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Carbon-13 Nuclear Magnetic Resonance of Organophosphorus Compounds. VIII. Triphenylphosphoranes and Triphenylphosphonium Salts

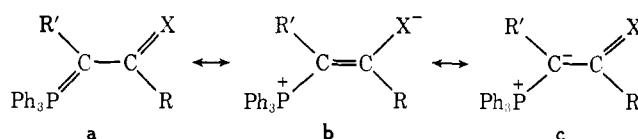
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Abstract: ^{13}C chemical shifts and ^{13}C - ^{31}P nuclear spin coupling constants have been obtained for six triphenylphosphoranes (phosphorus ylides), twelve triphenylphosphonium salts, triphenylphosphine oxide, and tetraphenylphosphonium bromide. In the salts the substituted phenyl carbon shifts vary slightly while the methylene resonance parallels analogously substituted carbon shifts in the series CH_3X , $\text{CH}_3\text{CH}_2\text{X}$, $\text{c-C}_6\text{H}_{11}\text{X}$, and $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CH}_2\text{X}$. The methylene carbon $^1J_{\text{CP}}$ varies through a range of over 30%. No correlation is found with the related $^1J_{\text{CP}}$'s in the above series. The ylides show strikingly high shieldings and one-bond ^{13}C - ^{31}P couplings for the ylide carbons. These shieldings are typical for *aliphatic* carbon and point toward high localization of negative charge on basically sp^2 carbons. Their $^1J_{\text{CP}}$ values are much larger than the one-bond couplings to the sp^2 carbons in the phenyl rings. The data indicate a delocalized cyclopentadienide phosphorane while the fluorenyl phosphorane has much more localization on the ylide carbon.

Organophosphorus compounds continue to provide demanding tests of our understanding of their syntheses, equilibria, and molecular electronic structure. We have been using ^{13}C nmr as a means of probing the structures, conformation, and bonding of different kinds of these interesting compounds.¹⁻⁷ As opposed to the (now) typical use of ^{13}C spectra for chemical shifts, organophosphorus compounds also exhibit both long and short range ^{13}C - ^{31}P nuclear spin couplings, which are especially useful in investigating stereochemistry and bonding. In part V⁵ considerable attention was given to the sensitivity of the ^{13}C shifts and ^{13}C - ^{31}P couplings in four-membered phosphorus heterocycles to the formal phosphorus oxidation state, particularly to the differences between P(IV) and P(V). In its higher oxidation "states," phosphorus has often been described as being able to form multiple bonds with adjacent atoms possessing lone-pair electrons *via* a $d\pi$ - $p\pi$ interaction. Thus, oxides are often written as $\text{R}_3\text{P}=\text{O}$ (even though both lone pairs on the oxygen are usually felt to be participating in what should be viewed as a pseudotriple bond). Another class of compounds in which it is common to invoke $d\pi$ - $p\pi$ bonding is that of phosphorus ylides, $\text{R}_3\text{P}=\text{CR}'\text{R}''$. These compounds are "stabilized" by using conjugating groups for R, R', and R''. A popular version of

stabilized ylides is that of $\text{Ph}_3\text{PC}(\text{R})\text{CO}_2\text{R}'$, for which ^1H nmr data are available.⁸⁻¹⁰ It has been common to interpret their stereochemistry and bonding in terms of the general valence-bond structures a-c. The elec-



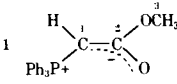
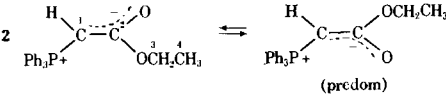
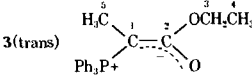
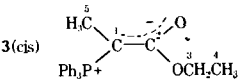
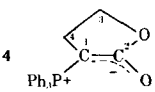
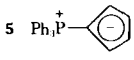
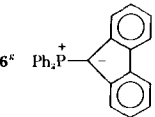
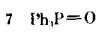
tronic differences within a-c should give rise to fundamental differences in the ^{13}C shieldings and ^{13}C - ^{31}P couplings for atoms in the ylide bond and/or those bound to them. Structure b is essentially that of a phosphonium salt and c a carbanion which could be, in principle, either trigonal or tetrahedral with formal sp^2 or sp^3 hybridization schemes for the ylide carbon. The $d\pi$ - $p\pi$ "back bonding" depicted by a presents an electronic distribution for which few ^{13}C data are available.¹¹

We have now determined the ^{13}C chemical shifts and ^{13}C - ^{31}P nuclear spin couplings in a series of phosphorus ylides of the type $\text{Ph}_3\text{PC}(\text{R})\text{CO}_2\text{R}'$ as well as the cyclopentadienyl- and fluorenyltriphenylphosphoranes. As examples of analogous P(IV) compounds and to explore

