SOME OBSERVATIONS ON THE PROTON MAGNETIC RESONANCE SPECTRA OF PHOSPHONIUM SALTS

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A study of the proton magnetic resonance (PMR) spectra of a number of tetra-alkyl(aryl)phosphonium salts has recently been reported by Hendrickson, Maddox, Sims and Kaesz[1]; chemical shifts and phosphorus–proton coupling constants were related to internuclear distance and the charge or covalency of the phosphorus atom by comparison with the corresponding phosphines. Less extensive studies of the PMR spectra of phosphonium salts have been reported by Martin and Mavel[2], Horn and Rothstein[3], Zimmer[4], Seyferth[5], Schweizer[6] and Griffin[7] and demonstrations of the utility of PMR spectra in the determination of the structure of complex salts[8] and in studies of the kinetics of reactions of salts[9] have been reported. This paper describes the PMR spectra of a number of representative alkyl-, benzyl- and allyl-triphenyl- and -trialkylphosphonium salts and alkylenebis(triphenylphosphonium) salts with an indication of the effects of factors such as solvent, concentration, temperature and substitution on chemical shifts and the geminal ^{31}P–H coupling constant.

The observed PMR parameters for the compounds studied are listed in Tables 1 and 2. The values obtained for compounds (I), (II) and (III) are in excellent agreement with those reported in the literature[1]. In each case for which chemical shift and coupling constant values are listed, the spectra were well resolved; the absorptions possessed the anticipated multiplicities and were interpretable by first order analysis. In only one case, ethylenebis(triphenylphosphonium) dibromide (XXX), was a second order spectrum observed; the methylene resonance of (XXX) was a poorly resolved doublet with a line separation of 5.0–5.2 cps. A similar deviation from first order multiplicity has been observed in the spectrum of the related ethylenebis(diphenylphosphine) dioxide[10].

The chemical shifts of the α-protons reflect the deshielding ability of the quaternary phosphorus with this effect being rapidly attenuated for β- and more remote protons; similar observations have been reported by Hendrickson *et al.*[1]. The observed ^{31}P–H coupling constants for α- (12.4–16.2 cps) and β- (18.7–20.0 cps) protons fall in the approximate ranges (α-, 12.4–15.7; β-, 17.2–19.6 cps) found by previous workers[1,2,5]. The only compound for which $|J_{PCH}|$ fell outside these ranges was benzhydryltriphenylphosphonium chloride (XVI). Both chemical shifts and geminal ^{31}P–H coupling constants are solvent-dependent; a marked upfield shift is observed consistently for α-protons in trifluoroacetic acid as compared to deuterochloroform.

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The solvent dependence of $|J_{PCH}|$ in the benzylphosphonium salts (VII), (XIII) and (XXV) has been discussed in an earlier study[11]. The use of trifluoroacetic acid as a solvent for these salts is highly advantageous since many of the salts have limited or negligible solubility in chloroform or other common solvents, including dimethyl sulfoxide. All of the salts studied, including the bisphosphonium salts, were found to be highly soluble in trifluoroacetic acid. Although this acid is known to add to olefins under mild conditions[12], no interaction with the olefinic salts was observed. The spectrum of (VI) was unchanged over a period of twenty-five hours in this solvent.

The geminal ^{31}P–H coupling constant was shown to be concentration independent over a range of 3–50 % (w/v) for (VII) in trifluoroacetic acid. However, a rather substantial change in the chemical shift of the methylene protons was observed for (VII) in solutions of greater than 15 % concentration: 15 %, $\tau = 5.50$ ppm; 50 %, $\tau = 5.32$ ppm. Temperature independence was observed for $|J_{PCH}|$ and $|J_{PCCH}|$ and the α- and β-proton chemical shifts for methyl- (I) and isopropyl-triphenylphosphonium (III) halides in deuterochloroform over a temperature range of 27–67°.

