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Magnetic Resonance Studies. I. Investigation of Phosphorus Compounds by ^{13}C and ^{31}P Nuclear Magnetic Resonance for Phosphonium Salts Containing Saturated Groups

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Abstract: It is found that the dominant effects observed for ^{13}C chemical shifts are also operative in the ^{31}P chemical shifts of alkyl substituted triphenylphosphonium salts. In this study β and γ effects are established in the ^{31}P NMR of the title compounds; steric effects are also evaluated in light of perturbations of the ^{31}P and ^{13}C chemical shifts. The influence of the triphenylphosphonium group on the ^{13}C chemical shifts for several types of alkyl groups including cycloalkanes is discussed. It is found that there is a relationship between phosphorus–carbon nuclear spin coupling and the hybridization of the carbon. Electronegativities of the substituents are also found to be reflected in ^{31}P–^{13}C coupling.

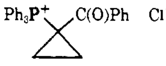
There have been few studies of the effect of the phosphonium substituent on ^{13}C chemical shifts.[1,2] Also structural and electronic effects on phosphorus–carbon nuclear spin coupling have not been well understood. In this study one substituent to phosphorus is varied in a systematic manner. By these minor structural variations the influence of phosphorus on ^{13}C chemical shifts and ^{31}P–^{13}C couplings can be examined.

The value of ^{31}P NMR for establishing structures of phosphorus containing molecules has been well documented.[3-5] However, the influence of the electronic environment on ^{31}P chemical shifts is not entirely clear. Totally empirical relationships have been developed which allow an accurate prediction of chemical shifts for phosphines, phosphine oxides, and phosphonium salts.[6] These relationships allow predictions of ^{31}P chemical shifts with a fair degree of accuracy; however, they do not clarify the mechanisms by which minor structural changes affect shifts in ^{31}P NMR. Quin and Breen[7] have shown that tetraalkylphosphonium salts exhibit α, β, and γ methyl substituent effects. They suggested that the factors influencing ^{31}P chemical shifts might have the same basis as those affecting ^{13}C NMR. It is interesting to note that the two theories of ^{31}P chemical shifts do not account for the β and γ substituent effects. For example, in going from $Me_4P^+I^-$ (25.3 ppm) to $Et_4P^+I^-$ (40.1 ppm) a 14.8 ppm decrease in shielding is observed.[8,9] Purdela's theory of ^{31}P chemical shifts is related only to changes in the bond angles around phosphorus,[10] and since all of the C–P–C bond angles in these two phosphonium salts must be tetrahedral because of symmetry, this theory cannot possibly account for the change in chemical shifts. Utilization of the computer program for the Van Wazer–Letcher theory of ^{31}P chemical shifts[11] predicts chemical shifts for Me_4P^+ of 31.3 ppm and Et_4P^+ of 29.3 ppm. In other words, a 2 ppm increase in chemical shift is predicted on going from $Me_4P^+I^-$ to $Et_4P^+I^-$, whereas a 14.8 ppm downfield shift is observed. The Van Wazer–Letcher approach has also been criticized because unrealistic assumptions must be made to deal with steric perturbations on ^{31}P chemical shifts for dioxaphosphorinanes.[12] In the present study factors influencing ^{31}P chemical shifts, particularly those of steric origin, are examined for a series of alkyl substituted triphenylphosphonium salts.

Results and Discussion

The results for the ^{31}P chemical shifts for compounds having the general structure Ph_3P^+–R X^-, where R is a saturated alkyl group and X is a chloride, bromide, or iodide anion, are presented in Table I. It should be noted that the counteranion has little, if any, influence on the ^{31}P chemical

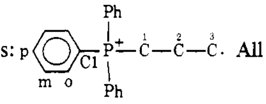
Table I. ^{31}P Chemical Shifts of Phosphonium Salts

