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H^1–H^1 AND H^1–P^{31} SPIN–SPIN INTERACTIONS
IN SOME NEW BICYCLO[2.2.2]OCTANE DERIVA-
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H^1-H^1 AND H^1-P^{31} SPIN-SPIN INTERACTIONS IN SOME NEW

BICYCLO[2.2.2]OCTANE DERIVATIVES

by

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INTRODUCTION

In 1952, Stetter and Steinacker (1) reported the preparation of 1-phospha-2,8,9-trioxaadamantane (I-1), and 8 years later, Verkade and Reynolds (2) reported the synthesis of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (I-2). Verkade and Piper later reported a study of the use of I-2
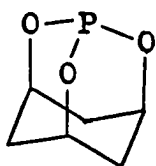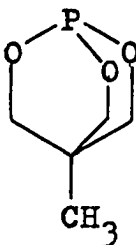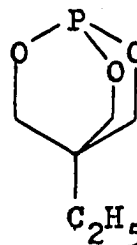
I-1   I-2   I-3

as a ligand toward transition metal ions (3, 4), and the properties of I-1 and I-2 as Lewis bases toward Group III acids were reported by Heitsch and Verkade (5, 6, 7, 8). The transition metal complexes of I-1 were reported by Huttemann in a doctoral dissertation (9) and the complexes of I-1, I-2, and 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (I-3) with cobalt(III), cobalt(I), nickel(II) and nickel(0) appeared in 1965 (10). In a doctoral dissertation (11), Hendricker described the metal carbonyl complexes of I-1, I-2, and I-3, some of which were subsequently reported elsewhere (12).

The general results of the above investigations are that crystalline metal complexes can be isolated most of which

exhibit maximum coordination numbers for the metal with only polycyclic phosphite in the coordination sphere. These findings differed from those obtained for trialkyl phosphites in that only color changes and intractable oils were observed in most cases (9). A comparison of the dipole moments of I-2 with triethyl phosphite showed I-2 to be more than twice as polar as the open chain phosphite (13). Oxidation of I-2 increased the dipole moment, indicating that the moment is directed toward the phosphorus. Presumably the difference in moments between the cyclic and open chain phosphites is a result of directed lone pair electron moments on the oxygens in the former. Dreiding models indicate that in $(C_2H_5O)_3P$ there is a large amount of steric repulsion between the alkoxy chains, whereas, I-2 is essentially strainless (9). It is of interest that transition metal complexes of open chain trialkyl phosphites have been isolated recently (9). Dreiding models show there is still ligand-ligand repulsion, although it can be minimized by restricting free rotation of the alkoxy groups and orientating these groups so that closest approach of the phosphorus to the metal can be attained. Although this process would not be favorable entropically, it could be compensated for by increasing the dipole moment of the ligand as a result of orientation of the oxygen lone pairs toward the phosphorus. Hence a stronger metal ion-dipole interaction could arise. Such an argument was used to explain the occurrence and stability of these complexes (9).

From the ultraviolet spectrum of $[Co(I-2)_6](ClO_4)_2$ (4),
a Dq value of 3320 cm^{-1} was calculated which compares well
with 3350 cm^{-1} obtained for $[Co(CN)_6]^{3-}$, indicating the
presence of a strong octahedral field. The probability of
d-pi-d-pi-bonding was invoked to explain the unusually large
ligand field strength of I-2. Furthermore, in the metal
carbonyl work published (12), the possibility of dative
pi-bonding from the metal d orbitals to the phosphorus d
orbitals was mentioned. Such pi-bonding could explain the
high CO stretching frequencies in these compounds.

A method of determining the possible presence or extent
of pi-bonding in these complexes might be to study similar
coordination compounds using a phosphine analogous in struc-
ture to I-2. Such a ligand would be a 1-phosphabicyclo[2.2.2]-
octane (I-4). Because of the difference in electronegativity
of oxygen and carbon, I-4 should be a better Lewis base than
I-2. However, when considering pi-bonding or back donation
of electrons from a transition metal to the d orbitals on
phosphorus, I-2 should pi-bond more strongly than I-4 because
of the superior electron withdrawing power of oxygen. Of
particular interest would be the synthesis of metal carbonyl
complexes of I-4 and a study of their CO, MC, and MP stretch-
ing frequencies in the infrared region. Hendricker (11)
tentatively assigned these frequencies for metal carbonyl

complexes of I-1, I-2, and I-3, and reviewed the metal car-
bonyl chemistry of phosphorus-containing ligands. Complexes
of trimethyl phosphite might be compared to those of triethyl
phosphine to determine the extent of pi-bonding; however, in
view of the steric problems indicated above, difficulties
might arise.
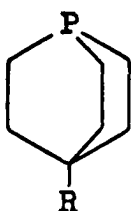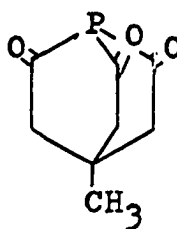
I-4   I-5

Attempts at isolating the free phosphine I-4 have been
the subjects of two theses. Cooper (14) tried to cyclize
$CH_3C(CH_2C(O)Cl)_3$ to I-5 with either sodium phosphide or phos-
phine but failed to isolate any characterizable organophos-
phorus compound. A reduction of the carbonyls on I-5 would
have produced I-4 (R=CH$_3$).

Mathews (15) isolated the phosphonium salt (I-6) of
I-4 (R=OH) by the reaction sequence shown below. Attempts to
reduce I-6 to I-4 (R=OH) by treatment with LiAlH$_4$ or by
pyrolysis failed.
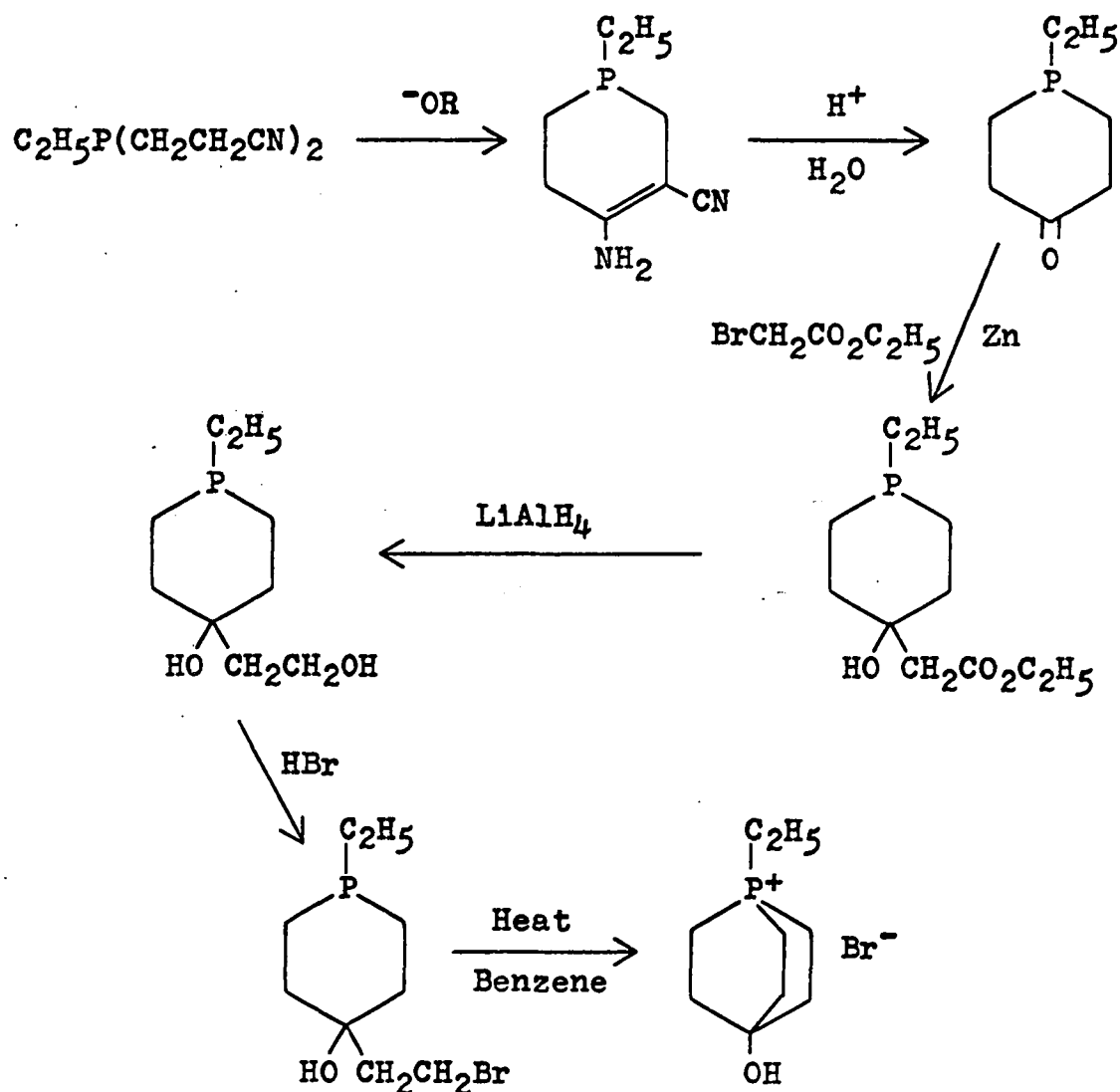
I-6

Previously, McEwen et al. (16) could not isolate I-4
(R=H) by treating the corresponding tribromide $HC(CH_2CH_2Br)_3$
with PH_3 or AlP. Wiley (17) also tried reacting the tri-
bromide with PH_3 in a sealed tube with negative results. This
led Mathews (15) to prophesy that a single-step synthesis of
I-4 would have little chance of success.

A review of the literature revealed few polycyclic phosphines or arsines with the Group V atom at the bridgehead. The first such compound reported by Hinton and Mann in 1959 (18) was the diphosphine I-7 prepared as outlined below.

$$R_3P \;+\; BrCH_2CH_2Br \longrightarrow R_3\overset{+}{P}(CH_2)_2\overset{+}{P}R_3 \quad 2Br^-$$

(R=CH₂C₆H₅) I-7
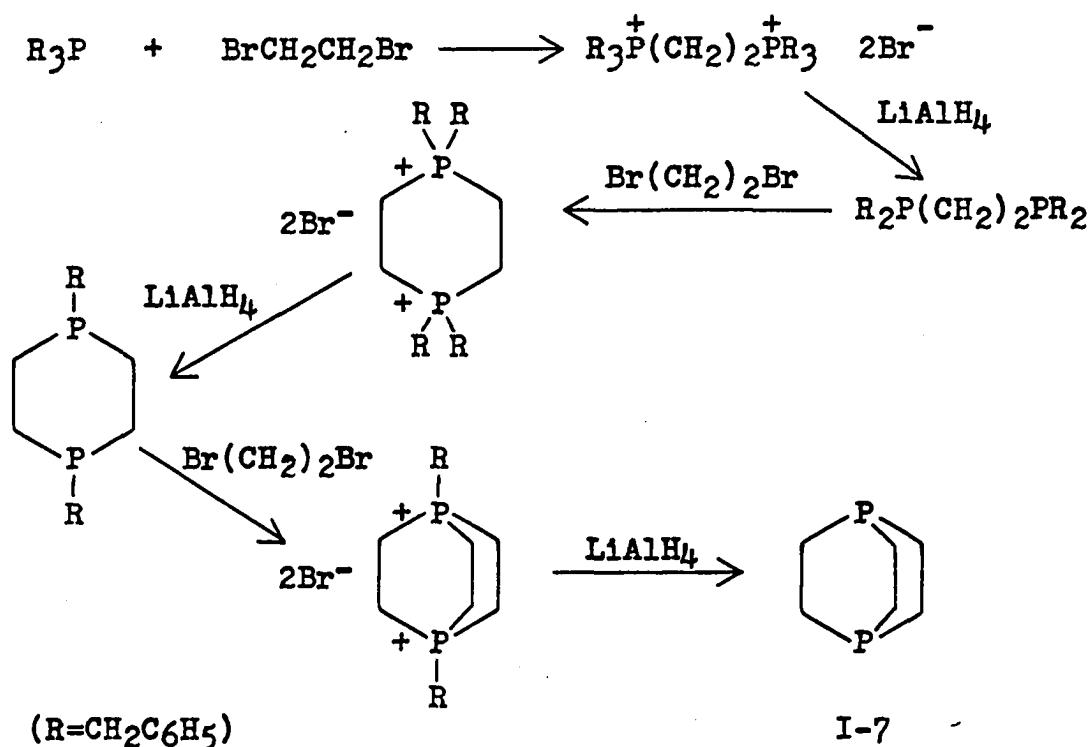
The last step in the synthesis of this very volatile compound was reported to proceed with considerable decomposition in low yield which might imply that the polycyclic phosphine is a strained unstable compound as Mathews (15) had observed in his dissertation. Five years previous to the reported synthesis of I-7, Jones and Mann (19) reported an attempt to isolate the 1,4-diarsa analogue by a similar reaction sequence. However, they isolated only the monocyclic $RAs(CH_2CH_2)_2AsR$.

In 1961, Krespan (20) reported the synthesis of I-8 by treating bis(trifluoromethyl)acetylene with red phosphorus and iodine in a heated autoclave. Compound I-8 is a stable volatile solid melting at 119°. In this report, Krespan also described the preparation of the analogous diarsine.

$$RC \equiv CR \ + \ I_2 \ \xrightarrow[P_{red}]{Heat}$$

(R=CF$_3$)

I-8
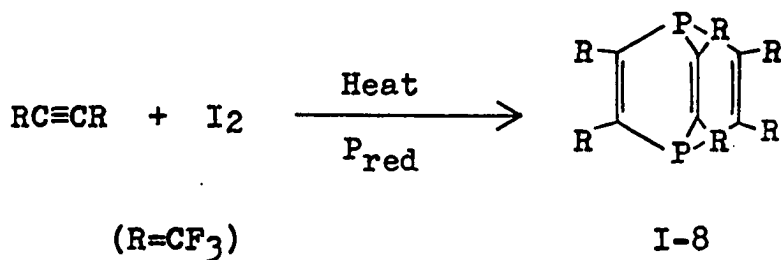
Heinekey et al. (21) reported the synthesis of 1-arsabicyclo[3.3.0]octane (I-9) in an overall yield of 1% by the reaction sequence shown.

$$C_2H_5O(CH_2)_3MgBr \ + \ C_2H_5OCHO \ \longrightarrow \ (C_2H_5O(CH_2)_3)_2CHOH$$

$$\downarrow PBr_3$$

$$(C_2H_5O(CH_2)_3)_2CHAs(CH_3)_2 \ \xleftarrow[2) \ IAs(CH_3)_2]{1) \ Mg} \ (C_2H_5O(CH_2)_3)_2CHBr$$

$$\downarrow CH_3Br$$

$$(C_2H_5O(CH_2)_3)_2CH\overset{+}{A}s(CH_3)_3 \ \xrightarrow[Heat]{HBr} \ (Br(CH_2)_3)_2CH\overset{+}{A}s(CH_3)_3$$

Br⁻   Br⁻

Heat

I-9
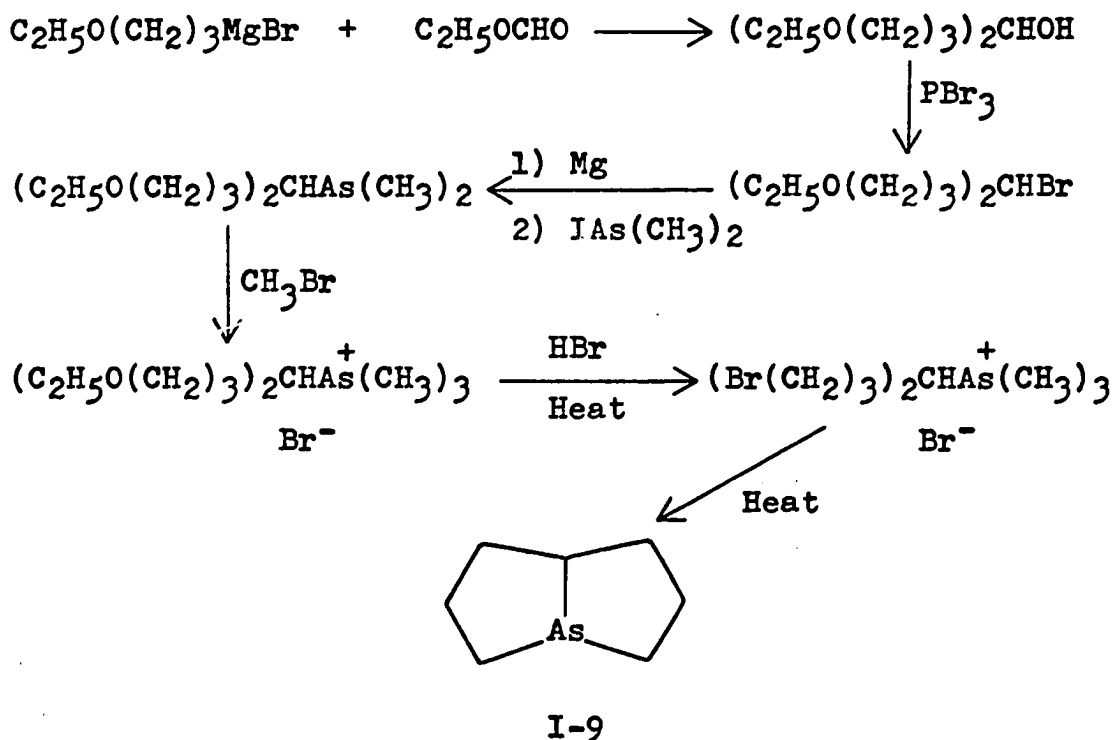
Finally, in 1965, Coskran and Verkade (22) reported the synthesis of the novel phosphite-phosphine I-10 by a trans-esterification reaction similar to that used in the preparation of I-1, I-2, and I-3 (23).

$$P(CH_2OH)_3 \ + \ (CH_3O)_3P \ \longrightarrow$$

I-10
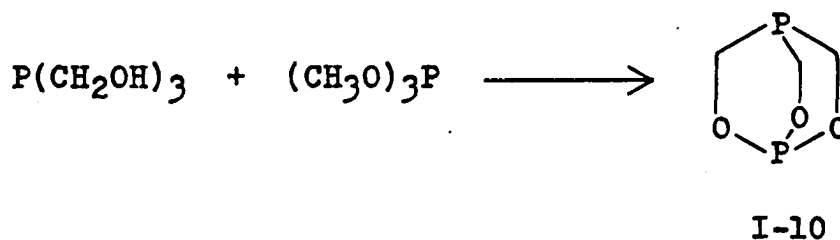
Other preparations of bicyclo[2.2.2]octane compounds with a hetero atom at the bridgehead which might offer feasible routes to the isolation of I-4 are those for quinuclidine (I-11) and for 1-silabicyclo[2.2.2]octane (I-12).

I-11
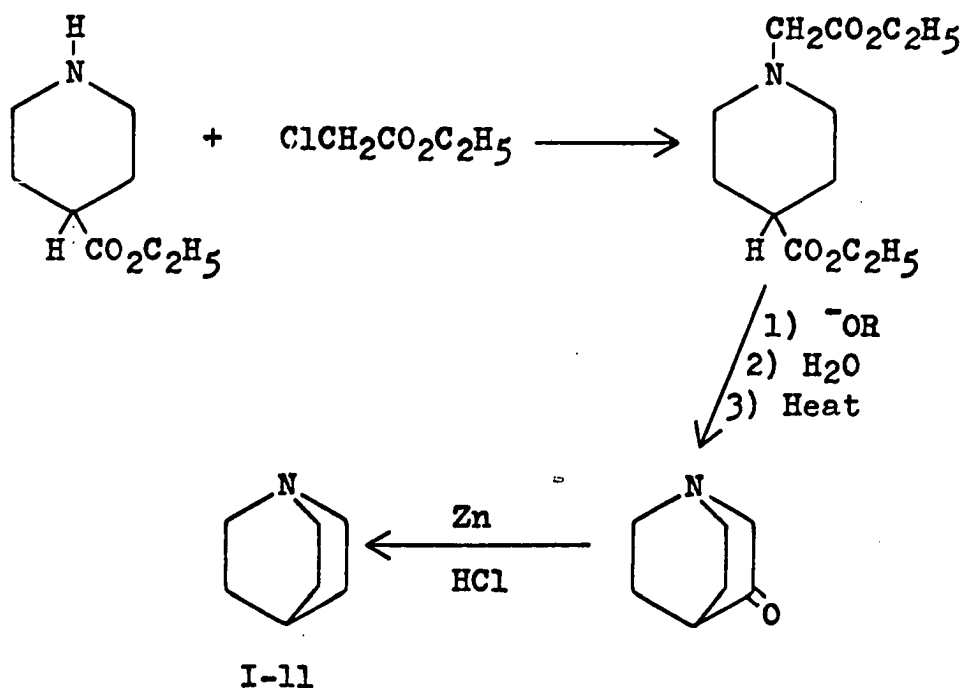
The synthesis of I-11 by Clemo and Metcalf (24) utilized a
Dieckmann reaction for the ring closure. Compound I-12 was
isolated by Sommer and Bennett (25), the cyclization being
affected by a Grignard reaction in 30% yield. They also
reported the synthesis of 1-silabicyclo[2.2.1]heptane (I-13)
by analogous reactions (26).

