in decalin at $110\text{-}125°$ with a 10 time molar excess of ethyl diazoacetate added in about 6 equal portions over a two day period, vinylferrocene was completely consumed. Separation of the addition products by column chromatography gave 35% of <u>trans-181</u> and 19.3% of <u>cis-181</u>.

The <u>trans</u> isomer was slightly less polar and the assignment of its configuration was made on the basis of its nmr spectrum which showed a quartet at δ 4.12 for 2 protons, singlets at δ 4.10 and δ 4.00 for 5 and 4 protons respectively, multiplets at δ 2.85-1.90 and δ 1.90-0.80 for 1 and 3 protons and a triplet at δ 1.22 for three protons. The <u>cis</u> isomer showed a multiplet from δ 4.40-4.07 for 4 protons, a singlet at δ 4.03 for 5 protons, a quartet at δ 4.08 for 2 protons, a multiplet at δ 2.40-1.67 for 2 protons, a multiplet at δ 1.67-1.0 for 2 protons and a triplet at δ 1.07 for three protons. The first spectrum is very similar to those obtained for the product of the Simmons-Smith reaction and as the major products of the addition of <u>182</u> to ethyl acrylate. The latter spectrum was similar to the minor methyl ester isolated from the ethyl acrylate addition.

In the nmr spectral of those compounds considered <u>trans</u>, the methyl or ethyl ester group protons all appear somewhat downfield compared to the corresponding groups in the minor isomers. This may be accounted for by additional shielding by ferrocene (238) when the ester group would have a <u>cis</u> configuration.

More convincing evidence was provided by synthesizing the corresponding 2-phenylcyclopropylcarboxylic acids <u>224</u>. The configuration of the <u>cis</u> and <u>trans</u> isomers had been established by oxidative degradation studies (236, 237).

An nmr spectrum of the ethyl esters <u>223</u> showed that the minor isomer (<u>cis-223</u>) exhibited ethyl ester group resonances at higher field than the corresponding <u>trans</u> isomer. The same difference was evident in the corresponding methyl esters of <u>224</u>.

The pattern of the cyclopropyl protons in the 60 MHz nmr spectra of <u>trans-181</u> and <u>trans-224</u> were strikingly similar and the patterns of the cyclopropyl protons of <u>cis-181</u> and <u>cis-224</u> were also clearly related. 100 MHz nmr spectra of the compounds accentuated the correlation in configurations (Figure 27-30) and allowed the calculation of coupling constants for the compounds (Table 7).

Of particular interest were the $J_{1,2}$ coupling constants. The <u>trans</u> compounds show coupling constants smaller than the <u>cis</u> compounds and since <u>trans</u> coupling constants have been observed to be always smaller within a given pair of compounds (239) the assignment would appear to be reasonable.

Shortly after <u>cis</u>- and <u>trans-181</u> were first synthesized an independent report appeared which confirmed the assignment of configurations (240). Mechtler and Schlögl (240) prepared the isomers in an analogous manner

Figure 27. 100 MHz nmr spectrum of cis-1-carboethoxy-
            2-ferrocenylcyclopropane 181 (top)

Figure 28. 100 MHz nmr spectrum of cis-2-phenylcyclo-
            propylcarboxylic acid 224 (bottom)

90 cps

1166   747   401

551 cps
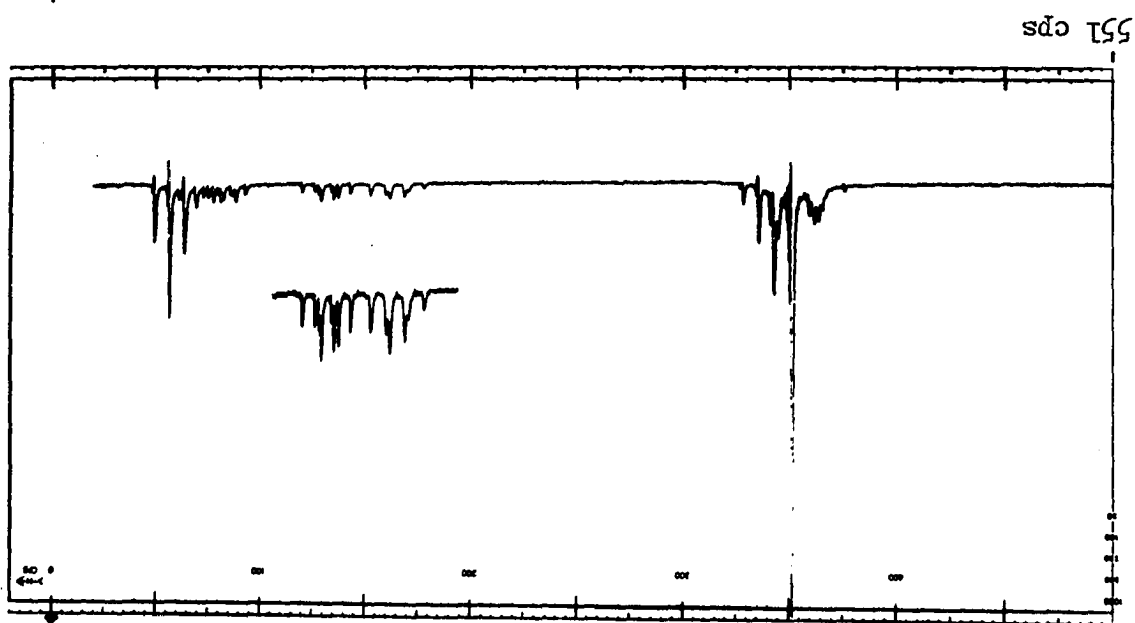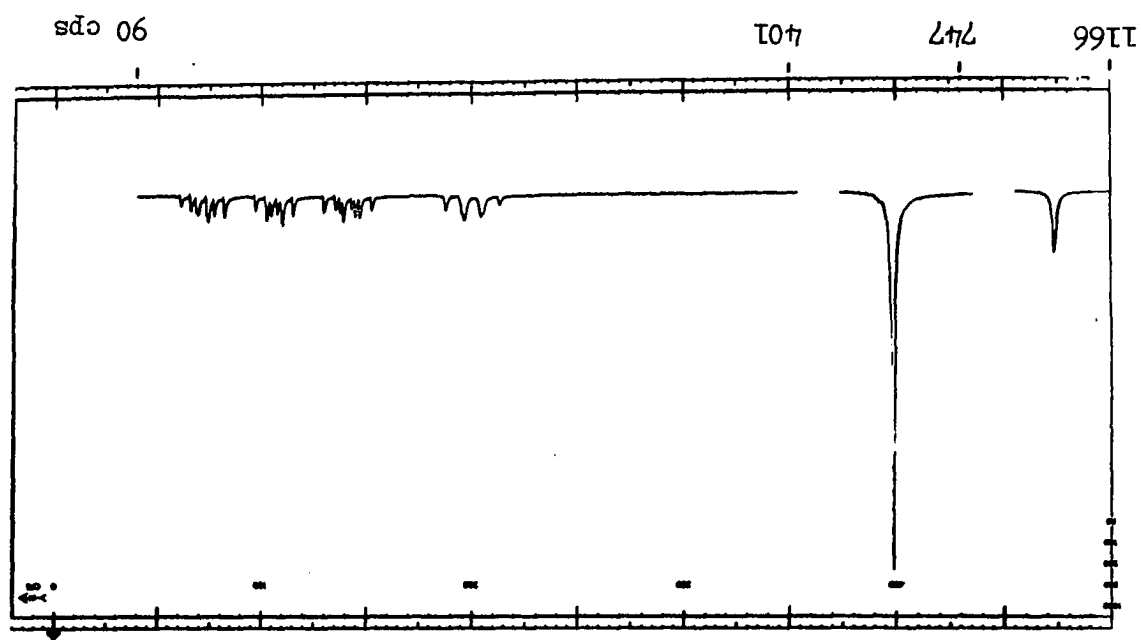
Figure 29. 100 MHz nmr spectrum of trans-1-carboethoxy-
          2-ferrocenylcyclopropane 181 (top)

Figure 30. 100 MHz nmr spectrum of trans-2-phenyl-
          cyclopropylcarboxylic acid 224 (bottom)

557 cps
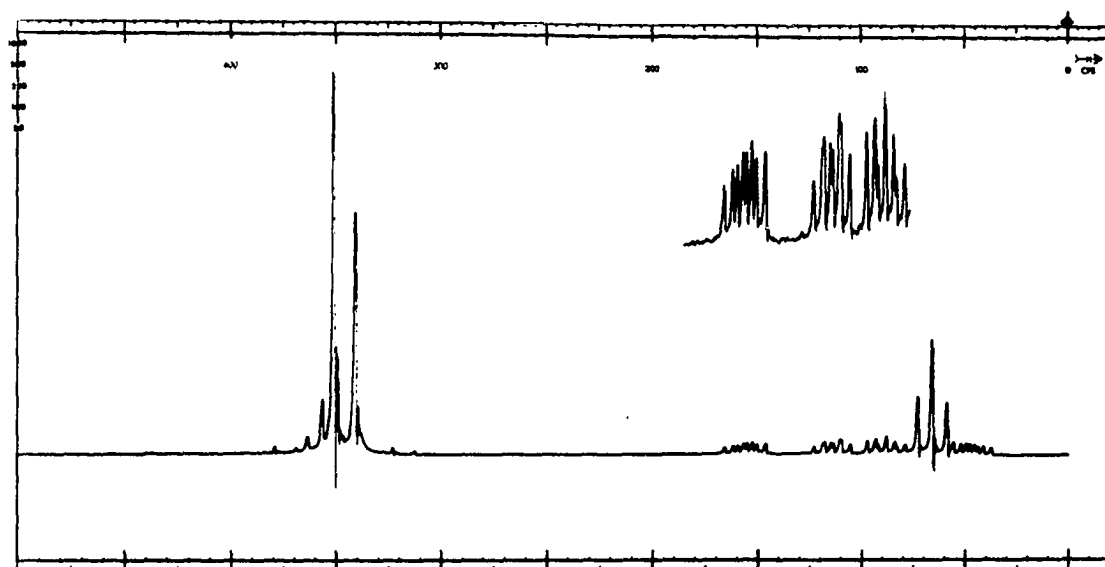
1248   764   674   312   101 cps
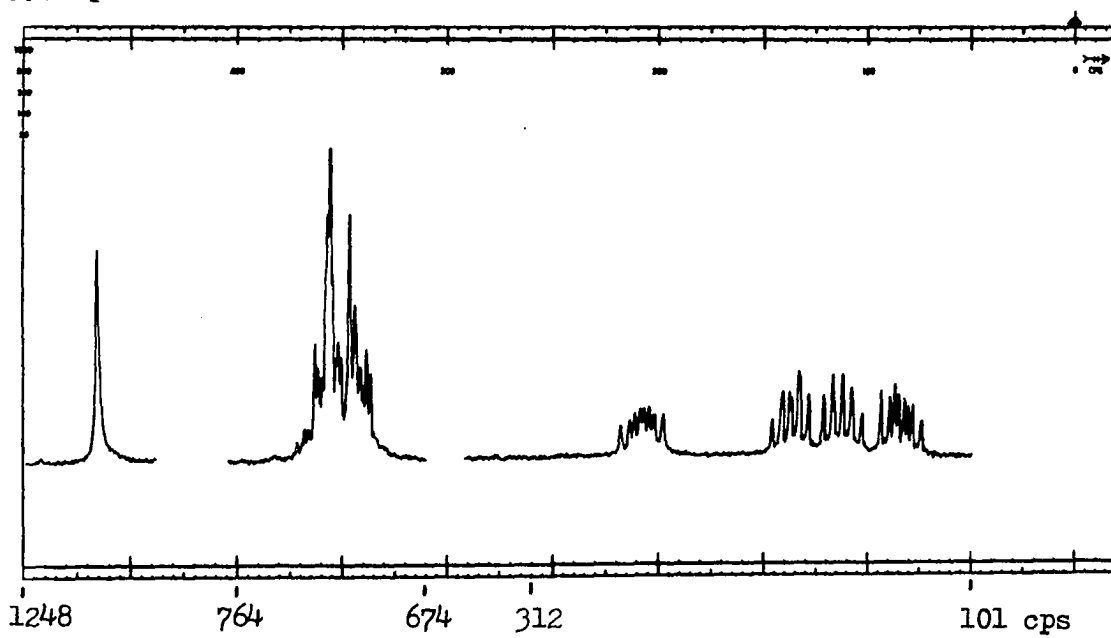
Table 7. Chemical shifts and coupling constants for cis- and trans-1-carboethoxy-2-ferrocenylcyclopropane 181 and cis- and trans-2-phenylcyclopropylcarboxylic acid 224

Structure[a]	Chemical shift[b]				Coupling constant[c]					
	H_1	H_2	H_3	H_4	$J_{1,2}$	$J_{1,3}$	$J_{1,4}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$
trans-224	258.1	189.5	164.1	136.1	4.4	9.1	6.8	5.2	8.4	4.6
trans-212	212.1	170.0	143.5	101.5	4.3	8.8	6.4	5.2	8.4	4.1
cis-224	251.5	191.9	157.7	122.9	9.2	7.8	9.0	5.8	7.9	5.0
cis-212	215.0	182.5	134.4	116.3	9.0	7.2	8.9	6.2	8.3	4.8

[a]Refer to the structure below:
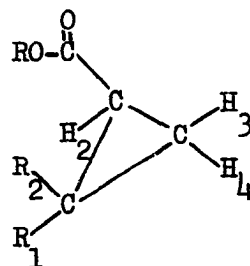
trans-224 $R = H$, $R_1 = Ph$, $R_2 = H_1$

trans-181 $R = C_2H_5$, $R_1 = Fer$, $R_2 = H_1$

cis-224 $R = H$, $R_1 = H_1$, $R_2 = Ph$

cis-185 $R = C_2H_5$, $R_1 = H_1$, $R_2 = Fer$

[b]In cps relative to TMS.

[c]In cps.

without solvent and with hydroquinone as a stabilizer in 70% yield (42% trans- and 28% cis-181).

The reaction of 2-ferrocenylpropene 220 with ethyl diazoacetate also proceeded to yield the corresponding cis- and trans-1-carboethoxy-2-methyl-2-ferrocenylcyclopropane 225 in 35% and 11.5% respectively. The assignment of configuration was based again upon their nmr spectra. The more abundant, less polar compound showed a quartet at δ 4.14 for 2 protons, a singlet at δ 4.13 for 5 protons, at singlet at δ 4.01 for 4 protons, a doublet of doublets at δ 1.92 for 1 proton, a multiplet at δ 1.60-1.05 for 2 protons, a singlet at δ 1.48 for 3 protons and a triplet at δ 1.25 for 3 protons. The absence of the proton at about δ 2.10 appeared to confirm the assignment of the proton H_1 as the cyclopropyl proton geminal to the ferrocenyl of phenyl groups in trans-181 and trans-224. A proton at about δ 2.15 was similarly missing in the spectrum of the minor and more polar component of the reaction mixture. Thus cis-225 showed a singlet at δ 4.13 for 9 protons, a quartet at δ 3.88 for 2 protons, a multiplet at δ 1.94-1.47 for 2 protons, a singlet at δ 1.55 for 3 protons and a triplet and a multiplet at δ 1.03 for 4 protons.

