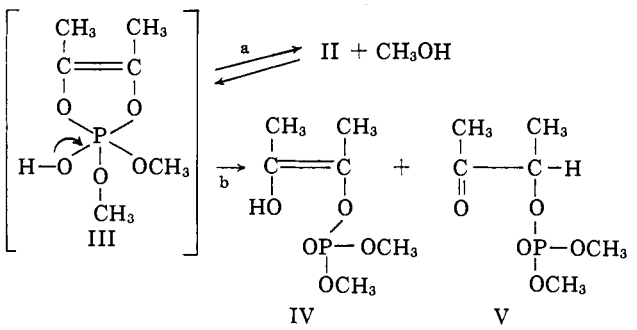
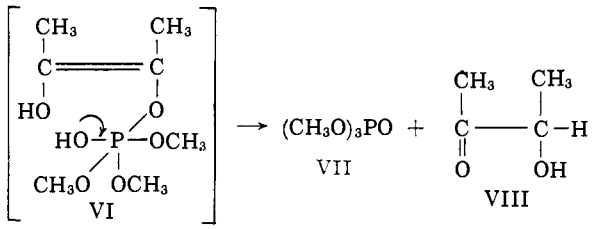
Spectral values are: $H^1$ n.m.r. ($\tau$ in p.p.m.): a 3 $H^1$ doublet, $J_{HP}$ = 11.5 c.p.s., at 6.24 ($CH_3O$), and a 6 $H^1$ singlet at 8.10 ($CH_3$ on olefin); $P^{31}$ n.m.r.[2e] (neat, at 40.5 Mc.p.s., in p.p.m. *vs.* 85% $H_3PO_4$): a 1:3:3:1 quartet, $J_{PH}$ = 12 c.p.s., at $-11.5 \pm 0.1$ (Figure 1). Strong bands in the infrared spectrum (in $CCl_4$) were caused by the P=O stretching vibrations (7.60 and 7.69 $\mu$), by the $POCH_3$ stretchings (9.48 and 8.40 $\mu$), and by the vinyl C–O stretching (8.30 $\mu$). Also, strong bands were found at 8.85, 10.10, and 11.20 $\mu$.

The course of the hydrolysis of the oxyphosphorane I was quite sensitive to temperature and to the nature of the solvent. Thus, when the temperature was allowed to rise to the boiling point of the benzene solution, the amount of II was very small and the amount of trimethyl phosphate (VII) increased considerably. The hydrolysis was conveniently followed by $H^1$ and $P^{31}$ n.m.r. spectroscopy; details will be given in the forthcoming paper.

The hydrolysis of the *unsaturated* oxyphosphorane I is a nucleophilic substitution[7] at quintuply connected phosphorus, *proceeding with considerable preservation of the ring*. It is suggested that an unstable oxyphosphorane III results from this substitution. Evidence has been given[8] for the operation of this mechanism in the hydrolysis of cyclic *saturated* oxyphosphoranes. III can collapse: (a) to the cyclic phosphate II and methanol; (b) to dimethylphosphoacetoin,[5] enol-IV, and keto-V. Some of the open phosphate V isolated in the hydrolysis came from the reaction of methanol with the cyclic phosphate II (*vide infra*); however, some V was formed directly, *i.e.*, from III.




Probably, the trimethyl phosphate (VII) obtained in the hydrolysis of I did not result from a secondary reaction of methanol with open phosphate V.[9] Compound VII could come from the unstable open oxyphosphorane VI resulting from an initial attack of water on I, with ring opening. Since acetoin (VIII) is more acidic than methanol, the collapse of VI should proceed to give VII + VIII.




(7) SN2, SN1, or *via* an intermediate with hexacoordinated phosphorus; no information is available on this point, which is under study in this laboratory.

(8) (a) F. Ramirez, O. P. Madan, N. B. Desai, S. Meyerson, and E. M. Banas, *J. Am. Chem. Soc.*, **85**, 2681 (1963); (b) F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963).

(9) Dimethylphosphoacetoin (V) and trimethyl phosphate are not affected by water in benzene solution under comparable conditions. The hydroxide ion catalyzed hydrolysis of V to acetoin and dimethylhydrogen phosphate in water is at least $2 \times 10^6$ times faster than that of trimethyl phosphate: F. Ramirez, B. Hansen, and N. B. Desai, *ibid.*, **84**, 4588 (1962).

