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FREE-RADICAL CHAIN REACTIONS OF ORGANIC MERCURY AND TIN COMPOUNDS

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Free-radical chain reactions of organic mercury and tin compounds

by

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PREFACE

This thesis has been divided into three parts. Part I includes the free radical substitution chain reactions of alkylmercury halides and dialkylmercurials with heteroatom-centered radicals. Part II covers the free radical substitution chain reactions of tri-$\underline{n}$-butyl-1-alkenyltin derivatives with carbon-centered as well as heteroatom-centered radicals. Part III is devoted to the reaction of tri-$\underline{n}$-butyl-Δ^3-butenyltin with phenyl disulfide.

Although a separate experimental section follows each presentation of results and discussion, descriptions of techniques and sources of starting materials are mentioned only once to avoid repetition. Most items utilized in subsequent sections are to be located at the beginning of the experimental section under the heading of "General considerations."

I. FREE RADICAL SUBSTITUTION REACTIONS OF ALKYLMERCURY HALIDES AND DIALKYMERCURIALS

A. Introduction

Organic mercury compounds are known since 1850 [1]. They are stable under normal conditions, fairly reactive and easy to obtain [2]. Organomercurials are known to undergo a wide range of chemical reactions. Electrophilic aliphatic substitution reactions of organomercurials have been extensively studied and a number of reviews [3-5] and one book [6] appeared on the subject. In contrast, homolytic substitution reactions of organomercurials have been studied to less extent. The homolytic reactions have been first recognized as side reactions accompanied the electrophilic processes [7, 8]. Keller, as cited by Winstein and Traylor, considered the possibility of radical chain process intervention in a study of iodine cleavage of alkylmercury iodide [7]. This cleavage was accelerated by light or peroxides and strongly retarded by oxygen. The observations were consistent with a chain reaction. Also, Winstein and Traylor showed that alkylmercury bromides react with hydrogen bromide by a radical rather than electrophilic mechanism [8].

In recent years, homolytic substitution reactions of organomercurials have attracted more attention. Jensen and co-workers observed a free radical chain reaction for the bromine cleavage of alkylmercury halides in nonpolar solvents in their attempt to establish the stereochemistry of electrophilic substitution reactions [9, 10]. Thus, the reaction of bromine with cis- or trans-4-methylcyclohexylmercury bromide in carbon

tetrachloride solution under an inert atmosphere gave a nearly statistical distribution of the two diastereomeric bromides from either starting material [10]. Under these conditions, the reaction likely proceeds by a radical chain mechanism involving the achiral 4-methylcyclohexyl radical as an intermediate. The propagation steps of the probable radical processes are shown in Scheme I. Similar results were obtained

Scheme I (R = CH$_3$, (CH$_3$)$_3$C)
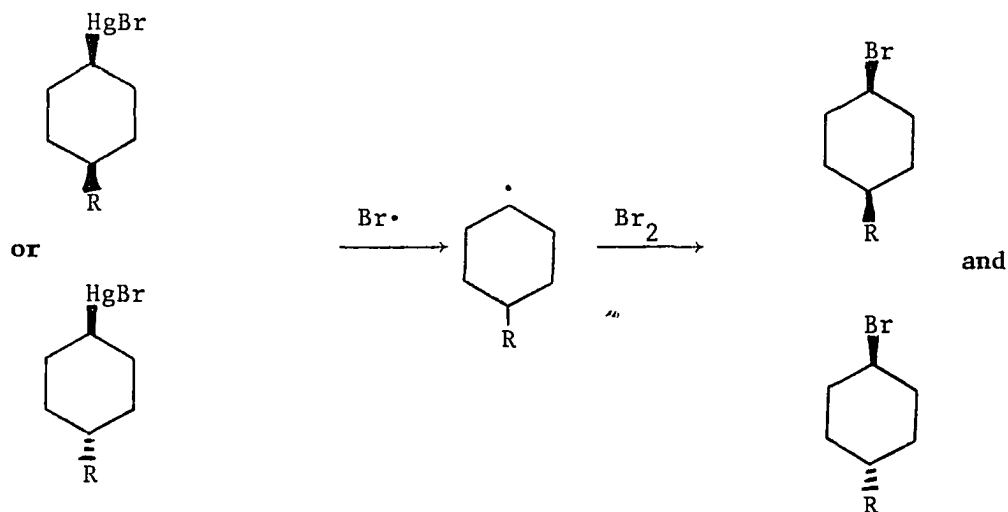
from the brominolysis of cis- or trans-tert-butylcyclohexylmercury bromide under similar reaction conditions [11]. In contrast, the sulfuryl chloride, SO$_2$Cl$_2$, cleavage of either cis- or trans-4-tert-butylcyclohexyl bromide yields a cis:trans distribution of 70:30 [11]. Again, the loss of stereochemistry indicates the intervention of a common radical intermediate. The authors have applied torsional effects to account for the different ratio of products

obtained in the sulfury chloride reaction. The reaction of 4-tert-butylcyclohexyl radical with SO_2Cl_2 has a higher heat of activation than the reaction with bromine and thus has greater bond formation in the transition state. Thus, the reaction with SO_2Cl_2 gives more of the product (axial chlorine) arising from the pathway having the smaller torsional strain.

Reductive demercuration reactions of alkylmercury halides by metal hydrides, such as sodium borohydride, appear to proceed via free radical chain processes [12]. The loss of stereochemical integrity [13-16], the observation of the rearranged product, 1,1,2-triphenylethane, from the sodium borohydride reduction of 2,2,2-triphenylethylmercury [17] and the efficient trapping of the alkyl radical intermediates by molecular oxygen [18] are evidence introduced to support the radical mechanism in these reactions. Scheme II outlines the most general accepted mechanism for the reduction of organomercurials. A key step in

Scheme II

$$RHgX + NaBH_4 \longrightarrow RHgH + NaX + BH_3$$

$$RHgH \longrightarrow RHg + H\cdot$$

$$RHg \longrightarrow R\cdot + Hg(0)$$

$$R\cdot + RHgH \longrightarrow RH + RHg$$
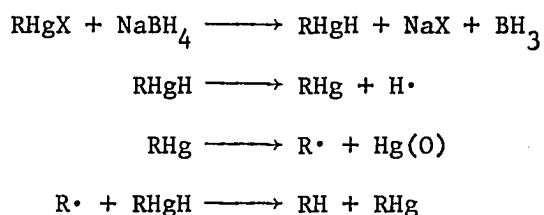
this mechanism is the decomposition of the alkylmercury (I) species to generate the alkyl radical and mercury metal, a process established to have an activation energy as low as 6 kcal mol^{-1} [19].

Further evidence to support a radical pathway for the reductive

demercurations was obtained by Quirk and Lea [20]. Thus, the reduction

of Δ^5-hexenylmercury bromide with sodium borohydride gave methylcyclo-

pentane as the major hydrocarbon product (Eq. 1). The formation of

$$\text{CH}_2=\text{CH-CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{HgBr} \xrightarrow[\text{THF}|\text{H}_2\text{O}]{\text{NaBH}_4} \bigcirc\text{CH}_3 + \diagup\diagdown\diagup\diagdown + \text{Hg(0)} \qquad (1)$$
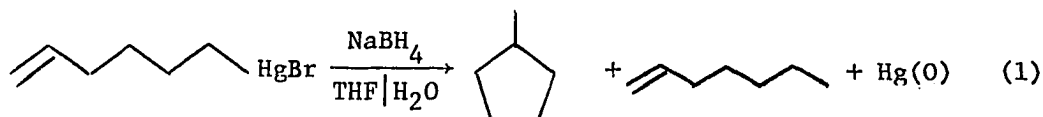
methylcyclopentane is consistent with the intermediacy of Δ^5-hexenyl

radical rather than the carbenium ion in this reaction, since the Δ^5-

hexenyl radical is known to undergo cyclization to the cyclopentyl-

carbinyl radical (Eq. 2), whereas the Δ^5-hexenyl cation cyclizes to

the cyclohexyl cation [21]. The ring closure in the above reaction

$$(2)$$
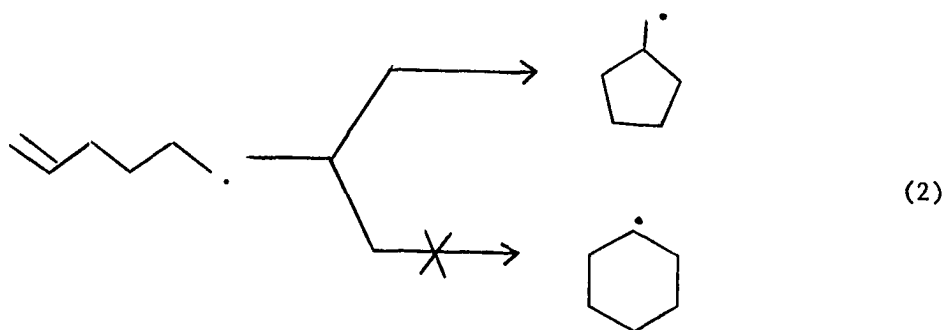
was completely suppressed in the presence of molecular oxygen due to

the trapping of the alkyl radicals [20].

In analogous reactions, the alkyl radicals, generated from the

sodium borohydride reduction of alkylmercury halides, have been effec-

tively trapped by electron deficient olefins (Eq. 3) [22-26]. The

$$\text{RHgCl} + \begin{array}{c}\text{H}\\ \diagdown\\ \text{X}\diagup\end{array}\text{C}=\text{C}\begin{array}{c}\diagup\text{Z}\\ \\ \diagdown\text{Y}\end{array} \xrightarrow{\text{NaBH}_4} \underset{\overset{|}{\text{X}}}{\text{RCHCHYZ}} + \text{Cl}^- + \text{Hg(0)} \qquad (3)$$
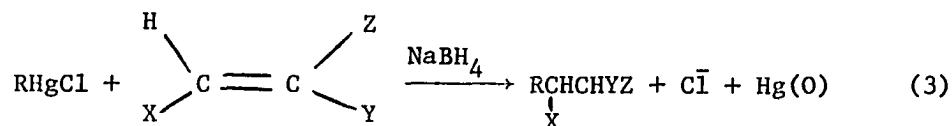
following chain mechanism has been proposed as a possible pathway for

this reaction, Scheme III. A key feature in this mechanism is the

Scheme III

X	Y	Z	
H	H	CO_2CH_3	
H	H	CN	, R = 1°,2°,3° alkyl
$CO_2C_2H_5$	H	C_2H_5	group.
CN	H	CN	
H	Cl	CN	

$$RHgCl + NaBH_4 \longrightarrow RHgH + NaCl + BH_3$$

$$RHgH \longrightarrow RHg + H\cdot$$

$$RHg \longrightarrow R\cdot + Hg(0)$$

1

$$1 + RHgH \longrightarrow \underset{X}{RCH} - CYZH + RHg$$

2
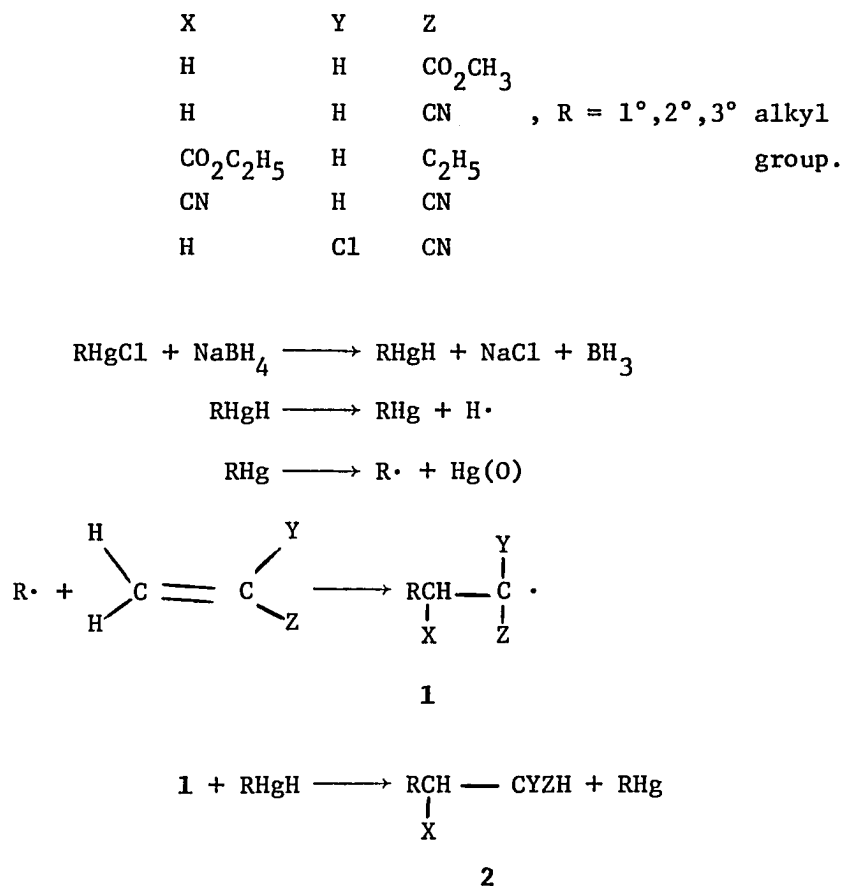
decomposition of alkylmercury(I) to afford the alkyl radicals R·, which

add to the olefins to yield the intermediate radicals **1**, which in turn

abstract hydrogen from RHgH to give the adduct **2** and RHg to continue

the chain. This reaction has been used to determine the selectivity of

1°, 2° and 3° alkyl radicals in addition reaction with alkenes [25].

Other free radical reactions of organomercurials have been re-
ported. Thus, treatment of Δ^5-hexenylmercury bromide with iodine in

dioxane gave cyclopentylmethyl iodide in 70% yield besides some Δ^5-

hexenyl iodide (Eq. 4) [27]. Free radical sources are known to

$$\text{\raisebox{0pt}{$\diagup\!\diagup\!\diagdown\!\diagup\!\diagdown$}HgBr} \xrightarrow[\text{dioxane}]{\text{I}_2} \text{\raisebox{0pt}{$\bigcirc$}}-CH_2I + \text{\raisebox{0pt}{$\diagup\!\diagup\!\diagdown\!\diagup\!\diagdown$}}I \quad (4)$$
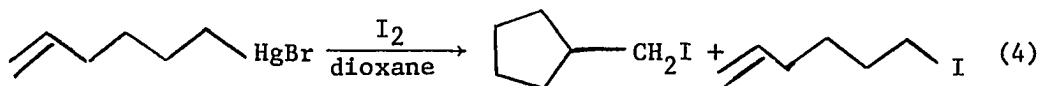
racemize the optically active alkylmercurials [28]. Thus, Jensen and

co-workers have reported that the bromine cleavage of optically active

sec-butylmercury bromide in nonpolar solvents led to complete racemiza-

tion [28]. Under these conditions, it is believed that free radical

pathways predominate. Similar results have been obtained by Reutov and

his collaborators who investigated both the kinetic and stereochemistry

of the bromine cleavage of optically active sec-butylmercury bromide in

carbon tetrachloride solution [29]. These racemization processes are

proposed to proceed through a tri-coordinate mercury radical intermedi-

ate [6].

Nugent and Kochi have shown that dialkylmercurials, RHgR', undergo

reductive elimination of olefins in carbon tetrachloride solutions [30].

The radical chain process outlined in Scheme IV was suggested as a

possible mechanism for the reaction. The course of the reaction is

governed by a β-hydrogen abstraction from the mercurials by trichloro-

methyl radical, followed by elimination and synchronous or subsequent

fragmentation of the alkylmercury(I) species. However, Nesmeyanov

and co-workers have proposed a completely different mechanism for the

Scheme IV

$$\cdot CCl_3 + HC(CH_3)_2CH_2HgR \longrightarrow \cdot C(CH_3)_2CH_2HgR + CHCl_3$$

$$\cdot C(CH_3)_2CH_2HgR \longrightarrow (CH_3)_2C = CH_2 + RHg$$

$$RHg \longrightarrow R\cdot + Hg(0)$$

$$R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3$$
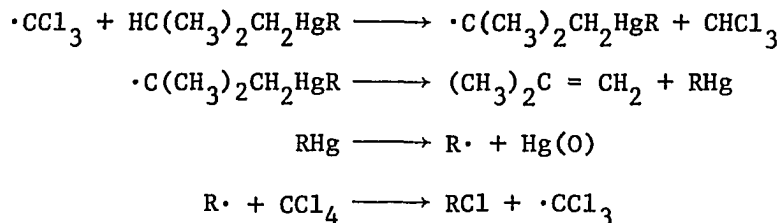
same reaction of the unsymmetrical dialkylmercurials with trichloro-methyl radical under similar reaction conditions, Scheme V [31]. These workers suggested that the chain reaction involved S_H^2 attack of

Scheme V   (R = phenyl; R' = n-butyl, ethyl, cyclohexyl)

$$(C_6H_5CO_2)_2 \longrightarrow C_6H_5\cdot + C_6H_5CO_2 + CO_2$$

$$C_6H_5\cdot + CCl_4 \longrightarrow C_6H_5Cl + \cdot CCl_3$$

$$\cdot CCl_3 + RHgR' \longrightarrow RCCl_3 + R'Hg$$

$$R'Hg + CCl_4 \longrightarrow R'HgCl + \cdot CCl_3$$
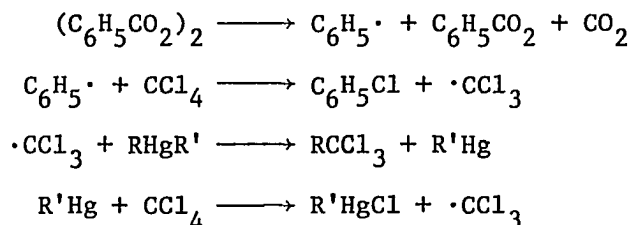
the trichloromethyl radical at the α-carbon of the mercurial. However, Jensen and Guard, in their reinvestigation of these processes, were unable to repeat the reactions reported by Nesmeyanov and co-workers [32]. Thus, the major products obtained from the reaction of di-n-butylmercury with carbon tetrachloride were 1,1,1,3-tetrachloropentane, n-butyl chloride, chloroform, n-butylmercury chloride and mercury. No 1,1,1-trichloropentane, the expected product according to Nesmeyanov results, was found [32]. These authors have proposed a mechanism for this reaction similar to the one given by Nugent and Kochi and presented in

Scheme IV.

Recently, Russell and Hershberger have reported that 1-alkenyl-mercury halides undergo facile photostimulated radical chain reactions with phenyl disulfide, phenyl ditelluride, phenyl diselenide and benzenesulfonyl chloride (Eq. 5, 6) [33]. Evidence to support the free

$$RCH = CHHgX + PhYYPh \xrightarrow{h\nu} RCH=CHYPh + PhYHgX \qquad [5]$$

$$Y = S, Se, Te$$

$$RCH = CHHgX + PhSO_2Cl \xrightarrow{h\nu} RCH=CHSO_2Ph + ClHgX \qquad [6]$$
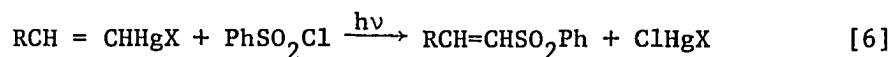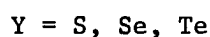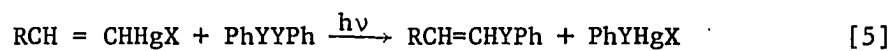
radical chain process in these reactions has been given [33]. This evidence includes the failure of the reaction to proceed in the dark and its complete inhibition by di-tert-butyl nitroxide. Scheme VI displays the suggested addition-elimination free radical chain mechanism

Scheme VI (Y = S, Se, Te)

$$RCH = CHHgX + PhY \cdot (PhSO_2 \cdot) \longrightarrow \underset{\cdot}{R}CH - \underset{|}{C}HYPh(SO_2Ph)$$
$$HgX$$

3

$$\mathbf{3} \longrightarrow RCH = CHYPh(SO_2Ph) + HgX$$

$$HgX + PhYYPh \longrightarrow PhY \cdot + PhYHgX$$

$$HgX + PhSO_2Cl \longrightarrow PhSO_2 \cdot + ClHgX$$
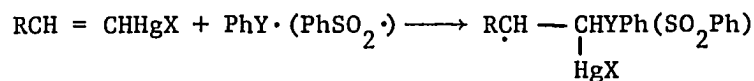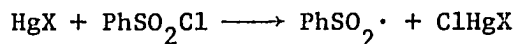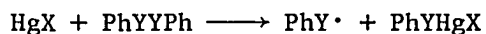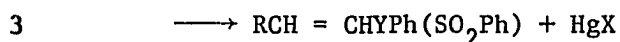
for this reaction. The key step in this mechanism is the addition of the heteroatom-centered radical to the α-carbon of the mercurial to afford the intermediate β-mercurio radical 3 which may be stabilized by the mercury substituent. The fragmentation of intermediate 3 yields

the substituted alkene and a mercury(I) species which continues the chain. It is worth noting that these reactions do not involve the free alkenyl radical as intermediates since the reaction with phenyl di-sulfide proceeds readily in the presence of benzenethiol to give alkenyl phenyl sulfide and not the alkene [33]. Similarly, a photo-stimulated coupling reaction between 1-alkenylmercury halides and the sodium salt of alkane- or arenesulfinic acids have been reported (Eq. 7)

$$R_1SO_2^-Na^+ + R_2CH = CHHgX \xrightarrow{h\nu} R_2CH = CHSO_2R_1 + NaX + Hg(0) \quad (7)$$
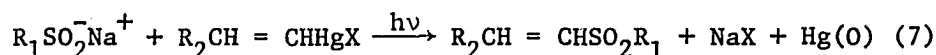
[34]. This reaction presumably follows a mechanism similar to the addition-elimination process of Scheme VI [33], e.g. Scheme VII. Other

Scheme VII

$$R_1SO_2 \cdot + R_2CH = CHHgX \xrightarrow{add.-elim.} R_2CH = CHSO_2R_1 + HgX$$

$$HgX + R_1SO_2^- \xrightarrow{\hspace{2cm}} RSO_2 \cdot + X^- + Hg(0)$$
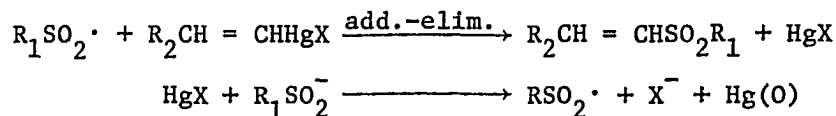
anions which will participate in the reaction of Scheme VII are $(RO)_2PO^-$ and $PhP(OR)O^-$ [33].

In analogy to the reactions of 1-alkenylmercurials with a hetero-atom-centered radical, alkylmercury halides would be expected to partici-pate in free radical chain reactions which might involve the alkyl radi-cal as an intermediate. Thus, in the presence of a radical source, the heteroatom-centered radicals $Q \cdot$ (Q = PhS, PhSe, PhTe, $PhSO_2$) might add to the alkylmercury halide, RHgX, to give the tricovalent mercury intermediate, RHgX(Q) (4). The decomposition of the intermediate 4

yields the alkyl radical which can propagate the reaction via S_H2 attack

at the radical precursor. The intermediacy of the tricovalent mercury

species 4 seems reasonable, since a similar intermediate was proposed

to account for the free radical racemization of some chiral organo-

mercurials [6] and the redistribution of some dialkylmercury compounds

[35].

The proposed reaction, free radical chain process, is shown in

Scheme VIII.

<u>Scheme VIII</u>   (Q = PhS, PhSe, PhTe, $PhSO_2$, $p-MeC_6H_4SO_2$, CCl_3)

(Y = PhS, PhSe, PhTe, Br, Cl)

Initiation

$$RHgX + Q\cdot \longrightarrow RHgX(Q)$$

$$4$$

$$4 \longrightarrow R\cdot + XHgQ$$

$$R\cdot + QY \longrightarrow RY + Q\cdot$$
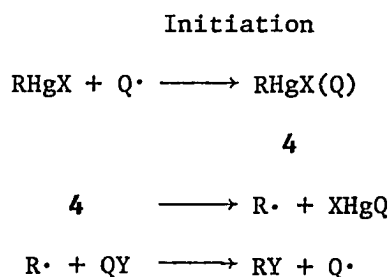
The scope and mechanism of the reaction of alkylmercurials with

heteroatom-centered radicals and $\cdot CCl_3$ is discussed in Parts (1-9) of

the following section. The reaction of dialkylmercurials with

PhSSPh and PhSeSePh is discussed in Parts (10, 11), whereas Part (12)

is devoted to the discussion of the reaction of benzylmercurials.

B. Results and Discussion

1. Reaction of alkylmercury halides with disulfides

Alkylmercury halides did not react with phenyl disulfide at any appreciable rate in the absence of a free radical initiator. Thus, Δ^3-butenylmercury chloride and phenyl disulfide in benzene solution did not react when kept in the dark at 50°C for several hours. However, the reaction occurred smoothly under the influence of radiation from a 275 W sunlamp placed 15 cm from the Pyrex reaction vessel to afford ClHgSPh as a white precipitate (almost completely insoluble in benzene), and Δ^3-butenyl phenyl sulfide in an excellent yield (see Table I). After the sunlamp was turned on, the white solid started to form within 15 minutes. Workup including the solid filtration and the solvent removal under reduced pressure gave an oily residue consisting of Δ^3-butenyl phenyl sulfide with a trace of ClHgSPh. The solid contaminant was removed by dissolving the residue in hexane and filtering. The hexane removal in vacuo gave the crude, but rather pure, Δ^3-butenyl phenyl sulfide as a light yellow oil. GLC analysis revealed the presence of ca. 5% of phenyl disulfide.

Results for the photoreaction of other alkylmercury halides with phenyl disulfide, some of which have been published in preliminary form [36], are summarized in Table I.

The thermal reaction of alkylmercurials with phenyl disulfide was also studied in the presence of a free radical initiator. Thus, Δ^3-butenylmercury chloride in benzene solution reacted with phenyl disulfide in the dark when the reaction mixture was heated at 80°C for

Table I. Photoreaction of alkylmercury halides with disulfides

$$R^1HgX + R^2SSR^2 \xrightarrow[PhH]{light} R^1SR^2 + R^2SHgX$$

R^1	R^2	Time (h)[a]	% Yield[b] R^1SR^2
$CH_2 = CHCH_2CH_2$	Ph	4	92
$CH_3(CH_2)_4CH_2$	Ph	3	78
$(CH_3)_3CCH_2$	Ph	12	74
$(CH_3)_2CH$	Ph	4	100
cyclo-C_6H_{11}[c]	Ph	18	65[d]
cyclo-$C_5H_9CH_2$	Ph	4	86 (73)[d]
7-norbornyl	Ph	6	43[e]
$CH_2 = CH(CH_2)_3CH_2$	Ph	3	88[f]
$CH_3(CH_2)_2CH_2$	Ph	6	84
$(CH_3)_2CHCH_2$	Ph	6	86
$CH_2 = CHCH_2CH_2$	n-Bu	20	60[g]
$CH_2 = CHCH_2CH_2$	Isopropyl	24	10
$CH_2 = CHCH_2CH_2$	$PhCH_2$	24	0
$CH_2 = CHCH_2CH_2$	tert-Bu	24	0

[a]Irradiation was carried out with a 275 W sunlamp positioned 15 cm from the Pyrex reaction vessel.

[b]^{1}H.N.M.R. yields.

[c]DMSO solvent.

[d]Isolated yield (5 mmol scale).

[e]A significant amount of the dimer R^1-R^1 was observed.

[f]Mixture of R^1 = Δ^5-hexenyl and cyclopentylcarbinyl.

[g]GLC yield.

several hours in the presence of 10 mol % of azobisisobutyronitrile

(AIBN). The reaction afforded Δ^3-butenyl phenyl sulfide in good yield

(see experimental section).

The inhibition of the free radical chain process was also explored.

Thus, the addition of 10 mole % of di-tert-butyl nitroxide to the photo-

reaction of Δ^3-butenylmercury chloride and phenyl disulfide resulted

in complete inhibition of the reaction for at least 4 hours.

It is worth mentioning that the reaction of Δ^3-butenylmercury

chloride with phenyl disulfide yielded no rearranged product, i.e. cyclo-

propylcarbinyl phenyl sulfide was not detected. However, other Δ^3-

butenyl organometallic derivatives are reported to give exclusively the

cyclized product. Thus, Ashcroft and co-workers have shown that tri-

chloromethyl radical and arylsulfonyl radicals react with Δ^3-butenyl-

bis-(dimethylglyoximato)pyridinecobalt(III) complexes to give the

corresponding cyclopropylcarbinyl derivatives (Eq. 8) [37].

$$\text{\raisebox{0pt}{$\diagdown\!\!\diagup\!\!\diagdown\!\!\diagup$}} \; CoLn + QY \xrightarrow{h\nu} \triangleright\!\!-\!\!/ Q + YCoLn \qquad (8)$$

$$Q = CCl_3, \; ArSO_2; \; Y = Cl$$
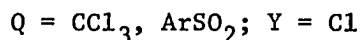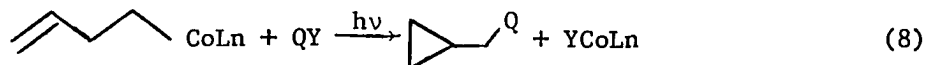
The reaction of alkylmercurials with phenyl disulfide seems to pro-

ceed via a free radical chain mechanism. Evidence for the free radical

nature of the reaction includes catalysis by free radical sources, such

as light irradiation or azobisisobutyronitrile, and complete inhibition

by the efficient free radical scavenger di-tert-butyl nitroxide as well

as the failure of the reaction to proceed in the dark. The detailed

mechanistic aspects of the reaction will be discussed in part 9 of this section.

In the photoreaction of Δ^5-hexenylmercury chloride with phenyl disulfide, a mixture of Δ^5-hexenyl phenyl sulfide and cyclopentycarbinyl phenyl sulfide was obtained in good yield. The product proportions were dependent on phenyl disulfide concentration. For kinetic purposes, the reaction was carried out in the presence of large excess phenyl disulfide in order to maintain an essentially constant concentration. Based on the relative yields of Δ^5-hexenyl phenyl sulfide and cyclo-pentylcarbinyl phenyl sulfide, and a unimolecular cyclization rate constant of 1×10^5 s^{-1} for the Δ^5-hexenyl radical [38], the rate constant k_2 for the $S_H{}^2$ attack of Δ^5-hexenyl radical upon phenyl disulfide was calculated to be 7.6×10^4 L/mol-s. Extensive cyclization in this reaction indicates the intermediacy of Δ^5-hexenyl radical which partitioned between rearrangement and $S_H{}^2$ substitution at phenyl disulfide, Scheme IX.

Scheme IX (Y = S, Se, Te)
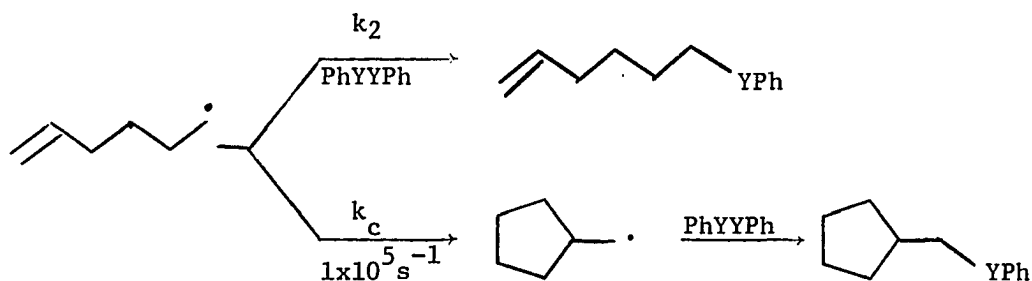
Allylmercury chloride showed a sluggish reaction with phenyl disulfide to afford a poor yield of ca. 30% of allyl phenyl sulfide. Phenylmercury chloride and cyclopropylmercury bromide failed to react with phenyl disulfide under these reaction conditions. In addition, phenylmercury thiophenoxide was neither decomposed by irradiation in a Rayonet photoreactor, nor reacted with phenyl disulfide. However, phenylmercury thiophenoxide undergoes a photostimulated reaction with isopropylmercury chloride to afford mainly isopropyl phenyl sulfide and a small amount of cumene. The formation of the former might involve the S_H2 attack of the alkyl radical on the sulfur mercury bond.

Alkyl disulfide showed different reactivities toward alkylmercurials. Thus, the photoreaction of Δ^3-butenylmercury chloride with n-butyl disulfide gave n-butyl Δ^3-butenyl sulfide in 60% yield. However, under the same conditions, the reaction of isopropyl disulfide afforded a very low yield of ca. 10% of isopropyl Δ^3-butenyl sulfide, whereas, tert-butyl disulfide completely failed to react with the alkylmercurial. The results parallel increasing steric hindrance in the disulfides and suggest that the reactions involve S_H2 of the alkyl free radical intermediate at the disulfide. Benzyl disulfide also failed to react with the alkylmercurials when the reaction mixture was irradiated with a sunlamp. The failure of benzyl disulfide to participate in this reaction may possibly be explained by abstraction of the benzylic hydrogen atoms of the disulfide by the alkyl radical.

2. Reaction of alkylmercury halides with phenyl diselenide

Solution of isopropylmercury chloride and phenyl diselenide in benzene showed no evidence of reaction in the dark at 50°C even after long periods of time. In dramatic contrast, a facile reaction occurred upon exposure of the reaction mixture to a 275 W sunlamp irradiation at ambient temperature (25-40°C). The reaction was evidenced by the formation of a light yellow precipitate of ClHgSePh, which was nearly insoluble in benzene, less than 15 minutes after irradiation was commenced. Workup consisted of filtering off the solid and removing the solvent in vacuo to give a quantitative yield of isopropyl phenyl selenide (see experimental section). Other alkylmercury halides were found to react with phenyl diselenide under similar reaction conditions to afford alkyl phenyl selenides in excellent yields. The results are tabulated in Table II.

The fact that the reaction of Δ^5-hexenylmercurial with phenyl diselenide gave a mixture of Δ^5-hexenyl phenyl selenide and cyclopentylcarbinyl requires the intermediacy of Δ^5-hexenyl radical in this reaction. From the ratio of the two selenides and the known rate constant of Δ^5-hexenyl radical cyclization, it was possible to calculate a rate constant of 1.2×10^7 L/mol-s for the S_H^2 displacement of Δ^5-hexenyl radical on phenyl diselenide. Clearly, phenyl diselenide is a better radical trap than phenyl disulfide, since less cyclization occurs with the former.

3. Reaction of alkylmercury halides with phenyl ditelluride

When benzene solutions of alkylmercury halides and phenyl ditelluride were irradiated with a sunlamp, a rapid reaction occurred as

Table II. Photoreaction of alkylmercury halides with phenyl diselenide

$$RHgX + PhSeSePh \xrightarrow[\text{PhH}]{\text{light}} RSePh + XHgSePh$$

R	Time (h)[a]	% Yield RSePh[b]
$CH_2 = CHCH_2CH_2$	5	85
$CH_3(CH_2)_4CH_2$	3	82
$(CH_3)_3CCH_2$	5	86
$(CH_3)_2CH$	5	100 (92)[c]
Cyclo-C_6H_{11}[d]	16	72[c]
Cyclo-$C_5H_9CH_2$	4	84
7-norbornyl	4	53[e]
$CH_2 = CH(CH_2)_3CH_2$	3	93[f]

[a]Irradiation was carried out with a 275 W sunlamp positioned 15 cm from the Pyrex reaction vessel.

[b]1H.N.M.R. yield.

[c]Isolated yield (5 mmol).

[d]DMSO solvent.

[e]A significant amount of the dimer R-R was detected.

[f]Mixture of R = Δ^5-hexenyl and cyclopentylcarbinyl.

evidenced by the formation of a deep yellow precipitate of ClHgTePh

after less than 15 minutes of irradiation. Workup afforded alkyl

phenyl tellurides in an excellent yield, Table III.

Table III. Photochemical reactions of alkylmercury halides with phenyl
ditelluride

$$RHgX + PhTeTePh \xrightarrow[\text{PhH}]{\text{light}} RTePh + XHgTePh$$

R	Time (h)[a]	% Yield[a] RTePh
$(CH_3)_2CH$	3	96
$CH_2 = CHCH_2CH_2$	3	92
$CH_3(CH_2)_4CH_2$	4	83
$(CH_3)_3CCH_2$	6	78
7-norbornyl	10	45[b]
$CH_2 = CH(CH_2)_3CH_2$	3	85[c]

[a] ^{1}H.N.M.R. yields.

[b] A significant amount of the dimer R–R was detected.

[c] Mixture of R = Δ^5-hexenyl and cyclopentylcarbinyl.

The reaction of Δ^5-hexenylmercury chloride with phenyl ditelluride

yielded a mixture of Δ^5-hexenyl phenyl telluride and cyclopentylcarbinyl

phenyl telluride. The formation of the latter is consistent with the

formation of alkyl radicals intermediates in this reaction. From the

yields of uncyclized and cyclized products and the known value of the

unimolecular cyclization of Δ^5-hexenyl radical, the rate constant of

S_H^2 substitution of this radical on phenyl ditelluride was found to be 4.8×10^7 L/mol-s. Obviously, diphenyl ditelluride is a better radical trap than either phenyl disulfide or phenyl diselenide.

4. Photoreaction of alkylmercury halides with Se-phenyl p-tolylselenosulfonate

Alkylmercury halides were found to react very rapidly with Se-phenyl p-tolylselenosulfonate 5 upon irradiation with a 275 W sunlamp.
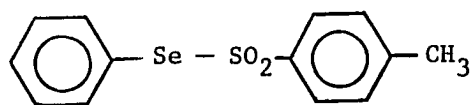
5

During the reaction, a white precipitate was formed. Workup by filtration and solvent removal in vacuo gave alkyl phenyl selenides as the exclusive organic products in good yields, Table IV. No alkyl p-tolyl sulfones were observed. The observation of alkyl phenyl selenides as the sole products of this reaction provided further evidence that the free alkyl radical is involved as an intermediate in the reaction of alkylmercurials with heteroatom-centered radicals.

Similar to the previous cases, Δ^5-hexenylmercurial reaction with Se-phenyl p-tolylselenosulfonate resulted in an extensive cyclization to yield a mixture of Δ^5-hexenyl phenyl selenide and cyclopentylcarbinyl phenyl selenide. From the ratio of the two products and the known cyclization rate constant of Δ^5-hexenyl radical, the second-order rate constant for the attack of Δ^5-hexenyl radical upon Se-phenyl p-tolylselenosulfonate was calculated to be 3.0×10^6 L/mol-s.

Table IV. Photoreaction of alkylmercury halides with Se-phenyl p-tolylselenosulfonate

$$RHgX + PhSe-SO_2C_6H_4Me\text{-}\underline{p} \xrightarrow{\text{light}} RSePh + XHgSO_2C_6H_4Me\text{-}\underline{p}$$

R	Time (h)	% Yield[a] RSePh
$CH_2 = CHCH_2CH_2$	5	87
$CH_3(CH_2)_4CH_2$	5	82
$(CH_3)_3CCH_2$	10	75
7-norbornyl	10	48[b]
$CH_2=CH(CH_2)_3CH_2$	6	81[c]

[a] ^{1}H.N.M.R. yields.

[b] A significant amount of the dimer R-R was observed.

[c] Mixture of R = Δ^5-hexenyl and cyclopentylcarbinyl.

5. Reaction of alkylmercury halides with benzenesulfonyl chloride

1-Chlorohexane was obtained as the only organic product from the photoreaction of $\underline{n}$-hexylmercury chloride with benzenesulfonyl chloride. The reaction was slow and performed in the Rayonet photoreactor at 350 nm under a nitrogen atmosphere. A white precipitate of $ClHgSO_2Ph$ was formed after several hours of irradiation. Workup consisting of filtration and solvent removal by distillation gave 1-chlorohexane in a fair yield.

Similarly, the reaction of Δ^5-hexenylmercury chloride with benzenesulfonyl chloride gave the alkyl chlorides as the sole products. However, a mixture of Δ^5-hexenyl chloride and cyclopentylcarbinyl chloride was found in the crude isolate of this reaction. Based on the ratio of the two products and the known value of unimolecular cyclization of

Δ^5-hexenyl radical, the rate constant of the S_H2 attack of Δ^5-hexenyl radical on benzenesulfonyl chloride was found to be 3.7×10^4 L/mol-s. It is worth noting that the extensive cyclization as well as the formation of the chlorides as the exclusive products support the intermediacy of the alkyl radicals in these reactions.