The esters cis- and trans-181 and cis- and trans-225 were easily converted to the corresponding cyclopropylcarbinyl alcohols with lithium aluminum hydride. Thus 181 was converted to 2-ferrocenylcyclopropylcarbinyl alcohol 227 in near quantitative yield and the cis-181 to the cis-226 in about 75% yield. The trans 225 was reduced in about 81% yield and the cis ester 225 was reduced to cis-2-ferrocenyl-2-methylcyclopropylcarbinyl alcohol 227 in about 65% yield. In all cases the starting materials could be recovered, therefore the yields should be considered percent conversions

and they could presumably be increased with longer reaction times.

Shono, Nishiguchi and Oda (205) reported the solvolysis of the 3,5-dinitrobenzoate of trans-228 in 75 weight percent aqueous dioxane at 130° (Scheme 62). They showed that the products 228 and 229 were stable under the reaction conditions and the 3,5-dinitrobenzoate of 229 did not give cyclopropyl products. Therefore the solvolysis did not give highly re-arranged products as the deamination reaction of trans-2-phenylcyclopropyl-carbinylamine (241). Further the methanolysis of the 3,5-dinitrobenzoate of trans-228 gave the methyl ethers of 228 and 229 indicating alkyl-oxygen cleavage in the solvolysis.

$$
\begin{array}{c}
\underset{\text{CH}_2}{\diagup\ \diagdown} \\
\text{Ph-CH}\text{———}\text{CH-CH}_2\text{O-3,5-DNB}
\end{array}
\quad
\xrightarrow[\text{dioxane}]{\text{75 wt \% aqueous}}
\quad
\begin{array}{c}
\underset{\text{CH}_2}{\diagup\ \diagdown} \\
\text{Ph-CH}\text{———}\text{CH-CH}_2\text{OH} \\
\underline{228}\ (12\text{-}15\%)
\end{array}
$$

3,5-DNB of trans-228

+

$$
\text{Ph-}\overset{\text{OH}}{\underset{|}{\text{CH}}}\text{-CH}_2\text{-CH=CH}_2
$$

$\underline{229}$ (85-88%)
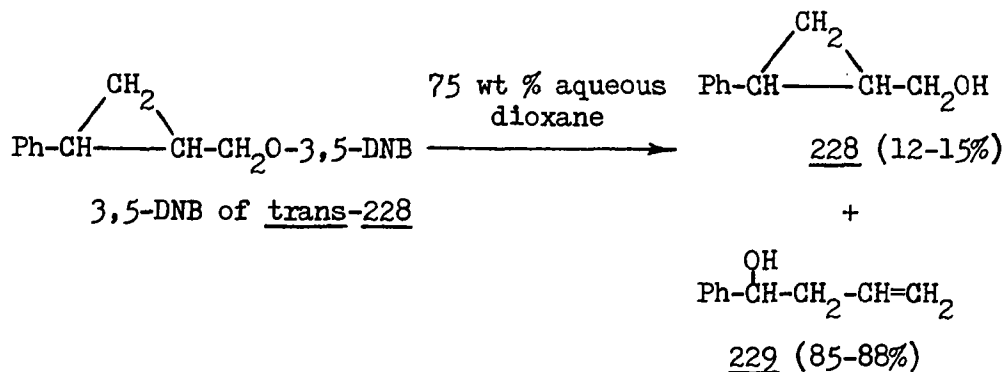
Scheme 62

The rates of solvolysis of the 3,5-dinitrobenzoates of trans-228 and 230-232 were first order and the Hammett plot of the relative rates versus σ_{p+} showed a straight line with slope -1.48. The trend in the solvolysis rates and the isolation of ring opened product from the solvolysis indi-cated charge delocalization to the 2 position of the cyclopropylcarbinyl cation. The value for the solvolysis of α-arylcyclopropylcarbinyl p-nitro-benzoates was -3.6 (242). The lower value of -1.48 (and the value of -1.8 obtained (243) for the solvolysis of trans-2-arylcyclopropyl tosylates)

could be rationalized by assuming that the conformation of the cyclopropylcarbinyl cation formed in the transition state of the solvolysis did not allow a sufficient π interaction between the π orbitals of the phenyl group and the p orbital of the carbonium ion.

p-X-Ph-CH——CH-CH$_2$OH (with CH$_2$ bridge)

230 X = OCH$_3$, relative rate = 15.4

231 X = CH$_3$, relative rate = 2.2

232 X = H, relative rate = 1.0

233 X = Cl, relative rate = 0.7
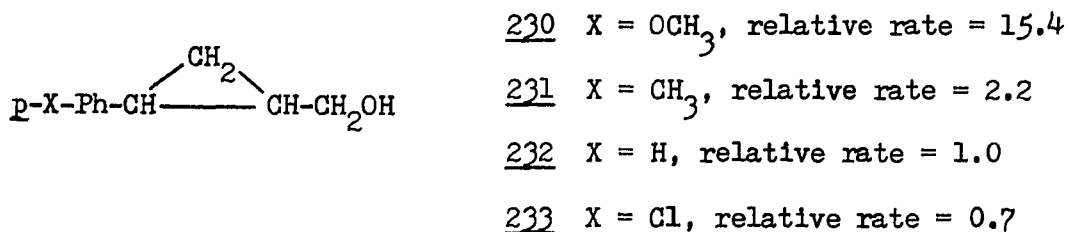
That analysis was substantiated by the finding that the rates of solvolysis of the 3,5-dinitrobenzoates of 234 and 235 were slower than that of the 3,5-DNB of trans-228. It had been shown that the 3,5-dinitrobenzoate of cis-228 was slower than that of the parent non-substituted compound (206). In the solvolysis of the 3,5-dinitrobenzoates of 234 or 235, steric interaction between 1-methylene and cis-2-phenyl groups of the intermediate cation would transform the conformation of the cation into one which would be unfavorable for the delocalization of the positive charge.

234

235
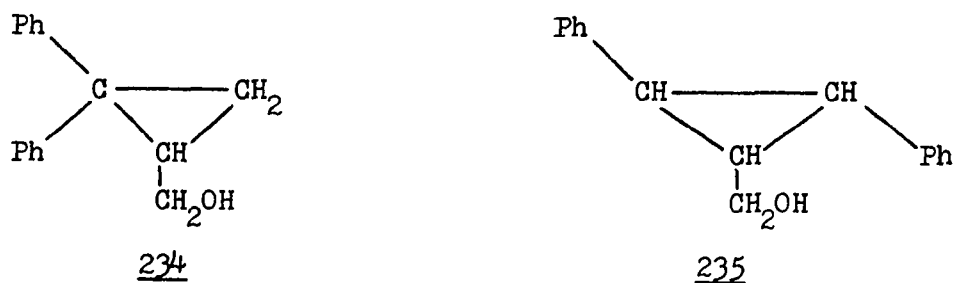
The solvolysis of the 3,5-dinitrobenzoates of 236 and 237 resulted in three-four fold rate increases relative to that of the 3,5-dinitrobenzoate of trans-228, suggesting the delocalization of positive charge to the 2 or 3 position of the 2-phenylcyclopropyl cation.

Ph
  \
   C————CH$_2$
  /   \
CH$_3$ CH
       |
      CH$_2$OH

<u>236</u>

Ph
  \
   CH————CH
      \   \
      CH   CH$_3$
       |
      CH$_2$OH
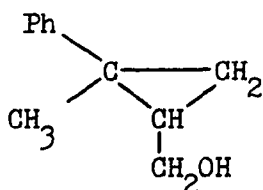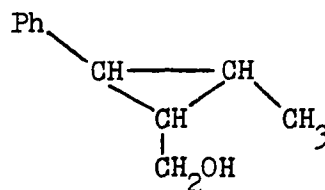
<u>237</u>

Schleyer and VanDine (244) had concluded that a symmetrically bisected cation <u>238</u> best fit their results with the solvolysis of the 3,5-dinitrobenzoates of 2,2-dimethylcyclopropylcarbinol <u>239</u> and 2,3-dimethylcyclopropylcarbinol <u>240</u>. They found that the rates of solvolysis was increased with substitution at both positions of the ring. Since the rates of solvolysis of the 3,5-dinitrobenzoates of <u>234</u> and <u>235</u> or those of the 3,5-dinitrobenzoates of <u>236</u> and <u>237</u> differed very little, it was concluded that the conformations of the cations formed was also similar to a symmetrical bisected cation with delocalization of charge to carbons 2 and 3 in such a way that the resonance effect of the 2-phenyl group was cancelled out by the inductive effect.

δ+

δ+

δ+ δ+
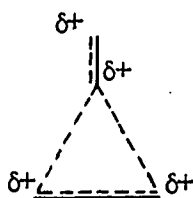
<u>238</u>

The 3,5-dinitrobenzoates of <u>cis</u>- and <u>trans-226</u> were prepared by treating <u>cis</u>- and <u>trans-226</u> with 3,5-dinitrobenzoylchloride in pyridine. Significantly the phenyl ring protons in the <u>trans</u> ester appeared as a singlet in an nmr but the same protons in the <u>cis</u> isomer appeared as a one proton triplet and a two proton doublet. It was found that the esters were not

sufficiently soluble to solvolyze in 75 weight percent aqueous dioxane
(to attain a concentration comparable to that employed by Shono and co-
workers) and that at 130°, the trans ester was thermally unstable, and
began to decompose in 100% acetone after about 8 hours. At 100° in 100%
acetone no apparent decomposition occurred until after 30 hours. The de-
composition was apparent by a darkening of the solution and the formation
of a precipitate. The addition of urea or lutidine to the reactions did
not appear to alter the decomposition.

Assuming that the decomposition appeared to be worse than it was, the
3,5-dinitrobenzoates of cis- and trans-226 were solvolyzed as 0.02 M
solutions in 10 weight percent aqueous acetone at 100°. The course of the
solvolysis was followed by titrating the 3,5-dinitrobenzoic acid with
aqueous sodium hydroxide using a pH meter. The equivalence points for the
titrations were obtained by taking a first derivative (245) of the data.

A first-order plot of the data is presented in Figure 31 and the
slopes of the plots were determined to be 1.8×10^{-6} second^{-1} for the cis
compound and 2.9×10^{-6} second^{-1} for the trans compound.

The rate of the solvolysis of the 3,5-dinitrobenzoate of trans-230
was 4.92×10^{-5} second in 75 weight percent aqueous dioxane at 130° (205).
By using the rule of thumb that a 10° difference in reaction temperature
will cause a two-fold difference in rate, the rate of the solvolysis of the
3,5-dinitrobenzoate of trans-226 would be about 2.3×10^{-5} second^{-1} at
130°. Additionally the rate of solvolysis of the 3,5-dinitrobenzoate of
trans-236 was found to be 4.1 times greater in 75 weight percent aqueous
dioxane than in 85 weight percent aqueous dioxane (205). Assuming that a
similar factor would apply to the difference in 90 weight percent aqueous

Figure 31. First order kinetic plots of the solvolysis of the 3,5-dinitrobenzoates of cis- and trans-2-ferrocenylcyclopropylcarbinyl alcohols 226 in 90% aqueous acetone at 100° C

Slope = 2.9 x 10^{-6}sec^{-1}

$\triangle$ Solvolysis of 3,5-dinitrobenzoate of trans-2-ferro-cenylcyclopropylcarbinyl alcohol 226

$\bigcirc$ Solvolysis of 3,5-dinitrobenzoate of cis-2-ferro-cenylcyclopropylcarbinyl alcohol 226

Slope = 1.8 x 10^{-6}sec^{-1}

$\log \left[\dfrac{a}{(a-x)} \right]$

time (hours)

238
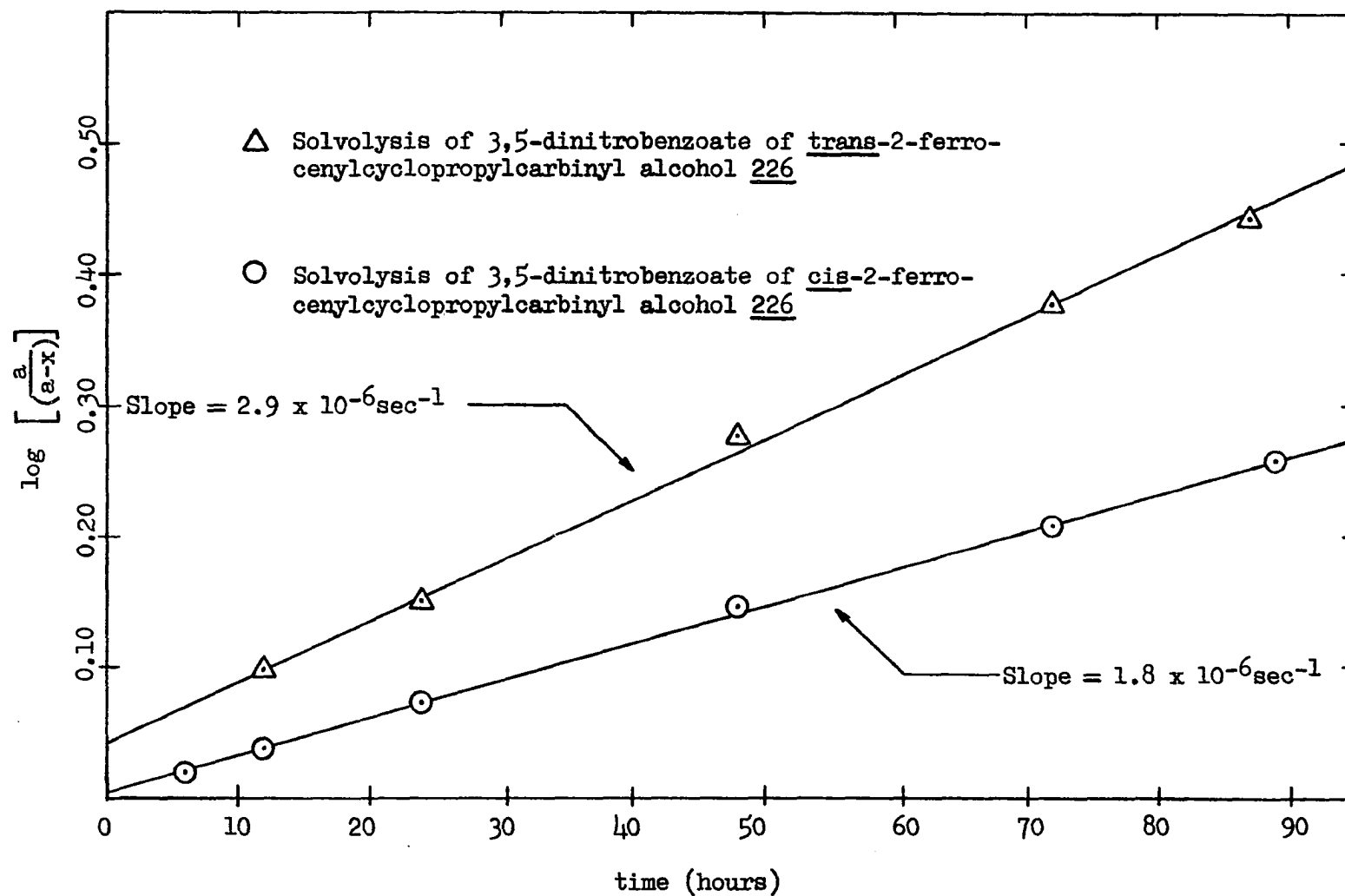
acetone to 75 weight percent aqueous dioxane, the rate of solvolysis of

the 3,5-dinitrobenzoate of trans-226 in 75 weight percent aqueous dioxane

may be estimated to be about 9.2×10^{-5} second^{-1}.

