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CORRELATION OF PROTON CHEMICAL SHIFT AND ^{31}P-H SPIN-SPIN COUPLING CONSTANTS FOR ORGANOPHOSPHORUS DERIVATIVES[1]

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Abstract—The chemical shifts and ^{31}P-H spin-spin coupling constants of protons on saturated C—H groups have been examined for a variety of model organophosphorus compounds. Correlations of these data with the charge on the phosphorus atom and proximity of hydrogen atoms to that nucleus are suggested. and related to other data previously reported in the literature.

INTRODUCTION

THE proton magnetic resonance spectra of organophosphorus compounds exhibit an extra facet of interest and information in that the phosphorus-31 nuclei (100% of the natural abundance of phosphorus) have a spin of 1/2 and so are capable of splitting the signals of proximate protons in the molecule. Some rudimentary correlations of ^{31}P-H coupling constants and structure in organophosphorus compounds have been obtained from ^{31}P magnetic resonance, summarized by Jones and Katritsky,[3a] as well as in a recent article[3b] not covered in that review. In general, however, because of the relatively small magnitude of most ^{31}P-H couplings, and the multiplicity of the ^{31}P signal arising from the splittings of nearby protons (i.e., for $(CH_3)_3P$, a decet is expected for the ^{31}P resonance, not easily resolved, while the proton resonance shows a well separated doublet at high resolution) these spectra have proved not to be a good source of ^{31}P-H coupling constants. A number of studies of proton resonance of organophosphorus compounds have been reported, and some useful data on chemical shift and spin-spin coupling constants are now known.[4]

Spurred by examples of splitting of proton resonances by ^{31}P in certain organophosphorus compounds prepared in connection with other work,[5] we have prepared and collected data from a number of model compounds for general NMR studies of this effect. In particular we sought to ascertain the chemical shifts and coupling constants of proton signals and their variation both with the distance of the proton from the ^{31}P nucleus and with the charge or covalency of that nucleus Our results are consistent with the earlier correlations that have been achieved in this field.

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[3a] R. A. Y. Jones and A. R. Katritsky, *Angew. Chem.* **74**, 60 (1962); [b] L. C. D. Groenweghe, L. Maier and K. Moedritzer, *J. Phys. Chem.* **66**, 901 (1962).

[4a] G. O. Dudek, *J. Chem. Phys.* 33, 624 (1960); [b] R. C. Axtmann, W. E. Shuler and J. H. Eberly, *Ibid.* **31**, 851 (1959); [c] H. David, G. Martin, G. Mavel and G. Sturtz, *Bull. Soc. chim. Fr.* 1616 (1962) and refs. *loc. cit.*

[5a] H. D. Kaesz and F. G. A. Stone, *J. Amer. Chem. Soc.* **82**, 6213 (1960); [b] J. B. Hendrickson, *Ibid.* **83**, 2018 (1961); [c] J. B. Hendrickson, J. J. Sims and R. E. Spenger, *Tetrahedron* **19**, 707 (1963).

EXPERIMENTAL

Trialkylphosphines. These were prepared by the Grignard reaction of the appropriate alkylmagnesium chloride (in tetrahydrofuran or diethyl ether) and PCl_3. The best yields were obtained when a large excess of the chloro-Grignard was used, at as high a dilution of this reagent as feasible (1 mole or less of RMgCl per liter of the ether and kept as at low a temperature as possible down to −78°) during the addition of the ether solution of PCl_3. In the case of $(CH_3)_3P$, this material is distilled out of the reaction flask along with the solvent, before the normal hydrolysis step. The phosphine may be precipitated from the ether solution by formation of the hydrochloride (using rigorously dried HCl gas, passed through a −78° trap). The extremely hygroscopic white precipitate is filtered (or separated from the ether by decantation) and the remaining ether removed by evaporation at red. press. A quantity of the hydrochloride may then be taken directly into $CHCl_3$ solution for proton magnetic resonance. The free phosphine is liberated from its hydrochloride using saturated NaOH solution, and finally dried (NaOH). On account of the volatility and air-sensitivity of $(CH_3)_3P$, it was handled, after regeneration from the hydrochloride, in a chemical high-vacuum system. $(C_2H_5)_3P$ is isolated by normal work-up of a Grignard reaction. $(CH_2{=}CH){-}(CH_3)_2P$ was prepared by the method outlined by Kaesz and Stone.[6]

Triphenylphosphonium salts. These were prepared from solutions of equimolar quantities of ϕ_3P and the appropriate halide in $CHCl_3$ by refluxing ½ hr. When the $CHCl_3$ was boiled off, ether was added to the resultant syrup, and crystals of the salt were obtained which were recrystallized from ether–methanol. In the cases of isopropyl and isobutyl iodides it was necessary to carry out the reaction in pressure flasks at 180°. The m.ps. corresponded with or were slightly higher than those previously reported and are given in parentheses in Table 1. $(CH_3{-}O{-}CH_2)(C_6H_5)_3P^+, Cl^-$ is apparently a new compound, m.p. 192–4°. (Found: C, 70·01; H, 5·75. Calc. for $C_{20}H_{20}POCl$: C, 70·07; H, 5·88%).