No effect of halide ion on either chemical shift or $|J_{PCH}|$ was observed in an examination of the spectra of benzyltriphenylphosphonium chloride and bromide in both deuterochloroform and trifluoroacetic acid and methyltriphenylphosphonium chloride and iodide in deuterochloroform. In contrast to the results with phosphonium salts, the chemical shifts of the α-proton resonances of tetra-*n*-butylammonium salts[13] have been shown to be dependent upon both concentration and anion. This dependence has been interpreted on the basis of ion pair association. For the very much larger phosphonium cations, ion pairing would be expected to be of less consequence and the concentration and anion insensitivity might be expected. It is significant that in the tetraalkylammonium salts, the lowest degree of association is observed with the larger anions (picrate and perchlorate) and the highest degree of association with the smallest anion (chloride)[13]. A modest anion dependence is observed for the aromatic proton signals of (I) and (VII), but the dependence is of a lower order than that observed for the aromatic protons of anilinium salts[14].

From an inspection of Table 1, it is obvious that $|J_{PCH}|$ is sensitive to changes in the nature of the substituent on the α-carbon and, in the benzyl salts, to changes in nuclear substituents. For the benzyl salts, $|J_{PCH}|$ showed a rough correlation with σ_{para}; the magnitude of $|J_{PCH}|$ decreases with the donor capacity of the nuclear substituent, reaching a maximum with the *p*-carbomethoxy salt [(XIII), 15.2 cps] and a minimum with the *m*-methyl salt [(IV), 14.0 cps].

It is interesting to note that while the coupling constant (13.1–13.2 cps) between the phosphorus atom and the methyl protons in a series of methylphosphonium salts (Table 2) remains constant regardless of the other substituents on phosphorus, the same structural insensitivity is not observed for the benzyl analogs [*cf.* (VII) and (XXV), (X) and (XXVI)]. A similar $|J_{PCH}|$ has been reported for (I) by Hendrickson *et al.*[1], but these investigators reported $|J_{PCH}| = 14.4$ cps for tetramethylphosphonium iodide. In the latter case, the divergence from the values cited in Table 2 may be due to specific solvation of the smaller symmetrical tetramethylphosphonium cation; specific solvation of the bulkier cations of Table 2 would be expected to be less likely. Horn and Rothstein[3] have reported a higher $|J_{PCH}|$ (14 cps) for methyltri-*n*-propylphosphonium iodide and picrate; however, their data appear to be accurate