- (1) G. A. Gray, *J. Amer. Chem. Soc.*, **93**, 2132 (1971).
- (2) G. A. Gray and S. E. Cremer, *Tetrahedron Lett.*, 3061 (1971).
- (3) G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3458 (1972).
- (4) G. A. Gray and S. E. Cremer, *Chem. Commun.*, 367 (1972).
- (5) G. A. Gray and S. E. Cremer, *J. Org. Chem.*, **37**, 3470 (1972).
- (6) G. A. Gray and S. E. Cremer, *J. Mag. Resonance*, in press.
- (7) G. A. Gray, *J. Amer. Chem. Soc.*, **95**, 5092 (1973).

- (8) H. J. Bestmann and J. P. Snyder, *ibid.*, **89**, 3936 (1967).
- (9) F. J. Randall and A. W. Johnson, *Tetrahedron Lett.*, 2841 (1968).
- (10) D. M. Crouse, A. T. Wehman, and E. E. Schweizer, *Chem. Commun.*, 866 (1968).
- (11) Very recently ^{13}C data have been reported for $(\text{CH}_3)_3\text{P}=\text{CH}_2$ showing a dipolar ylide structure containing an sp^2 carbanion and an sp^3 onium center, a bonding description very similar to that proposed here for the triphenylphosphoranes: H. Schmidbauer, W. Buchner, and D. Scheutzw, *Chem. Ber.*, **106**, 1251 (1973).

Table I. ¹³C Chemical Shifts in Some Phosphorus Ylides and Triphenylphosphine Oxide^a

Compd	Carbon								
	1	2	3	4	5	6	7	8	9
 1	29.78	171.96	49.67			128.18	133.20	129.02	130.08
 2	29.59	168.81	57.59	14.61		126.18	131.01	126.90	132.25
 3(trans)	32.96	<i>b</i>	57.91	15.45	12.15	128.28	<i>c</i>	<i>d</i>	<i>e</i>
 3(cis)	31.68	175.13	57.36	14.18	12.98	128.70	133.90	128.72	131.81
 4	30.83	180.20	65.89	30.63		126.16	133.51	129.09	132.55
		6	7	8	9	10	11	12	
 5 Ph ₃ P ⁺	126.62	133.98	129.17	132.94	78.26	117.21 ^f	114.57 ^f		
 6 ^a Ph ₃ P ⁺	126.26	134.66	129.53	133.08	53.28	131.26 ^f	142.09 ^f		
 7 Ph ₃ P=O	135.56	132.28	128.76	132.25					

^a Shifts are accurate to ± 0.02 ppm with respect to internal TMS-¹³C. ^b Insufficient signal-to-noise to assign. ^c No separate C-7 signal observed, line width of C-7 in **3(cis)** ~ 4 Hz. ^d No separate C-8 signal observed, line width of C-8 in **3(cis)** ~ 1.5 Hz. ^e No separate C-9 signal observed. ^f Assignment in pair not certain. ^g Outer ring aromatic shifts 116.36, 116.84, 123.23, and 119.80.

Table II. ^{13}C - ^{31}P Nuclear Spin Couplings in Some Phosphorus Ylides and Triphenylphosphine Oxide^a

Compd	Carbon								
	1	2	3	4	5	6	7	8	9
1	126.7	12.7	2.6			91.9	10.1	12.2	3.0
2	~130(trans) ~117(cis)	12.1	2.2	<1		91.6	9.9	12.2	2.7
3(trans)	127.7	<i>b</i>	<1	<1	12.4	89.8	9.5	12.0	2.4
3(cis)	120.7	12.5	<1	<1	13.2	89.8	9.5	12.0	2.4
4	135.1	21.9	13.8	12.6		92.0	10.2	12.5	2.9
	6	7	8	9	10	11	12		
5	89.6	10.0	12.1	2.9	113.1	15.7 ^c	18.0 ^c		
6	88.8	10.7	11.8	3.0	128.7	14.0 ^c	14.8 ^c		
7 Ph ₃ P=O	104.4	9.8	12.1	2.8					

^a In hertz, accurate to ± 0.2 Hz. ^b Signal-to-noise insufficient for assignment. ^c Assignment may be reversed within pair. ^d Outer aromatic ring couplings all < 1 Hz.

the function of substituent on the ^{13}C shifts and ^{13}C - ^{31}P couplings of a carbon bound to phosphorus coordinated *only* to carbon (as opposed to the compounds in part I,¹ $(\text{C}_2\text{H}_3\text{O})_2\text{P}(\text{O})\text{CH}_2\text{X}$), we have also studied the class $\text{Ph}_3\text{PCH}_2\text{X}^+\text{Y}^-$. It is the hope that these data may give a clearer delineation of the electronic differences (and similarities) between the formal P(IV) and P(V) "oxidation states," with the ultimate view of a useful description of the "stabilized" phosphorus-carbon ylide bond.