Other phosphonium salts. These were prepared by treating the appropriate alkyl phosphine with either HCl or an alkyl iodide in the chemical high-vacuum system. The resulting salt was freed from excess alkyl iodide, and dissolved in either $CDCl_3$, $CHCl_3$ or D_2O for magnetic resonance measurements. In all cases, the maximum concentration possible was used. $(CH_3)_3(CH_2{=}CH)P^+, I^-$ is apparently a new compound prepared from $(CH_3)_2(CH_2{=}CH)P$ (see above) and CH_3I. (Found: C = 25·96, H = 5·21. Calc. for $C_5H_{12}PI$: C = 26·10, H = 5·26%).

Other phosphorus valencies. $(CH_3)_3P{=}O$ and $(CH_3CH_2)_3PO$ were obtained through oxidation of the corresponding phosphine with 15% H_2O_2. After a period of 6 hr had elapsed, excess peroxide was destroyed by a catalase solution. The oxide was salted out of the aqueous medium by NaCl and Mg_2SO_4, and washed away from the salts with ether. The ether was evaporated at reduced pressure, and the resulting phosphine oxide studied as the neat liquid, or in solution in $CHCl_3$. $(CH_3)_3PCl_2$ was obtained as a hygroscopic precipitate resulting from the chlorination of an ether solution of $(CH_3)_3P$. Hydrolysis of this dihalide yielded a material in aqueous solution whose $^{31}P{-}CH_3$ coupling constant was the same as that for the $(CH_3)_3P{=}O$ prepared previously. *Triethylphosphine sulfide* was obtained by treating a solution of the phosphine in Et_2O under N_2 with an excess of sulfur.[7] Reaction was immediate. Solvent was evaporated in a stream of N_2 and residue extracted with boiling H_2O. The cooled solution deposited long needles m.p. 96–7°. A similar procedure[7] was used to obtain *trimethylphosphine sulfide.*

Proton magnetic resonances were obtained with a Varian A-60 Spectrometer. In each case where solubility permitted, tetramethylsilane was added to the contents of the sample tube as internal reference. In the aqueous solutions, a capillary tube containing that reference compound was used as external standard.

RESULTS

The observed chemical shifts and coupling constants are listed in Table 1. Only the resonances of the protons on alkyl groups are reported; those of the phenyl and vinyl groups, wherever these appear in the phosphorus derivatives are not being considered here nor reported in detail. These resonances appeared at a chemical shift and a multiplicity essentially as expected of them. The resonance of protons of

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[6] H. D. Kaesz and F. G. A. Stone, *J. Org. Chem.* **24**, 635 (1959).

[7] Cahours and Hofmann, *Liebigs Ann.* **104**, 1 (1857).

the phenyl group in phosphonium salts and other phenyl derivatives in which the phosphorus atom is more or less strongly positively charged, closely resembled those of phenyl groups on carbonium ions,[8] and an analysis of these could yield interesting information about the resonance interactions between phosphorus and phenyl rings in these derivatives In the multiplet pattern for each of the phenyl groups, the strongest peak was observed in each of the compounds at the following positions: $\phi_3PCH_3^+$, I^-, $\tau = 2{\cdot}35$; $\phi_3PCH_2CH_3^+$, I^-, $\tau = 2{\cdot}31$; $\phi_3PCH(CH_3)_2^+$, I^-, $\tau = 2{\cdot}23$; $\phi_3PCH_2CH(CH_3)_2^+$, I^-, $\tau = 2{\cdot}28$; $\phi_3PCH_2CO_2CH_3^+$, Cl^-, $\tau = 2{\cdot}29$; $\phi_3PCH_2OCH_3^+$, Cl^-, $\tau = 2{\cdot}32$; $\phi_3PCH_2COCH_3^+$, Cl^-, $\tau = 2{\cdot}42$. Under these same conditions, we observed ϕ_3P $\tau = 2{\cdot}90$. These resonances, as well as those of the vinyl group protons, will require separate study

