Conformation of the Enolate Forms of Ethoxycarbonylmethylenephosphoranes

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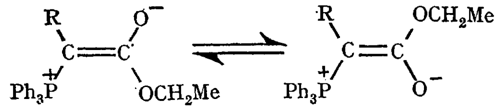
RECENT publications[1] on temperature-dependent structures of stable phosphoranes have led us to report an unexpected finding. The transoid conformer (Ia) is the major rotamer at low temperature. In phosphorane (b) and (c) the expected conformer (II) predominates.



(I) (II)

a; R=Me, b; R=H c; R=Ph

Investigation of the ethyl ester of alpha-substituted ethoxycarbonylmethylenetriphenylphosphoranes at low temperature has enabled the unambiguous assignment of the two conformers, (I) and (II), since the methyl group of the ester is diamagnetically shielded by the phenyl rings in the transoid conformer (I). The presence of an abnormally high-field methyl group in the transoid conformer (I) can only be explained on the basis of diamagnetic anisotropy, and not by inductive arguments, since the methylene protons of the ester experience this shielding effect to a lesser degree than does the methyl.†

From the coalescence-temperature data it is seen

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† Although these assignments are in direct contrast with those reported by Bestmann (ref. 1) for the methyl ester, there can be little doubt as to the validity of the assignment.

N.m.r. of the phosphoranes[a]

R	Temperature	Conformer ratio I:II	$-CH_2$Me		$-OCH_2Me$	
			Conformer 1	Conformer 2	Conformer 1	Conformer 2
	−60°	72:28	3·58 (q)	3·88 (q)	0·06 (t)	1·05 (t)
–Me	31	61:39	3·70 (q)	3·87 (s)	0·61 (t)	1·13 (s)
	62	coalesced[b]	3·78 (s)		0·61 (s)	
	−74	27:73	3·81 (s)		0·43 (t)	1·05 (t)
–H	32	coalesced[c]	3·88 (q)		0·91 (t)	
–Ph	−71	39:61	3·88 (s)		0·28 (s)	1·11 (s)
	39	coalesced[d]	3·91 (q)		0·80 (t)	

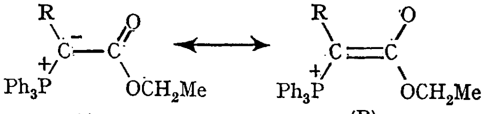
[a] All spectra obtained in $CDCl_3$ using $CHCl_3$ as an internal standard on a Varian A-60A n.m.r. spectrometer. $CHCl_3$ has δ 7·27 p.p.m. with respect to tetramethylsilane.

[b] Coalescence temperature of methyl + 60°.

[c] Coalescence temperature of methyl −20°.

[d] Coalescence temperature of methyl −45°.

the ease of rotation about the C–CO bond increases R = Me < H < Ph. The trend follows the inductive properties of the R-group. Rapid rotation around the C–CO bond indicates an increased contribution of form (A) to the resonance hybrid.



(A) (B)

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[1] H. J. Bestmann, G. Joachim, I. Lengyel, J. F. M. Oth, R. Merenyi, and H. Weitkarp, *Tetrahedron Letters*, 1966, 3355; H. J. Bestmann and J. P. Snyder, *J. Amer. Chem. Soc.*, 1967, **89**, 3936; H. Schmidbaur and W. Fronick, *Chem. Ber.*, 1968, **101**, 604.