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Nuclear Magnetic Resonance Studies. 5. Properties of Phosphorus–Carbon Ylides[1]

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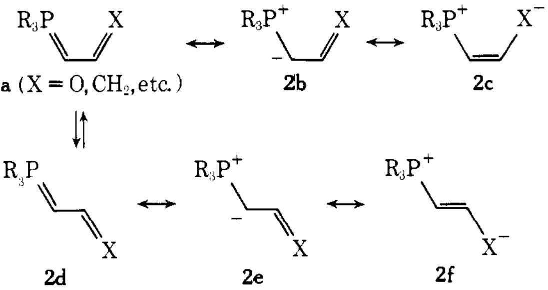
Abstract: The ^{13}C and ^{31}P NMR data for stabilized and nonstabilized phosphorus-carbon ylides are compared to CNDO/2 and MINDO/3 molecular orbital calculations. Evidence of both an experimental and theoretical nature is presented that indicates that the carbon adjacent to phosphorus exists in a trigonal conformation. The molecular orbital calculations predict substantial π interactions between the carbanion and phosphonium group. The various theoretical methods are compared to the trends in ^{13}C and ^{31}P chemical shifts developed for the compounds in this study. It is found that the negative charge in stabilized phosphoranes is delocalized over the π framework of the molecules to a smaller extent than for analogous carbanions. The conformational preferences of ethylidene, cyclopropylidene, allylidene, and formylmethylenephosphorane are studied by theoretical techniques and the results are in agreement with available experimental data.

Ylides occupy a unique position in the chemistry of carbanions, since the gegenion is incorporated in the framework of the molecules. Hence, no ion-pairing effects contribute to its electronic properties or structure. Phosphorus-carbon ylides, in particular, have enjoyed widespread use in synthesis.[4] Thus, these compounds are of considerable interest from the standpoint of their electronic structure and chemical reactivity.

A preliminary account of the carbon NMR of phosphorus ylides has been published.[5] The carbon and phosphorus NMR of methylenetrimethylphosphorane[6] and a series of stabilized phosphoranes[7] (ylides containing strong electron-withdrawing groups adjacent to the carbanion) have also appeared in the literature. This NMR information, as well as recent photoelectron spectroscopy studies on several ylides[8] indicate substantial negative charge on the carbon adjacent to phosphorus. These "carbanions" are, however, by no means unstable. Methylenetrimethylphosphorane can be distilled without decomposition[9] and an x-ray structural determination of methylenetriphenylphosphorane has been carried out.[10] The nonstabilized ammonium ylides, on the other hand, decompose rapidly.[11] The extra stability of phosphoranes compared to their nitrogen counterparts, short P-C bond distances, and numerous other physical properties have led many researchers to the conclusion that there is a multiple bond formed between phosphorus and carbon presumably via dπ-pπ overlap.[4,12] The involvement of d orbitals in a "chemically significant" manner has been challenged recently.[13,14] Thus, the following resonance structures may be considered to contribute by varying degrees to nonstabilized and stabilized phosphoranes.

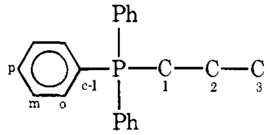
$$\underset{\textbf{1a}}{R_3P{=\!=}CR'_2} \longleftrightarrow \underset{\textbf{1b}}{R_3P^+{-}^-CR'_2}$$

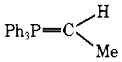
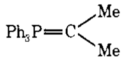
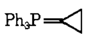
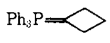
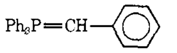
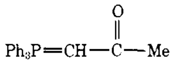
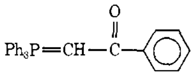
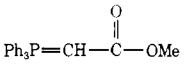
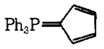

2a (X = O, CH$_2$, etc.) **2b** **2c**

2d **2e** **2f**

In the present work, a qualitative assessment of the importance of resonance structures outlined above is accomplished from two directions. First, by comparison of suitable, closely related compounds (in this case the parent phosphonium salts) the ^{13}C chemical shifts and ^{13}C–^{31}P coupling constants can provide a qualitative estimation of the electronic environment[15] in phosphoranes. This data is supplemented by ^{31}P chemical shifts. Second, CNDO/2[16] and MINDO/3[17] molecular orbital calculations were carried out on model phosphoranes. These calculations lend support for the arguments developed from

Table I. ^{13}C Chemical Shifts of Triphenylphosphonium Ylides and Their Corresponding Salts