The resonances of protons of methyl groups bonded to phosphorus are simple doublets due to $^{31}PCH_3$ coupling. The resonances of protons of ethyl groups involved analysis of more complexity. For an ethyl group bonded to a quaternary phosphorus atom, the CH_3 and CH_2 resonances are separated from each other by a sufficient chemical shift to yield essentially first order patterns for each. However, the methylene proton resonances appear as overlapping quartets owing to the closeness of constants between CH_3-CH_2 and CH_2-P^+ coupling as observed for the derivatives $(CH_3CH_2)_4P^+$ I^-, $(CH_3CH_2)(\phi)_3P^+$, I^-, see Figs. 1-A and 2. Our assignments were guided by the general trends of similar parameters observed elsewhere, and are given schematically on each of the figures containing such overlapping multiplet patterns. For instance, the methylene resonances for $(CH_3CH_2O)_3P$ are also observed to be overlapping multiplets. The symmetrical five line pattern has been previously analyzed through the use of ^1H-$\{^{31}P\}$ double resonance.[9] it was established that the observed pattern was composed of overlapping quartets.[9] We have used proton-proton double resonance,[10] CH_2-$\{CH_3\}$ and CH_3-$\{CH_2\}$, to single out the ^{31}P-H coupling, and confirm the assignments for the overlapping multiplets listed in Table 1.

The resonances for the protons of the ethyl groups in the other derivatives presented here, such as $(CH_3CH_2)_3PO$, $(CH_3CH_2)_3PS$ and $(CH_3CH_2)_3P$, were entirely second order owing to the small chemical shift separation between the CH_3 and CH_2 protons, and were analyzed by the aid of computer techniques using the self-iterating program of Swalen and Reilly[11] on the IBM 7090 computer at U.C.L.A. The observed second order patterns are presented in Figures 3 and 4 together with the spectra computed for these from the parameters listed in Table 1. In the calculations, it was necessary to assume that the protons of one ethyl group did not interact with the protons of a different ethyl group, so that we could treat this as a six spin system, A_3B_2X, rather than a sixteen spin system $(A_3B_2)_3X$. The calculation was further simplified by treating the system as two separate sets of superimposed A_3B_2 spectra, with the spin of "X" (phosphorus) fixed in one orientation for one set, and in the opposite orientation for the other set This method also yielded a cross-check, as the

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[8] cf. R. S. Berry, R. Dehl and W. R. Vaughan, *J. Phys. Chem.* **34**, 1460 (1961), and references *loc. cit.*

[9] J. N. Shoolery, cf. reference 95 and paragraph I, Section V in J. D. Baldeschweiler and E. W. Randall *Chemical Applications of Nuclear Double Resonance*, *Chem. Revs.* **63**, 81 (1963).

[10] Using the Varian V-3521 A integrator on a high-resolution spectrometer equipped with 60 Mc/s fixed frequency unit V-4311; we are indebted to Professor C. S. Foote of this Department for assistance in this phase of the work.

[11] J. D. Swalen and C. A. Reilly, *J. Chem. Phys.* 37, 21 (1962).

TABLE 1. MAGNETIC RESONANCE OF ALKYL GROUP PROTONS IN ORGANOPHOSPHOROUS COMPOUNDS

	H_α				H_β				H_γ				
	M^a	τ^a	J_{PH} c/s	J_{HH} c/s	M^a	τ^a	J_{PH} c/s	J_{HH} c/s	M^a	τ^a	J_{PH} c/s	J_{HH} c/s	Solvent
1. Trivalent phosphorus compounds													
$(CH_3)_3P$	2	9·11	2·7	—	—	—	—	—	—	—	—	—	Neat
$(CH_3)_2PCH{=}CH_2$	2	9·05	2·9	—	—	—	—	—	—	—	—	—	Neat
$(CH_3CH_2)_3P^b$	c	8·8	0·5	7·6	c	9·04	13·7	7·6	—	—	—	—	Neat
2. Tetravalent phosphonium salts													
$(CH_3)_4P^+$, I^-	2	7·53	14·4	—	—	—	—	—	—	—	—	—	$CDCl_3$
$(CH_3)_3PH^+$, Cl^{-d}	2	7·7	15·7	—	—	—	—	—	—	—	—	—	D_2O
$(CH_3)_3PCH{=}CH_2^+$, I^-	2	7·20	14·7	—	—	—	—	—	—	—	—	—	D_2O
$(CH_3CH_2)_4P^+$, I^-	$[2 \times 4]^e$	7·48	13	7·3	2×3	8·72	18·0	7·3	—	—	—	—	$CHCl_3$
$(CH_3CH_2)_4P^+$, I^{-f}	c	$7{\cdot}36_5$	$12{\cdot}7_6$	7·64	c	$8{\cdot}37_5$	$17{\cdot}9_8$	—	—	—	—	—	D_2O
$CH_3P\phi_3^+$, I^- (185–6°)	2	6·88	13·2	—	—	—	—	—	—	—	—	—	$CDCl_3$
	2	6·83	14	—	—	—	—	—	—	—	—	—	D_2O
$CH_3CH_2P\phi_3^+$, I^- (167–8°)	$[2 \times 4]^e$	6·35	14	7	2×3	8·70	19·6	7	—	—	—	—	$CDCl_3$
$(CH_3)_2CHP\phi_3^+$, I^- (199°)	c	~5	c	c	2×2	8·70	18·5	7	—	—	—	—	$CDCl_3$
$(CH_3)_2CHCH_2P\phi_3^+$, I^- (186–8°)	2×2	6·38	13·3	6·5	c	~7·8	c	c	2	8·98	0	7	$CDCl_3$