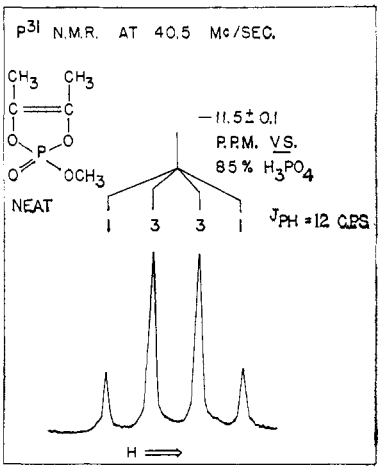
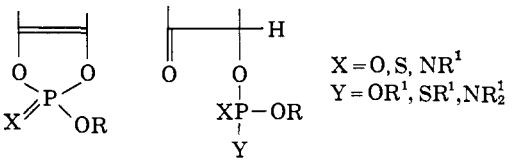



Figure 1.

The cyclic phosphate II reacted with 1 mole equiv. of methanol at 20°. $H^1$ n.m.r. disclosed the initial formation of the enol-IV and keto-V forms of dimethylphosphoacetoin.[2e,5] Finally, only the keto form remained. The methanolysis could involve the same intermediate III suggested for the hydrolysis of I, *i.e.*, the collapse of III to cyclic phosphate II is probably reversible. The addition of water to the phosphoryl group of five-membered cyclic phosphotriesters has been suggested[8] to explain the rapid hydrolysis of the latter to cyclic phosphodiesters.

The demonstration that both saturated[2e,8] and unsaturated cyclic oxyphosphoranes can be transformed stepwise into cyclic and open phosphates holds promise as a method of synthesis of a variety of phosphate derivatives, for example

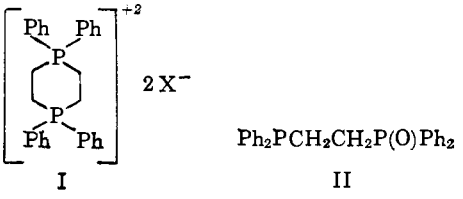



**Fausto Ramirez, O. P. Madan, C. P. Smith**
*Department of Chemistry*
*State University of New York at Stony Brook*
*Stony Brook, New York*
*Received December 14, 1964*

## The Abnormal Hydrolysis of Cyclic Diphosphonium Salts

*Sir:*

We wish to report the synthesis and basic hydrolysis of 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane dibromide (Ia, X = Br) to ethylenebis(diphenylphosphine) monoxide (II).



Reaction of equimolar amounts of ethylenebis(diphenylphosphine) and 1,2-dibromoethane in refluxing decalin or excess dibromoethane at atmospheric pressure led to precipitation of crystals of Ia (X = Br), m.p. 324–325°. *Anal.* Calcd. for $C_{28}H_{28}P_2Br_2$: C, 57.3; H, 4.8; P, 10.6; Br, 27.3. Found (after recrystallization from methanol–acetone): C, 56.91; H, 4.87; P, 10.72; Br, 27.53. The weight of product was essentially equal to that of the sum of the reagents used. It can therefore be concluded that I represents a 1:1 adduct of the reagents $[(Ph_2PCH_2)_2 \cdot (CH_2Br)_2]_n$.

The great solubility of Ia in water, the positive test for ionic halogen employing aqueous silver nitrate on the water solution of Ia, and the bands exhibited in the infrared spectrum of a KBr pellet of Ia show it to be a phosphonium salt. Treatment of an aqueous solution of Ia with aqueous solutions of sodium picrate or sodium salicylate produced immediate precipitates neither of which contained halogen, indicating that all of the bromine in Ia is ionic. The picrate Ib (X = picrate ion) was recrystallized from acetonitrile and methanol, m.p. 288–290°. *Anal.* Calcd. for $C_{40}H_{32}P_2N_6O_{14}$: N, 9.50. Found: N, 9.37. The salicylate Ic (X = salicylate ion) melted at 179–180° after recrystallization from water. *Anal.* Calcd. for $C_{42}H_{38}P_2O_6$: C, 72.0; H, 5.4; P, 8.8. Found: C, 72.13; H, 5.56; P, 8.76. Attempts at determination of the molecular weights of Ia, b, or c by ebullioscopic, cryoscopic, or osmometric methods gave unsatisfactory results. Direct evaporation of a sample of Ia into the ionization chamber of a high-resolution mass spectrometer from a small tube at 310° led to a mass spectrum in which the highest mass was 586, which would correspond to the molecular weight of Ia. There was no appreciable concentration of mass 293, which is the calculated molecular weight of the three-membered ring. High concentrations of masses 398 and 370 were found. Pyrolysis of Ia and similar salts have been shown to lead to ethylenebis(diphenylphosphine), mol. wt. 398.[1] Mass 370 corresponds to tetraphenylbiphosphine which is undoubtedly a major decomposition product.

