Formyl-, Aroyl, and Acyl-alkylidenetriphenylphosphoranes: Conformational Analysis by Proton Nuclear Magnetic Resonance Spectroscopy

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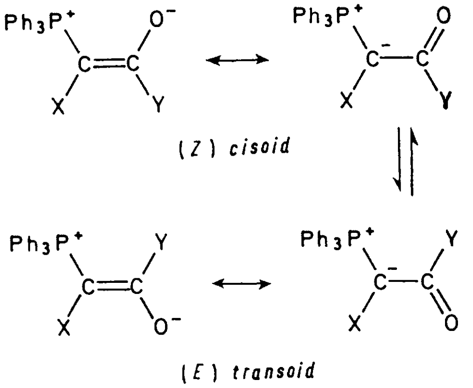
The conformations of eleven oxoalkylidenetriphenylphosphoranes have been assigned from their ^1H n.m.r. spectra. Mixtures of (*Z*) *cisoid* and (*E*) *transoid* conformers were detected in four compounds. The *Z*-geometry of β-oxomethylenetriphenylphosphoranes is favoured by the presence of β-substituents and the *E*-geometry is favoured by the presence of α-substituents. The conformational preferences are rationalised in terms of steric and electrostatic interactions. The absence of peak coalescence in the p.m.r. spectra up to 150° shows that interconversion of the conformers is very slow relative to the n.m.r. time scale.

VARIABLE-TEMPERATURE n.m.r. spectroscopy has been successfully applied to the study of restricted rotation in organic compounds. For β-oxomethylenetriphenylphosphoranes (1) rotation may be restricted about the α–β carbon–carbon bond and give rise to two preferred conformers, *i.e.* (*Z*) *cisoid* and (*E*) *transoid.*

The rate of interconversion of these conformers is suitable for study by p.m.r. spectroscopy when Y = OR or OAr, *i.e.* the alkoxycarbonyl derivatives.[1-3]



(1)

In contrast, the doubling of peaks which shows the presence of ' long-lived ' conformers, has not previously been observed in the p.m.r. spectra of oxomethylenetriphenylphosphoranes. An early report[4] of a variable-temperature spectrum for the acylmethylenephosphorane (1g) (X = H, Y = Me) was shown[5-7] to be due to reversible protonation at the α-carbon atom by trace amounts of phosphonium salt. Little work has been done on the assignment of the stereochemistry of these compounds and, consequently, the steric effects of substituents are largely unknown.

RESULTS

A series of formyl-, aroyl-, and acyl-methylenetriphenylphosphoranes have been prepared (see Table 1) in order to study steric and electronic effects in this class of compound and also to compare them with analogous alkoxycarbonyl compounds.

TABLE 1

Conformer ratios of β-oxoalkylidenetriphenylphosphoranes

Compound	Substituents		Solvent	% *cisoid* (*Z*) conformer
	X	Y		
(1a)	CN	*m*-MeC_6H_4	$C_6H_4Cl_2$	75
(1a)	CN	*m*-MeC_6H_4	$CDCl_3$	50
(1b)	PhCO	*m*-MeC_6H_4	C_6H_6	60
(1c) [27]	*p*-$NO_2C_6H_4CO$	Me	C_6H_6	60
(1d) [28]	H	H	CH_2Cl_2	50
	H	H	$CDCl_3$	40
	H	H	CH_3OH	25
(1e) [29]	Me	H	$CDCl_3$	0
(1f)	Cl	H	$CDCl_3$	0
(1g) [30]	H	Me	$CDCl_3$	100
(1h) [30]	H	Ph	$CDCl_3$	100
(1i) [31]	H	*p*-$NO_2C_6H_4$	$CDCl_3$	100
(1j) [31]	Me	Ph	$CDCl_3$	—

Compounds (1a—d) gave p.m.r. spectra[8] with doubling of peaks due to the presence of *Z*- and *E*-conformers. Tolyl or methyl groups were employed at the β-position in order to identify the two conformers. The spectra showed no temperature dependence in the range 30—150° apart from small changes in the relative intensities of the doubled peaks which is attributed to variations in conformer populations. A change of solvent affected the relative intensities more markedly (see Table 1).