TABLE 1. (contd)

$CH_3OCOCH_2P\phi_3^+$, Cl^- (196°)	2	4·30	13·6	—	—	—	—	—	—	—	—	—	$CDCl_3$
$CH_3OCH_2P\phi_3^+$, Cl^- (192–4°)	2	4·18	4	—	—	—	—	—	1	6·40	0	—	$CDCl_3$
$CH_3COCH_2P\phi_3^+$, Cl^- (241–2°)	2	3·87	11·5	—	—	—	—	—	1	7·58	0	0	$CDCl_3$
3. Other phosphorus valencies													
$(CH_3)_3PO$	2	8·07	13·4	—	—	—	—	—	—	—	—	—	D_2O
$(CH_3)_3PS$	2	8·26	13·0	—	—	—	—	—	—	—	—	—	$CDCl_3$
$(CH_3)_3PCl_2$	2	7·52	13·8	—	—	—	—	—	—	—	—	—	$CHCl_3$
$(CH_3CH_2)_3PO$[f]	c	8·35	11·9	7·75	c	8·9	16·3	7·75	—	—	—	—	$CHCl_3$
$(CH_3CH_2)_3PS$[f]	c	8·19	11·3	7·5	c	8·83	18·1	7·5	—	—	—	—	$CHCl_3$
$(CH_3CH_2)_3PBr_2$	2 × 4[e]	7·38	8·0	7·5	2 × 3[e]	8·91	23·0	7·5	—	—	—	—	$CHCl_3$

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[a] Resonances were observed at the multiplicity given under M. Centre of resonance given in τ-value, i.e. p.p.m. with respect to $(CH_3)_4Si\tau = 10{\cdot}00$, cf., G. V. D. Tiers, *J. Phys. Chem.* **62**, 1151 (1958).

[b] Previously reported by P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.* **34**, 1049 (1961); the parameters listed here differ significantly only in the chemical shift for the methylene protons (our assignment is 1·0 c.p.s. further downfield, in a total of 12 c.p.s.). The present parameters gave a calculated spectrum which was fit to the observed spectrum to within 0·001 c.p.s. (root mean square deviation).

[c] c = complex, second order

[d] Previously reported by B. Silver and Z. Luz, *J. Amer. Chem. Soc.* **83**, 786 (1961), 16·6 ± 0·8 c.p.s., for P—CH_3 coupling constant. We did not observe the PH resonance, nor its coupling on account of the pH of our medium.

[e] Overlapping multiplets; see Figs 1 and 2, and discussion in text.

[f] Second order resonances, see Figs 1a, 3 and 4, and discussion in text.