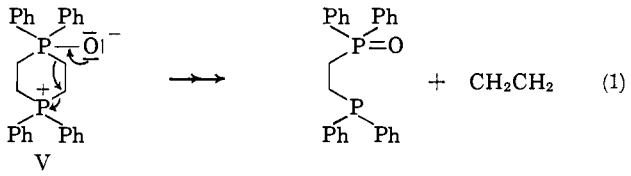
The proton magnetic resonance spectrum of a trifluoroacetic acid solution of Ia showed a doublet centered at $\delta$ = 4.0 p.p.m. with a $J_{P-CH}$ value of 6 c.p.s., as well as a rather sharp phenyl hydrogen peak at $\delta$ = 7.9 p.p.m. whose areas are in the ratio of 1:2.5. Griffin has found that an acetonitrile solution of ethylenebis(triphenylphosphonium) dibromide exhibits a doublet at $\tau$ 6.09 p.p.m. ($\delta$ 3.91), $J_{P-CH}$ = 5.0 c.p.s.[2] As expected, greater peak broadening is present in the cyclical compound. This is due to restricted rotation and noncoplanarity of the ring.

Mann has shown that ethylenebis(disubstituted phosphines) and 1,2 dibromoethane react to produce cyclical six-membered diphosphonium salts.[1,3] Rauhut, *et al.*, have shown that the cyclical six-membered diphosphonium salt is favored over polymer in the quaternization of $\beta$-acetoxyethyldialkylphosphines.[4]

Treatment of Ia with boiling aqueous sodium hydroxide gave ethylenebis(diphenylphosphine) monoxide (II).[5] Normal decomposition of quaternary phosphonium hydroxides is believed to involve an intermediate in which the hydroxyl group is covalently bonded to the phosphorus, which is then deprotonated by another hydroxide ion and finally decomposes in the rate-determining step to a tertiary phosphine oxide and a hydrocarbon.[6] Normal decomposition at the initially attacked phosphonium center would lead to IV, an analog of diethyldiphenylphosphonium hydroxide, expected to decompose normally to either ethylenebis(diphenylphosphine) dioxide or ethyldiphenylphosphine oxide.

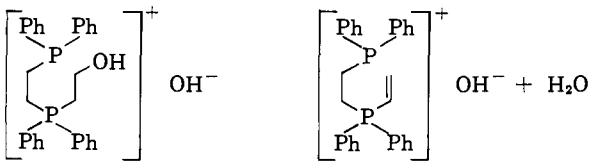
$$Ph_2P(O)CH_2CH_2P(Ph)_2CH_2CH_3^+\ OH^-$$
IV

Presumably the initial attack of hydroxide ion on Id (X = OH ion) follows the normal path to intermediate V (eq. 1). This intermediate may then

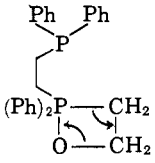



undergo a concerted $\beta$-elimination as shown in eq. 1.

Alternately, the initial attack may be at the carbon or hydrogen leading to either VI or VII, respectively.




Decomposition of VI *via* the "normal" path or by intramolecular attack *via* intermediate VIII would give ethylenebis(diphenylphosphine) monoxide. Decomposition of the vinylphosphonium salt VII is expected to proceed in the normal manner to give the same product.




VIII

A rationale for the lack of initial attack on phosphorus involves the fact that while the ring is intact both phosphorus atoms are constrained to an essentially tetrahedral $sp^3$-hybridization and are not free to assume the trigonal bipyramid structure of a pentacovalent phosphorus atom required in the "normal" decomposition. This is being investigated in cyclical monophosphonium salts.