No.	Compd	$\delta_{^{31}P}$[b]	No.	Compd	$\delta_{^{31}P}$[b]
1	Ph_3P^+-Me I^-	21.1	11		21.8
2	Ph_3P^+-Et Br^-	25.5			
3	Ph_3P^+-*n*-Pr Br^-	24.1[a]			
4	Ph_3P^+-*i*-Pr Br^-	31.3	12	Ph_3P^+-CH_2CN Cl^-	22.9
5	Ph_3P^+-*n*-Bu Br^-	24.1	13	Ph_3P^+-CH_2CH_2OMe Br^-	25.4
6	Ph_3P^+-*sec*-Bu Br^-	30.2[a]	14	Ph_3P^+-CH_2CH_2OH Cl^-	24.0
7	Ph_3P^+-*t*-Bu I^-	35.6	15	Ph_3P^+-c-Pr Br^-	28.5
8	Ph_3P^+-$CH_2C(O)OEt$ Br^-	21.0	16	Ph_3P^+-c-Bu Br^-	24.2
9	Ph_3P^+-$CH_2C(O)Me$ Cl^-	20.1	17	Ph_3P^+-c-Pe Br^-	30.4
10	Ph_3P^+-$CH_2C(O)Ph$ Br^-	22.2	18	Ph_3P^+-c-Hex I^-	27.3
			19	Ph_3P^+-c-Hep Br^-	30.1

[a] Values taken from S. O. Grim, et al., *J. Phys. Chem.*, **70**, 581 (1966). [b] Chemical shifts in ppm from 85% H_3PO_4. Positive values indicate deshielding.

Table II. ^{13}C Chemical Shifts of Phosphonium Salts[a]

Compd	No.	Carbon chemical shift, ppm 1	2	3	4	C1	o	m	p
Ph_3P^+-Me I^-	1	11.4				118.8	133,7	130.5	135,2
Ph_3P^+-Et Br^-	2	17,0	6.9			117,9	133,6	130,5	135.0
Ph_3P^+-*i*-Pr Br^-	4	21.5	16.4			117,5	133.8	130.6	134.9
Ph_3P^+-*t*-Bu I^-	7	35.3	28,2			117,1	134.4	130,9	135.3
Ph_3P^+-c-Pr Br^-	15	0,4	4.9			118,3	133.7	130.4	135,2
Ph_3P^+-c-Bu Br^-	16	25.4	23.1	20.3		118.0	133,8	130.7	135,2
Ph_3P^+-c-Pe Br^-	17	29.5	28.0	26.4		118,5	133.7	130.3	134.8
Ph_3P^+-c-Hex I^-	18	29.8	26,4	25.1	25.4	117,3	134.4	130.6	134,9
Ph_3P^+-c-Hep Br^-	19	28,6	27.7	26,9	26.9	117.9	133,7	130.2	134.5

[a] The numbering system is as follows:  All compounds were run in $CDCl_3$ and referenced to internal TMS.

shift for phosphonium salts.[13] This statement is borne out by the observation that a 2:1 solution of methyltriphenylphosphonium iodide and bromide in $CDCl_3$ shows only one unshifted resonance in which the line width observed is unchanged as compared to either pure salt.

From the data in Table I, a β effect for the replacement of a hydrogen atom with a methyl group β (i.e., P-C-H → P-C-C) to the phosphorus is observed to be +4.8 ppm (±0.3 ppm). A γ effect of −1.3 ppm (±0.2 ppm) is observed for the replacement of a γ hydrogen (i.e., P-C-C-H → P-C-C-C) for a methyl group. The δ effect for the ^{31}P NMR of phosphonium salts appears to be vanishingly small, e.g., compare *n*-butyl- with *n*-propyltriphenylphosphonium bromide (**3** and **5**). This is in good agreement with the β (+3.7 ppm) and γ (−1.5 ppm) constants proposed for tetraalkylphosphonium salts.[7] These effects have the same sign as those in ^{13}C NMR and thus it is possible that the same factors influencing ^{13}C chemical shifts might also be operative in ^{31}P NMR for the alkyl substituted triphenylphosphonium salts. In order to test this hypothesis further for a wide range of compounds with different electronic and steric factors, the graph in Figure 1 was constructed. In this graph the ^{31}P chemical shifts for Ph_3P^+-R X^- are plotted against the ^{13}C methyl resonances for H_3C-R. It is apparent that all of the compounds with the exception of the cyclohexyl substituent, **18**, fall on the line. Thus, the ^{31}P chemical shifts for the compounds reported in this study may be related to the ^{13}C methyl chemical shifts of their analogs by

$$\delta_{^{31}P} = 0.54\delta_{^{13}C} + 17.8$$

with a correlation coefficient $r = 0.969$. Therefore, in the absence of any changes in d orbital overlap on phosphorus,[14] the same factors affecting ^{13}C chemical shifts also appear to be operative in ^{31}P NMR.[15] A similar rationale has been developed for the relationship of ^{15}N chemical shifts and their carbon analogs for primary and secondary amines.[19]