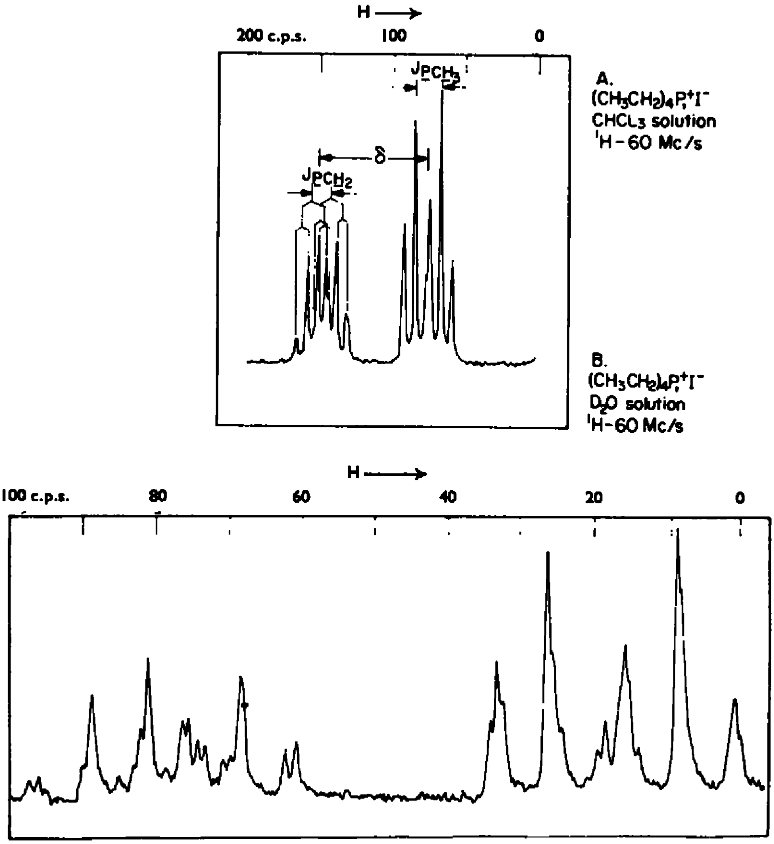

Fig. 1. Proton magnetic resonance spectra of $(CH_3CH_2)_4P^+$, I^-, 60 Mc/s/A. $CHCl_3$ solution (saturated). B. D_2O solution, (saturated), high resolution.

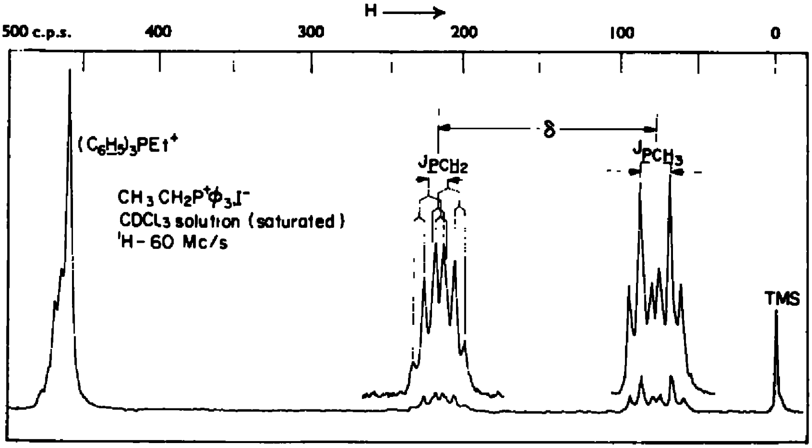

Fig. 2. Proton magnetic resonance spectrum of $CH_3CH_2P\phi_3^+$, I^-, 60 Mc/s, saturated $CHCl_3$ solution.

corresponding coupling constants from each set must be identical.[12] The parameters listed in Table 1 were obtained from computed spectra which were fit to the observed spectra with the following average deviations: Et_3P, 0·021; Et_3PO, 0·65; Et_3PS, 0·004; Et_4P^+, I^-, 0·084, c p s. We have avoided reporting relative signs for these calculated coupling constants because we were unable to make a sufficiently clear choice among the calculated spectra obtained from each of the possible permutations of relative signs. This is due to the nature of the spectra, as can be seen in Figs. 3 and 4, or in the spectrum of Et_3P, found in the literature reference cited in footnote (*b*) in Table 1. Because many of the required transitions are not separated from each other in the observed spectra, small changes in computed spectra did not markedly affect the comparison of calculated to observed spectra. For instance, in the case of Et_3P the average deviation reported above was obtained for the following combination of relative signs of the coupling constants: $\mp J_{p\text{-}H\alpha} \pm J_{p\text{-}H\beta} \pm J_{H\text{-}H}$. The average deviation of calculated to observed spectrum for the combination of signs $\mp$, $\pm$, $\mp$, respectively, was 0·22, and for the combination $\pm$, $\pm$, $\pm$, it was still only 0·028 c.p.s. This is insufficient evidence to base any assignment of relative signs of coupling constants at this time.