Similar results were obtained for the formylmethylenetriphenylphosphorane (1d) (X = H, Y = H) and no coalescence of peaks was observed for a benzene solution up to 150°. The spectrum showed the presence of an aldehydic proton which appeared as eight lines, a doublet of doublets for each conformer at τ 1·0 and 1·85 corresponding to the *Z*- and *E*-geometries respectively.[9] The α-proton possessed a similar splitting pattern, the *Z*- and *E*-conformers appearing at τ 6·3 and 5·9 respectively. Double-resonance experiments showed that all the coupling constants have the same sign, presumably positive.[9] This is in agreement with the positive PCH coupling constants usually observed when an sp^2-hybridised carbon atom is involved.[10]

For the remaining compounds (1e—i) only one conformer

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[9] Since this work was completed a report on this aspect was published by M. L. Filleux-Blanchard and M. G. J. Martin, *Compt. rend.*, 1970, **270C**, 1747.

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was detected. The p.m.r. spectrum of α-formylethylidenetriphenylphosphorane (1e) (X = Me, Y = H) contained a 1H doublet ($^3J_{PH}$ 4 Hz) at τ 1·78 (aldehydic proton) and a 3H doublet ($^3J_{PH}$ 13 Hz) at τ 8·11 (methyl group) which shows that this compound has a total preference for *E*-geometry. The aldehydic proton of the chloro-derivative (1f) (X = Cl, Y = H) was not observed and presumably coincided with the aromatic proton absorption which was centred at τ 2·4. This indicates that the aldehydic proton is shielded and that the compound has the same stereochemistry as (1e). In contrast the phosphorus ylides (1g—i) which do not possess α-substituents all showed a total preference for *Z*-geometry. The stereochemistry was deduced from the absence of shielding of the α-proton in the p.m.r. spectra (see Table 2) and their large geminal PCH coupling constants (24—27 Hz) which resemble that (25 Hz) for the *Z*-conformer of the parent formylphosphorane (1d). Also long-range coupling (1·8 Hz) to the methyl group was observed for the acylphosphorane (1g).

TABLE 2

P.m.r. parameters of the α-proton of β-oxoalkylidenetriphenylphosphoranes

	Z-Conformer		*E*-Conformer	
Compound	τ	$^2J_{PH}$	τ	$^2J_{PH}$
(1d)	6·3	25	5·9	20
(1g)	6·33	27		
(1h)	5·6 *	25		
(1i)	5·5 *	24		

* The downfield shift of these resonances is in accordance with deshielding by the β aryl rings.

The ^{31}P n.m.r. spectrum of the formyl phosphorane (1d) contained two resonance at δ_P −14 and −19 p.p.m. the relative intensities of which varied with solvent. In methanolic solution the lower field resonance at −19 p.p.m. was three times more intense than the higher field resonance. The p.m.r. spectrum of a methanolic solution showed that the predominant conformer possessed an *E*-geometry (see Table 1) which verifies the previously suggested assignment [11] for the ^{31}P resonances.

TABLE 3

Long wavelength absorption in the u.v. spectra of β-oxoalkylidenetriphenylphosphoranes in ethanol

Compound	$\lambda_{max.}$	ε
(1a)	292	11,000
(1b)	319	10,000
(1d)	288	4400
(1e)	290	2300
(1f)	315	1600
(1h)	323	10,600
(1i)	366	16,000
(1j)	318	6000
(1; X = H, Y = OMe) [32]	278	3000
(1; X = $\mathrm{CO_2Et}$, Y = OEt) [26]	272	3500

The i.r. spectra contained the usual low-frequency carbonyl bands. No bands attributable to specific geometries could be identified.

The u.v. spectra of the ylides contained a band in the 270—370 nm region,[12] see Table 3. An increase in conjugation *via* groups attached to the carbanionic centre has been shown [13] to lead to a bathochromic shift of this band. This effect is noticeable in the compounds which we have studied for the first substituent only and a second group does not affect the spectrum significantly except for compound (1j) (X = Me, Y = Ph). In this case the additional methyl group caused a reduction in the extinction coefficient.