Recognizing the potential for gross error in making these conversions,

it nevertheless would appear that the rate for the ferrocenyl compound was

comparable to the rate of the p-anisyl compound and possibly somewhat

greater (182).

The rate of solvolysis of the β-naphthalene sulfonates of cis- and

trans-228 was found to be in the ratio of 1:3.5 (206). The ratio of rates

for the ferrocenyl compounds would be 1:1.6. The ratio of rates for the

solvolysis of the 3,5-dinitrobenzoates of 234 to trans-228 and of 235 to

trans-228 may be estimated to be 1:5.4 and 1:7.1 respectively and were

considered to be considerable by Shono and coworkers (205).

The difference in solvolysis rates for the ferrocenyl esters was

smaller than for the phenyl compounds in both studies and may reflect some

interaction in the ferrocenyl compounds which was absent in the phenyl com-

pounds. However the differences noted were small and arose in different

systems, therefore far-reaching conclusions would probably be tenuous con-

cerning participation by ferrocenyl electrons at the carbinyl carbon until

the solvolyses of both the ferrocenyl and phenyl compounds were carried out

under equivalent conditions. Although if the two-fold increase in rate of

cis-226 relative to trans-226 might indicate that non-bonding iron elec-

trons may have participated.

Mechtler and Schlögl (240) have reported the reaction of the acetates

of the cis and trans alcohols 226 as a mixture with polyphosphoric acid at

room temperature for 30 minutes (Scheme 63).

The 87 hour solvolysis run was worked-up after titration and an nmr spectrum taken of the mixture obtained. The presence multiplets at about δ 6.4 and from δ 5.4-5.0 strongly indicated that the mixture contained ring opened products.

$$Fer-CH=CH-CH=CH_2$$

$$(30\%)$$

$$+$$

$$\underset{\overset{\displaystyle OH}{|}}{Fer-CH}-CH=CH-CH_3$$

$$(30\%)$$

$$+$$

$$\underset{\overset{\displaystyle OH}{|}}{Fer-CH}-CH_2-CH=CH_2$$

$$(20\%)$$

acetates of <u>226</u> $\xrightarrow{\text{PPA}}$

Fer-CH (triangle with CH$_2$) CH-CH$_2$OCCH$_3$ (O)
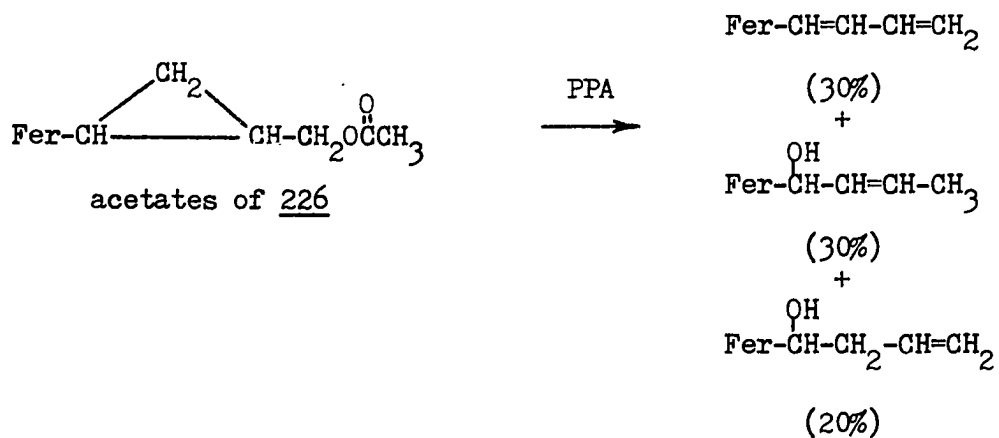
Scheme 63

EXPERIMENTAL

General

All boiling points and melting points are uncorrected and reported in degrees Centigrade.

The 60 MHz nmr spectra were recorded on a Varian A-60 spectrometer and 100 MHz nmr spectra were recorded on a Varian HA-100 spectrometer. All chemical shifts are reported in parts per million (ppm), units, relative to tetramethylsilane as internal standard unless otherwise noted. The number in parentheses indicating the number of protons causing the signal and the letter following designating the multiplicity of the signal: s, singlet; d, doublet; t, triplet; q, quartet; m, unresolved multiplet.

Infrared spectra were recorded on a Perkin-Elmer model 21, a Perkin-Elmer model 337 or Beckman IR 12 spectrometer and are reported in wave-numbers. Mass spectra were obtained on an Atlas CH-4 or an Atlas CH-7 spectrometer.

Photolysis was conducted using a 450 watt Hanovia type 673A high-pressure mercury arc lamp contained in a water cooled quartz immersion well.

Microanalytical data were obtained from Chemalytics, Inc., Tempe, Arizona or from Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Ferrocenylaldehyde 186

Ferrocenylaldehyde 186 was prepared by the previously reported (220) Vilsmeier-Haack reaction using ferrocene, phosphorous oxychloride and N-methylformanilide; 36.6% (lit. (246) 66%); nmr ($CHCl_3$): 9.95 (s, 1H), 4.79 (t, 2H), 4.59 (t, 2H) and δ 4.25 (s, 5H); ir (CCl_4): 2770 (w), 1688 (s), 1667 (shoulder), 1457 (m), 1373 (w), 1240 (m), 1107 (m), 1034 (m),

1025 (w) and 1002 cm^{-1} (w).

N-methylformanilide

N-methylformanilide was prepared according to an "Organic Syntheses" (246) procedure or purchased; bp 125-129°/9 mm (lit. (246) bp 114-121°/8 mm); nmr (CCl$_4$): 8.56 (s, 1H), 7.6-7.0 (m, 5H) and δ 3.22 (s, 3H).

Tosylhydrazone of ferrocenylaldehyde 185

To 25.0 g (0.117 mole) of 185 dissolved in 75 ml of methanol at 50° was added 21.7 g (0.117 mole) of tosylhydrazine in 50 ml of methanol at 50°. The reaction was exothermic and had to be moderated with a Dry-Ice-acetone bath to maintain a 50° reaction temperature for about 3 min before cooling the mixture to -78° for several hr. After that period the mixture was filtered to afford 42.3 g (94.7%) of 185; mp 155-160°. The material was found to be unstable in solution with several organic solvents, however recrystallization from methanol afforded 32.5 g (72.7%) of purified product; mp 157.5-159° (with decomp.) (lit. (225) mp 154-156° (with decomp.)). The compound was thermally unstable and the melting point reported was obtained with the temperature rising at 1°/min; nmr (CDCl$_3$, very dilute and decomposing): 7.59 (broad multiplet, about 1H), 7.55 (AB pattern, about 4H), 4.60-4.37 (m, about 2H), 4.28-4.05 (m) and 4.10 (s) for about 8H and δ 2.40 (s, about 3H); 100 MHz nmr (d$_6$-DMSO, sample decomposing as run): 776 (s, 1H), 760 (AB pattern, 4H), 449 (t, 2H), 430 (t, 2H), 394 (s) and 393 (s) for 10H and 231 cps (s, 3H); ir (KBr): 3190 (m), 1613 (m), 1599 (shoulder), 1475 (w), 1445 (w), 1410 (w), 1380 (w), 1365 (w), 1341 (shoulder), 1336 (m), 1312 (m), 1248 (m), 1886 (m), 1165 (s), 1106 (m), 1089 (m), 1038 (m), 1017 (w), 1004 (w), 962 (m), 946 (m) 905 (m), 848 (w),

837 (w), 810 (m) and 781 cm^{-1} (w); <u>Anal</u>. Calcd. for $C_{18}H_{18}FeN_2O_2S$:
C 56.56, H 4.75, N 7.33; Found: C 56.43, H 4.72, N 7.36.

Reaction of the tosylhydrazone of ferrocenylaldehyde <u>185</u> with sodium

methoxide in diethylene glycol at 60°

To 5.0 g (0.0131 mole) of <u>185</u> in a 250 ml flask was added 0.71 g

(0.0262 mole) of sodium methoxide and 90 ml of diethylene glycol. The con-

tents were warmed to 60° while stirring and after about 45 min at that

temperature a precipitate formed. The mixture was filtered and attempts to

extract the filtrate with cyclohexane, benzene and ether were unsuccessful.

The crystals collected were dissolved in $CHCl_3$ under reduced pressure

afforded about 2.1 g of crystals; nmr ($CDCl_3$): 8.14 (s, 1H), 7.56 (AB

pattern, 4H), 4.57 (t, 2H), 4.40 (t, 2H), 4.24 (s) and 4.13 (s) for 21H,

3.65 (m, unremoved diethylene glycol) and δ 2.45 (s, 3H); ir (CCl_4, very

weak): 3420 (m), 2900 (s), 1600 (m), 1358 (s), 1163 (s), 1126 (s), 1072

(s) and 1047 cm^{-1} (m); mass spectra: molecular ions at m/e 424, 396, 354,

304, 214 and 186 (the 580 m/e region was not scanned).

Reaction of the tosylhydrazone of ferrocenylaldehyde <u>185</u> with sodium

methoxide in ethylene glycol up to 100°

500 ml of ethylene glycol was distilled from CaH_2 through flame dried

glassware into a three-necked round bottom flask which had also been flame

dried (the first and last 50 ml portions were collected separately and

discarded). To the ethylene glycol was added 0.98 g (0.018 mole) of

sodium methoxide which had been dried under vacuum and the mixture was

stirred and degassed with nitrogen overnight. To the mixture was then

added 5.0 g (0.013 mole) of <u>185</u> and a gas collection tube attached. The

reaction mixture was then slowly warmed. Gas began to be collected slowly

when the reaction mixture reached about 40° but the 185 had not yet all

dissolved. As the temperature continued to rise, gas evolution increased

and the remaining 185 dissolved. When the temperature reached about 65°,

a fine precipitate began to form. At about 100°, the solid remained and

gas evolution ceased at 310 ml collected (theoretical N_2 yield: 310 ml).

Total reaction time was about 4.5 hr.

Mass spectral analysis of the gas sample collected indicated m/e 28

significantly above background.

Thin layer chromatography of the crude reaction mixture indicated the

presence of one major substance and at least five minor components.

The ethylene glycol was removed by vacuum distillation (a yellow-

orange substance co-distilled) to afford a yellow-orange residue. The

residue was taken up in $CHCl_3$ and extracted with water and sodium bicarbon-

ate solution. The organic layer was then dried over anhydrous $MgSO_4$, fil-

tered and the $CHCl_3$ removed under reduced pressure to afford 4.1 g of a

brown solid; nmr $(CDCl_3)$: 8.11 (s, 1H); 7.53 (AB pattern, 3H); 4.55 (t,

2H), 4.38 (t), 4.22 (s), 4.13 (s) and 4.07 (s) for 24H and 2.43 (s) and

δ 2.39 (s) for 3H.

The brown solid was recrystallized from ethyl acetate to afford brown

crystals; mp 198-199.5°; ir (KBr): 1600 (s), 1495 (w), 1470 (m), 1415 (m),

1378 (w), 1342 (s), 1329 (shoulder), 1305 (w), 1244 (m), 1235 (m), 1159

(s), 1105 (m), 1087 (m), 1053 (m), 1039 (m), 1026 (w), 1007 (m), 928 (w),

892 (m) and 867 cm^{-1} (w); mass spectrum: molecular ion at m/e 580. An nmr

of a less purified sample (small yellow crystals were present) was essen-

tially identical to that of the crude material. The data are consistent

with the compound being 187; Anal. Calcd. for $C_{29}H_{28}Fe_2N_2O_2S$: C 60.02, H 4.86, N 4.83; Found: C 59.93, H 4.84, N 4.84.

Column chromatography of the material afforded one isoluble fraction which was slightly more polar than 187 and not well separated; nmr ($CDCl_3$, omitting resonances due to 187): 7.35 (AB pattern), 4.07 (s) and δ 2.38 (s). The compound was identified later as 191.

Evaporation of the aqueous extracts of the original crude residue afforded white, water soluble crystals; nmr (H_2O): 7.45 (AB pattern, 4H) and δ 2.38 (s, 3H). The material was probably sodium tosylate.

Reaction of the tosylhydrazone of ferrocenylaldehyde 185 with sodium methoxide in diglyme at 30-40°

To 100 ml of diglyme and 200 ml of pentane was added, with stirring, 2.5 g (0.00654 mole) of 185 and 0.35 g (0.00654 mole) of sodium methoxide. The mixture was then warmed to 30-40 whereupon a precipitate formed with the evolution of a gas, however some 185 had not yet dissolved. Therefore, an additional 100 ml of pentane and 0.35 g (0.00654 mole) of sodium methoxide was added. The remaining 185 then dissolved after 3 hr and more precipitate formed but without the formation of a gas. The precipitate was then collected by filtration and washed with pentane; ir (KBr): 3400 (m), 1600 (w), 1441 (s), 1230 (s), 1123 (s), 1107 (w), 1090 (A), 1055 (w), 1030 (m), 960 (w), 917 (m), 880 (w), 810 (m), 756 (w), 708 (w) and 656 cm^{-1} (m). A portion of the material was found to be soluble in water and when the water solution was shaken with polar organic solvents, a brown substance could be extracted. Thin layer chromatography showed that the extracted material was 185. If the aqueous solution of the product was acidified, a

purple color developed initially and the extraction of the resultant 185 was facilitated.

Treatment of 185 with water produced no dissolution, but treatment of 185 with aqueous base did cause some dissolution. Acidification of the basic solution produced a purple color initially and subsequent extraction with polar organic solvents yielded 185.

Lithium salt of the tosylhydrazone of ferrocenylaldehyde 185

To 45 ml of dry diglyme under nitrogen atmosphere was added 6.54 g (0.0171 mole) of 185 with stirring. The solution was warmed to dissolve all of the hydrazone and then cooled to room temperature. To the cooled solution was added 10.4 ml of 2.07 M (0.0224 mole) phenyllithium in benzene/ether by means of a syringe through a septum over a 2-3 min period. The heat of reaction was sufficiently exothermic to boil the solvent momentarily. After about 1 hr a dense precipitate occurred and the mixture was stirred for an additional 3 hr. After that period the solid was collected by filtration and washed with dry benzene, ether and then hexane. The material was then dried under high vacuum, 5.66 g (85.3%).

Pyrolysis of the lithium salt of the tosylhydrazone of ferrocenylaldehyde 185 in ethylene glycol up to 145°

To 500 ml of dry ethylene glycol under nitrogen was added 2.0 g (0.00515 mole) of the lithium salt of 185. The temperature of the mixture was slowly raised to 120-145°. At about 120° rapid gas evolution was evident. At 145°, the gas evolution ceased and the mixture was maintained at 120-145° for about 1 hr and then allowed to cool to room temperature. The cooled mixture was then poured into water and extracted with ether. The

ether portions were washed in turn with water and then dried over anhydrous magnesium sulfate, filtered, and the ether removed under reduced pressure; ir (CCl_4). The residue obtained was chromatographed on silica gel to afford four fractions two of which were of sufficient size to isolate. Fraction two; mp 197-198°; 3580 (w), 3100 (w), 2930 (s), 1600 (w), 1455 (m), 1342 (m), 1259 (m), 1100 (s), 1053 (s), 927 (w) and 862 cm^{-1} (s), 0.20 g; nmr ($CDCl_3$): 7.35 (AB pattern, 4H), 4.06 (s, 11H) and δ 2.39 (s, 3H); mass spectrum: molecular ion at m/e 354. The data suggest the sulfone <u>191</u> (11.2%); <u>Anal</u>. Caldc. for $C_{17}H_{18}FeO_2S$: C 61.03, H 5.12; Found: C 61.19, H 5.05. Fraction four; mp about 45°; nmr ($CDCl_3$): 4.30 (s, 2H); 4.18 (m) and 4.11 (s) for about 11H and δ 3.54 (s, 2H); mass spectrum: molecular ion at m/e 260. The data suggest <u>196</u> (78%); <u>Anal</u>. Calcd. for $C_{13}H_{16}FeO_2$: C 60.02, H 6.21; Found: C 63.07, H 6.67.