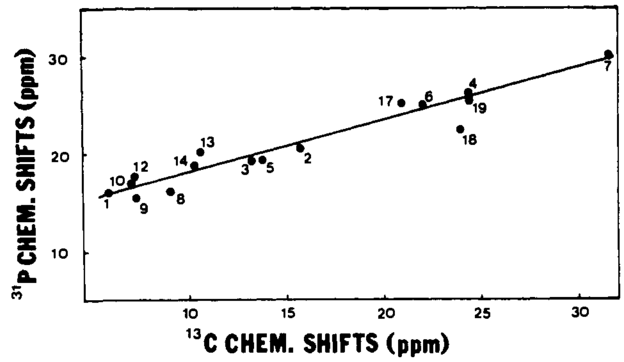


Figure 1. Comparison of ^{31}P chemical shifts of Ph_3P^+-R X^- versus ^{13}C chemical shifts of Me-R. The numbers refer to compounds listed in Table I and the line corresponds to that obtained by a linear regression analysis.

The ^{13}C chemical shifts for the compounds reported in this study are listed in Table II. The values for **1** and **2** agree with those reported by Gray.[1] It has been suggested that the triphenylphosphonium group exerts a constant effect on the ^{13}C chemical shift of the carbon directly bonded to phosphorus.[1] This is also found to be the case in the present study. A plot of the ^{13}C chemical shift of the first carbon in R-H versus the carbon directly bonded to phosphorus in Ph_3P^+-R is shown in Figure 2. It is seen that a better fit for the data occurs when separate lines are drawn for secondary and tertiary carbons; primary and quaternary carbons fall on the line drawn for secondary carbons. A linear regression analysis of the data gives, for secondary carbons, line A

$$\delta_{Ph_3P^+\text{-}R} = 0.91\delta_{R\text{-}CH_3} + 11.7$$

with a correlation coefficient $r = 0.996$. Here $\delta_{Ph_3P^+\text{-}R}$ rep-

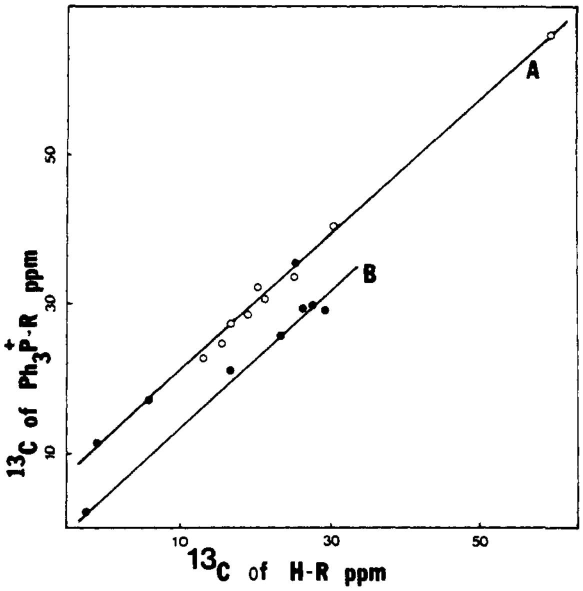
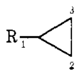
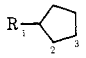
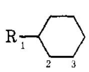
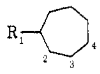


Figure 2. Comparison of ^{13}C chemical shifts of the alkyl carbon directly bonded to phosphorus in Ph_3P^+–R X^- versus the ^{13}C chemical shifts of the directly bonded carbon in H–R. Open circles refer to the data obtained by Gray in ref 1. Line A corresponds to primary, secondary, and quaternary carbons. Line B is drawn for tertiary carbons. The lines shown correspond to those obtained by separate linear regression analyses.