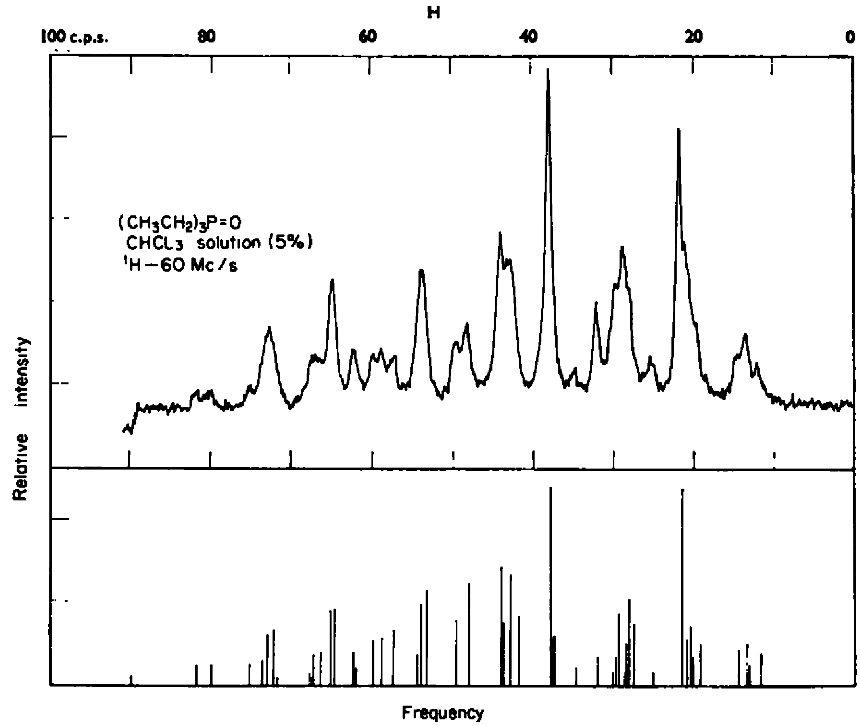

FIG. 3. Experimental (top) and theoretical (bottom) proton magnetic resonance spectra of $(CH_3CH_2)_3P{=}O$, 60 Mc/s, $CHCl_3$ solution (5%); the theoretical spectrum is calculated for the parameters listed in Table 1 for this compound.

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[12] cf. analysis of spectrum of trivinylphosphine, W. A. Anderson, R. Freeman and C. A. Reilly, *J. Chem. Phys.* 39, 1518 (1963).

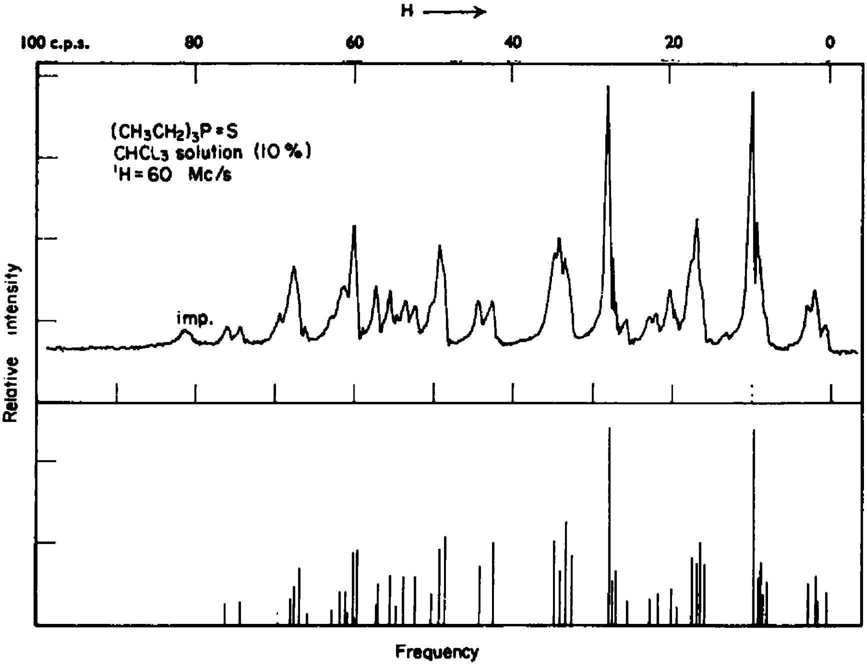

FIG. 4. Experimental (top) and theoretical (bottom) proton magnetic resonance spectra of $(CH_3CH_2)_3P{=}S$, 60 Mc/s, $CHCl_3$ solution (10%); the theoretical spectrum is calculated for the parameters listed in Table 1 for this compound.

DISCUSSION

The chemical shifts of the protons of the alkyl groups in the organophosphorus derivatives reported here depend largely on their proximity to the phosphorus atom and the charge on this atom as determined by the groups that are substituted on it, similar to observations[13a] made on other derivatives of phosphorus. In neutral phosphines, alkyl proton resonances are located near $\tau = 9$, and there is only a small chemical shift between resonance of the α and that of the β protons, as for instance, observed in $(CH_3CH_2)_3P$. On forming a quaternary salt, the α protons are shifted downfield by about 1·5 p.p.m. due to the presence of the positive charge on phosphorus. This effect is seen rapidly to decay; the beta protons in $(CH_3CH_2)_4P^+$ are found shifted downfield by only approximately 0·3 p.p.m. from their resonance in neutral phosphines. Gamma protons of alkyl groups in quaternary phosphorus salts are seen shifted downfield by approximately a little less than 0·1 p.p.m. of their resonance in neutral phosphines.