Mass spectrum of the sodium salt of the tosylhydrazone of ferrocenyl-aldehyde <u>185</u>

The sodium salt of <u>185</u> was submitted for mass spectral analysis. The vac lock inlet system was used and increasing heat was applied to the sample.

With 30 units of heat the largest ion was m/e 149 and m/e 211 and 226 were not above background. An ion at m/e 280 also appeared but did not contain iron.

With 50 units of heat the ion at m/e 226 was above background and larger than the m/e 280 ion which had not increased.

With 85 units of heat the m/e 211 ion began to appear and the m/e 226 ion increased somewhat.

With 120 units of heat applied the ion at m/e 211 was more intense than the ion at m/e 226 but very intense ions appeared at m/e 354, 396, 412 and 424, the m/e 396 ion being off scale and the m/e 226 ion being about 12% of scale.

Vacuum pyrolysis of the lithium salt of the tosylhydrazone of ferrocenylaldehyde 185 up to 170°

The lithium salt of 185 was taken up in chloroform and transferred to a large sublimation apparatus. The solvent was then removed under vacuum, the cold finger cooled to -78° and heat slowly applied. At about 100° some material was seen to condense upon the cold finger and the amount increased as the temperature was slowly increased to 170°. The condensed material was then washed from the cold finger with $CHCl_3$ and then concentrated under reduced pressure to afford a yellow-orange semi-solid which was partially soluble in pentane; ir ($CHCl_3$): 2930 (s), 2230 (w), 1625 (m, broad), 1600 (w), 1460 (m), 1385 (w), 1142 (w), 1105 (m) and 1000 cm^{-1} (m); mass spectrum: molecular ions at m/e 211, 276 (iron?), 292 and 396.

Treatment of the material with thin layer chromatography indicated many components in the mixture. The three most intense were isolated and submitted for mass spectral analysis but the samples did not contain enough materials to obtain spectra.

Vacuum pyrolysis of the sodium salt of the tosylhydrazone of ferrocenylaldehyde 185 up to 175°

Approximately 0.5 g of the sodium salt of 185 was placed in a large sublimation apparatus equipped with a cold finger cooled to -78°. Vacuum was then applied and the sample heated to $150 \pm 5°$ for two days. During that

period the sample darkened and the upper portions of the material seemed

to be orange-red in coloration. The condensate was then removed from the

cold finger by washing with chloroform into 0° pentane and the solvent re-

moved under reduced pressure to afford a residue which thin layer chroma-

tography indicated consisted of at least 3 components. More condensate

was collected from the same sample at $175 \pm 5^{\circ}$ over a two day period and thin

layer chromatography indicated the same mixture was present. Column chro-

matography on silica gel afforded two major fractions and several minor

ones.

Thin layer chromatography of the first major fraction indicated the

presence of at least five components; mass spectrum: molecular ions

observed at m/e 262 and 396.

The second major fraction appeared to consist of two materials by

thin layer chromatography; mass spectrum: only one molecular ion observed

at m/e 211 which suffered a metastable loss of 27 mass units to 185°. The

data suggest ferrocenylnitrile 197.

In a similar but separate experiment, the cold finger condensate

appeared distinctly reddish and the red coloration was lost on washing the

condensate from the cold finger with ether.

Attempted vacuum pyrolysis of the lithium salt of the tosylhydrazone of

ferrocenylaldehyde 185 with dimethyl fumarate as a trapping agent

A simple vacuum distillation apparatus was assembled and 2.05 g

(0.00528 mole) of the lithium salt of 185 placed in the pot. To the re-

ceiving flask was added 5.10 g (0.0389 mole) of dimethyl fumarate and the

flask cooled to -78°. Vacuum was then applied to the system and the pot

warmed slowly with an oil bath. At about 80-90° some orange condensate appeared in the distillation head and a few moments later a drop of yellow material condensed and dropped into the ester. The temperature was then increased to about 100° which caused a crystalline material to form in the condenser and the pot contents to appear pink. Further increasing the temperature caused the red coloration to intensify and more condensate to form in the distillation head. When the temperature reached 140° the contents of the pot appeared dull white but a reddish material had condensed just above the oil bath level. The system was then disassembled and thin layer chromatograms run for the condensates in the pot, distillation head and condenser which all appeared to consist of the same three major components. Column chromatography of the combined materials on silica gel also afforded three major fractions. The first fraction was a red solid which did not melt but darkened below 280°; nmr $(CDCl_3)$: 6.40 (s?), 4.38 (m), 4.26 (m), 4.09 (s) and δ 4.03 (s?); mass spectrum: molecular ion at m/e 262. The δ 4.38 and δ 4.26 multiplets appeared to be the protons on the substituted ring of a ferrocenyl compound with the non-substituted ring protons at δ 4.09. The second fraction was a yellow solid; mp 102-104°; nmr (CCl_4): 4.60 (t, 2H) and δ 4.30 (s, 7H); mass spectrum: molecular ion at m/e 211 with a metastable loss of 27 mass units to 185. The third major fraction appeared to be a mixture based upon the following spectral data; nmr $(CDCl_3)$: 7.60, 7.47 and 7.26 (part of an AB pattern, 4H), 4.80 (m, 3H), 4.61 (m, 2-3H), 4.29 (s, 7H), 4.15 (s?, 2H), 4.09 (s, 10H) and δ 2.41 (s, 3H); mass spectrum: molecular ions at m/e 211 and 214. The nmr indicated that at least a mixture of 197 and 191 was present however no ion at m/e 354 was observed (by the operator). The ion at m/e 214 would suggest

the presence of <u>186</u> and a small amount could be present in the nmr spectrum.

Ferrocenoyl chloride

Ferrocenoyl chloride was prepared from ferrocenic acid commercially available with oxalyl chloride by the method of Lan and Hart (247); red crystals (26.5%); ir (CCl$_4$): 1770 cm^{-1} (C=O) (lit. (247) 1767 cm^{-1}).

Nitrosomethylurea

Nitrosomethylurea was prepared according to an "Organic Syntheses" procedure (141) 47%.

Diazomethane ethereal solution

An ethereal solution of diazomethane was generally prepared by adding small amounts of nitrosomethylurea to a mixture of 50% KOH and ether with stirring. As the ether layer became saturated with diazomethane the excess was allowed to pass into a trap containing ether held at 0°. The trapped ethereal diazomethane solution was used unpurified except for drying the solution over KOH pellets or metallic sodium.

Ferrocenoyldiazomethane <u>199</u>

The procedure for preparing ferrocenoyldiazomethane <u>199</u> was adapted from the procedure of Yates and Shapiro (248) for preparing diazoketones. To an etheral solution of ferrocenoylchloride was added an equimolar amount of triethylamine in a non-standard taper flask. An excess of ethereal diazomethane was then added to the mixture at -10°, dropwise with stirring. After the addition was complete the stirring was stopped and the mixture allowed to stand for 3 hr at -10°. The ether was then removed under reduced pressure to afford a red-brown residue. The residue was taken up in

pentane or ether leaving the triethylamine hydrochloride precipitate and the solvents removed under reduced pressure to afford unpurified 199; ir (CCl_4): 2120 (m) (lit. (249) 2110), 1725 (s), 1740 (m) and 1460 cm^{-1} (m).

Hydrazone of ferrocenyldehyde 200

A. Attempted preparation according to the procedure of Closs and Moss (208) for the hydrazone of p-methoxybenzaldehyde. To 0.5 g (0.00233 mole) of 186 dissolved in the least amount of ether was added 1.49 g (0.00466 mole) of 97+% anhydrous hydrazine and the mixture was allowed to stir overnight at 0°. After an additional hour of stirring at room temperature, the aqueous base was removed; the ethereal phase was washed twice with 10 ml portions of water and dried over magnesium sulfate. After removal of the drying agent by filtration and evaporation of the solvent under reduced pressure a brown solid was afforded; mass spectrum: molecular ion at m/e 424 and no ion at 228.

B. Preparation by the procedure of Newkome and Fishel (221). To 5.0 g (0.0234 mole) of 186 in ethanol was added 5.62 g (0.0937 mole) of 1,1-dimethylhydrazine and the mixture heated to reflux for 22 hr under a positive nitrogen atmosphere. The excess hydrazine was then removed under reduced pressure to afford 5.7 g (96%, unpurified) of brown crystals of 201; mp 67.5-69°; Anal. Calcd. for $C_{13}H_{16}FeN_2$ C 60.95, H 6.29; Found: C 61.12, H 6.26; nmr $(CDCl_3)$: 7.04 (s, 1H), 4.48 (t, 2H), 4.17 (t, 2H), 4.08 (s, 5H) and δ 2.73 (s, 6H); ir $(CHCl_3)$: 3038 (s), 2870 (m), 2840 (m), 2800 (w), 1595 (w), 1479 (s), 1450 (m), 1385 (w), 1332 (w), 1272 (m), 1142 (s), 1108 (s), 1020 (s) and 833 cm^{-1} (m).

To 5.45 g (0.0213 mole) of 201 in 10 ml of ethanol was then added

3.2 g (0.10 mole) of anhydrous hydrazine and the mixture heated to reflux for 22 hr under an atmosphere of nitrogen. The solvent and excess hydrazine was then removed under vacuum to afford 200.

Reaction of the hydrazone of ferrocenylaldehyde 200 with silver oxide

To the hydrazone 200 derived from 2.0 g (0.00933 mole) of 186 by procedure B above was enough methylene chloride to effect dissolution at 0° and the 3.26 g (0.014 mole) of silver oxide was added which caused an immediate reaction to occur as evidenced by the material gushing up the neck of the flask. An ir spectrum was taken of the reaction mixture which exhibited bands at 3625 (s), 3410 (m), 2975 (m), 2990 (s), 2900 (s), 1605 (m), 1390 (m), 1292 (broad), 1150 (s), 880 (m) and 826 cm^{-1} (m). An ir spectrum run after adding the silver oxide showed no change except for a new band at 3700 cm^{-1}. No changes were then observed after one hour at 0° and several hours at room temperature. The addition of more silver oxide again caused no change.

Reaction of the hydrazone of ferrocenylaldehyde 200 with manganese dioxide

The reaction was carried out in essentially the same manner as the reaction above except that the silver oxide was replaced by an equimolar amount of manganese dioxide. The addition of the MnO_2 caused no immediate reaction at 0° as the silver oxide had and after one hr only a small band could be seen at 2070 cm^{-1} in an ir sample of the reaction mixture. After two hr at 0° however, the band at 2070 cm^{-1} was strong. Continued reaction caused the 2070 cm^{-1} band to decrease in importance and repeated scanning of the 2100-2000 cm^{-1} region of the spectrum caused the intensity of the 2070 cm^{-1} peak in the spectrum to drop to background after about 15 min.

Filtration of the reaction mixture after about seven hr of reaction time showed only a weak band at 2070 cm^{-1}.

Pyrolysis of the sodium salt of the tosylhydrazone of ferrocenylaldehyde 185 with cyclohexene

To 0.648 g (0.027 mole) of pentane washed sodium hydride was added 250 ml of pyridine (degassed with nitrogen) and 5.0 g (0.013 mole) of 185 with stirring in a flame dried three-necked round bottom flask under a nitrogen atmosphere. An immediate fluffy precipitate formed. To the mixture was then added 100 ml of degassed cyclohexene and the mixture slowly warmed. At about 75° distinct gas evolution was noted and the mixture then heated to 80°. After the gas evolution ceased the material was cooled to room temperature and filtered with suction and the residue washed with methanol. The residue was a light tan solid, 4.0 g. The filtrate afforded 3.65 g of material after removing the solvents under reduced pressure. Column chromatography of 2.74 g of the filtrate residue on silica gel afforded 3 major fractions and several minor ones. The first fraction was a yellow oil which decomposed standing at 0° to afford a methanol insoluble brown solid, 125 mg; nmr (CCl$_4$): 4.18 (m, 1.36H), 4.00 (s, 4.25H), 3.86 (s, 2.3H), δ 2.32-0.5 (m, 13H); ir (capillary film): 2910 (s), 1725 (w, in crude sample), 1448 (m), 1215 (w), 1105 (m), 1038 (w), 1023 (w), 1000 (m), 974 (w), 815 (s) and 759 cm^{-1} (s); mass spectrum: molecular ion at m/e 280 with metastable losses of 68 and 81 mass units from the molecular ion (m* calc. /m* obsd. respectively: 160.5/160.8 and 141.4/141.5) and small losses of 28 and 29 mass units from the molecular ion (additional higher mass ions were observed of low intensity containing iron); Anal. Calcd. for

$C_{17}H_{20}Fe$: C 72.88, H 7.19; Found: C 51.10, H 4.52. The data suggests 7-ferrocenylnorcarane but the analysis did not support that assignment.

Fraction two was an orange solid, 98 mg, crystals recrystallized from benzene did not melt but sublimed at about 200° (lit. (250) mp for 1,2-diferrocenylethene <u>188</u>, 265-267°); mass spectrum: molecular ion at m/e 396.

Fraction three was a brown solid, 53 mg, recrystallized from benzene, decomposed below 350° (lit. (220) mp for <u>189</u>, 245°); nmr (CDCl$_3$): 7.29 (s), 4.22 (s) and δ 4.13 (s) (spectrum was taken of unrecrystallized material and showed considerable evidence of impurities); mass spectrum: molecular ion at m/e 424.

Pyrolysis of the lithium salt of the tosylhydrazone of ferrocenylaldehyde <u>185</u> with dimethyl fumarate in diglyme

To 200 ml of THF was added 0.53 g (0.00136 mole) of the lithium salt of <u>185</u> and 0.4 g (0.0027 mole) of dimethyl fumarate with stirring. Dissolution of the salt was poor, therefore 100 ml of diglyme was added and the THF distilled from the mixture. At about 75° the salt dissolved and a gelatinous precipitate formed. The mixture was then heated to 145°. The reaction was then cooled to room temperature and filtered. The filtrate was then added to water and the aqueous layer extracted with ether. The organic solvents were then distilled affording a solid residue which was chromatographed on silica gel to afford one major band, 10.69 g, and several small more polar bands. The major band exhibited a molecular ion at m/e 342 corresponding to 1,2-dicarboethoxy-3-ferrocenylcyclopropane. Recrystallization of the fraction from benzene afforded brown crystals; mp

about 153°; mass spectrum: molecular ions at m/e 382 (for 185, lit (225) mp 154-156°), 396 (for 188) and 424 (for 189) when heat was applied to the sample.

The white residue of the filtration was dissolved in D_2O; nmr (D_2O): 7.43 (AB pattern, 4H), 6.52 (s, 1H) and δ 2.37 (s, 3H) (the tosyl leaving group).