DISCUSSION

Our results [8] and the results of other workers [9,11,14,15] for oxoalkylidenephosphoranes (1) show that the interconversion of the *Z*- and *E*-conformers is very slow relative to the n.m.r. time scale. This situation holds for oxophosphoranes even when the α-substituent is strongly electron-withdrawing as in compounds (1a—c). We note that for alkoxycarbonylmethylenephosphoranes electron-withdrawing α-substituents substantially reduce the barrier to rotation,[2] *e.g.* the methylmethoxycarbonyl compound (1; X = Me, Y = OMe) and the *p*-bromophenylmethoxycarbonyl compound (1; X = p-$\mathrm{BrC_6H_4}$, Y = OMe) have p.m.r. spectra which show peak coalescence at 68 and −59° respectively. Since the completion of this work a preliminary report [16] has appeared in which it is stated that formylmethylenephosphoranes which have electron-withdrawing α-substituents show variable-temperature p.m.r. spectra. Indeed two laboratories [16,17e] have now confirmed the withdrawn claim [15] that the parent compound (1d) also shows coalescence of peaks. In most of the reports it is not clear what solvent was used. Our own variable temperature p.m.r. spectra were carried out on a benzene solution of (1d). Rotation may be faster in more polar solvents,[18] a suggestion which is supported by the i.r. spectra.

The carbonyl stretching frequency which is related to the αβ double-bond character [17] is 1560 cm^{-1} or lower for all methylenephosphoranes which do not show frequent interconversion of conformers relative to the n.m.r. time scale. The formyl compound (1d) has the highest values (ν_{CO} 1560 cm^{-1} for a benzene solution). Furthermore this absorption rises to 1567 cm^{-1} for a chloroform solution and 1572 cm^{-1} for a methanolic solution, which may reflect a lower double-bond character and lower energy barrier to rotation. We predict that the recently reported formyl compounds with electron-withdrawing

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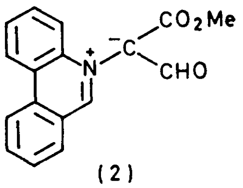
substituents will have carbonyl frequencies above 1560 cm^{-1}.*

The related formylmethoxycarbonylmethylene nitrogen ylide (2) [19] has a p.m.r. spectrum which shows coalescence of the methoxy resonances at 60°. Although it is not discussed in the report, restricted rotation may involve the formyl group or the methoxycarbonyl group. The high frequency of the methoxycarbonyl band ν_{CO} 1660 cm^{-1} [*cf.* ν_{CO} 1616 cm^{-1} for (1; X = H, Y = OMe)] indicates that restricted rotation of the ester group should not be detectable and that the rate process which is observed involves the formyl group (ν_{CO} 1570 cm^{-1}) as suggested by these workers.

Substituent effects on the conformer populations of oxoalkylidenephosphoranes may be summarised as follows: (*a*) in the absence of α- and β-substituents [*i.e.* (1d)] the stabilities of the *E*- and *Z*-conformers are similar and both forms are detected, (*b*) where there is an α-substituent only [*i.e.* (1e) and (1f) the *E*-conformer is favoured, (*c*) when there is a β-substituent only (1g—i) the *Z*-conformer is favoured,[14] (*d*) when there are α- and β-substituents the two conformers may have similar stabilities [*e.g.* (1a—c)] but there is a tendency to favour the *Z*-form.[20] The β-substituent presumably destabilises the *E*-conformer by its steric compression with the bulky triphenylphosphonium group. The effect of an α-substituent which increases the population of the *E*-conformer may be the result of several interactions. Firstly the $Ph_3P^+ \cdots Y$ steric repulsion which normally destabilises the *E*-conformer will be countered to some extent by a destabilising $X \cdots Y$ interaction in the *Z*-conformer; secondly $P^+ \cdots O^-$ attraction [21] in the *Z*-conformer may lead to the pseudo-trigonalbipyramidal structure (3) which is destabilised by the crowding of the α-substituent X and one of the P-phenyl groups; finally general crowding will twist the molecule about the α–β carbon–carbon bond and reduce the $P^+ \cdots O^-$ electrostatic stabilisation of the *Z*-conformer. The twisting is supported by the u.v. spectra (see Table 3) and is also believed to be the cause of reduced intensities of i.r. bands of α-substituted alkoxycarbonyl phosphoranes.[17d] The tendency to increase the population of the *E*-conformer upon the introduction of an α-substituent has also been observed for the alkoxycarbonyl derivatives.[22]

The conformational populations are also dependent on the medium. Solvent effects on the conformers of the formyl phosphorane (1d) are not easy to determine due to the extensive splitting of the formyl and α-protons. However in methanol a preference for the *E*-conformation is quite noticeable. This has not been noted before. The trend towards *E*-geometry in hydroxylic solvents is similar to that observed by Snyder [23] for alkoxycarbonylphosphoranes. The trend has been attributed to increased solvent aggregations of the oxy-anion. The fact that the solvent effect is also observed for the formyl compound indicates that the destabilisation of the *Z*-conformer in methanol is due to steric repulsion between the Ph_3P^+ group and the solvated oxyanion and reduced electrostatic stabilisation.