The formation of a phosphine oxide from a neutral phosphine creates essentially the same effects on the downfield shift of the protons as the quaternization of the phosphorus atom, only to a lesser extent. Through the expansion of the valency shell of phosphorus with empty 3d orbitals, there is some charge transfer back into these orbitals from unshared pairs on oxygen. In the phosphine sulfides, the phosphorus atom is even less positively charged, as reflected in the lesser downfield shift

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[13a] G. Mavel and G. Martin, *J. Chim. Phys.* **59**, 762 (1962); [b] G. Martin and G. Mavel, *C. R. Acad. Sci. Paris* **252**, 110 (1961).

of proton resonances from their position in the neutral phosphines. These observations are similar to those observed in the series $CH_3P(X)Cl_2$, X=O, S and Se, and $(CH_3)_4P^+$, I^-.[13b]

The spin-spin coupling ^{31}P-H in this series of derivatives also varies in a uniform manner, one which we believe can be correlated with positive charge on phosphorus. While the chemical shift of a proton is seen to move towards lower field in the series of derivatives $(CH_3)_3P$, $(CH_3)_3PS$, $(CH_3)_3PO$ and $(CH_3)_4P^+$, the coupling ^{31}P-CH_3 is seen to *increase*. This was also noted in the series mentioned above, reported by Martin and Mavel. Such an effect, we believe, may be explained by a combination of the theories of spin-spin coupling and the effects of electronegativity on the hybridization of a central atom. These have been noted before, for instance in the series of alkyltin halides[14] and also recently applied to hybridization of carbon in selected series of organometallic compounds.[15]

The sigma-electron contact contribution[16] to the spin-spin coupling constant between two nuclei is considered in the main to be directly proportional to the product of the electron densities of the two bonding orbitals, through which they interact, at their respective nuclei. For covalently bonded hydrogen, the contribution is considered to be essentially the same as that for hydrogen in the 1s state, but for atoms with hybridized bonding orbitals, the contact contribution is proportional to the percent *s*-character in the hybridized orbital used in forming the bond. In the P-CH_3 system, we take the contribution of the orbitals of carbon to be nearly constant in the series of derivatives. The most important factor in any of the changes observed in that coupling then is taken to be the change in hybridization of the phosphorus atom, i.e. the change in the percent *s*-character in the phosphorus orbital of the P-CH_3 bond. The hybridization of the orbitals of phosphorus will however depend on the relative electronegativities of the substituents. Making use of the concepts recently expressed and summarized by Bent[17] we can expect that the *s*-orbital of an atom tends to concentrate in the hybrid orbitals that are directed to the less electronegative groups. An unshared pair, such as that in the neutral phosphines, may generally be regarded as electrons bound to an atom of essentially zero electronegativity. If so, this would place a great deal of *s*-character in the lone pair, and decrease that in the phosphorus orbitals in the P-CH_3 bonds. The coupling ^{31}P-CH_3 is seen to be at a minimum in trimethyl phosphine, and slowly to increase as groups of increasing electronegativity are placed on phosphorus, rising to a maximum in $(CH_3)_4P^+$. This trend implies relative electronegativities of the substituents in the neutral phosphine in the order $CH_3^+ > Cl_2 > O > S$ as also reflected by the trends in chemical shift of the protons in these derivatives and thus the effects of these substituents on both chemical shift and ^{31}P-CH_3 coupling parameters are correlated. The electronegativity of a substituent leads to the placing of positive charge on the central phosphorus atom, and also serves to divert *s*-character into the orbitals of phosphorus directed towards relatively less electronegative groups. We assume that in the tetramethyl phosphonium salt, all four methyl groups are equivalently bonded

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[14] J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.* **83**, 3903 (1961).

[15] G. Mavel, *J. Chim. Phys.* **59**, 683 (1962).

[16a] N. F. Ramsey, *Phys. Rev.* **91**, 303 (1953); [b] M. Karplus and D. H. Anderson, *J. Chem. Phys.* **30**, 6 (1959).