Experimental Section

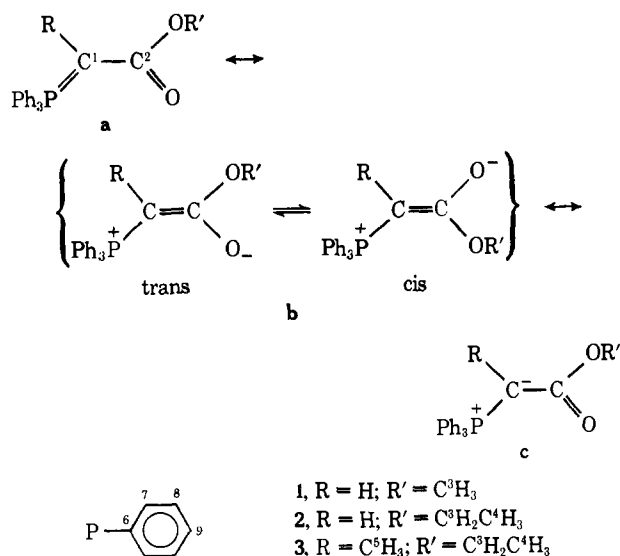
The ylides and one conjugate acid were run as received (except for 2 and 3 which were recrystallized from CH_2Cl_2 - $(\text{C}_2\text{H}_5)_2\text{O}$ and dried) from Aldrich Chemical Co. in saturated deuteriochloroform solution (usually 250–750 mg/ml) containing 1–5% tetramethylsilane as reference. Solutions were examined in 12-mm tubes using a Varian XL-100-15 nmr spectrometer in Fourier transform mode. Several hundred to several thousand transients were accumulated typically with acquisition times of 1.0 to 3.3 sec, with 1.7 sec being normal for coupling measurements. Line positions were determined automatically by computer software using the Varian S-124XL Fourier transform accessory. ^{13}C - ^1H couplings were eliminated using broadband ^1H noise-modulated decoupling.

The triphenylphosphonium salts were also purchased from Aldrich Chemical Co. and were run as received in deuteriochloroform solutions (usually 300–600 mg/ml) containing 1–5% tetramethylsilane. Most of the salts were examined in 10-mm tubes using an XL-100-WG12/S124-FT and acquisition times of 4–8 sec. Because of its low solubility (~ 50 mg/ml) the data for 19 were taken using an acquisition time of 1.14 sec, 47.3 thousand transients.

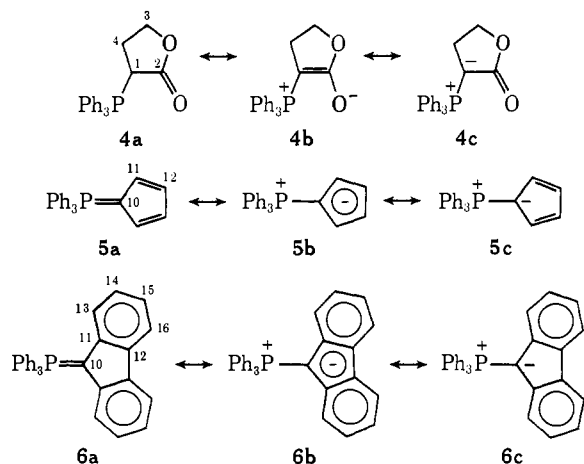
Results

Tables I and II contain the ^{13}C chemical shifts and ^{13}C - ^{31}P nuclear spin couplings for two major types of

phosphorus ylides. 1–4 are of the type $\text{Ph}_3\text{PC}(\text{R})\text{-CO}_2\text{R}'$ while 5 and 6 have the ylide carbon as part of a planar unsaturated ring. 1–3 have been shown to be equilibrium mixtures of cis and trans isomers (formally **b**), long lived enough to give separate signals for some of the protons in the ^1H nmr spectra. Only the trans configuration is possible for 4.



Recent work has shown that 1 is predominantly in the trans configuration,⁹ 2 is predominantly trans,¹⁰ and 3 is predominantly cis.¹⁰ Temperature-dependence studies¹⁰ show that the ease of cis-trans interconversion is



greater for **2** than **3**. This is borne out in the present work where separate signals are observed for the C-1, C-3, C-4, C-5, and C-6 carbons of the two isomers of **3** but only average shifts in **2** (at $\sim -33^\circ$) and also for **1**. The expected $^{10}2:1$ isomer ratio was observed for **3**.