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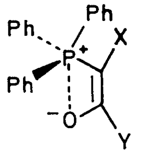

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EXPERIMENTAL

^{1}H and ^{31}P n.m.r. spectra were obtained on a Perkin-Elmer R10 instrument. I.r. and u.v. spectra were determined on a Unicam SP 200 and Beckman DB–G instruments.

Cyano-m-*toluoylmethylenetriphenylphosphorane* (1a).—*m*-Toluoylacetonitrile which was prepared by the method of Eby and Hauser [24] for benzoylacetonitrile had m.p. 58—59° (from ether) (lit.,[25] m.p. 74—75°); $\nu_{max.}$ (KBr) 685, 790, 1160, 1245, 1335, 1605, and 1685 cm^{-1}; τ ($CDCl_3$) 2·2—2·7 (4H, m), 5·88 (2H, s), and 7·62 (3H, s). The alkylidenephosphorane (1a) was prepared by the method of Horner and Oediger [26] in 20% yield, m.p. 215—216° (from ethanol–ethyl acetate) (Found: C, 79·6; H, 5·3; N, 3·2. $C_{28}H_{22}NOP$ requires C, 80·2; H, 5·3; N, 3·3%); $\nu_{max.}$ (KBr) 700, 720, 745, 760, 1110, 1190, 1350, 1440, 1555, and 2190 cm^{-1}; τ ($CDCl_3$) 2·5—2·9 (19H, m), 7·8 (2·2H, s), and 7·9 (0·8H, s).

Benzoyl-m-*toluoylmethylenetriphenylphosphorane* (1b).—Benzoylmethylenetriphenylphosphorane (2·5 g) was heated with *m*-toluic anhydride (1·9 g) at 120° for 5 h.[27] The crude product (1b) (82%) was purified by column chromatography, ethyl acetate and then ethanol being used as eluant. Recrystallisation from ethanol gave pale yellow yellow crystals of (1b), m.p. 182° (Found: C, 81·9; H, 5·4. $C_{34}H_{27}O_2P$ requires C, 81·9; H, 5·4%); $\nu_{max.}$ (KBr) 695, 715, 745, 780, 800, 880, 895, 925, 1005, 1030, 1110, 1290, 1305, 1335, 1395, 1445, 1490, 1525, 1590, 1605, and 3000 cm^{-1}; τ (benzene) 1·95—3·25 (Ar, m), 8·0 (Me, s), and 8·05 (Me, s).

Chloroformylmethylenetriphenylphosphorane (1f).—n-Butyl-lithium (20 ml; 0·054M) was added to a suspension of chloromethyltriphenylphosphonium chloride (3·8 g) in dry ether (50 ml) under nitrogen. After being stirred for 30 min the suspension was added slowly to ethyl formate (1·87 g) in ether (50 ml). After being stirred for a further

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* ν_{CO} for (1; X = p-$NO_2C_6H_4$, Y = H) was 1570 cm^{-1} (ref. 16) but the medium was not stated. For a meaningful comparison the i.r. spectra should be determined for solutions using the same solvent as used for the variable-temperature n.m.r. experiments.

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1½ h, the product was extracted into dilute hydrochloric acid (3 × 50 ml). The phosphorane was liberated by sodium hydroxide and taken up into benzene. Evaporation and recrystallisation from ethyl acetate gave (1f) (0·5 g, 15%), m.p. 212° (decomp.) (Found: C, 71·2; H, 4·9. $C_{20}H_{16}ClOP$ requires C, 70·9; H, 4·7%), $\nu_{max.}$ (KBr) 695, 720, 755, 760, 1105, 1230, 1390, 1440, 1480, 1565, 1585, 2800 (CHO), 3050, and 3100 cm^{-1}; τ ($CDCl_3$) 1·9 (1H, s) and 2·15—2·73 (15H, m).

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