Compd	No.	Carbon, ppm[a] 1	2	3	4	5	6	C-1	*o*	*m*	*p*
	3	3.2	11.0					133.3	132.9	128.5	130.6
	4	(17.0)	(6.9)					(117.9)	(133.6)	(130.5)	(135.0)
	5	9.0	20.8					133.6	133.8	128.3	130.6
	6	(21.5)	(16.4)					(117.5)	(133.8)	(130.6)	(134.9)
	7	4.3	7.7					*b*	132.8	128.8	130.8
	8	(0.4)	(4.9)					(118.3)	(133.7)	(130.4)	(135.2)
	9	14.6	28.5	22.8				131.8	132.5	128.6	130.7
	10	(25.4)	(23.1)	(20.3)				(118.0)	(133.8)	(130.7)	(135.2)
	11	28.0	127.1	121.6	128.3	115.1		130.4	133.4	129.1	131.8
	12[c]	(30.3)	(128.5)	(132.2)	(130.0)	(129.6)		(118.6)	(135.0)	(131.4)	(136.5)
$Ph_3P{=}CHCH{=}CH_2$	13	28.7	137.9	90.7				131.2	133.1	128.7	131.3
	14	(28.6)	(126.3)	(123.1)				(117.7)	(133.9)	(130.4)	(135.1)
 $Ph_3P{=}CH{-}C({=}O){-}Me$	15	51.3	190.5	28.4				127.4	133.0	128.7	131.8
	16	(40.1)	(201.4)	(32.4)				(119.0)	(134.2)	(130.3)	(134.9)
	17	50.4	184.9	141.4	127.0	127.7	129.3	127.2	133.2	128.8	132.0
	18[c]	(38.7)	(196.5)	*b*	(135.0)	(129.2)	(130.1)	(119.0)	(134.3)	(130.4)	(135.1)
 $Ph_3P{=}CH{-}C({=}O){-}OMe$	19[c]	29.8	172.0	49.7				128.2	133.2	129.0	130.1
	20[c]	(40.1)	(201.4)	(32.4)				(119.0)	(134.2)	(130.3)	(134.9)
	21[c]	78.3	117.2	114.6				126.6	134.0	129.2	133.1

[a] The salts are listed within the parentheses. The carbon chemical shifts are referenced to internal Me_4Si. The numbering of the compounds is shown at the top of the table. [b] One resonance was obscured by another peak. [c] Values taken from G. A. Gray, *J. Am. Chem. Soc.*, 95, 7736 (1973).

experimental methods with respect to electron distribution. Additionally, by minimizing the energy of molecules with respect to geometrical variables, the calculations provide clues to the conformation of phosphorus-carbon ylides. Previous theoretical treatments include extended Hückel calculations which were performed on a variety of phosphoranes by Hoffmann et al.[18] and there has been an ab initio calculation of methylenephosphorane using assumed geometries.[19] Also π-electron models have been considered for phosphoranes.[20] All of these studies have indicated appreciable interaction of d orbitals on phosphorus.

Results

NMR Results. The ^{13}C chemical shifts, ^{13}C–^{31}P couplings, and ^{31}P chemical shifts of the phosphoranes are given in Tables I–III, respectively. The ^{13}C and ^{31}P NMR of the phosphonium salts has been recently published;[21] these compounds are used as a reference to the phosphoranes and will not be discussed here. That the compounds were the ylides and not the lithium adducts of the nonstabilized phosphoranes is evidenced by the large P–C coupling of alkyl C-1 (77.3–132.8 Hz), whereas the lithium adduct of methylenetriphenylphosphorane has a P–C coupling of 50–65 Hz and a ^{31}P chemical shift which is identical with that of methyltriphenylphosphonium iodide,[22] in contrast to the other ylides in Table III.

The ^{13}C chemical shifts for the alkyl C-1 of all of the phosphoranes are found to be shielded by an extraordinary amount compared to typical conjugated carbanions.[15,23] This does not explicitly rule out resonance structures **1a**, **2a**, or **2d**, since d orbitals are expected to be diffuse, leaving significant electron density near the α carbon.[12] There is also evidence that some delocalization of electron density occurs via resonance structures analogous to **2c** and **2f**. For example, C-5 in benzylidenetriphenylphosphorane (**11**) and C-3 in allylidenetriphenylphosphorane (**13**) are shielded by 14.5 and 32.4 ppm, respectively, from their phosphonium salt protomers, **12** and **14**. These carbons are, however, deshielded with respect to benzyl or pentadienyl carbanions.[23] C-3 in acetonylidenetriphenylphosphorane (**15**) and C-4 and C-6 in **17** are also shielded compared to their phosphonium salts, which may be taken as indirect evidence for some delocalization of charge onto the carbonyl oxygen, since the electron-withdrawing nature of an enolate anion is expected to be less than that of a carbonyl group. However, the highly shielded alkyl C-1 for **15**, **17**, and **19** again precludes **2c** and **2f** as the sole resonance contributors to the electronic structure of these compounds.[7] The alkyl C-1 in cyclopentadienyltriphenylphosphorane (**21**) is shielded by 24.1 ppm from the carbons in cyclopentadienyl carbanion,[24] while C-2 and C-3 are deshielded by 14.2 and 11.6 ppm, respectively. This implies some localization of charge; however, this effect is small compared to the other stabilized phosphoranes (vide infra).