Pyrolysis of the lithium salt of the tosylhydrazone of ferrocenylaldehyde 185 with dimethyl fumarate as solvent

To 2.0 g (0.00505 mole) of the lithium salt of 185 was added 3.7 g (0.0258 mole) of dimethyl fumarate and the mixture heated. At 110° the ester melted and the components mixed. The mixture was then heated to 135°. The reaction was then cooled to room temperature and added to water. The aqueous layer was then extracted with ether and the organic layer washed with water and dilute aqueous base. The aqueous portions were evaporated to afford a white solid and the organic layer stripped of solvent under reduced pressure to afford brown residue which was chromatographed on silica gel to afford two small fractions less polar than the major fraction. Recrystallization of the major fraction afforded brown crystals; mp about 153° (lit. (225) mp for 185 154-156°). The two small non-polar fractions were adsorbed on alumina and purified by thin layer chromatography. The alumina adsorbed spots were submitted for mass spectral analysis. Fraction one, orange; mass spectrum: not enough sample obtained. Fraction 2, yellow; mass spectrum: molecular ion at m/e 342 (for 1,2-dicarboethoxy-3-ferrocenylcyclopropane).

Photolysis of the lithium salt of the tosylhydrazone of ferrocenylaldehyde
185 in THF with dimethyl fumarate

The lithium salt of 185 was added to 5.1 g (0.039 mole) of dimethyl
fumarate in THF and the mixture photolyzed for 18 hr. The solvent was
then removed under reduced pressure and the residue chromatographed on sil-
ica gel to afford four fractions. The last fraction afforded brown
crystals which had an R_f value identical to 185. Fraction one, by thin
layer chromatography was contaminated with the excess dimethyl fumarate
and was distilled, the residue afforded a molecular ion at m/e 342. The
distillate of fraction one afforded a molecular ion at m/e 244 which con-
tained iron. Fraction two also afforded a molecular ion at m/e 342 in its
mass spectrum along with molecular ions at 396 and 424. Fraction three
exhibited molecular ions at 354, 396 and 440. The separation appeared to
be poorly made possibly due to the large excess of dimethyl fumarate
present.

Pyrolysis of the lithium salt of the tosylhydrazone of ferrocenylaldehyde
185 with methyl cinnamate in glyme

To 13.7 g of glyme distilled from potassium metal was added 0.666 g
(0.00174 mole) of 185 with stirring followed by 1.09 ml of 1.6 M n-butyl
lithium (0.00174 mole). Immediate formation of a precipitate gas evolution
occurred and the mixture was cooled by an ice water bath and stirred for
an hr. After that period the mixture was allowed to warm to room temper-
ature which produced a thick slurry. Approximately 2 g (0.012 mole) of
methyl cinnamate was then added and the mixture heated to 87° for 15 min
and then cooled to room temperature. Thin layer chromatography of the

material obtained showed the presence of at least eight fractions. Thick layer chromatography of the material afforded nine fractions. Fraction one was a yellow liquid which when concentrated produced a brown precipitate, 13 mg; nmr (CCl_4): 3.99, 3.97 and 3.82 (singlets, 9H), 2.3 (m, 2H) and δ 1.7-0.6 (m, 13H); ir (capillary film): 2920 (s), 1466 (m), 1105 (m), 1039 (w), 1022 (w), 1000 (m) and 815 cm^{-1} (m); mass spectrum: molecular ion at m/e 256; possibly insertion product of <u>182</u> into butane. Fraction two was an orange liquid, 3 mg; mass spectrum: molecular ion at m/e 288; possibly the insertion of <u>182</u> into DME. Fraction three was a red-brown liquid, 3 mg. Fraction four was a red-brown liquid, 8 mg; mass spectrum: molecular ion at m/e 162; apparently impure methyl cinnamate. Fraction five was a brown solid, 49 mg; mass spectrum: molecular ions at m/e 162 and 211 (with m* loss of HCN) for possibly methyl cinnamate and <u>197</u>. Fraction six was a dark brown liquid, 6 mg; mass spectrum: molecular ions at m/e 162, 211 (with m* loss of HCN) and 254 for possibly methyl cinnamate, <u>197</u> and <u>191</u> respectively. Fraction seven was a dark red liquid, 67 mg; nmr ($CDCl_3$): 7.25 (s, $CHCl_3$?), 4.4-3.8 (m, 9H) and 2.50-0.50 (m, 150-160 H) with a sharp singlet at δ 1.27 (90H); ir (capillary film): 2920 (s), 1737 (s), 1460 (m), 1375 (w), 1253 (w), 1165 (w) and 1105 cm^{-1} (w); mass spectrum: molecular ions at m/e 214 with metastable loss of 28 mass units from the molecular ion (m* calcd./m* obsd.: 161.6/161.8) and 376, the former for <u>186</u>. Thin layer chromatography of fraction seven showed the presence of at least four components. Fraction eight was a brown black, 54 mg; nmr ($CDCl_3$): 8.0-6.9 (m) with sharp resonance at 7.25 ($CHCl_3$?), 5.2-3.2 (m) with sharper resonances at 4.19 and 3.69, 2.38 (s), 2.0 (s) and δ 1.4-1.0 (m); ir (capillary film): 2920 (s), 1738 (w), 1460

(m), 1378 (w), 1259 (m), 1122 (m), 1104 (m) and 1028 cm^{-1} (m); mass spectrum: molecular ion at m/e 360 for 1-carbomethoxy-2-ferrocenyl-3-phenyl-cyclopropane but the nmr and ir indicate significant impurities.

Pyrolysis of the sodium salt of the tosylhydrazone of ferrocenylaldehyde
185 in ethyl acrylate

To a flame dried, nitrogen flushed round bottom flask was added 0.1 g
(0.0042 mole) of pentane washed sodium hydride, 1.3 g (0.0034 mole) of
carefully dried 185. The mixture was cooled to -78° and DME freshly distilled from potassium metal and degassed was added with stirring. The mixture was then warmed to -60° for several hr. The solvent was then removed
by vacuum overnight. To the dried salt was then added 20 ml of ethyl
acrylate and the mixture heated while stirring. Gas evolution was monitored and the greatest gas evolution occurred between 80-100°. After the
mixture was held at 110° for 5 min no further gas evolution occurred and
the mixture was cooled to room temperature, then cooled in a liquid nitrogen bath while removing the excess ethyl acrylate by vacuum. The residue
was taken up in an organic solvent and filtered to afford a white residue,
0.65 g (0.6 g of sodium salt of leaving group expected). The solvents were
removed from the filtrate to afford a thick brown viscous liquid, 5.3 g.
Column chromatography of 0.37 g of the filtrate residue afforded three
small fractions (2, 14 and 16 mg respectively) less polar than the fourth
major fraction which accounted for the remainder of the material less a
small uneluted residue. Thin layer chromatography of the fourth fraction
showed only one component. An nmr spectrum of the chromatographed material fraction four was unresolved but the crude material afforded somewhat

better resolution. The spectrum exhibited two unresolved multiplets from

4.6-3.0 and from 3.0 to δ 0.5 in the ratio 1:2. Prominent peaks could be

discerned at 4.29, 4.17 (largest in ferrocenyl region), 4.05 (second

largest in ferrocenyl region), 3.93, 3.82 and a triplet at δ 1.25 (largest

peak in the spectrum). Peaks for the quartet appear to be at 4.29, 4.17,

4.05 and δ 3.93 underlying the ferrocenyl ring protons. An ir spectrum of

the material showed (capillary film): 2960 (m), 1724 (s), 1548 (w), 1448

(m), 1380 (m), 1297 (m), 1172 (s, broad), 1102 (m), 1026 (m) and 853 cm^{-1}

(w). A mass spectrum of the crude material exhibited a molecular ion at

m/e 298 accountable for 181.

An attempt was made to sublime or distill 181 from the apparent poly-

mer under vacuum at temperatures up to 100° but to no result. Pentane

extractions of the syrup were then made by vigorously stirring the materi-

al with pentane for five hr periods. The combined extracts of five ex-

tractions were then chromatographed to afford one small non-polar band and

a larger polar band which exhibited an nmr spectrum somewhat better re-

solved but essentially identical to that of the crude mixture. An nmr

spectrum of the residue of the extraction appeared unaltered compared to

the original material except for two small singlets appearing at δ 3.50

and δ 3.57 which were apparently methyl ester group singlets which could

have arisen by ester exchange since methanol was used several times in

transferring and washing the material. The small chromatography fraction

was further chromatographed by thick layer to afford a yellow orange oil,

60 mg; nmr (CCl$_4$): 4.29, 4.17 and 3.83 (parts of quartets) and 4.06 and

3.95 (singlets) for about 10H; 3.64 and 3.44 (singlets in the ratio 2:1)

for about 2H and 2.8-0.5 (m, 7H) with a triplet appearing at δ 1.25.

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Thin layer chromatography of the material indicated the presence of at least three components. Thick layer chromatography of the material on silica gel with 2% ethyl acetate in Skelly B afforded three fractions with repeated elutions. Fraction one (least polar) afforded an orange solid; mp about 50° (lit. (240) mp 56-58°); nmr (CDCl$_3$): 4.17 (q), 4.16 (s), 4.06 (s or m), 2.5-0.8 (m) and δ 1.28 (t); mass spectrum: molecular ion at m/e 298 for __185__. Fraction two afforded an orange solid, mp about 50°; nmr (CCl$_4$): 4.05 and 3.95 (singlets, 9H), 3.66 (s, 2.2H) and δ 2.5-0.8 (m); mass spectrum: molecular ions at m/e 284 and 298 for __181__ and a corresponding methyl ester. Fraction three afforded an orange solid, mp 57-60°; nmr (CCl$_4$): 4.25-3.84 (m) and 4.02 (s) for 9H, 4.47 (s, 1.6H), δ 2.4-0.8 (m, 6H);mass spectrum: molecular ions at m/e 284 and 298 for __181__ and a corresponding methyl ester.

1-carboethoxy-2-ferrocenylethene __213__

To 0.168 g (0.007 mole) of sodium hydride washed free of oil with pentane was added about 10 ml of DME. To that mixture was added 1.6 g (0.007 mole) of triethylphosphonoacetate dropwise with stirring. Not all of the NaH was consumed therefore additional triethylphosphonoacetate was added until all NaH was taken up. The reaction mixture was then cooled with an ice water bath and 1.5 g (0.007 mole) of __186__ added dissolved in DME. The mixture turned bright red and a syrupy residue formed but stirring was continued for about 6 hr. The solvent was then removed by vacuum and the residue taken up in CH$_2$Cl$_2$ and adsorbed on silica gel. Chromatography of the material afforded a bright red fraction, 2.14 g, which was recrystallized from benzene to afford red crystals, 1.88 g (94%); nmr

(CCl$_4$): 7.65, 7.39, 6.11 and 5.86 (AB pattern, 2H), 4.45 (t), 4.31 (t), 4.19 (q) and 4.11 (s) for 11H and δ 1.3 (t, 3H); (lit. (231) mp 58-60.5°).

(Dimethylamino)methylphenyloxosulfonium fluoroborate

The title compound was prepared by the method of Johnson, Haake and Schroeck (229) from 26 g (0.168 mole) of methyl phenyl sulfoximine and 102 g (0.42 mole) of trimethyloxonium fluoroborate, 19.1 g (41%); mp 118-119° (lit. (229) mp 118-119°). The methyl phenyl sulfoximine was prepared by the method of Johnson, Haake and Schroeck (229) from 45.9 g (0.328 mole) of methyl phenyl sulfoxide with sodium azide in sulfuric acid, 50 g (98%). The methyl phenyl sulfoxide was prepared by oxidation of thioanisole by sodium metaperiodate according to an "Organic Syntheses" procedure (251). The trimethyloxonium fluoroborate was prepared according to an "Organic Syntheses" procedure (252) from triethyloxonium fluoroborate also prepared according to an "Organic Syntheses" procedure (252).

(Dimethylamino)phenyloxosulfonium methylide 212

The (dimethylamino)phenyloxosulfonium methylide 212 was prepared according to the procedure of Johnson, Haake and Schroeck (229). To 0.425 g (0.0177 mole) of sodium hydride washed free of mineral oil with pentane was added, with stirring and a room temperature water bath, 4.0 g (0.147 mole) of (dimethylamino)methylphenyloxosulfonium fluoroborate dissolved in 15 ml of DMSO freshly distilled from CaH$_2$. The reaction was exothermic and occasionally was cooled with an ice water bath. When hydrogen evolution ceased a clear yellow solution of 212 was obtained.

Reaction of (dimethylamino)phenyloxosulfonium methylide <u>212</u> with 1-carbo-
ethoxy-2-ferrocenylethene <u>213</u>

A. At room temperature for 4 hr 4.0 g (0.014 mole) of <u>213</u> was dis-

solved in 20 ml of dry DMSO and added to <u>29</u> generated from 4.0 g (0.0147

mole) of (dimethylamino)methylphenyloxosulfonium fluoroborate and 0.425 g

(0.0177 mole) of NaH with stirring. The reaction was stirred for 4 hr at

room temperature and at the end of that period the reaction was terminated

by adding water to the reaction. The aqueous solution was then extracted

with CH_2Cl_2 and the organic layer dried over anhydrous magnesium sulfate,

filtered and then the solvent removed under reduced pressure to afford red

crystals; nmr $(CDCl_3)$: identical to that of <u>213</u>.

B. At room temperature for 7 days. To 0.0221 mole of <u>212</u> generated

as above was added in DMSO with stirring 4.18 g (0.0147 mole) of <u>213</u>. The

reaction was stirred at room temperature for a week and then terminated by

adding water to the mixture, the aqueous layer extracted with CH_2Cl_2, the

organic layer dried over $MgSO_4$, filtered and the solvents removed under re-

duced pressure to afford red crystals; nmr $(CDCl_3)$: identical to that of

<u>213</u>.

C. At room temperature overnight and at 50° for 1.5 hr. To 0.0267

mole of <u>212</u> generated as described above was added 6.49 g (0.0225 mole) of

<u>213</u> and the reaction stirred at room temperature overnight. The mixture

was then warmed to 50° for 1.5 hr and then terminated by addition of H_2O

and worked up as before to afford a red brown oil; nmr (CCl_4): unresolved

but identical to that of the starting material <u>213</u>.

Reaction of dimethyloxosulfonium methylide 214 with 1-carboethoxy-2-ferro-cenylethene 213 in DMSO

To 3.3 g (0.015 mole) of trimethyloxosulfonium iodide in 20 ml of CaH$_2$ dried DMSO was added 0.632 g (0.015 mole) of a 57% oil dispersion of NaH with stirring and cooling. When the evolution of hydrogen ceased, 3.5 g (0.015 mole) of 213 was added and the reaction stirred at room temperature for 3 hr. After that period, water was added to the reaction mixture and the aqueous solution extracted with ether, the organic layer dried over MgSO$_4$, filtered and the solvent removed under reduced pressure to afford a brown oil; nmr (DMSO): 4.41-4.12 (m) and 4.25 (s) for 9H and δ 3.72-3.2 (m, 6.6H).