The ^{13}C shifts are easily assigned on the basis of the large carbonyl shift, small methyl shift, data from previously studied phenyl-substituted phosphorus compounds,^{3,5} and the observed $^{13}\text{C}-^{31}\text{P}$ couplings.

5 and **6** are assigned using the signals expected from the Ph_3P^+ group as determined from **1-4**. The unsubstituted cyclopentadienyl ring carbons are so close in shift and coupling that their assignment may be the reverse of that shown. A similar situation prevails for the fluorenyl compound **6**. The reduced intensity of C-11 and C-12 quaternary carbons (long T_1) allows them to be identified, but their exact assignment as well as those within C-13 to C-16 remains open. **7** was examined as a model for the effect of extensive $d\pi-p\pi$ bonding on the phenyl carbons. Shifts and couplings for the triphenylphosphonium salts are given in Tables III and IV.

Table III. ^{13}C Chemical Shifts^a in

X	Carbon, ppm ^b				
	6	7	8	9	1
8 H	119.30	133.51	130.66	135.36	10.56
9 CH_3^c	119.00	134.42	131.52	136.27	16.39
10 CH_2CH_3^d	118.27	133.76	130.73	135.23	24.20
11 $\text{CH}_2\text{CH}_2\text{CH}_3^e$	118.34	133.79	130.76	135.30	22.50
12 $\text{CH}=\text{CH}_2^f$	117.95	134.09	130.57	135.33	28.53
13 C_6H_5^g	118.57	134.99	131.35	136.50	30.32
14 CH_2OH^h	119.02	133.14	130.55	135.13	27.10
15 COCH_3^i	119.05	134.15	130.30	134.90	40.14
16 $\text{CO}_2\text{CH}_2\text{CH}_3^j$	117.96	134.11	130.65	135.63	32.89
17 OCH_3^k	117.02	134.58	130.98	135.93	66.19
18 Cl	116.48	134.62	130.89	136.01	33.79
19 COC_6H_5^l	119.04	134.27	130.40	135.06	38.66

^a In CDCl_3 . ^b Shifts are accurate to ± 0.01 ppm and are with respect to 1-5% internal $\text{TMS}-^{13}\text{C}$ (natural abundances). ^c Methyl, 6.94 ppm. ^d CH_2 , 16.40; CH_3 , 15.20 ppm. ^e CH_2 , 24.48; CH_2 , 23.56; CH_3 , 13.68 ppm. ^f CH , 126.12; CH_2 , 123.58 ppm. ^g C-6', 128.46; C-7', 132.19; C-8', 129.95; and C-9', 129.57 ppm. ^h CH_2 , 55.52 ppm. ⁱ $\text{C}=\text{O}$, 201.45; CH_3 , 32.35 ppm. ^j $\text{C}=\text{O}$, 164.47; CH_2 , 62.81; and CH_3 , 13.69 ppm. ^k CH_3 , 62.86 ppm. ^l $\text{C}=\text{O}$, 196.49; C-6', insufficient signal-to-noise to assign; C-7', 135.01; C-8', 129.16; and, C-9', 130.13 ppm.

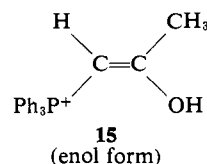
Table IV. $^{13}\text{C}-^{31}\text{P}$ Nuclear Spin Couplings^{a, b} in

X	Carbon				
	6	7	8	9	1
8 H	88.6	10.7	12.8	3.0	56.8
9 CH_3^c	86.0	9.7	12.5	3.0	52.6
10 CH_2CH_3^d	85.6	10.0	12.4	2.9	49.6
11 $\text{CH}_2\text{CH}_2\text{CH}_3^e$	85.8	9.9	12.5	3.0	50.3
12 $\text{CH}=\text{CH}_2^f$	85.9	9.9	12.5	2.8	50.2
13 C_6H_5^g	86.0	9.7	12.5	3.0	47.7
14 CH_2OH^h	86.6	10.2	12.6	3.1	50.0
15 COCH_3^i	89.3	10.6	13.2	2.1	58.8
16 $\text{CO}_2\text{CH}_2\text{CH}_3^j$	89.0	10.7	13.2	3.0	55.5
17 OCH_3^k	85.9	10.0	12.8	3.1	69.4
18 Cl	88.3	10.2	13.0	3.0	56.8
19 COC_6H_5^l	89.4	10.6	13.2	2.2	61.9

^a Couplings are accurate to ± 0.2 Hz. ^b In CDCl_3 . ^c CH_3 , 5.3 Hz. ^d CH_2 , 4.4; CH_3 , 17.3 Hz. ^e CH_2 , 4.4; CH_2 , 16.4; and CH_3 , 1.0 Hz. ^f CH , 13.3; CH_3 , 9.7 Hz. ^g C-6', 8.5; C-7', 5.5; C-8', 3.2; and C-9', 3.9 Hz. ^h CH_2 , 4.9 Hz. ⁱ $\text{C}=\text{O}$, 3.0; CH_3 , 7.0 Hz. ^j $\text{C}=\text{O}$, 4.0; CH_2 , 0.0; and CH_3 , 0.0 Hz. ^k CH_3 , 13.1 Hz. ^l $\text{C}=\text{O}$, 5.2 Hz.