It is interesting that the C-1 phenyl carbons are uniformly deshielded by 12–16 ppm from those in the phosphonium salts. Likewise the alkyl carbons β to the phosphorus for the nonstabilized ylides **3**, **5**, **7**, and **9** are deshielded from their phosphonium salt counterparts. This effect, which is also seen for phosphine oxides and other compounds containing a P=X bond,[1] may be in part due to an electric field effect of the P=C bond.

The chemical shifts for the ortho phenyl carbons are likely to be obscured by steric differences between the ylides and salts in Table I; however, the meta and para chemical shifts are consistently shielded with respect to the phosphonium salts. This is in accord with increased electron density on the phosphorus for the ylides compared to the salts.

The ^{31}P chemical shifts of nonstabilized phosphoranes are shielded by 7.7–20.5 ppm from their phosphonium salt protomers. The ^{31}P chemical shifts of **3** and **5** are similar to those obtained in Me_2SO.[25] It is normal in tetravalent phosphorus

Table II. $^{31}P-^{13}C$ Couplings of Triphenylphosphonium Ylides and Their Corresponding Salts

Compd No.	$^{31}P-^{13}C$ couplings, Hz[a]							
	1	2	3	4	C-1	*o*	*m*	*p*
3	110.7	4.3			82.8	9.0	11.0	2.7
4	(51.6)	(5.1)			(86.2)	(9.9)	(12.4)	(2.9)
5	121.5	13.4			81.2	8.5	11.6	2.4
6	(47.0)	(2.0)			(83.1)	(9.2)	(12.1)	(3.0)
7	132.8	*b*			*c*	9.6	11.5	2.7
8	(86.9)	(4.3)			(89.6)	(9.8)	(12.6)	(2.8)
9	77.3	*b*	25.0		81.2	8.8	10.8	2.6
10	(45.0)	(2.8)	(16.8)		(85.0)	(9.6)	(12.3)	(2.9)
11	128.0	*b*	14.2	2.0	94.2	9.8	11.7	2.9
12[d]	(47.7)	(8.5)	(5.5)	(3.2)	(86.0)	(9.7)	(12.5)	(3.0)
13	131.4	7.2	20.4		86.3	9.5	11.8	2.7
14	(49.7)	(13.4)	(9.8)		(85.9)	(9.8)	(12.4)	(2.6)
15	108.0	2.4	16.5		90.3	9.8	12.2	2.4
16	(58.8)	(3.0)	(7.0)		(89.3)	(10.6)	(13.2)	(2.1)
17	111.7	3.0	14.1	*b*	90.2	10.2	12.7	2.6
18[d]	(61.9)	(5.2)	*b*	*b*	(89.4)	(10.6)	(13.2)	(2.2)
19[d]	126.7	12.7	2.6		91.9	10.1	12.2	3.0
20[d]	(58.8)	(3.0)	(7.0)		(89.3)	(10.6)	(13.2)	(2.1)
21[d]	113.1	15.7	18.0		89.6	10.0	12.1	2.9

[a] Salts are listed within the parentheses. The numbering system is identical with that used in Table I. The digital resolution used was ±0.1 Hz. [b] No coupling to phosphorus was observed. [c] One resonance was obscured by another peak. [d] Values taken from G. A. Gray, *J. Am. Chem. Soc.*, 95, 7736 (1973).