6. Reaction of Δ^5-hexenylmercury chloride with benzene thiol

Δ^5-hexenylmercury chloride reacts rapidly with benzene thiol under sunlamp irradiation as evidenced by the formation of a white precipitate after less than 20 minutes of irradiation. Normal workup afforded a mixture of 1-hexene and methylcyclopentane as the exclusive products. From the ratio of the two isomeric compounds and the rate of unimolecular cyclization of Δ^5-hexenyl radical, the rate constant for the hydrogen abstraction reaction of Δ^5-hexenyl radical with benzene thiol was calculated to be ca. 8×10^7 L/mol-s. The above reaction did not proceed in the dark, and was completely inhibited by di-_tert_-butyl nitroxide which eliminates the electrophilic cleavage of Δ^5-hexenyl moiety. When the reaction of Δ^5-hexenylmercurial and benzene thiol was repeated in the presence of phenyl disulfide, the formation of 1-hexene and methylcyclopentane by H-abstraction from PhSH remained the main reaction channel. These results are in agreement with the conclusion that primary alkyl radicals abstract hydrogen from PhSH ca. 20 times faster than the S_H2 attack at phenyl disulfide and has essentially no reactivity toward PhS$^-$ [39]. Also, it has been reported that the phenyl radicals abstract hydrogen from PhSH at an essentially diffusion-controlled rate [40]. The trapping

of the alkyl radical by benzene thiol, together with the formation of

methylcyclopentane provide further evidence that this reaction involves

the alkyl radical as an intermediate.

7. Reaction of monoalkylmercurials with bromotrichloromethane
   and carbon tetrachloride

A slow reaction occurred between $\underline{n}$-hexylmercury chloride and bromo-

trichloromethane when the reaction mixture in CH_2Cl_2 solution was

irradiated in the Rayonet reactor at 350 nm. A white precipitate was

formed several hours after the irradiation began. When the reaction was

complete, the precipitate was filtered. GLC analysis of the filtrate

determined $\underline{n}$-hexyl bromide as the main product (52% yield). In addi-

tion, small amounts of $CHCl_3$ (8%) and 1,1,1-trichloro-3-bromoheptane

were detected. When the above reaction was performed thermally at 80°C

in the presence of 10 mole % AIBN, the main product was again $\underline{n}$-hexyl

bromide with little $CHCl_3$ and 1,1,1-trichloro-3-bromoheptane. The photo-

reaction of $\underline{n}$-hexylmercury chloride with $BrCCl_3$ was completely inhibited

by di-$\underline{tert}$-butyl nitroxide. Comparable results were obtained with other

alkylmercury halides. Thus, $\underline{n}$-butylmercury chloride reacted with $BrCCl_3$

to give 1-bromobutane as the main product. Only small amounts of $CHCl_3$

and 1,1,1-trichloro-3-bromopentane were detected. The reaction of

alkylmercurial salts with CCl_4 was also investigated. A very slow reac-

tion took place when a CCl_4 solution of $\underline{n}$-hexylmercury chloride was

irradiated in the Rayonet reactor at 350 nm. Workup afforded $\underline{n}$-hexyl

chloride (32% yield), $CHCl_3$ (14%) and 1,1,1,3-tetrachloroheptane.

The formation of $\underline{n}$-hexyl bromide and $\underline{n}$-hexyl chloride as the main

products of the reactions of n-hexylmercury chloride with $BrCCl_3$ and

CCl_4 suggests the formation of n-hexyl radical, which attacks these

substrates to give halogen atom transfer. It has been reported that

$BrCCl_3$ has a tendency to give a bromine atom chain process in its reac-

tions with some hydrocarbons under free radical conditions [41]. Such a

process can be prevented by use of K_2CO_3 to neutralize the resulting

HBr and prevent the formation of molecular bromine [41]. Thus, to

exclude this possibility in the present study, the reaction of n-

hexylmercury chloride with $BrCCl_3$ was performed in the presence of K_2CO_3.

However, it was found that K_2CO_3 had no effect on the outcome of the

reaction and n-hexyl bromide remained the main product. This observa-

tion rules out any bromine involvement in the reaction of n-hexylmercuri-

al and $BrCCl_3$ and confirms the intermediacy of the alkyl radical prior

to the halogen atom transfer reaction.

The formation of polyhalogenated hydrocarbons as the minor products

in these reactions may be due to a β-elimination process to give 1-

alkenes, which would react further with $BrCCl_3$ and CCl_4 to give the

adduct as anticipated from the well-known addition of CCl_4 to olefins

under free radical conditions [42]. β-Elimination has been reported to

be the sole pathway for the reaction of dialkylmercury compounds with

CCl_4 [30]. However, the reaction of alkylmercury halides seems to pro-

ceed through alkyl radical intermediates with limited involvement of β-

elimination. The formation of the alkyl radicals in the reaction of

alkylmercurials with $BrCCl_3$ and CCl_4 requires the addition of $\cdot CCl_3$ to

the mercury atom of the mercurial to give the tricovalent mercury

intermediate, $RHgCl(CCl_3)$ which decomposes to yield R·. Note that once

the intermediate $RHgCl(CCl_3)$ is invoked, its decomposition to alkene,

$HCCl_3$ and HgCl must also be considered.

The unsymmetrical mercurial n-butylphenylmercury was found to re-

act with $BrCCl_3$ under sunlamp irradiation. The products were n-butyl

bromide (48%), $CHCl_3$ (7%) and 1,1,1-trichloro-3-bromopentane. Phenyl-

trichloromethane was observed in a small amount, ca. 5%. Similarly, the

reaction with CCl_4 occurred photochemically or thermally in the presence

of benzoyl peroxide as the initiator. The products were n-butyl chloride

(31%), $CHCl_3$ (17%) and 1,1,1,3-tetrachloropentane. Again, phenyltri-

chloromethane was detected only in a small amount. These results are in

dramatic contrast to those reported for this reaction by Nesmeyanov and

his collaborators [31]. These authors report that the main products of

the catalyzed thermal reaction between n-butylphenylmercury and carbon

tetrachloride were n-butylmercury chloride and phenyltrichloromethane.

The presence of phenyltrichloromethane was inferred by the isolation of

benzoic acid from the alkaline hydrolysis of the reaction products. No

n-butyl chloride or polyhalogenated pentane were reported as products.

These workers proposed the formation of phenyltrichloromethane by S_H^2

attack at the phenyl mercury bond (Eq. 9). The fact that phenyltri-

$$\text{n-BuHgPh} + \cdot CCl_3 \longrightarrow PhCCl_3 + BuHg \qquad (9)$$
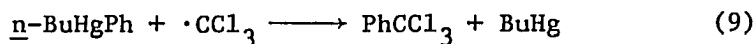
chloromethane is formed only in negligible amount indicates that this

proposal is erroneous. The results of the present study are in good

agreement with those reported by Jensen and Guard, who also were unable

to reproduce another part of the Nesmeyanov work [32].

One reaction was performed between n-butylphenylmercury and benzenesulfonyl chloride with sunlamp irradiation for 48 h. This reaction gave n-butyl chloride, diphenyl sulfone and mercury metal. The formation of n-butyl chloride requires the formation of n-butyl radical prior to the halogen atom transfer reaction. The precipitation of mercury metal may arise from the decomposition of phenylmercury benzenesulfinate intermediate which would give diphenyl sulfone. Phenylmercury benzenesulfinate, prepared from the reaction of diphenylmercury and mercury diphenylsulfinate, was found to undergo a slow photostimulated decomposition under sunlamp irradiation to give diphenyl sulfone and mercury metal.

8. Reaction of dialkylmercurials with bromotrichloromethane
   and carbon tetrachloride

Diisobutylmercury was found to react very rapidly with $BrCCl_3$ at $-50°C$ under sunlamp irradiation in methylene chloride solutions to give isobutyl bromide as the main product. This reaction was accompanied by the formation of a white precipitate, presumably $(CH_3)_2CHCH_2HgCCl_3$. In addition, small amounts of $CHCl_3$ and 1,1,1-trichloro-3-bromo-3-methyl-butane were identified among the products. The yields of isobutyl bromide and chloroform were monitored as a function of time as shown in Table V; and graphically displayed in Figure 1. It is clear that the formation of isobutyl bromide predominates. The reaction must occur via a radical chain process since the addition of 12 mole % of di-tert-butyl nitroxide completely inhibited the photostimulated reaction for 2 h and

Table V. Photoreaction of diisobutylmercury with $BrCCl_3$ in methylene chloride solutions at $-50°C$

Time (h)	% Yield (mole/mole of $((CH_3)_2CHCH_2)_2Hg$	
	$(CH_3)_2CHCH_2Br$	$CHCl_3$
0.5	54	3.3
1.0	80	5.2
1.5	105	7.4
1.5	89	6.0
3.0	104	7.2
3.0	93	6.5
6.0	92	7.3
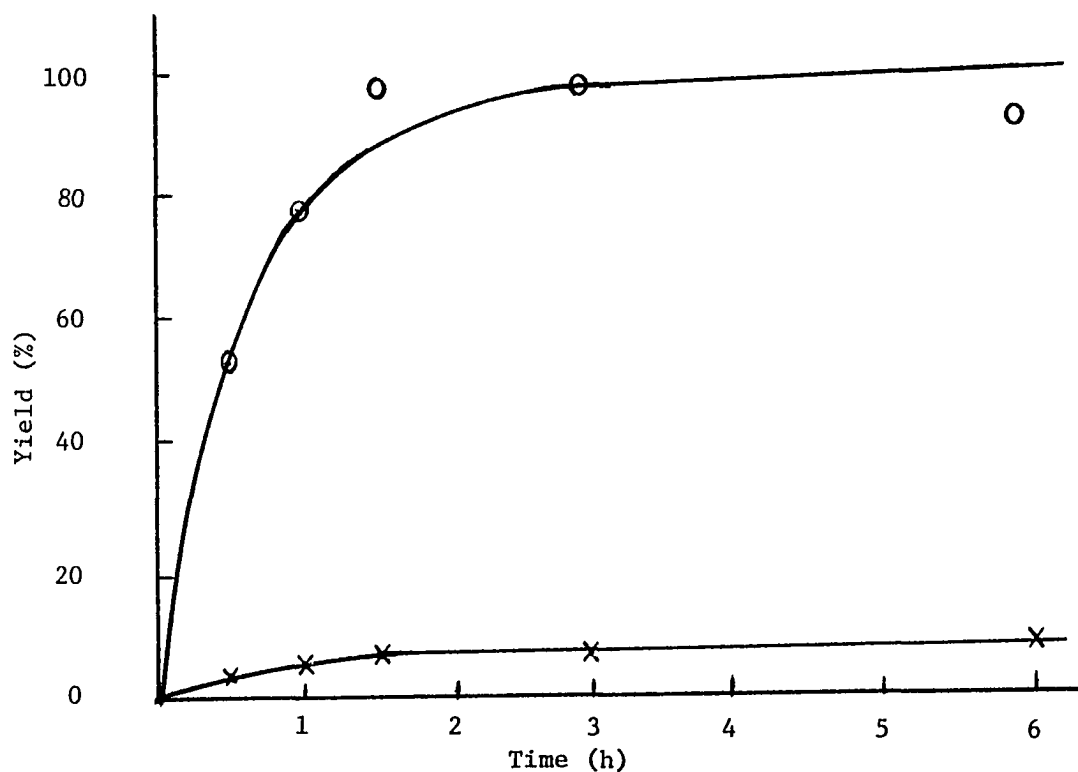
Figure 1. Reaction of diisobutylmercury with $BrCCl_3$. Formation of isobutyl bromide [O] and $CHCl_3$ [x] vs. time

no reaction was observed in the absence of irradiation. The formation
of isobutyl bromide in the photostimulated reaction can be rationalized
in terms of a radical chain process, Scheme X. The initial step of

<u>Scheme X</u>

$$(CCH_3)_2CHCH_2)_2Hg + \cdot CCl_3 \xrightarrow{k_{add}} ((CH_3)_2CHCH_2)HgCCl_3$$

6

$$\textbf{6} \longrightarrow (CH_3)_2CH\overset{\cdot}{C}H_2 + (CH_3)_2CHCH_2HgCCl_3$$

$$(CH_3)_2CH\overset{\cdot}{C}H_2 + BrCCl_3 \longrightarrow (CH_3)_2CHCH_2Br + \overset{\cdot}{C}Cl_3$$
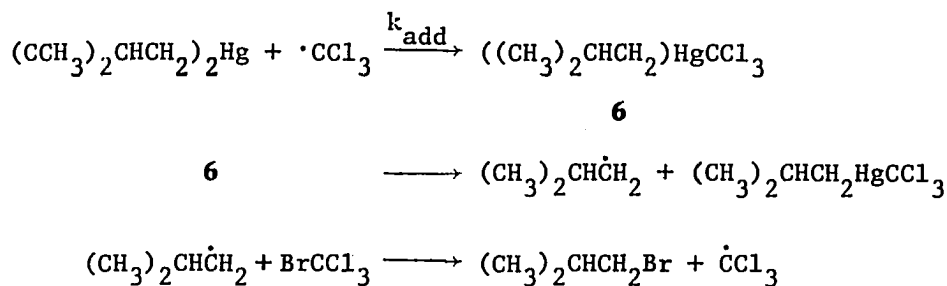
this process involves the addition of $\cdot CCl_3$ to the mercury atom of the

mercurial to give the tricovalent mercury species **6**. Intermediate **6**

dissociates to produce the alkyl radical which abstracts a bromine atom

from $BrCCl_3$ to yield the isobutyl bromide. The formation of the small

amounts of $CHCl_3$ and $Cl_3CH_2CHBr(CH_3)_2$ may occur via a β-elimination

process involving the attack of $\cdot CCl_3$ at the β-hydrogen of the mercurial

(Eq. 10) followed by reaction (11). It is important to emphasize that

$$\cdot CCl_3 + ((CH_3)_2CHCH_2)_2Hg \xrightarrow{k_H} HCCl_3 + (CH_3)_2C=CH_2 + (CH_3)_2CHCH_2Hg \qquad (10)$$

$$(CH_3)_2CHCH_2Hg \longrightarrow Hg(0) + (CH_3)_2CHCH_2 \xrightarrow{BrCCl_3} (CH_3)_2CHCH_2Br + \cdot CCl_3 \qquad (11)$$
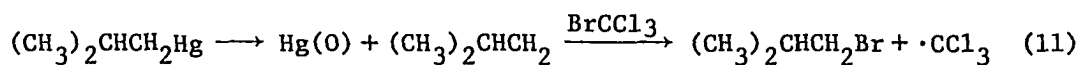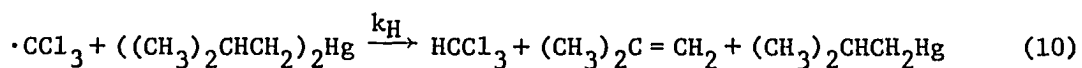
the chloroform was formed only in a very limited amount, which indi-
cates that $\cdot CCl_3$ prefers to add to the mercury atom rather than attack
at the β-hydrogen atom. From the relative yields of isobutyl bromide
and chloroform (Table V), it is possible to estimate a value for

k_{add}/k_H of ~15, where k_{add} is the rate constant for the addition of
$\cdot CCl_3$ to the mercury and k_H is the rate constant for the attack at β-
hydrogen. The reaction at -50°C is simplified by the fact that i-
BuHgCCl$_3$ is apparently unreactive, possibly because of insolubility.
Thus, ~6% of the diisobutylmercury reacts by equations 10 and 11 and
~94% reacts by Scheme X. At -50°C, the photostimulated reaction of
diisobutylmercury with CCl_4 (0.1 M) in CH_2Cl_2 failed to give any de-
tectable reaction in 1.5 h.

The reaction of diisobutylmercury with $BrCCl_3$ also occurred under
sunlamp irradiation at ambient temperature (35-45°C) to give after 6 h
isobutyl bromide (0.78 equiv), whereas $CHCl_3$ was formed in a lower
yield (0.18 equiv). Surprisingly, the disappearance of the mercurial
was slower at this temperature than at -50°C. A typical experiment at
35-45° required 6 h for completion while at -50°C the reaction was over
in ~1.5 h. The results show that the amount of attack of $\cdot CCl_3$ at the
β-hydrogen increases with an increase in the temperature, but that the
addition of $\cdot CCl_3$ to the mercury remains the most important reaction
pathway. The formation of isobutyl bromide as the main product under
these conditions gives further support for the mechanism in which the
$\cdot CCl_3$ adds to the mercury atom, as previously shown in Scheme X.

The reaction of certain dialkylmercurials with CCl_4 at higher
temperature (100°C) and in the presence of di-n-butyryl peroxide has
been reported by Nugent and Kochi [30]. The results obtained by these
workers are summarized in Table VI. The reaction is reported to pro-
ceed by a radical chain mechanism involving $\cdot CCl_3$ attack at the

Table VI. Copy of table I, Ref. [30]

Table I. Reductive Elimination of Dialkylmercury in Carbon Tetra-
          chloride Solutions[a]

Mercurial[b]	Conversion[c]	Products (mmol)[d]			
R-Hg-R'	(%)	$R(-H)^3$	R'-Cl	$CHCl_3$	Hg^0
i-BuHgMe	51	1.01	0.93	0.93	1.02
i-BuHgNp	88	0.96	0.87	0.91	0.97
$Hg(CH_2)_6$[f]	--[g]	0.84	0.86	1.07	0.80

[a]At 100°C, no initiator added. [b]2.25 mmol in 5 ml CCl_4. [c]Based on
recovered RHgR' after 300 hrs. [d]Per mmol of unrecovered RHgR'. [e]Alkene
plus CCl_4 adduct. [f]Contains 0.28 mmol di-n-butyryl peroxide, yields
based after 7 hrs on reactant charged. [g]Not determined.

β-hydrogen of the mercurial (i.e., reaction 10). The general conclusion

of Nugent and Kochi was confirmed when diisobutylmercury in CCl_4 was

irradiated for 48 h in the Rayonet reactor at 350 nm. GLC and GCMS

analysis indicated the formation of isobutyl chloride, $HCCl_3$ and 1,1,1,3-

tetrachloro-3-methylbutane in an approximate 1:1:1 ratio. The results

obtained for the reaction of diisobutylmercury with $BrCCl_3$ at low as

well as at ambient temperatures contradicts the β-elimination mechanism

of Nugent and Kochi as being the sole or preferred pathway for the reac-

tion of a dialkylmercurial with $\cdot CCl_3$. However, the results support a

mechanism in which the $\cdot CCl_3$ adds to the mercury atom displacing an

alkyl radical, Scheme X.

The striking dependency of the product of the reaction of

diisobutylmercury on the substrate, i.e., $BrCCl_3$ or CCl_4, might be

explained by the reversible formation and dissociation of the trico-

valent mercury species 6, Scheme XI. $BrCCl_3$ is known to be a better

trap for an alkyl radical than CCl_4. For example, the rate constants

Scheme XI

$$(Me_2CHCH_2)_2Hg + \cdot CCl_3 \; \rightleftarrows \; (Me_2CHCH_2)_2HgCCl_3$$

$$\Big\downarrow \beta\text{-elimination} \qquad \mathbf{6}$$

$$\Big\updownarrow$$

$$CHCl_3 + Me_2CH\overset{\bullet}{C}H_2 + Me_2C = CH_2 + Hg(0)$$

$$\cdot CCl_3 + Me_2CHCH_2Cl \;\underset{slow}{\overset{CCl_4}{\longleftarrow}}\; Me_2CH\overset{\bullet}{C}H_2 + Me_2CHCH_2HgCCl_3$$

$$Fast \Big\downarrow BrCCl_3$$

$$\cdot CCl_3 + Me_2CHCH_2Br$$
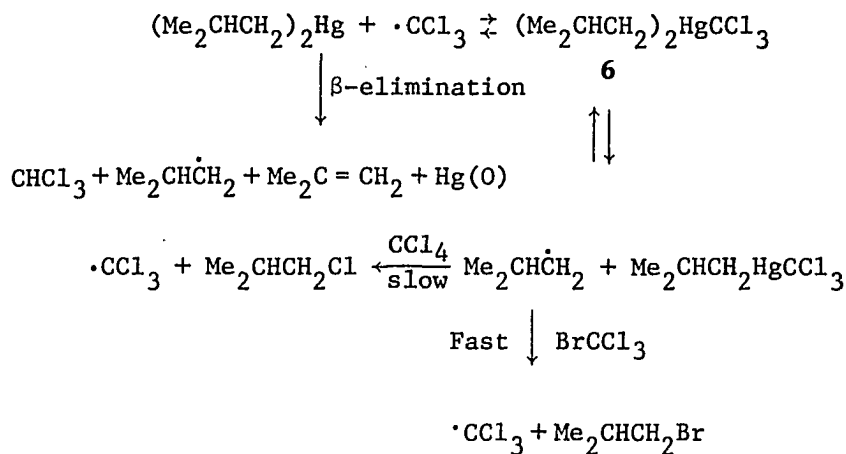
for attack of $\cdot CH_3$ on $BrCCl_3$ and CCl_4 are 2.2×10^6 and $4(1.3 \times 10^2)$ L/mol-s, respectively [43]. Thus, the isobutyl radical intermediate will rapidly abstract a bromine atom from $BrCCl_3$ to give isobutyl bromide and $\cdot CCl_3$ which continues the chain. This leads to a shift in the equilibrium in Scheme XI to the right and decreases the chances for the β-elimination reaction. On the other hand, the abstraction of a chlorine atom by the isobutyl radical from CCl_4 proceeds much slower than with $BrCCl_3$ (the difference in reactivity toward $\cdot CH_3$ is >1000). This leads to an increase in the steady-state concentrations of $Me_2CH\overset{\bullet}{C}H_2$, $\mathbf{6}$ and $\cdot CCl_3$. The net result will be a build-up in the steady-state concentration of $\cdot CCl_3$ which might enhance the β-elimination process.

Scheme XI also explains the unusual temperature dependence observed in the reaction of diisobutylmercury with $BrCCl_3$. Under the same conditions, the reaction is much faster at $-50°C$ than at $35-45°$. The equilibrium of Scheme XI could allow a higher steady state concentration

of $\cdot CCl_3$ to be achieved at the higher temperature if $\underline{\Delta H}$ is negative for

the following equilibrium (Eq. 12). This not only increases the

$$R_2Hg + \cdot CCl_3 \rightleftarrows RHgCCl_3 + R \cdot \qquad (12)$$
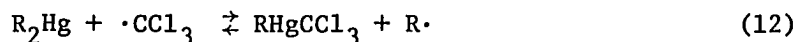
possibility for the occurrence of the irreversible β-elimination reac-

tion (Eq. 13), but also increases the probability of termination between

$$R_2Hg + \cdot CCl_3 \longrightarrow HCCl_3 + R(-H) + RHg \longrightarrow R \cdot + Hg(0) \quad (13)$$
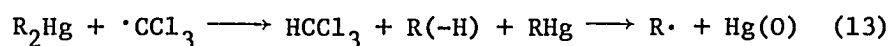
two trichloromethyl radicals. Traces of C_2Cl_6 were observed in these

reactions, whereas $RCCl_3$ was never detected. Thus, a fast and clean

substitution reaction $(XCCl_3 + R_2Hg \rightarrow RX + RHgCCl_3)$ is best achieved at

low temperatures with a polyhalomethane that is reactive in halogen

atom transfer with the alkyl radical. Whether a Hg(III) species, $\underline{e.g.}$ 6

in Scheme XI, is a true intermediate in these substitution reactions

must remain a matter of speculation since all the experimental evidence

can also be accounted by a classical S_H^2 process in which the transition

state has the composition R_2HgCCl_3.

Further support for the mechanism shown in Scheme X came from the

observation that mercurycycloheptane reacted with CCl_4 to yield exclu-

sively Δ^5-hexenyl chloride and its CCl_4 adduct, 1,1,1,3,7-pentachloro-

heptane. Despite a previous report that the reaction of 0.45 M mercury-

cycloheptane in CCl_4 at 100°C gave a measurable amount of cyclopentyl-

carbinyl chloride [30], none of the latter product was observed when

the reaction with 0.1 M solutions of the mercurial was repeated either

photochemically at 35° or at 100° with benzoyl peroxide as the initiator.

The Δ^5-hexenyl radical in CCl_4 solution would have to undergo an appreciable amount of ring closure because of the known rate constants (Scheme XII) [38]. Attack of $\cdot CCl_3$ on mercury cycloheptane by a β-hydrogen abstraction would have to form the Δ^5-hexenyl radical and at least some

Scheme XII
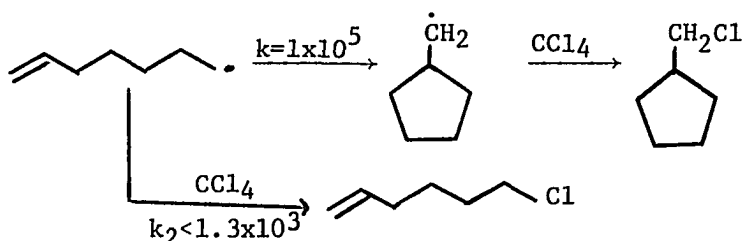
cyclopentylcarbinyl chloride (Eq. 14). We can conclude that with

$$\text{(14)}$$
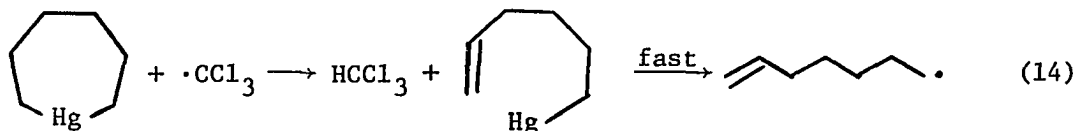
mercurycycloheptane, the preferred reaction pathway must be exclusive S_H^2 substitution at Hg leading to $CCl_3Hg(CH_2)_5\dot{C}H_2$ and presumably to $CCl_3Hg(CH_2)_5CH_2Cl$ (**7**). Further reaction of **7** appears to form only the β-elimination product, Δ^5-hexenyl chloride which can undergo the free radical addition of CCl_4 to form $CCl_3CH_2CH(Cl)(CH_2)_4CH_2Cl$. A possible rationalization for the above sequence of events is as follows. Attack of $\cdot CCl_3$ on mercurycycloheptane may occur preferentially at mercury in an irreversible manner to yield eventually **7**. The reaction may be irreversible because of the steric effects associated with the ring closure of the intermediate $CCl_3Hg(CH_2)_5\dot{C}H_2$. For the attack of $\cdot CCl_3$

upon **7** apparently leads exclusively to elimination, perhaps because attack upon mercury is a reversible process. There is also a possibility that when the mercury contains one trichloromethyl substituent as in **7**, that the β-elimination process is now favored because a concerted two bond cleavage process (Eq. 15). Reaction 15 thus represents

$$\cdot CCl_3 + RCH_2CH_2HgCCl_3 \rightarrow RCH = CH_2 + CHCl_3 + Hg(0) + \cdot CCl_3 \qquad (15)$$
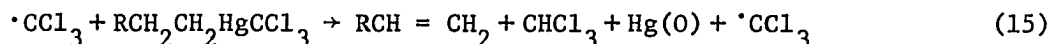
a free radical chain decomposition of $RCH_2CH_2HgCCl_3$ to $HCCl_3$, $Hg(0)$ and $RCH = CH_2$. A two bond cleavage process may also occur in the β-elimination of dialkylmercurials with $\cdot CCl_3$. In reaction with CCl_4, there appears to be much more elimination observed for $(RCH_2CH_2)_2Hg$ than for RCH_2CH_2HgCl. This may reflect the preferred reaction of $RCH_2CH_2HgCCl_3$ towards elimination. However, it may also reflect a preference for elimination in $(RCH_2CH_2)_2Hg$ when compared with RCH_2CH_2HgCl. The possibility exists that reaction 16 is faster than reaction 17 because

$$\cdot CCl_3 + RCH_2CH_2HgR' \xrightarrow{\text{fast}} HCCl_3 + RCH = CH_2 + Hg(0) + R \cdot \qquad (16)$$

$$\cdot CCl_3 + RCH_2CH_2HgCl \xrightarrow{\text{slow}} HCCl_3 + RCH = CH_2 + HgCl \qquad (17)$$
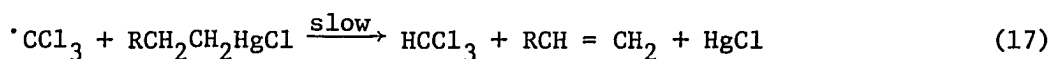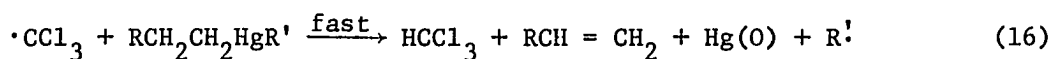
reaction 16 can involve the cleavage of both carbon mercury bonds in a concerted fashion. However, our results using $BrCCl_3$ conclusively demonstrate that for both RCH_2CH_2HgCl and $(RCH_2CH_2)_2Hg$, attack of $\cdot CCl_3$ on the mercury atom occurs more readily than the β-elimination process of reactions 16 and 17.

9. Mechanistic considerations

The reaction of alkylmercurial salts, RHgX (X = Cl, Br) with phenyl
disulfide, phenyl diselenide, phenyl ditelluride, Se-phenyl p-tolyl-
selenosulfonate, benzenesulfonyl chloride, bromotrichloromethane,
carbon tetrachloride and benzenethiol show all the characteristics of
an efficient radical chain process. Thus, the reactions are initiated
photochemically or by the decomposition of AIBN. They are completely
inhibited by efficient radical scavengers such as di-tert-butyl
nitroxide. Moreover, the formation of cyclopentylcarbinyl derivatives
from the reaction of Δ^5-hexenylmercurial indicates the intermediacy of
the Δ^5-hexenyl radical, which would cyclize to the cyclopentylcarbinyl
radical [21]. Further evidence for the alkyl radical involvement in
these reactions is provided by the observation that the reaction of
alkylmercury halides with benzenesulfonyl chloride yields only alkyl
chlorides and no alkyl phenyl sulfone. Similarly, the reaction with
$PhSeSO_2PhMe$-p gives only alkyl phenyl selenides, while the reactions
with $BrCCl_3$ and CCl_4 give mainly alkyl halides. It is worth mention-
ing, that the alkyl radical intermediates in these reactions are also
trapped, as previously discussed, by benzenethiol to give the alkane
(Eq. 18).

$$RHgX + PhSH \xrightarrow{light} RH + PhSHgX \qquad (18)$$

Scheme XIII outlines the simplest free radical chain mechanism which
can account for the above-mentioned facts. The initial step of the
reaction may be the homolytic scission of the heteroatom-centered

Scheme XIII (Q = PhS, PhSe, PhTe, $PhSO_2$, p-$MePhSO_2$, CCl_3)

(Y = PhS, PhSe, PhTe, Cl, Br)

(X = Cl, Br)

Initiation or $Q - Y \xrightarrow{h\nu} Q\cdot + Y\cdot$

$RHgX \xrightarrow{h\nu} R\cdot + HgX$

$RHgX + Q\cdot \longrightarrow RHgX(Q)$

8

Propagation **8** $\longrightarrow R\cdot + XHgQ$

$R\cdot + Q-Y \longrightarrow RY + Q\cdot$
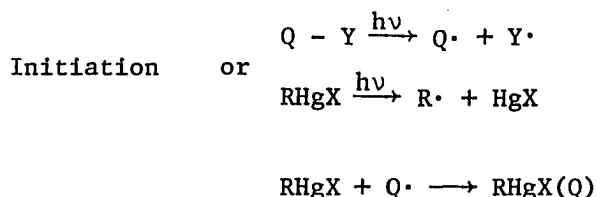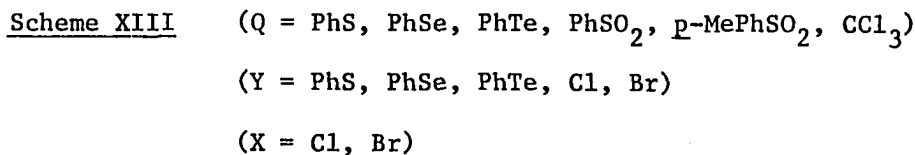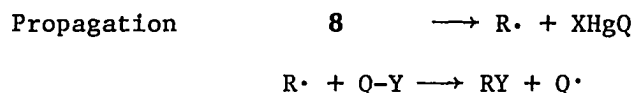
radical precursors, QY. This suggestion seems reasonable because di-
sulfides are well-known to homolytically photo-dissociate [44]. How-
ever, production of free radicals by the fragmentation of the alkyl-
mercurials cannot be ruled out. The tricovalent mercury species **8** is
included as a possible intermediate in the reaction, although there is
no direct evidence to support its existence. Such species were previ-
ously proposed as intermediates to account for the racemization [6],
or distribution [35] of mercurials by alkyl or aryl radicals. Decomposi-
tion of intermediate **8** affords the alkyl radical which reacts with the
substrate QY to yield the product RY and the radical Q· which continues
the chain. The observation that phenylmercury chloride and cyclopropyl-
mercury bromide do not react with phenyl disulfide under these reaction
conditions may be explained by the high bond-dissociation energies for

intermediate 8.

Organomercury halides are reported to participate in free radi-
cal chain reactions [33, 45]. Thus, alkylmercury halides react with
nitronate anions via a chain process to give the tertiary nitro com-
pounds (Eq. 19). Similarly, 1-alkenylmercurial salts undergo a facile

$$R_1HgX + \begin{matrix} R_2 \\ \diagdown \\ R_3 \diagup \end{matrix} C=NO_2^- \xrightarrow{\text{light}} R_1 \overset{R_2}{\underset{R_3}{-\overset{|}{\underset{|}{C}}-}} NO_2 + Hg(0) + X^- \quad (19)$$
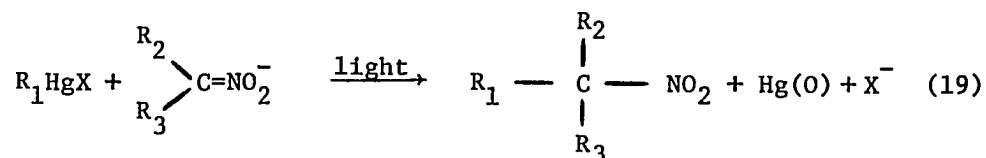
photostimulated chain reaction with phenyl dichalcogenide, PhYYPh
(Y = S, Se, Te) (Eq. 20) to give the corresponding alkyl phenyl

$$RCH = CHHgX + PhYYPh \xrightarrow{\text{light}} RCH = CHYPh + PhYHgX \quad (20)$$

chalcogenide in excellent yields. Evidence to support the chain
mechanism in these reactions has been given [46].

Analogous chain reactions were encountered in other organometallic
compounds. Thus, alkyl-bis(dimethylglyoximato)pyridinecobalt(III) com-
plexes are reported to react photochemically or thermally with phenyl
disulfide and phenyl diselenide to give alkyl phenyl sulfides and
selenides, respectively (Eq. 21) [47]. These reactions were interpreted

$$RCo(dmgH)Py + PhYYPh \xrightarrow{\text{light}} RYPh + PhYCo(dmgH)Py \quad (21)$$
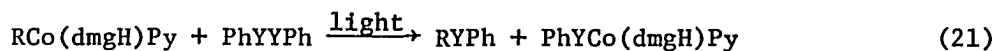
in terms of radical chain processes in which the alkyl radicals attack
via S_H^2 process at the radical precursors to give the mentioned products.

The intermediacy of the alkyl radicals was supported by the formation

of a racemic mixture of sec-octyl phenyl sulfide from both (R)- and

(S)-sec-octylcobaloxime. Also, Δ^5-hexenylbis(dimethylglyoximato)-

(pyridine)cobalt(III) has been reported to undergo a photostimulated

reaction with a limited excess of carbon tetrachloride to afford a

mixture of Δ^5-hexenyl chloride and cyclopentylmethyl chloride [48]. A

radical chain mechanism involved the Δ^5-hexenyl radical as an intermedi-

ate has been postulated to rationalize the formation of the cyclic

product, Scheme XIV. However, in the presence of large excess carbon

Scheme XIV

$$CH_2 = CH(CH_2)_3CH_2Cl$$

$$k_2 \uparrow \ CCl_4$$

$$CH_2 = CH(CH_2)_3CH_2Co(dmgH)Py \xrightarrow{h\nu} CH_2 = CH(CH_2)_3\dot{C}H_2 + Co^{II}(dmgH)Py$$
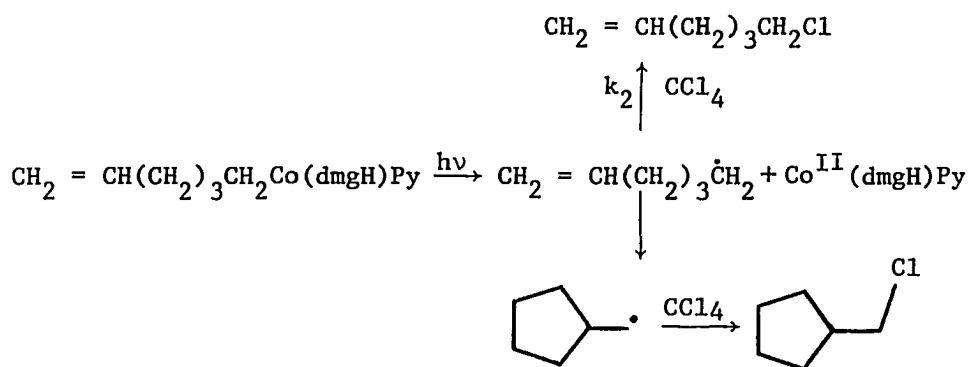
tetrachloride, the main product was tetrachloroheptylcobaloxime(III)

resulted from the radical chain addition of the elements of CCl_4 to the

double bond of the alkenylcobaloxime(III). The tetrachloroheptylco-

baloxime(III) underwent further reaction with CCl_4 to yield 1,1,1,2,7-

pentachloroheptane as the final product [48].

10. Reaction of dialkylmercury with phenyl disulfide

Although a benzene solution of di-n-butylmercury (1 equiv) and

phenyl disulfide (1.2 equiv) did not exhibit any sign of a chemical

reaction when kept in dark at 45°C even after a long period of time,

a facile reaction took place when the solution was irradiated with a

sunlamp positioned 15 cm from the reaction vessel. Di-n-butylmercury

was completely consumed within the first 2.5 hours of the reaction as

revealed by GLC analysis. The same analysis indicated the formation of

two products, which were identified to be n-butyl phenyl sulfide and

n-butylmercury thiophenoxide. The identity of both compounds was veri-

fied by GLC retention time matching with the authentic compounds, and

by GCMS analysis (see experimental section).

The formation of these two products can be explained by a radical

chain process involving the formation of tricovalent mercury intermedi-

ate, **9**. The propagation steps of such a process are outlined in Scheme

XV. This mechanism is similar to the one previously described for the

Scheme XV

$$PhS\cdot + Bu_2Hg \longrightarrow Bu_2HgSPh$$

9

$$\textbf{9} \qquad \longrightarrow Bu\cdot + BuHgSPh$$

$$Bu\cdot + PhSSPh \longrightarrow BuSPh + PhS\cdot$$
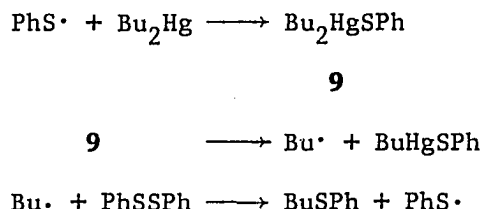
reaction of alkylmercurial salts. A key feature in this mechanism is

the decomposition of intermediate **9** to the alkyl radical and

n-butylmercury theophenoxide followed by S_H^2 attack of the alkyl radical at the phenyl disulfide to give n-butyl pheny sulfide and the thiyl radical which continues the chain. Further irradiation of the reaction mixture resulted in mercury metal precipitation, presumably from the decomposition of n-butylmercury thiophenoxide. At the end of the reaction, n-butyl phenyl sulfide was obtained in an 85% yield (1.7 equiv).

n-Butylmercury thiophenoxide was prepared independently, and was found to decompose slowly under sunlamp irradiation to give n-butyl phenyl sulfide and mercury metal. This photodecomposition might occur by reactions 22 and 23. Moreover, n-butylmercury thiophenoxide was

$$\text{Bu} \cdot + \text{PhSHgBu} \longrightarrow \text{BuSPh} + \text{BuHg} \qquad (22)$$

$$\text{BuHg} \longrightarrow \text{Bu} \cdot + \text{Hg(0)} \qquad (23)$$
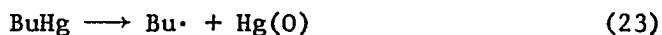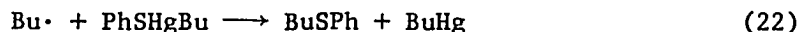
found to react very rapidly with phenyl disulfide to yield n-butyl phenyl sulfide in good yield and a white precipitate of mercury(II) sulfide salt. No mercury metal was formed under these conditions. This reaction can be explained in terms of a radical chain process as shown in Scheme XVI.

