

1.0, EtOH) – 20.4° (c 1.0, CH₂Cl₂).

Determination of the absolute configuration of 2-hydroxylamino-1-phenylpropane (1). An ethereal solution (25 ml) of (+)-1 (200 mg, 1.3 mmol) was added dropwise to a well stirred slurry of LiAlH₄ (326 mg, 8.6 mmol) in dry ether (40 ml). The mixture was refluxed for 2 h. After cooling the LiAl-complex was decomposed by cautious addition of H₂O (0.3 ml), 15 % NaOH (0.3 ml) and finally H₂O (0.9 ml). The resulting suspension was refluxed for 30 min, then filtered and the precipitate washed with ether. The combined filtrate and washings were dried (K₂CO₃) and the solvent evaporated *in vacuo*, affording 142 mg of the crude base. The base was converted to the sulfate by addition of an equivalent amount of ethereal H₂SO₄ to a cold ethereal solution of the base. Two recrystallizations from diluted ethanol yielded 50 mg of pure amphetamine sulfate, m.p. 318–320 °C decomp. [α]_D²⁵ +22.2° (c 1.0, H₂O), (Lit.¹¹ (S)-1-phenyl-2-aminopropane sulfate m.p. > 300 °C decomp. [α]₅₈₉²³ +22.1° (c 2.0, H₂O).

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Substituent Effects on ¹³C Chemical Shifts of Benzoyl Stabilised Phosphonium Ylides

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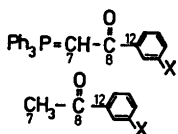
Recent studies of ¹³C chemical shifts, *inter alia*, of phosphorus ylides have indicated that the ylide carbon is best described as *sp*² hybridised and carries a significant negative charge.^{1,2} Additionally, the existence of *d_π-p_π* bonding between phosphorus and the ylide carbon has been recognised, although the extent of this bonding is thought to be moderate;¹ for calculated values of a non-stabilised ylide see Ref. 3. As a result of these studies and in extension of our own studies on ¹³C chemical shifts in arsenic ylides,⁴ we have investigated the ylide, C(7), and carbonyl carbon, C(8), chemical shift variation as a function of substituent, X, in a series of phosphonium ylides containing an *m*-substituted benzoyl group 1–8. The relevant ¹³C chemical shifts are given in Table 1.

The present results confirm¹ that the ylide carbon C(7) in stabilised phosphonium ylides absorbs at rather high field; the C(7) shifts correlate with the linear free energy parameter σ_m (from Ref. 5) in the sense that electron-withdrawing substituents cause deshielding. The carbonyl carbons, C(8), are however

Table 1. ¹³C chemical shifts of exocyclic carbons in metasubstituted acetophenones and phosphorus ylides. ¹³C chemical shifts (ppm) determined on solutions (0.2 M) in CDCl₃ with internal TMS as standard are accurate to 0.05 ppm. σ_m from Ref. 5.

	Ylide		Substituent	Acetophenone		σ_m
	C(7) ^a	C(8) ^b		C(7)	C(8)	
1	50.54	184.80	H	26.52	198.00	0.0
2	50.47	185.12	Me	26.54	198.13	-0.7
3	50.79	184.45	OMe	26.63	197.74	0.12
4	51.31	182.95	F	26.59	196.56	0.34
5	51.36	182.79	Cl	26.58	196.60	0.37
6	51.33	182.90	Br	26.55	196.51	0.39
7	52.01	181.91	CN	26.64	196.06	0.68
8	52.33	181.47	NO ₂	26.71	195.75	0.71

^a ¹J_{P-C(7)} 111.4–112.4 Hz. ^b ²J_{P-C(8)} = 3.4–3.8 Hz.



shielded by electron-withdrawing substituents; again a correlation of the chemical shifts with σ_m is obtained. The alternate response of C(7) and C(8) to substituent change may be rationalised on the basis of substituent induced charge alternation^{6,7} with chemical shift changes influenced primarily by charge density variation.¹ See however Ref. 8. We find further, that the substituent induced range of shifts for the carbonyl carbon C(8) is twice that of the more remote ylide carbon C(7). The regular behaviour of C(8) in *m*-methoxy ylide 3 contrasts with that of the *p*-methoxy analogue in both phosphorus⁹ and arsenic⁴ series and thus indicates a non-enhanced C(8)–C(12) bond order in 3. Whereas infra-red spectral data¹⁰ indicate a greater polarity of the carbonyl bond in the arsenic ylides, the carbonyl carbon is more deshielded in the parent phosphorus ylide 1 than in its arsenic counterpart⁴ by 3.0 ppm. Accordingly, we conclude that it is risky to draw unambiguous conclusions regarding bond polarity from ¹³C chemical shifts especially in complex multiply bonded systems.

The remaining carbons of the series 1–8 showed unexceptional chemical shift behaviour, however we note a hitherto unreported¹¹ coupling $^3J[\text{P}–\text{CH}–\text{C}(\text{O})–\text{C}(12)]$ of magnitude 14.4–15.2 Hz.

We have also examined the ¹³C chemical shifts of a series of *m*-acetophenones (Table 1) and here again carbonyl carbon shieldings correlate with σ_m , although the range of substituent induced shift is now about two-

thirds of that found in the ylide series 1–8, whereas methyl carbon shifts are essentially invariant to substituent variation.

It is possible that this regularity of chemical shift behaviour with substituent variation (Table 1) may be associated more generally with *m*-substituted series. We hope to consider the more involved shift variation in the corresponding *p*-substituted phosphonium ylides in a future publication.

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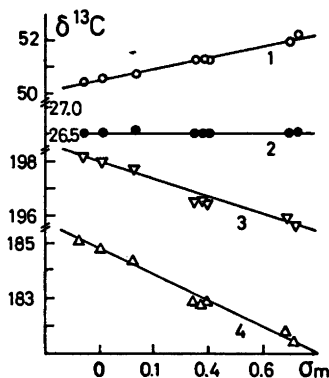


Fig. 1. Plot of ¹³C shifts in Table 1 against σ_m . 1, ylide C(7); 2, acetophenone C(7); 3, acetophenone C(8); 4, ylide C(8).