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About the Structure of Phosphorus Ylids: Electron Distribution and Geometry

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ABSTRACT

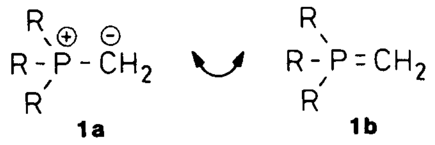
Using ^{13}C-chemical shifts as a probe for the electronic environment of carbon centers, triphenylphosphonio-methanide, the model case of a "reactive" phosphorus ylid, was found to have much more zwitterion than PC double bond character (resonance structure **1a** *being dominant). Triphenylphosphonio-propenide ("triphenylphosphonium-allylid"), a "moderated" ylid, accumulates electron excess mainly at the α-carbon atom (resonance structure* **6a** *being dominant) whereas triphenylphosphonio-ethenoate (formyl-methylene-triphenylphosphorane) and other "stabilized" ylids carry roughly equal fractions of negative charge at the α-carbon and the oxygen atom (resonance formulas* **a** *and* **b** *being of comparable importance). The one-bond C,H coupling constant of triphenylphosphonio-methanide* (**1**) *argues against a perfectly planar ylid center. The three-bond P,C coupling constants permit the assignment of* endo- *or* exo-*configurations to ylids having an allyl-type side-chain.*

INTRODUCTION

Wittig [1] coined the word "ylid" to call attention to the unusual structural features of newly discovered zwitterions having a positively charged nitrogen atom linked to a carbanionic center. Unlike nitrogen, phosphorus is not forbidden to expand its valence electron shell beyond an octet. Hence, the same author considered the species obtained upon deprotonation of phosphonium salts as hybrids between an "ylid" and an "ylene" form (**1a** and **1b**, R = H_3C, H_5C_6) [2] (Scheme 1).

The postulated resonance stabilization of phosphorus ylids was in qualitative agreement with the relative ease of their generation under irreversible [2, 3] or reversible conditions [4]. The concept of "*d*-orbital resonance" soon became popular although the nature of the invoked P,C double bond still remains unspecified. Several molecular orbital calculations [5] have cast doubt on the alleged d_π-p_π interaction and favor instead a "polarization" of the lone pair at the ylid α-carbon atom. An extended Gillespie-Nyholm model approach may help us to rationalize and even to visualize what is probably happening: without mixing with the d_π-orbital, the p_π-orbital expands toward the heteroatom in which direction it experiences little repulsion due to the relatively long bond distance and the flexibility of the geminal phosphorus—carbon bonds [6] (Scheme 2).

There is general agreement that the ylene from (**1b**) contributes substantially to the resonance hybrid but that the zwitterionic ylid (**1a**) form is dominant. We are, however, aware of only two attempts



SCHEME 1

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dπ - pπ interaction   pπ polarization

SCHEME 2

to *quantify* the relative importance of these limiting structures. On the basis of infrared and Raman frequencies, bond orders of 1.65 and 1.30 were assigned to trimethyl- and triphenylphosphonio-methylid, respectively [7]. We wondered whether nuclear magnetic resonance (NMR) spectroscopic data could provide a clearer answer. In particular, we wanted to test the suitability of ^{13}C chemical shifts as a probe for local electron densities.

At the same time, a reinvestigation of the relationship between $^{1}J_{C,H}$ coupling constants and ylid geometery was deemed to be warranted. A long time ago [8] we had postulated the ylid carbon to have a pyramidal shape, although a flat one, rather than to be planar as generally assumed. This idea was refuted as being incompatible with spectroscopic [9] and computational [10] evidence. Very recently, however, an advanced X-ray diffraction study [11] of triphenylphosphonio-methanide (**1**) did confirm the pyramidal deformation. These findings call for a reappraisal of earlier NMR work.

Finally, we hoped to gain insight into the *endo/exo* isomerism of resonance stabilized ylids by focusing on the $^{3}J_{P,C}$ coupling constants. This conformational problem has not yet received the attention it deserves and even has never been addressed at all with respect to allyl-type ylids. It may, however, provide the key to an understanding of the still-enigmatic stereoselectivities [12] of many Wittig reactions. Thus, for the moment the effect of allkyl groups on the stereochemical outcome of olefinations with triphenylphosphonio-2-alkenides [13] remains as unexplained as the marked solvent dependence of olefinations with alkoxycarbonyl substituted ylids [14].