Scheme XVI

$$\text{PhS} \cdot + \text{BuHgSPh} \longrightarrow \text{BuHg(SPh)}_2$$

10

$$\textbf{10} \qquad \longrightarrow \text{Bu} \cdot + \text{Hg(SPh)}_2$$

$$\text{Bu} \cdot + \text{PhSSPh} \longrightarrow \text{BuSPh} + \text{PhS} \cdot$$
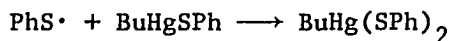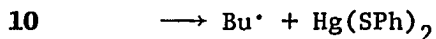
The formation of n-butylmercury thiophenoxide as an intermediate in the reaction of dialkylmercurials with phenyl disulfide can be accounted for by a different chain process, Scheme XVII. This mechanism involves the $S_H{}^2$ attack of the thiyl radical at the α-carbon of the

Scheme XVII

$$R_2Hg + PhS\cdot \xrightarrow{S_H} RSPh + RHg$$

$$RHg + PhSSPh \longrightarrow RHgSPh + PhS\cdot$$
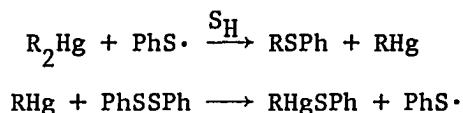
mercurial to give RSPh and RHg. However, this process can be dismissed, since the reaction of di-Δ^5-hexenylmercury showed extensive cyclization to give the cyclopentylcarbinyl derivatives. In addition, thermochemical studies [49] and N.M.R. CIDNP studies [50] showed that RHg is extremely unstable and too short-lived a species to participate effectively in bimolecular processes.

Interestingly, di-n-butylmercury (1 equiv) reacted very rapidly with excess phenyl disulfide (2.5 equiv) to afford a quantitative yield (2 equiv) of n-butyl phenyl sulfide and a white precipitate of mercury(II) sulfide salt, $Hg(SPh)_2$. The fate of the mercury in the reaction of dialkylmercurials with phenyl disulfide clearly depends on the concentration of the latter. Thus, mercury metal was formed with limited amount of the disulfide, whereas the mercury(II) salt was formed when excess phenyl disulfide was used. In the latter case, it seems reasonable that both di-n-butylmercury and n-butylmercury thiophenoxide react according to the chain mechanism shown in Scheme XVIII. The key steps in this mechanism are the decomposition of

Scheme XVIII

$$\text{PhS}\cdot + \text{Bu}_2\text{Hg} \longrightarrow \text{Bu}_2\text{HgSPh}$$

9

$$\textbf{9} \longrightarrow \text{Bu}\cdot + \text{BuHgSPh}$$

$$\text{Bu}\cdot + \text{PhSSPh} \longrightarrow \text{BuSPh} + \text{PhS}\cdot$$

$$\text{PhS}\cdot + \text{BuHgSPh} \longrightarrow \text{BuHg(SPh)}_2$$

10

$$\textbf{10} \longrightarrow \text{Bu}\cdot + \text{Hg(SPh)}_2$$
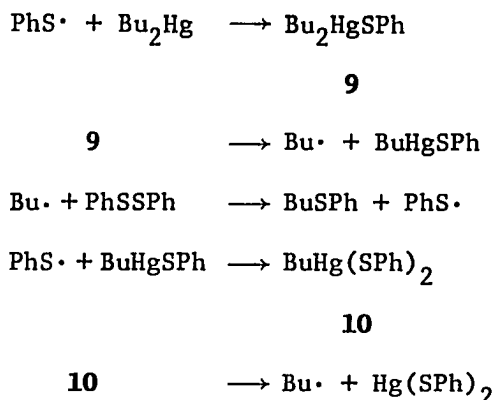
intermediate **9** and **10** to afford the alkyl radicals which attack at the radical precursor to give the sulfide product and the thiyl radical which continues the chain. The S_H2 attack of the alkyl radical occurs at PhSSPh rather than PhSHgBu, possibly because PhSSPh is more reactive. Hence, no mercury metal was formed in the presence of excess phenyl disulfide.

Similar results were observed with other dialkylmercurials. These results are summarized in Table VII. Treatment of di-isobutylmercury (1 equiv) with phenyl disulfide (1.2 equiv) under the influence of a sunlamp irradiation resulted in a 92% yield (1.84 equiv) of isobutyl phenyl sulfide together with mercury metal. However, the use of excess phenyl disulfide (2.5 equiv) resulted in the formation of mercury(II) sulfide salt as a white precipitate besides a 95% yield (1.9 equiv) of isobutyl phenyl sulfide. Also, treatment of di-Δ^5-hexenylmercury (1 equiv) with phenyl disulfide (1.2 equiv) gave mercury metal and a mixture of Δ^5-hexenyl phenyl sulfide and cyclopentylcarbinyl phenyl sulfide in good yield. However, when di-Δ^5-hexenylmercurial was

Table VII. Photochemical reaction of dialkulmercury with phenyl
disulfide

$$R_2Hg + PhSSPh \xrightarrow{\text{light}} 2 \text{ RSPh} + Hg(0) \text{ or } Hg(SPh)_2$$

R	Time (h)	% Yield[a] RSPh
$CH_3CH_2CH_2CH_2$[b]	2.5	100
$CH_3CH_2CH_2CH_2$[c]	21	85
$(CH_3)_2CHCH_2$[b]	2	95
$(CH_3)_2CHCH_2$[c]	12	92
$CH_2=CH(CH_2)_3CH_2$[b]	4	88[d]
$CH_2=CH(CH_2)_3CH_2$[c]	15	83[d]

[a] ^{1}H.N.M.R. yields.

[b] R_2Hg (1 equiv) and PhSSPh (2.5 equiv).

[c] R_2Hg (1 equiv) and PhSSPh (1.2 equiv).

[d] Mixture of $R=\Delta^5$-hexenyl and cyclopentylcarbinyl.

reacted with excess phenyl disulfide (2.5 equiv), a mixture of Δ^5-
hexenyl phenyl sulfide and cyclopentylcarbinyl phenyl sulfide was formed.
In addition, mercury(II) sulfide salt was formed.

Mercurycycloheptane undergoes a facile reaction with phenyl
disulfide (2 equiv) under sunlamp irradiation to afford 1,6-dithiophenoxy-
hexane as the exclusive product. No Δ^5-hexenyl phenyl sulfide or cyclo-
pentylcarbinyl phenyl sulfide was detected. The absence of the last two
products indicates that the reaction occurs through a mechanism different
from that reported for the reaction of mercurycycloheptane with tri-
chloromethyl radical, namely β-elimination leading to the Δ^5-hexenyl

radical [30]. The results are in agreement with those observed for
the reaction of other alkylmercurials or dialkylmercurials with PhSSPh
in that no β-elimination was observed in either case. The formation
of 1,6-dithiophenoxyhexane can be explained by a radical chain
mechanism involving the tricovalent mercury intermediate as presented
in Scheme XIX.

Scheme XIX
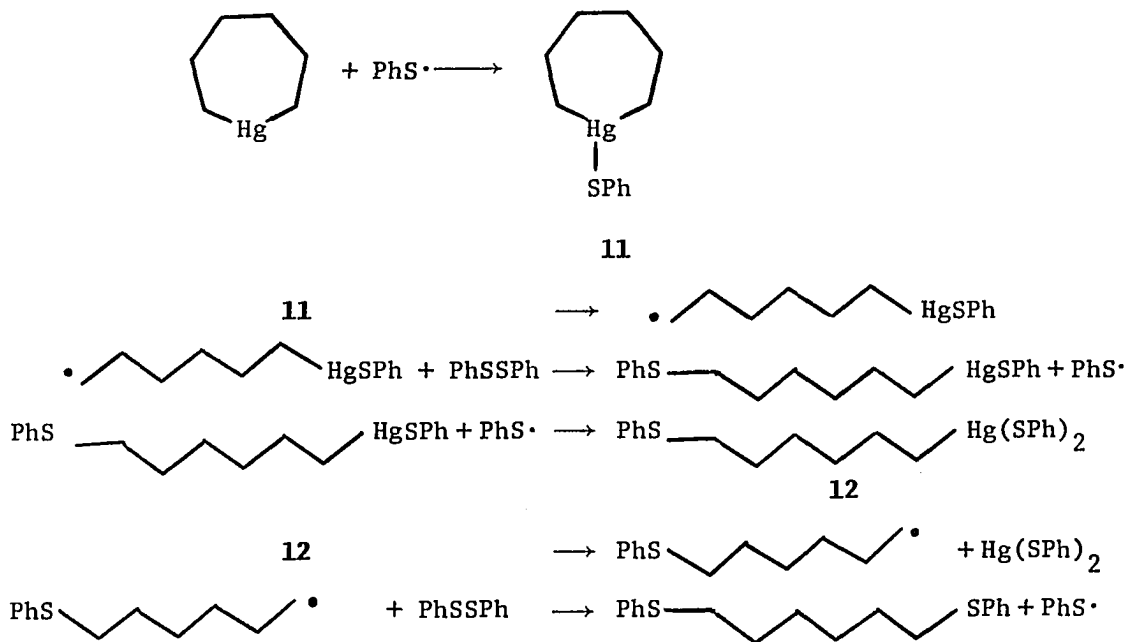
11. Reaction of dialkylmercury with phenyl diselenide

Di-n-butylmercury (1 equiv) and phenyl diselenide (1.2 equiv) under-
went a rapid reaction under sunlamp irradiation. After ca. 1 hour of
irradiation, a pale yellow precipitate, presumably n-butylmercury

selenophenoxide, was formed. GLC analysis at this point revealed n-butyl phenyl selenide to be present in high yield. Further irradiation resulted in dissolution of the solid followed by mercury metal precipitation. Workup consisted of the decantation of the solution from the mercury and the solvent removal in vacuo to yield pure n-butyl phenyl selenide in a 92% yield (1.84 equiv). Excess phenyl diselenide resulted in a faster reaction. Thus, di-n-butylmercury (1 equiv) and phenyl diselenide (2.5 equiv) reacted very rapidly under sunlamp irradiation as evidenced by the formation of a yellow precipitate after less than 10 minutes of irradiation. The precipitate did not dissolve upon further irradiation and was identified to be the mercury(II) selenide salt, $Hg(SePh)_2$ which is reported to be thermally unstable (Eq. 24) [51]. The reaction gave a quantitative yield (2 equiv) of n-butyl phenyl selenide.

$$(PhSe)_2Hg \xrightarrow[\text{reflux}]{\text{dioxane}} PhSeSePh + Hg(0) \qquad (24)$$
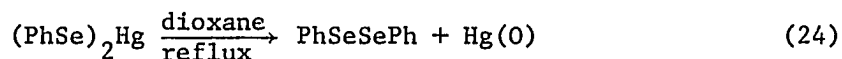
Other dialkylmercurials showed comparable behavior when allowed to react with phenyl diselenide. The results are tabulated in Table VIII. Thus, di-isobutylmercury (1 equiv) and phenyl diselenide (1.2 equiv) underwent a photostimulated reaction under sunlamp irradiation to give a 90% yield (1.8 equiv) of isobutyl phenyl selenide and metallic mercury. Again, the use of excess phenyl diselenide (2.5 equiv) led to a quantitative yield (2 equiv) of isobutyl phenyl selenide and mercury(II) selenide salt. The reaction is faster in the presence of excess phenyl diselenide. With di-Δ^5-hexenylmercury, not only similar results were

Table VIII. Photoreaction of dialkylmercurials with phenyl diselenide

$$R_2Hg + PhSeSePh \xrightarrow[PhH]{light} 2RSePh + Hg(0) \text{ or } Hg(SePh)_2$$

R	Time (h)	% Yield[a] RSePh
$CH_3CH_2CH_2CH_2$[b]	1.5	100
$CH_3CH_2CH_2CH_2$[c]	4	92
$(CH_3)_2CHCH_2$[b]	1.5	100
$(CH_3)_2CHCH_2$[c]	5	90
$CH_2=CH(CH_2)_3CH_2$[b]	1.5	100[d]
$CH_2=CH(CH_2)_3CH_2$[c]	6	95[d]

[a] ^{1}H.N.M.R. yields.

[b] R_2Hg (1 equiv) and PhSeSePh (2.5 equiv).

[c] R_2Hg (1 equiv) and PhSeSePh (1.2 equiv).

[d] Mixture of R = Δ^5-hexenyl and cyclopentylcarbinyl.

obtained, but also the reaction gave a mixture of Δ^5-hexenyl selenide
and cyclopentylcarbinyl phenyl selenide.

The reaction of dialkylmercury with phenyl diselenide shows the
characteristic features of a radical chain process. Not only was the
reaction initiated by light, but the Δ^5-hexenyl moiety showed an ex-
tensive cyclization to the cyclopentylcarbinyl derivative, which requires
the intermediacy of the Δ^5-hexenyl radical. Mechanistically, it is
believed that the reaction proceeds through a chain process similar
to the one previously discussed for phenyl disulfide and shown in Scheme
XVIII.

It is worth noting that alkyl phenyl selenides and alkyl phenyl

tellurides are reported to be the products of the thermal reaction of

dialkylmercurials with phenyl diselenide or phenyl ditelluride (Eq.

25) [51]. However, the authors did not mention the mechanistic aspects

$$R_2Hg + PhYYPh \xrightarrow[\text{reflux}]{\text{dioxane}} 2RYPh + Hg(0) \tag{25}$$

$$Y = Se, Te \quad .$$
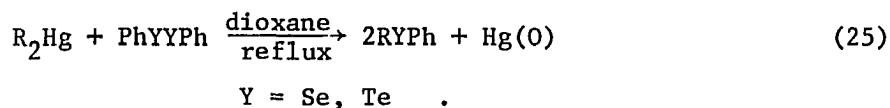
of this reaction.

12. Reaction of benzylmercurials with phenyl disulfide, phenyl diselenide and phenyl ditelluride

Benzylmercury chloride and phenyl disulfide were found to undergo

a photostimulated reaction under sunlamp irradiation to afford bibenzyl

as the main product together with a small amount of benzyl phenyl sulfide

(see Table IX). The reaction failed to proceed in the dark, while it

was inhibited by 7 mole.% of di-tert-butyl nitroxide for an extended

period of time. Similarly, a rapid photostimulated reaction occurred

between benzylmercury chloride and phenyl diselenide. However, the

prime product of this reaction was found to be benzyl phenyl selenide,

whereas bibenzyl was formed in only a small amount. Essentially, the

same results were obtained for the reaction of benzylmercury chloride

and Se-phenyl p-tolylselenosulfonate (see Table IX). On the other hand,

the reaction of benzylmercury chloride with phenyl ditelluride afforded

benzyl phenyl telluride as the exclusive product. No bibenzyl was

formed.

Dibenzylmercury undergoes a facile photostimulated decomposition

Table IX. Photoreaction of benzylmercurials with phenyl disulfide,
phenyl diselenide and phenyl ditelluride

$$PhCH_2HgX + QY \xrightarrow{\text{light}} PhCH_2Y + PhCH_2CH_2Ph + Hg(0)$$

X	QY	Time (h)	% Yield[a] $PhCH_2Y$
Cl	PhSSPh	4	15 (66)[b]
Cl	PhSeSePh	2	72 (7)[b]
Cl	PhTeTePh	1	80 (0)[b]
Cl	p-MePhSO$_2$SePh	6	68 (5)[b]
$PhCH_2$	PhSSPh	6	8 (72)[b]
$PhCH_2$	PhTeTePh	1	100 (0)[b]
$PhCH_2$	--	21[c]	(82)[b]
SPh	--	6[c]	--[d] (85)[b]

[a]^{1}H.N.M.R. yields.

[b]Yield of bibenzyl.

[c]Irradiation in Rayonet photoreactor at 350 nm.

[d]Trace of benzyl phenyl sulfide was detected.

under UV (350 nm) irradiation to give bibenzyl and mercury metal. The

decomposition did not proceed in the dark and was inhibited by 10 mole %

di-tert-butyl nitroxide. Although benzylmercury chloride did not under-

go photostimulated decomposition, bibenzyl is reported to be the product

of this reaction in the presence of anions (A$^-$), such as $(EtO)_2PO^-$ and

NO_2^- (Eq. 26) [46]. It is believed that anions A$^-$ promote the

$$PhCH_2HgCl \xrightarrow[h\nu]{A^-/DMSO} PhCH_2CH_2Ph + Hg(0) + X^- \qquad (26)$$
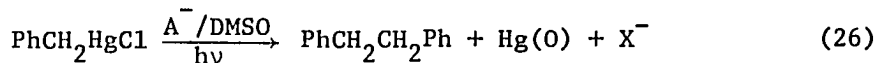
symmetrization of benzylmercury chloride to dibenzylmercurial which in turn photodecomposed to bibenzyl and mercury metal [46]. Benzylmercury thiphenoxide was found to decompose under UV irradiation to give bibenzyl, mercury(II) sulfide salt and mercury metal.

A photostimulated reaction occurred between dibenzylmercury and phenyl disulfide (2 equiv) when the reaction mixture irradiated with a sunlamp. Bibenzyl was obtained as the primary product in a 72% yield, while benzyl phenyl sulfide was formed in only 8% yield. In dramatic contrast, the photoreaction of dibenzylmercury with phenyl ditelluride (2 equiv) yielded benzyl phenyl telluride as the sole product. The formation of bibenzyl was completely suppressed.

The results presented above clearly indicate that the reactions of benzylmercurials took a somewhat different course than the reactions of other $1°$-alkylmercurials in that significant yields of bibenzyl were often observed. Bibenzyl must be formed by a radical chain process, not only because the reactions were induced by light, but also because they were significantly inhibited by di-_tert_-butyl nitroxide. Bibenzyl could be formed in these reactions by the S_H2 attack of the benzyl radical at the α-carbon of the mercurial (Eq. 27) or by the decomposition of the tricovalent mercury intermediate $(PhCH_2)_2HgQ$, **13** (Eq. 28) (Q = $PhCH_2$, Cl, PhS, PhSe, PhTe) directly to bibenzyl and HgQ which will

$$PhCH_2\cdot + PhCH_2HgQ \xrightarrow{\text{S}_H2} PhCH_2CH_2Ph + HgQ \qquad (27)$$

$$(PhCH_2)_2HgQ \longrightarrow PhCH_2CH_2Ph + HgQ \qquad (28)$$
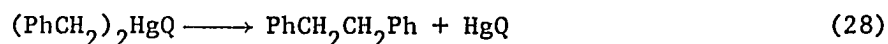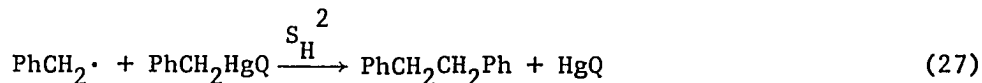
continue the chain. The mechanistic distinction between these two

alternatives was accomplished by comparing the results of the reaction

of dibenzylmercurial with phenyl disulfide and phenyl ditelluride.

The fact that the photostimulated reaction of dibenzylmercurial with

phenyl ditelluride gave exclusively benzyl phenyl telluride and

mercury(II) telluride salt led to the conclusion that intermediate 13

decomposes to the benzyl radical and not directly to the bibenzyl.

The benzyl radical is then effectively trapped by PhTeTePh via S_H^2

attack at the ditelluride (Eq. 29). S_H^2 attack of PhTe· at the benzyl

$$PhCH_2· + PhYYPh \longrightarrow PhCh_2YPh + PhY· \qquad (29)$$
$$Y = S, Te$$
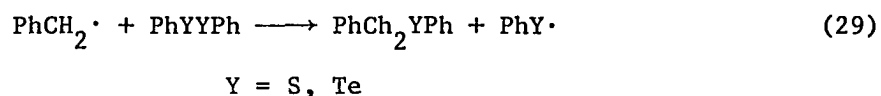
carbon of the mercurial or decomposition of intermediate 13 directly to

$PhTeCH_2Ph$ were dismissed because of the cyclization observed in the

reaction of Δ^5-hexenylmercury chloride with PhYYPh. With PhSSPh, a

poorer trap for the benzyl radical than PhTeTePh, the major product was

bibenzyl. Thus, it can be concluded that bibenzyl is formed by S_H^2

attack of the benzyl radical at the benzyl position of the mercurial

with $k_{27} > k_{29}$ for Y = S, but $k_{27} < k_{29}$ for Y = Te.

Scheme XX outlines a general radical chain mechanism for the reac-

tion of benzylmercurials with phenyl dichalcogenide. A key step in this

mechanism is the S_H^2 attack of the alkyl radical at the α-carbon of the

benzylmercurial to afford bibenzyl and another radical which continues

the chain.

The S_H^2 attack of the benzyl radical on the α-carbon of the

<u>Scheme XX</u>   (Q = PhCH$_2$, Cl, PhY; Y = S, Se, Te)

$$PhCH_2\cdot \; + \; PhCH_2HgQ \xrightarrow{S_H^2} PhCH_2CH_2Ph \; + \; HgQ$$

$$PhCH_2\cdot \; + \; PhYYPh \longrightarrow PhCH_2YPh \; + \; PhY\cdot$$

$$HgQ(Q=PhCH_2, \; PhY) \longrightarrow Q\cdot \; + \; Hg(0)$$

$$HgQ \; + \; PhYYPh \longrightarrow PhYHgQ \; + \; PhY\cdot$$

$$PhY\cdot \; + \; PhCH_2HgQ \longrightarrow PhCH_2HgQ(YPh)$$

$$PhCH_2HgQ(YPh) \longrightarrow PhCH_2\dot{} \; + \; QHgYPh$$
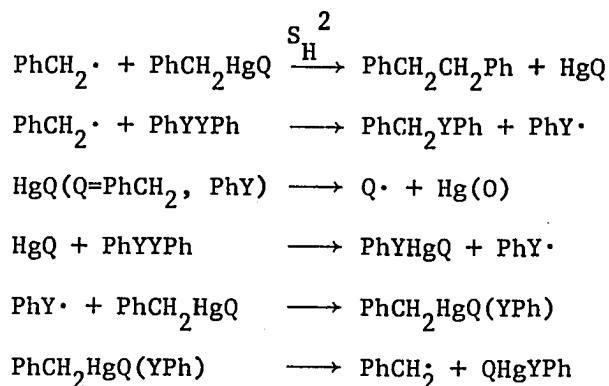
mercurials furnished an interesting example of S_H^2 displacement at sp^3 hybridized carbon. Despite the fact that the S_H^2 substitution reactions at sp^3 hybridized carbon are rare [52], recently Funabiki and co-workers have shown that cobaloxime(II) complexes are potential leaving groups in some S_H^2 processes involving displacement at saturated carbon [53]. Thus, benzylcobaloxime complex was found to react with trichloromethyl radical thermally or photochemically to give good yield of trichloro-ethylbenzene (Eq. 30). The reaction is believed to involve a radical

$$[PhCH_2Co(dmgH)_2 \; (imid)] \; + \; \cdot CCl_3 \xrightarrow{S_H^2} PhCH_2CCl_3 + [Co^{II}(dmgH)(imid)]$$

(30)
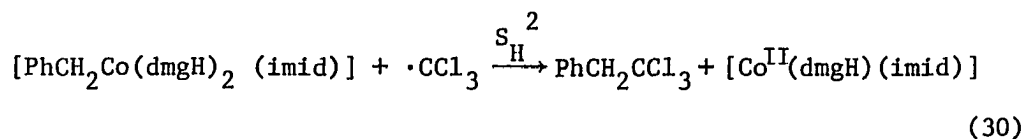
imidH = imidazole; dmgH = dimethylglyoximate

chain process in which a key step is the S_H^2 attack of trichloromethyl radical at the α-carbon [53]. Similarly, ally and substituted allyl-cobaloximes react with trichloromethyl radical and arylsulfonyl radi-cals via $S_H^{2'}$ mechanism to give the corresponding rearranged allyl

derivatives (Eq. 31, 32) [54-56]. More recently, the same workers have

$$\cdot CCl_3 + R_1R_2 = CHCH_2Co(dmgH)_2Py \xrightarrow{S_H^{2'}} CCl_3-CR_1R_2CH = CH_2 + [Co^{II}(dmgH)_2Py] \quad (31)$$

$$ArSO_2\cdot + R_1R_2C = CHCH_2Co(dmgH)_2Py \xrightarrow{S_H^{2'}} ArSO_2-CR_1R_2RCH = CH_2 + [Co^{II}(dmgH)Py] \quad (32)$$
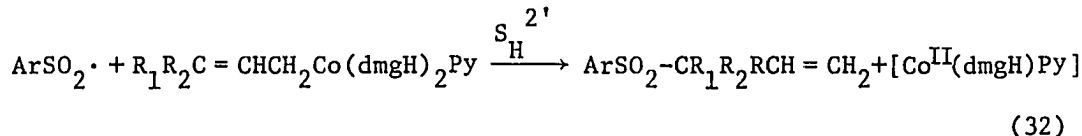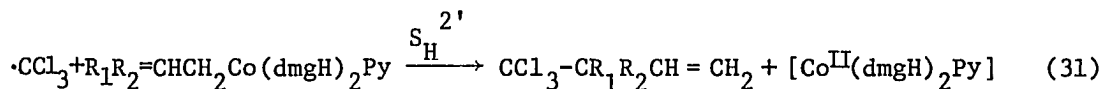
shown that the cobaloxime complexes can participate in an intramolecular

homolytic substitution reactions, S_H^i at sp^3 hybridized carbon [37, 57].

Thus, Δ^3-butenylcobaloxime(III) complexes react with carbon- or sulfur-

centered radicals to give the cyclopropyl derivatives (Eq. 33, 34).

$$CH_2=CHCH_2CH_2Co(dmgH)_2Py + \cdot CCl_3 \xrightarrow{S_H^i} \text{[cyclopropyl-}CCl_3\text{]} + [Co^{II}(dmgH)_2Py] \quad (33)$$

$$CH_2=CHCH_2CH_2Co(dmgH)_2Py + ArSO_2\cdot \xrightarrow{S_H^i} \text{[cyclopropyl-}SO_2Ar\text{]} + [Co^{II}(dmgH)_2Py] \quad (34)$$
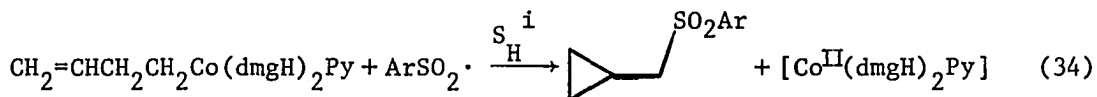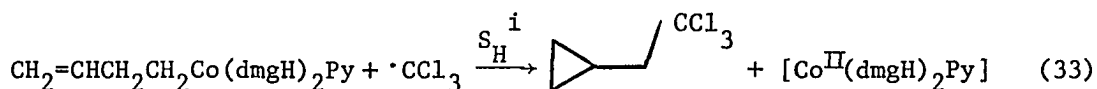
The reaction proceeds via a chain process in which one of the propagation

steps involve a homolytic attack of the carbon- or sulfur-centered

radicals at δ-carbon of the butenyl ligand followed by synchronous or

subsequent attack of the incipient γ-carbon radical on the α-carbon,

causing cyclization and displacement of cobaloxime(II) complex. Since

the analogous process was not observed with Δ^3-butenylmercury chloride

in reaction with $PhSeSO_2C_6H_4Me$-$\underline{p}$, a process demonstrated to include $\underline{p}$-

$MeC_6H_4SO_2\cdot$ as an intermediate, it follows that either the carbon-carbon

double bond of the Δ^3-butenylcobaloxime(III) complex is much more reactive

towards $ArSO_2^-$ than the double bond of Δ^3-butenylmercury chloride or the

mercury atom of RHgCl is much more reactive than the cobalt atom of an

organocobaloxime complex. It seems most reasonable that the latter explanation is correct.

C. Conclusion

Alkylmercury halides (RHgX, R = n-butyl, n-hexyl, Δ^3-butenyl, Δ^5-hexenyl, isopropyl, cyclohexyl, cyclopentylcarbinyl and 7-norbornyl) rapidly react under the influence of ordinary sunlamp irradiation with PhSSPh, PhSeSePh, PhTeTePh, p-MeC$_6$H$_4$SO$_2$SePh, PhSO$_2$Cl and PhSH to afford respectively, RSPh, RSePh, RTePh, RCl and RH in good yields. Mechanistically, the reactions have been shown to proceed by free radical chain processes involving alkyl radicals. Evidence to support this mechanism includes the facts that the reactions fail to proceed in the dark but can be initiated either photochemically or by the thermolysis of AIBN. The reactions are completely inhibited by di-tert-butyl nitroxide. Moreover, Δ^5-hexenylmercury chloride exhibits cyclization to yield the cyclopentylcarbinyl derivatives, which requires the intermediacy of the Δ^5-hexenyl radical. Further evidence for the radical intermediates in this reaction comes from the observation that the reaction of RHgX with the unsymmetrical radical precursors, such as PhSO$_2$Cl or p-MePhSO$_2$SePh gives RCl and RSePh, respectively, as the sole products.

Dialkylmercurials (R$_2$Hg, R = n-butyl, isobutyl and Δ^5-hexenyl) readily react with PhSSPh and PhSeSePh under sunlamp irradiation to give RSPh and RSePh. The reaction is inhibited by di-tert-butyl nitroxide. The mercurial side product of this reaction is either mercury metal or mercury(II) salts depending on the concentration of the phenyl dichalcogenide. Free radical chain mechanism involving R· and

Hg(III) intermediate has been proposed for this reaction.

Benzylmercurials ($PhCH_2HgQ$, Q = Cl and $PhCH_2$) have been found to react with PhSSPh, PhSeSePh and PhTeTePh somewhat differently from other 1°-alkylmercurials, in that bibenzyl is formed in the reactions of benzylmercurials, and in some cases is the main product. Bibenzyl is also the product of the photostimulated decomposition of dibenzyl-mercurial and benzylmercury thiophenoxide. Based on experimental evidence, a chain mechanism involving S_H2 attack of the benzyl radical on the benzyl mercury bond has been postulated.

Synthetically, the described reactions of RHgX and R_2Hg provide a convenient method for the preparation of alkyl phenyl sulfides, alkyl phenyl selenides and alkyl phenyl tellurides in good yields. The reactions can be carried out under neutral conditions and at room temperature. Alkyl phenyl sulfides are usually prepared by the reaction of benzene thiol with the alkyl halides under alkaline conditions, or by the addition of PhSH to olefins [58]. Thus, the reaction of RHgX or R_2Hg with PhSSPh complements these existing methods. Alkyl phenyl selenides or tellurides can be prepared using methods similar to those used in the preparation of organic sulfides [59]. However, there is some limitation since selenide and telluride anions are easily oxidized by air to the corresponding diselenide and ditelluride. Thus, the reaction of RHgX or R_2Hg with PhSeSePh and PhTeTePh seems to be more convenient method for the preparation of RSePh and RTePh. Furthermore, the formation of neopentyl (and perhaps tert-alkyl) sulfides, selenides, and tellurides occurs readily in these free radical chain processes.

D. Experimental Section

1. General considerations

All melting points were determined on a Thomas-Hoover capillary

melting point apparatus and are uncorrected. Analytical gas chromatog-

raphy (GLC) was performed on a Varian 3700 gas chromatograph with an

attached Hewlett-Packard 3390A data system. G.C. mass spectra (GCMS)

were recorded on a Finnegan 4000 data system. High resolution mass

spectra (MS) were recorded on an AEI MS 902 mass spectrometer. [1]H.N.M.R.

spectra (60 MHz) were recorded on a Varian EM 360A, or a Hitachi-Perkin

Elmer R-20B instrument in $CDCl_3$ or C_6D_6 with tetramethylsilane (TMS) as the

internal standard. [1]H.N.M.R. yields were determined by integrated com-

parison with a known amount of an appropriate reference (usually CH_2Br_2).

Solvents were purchased from Fisher or Baker. Dimethyl sulfoxide

(DMSO) and benzene were distilled from calcium hydride before use and

stored over 4A molecular sieves under nitrogen. Tetrahydrofuran (THF) was

distilled from lithium aluminum hydride before use and stored over 4A

molecular sieves.

Phenyl disulfide, benzyl disulfide, n-butyl disulfide, isopropyl

disulfide and tert-butyl disulfide were purchased from Aldrich Chemical

Co. Phenyl diselenide, benzenesulfonyl chloride, bromotrichloromethane

and phenylboric acid were also products of Aldrich. Benzenethiol was

product of Eastman Organic. Phenyl ditelluride [60], and Se-phenyl p-

tolylselenosulfonate [61] were prepared by literature methods.

2. Preparation of organic mercury compounds

Alkylmercury halides were prepared in the usual manner [2] by treating the Grignard reagent in THF with slight excess of the appropriate mercury halide. Thus prepared were benzylmercury chloride [62], Δ^5-hexenylmercury chloride [63], n-hexylmercury chloride [64], isopropylmercury chloride [65] and cyclohexylmercury chloride [66]. The alkylmercurial salts were purified by crystallization from ethanol. Symmetrical dialkylmercurials were prepared by the method of Gilman and Brown [67]. Thus prepared were di-n-butylmercury [68], di-isobutyl-mercury [69] and di-Δ^5-hexenylmercury [20]. The asymmetrical mercurial, n-butylphenylmercury was obtained by the interaction of n-butylmercury chloride and phenylboric acid [70]. Mercurycycloheptane was prepared from the reaction of 1,6-dibromohexane with sodium amalgam [71]. Benzylmercury thiophenoxide [72] and phenylmercury phenylsulfinate [73] were obtained following published procedures. Other organomercurials employed in were prepared by Dr. J. Hershberger.

3. General procedure for the photoreaction of alkylmercury halides with phenyl disulfide

Alkylmercury halide (1.0 mmol) and phenyl disulfide (1.2 mmol) were dissolved in 10 ml of benzene in a Pyrex flask equipped with a magnetic stirring bar and rubber septum. After a nitrogen purge, the reaction mixture was irradiated for several hours with a 275 W sunlamp placed 15 cm from the reaction vessel. During the reaction, a white precipitate had formed. After the reaction completion, the precipitate was filtered. The solvent removal from the filtrate under reduced pressure gave a light

yellow oil containing a little of the white solid chloromercury

thiophenoxide salt. The oily residue was dissolved with hexane and

filtered to remove the solid contaminant. The hexane was evaporated

in vacuo to give an oil. GLC and ^{1}H.N.M.R. analysis revealed alkyl

phenyl sulfides as the exclusive products. The products were further

identified by GCMS analysis. The yield of products and reaction times

are given in Table I. The GCMS and ^{1}H.N.M.R. data of alkyl phenyl

sulfides are given in Table X.

4. Dark reaction of Δ^3-butenylmercury chloride
   with phenyl disulfide

Δ^3-Butenylmercury chloride (0.292 g, 1.0 mmol) and phenyl disulfide

(0.261 g, 1.2 mmol) were dissolved in 10 ml of benzene under a nitrogen

atmosphere. The flask was tightly wrapped with aluminum foil to exclude

light. After stirring the reaction mixture for 6.5 h at 50°C, the

solvent was removed under vacuum. GLC analysis of the crude isolate

indicated that no Δ^3-butenyl phenyl sulfide was formed. The unchanged

starting materials were recovered.

5. Effect of di-tert-butyl nitroxide on the photoreaction between
   Δ^3-butenylmercury chloride and phenyl disulfide

Δ^3-Butenylmercury chloride (0.292 g, 1.0 mmol), phenyl disulfide

(0.261 g, 1.2 mmol) and di-tert-butyl nitroxide (13 mg, 0.1 mmol) were

dissolved in 10 ml of nitrogen-purged benzene in a Pyrex flask. The

solution was irradiated with a sunlamp for 4 h, during which time no

precipitate was formed. The solvent was removed under vacuum and the

crude residue was analyzed by GLC which showed that Δ^3-butenyl phenyl

Table X. GCMS and [1]H.N.M.R. data of alkyl phenyl sulfides, RSPh

R	GCMS m/e (relative intensity)	[1]H.N.M.R.[a] δ (ppm)
$CH_2=CHCH_2CH_2$	166 (1.7), 164 (37, M+), 123 (100), 110 (18).	7.4-7.0 (m, 5H), 5.7-5.42 (m, 1H), 5.15-4.8 (m, 2H), 2.85-2.6 (m, 2H), 2.13-2.15 (m, 2H).
$CH_3(CH_2)_4CH_2$	196 (7), 194 (21, M+), 123 (17), 110 (100).	7.45-7.0 (m, 5H), 2.71 (t, 2H, J=6.5 Hz), 1.7-0.8 (m, 11H).[b]
$(CH_3)_3CCH_2$	182 (2), 180 (47, M+), 124 (83), 110 (50), 57 (100).	7.4-7.0 (m, 5H), 2.65 (s, 2H) 0.93 (s, 9H).[b]
$(CH_3)_2CH$	154 (2.3), 152 (50, M+), 110 (100.	7.4-7.1 (m, 5H), 3.02 (septet, 1H, J = 6 Hz), 1.1 (d, 6H, J = 6.5 Hz).[b]
Cyclo-$C_5H_9CH_2$	194 (1), 192 (22, M+), 123 (12), 110 (100).	7.5-7.0 (m, 5H), 2.85 (d, 2H, J = 6.5 Hz), 2.1-1.1 (m, 9H).
Cyclo-C_6H_{11}	194 (7), 192 (20, M+), 110 (100), 56 (66).	7.5-7.1 (m, 5H), 3.2-2.78 (m, 1H), 1.7-0.9 (m, 10H).
7-norbornyl	206 (3.7), 204 (76, M+), 110 (73), 95 (94), 67 (100).	
$CH_2=CH(CH_2)_3CH_2$	194 (1), 192 (22, M+), 123 (49), 110 (100).	7.45-7.05 (m, 5H), 5.95-5.4 (m, 1H), 5.1-4.8 (m, 2H), 2.9 (t, 2H, J = 6.5 Hz), 1.9-0.9 (m, 6H).
$CH_3(CH_2)_2CH_2$	168 (1.8), 166 (39, M+), 123 (22), 110 (100).	7.5-7.15 (m, 5H), 3.01 (5, 2H, J = 6 Hz), 1.8-0.7 (m, 7H).
$(CH_3)_2CHCH_2$	168 (2.1), 166 (47, M+), 123 (46), 110 (100).	7.5-7.1 (m, 5H), 2.85 (d, 2H, J = 7 Hz), 2.3-1.8 (m, 1H), 1.15 (d, 6H, J = 7 Hz).
$PhCH_2$	202 (0.6), 200 (12, M+), 91 (100).	7.6-7 (m, 5H), 4.1 (s, 2H).

[a]$CDCl_3$ solutions unless otherwise mentioned.

[b]C_6D_6 solutions.

sulfide was not formed. The starting materials were recovered un-
changed.

6. Thermal reaction of Δ^3-butenylmercury chloride with phenyl
   disulfide in the presence of AIBN

Δ^3-Butenylmercury chloride (1.46 g, 5.0 mmol), phenyl disulfide

(1.308 g, 6.0 mmol) and azobisisobutyronitril (AIBN) (0.08 g, 0.5 mmol)

were dissolved in 30 ml of benzene under a nitrogen atmosphere. The

flask was wrapped with aluminum foil to exclude light. The reaction

vessel was immersed in an oil bath at temperature of 80°C. The reaction

mixture was heated for 10 h during which time a white precipitate was

formed. Workup as previously described for the photoreaction yielded

Δ^3-butenyl phenyl sulfide in an 86% yield as determined by ^{1}H.N.M.R.

Distillation gave the sulfide as a colorless oil in a 64% yield, b.p. =

81-83°C (1.2 mm); lit. [74] b.p. = 85.5-86.5 (1.5 mm).

7. Photoreaction of Δ^5-hexenylmercury chloride
   with phenyl disulfide

Δ^5-Hexenylmercury chloride (0.96 g, 3 mmol) and phenyl disulfide

(2.62 g, 12 mmol) were dissolved in 20 ml of nitrogen-purged benzene in

a Pyrex flask. The solution was irradiated with a sunlamp for 8 h dur-

ing which time a large amount of white precipitate was formed. Workup

as previously described afforded an oily residue. Analysis by GLC

showed that the residue contained a mixture of two isomeric alkyl phenyl

sulfides together with phenyl disulfide. The two sulfides were identi-

fied to be Δ^5-hexenyl phenyl sulfide and cyclopentylcarbinyl phenyl

sulfide. The two sulfides were separated by preparative GLC on a 15%

OV-3 on Chromosorb W column (10'x1/8"). The ratio of the two isomers
was determined by quantitative GLC as being 31.3% Δ^5-hexenyl phenyl
sulfide and 67.8% cyclopentylcarbinyl phenyl sulfide. Octadecane was
used as an internal standard.

8. Photoreaction of Δ^3-butenylmercury chloride with n-butyl disulfide

Δ^3-Butenylmercury chloride (0.292 g, 1.0 mmol) and n-butyl disulfide
(0.214 g, 1.2 mmol) were dissolved in 10 ml of benzene. After a nitrogen
purge, the solution was irradiated in the Rayonet photoreactor (350 nm) for
20 h during which time a white precipitate was formed. The usual work-
up gave an oily residue. Quantitative GLC analysis revealed a 60% yield
of n-butyl Δ^3-butenyl sulfide. The identity of the product was verified
by GLC (10'x1/8", 15% OV-3, 100-280°/15°C) retention time matching of an
authentic sample.

GCMS, m/e (relative intensity) 146 (0.16), 144 (2, M+), 103 (13),
88 (24), 61 (100).