I-12   I-13
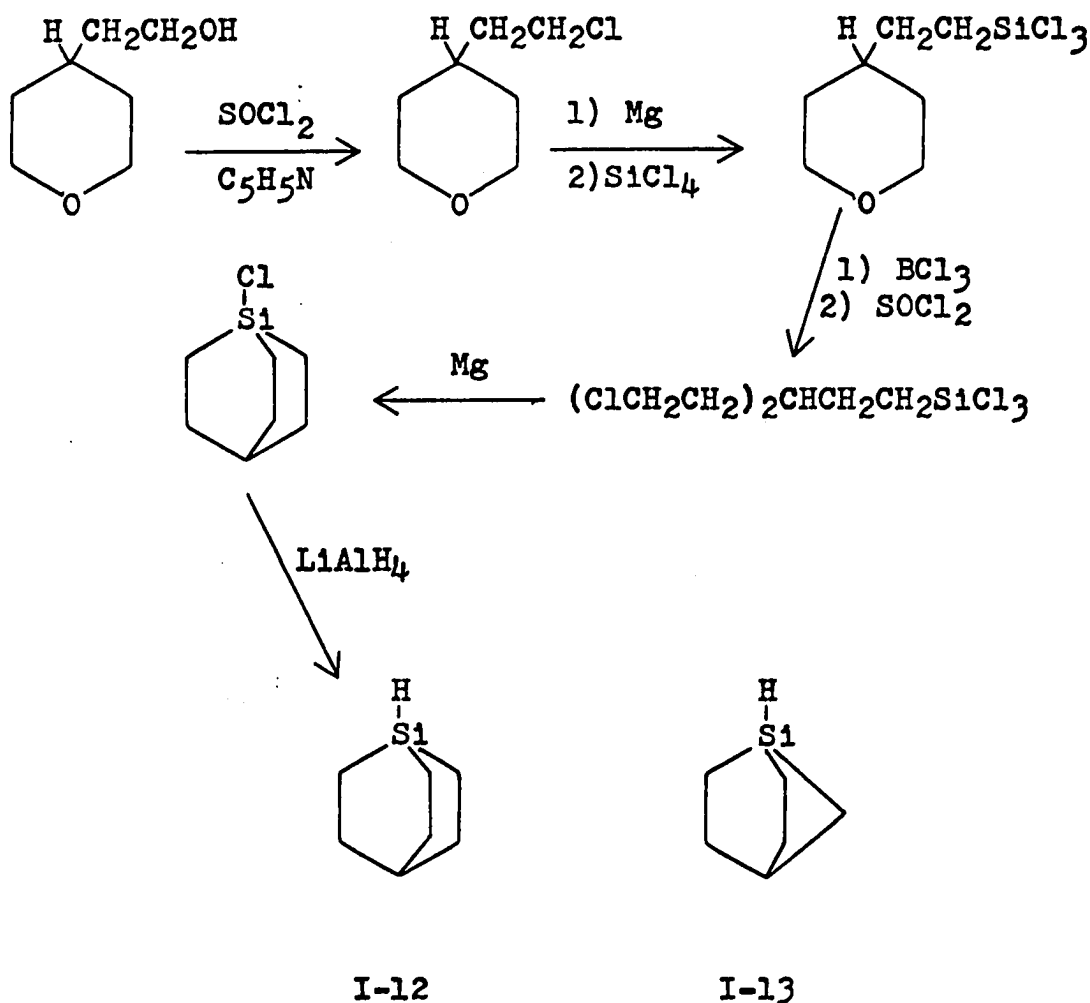
Maier has reviewed the chemistry and synthesis of mono-,
di-, and trialkyl phosphines (27). In addition to the

methods of synthesis outlined above, organometallic reagents
are frequently used to obtain alkyl phosphines. Issleib has
reported reactions of MPR_2 and M_2PR (M=Li, Na, K; R=H, alkyl,
aryl) with organic halides, an example of which is indicated
in reaction (a) (28). For the preparation of noncyclic tri-
alkyl phosphines, see, for example, reference 29. Issleib
et al. have also reported the reaction of $LiPR_2$ with ethylene
oxide as shown in reaction (b) (29), and the reaction of
$(C_6H_5)_2PCl$ with CH_2N_2 as shown in reaction (c) (30). The
preparation of alkali metal phosphides used here has been
reviewed recently by Issleib (31).

$$Li_2PR \quad + \quad Br(CH_2)_nBr \longrightarrow \qquad \qquad \qquad (a)$$

$$n=4 \qquad n=5$$

$$LiPR_2 \quad + \quad CH_2CH_2 \xrightarrow[2) \ H_2O]{} \quad HOCH_2CH_2PR_2 \qquad (b)$$

$$(C_6H_5)_2PCl \quad + \quad CH_2N_2 \xrightarrow[2) \ H_2O]{} \quad (C_6H_5)_2PCH_2P(C_6H_5)_2 \ (c)$$
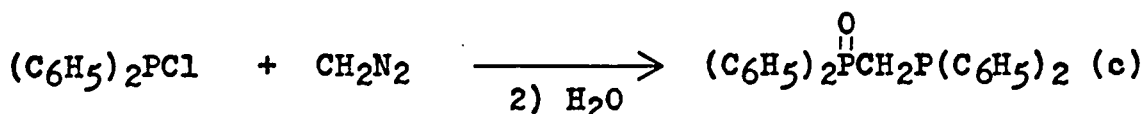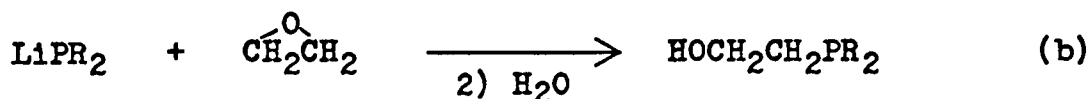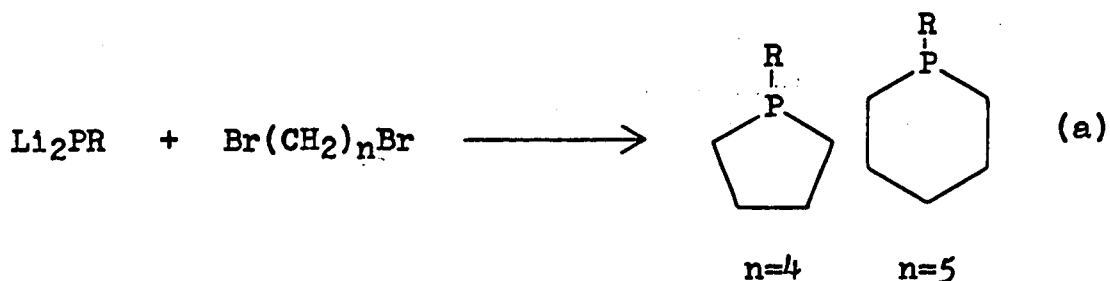
Another method of P-C bond formation has been the action
of organic Grignard reagents on P-Cl (32), P-Br (33), and
P-OR (34) bonds. Three examples are shown in (d), (e),
and (f).

$$C_6H_5\overset{\overset{O}{\|}}{P}{<}^{Cl}_{CH_2Cl} \quad + \quad CH_3MgBr \quad \longrightarrow \quad C_6H_5\overset{\overset{O}{\|}}{P}{<}^{CH_3}_{CH_2Cl} \qquad (d)$$

$$Br(CH_2)_5Br \quad \xrightarrow[\text{2) } CH_3P(S)Br_2]{\text{1) Mg}} \qquad (e)$$

$$Br(CH_2)_5\overset{\overset{O}{\|}}{P}(OR)_2 \quad \xrightarrow{\text{Mg}} \qquad (f)$$
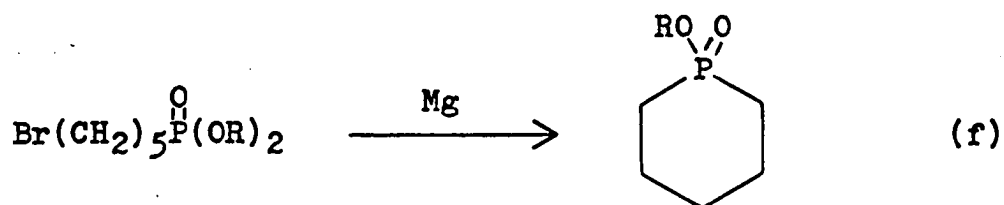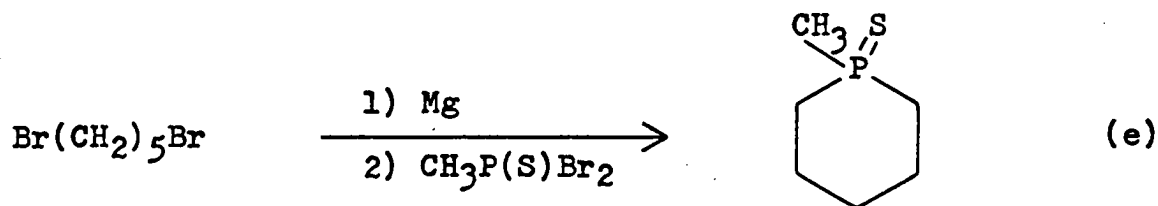
Recently, Angstadt reported the alkylation of elemental phosphorus (35). The reactions were carried out in carbon disulfide using an alkyl halide, white phosphorus, and aluminum trichloride in a hydrogen chloride atmosphere. Generally, dialkyl derivatives were obtained. According to a recent review concerning the alkylation of elemental phosphorus (36), reactions are generally performed in sealed tubes or autoclaves at elevated temperatures. It was concluded that the reaction proceeds by a radical process, and copper metal was sometimes used as a catalyst. Usually, mono- and dialkylchlorophosphines resulted rather than trialkylphosphines, the latter being apparently less stable at elevated temperatures.

In deciding upon a synthetic route to the desired bicyclic phosphine (I-4), a major concern was the overall yield. If a significant study is to be made of the use of this phosphine as a ligand, substantial quantities must be

available. Thus, as a result of low yields, syntheses of the type described by Mann et al. (8, 21), wherein many steps are involved, were not initially considered.

Cooper has outlined the synthesis of $CH_3C(CH_2CO_2H)_3$ in reputable yields (14), and Lukes and Ferles have converted this acid to the tribromide in good yields (37). Using this as a starting material, its reactions with $NaPH_2$, magnesium followed by PCl_3, and elemental phosphorus were studied. In the synthesis of I-10, cyclization was accomplished at the bridgehead opposite the phosphine. A similar approach was also studied as a route to I-4 by attempting to cyclize $P(CH_2CH_2CN)_3$ (38).

In addition to the synthesis of the bicyclic phosphine I-4, a proton nuclear magnetic resonance (n.m.r.) study of polycyclic phosphorus compounds became of interest. In 1962, Verkade and King (39) reported the H^1 and P^{31} n.m.r. spectra of I-1, I-2 and their 1-oxo and 1-sulfo derivatives. For the compounds therein considered, there seemed to be a dihedral angle dependence of the POCH coupling constants analogous to that reported by Karplus for HCCH interactions (40). The B^{11}, F^{19}, H^1 and P^{31} n.m.r. spectra of Group III acid complexes of I-1 and I-2 were reported later by Verkade et al. and a long-range (four-bond) POCCH coupling of 2 cycles per second (c.p.s.) was reported for the 1-oxo derivative of I-1 (8).

A review of P^{31} n.m.r. in 1962 revealed no four-bond (PXXXH) coupling interactions and indicated that little work

had been done on P-H spin interactions in general (41).

Similarly, Groenweghe et al. later that year reported no long-
range coupling constants, but observed that two-bond (PXH)
and three-bond (PXXH) coupling constants seemed to be depen-
dent on the type of atom (X) separating the coupling nuclei
and the hybridization of phosphorus (42).

Long-range (four-bond) interactions have been noted in
unsaturated organophosphorus compounds. Cotton and Schunn
(43) reported a PC=CCH coupling constant of 2.0 c.p.s. in a
transition metal complex, and Singh et al. reported P=NCCH
couplings of 0.6 to 1.0 c.p.s. (44). More recently they used
this type of long-range interaction to verify structures (45).

Bene et al. in 1963 (46, 47) reported POCCH interactions
of 0.55 and 0.84 c.p.s. in $(C_2H_5O)_3P$ and $(C_2H_5O)_3PO$, respec-
tively. Later that year, Burgada et al. (48) reported simi-
lar long-range interactions in some t-butoxy phosphorus
compounds of approximately 0.5 c.p.s. Within the last year,
several articles have appeared reporting more four-bond P-H
coupling constants in saturated organophosphorus compounds.
Reddy and Schmutzler estimated a POCCH coupling of 0.5 c.p.s.
for a ternary alkoxy phosphorus fluoride and observed some
four-bond F-H coupling constants (49). Ramirez et al. found
similar values for some alkoxy phosphoranes $((RO)_3P(OR)_2)$
(50). Seyferth and Singh reported two PCCCH interactions of
0.76 and 0.50 c.p.s. for an alkyl aryl phosphonium salt and
a phosphine oxide respectively (51).

Because of the generally low values obtained for these long-range coupling constants and the similarity in the magnitudes of those reported, their sporatic appearance has been explained by changes in the hybridization about phosphorus giving rise to changes in the Fermi contact interaction (47, 51).

The comparatively large long-range four-bond coupling value of 2 c.p.s. obtained for the oxo derivative of I-1 (8) suggests that a second effect or mechanism is needed to explain this interaction. Meinwald and Lewis have proposed a spatial interaction to explain four-bond H-H coupling interactions in saturated rigid organic compounds (52). In a review of these H-H interactions (53), the majority of compounds showing four-bond H-H couplings possessed the "W" conformation, and thus could be explained by a spatial interaction between two carbon atoms (dashed line) as shown in the representation below. Similar coupling constants have been

$$
\begin{array}{ccc}
H & C & H \\
\backslash & \diagup\ \diagdown & \diagup \\
& C\text{-----}C &
\end{array}
$$
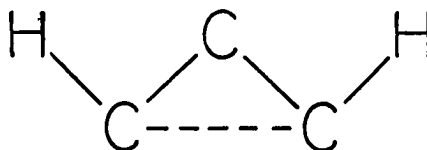
found recently in acyclic, bicyclic and steroid systems where the intermediate skeleton is in the "W" conformation (54, 55). Sternhell did point out in his review (53) that there were some four-bond couplings which could not be explained by this conformational arrangement. Ng and Sederholm

proposed similar "through-space" coupling to explain some F-F coupling constants (56), a proposition which has been questioned recently (57, 58).

Koide and Duval have presented a theory to account for the appearance of long-range coupling constants and the differences in signs which have occurred (59). One mechanism is a direct non-bonded orbital overlap between the two atoms undergoing coupling. The second is a "through-bond" mechanism involving (a) interaction of the proton nuclear spin with interatomic covalent bonds and (b) interatomic Hund couplings between spins of localized electrons. For an odd number of

$$|H\!\downarrow\!+\!C\!-\!\uparrow\!C\!+\!\downarrow\!H \qquad |H\!\downarrow\!\uparrow\!C\!\downarrow\!\uparrow\!C\!\downarrow\!\uparrow\!H$$

(a)   (b)

bonds, these latter two interactions tend to cancel, while for an even number of bonds they will reinforce one another.

No five-bond H-H coupling constants have been reported for saturated systems. Of those reported, the systems closest to saturation are those involving long-range coupling to a formyl proton. Kowalewski and Kowalewski found values of 0.45-0.60 c.p.s. for the coupling constant $J_{HC(O)OCCH}$ in alkyl formates (60). They mention that these interactions probably result from partial double bond character in the CO bond.

To better understand long-range H-P interactions (coupling through four bonds or more), it would be beneficial to review what is known about PXH and PXXH coupling constants. Most of the data presented in the literature can be understood by considering Bent's comments on the distribution of s-character in the bonds around a central atom (61), and by considering the Fermi contact interaction (62, 63) as the dominant coupling mechanism. In general, the s-character tends to concentrate in those bonds directed toward the less electronegative substituents which would consequently increase the p-character in the bonds to the more electronegative groups. For a ternary phosphorus compound, the lone pair is considered to be directed toward a substituent of zero electronegativity. Thus, the non-bonded electrons are considered to be mainly s in character. So in considering a series of compounds R_3PX, the PX bond will increase in p-character, thus leaving more s-character in the PR bonds as the X group becomes more electronegative. Such an increase in s-character would increase the P-H coupling constant between phosphorus and the protons in the alkyl chain R as a result of increasing the Fermi contact interaction.

In 1965, a proton n.m.r. study of adducts and phosphonium salts of I-1 and I-2 was presented in which a linear correlation was found between the proton chemical shifts and POCH coupling constants (23). The trends in chemical shifts were explained in terms of the electron withdrawing power of

of the substituent attached to the phosphorus, the more acidic substituents giving a greater downfield shift to the proton resonances. The linear increase in POCH coupling that accompanied the downfield shift of proton resonances was explained using the arguments outlined above. It is interesting that no relation was found between J_{POCH} and the substituent attached to phosphorus in open chain trialkyl phosphites and that there was little change in the coupling value in their adducts and phosphonium salts (23).

Hendrickson, et al. (64) reported a similar correlation for J_{PCH} and J_{PCCH} for some trialkyl phosphine derivatives where the coupling constants increased with the positive charge on phosphorus although there was no linear correlation. The charge on phosphorus was rationalized from the electronegativity or electron attracting power of the substituents attached to the trialkyl phosphines. Later, Griffin and Gordon reported there to be no dependence of J_{PCH} on the substituent attached to phosphorus for a series of phosphonium salts (65), but did find that J_{PCH} was solvent dependent. The solvent dependence, however, could not be correlated with any solvent properties (66).

Correlations for J_{PNCH} in some tris(dialkylamino) phosphine derivatives have been reported, and the results were analogous to the above two systems (67). However, it was pointed out that the PNCH coupling constant in the sulfide derivative was larger than that for the oxide. This reversal

between the oxide and sulfide was also found in the PCCH coupling constants reported by Hendrickson et al. (64).

A variety of correlations analogous to the three outlined above have been reported in the literature. In 1963, Flitcroft and Kaesz reported SnH and SnCH coupling constants for a series of alkyl substituted stannanes, and similar interactions for some analogous lead compounds (68). The results were explained in terms of the above arguments of Bent. Similar correlations were found by Patil and Graham for some alkyl tin compounds substituted with metal carbonyl anions (69). Massey et al. reported that both J_{PCH} and J_{PCCH} decrease in a series of phosphonium salts as methyl groups are replaced by ethyl groups (70), and they explained this trend using the concepts outlined by Bent. More recently, Burdett and Burger reported similar correlations using alkyl phosphonates $(RP(O)(OR)_2)$ (71).

Other data have appeared correlating J_{POCH} (72, 73), J_{SnH} (74), and J_{NCCH} (75) with the Taft polar substituent constant (sigma*) (76). In each of these series of compounds, the coupling constant increased as sigma* increased, that is, as the substituents increased in their electron attracting ability. These data were only for electron induction substituents (negative sigma*). Dudek reported that for electron withdrawing substituents (positive sigma*) J_{POCH} could not be correlated with the polar substituent constant (73).

David et al. have presented some J_{PCH} values for alkyl phosphonates (77), Seyferth and Singh have presented some for phosphonium salts (51), and Schmutzler and Reddy have presented J_{PCCH} data for some t-butyl phosphonate derivatives (78). Their results can be correlated with a few exceptions (77, 78) according to the concepts described above, although there were no comments concerning this in these articles.

Reddy and Schmutzler found correlations analogous to those above for alkoxy and amine substituted phosphorus(III) fluorides in which J_{PF} decreased as fluorine was replaced by a less electronegative group (49). Whitesides et al. published data on methyl substituted phosphines in which J_{PCH} decreased with increased alkylation, but contrary to the results obtained for J_{SnH}, J_{PH} increased with alkylation (79). Fluck and Issleib found a similar correlation for J_{PH} in some alkyl and aryl substituted phosphines (80).

In general, all of the data, except for directly bonded P-H coupling constants, can be correlated so that for a given geometry, oxidation state, and series of compounds, the heavy atom-hydrogen coupling constants increase as substituents of low sigma* (or low electronegativity) are replaced by substituents of high sigma* (or high electronegativity). These are the same results Juan and Gutowski obtained for J_{CH} (81), wherein they found that the s-character in the separate carbon hybrid orbitals could be determined by the electronegativity of the substituents provided that the total

s-character is conserved. This is to be contrasted with the correlations of Abraham and Pachler for HCCH coupling constants which decreased as the sum of electronegativities of substituents attached to the C-C fragment increased (82). Grant and Litchmann have also correlated J_{CH} with the effective nuclear charge of the R_3C moiety (83).

The above correlations would seem to imply that the coupling mechanism of primary importance is the Fermi contact interaction. This is generally accepted to be the important mechanism for proton-proton interactions (62, 63, 84, 85), electron-orbital and electron-dipole interactions being of relatively little importance (62, 63). Karplus considered only the Fermi term to explain F-F and H-F couplings (86), and Smith did likewise to explain Group IV atom-proton interactions (87, 88). Furthermore, Klose used only the Fermi term to describe the PCH and PCCH coupling constants in $(C_2H_5)_3P$ (89).

Whitesides et al. suggested that electron-orbital and electron-dipole interactions would be expected to be relatively more important in coupling to phosphorus due to greater anisotropy of screening around phosphorus (79). Previously, McConnell had stated that coupling between nuclei not directly bonded but which made use of both s and p orbitals in bonding will involve significant contributions from both electron-dipole and electron-orbital interactions with the nuclei (90). Recently, Pople and Santry found by a molecular

orbital calculation that J_{FF} in fluorine involves a large contribution from the electron-dipole interaction (91).

The purpose of the nuclear magnetic resonance study reported herein was to observe long-range coupling constants in some polycyclic compounds to determine what geometrical criteria were necessary for these interactions. It was also of interest to see if the hybridization considerations outlined above were applicable to long-range interactions or if this type of coupling was better explained by some sort of direct spatial interaction.

In addition to compounds I-1 and I-2, two bicyclic orthoformates reported in the literature were of interest. Stetter (92) reported the synthesis of the orthoformyl derivative of I-1 (CH in place of P), and Doering and Levy (93) reported the isolation of the orthoformyl derivative of I-2. Two trialcohols have been reported in the literature which were of interest in affording new bicyclic compounds for n.m.r. study. Breusch and Oguzer (94) reported the synthesis of $HC(CH_2OH)_3$, and Grayson (95) described the preparation of $P(CH_2OH)_3$. Cyclizations of trialcohols to orthoformate esters (93) or phosphite esters (23) have been described previously, and these procedures were carried out to form the bicyclic derivatives of the aforementioned trialcohols.

EXPERIMENTAL

All preparations were carried out under nitrogen flush
except for some of the organic intermediates (those for which
a nitrogen atmosphere was used are specified). For the inter-
mediate preparations, yields were based upon the major organic
precursor; for the polycyclic preparations, yields were based
upon the trialcohols or the precursory cyclic compound; and
for the complexes prepared, yields were based upon that
reactant in deficiency according to the molar ratios.

Materials

All solvents were reagent grade and those used in con-
nection with polycyclic compounds or complexes were dried
with Linde 4-A Molecular Sieve. Trimethylorthoformate,
trimethylorthoacetate, ethylacetoacetate, cyanoethylacetate,
and trimethyl phosphite were purchased from Eastman Organic
Chemicals; aluminum phosphide from Alfa Inorganics, Inc.;
2-hydroxymethyl-2-methyl-1,3-propanediol and acrylonitrile
from Matheson Coleman and Bell; triethylmethanetricarboxyl-
ate from Aldrich Chemical Company, Inc.; and nickel tetra-
carbonyl and iron pentacarbonyl from A. D. MacKay, Inc.
Tetrakis(hydroxymethyl)phosphonium chloride was generously
supplied by the Hooker Chemical Corporation, 1,3,5-trihydroxy-
cyclohexane by T. J. Huttemann (9), and tris(dimethylamino)
phosphine by G. Casedy (96).

Intermediates Prepared

Ethyl-4,6-dimethyl coumalate, $\overline{OC(O)CH=C(CH_3)C(CO_2C_2H_5)=CCH_3}$

.This compound was prepared from ethylacetoacetate following a method previously described (14, 97).

Diethyl-3-methyl glutaconate, $C_2H_5O_2CCH=C(CH_3)CH_2CO_2C_2H_5$

By modification of a procedure outlined by Bland and Thorpe (14, 98) this diester was obtained in 94% yield. A solution of 36.0 g. of sodium (1.57 moles) in 500 cc. of absolute ethanol was simultaneously combined with 153 g. of the above cyclic ester (0.78 moles) over a 30-minute period while stirring and cooling with cold water. The solution was stirred an additional 30 minutes and allowed to stand 2 hours at room temperature. Addition of 2-3 liters of water precipitated the liquid product which was separated and extracted with ether. Acidification of the aqueous phase resulted in an equal amount of oil which was similarly treated, and the two extracts were combined and dried with magnesium sulfate. After filtering and concentrating, the material isolated by vacuum distillation ($b_{0.2-0.5}=95-125^{\circ}$) proved to be a mixture of the cis and trans isomers (see discussion).

Diethyl-3-methyl-3-(cyanocarbethoxymethyl)-glutarate, $CH_3C(CH_2CO_2C_2H_5)_2CH(CN)CO_2C_2H_5$

This Michael addition product of sodium cyanoethylacetate and the preceding diester has been described elsewhere (14, 99).

If the cyanoethylacetate was not distilled prior to use,
low yields resulted.