Table III. ^{31}P Chemical Shifts of Triphenylphosphonium Ylides and Their Corresponding Salts

Compd no.	δ_P[a]	$\Delta\delta_P$[b]	Compd no.	δ_P[a]	$\Delta\delta_P$[b]
3	15.0		13	10.7	
4	(25.5)	10.5	14	(20.8)	10.1
5	9.8		15	14.6	
6	(31.3)	21.5	16	(20.1)	5.5
7	16.7		17	16.8	
8	(28.5)	11.8	18	(22.2)	5.4
9	16.5		19	17.8	
10	(24.2)	7.7	20	(21.0)	3.2
11	7.0				
12	(23.2)	16.2			

[a] The ^{31}P chemical shifts of the phosphonium salts are given in parenthesis. The shifts are reported in parts per million downfield from external 85% H_3PO_4. [b] The difference in chemical shift between the salt and the ylide.

compounds that replacement of a hydrogen with a methyl group β to the phosphorus causes a downfield ^{31}P chemical shift.[1,22,26] This does not appear to be the case for phosphorus ylides. For example, isopropylidenetriphenylphosphorane (**5**) is shielded by 5.2 ppm from ethylidenetriphenylphosphorane (**3**). This situation is also found for alkylidenetriethyl- and triisopropylphosphoranes.[27]

The one-bond P-C couplings to alkyl C-1 in Table II for the ylides are at least twice the magnitude of the corresponding salts with the exception of **7** and **9** (a discussion of the reduction of $^1J_{P-C}$ in **7** and **9** is given in the theoretical section). It should be noted that $^1J_{P-C}$ has been determined to be positive for phosphonium ylides and salts.[6] The magnitude of the P-C coupling has been successfully related to the percent s character in the carbon hybrid orbital comprising the P-C bond for a variety of tetravalent phosphorus compounds.[1,21,22,28] Therefore, the large P-C couplings for alkyl C-1 in the phosphoranes implies that these carbons must be approximately sp^2 hybridized, i.e., trigonal with the lone pair of electrons in a p orbital. This is in agreement with all of the x-ray structures of phosphorus-carbon ylides.[10,29] The only other significant difference in the P-C couplings of the ylides compared to their phosphonium salts is a larger $^3J_{P-C}$ for alkyl C-3 in **9**, **11**, **13**, **15**, and **17**. Since the mechanism for the three-bond P-C coupling has not been elucidated at this time, little information can be attached to this result.

Theoretical Results for Nonstabilized Phosphoranes. In conjunction with and to confirm some of the conclusions concerning the electronic nature and conformation of phosphoranes deduced from ^{13}C and ^{31}P NMR parameters, a series of molecular orbital calculations was carried out. The CNDO/2 method (spd basis set) has been shown to give generally reliable bond distances and angles for molecules containing a second-row atom, particularly where the difference in electronegativity of the second-row atom and its nearest neighbors is small.[30] It is known that the CNDO/2 and other semiempirical methods such as extended Hückel overestimate d-orbital importance;[30,31] however, ab initio data for methylenephosphorane[19] and the isoelectronic phosphine oxide[32] indicate significant d-orbital involvement for these molecules. Thus, deleting d orbitals from the CNDO/2 basis set should effectively bracket a reasonable situation. The optimized geometries, ionization potentials, and proton affinities with MINDO/3 for molecules containing a second-row element are excellent.[33] It should be noted that MINDO/3 has not been parameterized for the inclusion of d orbitals and phosphorus-oxygen or fluorine overlap.

The optimized bond angles and lengths for methylenetriphenylphosphorane and the methyl triphenylphosphonium salt were found to be in excellent agreement with experimental results.[10,29]

In general, the results of the calculations[34] show that the electron density on phosphorus increases (i.e., becomes less positive) with the sequential substitution of methyl groups for hydrogen atoms on the carbon adjacent to phosphorus for model phosphoranes of the type $H_3P{=}CH_2$ (**22**), $H_3P{=}CHCH_3$, (**23**), and $H_3P{=}C(CH_3)_2$ (**24**) in all three types of calculation. This is in accord with the ^{31}P chemical shifts of **3**, **5**, and other trialkylphosphoranes[27] in which the β effect for methyl substitution causes the ^{31}P chemical shift to become shielded. Likewise, the charge on the carbon adjacent to phosphorus decreases in the order **22** > **24** > **23**, which is consistent with the ^{13}C chemical shifts of analogous compounds (Table I).[35,36]

The predicted charge on phosphorus for methyl-, ethyl-, and isopropylphosphonium cations show a trend opposite to that given for the CNDO/2 (spd) and (sp) methods. MINDO/3 gives the proper order. However, it predicts that there should be essentially no difference in the charge on the carbon adjacent to phosphorus for these compounds, whereas, the CNDO/2 data for both methods are in line with the ^{13}C chemical shifts of methyltriphenylphosphonium iodide,[21] **4**, and **6**.

Comparison of the charges on phosphorus and their corresponding phosphonium cations provides some interesting results. CNDO/2 (sp) and MINDO/3 indicate that the phosphorus loses charge in going from the phosphonium cation to the ylide.