*Acknowledgments.* This work was carried out under a grant from the Petroleum Research Fund of the American Chemical Society. All of the proton n.m.r. work was done by Mr. Gordon Boudreaux of the Spectroscopy Investigation of Cotton Physical Properties Laboratory, U. S. Southern Regional Utilization Research Center in New Orleans, La. The mass

(1) C. H. S. Hitchcock and F. G. Mann, *J. Chem. Soc.*, 2081 (1958).
(2) Private communication.
(3) R. C. Hinton and F. G. Mann, *J. Chem. Soc.*, 2835 (1959).
(4) M. M. Rauhut, G. B. Borowitz, and H. C. Gillham, *J. Org. Chem.*, **28**, 2565 (1963).
(5) A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, **86**, 5354 (1964).
(6) M. Zanger, C. A. VanderWerf, and W. E. McEwen, *ibid.*, **81**, 3806 (1959).

spectral work was done at the Humble Oil and Refining Company in Baytown, Texas and Baton Rouge, La.

**Adam M. Aguiar, Harriet Aguiar, Donald Daigle**
*Department of Chemistry, Tulane University*
*New Orleans 18, Louisiana*
*Received October 8, 1964*

## Metal–Metal Bonding Sequences Involving Three Different Metals

*Sir:*

A number of compounds have been reported which involve covalent bonds between two different metals in the sequence M–M′–M. A partial listing of some of the more recent would include Fe–Sn–Fe,[1a] Au–Fe–Au,[1b] Ge–Pt–Ge,[1c] Mn–Sn–Mn,[1d] Mn–Ge–Mn,[1e] and Ge–Hg–Ge.[1f] Dighe and Orchin[2] have now described a compound having a sequence of three different metals, $\pi$-$C_5H_5Fe(CO)_2HgCo(CO)_4$, which is evidently the first example of its type to be reported. We are therefore prompted to communicate a portion of our own work involving sequences M–M′–M″.

We have prepared several compounds of this general type by stepwise replacement of chlorine in dimethyltin dichloride. Thus pentacarbonylmanganesedimethyltin chloride (I) readily forms $\pi$-cyclopentadienyltricarbonylmolybdenum(pentacarbonylmanganese)dimethyltin (II) by reaction with $\pi$-cyclopentadienylmolybdenumtricarbonyl anion.

$$\underset{\text{I}}{(OC)_5Mn\text{–}Sn(CH_3)_2\text{–}Cl} \longrightarrow \underset{\text{II}}{(OC)_5Mn\text{–}Sn(CH_3)_2\text{–}Mo(CO)_3(\pi\text{-}C_5H_5)}$$

Compound II can be isolated from pentane–methylene chloride as yellow crystals, melting without decomposition at 95–96°. *Anal.* Calcd. for $C_{15}H_{11}O_8MoSnMn$: C, 30.60; H, 1.87; mol. wt., 589. Found: C, 31.2; H, 1.8; mol. wt.,[3] 565. The n.m.r. spectrum shows cyclopentadienyl protons at $\tau$ 4.65 and methyltin protons centered at $\tau$ 9.20; the ratio of areas is 5:6.4 (calcd. 5:6). Infrared carbonyl stretching bands are observed in carbon tetrachloride solution at 2090, 2085, 2056, 2001, 1924, and 1895 cm.$^{-1}$. These may be compared with the values 1997, 1922, and 1895 cm.$^{-1}$ observed[4] in the related compound $(CH_3)_3Sn$-$Mo(CO)_3(\pi$-$C_5H_5)$.

Other compounds which we have prepared are listed in Table I. An aspect of particular interest is the magnitude of spin coupling between methyl protons and the isotopes $^{117}Sn$ and $^{119}Sn$. A progressive decrease in the coupling constant occurs as the methyl groups of tetramethyltin are successively replaced by transition metal atoms.

The trend of coupling constants in relation to bond type can be understood in terms of two concepts applied by Flitcroft and Kaesz[5] in their study of spin–spin coupling in the methylstannanes: (a) that $H_3C$–*Sn* coupling will be proportional to the s-character of the hybrid tin orbital used in the bond to carbon, and (b) the s-character of an atom tends to concentrate in orbitals that are directed toward electropositive groups.[6] It thus appears that tin orbitals engaged in bonding to transition metals have more than 25% s-character, leaving the methyl-bonded tin orbitals with reduced s-character and diminished coupling constants.