4-Methyl-2,6-dioxo-4-piperidineacetic acid, CH₃C(CH₂CO₂H)(CH₂CO)₂NH

<u>4-Methyl-2,6-dioxo-4-piperidineacetic acid,</u>
$CH_3C(CH_2CO_2H)(CH_2CO)_2NH$
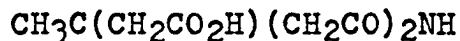
The preparation of this piperidine derivative by acid
hydrolysis of the previous Michael addition product has been
described previously (14, 99). This derivative was never puri-
fied, the crude material isolated being used directly in the
following procedure.

<u>3-Methyl-3-(carboxymethyl)-glutaric acid,</u> $CH_3C(CH_2CO_2H)_3$

This compound was isolated by base hydrolysis of the
preceding compound as described by Kohler and Reid (14, 99).

<u>Triethyl-3-methyl-3-(carboxymethyl)-glutarate,</u>
$CH_3C(CH_2CO_2C_2H_5)_3$
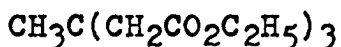
Following a method outlined by Lukes and Ferles (37),
133 g. of $CH_3C(CH_2CO_2H)_3$ (0.62 moles) was dissolved in a mix-
ture of 160 cc. of absolute ethanol, 200 cc. of benzene, and
one cc. of concentrated sulfuric acid. After azeotropically
removing the water, the solvents were removed by atmospheric
distillation and the residue extracted into ether. The
extract was filtered, washed with sodium bicarbonate solution
and dried with magnesium sulfate. Filtration of the solid
and removal of the solvent under reduced pressure followed by

vacuum distillation ($b_{0.1}$= 120°) gave 156.5 g. (87.5% yield) of the product.

3-Hydroxyethyl-3-methyl-1,5-pentanediol, $CH_3C(CH_2CH_2OH)_3$

This compound was obtained by reduction of the preceding triester (37). To 12 g. of lithium aluminum hydride (0.32 moles) dissolved in 400 cc. of ether was added dropwise under nitrogen flush 49 g. of the ester (0.17 moles) in 100 cc. of ether while cooling with ice and stirring. After stirring for 2 hours at room temperature, 200 cc. of water was added dropwise followed by dry ice until the aqueous layer froze. The ether phase was removed and discarded while the aqueous layer was filtered after melting and neutralized with concentrated sulfuric acid. After evaporating the water under vacuum, the residue was extracted into absolute ethanol. The extract was dried azeotropically with benzene and distilled, giving 17.5 g. ($b_{1.0}$=175-80°) of the product (64% yield).

3-Bromoethyl-3-methyl-1,5-dibromopentane, $CH_3C(CH_2CH_2Br)_3$

Using a procedure analogous to one reported by Lukes and Galik (100), 5.0 g. of the above trialcohol (31 mmoles) was dissolved in 50 cc. of a 27% glacial acetic acid solution of hydrogen bromide containing a crystal of cupric nitrate. This solution was placed in a 9-inch pyrex vacuum sealed tube (30 mm.) which was heated at 100° for 24 hours. After the tube was opened, the liquid product was precipitated by combining the contents with 200 cc. of water. The product was

then extracted into 200 cc. of chloroform after which the extract was neutralized by washing with a sodium bicarbonate solution and dried with magnesium sulfate. A vacuum distillation yielded 10.5 g. (97.2% yield) of the product ($b_{0.05}=127-32^{\circ}$).

3-Iodoethyl-3-methyl-1,5-diiodopentane, $CH_3C(CH_2CH_2I)_3$

Following a general procedure (93), 10.5 g. of the above tribromide (30.0 mmoles) and 20.0 g. of sodium iodide (133 mmoles) were placed in 100 cc. of butanone and the solution refluxed for 72 hours. After removing the solvent under vacuum, the product was precipitated with 100 cc. of water and extracted into benzene. The benzene extract was washed twice with a sodium thiosulfate solution and once with a sodium bicarbonate solution and then dried with magnesium sulfate. Concentrating and cooling the filtered solution gave 13.0 g. (88% yield) of the white crystalline product (m.p.=89-92°).

4-Hydroxyethyl-4-methyltetrahydropyran, $O(CH_2CH_2)_2C(CH_3)CH_2CH_2OH$
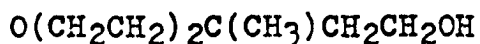
This material was isolated as a by-product by Lukes and Ferles in the reduction of $CH_3C(CH_2CO_2C_2H_5)_3$ (37). To obtain it in good yields, the following procedure was used. While flushing with nitrogen, a solution of 49 g. of the above mentioned ester (0.17 moles) in 100 cc. of ether was added dropwise to a solution of 20 g. of lithium aluminum hydride (0.53 moles) in 400 cc. of ether while stirring and cooling

with ice. This mixture was refluxed vigorously for 3 hours followed by decomposition with 50 cc. of water (2.8 moles), then with 103 g. of concentrated sulfuric acid (1.06 moles). After stirring for 2 hours, additional water was added and the solution was neutralized with sodium bicarbonate. The ether phase was discarded and the aqueous layer filtered and evaporated under vacuum, the residue being extracted into ethanol. The extract was dried azeotropically with benzene and distilled, giving 14.8 g. (60.5% yield) of the liquid product ($b_{0.1}$=88-90°).

4-Chloroethyl-4-methyltetrahydropyran, $O(CH_2CH_2)_2C(CH_3)CH_2CH_2Cl$
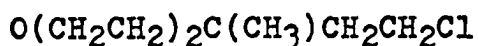
Sommer and Bennett reported the preparation of $O(CH_2CH_2)_2CHCH_2CH_2Cl$ (25). Following their procedure, 14 g. of $O(CH_2CH_2)_2C(CH_3)CH_2CH_2OH$ (0.10 moles) was dissolved in 8.7 g. of pyridine (0.11 moles), and 13 g. of thionyl chloride (0.11 moles) was added dropwise while stirring and flushing with nitrogen. The resulting mixture was heated at 80° for 20 hours, then cooled to room temperature and extracted with n-heptane. Distillation of the magnesium sulfate-dried extract gave 11.7 g. (72% yield) of the desired product ($b_{3.7}$=70-5°).

Sodium phosphide, $NaPH_2$

This material was prepared by a method previously described (14).

Tribenzyl phosphine, $(C_6H_5CH_2)_3P$

The preparation of this compound has been outlined by Hinton and Mann (18).

Tris(cyanoethyl) phosphine, $P(CH_2CH_2CN)_3$

This compound was obtained following a procedure outlined by Mathews (15).

Tris(carbethoxyethyl) phosphine, $P(CH_2CH_2CO_2C_2H_5)_3$

By a one step hydrolysis-esterification of $P(CH_2CH_2CN)_3$, this compound was isolated in a 47% yield following a procedure described by Rauhut (38).

2-Hydroxymethyl-1,3-propanediol, $HC(CH_2OH)_3$

This trialcohol was obtained by modification of a procedure previously reported (94). To 40 g. of lithium aluminum hydride (1.1 moles) in 300 cc. of diethyl ether was added dropwise 40 g. of triethylmethanetricarboxylate (170 mmoles) in 200 cc. of diethyl ether while cooling with ice. The resulting solution was refluxed under nitrogen while stirring for 72 hours, after which it was decomposed by dropwise addition of water, and partially neutralized by saturating with carbon dioxide. After siphoning off the ether phase, the bulky white precipitate was filtered and the filtrate neutralized with concentrated sulfuric acid. The water was then removed by vacuum distillation and the residue dried azeotropically with benzene. Distillation of the dried residue

extracted into ethanol yielded 2.5 g. (18% yield) of a low-melting solid ($b_{0.3}$=140-4°).

Tris(hydroxymethyl) phosphine, $P(CH_2OH)_3$

A procedure described previously (95) was followed which involved the use of tetrakis(hydroxymethyl)phosphonium chloride. This material was not characterized for each preparation and was used directly as outlined in the following section.

Polycyclic Compounds Prepared

2,8,9-Trioxaadamantane, $(CH_2)_3(CHO)_3CH$ (I)

The method used for preparing this orthoformate ester was previously described by Stetter (92).

2,8,9-Trioxa-1-phosphaadamantane, $(CH_2)_3(CHO)_3P$ (II)*

This tricyclic phosphite and its 1-oxo derivative (III) were prepared as described previously (23).

4-Methyl-2,6,7-trioxabicyclo[2.2.2]octane, $CH_3C(CH_2O)_3CH$ (IV)

This orthoformate ester was prepared according to a method originally described by Doering and Levy (93).

4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $CH_3C(CH_2O)_3P$ (V)*

The preparation of this bicyclic phosphite and its 1-oxo

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*These two compounds were formerly numbered I-1 and I-2. The numbers II and V will be used henceforth.

derivative (VI) have been described elsewhere (2, 23).

2,6,7-Trioxabicyclo[2.2.2]octane, $HC(CH_2O)_3CH$ (VII)

A mixture of 1.0 g. of 2-hydroxymethyl-1,3-propanediol (9.4 mmoles), 1.1 g. of trimethylorthoformate (10.0 mmoles), and two drops of triethylamine was refluxed for 3 hours, followed by removal of methanol by atmospheric distillation at 90° over a 20-hour period. Sublimation of the oily residue at room temperature and 0.01 mm. into a liquid nitrogen trap produced 0.06 g. (5.0% yield) of the orthoformate which collected at the top of the trap. This material was resublimed for purification.

2,6,7-Trioxa-1-phosphabicyclo[2.2.2]octane, $HC(CH_2O)_3P$ (VIII)

A mixture of 0.4 g. of 2-hydroxymethyl-1,3-propanediol (4 mmoles), 0.5 g. of trimethyl phosphite (4 mmoles), and two drops of triethylamine was refluxed at 100° for 30 minutes. After methyl alcohol was removed from the reaction mixture by atmospheric distillation, the residue was solidified by cooling to 0°. Sublimation of this mixture at room temperature and 0.01 mm. produced 0.25 g. (30% yield) of colorless crystals which were purified by resublimation.

1-Oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $HC(CH_2O)_3PO$ (IX)

A solution of 0.1 g. of the above phosphite VIII (0.8 mmoles) in 10 cc. of ethanol was oxidized by dropwise

addition of 0.1 g. of 30% hydrogen peroxide (0.9 mmoles of H_2O_2). Colorless crystals formed when this solution was cooled, and sublimation at $100°$ and 0.01 mm. gave 0.07 g. (70% yield) of the phosphate.

<u>1-Sulfo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $HC(CH_2O)_3PS$ (X)</u>

An intimate mixture of 0.10 g. of the phosphite ester VIII (0.7 mmoles) and 0.05 g. of sulfur (1.5 mmoles) was heated at $110°$ in a sealed tube for 30 minutes. The resulting solid was extracted into 30 cc. of acetone and the solution filtered and evaporated leaving a solid which, when sublimed at $100°$, produced 0.11 g. (95% yield) of white crystals.

<u>3,5,8-Trioxa-1-phosphabicyclo[2.2.2]octane, $P(CH_2O)_3CH$ (XI)</u>

To the trialcohol $P(CH_2OH)_3$ obtained from 9.0 g. of $ClP(CH_2OH)_4$ (47 mmoles) was added 5.0 g. of trimethylorthoformate (47 mmoles) and two drops of triethylamine. The procedure was the same as that used for VII giving 1.6 g. (25% yield) of the orthoformate ester.

<u>1-Oxo-3,5,8-trioxa-1-phosphabicyclo[2.2.2]octane, $OP(CH_2O)_3CH$ (XII)</u>

According to a general procedure reported by Baltz and Fischer (101), molecular oxygen was bubbled into a solution of 0.31 g. of the phosphine orthoformate XI, (2.1 mmoles) in 50 cc. of diethyl ether contained in a quartz tube while

irradiating with an ultraviolet light (Hanovia lamp No. 658A)
for 30 minutes. Evaporation of the ether gave a white solid
which sublimed at 50° and 0.01 mm. pressure, forming 0.03 g.
(10% yield) of colorless crystals. If the oxygen and diethyl
ether were dried, no phosphine oxide was isolated.

1-Sulfo-3,5,8-trioxa-1-phosphabicyclo[2.2.2]octane, SP(CH$_2$O)$_3$CH (XIII)

An intimate mixture of 0.35 g. of XI (2.6 mmoles) and
0.1 g. of sulfur (3.1 mmoles) was heated at 110° for 1 hour
in a sealed tube. The contents of the tube were then extracted
with acetone and the solution filtered and evaporated giving a
white solid. Sublimation of this residue under vacuum at room
temperature gave 0.1 g. of XI. Continued sublimation of the
remaining residue at 40° produced 0.12 g. (28% yield) of the
white product which was resublimed for purification.

4-Methyl-3,5,8-trioxa-1-phosphabicyclo[2.2.2]octane, P(CH$_2$O)$_3$CCH$_3$ (XIV)

The _tris_(hydroxymethyl) phosphine obtained from 22.0 g.
of ClP(CH$_2$OH)$_4$ (115 mmoles) was combined with 13.8 g. of
trimethylorthoacetate (115 mmoles) and a few drops of tri-
ethylamine. This mixture was heated at 80-100°, thus removing
the methanol formed while flushing with nitrogen. Upon cool-
ing, the oily residue solidified, and the product was sublimed
giving 17.0 g. (67.5% yield) of clear crystals which were
purified by resublimation.

4-Methyl-1-oxo-3,5,8-trioxa-1-phosphabicyclo[2.2.2]octane, OP(CH₂O)₃CCH₃ (XV)

$\text{4-Methyl-1-oxo-3,5,8-trioxa-1-phosphabicyclo[2.2.2]octane,}$ $\text{OP(CH}_2\text{O)}_3\text{CCH}_3 \text{ (XV)}$

To 1.0 g. of the above phosphine XIV (6.7 mmoles) dis-
solved in 10 cc. of absolute ethanol and protected from water
with Molecular Sieve was added 0.8 g. of 30% hydrogen peroxide
solution (6.7 mmoles of H_2O_2). After standing 15 minutes, the
reaction mixture was filtered and concentrated to 5 cc. under
vacuum. Cooling this solution at 0° for several hours gave
0.2 g. of colorless crystals representing a 20% yield.

4-Methyl-1-sulfo-3,5,8-trioxa-1-phosphabicyclo[2.2.2]octane, SP(CH₂O)₃CCH₃ (XVI)

$\text{4-Methyl-1-sulfo-3,5,8-trioxa-1-phosphabicyclo[2.2.2]octane,}$ $\text{SP(CH}_2\text{O)}_3\text{CCH}_3 \text{ (XVI)}$

An intimate mixture of 1.0 g. of XIV (6.7 mmoles) and
0.2 g. of sulfur (6.7 mmoles) was heated in a sealed tube at
110° for 1 hour. The contents of the tube were extracted
with acetone which upon concentration and the addition of
methanol gave a white solid. Sublimation of this solid under
vacuum at 60° gave 0.4 g. (33% yield) of clear colorless
crystals.

Complexes Prepared

Bis-(XIV)-dicarbonylnickel(0)

To 3.2 cc. of Ni(CO)₄ (24 mmoles) dissolved in 20 cc. of
chloroform was added 2.5 g. of XIV (17 mmoles) dissolved in
5 cc. of chloroform. After stirring the mildly exothermic
reaction for 2 hours at room temperature, the solution was

filtered and evaporated under vacuum giving a light brown solid. Recrystallization from pentane gave 2.5 g. (73% yield) of white crystals.

Tris-(XIV)-carbonylnickel(O)

1.0 g. of $Ni(CO)_2(XIV)_2$ (2.4 mmoles) and 0.36 g. of XIV (2.4 mmoles) were combined in 20 cc. of ethylbenzene and the mixture was refluxed for 3 hours. The resulting solution was filtered, concentrated to half of its original volume and cooled giving 1.0 g. (79% yield) of the white crystalline product which was filtered and washed with pentane.

Tetrakis-(XIV)-nickel(O)

A solution of 0.45 g. of $Ni(CO)_2(XIV)_2$ (1.1 mmoles) and 0.40 g. of XIV (2.5 mmoles) in 20 cc. of ethylbenzene was refluxed for 3 hours. Filtration of this solution, concentration to half-volume and cooling deposited the impure product which was recrystallized from a benzene-pentane mixture giving 0.4 g. (56% yield) of white crystals.

Mono-(XIV)-tetracarbonyliron(O)

A mixture of 2.0 g. of XIV (14 mmoles) and 1.8 cc. of $Fe(CO)_5$ (14 mmoles) was combined in 25 cc. of ethylbenzene. The resulting solution was placed in a quartz tube (11) and irradiated with an ultraviolet light (Hanovia lamp No. 658A) for 2 hours. The decomposition products were filtered and the solution evaporated giving a light yellow solid. Upon

recrystallization from pentane, 0.8 g. (20% yield) of yellow-white crystals was found.

Bis-(XIV)-tricarbonyliron(0)

A 25 cc. ethylbenzene solution of 1.7 g. of XIV (12 mmoles) and 0.8 cc. of $Fe(CO)_5$ (5.7 mmoles) was irradiated as in the preceding preparation for 5 hours. The resulting solution was cooled and filtered giving a brown solid which was extracted into dichloromethane. Concentration and cooling of this solution gave 0.8 g. (32% yield) of light yellow crystals.

Attempted Preparations

5-Methyl-2,8,9-trioxa-1-phosphabicyclo[3.3.3]undecane, $CH_3C(CH_2CH_2O)_3P$

Three procedures have been outlined for the preparation of $CH_3C(CH_2O)_3P$. Following one (8), $CH_3C(CH_2CH_2OH)_3$ and trimethyl phosphite were refluxed, followed by removal of methanol and unreacted trimethyl phosphite under vacuum. Only an insoluble, involatile oil resulted.

Following the second (2), the above trialcohol and phosphorus trichloride were combined in pyridine and tetrahydrofuran. Filtration and evaporation again left only an insoluble, involatile oil.

As described in the third procedure (96), the trialcohol and tris(dimethylamino) phosphine were combined neat and

heated at 100°. After evolution of dimethylamine ceased, an intractable oil was left.

5-Aza-2,8,9-trioxa-1-phosphabicyclo[3.3.3]undecane, N(CH₂CH₂O)₃P
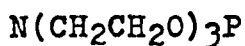
Using vacuum-distilled triethanolamine which had been stored over Molecular Sieve, the reactions outlined for the previous compound were attempted. From these reactions, an uncharacterizable semisolid resulted. On one occasion a trace of volatile solid was obtained which could not be reproduced in subsequent attempts.

4,6-Dioxo-1-phosphabicyclo[3.3.1]nonane, CH₂P(CH₂CH₂CO)₂CH
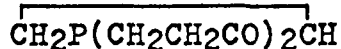
Mathews reported the synthesis of $C_2H_5P(CH_2CH_2)_2CO$ (15). Using an analogous procedure, tris(cyanoethyl) phosphine was added dropwise to a t-butanol solution of potassium t-butoxide. This solution was refluxed several hours, followed by decomposition with acetic acid. Hydrolysis with hydrochloric acid and evaporation of this acid solution left only a viscous water-soluble oil containing no volatile material. Whether this was starting material, polymer, or a monocyclic derivative was not ascertained.

In another attempted preparation, $P(CH_2CH_2CO_2C_2H_5)_3$ was added to an ethanol solution of sodium ethoxide giving a white precipitate. After refluxing for several hours, the

solution was neutralized, filtered and evaporated giving the starting material.

4-Methyl-1-phosphabicyclo[2.2.2]octane, $CH_3C(CH_2CH_2)_3P$

Six different methods were used in attempting to prepare this compound.

First, equimolar quantities of sodium phosphide and $CH_3C(CH_2CH_2Br)_3$ dissolved in xylene were combined. After refluxing this heterogeneous reaction mixture for several hours, the solution was filtered and evaporated giving only the starting material.

In the second attempt, the above two reactants in the same molar ratio were combined with two equivalents of pyridine and heated at 100° in a sealed tube for several hours. An insoluble, involatile solid resulted.

Third, the above tribromide was combined with excess magnesium in dry ether. A drop of methyl iodide and a strip of magnesium were combined in ether, and when a reaction commenced, the mixture was added to the above solution as an initiator. After 24 hours of refluxing, the magnesium and the tribromide were recovered. The use of $CH_3C(CH_2CH_2I)_3$ gave similar results.

Following a procedure outlined by Hinton and Mann (18) in the fourth attempt, an equivalent of tribenzyl phosphine dissolved in ether was added to an ether solution of one equivalent each of $CH_3C(CH_2CH_2Br)_3$ and lithium aluminum

hydride, and the resulting solution was refluxed for several hours. Water was added to decompose the mixture and the ether phase was separated, dried with magnesium sulfate and evaporated giving an intractable oil.

Fifth, several attempts were made to prepare the bicyclic phosphine using the tribromide and red or white phosphorus in 1:2 molar ratios. The two were combined in either a static or dynamic vacuum and heated at 100° for several hours. No volatile materials resulted and only an intractable water soluble solid was isolated. When the triiodide was used, some volatile PH_4I was obtained.

Sixth, in an attempt to isolate $O(CH_2CH_2)_2C(CH_3)CH_2$-CH_2MgCl, a precursor to the desired bicyclic phosphine, $O(CH_2CH_2)_2C(CH_3)CH_2CH_2Cl$ was combined with one equivalent of magnesium in dry ether. After initiating the reaction with methyl iodide, the mixture was refluxed for 24 hours. Only magnesium and the starting material were isolated.

Analyses of New Compounds

Carbon-hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Melting points were taken in capillaries and are uncorrected. Analytical data for the new compounds prepared are listed in Table 1.

Infrared Spectra

Infrared spectra in the sodium chloride region were obtained on carbon tetrachloride, chloroform or dichloromethane

solutions where possible. Spectra for III, VI, and IX were obtained on KBr pellets and those for X, XIII, and XVI on nujol mulls. The instrument used was a Perkin-Elmer model 21 double beam spectrometer. Far infrared spectra from 800 to 140 cm^{-1} were obtained on nujol mulls using a Beckman IR-11 grating spectrometer. The far infrared spectrum of the ligand XIV was obtained on a cesium iodide pellet.

Nuclear Magnetic Resonance Spectra

Proton n.m.r. spectra were obtained on 5 to 20% by weight solutions on a Varian Associates Model HR-60 spectrometer or a Model A-60 spectrometer operating at 14,100 gauss. Tetramethylsilane (TMS) was used as an internal standard throughout, and absorptions were measured in parts per million (p.p.m.) downfield from TMS.

Table 1. Analytical data for new compounds

Compound	% Carbon		% Hydrogen		Melting Point
	Calc.	Obs.	Calc.	Obs.	
$HC(CH_2O)_3CH$ (VII)	51.70	50.30	6.89	6.87	90-2
$HC(CH_2O)_3P$ (VIII)	35.79	35.98	5.23	5.40	126-7
$HC(CH_2O)_3PO$ (IX)	32.00	31.82	4.66	4.74	245-7
$HC(CH_2O)_3PS$ (X)	28.97	27.08	4.21	4.00	198-200
$P(CH_2O)_3CH$ (XI)	35.79	35.73	5.23	5.28	88-9
$OP(CH_2O)_3CH$ (XII)	32.00	32.94	4.66	5.12	152-5
$SP(CH_2O)_3CH$ (XIII)	28.97	28.99	4.21	4.23	127-30
$P(CH_2O)_3CCH_3$ (XIV)	40.54	40.27	6.08	5.90	80-2
$OP(CH_2O)_3CCH_3$ (XV)	36.59	35.35	5.49	5.34	175-9
$SP(CH_2O)_3CCH_3$ (XVI)	33.32	33.28	5.00	5.07	174-7
$Ni(CO)_2(XIV)_2$	35.06	35.32	4.38	4.42	114-16
$Ni(CO)(XIV)_3$	36.15	33.92	5.08	4.84	175[a]
$Ni(XIV)_4$	36.90	37.62	5.53	5.90	260[a]
$Fe(CO)_4(XIV)$	34.25	34.75	2.84	2.76	132-3
$Fe(CO)_3(XIV)_2$	35.82	36.12	4.04	4.28	160[b]

[a]Decomposition point.