EXPERIMENTAL

Sample Preparation

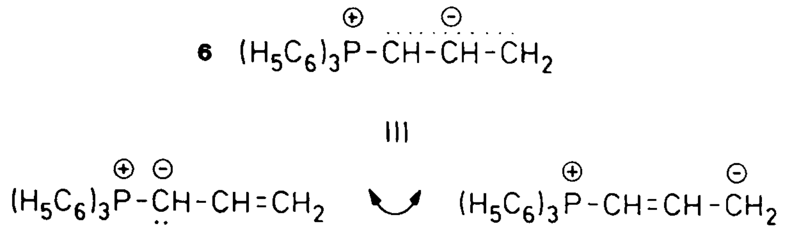
All manipulations were carried out under an atmosphere of 99.995% pure nitrogen. Commercial-grade sodium hydride (0.7 g, 0.03 mol) was washed several times with diethyl ether to remove the adherent mineral oil. The alk(en)yltriphenylphosphonium bromide (0.02 mol) and tetrahydrofuran (50 mL) were added. After 5 h of vigorous stirring at 25°C the colored (yellow or orange-red) solution was filtered through a glass frit (G4) into an empty flask. A small volume (2 mL) of the filtrate was placed in a tiny (5-mL) Schlenk tube. Upon evaporation of the solvent under reduced pressure (0.1 mmHg) a solid, although smeary residue was obtained. It was dissolved in anhydrous perdeuterated tetrahydrofuran (2.5 mL). By means of a syringe roughly half of this quantity was transferred into a 5- or 10-mm-wide NMR tube which was sealed by flame.

Spectra Recording

^{1}H and ^{13}C NMR spectra were obtained in the pulsed Fourier transform mode at 360- and 90.6-MHz frequency, respectively; a Bruker CXP-200 instrument (at 81.0 MHz) was available for ^{31}P NMR spectra. The chemical shifts given refer to tetramethylsilane ($\delta_H^1 = 0.00$; $\delta_C^{13} = 0.0$) as an internal and 85% aqueous phosphoric acid ($\delta_P^{31} = 0.0$) as an external standard.

RESULTS AND DISCUSSION

We first compared (see Table 1 [15–19]) triphenylphosphonio-methanide (**1**), the most common Wittig reagent, with one imide/carbanide-hybridized, 1,3-dipolar zwitterion (**2**) and three typical "phospha-alkenes" [20] (**3–5**). As expected, the latter compounds have ^{13}C-resonances at low field. For an imaginary, pure "ylene" form (**1b**) we would predict a number in the order of δ + 140. In contrast, a



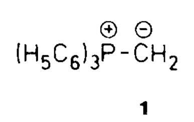
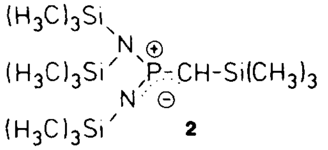
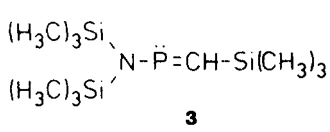
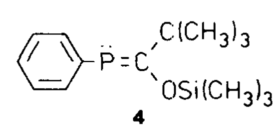
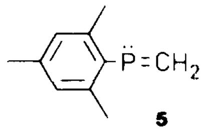
$$(H_5C_6)_3\overset{\oplus}{P}\text{-CH-}\overset{\ominus}{\text{CH}}\text{-CH}_2$$

$$(H_5C_6)_3\overset{\oplus}{P}\text{-}\overset{\ominus}{\ddot{\text{C}}}\text{H-CH=CH}_2 \qquad (H_5C_6)_3\overset{\oplus}{P}\text{-CH=CH-}\overset{\ominus}{\text{CH}_2}$$