Reaction of dimethyloxosulfonium methylide 214 with 1-carboethoxy-2-ferro-cenylethene 213 in THF

To 0.37 g (0.0088 mole) of sodium hydride in 57% oil dispersion was added 13.8 ml of THF distilled from LiAlH$_4$ and 1.94 g (0.0088 mole) of trimethyloxosulfonium iodide with stirring. The mixture was stirred at room temperature for about 1.5 hr and then 2.5 g (0.0088 mole) of 213 added. The reaction was stirred at room temperature under a positive ni-trogen atmosphere overnight and then terminated by adding water. The aqueous solution was extracted with CH$_2$Cl$_2$, the organic layer dried over MgSO$_4$, filtered and the solvent removed from the filtrate to afford a brown residue. The residue was partially soluble in petroleum ether and several petroleum ether extractions were combined and the solvent removed to afford a red oil, nmr (CDCl$_3$): identical to the spectrum of starting material with alkane residues present upfield. The petroleum ether

insoluble residue; nmr (CDCl$_3$): unresolved multiplets from about 5.0 to

3.0 with a singlet at δ 4.20. The aqueous layer was then acidified and

extracted with CH$_2$Cl$_2$, the organic fractions dried over MgSO$_4$, filtered

and the solvent removed under reduced pressure to afford a yellowish solid;

nmr (CDCl$_3$): 10.1 (m, 1H), 7.88, 7.62, 7.29, 6.19 and 5.93 (singlets, 2H),

4.6–4.4 (m, 2.5H), 4.19 (s, 6.5H) and δ 4.07 (s, 2H). In addition two

very small multiplets could be just barely discerned at about 2.45-1.9 and

1.9-0.83 but were not integrated. Therefore some 2-ferrocenylcyclopropyl-

carboxylic acid may have been produced.

Attempted preparation and photolysis of 1-ethoxycarbonyl-4-ferrocenyl-2,3-diazocyclobut-2-ene 219

To 0.521 g (0.00184 mole) of 213 was added a five times mole excess

of ethereal diazomethane and the mixture allowed to set overnight at room

temperature in the dark. After that period the excess diazomethane and

ether were removed under reduced pressure. The residue was taken up in

ether again and filtered, the ether removed to afford a residue; nmr

(CCl$_4$): 6.71 (AB pattern, 0.73H), 5.41-5.02 (m, 0.84), 5.02-4.52 (m,

1.4H), 4.41 (m, 1H), 4.32 (m, 1H), 4.20 (s, 1H), 4.09 and 4.03 (singlets,

5.72H), 3.93-3.73 (m, 1.6H), 3.47-2.5 (m, 1H), 1.33 and δ 1.29 (triplets,

3H).

The residue was then redissolved in an excess of ethereal diazomethane

and allowed to stand at room temperature for a total of two days. After

that period the red solution had become light orange and a precipitate had

formed. The solvents and any excess diazomethane of a small portion was

removed under reduced pressure to afford an oil; nmr (CDCl$_3$): 8.00 (s,

too small to integrate), 7.37 (s, too small to integrate), 5.51-5.12 (m, 0.53H), 4.89 (m, 0.82H), 4.81-4.61 (m, 0.53H), 4.5-3.75 (m, 10H) with a singlet at 4.11, 3.52 (s) and 3.43-3.12 (m) for 0.41H, 1.32, 1.27 and δ 1.18 (triplets, 3H); ir (capillary film): 3420 (m), 3100 (w), 2990 (m), 1710 (s), 1630 (m), and 1558 cm^{-1} (w).

The residue was then taken up in ether, a small amount of benzophenone added and the solution transferred to a quartz photolysis well and irradiated for five hr. At no time was gas evolution detected. After the five hour period the mixture was filtered and the solvent removed from the filtrate under reduced pressure to afford an oil; thin layer chromatography showed many components but none with R_f values corresponding to 181; nmr (CDCl$_3$): 7.6 (m, 1H), 4.88 (m, 0.4H), 4.5-3.5 (m) with a slightly split singlet at 4.11 for 11H, 3.3-2.3 (m, 1H) and δ 2.0-0.6 (m, polymeric material): ir 3390 (w), 3100 (w), 2970 (m), 1730 (s), 1634 (w) and 1558 cm^{-1} (w).

Methyltriphenylphosphonium Iodide

The title compound was prepared according to the procedure of Foerst (253) for the preparation of methyltriphenylphosphonium bromide.

To 35.6 g (0.136 mole) of triphenylphosphine was added 150 ml of benzene. This solution was cooled and while magnetically stirring, 26.7 g (0.188 mole) of methyl iodide was added. Almost immediately the salt separated from the solution as a white precipitate. The mixture was allowed to stand several days at room temperature and then filtered washing with benzene. The yield was 54.6 g (99%); mp 187-187.5° (lit. (252) mp 182-184°).

Vinylferrocene <u>205</u>

<u>205</u> was prepared by a Wittig reaction in DMSO by a procedure developed by Greenwald, Chaykovsky and Corey (254).

In a three neck, round bottom flask equipped with a reflux condenser, magnetic stirrer, nitrogen inlet and a septum was placed 6.18 g (0.257 mole) of sodium hydride washed free of mineral oil with pentane. To the NaH was added 40 ml of dry DMSO under a nitrogen atmosphere. The mixture was then warmed to 60-80° with stirring. Gas evolution would begin and when the solution would change from a milky appearance and darken, the heat was removed and the solution cooled rapidly. To the cooled solution was added 104 g (0.257 mole) of methyltriphenylphosphonium iodide dissolved in warm DMSO by means of a syringe. After about 10 min, 22 g (0.103 mole) of ferrocenylaldehyde <u>186</u> was added dissolved in warm DMSO by means of a syringe. After 0.5 hr the excess dimsyl anion was destroyed by adding an ice-water mixture. The aqueous solution was then extracted with cyclohexane until the organic portions were clear, then the combined organic portions were washed with water, dried over anhydrous $MgSO_4$, filtered, the solvent removed under reduced pressure and the residue chromatographed on silica gel to afford three bands. Band one was rechromatographed to collect 14.8 g (68%) of <u>205</u>; mp 48.5-49.5° (lit. (144) mp 48-49°); nmr (CCl_4): 6.64 (s), 6.47 (s), 6.36 (s) and 6.18 (s) for 1H, 5.41 (d), 5.09 (q), and 4.88 (d) for 2H, 4.27 (t) and 4.11 (t) for 4H and δ 4.01 (s, 5H); ir (CCl_4): 1630 cm^{-1}. Band two was a yellow-orange oil with a foul odor, 1.03 g; nmr (CCl_4): 7.15-6.60 (m, 1.65H), 5.18 (m, 0.9H), 4.83 (m, 1H), 4.29 (t, 2H), 4.10 (t, 2H), 4.00 (s, 5H), 3.9-1.96 (m, 10.8H) with a singlet at δ 2.38 for 2.4H; ir (CCl_4): 2540 (m), 3011 (w), 2940 (s), 2530 (s),

1625 (m), 1451 (m), 1028 (m) 1107 (m), 1032 (m), 1000 (m), 951 (w) and 878 cm^{-1} (m); mass spectrum: molecular ion at m/e 318 with mass losses of 32, 47, 78 and 79. Thin layer chromatography of the material showed that there was a mixture present and it was evident that the material was unstable and decomposing, the band at 2530 cm^{-1} increasing as it decomposed. The data in part support compound 240 as a possibility:

$$\underset{\text{240}}{\text{Fer-}\overset{\overset{\displaystyle CH_2}{\|}}{C}\text{-}CH_2CH_2SSCH}$$
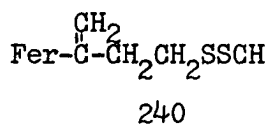
Band three was a yellow-orange solid, 1.4 g; nmr (CCl$_4$): 5.20 (m, 1H), 4.87 (m, 1H), 4.32 (t, 2H), 4.12 (m, 2H), 4.00 (s, 6H) and δ 3.15-2.50 (m, 4H), treatment of the sample with D$_2$O caused no change; ir (CCl$_4$): 3120 (m), 2940 (m), 1770 (w), 1715 (w), 1625 (s), 1412 (m), 1105 (m), 1031 (m), 1000 (m) and 879 cm^{-1} (s); mass spectrum: molecular ion at m/e 272 with mass losses of 33, 34 and 46. Band three was also unstable and decomposed on standing. A possible structure could be 241:

$$\underset{\text{241}}{\text{Fer-}\overset{\overset{\displaystyle CH_2}{\|}}{C}\text{-}CH_2CH_2SH}$$
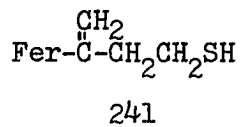
The side products were essentially eliminated when less of an excess of dimsyl anion was generated.

Acetylferrocene

Acetylferrocene was prepared by a Friedal-Crafts reaction according to the procedure of Broadhead, Osgerby and Pauson (255), 50%; mp 82.5-

83.5° (lit. (255) mp 85-86°).

2-ferrocenylpropene 220

Prepared by the same procedure used for vinylferrocene 205. Thus 2.11 g (0.088 mole) of NaH, about 25 ml of DMSO, 25.6 g (0.088 mole) and 10 g (0.0438 mole) of acetylferrocene afforded 9.2 g (93%) of 220 after chromatographically purifying it; mp 66.5-68° (lit. (256) mp 64.5-66.5°); nmr (CCl$_4$): 5.06 (m, 1H), 4.76 (m, 1H), 4.28 (t, 2H), 4.09 (t, 2H), 3.98 (s, 5H) and δ 2.02 (s, 3H) (lit. (257) nmr identical).

Treatment of vinylferrocene 205 with ethereal diazomethane

To 1 g (0.005 mole) of 205 was added 0.01 mole of diazomethane in 25 ml of ether. The mixture was allowed to set in the dark for 2 weeks during which time the solvent evaporated, the residue afforded an nmr spectrum identical to that of starting material 205.

Treatment of 2-ferrocenylpropene 220 with ethereal diazomethane

To 1 g (0.004 mole) of 220 was added 0.1 mole of diazomethane in 25 ml of ether. The mixture was allowed to set in the dark for 2 weeks during which time the solvent evaporated, the residue afforded an nmr spectrum identical to that of starting material 220.

Preparation of zinc/copper couple

A. Prepared according to the procedure of LeGoff (258) from cupric acetate and zinc dust.

B. Prepared according to the procedure of Rawson and Harrison (259) from cuprous chloride and zinc dust. Occasionally anhydrous cuprous chloride was prepared according to the procedure of Drago and Brown (260)

from cupric chloride, copper turnings and HCl.

Reaction of vinylferrocene 205 with methylene iodide and zinc/copper couple

To 0.102 g (0.005 mole) of 205, 3 ml of anhydrous ether, an excess of zinc/copper couple prepared by procedure A above and 0.167 g (0.0063 mole) of methylene iodide. The mixture was maintained at reflux for 46 hr with occasional shaking. After that period the reaction was stopped by adding 1 ml of 1 N HCl and ice. The aqueous layer was then extracted with ether, the ether portions dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue had a white precipitate and black-green oil present. Chromatography afforded one large yellow fraction and several small, more polar fractions which were not collected. The yellow fraction afforded a yellow oil; nmr (CCl_4): 4.53-3.82 (m, 1H), 4.02 (s, 5H), 3.91 (s, 4H), 1.7-1.21 (m) and δ 1.05-0.32 (m) for 5H. Thin layer chromatography of the material showed the presence of at least three components.

Reaction of 2-ferrocenylpropene 220 with methylene iodide and zinc/copper couple

To zinc/copper couple freshly prepared according to procedure A from 0.72 g (0.011 mole) of zinc dust was added 15 ml of anhydrous ether, 1.0 g (0.0044 mole) of 220 and 2.95 g (0.011 mole) of methylene iodide. The reaction was warmed to reflux and stirred for 29 hr under a positive pressure of nitrogen. The reaction was then terminated by adding a 0° solution of NH_4Cl, the aqueous solution extracted with ether, the ether portions combined, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was adsorbed on alumina and one large band eluted with pentane. The pentane removed under reduced pressure

afforded 1.05 g of a yellow oil; nmr (CCl_4): indicated that about 44% of the material was methylene iodide and that about 20% of the ferrocenyl protons were due to unreacted 220. The mixture was then purified using a vapor phase chromatograph to obtain a yellow oil; nmr (CCl_4): 4.00 (s, 5H), 3.88 (s, 4H), 1.34 (s, 3H) and δ 0.64 (m, 4H); ir (capillary film, unpurified): 2940 (s), 1461 (m), 1381 (m), 1307 (w), 1148 (m), 1107 (s), 1031 (m), 1000 (m), 912 (m) and 817 cm^{-1} (s); mass spectrum: molecular ion at m/e 240.

Reaction of 1-carboethoxy-2-ferrocenylethene 213 with methylene iodide and zinc/copper couple

To zinc/copper couple prepared from 12.8 g (0.195 mole) of zinc dust and 20.1 g (0.195 mole) of freshly prepared cuprous chloride by method B was added about 32 ml of anhydrous ether, 20 g (0.075 mole) of 213 and 8 ml (0.075 mole) of methylene iodide with stirring under a positive nitrogen atmosphere. The mixture was heated to reflux for 22 hr and after that period terminated by addition of cold NH_4Cl/Na_2CO_3 solution. The mixture was filtered and the filtrate extracted with ether, the ether portions combined, dried over $MgSO_4$, filtered and the solvent removed. An nmr spectrum of the material indicated that about 67% of the mixture was 213. The mixture was then recombined with the same proportions of reactants and again heated to reflux for an additional 22 hr. After that period the reaction was terminated and worked-up as before. An nmr spectrum of the reaction mixture indicated that about 58.5% of the material was unreacted 213. Therefore the same sequence of steps was followed a third time. An nmr spectrum of the reaction mixture then showed that 213 was present in

about 50%. The material was then chromatographed on silica gel to afford orange crystals and with continued elution another fraction to afford unreacted 213. The orange crystal were recrystallized; mp 56-57° (lit. (250) mp 56-58°); nmr (CDCl$_3$): 4.12 (q, 2H), 4.12 (s, 5H), 4.02 (s, 4H), 2.4-1.97 (m, 1H), 1.97-0.7 (m, 3H) and δ 1.22 (t, 3H).

Reaction of vinylferrocene 213 with ethyl diazoacetate

The reaction was carried out several times with different solvents. With toluene as solvent, the reaction was conducted over a 64 hr period at reflux with four moles of ethyl diazoacetate to afford cis- and trans-1-carboethoxy-2-ferrocenylcyclopropane 181 in 72%. The following procedure for the reaction in decalin is general and applies to all of the reactions carried out.

To 1.96 g (0.0092 mole) of 205 was added 25 ml of decalin and about 2 ml (0.019 mole) of ethyl diazoacetate. The mixture was heated to 110-125° and after about hr an additional 2 ml of ethyl diazoacetate was added. Within a two day period four more additions of ethyl diazoacetate were made. At the end of that period, thin layer chromatography indicated that very little starting material remained. The reaction mixture was then cooled to room temperature and the decalin removed under reduced pressure to afford a viscous oil. The material was chromatographed on alumina repeatedly with 1-3% ether in Skelly B to afford two fractions (besides impurities). The first fraction, (0.945 g (35%), recrystallized from pentane was an orange solid; mp 56-57° (lit. (240) mp 56-58°); nmr (CDCl$_3$): 4.12 (q, 2H), 4.10 (s, 5H), 4.00 (s, 4H), 2.35-1.90 (m, 1H), 1.90-0.8 (m, 3H) and δ 1.22 (t, 3H); 100 MHz nmr (CDCl$_3$): see Figure 29: mass

spectrum: molecular ion at m/e 298; <u>Anal</u>. Calcd. for $C_{16}H_{18}FeO_2$: C

64.44, H 6.10; Found: C 64.30, H 5.76. Fraction two, 0.520 g (19.3%),

recrystallized from pentane to afford orange crystals; mp 37-38° (lit. (86)

mp oil); nmr (CCl_4): 4.40-4.07 (m, 4H), 4.03 (s, 5H), 4.08 (q, 2H), 2.40-

1.67 (m, 2H), 1.67-1.0 (m, 2H) and δ 1.07 (t, 3H); 100 MHz nmr (CCl_4): see

Figure 27: <u>Anal</u>. Calcd. for $C_{16}H_{18}FeO_2$: C 64.44, H 6.10; Found: C 64.23,

H 6.06.