[b]Decomposes slowly.

DISCUSSION

Intermediates

The intermediates were prepared following literature procedures and thus were characterized only by their melting points or boiling points and by their n.m.r. spectra.

In the preparation of $C_2H_5O_2CCH=C(CH_3)CH_2CO_2C_2H_5$, a boiling range of $30°$ was observed in the distillation of the product. The n.m.r. spectra for the first and last fractions of the distillation are shown in Figure 1. The $C\underline{H}_3CH_2-$ protons appear as a high-field triplet and the $CH_3C\underline{H}_2-$ protons as a low-field quartet while the methine $C\underline{H}$ appears as a broad peak at 5.7 p.p.m. It is apparent that the spectra are the same except for the relative intensities of the four peaks between 1.8 and 3.8 p.p.m. From the integration of the spectra the ratio of the two intensities at low field to the two at high field was 2:3 in keeping with the assignments of these pairs of peaks to methylene and methyl protons, respectively. A similar ratio was found between the peak at 3.1 and that at 2.2 p.p.m., and between the peak at 3.7 and that at 1.9 p.p.m. Although assignment of peaks to specific isomers cannot be made, the absorptions at 1.9 and 2.2 p.p.m. are assigned to the two different $C\underline{H}_3C=$ protons and those at 3.1 and 3.7 p.p.m. are assigned to the two different $CC\underline{H}_2C$ protons. It is postulated, therefore, that each sample consists of a mixture of cis and trans olefinic isomers in

Figure 1. The n.m.r. spectra of $C_2H_5O_2CCH_2C(CH_3)=CHCO_2C_2H_5$

in CCl_4 for different cis-trans mixtures

CH₃ CH₂CH₃

CH₂CH₃

CH₂

CH

PPM (δ)

CH₂CH₃

CH₃

CH₂CH₃

CH₂

CH

PPM (δ)
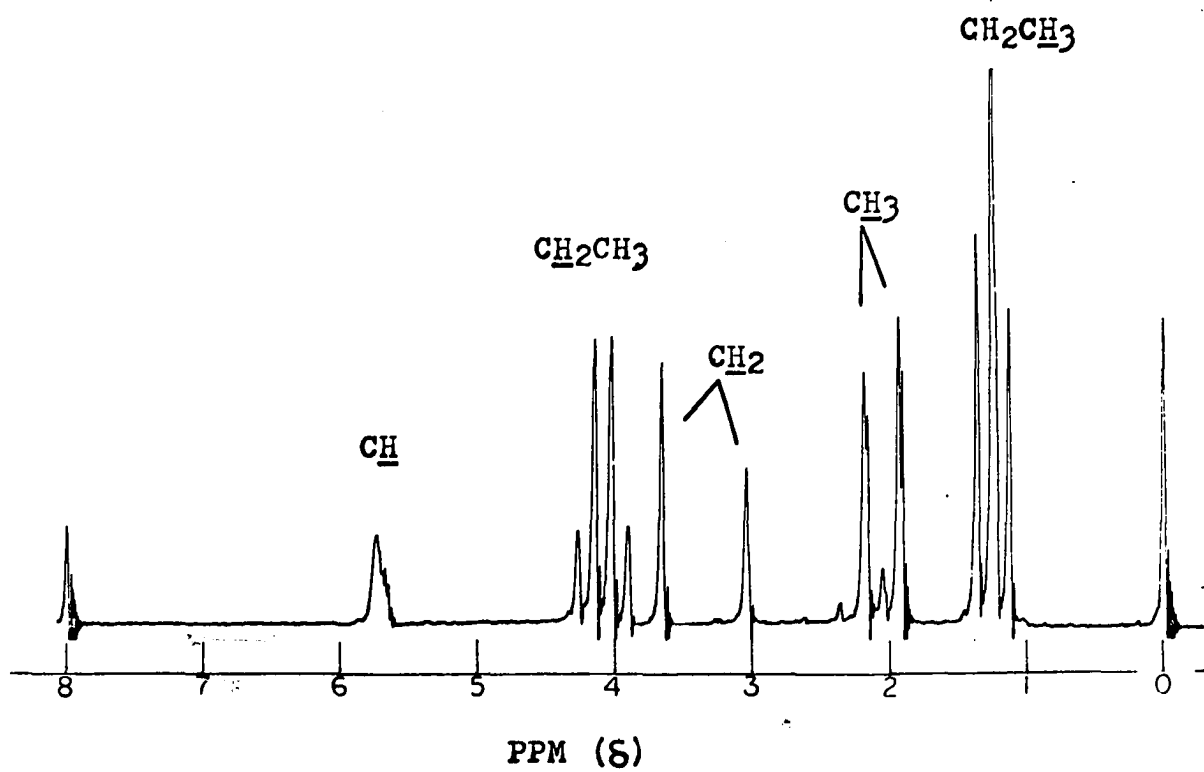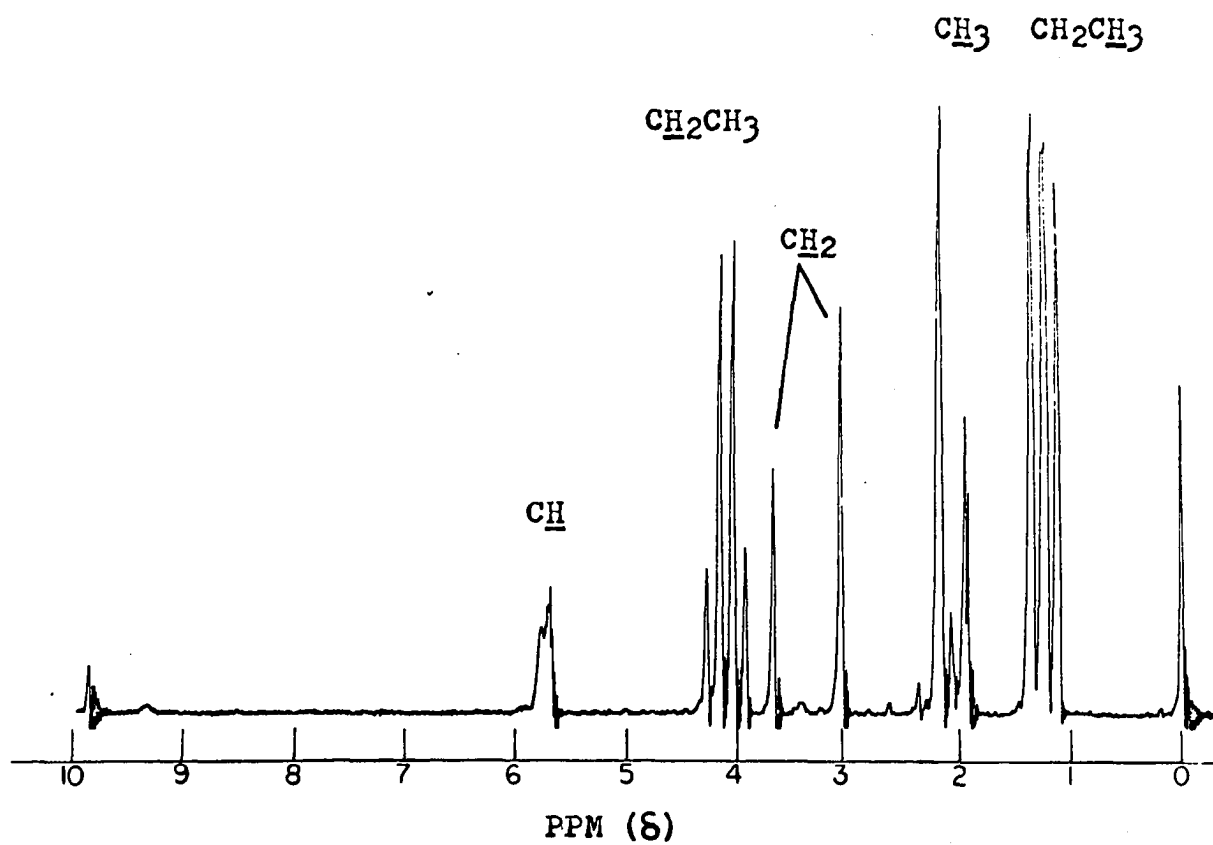
different ratios. Such a _cis_-_trans_ mixture could explain the wide boiling range and the appearance of additional peaks in the n.m.r. spectra as well as the varying intensities of the four absorptions in the distillation fractions. This type of isomerization was not reported in the original preparation in which a constant boiling material was obtained in 75% yield (98). The isomerization reported here is perhaps due to the somewhat different procedure used affording the better overall yield (94%).

In the preparation of the tribromide $CH_3C(CH_2CH_2Br)_3$ it was accidently found* that with a trace of copper in the glacial acetic acid, the yield increased from 75 to 97%. Because of the small amount present, the copper may complex the intermediate organic acetate and facilitate its removal on replacement by bromide ion. The point of equilibrium in the reaction may therefore be shifted toward a higher concentration of bromide-containing product.

Most of the n.m.r. spectra obtained for the intermediates were easily interpretable. However, A_2B_2 patterns were obtained for the methylene protons in $CH_3C(CH_2CH_2X)_3$ where X is Br or Cl. In the cyclic compounds $XCH_2CH_2C(CH_3)(CH_2CH_2)_2O$ where X is OH or Cl, the methylene portions of the spectra
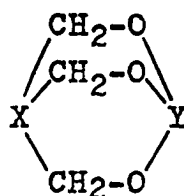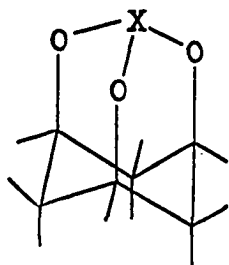
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*This discovery was made by A. C. Vandenbroucke, Jr., Ph.D. candidate, Department of Chemistry, Iowa State University, Ames, Iowa.

were complex because of the overlapping of an A_2B_2 pattern ($XC\underline{H}_2C\underline{H}_2C$) with an $A_2A'_2B_2B'_2$ pattern ($C(C\underline{H}_2C\underline{H}_2)_2O$). The integration of the total $C\underline{H}_2$ to $C\underline{H}_3$ intensities was 6:2 in each spectrum. Otherwise, these spectra were not analyzed.

An unanalyzed A_2B_2X spectrum was obtained for $P(CH_2CH_2CN)_3$. The low-field multiplet of peaks (due to $C\underline{H}_2CN$) had a greater width than the high-field multiplet indicating a larger amount of coupling to the $C\underline{H}_2CN$ protons. This implies that J_{PCCH} is larger than J_{PCH}. For most phosphines studied, PCH coupling constants have been found to be less than PCCH couplings (64). This is generally rationalized in terms of two canceling coupling mechanisms for PCH interactions, one of which is inapplicable to PCCH couplings (89). It is interesting, however, that from the spectrum of $P(CH_2CH_2CO_2C_2H_5)_3$, J_{PCH} and J_{PCCH} appear to be equal. That is, this unanalyzed A_2B_2X spectrum contained a mirror line of symmetry between the absorptions implying equal P^{31} coupling to both $PC\underline{H}_2$ and $C\underline{H}_2CN$ protons. This equality is puzzling in view of previous results for P-H coupling constants (64), but may be a result of CPC angle changes from $P(CH_2CH_2CN)_3$ to $P(CH_2CH_2CO_2C_2H_5)_3$ (see discussion of H-P coupling constants, specifically that in connection with XI).

Polycyclic Compounds

The polycyclic compounds prepared are shown in Figure 2. The structures given are in keeping with their melting points,

	X
I	CH
II	P
III	P=O

	X	Y
IV	H3CC	CH
V	H3CC	P
VI	H3CC	P=O
VII	HC	CH
VIII	HC	P
IX	HC	P=O
X	HC	P=S
XI	P	CH
XII	O=P	CH
XIII	S=P	CH
XIV	P	CCH3
XV	O=P	CCH3
XVI	S=P	CCH3

Figure 2. Polycyclic compounds prepared

volatility, and analyses, as well as their infrared and n.m.r. spectra.

From the melting point data presented in Table 1, it is evident that the thermal stability of the crystal increases from the free ligands VIII, XI, and XIV to the sulfide X, XIII, and XVI to the oxide IX, XII, and XV derivatives, respectively. The effect of substituting a methyl group for a proton in comparing compounds XI and XIV, XII and XV, and XIII and XVI is not reflected consistently in the melting points. However, the added stability of methyl-substituted compounds V and XIV over VIII and XI to attack by nucleophilic agents may be reflected in the yields reported for their preparation. For the phosphite esters V and VIII, the yields were 85 (23) and 30%, respectively, and for the phosphines XI and XIV, the yields were 25 and 67.5%, respectively. The attack of nucleophiles such as methanol or the appropriate trialchohol on the bicyclic compounds would reverse the equilibrium of the reaction to give starting materials or could perhaps give rise to polymerization. In the methyl substituted compounds V and XIV, the methyl group would sterically inhibit such an attack on the methylene carbon.

The analyses obtained for the polycyclic compounds shown in Table 1 are in agreement with the calculated values. Those obtained for VII and X differ from the calculated values by 1 and 2% for carbon, respectively. Doering and Levy reported that IV was very susceptible to hydrolysis (93) and considering

this possibility, the low carbon analysis obtained for VII can be explained. The purification of X consisted of sublimation at 100° at which temperature unreacted sulfur could have sublimed thus contaminating the product and causing the low carbon and hydrogen analyses.

Some infrared stretching frequencies obtained for the polycyclic compounds are shown in Table 2. In addition to those absorptions listed in the table, each of the spectra (except for that of VIII) possessed a medium absorption around 1180-1210 cm^{-1}. Because of its frequent appearance, this absorption may correspond to a molecular mode characteristic of polycyclic compounds.

The absorptions listed between 900 and 1200 cm^{-1} may correspond to C-O or P-O stretching modes or to POC or COC bending modes (102, 103). For the orthoformate and orthoacetate derivatives I, IV, VII, and XI through XVI, there are two sets of three identical C-O bonds; three involving the bridgehead carbon and three involving the methylene carbons. Each set possesses C_{3v} symmetry and from a group theoretical treatment, two C-O stretching frequencies would be expected for each set giving a total of four (104). For the compounds I, IV, VII, and XIII, more than four absorptions are obtained, four of which may be due to C-O stretching modes and the others to COC bending modes. Contrary to expectation, spectra of compounds XI, XII, and XIV-XVI show no more than three absorptions in spite of the fact that all these compounds are

Table 2. Some infrared stretching frequencies for polycyclic compounds in cm^{-1}

Compound	Phase	C-O Region 900-1200 cm^{-1}		P=O	P=S	P-C
$(CH_2)_3(CHO)_3CH$ (I)	CCl$_4$	1170(s)[a], 1135(s), 1055(s) 978(s), 923(s)				
$(CH_2)_3(CHO)_3P$ (II)	CHCl$_3$	1107(s), 1050(w)[b], 935(s) 917(s), 902(s)				
$(CH_2)_3(CHO)_3PO$ (III)	KBr	1100(s), 1085(s), 1057(m)[c] 1037(m)		1295(s)		
$(CH_2)_3(CHO)_3PS$[d]	nujol	1098(s), 1085(s), 1056(m) 1037(m), 935(s), 917(m)			777(s)	
$CH_3C(CH_2O)_3CH$ (IV)	CCl$_4$	1060(s), 1046(s), 990(s) 945(s), 910(s)				
$CH_3C(CH_2O)_3P$ (V)	CHCl$_3$	1035(s), 955(m), 923(m)				
$CH_3C(CH_2O)_3PO$ (VI)	KBr	1040(sh)[e], 1014(s), 955(s) 930(m)		1295(s)		

[a] Strong.

[b] Weak.

[c] Medium.

[d] Preparation described by Stetter (1).

[e] Shoulder.

Table 2. (Continued)

Compound	Phase	C-O Region 900-1200 cm^{-1}	P=O	P=S	P-C
CH$_3$C(CH$_2$O)$_3$PS[f]	nujol	1040(s), 995(s), 940(s)		825(s)	
HC(CH$_2$O)$_3$CH (VII)	CCl$_4$	1162(s), 1114(m), 1085(m) 982(s), 970(s), 885(s)			
HC(CH$_2$O)$_3$P (VIII)	CHCl$_3$	1107(m), 1070(s), 1040(sh) 900(s)			
HC(CH$_2$O)$_3$PO (IX)	KBr	1103(m), 1063(s), 964(m) 940(s), 930(s)	1307(s)		
HC(CH$_2$O)$_3$PS (X)	nujol	1055(sb)[g], 910(sb)		808(s)	
P(CH$_2$O)$_3$CH (XI)	CCl$_4$	1142(s), 1007(s), 926(s)			
OP(CH$_2$O)$_3$CH (XII)	CHCl$_3$	1132(s), 1030(sb)	1208(s)		
SP(CH$_2$O)$_3$CH (XIII)	nujol	1128(s), 1020(s), 1010(s) 913(s), 889(s)		742(s)	
P(CH$_2$O)$_3$CCH$_3$ (XIV)	CCl$_4$	1120(s), 1055(s), 1004(s)			763(m), 696(m)[h]
OP(CH$_2$O)$_3$CCH$_3$ (XV)	CHCl$_3$	1119(s), 1032(s), 1016(s)	1200(s)		798(m), 698(m)[h]
SP(CH$_2$O)$_3$CCH$_3$ (XVI)	nujol	1118(s), 1032(s), 1007(s)		744(m)	779(m), 689(m)

[f] Preparation described by Verkade and Reynolds (2).

[g] Strong-broad.

[h] Obtained on nujol mulls.

also orthoformate or orthoacetate esters. No ready explanation for these absences is apparent.

For the phosphites, phosphates, and thiophosphates II, III, V, VI, VIII, IX, X, and the thiophosphates of esters II and V, two C-O stretching modes would be expected as well as P-O stretching and POC bending vibrations. Although POC bending absorptions have been assigned for II and III at 1040 and 1037 cm^{-1}, respectively (9), and for other phosphorus compounds in the range of 1030 to 1090 cm^{-1} (103), there is no consistent absorption listed in Table 2 which can be assigned to the POC bending mode.

The P=O and P=S stretching absorptions were easily assigned by comparison of spectra obtained for the phosphates and thiophosphates with those of the parent phosphites and by a similar comparison of spectra of the phosphine derivatives. The P=O and P=S stretching frequencies for the phosphine derivatives XII, XIII, XV, and XVI are approximately 100 cm^{-1} lower in frequency than the absorptions for the phosphite derivatives III, VI, IX, X, and the 1-sulfo derivatives of II and V. This is in agreement with the observation by Zingaro that the P=S frequency increases as more electronegative substituents are placed on the phosphorus in a series of phosphine sulfide derivatives (105). Thus, oxygen being more electronegative than carbon, P=S and P=O stretching frequencies for the phosphite derivatives should appear at higher frequencies than those for phosphine derivatives.

The reason for the variation in the P=S absorptions obtained for X and the l-sulfo derivatives of II and V compared to the relatively constant values of the P=O absorptions obtained for III, VI, and IX is not known.

P-C stretching frequencies are tentatively assigned in spectra of XIV, XV, and XVI. A group theoretical treatment implies that two stretching modes should be present in these molecules (104) and the assigned absorptions are found at the appropriate frequencies (103). Furthermore, that the higher frequency is more sensitive to oxidation and sulfuration of the phosphorus than the lower one is consistent with the P-C stretching frequencies reported by Daasch and Smith (103) for trialkyl phosphines.

The n.m.r. spectra obtained for the polycyclic compounds are shown in Figures 3, 4, 5, 6, 7, and 8. Also shown on these spectra are expansions of certain absorptions and the results of some decoupling experiments. The spectra for compounds I, II, III, V, and VI have been presented elsewhere (8, 23, 39).

