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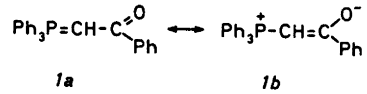
# $^{13}C$ Chemical Shifts of Phosphonium Ylides Stabilised by *p*-Substituted Phenacyl Groups; Substituent Effects and Comparison with Arsonium Analogues

PAUL FRØYEN [a] and DAVID G. MORRIS [b]

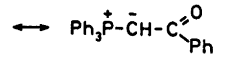
[a] Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway and
[b] Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

$^{13}C$ Chemical shift assignments are presented for a series of triphenylphosphonium ylides in which a *p*-substituted phenacyl group is linked to the carbanion. The ylide carbon is deshielded by electron-withdrawing substituents such that their chemical shifts correlate linearly with the dual substituent parameters of Swain and Lupton with the resonance term predominant. Chemical shifts of the carbonyl carbon do not show an analogous correlation and enhanced conjugation is indicated for the *p*-methoxy derivative from, *inter alia*, the carbonyl carbon chemical shift. A comparison of the shieldings of the carbons of the phenyl rings bound to phosphorus with those of the corresponding carbons of the analogous arsonium ylides indicates minor but subtle differences which are discussed in terms of the transmission modes of substituent effects. For these carbons the probable relevance of $\pi$ polarisation as a mechanism for redistribution of electron density is indicated from a comparison of chemical shifts of the ylide, triphenylphosphine and a triphenylphosphonium salt.

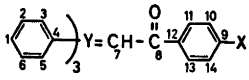
Recently a number of studies have been made of the $^{13}C$ and $^{31}P$ NMR spectra of phosphorus ylides;[1–3] in most of these cases greater stability has been conferred on the ylide by delocalisation of the formal negative charge on the ylide carbon over a stabilising group. Accordingly the ylide may, in the case of a stabilising phenacyl group be represented by a number of resonance structures *1a-c*, where additionally there exists the possibility of delocalisation of the negative charge on the ylide carbon onto phosphorus by means of $d\pi-p\pi$ bonding; this latter feature is denied to ylides derived from first row elements. The extent of this $d\pi-p\pi$ bonding is considered to be relatively small,[3,4] although P–C interatomic distances in several ylides have been found [5] to be intermediate between estimated values of the corresponding single and double bond lengths.[4]



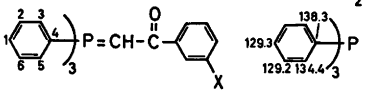
*1a* *1b*



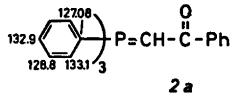
*1c*



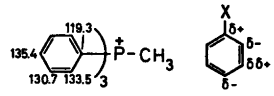
Series *2* Y=P *a* X=H *e* X=Cl
Series *3* Y=As *b* X=Me *f* X=Br
*c* X=OMe *g* X=CN
*d* X=F *h* X=$NO_2$



*4* *5*



*2a*



*6* *7*

Recent calculations [5] which include 3*d* orbitals on phosphorus indicated, with respect to analogous calculations not involving 3*d* orbitals, a significantly reduced charge separation in an unstabilised prototype phosphonium ylide with concomitant increase in P–C overlap population which arises from bonding between $P_{3dxz}$ and $C_{2px}$ orbitals together with a smaller, although significant, involvement of the $P_{3dyz}$ orbital in bonding which results in the ability of phosphorus to conjugate in two perpendicular planes. Further, calculations showed that the electron density in the phosphorus carbon $\sigma$ bond was small.

In order to extend our previous studies on $^{13}$C chemical shifts of the corresponding *p*-substituted arsonium [6] and *m*-substituted phosphonium [7] ylides and to effect comparison between these series we have examined the $^{13}$C chemical shifts of a series of nine ylides *2a–h* where a *p*-substituted phenacyl group is bonding to the ylide carbon C(7).

## RESULTS AND DISCUSSION

$^{13}$C Chemical shifts for the series *2a–h* were determined in $CDCl_3$ at a common concentration and are presented in Table 1, with the coupling constant between the particular carbon and phosphorus given in parentheses. The assignment of carbon shifts was carried out as in our earlier paper [6] with additional assistance from the couplings to phosphorus in the case of carbons (1)–(8), where ample precedent exists. Additionally, we note, as with the corresponding *m*-substituted series,[7] a coupling $^3J_{P-C-C-C(12)} \approx 15$ Hz.