2-phenylcyclopropylcarboxylic acid <u>224</u>

1-carboethoxy-2-phenylcyclopropane <u>223</u> as a mixture of <u>cis</u> and <u>trans</u>

esters was prepared according to the procedure of Burger and Yost (261);

71.5%. The esters were saponified and the <u>cis</u> and <u>trans-224</u> separated

according to the same procedure. <u>Trans-224</u>; mp 86-88° (lit. (261) mp 93°);

nmr $(CDCl_3)$: 13.18 (s, 1H), 7.41-6.93 (m, 5H), 2.8-2.42 (m, 1H) and δ 2.09-

1.15 (m, 3H); 100 MHz nmr $(CDCl_3)$: see Figure 30. <u>Cis-224</u>; mp 103-105.5°

(lit. (262) mp 106-107°); nmr $(CDCl_3)$: 12.24 (s, 1H), 7.16 (s, 5H), 2.76-

2.05 (m, 1H) and δ 2.05-1.00 (m, 3H); 100 MHz nmr $(CDCl_3)$: see Figure 28.

The <u>cis</u>- and <u>trans</u>-1-carbomethoxy-2-phenylcyclopropanes were prepared

by adding ethereal diazomethane to the appropriate acid <u>224</u> until the yellow

coloration was no longer discharged. The ethereal solutions were then left

overnight at room temperature. Then the ether was removed under reduced

pressure and the residue filtered. <u>Trans</u>-1-carbomethoxy-2-phenylcyclopro-

pane; nmr (CCl_4): 7.32-6.83 (m, 5H), 3.58 (s, 3H), 2.67-2.28 (m, 1H) and

δ 2.02-0.98 (m, 3H). <u>Cis</u>-1-carbomethoxy-2-phenylcyclopropane; nmr (CCl_4):

7.13 (s, 5H), 3.23 (s, 3H) and δ 2.74-0.91 (m, 4H).

Reaction of 2-ferrocenylpropene 220 with ethyl diazoacetate

The reaction was carried out in a manner analogous to that with vinyl-ferrocene 205 in toluene with 2.75 g (0.0122 mole) of 220 and 10.4 ml (0.10 mole) of ethyl diazoacetate over a 45 hr period. The solvent was then removed and the brown-black, viscous residue chromatographed on silica gel to afford three fractions. Fraction one, 0.218 g, recovered 220. Fraction two was rechromatographed repeatedly to obtain separation of two new fractions, 2A and 2B. Fraction 2A, orange crystals, recrystallized from pentane, 1.3 g; mp 74-75°; nmr $(CDCl_3)$: 2960 (m), 1725 (s), 1430 (w), 1375 (m), 1280 (m), 1270 (m), 1180 (s), 1140 (m) and 1060 cm^{-1} (m); mass spectrum: molecular ion at m/e 312 with mass losses of 28, 45, 65, 66 and 73; Anal. Calcd. for $C_{17}H_{20}FeO_2$: C 65.40, H 6.46; Found: C 65.27, H 6.48. The data support trans-225. Fraction 2B, orange crystals, recrystallized from pentane, 0.43 g; mp 73.5-74°; nmr $(CDCl_3)$: 4.13 (s, 9H), 3.88 (q, 2H), 1.94-1.47 (m, 2H), 1.55 (s, 3H) and 1.15-0.91 (m) and δ 1.03 (s) for 4H; ir $(CDCl_3)$: 2970 (w), 1710 (s), 1430 (w), 1370 (m), 1245 (m), 1195 (m), 1170 (s) and 1080 cm^{-1} (m); mass spectrum: molecular ion at m/e 312 and mass losses of 28, 45, 65 and 73; Anal. Calcd. for $C_{17}H_{20}FeO_2$: C 65.40, H 6.46; Found: C 65.29, H 6.52. The data supports cis-225. Fraction three, oil, 0.050 g; nmr (CCl_4): 4.11 (s, 5H), 4.06 (s, 4H), 1.72 (s, 1H) and δ 1.41 (s, 6H); mass spectrum: molecular ion at m/e 244 with metastable loss of 18 mass units. The data suggest that fraction three may have been 2-ferrocenyl-2-hydroxypropane.

Reduction of cis-carboethoxy-2-ferrocenylcyclopropane 181 with lithium

aluminum hydride

To 0.138 g (0.00362 mole) of crushed lithium aluminum hydride was

added about 10-20 ml of anhydrous ether and the mixture heated to reflux

for 0.4 hr. To the cooled solution was added 0.54 g (0.00181 mole) of

cis-181 with stirring under a nitrogen atmosphere and the reaction was

heated to reflux for 4 hr. After that period was added slowly 0.14 ml of

water, then 0.14 ml of 15% NaOH and finally 0.42 ml of water to the reac-

tion mixture (262). The white precipitate was filtered and the filtrate

washed with $NaHCO_3$ solution and then water. The ether layer was then

dried over $MgSO_4$, filtered and the solvent removed under reduced pressure.

The residue was chromatographed on alumina to obtain two fractions. Frac-

tion one was unreacted starting material, 0.134 g (25%). Fraction two was

the rest of the ferrocenyl material contaminated with silicone oil (about

75%), recrystallized from pentane to afford orange crystals; mp 62-63°

(lit. (250) mp oil); nmr ($CDCl_3$): 4.28-3.89 (m) and 4.12 (s) for 9H, 3.66-

3.06 (m 2H), 2.12-1.69 (m, 1H), 1.64 (s, 1H, treatment with D_2O lost),

1.50-0.71 (m, 2H) and δ 0.60-0.30 (m, 1H); ir ($CHCl_3$): 3615 (m), 3460 (w),

3045 (s), 1410 (m), 1248 (m), 1107 (m) and 1015 cm^{-1} (s); Anal. Calcd. for

$C_{14}H_{16}FeO$: C 65.64, H 6.31; Found: C 65.46, H 6.42.

Reduction of trans-1-carboethoxy-2-ferrocenylpropane 181 with lithium

aluminum hydride

The reduction of trans-181 was carried out in a manner analogous to

that given above for cis-181. Column chromatography of the reaction prod-

uct from 5.6 g (0.0188 mole) of trans-181 was isolated 4.7 g (98%) trans-

<u>226</u> as an oil (lit. (249) oil) which was unstable and decomposed producing

a sharp odor; nmr (CDCl$_3$): 4.12 (s, 5H), 4.01 (broad singlet, 4H), 3.45

(d, 2H), 2.68 (s, 1H, lost on treatment with D$_2$O), and δ 1.58-0.54 (m, 4H);

ir (CHCl$_3$): 3630 (m), 3480 (w), 3035 (m), 1415 (m), 1108 (m), 1015 (s) and

832 cm^{-1} (m); <u>Anal</u>. Calcd. for C$_{14}$H$_{16}$FeO: C 65.64, H 6.31; Found: 65.18,

H 6.36.

Reduction of <u>trans-1-carboethoxy-2-methyl-2-ferrocenylcyclopropane</u> <u>225</u> with lithium aluminum hydride

The reduction of <u>trans-225</u> was carried out as with the compounds

above, from 1.3 g (0.0042 mole) of <u>trans-225</u> was obtained 0.91 g (81%, un-

purified <u>trans-227</u>): mp 41.5-43°; nmr (CDCl$_3$): 4.09 (s, 5H), 3.97 (m,

4H), 3.45 (doublet of doublets, 2H), 3.01 (s, 1H, lost on addition of D$_2$O),

1.50-0.33 (m, 3H) and δ 1.31 (s, 3H); ir (CHCl$_3$): 3640 (m), 3040 (s),

1246 (s), 1109 (m), 1050 (m) and 1005 cm^{-1} (m); mass spectrum: molecular

ion at m/e 270 with mass losses of 31, 46 and 57; <u>Anal</u>. Calcd. for

C$_{15}$H$_{18}$FeO: C 66.68, H 6.72; Found: C 66.90, H 6.56.

Reduction of <u>cis-1-carboethoxy-2-methyl-2-ferrocenylcyclopropane</u> <u>225</u> with lithium aluminum hydride

The reduction of <u>cis-225</u> was carried out as with the compounds above,

from 0.393 g (0.00126 mole) of <u>cis-225</u> was obtained about 65% <u>cis-227</u>; mp

47-48°; nmr (CDCl$_3$): 4.21-4.00 (m) and 3.95-3.78 (m) for 4H, 4.14 (s, 5H),

3.50-3.19 (m, 3H), 1.45 (s, 3H) and δ 1.31-0.60 (m, 3H); ir (CHCl$_3$): 3620

(m), 3030 (m), 1109 (m), 1030 (m) and 1003 cm^{-1} (s); mass spectrum:

molecular ion at m/e 270 with losses of 31, 44, 46 and 57; <u>Anal</u>. Calcd.

for C$_{15}$H$_{18}$FeO: C 66.68, H 6.72; Found: C 66.25, H 6.58.

3,5-dinitrobenzoate of <u>trans-2-ferrocenylcyclopropylcarbinyl</u> alcohol <u>226</u>

To 4.2 g (0.0164 mole) of <u>trans-226</u> in about 15-20 ml of dry pyridine was added with stirring under a nitrogen atmosphere 5.7 g (0.0246 mole) of 3,5-dinitrobenzoyl chloride. The mixture was then heated to 90° for 1 hr. After that period the mixture was poured into ice and sodium bicarbonate solution and the aqueous layer extracted with CH_2Cl_2. The combined organic portions were washed with aqueous bicarbonate and then several times with water, dried over $MgSO_4$, filtered and the solvents removed under reduced pressure. The residue was a black oil and retained the odor of pyridine and therefore was subjected to high vacuum until all of the pyridine was removed. The residue was then taken up in ether, filtered and the 3,5-dinitrobenzoate recrystallized to afford 3.7 g of a purplish powder. A second crop was obtained from the filtrate to afford a total of 5.65 g (81%); mp 104-105.5°; nmr (d_6-acetone): 9.23 (s, 3H), 4.53 (m, 1H), 4.42 (m, 1H), 4.14 (s, 5H), 4.05 (m, 4H), 1.92-1.37 (m, 2H) and δ 1.20-0.68 (m, 2H); ir (KBr): 3425 (w, broad), 3075 (m), 1710 (s), 1620 (m), 1530 (s), 1450 (m), 1330 (s), 1270 (s), 1170 (s), 1100 (m), 1072 (m), 1045 (m), 994 (w), 969 (m), 919 (m), 912 (m), 817 (m), 773 (m), 731 (m) and 719 cm^{-1}(m).

3,5-dinitrobenzoate of <u>cis-2-ferrocenylcyclopropylcarbinyl</u> alcohol <u>226</u>

The title compound was prepared in the same manner as the <u>trans</u> compound. Thus from 1.05 g (0.0041 mole) of <u>cis-226</u> and 1.38 g (0.00485 mole) of 3,5-dinitrobenzoyl chloride was obtained 1.65 (89.5%) g from ether; mp 120-122°; nmr ($CDCl_3$): 9.28 (t, 1H), 9.14 (d, 2H), 4.75-3.85 (m) and 4.17 (s) for 11H and δ 2.38-0.5 (m, 4H); ir (KBr): 3400 (w, broad), 3085 (w), 3070 (w), 2980 (w), 2930 (w), 1720 (s), 1625 (m), 1043

(m), 1020 (w), 992 (m), 961 (m), 927 (m), 912 (m), 880 (w), 820 (m), 788 (w), 771 (m) and 721 cm^{-1} (s).

Preliminary solvolysis of the 3,5-dinitrobenzoate of trans-2-ferrocenyl-cyclopropylcarbinyl alcohol 228 in sealed nmr sample tubes at various conditions and temperatures

A. To 0.0281 g (0.0000625 mole) of the 3,5-DNB of trans-226 in an nmr sample tube was added 0.25 ml of 75 wt % aqueous dioxane (0.25 M). The tube was sealed with the contents at -78° under vacuum and then heated to 130° for 24 hr. A precipitate was present after 1 hr and at the end of that period the contents of the tube had also produced a black precipitate. The tube was opened and the solvents evaporated under vacuum to afford a black residue. The residue was extracted with CDCl$_3$, filtered and an nmr spectrum taken of the filtrate: very small singlet or multiplet at 9.25, very small singlet or multiplet at 7.34, small multiplet at 4.62, singlet at 3.77 and a possible multiplet at δ 0.73.

B. To 281 mg (0.0000625 mole) of the 3,5-DNB of trans-226 in an nmr sample tube was added 3.7 mg (0.000062 mole) of urea and 0.25 ml of 75 wt % of d$_6$-acetone in D$_2$O. The tube was sealed as before and heated for 24 hr at 130°. An attempt was made to run spectra periodically but the material was insoluble at room temperature and signal too weak. After 1 hr some decomposition was present but not as much as in A above. At the end of the 24 hr period a significant amount of black precipitate was again present.

C. To 281 ml (0.000625 mole) of the 3,5-DNB of trans-226 was added 14.25 μl (0.000125 mole) of lutidine and 0.25 ml of 90 wt % of d$_6$-acetone

in D_2O, the tube sealed and heated to 130° for 23 hr. Decomposition was again reduced but the signal was essentially lost after 4 hr, but two new multiplets momentarily appeared at δ 6.42 and δ 4.25.

D. A 281 mg sample of the 3,5-DNB of trans-226 was dissolved in 0.25 ml d_6-acetone and the tube sealed and heated to 130° for 19 hr. After 3 hr some resolution had been lost and the strength of the signal had decreased somewhat. After 8 hr the solution appeared to be darker and a deposit had formed, the strength of the signal was about 50% of its original value. After 19 hr the signal was very weak and two very small multiplets appeared at δ 8.0 and δ 7.71.

E. A 281 sample of the 3,5-DNB of trans-226 was dissolved in 0.25 ml of d_6-acetone, the tube sealed and heated to 100° for 50 hr. After 30 hr the sample appeared to be somewhat darker but no deposit had formed. After 50 hr some decomposition was noticeable.

F. To 281 mg (0.0000625 mole) of the 3,5-DNB of trans-226 was added 14.25 μl (0.000125 mole) of lutidine and 0.25 ml of 90 wt % of d_6-acetone in D_2O, the tube sealed and heated to 100° for 61 hr. After 7 hr a small multiplet began to appear at δ 4.29. After 20 hr some slight residue was present. After 28 hr more deposit was present and small multiplets were present at δ 5.93, δ 5.05 and δ 4.28. The deposit continued to form as the sample signal was decreasing. The multiplet at δ 5.05 also appeared to be lost.

G. A sample of the 3,5-DNB of trans-226 identical to that run in F was also run concurrently at 100° except that the lutidine was not added. The observations noted for the F run were no different in this run including the appearance of the small multiplets and loss of the δ 5.05 multiplet

at the same time interval.