9. Photoreaction of Δ^3-butenylmercury chloride with isopropyl disulfide

Δ^3-Butenylmercury chloride (0.292 g, 1.0 mmol) and isopropyl
disulfide (0.187 g, 1.2 mmol) were dissolved in nitrogen-purged benzene.
The mixture was irradiated in the Rayonet photoreactor at 350 nm. Only
a small amount of white precipitate was formed. After 24 h of irradia-
tion, the solution was washed with 20 ml of 15% sodium thiosulfate solu-
tion to remove the unreacted mercury compounds. The organic layer was
dried over $MgSO_4$, then the solvent was removed in vacuo to give a light

yellow oil. Quantitative GLC analysis indicated that the residue con-
sisted mainly of unchanged isopropyl disulfide, whereas isopropyl Δ^3-
butenyl sulfide was formed only in ca. 10% yield.

GCMS, m/e (relative intensity) 132 (0.3), 130 (6.4, M$^+$), 89 (90),
55 (100).

10. Photoreaction of Δ^3-butenylmercury chloride with tert-butyl disulfide

Δ^3-Butenylmercury chloride (0.292 g, 1.0 mmol) and tert-butyl
disulfide (0.214 g, 1.2 mmol) were dissolved in 10 ml of benzene under
a nitrogen atmosphere. The solution was irradiated in the Rayonet
reactor at 350 nm. After 24 h, no precipitate was formed. Workup as
discussed above gave an oily residue. GLC analysis of the residue re-
vealed only tert-butyl disulfide. No Δ^3-butenyl tert-butyl sulfide was
detected.

11. Photoreaction of Δ^3-butenylmercury chloride with benzyl disulfide

Δ^3-Butenylmercury chloride (0.292 g, 1.0 mmol) and benzyl disulfide
(0.295 g, 1.2 mmol) were dissolved in 10 ml of benzene. After a nitrogen
purge, the solution was irradiated for 24 h with a sunlamp positioned
15 cm from the reaction vessel. No precipitate was formed. The usual
workup yielded a solid residue, which was found by GLC analysis to
contain benzyl disulfide only. No benzyl Δ^3-butenyl sulfide was ob-
served. Similarly, 19 h irradiation in the Rayonet reactor at 350 nm
failed to initiate the above reaction.

12. Photoreaction of cyclopropylmercury bromide
    with phenyl disulfide

Cyclopropylmercury bromide (0.32 g, 1.0 mmol) and phenyl disulfide

(0.261 g, 1.2 mmol) were dissolved in 10 ml of nitrogen-purged DMSO.

The reaction mixture was irradiated in the Rayonet photoreactor at 350

nm for 15 h. The reaction mixture was poured into 50 ml of 20% brine

solution containing 1 g of sodium thiosulfate to remove the unreacted

cyclopropylmercurial. The resulting solution was extracted with 25 ml

of benzene and the extract was dried over $MgSO_4$. The benzene was re-

moved under reduced pressure to give a light yellow oil. GLC analysis

showed that the oil contained exclusively phenyl disulfide. No alkyl

phenyl sulfide was detected.

13. Photoreaction of allylmercury chloride with
    phenyl disulfide

Allylmercury chloride (0.276 g, 1.0 mmol) and phenyl disulfide

(0.261 g, 1.2 mmol) were dissolved in 10 ml of nitrogen-purged benzene.

The solution was irradiated with a sunlamp for 18 h during which time

a small amount of white precipitate was formed. Normal workup afforded

a 30% yield of allyl phenyl sulfide as determined by quantitative GLC.

The identity of allyl phenyl sulfide was confirmed by GLC (10'x1/8",

15% OV-3, 100°C) retention time matching with an authentic sample.

14. Photoreaction of phenylmercury iodide
    with phenyl disulfide

Phenylmercury iodide (0.404 g, 1.0 mmol) and phenyl disulfide (0.261

g, 1.2 mmol) were dissolved in 15 ml of DMSO under a nitrogen atmosphere.

The solution was irradiated in the Rayonet reactor at 350 nm for 15 hr.

Workup as described above resulted in an oily residue. GLC analysis

revealed phenyl disulfide. No diphenyl sulfide was detected.

15. Photodecomposition of phenylmercury thiophenoxide

Phenylmercury thiophenoxide (1.0 g, 2.6 mmol) in 20 ml of nitrogen-

purged DMSO was irradiated in the Rayonet photoreactor at 350 nm for 24

h, during which time a trace of mercury metal precipitated. Workup as

previously described afforded a solid residue which was shown by GLC

analysis to contain no diphenyl sulfide.

16. Photoreaction of phenylmercury thiophenoxide
    and phenyl disulfide

Phenylmercury thiophenoxide (0.386 g, 1.0 mmol) and phenyl disulfide

(0.261 g, 1.2 mmol) were dissolved in 15 ml of DMSO. After a nitrogen

purge, the solution was irradiated in the Rayonet reactor at 350 nm for

24 h. Workup afforded an oily residue, which was shown by GLC analysis

to contain only phenyl disulfide. No diphenyl sulfide was observed.

17. Photoreaction of phenylmercury thiophenoxide
    with isopropylmercury chloride

Phenylmercury thiophenoxide (0.772 g, 2.0 mmol) and isopropylmercury

chloride (0.69 g, 2.5 mmol) were dissolved in 20 ml of DMSO under a

nitrogen atmosphere. The reaction mixture was irradiated with a sunlamp

for 12 h. A trace of mercury metal precipitated. The usual workup gave

a light yellow oil, which was shown by GLC to contain a mixture of

isopropyl phenyl sulfide and isopropylbenzene in a 4:1 ratio and an

overall yield of 59%. The presence of the two compounds was verified

by GLC (10'x1/8", 15 OV-3, 80-280°C/10°C) retention time matching with

the authentic compounds.

18. General procedure for the photoreaction of alkylmercurials
    with phenyl diselenide

Alkylmercury halide (1.0 mmol) and phenyl diselenide (1.2 mmol)

were dissolved in 10 ml of benzene. After a nitrogen purge, the solu-

tion was irradiated with a 275 W sunlamp for few hours during which time

a pale yellow precipitate was formed. When the reaction was complete,

the precipitate was filtered and the solvent was removed under vacuum

to afford a light yellow oil. The oil was shown by GLC and ^{1}H.N.M.R.

analysis to consist exclusively of alkyl phenyl selenides. The

products were further identified by GCMS analysis. The results are

tabulated in Table II. The GCMS and ^{1}H.N.M.R. data are summarized in

Table XI.

19. Dark reaction between isopropylmercury chloride
    and phenyl diselenide

Isopropylmercury chloride (0.278 g, 1.0 mmol) and phenyl diselenide

(0.377 g, 1.2 mmol) were dissolved in 10 ml of nitrogen-purged benzene.

The reaction flask was wrapped with aluminum foil to exclude light.

After stirring the reaction at 50°C for 6 h, the solvent was removed

under reduced pressure. GLC and ^{1}H.N.M.R. analysis of the crude isolate

revealed unchanged starting materials. No alkyl phenyl selenide was

formed.

Table XI. GCMS and [1]H.N.M.R. data for alkyl phenyl selenides, RSePh

R	GCMS[a] m/e (relative intensity)	[1]H.N.M.R.[b] δ (ppm)
$CH_2=CHCH_2CH_2$	212 (17, M[+]), 158 (21), 55 (100).	7.45-6.95 (m, 5H), 5.9-5.3 (m, 1HO, 5.1-4.75 (m, 2H), 2.8-2.4 (m, 2H), 2.3-2.1 (m, 2H).[c]
$CH_3(CH_2)_4CH_2$	242 (21, M[+]), 158 (100), 78 (65).	7.6-7.1 (m, 5H), 2.9 (5, 2H, J = 6.5 Hz), 1.9-0.7 (m, 11H).
$(CH_3)_3CCH_2$	228 (15, M[+]), 158 (35), 71 (100).	7.45-6.9 (m, 5H), 2.75 (s, 2H), 0.9 (5, 9H).[c]
$(CH_3)_2CH$	200 (21, M[+]), 158 (61), 78 (100).	7.7-7.1 (m, 5H), 3.42 (septet, 1H, J = 6 Hz), 1.33 (d, 6H, J = 6 Hz).
Cyclo-$C_5H_9CH_2$	240 (6, M[+]), 158 (31), 83 (38), 55 (100).	7.4-6.85 (m, 5H), 2.75 (d, 2H, J = 6.5 Hz), 1.8-0.9 (m, 9H).[c]
Cyclo-C_6H_{11}	240 (6, M[+]), 158 (44), 83 (27), 55 (100).	7.65-7.1 (m, 5H), 3.5-3.0 (m, 1H), 2.2-0.9 (m, 10H).
$CH_2=CH(CH_2)_3CH_2$	240 (7, M[+]), 158 (25), 83 (43), 55 (100).	7.65-7.1 (m, 5H), 5.8-5.2 (m, 1H), 5.0-4.75 (m, 2H), 2.65 (t, 2H, J = 7 Hz), 2.0-1.2 (m, 6H).
7-norbornyl	252 (12, M[+]), 158 (18), 95 (93), 67 (100).	
$CH_3(CH_2)_2CH_2$	214 (31, M[+]), 158 (100), 78 (76).	7.6-7.1 (m, 5H), 2.82 (5, 2H, J = 7 Hz), 1.85-0.9 (m, 7H).
$(CH_3)_2CHCH_2$	214 (22, M[+]), 158 (58), 78 (40), 57 (100).	7.6-7.15 (m, 5H), 2.92 (d, 2H, J = 6.5 Hz), 2.1-1.7 (m, 1H), 1.05 (d, 6H, J = 6.5 Hz).
$PhCH_2$	248 (3, M[+]), 91 (100).	7.6-7.0 (m, 10H), 4.0 (s, 2H).

[a]m/e for M[+] is based on [80]Se.

[b]$CDCl_3$ solutions unless otherwise mentioned.

[c]C_6D_6 solutions.

20. Photoreaction of Δ^5-hexenylmercury chloride
    with phenyl diselenide

Δ^5-Hexenylmercury chloride (0.318 g, 1.0 mmol) and phenyl diselenide

(1.57 g, 5.0 mmol) were dissolved in 40 ml of benzene. After a nitrogen

purge, the solution was irradiated with a sunlamp for 3 h, during which

time a yellow precipitate was formed. The reaction was worked up as

previously described. Analysis by GLC showed that the residue contained

a mixture of Δ^5-hexenyl phenyl selenide and cyclopentylcarbinyl phenyl

selenide. The ratio of the two isomers was determined by quantitative

GLC as being 93.8% Δ^5-hexenyl phenyl selenide and 6.2% cyclopentyl-

carbinyl phenyl selenide.

21. General procedure for the photoreaction of alkyl-
    mercury halides with phenyl ditelluride

Alkylmercury halide (1.0 mmol) and phenyl ditelluride (1.2 mmol)

were dissolved in 10 ml of nitrogen-purged benzene. The reaction mix-

ture was irradiated with a sunlamp for several hours. During the ir-

radiation, a deep yellow precipitate was formed. Usual workup afforded

a yellow oily residue. GLC and [1]H.N.M.R. analysis revealed alkyl phenyl

tellurides in good yield. The products were further identified by

GCMS. The yield of products and reaction times are given in Table III,

whereas the GCMS and [1]H.N.M.R. data are given in Table XII.

22. Photoreaction of Δ^5-hexenylmercury chloride
    with phenyl ditelluride

Δ^5-Hexenylmercury chloride (0.19 g, 0.6 mmol) and phenyl ditel-

luride (1.24 g, 3.0 mmol) were dissolved in 20 ml of benzene under a

Table XII. GCMS and ^{1}H.N.M.R. data for alkyl phenyl tellurides, RTePh

R	GCMS m/e (relative intensity)	^{1}H.N.M.R. δ (ppm)
$CH_2=CHCH_2CH_2$	260 (15, M$^+$), 77 (43), 55 (100).	7.7-6.8 (m, 5H), 5.8-5.1 (m, 1H), 4.9-4.6 (m, 2H), 3.0-2.7 (m, 2H), 2.45-2.1 (m, 2H).[a]
$CH_3(CH_2)_4CH_2$	290 (6, M$^+$), 206 (13), 77 (100).	7.75-7.1 (m, 5H), 2.85 (5, 2H, J = 7 Hz), 1.8-0.8 (m, 11H).[b]
$(CH_3)_3CCH_2$	276 (3, M$^+$), 77 (51), 71 (100).	7.72-6.95 (m, 5H), 3.0 (s, 2H), 0.85 (s, 9H).[a]
$CH_2=CH(CH_2)_4CH_2$	288 (2, M$^+$), 83 (31), 77 (45), 55 (100).	7.8-6.9 (m, 5H), 6.0-5.3 (m, 1H), 5.1-4.7 (m, 2H), 2.82 (t, 2H, J = 6.5 Hz), 2.1-0.9 (m, 6H).[a]
Cyclo-$C_5H_9CH_2$	288 (1, M$^+$), 83 (44), 77 (58), 55 (100).	
$(CH_3)_2CH$	248 (8, M$^+$), 77 (100).	7.7-7.1 (m, 5H), 3.25 (septet, 1H, J = 7 Hz), 1.3 (d, 6H, J = 6 Hz).[b]
7-norbornyl	300 (3, M$^+$), 95 (92), 77 (42), 67 (100).	
$PhCH_2$	296 (3, M$^+$), 91 (100)	7.4-6.8 (m, 10H), 3.95 (s, 2H).[a]

[a] C_6D_6 solution.

[b] $CDCl_3$ solution.

nitrogen atmosphere. The solution was irradiated with a sunlamp for

3 h. Workup, as previously described, gave a solid residue. GLC

analysis revealed a mixture of Δ^5-hexenyl phenyl telluride as the major

product and cyclopentylcarbinyl phenyl telluride in a small amount.

The ratio of the two isomers was determined by quantitative GLC as

being 98.9% Δ^5-hexenyl phenyl telluride and 1.1% cyclopentylcarbinyl

phenyl telluride.

23. **Photoreaction of alkylmercury halides with Se-phenyl p-tolylselenosulfonate**

Alkylmercury halides (1.0 mmol) and Se-phenyl p-tolylselenosulfonate

(1.2 mmol) were dissolved in 10 ml of nitrogen-purged benzene. The solu-

tion was irradiated with a sunlamp for several hours, during which time

a white precipitate was formed. After the reaction was complete, the

usual workup gave a light yellow oil. GLC and ^{1}H.N.M.R. analysis

revealed alkyl phenyl selenides as the exclusive products. No alkyl

p-tolyl sulfone was detected. The yield of products and the reaction

times are tabulated in Table IV.

24. **Photoreaction of Δ^5-hexenylmercury chloride and Se-phenyl p-tolylselenosulfonate**

Δ^5-Hexenylmercury chloride (0.32 g, 1.0 mmol) and Se-phenyl p-

tolylselenosulfonate (1.56 g, 5.0 mmol) were dissolved in 25 ml of

benzene. After a nitrogen purge, the reaction mixture was irradiated

with a sunlamp for 6 h during which time a white precipitate was formed.

Workup yielded a mixture of Δ^5-hexenyl phenyl selenide and cyclopentyl-

carbinyl phenyl selenide in good yield. The ratio of the two isomers

was determined by quantitative GLC as being 86% Δ^5-hexenyl phenyl

selenide and 14% cyclopentylcarbinyl phenyl selenide.

25. Photoreaction of n-hexylmercury chloride with benzenesulfonyl chloride

n-Hexylmercury chloride (0.32 g, 1.0 mmol) and benzenesulfonyl

chloride (0.211 g, 1.2 mmol) were dissolved in 10 ml of benzene. The

stirred solution was irradiated under nitrogen in a Rayonet photo-

reactor equipped with fourteen "350 nm" bulbs. After 48 h of irradia-

tion, the precipitation which had formed was filtered off. The solvent

was removed by fractional distillation to afford an oily residue. GLC

and ^{1}H.N.M.R. analysis of the crude residue revealed n-hexyl chloride

as the sole product in a 46% yield. No n-hexyl phenyl sulfone was

observed.

GCMS, m/e (relative intensity) 91 (100, M^+-29), 55 (99).

26. Photoreaction of Δ^5-hexenylmercury chloride with benzenesulfonyl chloride

Δ^5-Hexenylmercury chloride (0.32 g, 1.0 mmol) and benzenesulfonyl

chloride (0.88 g, 5.0 mmol) were dissolved in 25 ml of nitrogen-purged

benzene. The solution was irradiated for 48 h in a Rayonet reactor at

350 nm. When the reaction was complete, the white precipitate was

filtered and the solvent was removed by fractional distillation.

Analysis of the residue by quantitative GLC revealed a mixture of Δ^5-

hexenyl chloride and cyclopentylcarbinyl chloride. The ratio of the

two isomers was determined to be 7% Δ^5-hexenyl chloride and 93% cyclo-

pentylcarbinyl chloride.

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27. Photoreaction of Δ^5-hexenylmercury chloride with benzene thiol

Δ^5-Hexenylmercury chloride (0.032 g, 0.1 mmol) and benzenethiol (0.033 g, 0.3 mmol) were dissolved in 5 ml of benzene. After a nitrogen purge, the solution was irradiated with a sunlamp for 5 h. A white precipitate was formed. The precipitate was filtered and the filtrate was analyzed by GLC, which revealed a mixture of 1-hexene and methyl-cyclopentane as the exclusive products of the reaction. The identity of both compounds was verified by GLC (10'x1/8", 15% OV-3, 45°C) retention time matching with authentic samples. The ratio of the two isomers was determined by quantitative GLC as being 98.1% 1-hexene and 1.9% methylcyclopentane.

28. Effect of di-tert-butyl nitroxide on the reaction of Δ^5-hexenylmercury chloride and benzenethiol

To a solution of Δ^5-hexenylmercury chloride (0.16 g, 0.5 mmol) and benzenethiol (0.11 g, 1.0 mmol), di-tert-butyl nitroxide (13 mg, 0.05 mmol) was added. The flask was wrapped with aluminum foil to exclude light. The reaction mixture was kept at 80°C for 38 h. No precipitate was formed. GLC analysis revealed the unchanged starting materials. No hydrocarbon products were detected.

29. Photoreaction of n-hexylmercury chloride with bromotrichlormethane

n-Hexylmercury chloride (0.32 g, 1.0 mmol) and $BrCCl_3$ (0.235 g, 3.6 mmol) were dissolved in 10 ml of CH_2Cl_2. The reaction mixture was irradiated in the Rayonet reactor at 350 nm for 36 h. The precipitate

was filtered. GLC analysis of the filtrate revealed n-hexyl bromide

(52% yield) as the main product. The identity of this compound was con-

firmed by GLC retention time matching with an authentic sample and GCMS

analysis.

GCMS, m/e (relative intensity) 166 (3), 164 (3, M^+), 137 (40),

135 (40), 85 (75), 55 (100).

In addition, $CHCl_3$ (7%), hexachloroethane and 1,1,1-trichloro-3-bromo-

heptane were formed. The identity of the latter product was established

by the GCMS analysis.

GCMS, m/e (relative intensity) 203 (0.25), 201 (0.32, M^+-Br), 167

(8), 165 (12), 131 (10), 129 (31), 93 (100).

The photoreaction of n-hexylmercury chloride and $BrCCl_3$ was completely

inhibited by 10 mole % of di-tert-butyl nitroxide for 16 h.

Similar procedure was applied for the reaction of n-butylmercury

chloride and $BrCCl_3$. The reaction time was 40 h. n-Butyl bromide was

formed as the main product in a 42% yield; whereas $CHCl_3$ (6%) and

1,1,1-trichloro-3-bromopentane were observed as the minor products.

30. Photoreaction of n-hexylmercury chloride with bromo-
     trichloromethane in the presence of K_2CO_3

n-Hexylmercury chloride (0.32 g, 1.0 mmol) and $BrCCl_3$ (0.235 g, 1.2

mmol) were dissolved in 10 ml of nitrogen-purged CH_2Cl_2 containing 0.5 g

of K_2CO_3 suspended by gentle stirring. The reaction mixture was irradi-

ated in the Rayonet reactor at 350 nm for 36 h. Workup afforded n-hexyl

bromide as the main product (49%) and $CHCl_3$ (5) as determined by quanti-

tative GLC. In addition, GCMS analysis determined small amounts of

1,1,1-trichloro-3-bromoheptane and hexachloroethane.

31. Photoreaction of n-hexylmercury chloride and carbon tetrachloride

A solution of $\underline{n}$-hexylmercury chloride (0.32 g, 1.0 mmol) in 8 ml of CCl_4 and 2 ml of CH_2Cl_2 was irradiated in the Rayonet reactor at 350 nm under a nitrogen atmosphere. The irradiation was continued for 84 h during which time a white precipitate was formed. When the reaction was complete, the solid was filtered. Quantitative GLC analysis revealed $\underline{n}$-hexyl chloride (32%) and $CHCl_3$ (17%), using decane as the internal standard. The identity of the products was verified by GLC (10'x1/8", 15% OV-3, 50-280/10°C) retention time matching with authentic samples.

$\underline{n}$-Hexyl chloride:

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 93 (32), 91 (100, M^+-Et), 55 (85). In addition, 1,1,1,3-tetrachloroheptane was formed. This compound was identified by GCMS analysis.

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 203 (0.48), 201 (0.5, M^+-Cl), 167 (11), 165 (17), 131 (9), 129 (28), 55 (100).

32. General procedure for the photoreaction of dialkyl-mercurials and phenyl disulfide

The dialkylmercury (1.0 mmol) and phenyl disulfide (1.2 mmol) were dissolved in 10 ml of benzene under a nitrogen atmosphere. The stirred solution was irradiated with a sunlamp placed 15 cm from the reaction vessel. After 2.5 h of irradiation, GLC analysis showed the complete disappearance of the dialkylmercurial peak and the formation of two new peaks. One peak occurs at the proper retention time for the alkyl phenyl

sulfide, while the other peak may have been the alkylmercury thiophen-
oxide. In one case, the latter was identified by GLC retention time
matching with an authentic sample (6'x1/8", 7% OV-3, 100-280°C/10°C).
Further irradiation for an additional several hours resulted in mercury
metal precipitation. When the reaction was complete, the solution was
decanted from the mercury metal, and the solvent was concentrated under
vacuum to afford an oily residue. [1]H.N.M.R. and GLC examinations re-
vealed alkyl phenyl sulfides in excellent yield. The yield of products
and reaction times are summarized in Table VII.

33. Photoreaction of dialkylmercurials with excess phenyl disulfide

The dialkylmercurial (1.0 mmol) and phenyl disulfide (2.5 mmol)
were dissolved in 10 ml of nitrogen-purged benzene. The mixture was
irradiated with a sunlamp for a few hours, during which time a white
precipitate, presumably mercury(II) sulfide salt, was formed. After
the reaction was complete, the precipitate was filtered and the solvent
was evaporated in vacuo to give a light yellow oil residue. [1]H.N.M.R.
and GLC analysis revealed alkyl phenyl sulfides as the sole organic
product of the reaction. The results are included in Table VII. It
is noteworthy that no mercury metal was formed under these conditions.

34. Dark reaction of di-n-butylmercury and phenyl disulfide

Di-n-butylmercury (0.471 g, 1.5 mmol) and phenyl disulfide (0.652
g, 3.0 mmol) were dissolved in 10 ml of benzene. The reaction flask
was wrapped with aluminum foil to exclude light. The reaction mixture

was heated at 45°C for 4 h. No precipitate was formed. The usual work-up gave a solid residue. [1]H.N.M.R. and GLC analysis revealed the un-changed starting materials. No n-butyl phenyl sulfide was detected.

35. Effect of di-tert-butyl nitroxide on the reaction of di-n-butylmercury with phenyl disulfide

Di-n-butylmercury (0.314 g, 1.0 mmol), phenyl disulfide (0.545 g, 2.5 mmol) and di-tert-butyl nitroxide (14 mg, 0.1 mmol) were dissolved in 10 ml of benzene. After a nitrogen purge, the solution was irradi-ated with a sunlamp. After 1.5 h, only a small amount of a white pre-cipitate was formed. Workup gave an oil, which was shown by GLC to contain mainly unchanged starting materials. n-Butyl phenyl sulfide was formed only in a 15% yield (0.3 mmol).

36. Preparation of n-butylmercury thiophenoxide

n-Butylmercury chloride (2.92 g, 10.0 mmol) was added slowly to a gently stirred solution containing potassium tert-butoxide (1.31 g, 11.6 mmol) and benzenethiol (1.29 g, 11.6 mmol) in 30 ml of nitrogen-purged DMSO. After 5 min., the solution was poured into 250 ml of aqueous 10% potassium carbonate. The resulting solution was extracted with benzene. The extract was washed with aqueous carbonate and dried over $MgSO_4$. The benzene solvent was removed under reduced pressure to give 3.3 g of crude product. Distillation, using short path apparatus, yielded 2.3 g (63% yield) pure n-butylmercury thiophenoxide. b.p. = 135-8°C at 0.3 mm. Extensive decomposition occurred upon distillation to give n-butyl phenyl sulfide and mercury metal.

[1]H.N.M.R. (CDCl$_3$) δ 7.55-7.05 (m, 5H), 1.9-0.8 (m, 9H).

M.S. Calculated for C$_{10}$H$_{14}$HgS: 368.05225. Measured 368.05104. Error -1.7 ppm.

GCMS, m/e (relative intensity) 368 (1, M$^+$), 112 (4.8), 110 (100) 57 (65).

37. Photodecomposition of n-butylmercury thiophenoxide

n-Butylmercury thiophenoxide (1.0 g, 2.75 mmol) was dissolved in 10 ml of benzene under a nitrogen atmosphere. Although the solution was stable in the dark at room temperature, a slow decomposition with precpitation of mercury metal occurred under sunlamp irradiation for 20 h. The solution was decanted from the mercury bead and the mercury rinsed with a little benzene and the combined solution was concentrated under reduced pressure to give 0.4 g (88% yield) of n-butyl phenyl sulfide.

38. Photoreaction of n-butylmercury thiophenoxide

n-Butylmercury thiophenoxide (0.368 g, 1.0 mmol) and phenyl disulfide (0.261 g, 1.2 mmol) were dissolved in 10 ml of nitrogen-purged benzene. The solution was irradiated with a sunlamp for 2 h during which time a white precipitate was formed. Workup consisted of the precipitate filtration and the solvent removal gave a light yellow oil. GLC analysis revealed n-butyl phenyl sulfide as the only component of the residue. The yield by quantitative [1]H.N.M.R. was 92%.

39. Photoreaction of n-butylphenylmercury with
    phenyl disulfide

n-Butylphenylmercury (0.334 g, 1.0 mmol) and phenyl disulfide (0.436

g, 2.0 mmol) were dissolved in 10 ml of benzene. After a nitrogen purge,

the solution was irradiated with a sunlamp for 8 h. A white precipitate

and a trace of mercury metal were formed. Workup gave an oil, which was

shown by GLC analysis to consist mainly of n-butyl phenyl sulfide (68%

yield). In addition, diphenyl sulfide was also observed in a 14% yield.

40. Photoreaction of n-butylphenylmercury and
    benzenesulfonyl chloride

n-Butylphenylmercury (0.334 g, 1.0 mmol) and benzenesulfonyl

chloride (0.211 g, 1.2 mmol) were dissolved in 10 ml of benzene. After

a nitrogen purge, the solution was irradiated with a sunlamp for 48 h.

When the reaction was complete, n-butyl chloride and diphenyl sulfone

were determined to be the products of the reaction. The yield of di-

phenyl sulfone by quantitative ^{1}H.N.M.R. was 65%. The identity of the

product was confirmed by GLC (10'x1/8", 15% OV-3, 100-280°C/15°C) reten-

tion time matching with an authentic sample.

^{1}H.N.M.R. (CDCl$_3$) δ 7.6-7.2 (m).

GCMS, m/e (relative intensity) 220 (0.8), 218 (7, M$^+$), 125 (100).

41. Photodecomposition of phenylmercury phenylsulfinate

A solution of phenylmercury phenylsulfinate (0.418 g, 1.0 mmol) in

10 ml of DMSO was irradiated for 48 h with a sunlamp under a nitrogen

atmosphere. The reaction mixture was poured in 50 ml of aqueous 10%

sodium thiosulfate solution and extracted with benzene. The extract was

dried over $MgSO_4$ and the solvent was removed in vacuo to give 0.12 g

(55% yield) of diphenyl sulfone. The compound was identified by

[1]H.N.M.R. and GCMS as described above.

42. Photoreaction of mercurycycloheptane with phenyl disulfide

Mercurycycloheptane (0.142 g, 0.5 mmol) and phenyl disulfide (0.261

g, 1.2 mmol) were dissolved in 5 ml of nitrogen-purged benzene. The

solution was irradiated for 2.5 h with a sunlamp positioned 15 cm from

the reaction vessel. A white precpitate was formed during the reaction.

When the reaction was complete, workup afforded 1,6-dithiophenoxyhexane

as the exclusive product. The identity of this product was verified by

GLC (10'x1/8", 15% OV-3, 150-280°C/20°C) retention time matching with an

authentic sample prepared by a published procedure [75].

[1]H.N.M.R. (CDCl$_3$) δ 7.25 (broad singlet, 10H), 2.95 (t, 4H, $\underline{J}$ = 6.5

Hz), 1.8-1.15 (m, 8H).

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 304 (1.2), 302 (14, M^+), 195 (1.5),

193 (33), 123 (88), 55 (100).

43. Photoreaction of dialkylmercury with phenyl diselenide

The dialkylmercury (1.0 mmol) and phenyl diselenide (1.2 mmol) were

dissolved in 10 ml of benzene under a nitrogen atmosphere. The solution

was irradiated with a 275 W sunlamp. After one hour, a pale yellow pre-

cipitate was formed. Further irradiation for an additional several

hours resulted in the dissolution of the precipitate and mercury metal

formation. The usual workup gave alkyl phenyl selenides as the sole

products. The yield of products and reaction times are summarized in

Table VIII.

44. Photoreaction of dialkylmercurys with excess phenyl diselenide

The dialkylmercury (1.0 mmol) and phenyl diselenide (2.5 mmol) were dissolved in 10 ml of nitrogen-purged benzene. The reaction mixture was irradiated with a sunlamp for a few hours during which time a yellow precipitate was formed, which did not dissolve upon prolonged irradiation. After the reaction was complete, the precipitate was filtered and the solvent removed under reduced pressure to yield alkyl phenyl selenides in excellent yields. Results are included in Table VIII.

45. Photoreaction of benzylmercury chloride with phenyl disulfide

Benzylmercury chloride (0.326 g, 1.0 mmol) and phenyl disulfide (0.261 g, 1.2 mmol) were dissolved in 10 ml of benzene. After a nitrogen purge, the solution was irradiated in a Rayonet photoreactor equipped with fourteen "350 nm" bulbs for 4 h. When the reaction was complete, the white precipitate was filtered and the solvent evaporated in vacuo. Quantitative ^{1}H.N.M.R. revealed a mixture consisted of bibenzyl (66% yield) and benzyl phenyl sulfide (15% yield) in the residue. The two compounds were identified by the methylen absorptions at 3.03 and 4.12 ppm in $CDCl_3$, respectively, in agreement with that of the authentic samples. Both products were further identified by GCMS analysis.

46. Photoreaction of benzylmercury chloride
    with phenyl diselenide

Benzylmercury chloride (0.326 g, 1.0 mmol) and phenyl diselenide

(0.378 g, 1.2 mmol) were dissolved in 10 ml of nitrogen purged benzene.

The solution was irradiated with a sunlamp for 2 h, during which time

a light yellow precipitate was formed. The usual workup gave an oily

residue. Quantitative ^{1}H.N.M.R. indicated a mixture of bibenzyl (7%

yield) and benzyl phenyl selenide (72% yield) as the product of this

reaction. GCMS analysis confirmed the presence of both products.

47. Photoreaction of benzylmercury chloride with
    phenyl ditelluride

Benzylmercury chloride (0.326 g, 1.0 mmol) and phenyl ditelluride

(0.494 g, 1.2 mmol) were dissolved in 10 ml of benzene. After a nitrogen

purge, the solution was irradiated with a sunlamp for 1 h. Normal workup

afforded an oily residue, which was shown by quantitative ^{1}H.N.M.R. to

contain exclusively benzyl phenyl telluride (80% yield). No bibenzyl

was formed.

48. Photoreaction of benzylmercury chloride with
    Se-phenyl p-tolyselenosulfonate

Benzylmercury chloride (0.326 g, 1.0 mmol) and Se-phenyl p-tolyl-

selenosulfonate (0.374 g, 1.0 mmol) were dissolved in 10 ml of nitrogen-

purged benzene. The solution was irradiated with a sunlamp for 6 h,

during which a white precipitate was formed. Workup gave a yellow oil,

which was shown by quantitative ^{1}H.N.M.R. to consist of a mixture of

benzyl phenyl selenide (68% yield) and bibenzyl (5% yield).

49. Photodecomposition of dibenzylmercury

A solution of dibenzylmercury (0.764 g, 2.0 mmol) in 10 ml of benzene was irradiated in the Rayonet reactor at 350 nm under a nitrogen atmosphere. Irradiation was continued for 21 h until the complete disappearance of the mercurial as indicated by [1]H.N.M.R. analysis of a sample of the reaction mixture. Mercury metal was precipitated. The solution was decanted from the mercury and the solvent was removed under vacuum to give 0.31 g (86%) of bibenzyl.

[1]H.N.M.R. ($CDCl_3$, δ) 7.5-7.15 (m, 10H), 3.03 (s, 4H).

GCMS, m/e (relative intensity) 182 (16, M^+), 91 (100).

50. Photoreaction of dibenzylmercury with phenyl disulfide

Dibenzylmercury (0.382 g, 1.0 mmol) and phenyl disulfide (0.545 g, 2.5 mmol) were dissolved in 10 ml of nitrogen-purged benzene. The solution was irradiated with a sunlamp for 6 h, during which time mercury metal and a little white precipitate were formed. Workup gave a light yellow oil, which was shown by quantitative [1]H.N.M.R. to consist of bibenzyl (72% yield) and benzyl phenyl sulfide (8% yield).

51. Photodecomposition of benzylmercury thiophenoxide

A solution of benzylmercury thiophenoxide (0.8 g, 2.0 mmol) in 10 ml of benzene under a nitrogen atmosphere was irradiated in the Rayonet photoreactor at 350 nm for 8 h. Mercury metal and a white precipitate were formed. Normal workup gave an oily residue. Quantitative [1]H.N.M.R. revealed bibenzyl as the major product in an 86% yield. Only a trace amount of benzyl phenyl sulfide was detected by GCMS analysis.

52. Photoreaction of dibenzylmercury and phenyl ditelluride

Dibenzylmercury (0.382 g, 1.0 mmol) and phenyl ditelluride (0.82 g, 2.0 mmol) were dissolved in 10 ml of nitrogen-purged benzene. The solution was irradiated with a sunlamp for 1 h, during which time a deep yellow precipitate was formed. Workup gave a light yellow oil, which was shown by quantitative ^{1}H.N.M.R. to consist exclusively of benzyl phenyl telluride (100% yield). No bibenzyl was observed.

53. Photoreaction of n-butylphenylmercury with carbon tetrachloride

A solution of n-butylphenylmercury (0.5 g, 1.5 mmol) in 5 ml of carbon tetrachloride was irradiated in a Rayonet photoreactor at 350 nm under a nitrogen atmosphere. The irradiation was continued for 24 h during which time a white precipitate was formed. When the reaction was complete, the precipitate was filtered. Quantitative GLC analysis of the filtrate indicated n-butyl chloride (33% yield), $CHCl_3$ (17% yield) and 1,1,1,3-tetrachloropentane as the major products of the reaction.

n-Butyl chloride:

GCMS, m/e (relative intensity) 94 (0.3), 92 (0.9, M^+), 56 (100).

1,1,1,3-Tetrachloropentane:

GCMS, m/e (relative intensity) 175 (10), 173 (11, M^+-Cl), 139 (73), 137 (100), 76 (79), 55 (45).

In addition, GCMS analysis revealed chlorobenzene and biphenyl as minor products of this reaction. Also, a small amount of ca. 5% of phenyltrichloromethane was detected.

54. Thermal reaction of n-butylphenylmercury with carbon tetrachloride in the presence of benzoyl peroxide

n-Butylphenylmercury (0.5 g, 1.5 mmol) and benzoyl peroxide (36 mg, 0.15 mmol) were dissolved in 5 ml of carbon tetrachloride under a nitrogen atmosphere. The reaction flask was wrapped with aluminum foil to exclude light. The mixture was heated at reflux in an oil bath kept at 100°C for 18 h during which time a white precipitate was formed. Workup as described previously gave an oily residue. Quantitative GLC analysis revealed n-butyl chloride (31%), $CHCl_3$ (17%) and 1,1,1,3-tetrachloropentane as the major products. The products were further identified by GCMS analysis. In addition, GCMS analysis indicated the formation of other side products including chlorobenzene and biphenyl. Only a small amount of phenyltrichloromethane was detected.

55. Photoreaction of n-butylphenylmercury with bromotrichloromethane

n-Butylphenylmercury (0.5 g, 1.5 mmol) and bromotrichloromethane (0.49 g, 2.5 mmol) were dissolved in 10 ml of nitrogen-purged benzene. The solution was irradiated with a sunlamp for 20 h during which time a white precipitate was formed. Workup as previously described gave an oil, which was shown by quantitative GLC analysis to contain n-butyl bromide (48%) $CHCl_3$ (7%) and 1,1,1-trichloro-3-bromopentane as the main products. The compounds were identified by GCMS analysis.

n-Butyl bromide:

GCMS, m/e (relative intensity) 138 (7), 136 (7, M^+), 109 (3), 107 (3), 57 (100).

1,1,1-trichloro-4-bromopentane:

GCMS, $\underline{m/e}$ (relative intensity) 254 (0.18), 252 (0.08, M^+), 175 (4), 173 (4, M^+-Br), 139 (62), 137 (100).

Other minor products identified by GCMS analysis included bromobenzene and traces of biphenyl and phenyltrichloromethane.

56. Photoreaction of diisobutylmercury with bromotrichloromethane

Diisobutylmercury (0.314 g, 1.0 mmol) was dissolved in 5 ml of CH_2Cl_2 and the solution was cooled to -50°C using $CHCl_3$-dry ice slush. A precooled bromotrichloromethane solution (0.49 g, 2.5 mmol) in 5 ml of CH_2Cl_2 was added. The reaction mixture was irradiated at -50°C with a sunlamp placed 15 cm from the reaction vessel. For analysis, the reaction mixture was filtered and the filtrate washed with 10 ml of 5% aqueous sodium thiosulfate solution and dried (Na_2SO_4). GLC analysis revealed isobutyl bromide as the main product besides small amounts of $CHCl_3$ and 1,1,1-trichloro-3-bromo-3-methylbutane. The yields of iso-butyl bromide and $CHCl_3$ were determined at different periods of time by quantitative GLC analysis using decane as the internal standard. The results are summarized in Table V.

57. Photoreaction of diisobutylmercury with bromotrichloromethane

Diisobutylmercury (0.314 g, 1.0 mmol) and bromotrichloromethane (0.49 g, 2.5 mmol) were dissolved in 10 ml of CH_2Cl_2. A precipitate was formed a few minutes after the mixing in room light. GLC analysis at this point revealed the formation of isobutyl bromide and a small

amount of $CHCl_3$. The reaction mixture was irradiated with a sunlamp

at ambient temperature (35-45°C). The progress of the reaction was

monitored by GLC. When the reaction was complete (6 h), the precipi-

tate was filtered. The filtrate was washed with 10 ml of 5% aqueous

sodium thiosulfate solution and dried over Na_2SO_4. Quantitative GLC

analysis established a 78% yield of isobutyl bromide and an 18% yield of

$CHCl_3$. In addition, 1,1,1-trichloro-3-bromo-3-methylbutane was observed.

58. Effect of di-tert-butyl nitroxide on the reaction of
    diisobutylmercury with bromotrichloromethane

Diisobutylmercury (0.314 g, 1.0 mmol) and di-tert-butyl nitroxide

(17 mg, 0.012 mmol) were dissolved in 5 ml of CH_2Cl_2 and the solution was

cooled to -50°C. Bromotrichloromethane (0.49 g, 2.5 mmol) in 5 ml of

CH_2Cl_2 was cooled to -50° and added to the solution. The reaction mix-

ture was irradiated with a sunlamp at -50° for 2 h. GLC analysis re-

vealed the unchanged starting materials. Neither isobutyl bromide nor

$CHCl_3$ was observed.

59. Photoreaction of diisobutylmercury with
    carbon tetrachloride

Diisobutylmercury (0.314 g, 1.0 mmol) and CCl_4 (0.38 g, 2.5 mmol)

were dissolved in 10 ml of CH_2Cl_2. The solution was cooled to -50°C and

irradiated with a sunlamp for 1.5 h. GLC analysis revealed exclusively

the starting materials. Isobutyl chloride and chloroform were not

observed.