The ylide carbon C(7) in the series *2a–h* is deshielded by electron-withdrawing substituents and the chemical shift variation of this carbon correlates with the dual substituent field (*F*) and resonance (*R*) parameters of Swain and Lupton [8] as indicated in eqn. (1), with a correlation coefficient of 0.925; in this equation the

$$\delta[C(7)] = 1.57F + 3.11R \quad (1)$$

weighting of *R* is 55.8 %. This latter value is rather lower than that obtained for the corresponding *p*-substituted acetophenones [9] and arsonium ylides.[6] With respect to arsonium ylides the lower weighting of *R* arises from both an enhancement of *F* and an attenuation of *R*, although in both these ylide series the *R* weighting is appreciably higher than that obtained for the corresponding carbon, $\beta$ to the aromatic ring, in both *p*-substituted styrenes [10] and phenylacetylenes.[11]

By way of contrast no correlation of carbonyl, C(8) chemical shifts with *F* and *R* is obtained; for this carbon electron-withdrawing

*Table 1.* $^{13}$C Chemical shifts (ppm) in *p*-substituted phosphonium ylides *2a-h*.

| Compound | Substituent | C(4) | C(3), C(5) | C(2), C(6) | C(1) | C(7) | C(8) |
|---|---|---|---|---|---|---|---|
| *2a* | H | 127.08(91.5) | 133.07(10.3) | 128.82(12.2) | 132.01(2.0) | 50.54(112.1) | 184.80(3.4) |
| *2b* | Me | 127.51(91.1) | 133.23(10.1) | 128.87(12.4) | 132.00(1.9) | 50.03(112.6) | 185.06(3.2) |
| *2c* | MeO | 127.06(91.1) | 133.15(10.2) | 128.91(12.1) | 132.12(1.8) | 50.12(113.0) | 182.71(3.2) |
| *2d* | F | 126.96(90.6) | 133.10(10.1) | 128.91(12.2) | 132.11(1.8) | 50.47(112.5) | 183.56(3.8) |
| *2e* | Cl | 126.92(90.0) | 133.17(10.1) | 128.99(12.2) | 132.15(–) | 50.98(112.3) | 183.56(3.4) |
| *2f* | Br | 126.86(91.7) | 133.14(10.1) | 128.93(12.2) | 132.15(2.1) | 50.98(111.8) | 183.57(4.3) |
| *2g* | CN | 126.27(91.5) | 133.06(10.3) | 128.99(12.3) | 132.32(–) | 52.93(111.2) | 182.14(3.6) |
| *2h* | $NO_2$ | 126.26(91.4) | 133.12(10.4) | 129.06(12.3) | 132.41(2.4) | 53.55(110.7) | 181.16(3.6) |
| | | C(12) | C(11), C(13) | C(10), C(14) | C(9) | C(15) | |
| *2a* | H | 129.26 | 127.67 | 126.89 | 141.30(15.0) | – | |
| *2b* | Me | 139.32 | 128.47 | 127.03 | 138.80(15.1) | 21.34 | |
| *2c* | MeO | 156.76 | 110.90 | 128.32 | 135.48(15.1) | 56.29 | |
| *2d* | F | 163.67 | 114.35 | – | 137.64(15.1) | – | |
| *2e* | Cl | 135.18 | 128.42 | 127.82 | 139.98(15.4) | – | |
| *2f* | Br | 123.65 | 130.78 | 128.68 | 140.21(15.0) | – | |
| *2g* | CN | 112.33 | 131.94 | 127.47 | 145.42(15.0) | 119.09 | |
| *2h* | $NO_2$ | 148.25 | 123.02 | 127.76 | 147.40(15.1) | – | |

substituents cause deshielding. As in the corresponding arsonium ylide series [6] greater shielding than expected is shown for C(8) of the *p*-methoxy derivative *2c*. Together with a smaller than usual substituent chemical shift for C(12) and greater than normal deshielding of the methoxy carbon in *2c* this suggests enhanced conjugation by the electrons of the methoxy oxygen lone-pair as has been found for carboxyl carbons in *p*-substituted benzoic acids,[12] where the substituents $Me_2N$, MeO, F which cause enhanced shielding can be brought into line by means of the Yukawa-Tsuno equation which uses a common extra-conjugative coefficient. In *2d* we do not find excessive shielding of C(8) and we were unable to extend the series *2a–h* to include the substituent $Me_2N$.

In the phosphonium ylides *2a–h* the ylide carbon C(7) is shielded by *ca.* 7 ppm from C(7) in the corresponding arsonium series *3a–h*, whereas the carbonyl carbon C(8) in *2a–h* is deshielded by 3 ppm from the series *3a–h* for a given substituent. This behaviour may be rationalised by a greater electron density on C(7) and smaller electron density on C(8) in the phosphonium ylide series. The more ketone like behaviour of C(8) in the phosphonium ylides is in accord with greater polarity of the formal carbonyl bond in arsonium ylides.[15]

Although originally chosen as ballast the triphenylphosphonium and arsonium moieties of the *p*-substituted ylides show interesting trends in their $^{13}C$ chemical shifts. Thus the heteroatom bonded C(4) and C(2),C(6) are more shielded in the phosphonium series *2a–h* for a given substituent, whereas C(3), C(5) and C(1) are more shielded in the arsonium series *3a-h*. This pattern of alternation is accompanied by attenuation with increasing separation from the heteroatom, P or As (Table 2). Interpretation of these effects, which are novel to monosubstituted aromatic rings, is something of a problem, particularly since $^{13}C$ chemical shifts of triphenyl phosphine [1] and arsine oxides * do not conform to the above pattern. Here the heteroatom bonded carbon is more shielded in $Ph_3AsO$, in contrast to the corresponding carbon in triphenylphosphine and arsine.[15] We also note that carbons bonded to chlorine generally absorb at lower field than those bonded to bromine.[16]