Spectra obtained for the series of compounds VII, VIII, IX, and X are shown in Figures 3, 4, and 5. In each case, the methine ($\underline{H}C(C-)_3$) resonance appears as a doublet of septuplets due to coupling with six equivalent methylene protons and phosphorus for VIII, IX and X. Similarly, a doublet of septuplets is observed for the methine resonance due to coupling with six equivalent methylene protons and the

Figure 3.   The n.m.r. spectra of HC(CH$_2$O)$_3$CH (VII) and
            HC(CH$_2$O)$_3$P (VIII)

$HC(CH_2O)_3CH$ (VII) In CCl_4

Top spectrum labels: CH_2; Irradiate CH_2 Scan $HC(C-)_3$; Irradiate $HC(O-)_3$ Scan $HC(C-)_3$; $HC(O-)_3$; $HC(C-)_3$

PPM (δ)

$HC(CH_2O)_3P$ (VIII) In CCl_4

Bottom spectrum labels: Scan CH_2; CH_2; Scan CH; Irradiate CH_2 Scan CH; CH

PPM (δ)
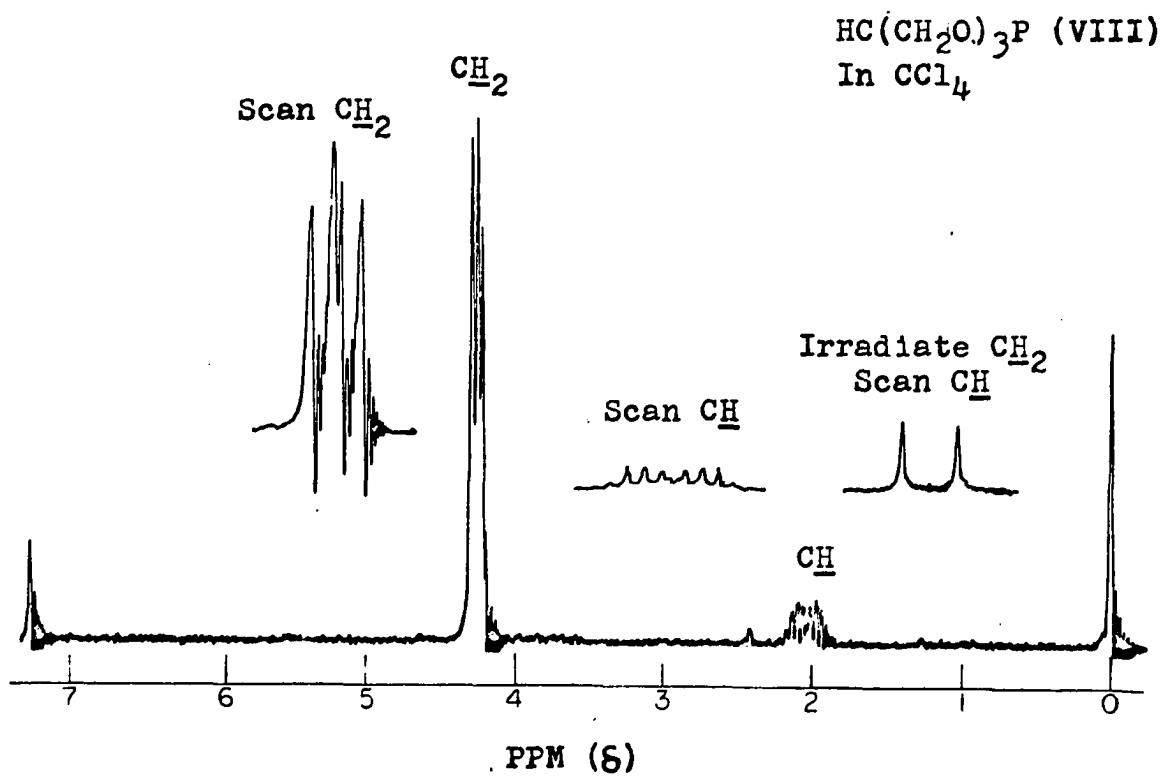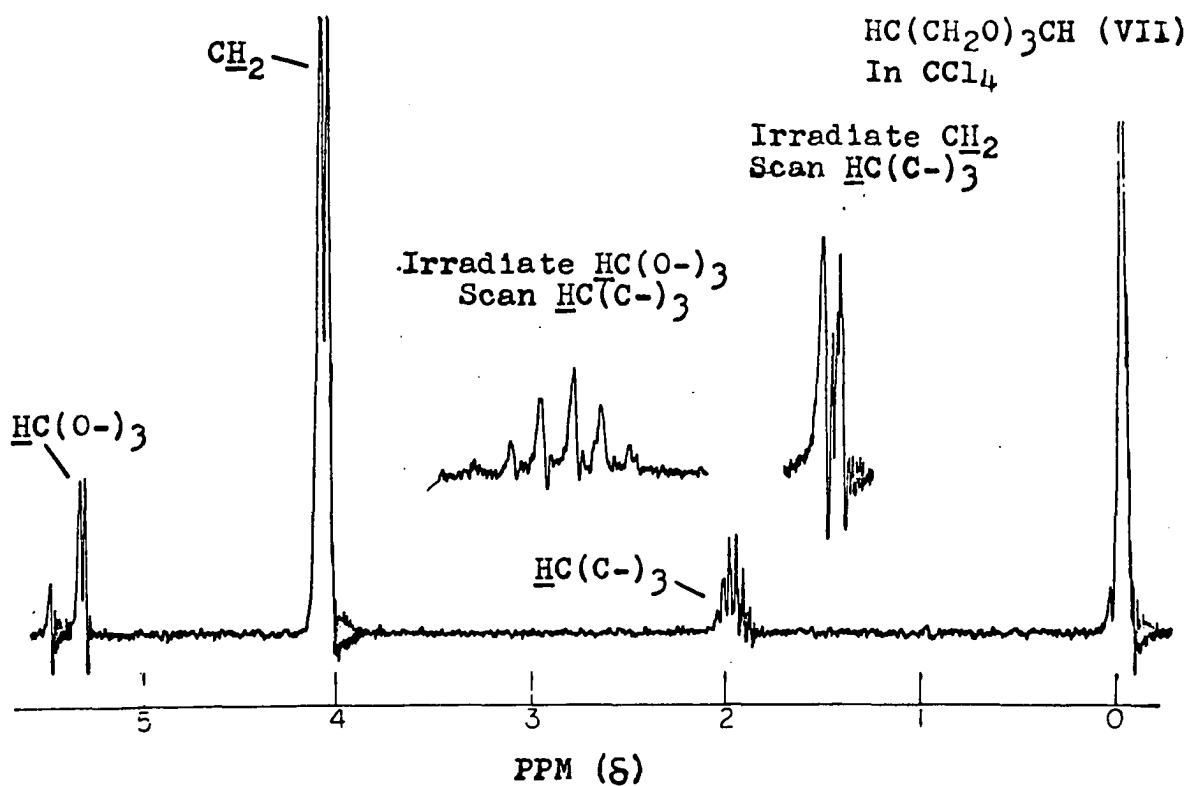
Figure 4.   The n.m.r. spectrum of HC(CH$_2$O)$_3$PO (IX)

HC(CH$_2$O)$_3$PO (IX)
In (CD$_3$)$_2$SO
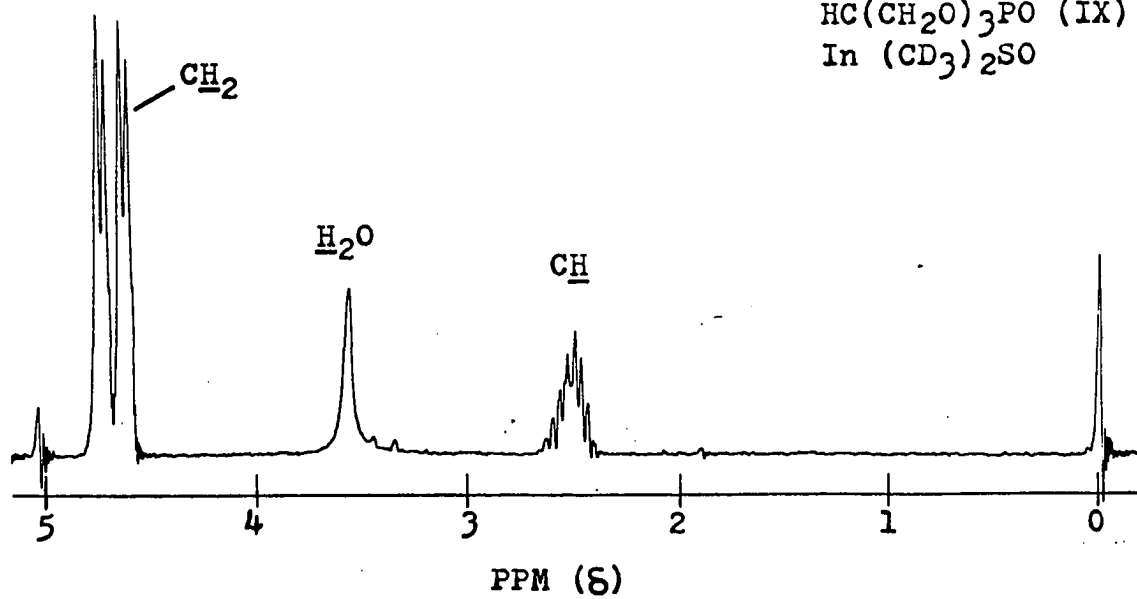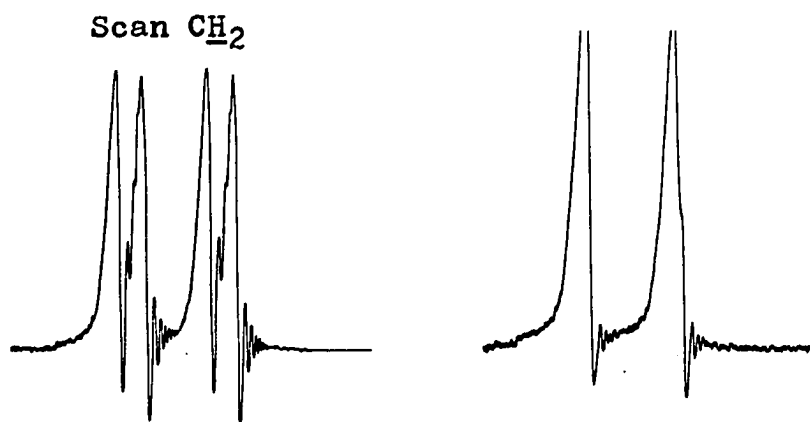
Figure 5. The n.m.r. spectra of $HC(CH_2O)_3PS$ (X) and
$SP(CH_2O)_3CH$ (XIII)

Scan CH₂ — impurity — CH₂ — Scan CH — CH — HC(CH₂O)₃PS (X) In C₅H₅N

CH₂ — HC(CH₂O)₃PS (X) In (CH₃)₂SO

Scan CH — CH₂ — CH — SP(CH₂O)₃CH (XIII) In CDCl₃ — Scan CH₂
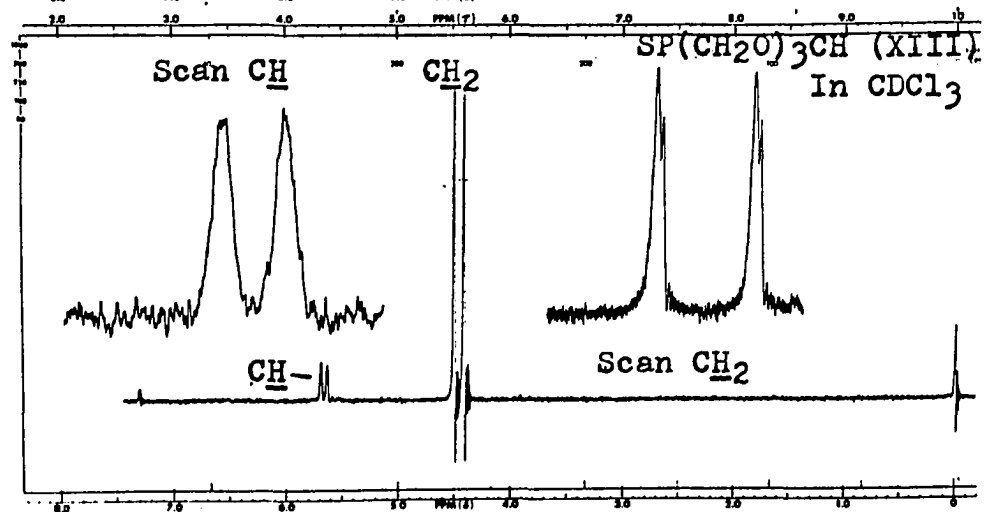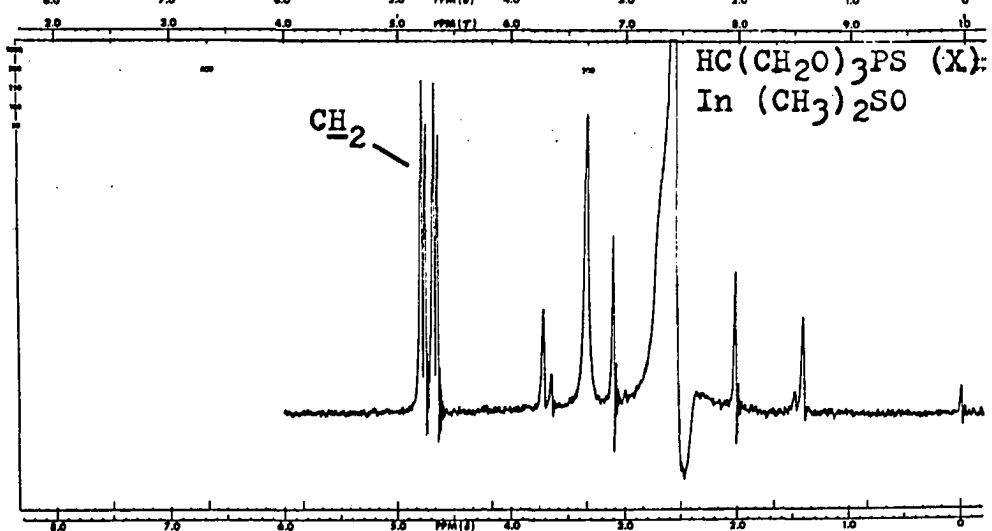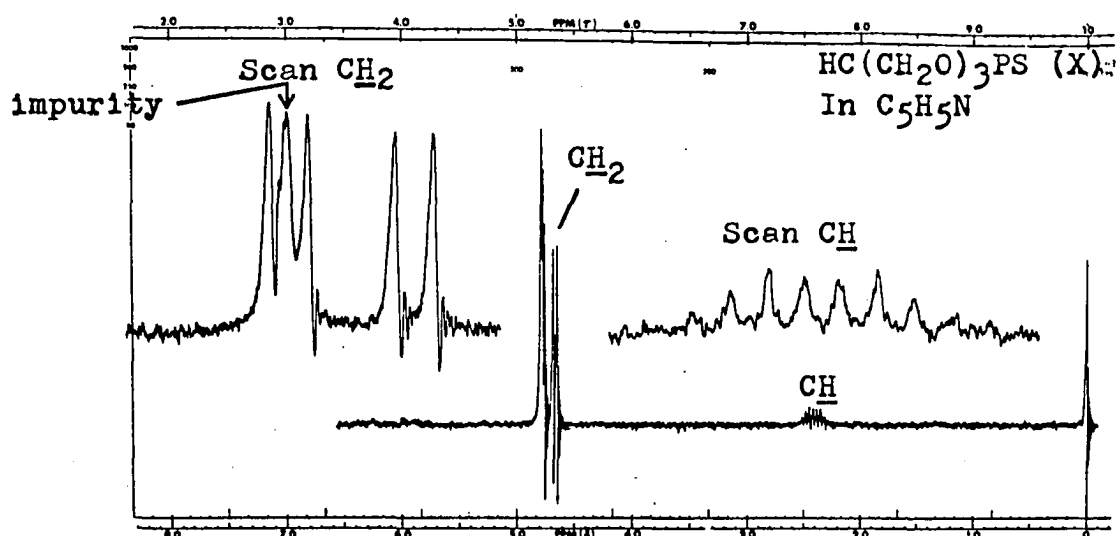
Figure 6. The n.m.r. spectra of $P(CH_2O)_3CH$ (XI) and $OP(CH_2O)_3CH$ (XII)

Scan CH

Irradiate CH₂
Scan CH

CH

$P(CH_2O)_3CH$ (XI)
In CCl_4

CH₂

PPM (δ)

$OP(CH_2O)_3CH$ (XII)
In $CDCl_3$

CH₂

CH

PPM (δ)
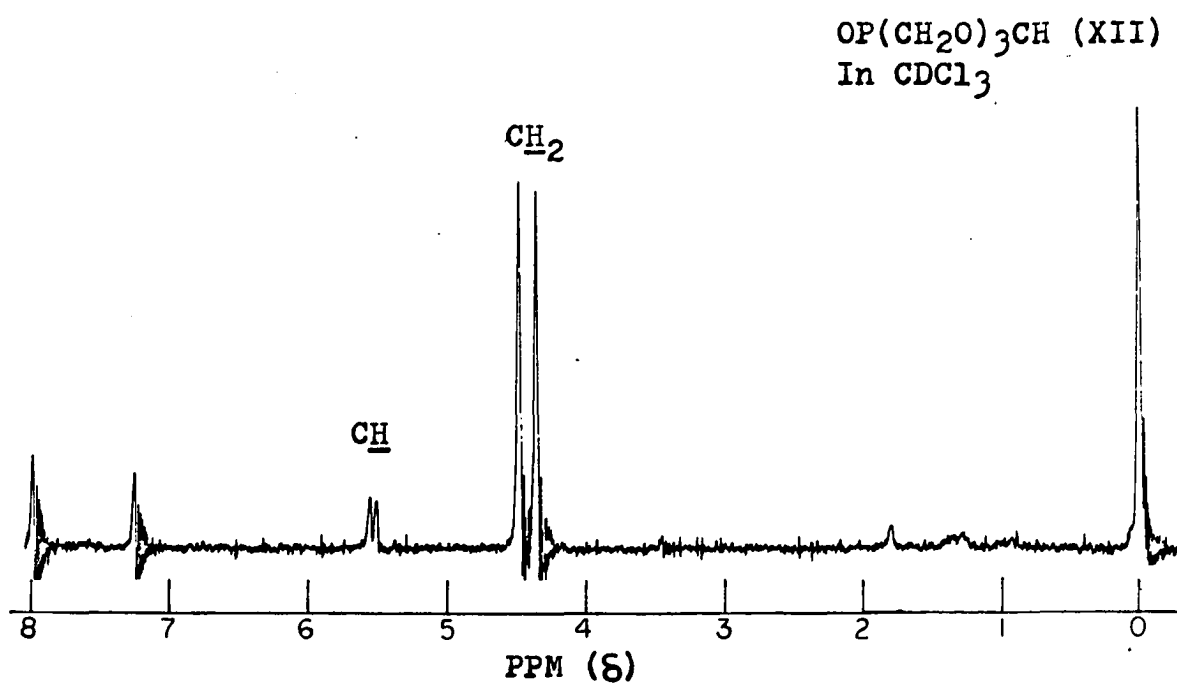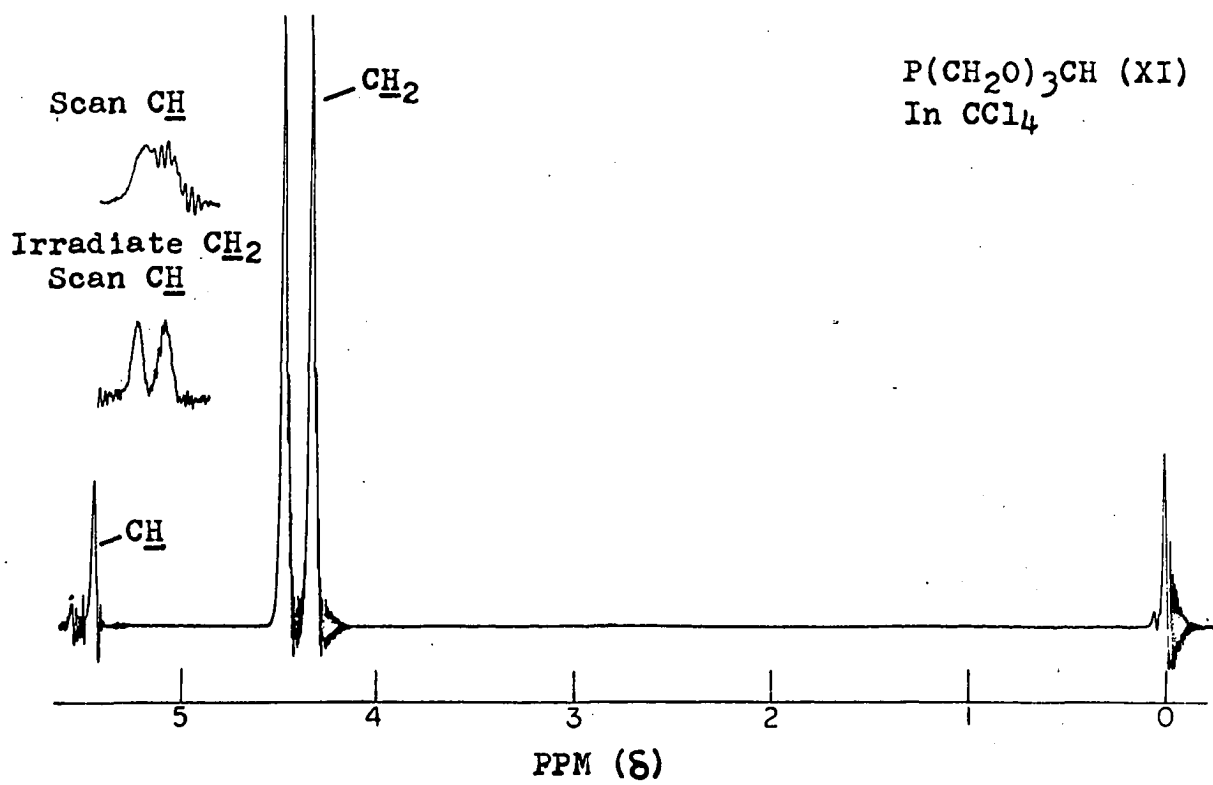
Figure 7. The n.m.r. spectra of $P(CH_2O)_3CCH_3$ (XIV),

OP$(CH_2O)_3CCH_3$ (XV), and SP$(CH_2O)_3CCH_3$ (XVI)

$P(CH_2O)_3CCH_3$ (XIV) In CCl_4

Scan $C\underline{H}_2$

$C\underline{H}_2$

Scan $C\underline{H}_3$

$C\underline{H}_3$

$OP(CH_2O)_3CCH_3$ (XV) In $CDCl_3$

$C\underline{H}_2$

$C\underline{H}_3$

Scan $C\underline{H}_3$

$SP(CH_2O)_3CCH_3$ (XVI) In $(CH_3)_2CO$

Scan $C\underline{H}_2$

Scan $C\underline{H}_3$

$C\underline{H}_2$

$C\underline{H}_3$

TMS
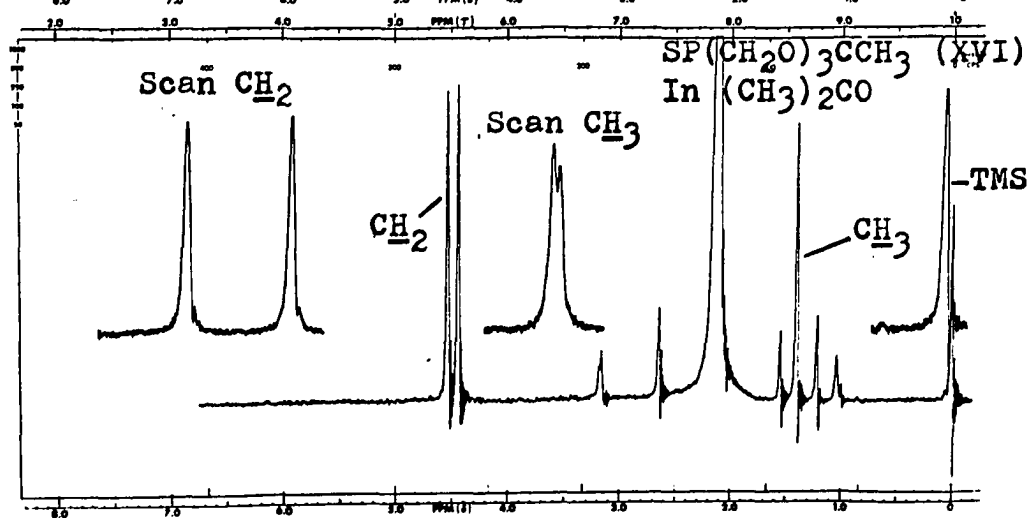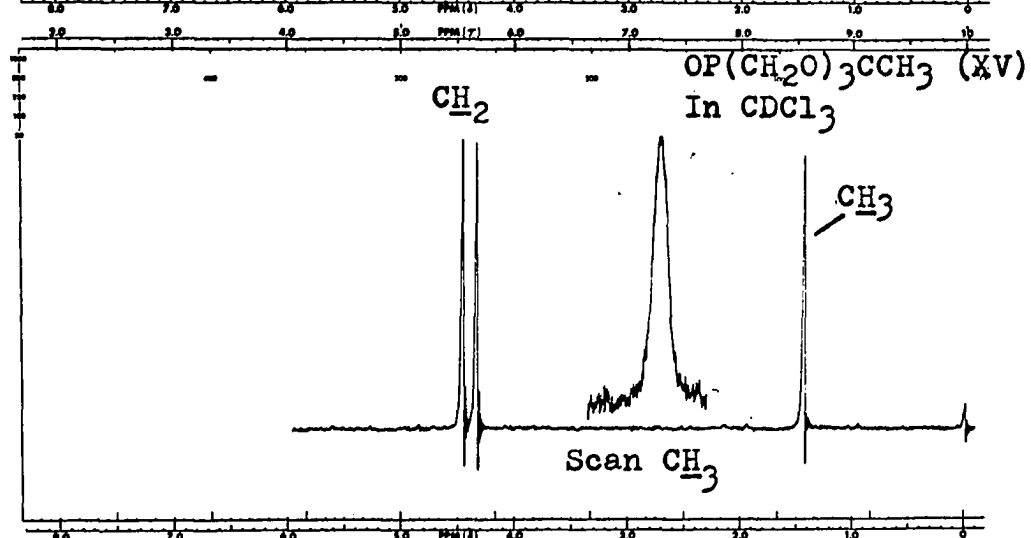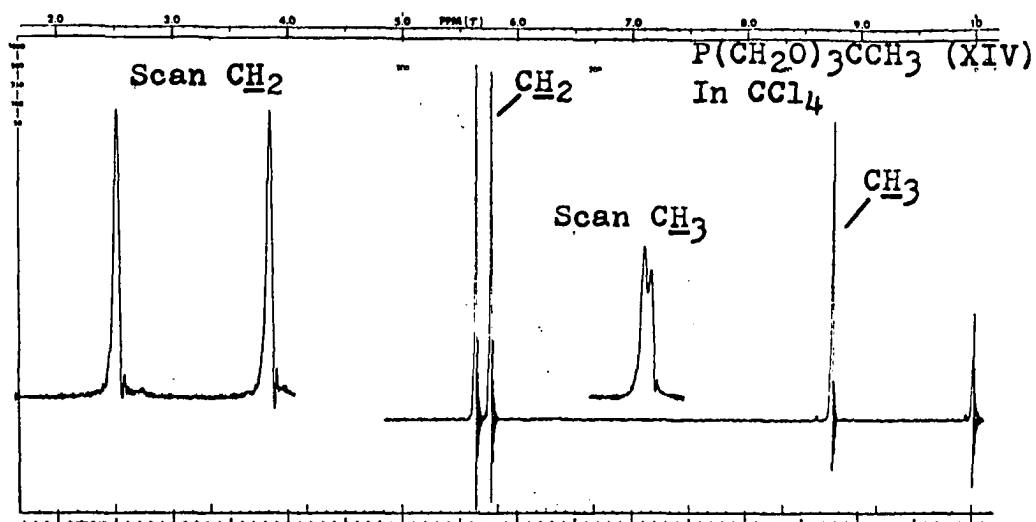
Figure 8. The n.m.r. spectra of $CH_3C(CH_2O)_3CH$ (IV), $CH_3C(CH_2O)_3As$, and $CH_3C(CH_2O)_3P$ (V)