Table III. Comparison of ^{13}C Chemical Shifts for Model Cycloalkanes

Cycloalkane	R	Carbon, ppm 1	2	3	4
	H^a	−2.9	−2.9		
	CH_2Ph^a	10.1	5.1		
	CN^a	−3.9	6.7		
	P^+Ph_3	0.4	4.9		
	H^b	26.5	26.5	26.5	
	Me^b	35.4	35.4	25.8	
	P^+Ph_3	29.5	28.0	26.4	
	$\Delta\delta^c$	5.9	7.4	−0.6	
	H^b	27.8	27.8	27.8	27.8
	Me^d	33.4	36.0	27.1	27.0
	P^+Ph_3	29.8	26.4	25.1	25.4
	$\Delta\delta$	3.6	9.6	2.0	1.6
	H^b	29.4	29.4	29.4	29.4
	Me^e	34.9	37.5	26.9	28.9
	P^+Ph_3	28.6	27.7	26.9	26.9
	$\Delta\delta$	6.3	9.8	0	2.0

[a] Reference 20, p 161. [b] Reference 20, p 67. [c] $\Delta\delta = (\delta_{Me-c\text{-}alkane} = \delta_{Ph_3P^+-c\text{-}alkane})$. [d] T. Pehk and E. Lippmaa, *Org. Magn. Reson.*, 3, 679 (1971). [e] M. Christl and J. D. Roberts, *J. Org. Chem.*, 37, 3443 (1972).

resents the carbon chemical shifts for the carbon in R directly bonded to phosphorus in the phosphonium salts and δ_{R-CH_3} represents that for the hydrocarbon analogs. The equation for tertiary carbons, line B, is given by

$$\delta_{Ph_3P^+-R} = 0.92\delta_{R-CH_3} + 4.0$$

with a correlation coefficient $r = 0.987$. That the α effect for the triphenylphosphonium substituent is not constant, but depends upon the degree of branching at the site of substitution on carbon, is a well known phenomena. Similar effects have been noted for NO_2, OH, CN, -C(O)-, and other substituents.[20]

To examine steric effects in phosphonium salts a homologous series of cycloalkyl substituted triphenylphosphonium salts was studied. It can be seen in Table I that the ^{31}P chemical shifts for cyclobutyl- and cyclohexyltriphenylphosphonium salts, **16** and **18**, are shielded by 2.8 and 6.2 ppm, respectively, relative to those for cyclopentyl- and cycloheptyltriphenylphosphonium bromide, **17** and **19.** Examination of Fisher-Hirschfelder-Taylor and Framework molecular models shows that **16** and **18** possess significant steric interactions between the phenyl groups around phosphorus and the C-H bonds β to the phosphorus in the cycloalkyl ring. However, in **17** and **19** the C-H bonds are directed at an angle away from the phenyl groups. Thus the upfield ^{31}P chemical shifts of **16** and **18** can be interpreted as a consequence of steric compression. It was previously shown herein and it has been noted by other workers[6,7] that there appears to be no additional effect beyond the γ carbon in determining ^{31}P chemical shifts of acyclic derivatives.

In Table III a number of ^{13}C chemical shifts for several cycloalkyltriphenylphosphonium salts are compared to analogs. It is apparent that the carbon β to the site of substitution (C2) is relatively shielded for the cyclic phosphonium salts compared to their methyl analogs. This steric compression for C2 is in agreement with the previous discussion of the influence of steric factors on ^{31}P chemical shifts. However, it must be pointed out that the chemical shifts for the methylcycloalkanes represent average perturbations from the relative populations of the methyl groups in axial and equatorial positions. The bulk of the triphenylphosphonium group is expected to cause the axial isomer to become energetically unfavorable. Thus any comparison of the magnitudes of the steric perturbations in the ^{13}C shifts of C2 among the cycloalkyl derivatives is likely to be obscured.