The $^{13}C$ shift variations in Table 2 do not conform to the effects of substituent induced orbital repulsion [17–19] as formulated for first row elements; presently we expect greater orbital repulsion for the less diffuse phosphorus orbitals with the effect that C(4) in the series *2a-h* would be deshielded relative to the series *3a-h*. Recently Reynolds [18] has invoked $\pi$-polarisation effects to explain the large high field ipso shift in the cation form of phenylalanine with respect to the zwitterionic form; however, this change is accompanied by much smaller low field shifts for the remaining carbons. Other postulated substituent effects include the ill-defined inductoelectromeric ef-

* Chemical shifts of $Ph_3AsO$ (numbering as in series *2* and *3*) are C(4) 132.83, C(3) 131.54, C(2) 129.39, C(1) 132.19 ppm.

*Table 2.* $^{13}C$ Chemical shifts (ppm) of carbons of unsubstituted aromatic rings in *m*-substituted phosphonium ylides *4a–h*. Values in parentheses denote the relevant coupling constant to phosphorus.

| Compound | Substituent | C(4) | C(3) | C(2) | C(1) |
|---|---|---|---|---|---|
| *4a* | H | 127.08(91.5) | 133.07(10.3) | 128.82(12.2) | 132.01(2.0) |
| *4b* | Me[a] | – | 133.24(10.2) | 128.93(12.0) | 132.07(2.2) |
| *4c* | MeO[b] | 126.97(91.2) | 133.07(10.1) | 128.83(12.5) | 132.02(2.0) |
| *4d* | F | 126.71(91.4) | 133.07(10.5) | 128.89(11.7) | 132.15(2.5) |
| *4e* | Cl | 126.55(91.5) | 132.98(10.3) | 128.85(12.1) | 132.13(1.8) |
| *4f* | Br | – | 133.13(10.2) | 128.93(12.0) | 132.17(2.9) |
| *4g* | CN[c] | 126.46(91.4) | 133.15(10.1) | 129.05(12.3) | 132.38(3.2) |
| *4h* | $NO_2$ | 126.34(91.5) | 133.13(10.4) | 129.04(12.6) | 132.41(1.8) |

[a] $\delta$C(15) = 21.50 ppm. [b] $\delta$C(15) = 55.24 ppm. [c] $\delta$C(15) = 111.80 ppm.

fect [17] which lacks experimental support, the short range $\sigma$ inductive effect and the $\pi$ inductive effect which effects $\pi$ electron changes as in *7* for a $+I_\pi$ substituent.

The data of Table 2 are accommodated most economically in terms of differential inductive effects of the partially positively charged phosphorus and arsenic atoms as these are considered to be transmitted through both saturated and unsaturated frameworks. The pattern obtained in Table 2 does not correspond to differential $\pi$ polarisation effects between phosphorus and arsenic except for C(4) and C(1); however the point has been made that when the substituents which form the basis for comparison are directly bonded to the aromatic ring explicit manifestation of the $\pi$ polarisation pattern may not be observed on account of other factors, in particular conjugative effects.[18] Although conjugative effects are considered to be absent between phosphorus and the three associated phenyl rings in certain phosphonium ylides on the basis of earlier basicity measurements,[23] $^{13}$C chemical shifts may provide a more sensitive measure for such effects.

A possible incursion of $\pi$ polarisation can be seen from comparison of the triphenylphosphorus carbon shifts in the sequence *5*, *2a* and *6* where the progressive increase of positive charge on the phosphorus brings about corresponding greater shielding at C(4), the phosphorus bound carbon, accompanied by deshielding at C(1), with rather small variations at C(2) and C(3). The shifts at C(4) and C(1) are in accord with enhancement and reduction, respectively, of electron density at these carbons.

Additionally in this series we note that the $^{31}$P chemical shifts of $+6$,[24] $-16.5$,[25] and $-21.1$ [3b] ppm (a negative value indicates deshielding with respect to external 85 % $H_3PO_4$) for *5*, *2a* and *6* agree with expectation based on progressively greater positive charge on phosphorus. However, for the series *2a–h* the $^{31}$P chemical shifts are, within experimental error, invariant to the nature of the substituent.

Currently we are investigating the chemical shift variations in the series of phosphorus salt precursors of the ylide series *2a-h* in order to investigate further and clarify the substituent dependence of chemical shifts.

## EXPERIMENTAL

$^{13}$C NMR spectra were recorded at 25.2 MHz with a Varian XL 100 spectrometer operating in the Fourier transform mode with proton noise decoupling. The radio-frequency pulse width was 10 $\mu$s. The accuracy of individual line positions was 0.05 ppm except for carbonyl carbons where the accuracy was 0.02 ppm. The probe temperature was 35 °C. The spectral data refer to solutions of ylide (0.1 M) in $CDCl_3$ (lock signal) and are quoted relative to internal tetramethylsilane as standard.

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