CH₃C(CH₂O)₃CH (VII)
In CCl₄

CH₃C(CH₂O)₃As
In CCl₄

CH₃C(CH₂O)₃P (V)
In CCl₄
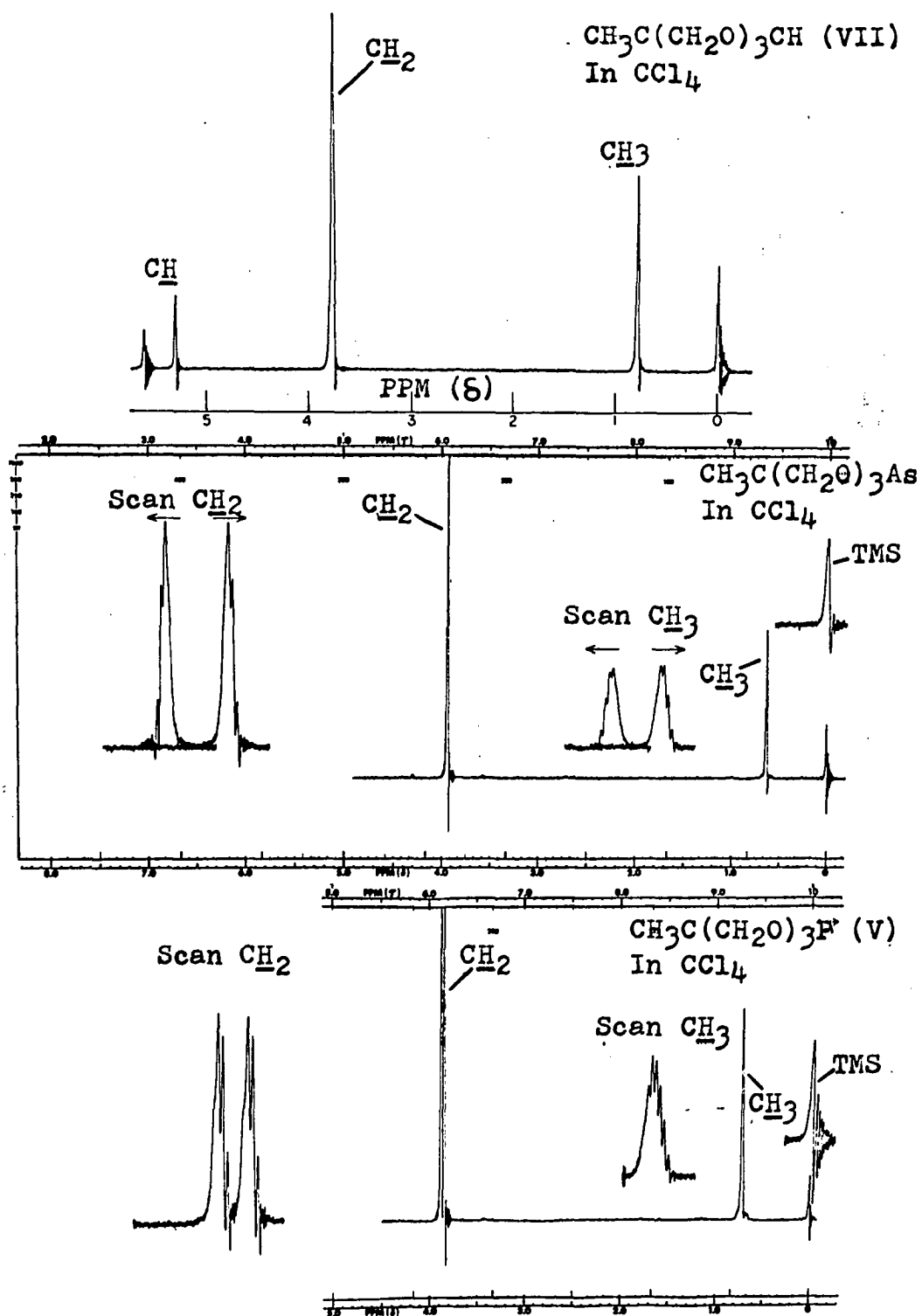
orthoformyl ($\underline{H}C(O-)_3$) proton for VII. For the orthoformate VII, the methylene resonance appears as a doublet due to coupling with the methine proton. Because coupling of the methylene and orthoformyl protons is too small to be observed, the orthoformyl resonance appears as a doublet due to coupling to the methine proton at the opposite bridgehead. For the phosphorus compounds VIII, IX and X, the methylene resonance appears as a doublet of doublets arising from interactions with the methine proton and the phosphorus. In the spectrum of the thiophosphate X in pyridine, an additional peak is present near the methylene resonance. That this absorption probably arises from a slight decomposition was shown by obtaining the spectrum in dimethyl sulfoxide in which it was absent.

Shown in Figures 5 and 6 are the proton n.m.r. spectra obtained for the phosphine derivatives XI, XII and XIII. In each spectrum the orthoformyl resonance is a low-field doublet because of coupling with the phosphorus four bonds removed. The methylene absorption likewise appears as a doublet arising from coupling with the phosphorus.

In Figure 7, the n.m.r. spectra for the phosphine derivatives XIV, XV, and XVI are shown. The methylene resonance in each spectrum appears as a doublet due to coupling to the phosphorus while the methyl resonance appears as a high-field singlet. Upon expansion, this singlet is resolved

into a doublet in two of the spectra presumably due to a five-bond interaction with the phosphorus.

The n.m.r. spectrum of the orthoformate ester IV is shown in Figure 8 along with the spectra of V and the bicyclic arsenite $CH_3C(CH_2O)_3As$ whose preparation is described elsewhere (2). The orthoformate spectrum consists of three singlets, no coupling larger than 0.2 c.p.s. being observed. The expanded methyl resonance in the spectrum of $CH_3C(CH_2O)_3As$ appears as an incompletely resolved septuplet which would be expected if coupled to six equivalent methylene protons. Arsenic has a nuclear spin of $3/2$, but also possesses an electric quadrupole moment which would inhibit coupling to the protons in the molecule. In the spectrum of V, the expanded methyl resonance is better resolved than that of the arsenite and appears to be an octet which would indicate coupling to the six methylene protons and equal coupling to the phosphorus five bonds removed. The postulated five-bond P-H coupling is tentative until a decoupling experiment is performed.

The proton chemical shifts observed for the polycyclic compounds are listed in Table 3. An interpretation of the coupling constants will be deferred to later sections.

The trends in the chemical shifts reported in Table 3 can be interpreted in terms of inductive considerations (106). The chemical shift of the methine protons $(CH_2)_3$-$(C\underline{H}O)_3X$ progresses to lower field as X changes from CH to P

Table 3. Proton chemical shifts of polycyclic compounds in p.p.m.

Compound	Solvent	CH_3	CH_2	$HC(O-)_3$	$HC(C-)_3$	$HC(C-)_2O-$
$(CH_2)_3(CHO)_3CH$ (I)[a]	CCl_4		1.65^b 2.65^c	5.38		4.24
$(CH_2)_3(CHO)_3P$ (II)[d]	$CDCl_3$		1.87^b 3.03^c			4.32
$(CH_2)_3(CHO)_3PO$ (III)[d]	$(CH_3)_2SO$		1.85^b 2.73^c			4.97
$H_3CC(CH_2O)_3CH$ (IV)	CCl_4	0.79	3.79	5.31		
$H_3CC(CH_2O)_3P$ (V)[d]	$CDCl_3$	0.72	3.93			
$H_3CC(CH_2O)_3PO$ (VI)[d]	$(CH_3)_2SO$	0.87	4.48			
$HC(CH_2O)_3CH$ (VII)	CCl_4		4.04	5.25	1.94	
$HC(CH_2O)_3P$ (VIII)	$CDCl_3$		4.12		2.03	
$HC(CH_2O)_3PO$ (IX)	$(CD_3)_2SO$		4.72		2.53	

[a] Values taken from reference 8.

[b] Axial methylene resonance.

[c] Equatorial methylene resonance.

[d] Values taken from reference 39.

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Table 3. (Continued)

Compound	Solvent	$C\underline{H}_3$	$C\underline{H}_2$	$\underline{H}C(O-)_3$	$\underline{H}C(C-)_3$	$\underline{H}C(C-)_2O-$
$HC(CH_2O)_3PS$ (X)	C_5H_5N		4.72		2.41	
$P(CH_2O)_3CH$ (XI)	CCl_4		4.33	5.32		
$OP(CH_2O)_3CH$ (XII)	$CDCl_3$		4.42	5.54		
$SP(CH_2O)_3CH$ (XIII)	$CDCl_3$		4.46	5.67		
$P(CH_2O)_3CCH_3$ (XIV)	CCl_4	1.23	4.30			
$OP(CH_2O)_3CCH_3$ (XV)	$CDCl_3$	1.43	4.40			
$SP(CH_2O)_3CCH_3$ (XVI)	$(CH_3)_2CO$	1.40	4.49			

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to PO in the series I, II, III. Inasmuch as the methylene
protons in this series are removed by an additional bond, the
effect of the bridgehead substituent on their chemical shift
is not expected to be as significant as on the methine shift,
and the lack of any trend here has been discussed elsewhere
(8). Trends analogous to the above are noted in the methyl-
ene chemical shifts for the series of compounds IV, V, VI and
VII, VIII, IX and in the methine ($\underline{H}C(C-)_3$) chemical shift for
the series VII, VIII, IX. The downfield trend in these shifts
can be attributed to the O_3X portion of the molecule (where
X=CH, P, and PO) which becomes more electron withdrawing in
character from the orthoformate to phosphite to phosphate
derivatives. The absence of a significant trend in the
methyl chemical shifts for the series IV, V, VI might be a
result of their large distance from the O_3X moiety. The
deshielding of the orthoformyl protons ($\underline{H}C(O-)_3$) and the
methylene protons from VII to XI to XII and of the methyl and
methylene protons from XIV to XV is also consistent with the
above trends. In the latter compounds, $X(CH_2-)_3$ may be con-
sidered to function as the electron withdrawing moiety. The
above trends seem to imply that the electronegativity of
carbon in the orthoformates is less than that of phosphorus
in either the phosphite or phosphate compounds if it can be
assumed that the hybridization around all the atoms in the
various esters is relatively constant because of the rigid

molecular geometries. The apparent smaller electronegativity of carbon compared to that of phosphorus is contrary to the values listed in three accepted electronegativity scales (107).

The above conclusions on electronegativities might also explain the deshielding of the methylene protons from V to XIV and from VIII to XI. However, the trend does not hold for the 1-oxo derivatives VI to XV and IX to XII which might indicate that the structural differences of these compounds preclude any such comparisons.

The 1-sulfo derivatives X, XIII, XVI were not included in any of the trends outlined above because of their somewhat variable chemical shifts. This behavior might indicate that solvent effects must be considered and in view of the relatively small differences in chemical shifts observed between the 1-oxo and 1-sulfo derivatives IX and X, XII and XIII, and XV and XVI, such a consideration might place the sulfo derivatives in their proper order in the above trends (8).

The large differences in chemical shift between the methine protons ($\underline{H}C(C-)_3$) in the compounds VII, VIII, IX, X and the orthoformyl protons ($\underline{H}C(O-)_3$) in the compounds I, IV, VII, XI, XII, XIII are indicative of the difference in electronegativities of carbon and oxygen. Thus, it is logical that the methine proton ($\underline{H}C(C-)_2O-$) chemical shifts should be intermediate between the $\underline{H}C(C-)_3$ and $\underline{H}C(O-)_3$ shifts as is shown in Table 3.

Finally, upon comparing the chemical shifts of the methylene protons in the series IV, V, VI and VII, VIII, IX, the inductive effect of the methyl group is apparent. Inasmuch as the methyl group is given a Taft polar substituent value of 0.00 and the electron-withdrawing hydrogen substituent a value of +0.49 (76), the above might better be attributed to the superior electron-withdrawing ability of the hydrogen substituent compared to that of the methyl group.

Complexes

As will be elaborated upon in a later section, the desired bicyclic phosphine I-4 has not been isolated. However, the preparation of the closely related phosphine $P(CH_2O)_3CCH_3$ (XIV) has been described herein for the first time and a brief account of its use as a ligand toward metal carbonyls will now be given.

The carbonyl complexes of XIV that have been characterized are $Ni(CO)_x(XIV)_{4-x}$ (x=0, 1, 2) and $Fe(CO)_x(XIV)_{5-x}$ (x=3, 4). The nickel compounds are taken to be tetrahedral by their analogy to known compounds (11) and as indicated by their infrared spectra. Similarly, the iron complexes are assumed to be trigonal bipyramidal in structure. Attempts were made to isolate $Ni(CO)_3(XIV)$, but only $Ni(CO)_2(XIV)_2$ resulted from these reactions. In fact, the preparation of $Ni(CO)_2-(XIV)_2$ described herein was intended as an attempt to isolate the monosubstituted complex. Even when a low temperature (0°)

and a two-fold excess of $Ni(CO)_4$ was used, only $Ni(CO)_2(XIV)_2$ was obtained.

All of the above complexes were found to be susceptible to oxidation by air in varying degrees. The two iron complexes and $Ni(CO)_2(XIV)_2$ were found to be relatively stable, their non-aqueous solutions withstanding decomposition over a period of hours. Conversely, $Ni(CO)(XIV)_3$ and $Ni(XIV)_4$ were so susceptible to oxidation that their n.m.r. spectra could not be obtained because of small amounts of paramagnetic oxidation product which precipitated. The ease with which these samples decomposed and hydrolyzed could explain the low carbon-hydrogen analysis obtained for a recrystallized sample of $Ni(CO)(XIV)_3$. It would appear from the analytical data listed in Table 1 that the thermal stability of these complexes increases with the degree of substitution of XIV.

The near infrared stretching frequencies obtained for these complexes are given in Table 4. The presence of XIV in the complexes was ascertained from the appearance of three strong C-O stretching frequencies between 1000 and 1120 cm^{-1}. The C-O frequencies in most of the spectra tend to shift only two to eight cm^{-1} to lower wave lengths from the free ligand to the complex and in no ordered manner.

That three carbonyl stretching frequencies are observed is expected from a group theoretical treatment (104). The frequencies reported here are five to twenty cm^{-1} lower than

Table 4. Near infrared stretching frequencies of carbonyl complexes of $P(CH_2O)_3CCH_3$ (XIV) in cm^{-1}

Compound[a]	Carbonyl CO	C-O
$Fe(CO)_4$(XIV)	2059(s)[b], 1988(s) 1949(vs)[c]	1118(s), 1052(s) 1012(s)
$Fe(CO)_3$(XIV)$_2$	1904(vs)	1116(s), 1049(s) 1011(s)
$Ni(CO)_2$(XIV)$_2$	2030(s), 1978(s)	1119(s), 1050(s) 1007(s)
$Ni(CO)$(XIV)$_3$	1971(s)	1117(s), 1049(s) 1005(s)
Ni(XIV)$_4$		1117(s), 1047(s) 1000(s)

[a]Taken on CH_2Cl_2 solutions.

[b]Strong.

[c]Very strong.

those reported for analogous complexes of $C_2H_5C(CH_2O)_3P$ (I-3) (11). As was pointed out in Hendricker's dissertation (11), there are two alternatives to explain this difference in frequencies. First, the ligand with better pi-bonding ability will give higher carbonyl stretching frequencies, and second, as the base strength of the ligand increases, the carbonyl stretching frequency decreases. As was pointed out in the introduction, XIV should be more basic than I-3, but the latter should be a better pi-bonding ligand. Thus, either of these alternatives or a combination of them could explain these results.

The far infrared absorptions of the ligand XIV are listed in Table 5 along with those observed for Ni(XIV)$_4$. In the complex, the only absorption which should be present in addition to the ligand absorptions is the Ni-P stretching frequency. The ligand absorption at 265 cm^{-1} was found to be present in all far infrared spectra of the complexes varying by only one to two cm^{-1}. Thus, the shoulder which appears in Ni(XIV)$_4$ at 250 cm^{-1} is assigned to the Ni-P stretching mode, all other absorptions observed for Ni(XIV)$_4$ being attributed to the ligand. It is apparent from the frequencies listed for free XIV and Ni(XIV)$_4$, that there is a marked difference in ligand absorptions in the two cases. A comparison of the spectra obtained for the other complexes and free XIV revealed this same type of change in ligand absorptions upon complex formation. The absorptions remaining in the spectra of the complexes after removing those due to the ligand are listed in Table 6 along with their tentative assignments. The numbers of M-C, MCO, and M-P frequencies obtained in this manner agree with the number of modes expected from a group theoretical treatment (104).

The general ranges of frequencies obtained here are 482-600 cm^{-1} for MCO, 364-484 cm^{-1} for the M-C stretch and 187-270 cm^{-1} for the M-P mode which fall within the accepted wave length limits reported for these modes (11). It should be pointed out that a M-P stretching frequency as high as

Table 5. Far infrared ligand (XIV) absorptions (cm^{-1}) as free ligand and in $Ni(XIV)_4$

$P(CH_2O)_3CCH_3$ (XIV)[a]	$Ni(XIV)_4$[b]
766(m)[c]	700-50[d]
716(w)[e]	
697(w)	670(sh)[f]
644(s)[g]	662(vs)[h]
553(m)	
456(s)	497(vs)
444(s)	440(w)
297(sh)	295(s)
289(s)	265(m)
265(s)	250(sh)
201(w)	150(w)

[a] Taken on CsI pellet.

[b] Taken on nujol mull.

[c] Medium.

[d] Obscured by polyethylene absorption.

[e] Weak.

[f] Shoulder.

[g] Strong.

[h] Very strong.

Table 6. Far infrared stretching frequencies of carbonyl complexes of $P(CH_2O)_3CCH_3$ (XIV) in cm^{-1}

Compound[a]	M-C-O	M-C	M-P
$Fe(CO)_4(XIV)$	600[b] 572 547	484 419 384	250-60[c]
$Fe(CO)_3(XIV)_2$	562 550	·387	270[c]
$Ni(CO)_2(XIV)_2$	513 482	446 364	233 200
$Ni(CO)(XIV)_3$	519	442	244[d] 187
$Ni(XIV)_4$			250[c]

[a]Taken on nujol mulls.

[b]All absorptions were of medium intensity.

[c]Partially obscured by ligand absorption at approximately 265 cm^{-1}.

[d]Partially obscured by $Ni(XIV)_4$ impurity at 250 cm^{-1}.

424 cm^{-1} has recently been reported (108) which may allow quite an extensive latitude in assigning M-P absorptions.