Discussion

In an earlier communication⁷ we reported the very high shieldings and directly bonded C-P coupling in the ylides **1-7**. The large contrasts between these data and the shieldings and couplings of the phosphorus-bound carbons in the triphenyl groups and those of C-1 in the enol form of **15**¹² (a **b** type carbon) clearly show that **b**



does not provide a reasonable bonding description for these phosphorus ylides. Taking into account other ^{13}C shift data on delocalized carbanions¹³ and the X-ray results of various ylides,¹⁴ a bonding description involving basically sp^2 hybridization with high negative charge best fits the data. It is interesting to note that the ylide couplings are larger than those of the sp^2 carbons in the triphenyl group, in spite of the fact that effective nuclear charge arguments¹⁵ would predict a smaller coupling. The shift and coupling data for the ylide carbons in **5** and **6** in conjunction with previously reported data on odd-numbered delocalized carbanions^{16,17} imply a greater localization of the anionic

(12) Only one set of enol resonances (out of two possible isomers were observed for **15** in CDCl_3 . The observed ratio was 2.5 keto:enol. The enol form above is shown as an example, but the arguments above are unaffected by choice of isomer. Using the numbering system employed for the ylides: C-1, 70.92 ppm, 99.2 Hz; C-2, 180.90, 0.0; C-3, 23.80, 12.7; C-6, 121.88, 92.5; C-7, 133.40, 10.6; C-8, 130.16, 13.2; and C-9 134.90, 2.1.

(13) R. Waack, M. A. Doran, E. B. Baker, and G. A. Olah, *J. Amer. Chem. Soc.*, **88**, 1272 (1966); L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *ibid.*, **91**, 1057 (1969); R. Waack, L. D. McKeever, and M. A. Doran, *Chem. Commun.*, 117 (1969).

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(16) R. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson, G. D. Forsythe, D. A. McCombs, and A. S. Roth, *ibid.*, **95**, 926 (1973).

(17) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).

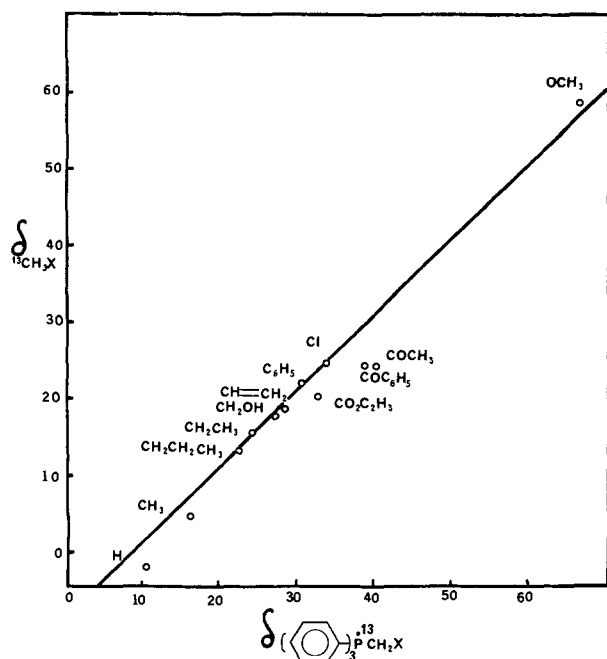


Figure 1. Correlation of the substituted carbon shifts in CH_3X and $\text{Ph}_3\text{P}^+\text{CH}_2\text{X}$. Line drawn for slope = 1.00.

charge on the ylide carbon in **6** than **5** and thus may be better depicted as delocalized in **5** and localized in **6**.^{17a}

The C-11 and C-12 shifts in **5** and **6** are difficult to explain on an additivity basis. Other model compounds¹⁸ are considered in Chart I for reference. The effect of going from cyclopentadiene to fluorene is an approximate 10-ppm deshielding for C-11. In aromatic cases such as benzene or pyridine only a small change is evident. For **5** \rightarrow **6** (assuming that C-12 is assigned from the similarity of shift to the analogous fluorene carbon) C-11 is deshielded by 14 ppm and C-12 by 25 ppm. These large changes re-enforce the localized character of **6** since a fully delocalized **6** would probably have C-11 and C-12 shifts of more comparable magnitude.