TABLE 1

PMR PARAMETERS FOR PHOSPHONIUM SALTS

	R	X	Solvent	τ-αCH[a]	J_{PCH}[a]	Remarks
$[(C_6H_5)_3PR]^+ X^-$						
(I)	CH_3	Cl	$CDCl_3$	6.83	13.1	
			CF_3COOH	7.17	13.4	
(II)	CH_2CH_3	Br	$CDCl_3$	6.21	12.4	τ_{CH_3} = 8.62; J_{PCCH} = 20.0; J_{HCCH} = 7.5
(III)	$CH(CH_3)_2$	Br	$CDCl_3$	5.21	—[b]	τ_{CH_3} = 8.60; J_{PCCH} = 18.7; J_{HCCH} = 6.9
(IV)	$C(CH_3)_3$[c]	Br	$CDCl_3$	—	—	τ_{CH_2} = 8.32; J_{PCCH} = 17.2
(V)	$CH_2CH{=}C(CH_3)_2$	Br	$CDCl_3$	5.57	14.2	
(VI)	$CH_2CH{=}CHC_6H_5$	Cl	$CDCl_3$	5.06	15.7	J_{HCCH_2} = 7.2
			CF_3COOH	5.89	14.8	J_{HCCH_2} = 6.9
			DMSO	*ca.* 5.0	15.9	J_{HCCH_2} = 6.8
(VII)	$CH_2C_6H_5$	Br	$CDCl_3$[d]	4.71	14.1	
(VIII)	$CH_2C_6H_4CH_3$-*o*	Br	$CDCl_3$	4.68	14.1	τ_{CH_3} = 8.28
(IX)	$CH_2C_6H_4CH_3$-*m*	Br	$CDCl_3$	4.85	14.0	τ_{CH_3} = 7.93
			CF_3COOH	5.57	13.6	τ_{CH_3} = 8.83
(X)	$CH_2C_6H_4CH_3$-*p*	Cl	$CDCl_3$	4.66	14.3	τ_{CH_3} = 7.77
			CF_3COOH	5.52	13.6	τ_{CH_3} = 7.65
(XI)	$CH_2C_6H_4OCH_3$-*p*	Br	$CDCl_3$	4.85	14.8	τ_{CH_3} = 6.30
			CF_3COOH	5.45	13.5	τ_{CH_3} = 6.05
			DMSO	4.74	15.1	
(XII)	$CH_2C_6H_4Cl$-*p*	Cl	$CDCl_3$	4.26	14.7	
(XIII)	$CH_2C_6H_4COOCH_3$-*p*	Cl	$CDCl_3$[d]	4.29	15.2	τ_{CH_3} = 6.15
(XIV)	$CH_2C_6H_4NO_2$-*m*	Br	DMSO	4.50	16.1	
(XV)	$CH_2C_6H_4NO_2$-*p*	Cl	CF_3COOH	5.23	14.8	$J_{PCH\text{-}o}$ = 2.3; J_{HCCH} ring = 8.7
(XVI)	$CH(C_6H_5)_2$	Cl	$CDCl_3$	1.72	17.9	
(XVII)	CH_2COOH	Br	CF_3COOH	5.43	14.1	
(XVIII)	$CH_2COOC_2H_5$	Br	$CDCl_3$	4.58	13.9	
(XIX)	$CH_2COOCH_2C_6H_5$	Cl	$CDCl_3$	4.21	14.0	
(XX)	$CH(C_6H_5)COC_6H_5$	Br	DMSO	1.30	12.5	
$[(n\text{-}C_4H_9)_3PR]^+ X^-$						
(XXI)	CH_3[e]	I	$CDCl_3$	7.93	13.2	
			CF_3COOH	8.14	13.1	
(XXII)	$CH_2CH{=}CH_2$	Cl	$CDCl_3$	6.42	15.9	

[a] All chemical shifts are taken as the centers of multiplets in ppm from TMS (τ = 10.00). All coupling constant values are given in cps. [b] Broad unresolved multiplet. See ref. 1. [c] Ref. 5. [d] For τ and J values in other solvents, see ref. 11. [e] For compounds (XXI)–(XXIX) *n*-butyl proton resonances were observed at τ_{CH_3} = 9.02–9.10 ppm, $\tau_{(CH_2)_2}$ = 8.40–8.55 ppm, τ_{PCH_2} = 7.47–7.58 ppm.

(*continued on p. 417*)

TABLE 1 (*continued*)

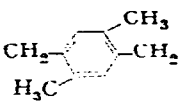
	R	*X*	*Solvent*	τ-αCH[a]	J_{PCH}[a]	*Remarks*
(XXIII)	$CH_2C(CH_3)=CH_2$	Cl	$CDCl_3$	6.38	16.2	
(XXIV)	$CH_2CH=C(CH_3)_2$	Br	$CDCl_3$	6.64	15.0	
(XXV)	$CH_2C_6H_5$	Cl	$CDCl_3$[d]	5.67	15.4	
(XXVI)	$CH_2C_6H_4CH_3$-*p*	Cl	$CDCl_3$	5.79	15.0	τ_{CH_3} = 7.70; $J_{PCH\text{-}O}$ = 2.2; J_{HCCH} ring = 8.0
XXVII)	$CH_2COC_6H_5$	Br	$CDCl_3$	4.96	13.0	
(XXVIII)	CH_2COOH	Cl	$CDCl_3$	6.12	12.7	
(XXIX)	CH_2CN	I	$CDCl_3$	5.35	14.3	
$[(C_6H_5)_3PRP(C_6H_5)_3]^{2+}$ $2X^-$						
(XXX)	CH_2CH_2	Br	CH_3CN	6.09		Doublet, not well resolved, line separation = 5.0 cps
			CF_3COOH	6.22		Doublet, not well resolved, line separation = 5.2 cps
(XXXI)	$CH_2C_6H_4CH_2$-*o*	Br	CF_3COOH	5.95	14.0	
(XXXII)	$CH_2C_6H_4CH_2$-*p*	Cl	CF_3COOH	5.39	13.2	
(XXXIII)		Cl	CF_3COOH	5.46	13.3	τ_{CH_3} = 8.40

