

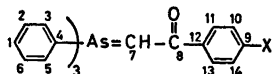
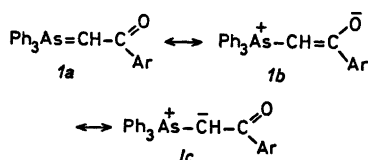
Substituent Effects in ^{13}C NMR Spectra of Stabilised Arsenic Ylides

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^{13}C chemical shift assignments are presented for a series of arsenic ylides with a *p*-substituted phenacyl group linked to the carbanion. Chemical shifts of the ylide carbon in this series show a linear dependence with the dual substituent parameters of Swain and Lupton, the resonance term being predominant. However, chemical shifts of the carbonyl carbon do not exhibit an analogous correlation. The chemical shifts of the carbon atoms in the phenyl groups linked to arsenic indicate limited interaction between aromatic ring and arsenic.

In ylides greater stability is conferred upon the molecule by attachment of electron-withdrawing groups to the site which bears a formal negative charge. In arsenic and phosphorus ylides there exists the further possibility of $d\pi-p\pi$ bonding between the heteroatom and the ylide carbon.¹ The bonding situation in these molecules is typically represented in



- 2a X = H
 2b X = Me
 2c X = OMe
 2d X = F
 2e X = Cl
 2f X = Br
 2g X = CN
 2h X = NO₂
 2i X = Ph

terms of contributions from resonance hybrids of the type *1a-c*. Since ^{13}C chemical shifts represent sensitive indicators of physical environment we have undertaken an investigation of these shieldings in a number of ylide series containing substituted aroyl stabilising groups in order to assess the effect of ylide structure on the transmission of substituent effects against a background of work on other aromatic systems.²⁻⁴ In this paper we present results obtained with a series of nine triphenylarsonium ylides *2a-i*. Previously it had been found that the bimolecular rate constants for reaction of a series of *p*-substituted triphenylarsonium ylides with *p*-nitrobenzaldehyde⁵ correlated fairly successfully with the Hammett constant σ_p ; accordingly a σ_p -like correlation might be expected for the chemical shifts of the ylide carbon C(7) in the series *2a-i*.

RESULTS AND DISCUSSION

^{13}C chemical shifts for the series *2a-i*, determined at a common concentration in CDCl₃, are given in Tables 1 and 2. The ylide, C(7) and carbonyl, C(8), carbon absorptions were readily assigned. However, assignment of aromatic ring carbon absorptions presented more of a problem. Differentiation between carbons C(1)–C(6) and C(9)–C(14) could be made on the basis of signal intensities. Additionally the shieldings of C(1)–C(6) are related to those of the corresponding phosphorus ylides⁶ and, in general, the C(9)–C(14) shieldings may be derived with reasonable accuracy from those for *2a* and the corresponding mono-substituted benzene.⁷

Table 1. ^{13}C chemical shifts of C(1)–C(8) in ylides (2a–i).

Compound	Substituent	C(1)	C(2), C(6)	C(3), C(5)	C(4)	C(7)	C(8)
2a	H	131.64	129.41	132.42	128.88	57.13	181.80
2b	Me	131.60	129.38	132.41	128.88	56.59	181.75
2c	MeO	131.70	129.44	132.40	128.73	56.54	179.71
2d	F	131.74	129.47	132.44	128.90	56.88	180.67
2e	Cl	131.75	129.47	132.38	—	57.43	180.31
2f	Br	131.76	129.48	132.41	128.48	57.48	180.40
2g	CN	131.92	129.54	132.30	127.94	59.23	179.01
2h	NO_2	132.01	129.60	132.37	127.93	59.90	178.76
2i	Ph	131.72	129.46	132.50	—	57.35	180.50

Table 2. ^{13}C chemical shifts of C(9)–C(14)/C(15) in ylides (2a–i).

Compound	Substituent	C(9)	C(10), C(14)	C(11), C(13)	C(12)	C(15)
2a	H	128.88	127.62	127.09	140.49	—
2b	Me	138.86	128.35	126.96	137.62	21.29
2c	MeO	156.51	110.91	—	134.64	56.20
2d	F	163.60 ^a	114.34 ^b	128.98 ^c	136.87 ^d	—
2e	Cl	134.74	128.68	128.08	138.77	—
2f	Br	123.26	130.72	128.48	139.36	—
2g	CN	111.97	131.56	127.47	144.68	119.10
2h	NO_2	148.01	123.02	127.76	146.63	—
2i	Ph	—	—	—	—	—

^a $^1J_{\text{C-F}} = 247.2$ Hz. ^b $^2J_{\text{C-F}} = 21.1$ Hz. ^c $^3J_{\text{C-F}} = 8.6$ Hz. ^d $^4J_{\text{C-F}} = 2.8$ Hz.

Of particular interest is the chemical shift of the ylide carbon, C(7) which may be regarded as sp^3 hybridised. With respect to a 'normal' *i.e.* olefinic, sp^2 hybridised carbon C(7) in 2a–i is shielded by *ca.* 100 ppm. Such behaviour is consistent with the presence of high electron density on the ylide carbon as is indicated, in the general case, by the resonance structure 1c. A similar finding has been reported for a number of phosphorus ylides⁶ and other examples of formally sp^3 hybridised carbons which absorb at higher field, than might be expected, include the terminal carbons of allene,⁹ ketene¹⁰ and diazomethane;¹¹ in the latter cases the enhanced shielding is attributed to high electron density.