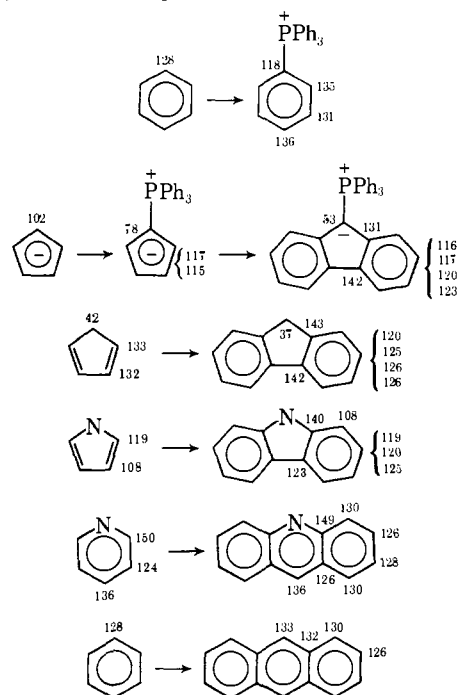
The remaining carbon directly bound to the phosphorus is C-6. Within **1-6**, it is deshielded with respect to the phosphonium analogs **8-19** while variations apparently seem only reflective of the cyclic or acyclic nature of the ylide carbon. Although the ylide carbon shifts and couplings in **5** and **6** differ significantly, their C-6 (and other phenyl carbon) shifts and couplings differ only slightly. It then appears that the electronic redistribution on going from **5** to **6** does not involve the Ph_3P^+ group to any significant extent. The C-6 couplings do have a 3-Hz spread within the ylides, a sensitivity to changes taking place several bonds away. The largest C-6 variation is noted in triphenylphosphine oxide.

The increase in C-6 coupling is similar to the 10–20%

(17a) NOTE ADDED IN PROOF. X-Ray and photoelectron spectroscopic studies on **5** and **6** have appeared very recently (H. L. Ammon, G. L. Wheeler, and P. H. Watts, Jr., *J. Amer. Chem. Soc.*, **95**, 6158 (1973)). A similar pattern of delocalization in **5** and **6** was inferred.

(18) Data obtained from J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972, unless otherwise noted. Triphenylphosphonium bromide, this laboratory, saturated solution in CDCl_3 : C-6, 117.94 ppm, 89.3 Hz; C-7, 134.82, 10.4; C-8, 131.36, 12.8; and C-9, 136.28, 3.0. Cyclopentadienyl and fluorenyltriphenylphosphoranes, this work.

Chart I. Comparison of ^{13}C Chemical Shifts (with Respect to $\text{TMS-}^{13}\text{C}$) in Model Compounds



increase in directly bonded phenyl carbon coupling in replacing a phosphonium methyl with oxide in the phenyl-substituted 1,2,2,3,4,4-hexamethylphosphetanium salts reported earlier.⁵ The same carbon also undergoes an ~ 11 -ppm deshielding in the salt to oxide process. Methyltriphenylphosphonium iodide has a substituted phenyl carbon shift of 119.3 ppm and is similarly deshielded by 13.3 ppm on going to the oxide. The importance of $d\pi-p\pi$ bonding to the oxide oxygen is not readily assessed since the deshielding of C-6 and its increased coupling may only reflect an oxygen substituent (inductive) effect.

Triphenylphosphonium Salts. The triphenylphosphonium group has found widespread use in organophosphorus chemistry for synthetic and stability reasons. It is important to have sensitive indicators of any electronic perturbations this group has when used as a substituent, a role that ^{13}C chemical shifts and ^{13}C - ^{31}P couplings can fill usefully. Attempts at decomposition of ^{13}C shifts into sums of substituent effects have resulted in a large body of data for the general system $\text{Y-}^{13}\text{C}_2\text{-X}$, where X represents a site of variable substitution and Y a group containing a directly bound spin-coupled nucleus such as ^1H , ^{13}C , or ^{31}P . These have been useful in examining the effect of substituents and their transferability. In part I¹ we studied the series $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{CH}_2\text{X}$ and compared it (primarily) to the series CH_3X . An excellent ^{13}C shift correlation (slope = 1.0) was evident, indicating additivity of effects on the methylene carbon shift. The phosphonate series can be envisioned primarily as coordination of a O_3P group to a CH_2X fragment. The triphenylphosphonium series reported here represents coordination of a C_3P group to CH_2X . Figure 1 illustrates again the additivity of phosphonium and X substituent effects. The correlation is excellent as is the cross correlation of the two types of (formally) P(IV) and P(V) series in Figure 2. Also embodied in Figure 2 are correlations