TABLE 2

PMR PARAMETERS FOR METHYLPHOSPHONIUM SALTS[a]

	Compound	τ_{CH_3}[b]	J_{PCH_3}[b]
(I)	$[(C_6H_5)_3PCH_3]^+ Cl^-$	6.83	13.1
(XXXIV)	$[(C_6H_5)_2(n\text{-}C_4H_9)PCH_3]^+ I^-$	7.19	13.2
(XXXV)	$[C_6H_5(n\text{-}C_4H_9)_2PCH_3]^+ I^-$	7.48	13.2
(XXI)	$[(n\text{-}C_4H_9)_3PCH_3]^+ I^-$	7.93	13.2
(XXXVI)	$[(p\text{-}CH_3OC_6H_4)_3PCH_3]^+ I^-$	6.91	13.1[c]

[a] All spectra are recorded in $CDCl_3$ solution. [b] All chemical shifts are taken as the centers of doublets in ppm from TMS (τ = 10.00). All coupling constant values are given in cps. [c] τ_{OCH_3} = 6.08, ref. 7.

to $\pm$ 1 cps and consequently may be consistent with the results of this study. There are several possible explanations for the differing behavior of P–methyl and P–benzyl couplings toward changes in the substituents on phosphorus, the most attractive being a specific solvation of the benzyl aromatic ring[15].

Hendrickson *et al.* have indicated that for trimethylphosphine, the oxide and tetramethylphosphonium cation, the geminal ^{31}P–H coupling increases grossly with

the increasing *s*-character of the P–C bond. Similar results were observed with the corresponding ethyl analogs, although the observed coupling constants for triethylphosphine sulfide and dibromide did not support this interpretation[1]. The results of this study provide evidence against such an interpretation; $|J_{PCH}|$ for methyltri-*n*-butylphosphonium (XXI) and methyltris(*p*-methoxyphenyl)phosphonium (XXXVI) cations are identical within experimental error, but it is highly unlikely that the degree of *s*-character in the P–methyl bond is the same in each compound. No correlation of $|J_{PCH}|$ with σ^* was observed for any of the salts studied and it is obvious that more than simple inductive effects are involved in the determination of the magnitude of $|J_{PCH}|$. In regard to the preceding discussion, it has been found in this laboratory that the behavior of benzylphosphonates is completely different than that of the benzylphosphonium salts. In dimethyl *p*-methoxy-, *p*-methyl- and *p*-bromo-benzylphosphonates, $|J_{PCH}|$ (21.5–21.8 cps) was found to be essentially independent of the nature of the nuclear substituent[16].