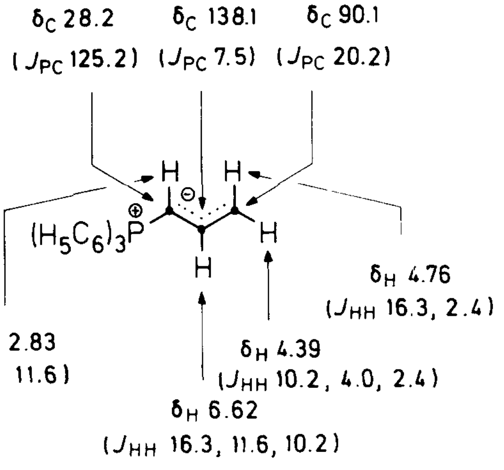
6 **6a** **6b**

SCHEME 3

TABLE 1 ^1H, ^{13}C- and ^{31}P-Chemical Shifts of Triphenylphosphonio-methanide (**1**), a 1,3-dipolar species (**2**), and three "phospha-alkenes" (**3–5**)

organophosphorus compound	$\delta_{^1H}$	$\delta_{^{13}C}$	$\delta_{^{31}P}$	ref.
 $(H_5C_6)_3\overset{\oplus}{P}-\overset{\ominus}{C}H_2$ **1**	0.21	-5.4	18.4	[15,16]
 **2**	2.25	58.3	102.6	[17]
 **3**	7.09	148.3	309.9	[17]
 **4**	-	216	135	[18]
 **5**	7.05 6.77	155.8	288.6	[19]

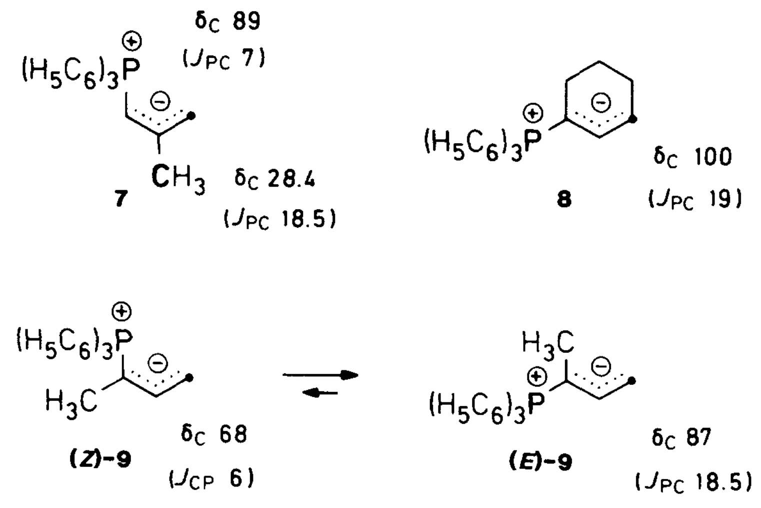
6



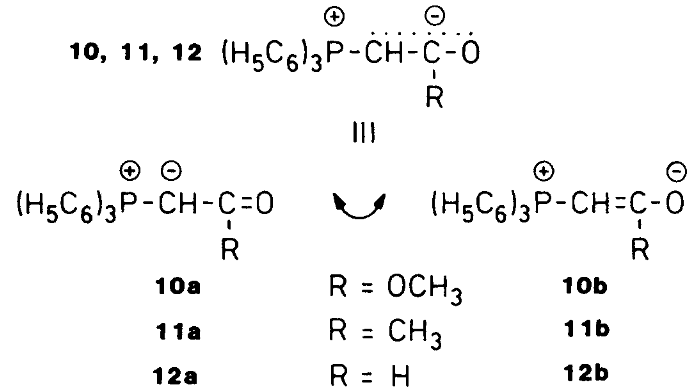
SCHEME 4

pure "ylid" form should give rise to a signal at the high-field end of the nmr scale [21]. Obviously the true phosphorus species behaves in this respect very much like a P-C zwitterion. Its double-bond character should not exceed 20% as an upper limit. The marked differences in ^1H and ^{31}P chemical shifts between species **1** and the phospha-alkenes **3–5** may be taken as additional evidence in favor of an ylid structure. Hence, α-deprotonated phosphonium salts are perfectly well represented by a zwitterionic formula and, consequently, should be called *phosphonio-alkanides* rather than alkylidene-phosphoranes.