60. Photoreaction of diisobutylmercury with carbon tetrachloride

Diisobutylmercury (0.34 g, 1.0 mmol) in 5 ml of CCl_4 was irradiated in the Rayonet reactor at 350 nm for 48 h during which time mercury metal was formed. The solution was decanted from the mercury bead and washed with sodium thiosulfate solution. GLC analysis revealed isobutyl chloride, $CHCl_3$ and 1,1,1,3-tetrachloro-3-methylbutane. The ratio of these products was determined by GCMS analysis to be approximately 1:1:1.

61. Photoreaction of mercurycycloheptane and carbon tetrachloride

Mercurycycloheptane (0.15 g, 0.5 mmol) was dissolved in 5 ml of CCl_4. After a nitrogen purge, the solution was irradiated with a sunlamp for 10 h during which time a white precipitate and mercury metal were formed. When the reaction was complete, quantitative GLC of the reaction mixture revealed Δ^5-hexenyl chloride (8%) and its CCl_4 adduct, 1,1,1,3,7-pentachloroheptane (62%). No cyclopentylcarbinyl chloride was detected. The products were identified by GCMS analysis.

Δ^5-Hexenyl chloride:

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 120 (1), 118 (3.6, M^+), 82 (50), 69 (58), 55 (100).

1,1,1,3,7-Pentachloroheptane:

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 241 (0.01), 239 (0.11), 237 (0.3), 235 (0.26, M^+-Cl), 205 (0.5), 203 (5), 201 (15), 199 (16), 165 (13), 163 (21), 140 (26), 138 (43), 55 (100).

62. <u>Thermal</u> <u>reaction</u> <u>between</u> <u>mercurycycloheptane</u> <u>and</u> <u>carbon</u>
    <u>tetrachloride</u> <u>in</u> <u>the</u> <u>presence</u> <u>of</u> <u>benzoyl</u> <u>peroxide</u>

Mercurycycloheptane (0.15 g, 0.5 mmol) and benzoyl peroxide (12 mg,

0.05 mmol) were dissolved in 5 ml of carbon tetrachloride. The reaction

mixture was wrapped with aluminum foil to exclude light. The solution

was heated under a nitrogen atmosphere in an oil bath kept at 100°C for

10 h. Workup as previously described afforded Δ^5-hexenyl chloride and

1,1,1,3,7-pentachloroheptane, exclusively, in yields comparable to

those observed in the photoreaction. Again, no cyclopentylcarbinyl

chloride was detected.

## II. SUBSTITUTION REACTIONS OF TRI-n-BUTYL-1-ALKENYLTINS

BY A FREE RADICAL CHAIN MECHANISM

A. Introduction

Trialkyl-1-alkenyltin compounds are usually prepared from the reaction of 1-alkenylmagnesium halides (Gringard reagent) with the appropriate trialkyltin halides, or by the hydrostannylation of the unsaturated alkenyl compounds [76-78]. They are thermally stable and can be stored at room temperature for extended periods of time. However, these tin compounds are very sensitive toward electrophilic reagents, and their reactions with electrophilic species have been reported on numerous occasions [79-82]. In principle, both cleavage of the alkenyl-tin bond and addition to the double bond can occur. Of these two processes, cleavage has been observed more often. Thus, halogens, hydrogen halides, organic acids and thiols are reported to cleave the alkenyl group in the alkenyl derivatives of tin [79]. No addition reactions were observed under these conditions. This behavior was attributed to the relatively low carbon-tin bond energy [79]. The sequence of cleavage of organic groups from tin by the halogens has been established to be phenyl > alkenyl > alkyl [79]. Thus, in reaction with iodine, $Ph_3SnCH=CH_2$ gave iodobenzene and $Ph_2ISnCH=CH_2$, while $Me_3SnCH=CH_2$ gave vinyl iodide and Me_3SnI [79,82].

Electrophilic addition to the vinyl group in trialkyl-1-alkenyltin compounds has also been reported [83, 84]. Sulfenyl chlorides and thiocynates (R'SX, X = Cl or SCN) react with $R_3SnCH=CH_2$ in aprotic

solvents to give products of Markovnikov addition to the double bond

and cleavage of the vinyl-tin bond (Eq. 35) [84]. The cleavage products

$$R_3SnCH{=}CH_2 + R'SX \xrightarrow[\Delta]{CH_2Cl_2} R_3SnCHXCH_2SR' + CH_2{=}CHSR' + R_3SnX \qquad (35)$$
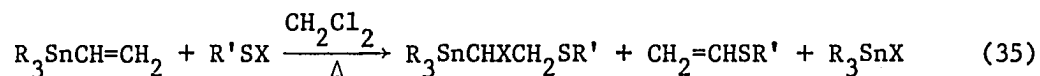
are exclusively obtained from the most reactive sulfenyl chloride used,

p-MeC$_6$H$_4$SCl, while cleavage and addition occur with the less-electro-

philic species, 2-O$_2$N-4-Y-C$_6$H$_3$SX (X = Cl and SCN; Y = H, Me and NO$_2$)

[83].

Free radical addition reactions to the double bond in trialkyl-1-

alkenyltin derivatives are quite common. Seyferth has reported that

polyhalomethanes, CCl$_3$Z (Z = H, Cl, Br), add to triethyl-1-ethenyltin

in the presence of benzoyl peroxide to give moderate yields of adduct

14 (Eq. 36) [85]. The reaction is believed to proceed through a radical

$$(C_2H_5)_3SnCH{=}CH_2 + CCl_3Z \xrightarrow[90°C]{Bz_2O_2} (C_2H_5)_3SnCHZCH_2CCl_3 \qquad (36)$$
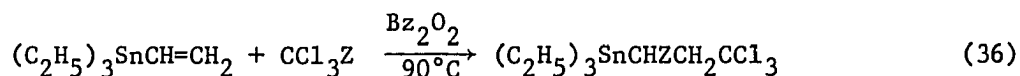
14

chain mechanism involving β-addition of trichloromethyl radical to the

vinyl group to give α-alkylstannyl radical, which abstracts a halogen

atom or hydrogen from the polyhalomethanes. Similarly, p-toluenethiol

was shown to undergo free radical, azo-catalyzed addition to triphenyl-

1-ethenyltin to afford the β-sulfur substituted tin compound **15** (Eq.

37) [86]. Stamm has also reported that the free radical addition of

$$Ph_3SnCH{=}CH_2 + p\text{-}MeC_6H_4SH \xrightarrow{AIBN} Ph_3SnCH_2CH_2SC_6H_4Me\text{-}p \qquad (37)$$
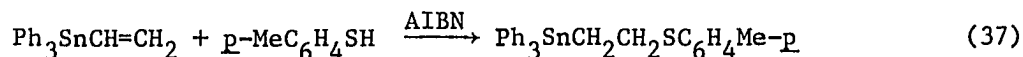
15

thioacetic acid, CH_3COSH, to tri-n-butyl-1-ethenyltin proceeded with

reasonable ease under UV irradiation at or below room temperature to

give 2-(tri-n-butyl)ethylthioacetate in good yield [87]. No cleavage

of the alkenyl-tin bond was observed. Other alkanethiols were reported

to react with triethyl-1-ethenyltin under UV irradiation with predomi-

nant formation of the addition product 2-(triethyltin)ethyl alkyl

sulfide (Eq. 38) [88-90]. Besides adduct **16**, the addition-elimination

$$Et_3SnCH=CH_2 + RSH \xrightarrow{UV} Et_3SnCH_2CH_2SR + RSCH_2CH_2SR + (Et_3SnCH_2)_2 \quad (38)$$

$$\textbf{16} \qquad\qquad \textbf{17} \qquad\qquad \textbf{18}$$
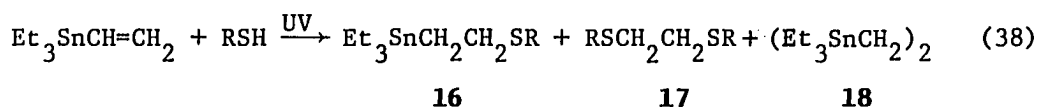
products **17** and **18** were also observed (Eq. 38). The following mechanis-

tic picture was postulated to account for the formation of these

products, Scheme XXI. It is worth mentioning that the yield of the main

Scheme XXI   (R = n-butyl, isopropyl and tert-butyl)

$$RSH \xrightarrow{UV} RS\cdot + H\cdot$$

$$RS\cdot + Et_3SnCH=CH_2 \underset{\longleftarrow}{\overset{\beta\text{-add.}}{\longrightarrow}} Et_3Sn\dot{C}H-CH_2SR \xrightarrow{RSH} \textbf{16}$$

$$RS\cdot + Et_3SnCH=CH_2 \underset{\longleftarrow}{\overset{\alpha\text{-add.}}{\longrightarrow}} Et_3SnCH(SR)\dot{C}H_2 \xrightarrow{\beta\text{-elim.}} CH_2=CHSR + Et_3Sn\cdot$$

$$Et_3Sn\cdot + CH_2=CHSnEt_3 \xrightarrow{RSH} \textbf{18}$$

$$RSH + CH_2=CHSR \longrightarrow \textbf{17}$$
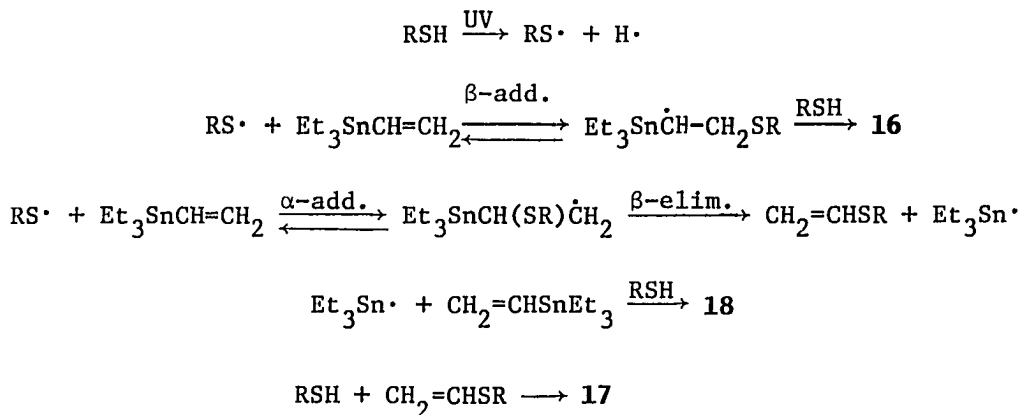
product **16** decreases in going from tert-butyl thiol to isopropyl thiol

and further to n-butyl thiol. This was attributed both to an increase

in electrophilicity of the corresponding thiyl radicals and to a decrease in steric hindrance to the attack at the α-carbon atom [88].

Free radical hydrostannylation reactions of trialkyl-1-alkenyltin with trialkyltin hydrides have been explored [91]. Thus, trialkyltin hydrides R_3SnH (R = methyl or ethyl) were found to add to trialkyl-1-ethenyltin, $R_3SnCH=CH_2$ (R = methyl or ethyl) under free radical conditions to give both α- and β-adducts (Eq. 39), rather than the β-adduct

$$R_3SnCH=CH_2 + R_3SnH \xrightarrow{AIBN} (R_3Sn)_2CHCH_3 + R_3SnCH_2CH_2SnR_3 \qquad (39)$$
$$\alpha\text{-adduct} \qquad \beta\text{-adduct}$$
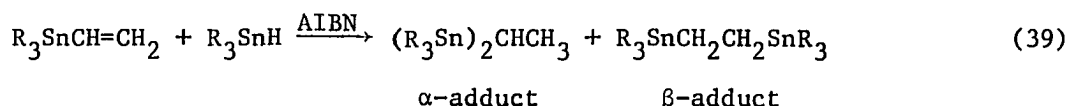
exclusively, as expected. Interestingly, triphenyltin hydride added to triphenyl-1-ethenyltin to give exclusively the β-adduct. In a somewhat related reaction, free radical addition-elimination was observed for the reaction of trialkyltin hydrides and trialkyl-1-alkenyltin [92]. The exchange reaction (Eq. 40) was established to be the main reaction

$$RCH=CHSnR'_3 + R''_3SnH \underset{\longleftarrow}{\xrightarrow{AIBN}} RCH=CHSnR''_3 + R'_3SnH \qquad (40)$$
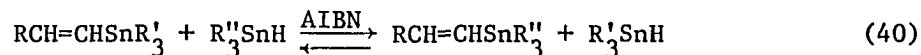
channel, and it was accompanied by isomerization. When R was electron withdrawing group, i.e. CO_2Me, both exchange and hydrostannylation products were obtained. Rykov and co-workers have shown that the alkenyl-tin bond cleavage occurred when the mixture of isomers 19 and 20 was treated with carbon tetrachloride (Eq. 41) [93]. CIDNP was observed at temperature above 20°C for isomer 20.

Tin-centered radicals are well-known to participate in free radical chain processes [94]. The most common reactions involve the tin-centered

$$\underset{\mathbf{19}}{\overset{Pr_3Sn}{\underset{Et}{\diagdown}}C=C\overset{OMe}{\underset{H}{\diagup}}} \quad + \quad \underset{\mathbf{20}}{\overset{Pr_3Sn}{\underset{MeO}{\diagdown}}C=C\overset{Et}{\underset{H}{\diagup}}} \quad \xrightarrow[\Delta]{CCl_4} Pr_3SnCl + HCCl_3 + EtC\equiv COMe \tag{41}$$
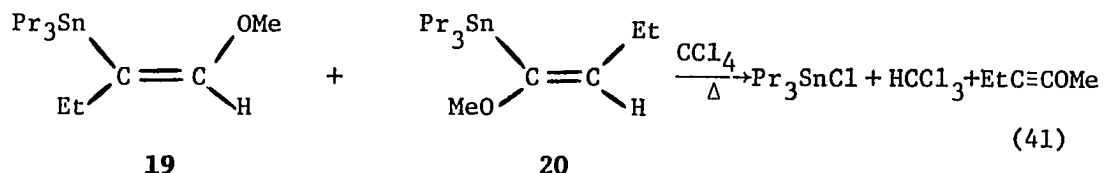
radicals are the organotin hydrides reduction of alkyl halides [95-97] and hydrostannylation of alkenes and alkynes [98]. The reduction of alkyl halides by trialkyltin hydrides was discovered in 1957 [95] and was established to proceed via a chain process a few years later [96, 97]. The tri-n-butyltin hydride reduction of Δ^5-hexenyl bromide gave methylcyclopentane as the main product (>90%) which is consistent with the intermediacy of the alkyl radical in this reaction [99]. The propagation steps of the most accepted mechanism for this reduction reaction is shown in Scheme XXII. The halogen transfer reaction (Eq.

Scheme XXII

$$R_3Sn\cdot + R'X \longrightarrow R_3SnX + R\cdot \tag{42}$$

$$R\cdot + R_3SnH \longrightarrow R'H + R_3Sn\cdot \tag{43}$$
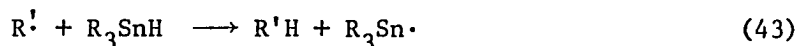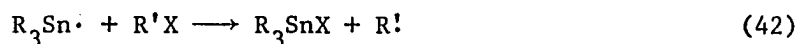
42) may proceed either directly via S_H2 attack on the halogen atom or by a two step mechanism involving prior electron transfer to form the radical-anion [100]. However, no evidence for the electron transfer step has been given. The reactivities of various alkyl halides toward tin-centered radicals in the halogen transfer reaction (Eq. 42) were found to decrease in the order I > Br > Cl.

The reduction of alkyl and aryl disulfides with triorganotin hydrides has also been studied [101, 102]. The products were alkyl or

aryl thiols and the corresponding triorganotin alkyl (aryl) sulfides. The reaction is believed to occur by a free radical chain process in which one of the propagation steps involves the homolytic substitution reaction at the disulfide by an attacking tin-centered radical (Eq. 44) [102].

$$R_3Sn\cdot + R'SSR' \longrightarrow R'S\cdot + R_3SnSR' \tag{44}$$
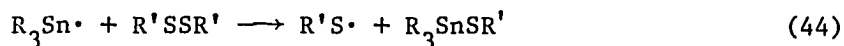
Recently, 1-alkenylmercurial salts were found to undergo a photo-stimulated reactions with heteroatom-centered radicals, such as PhS·, PhSe·, PhTe· and $PhSO_2$·, to give the corresponding olefinic derivatives [33, 34]. These reactions were established to proceed through a radical chain addition-elimination mechanism, which does not involve a free vinyl radical [33].

Analogous to the reactions of 1-alkenylmercurials, and based on the well-established involvement of tin-centered radicals in free radical chain processes, we reasoned that tri-$\underline{n}$-butyl-1-alkenyltin compounds, $\underline{n}$-$Bu_3SnCH=CR_1R_2$ (R_1, R_2 = H and Ph), under free radical reaction conditions would participate in chain reactions with carbon-centered and/or heteroatom-centered radicals to afford the corresponding substituted alkenes (Eq. 45). The suggested reaction, a radical chain process, is

$$R_1R_2C = CHSnBu_3 + QY \longrightarrow R_1R_2C = CHQ + Bu_3SnY \tag{45}$$
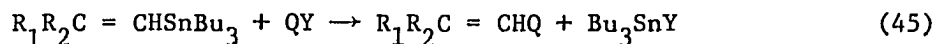
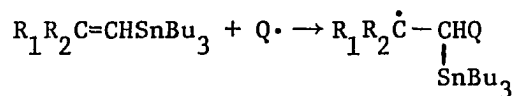outlined in Scheme XXIII.

The scope and mechanism of the above reaction will be the subject of the discussion in the next section. Parts (1-3) will cover the

<u>Scheme XXIII</u> $(Q = PhS, PhSO_2, \underline{p}-MeC_6H_4SO_2, CCl_3, R)$

$(Y = PhS, Cl, PhSe, Br, SO_2Cl, HgCl, X; X = I, Br, Cl)$

Initiation $Q - Y \rightarrow Q\cdot + Y\cdot$

$$R_1R_2C{=}CHSnBu_3 + Q\cdot \rightarrow R_1R_2\overset{\displaystyle\cdot}{C}-\underset{\displaystyle SnBu_3}{\underset{|}{CHQ}}$$

21

Propagation

$$\mathbf{21} \longrightarrow R_1R_2C = CHQ + Bu_3Sn\cdot$$

$$Bu_3Sn\cdot + Q - Y \longrightarrow Q\cdot + Bu_3SnY$$
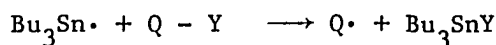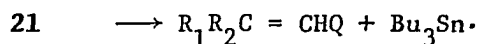
reactions of tri-<u>n</u>-butyl-1-alkenyltin with carbon-centered radicals.

Part (4) will cover the reactions of some β-substituted styrenes,

PhCH=CHQ $(Q = I, SO_2Ph, HgCl, SPh)$, with alkylmercury halides. Whereas

Part (5) is considered with the reaction of tri-<u>n</u>-butyl-1-alkenyltin

with heteroatom-centered radicals.

B. Results and Discussion

1. <u>Reaction of tri-n-butyl-1-alkenyltin compounds
    with alkylmercury halides</u>

Tri-<u>n</u>-butyl-1-alkenyltin compounds were found to undergo a photo-

stimulated reaction with alkylmercurial salts to yield the substituted

1-alkenes, tri-<u>n</u>-butyltin halides and mercury metal. Thus, when a

benzene solution of tri-<u>n</u>-butyl-(<u>E</u>)-2-phenyl-1-ethenyltin and isopropyl-

mercury chloride was irradiated with a 275 W sunlamp placed 15 cm from

the Pyrex reaction vessel, a reaction took place as evidenced by

mercury metal precipitation about 1 h after the reaction began. The

workup consisted of decanting the reaction solution from the beads of

mercury and concentrating the solution under reduced pressure to give

a yellow oily residue. Upon distillation, 1-phenyl-3-methyl-1-butene

was isolated in a 72% yield as a mixture of cis- and trans-isomers.

The trans:cis ratio was established to be 92:8 by quantitative GLC

analysis. Tri-n-butyltin chloride was formed as the other final product

in comparable yield.

The reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin and isopropyl-

mercury chloride can be accomplished thermally in the presence of free

radical sources. Thus, when the above reaction mixture in benzene was

heated at 80°C with 10 mole % of AIBN, a reaction occurred as indicated

by mercury metal precipitation. Normal workup afforded a 73% yield of

1-phenyl-3-methyl-1-butene. Again, the trans-isomer predominates and

the GLC trans:cis ratio was calculated to be 94:6. In addition, tri-n-

butyltin chloride was formed.

The necessity of free radical initiator, such as sunlamp irradia-

tion or AIBN, for the reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin

and isopropylmercurial was demonstrated by the observation that the

reaction did not proceed in the dark. Thus, no reaction was observed

when the reaction mixture was heated at 50°C in the dark for 24 h.

Mercury metal did not form and GLC analysis revealed the unchanged

starting materials almost quantitatively. The failure of the reaction

to occur in the dark indicates the possibility of radical chain process

in this reaction.

The participation of free radical chain process was examined with

di-tert-butyl nitroxide, which is known to be an effective suppressor of radical intermediates. Its inhibitory effect was studied under photo-irradiation with a sunlamp. It is found that this inhibitor strongly retarded the formation of the coupling product. However, the reaction proceeded after prolonged irradiation, presumably after the total consumption of di-tert-butyl nitroxide. The yield of the coupling product after 16 h of sunlamp irradiation in the presence of 10 mole % of di-tert-butyl nitroxide was drastically reduced to 35% as determined by quantitative [1]H.N.M.R. analysis.

The reaction of a series of alkylmercurial salts, RHgX, with tri-n-butyl-(E)-2-phenyl-1-ethenyltin, the stoichiometry of which is presented in reaction 46, proceeds effectively under sunlamp irradiation to

$$(\underline{E})\text{-PhCH=CHSnBu}_3 + \text{RHgX} \xrightarrow[\text{PhH}]{\text{light}} \text{PhCH=CHR} + \text{Bu}_3\text{SnX} + \text{Hg(0)} \qquad (46)$$
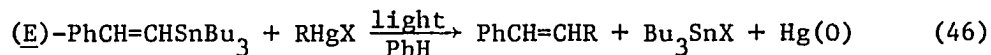
give the corresponding β-alkyl substituted styrenes, tri-n-butyltin chloride and mercury metal. In general, 3°-alkylmercurials react faster than the 2°-alkylmercurials which react faster than primary ones. In all cases, the trans-isomer was formed as the main product, whereas the cis-isomer was formed only in a small amount. The results are summarized in Table XIII.

The experimental evidence presented above has an interesting mechanistic implication. This evidence includes the reaction catalysis by free radical sources, such as sunlamp irradiation or thermolysis of AIBN, and retardation by the efficient radical scavenger di-tert-butyl nitroxide as well as the failure of the reaction to proceed in the dark.
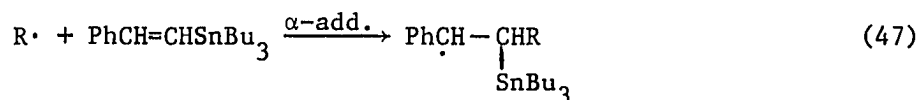
Table XIII. Reaction of tri-n̲-butyl-1-alkenyltin with alkylmercurials

$R_1R_2C{=}CHSnBu_3 + R_3HgCl \rightarrow R_1R_2C{=}CHR_3 + Hg(0) + Bu_3SnCl$

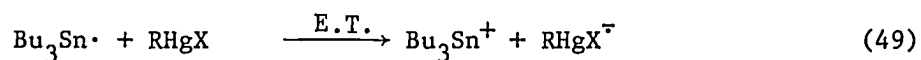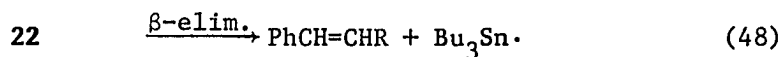| R_1	R_2	R_3	Conditions	% Yield[a] $R_1R_2C{=}CHR_3$	trans/cis[b]
Ph	H	iso-C_3H_7	PhH, hν, 18[c]	86 (72)[d]	92/8
Ph	H	iso-C_3H_7	PhH, AIBN, 80°C, 16 h	73	94/6
Ph	H	iso-C_3H_7	PhH, dark, 50°C, 24 h	0	
Ph	H	iso-C_3H_7	PhH, hν, DTBN, 16 h[c]	35	91/9
Ph	H	Cyclo-C_6H_{11}	DMSO, hν, 16 h[c]	88	95/5
Ph	H	Cyclo-C_5H_9	PhH, hν, 18 h[c]	77	95/5
Ph	H	tert-C_4H_9	PhH, hν, 14 h[c]	83	98/2
Ph	H	Δ^5-C_6H_{11}	PhH, hν, 32 h[e]	55[f]	88/12
Ph	H	n-C_4H_9	PhH, hν, 40 h[e]	46	86/14
Ph	H	Δ^3-C_4H_7	PhH, hν, 36 h[e]	45	88/12
Ph	H	Cyclo-$C_5H_9CH_2$	PhH, hν, 48 h[e]	52	85/15
Ph	H	$PhCH_2$	PhH, hν, 15 h[c]	18[g]	91/9
H	H	Cyclo-C_5H_9	PhH, hν, 24 h[e]	~10	
H	H	Cyclo-C_6H_{11}	DMSO, hν, 24 h[e]	~8	
Me	Me	Cyclo-$C_5H_9CH_2$	PhH, hν, 96 h[e]	0	
Ph	Ph	iso-C_3H_7	PhH, hν, 28 h[e]	73	
Ph	Ph	tert-C_4H_9	PhH, hν, 18 h[e]	78	
Ph	Ph	Cyclo-C_6H_{11}	DMSO, hν, 32 h[e]	76	
Ph	Ph	neo-C_5H_{11}	PhH, hν, 72 h	~10	

[a] ^{1}H.N.M.R. yields.
[b] Stereochemistry was determined by GLC.
[c] Irradiation period with a 275 W sunlamp placed 15 cm from the reaction vessel.
[d] Isolated yield.
[e] Irradiation time in the Rayonet reactor at 350 nm.
[f] Only cyclized products were observed.
[g] Bibenzyl was formed as the main product.

This evidence indicates the free radical nature of the reaction. The assumption is that the reaction proceeds via free radical addition-elimination chain process, in which one of the propagation steps involves electron transfer from the tin-centered radical to the alkyl-mercurial to give the radical anion. A reasonable suggestion for the propagation stage of such a mechanism is shown in Scheme XXIV. The first

Scheme XXIV   (X = Cl, Br)

$$R\cdot + PhCH=CHSnBu_3 \xrightarrow{\alpha-add.} \underset{\underset{\displaystyle SnBu_3}{|}}{PhCH-CHR} \qquad (47)$$

22

$$\textbf{22} \quad \xrightarrow{\beta-elim.} PhCH=CHR + Bu_3Sn\cdot \qquad (48)$$

$$Bu_3Sn\cdot + RHgX \quad \xrightarrow{E.T.} Bu_3Sn^+ + RHgX^{-} \qquad (49)$$

23

$$\textbf{23} \quad \longrightarrow R\cdot + X^{-} + Hg(0) \qquad (50)$$
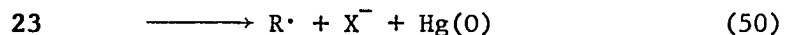
step in this mechanism involves the addition of the alkyl radical, R·, to the α-carbon of 1-alkenyltin compound to give the β-alkylstannyl radical intermediate 22. The regioselective addition of the alkyl radical to the α-carbon of the tin compound can be rationalized in terms of the stability of the resulting benzylic radical **22** which is stabilized by delocalization of the unpaired electron into the phenyl ring. The importance of this stabilization was demonstrated by the observation that the unsubstituted tri-n-butyl-1-ethenyltin reacts with

alkylmercurials sluggishly and to a very limited extent under similar reaction conditions (the reaction of tri-n-butyl-1-ethenyltin will be discussed later in this section). Furthermore, the β-alkylstannyl radical 22 may be stabilized by a possible interaction of the β-radical center with the d^5-orbitals of the tin substituent. However, this would not expect to occur to a large extent, since tri-n-butyl-1-ethenyltin reacts very slowly, as mentioned above. Thus, this interaction, if it exists at all, is not enough of a driving force to affect the regioselectivity of the addition of the alkyl radical. The intermediate β-alkylstannyl radical undergoes a β-elimination reaction to give the product, the β-alkylstyrene, and the tri-n-butyltin radical, $Bu_3Sn\cdot$. Electron transfer from the tin radical to the alkylmercurial (Eq. 49) gives the alkylmercury halide radical-anion, 23. The decomposition of this intermediate (Eq. 50) yields mercury metal, halide anions and the alkyl radical which will continue the chain.

Electron transfer reaction has been suggested as a possible propagation step in the free radical reduction of alkyl halides with triorganotin hydrides [100]. Recently, Bloodworth and Courtneidge have reported that tri-n-butyltin hydride reduction of alkylmercurials proceeds through free radical chain process to give alkanes, tri-n-butyltin halides and mercury metal [103]. These workers have suggested that the generation of the alkyl radicals in this reaction involved a S_H2 attack of the tri-n-butyltin radical at the halogen-mercury bond (Eq. 51). However, alkylmercury halides were established to react under free radical conditions (Part I of this dissertation) without any

$$\underline{n}-Bu_3Sn\cdot + BrHgR \longrightarrow \underline{n}-Bu_3SnBr + RHg \longrightarrow R\cdot + Hg(0) \qquad (51)$$
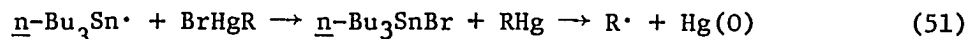
involvement of a S_H^2 attack at the halogen-mercury bond, i.e. reaction

52 has never been encountered. Thus, if the alkyl radical fails to

$$R\cdot + BrHgR \xrightarrow{\quad\not\longrightarrow\quad} RBr + RHg \qquad (52)$$

show any sign for S_H^2 attack at the halogen-mercury bond, it is unlikely

that the tin-centered radicals will attack the halogen-mercury bond in

a S_H^2 fashion. Moreover, the S_H^2 attack is highly unlikely at the

strong RHg-Br bond (70 Kcal/mol) [104]. However, it is difficult to

completely exclude reaction 51 from the free radical chain reaction and

the possibility of competing reactions 49 and 51 exists.

The intermediacy of the alkyl radicals in the reaction of 1-alkenyl-

tin compounds with alkylmercury halides was demonstrated by the observa-

tion that Δ^5-hexenylmercury chloride reacted with tri-$\underline{n}$-butyl-($\underline{E}$)-2-

phenyl-1-ethenyltin to give only the cyclized product 1-phenyl-3-

cyclopentyl-1-propene with an 88:12 trans:cis ratio. No 1-phenyl-1,7-

octadiene or 1-phenyl-2-cyclohexylethene was detected by [1]H.N.M.R. or

GLC analysis. The formation of cyclopentyl derivative is consistent

with the formation of Δ^5-hexenyl radical, which is well-known to cyclize

to the cyclopentylcarbinyl radical [21].

The reaction of other 1-alkenyltin compounds with alkylmercurials

has also been investigated under free radical reaction conditions. Thus,

tri-$\underline{n}$-butyl-2,2-diphenyl-1-ethenyltin and isopropylmercury chloride

underwent a photostimulated reaction under UV irradiation to give

1,1-diphenyl-3-methyl-1-butene in a 73% yield. Mercury metal was pre-
cipitated and tri-n-butyltin chloride was formed. Comparable results
were obtained when the reaction was performed thermally at 80°C with 10
mole % AIBN added. The above reaction failed to proceed in the dark
and strongly retarded by free radical inhibitor, di-tert-butyl nitroxide.
Similarly, tri-n-butyl-2,2-diphenyl-1-ethenyltin and cyclohexylmercury
chloride reacted under sunlamp irradiation to give 1,1-diphenyl-2-
cyclohexylethene in a 76% yield together with mercury metal and tri-n-
butyltin chloride. However, neopentylmercury chloride reacted very
slowly with tri-n-butyl-2,2-diphenyl-1-ethenyltin under similar reac-
tion conditions. The substituted alkene was detected in a low yield
of ca. 10%. It is worth mentioning that the reaction of alkylmercurials
with $Ph_2C=CHSnBu_3$ proceeds faster in the presence of excess (3-5 equiv)
alkylmercurials. Mechanistically, the reaction is believed to proceed
by a radical chain process, which involves β-alkylstannyl radical inter-
mediate, as previously described and shown in Scheme XXIV.

Tri-n-butyl-1-ethenyltin reacted very slowly with alkylmercurials
to give very low yields of 1-alkenes. Thus, irradiation of a benzene
solution of tri-n-butyl-1-ethenyltin and cyclopentylmercury chloride in
the Rayonet at 350 nm yielded vinylcyclopentane in only 10% yield. In
addition, slow reactions and poor yields were observed in the reaction
of $CH_2=CHSnBu_3$ with other alkylmercurials, RHgCl (R = cyclohexyl, n-
hexyl and Δ^5-hexenyl). The results demonstrate the importance of the
β-phenyl substituents as driving force in accomplishing the α-addition
of the alkyl radical to 1-alkenyl tin compounds.

Surprisingly, tri-n-butyl-2,2-dimethyl-1-ethenyltin did not react
with cyclopentylmethylmercury chloride, even after prolonged irradia-
tion in the Rayonet at 350 nm. The substituted 1-alkene was not formed
and only a trace of mercury metal was precipitated. The reaction
also failed to occur thermally at 80°C with 10 mole % AIBN. The lack
of success in this reaction indicates that the alkyl radical did not
propagate the reaction, probably because of the abstraction of the
allylic hydrogen of the tin substrate by the alkyl radical.

The triorganotin enolate, tri-n-butyl-(1-cyclohexenyloxy)tin (24)
undergoes a photostimulated substitution reaction with alkylmercurials
to afford monoalkylated products in low yield. Thus, sunlamp irradia-
tion of a benzene solution of 24 and n-butylmercury chloride for 16 h
resulted in the formation of 2-n-butylcyclohexanone in a 24% yield.
Similarly, the reaction of 24 with isopropylmercury chloride under sun-
lamp irradiation gave a 36% yield of 2-isopropylcyclohexanone.
Analogous to the reaction of tri-n-butyl-1-alkenyltin derivatives, the
reaction of organotin enolate might proceed through a radical chain
process. A plausible propagation steps of such a process are shown in
Scheme XXV. The addition of R· to the β-carbon of the organotin enolate
gives the stabilized tertiary radical 25 as an intermediate, which under-
goes β-elimination of Bu_3Sn· to give the product, 2-alkylcyclohexanone.
Bu_3Sn· continues the chain through an electron transfer process to give
the radical anion, followed by the dissociation of the latter to give
mercury metal, X^- and R·. Organotin enolates have been reported to
undergo substitution reactions with various alkyl halides to give

Scheme XXV

$$Bu_3Sn\cdot + RHgCl \longrightarrow Bu_3Sn^+ + RHgCl^{\tau}$$

$$RHgCl^{\tau} \longrightarrow R\cdot + Cl^- + Hg(0)$$
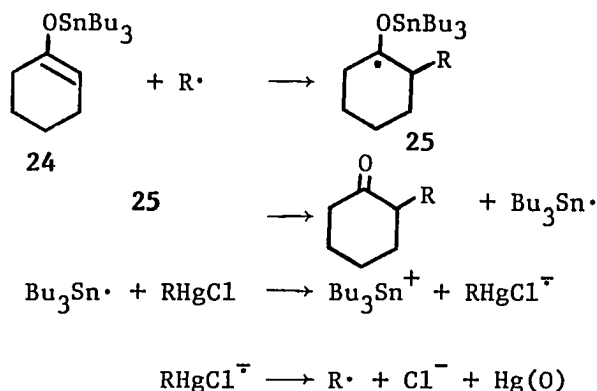
monoalkylated products (Eq. 53) [105, 106]. The alkyl iodides were found to react more readily than the corresponding bromides.

$$\text{OSnBu}_3 + RI \xrightarrow[\text{16 h}]{80°C} \text{O} + Bu_3SnI \qquad (53)$$
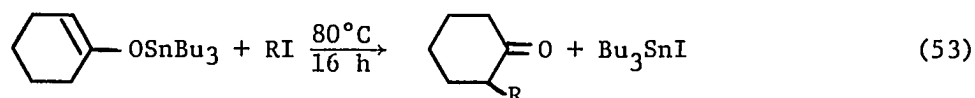
Attempts to use Grignard reagents as alkyl radical sources were, unfortunately, unsuccessful. Thus, sunlamp irradiation of a THF solution of n-hexylmagnesium bromide or Δ^5-hexenylmagnesium bromide and tri-n-butyl-(E)-2-phenyl-1-ethenyltin for 12 h gave no coupling product and the starting stannane was recovered unchanged.
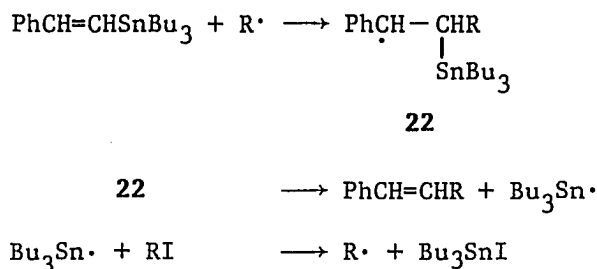
2. Reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with alkyl halides

When tri-n-butyl-(E)-2-phenyl-1-ethenyltin was treated with n-butyl iodide in benzene solution under UV (350 nm) irradiation, the coupling product was obtained in significant yield. The product, 1-phenyl-1-hexene, was found as a mixture of both cis- and trans-isomers. The GLC

ratio of <u>trans</u>:<u>cis</u> isomers was determined to be 84:16. Tri-<u>n</u>-butyltin

iodide was formed as the other product. The first indication that the

reaction might proceed via a radical chain process came when the reac-

tion failed to proceed in the dark. Thus, treatment of tri-<u>n</u>-butyl-

(<u>E</u>)-2-phenyl-1-ethenyltin with <u>n</u>-butyliodide in the dark at 50°C for 10

h led to no change in the starting materials. Moreover, the reaction

was strongly inhibited by di-<u>tert</u>-butyl nitroxide. When the photoreac-

tion was repeated with 10 mole % di-<u>tert</u>-butyl nitroxide added, the

yield dropped to 23% after prolonged irradiation at 350 nm. However,

the reaction between <u>n</u>-butyl iodide and tri-<u>n</u>-butyl-(<u>E</u>)-2-phenyl-1-

ethenyltin occurred smoothly upon heating the solution in the dark at

80°C in the presence of AIBN. 1-Phenyl-1-hexene was formed in a 64%

yield as determined by quantitative ^{1}H.N.M.R. In a similar manner, <u>n</u>-

pentyl iodide was found to react cleanly with tri-<u>n</u>-butyl-(<u>E</u>)-2-phenyl-

1-ethenyltin under UV 9350 nm) irradiation to afford 1-phenyl-1-heptene

in a moderate yield. Again, the product consisted of both <u>trans</u>- and

<u>cis</u>-isomers with the <u>trans</u>-isomer predominating.

The results presented above indicate a possible free radical chain

process in which a key step is the S_H2 attack of the tin-centered radi-

cal at the alkyl iodide. A proposed propagation steps for this mechanism

are shown in Scheme XXVI. The regioselective addition of R· to the

α-carbon of the tin compound, which may be enhanced by the phenyl sub-

stituent, would give the β-alkylstannyl radical **22**. Intermediate **22**

undergoes β-elimination of Bu₃Sn· to afford the product. The S_H2 attack

of the tin-centered radical at R-I gives Bu₃SnI and R· which continues

Scheme XXVI

$$PhCH=CHSnBu_3 + R\cdot \longrightarrow PhCH-CHR$$
$$\qquad\qquad\qquad\qquad\qquad \cdot\ \ \ |$$
$$\qquad\qquad\qquad\qquad\qquad\quad SnBu_3$$

22

$$\textbf{22} \qquad\qquad \longrightarrow PhCH=CHR + Bu_3Sn\cdot$$

$$Bu_3Sn\cdot + RI \qquad \longrightarrow R\cdot + Bu_3SnI$$

the chain. Analogous S_H^2 attack was proposed for the organotin hydrides reduction of the alkyl halides, which is known to proceed through a radical chain mechanism [97].

The use of other alkyl halides as sources for the alkyl radicals was also studied. However, a limited success was encountered in several occasions. For example, the reaction of isopropyl iodide with tri-_n_-butyl-(_E_)-2-phenyl-1-ethenyltin under UV (350 nm) irradiation was complicated with the formation of unidentified yellow precipitate. Only a low yield of the coupling product, 1-phenyl-3-methyl-1-butene was detected. In addition, β-styryl iodide (both _cis_- and _trans_-isomers) was also formed. This is in contrast to the reactions of 1°-alkyl iodides. Also, benzyl bromide reacted very slowly with tri-_n_-butyl-(_E_)-2-phenyl-1-ethenyltin under UV (350 nm) irradiation to give a low yield (15%) of 1,3-diphenyl-1-propene. Both _cis_- and _trans_-isomers were detected and again the _trans_-isomer predominated. Under similar reaction conditions, benzyl chloride completely failed to react with the 1-alkenyltin compound $PhCH=CHSnBu_3$. Similarly, iodobenzene, 2-chloro-2-nitropropane, and 2-bromo-2-nitropropane failed to react with $PhCH=CH_2SnBu_3$ under UV (350) irradiation. Methyl bromoacetate and

tri-n-butyl-(E)-2-phenyl-1-ethenyltin underwent a slow photostimulated reaction to give a fair yield of the coupling product, PhCH=CHCH$_2$CO$_2$Me. Both cis- and trans-isomers were formed. In contrast, chloroaceto-nitrile did not react under similar reaction conditions. Additionally, benzoyl chloride failed to react with tri-n-butyl-(E)-2-phenyl-1-ethenyltin under UV irradiation or thermally at 80°C in the presence of AIBN. It is noteworthy that triorgano-1-alkenyltin compounds have been reported to react with acid chlorides in the presence of Lewis acid catalysis, such as pallidium(II) complexes [107] or aluminum chloride [108] to yield the α,β-unsaturated ketones and trialkyltin chlorides.