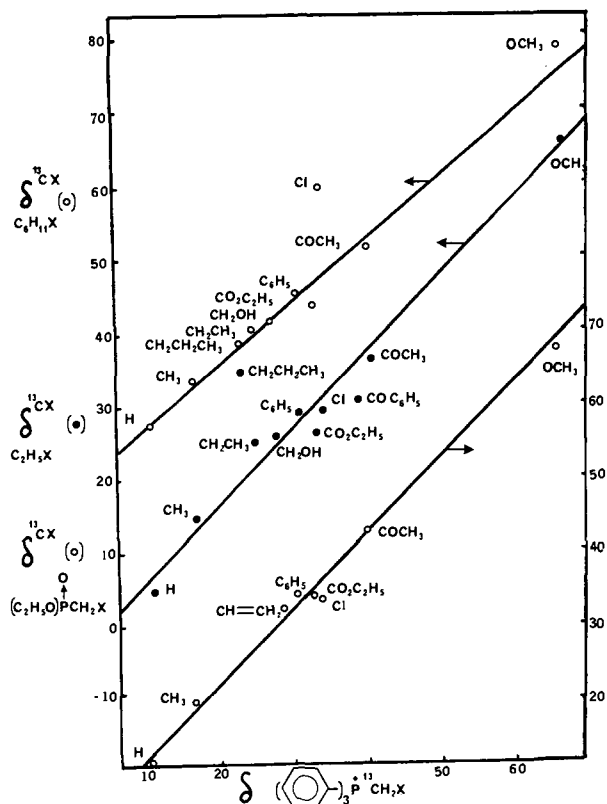


Figure 2. Correlations of the substituted carbon shifts in C_2H_5X , $(C_2H_5O)P(O)CH_2X$, substituted cyclohexanes, and $Ph_3P^+CH_2X$.

of the methylene carbon shift with similarly substituted ethyl¹⁹ and cyclohexyl groups.²⁰ It is clear that the triphenylphosphonium group contributes its own characteristic shielding but does not strongly interact with other substituents to produce nonlinear effects. Hence, additivity relations should be possible for chemical shifts. Similar attempts at examining trends in ^{13}C - ^{31}P couplings with substituent reveal poorer patterns of agreement. As Figure 3 shows, $^1J_{CC}$ in substituted ethanes seems to most faithfully follow the trend of the $^1J_{CP}$ in the triphenylphosphonium salts. While a more scattered pattern is provided for $^1J_{CH}$ in CH_3X , $^1J_{CP}$ in the phosphonates seems to have opposite patterns of correlation, as a function of X. The phenyl carbon couplings in the triphenylphosphonium series are essentially independent of substituent with a few exceptions. The C-6 couplings cluster around 86 Hz except for the H, $COCH_3$, $CO_2CH_2CH_3$, COC_6H_5 , and Cl substituents which range from 88.3–89.4 Hz. These same substituents also produce slightly higher C-7 couplings (except Cl).

^{13}C - ^{31}P Couplings and Bond Character. The various theoretical approaches in the study of nuclear spin couplings were reviewed in part I.¹ In that work SCF-MO finite perturbation calculations using the INDO approximation based on the theory of Pople, McIver, and Ostlund²¹ were shown to be successful in calcula-

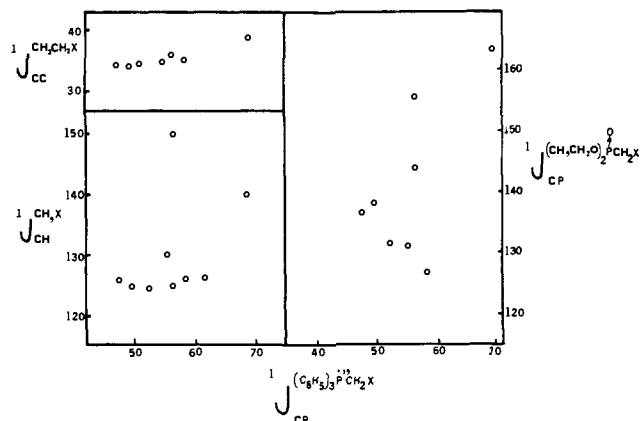


Figure 3. Correlations of $^1J_{CY}$ coupling in $Y-^{13}CH_2-X$ with $^1J_{CP}$ in $Ph_3P^+CH_2X$ for $Y = ^1H, ^{13}C,$ and ^{31}P .

tion of ^{13}C - ^{31}P one-bond couplings in a series of diethyl phosphonates.¹ For these four-coordinate phosphorus compounds the coupling followed the calculated $2S_C-3S_P$ bond order but varied about twice as fast. The site of variable substitution was not on the phosphorus but on the phosphonate carbon. In the triphenylphosphonium salts we have a somewhat similar situation. The phenyl data indicate that the phosphorus is changing very little in its electronic character within the series. It then appears that, while the chemical shift perturbations caused by X are fairly independent of Y, the coupling of the methylene carbon to the directly bonded atom in Y is affected electronically by X in a way dependent on the nature of the coupled atom in Y. Use of any one of these couplings as reflective of s character in the bonding orbital may have some validity, but any attempt at ascribing a change in this bonding orbital s character as a sole property of the X substituent must fail. Hopefully, full molecular orbital calculations of the couplings may bring out the factors responsible for this complex behavior.