At the same time we have reevaluated the $^1J_{C,H}$ and $^1J_{P,C}$ coupling constants of the parent ylid **1**. In our opinion, the measured values of 153 and 101 Hz, respectively, are too small to really fit a planar configuration at the α-carbon and agree well with the suggested flat pyramid. Actually,



SCHEME 5



SCHEME 6

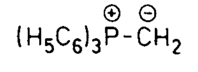
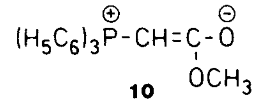
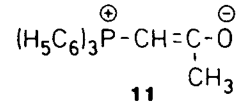
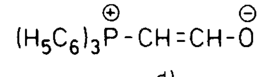
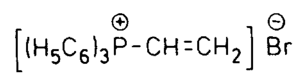
triphenylphosphonio-2-propenide (**6**), -2-methyl-2-propenide (**7**), and triphenylphosphonio-phenylmethanide [22], all of which should be virtually, if not perfectly planar, exhibit substantially larger one-bond coupling constants ($J_{C,H}$ 158, 153 and 160 Hz; $J_{P,C}$ 125, 121, and 129 Hz). On the other hand, we assume electronegatively substituted ylids such as triphenylphosphonio-methoxymethanide, -fluoromethanide and -chloromethanide to form relatively steep pyramids. This may explain the lack of *cis*-stereoselectivity encountered in reactions with these ylids [23], since our "leeward approach" model [24] implies an α-carbon center that should not deviate much from planarity.

The same approach which has provided insight into the nature of the PC bond in the "reactive" ylid **1** permits also an evaluation of the electron distribution of "moderated" and "stabilized" ylids, the side-chains of which offer the possibility of charge delocalization. Let us treat the limiting structures **a** and **b** of the allyl-type ylid **6** as if they were isolated, individual entities (Scheme 3). The ^{13}C signals of their negatively charged carbon atoms should then appear in the range around −5 ppm while olefinic carbon atoms, regardless of whether located at the α- or γ-position, ought to be found in the neighborhood of +120 ppm.

The real spectrum shows magnetically quite different α- and γ-carbons. If one judges on the basis of their chemical shifts ($\delta_C\alpha$ 28.2 ppm, $\delta_C\gamma$ 90.1 ppm), the resonance structure **6a** contributes approximately three times more to the overall electronic situation than resonance structure **6b** (Scheme 4).

The observed $^3J_{PC}$-constant of 20 Hz means that the phosphonio group occupies the *exo*-position. As can be concluded from ylids **7**, **8** [25] and **9** (Scheme 5), the configurations of which are unambiguously known, $^3J_{PC}$ values of 15–20 Hz belong to an *anti*-periplanar arrangement of the phosphorus and carbon nuclei whereas $^3J_{PC}$ values of 5–10 Hz reveal a *syn*-relationship. For a long time the *endo*- or *exo*- (*Z*- or *E*-) geometry of such allyl-type ylids has been a neglected structural feature.

TABLE 2 $^1H^\alpha$, $^{13}C^\alpha$ and, ^{31}P-Chemical Shifts of Triphenylphosphonio-methanide (**1**), 2-Triphenylphosphonio-1-methoxy-ethenoate (**10**), 2-Triphenylphosphonio-1-methyl-ethenoate (**11**), 2-Triphenylphosphonio-ethenoate (**12**) and Triphenylvinylphosphonium Bromide

organophosphorus compound	$\delta_{^1H}$	$\delta_{^{13}C}$	$\delta_{^{31}P}$	ref.
 $(H_5C_6)_3\overset{\oplus}{P}-\overset{\ominus}{C}H_2$ **1**	0.21	-5.4	18.4	[15,16]
 $(H_5C_6)_3\overset{\oplus}{P}-CH=\underset{OCH_3}{C}-\overset{\ominus}{O}$ **10**	2.91 3.36	29.8 -	17.8 -	[15,27][c]
 $(H_5C_6)_3\overset{\oplus}{P}-CH=\underset{CH_3}{C}-\overset{\ominus}{O}$ **11**	3.78[a]	51.3[a]	14.6[a]	[15,27]
 $(H_5C_6)_3\overset{\oplus}{P}-CH=CH-\overset{\ominus}{O}$ **12**[d]	4.16[a] 3.69[b]	52.2[a] -	14[a] 19[b]	[15,27]
 $\left[(H_5C_6)_3\overset{\oplus}{P}-CH=CH_2\right]\overset{\ominus}{Br}$	8.09	119.2	19.3	[15,28]

[a] Positively and negatively charged heteroatoms occupying a *cis*-position.