The reactivities of alkyl halides in the reaction with PhCH=CHSnBu$_3$ reflect the ease of the abstraction of the halogen atom by the tin-centered radicals. The results are in agreement with those reported for the reaction of alkyl halides with triorganotin hydrides, i.e. I > Br > Cl [109, 110].

In 1977, Saihi and Pereyre reported that tri-n-butyl-1-alkenyltin derivatives reacted with ethyl haloacetates, XCH$_2$CO$_2$Et (X = Br or I), at high temperatures to give a low yield of the corresponding α,β-unsaturated esters, R$_1$R$_2$C=CHCH$_2$CO$_2$Et [108]. The results obtained by these workers are summarized in Table XIV. These workers have also reported that n-butyl bromide, sec-butyl iodide, benzyl chloride and propargyl bromide failed to react with 1-alkenyltin compounds under UV irradiation or by the thermolysis of AIBN. However, these authors did not specify which 1-alkenyltin derivative was used in the reaction with these halides.
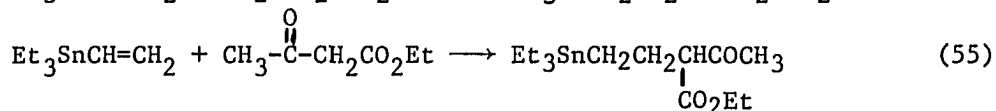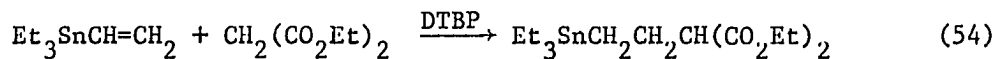
Table XIV. Thermal reaction of 1-alkenyltin derivatives with ethyl
haloacetates [108]

$$Bu_3SnCH=CR_1R_2 + XCH_2CO_2Et \xrightarrow{\Delta} R_1R_2C=CHCH_2CO_2Et$$

R_1	R_2	X	Temperature °C	Yield %
H	H	Br	120	0
H	H	I	130	19
Me	H	Br	140	15[a]
Me	H	I	140	28[a]
Me	Me	Br	140	16
Me	Me	I	140	38
Ph	H	Br	150	14[b]
Ph	H	I	150	41[b]

[a]A mixture of _cis_ and _trans_ isomers.

[b]_Trans_ isomer only.

The photostimulated reaction of $BrCH_2CO_2Me$ with $CH_2{=}CHSnBu_3$ at

40°C was performed and the product, although not completely identified,

appeared to be the 1:1 addition product, $MeO_2CCH_2CH_2CH(Br)SnBu_3$. The β-

addition of carbon-centered radicals to triethylvinyltin has been

reported. In addition to the reactions involving ·CCl_3 mentioned in

the introduction [85], triethylvinyltin reacts with diethylmalonate or

ethylacetoacetate in the presence of di-_tert_-butylperoxide to give only

β-addition products (Eq. 54, 55) [111]). No substitution products were

$$Et_3SnCH=CH_2 + CH_2(CO_2Et)_2 \xrightarrow{DTBP} Et_3SnCH_2CH_2CH(CO_2Et)_2 \quad (54)$$

$$Et_3SnCH=CH_2 + CH_3\overset{O}{\overset{\|}{C}}{-}CH_2CO_2Et \longrightarrow Et_3SnCH_2CH_2\underset{\underset{CO_2Et}{|}}{CH}COCH_3 \quad (55)$$

observed. Diethyl (β-triethylstannylethyl)malonate was obtained in a

37% yield, whereas 3-ethoxycarbonyl-5-triethylstannyl-2-pentanone
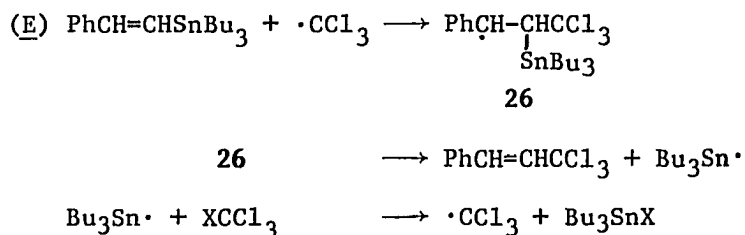
resulted in a 44% yield [111].

3. Reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin
   with polyhalomethanes

When a carbon tetrachloride solution of tri-n-butyl-(E)-2-phenyl-

1-ethenyltin was irradiated in the Rayonet at 350 nm, a slow reaction

occurred. The progress of the reaction was followed by ^{1}H.N.M.R. When

the reaction was complete, the solvent was removed under reduced pres-

sure to give a light yellow residue. GLC and ^{1}H.N.M.R. analysis revealed

1-phenyl-3,3,3-trichloropropene as the only organic product of the reac-

tion. The reaction was not completely stereoselective in that both

trans- and cis-isomers were formed. However, as in the reaction of

other carbon-centered radicals, the trans-isomer predominated. The GLC

trans:cis ratio was determined to be 95:5. Tri-n-butyltin chloride was

formed as the other product. The product of the addition of CCl_4 to

the double bond of the tin compound was not observed. The above reac-

tion was also found to occur thermally in the dark in the presence of

free radical initiator. Thus, heating the above reaction mixture in

the dark at 80°C, with 10 mole % AIBN was added, led to the formation

of both isomers of 1-phenyl-3,3,3-trichloro-1-propene and tri-n-butyltin

chloride. Again, no addition product was detected. The formation of

the coupling product was completely inhibited by di-tert-butyl

nitroxide. This observation supports the free radical nature of the

reaction.

Comparable results were obtained from the reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin and bromotrichloromethane. Both photochemical reaction and thermal reaction in the presence of AIBN afforded 1-phenyl-3,3,3-trichloro-1-propene and tri-n-butyltin bromide as the exclusive products. The product was a mixture of trans- and cis- in a ratio of 93:7 as determined by GLC analysis. When the same reaction was repeated with trichloromethanesulfonyl chloride, as the $\cdot CCl_3$ source, 1-phenyl-3,3,3-trichloro-1-propene was obtained as the exclusive product. No addition products were observed with either $BrCCl_3$ or CCl_3SO_2Cl.

The reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with poly-halomethanes showed the characteristics of a free radical chain process. The reaction was catalyzed by free radical sources, such as UV irradiation or by the thermolysis of AIBN. Furthermore, the reaction was completely inhibited by di-tert-butyl nitroxide. A plausible reaction mechanism involves addition-elimination chain process presented in Scheme XXVII. The first propagation step involves the α-addition of

Scheme XXVII   (X = Cl, Br, SO_2Cl)

(E) PhCH=CHSnBu$_3$ + $\cdot CCl_3$ $\longrightarrow$ PhĊH-CHCCl$_3$
                                                                    |
                                                                  SnBu$_3$

26

26 $\longrightarrow$ PhCH=CHCCl$_3$ + Bu$_3$Sn·

Bu$_3$Sn· + XCCl$_3$ $\longrightarrow$ $\cdot CCl_3$ + Bu$_3$SnX

$\cdot CCl_3$ to the 1-alkenyltin compound to give the benzylic-stabilized β-alkylstannyl radical intermediate, **26**. Intermediate **26** undergoes

(step 2) β-elimination of $Bu_3Sn\cdot$ to yield the product. The tin-centered radical abstracts a halogen atom from the substrate to generate $\cdot CCl_3$ and yield Bu_3SnX. In the case of trichloromethane-sulfonyl chloride, it seems that the trichloromethanesulfonyl radical dissociated to $\cdot CCl_3$ and SO_2 (Eq. 56) before the α-addition to the tin

$$CCl_3SO_2^{\cdot} \longrightarrow \cdot CCl_3 + SO_2 \tag{56}$$
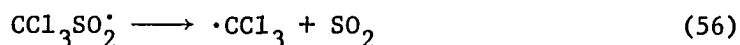
compound occurred. Thus, in this case, regeneration of $\cdot CCl_3$ by reaction 56 provides one of the propagation steps required for the chain reaction.

Polyhalomethanes CCl_3Z (Z = H, Cl and Br) are reported to add to triethyl-1-ethenyltin under free radical reaction conditions to yield adduct **14** (Eq. 57) [85]. The adduct was presumably formed via the

$$(C_2H_5)_3SnCH=CH_2 + CCl_3Z \xrightarrow[90°C]{Bz_2O_2} (C_2H_5)_3SnCH(Z)CH_2CCl_3 \tag{57}$$
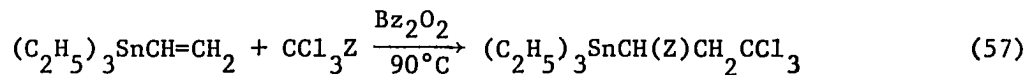
$$\textbf{14}$$

addition of $\cdot CCl_3$ radical to the β-carbon of the vinyltin compound followed by the abstraction of the atom Z from the substrate. Thus, it is obvious that the β-phenyl substituent in tri-n-butyl-(E)-2-phenyl-1-ethenyltin plays an important role in enhancing the regioselective addition of $\cdot CCl_3$ to the α-carbon of the 1-alkenyltin compound, which leads to substitution rather than addition reaction. It is worth mentioning that unsubstituted triorgano-1-ethenylsilanes [112] and triorgano-1-ethenylgermanes [113] undergo similar addition reactions with polyhalomethanes in the presence of free radical sources, such as benzoyl

peroxide, in which $X_3C\cdot$ adds to the unsubstituted β-carbon atom.

4. Reaction of β-substituted styrenes with alkylmercurials

Trans-β-substituted styrenes, PhCH=CHQ (Q = I, $PhSO_2$, HgCl and PhS), were found to undergo photostimulated reactions with alkylmercury halides to give mainly the trans-β-alkylated styrene. The cis-isomer was formed only in a small amount. The reaction of (E)-β-iodostyrene with iso-propylmercury chloride was performed in DMSO under UV irradiation. The reaction gave (E)-1-phenyl-3-methyl-1-butene as the major product. IHgCl was presumably formed as the other reaction product, and only a trace of mercury metal was precipitated. When the same reaction was re-peated thermally in the dark at 100°C, with 10 mole % benzoyl peroxide added, the reaction occurred to give the same product in significant yield (see experimental section). Di-tert-butyl nitroxide is known to be a power-ful inhibitor of the free radical reactions. When the photoreaction was repeated in DMSO with 10 mole % of di-tert-butyl nitroxide added, the yield of the coupling product, 1-phenyl-3-methyl-1-butene, was drastically reduced (see Table XV). Consequently, the reaction must pro-ceed through a free radical chain process. In addition, the reaction of β-iodostyrene with isopropylmercurial failed to occur when the reaction mixture was heated in the dark at 50°C. Other alkylmercurials were found to participate in free radical chain reactions with (E)-β-iodo-styrene. The results are tabulated in Table XV. In general, 1°-alkyl-mercurial salts reacted slower than the 2°-alkylmercurials and the yields usually are better with the latter.

Table XV. Reaction of β-substituted styrene with alkylmercurials

$$PhCH=CHQ + RHgCl \xrightarrow{\text{light}} PhCH=CHR + QHgCl$$

Q	R	Time (h)[a]	% Yield[b] PhCH=CHR	trans/ cis[c]
I	$(CH_3)_2CH$	14	76	90/10
I	cyclo-C_6H_{11}	14	84	92/8
I	n-C_4H_9	48	22[d]	
I	neo-C_5H_{11}	48	~10[d]	
SO_2Ph	$(CH_3)_2CH$	38	68	85/15
SO_2Ph	cyclo-C_6H_{11}	48	74	88/12
SO_2Ph	tert-C_4H_9	16	43	89/11
HgCl	$(CH_3)_2CH$	30	36	85/15
HgCl	cyclo-C_6H_{11}	22	42	90/12
SPh	$(CH_3)_2CH$	43	32	84/16
SPh	cyclo-C_6H_{11}	38	43	83/17

[a]Irradiation period in the Rayonet reactor at 350 nm. The reactions were performed in DMSO under nitrogen at ambient temperature (35°C).

[b]^{1}H.N.M.R. yields.

[c]Stereochemistry ratio was determined by GLC.

[d]Isomerized starting material was observed.
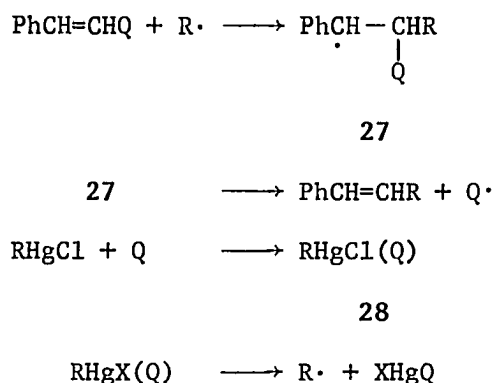
The substitution reaction has been successfully extended to the phenyl trans-β-styryl sulfone and (E)-2-phenyl-1-ethenylmercury chloride. The results are included in Table XV. The corresponding sulfide gave practically the same results, though the reactions proceeded rather sluggishly and the yields are much lower.

The results discussed above demonstrated that the reaction of

β-substituted styrenes with alkylmercurials must proceed via a radical chain mechanism. The initiation of the reaction photochemically or by thermolysis of AIBN, besides the significant inhibition by di-tert-butyl nitroxide support this conclusion. The possible propagation steps for such a mechanism are shown in Scheme XXVIII. A key step in this mechanism is the α-addition of R· to the substrate to yield the

Scheme XXVIII   (Q = I, $PhSO_2$, HgCl, PhS)

$$PhCH=CHQ + R· \longrightarrow PhCH - CHR$$
$$\underset{·}{} \quad \underset{Q}{|}$$

27

$$27 \longrightarrow PhCH=CHR + Q·$$

$$RHgCl + Q \longrightarrow RHgCl(Q)$$

28

$$RHgX(Q) \longrightarrow R· + XHgQ$$

benzylic-stabilized carbon-centered radical intermediate, **27**, which undergoes a β-elimination to give the product and Q·. The Q· radical can add to the alkylmercurial to afford the tricovalent mercury species **28** (as discussed in Part I of this dissertation). Decomposition of **28** gives the mercury(II) salt and generates the alkyl radical which continues the chain.

(E)- or (Z)-Methyl β-styryl sulfone or sulfoxide are reported to react with trialkylboranes by a free radical chain mechanism to give mainly or exclusively the (E)-β-alkyl styrenes in good yield [114].

This reaction has been explained by postulating a vinyl radical inter-
mediate [114]. However, the reaction most likely proceeds by the chain
sequence of Scheme XXVIII with R_3B taking the place of RHgCl. The
reaction failed with the methyl β-styryl sulfide or with vinyl sulfoxides
or sulfones containing an alkyl β-substituent [114]. The reaction was
extended to methyl phenylethynyl sulfone and sulfoxide which with Bu_3B
and $(i\text{-}Pr)_3B$ gave good yields of the 1-phenylalkyne-1 [114].

It has been established that alkyl radicals, substituted at the β-
position with a sulfur, often eliminate a sulfur-centered radical to
generate an alkene [115-117]. Although the elimination of phenylthio
or phenylsulfonyl radical is reported to be not stereoselective, in
that a mixture of (E)- and (Z)-isomers was formed [115, 116], the
elimination of phenylsulfinyl radical is reported to be completely
stereoselective [117].

In addition to these vinylic substitution reactions, homolytic
aromatic substitution reactions between alkylmercury halides and 2-
substituted benzothiazole (29) were also investigated. It was found

X = I and $PhSO_2$

29
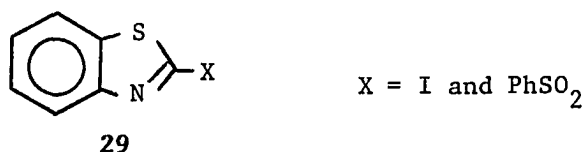
that 2-iodobenzothiazole reacted with isopropylmercury chloride under
UV (350 nm) irradiation to give a moderate yield of 2-isopropylbenzo-
thiazole. A similar reaction was observed between cyclohexylmercury
chloride and 2-iodobenzothiazole to yield 2-cyclohexylbenzothiazole.
However, the reaction of 1°-alkylmercurials with 2-iodobenzothiazole was

found to be slower and the yields were lower. The results are sum-

marized in Table XVI. The reaction was significantly inhibited by

Table XVI. Photoreaction of 2-substituted benzothiazole with alkyl
mercury halides

X	R	Time[a] (h)	% Yield[b] 30
I	$(CH_3)_2CH$	22	55
I	Cyclo-C_6H_{11}	18	62
I	$CH_3CH_2CH_2CH_2$	43	38
I	$(CH_3)_3CCH_2$	72	~10[c]
SO_2Ph	$(CH_3)_2CH$	38	35
SO_2Ph	Cyclo-C_6H_{11}	38	38
SO_2Ph	$(CH_3)_3CCH_2$	80	~5[c]

[a]Irradiation period in a Rayonet photoreactor equipped with 14
"350 nm" bulbs. Reactions were performed in DMSO under nitrogen at
ambient temperature (35°C).

[b]1H.N.M.R. yields.

[c]Unchanged starting material was detected,

di-tert-butyl nitroxide and failed to proceed in the dark. The reac-

tion was successfully extended to the 2-(phenylsulfonyl)benzothiazole,

though its reactions proceeded somewhat slower. The results are sum-

marized in Table XVI.

The reaction is believed to occur via the addition-elimination

mechanism of Scheme XXIX; i.e., by the generally accepted mechanism

for homolytic aromatic substitution. The addition of the alkyl radical

Scheme XXIX   (X = I, $PhSO_2$)

RHgCl + X ———→ RHgCl(X)

RHgCl(X) ———→ R· + XHgCl
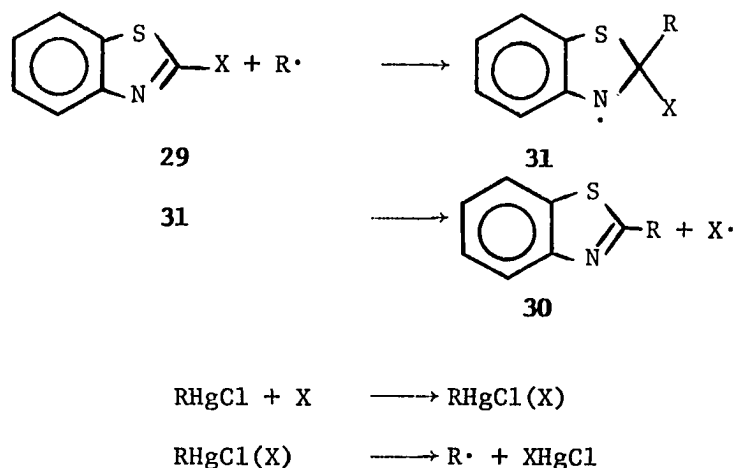
to the substrate gives the ipso intermediate **31**, which is stabilized

by the delocalization of the odd electron by the phenyl ring. Subse-

quent elimination of group X from **31** affords the product. Group X

adds to the alkylmercurial to yield the tricovalent mercury species

which decomposes to mercury(II) salt and R· which continues the chain.

Ipso-substitution is reported to be the main reaction pathway for the

reaction of 2-substituted benzothiazole **29** (X = I, $PhSO_2$, NO_2 and COMe)

with adamantyl radical [118].

Attempts to extend these ipso substitution processes to other

aromatic substrates were unsuccessful. Thus, α-iodonaphthalene failed

to react with isopropylmercury chloride under UV (350 nm) irradiation.

Similarly, iodobenzene failed to react with isopropylmercurial under comparable reaction conditions. However, the reaction of 4-phenyl-thiopyridine with excess alkylmercurials RHgCl (R = isopropyl and cyclohexyl) afforded mainly the products of substitution at the 2-position and only a small amount of the ipso substitution product. The latter reaction proceeded with a limited conversion.

5. Reaction of tri-n-butyl-1-alkenyltin with
   heteroatom-centered radicals

No reaction was observed between tri-n-butyl-1-ethenyltin and phenyl disulfide upon prolonged heating (50°C) in benzene solution in the dark. In contrast, a facile reaction occurred when the reaction mixture was irradiated with a sunlamp placed 15 cm from the reaction vessel. The progress of the reaction was monitored by GLC. After the reaction was complete, the solvent was removed under reduced pressure to give a light yellow oil. The residue was shown by GLC analysis to contain two compounds which were identified to be vinyl phenyl sulfide and tri-n-butyltin phenyl sulfide. Upon distillation, vinyl phenyl sulfide was isolated as a colorless liquid in a 92% yield. The same reaction was found to be effectively initiated with AIBN at 80°C. Thus, vinyl phenyl sulfide was obtained in almost quantitative yield when a benzene solution of tri-n-butyl-1-ethenyltin and phenyl disulfide was heated at 80°C in the dark in the presence of 10 mole % AIBN. However, when the photoreaction was repeated with 10 mole % di-tert-butyl nitroxide added, the formation of vinyl phenyl sulfide was completely suppressed. This indicates the free radical nature of the reaction.

Other tri-n-butyl-1-alkenyltin compounds were also found to react

very rapidly with phenyl disulfide in similar manner to afford the

corresponding 1-alkenyl phenyl sulfides in good yields. The results

are summarized in Table XVII. Thus, tri-n-butyl-(E)-2-phenyl-1-ethenyl-

tin and phenyl disulfide underwent a rapid photostimulated reaction

Table XVII. Reaction of tri-n-butyl-1-alkenyltin with heteroatom-
centered radicals

$$RCH=CHSnBu_3 + QY \longrightarrow RCH=CHQ + Bu_3SnY$$

R	QY	Conditions[a]	% Yield[b] RCH=CHQ
H	PhSSPh	PhH, hv, 4h	91
H	PhSSPh	PhH, AIBN, 80°C	82
H	PhSSPh	PhH, dark, 50°C	0
H	PhSSPh	PhH, hv, $\overset{X}{\underset{X}{N}}$-O· 2h	0
H	$PhSO_2Cl$	PhH, hv, 6 h	90
H	$PhCH_2SSCH_2Ph$	PhH, hv, 12 h	82
Ph	PhSSPh	PhH, hv, 4 h	86
Ph	$PhSO_2Cl$	PhH, hv, 4 h	88
Ph	$PhCH_2SSCH_2Ph$	PhH, hv, 10 h	85
Ph	PhSeSO2PhMe-p	PhH, hv, 6 h	84
H	PhSeSePh	PhH, hv, 24 h	0
Ph	PhSeSePh	PhH, hv, 24 h	0

[a]Reactants were irradiated with a 275 W sunlamp approximately 15
cm from the Pyrex reaction vessel, reactions were performed under
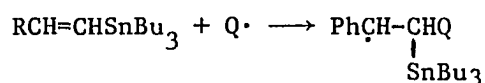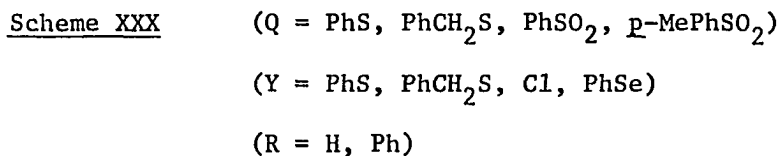nitrogen at ambient temperature (25-40°C).

[b]Isolated yields.

under sunlamp irradiation to give β-styryl phenyl sulfide in an 86%

yield. Surprisingly, only the trans-isomer was observed, whereas the

cis-isomer was not detected by either ^{1}H.N.M.R. or GLC analysis.

Again, the reaction can be initiated thermally with AIBN, and was com-

pletely inhibited by di-tert-butyl nitroxide.

Alkyl disulfides were also found to participate in a free radical

reaction with tri-n-butyl-1-alkenyl derivatives to yield the correspond-

ing 1-alkenyl alkyl sulfides. Thus, treatment of $RCH=CHSnBu_3$ (R = H

and Ph) with benzyl disulfide under the influence of a sunlamp irradia-

tion gave $RCH=CHSCH_2Ph$ (R = H and Ph) in significant yield. The results

are included in Table XVII. The reaction was successfully extended to

other sulfur-centered radicals. Thus, benzenesulfonyl chloride reacted

with $RCH=CHSnBu_3$ (R = H and Ph) under sunlamp irradiation to afford

$RCH=CHSO_2Ph$ exclusively. Similarly, Se-phenyl p-tolylselenosulfonate

reacted with $RCH=CHSnBu_3$ under similar reaction conditions to yield

exclusively $RCH=CHSO_2PhMe-p$ in good yields. The results are shown in

Table XVII. In the reaction of $PhCH=CHSnBu_3$ with all these substrates,

only the trans-isomers were obtained. The cis-isomers were not

detected.

The reaction of 1-alkenyltin compounds with sulfur-centered radi-

cals exhibits all the characteristics of an efficient radical chain

process. The reaction can be effectively initiated with free radical

sources, such as sunlamp irradiation or thermolysis of AIBN. Also,

the reaction failed to proceed in the dark and was completely inhibited

by di-tert-butyl nitroxide. It is believed that the reaction occurs

through an addition-elimination radical chain process. Scheme XXX out-
lines a possible propagation steps for such process, which is analogous

Scheme XXX   (Q = PhS, PhCH$_2$S, PhSO$_2$, p-MePhSO$_2$)

(Y = PhS, PhCH$_2$S, Cl, PhSe)

(R = H, Ph)

$$RCH=CHSnBu_3 + Q\cdot \longrightarrow Ph\overset{\cdot}{C}H-CHQ$$
$$\underset{\displaystyle SnBu_3}{|}$$

32

32 $\longrightarrow$ PhCH=CHQ + Bu$_3$Sn$\cdot$

Bu$_3$Sn$\cdot$ + Q - Y $\longrightarrow$ Q$\cdot$ + Bu$_3$SnY
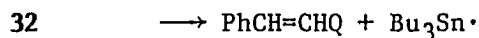
to the one previously described for the reaction of 1-alkenyltin com-
pounds with CCl$_4$ and BrCCl$_3$. A key step in this mechanism is the S$_H^2$
attack of Bu$_3$Sn$\cdot$ at the radical precursors QY to generate the sulfur-
centered radicals Q$\cdot$. Tri-n-butyltin radical has been reported to
participate in a S$_H^2$ attack at aryl or alkyl disulfides (Eq. 58) [102].

$$\underline{n}\text{-Bu}_3Sn\cdot + RSSR \longrightarrow \underline{n}\text{-Bu}_3SnSR + RS\cdot \qquad (58)$$
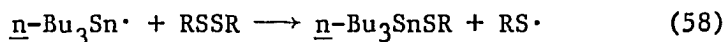
Spanswick and Ingold determined the rate constants for the bimolecular
homolytic displacement at phenyl disulfide and benzyl disulfide to be
9x10^6 and 7x10^5 L/mol·s·, respectively.

Triethyl-1-ethenyltin is reported to react with alkanethiols under
UV irradiation with predominant formation of the addition product 2-
(triethyltin)ethyl alkyl sulfide (Eq. 59) [88, 89]. In addition,

$$Et_3SnCH=CH_2 + RSH \xrightarrow{UV} Et_3SnCH_2CH_2SR \qquad (59)$$

16
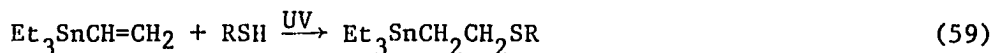
products of the α-addition of RS· to the double bond of the tin sub-
strate followed by β-elimination of Et_3Sn· were also observed. The
formation of the addition product **16** is believed to proceed through a
free radical addition of RS· to the β-carbon of the vinyltin compound
to give the α-alkylstannyl radical **33**, which abstracts a hydrogen atom
from RSH. Both α- and β-additions are believed to be reversible (Eq.
60, 61) [88]. β-Alkylstannyl radical (**34**) will rapidly undergo a β-

$$RS· + Et_3SnCH=CH_2 \underset{\longleftarrow}{\xrightarrow{\beta\text{-add}}} Et_3Sn\overset{\bullet}{C}H-CH_2SR \xrightarrow{RSH} \textbf{16} \qquad (60)$$
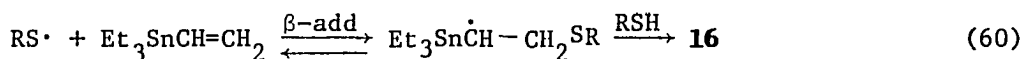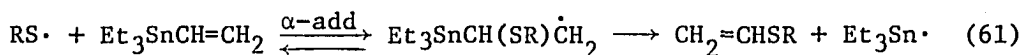
33

$$RS· + Et_3SnCH=CH_2 \underset{\longleftarrow}{\xrightarrow{\alpha\text{-add}}} Et_3SnCH(SR)\overset{\bullet}{C}H_2 \longrightarrow CH_2=CHSR + Et_3Sn· \qquad (61)$$

34

elimination of Et_3Sn· to give vinyl alkyl sulfide, whereas α-alkyl-
stannyl radical, which cannot undergo a β-elimination reaction, will
readily abstract a hydrogen atom from the mercaptans, which are known
to be good hydrogen donors, to give adduct **16**. In the reaction of
PhSSPh with $CH_2=CHSnBu_3$, if the β-addition of the thiyl radical occurred
the resulting α-alkylstannyl radical must dissociate back to its com-
ponents due to the lack of a potential atom donor under these condi-
tions. Consequently, the equilibrium in reaciton 60 will be generally
in favor of the left side and, thus, reaction 61 will be the exclusive
pathway for the reaction of PhSSPh and $CH_2=CHSnBu_3$. Other mercaptans
have been reported to add to triorgano-1-alkenyltin derivatives under

free radical reaction conditions [86, 87].

1-Alkenylmercurials are established to undergo a photostimulated free radical chain substitution reaction with phenyl dichalcogenide, PhYYPh (Y = S, Se and Te), and benzenesulfonyl chloride (Eq. 62, 63)

$$RCH=CHHgX + PhYYPh \longrightarrow RCH=CHYPh + PhYHgX \qquad (62)$$

$$RCH=CHHgX + PhSO_2Cl \longrightarrow RCH=CHSO_2Ph + ClHgX \qquad (63)$$
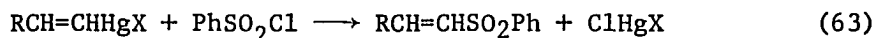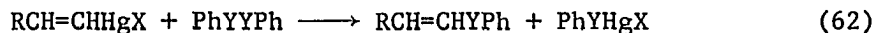
[33]. In all cases, the reactions are completely inhibited by 5-10 mole % of di-tert-butyl nitroxide and failed to proceed significantly in the dark. The reactions are explained by proposing a free radical addition-elimination mechanism analogous to the one presented in Scheme XXX. Other tri-n-butyl-1-alkenyltin compounds, $R_2C=CHSnBu_3$ (R = Ph and Me) are found to react with sulfur-centered radicals, such as PhS· and $PhSO_2·$, to give the corresponding sulfide and sulfone derivatives in good yields [119].

In one case, the reaction of tri-n-butyl-2-phenyl-1-ethynyltin with phenyl disulfide was examined, unfortunately, without success. Thus, UV (350 nm) irradiation of a benzene solution of the above reactants for 24 h resulted only in a trace amount of the substitution product PhC≡CSPh, whereas most of the unchanged starting materials were recovered.

Despite the success encountered with the reaction of trialkyl-1-alkenyltin derivatives with sulfur-centered radicals, attempts to extend this reaction to other heteroatom-centered radicals were un-successful. Thus, 1-alkenyltin compounds completely failed to react

with phenyl diselenide under prolonged sunlamp or UV (350 nm) irradiation. Similarly, the reaction failed to proceed thermally at 80°C in the presence of AIBN. In all cases, the unchanged starting materials were accounted for approximately quantitatively. The observation that PhSe· is less reactive than PhS· toward 1-alkenyltin compounds is compatible with the fact that the Se atom is less reactive than the S atom in the addition reaction with alkenes [120]. Recently, Ito has reported that the addition rate constants of PhSe· for alkenes are generally smaller than those of PhS· (Eq. 64) [121]. The photodecomposition of phenyl diselenide was established to be a reversible process

$$CH_2=CHY + PhX· \longrightarrow PhXCH_2\overset{·}{C}HY \qquad (64)$$

$$X = S \text{ and } Se$$
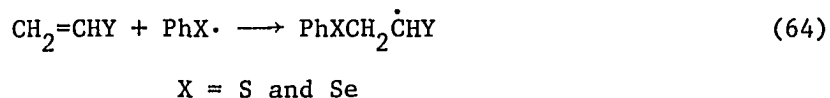
(Eq. 65) with k_r value estimated to be $7x10^9$ L/mole·s· in carbon

$$PhSeSePh \underset{k_r}{\overset{h\nu}{\rightleftarrows}} 2 \text{ PhSe·} \qquad (65)$$

tetrachloride, which is close to the diffusion rate constant [121]. The low reactivity of PhSe· compared with PhS· in the addition reaction with alkenes may be due to greater stabilization of an unpaired electron in PhSe· than that in PhS· [121]. The bond dissociation energy data suggested that the selenium-centered radicals are in general more stable than the sulfur-centered radicals [122].

The results observed for the reaction of tri-n-butyl-1-alkenyltin compounds with phenyl diselenide are in dramatic contrast to those reported for the reaction of 1-alkenylmercurials with PhSeSePh [33].

1-Alkenylmercurial salts are reported to react with PhSeSePh under sun-
lamp irradiation to give the corresponding alkenyl phenyl selenides in
excellent yields. These results indicate that 1-alkenylmercurials are
better traps for PhSe· than 1-alkenyltin compounds. The difference
can be rationalized by assuming that PhSe· adds first to the mercury
atom of the mercurial to give the tricovalent mercury species **35**, which
undergoes rearrangement to give the β-alkylmercuri radical **36**, Scheme
XXXI. Since an analogous reaction is not particularly feasible for the

Scheme XXXI

$$RCH+CHHgX + PhSe· \longrightarrow RCH=CHHg(SePh)X$$

35

$$\textbf{35} \qquad \longrightarrow RCH-CH(SePh)HgX$$

36

$$\textbf{36} \qquad \longrightarrow RCH=CHSePh + HgX$$

$$HgX + PhSeSePh \longrightarrow PhSe· + PhSeHgX$$
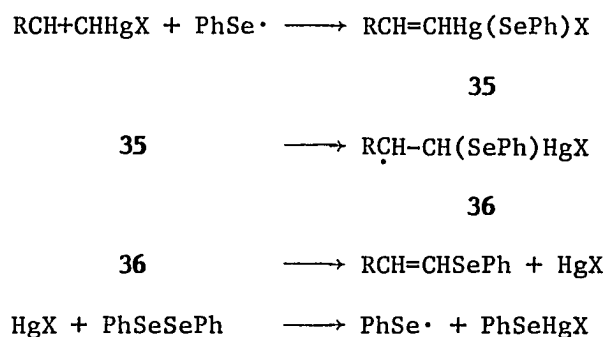
tin compound, PhSe· failed to react with 1-alkenyltin compounds.

Attempts to generate and react nitrogen-centered radicals were
also unsuccessful. A spontaneous reaction occurred upon mixing tri-n-
butyl-1-ethenyltin and N-bromosuccinimide in THF solution to give vinyl
bromide as the sole product. No N-ethenylsuccinimide was observed.
The spontaneity of the reaction and the formation of the vinyl bromide
as the exclusive product indicate that the reaction may involve an
electrophilic substitution process rather than the homolytic addition-

elimination process. It is well-known that the tin-vinyl bond can be cleaved readily by electrophilic species, such as halogens or hydrogen halides, to give vinyl halides or ethene, respectively [79]. Similar results were obtained from the reaction of N-phenylthiophthalimide with PhCH=CHSnBu$_3$, where β-styryl phenyl sulfide was formed as the exclusive product. However, N-chlorosuccinimide failed to react with 1-alkenyl-tin derivatives under either sunlamp or UV (350 nm) irradiation.

Oxygen-centered radicals did not react with 1-alkenyltin compounds. Thus, the tert-butoxy radical generated from the thermolysis of tert-butylperoxybenzoate failed to react with PhCH=CHSnBu$_3$ when the reaction mixture in chlorobenzene was heated at reflux for 5 h. Acetone was obtained as the only organic product, whereas the tin starting material was recovered. In addition, phosphorous-centered radicals also failed to react with PhCH=CHSnBu$_3$. The reaction between chlorodiphenylphos-phine or chlorodiethylphosphate with tri-n-butyl-(E)-2-phenyl-1-ethenyltin under UV (350 nm) irradiation gave only a trace amount of the coupling product.

C. Conclusion

Tri-n-butyl-1-alkenyltin compounds, PhCH=CHSnBu$_3$ and Ph$_2$C=CHSnBu$_3$, were found to react with alkylmercury halides, RHgCl, under sunlamp irradiation to give 1-substituted alkenes, tri-n-butyltin chloride and mercury metal. The reaction of (E)-PhCH=CHSnBu$_3$ is not completely stereoselective in that both cis- and trans-PhCH=CHR were formed. However, the trans-isomer is usually formed as the main product.

Evidence has been presented for a radical chain process in which one of the propagation steps involves an electron transfer from the tin-centered radical to the alkylmercurial. Other β-substituted styrenes, PhCH=CHQ (Q = I, $PhSO_2$, HgCl, PhS) were also found to couple with alkylmercurial salts to yield mainly the trans-isomer of PhCH=CHR and mercury(II) salts, QHgX. These reactions are believed to proceed through an addition-elimination radical chain process, which involves the free alkyl radicals and tricovalent mercury intermediate.

The above reactions, however, are of more mechanistic interest than value in synthesis. Although these reactions furnished a convenient way to synthesize substituted 1-alkenes, it is doubtful that they can compete with the well-established literature procedure, namely, Wittig reaction [123, 124]. Another disadvantage in the above reactions is that the side products, i.e. Bu_3SnCl, Hg(0) and XHgQ, represent a high portion of the starting materials, which means a great loss in mass upon the formation of the product.

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin reacts with polyhalomethanes, CCl_3Z (Z = Cl, Br, SO_2Cl) via a free radical addition-elimination mechanism to give mainly the trans-isomer of $PhCH=CHCl_3$. No addition of CCl_3Z to the double bond of the substrate was observed. The results are in contrast to those reported for the reaction of $CH_2=CHSnEt_3$ with CCl_3Z (Z = Br, Cl, H), where the addition product $CCl_3CH_2CHZSnEt_3$ was reported to be the exclusive product [85]. The results demonstrate the importance of the β-phenyl substituent, which changes the regioselectivity of the addition step.

Tri-n-butyl-1-alkenyltin derivatives, $RCH=CHSnBu_3$ (R = H, Ph), undergo a photostimulate reaction with phenyl disulfide, benzyl disulfide, benzenesulfonyl chloride and Se-phenyl p-tolylselenosulfonate to give good yields of the corresponding alkenyl derivatives. The reaction can also be initiated by the thermolysis of AIBN and it is completely inhibited by di-tert-butyl nitroxide. Again a radical chain addition-elimination mechanism involving the $S_H{}^2$ attack at the radical precursors by the tin-centered radicals was proposed. Attempts to extend this reaction to other heteroatom-centered radicals, i.e. oxygen-, nitrogen- and phosphorous-centered radicals, were unsuccessful.

Synthetically, the reaction of 1-alkenyltin compounds with sulfur-centered radicals provided a convenient method to prepare 2-substituted-1-ethenyl phenyl or alkyl sulfides. Existing methods to synthesize this group of compounds include the Hörner-Witting reaction of trialkoxy-methylphosphate esters with aldehyde [125], the reaction of 1-alkenyl-mercurials with disulfides [33], the addition reaction of mercaptans to acetylens [126] and the coupling of mercaptide ion with vinyl bromides by catalytic pallidium(O) [127].