It is of interest to compare the CO, M-C, and M-P stretching values obtained for complexes of XIV with the values reported for I-3 (11). As was pointed out previously, the CO stretching frequencies for complexes of XIV were five to twenty cm^{-1} lower than those reported for complexes of I-3. The M-C stretching frequencies reported in Table 6 are

approximately two to sixty cm^{-1} higher than those reported for I-3, and the M-P stretching frequencies reported here are fifteen to seventy-five cm^{-1} higher than those observed for I-3. These differences in frequencies can be explained in terms of a combination of sigma- and pi-bonding effects in the metal-phosphorus bonds. For a detailed discussion of these effects, see reference 11. If the phosphine XIV is considered to be a better Lewis base than the phosphite I-3 (see introduction), coordination of XIV to a metal carbonyl would build up a greater charge density on the metal than would I-3. Such a build up of charge could be relieved by pi-bonding between the metal and carbon (giving a higher M-C stretching frequency for XIV complexes) forcing a reduction of bond order in the CO bond (giving a lower CO stretching frequency for complexes of XIV) as is illustrated below. The larger M-P frequencies

$$XIV: \longrightarrow M \longrightarrow C \equiv O:$$
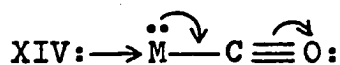
obtained for complexes of XIV compared to those of I-3 can be explained by added sigma M-P bonding in the former if XIV is considered to be a better Lewis base than I-3.
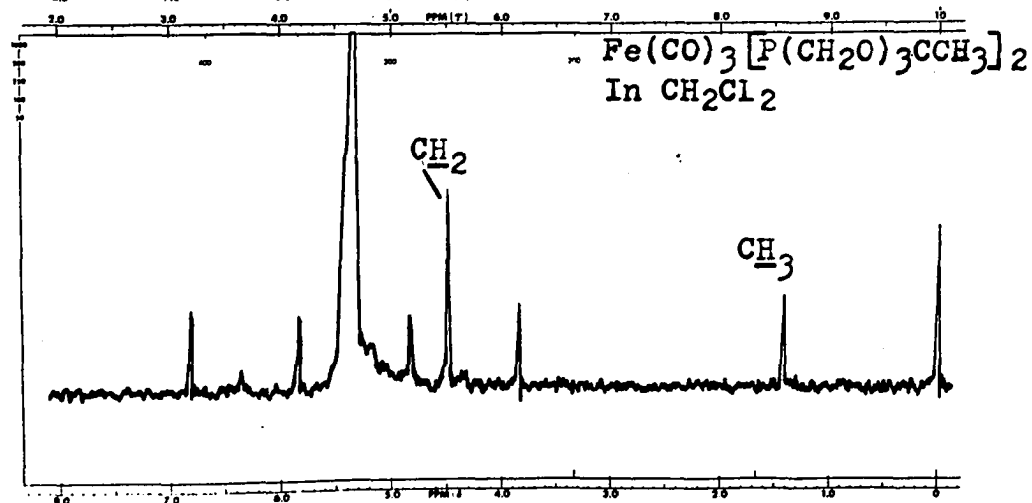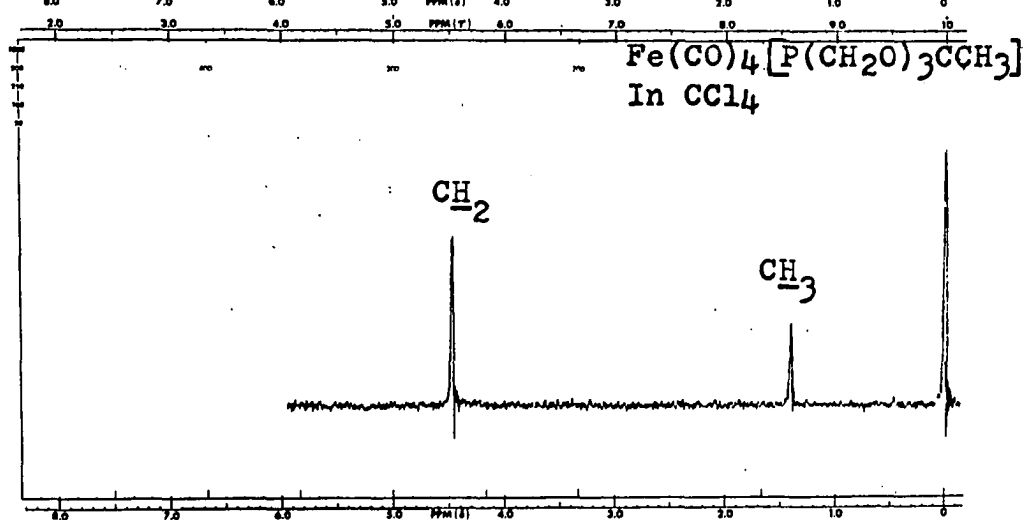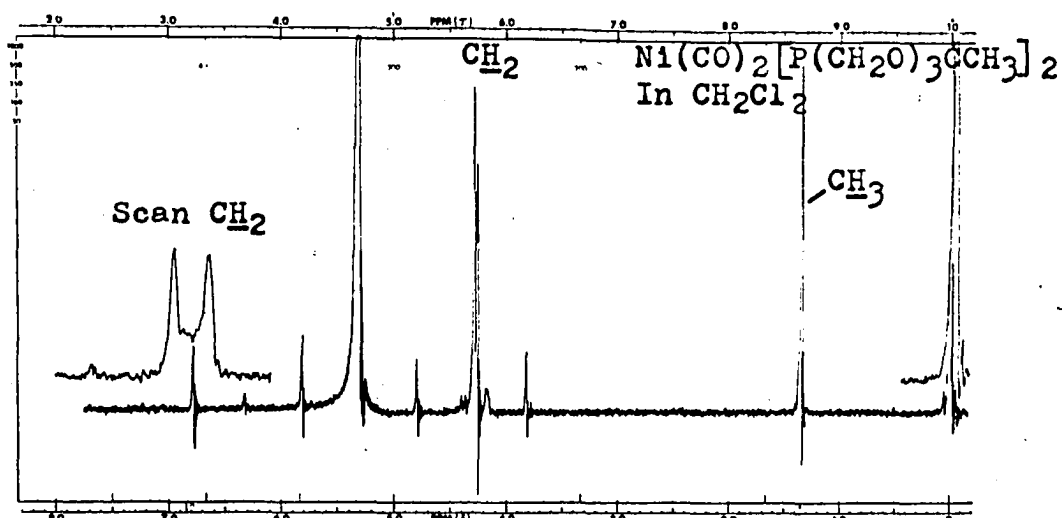
Hendricker (11) reported no perceptible changes in M-C or M-P stretching frequencies among the various carbonyl compounds considered which is contrasted with the report of Bigorgne and Zelwer (109) that a linear increase of the M-C stretching frequency accompanied increased substitution. From

the data reported in Table 6, it is evident that the M-P stretching frequency increases with increased substitution of XIV, but nothing definitive can be said about the M-C stretching frequency. Such an increase in the M-P frequency may imply the presence of dative d-pi-d-pi bonding between the metal and phosphorus which would increase as the charge density on the metal increases as a result of increased substitution of XIV.

It appears then that the differences in infrared spectral frequencies between complexes of I-3 and XIV can be explained in terms of the sigma-bonding differences between XIV and I-3. Thus, there is as yet insufficient information to either substantiate or contradict the empirical ordering of pi-bonding ligands of $PX_3 > V \sim (C_6H_5O)_3P \sim II > (CH_3O)_3P > PR_3 > NR_3$ (X = halogen, R = alkyl) (11). Additional data from adducts of XIV with boron Lewis acids would be helpful to ascertain whether or not XIV is indeed more basic in a Lewis sense than I-3.

The proton n.m.r. spectra obtained for three carbonyl complexes of XIV are shown in Figure 9. In the spectrum of $Ni(CO)_2(XIV)_2$, the methyl resonance appears at high-field as a singlet and the methylene at low-field as a doublet due to PCH coupling. Expansion of the methylene resonance showed a broad center absorption analogous to that reported for the corresponding complex of V which is an example of minimum P-P coupling (11). The spectra of $Fe(CO)_4(XIV)$ and $Fe(CO)_3(XIV)_2$

Figure 9. The n.m.r. spectra of $Ni(CO)_2(XIV)_2$, $Fe(CO)_4(XIV)$, and $Fe(CO)_3(XIV)_2$

$Ni(CO)_2[P(CH_2O)_3CCH_3]_2$
In CH_2Cl_2

CH_2

Scan CH_2

CH_3

$Fe(CO)_4[P(CH_2O)_3CCH_3]$
In CCl_4

CH_2

CH_3

$Fe(CO)_3[P(CH_2O)_3CCH_3]_2$
In CH_2Cl_2

CH_2

CH_3

show only two singlets each, the PCH coupling being approximately zero. Absence of the PCH coupling precluded the observation of P-P coupling.

The chemical shifts observed for these complexes are listed in Table 7 and the coupling constants will be discussed in a later section. The chemical shifts listed in Table 7 are very similar and represent a deshielding of about 0.2 p.p.m. from those of the free phosphine as a result of coordination to the metal carbonyl.

Table 7. Proton chemical shifts for complexes in p.p.m.

Compound	Solvent	$C\underline{H}_3$	$C\underline{H}_2$
$Fe(CO)_4(XIV)$	CCl_4	1.40	4.48
$Fe(CO)_3(XIV)_2$	CH_2Cl_2	1.42	4.49
$Ni(CO)_2(XIV)_2$	CH_2Cl_2	1.34	4.38

H^1-H^1 Coupling Constants

Proton-proton coupling constants obtained for polycyclic compounds are listed in Table 8. The magnitudes of the HCCH interactions can be understood by application of the Karplus theory for dihedral angle dependence of vicinal coupling constants (40). According to this theory, J_{HCCH} will attain a value of about 10 c.p.s. when the two C-H bonds make a dihedral angle of zero degrees. J_{HCCH} decreases to

Table 8. H^1-H^1 coupling constants for polycyclic compounds in c.p.s.

Compound	J_{HCCH}	J_{HCOCH}	J_{HCCCH}	J_{HCOCCH}
$(CH_2)_3(CHO)_3CH$ (I)[a]	2.7[b]	<0.2		1.25[c]
$(CH_2)_3(CHO)_3P$ (II)[a]	−[d]			
$(CH_2)_3(CHO)_3PO$ (III)[a]	2.5[b]			
$H_3CC(CH_2O)_3CH$ (IV)		<0.2	−[d]	
$H_3CC(CH_2O)_3P$ (V)			~0.3	
$H_3CC(CH_2O)_3PO$ (VI)			−[d]	
$H_3CC(CH_2O)_3As$[e]			~0.2	
$HC(CH_2O)_3CH$ (VII)	2.3	<0.2		1.7
$HC(CH_2O)_3P$ (VIII)	2.3			
$HC(CH_2O)_3PO$ (IX)	1.9			
$HC(CH_2O)_3PS$ (X)	2.0			
$P(CH_2O)_3CH$ (XI)		<0.2		
$OP(CH_2O)_3CH$ (XII)		<0.2		
$SP(CH_2O)_3CH$ (XIII)		~0.3		
$P(CH_2O)_3CCH_3$ (XIV)				−[f]
$OP(CH_2O)_3CCH_3$ (XV)				−[f]
$SP(CH_2O)_3CCH_3$ (XVI)				−[f]

[a]Values reported in reference 8.

[b]Coupling to equatorial methylene proton only.

[c]Coupling to axial methylene proton only.

[d]Not resolved.

[e]Preparation described in reference 2.

[f]Not observed (~0).

approximately 1 c.p.s. as the dihedral angle increases from zero to 90 degrees and then increases to about 12 c.p.s. as the dihedral angle increases to 180 degrees. For each of the HCCH coupling constants listed in Table 8, the HCCH system is gauche having a dihedral angle close to 60 degrees. Thus, each coupling constant should be approximately 2 c.p.s. as observed. For compound II, this coupling interaction was not resolved, and for I and III, the coupling between the methine and axial methylene protons was not observed. This may be a result of the postulated distortion of these adamantane like compounds (8). From Drieding models, it is necessary to push the three oxygens toward the three-fold axis of the molecule. The result of this is an increase in the dihedral angle from 60 degrees between the methine and axial methylene protons which would decrease J_{HCCH} by application of the Karplus theory. A small decrease in J_{HCCH} for the methine-axial methylene coupling is expected on the basis of the slight distortion postulated since even a 90° dihedral angle still allows approximately 1 c.p.s. coupling. That no such coupling is observed in I (8), however, is somewhat unexpected. It is also of interest to note that the HCCH coupling in the tri-alcohol $HC(CH_2OH)_3$ from which VII, VIII, IX and X were synthe-sized is 6.0 c.p.s. which corresponds to an averaging of the coupling values expected for the gauche and trans conforma-tions.

HCOCH coupling constants could not be resolved but were estimated from expanded line widths to be less than 0.2 c.p.s. for compounds I, IV, VII, XI and XII. A J_{HCOCH} value of approximately 0.3 c.p.s. was resolved for XIII as is shown in Figure 5. Similarly, HCCCH coupling constants of approximately 0.3 and 0.2 c.p.s. were observed for V and CH_3C-$(CH_2O)_3As$ as is shown in Figure 8. Unexpectedly large HCOCCH coupling constants of 1.25 and 1.7 c.p.s. were observed for I and VII, respectively. The latter is shown in Figure 3.

Four-bond proton-proton coupling constants although not common are known (53), but five-bond coupling constants in saturated systems were heretofore unknown. A spatial coupling mechanism as proposed by Meinwald and Lewis (52) might be invoked to explain the HCOCCH coupling interactions in that the C-H bonds involved are colinear in VII and parallel in I. Support for the postulate that a spatial interaction is of importance in these two compounds might stem from the lack of any five-bond coupling in XIV, XV and XVI wherein there is no fixed conformational arrangement due to the rotating methyl group. The data in Table 8 at least show the strong geometrical dependence of five-bond coupling constants and may also imply a spatial interaction through the polycyclic system. In this context it is of interest to note that Tori et al. (110) found a five-bond coupling constant of similar magnitude (1.8 c.p.s.) in a highly substituted bicyclo[2.2.2]-oct-2-ene. The similarity in magnitude between this coupling

and that for VII might imply that the coupling mechanism is analogous in each compound and thus independent of any unsaturation in the systems and the nature of any substituents attached.

There is some support for a "through-bond" coupling mechanism to explain these five-bond interactions. The ratio of J_{HCOCCH} for VII to J_{HCOCCH} for I is approximately 3:2 which corresponds exactly to the ratio of the number of paths available for "through-bond" coupling in VII and I, respectively. Furthermore, if the magnitudes of five-bond coupling constants obtained by Kowalewski and Kowalewski (60) of 0.45 to 0.6 c.p.s. for alkyl formates are taken to be representative of coupling constants in saturated systems, then the magnitude of coupling through two bonding paths as in I would give a coupling constant of 0.9 to 1.2 c.p.s., while the magnitude through three bonding paths as in VII would give a J_{HCOCCH} value of 1.35 to 1.8 c.p.s. These values compare favorably with those obtained for I and VII. It is also important to note that if a spatial interaction is considered for the adamantane type molecule I, the C-H bonds are not properly aligned as they are in VII. Furthermore, if a direct interaction dependent on the distance between these two carbon atoms is of importance, the coupling constants of I and VII do not reflect the shorter C-C distance (by 0.4 Å) in VII compared to I as obtained from Drieding models.

If the spatial interaction described above is of impor-
tance, it should be applicable as well to the HCOCH couplings
noted in Table 8 where each compound possesses the "W" con-
formation. Furthermore, HCCCH couplings are noted for V and
$CH_3C(CH_2O)_3As$ wherein the "W" conformation is not present
since the methyl group is free to rotate. Thus, the similar-
ity of the magnitudes of J_{HCOCH} and J_{HCCCH} would seem to imply
that a spatial coupling mechanism is not of importance for
these four-bond systems.

In addition to the long-range coupling theory of Koide
and Duval (59), Barfield (111) has found a dihedral angle
dependence of four-bond H-H coupling constants analogous to
that reported for vicinal interactions described above (40).
Barfield found that the coupling constant has a value of
about 1.0 c.p.s. at a dihedral angle of zero degrees which
passes through a minimum of 0.0 c.p.s. at 90 degrees and rises
to approximately 1.2 c.p.s. at 180 degrees. In compound I,
the HCOCH dihedral angle is zero degrees, while in IV, VII,
XI, XII and XIII, it is 60 degrees, and no HCCCH dihedral
angle can be described for IV, V, VI and $CH_3C(CH_2O)_3As$. In
contrast to Barfield's conclusions then, there is no dihedral
dependence from the data reported in Table 8 for four-bond
coupling constants.

The theory of Koide and Duval (59), which considers a
two-fold "through-bond" coupling mechanism, predicts that the
two mechanisms will reinforce for four-bond coupling and will

cancel for five-bond coupling. If the two five-bond couplings for I and VII are ignored, this theory would then explain the observed four-bond couplings in Table 8 and the absence of five-bond couplings in XIV, XV and XVI. Furthermore, Koide and Duval would very probably explain the large J_{HCOCCH} values of 1.25 and 1.7 c.p.s. obtained for I and VII, respectively, by a direct coupling through the cage, as mention of this type of direct interaction was made in their publication.

A determination of the signs of the four-bond coupling constants listed in Table 8 would greatly facilitate a study of the coupling mechanism which gives rise to their occurrence. Generally, coupling between nuclei separated by an even number of bonds gives a negative coupling constant while coupling over an odd number of bonds gives a positive coupling constant (59, 86, 112). Thus, if the four-bond coupling constant arises from a "through-bond" mechanism, it should be negative. But if there is a spatial interaction as illustrated in the introduction, the bonding path would be reduced to three "bonds" and the coupling constant should be positive. For compounds I and VII, both the "through-bond" mechanism (coupling through five bonds) and the "through-space" mechanism (reduction of the path to three "bonds") should give a positive coupling constant. Thus, a differentiation of these two mechanisms would not be possible. However, this does raise the interesting point that the large

coupling values obtained for I and VII may be a result of a reinforcing of both the "through-bond" and "through-space" mechanisms.

It should also be pointed out that the intervening oxygen atoms may play an important role in the long-range coupling values. Holmes et al. (113) found that two coupling interactions of different sign were needed to explain the H-D coupling observed in HOD. One of the interactions involved the non-bonded electron density on oxygen which constituted about thirty percent of the "through-bond" interaction.

H^1-P^{31} Coupling Constants

The phosphorus-proton coupling constants that were obtained for the polycyclic compounds and complexes are listed in Table 9. The POCH interactions discussed first are analogous to results published elsewhere (23, 39, 106). J_{POCH} is seen to increase from the phosphites II, V, and VIII to the sulfides $(CH_2)_3(CHO)_3PS$, $CH_3C(CH_2O)_3PS$, and X to the oxides III, VI, and IX, although the difference between IX and X is zero. These results are consistent with the concepts outlined by Bent (61), in that the electronegativity of the substituents increases from the lone pair (phosphites) to sulfur (thiophosphates) to oxygen (phosphates). Such an increase would then increase the s-character in the POCH bonding system and account for the increased coupling by an increase in the Fermi contact interaction. The larger

Table 9. H^1-P^{31} coupling constants for polycyclic compounds and complexes in c.p.s.

Compound	J_{PCH}	J_{POCH}	J_{PCOCH}	J_{POCCH}	J_{PCOCCH}	J_{POCCCH}
$(CH_2)_3(CHO)_3P$ (II)[a]		6.0		<0.5		
$(CH_2)_3(CHO)_3PO$ (III)[a]		20.0		~2.0		
$(CH_2)_3(CHO)_3PS$[a]		19.0		—[b]		
$H_3CC(CH_2O)_3P$ (V)[a]		2.0				~0.3
$H_3CC(CH_2O)_3PO$ (VI)[a]		7.0				—[b]
$H_3CC(CH_2O)_3PS$[a]		6.0				—[b]
$HC(CH_2O)_3P$ (VIII)		1.6		7.2		
$HC(CH_2O)_3PO$ (IX)		6.5		6.2		
$HC(CH_2O)_3PS$ (X)		6.5		5.9		
$P(CH_2O)_3CH$ (XI)	8.5		1.0			
$OP(CH_2O)_3CH$ (XII)	7.4		3.0			
$SP(CH_2O)_3CH$ (XIII)	5.3		3.3			
$P(CH_2O)_3CCH_3$ (XIV)	8.0				~0.3	
$OP(CH_2O)_3CCH_3$ (XV)	7.3				—[b]	
$SP(CH_2O)_3CCH_3$ (XVI)	5.6				~0.3	
$Fe(CO)_4$(XIV)	—[c]				—[c]	
$Fe(CO)_3$(XIV)$_2$	—[c]				—[c]	
$Ni(CO)_2$(XIV)$_3$	1.8				—[c]	

[a] Values taken from reference 39.

[b] Not resolved.

[c] Not observed (~0).

magnitude of POCH coupling in II, III, and the 1-sulfo deriva-
tive of II compared to similar derivatives of V suggests a
dihedral angle dependence of POCH coupling as has been dis-
cussed previously (30).

The difference between POCH coupling values reported here
and POCH, PNCH, and PCCH values reported in the literature for
open chain systems merits some speculative consideration. The
coupling value of J_{PCCH} for $(C_2H_5)_3P$ is 13.7 c.p.s. (64),
J_{PNCH} for $((CH_3)_2N)_3P$ is 8.82 c.p.s. (67), and J_{POCH} for
$(C_2H_5O)_3P$ is 7.9 c.p.s. (47). The coupling constants for the
corresponding oxides are 16.3, 9.47, and 8.4 c.p.s., respec-
tively. In each case, $J_{PCCH} > J_{PNCH} > J_{POCH}$, and the decreasing
trend in J is in the same order as the increase in the number
of lone-pair electrons present on intervening atoms. Holmes
et al. (113) found that interaction of nuclear spins with such
non-bonded electrons on intervening atoms gives rise to a
coupling interaction of opposite sign to the interaction which
is strictly through-bond in nature. Consideration of this
additional interaction would explain the above results for
PCCH, PNCH, and POCH coupling constants. The POCH inter-
actions listed in Table 9 are seen to increase on oxidation
of the polycyclic compounds by a larger magnitude than the
increase noted for the three open chain compounds above. This
might be a result of the difference in rigidity of structure
between the polycyclic and open chain compounds, where the
latter may undergo more radical change in structure upon

oxidation. Any structural changes would effect the percent of s-character in the bonds to phosphorus.

If there is a dihedral angle dependence for POCH coupling constants, a maximum value should be attained for II (J_{POCH} = 6.0 c.p.s.) where the POCH dihedral angle is 180 degrees, and a value close to minimum should be observed for V and VIII (J_{POCH} = 2.0-1.6 c.p.s.) where the POCH dihedral angle is 60 degrees. Thus, by analogy to the Karplus relation (40), an approximate range for J_{POCH} would be 1 to 6 c.p.s. for a dihedral angle range of 90 to 180 degrees. For an open chain trialkyl phosphite, a POCH coupling constant should be observed representing an average value of the gauche (60 degrees) and trans (180 degrees) conformations. Such an average value would be 3.5 c.p.s. which is low compared to the value of 7.9 c.p.s. reported for $(C_2H_5O)_3P$ (47). The higher observed value might then be rationalized as a result of a larger OPO angle in the open chain phosphite compared to the polycyclic phosphites and, thus, a larger percent s-character in the P-O bonds resulting in a larger Fermi contact interaction.

The PCH coupling constants listed in Table 9 are seen to attain a maximum absolute value for the free phosphines XI and XIV, and decrease to the oxides XII and XV, and then to the sulfides XIII and XVI. Furthermore, complexation of XIV reduces J_{PCH} to 1.8 c.p.s. for $Ni(CO)_2(XIV)_2$ and to zero for

the iron carbonyl compounds. These results are inexplicable in terms of the concepts outlined above for POCH coupling constants. Hendrickson et al. (64) reported J_{PCH} values for substituted trialkyl phosphines of 0.5, 11.3, and 11.9 c.p.s. for $(C_2H_5)_3P$, $(C_2H_5)_3PS$, and $(C_2H_5)_3PO$, respectively, giving a trend analogous to that reported herein for POCH coupling constants. Also the values of 8.5 and 8.0 c.p.s. obtained for XI and XIV are anomolously high compared to the J_{PCH} value obtained for $(C_2H_5)_3P$ and other alkyl phosphines (64). The PCH coupling constant observed for the trialcohol $P(CH_2OH)_3$ is 2.0 c.p.s. (22).

A consideration of bond angles has been invoked to explain the increase in J_{PCH} from $P(CH_2OH)_3$ to the cyclic compounds XI through XVI (22, 106). The CPC bond angle in $(CH_3)_3P$ has been determined by an electron diffraction structural study to be $98.9°$ (114) which might be assumed to hold approximately for $P(CH_2OH)_3$. In the polycyclic phosphines reported in Table 9, the CPC angles might be considered to be nearly tetrahedral because of their rigid cyclic structures. If this is the case, cyclization of the above trialcohol would increase the CPC bond angles giving an increase in the percent s-character in the C-P bonds which would explain the increased coupling by the Fermi contact interaction.

Cullingworth et al. (115) have recently observed that J_{PCH} changes sign when $(CH_3)_3P$ is coordinated to $Al(C_2H_5)_3$.

By plotting the PCH coupling constant against the ratio of $Al(C_2H_5)_3$ to $(CH_3)_3P$ they observed that J_{PCH} passed through a value of zero, although they were not able to discern the sign of the values.

If a change in sign of the PCH coupling can be assumed upon coordination of the phosphine XIV, then the data in Table 9 can be explained by the concepts outlined above for POCH coupling. If for the sake of argument J_{PCH} is taken to be negative for the phosphine XIV and $Ni(CO)_2(XIV)_2$, and all other derivatives of XIV are considered to have positive coupling constants, the following order of increasing J_{PCH} is obtained: $XIV < Ni(CO)_2(XIV)_2 < Fe(CO)_4(XIV) \sim Fe(CO)_3(XIV)_2 <$ $XVI < XV$. The same order holds for the series $XI < XIII < XII$. The J_{POCH} values listed in Table 9 for derivatives of V and the values of 4.0, 5.1 and 5.0 c.p.s. obtained for $Ni(CO)_2$-$(V)_2$, $Fe(CO)_4(V)$ and $Fe(CO)_3(V)_2$, respectively (12), follow the order $V < Ni(CO)_2(V)_2 < Fe(CO)_4(V) \sim Fe(CO)_3(V)_2 < CH_3C$-$(CH_2O)_3PS < VI$. Not only do these two orders agree completely, but the multiple of increase is seen to be approximately the same through both orders. For example, both J_{POCH} and J_{PCH} increase from the free ligands to the complexes by one-half the magnitude of increase from the ligands to the oxides. Thus, if a change in the sign of the PCH coupling constant is assumed, the order of the trend observed may be explained by the concepts of electronegativity as outlined by Bent (61).