In the series 2a–i the ylide carbon, C(7), is deshielded by electron-withdrawing substituents, such that C(7) chemical shifts correlate with the dual substituent parameters¹² F and R according to eqn. 1

$$\delta_{\text{C}(7)} = 1.198F + 4.11R \quad (1)$$

where the correlation coefficient, $r = 0.949$. The weighting of R in eqn. (1) is 69.6 % and it is noted that a closely related weighting of R , 70.9 %, is obtained in the methyl proton chemical shift dependence on substituent character in *p*-substituted acetophenones¹³ which is given in eqn. (2).

$$\delta_{\text{H}_3\text{C}} = 0.046F + 0.153R \quad (2)$$

The figures in eqn. (1), which represent a pronounced weighting in favour of R are thus in accord with comparable data for related systems, *e.g.* *p*-substituted phenylacetylenes⁴ and styrenes³ where for the ^{13}C chemical shifts of carbons β to the aromatic ring, ($\lambda = r/f$) is > 1 ; here r and f are the numerical coefficients in the dual substituent parameter (D.S.P) eqn. (3). We feel that, in general, the dual substituent parameter approach can provide for a

meaningful analysis of ¹³C chemical shifts in substituted aromatic systems and a reaffirmation of the validity of this approach has recently been given.²

$$\delta C_{\beta} = fF + rR \quad (3)$$

By way of contrast the carbonyl chemical shifts in *2a-i* show no overall correlation with substituent parameters although it is observed that greater shielding of C(8) is associated with increased electron-withdrawing character of the substituent. This response of C(8) to substituent variation is opposite to that of C(7). However, the behaviour of C(8) in the *p*-methoxy derivative of *2c* is noteworthy in that here the carbonyl carbon absorbs at higher field than would be expected on any basis of substituent character. Preliminary results on the analogous phosphorus ylides⁶ indicate similar 'anomalous' behaviour of the methoxy derivative. It is probable that the high field C(8) shift in *2c* is a reflection of enhanced conjugation between the methoxy substituent and the carbonyl group, mediated by the aromatic ring. This contention finds support in the fact that the methoxy induced substituent chemical shift for C(9), 27.6 ppm, is *ca.* 4 ppm less than found normally; in *p*-methoxyacetophenone the corresponding value is 30.4 ppm. Further, the C(12) substituent chemical shift in *2c*, 5.85 ppm, is again smaller than typically found for ring carbons *para* to a methoxy substituent, and the chemical shift of the methoxy carbon in *2c*, 56.2 ppm, shows deshielding by 1 ppm from its typical values; this deshielding is in accord with conjugative release of oxygen lone-pair electrons.

The carboxyl carbons in *p*-substituted benzoic acids experience enhanced shielding in the case of electron-donating substituents over that anticipated by σ values, and here calculations associate this effect with an increased bond order between the carboxyl carbon and the aromatic ring.¹⁴ A parallel therefore appears to exist between the present results and those of Niwa and Yamazaki.¹⁴

In the series *2a-i* only methoxy, the most strongly electron releasing substituent, gives evidence for enhanced conjugation. In this connection the chemical shift behaviour brought about by the more strongly electron releasing *p*-dimethylamino substituent would be of con-

siderable interest; however, we have been unable to extend the series *2a-i* to include this substituent.

Within the triphenylarsonium moiety minor but significant variation is found for the C(1) and C(4) shifts whereas those for C(2) and C(3) are essentially insensitive to C(9) substituent variation. It has been shown previously^{15,16} in triphenylphosphonium ylides that resonance interaction of these phenyl rings across phosphorus is essentially absent and a similar situation probably obtains in the analogous triphenylarsonium ylides. At present it is not possible to be definitive about the C(1) and C(4) shift variation in the series *2a-i*. A number of proposals have been made in order to account for substituent chemical shifts of aromatic ring carbons. In the series *2a-i* an attractive possibility is that substituent induced variations of electron density on arsenic bring about π -polarisation of the three arsenic bonded aromatic rings thereby accounting for the observed chemical shift variation. It is extremely unlikely that the substituent inductive effect could act directly over such large distances.

EXPERIMENTAL

¹³C NMR spectra were recorded with a Varian XL 100 spectrometer operating in the Fourier transform mode at 25.2 MHz. The spectra were determined at the University of Edinburgh by Dr. A. Boyd. Spectral data in Tables 1 and 2 pertain to solutions of ylide (0.1 M) in CDCl₃ and are quoted relative to internal tetramethylsilane as standard.

Triphenylarsonium 2-(4-cyanophenyl)-2-oxoethylide. To a stirred solution of 5.0 g (3.4×10^{-2} mol) *p*-cyanoacetophenone in 30 ml chloroform 5.5 g (3.4×10^{-2} mol) of bromine was slowly added. After the addition, the solution was evaporated to dryness in vacuum. The resulting α -bromo-*p*-cyanoacetophenone was dissolved in 40 ml chloroform together with 8.7 g (3.4×10^{-2} mol) triphenylarsine and refluxed for 5 h. The solution was cooled and 500 ml of ether was added. The precipitated arsonium salt was washed with ether, dissolved in methanol and a slight excess of sodium methoxide was added. The solvent was removed on a rotary evaporator and the crude ylide was purified by column chromatography using aluminium oxide as the substrate and chloroform as eluent, followed by recrystallisation from benzene-ether. For NMR data see Tables 1 and 2. M.p. 177 °C (dec.) (Found: C 72.21; H 4.43. Calc. for C₂₇H₂₀AsNO: C 72.16; H 4.49).

Triphenylarsonium 2-(4-fluorophenyl)-2-oxoethylide was prepared from *p*-fluoroacetophenone and triphenylarsine as described above. For NMR data see Tables 1 and 2. M.p. 152–153 °C. Found: C 70.42; H 4.59. Calc. for C₂₀H₂₀AsFo: C 70.59; H 4.56.

The other arsonium ylides were prepared as previously described.⁵ For NMR data see Tables 1 and 2.

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