This is interpreted as primarily a charge polarization effect in that going from a nearly neutral carbon in the phosphonium cations to a negatively charged one for the ylides creates a large positive charge on phosphorus for the ylides. The CNDO/2 (spd) method, however, shows that phosphorus gains electron density in the phosphoranes with the intervention of d orbitals. This result is in accord with the ^{13}C chemical-shift differences for the meta and para carbons in the ylides compared to their salts (Table I). The ^{31}P chemical-shift differences in Table III follow the CNDO/2 (spd) results if one can assume that charge densities on phosphorus reflect ^{31}P chemical shifts.[37]

The conformation of the carbon adjacent to phosphorus in the nonstabilized ylides was found to be trigonal by the

CNDO/2 (spd) and MINDO/3 methods. For example, the pyramidal geometry of cyclopropylidenephosphorane is predicted by CNDO/2 (spd) to be more stable than the trigonal conformation by 7.4 kcal/mol.

Further evidence that the trigonal conformation is the most stable for nonstabilized phosphoranes is given by calculation of P–C couplings by the finite perturbation method.[38] This method has been shown to give reliable one-bond P–C couplings for a variety of tetravalent phosphorus compounds.[28,29] The calculated $^1J_{\mathrm{P-C}}$ for ethylidenephosphorane with a trigonal geometry was 116.8 Hz using the CNDO/2 (spd) wave function, in excellent agreement with that found for **3** in Table II. However, this coupling becomes −163.2 Hz with the pyramidal geometry, which is contrary to the experimentally determined sign of $^1J_{\mathrm{P-C}}$ for methylenetrimethylphosphorane.[6] Likewise $^1J_{\mathrm{P-C}}$ for cyclopropylidenephosphorane was calculated to be 194.4 and −412.1 Hz with a trigonal and pyramidal conformation, respectively. This indicates that the phosphonium group in cyclopropylidenetriphenylphosphorane (**7**) (and cyclobutylidenetriphenylphosphorane (**9**)) may be tipped slightly out of the plane of the cyclopropyl ring ($\sim$5–10°), since $^1J_{\mathrm{P-C}}$ for **7** was 132.8 Hz (Table II). Therefore, a smaller P–C coupling is observed in going from the salt to the ylide for **7** and **9** than that for the other phosphoranes in Table II. A detailed account of the conformational dependence on P–C couplings for phosphonium salts and ylides will be presented elsewhere.[39]

The molecular orbital calculations imply substantial π interactions between the carbanion and phosphorus in phosphorus–carbon ylides. This accounts in a large part for their increased stability over ammonium ylides. The CNDO/2 (spd) method seems to offer the best predictions for conformational and charge-distribution properties in relation to the ^{13}C and ^{31}P NMR results. The MO methods predict only modest delocalization of negative charge into the π framework of stabilized phosphoranes. A large share of this excess negative charge is transferred to phosphorus via dπ–pπ overlap in CNDO/2 (spd) for these compounds. All of the MO methods are consistent with the shielded C-1 resonances for the stabilized phosphoranes compared to analogous carbanions by ^{13}C NMR. However, it is difficult to reconcile the observation that phosphorus gains negative charge in going from the salt to the ylide on the basis of meta and para ^{13}C chemical shifts for the triphenylphosphonium substituent in all of the ylides considered in this study, with the charges calculated on phosphorus by CNDO/2 (sp).

Experimental Section

Compounds **3**, **5**, **7**, **9**, **11**, and **13** were prepared in a dry box by dropwise addition of an equimolar amount of *n*-butyllithium in hexane (Alfa Chemicals) to a suspension of the recrystallized phosphonium salt in diethyl ether (dried and distilled over NaH). The resulting red solutions were stirred for approximately 2 h and concentrated in vacuo. The remaining solid was dissolved in C_6D_6 to a concentration of approximately 0.5 M and filtered several times through a pipet packed with glass wool. The NMR tube was sealed with wax prior to removal from the dry box. Compounds **15** and **17** were not air sensitive and, hence, recrystallized before use and run in C_6D_6. The ^{13}C and ^{31}P data were taken at operating frequencies of 22.63 and 36.43 MHz, respectively, on a Bruker HFX-90 spectrometer. All samples were run at 28 °C with broad-band ^{1}H decoupling. Assignment of peaks was accomplished by comparison of the ^{13}C chemical shifts and P–C couplings of the phosphonium salts[22] and other stabilized phosphoranes.[7] All calculations were carried on a Burroughs B6700 or Univac 1108 computer.

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