The ^{31}P chemical shift of cyclopropyltriphenylphosphonium bromide (**15**) is found at 28.5 ppm. Comparison of this value with those obtained for cyclopentyltriphenylphosphonium bromide (**17**) and isopropyltriphenylphosphonium bromide (**4**) of 30.4 and 31.3 ppm, respectively, reveals that the phosphorus in the cyclopropyl compound is shielded by approximately 2–3 ppm. This slight shielding effect produced by the cyclopropyl ring is also observed in the ^{13}C chemical shifts of carbonyls directly attached to a cyclopropyl ring.[21] Molecular models of **15** indicate that there are probably no significant interactions between C2 of the cyclopropyl ring and the triphenylphosphonium group. Therefore, the upfield ^{31}P shift in **15** is probably not due to steric effects. Boyd and Hoffmann[22] have shown by extended Hückel calculations that one of the degenerate set of Walsh orbitals in a cyclopropane substituent interacts with an empty d orbital or phosphorus in cyclopropylidenephosphorane. However, a comparison of the ^{13}C chemical shifts of the cyclopropyl ring with several analogs in Table III reveals no unusual substituent effects for the triphenylphosphonium group. Thus interaction of the highest occupied MO of the cyclopropyl ring with an empty d orbital on phosphorus in **15** is not considered to be significant. Rather, it is felt that the magnetic anisotropy of the cyclopropyl ring[23] is the agent principally responsible for this increased shielding in **15.**

In the case of 1-benzoylcycloprop-1-yltriphenylphosphonium chloride (**11**) the effect of the cyclopropyl substituent is not as clear. The ^{31}P resonance of phenacyltriphenylphosphonium bromide (**10**) is deshielded by only 0.4 ppm relative to **11.** Inspection of molecular models indicates that the edge of the carbonyl π system must lie in proximity to the phosphorus atom. Thus an opposing downfield shift due to anisotropy of the carbonyl group would be expected, which is in opposition to any anisotropy effects of the cyclopropyl group.

The values of the ^{13}C-^{31}P nuclear spin couplings are given in Table IV. It has been shown[1] that there is no correlation of directly bonded C-H couplings with corresponding P-C couplings. This is also apparent in this study. There

Table IV. $^{31}P-^{13}C$ Coupling Constants[a]

Compd	No.	$^{31}P-^{13}C$ coupling, Hz							
		1	2	3	4	C1	o	m	p
$Ph_3P^+-Me\ I^-$	1	57.1				88.6	10.7	12.9	3.0
$Ph_3P^+-Et\ Br^-$	2	51.6	5.1			86.2	9.9	12.4	2.9
$Ph_3P^+-i\text{-}Pr\ Br^-$	4	47.0	2.0			83.1	9.2	12.1	3.0
$Ph_3P^+-t\text{-}Bu\ I^-$	7	42.5	0.6			80.1	8.8	12.0	3.0
$Ph_3P^+-c\text{-}Pr\ Br^-$	15	86.9	4.3			89.6	9.8	12.6	2.8
$Ph_3P^+-c\text{-}Bu\ Br^-$	16	45.0	2.8	16.8		85.0	9.6	12.3	2.9
$Ph_3P^+-c\text{-}Pe\ Br^-$	17	49.2	*b*	8.9		84.5	9.5	12.1	2.7
$Ph_3P^+-c\text{-}Hex\ I^-$	18	45.4	1.7	14.3	*b*	83.0	9.5	11.5	*b*
$Ph_3P^+-c\text{-}Hep\ Br^-$	19	42.6	*b*	15.8	*b*	82.8	9.4	12.0	*b*

[a] The numbering system is identical to that in Table II. The digital resolution was ±0.1 Hz. [b] Unresolved coupling.

are, however, several systematic trends in these data, the coupling of phosphorus to the directly bonded alkyl carbon decreases regularly where hydrogens β to phosphorus are replaced by methyl groups *in seriatum*, i.e., going from methyl- to *tert*-butyltriphenylphosphonium salts. Also coupling to the C1 phenyl carbon decreases in this series. That these two trends might be interrelated is evidenced by Figure 3.

The reduction of $^1J_{^{31}P-^{13}C}$ for the alkyl carbon of *tert*-butyltriphenylphosphonium iodide (**7**) compared to methyltriphenylphosphonium iodide (**1**) is consistent with the fact that the percent s character in the carbon hybrid making up the P–C bond is decreasing. The C–C–C bond angles in **7** should be larger than the H–C–H bond angles in **1** because of nonbonded interactions between the methyl C–H bonds. Therefore the percent of s character in the central carbon hybrid orbital of the C–C (or C–H) bonds must increase in going from **1** to **7** at the expense of decreasing the s character in the hybrid orbital comprising the P–C bond. Since the magnitude of coupling between two elements is directly related to the product of the percent s character in the hybrid orbitals forming the bond,[24] the coupling constant decreases regularly in the order:

$$J_{Me} > J_{Et} > J_{i\text{-}Pr} > J_{t\text{-}Bu}$$

This is further supported by the work of Summerhays and Maciel[25] where $^{13}C-^{13}C$ coupling was studied for X-Et, X-CHMe$_2$, and X-CMe$_3$. It was found that generally J_{C-C} increased in the order $J_{Et} > J_{i\text{-}Pr} > J_{t\text{-}Bu}$ for a variety of derivatives with widely different electronic and steric factors. It was shown by the finite perturbation-INDO method that the C–C–C bond angles must increase, thus increasing their percent s character for this series in order to account for this trend.

An alternate, but similar, rationale for the relationship of the directly bonded $^{31}P-^{13}C$ couplings in this series of compounds which does not necessitate any change in the P–C–C bond angles is that in going from Ph_3P^+-Me to Ph_3P^+-*t*-Bu the phosphorus-alkyl carbon bond distance might increase. This would minimize the steric interactions between the phenyl and methyl groups. This has the same net effect as described before, namely the percent s character in the P–C bond decreases.

The electronegativity of substituent, R, in Ph_3P^+–R seems to determine, in part, the magnitude of coupling from phosphorus to the C1 phenyl carbon. The electronegativity of a group decreases as the percent s character in the valence orbital decreases.[26] Therefore, the electronegativity of these substituents on the triphenylphosphonium group should decrease in the following order, Me > Et > *i*-Pr > *t*-Bu. The $^1J_{^{31}P-^{13}C1\ phenyl}$ coupling decreases in parallel with this order.

Further evidence for the relationship between the electronegativity of the substituent and the magnitude of $^1J_{^{31}P-^{13}C1\ phenyl}$ is provided by cyclopropyltriphenylphosphonium bromide (**15**) where the hybrid orbital on carbon in the cyclopropyl ring making up the P–C bond is expected to be approximately sp^2.[26] Since the electronegativity of an sp^2 hybridized group is greater than that for an sp^3 hybrid, the coupling to the C1 phenyl carbon should increase. This is indeed the case; $^1J_{^{31}P-^{13}C1\ phenyl}$ for **15** is larger than any of the other compounds in this study. Substitution of a more electronegative element than carbon for the substituent is expected to increase $^1J_{^{31}P-^{13}C1\ phenyl}$ further. In anilino-*N*-triphenylphosphonium bromide where the substituent contains a nitrogen atom directly bonded to phosphorus $^1J_{^{31}P-^{13}C1\ phenyl}$ is 102.5 Hz.[27] It is also noted in Figure 3 that all of the cycloalkyl phosphonium salts fall nearly on the line with the exception of cyclobutyltriphenylphosphonium bromide and cyclopropyltriphenylphosphonium bromide (**15** not shown on graph). This may be due, in part, to the ring strain associated with these compounds and other steric effects.

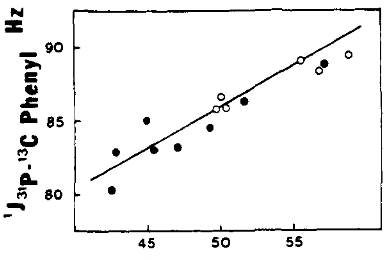


Figure 3. Comparison of the $^{31}P-^{13}C$ coupling to the C1 phenyl carbon versus the $^{31}P-^{13}C$ coupling to the alkyl carbon directly bonded to phosphorus. Open circles refer to the data reported by Gray in ref 1. The correlation coefficient for these data was found to be 0.960 (not including **15** and **16**).

Experimental Section

Spectra were obtained on a Bruker HFX-90 spectrometer equipped for Fourier transform pulsed NMR with a Nicolet 1085 data system. The ^{31}P and ^{13}C data were taken at operating frequencies of 36.43 and 22.63 MHz, respectively. The ^{31}P chemical shifts are reported as referenced to external 85% H_3PO_4 with shifts occurring downfield from the reference taken as positive. The ^{13}C chemical shifts are reported with respect to internal TMS with downfield shifts again reported as positive. All samples were run as 0.1 to 0.05 *M* solutions of CDCl$_3$ at 28° with broad band ^1H decoupling. Spectral assignments were made with the aid of off-resonance decoupling and model compounds as appropriate. The tabulated values reported in Table I represent the average chemical shift for each compound taken over several runs; no compound varied by more than ±0.3 ppm with the average being ±0.17 ppm.