[b] Positively and negatively charged heteroatoms occupying a *trans*-position.

[c] See also: F.J. Randall, A.W. Johnson, *Tetrahedron Lett. 24*, 1968, 2841; H.I. Zeliger, J.P. Snyder, H.J. Bestmann, *Tetrahedron Lett., 25*, 1969, 2199; G.A. Gray, *J. Am. Chem. Soc., 95*, 1973, 5092, 7736.

[d] In perdeuterobenzene at 25°C a (*Z*/*E*)-equilibrium of 95 : 5 is established. Full ^1H NMR data (360 MHz): 9.69 (0.95 H, dd, *J* 38.5, 2.9); 9.04 (0.05 H, dd, *J* 10.3, 1.5); 7.8 (6 H, m); 7.0 (9 H, m); 4.16 (0.05 H, dd, *J* 20.5, 10.3); 3.69 (0.95 H, dd, *J* 25.8, 2.9); ^{13}C NMR (90.6 MHz) of the (*Z*)-isomer: 181.8 (1 C, d, J_{CH} 159.9, J_{PH} ~0); 133.5 (6 C, dq, J_{CH} 163.6, ~10, J_{CP} 10.4); 131.9 (3 C, dt, J_{CH} 161.3, ~2, J_{CP} 2.0); 128.9 (6 C, ddd, J_{CH} 167.3, 7.4; J_{CP} 12.1); ~128 (?, 3 C, d, J_{CP} ~70); 52.2 (1 C, ddd, J_{CH} 165.7, 29.9, J_{CP} 100.8).

Finally, we turned to α-acyl-substituted ylids **10**, **11**, and **12** which are oxa-analogs of the just mentioned allyl-type ylids. Once more two principal resonance structures, **a** and **b**, have to be considered. Again, if they could be studied separately, the "ylid" forms **a** should continue to produce a ^{13}C-signal around -5 ppm and, on the other hand, the "betaïne" forms should emerge in the range of 100–120 ppm (**10b**, **11b**) or around 130 ppm (**12b**) [26] (Scheme 6).

As can be deduced from the collected data (Table 2) [15–16, 27–29], the true electronic situation is roughly halfway between betaine-like and ylid-like. Therefore, both *2-phosphonio-1-alkenoates* and *1-phosphonio-2-oxo-alkanides* are appropriate names for such α-deprotonated α-acylphosphonium salts.

Acknowledgment

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[20] R. Appel, F. Knoll, I. Ruppert, *Angew. Chem.*, *93*, 1981, 771; *Angew. Chem., Int. Ed. Engl.*, *20*, 1981, 731.
[21] Although one may blame us for gambling, we dare

to give an estimate for the chemical shifts of the hypothetical pure "ylid" form **1a**: $\delta_H^1 \sim 1$ ppm, $\delta_C^{13} \sim -30$ ppm. Extrapolation leads then to these approximations for the (planar) free methane anion: $\delta_H^1 \sim -4$ ppm, $\delta_C^{13} \sim -40$ ppm. Previously H. H. Vogt and R. Gompper (*Chem. Ber.*, *114*, 1981, 2884) have proposed a somewhat different number (+30 ppm) for the same ^{13}C shift. After completion of this work Prof. W. Kutzelnigg, Bochum, kindly informed us about recent results of a computational approach to relevant ^{13}C chemical shifts: CH_3 [anion, pyramidal] −50, CH_3 [anion, planar] −70 ppm (M. Schindler, unpublished results); $HP = CH_2$ [phosphaalkene] +200, $H_4P\text{-}CH_3$ [phosphorane] +20, H_3PCH_2 [ylid] −40 ppm (U. Fleischer, M. Schindler, W. Kutzelnigg, unpublished research; see also W. Kutzelnigg, *Angew. Chem.*, *96*, 1984, 262; *Angew. Chem., Int. Ed. Engl.*, *23*, 1984, 272).

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