From the arguments presented above, it is apparent on comparing J_{PCH} and J_{POCH} values for the ligands XIV and V, respectively, and their derivatives, that a change in sign for the PCH coupling is necessary for consistency in the two trends. J_{PCH} is noted to increase on cyclization of $P(CH_2OH)_3$ to XIV (or increase in negative magnitude if the assignment of signs given above is accepted), to approach zero from XIV to $Fe(CO)_4(XIV)$, and then to increase in positive magnitude to XV. As was outlined in the introduction, many data for quaternary phosphorus and tin compounds have been presented which were interpreted using only the Fermi contact interaction. On the other hand, no structural data are available for polycyclic phosphines from which a CPC bond angle can be estimated for XIV. Thus, it seems reasonable to explain the variation of J_{PCH} from XIV to XV in the aforementioned series using the Fermi contact mechanism, and to propose an alternative coupling mechanism to explain the increased PCH interaction from $P(CH_2OH)_3$ to XIV.

The generally low values of PCH coupling constants compared to the larger PCCH coupling constants have been rationalized in the following manner (64, 79, 116). The PCH coupling is considered to be small as a result of two different coupling mechanisms of different signs giving rise to a cancellation of terms, whereas the PCCH coupling is considered to arise mainly by the Fermi contact interaction. The added interaction in PCH coupling has been vaguely described as a

spin-orbital, spin-electron-dipole, spin-d orbital interaction, or as a spin interaction with the non-bonded electrons on the phosphorus (79). Participation of phosphorus d orbitals in bonding would probably not be of importance for phosphines, but by analogy to the work of Holmes et al. (113), interaction of the nuclear spins with the non-bonded electrons on phosphorus could account for perhaps 30% of this additional PCH interaction. Specifically what interaction gives rise to the increase in J_{PCH} on cyclization is obscure. Consideration of the interaction with non-bonded electrons would explain the rather large increase in J_{PCH} on quaternization that is observed in Table 9 and on quaternization of other trialkyl phosphines mentioned previously in that not only would the Fermi interaction increase, but the interaction of nuclear spins with the non-bonded electrons (presumably of opposite sign) would vanish.

Speculation can be made about the signs of J_{PCH} reported herein. Although J_{POCH} is generally considered to be positive (71), there is controversy concerning the sign of J_{PCH} and J_{PCCH} (70, 79, 116), except that they are considered to be of opposite sign (70, 117). The signs may be considered analogous to those reported for proton-proton interactions where J_{HCH} and J_{HCCH} are taken to be negative and positive, respectively (112). Only the Fermi contact interaction is considered to be dominantly responsible for the signs of these

interactions. As discussed above, the Fermi interaction was taken to be the major mechanism in describing the PCH coupling constant for the phosphine oxides XII and XV, thus by analogy to the accepted sign for J_{HCH}, J_{PCH} may also be considered as negative for these two compounds. As a result of this, the series of derivatives of XIV would be ordered as follows in terms of increasing Fermi contact interaction and increasing negative coupling: XIV(+8.5 c.p.s.)$<$Ni(CO)$_2$(XIV)$_2$ (+1.8 c.p.s.)$<$Fe(CO)$_4$(XIV)$\sim$Fe(CO)$_3$(XIV)$_2$(0 c.p.s.)$<$XVI(-5.6 c.p.s.)$<$XV(-7.3 c.p.s.).

Two types of four-bond P-H coupling constants are listed in Table 9, PCOCH and POCCH interactions (106). As was pointed out in the introduction, four-bond P-H couplings have been observed before and are generally of low magnitude. For example, in $(C_2H_5O)_3P$ and $(C_2H_5O)_3PO$, J_{POCCH} was found to be 0.55 and 0.84 c.p.s., respectively (47). The various substituent groups in these latter two compounds can be considered to undergo free rotation about all bonds, and thus from a lack of any specific geometrical arrangement, the long-range coupling can be considered to arise from a "through-bond" Fermi contact interaction. If this is accepted to be the case, then the long-range coupling noted for XI, XII, XIII and II, III may also be explained in terms of a Fermi contact interaction. There are three equivalent routes available for "through-bond" coupling in XI, XII and XIII, and thus the Fermi terms might be 1.6 c.p.s. for XI (three times 0.55 c.p.s.) and 2.5 c.p.s.

for XII and XIII (three times 0.84 c.p.s.). Inasmuch as there are two equivalent paths available for "through-bond" coupling for II and III, the Fermi terms might be 1.1 c.p.s. (two times 0.55 c.p.s.) and 1.7 c.p.s. (two times 0.84 c.p.s.), respectively. The approximate agreement in magnitudes between the values calculated above and those listed in Table 9 suggests that a "through-bond" coupling mechanism is dominant in the coupling observed in these compounds. Furthermore, the increase of these four-bond coupling constants on oxidation or quaternization from XI to XII or XIII and from II to III is consistent with the arguments outlined by Bent (61) for an increase in s-character in the P-O bonds upon oxidation and hence is also consistent with a Fermi coupling mechanism.

The decrease of J_{POCCH} from 7.2 to 6.2 to 5.9 c.p.s. from VIII to IX to X is completely inconsistent with the trends observed for other coupling constants listed in Table 9. Consideration of this trend and the large magnitudes observed for these three POCCH interactions suggests that an interaction in addition to the Fermi contact one is of importance here. An indication of what this added term might be becomes apparent upon considering the structures of II, VIII, and XI. Molecule VIII differs from XI in the relative positions of the CH_2O groups and is different from II in the orientation of the C-H bonds four bonds removed from the coupling phosphorus atom. Speculation might allow for a direct interaction between the phosphorus and carbon at the opposite bridgehead in VIII

facilitated in some manner by the oxygen atoms around phosphorus to explain the high POCCH coupling observed. This type of interaction would likely decrease on oxidation or sulfuration due to withdrawal of electron density by the substituent attached to phosphorus. This postulate is in keeping with the observed decrease in J_{POCCH} from VIII to IX and X. That J_{POCCH} in IX and X is twice the size of J_{PCOCH} in XII and XIII might indicate that this added interaction is still present in the oxide IX and the sulfide X.

This secondary interaction would be of no importance for the four-bond couplings in the phosphine XI or its derivatives XII and XIII where the phosphorus is surrounded by carbon atoms or in the adamantane derivatives II and III where the C-H bond involved is not colinear with the phosphorus lone-pair orbital. Support for this conclusion stems from the increase in four-bond coupling upon oxidation of XI or II which would be expected for a "through-bond" mechanism. Furthermore, from Drieding models, the distance from phosphorus to the apical carbon is 2.2 $\overset{o}{A}$ in VIII and 2.6 $\overset{o}{A}$ from the phosphorus to the methylene carbon in II. This difference of 0.4 $\overset{o}{A}$ might explain the absence of a direct interaction in II and III in addition to the above geometrical argument.
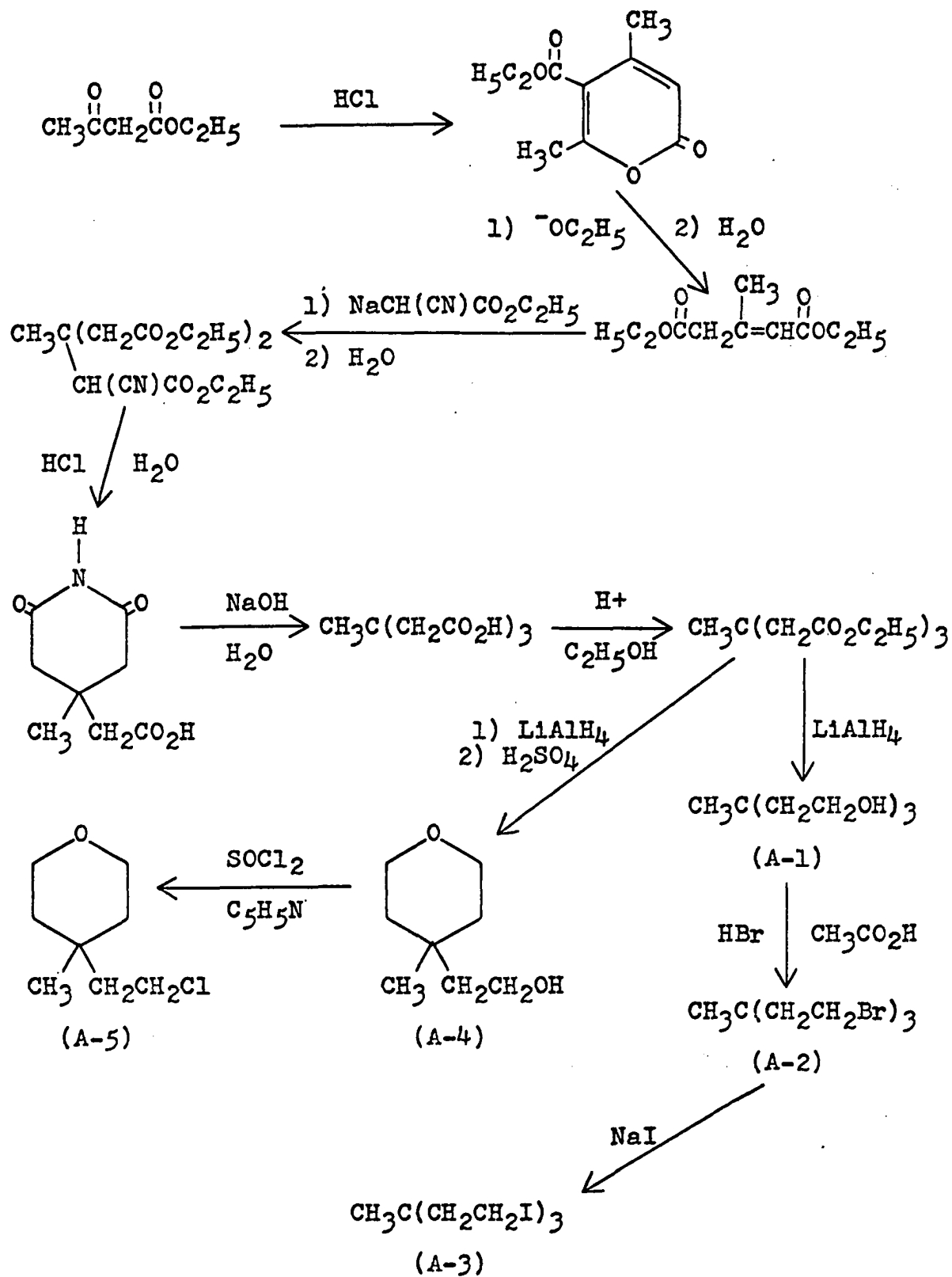
No five-bond P-H coupling constants have been previously reported for saturated organophosphorus compounds. The

magnitudes of J_{POCCCH} and J_{PCOCCH} are seen to be small (~ 0.3 c.p.s.) and the same for both the phosphite V and the phosphine XIV. From the arguments above, these couplings probably are a result of a "through-bond" interaction in these compounds although a partial "through-space" interaction cannot be ruled out in the case of V. Again there are three equivalent bonding paths from the phosphorus to the coupling protons under consideration which might explain the presence of five-bond coupling here and its absence in open chain compounds.

Attempted Preparations

The reaction sequence used for the preparation of the intermediate precursors to $CH_3C(CH_2CH_2)_3P$ (I-4) is shown below. Compounds A-1, A-2, A-3, and A-5 were then used separately in attempts to prepare I-4.

If the trialcohol A-1 were cyclized to the corresponding phosphite ester $CH_3C(CH_2CH_2O)_3P$, a stepwise Arbuzov rearrangement and reduction might give I-4 as outlined by Cooper (14). The first intermediate in this sequence would be CH_3- $\overline{C(CH_2CH_2O)_2P(O)CH_2CH_2}$, obtained by heating the above phosphite. Reduction of the oxo group and two successive treatments with heat followed by reduction would give I-4. As was outlined in the experimental section, three attempts were made to isolate this bicyclic phosphite without success. Presumably, the added length of the alkyl chain

$$CH_3CCH_2COC_2H_5 \xrightarrow{\text{HCl}}$$ (diketoester with two C=O)

[Structure: pyranone ring with $H_5C_2O_2C$, CH_3, H_3C, =O substituents]

$$\xrightarrow{\text{1) } ^-OC_2H_5 \quad \text{2) } H_2O}$$

$$H_5C_2OCCH_2\overset{CH_3}{\underset{}{C}}=CHCOC_2H_5$$

$$\xleftarrow[\text{2) } H_2O]{\text{1) } NaCH(CN)CO_2C_2H_5} \quad CH_3C(CH_2CO_2C_2H_5)_2$$
$$CH(CN)CO_2C_2H_5$$

$$\xrightarrow{\text{HCl} \quad H_2O}$$

[Glutarimide ring structure with N–H, two C=O, CH_3 and CH_2CO_2H substituents]

$$\xrightarrow[H_2O]{\text{NaOH}} CH_3C(CH_2CO_2H)_3 \xrightarrow[C_2H_5OH]{\text{H+}} CH_3C(CH_2CO_2C_2H_5)_3$$

$$\xrightarrow[\text{2) } H_2SO_4]{\text{1) } LiAlH_4}$$

[Tetrahydropyran ring with CH_3 and CH_2CH_2OH substituents]
(A-4)

$$\xleftarrow[C_5H_5N]{\text{SOCl}_2}$$

[Tetrahydropyran ring with CH_3 and CH_2CH_2Cl substituents]
(A-5)

$$CH_3C(CH_2CO_2C_2H_5)_3 \xrightarrow{\text{LiAlH}_4} CH_3C(CH_2CH_2OH)_3$$
(A-1)

$$\xrightarrow[CH_3CO_2H]{\text{HBr}} CH_3C(CH_2CH_2Br)_3$$
(A-2)

$$\xrightarrow{\text{NaI}} CH_3C(CH_2CH_2I)_3$$
(A-3)

in $CH_3C(CH_2CH_2OH)_3$ compared to $CH_3C(CH_2OH)_3$ is sufficient to separate the hydroxyl groups enough so that polymerization is more likely than cyclization when the trialcohol is treated with either $(CH_3O)_3P$, PCl_3, or $P(N(CH_3)_2)_3$.

In this connection, the preparation of the bicyclic amine-phosphite $N(CH_2CH_2O)_3P$ became of interest. This molecule would contain two different sites for coordination to a transition metal (R_3N versus $(RO)_3P$), and a study of its use as a ligand would allow a direct comparison of the coordinating ability of amines and phosphites. Cyclizations of triethanolamine have been described previously in preparing $N(CH(CH_3)CH_2O)_3B$ (118), $N(CH_2CH_2O)_3Al$ (119), and $N(CH_2CH_2O)_3$-Si-R (R = alkyl) (120). The latter two were isolated from transesterification reactions involving $N(CH_2CH_2OH)_3$ and either $Al(OC_2H_5)_3$ or $RSi(OC_2H_5)_3$, and the former was made by combining the trialcohol with boric acid. Not only was this type of transesterification reaction attempted herein using $N(CH_2CH_2OH)_3$ and $P(OCH_3)_3$, but also the reaction of this trialcohol with PCl_3 and $P(N(CH_3)_2)_3$. In each instance, the desired bicyclic compound was not formed, but rather a polymer judging from the insolubility and viscosity of the resulting syrup.

A heterogeneous reaction between the tribromide A-2 and $NaPH_2$ in xylene was attempted with negative results. If the desired $CH_3C(CH_2CH_2Br)_2CH_2CH_2PH_2$ had been obtained, it would have been treated with a base to abstract HBr and cyclize

the compound to I-4. It was rationalized that the reaction
did not occur because the two components did not come into
sufficient contact. Combining the reactants with two equiva-
lents of pyridine in a heated sealed tube resulted in the
formation of a supposed polymeric material. This product may
have been analogous to one reported by McEwen et al. (16) who
reported a material with the repeating unit $-[CH_2CH_2C(CH_2CH_2)_2-$
$\overset{+}{P}(C_6H_5)]_n$ nBr^- as the product of a reaction between $HC(CH_2CH_2-$
$Br)_3$ and $K_2PC_6H_5$.

Attempts were made to prepare the desired phosphine I-4
(R=CH$_3$) by reacting the tribromide A-2 or triiodide A-3 with
either red or white phosphorus in a heated vacuum system.
Presumably considerable decomposition took place as indicated
by the tar-like gum that remained after reaction. Grayson
indicated that trialkyl phosphines rarely resulted from these
reactions since they apparently are unstable at elevated tem-
peratures (36).

Under the conditions outlined in the experimental section,
Grignard reagents of A-2, A-3, or A-5 did not form. This
might be a result of steric hindrance in that each of the
compounds possesses three substantial alkyl chains and a
methyl group. However, Sommer and Bennett did report the
preparation of $O(CH_2CH_2)_2CHCH_2CH_2MgCl$ (25) which differs from
A-5 only in the absence of a methyl group two bonds removed
from the reaction center. If the Grignard reagents of A-2
or A-3 had been formed, they would have been treated with

PCl$_3$ to obtain I-4. After forming the Grignard derivative of A-5, it would have been reacted with PCl$_3$ to give O(CH$_2$CH$_2$)$_2$-C(CH$_3$)CH$_2$CH$_2$PCl$_2$ which could have yielded I-4 by the reaction sequence Sommer and Bennett used to form a polycyclic silane as illustrated in the introduction.

An attempt was also made to cyclize P(CH$_2$CH$_2$CN)$_3$ or P(CH$_2$CH$_2$CO$_2$C$_2$H$_5$)$_3$ using an alkoxide base to isolate I-4. Upon examination of the first intermediate (A-6) which would be formed in treating P(CH$_2$CH$_2$CO$_2$C$_2$H$_5$)$_3$ with NaOC$_2$H$_5$, it seems apparent that Ha, being the most acidic proton due to the withdrawing carbonyl groups, would be lost to $^-$OR and intramolecular cyclization could take place as shown to give the bicyclo[3.3.1] nonane A-7. However, as was reported in the experimental section, this cyclization did not take place. When P(CH$_2$CH$_2$CN)$_3$ was used, the product isolated after basic hydrolysis was not characterized because no volatile material resulted. By analogy to the volatile compounds I-XVI, poly-cyclic phosphines would be expected to be volatile as well.

A-6   A-7
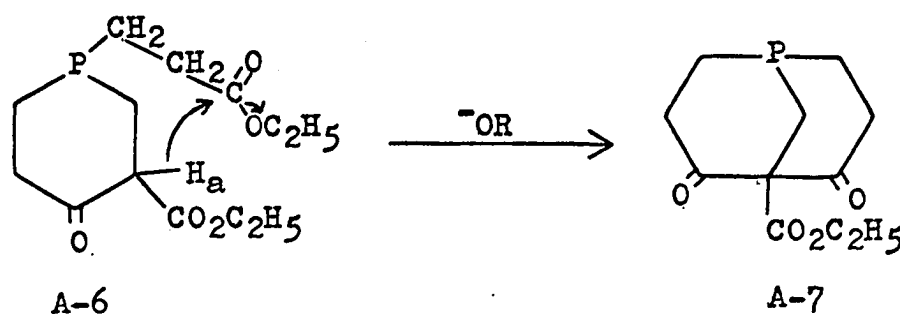
SUGGESTIONS FOR FUTURE WORK

It would be of interest to prepare the iron and nickel carbonyl derivatives of VIII and XI to see if a correlation could be found for the four-bond coupling constants analogous to that reported herein for J_{PCH}. Correlations of these interactions and POCCH and PCOCH interactions obtained from Lewis acid adducts of VIII and XI, respectively, would perhaps yield additional information concerning the additional coupling mechanism postulated for VIII, IX, and X. A determination of the signs of the four-bond interactions for compounds VIII to XIII might also be beneficial in describing this additional mechanism.

If J_{PCH} can be described in terms of the Fermi interaction alone, as proposed, then the preparation of the adducts of BF_3, $B(CH_3)_3$, and BH_3 of XIV as well as the preparation of phosphonium salts of XIV in conjunction with a study of their n.m.r. spectra should provide a check on this postulate. If the Fermi mechanism is dominant, then a good correlation between J_{PCH} for these derivatives and the electronegativity of substituents attached to phosphorus should be obtained analogous to those outlined in the introduction.

The study of metal carbonyl derivatives of XIV reported here is very incomplete. To better compare the donor ability of XIV to that of V, the XIV derivatives of chromium, molybdenum, and tungsten carbonyls should be synthesized and their

infrared spectra from 5000 to 50 cm^{-1} studied. From these spectra, CO, MC, and MP stretching frequencies could be assigned for derivatives of XIV. With this data and that obtained herein, a substantial comparison of these two ligands could be made using the far infrared data reported by Hendricker (11) for phosphite metal carbonyl derivatives.

The attempted preparation of $CH_3C(CH_2CH_2)_3P$ described in this dissertation might suggest that organometallic reactions will not afford the desired bicyclic phosphine. On the other hand, perhaps all that is needed is a suitable medium in which to carry out the reaction of a dilute solution of $CH_3C-(CH_2CH_2Br)_3$ with $NaPH_2$ in that these two do react when combined neat.

In addition to the above sodium phosphide reactant, salts such as $NaP(CH_2C_6H_5)_2$ or $Na_2PCH_2C_6H_5$ might be used. Reaction of these phosphides with the above tribromide would yield $BrCH_2CH_2C(CH_3)(CH_2CH_2)_2PCH_2C_6H_5$ or $(BrCH_2CH_2)_2C(CH_3)CH_2CH_2P-(CH_2C_6H_5)_2$ which would be analogous to the intermediates in the synthesis of $P(CH_2CH_2)_3P$ as outlined in the introduction. On heating either of these two intermediates, the cyclic phosphonium salts $[CH_3C(CH_2CH_2)_3PCH_2C_6H_5]^+$ Br^- or $[BrCH_2CH_2C(CH_3)-(CH_2CH_2)_2P(CH_2C_6H_5)_2]^+$ Br^- would form which could be reduced to $CH_3C(CH_2CH_2)_3P$ (I-4, R=CH_3) or $BrCH_2CH_2C(CH_3)(CH_2CH_2)_2-PCH_2C_6H_5$. The latter could be converted to the desired product by heating followed by reduction.

It might also be rewarding to react $CH_3C(CH_2CH_2Br)_3$ with

$(CH_3O)_3P$, which should give the Arbuzov product $(BrCH_2CH_2)_2$-$C(CH_3)CH_2CH_2P(O)(OCH_3)_2$. Treatment of this material with magnesium might give the phosphine oxide $CH_3C(CH_2CH_2)_3PO$. Alternately, the Arbuzov product might be reduced, followed by heating to give $BrCH_2CH_2C(CH_3)(CH_2CH_2)_2P(O)OCH_3$. Reduction of this last compound followed by heat would give the desired phosphine oxide, which should be reducible to I-4 ($R=CH_3$).

It would also be of interest to attempt a reaction between the trialcohol $CH_3C(CH_2CH_2OH)_3$ and PH_3 in hopes of forming the bicyclic phosphine I-4 ($R=CH_3$). In this connection, Maier (121) has reported the reaction of $H_2P(CH_2)_x$-PH_2 with R_2NCH_2OH to give $(R_2NCH_2)_2P(CH_2)_xP(CH_2NR_2)_2$ in excellent yields.

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