In the spectra of the (*p*-nitrobenzyl)triphenylphosphonium (XVI) and (*p*-methylbenzyl)tri-*n*-butylphosphonium (XXVI) cations, coupling of the phosphorus atom with the ring protons *ortho* to the methylene group with magnitudes of 2.3 and 2.2 cps respectively was observed. The observed spectra were of the A_2B_2X classification with $J_{BX} = 0$ or less than detectable under the experimental conditions. This four-bond coupling is of the same order of magnitude as the four-bond coupling (J = 2.4–3.4 cps) found between the phosphorus atom and the *meta*-protons in a series of *para*-substituted triarylphosphine oxides[7]; in the latter cases, the phosphorus atom was attached directly to the conjugated system while in the benzylphosphonium salts a saturated carbon intervenes. Previous examples of four-bond phosphorus–proton couplings have been reported for the sodium salt and zinc derivative of diethyl acetonylphosphonate (J = *ca.* 2 cps)[17] and for the P–N–C–C–H system (J = 0.58–1.21 cps)[4]. Five-bond phosphorus–proton couplings have been observed in dialkyl allyl phosphites (J = 1.5–3.0 cps)[18]. The results obtained in this study provide further evidence for the generality of long range ^{31}P–H couplings in organophosphorus compounds.

EXPERIMENTAL

All spectra were obtained on a Varian A-60 spectrometer at a probe temperature of 27 or 32°; unless noted otherwise 3–8 % (w/v) solutions with tetramethylsilane as an internal standard were employed. The chemical shifts and coupling constants are accurate to ± 0.01 ppm and ± 0.1 cps respectively and are the average of at least three separate spectrum determinations. The coupling constants were obtained from 50 cps sweep width spectra.

Compounds (V), (VIII), (IX), (XXII), (XXIII), (XXIV) and (XXVI) were prepared by warming approximately equimolar mixtures of the appropriate phosphine and alkyl halide in the absence of solvent; a solid formed and the phosphonium salt was isolated by trituration with petroleum ether (30–60°) and ether. The allyltri-*n*-butylphosphonium salts, (XXII), (XXIII) and (XXIV), were found to be extremely hygroscopic and no attempts were made to obtain melting points or analytical data. The PMR spectra of these compounds were completely consistent in all respects with the anticipated structures. The following compounds were obtained in analytical

purity: (*3-methyl-2-butenyl*)*triphenylphosphonium bromide* (V), m.p. 231–232° (Found: C, 67.38; H, 5.76; P, 7.77. $C_{23}H_{24}BrP$ calcd.: C, 67.15; H, 5.88; P, 7.53 %.); (*o-methylbenzyl*)*triphenylphosphonium bromide* (VIII), m.p. 253–255° (dec.) (Found: C, 70.11; H, 5.38; P, 7.04. $C_{26}H_{24}BrP$ calcd.: C, 69.81; H, 5.41; P, 6.92 %.); (*m-methylbenzyl*)-*triphenylphosphonium bromide* (IX), m.p. 271–272° (dec.). (Found: C, 70.01; H, 5.22; P, 6.89. $C_{26}H_{24}BrP$ calcd.: C, 69.81; H, 5.41; P, 6.92 %.); (*p-methylbenzyl*)*tri-n-butylphosphonium chloride* (XXVI), m.p. 154.5–155°. (Found: C, 70.30; H, 10.67; P, 9.31. $C_{20}H_{36}ClP$ calcd.: C, 70.05; H, 10.58; P, 9.03 %.)

Compound (XX) and compounds (XVII)–(XIX) and (XXVIII) were provided by Dr. I. J. BOROWITZ and D. J. MARTIN, respectively. The source of the remaining compounds in Tables 1 and 2 has been cited in the literature[19].

SUMMARY

The proton magnetic resonance spectra of a series of alkyl-, benzyl- and allyltriphenyl and -trialkylphosphonium salts and alkylenebis(triphenylphosphonium) salts have been determined. Chemical shifts of α-protons are dependent upon solvent and concentration and independent of temperature and halide ion; phosphorus–proton coupling constants are dependent only on solvent. In a series of methylphosphonium salts, the geminal $|J_{PCH_3}|$ is constant and independent of the nature of the other groups (alkyl, aryl) attached to phosphorus. A four-bond phosphorus–aromatic proton coupling was observed in two *para*-substituted benzylphosphonium salts.

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