D. Experimental Section

1. General considerations

Alkylmercury halides were prepared as previously described in Part I. Tri-n-butyl-1-ethenyltin [77], tri-n-butyl-2-phenyl-1-ethynyltin [128] and tri-n-butyl-(1-cyclohexenyloxy)tin [129] were prepared according to published procedures. Trans-β-styryl iodide [130], trans-β-styryl

phenyl sulfide [131], trans-β-styryl phenyl sulfone [132], N-phenyl-
thiophthalimide [133], 2-chloro-2-nitropropane [134] and 2-bromo-2-
nitropropane [134] were also prepared following literature methods.
2-Iodobenzothiazole [135], 2-(phenylsulfonyl)benzothiazole [136] and
4-phenylthiopyridine [137] were prepared by published procedures.
Tri-n-butyl-2,2-diphenyl-1-ethenyltin and tri-n-butyl-2,2-dimethyl-1-
ethenyltin were prepared by P. Ngoniwatchai.

n-Butyl iodide, n-pentyl iodide, isopropyl iodide, 2-iodo-
naphthalene and trichloromethanesulfonyl chloride were purchased from
Eastman Organic. Benzyl bromide, N-chlorosuccinimide, methyl bromo-
acetate, chloroacetonitrile, tert-butyl perbenzoate, β-bromostyrene,
chlorodiethylphosphate and chlorodiphenylphosphine were purchased from
Aldrich Chemical Co. Iodobenzene was a product of Baker Chem. Co.
Benzoyl chloride was a product of Mallinkrodt Chem. Co. and was distilled
prior to use. N-Bromosuccinimide was purchased from Fisher Scientific
Co. and crystallized from water before use. Azobisisobutyronitrile was
used as received from Aldrich Chemical Co., whereas benzoyl peroxide was
crystallized from water before use. Diethyl ether was distilled from
lithium aluminum hydride and stored over 4 A molecular sieves.

^{1}H.N.M.R. (300 MHz) and ^{13}C.N.M.R. (75.473 MHz) spectra were recorded
on a Bruker WM 300 in $CDCl_3$ solutions. Infrared spectra (I.R.) were
recorded on a Beckman 4250 spectrophotometer. The GLC yields and
isomer ratios were determined using a column packed with 15% OV-3 on
Chromosorb W, with the proper standard (usually biphenyl) added.

2. Preparation of tri-n-butyl-(E)-2-phenyl-1-ethenyltin

The title compound was prepared by a literature procedure [138].
Thus, a solution of 45.6 g (0.14 mole) of tri-n-butyltin chloride in
30 ml of THF was added to a Grignard reagent prepared from 4.1 g (0.17
g atom) of magnesium and 33.7 g (0.185 mole) of β-bromostyrene in 175
ml of ether and 25 ml of THF. The mixture was heated at reflux for 2
h, then cooled to room temperature and hydrolyzed by an ammonium
chloride solution. The salts were washed with 50 ml of ether, the
combined ether layers were filtered, dried ($MgSO_4$) and the solvent was
removed under reduced pressure. The residue was distilled under vacuum
to yield two fractions: Fraction I b.p. range 138-150°C (1.2 mm) and
fraction II b.p. range 155-160°C (1.2 mm). GLC analysis of fraction I
revealed a mixture of cis- and trans-tri-n-butyl-2-phenyl-1-ethenyltin
of a ratio ca. 30:70. However, fraction II consisted mainly of the
trans-isomer (>97%) which has a reported b.p. = 130-132°C (0.1 mm)
[108].

^{1}H.N.M.R. (300 MHz, $CDCl_3$) δ 7.4 (d, 2H, J = 6 Hz), 7.37-7.16 (m,
3H), 6.9 (d, 2H, J = 3 Hz), 1.74-1.5 (m, 6H), 1.45-1.22 (m, 6H), 1.1-
0.8 (m, 15 H).
Small satellite signals arising from coupling of the ^{117}Sn and ^{119}Sn
with the geminal proton were observed at 6.21 and 7.6 ppm.

^{13}C.N.M.R. (proton decoupled, $CDCl_3$, reported in ppm from TMS)
146.5, 139.1, 129.4, 128.5, 127.6, 126, 29.5, 27.6, 13.9, 10.

I.R. (neat, NaCl plates, cm^{-1}) 3100 (m), 2960 (s), 2900 (m), 1595
(m), 1495 (5), 1190 (m), 1175 (m), 1030 (m), 990 (s), 775 (s), 690 (s).

3. <u>General procedure for the photoreaction of tri-n-butyl-(E)-</u>
   <u>2-phenyl-1-ethenyltin with alkylmercury halides</u>

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (1.0 mmol) and alkylmercury

halide (1.2 mmol) were dissolved in 10 ml of benzene in a Pyrex flask

equipped with magnetic stirrer and rubber septum. After a nitrogen

purge, the solution was irradiated for several hours with a 275 W sun-

lamp placed 15 cm from the reaction vessel. The progress of the reac-

tion was monitored by GLC analysis which showed the complete dis-

appearance of the tin starting material. Mercury metal was precipitated

as a shiny globule. When the reaction was complete, the solution was

decanted from the mercury bead, and washed with 10 ml of 10% aqueous

sodium thiosulfate solution to remove the excess alkylmercurial. The

benzene layer was dried over $MgSO_4$. The solvent was removed in vacuo

to afford an oily residue, which was shown by GLC analysis to consist

of two compounds which were identified by GCMS analysis to be the

coupling product (the β-alkylstyrene) and tri-n-butyltin chloride.

Quantitative [1]H.N.M.R. revealed the formation of the β-alkylstyrenes

in good yields. The product identification was based on the chemical

shift of the vinylic protons compared with those of the authentic com-

pounds. The yield of products and the reaction times for different

alkylmercurials are summarized in Table XIII.

4. <u>Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin</u>
   <u>with isopropylmercury chloride</u>

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (1.96 g, 5.0 mmol) and iso-

propylmercury chloride (1.668 g, 6.0 mmol) were dissolved in 30 ml of

nitrogen-purged benzene. The solution was irradiated with a sunlamp

for 18 h during which time mercury metal was precipitated. After the reaction was complete, the solution was decanted from the mercury metal and the mercury was washed with a small amount of benzene. The combined benzene solution was washed with 25 ml of 10% sodium thiosulfate solution. The organic layer was dried (MgSO$_4$), and the solvent was removed under vacuum to give a light yellow oil. Distillation of the residue, using short path apparatus, afforded 0.52 g (72% yield) of 1-phenyl-3-methyl-1-butene, b.p. 44-45°C (0.33 mm), lit. [139] 84-85°C (12 mm). The product contained two isomers, the GLC (10'x1/8", 15% OV-3, 100-280°C/10°C) trans:cis ratio was determined to be 92:8 using biphenyl as the internal standard.

^{1}H.N.M.R. (CDCl$_3$) δ 7.32-7.05 (m, 5H), 6.32-6.2 (m, 2H), 2.7-2.2 (m, 1H), 1.05 (d, 6H, J = 6.5 Hz).

GCMS, m/e (relative intensity) 146 (31, M$^+$), 131 (100), 91 (50).

5. Dark reaction between tri-n-butyl-(E)-2-phenyl-1-ethenyltin
    with isopropylmercury chloride

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) and isopropylmercury chloride (0.333 g, 1.2 mmol) were dissolved in 10 ml of benzene under a nitrogen atmosphere. The reaction flask was wrapped with aluminum foil to exclude light. The reaction mixture was heated at 50°C for 24 h during which time no mercury metal was precipitated. The usual workup afforded an oily residue which was shown by GLC to consist exclusively of the tin starting material. None of the coupling product, 1-phenyl-3-methyl-1-butene, was detected.

6. **Effect of di-tert-butyl nitroxide on the reaction between tri-n-butyl-(E)-2-phenyl-1-ethenyltin and isopropyl-mercury chloride**

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol), isopropyl-mercury chloride (0.333 g, 1.2 mmol) and di-tert-butyl nitroxide (14 mg, 0.1 mmol) were dissolved in 10 ml of nitrogen-purged benzene. The solution was irradiated with a sunlamp positioned 15 cm from the reaction vessel for 16 h. Some mercury metal was precipitated. Workup as previously described gave a 35% yield of 1-phenyl-3-methyl-1-butene as determined by [1]H.N.M.R. The compound was further identified by GCMS analysis.

7. **Thermal reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with isopropylmercury chloride in the presence of AIBN**

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (1.96 g, 5.0 mmol), isopropyl-mercury chloride (1.668 g, 6.0 mmol) and AIBN (33 mg, 0.2 mmol) were dissolved in 30 ml of benzene. The reaction flask was wrapped with aluminum foil to exclude light. The solution was immersed in an oil bath and heated for 16 h at 80°C under a nitrogen atmosphere. Mercury metal was precipitated. Upon workup, 1-phenyl-3-methyl-1-butene was isolated in a 73% yield. The GLC trans-cis ratio was established to be 94:6. The product was identified by [1]H.N.M.R. and GCMS as previously mentioned.

8. **Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with Δ5-hexenylmercurial**

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (1.96 g, 5.0 mmol) and Δ^5-hexenylmercury chloride (1.91 g, 6.0 mmol) were dissolved in 30 ml of

benzene. After a nitrogen purge, the solution was irradiated in a
Rayonet photoreactor equipped with fourteen "350 nm" bulbs for 32 h
during which time mercury metal was precipitated. Normal workup gave
an oil, which was shown by GLC analysis to contain two isomers of the
coupling product besides Bu_3SnCl. [1]H.N.M.R. analysis revealed a 55%
yield of the coupling product. The same analysis indicated the com-
plete absence of the vinylic protons of the Δ^5-hexenyl moiety, which
means that complete cyclization to give the cyclopentylcarbinyl product
had occurred. The formation of this product, i.e. 1-phenyl-3-cyclo-
pentyl-1-propene, was confirmed by GLC (10'x1/8", 15% OV-3, 180°C)
retention time matching with an authentic sample prepared by the reac-
tion of cyclopentylcarbinylmercury chloride and tri-n-butyl-(E)-2-
phenyl-1-ethenyltin.

[1]H.N.M.R. (CDCl$_3$) δ 7.55-7.2 (m, 5H), 6.3-6.05 (m, 2H), 2.25-
1.1 (m, 11H).

GCMS, m/e (relative intensity) 186 (14, M[+]), 117 (98), 104 (100),
91 (25).

9. General procedure for the photoreaction of tri-n-butyl-
   2,2-diphenyl-1-ethenyltin with alkylmercurials

Tri-n-butyl-2,2-diphenyl-1-ethenyltin (1.0 mmol) and alkylmercury
halide (5 mmol) were dissolved in 10 ml of benzene under a nitrogen
atmosphere. The reaction mixture was irradiated with a sunlamp for
several hours during which time mercury metal was precipitated. Workup
as previously described gave a light yellow oily residue. GLC analysis
revealed the coupling product, i.e., 1,1-diphenyl-1-alkenes in

significant yields. All products were further identified by [1]H.N.M.R.
and GCMS.

10. Photoreaction of tri-n-butyl-1-ethenyltin with
    cyclopentylmercury chloride

Tri-n-butyl-1-ethenyltin (0.312 g, 1.0 mmol) and cyclopentylmercury

chloride (0.365 g, 1.2 mmol) were dissolved in 10 ml of nitrogen-

purged benzene. The solution was irradiated with a sunlamp for 24 h. A

trace of mercury metal was precipitated. The solvent was removed by

fractional distillation to afford an oily residue. GLC analysis indi-

cated a low yield of ca. 10% of the coupling product vinylcyclopentane

and the unchanged tin starting material. A 24 h irradiation in the

Rayonet at 350 nm failed to improve the yield in the above reaction.

The same procedure was applied for the photoreaction of tri-n-

butyl-1-ethenyltin with other alkylmercurials RHgCl (R = cyclohexyl, n-

hexyl and Δ^5-hexenyl). Essentially, similar results were obtained in

all cases.

11. Photoreaction of tri-n-butyl-2,2-dimethyl-1-ethenyltin
    with cyclopentylcarbinylmercury chloride

Tri-n-butyl-2,2-dimethyl-1-ethenyltin (0.342 g, 1.0 mmol) and

cyclopentylcarbinylmercury chloride (0.82 g, 1.2 mmol) were dissolved

in 10 ml of benzene under a nitrogen atmosphere. The solution was ir-

radiated in the Rayonet at 350 nm for 4 days. A trace amount of mercury

was precipitated. The solution was decanted from the mercury metal and

the solvent was removed in vacuo to give a solid residue. [1]H.N.M.R.

analysis revealed the disappearance of the tin substrate as evidenced by

the disappearance of the vinylic proton at 5.6 ppm (singlet). However,

a new singlet appeared at 5.85 ppm. GCMS analysis indicated that the

coupling product, 1,1-dimethyl-3-cyclopentyl-1-propene, was formed only

in a trace amount, whereas Bu_3SnCl was a major product. In addition,

GCMS indicated a mercury compound was formed in a significant amount.

The structure of this compound was tentatively assigned to be $Me_2C=CH-$

$HgCH_2C_5H_9-c$. The reaction was not investigated further.

GCMS, m/e (relative intensity) 338 (0.3, M^+), 255 (0.6), 83 (43),

55 (100).

12. <u>Photoreaction</u> <u>of</u> <u>tri-n-butyl-(1-cyclohexenyloxy)tin</u>
    <u>with</u> <u>alkylmercury</u> <u>halides</u>

Tri-n-butyl-(1-cyclohexenyloxy)tin (0.193 g, 0.5 mmol) and n-butyl-

mercury chloride (0.584 g, 2.0 mmol) were dissolved in 10 ml of benzene

under a nitrogen atmosphere. The reaction mixture was irradiated with

a sunlamp for 16 h during which time mercury metal was precipitated.

Normal workup afforded a 24% yield of 2-n-butylcyclohexanone as

determined by GLC using biphenyl as the internal standard. The product

was further identified by GCMS analysis.

GCMS, m/e (relative intensity) 154 (5, M^+), 98 (100).

The same procedure was applied for the reaction of tri-n-butyl-

(1-cyclohexenyloxy)tin with isopropylmercurial. Thus, a 14 h sunlamp

irradiation of the above reaction mixture gave a 36% yield of 2-

isopropylcyclohexanone.

GCMS, m/e (relative intensity) 140 (24, M^+), 125 (31), 98 (100).

13. **Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin
with n-hexylmagnesium chloride**

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) was added

to the Grignard reagent prepared from n-hexyl bromide (0.36 g, 2.2

mmol) and magnesium (48 mg, 2.0 mg.atom) in 5 ml of THF under nitrogen.

The reaction mixture was irradiated with a sunlamp for 24 h. The solu-

tion was hydrolyzed with an ammonium chloride solution and the organic

products were extracted with benzene. The extract was dried (MgSO$_4$)

and the solvent was removed under reduced pressure to give a light

yellow oil. Quantitative ^{1}H.N.M.R. indicated exclusively the unchanged

tri-n-butyl-(E)-2-phenyl-1-ethenyltin. None of the coupling product,

1-phenyl-1-octene, was observed. Similar results were obtained from the

reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with Δ^5-hexenylmagnesi-

um bromide under the same reaction conditions.

14. **Photoreaction of tri-n-butyl-(E)-2-phenyl-1-
ethenyltin with n-butyl iodide**

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) and n-

butyl iodide (0.368 g, 2.0 mmol) were dissolved in 10 ml of benzene.

After a nitrogen purge, the solution was irradiated in the Rayonet for

30 h. The solvent was removed under reduced pressure to give an oily

residue. Quantitative GLC revealed 1-phenyl-1-hexene in a 62% yield.

The trans:cis ratio was determined to be 87:13.

GCMS, m/e (relative intensity) 160 (25, M$^+$), 117 (100), 104 (68).

Under similar reaction conditions, the reaction of tri-n-butyl-

(E)-2-phenyl-1-ethenyltin with n-pentyl iodide gave a 67% yield of

1-phenyl-1-heptene as determined by quantitative GLC. The trans:cis

ratio was established to be 88:12.

GCMS, m/e (relative intensity) 174 (21, M$^+$), 117 (100), 104 (98).

15. Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin
    with isopropyl iodide

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) and

isopropyl iodide (0.85 g, 5.0 mmol) were dissolved in 10 ml of benzene

under a nitrogen atmosphere. The solution was irradiated in the Rayonet

at 350 nm for 15 h during which time an unidentified yellow precipitate

was formed. The precipitate was filtered and the solvent was removed

in vacuo to yield a light yellow oil. Quantitative GLC determined

1-phenyl-3-methyl-1-butene in an 18% yield and the tin substrate (35%).

In addition, β-iodostyrene (two isomers) was observed in significant

yield. The latter was identified by GCMS analysis (m/e = 230 observed

for the parent ion).

16. Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin
    with benzyl bromide

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) and

benzyl bromide (0.364 g, 2.0 mmol) were dissolved in 10 ml of nitrogen-

purged benzene. The reaction mixture was irradiated in the Rayonet at

350 nm for 48 h. Workup as previously described afforded 1,3-diphenyl-

1-propene in a 15% yield as determined by quantitative GLC analysis.

GCMS, m/e (relative intensity) 194 (69, M$^+$), 115 (100), 91 (51).

In addition, a small amount of bibenzyl was detected.

17. Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with methyl bromoacetate

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) and

methyl bromoacetate (0.456 g, 3 mmol) were dissolved in 10 ml of

benzene. After a nitrogen purge, the solution was irradiated in the

Rayonet at 350 nm for 44 h. Normal workup afforded a 38% yield of

methyl 1-phenyl-1-propenylacetate, besides unchanged starting

material (47%) as determined by GLC analysis. The GLC ratio of trans:

cis isomers of the coupling product was established to be 83:17.

GCMS, m/e (relative intensity) 176 (25, M$^+$), 117 (100), 91 (25).

The same procedure was applied for the reaction of chloro-

acetonitrile with tri-n-butyl-(E)-phenyl-1-ethenyltin. However, 3 days

irradiation of the above reaction mixture in the Rayonet resulted in no

change in the starting materials. No substitution product was detected.

18. Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with 2-bromo-2-nitropropane

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) and

2-bromo-2-nitropropane (0.501 g, 3.0 mmol) were dissolved in 10 ml of

benzene under nitrogen. The reaction mixture was irradiated in the

Rayonet at 350 nm for 48 h. The usual workup afforded the unchanged

starting materials. No coupling product was observed as determined by

GLC analysis. Under similar reaction conditions, 2-chloro-2-nitro-

propane also failed to react with tri-n-butyl-(E)-2-phenyl-1-ethenyltin.

19. Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin
    with benzoyl chloride

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) and

benzoyl chloride (0.42 g, 3.0 mmol) in 10 ml of benzene were irradiated

in the Rayonet at 350 nm for 28 h. Normal workup afforded the unchanged

starting materials as indicated by GLC analysis. No substitution

product was detected.

20. Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin
    with iodobenzene

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) and

iodobenzene (0.612 g, 3.0 mmol) were dissolved in 10 ml of nitrogen-

purged benzene. The solution was irradiated in the Rayonet at 350 nm

for 48 h. The usual workup gave only a trace amount of 1,2-diphenyl-

ethylene as revealed by GCMS analysis (m/e = 180 was observed for the

parent ion). The unchanged starting tin substrate was recovered.

21. Reaction of tri-n-butyl-1-ethenyltin with
    methyl bromoacetate

Tri-n-butyl-1-ethenyltin (0.948 g, 3.0 mmol) and methyl bromo-

acetate (0.547 g, 3.6 mmol) were dissolved in 25 ml of benzene. After

a nitrogen purge, the solution was irradiated in the Rayonet at 350 nm

for 24 h. The solvent was removed under vacuum. ^{1}H.N.M.R. of the

crude isolate determined the absence of any vinylic protons and the

appearance of a new multiplet at 2.2-3.0 ppm, which might be due to the

formation of the addition product, $MeO_2CH_2CH_2CHBrSnBu_3$. The structure

of the product was not fully determined, but GCMS analysis provides

some support for this structure.

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 470 (0, M^{+}), 413 (3), 313 (8),

257 (8), 199 (17), 177 (47), 57 (100).

A possible rationalization of the MS results is given in Scheme

XXXII, where masses have been calculated for ^{120}Sn.

Scheme XXXII

$$[MeO_2CCH_2CH_2CHBrSnBu_3]^{+\cdot}$$

$-Bu\cdot$ $*$

$MeO_2CCH_2CH_2CHBrSn^{+}Bu_2$ $Bu^{+} + MeO_2CCH_2CH_2CHBr\dot{S}nBu_2$

$\underline{m}/\underline{e} = 413$ (3)   rearrangement $\underline{m}/\underline{e} = 57$ (100)

$MeO_2CCH_2CH_2\overset{+}{C}HSnBu_2$

|Br

$\underline{m}/\underline{e} = 413$

|-100

$Bu_2\overset{+}{Sn}Br$

$\underline{m}/\underline{e} = 313$ (8)

| $-(CH_2=CHCH_2CH_3)$ (56)

$Bu\overset{+}{Sn}Br$

|

H

$\underline{m}/\underline{e} = 257$ (8) $\xrightarrow[-HBr]{red.-elim.}$ $BuSn^{+}$ $\underline{m}/\underline{e} = 177$ (47)

red.-elim. $-BuH$

$\overset{+}{Sn}Br$

$\underline{m}/\underline{e} = 199$ (17)

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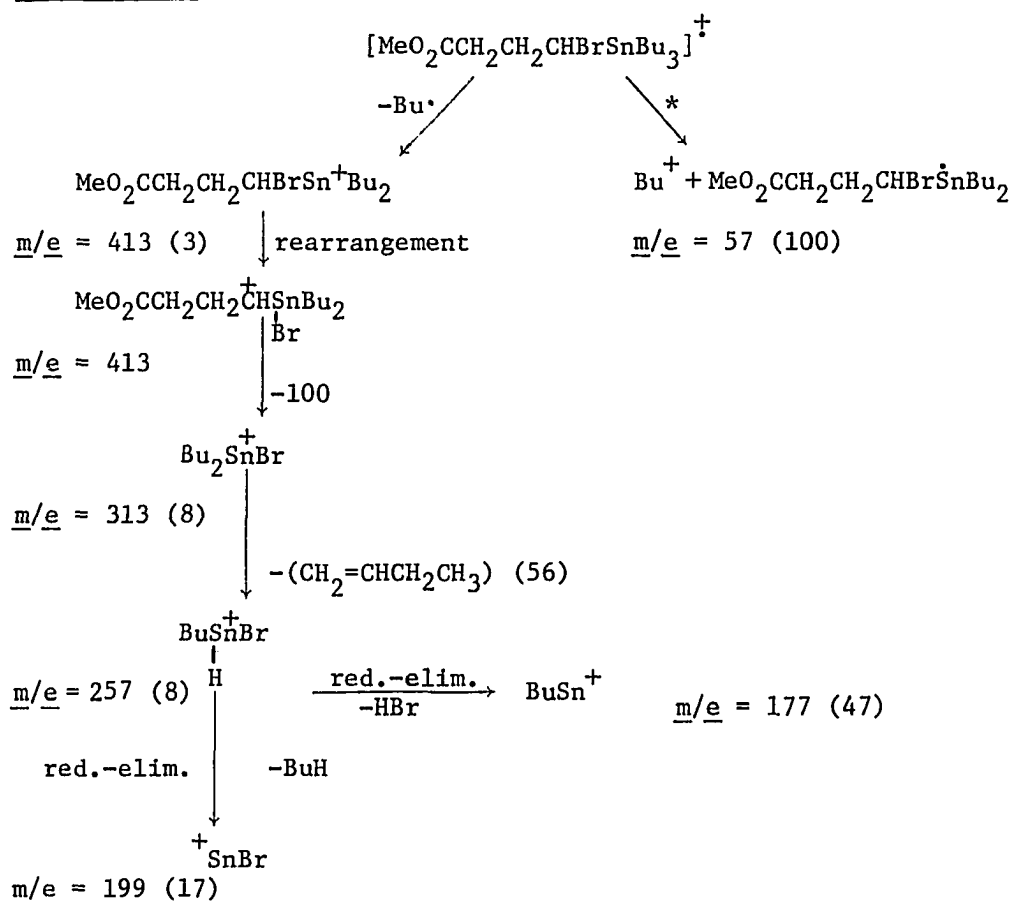
*The loss of Bu3Sn· is less likely because it will give the less

stable carbonium ion $MeO_2CCH_2CH_2\overset{+}{C}HBr$.

22. <u>General procedure for the reaction of</u> β-<u>substituted</u>
    <u>styrenes with alkylmercury halides</u>

The β-substituted styrene, PhCH=CHQ (Q = I, PhSO$_2$, HgCl or PhS),

(1.0 mmol) and alkylmercury halide (2.0 mmol) were dissolved in 10 ml

of nitrogen-purged DMSO. The solution was irradiated with a sunlamp

or in the Rayonet at 350 nm for several hours during which time a trace

of mercury metal was precipitated. When the reaction was complete,

the reaction mixture was poured into 25 ml of aqueous 10% sodium

thiosulfate and the organic products were extracted with benzene. The

extract was washed with aqueous thiosulfate, dried (MgSO$_4$), and concen-

trated in vacuo to yield a light yellow oil. The oil was determined

by GLC to be the β-alkylstyrenes (mainly the <u>trans-isomers</u>). The

products were further identified by ^{1}H.N.M.R. and GCMS analysis. The

yield of products and the reaction conditions are summarized in Table

XV.

23. <u>Thermal reaction of trans-</u>β-<u>styryl iodide with isopropylmercury</u>
    <u>chloride in the presence of benzoyl peroxide</u>

<u>Trans</u>-β-styryl iodide (0.23 g, 1.0 mmol), isopropylmercury chloride

(0.556 g, 2.0 mmol) and benzoyl peroxide (24 mg, 0.1 mmol) were dis-

solved in 10 ml of nitrogen-purged DMSO. The reaction flask was wrapped

with aluminum foil to exclude light. The reaction mixture was heated at

100°C for 24 h. Workup as discussed above yielded an oily residue.

Quantitative ^{1}H.N.M.R. revealed 1-phenyl-3-methyl-1-propene in a 68%

yield. The GLC <u>trans</u>:<u>cis</u> ratio was determined to be 95:5, using bi-

phenyl as the internal standard.

24. **Effect of di-tert-butyl nitroxide on the photoreaction of trans-β-styryl iodide with isopropylmercury chloride**

Trans-β-styryl iodide (0.23 g, 1.0 mmol), isopropylmercury chloride (0.556 g, 2.0 mmol) and di-tert-butyl nitroxide (14 mg, 0.1 mmol) were dissolved in 10 ml of DMSO under a nitrogen atmosphere. The solution was irradiated for 10 h with a sunlamp positioned 15 cm from the reaction vessel. The usual workup gave a light yellow oil, which was shown by quantitative GLC analysis to contain 1-phenyl-3-methyl-1-butene (21% yield) and mainly the starting β-styryl iodide (both cis- and trans-isomers).

25. **Dark reaction between trans-β-styryl iodide and isopropylmercury chloride**

Trans-β-styryl iodide (0.23 g, 1.0 mmol) and isopropylmercury chloride (0.556 g, 2.0 mmol) were dissolved in 10 ml of nitrogen-purged DMSO. The flask was wrapped with aluminum foil to exclude light. The reaction mixture was heated for 24 h in an oil bath at 50°C. Normal workup yielded exclusively the unchanged starting material as determined by GLC analysis. None of the coupling product, 1-phenyl-3-methyl-1-butene, was observed.

26. **Photoreaction of 2-substituted benzothiazole with alkylmercury halides**

2-Iodobenzothiazole (0.13 g, 0.5 mmol) and alkylmercury halide (2.5 mmol) were dissolved in 10 ml of nitrogen-purged DMSO. The reaction mixture was irradiated in the Rayonet at 350 nm for several hours. The solution was poured into 25 ml of aqueous sodium thiosulfate and the organic products were extracted with benzene. The benzene solution

was washed with aqueous thiosulfate, dried ($MgSO_4$) and concentrated in vacuo to give an oily residue. GLC analysis revealed 2-alkylbenzothiazole in a moderate yield. The yield of products and reaction times are summarized in Table XVI.

The following data were obtained for the 2-alkylbenzothiazoles.

2-Cyclohexybenzothiazole:

^{1}H.N.M.R. ($CDCl_3$) δ 8.05-7.8 (m, 2H), 7.55-7.2 (m, 2H), 3.05-2.7 (m, 1H), 2.2-1.4 (m, 10 H).

GCMS, m/e (relative intensity) 219 (0.5), 217 (9, M^+), 162 (100), 149 (86).

2-Isopropylbenzothiazole:

^{1}H.N.M.R. ($CDCl_3$) δ 7.95-7.7 (m, 2H), 7.5-7.2 (m, 2H), 3.1-2.7 (m, 1H), 1.21 (d, 6H, J = 7 Hz).

GCMS, m/e (relative intensity) 179 (1.5), 177 (34, M^+), 162 (100).

2-n-Butylbenzothiazole:

GCMS, m/e (relative intensity) 193 (1.2), 191 (26, M^+), 149 (100).

The same procedure was applied for the reaction of 2-(phenylsulfonyl)benzothiazole and alkylmercurials. The results are included in Table XVI.

27. Photoreaction of 4-phenylthiopyridine with alkylmercury halides

4-Phenylthiopyridine (0.187 g, 1.0 mmol) and isopropylmercury chloride (0.331 g, 1.2 mmol) were dissolved in 10 ml of DMSO under a nitrogen atmosphere. The solution was irradiated in the Rayonet at 350 nm for 16 h. Workup as mentioned above gave an oily residue. GLC

analysis revealed mainly the unchanged starting material (68%), 4-isopropylpyridine (5%) and 2-isopropyl-4-phenythiopyridine (13%). The products were identified by GCMS analysis, which also indicated that isopropyl phenyl sulfide was formed in a small amount.

4-Isopropylpyridine:

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 121 (2, M^+), 120 (55), 105 (100).

2-Isopropyl-4-phenylthiopyridine:

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 231 (0.65), 229 (14, M^+), 214 (10), 152 (100).

The same procedure was followed in the reaction of 4-phenylthio-pyridine (0.1 g, 0.5 mmol) and cyclohexylmercury chloride (0.477 g, 1.5 mmol). The solution was irradiated in the Rayonet for 24 h. The usual workup gave a trace of 4-cyclohexylpyridine and a 28% yield of 2-cyclohexyl-4-phenylthiopyridine as determined by GLC analysis. In addition, the starting material was observed (53%). 2-Cyclohexyl-4-phenylthiopyridine was identified by GCMS, which also revealed a small amount of cyclohexyl phenyl sulfide.

2-Cyclohexyl-4-phenylthiopyridine:

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 271 (0.5), 269 (11, M^+), 214 (100), 201 (37).

28. **Photoreaction of 2-iodonaphthalene with isopropylmercury chloride**

1-Iodonaphthalene (0.063 g, 0.25 mmol) and isopropylmercury chloride (0.345 g, 1.25 mmol) were dissolved in 5 ml of DMSO. After a nitrogen purge, the solution was irradiated in the Rayonet at 350 nm for 48 h.

Normal workup afforded mainly the unchanged starting material as determined by GLC analysis. Only a trace of the substituted product, 1-isopropylnaphthalene, was observed.

The same procedure was applied for the reaction of iodobenzene with isopropylmercury chloride. Essentially, none of the substitution product, 2-isopropylbenzene, was detected.

29. Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with carbon tetrachloride

A solution of tri-$\underline{n}$-butyl-($\underline{E}$)-2-phenyl-1-ethenyltin (1.96 g, 5.0 mmol) in 20 ml of nitrogen-purged carbon tetrachloride was irradiated in the Rayonet at 350 nm for 38 h. The progress of the reaction was monitored by ^{1}H.N.M.R. which showed the gradual disappearance of the starting material (δ = 6.9, s) and the appearance of a new vinylic compound (δ = 6.0, q, $\underline{J}_{AB}$ = 12 Hz, ν_{AB} = 0.59 ppm). When the reaction was complete, the solvent was removed in vacuo and the residue was distilled, using short path apparatus to give 0.68 g (62% yield) of 3,3,3-trichloro-1-phenyl-1-propene as the exclusive product, b.p. = 86-90°C (0.7 mm). Both trans- and cis-isomers were formed in a ratio of 95:5 as determined by GLC analysis.

^{1}H.N.M.R. (CDCl$_3$) δ 7.65-7.2 (m, 5H), 6.0 (q, $\underline{J}_{AB}$ = 12 Hz, ν_{AB} = 0.59 ppm).

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 222 (0.2), 220 (0.2, M$^+$), 189 (3), 187 (20), 185 (32, M+-Cl), 151 (31), 149 (100), 115 (14).

MS, Calculated for C$_9$H$_7$Cl$_3$: 219.96151, measured for C$_9$H$_7$Cl$_3$: 219.96168. Error: 0.8 ppm.

In addition, 1.0 g (61% yield) of tri-n-butyltin chloride was collected. Also, a trace of β-styryl chloride was identified by GCMS (m/e = 138 was observed for the parent ion). However, no addition product was observed.

30. Thermal reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with carbon tetrachloride in the presence of AIBN

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (1.96 g, 5 mmol) and AIBN (41 mg, 0.25 mmol) were dissolved in 20 ml of carbon tetrachloride. The reaction mixture was wrapped with aluminum foil to exclude light. The reaction mixture was immersed in an oil bath and heated at 80°C for 24 h under a nitrogen atmosphere. Workup as described above gave 0.58 g (53% yield) of 3,3,3-trichloro-1-phenylpropene. The product was identified by [1]H.N.M.R. and GCMS as described above. Tri-n-butyltin chloride was obtained in comparable yield.

31. Dark reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with carbon tetrachloride

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) was dissolved in 10 ml of carbon tetrachloride. The reaction mixture was wrapped with aluminum foil to exclude light. The solution was heated in an oil bath at 50°C for 24 h. The usual workup gave exclusively the starting tin compound. None of the substitution product, 3,3,3-tri-chloro-1-phenyl-1-propene, was observed.

32. Effect of di-tert-butyl nitroxide on the photoreaction between
     tri-n-butyl-(E)-2-phenyl-1-ethenyltin and carbon tetrachloride

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (1.96 g, 5.0 mmol) and

di-tert-butyl nitroxide (36 mg, 0.25 mmol) were dissolved in 25 ml of

nitrogen-purged carbon tetrachloride. The solution was irradiated in

the Rayonet at 350 nm for 18 h. The usual workup afforded a light

yellow oil residue. GLC and [1]H.N.M.R. indicated the unchanged starting

tin substrate. No substitution product, i.e. PhCH=CHCCl$_3$, was

observed.

33. Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin
     with bromotrichloromethane

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) and

bromotrichloromethane (0.294 g, 1.5 mmol) were dissolved in 10 ml of

nitrogen-purged benzene. The reaction mixture was irradiated in the

Rayonet at 350 nm for 15 h. Normal workup afforded 3,3,3-trichloro-1-

phenyl-1-propene in a 55% yield as determined by quantitative [1]H.N.M.R.

The product was further identified by GCMS. Comparable results were

obtained when the above reaction was performed thermally in the dark

at 80°C with 10 mole % AIBN added (16 h).

34. Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin
     with trichloromethanesulfonyl chloride

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) and tri-

chloromethanesulfonyl chloride (0.31 g, 1.5 mmol) were dissolved in 10

ml of benzene. After a nitrogen purge, the solution was irradiated in

the Rayonet at 350 nm for 24 h. The usual workup yielded 3,3,3-tri-

chloro-1-phenyl-1-propene in a 48% yield. No sulfone derivative was

observed. The product was identified by [1]H.N.M.R. and GCMS analysis, as previously described.

35. Photoreaction of tri-n-butyl-1-ethenyltin with phenyl disulfide

Many details of the following procedure, and especially for the workup procedure, are general for the reactions of 1-alkenyltin compounds with the heteroatom-centered radicals.

Tri-n-butyl-1-ethenyltin (0.942 g, 3.0 mmol) and phenyl disulfide (0.785 g, 3.6 mmol) were dissolved in 25 ml of benzene. After a nitrogen purge, the solution was irradiated with a sunlamp for 4 h. When the reaction was complete, the solvent was removed in vacuo to give an oily residue. Quantitative [1]H.N.M.R. determined vinyl phenyl sulfide in a quantitative yield. When the residue was distilled under vacuum, using a short path apparatus, 0.37 g (91% yield) of vinyl phenyl sulfide was isolated as a colorless liquid, b.p. = 35-37°C (0.5 mm); lit. [140] b.p. = 75-76°C (11 mm).

[1]H.N.M.R. (CDCl$_3$) δ 7.35-7.10 (m, 5H); 6.44 (dd, 1H, $\underline{J}$(trans) = 16.5 Hz, $\underline{J}$(cis) = 9 Hz), 5.33 (d, 1H, $\underline{J}$ = 9 Hz), 5.24 (d, 1H, $\underline{J}$ = 16.5 Hz).

GCMS, m/e (relative intensity) 138 (0.5), 136 (11, M$^+$), 135 (100), 109 (65).

36. Thermal reaction of tri-n-butyl-1-ethenyltin with phenyl disulfide in the presence of AIBN

Tri-n-butyl-1-ethenyltin (0.942 g, 3.0 mmol), phenyl disulfide (0.785 g, 3.6 mmol) and AIBN (50 mg, 0.3 mmol) were dissolved in 25 ml

of nitrogen-purged benzene. The reaction mixture was wrapped with

aluminum foil to exclude light. The solution was heated in an oil bath

at 80°C for 4 h. Normal workup afforded 0.33 g (82% yield) of vinyl

phenyl sulfide. The product was identified by [1]H.N.M.R. and GCMS as

mentioned above.

37. Dark reaction between tri-n-butyl-1-ethenyltin
    and phenyl disulfide

Tri-n-butyl-1-ethenyltin (0.942 g, 3.0 mmol) and phenyl disulfide

(0.785 g, 3.6 mmol) were dissolved in 25 ml of benzene. The reaction

mixture was wrapped with aluminum foil to exclude light. After a

nitrogen purge, the solution was heated in an oil bath at 50°C for 4 h.

Workup as previously described afforded the unchanged starting materials

as determined by GLC. No vinyl phenyl sulfide was formed.

38. Effect of di-tert-butyl nitroxide on the photoreaction of
    tri-n-butyl-1-ethenyltin with phenyl disulfide

Tri-n-butyl-1-ethenyltin (0.942 g, 3.0 mmol), phenyl disulfide

(0.785 g, 3.6 mmol) and di-tert-butyl nitroxide (42 mg, 0.3 mmol) were

dissolved in 25 ml of benzene under a nitrogen atmosphere. The solution

was irradiated with a sunlamp for 3 h. Normal workup gave the unchanged

starting materials almost quantitatively as determined by GLC analysis.

No vinyl phenyl sulfide was observed.

39. Photoreaction of tri-n-butyl-1-ethenyltin
    with benzenesulfonyl chloride

Tri-n-butyl-1-ethenyltin (0.942 g, 3.0 mmol) and benzenesulfonyl

chloride (0.633 g, 3.6 mmol) were dissolved in 25 ml of benzene. After

a nitrogen purge, the solution was irradiated with a sunlamp for 6 h.
The solvent was removed under reduced pressure to give a light yellow
oil. Distillation under vacuum gave 0.8 g of Bu_3SnCl. Crystallization
of the residue from methanol afforded 0.45 g (89% yield) of vinyl
phenyl sulfone as a colorless solid, m.p. = 67-68°C; lit. [141] m.p. =
67-68°C.

[1]H.N.M.R. ($CDCl_3$) δ 7.9-7.4 (m, 5H), 6.7 (dd, J(trans) = 16 Hz,
J(cis) = 9 Hz), 6.47 (d, 1H, J = 9 Hz), 6.05 (d, 1H, J = 16 Hz).

GCMS, m/e (relative intensity) 170 (0.72), 168 (15, M^+), 125 (91),
77 (100).

The above reaction was performed thermally at 80°C in the presence
of 10 mole % AIBN, the reaction time was 8 h. Vinyl phenyl sulfone
was isolated in an 85% yield. The photoreaction was repeated in the
presence of 10 mole % di-tert-butyl nitroxide following the same pro-
cedure. No vinyl phenyl sulfone was detected under these conditions.

40. Photoreaction of tri-n-butyl-1-ethenyltin with benzyl disulfide

Tri-n-butyl-1-ethenyltin (0.314 g, 1.0 mmol) and benzyl disulfide
(0.295 g, 1.2 mmol) were dissolved in 10 ml of nitrogen-purged benzene.
The reaction mixture was irradiated with a 275 W sunlamp for 12 h.
Normal workup gave benzyl vinyl sulfide in a 78% yield as determined
by [1]H.N.M.R. analysis.

[1]H.N.M.R. ($CDCl_3$) δ 7.38-7.1 (m, 5H), 6.4 (dd, J(trans) = 16 Hz,
J(cis) = 9 Hz), 5.35 (d, 1H, J = 9 Hz), 5.2 (d, 1H, J = 16 Hz), 3.92
(s, 2H).

GCMS, m/e (relative intensity) 152 (1.2), 150 (27, M$^+$), 91 (100).

41. **Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with phenyl disulfide**

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (1.176 g, 3.0 mmol) and phenyl disulfide (0.785 g, 3.6 mmol) were dissolved in 25 ml of nitrogen-purged benzene. The solution was irradiated for 4 h with a sunlamp placed 15 cm from the reaction vessel. When the reaction was complete, the solvent was removed in vacuo. The crude isolate was shown by quantitative ^{1}H.N.M.R. to contain exclusively trans-β-styryl phenyl sulfide in a 95% yield. Short path distillation gave 0.55 g (86% yield) of the product, b.p. = 142-5°C (0.6 mm). This compound is already reported in the literature [131]. No cis-β-styryl phenyl sulfide was detected.