If $^1J_{CP}$ does reflect the s character of the ylide bond, comparison of the enol form of **15** with ylides **1** and **2** gives the safest comparison since the coordination and geometry of the important atoms are very similar. The 99-Hz enol carbon coupling is to be contrasted to the 117–130-Hz range shown in the ylides. Within the argument that increased coupling results from increased s character (Fermi contact mechanism), the ylides should have a higher s character in the ylide bonding orbital. It might be argued that the additional s-orbital contribution comes from a rehybridization of phosphorus. The observed phenyl ^{13}C - ^{31}P couplings do not suggest this, however. It would then seem that the ylide carbon would have to contribute the major share of rehybridization, although it must be emphasized that attaching too much credibility to this simple mechanism would be unwise since our understanding of coupling between heavy atoms is still evolving.

Stereospecificity in ^{13}C - ^{31}P Coupling. As noted in our earlier studies on phosphetanes, ^{13}C - ^{31}P couplings are very sensitive to stereochemistry.²⁻⁵ Stereospecificities are largest for $^2J_{CP}$ in phosphines⁴ but they are also evident in one-bond couplings in P(IV) and P(V) compounds.² Other workers have also had simi-

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lar results in other cyclic and acyclic compounds.²²⁻²⁵ As evident in Table II, the coupling of the ylide carbon is sensitive to isomer, larger in the trans isomers of **2**, **3**, and (trans by definition) **4**. The relative positions of the coupled atoms remain constant in both isomers, *i.e.*, no dihedral angle dependence. While no simple explanation of the stereospecificity is apparent, its utility can still be recognized as a means of isomer identification, particularly in those instances where the ¹H nmr methods are difficult or impossible.

Conclusions

The data reported here show clear and basic differences in molecular electronic structure among phos-

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phorus ylides and triphenylphosphonium salts, although it appears that the electronic differences do not arise out of significant changes in the phosphorus bonding but primarily in the ylide carbon electronic nature. The triphenylphosphonium group has additive effects on ¹³C shifts as a substituent although the directly bonded coupling to a coordinated carbon reflects changes in the electronic nature of that carbon in a rather complex way as a function of further substitution on that carbon. The ylide carbons in the apparently similar cyclopentadienyl and fluorenyl ylides are indeed of substantially different character with subsequently different degrees of localization of anionic charge. Ylides of the type Ph₃PC(R)CO₂R' should not be considered to have primarily **b** type electronic character. Instead, they show greater localization, as exemplified by **c** type bonding.

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Selective Measurement of Nuclear Relaxation Times of Carbohydrate Derivatives¹

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Abstract: The proton nuclear relaxation times (T_1 values) of 3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-bromo-2-deoxy- β -D-glucopyranose (**1**), of its α anomer (**2**), of the corresponding 2-chloro-glucosyl derivatives (**3**, **4**), and of the 2-bromo- α -D-manno derivative (**5**) have been measured by a Fourier transform method; the T_1 and T_2 values of some resonances of **1** and **3** were also measured *via* the audiofrequency pulse technique. Characteristic differences in T_1 values exist between protons having an axial or an equatorial disposition with respect to the ring system, and between vicinal protons that have a *gauche* interaction.

Although the phenomenon of nuclear relaxation is of fundamental importance to the measurement of nuclear magnetic resonance (nmr) spectra, it has been largely neglected by organic chemists.⁵ There are many good reasons for this lack of interest, of which the most cogent is that until very recently, instrumentation suitable for the *routine* and selective measurement of the nuclear relaxation times of anything other than very simple molecules has been unavailable. However, the development of the selective, audiofrequency pulse (nmr) technique by Freeman and Wittekoek⁶ and of Fourier transform methods by Ernst and Anderson, by Waugh and coworkers, and by Freeman and Hill⁷ has

made possible, at least in principle, relaxation studies of complex organic systems. Several laboratories, notably that of Allerhand,⁸ have measured the longitudinal relaxation times of ¹³C in natural abundance using Fourier transform methods, but few laboratories have shown much interest in equivalent studies of proton relaxation times. As part of a general program⁹ to evaluate the very considerable potential of this area, we have chosen to study five pyranose derivatives which were known¹⁰ to give reasonably simple proton nmr spectra. As will be seen, the audiofrequency pulse techniques does not satisfy entirely the selectivity

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