[17] H. A. Bent, *Chem. Revs.* **60**, 275 (1960) and *Canad. J. Chem.* **38**, 1235 (1960).

to phosphorus so that in this derivative all four phosphorus hybrid orbitals contain the same, i.e. 25%, *s*-character. This comes to a minimum in the free phosphine, where the lone pair receives the dominant contribution of *s*-character. The same trends observed for the α protons in the methyl groups are also observed for both α and β protons in the ethyl groups, in the series Et_3P, Et_3PO and Et_4P^+. Starting in the neutral phosphine, the couplings ^{31}P-CH_2- and ^{31}P-CH$_2$-CH$_3$ are both seen to increase in the series of ethyl derivatives, just as the ^{31}P-CH$_3$ coupling constant was found to increase in the series of methyl derivatives. However, the proton chemical shifts and ^{31}P-H coupling constants in the derivatives $(CH_3CH_2)_3PS$ and $(CH_3CH_2)_3$ PBr_2 do not seem to fit into these correlations. It is entirely possible that these might not apply, without some modification, to groups more complicated than methyl. The breakdown of simple valence-bond picture of coupling is manifest already in the observed greater coupling ^{31}P-CH$_2$-CH_3 over that for ^{31}P-CH_2CH$_3$. This has been discussed by Mavel[15] and attributed to effects of second order hybridization on the *alpha* carbon atom (reflecting the greater electronegativity of the H atom compared to the CH$_3$ group as substituents on carbon). But it is evident that a more sophisticated view will be necessary, as can be seen for instance from the discussion by Klose.[18] There are positive and negative contributions to the coupling constant, and the interplay of factors regulating these might perhaps rival the effects of second-order hybridization.[19]

SUMMARY AND CONCLUSION

The values for the chemical shifts and coupling constants obtained, given in Table 1, permit a number of useful inferences to be made. It is clear that phosphorus nuclei cause splitting of the proton signal for protons attached to saturated carbon either α- or β- to the phosphorus atom, but in no case is splitting observed for more remote protons (γ- or beyond). Several further cases have been recently reported[20] in which no coupling of phosphorus with γ protons was observed. This is in direct conflict with the assignments by Martin and Mavel[21] of proton resonances of a series of propyl substituted phosphorus derivatives. The resonances are mostly second order, and we do not believe the assignments presented by these workers to be reasonable.

The magnitude of phosphorus coupling is greater at the β-hydrogen than at the α-hydrogen. The change from trivalent neutral phosphorus to the tetravalent and positively charged phosphonium ion is accompanied by a chemical shift in the proton resonance to lower field, as anticipated from the change in electronegativity of the phosphorus atom. The P-H coupling constants also show a considerable enhancement on changing from neutral trivalent to charged tetravalent phosphorus, the slight 3 c.p.s. coupling of the α-protons in the former being raised to 8–15 c.p.s. in the latter, while the β-protons in the phosphonium salts are split by 18–23 c.p.s. This behavior is summarized in Table 2.

[18] G. Klose, *Ann. Physik.* **7**, 262 (1962) and references *loc. cit.*

[19] For instance, it has been pointed out that for atoms containing nonbonding electrons, a configuration interaction of low-lying triplet states with bonding M.O.'s joining the coupled atoms can lead to a contribution to the coupling of *opposite* sign to the sigma contribution, and result in a lowered net observed coupling constant, cf. J. R. Holmes, D. Kivelson and W. C. Drinkard, *J. Chem. Phys.* **37**, 150 (1962).

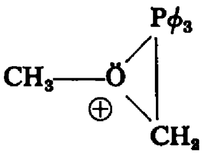
[20] T. H. Siddall and C. A. Prohaska, *J Amer Chem. Soc.* **84**, 2502 (1962).

[21] G. Martin and G. Mavel, *C. R. Acad. Sci., Paris* **253**, 2523 (1961).

TABLE 2. SUMMARY OF PROTON RESONANCES

		H_α	H_β	H_γ
Trivalent P:	$\tau =$	9·1	9·1	
	J_{PH}	3 c.p.s.	10 c.p.s.	
Tetravalent $P^{\oplus}$	$\tau =$	6·4–6·9	8·7	9·0
	J_{PH}	8–15 c.p.s.	18–23 c.p.s.	0 c.p.s.

In two of the phosphonium salts the α-protons exhibit significantly lower splitting by the adjacent phosphorus; in acetonyl-triphenylphosphonium chloride the constant is 11·5 c.p.s. while in methoxymethyl-triphenylphosphonium chloride the splitting is only 4 c.p.s. It is tentatively suggested that the oxygen in these compounds is partially bound to the positive phosphorus affording resonance forms such as I in which the phosphorus atom becomes pentacovalent and its positive charge much diffused and reduced.



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