^{1}H.N.M.R. (CDCl$_3$) δ 7.55-7.1 (m, 10 H), 6.83 (d, 1H, J = 15 Hz), 6.68 (d, 1H, J = 15 Hz).

GCMS, m/e (relative intensity) 214 (4.4), 212 (93, M$^+$), 121 (69), 77 (100).

42. **Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with benzenesulfonyl chloride**

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (1.176 g, 3.0 mmol) and benzenesulfonyl chloride (0.563 g, 3.6 mmol) were dissolved in 25 ml of nitrogen-purged benzene. The solution was irradiated with a sunlamp for 4 h. The usual workup gave an oil, which upon short path distillation afforded 0.85 g of tri-n-butyltin chloride. Crystallization of the residue from methanol gave 0.62 g (85% yield) of trans-β-styryl

phenyl sulfone, m.p. = 73-74°C; lit [132] m.p. = 74-75°C. No cis-β-styryl phenyl sulfone was detected.

[1]H.N.M.R. (CDCl$_3$) δ 7.75 (d, 1H, partially obscured), 7.7-7.2 (m, 10H), 6.9 (d, 1H, J = 16 Hz).

GCMS, m/e (relative intensity) 246 (0.48), 244 (10, M[+]), 102 (89), 91 (100), 77 (94).

43. **Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with Se-phenyl p-tolylselenosulfonate**

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.394 g, 1.0 mmol) and Se-phenyl p-tolylselenosulfonate (0.374 g, 1.2 mmol) were dissolved in 10 ml of nitrogen-purged benzene. The solution was irradiated with a sun-lamp for 8 h. Normal workup afforded a yellow oily residue. [1]H.N.M.R. revealed trans-β-styryl p-tolyl sulfone as the sole product in an 86% yield. No cis-isomer was detected either by [1]H.N.M.R. or GLC analysis.

[1]H.N.M.R. (CDCl$_3$) δ 7.75-7.15 (m, 9H), 7.69 (d, 1H, partially obscured), 6.79 (d, 1H, J = 15 Hz), 2.37 (s, 3H).

GCMS, m/e (relative intensity) 260 (0.8), 258 (16, M[+]), 139 (71), 102 (45), 91 (100), 77 (68).

44. **Photoreaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with benzyl disulfide**

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (1.176 g, 3.0 mmol) and benzyl disulfide (0.886 g, 3.6 mmol) were dissolved in 10 ml of benzene. After a nitrogen purge, the solution was irradiated with a sunlamp for 10 h. The usual workup gave 0.55 g (81% yield) of trans-β-styryl benzyl sulfide as a colorless solid, m.p. = 65-67°C; lit. [142] m.p. =

67.5-68°C. No cis-β-styryl benzyl sulfide was detected either by ^{1}H.N.M.R. or GLC analysis.

^{1}H.N.M.R. (CDCl$_3$) δ 7.5-7.1 (m, 10H), 6.58 (d, 1H, J = 15 Hz) 6.42 (d, 1H, J = 15 Hz), 4.05 (s, 2H).

GCMS, m/e (relative intensity) 228 (0.4), 226 (9, M$^+$), 91 (100).

45. Photoreaction of tri-n-butyl-1-alkenyltin with phenyl diselenide

Tri-n-butyl-1-ethenyltin (0.314 g, 1.0 mmol) and phenyl diselenide (0.377 g, 1.2 mmol) were dissolved in 10 ml of nitrogen-purged benzene. The solution was irradiated with a sunlamp for 24 h. Normal workup gave a light yellow residue, which was shown by GLC analysis to contain exclusively the unchanged starting materials. No vinyl phenyl selenide was detected. Similarly, a 12 h irradiation in the Rayonet at 350 nm failed to initiate the above reaction.

The same procedure was applied for the reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.394 g, 1.0 mmol) and phenyl diselenide (0.377 g, 1.2 mmol). The reaction mixture was irradiated in the Rayonet reactor for 24 h. No β-styryl phenyl selenide was observed.

46. Thermal reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin with phenyl diselenide in the presence of AIBN

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.394 g, 1.0 mmol), phenyl diselenide (0.377 g, 1.2 mmol) and AIBN (16 mg, 0.1 mmol) were dissolved in 10 ml of benzene under a nitrogen atmosphere. The reaction mixture was wrapped with aluminum foil to exclude light. The reaction mixture was heated at 80°C for 24 h. The usual workup gave the unchanged

starting materials as determined by GLC analysis. No substitution

product was observed.

47. Reaction of tri-n-butyl-1-alkenyltin
     with N-halosuccinimides

Tri-n-butyl-1-ethenyltin (0.312 g, 1.0 mmol) was added to a solu-

tion of N-bromosuccinimide (0.212 g, 1.2 mmol) in 10 ml of THF. A

highly exothermic reaction occurred. The product of the reaction was

identified to be vinyl bromide. The identity of this compound was

confirmed by GLC (5'x1/8", 15% OV-3, 60°C) retention time matching of

an authentic sample.

N-Chlorosuccinimide (1.2 mmol) failed to react with either tri-n-

butyl-1-ethenyltin (1.0 mmol) or tri-n-butyl-(E)-2-phenyl-1-ethenyltin

(1.0 mmol) under UV (350 nm) irradiation for 24 h. In both cases, no

substitution product was observed and the unchanged starting materials

were recovered.

48. Reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin
     with N-phenylthiophthalimide

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (1.176 g, 3.0 mmol) and N-

phenylthiophthalimide (0.868 g, 3.2 mmol) were dissolved in 25 ml of

benzene. After a nitrogen purge, the solution was irradiated with a

sunlamp for 8 h. Normal workup afforded trans-β-styryl phenyl sulfide

as the exclusive product in a 76% yield as determined by quantitative

[1]H.N.M.R. analysis. The product was further identified by GCMS analy-

sis. No N-β-styrylphthalimide was detected.

49. Reaction of tri-n-butyl-(E)-2-phenyl-1-alkenyltin
    with chlorodiphenylphosphine

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (0.392 g, 1.0 mmol) and

chlorodiphenylphosphine (0.264 g, 1.2 mmol) were dissolved in 10 ml

of benzene. The solution was irradiated in the Rayonet at 350 nm for

24 h under a nitrogen atmosphere. The usual workup gave an oily resi-

due, which was shown by GLC to consist mainly of the starting

materials. However, GCMS analysis indicated a trace amount of the

substituted product, $PhCH=CHPPh_2$ (m/e = 288 was observed for the parent

ion). Following the same procedure, the reaction of tri-n-butyl-1-

ethenyltin with chlorodiphenylphosphine did not occur after 24 h of UV

(350 nm) irradiation.

50. Reaction of tri-n-butyl-1-alkenyltin
    with chlorodiethylphosphate

Tri-n-butyl-1-ethenyltin (0.314 g, 1.0 mmol) and chlorodiethyl-

phosphate (0.206 g, 1.2 mmol) were dissolved in 10 ml of nitrogen-

purged benzene. The solution was irradiated in the Rayonet at 350 nm

for 18 h. Workup as previously described gave the unchanged starting

materials as evidenced by [1]H.N.M.R. and GLC analysis. No substitution

product was observed. The above reaction did not occur when the reac-

tion was performed thermally in the presence of 10 mole % AIBN at 80°C

for 18 h.

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (1.0 mmol) also failed to

react with chlorodiethylphosphate (1.2 mmol) under photochemical or

thermal conditions similar to those described above. In both cases,

the unchanged starting materials were detected.

51. **Thermal reaction of tri-n-butyl-(E)-2-phenyl-1-ethenyltin**
    with tert-butyl peroxybenzoate

Tri-n-butyl-(E)-2-phenyl-1-ethenyltin (1.176 g, 3.0 mmol) and

tert-butyl peroxybenzoate (0.7 g, 3.6 mmol) were dissolved in 25 ml of

chlorobenzene. The reaction mixture was wrapped with aluminum foil to

exclude light. The solution was heated at reflux for 5 h. The volatile

products were distilled directly while the reaction was in progress.

[1]H.N.M.R. and GLC analysis of the distillate revealed acetone exclusive-

ly. Chlorobenzene was distilled to give a light yellow oil. [1]H.N.M.R.

analysis determined the starting tin compound approximately quanti-

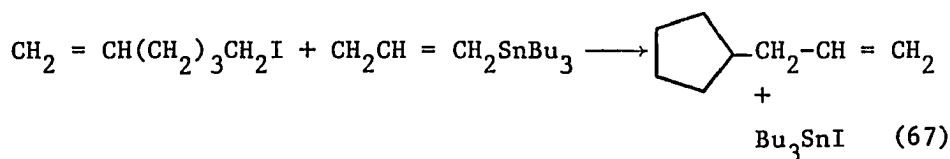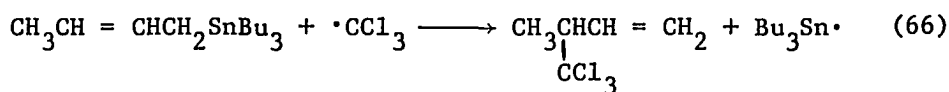tatively. No substitution product, i.e. t-BuOCH=CHPh, was detected.

52. **Photoreaction of tri-n-butyl-2-phenyl-1-ethynyltin**
    with phenyl disulfide

Tri-n-butyl-2-phenyl-1-ethenyltin (0.39 g, 1.0 mmol) and phenyl

disulfide (0.261 g, 1.2 mmol) were dissolved in 10 ml of nitrogen-

purged benzene. The reaction mixture was irradiated with a sunlamp for

12 h. Normal workup gave a residue which was shown by GLC to contain

mainly the starting materials. GCMS analysis determines a trace amount

of the expected product PhC≡CSPh (m/e = 210 was observed for the parent

ion). Similarly, a 24 h irradiation in the Rayonet reactor failed to

initiate the above reaction.

III. FREE RADICAL REACTIONS OF TRI-n-BUTYL-Δ^3-BUTENYLTIN

A. Introduction

Allylic triorganotin compounds are reported to react with numerous organic halides and polyhalomethanes via a homolytic substitution mechanism with allylic rearrangement (Eq. 66, 67) [143]. A radical chain process was proposed for this reaction and was supported by the
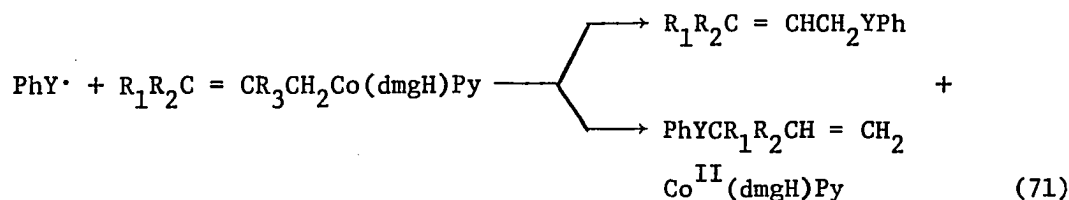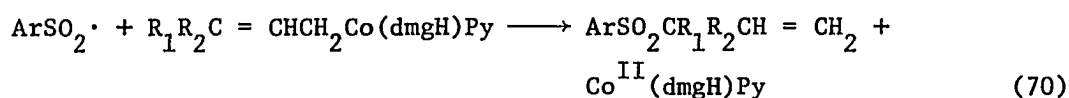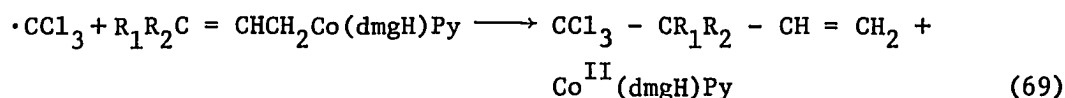
$$CH_3CH = CHCH_2SnBu_3 + \cdot CCl_3 \longrightarrow CH_3\underset{\underset{CCl_3}{|}}{CH}CH = CH_2 + Bu_3Sn \cdot \qquad (66)$$

$$CH_2 = CH(CH_2)_3CH_2I + CH_2CH = CH_2SnBu_3 \longrightarrow \text{⬠} - CH_2-CH = CH_2$$
$$+$$
$$Bu_3SnI \qquad (67)$$

reactivity sequence of alkyl halides, the stereochemistry, the rearrangement of Δ^5-hexenyl moiety into the cyclopentylcarbinyl radical and the influence of free radical initiators and inhibitors [143]. In addition, allytri-n-butyltin derivatives have been established to react with heteroatom-centered radicals PhY· (Y = S, Se, SO_2) to give the corresponding allyl derivatives (Eq. 68) [144]. Somewhat related reactions

$$PhY \cdot + RCH = CHCH_2SnBu_3 \longrightarrow RCH(YPh)CH = CH_2 + Bu_3Sn \cdot \qquad (68)$$
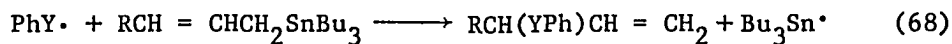
are encountered in allyl derivatives of other metals, especially cobalt. Thus, allylcobaloxime complexes are reported to react with polyhalomethanes [55], arylsulfonyl chlorides [54], and heteroatom-centered radicals PhY· (Y = S, Se) under free radical reaction conditions to

yield the corresponding allyl derivatives (Eq. 69-71). Although reactions 69 and 70 showed complete allylic rearrangement, reaction 71 gave a mixture of both rearranged and unrearranged products [47]. Each of these

$$\cdot CCl_3 + R_1 R_2 C = CHCH_2 Co(dmgH)Py \longrightarrow CCl_3 - CR_1 R_2 - CH = CH_2 +$$
$$Co^{II}(dmgH)Py \qquad (69)$$

$$ArSO_2 \cdot + R_1 R_2 C = CHCH_2 Co(dmgH)Py \longrightarrow ArSO_2 CR_1 R_2 CH = CH_2 +$$
$$Co^{II}(dmgH)Py \qquad (70)$$

$$PhY \cdot + R_1 R_2 C = CR_3 CH_2 Co(dmgH)Py \longrightarrow$$

$$\longrightarrow R_1 R_2 C = CHCH_2 YPh$$
$$+$$
$$\longrightarrow PhYCR_1 R_2 CH = CH_2$$
$$Co^{II}(dmgH)Py \qquad (71)$$

reactions represents part of a chain process (Eq. 72, 73) in which the metal-centered radical plays a crucial role in the production of the organic radical.

$$M^o + Q - Y \longrightarrow MY + Q \cdot \qquad (72)$$

$$Q \cdot + RM \longrightarrow R'Q(RQ) + M \cdot \qquad (73)$$

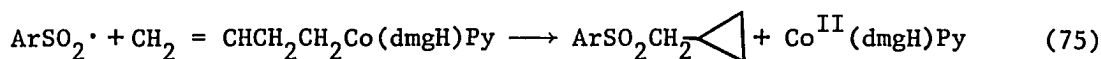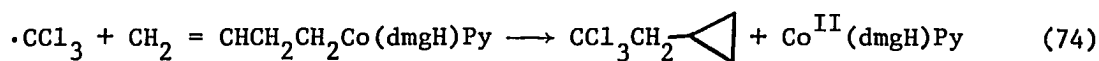R = allyl or substituted allyl group .

R' = the rearranged allyl group .
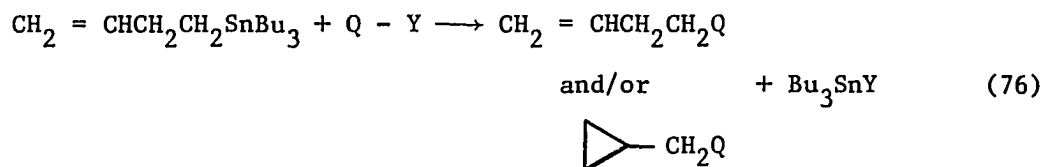
Q = CCl_3, $ArSO_2$, PhS, PhSe .

Y = Cl, PhS, PhSe .

Δ^3-Butenylcobaloxime complexes are reported to undergo a free radical chain reaction with electrophilic radicals, such as $\cdot CCl_3$ and $ArSO_2 \cdot$, to yield exclusively the corresponding cyclopropylcarbinyl derivatives

(Eq. 74, 75) [37]. The formation of these cyclized products is consistent

with a process involving attack of a reactive species at the δ-carbon of

$$\cdot CCl_3 + CH_2 = CHCH_2CH_2Co(dmgH)Py \longrightarrow CCl_3CH_2\text{---}\triangleleft + Co^{II}(dmgH)Py \qquad (74)$$

$$ArSO_2\cdot + CH_2 = CHCH_2CH_2Co(dmgH)Py \longrightarrow ArSO_2CH_2\text{---}\triangleleft + Co^{II}(dmgH)Py \qquad (75)$$

the butenyl ligand with synchronous or subsequent cyclization and dis-

placement of the metal complex. The reactions do not involve the Δ^3-

butenyl radical intermediate, which would react to give predominantly

open chain products.

Considering the close relationship encountered in allylic organotin

and allylic cobaloxime compounds in their reactions with polyhalomethanes

and heteroatom-centered radical precursors, it seemed reasonable to

expect that Δ^3-butenyltin derivatives might undergo homolytic substitu-

tion reactions (Eq. 76) similar to those observed for Δ^3-butenylco-

baloxime compounds. This reaction will be the subject of discussion in

$$CH_2 = CHCH_2CH_2SnBu_3 + Q - Y \longrightarrow CH_2 = CHCH_2CH_2Q$$

$$\text{and/or} \qquad + Bu_3SnY \qquad (76)$$

$$\triangleright\text{---}CH_2Q$$

the next section, which will cover a limited amount of work done in this

area.

It is noteworthy that tri-n-butyl-Δ^3-butenyltin derivatives are

reported to react with numerous electrophilic species E^+ (E = Cl, Br, I,

PhS, p-MePhS and SCl) to give mainly the corresponding cyclopropylcarbinyl

derivatives in good yields (Eq. 77) [145]. The initial stage of this

$$CH_2 = CHCH_2CH_2SnBu_3 + E^+ \longrightarrow \triangleright\!\!-CH_2E + Bu_3Sn^+ \qquad (77)$$

reaction is thought to involve addition of electrophiles to the double

bond of the Δ^3-butenyl ligand to form electron deficient carbon atom δ

to tin. These incipient carbonium ions then electrophilically induce

heterolytic fragmentations of the carbon-tin bond with concurrent ring

formation [145].

B. Results and Discussion

Tri-n-butyl-Δ^3-butenyltin underwent a slow photostimulated reaction

with phenyl disulfide under UV (350 nm) irradiation to give, exclusively,

Δ^2-butenyl phenyl sulfide (37). The structure of this compound was

$$CH_3 - CH = CH_2 - CH_2SPh$$

37
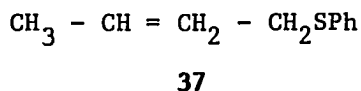
confirmed by ^{1}H.N.M.R., mass spectrum and GLC retention time match-

ing with those of an authentic sample. The formation of **37** was completely

unexpected. No Δ^3-butenyl phenyl sulfide (38) or cyclopropylcarbinyl

phenyl sulfide (39) was observed. Compound 37 must be formed via a free

$$CH_2 = CHCH_2CH_2SPh \qquad\qquad \triangleright\!\!-CH_2SPh$$

38   **39**
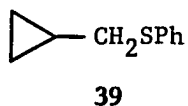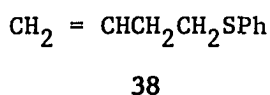
radical chain process, since the reaction failed to proceed in the dark

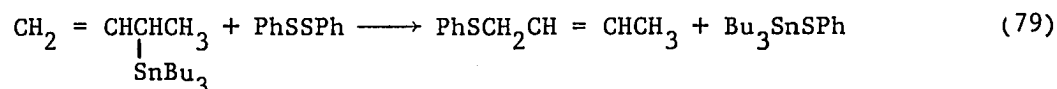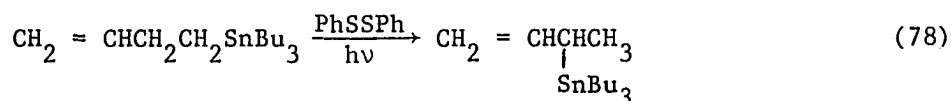and was strongly retarded by di-tert-butyl nitroxide. In addition, the

reaction was effectively initiated by AIBN at 80°C.

Several experiments were performed, under similar reaction condi-tions, to preclude the formation of either Δ^3-butenyl phenyl sulfide or cyclopropylcarbinyl phenyl sulfide as an intermediate prior to the formation of **37**. Thus, UV (350 nm) irradiation of a benzene solution of **38** for 28 h led to no isomerization. The unchanged Δ^3-butenyl phenyl sulfide was recovered approximately quantitatively. Comparable results were obtained when the irradiation of compound **38** was performed in the presence of Bu_3SnCl in the Rayonet at 350 nm. In one case, a known amount of Δ^3-butenyl phenyl sulfide was added to the reaction mixture of tri-<u>n</u>-butyl-Δ^3-butenyltin and phenyl disulfide, and the whole solution was irradiated in the Rayonet for 48 h. Although Δ^2-butenyl phenyl sulfide was formed in a respectable yield, the starting Δ^3-butenyl phenyl sulfide was accounted for almost quantitatively. A similar set of experiments was carried out on the cyclopropylcarbinyl phenyl sulfide. Thus, irradiation of a benzene solution of compound **39**, alone or in the presence of Bu_3SnCl, in the Rayonet at 350 nm resulted in no isomeriza-tion. The starting sulfide was recovered.

The results presented above exclude the intermediacy of either Δ^3-butenyl phenyl sulfide or cyclopropylcarbinyl phenyl sulfide in the formation of Δ^2-butenyl phenyl sulfide (**37**) from the reaction of the Δ^3-butenyltin compound with phenyl disulfide. Although it is difficult to propose an unambiguous mechanism to explain the results of this perplex-ing reaction, there are two possible explanations which warrant consider-ation. First, it is possible that the Δ^3-butenyltin compound rearranged

under the reaction conditions to give 3-(tri-$\underline{n}$-butylstannyl)-1-butene (Eq. 78), Scheme XXXIII. The 3-(tri-$\underline{n}$-butylstannyl)-1-butene would

Scheme XXXIII

$$CH_2 = CHCH_2CH_2SnBu_3 \xrightarrow{\text{PhSSPh}}{\text{h}\nu} CH_2 = CHCHCH_3 \qquad (78)$$
$$\underset{SnBu_3}{|}$$

$$CH_2 = CHCHCH_3 + PhSSPh \longrightarrow PhSCH_2CH = CHCH_3 + Bu_3SnSPh \qquad (79)$$
$$\underset{SnBu_3}{|}$$

rapidly undergo the known $S_H^{2'}$ reaction with allylic transposition to give the product **37**. A possible mechanism for the isomerization of the Δ^3-butenyltin compound to 3-(tri-$\underline{n}$-butylstannyl)-1-butene is shown in Scheme XXXIV. Of course, reactions 80 and 81 might occur in a concerted

Scheme XXXIV

$$(80)$$

$$(81)$$

$$(82)$$
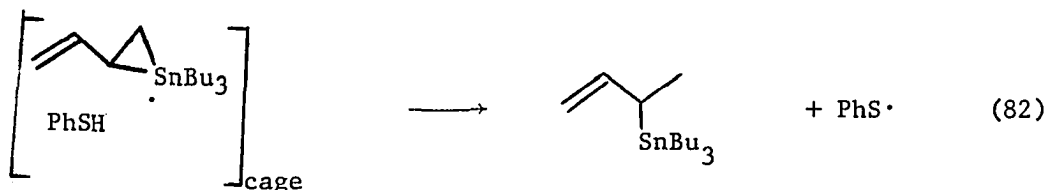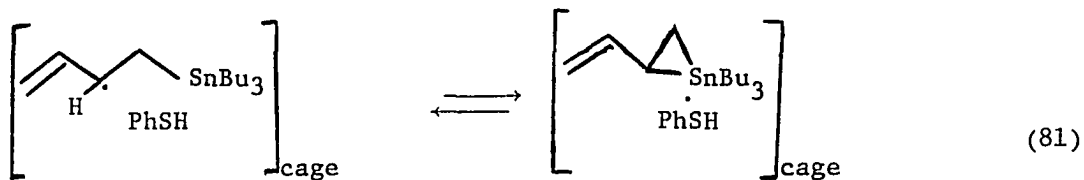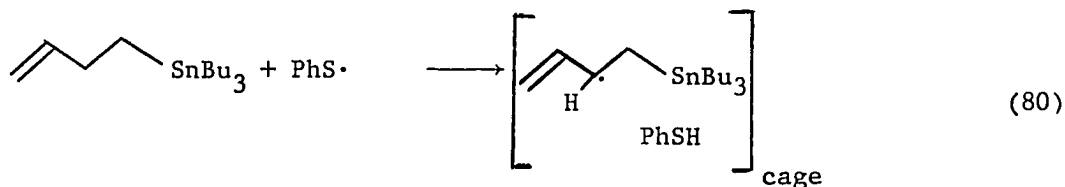
fashion with allylic attack leading directly to the bridged radical. Reaction with PhSH could then regenerate PhS· and the isomerized butenyltin.

Another possible explanation for this reaction is a radical chain process involving an unusual 1,2-hydrogen shift as shown in Scheme XXXV.

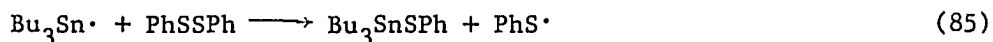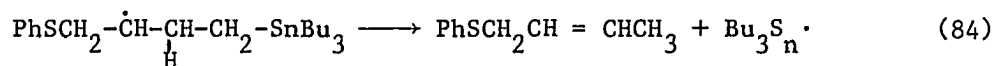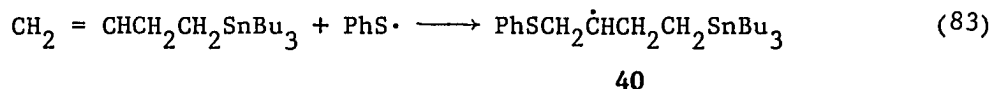Scheme XXXV

$$CH_2 = CHCH_2CH_2SnBu_3 + PhS· \longrightarrow PhSCH_2\overset{\cdot}{C}HCH_2CH_2SnBu_3 \qquad (83)$$
$$\mathbf{40}$$

$$PhSCH_2-\overset{\cdot}{C}H-\underset{\overset{|}{H}}{C}H-CH_2-SnBu_3 \longrightarrow PhSCH_2CH = CHCH_3 + Bu_3S_n· \qquad (84)$$

$$Bu_3Sn· + PhSSPh \longrightarrow Bu_3SnSPh + PhS· \qquad (85)$$

The initial stage of this mechanism involves the addition of the thiyl radical to the δ-carbon of the butenyl group to yield radical **40**. It can be postulated that intermediate **40** undergoes a 1,2-hydrogen shift to the α-carbon of the butenyl substituent with the elimination of $Bu_3Sn·$ and the formation of **37**. It should be mentioned that this process is unprecedented and it is very questionable. Since the δ-position in **40** is more capable than the α-position for accepting a hydrogen atom, it seems that if a 1,2-hydrogen shift were to occur, it would be most reasonable to expect it to yield $PhSCH_2CH_2\overset{\cdot}{C}HCH_2SnBu_3$ rather than $PhSCH_2CH=CHCH_3$. It is important to emphasize that the mechanism of Scheme XXXV is highly speculative, and no evidence is available to support or disprove it.

Interestingly, the δ-alkylstannyl radical **40** did not undergo

cyclization to afford the cyclopropylcarbinyl derivatives. This is in contrast to the behavior observed for the reaction of Δ^3-butenylcobalox-ime complexes with sulfur-centered radicals [37]. In addition, the reaction of the Δ^3-butenyltin compound is different from that observed for Δ^3-butenylmercury chloride. In the latter reaction with phenyl disulfide, Δ^3-butenyl phenyl sulfide was isolated exclusively, as discussed in Part I of this thesis. The reasons behind these discrepancies are not clear, and further work on this reaction is planned for the future. However, it appears that the results can be explained qualitatively by the relative rate constants in Scheme XXXVI.

Scheme XXXVI
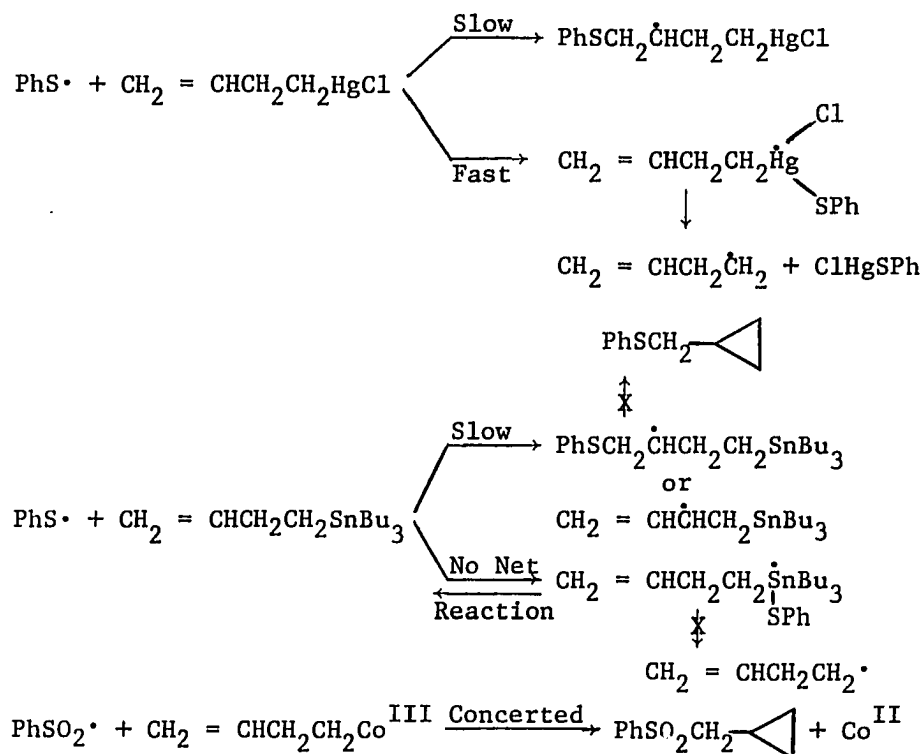
Tri-n-butyl-Δ^3-butenyltin failed to react with pheny diselenide under UV (350 nm) irradiation for 24 h. The unchanged starting materials were recovered. This result is consistent with those observed for 1-alkenyltin derivatives. However, tri-n-butylallyltin compounds have been established to react with phenyl diselenide to yield the corresponding allyl phenyl selenides with complete allylic shift [144].

A preliminary study showed that trichloromethanesulfonyl chloride reacted with tri-n-butyl-Δ^3-butenyltin under UV (350 nm) irradiation to give very low yields of two products. Both were identified only by GCMS analysis. One product had the elemental composition $C_5H_7Cl_3$, while the other product was identified to be 1,1,1,3-5-pentachloropentane. The formation of the latter might involve S_H^2 attack of $\cdot CCl_3$ at the tin atom of the substrate after the addition of the elements CCl_3 and Cl to the double bond had taken place. The S_H^2 attack of a radical at $S_n(IV)$ is not uncommon [52]. Carbon tetrachloride showed a very slow reaction with the Δ^3-butenyltin compound, and after 48 h of UV irradiation only a trace of a product, with elemental composition $C_5H_7Cl_3$, was observed. Similarly, the reaction of tri-n-butyl-Δ^3-butenyltin with benzenesulfonyl chloride afforded a very low yield of the substitution product, $C_4H_7SO_2Ph$, whose structure has not been fully determined.

C. Conclusion

Tri-n-butyl-Δ^3-butenyltin reacted with phenyl disulfide under UV (350 nm) irradiation to give, unexpectedly, Δ^2-butenyl phenyl sulfide in a fair yield. The mechanism leading to this product is not known.

However, Δ^3-butenyl phenyl sulfide and cyclopropylcarbinyl phenyl sulfide are not involved as intermediates in the reaction.

D. Experimental Section

1. General considerations

Tri-$\underline{n}$-butyl-Δ^3-butenyltin was prepared following a literature procedure [76]. Cyclopropylcarbinyl phenyl sulfide was prepared from the reaction of tri-$\underline{n}$-butyl-Δ^3-butenyltin with phenylsulfenyl chloride [145]. Δ^3-Butenyl phenyl sulfide was prepared by a published procedure [72].

2. Photoreaction of tri-n-butyl-Δ^3-butenyltin with phenyl disulfide

Tri-$\underline{n}$-butyl-Δ^3-butenyltin (1.032 q, 3.0 mmol) and phenyl disulfide (0.785 g, 3.6 mmol) were dissolved in 25 ml of benzene. After a nitrogen purge, the solution was irradiated in the Rayonet at 350 nm for 72 h. The solvent was removed under vacuum to give a light yellow residue. Upon distillation, using short path apparatus, 0.22 g (45% yield) of Δ^2-butenyl phenyl sulfide was isolated, b.p. = 70-72°C (0.8 mm); lit [146] b.p. = 109°C (10 mm). The identity of the compound was verified by [1]H.N.M.R., GCMS and GLC (10'x1/8", 15% OV-3, 100°C) retention time matching with those of an authentic sample.

[1]H.N.M.R. (CDCl$_3$) δ 7.35-7 (m, 5H), 5.6-5.35 (m, 2H), 3.65-3.3 (m, 2H), 1.7-1.4 (m, 3H).

GCMS, $\underline{m}/\underline{e}$ (relative intensity) 166 (0.9), 164 (19, M[+]), 110 (69), 55 (100).

I.R. (neat, NaCl plates, cm^{-1}) 1580 (m), 1470 (s), 950 (s), 730 (s), 680 (s).

The product was a mixture of both <u>cis</u>- and <u>trans</u>-isomers.

2. <u>Thermal reaction of tri-n-butyl-Δ³-butenyltin with phenyl disulfide in the presence of AIBN</u>

Tri-<u>n</u>-butyl-Δ³-butenyltin (0.344 g, 1.0 mmol) and phenyl disulfide (0.263 g, 1.2 mmol) and AIBN (16 mg, 0.1 mmol) were dissolved in 10 ml of nitrogen-purged benzene. The reaction mixture was wrapped with aluminum foil to exclude light. The reaction mixture was heated at 80°C for 50 h. Workup as described above gave an oily residue, which was shown by a quantitative GLC to contain Δ²-butenyl phenyl sulfide in a 41% yield. The product was identified by GCMS as described above.

3. <u>Effect of di-tert-butyl nitroxide on the reaction of tri-n-butyl-Δ³-butenyltin with phenyl disulfide</u>

Tri-<u>n</u>-butyl-Δ³-butenyltin (0.344 g, 1.0 mmol), phenyl disulfide (0.263 g, 1.2 mmol) and di-<u>tert</u>-butyl nitroxide (14 mg, 0.1 mmol) were dissolved in 10 ml of benzene. After a nitrogen purge, the reaction mixture was irradiated in the Rayonet at 350 nm for 48 h. Workup as previously described afforded Δ²-butenyl phenyl sulfide in an 18% yield as determined by GLC analysis.

4. <u>Dark reaction of tri-n-butyl-Δ³-butenyltin with phenyl sulfide</u>

Tri-<u>n</u>-butyl-Δ³-butenyltin (0.344 g, 1.0 mmol) and phenyl disulfide (0.263 g, 1.2 mmol) were dissolved in 10 ml of benzene. The reaction mixture was heated at 50°C for 24 h under nitrogen. The usual workup afforded the unchanged starting materials. No Δ²-butenyl phenyl sulfide

was detected.

5. Attempts to photo-isomerized Δ^3-butenyl phenyl sulfide

Δ^3-Butenyl phenyl sulfide (0.328 g, 2.0 mmol) in 5 ml of benzene was irradiated in the Rayonet at 350 nm for 28 h. The solvent was removed in vacuo to afford an oil. ^{1}H.N.M.R. and GLC analysis determined the residue to contain, exclusively, Δ^3-butenyl phenyl sulfide. No isomerization was observed. When the above reaction was repeated, with tri-n-butyltin chloride (0.16 g, 0.5 mmol) added, similar results were obtained after 24 h of UV (350 nm) irradiation. In either case, Δ^3-butenyl phenyl sulfide was recovered.

6. Photoreaction of tri-n-butyl-Δ^3-butenyltin with phenyl
   disulfide in the presence of Δ^3-butenyl phenyl sulfide

Tri-n-butyl-Δ^3-butenyltin (0.344 g, 1.0 mmol), phenyl disulfide (0.263 g, 1.2 mmol) and Δ^3-butenyl phenyl sulfide (0.164 g, 1.0 mmole) were dissolved in 10 ml of nitrogen-purged benzene. The reaction mixture was irradiated in the Rayonet at 350 nm for 35 h. The solvent was removed in vacuo and the residue was analyzed by GLC, which indicated Δ^3-butenyl phenyl sulfide almost quantitatively. In addition, GLC analysis revealed a 42% yield of Δ^2-butenyl phenyl sulfide.

7. Attempts to photo-isomerize cyclopropylcarbinyl
   phenyl sulfide

Cyclopropylcarbinyl phenyl sulfide (0.164 g, 1.0 mmol) in 5 ml of benzene was irradiated in the Rayonet for 46 h under a nitrogen atmosphere. After the solvent was removed under vacuum, GLC analysis revealed, exclusively, the starting cyclopropylcarbinyl phenyl

sulfide. No Δ^2-butenyl phenyl sulfide was observed. When the above

reaction was repeated with tri-n-butyltin chloride (0.16 g, 0.15 mmol)

added, no isomerization was observed after 32 h of irradiation in the

Rayonet reactor at 350 nm.

8. **Photoreaction of tri-n-butyl-Δ^3-butenyltin with phenyl diselenide**

Tri-n-butyl-Δ^3-butenyltin (0.344 g, 1.0 mmol) and phenyl diselenide

(0.377 g, 1.2 mmol) were dissolved in 10 ml of nitrogen-purged benzene.

The reaction mixture was irradiated in the Rayonet at 350 nm for 24 h.

Normal workup gave an oily residue, which was shown by GLC to con-

tain, exclusively, the starting materials. No substitution product, i.e.

butenyl phenyl selenide, was observed.

9. **Photoreaction of tri-n-butyl-Δ^3-butenyltin with trichloromethanesulfonyl chloride**

Tri-n-butyl-Δ^3-butenyltin (0.344 g, 1.0 mmol) and trichloro-

methanesulfonyl chloride (0.259 g, 1.2 mmol) were dissolved in 10 ml of

benzene under a nitrogen atmosphere. The solution was irradiated in the

Rayonet at 350 nm for 36 h. The solvent was distilled to give a yellow

residue. GCMS analysis of the residue revealed small amounts of the

trichloro-substituted product, $C_4H_7Cl_3$, and 1,1,1,3,5-pentachloropen-

tane.

$C_4H_7Cl_3$:

GCMS m/e (relative intensity) 139 (4.7), 137 (7, M^+-Cl), 103

(14), 101 (40), 100 (7.8), 98 (45), 96 (64), 55 (100.

1,1,1,3,5-pentachloropentane:

GCMS $\underline{m}/\underline{e}$ (relative intensity) 208 (0.7), 206 (0.8, M^+-HCl), 173 (3.9), 171 (4, M^+-2Cl-H), 137 (8), 135 (12), 109 (100), 89 (71), 75 (90), 53 (82).

Under similar reaction conditions, CCl_4 reacted with tri-$\underline{n}$-butyl-Δ^3-butenyltin much slower and gave only a trace of the substituted product as shown by GCMS.

10. **Photoreaction of tri-n-butyl-Δ^3-butenyltin with benzenesulfonyl chloride**

Tri-$\underline{n}$-butyl-Δ^3-butenyltin (0.344 g, 1.0 mmol) and benzenesulfonyl chloride (0.211 g, 1.2 mmol) were dissolved in 10 ml of nitrogen-purged benzene. The solution was irradiated in the Rayonet for 36 h. The usual workup gave only a trace of the substituted product as determined by GCMS analysis.

$C_4H_7SO_2Ph$:

GCMS $\underline{m}/\underline{e}$ (relative intensity) 198 (0.1), 196 (1.8), 142 (12), 126 (12), 77 (50), 55 (100).

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VI. APPENDIX

Literature references to phenyl alkyl chalcogenide (PhYR) prepared in Part I of this thesis.

R	Y	Literature Ref.
$(CH_3)_2CH$	S	47
$CH_3(CH_2)_2CH_2$	S	47
$(CH_3)_3CCH_2$	S	˙147
$CH_3(CH_2)_4CH_2$	S	148
$PhCH_2$	S	148
$c-C_6H_{11}$	S	149
$(CH_3)_2CHCH_2$	S	150
$(CH_3)_2CH$	Se	51
$CH_3(CH_2)_2CH_2$	Se	51
$CH_3(CH_2)_5CH_2$	Se	148
$PhCH_2$	Se	51
$c-C_6H_{11}$	Se	151
$CH_2=CH(CH_2)_3CH_2$	Se	152
$c-C_5H_9CH_2$	Se	152
$(CH_3)_2CH$	Te	51
$PhCH_2$	Te	51