**Table I.** Chemical Shifts and Coupling Constants for Methyltin Derivatives[a]

| Compound | $\tau_{CH_3}$ | $\tau_{C_5H_5}$ | $J(^{119}Sn\text{–}CH_3)$ |
|---|---|---|---|
| $(CH_3)_4Sn$[b] | 9.86 | | 54.0 |
| $(CH_3)_3Sn\text{–}Mo(CO)_3(\pi\text{-}C_5H_5)$ | 9.56 | 4.59[c] | 48.5 |
| $(CH_3)_3Sn\text{–}Fe(CO)_2(\pi\text{-}C_5H_5)$[c,d] | 9.55 | 5.11 | ~49 |
| $(CH_3)_2Sn[Mo(CO)_3(\pi\text{-}C_5H_5)]$-$[Mn(CO)_5]$ | 9.20 | 4.65[c] | 36.9 |
| $(CH_3)_2Sn[W(CO)_3(\pi\text{-}C_5H_5)][Mn(CO)_5]$ | 9.18 | 4.59 | 37.3 |

[a] Measured in $CCl_4$ using a Varian HR-100 spectrometer; $\tau$-values relative to tetramethylsilane as internal standard; coupling constant $J$ in c.p.s. [b] From ref. 5. [c] In $CHCl_3$ solution, using A-60 spectrometer. [d] J. Kenney and W. A. G. Graham, unpublished.

*Acknowledgment.* We thank the National Research Council of Canada for partial support of this work.

(1) (a) F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 179 (1964); (b) E. C. Coffey, J. Lewis, and R. S. Nyholm, *ibid.*, 1741 (1964); (c) R. J. Cross and F. Glockling, *Proc. Chem. Soc.*, 143 (1964); (d) R. D. Gorsich, *J. Am. Chem. Soc.*, **84**, 2486 (1962); (e) A. G. Massey, A. J. Park, and F. G. A. Stone, *ibid.*, **85**, 2021 (1963); (f) N. S. Vyazankin, G. A. Razuvaev, and E. N. Gladyshev, *Dokl. Akad. Nauk SSSR*, **151**, 1326 (1963); *Chem. Abstr.*, **59**, 14014 (1963).
(2) S. V. Dighe and M. Orchin, *J. Am. Chem. Soc.*, **86**, 3895 (1964).
(3) Mechrolab osmometer in chloroform solution.
(4) H. R. H. Patil and W. A. G. Graham, to be published.
(5) N. Flitcroft and H. D. Kaesz, *J. Am. Chem. Soc.*, **85**, 1377 (1963).
(6) H. A. Bent, *Can. J. Chem.*, **38**, 1235 (1960).

**H. R. H. Patil, W. A. G. Graham**
*Department of Chemistry, University of Alberta*
*Edmonton, Alberta*
*Received November 12, 1964*

## Hyperconjugative Enhancement of Geminal Coupling Constants

*Sir:*

Recent symposia[1,2] have emphasized that use of hyperconjugation for explaining certain molecular properties is a matter of considerable controversy. The disagreement centers on whether electron delocalization involving $\sigma$- and $\pi$-bonds or hybridizational changes in the connecting C–C $\sigma$-bond offers the best means for rationalizing the physical and chemical data. We now wish to present evidence which supports the former.

Work by Barfield and Grant[3] on $\pi$-bond enhancement of geminal coupling constants in adjacent methylene groups has impinged upon the problem by exhibiting the importance of hyperconjugative terms in the transmission of spin–spin couplings in a large number of unsaturated molecules. In this study the symmetry and molecular orientation were shown experimentally and theoretically to affect the degree of delocalization as detected by the modification of the spin–spin coupling constants.

The cumulated systems, allene and ketene, constitute pertinent cases for studying possible hyperconjugative effects. This is illustrated by structures I and II where the methylene group in each compound exhibits an unusually favorable orientation relative to the vicinal $\pi$-bond. Not only are these hydrogens locked into the same symmetry plane as the vicinal $\pi$-electron systems, but the C=C bond distances between the

(1) "The Conference on Hyperconjugation," Indiana University; *Tetrahedron*, **5**, 105 (1959).
(2) "Paper Symposium," *ibid.*, **17**, 123 (1962).
(3) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).