All phosphonium salts were prepared by standard methods.[28] Compound 11 was prepared by Labow.[29] Cycloheptyltriphenylphosphonium bromide (**19**) was prepared by heating equimolar quantities of cycloheptyl bromide and triphenylphosphine for 36 hr. The resulting solid was washed several times with ethyl acetate and recrystallized twice from methylene chloride-ethyl acetate to give white crystals, mp 175–177°. Anal. Calcd for $C_{25}H_{28}PBr$: C, 68.34; H, 6.42. Found: C, 68.03; H, 6.38.

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Magnetic Resonance Studies. II. Investigation of Phosphonium Salts Containing Unsaturated Groups by ^{13}C and ^{31}P Nuclear Magnetic Resonance[1]

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Abstract: The β carbon in vinyltriphenylphosphonium bromide is found to be substantially deshielded in the ^{13}C NMR. Other phosphonium salts containing unsaturated groups adjacent to phosphorus also show this effect. The extent of the deshielding of the β carbon is interpreted to be a consequence of $d\pi-p\pi$ bonding between phosphorus and carbon. The β carbon of propynyltriphenylphosphonium bromide resonates at 121.8 ppm which is also consistent with $d\pi-p\pi$ bonding. A comparison of the ^{31}P chemical shifts of Ph_3P^+-R with the methyl ^{13}C chemical shifts of Me-R shows a consistent increased shielding in the ^{31}P NMR of the title compounds and is interpreted in light of $d\pi-p\pi$ overlap.

Phosphonium salts have enjoyed a great deal of emphasis as useful intermediates in organic synthesis.[2] Therefore, a detailed account of the electronic structure of these compounds may provide clues to the nature of the reactions in which phosphonium salts, and by analogy other organophosphorus compounds, participate. Vinylphosphonium salts undergo facile Michael addition with a wide variety of nucleophiles,[3] thus it is expected that the β vinyl carbon exhibits some degree of positive charge. A rationale for this fact is the overlap of the π orbital of the vinyl group with an empty d orbital on phosphorus. Utilization of d orbitals on phosphorus is still a matter of controversy with conflicting ideas often being presented.[4] There have been no studies of the ^{13}C and ^{31}P NMR of phosphonium salts containing unsaturated groups to date. Since ^{13}C and ^{31}P NMR are sensitive probes for the electronic environment about molecules,[5,6] it is expected than an examination of these parameters can shed light on the nature of $d\pi-p\pi$ interactions and the bonding in the title compounds.

Results and Discussion

The results of this NMR study of phosphonium salts having the general structure $Ph_3P^+-RX^-$, where R is an unsaturated group and X^- is either a bromide or chloride anion, are presented in Tables I, II, and III. Table I lists the ^{31}P chemical shifts, Table II lists the ^{13}C chemical shifts, and Table III gives the $^{31}P-^{13}C$ couplings taken from the carbon NMR. The values reported for **5** and **10** in the ^{13}C NMR agree with those reported by Gray.[7] Table IV compares the ^{13}C chemical shifts of several unsaturated phosphonium salts to model analogs.

^{13}C NMR. The α effect has been related to the electronegativity of a group and has been interpreted to be largely due to inductive effects.[8,9] In the previous work substitution of a triphenylphosphonium group for a hydrogen in compounds of the type $Ph_3P^+-CHRR^1$ has been shown to produce an α effect for the carbon directly bonded to the phosphorus of 4 ppm downfield. On this basis, the electronegativity of the triphenylphosphonium group is estimated to be between that of hydrogen and a methyl group.[10] Inductive effects for the β position are much smaller than those for the α position. The β carbon in vinyltriphenylphosphonium bromide is found to be deshielded by 22.4 ppm as compared to ethylene (Table IV). An inductive effect can only account for a minor portion of this relatively large shift. Magnetic anisotropy effects can also be discounted in interpreting this shift since they contribute only a few parts per million.[11]