Solvolysis of the 3,5-dinitrobenzoates of cis- and trans-2-ferrocenylcyclo-propylcarbinyl alcohols 226

A.   Into glass ampules were placed 10.0 ml samples of a 0.020 M

solution of the 3,5-dinitrobenzoate of trans-2-ferrocenylcyclopropyl-

carbinyl alcohol 226 with a syringe. The samples were cooled to -78° and

sealed under 226 with a syringe. The samples were then placed in a 100°

constant temperature bath (contact thermometer). Periodically samples

were withdrawn, cooled to 0° and the contents titrated with an aqueous

0.022 M NaOH solution restandardized periodically with a 0.00959 M solution

of benzoic acid in 50% aqueous acetone. The titrations were done with a

pH meter and the data subjected to first derivative analysis (245) to

obtain the end point. During the titration the titrated solution darkened

particularly near the end-point and eventually turned blue in excess base.

Single samples were titrated at t = 0, 12, 24 and 48 hr. Duplicate samples

were titrated at t = 72 and 87 hr. A first order plot of the results was

presented in Figure 31. The slope was determined to be 2.93 x 10^{-6} sec^{-1}.

The t = 87 hr samples were titrated and the solutions then acidified

with 2 M HCl, the aqueous solution extracted with CH_2Cl_2, the organic por-

tions washed with aqueous sodium bicarbonate and then water, the organic

layer was then dried over $MgSO_4$, filtered and the solvents removed under

reduced pressure to afford a brown-black semi-solid; nmr ($CDCl_3$): 9.16

(s, 3H); 6.72-6.5 (m, 1.5H); 6.5-6.0 (m, 4.6H); 5.68-5.4 (m, 2H); 5.4-

5.0 (m, 3.3H); 4.48 (s), 4.35 (m), 4.25 (m), 4.15 (s, unsubstituted ferro-

cene ring) and 4.05 (s, substituted ferrocene ring?) for 33 H; 2.7 (s,

1.3) and δ 2.0-0.7 (m, 20H).

B. Into glass ampules were placed 5.0 ml samples of a 0.020 M solution

of the 3,5-dinitrobenzoate of cis-2-ferrocenylcyclopropylcarbinyl alcohol

226 with a syringe. The samples were cooled to liquid nitrogen tempera-

ture and sealed under vacuum. The samples were then placed in a 100°

constant temperature bath. Periodically samples were withdrawn, cooled to

0°, the ampules opened and the contents washed into a beaker with acetone

and water to a volume of about 30 ml. The samples were then titrated with

an aqueous 0.013 M solution of NaOH restandardized periodically with a

0.00961 M solution of benzoic acid in acetone. The titrations were done

with a pH meter and the data subjected to a first derivative analysis (245)

to obtain the end-point. Duplicate samples were titrated at t = 0, 6, 12,

24, 48, 72 and 89 hr. A first order plot of the results was presented in

Figure 31. The slope was determined to be 1.80 x 10^{-6} sec^{-1}.

SUGGESTIONS FOR FURTHER RESEARCH

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SUGGESTIONS FOR PART I

In part I a correlation was attempted for $M^{+}\text{-}N_2\text{-}CO$ with respect to para substituent in the diazoacetophenones studied. It was noted that the spectra of the compounds were not obtained under standardized conditions and that therefore only a qualitative trend for Wolff-type rearrangement might be reasonably expected. A better correlation might be obtained if an internal standard were incorporated into the molecules being investigated (263). Zeller, Meier and Müller began such a system with $[2\text{-}^{13}C]$ - 2,4-dioxo-3-diazo-4-phenylbutane 20 (9).

Synthesis of a series of dibenzoyldiazomethanes 242 with the benzoyl-carbon atom of the unsubstituted phenyl labelled by incorporation of ^{13}C at that position would allow the comparison of migration abilities of the substituted phenyl groups internally in each case with that of the common unsubstituted phenyl group by determining the $M^{+}\text{-}N_2\text{-}CO/M^{+}\text{-}N_2\text{-}^{13}CO$ ratio.
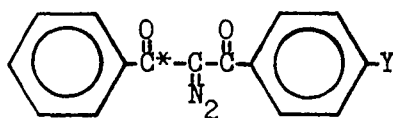
242

Systematic investigations of other classes of diazocompounds by mass spectrometry have still not yet been reported. The instability of these compounds is probably a factor since the compounds may be both difficult (and dangerous) to purify. Their instability would also cast some doubt upon the spectra obtained since decomposition prior to ionization would be conceivable. Diazoesters and, in particular, α-organometallic diazoesters, however, probably possess stabilities sufficient to allow such a study.

SUGGESTIONS FOR PART II

In Part II the discussion concerning the results of the addition of nucleophiles on dimethylphenylsilylethoxy ketene 82 and triphenylsilyl-ethoxyketene 121 was based upon spectral data obtained upon crude reaction mixtures. Such a treatment was necessitated for several reasons. The precurser diazocompounds 75 and 117 which now appear to be available with relative ease, were the result of multiple step syntheses. The procedures were not practiced and therefore the diazocompounds were obtained in suffi-cient but small quantities. Of more importance was the difficulty in ob-taining quantities of the ketenes. The ketene 82 was obtainable in good quality by decomposition of 75 in a gc, the process however was tedious and resulted in amounts for only very small scale reactions. The ketene 121 could be collected by vacuum pyrolysis in a purer state than 82 but only small amounts of 117 could be pyrolyzed at a time and the product would be difficult to purify further. Therefore the reactions studied were done on a very small scale and the products obtained were in quite small quantity. Uncertainty as to the source of the rearranged products and the possibility of losing the products in trying to isolate and purify them made the in situ study of the reactions more attractive.

Since the only way to obtain 121 and 82 in larger quantities seems to be by expending the time and effort to collect them by vacuum pyrolysis or gc respectively, perhaps a better approach would be to independently syn-thesize the proposed products.

The compounds might be accessible using the ketenes synthesized by the Soviet workers as starting materials (106) as shown in Scheme 64.

$$R_3SiCH=C=O$$

$$\downarrow Br_2$$

$$\overset{\underset{|}{Br}}{R_3SiCH-COBr}$$

$$\theta_{OH}$$

$$\downarrow \theta_{OR'}$$

$$\overset{\underset{|}{OH}}{R_3SiCH-CO_2H}$$

243

$$\downarrow R'''CHN_2$$

$$\overset{\underset{|}{OH}}{R_3SiCH-CO_2R''}$$

$$\overset{\underset{|}{OR'}}{R_3SiCH-CO_2R'} \xrightarrow{R''OH} \overset{\underset{|}{OR'}}{R_3SiCH-CO_2R''}$$

$$\downarrow H^{\oplus}, HOH \qquad\qquad \uparrow R''OH$$

$$\overset{\underset{|}{OR'}}{R_3SiCH-CO_2H} \xrightarrow{SOCl_2} \overset{\underset{|}{OR'}}{R_3SiCH-COCl}$$

244   **245**

$$\downarrow Et_3N$$

$$\overset{\underset{|}{OR'}}{R_3Si-C}\diagdown_{C}\diagdown_{\diagup}^{O}$$
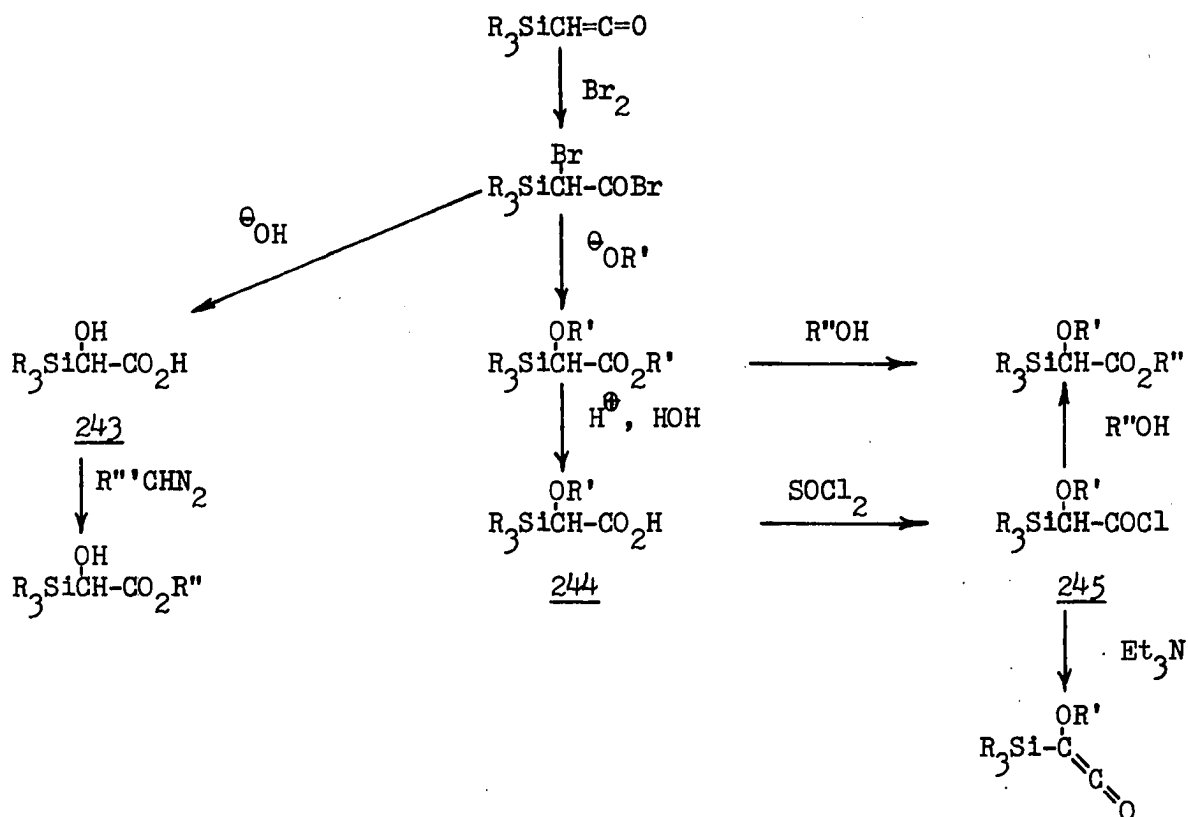
Scheme 64

Of some particular interest would be the isolation of compounds **243** and **244** to determine whether they would, in fact, rearrange to produce phenylacetic acid. And as can be seen the production of **245** would afford the possibility of synthesizing triorganosilylalkoxyketenes by an independent route.

The original purpose for preparing the α-silyldiazocompounds was never carried out--that is, utilizing them as potential sources of sila-cyclopropanes. A recent report by Ando, Sekiguchi, Hagiwara and Migita (264) suggests that 1,3-intramolecular insertion of a silylcarbene may indeed yield silacyclopropanes. They reported that the pyrolysis of phenyltrimethylsilyldiazomethane **246** in a nitrogen flow system at 500°

yielded two products 247 and 248. The product 248 was rationalized as being derived from the silacyclopropane 249 (Scheme 65).
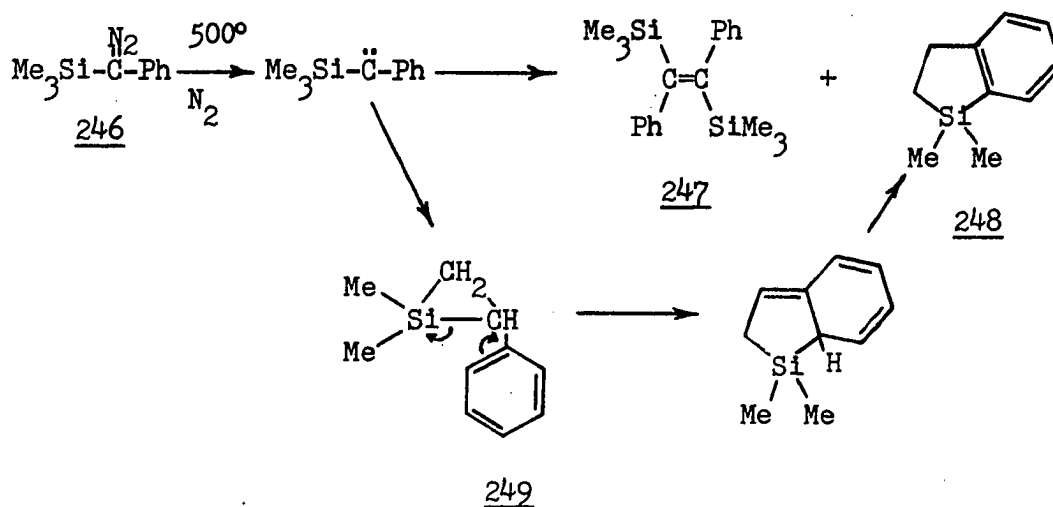
Scheme 65

Of some interest was the observation that pyrolysis of phenyldimethyl-silylphenyldiazomethane did not give a benzosilacyclopentene derivative. Additionally the photolysis of 246 in alcohols gave high yields of the O-N insertion products of the silylphenylcarbene and no 247 or 248. Photolysis of 246 in benzene gave 247 as the main product.

Considering these results the photolysis of α-silyldiazomethanes at low temperatures in an inert matrix (such as a Freon) would still be of considerable interest.

SUGGESTIONS FOR PART III

In order to establish firmly whether the 3,5-dinitrobenzoate of trans-226 solvolyses at a rate comparable to that of the 3,5-dinitrobenzoate of trans-230, the latter compound should be solvolyzed under comparable conditions. The solvolysis of the 3,5-dinitrobenzoates of cis- and trans-228 under the same conditions would also establish the exact relationship between the rates of reaction for the corresponding cis and trans isomers to determine whether any rate enhancement did occur with the cis-ferrocenyl compound.

As was noted in the discussion in Part III, some slight rate increase of the cis-ferrocenyl compound relative to the cis-phenyl compound does appear to be evident. The rate enhancement for the cis-ferrocenyl compound does not appear to be strikingly large however and, perhaps, a better approach to determine whether any additional assistance by the ferrocenyl group in the solvolysis of the cis compound would be to determine the $\Delta S^{\dagger}$ for the cis- and trans-ferrocenyl compounds. Both compounds might be expected to experience about the same effects by the ferrocenyl group at cyclopropyl carbon-2 and any additional assistance by the ferrocenyl group in the cis compound at the carbinyl carbon atom could be reflected in the $\Delta S^{\dagger}$ term.

Shono, Nishiguchi and Oda (205) have shown however that delocalization of charge to cyclopropyl carbon-2 is of some significance. Recent reports (171, 265) have shown that there is a significant barrier to rotation about the bond from the substituted ferrocenyl ring and carbinyl carbon in α-ferrocenylcarbonium ions, therefore significant interaction

between the ferrocenyl group and cyclopropyl carbon-2 in the solvolysis process might in itself preclude any major assistance by iron at the carbinyl carbon in the solvolysis of the 3,5-dinitrobenzoate of cis-226.

It might therefore be of some interest to determine the rates of solvolysis of the 3,5-dinitrobenzoates of the ferrocenyl compounds 250-252 and of the corresponding phenyl compounds. Though the alkyl group in 250 may assume many conformations, it is of interest to note that hydrogen bonding to the iron has been observed in the ir spectra of 2-ferrocenylethanol (266, 267) and 3-ferrocenylpropanol (266).
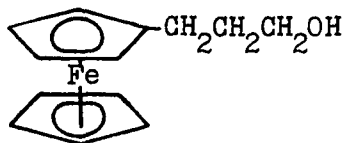
$CH_2CH_2CH_2OH$

250
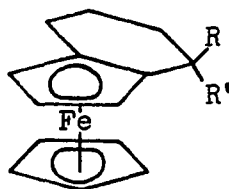
251 R = H, R' = CH_2CH_2OH

252 R = CH_2CH_2OH, R' = H

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