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THE CONFORMATIONS OF KETO AND FORMYL METHYLENETRIPHENYLPHOSPHORANES

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Variable temperature p.m.r. spectra have been observed for alkoxycarbonyl alkylidenephosphoranes (1, Z = OR)[1] and there is general agreement that the variation is due to infrequent rotation about the α-β carbon-carbon bond. At low temperatures, the spectra usually correspond to a mixture of *cisoid* and *transoid* conformers.

cisoid (1) *transoid*

A second variable temperature effect which involves the α-protons of phosphorus ylides in general, has been observed[2] and shown[3,4] to be due to reversible protonation by trace amounts of phosphonium salt. Two acyl methylenephosphoranes[2] showed this effect only. Restricted rotation about the α-β carbon-carbon bond in phenacyl methylenephosphorane (1; Y=H, Z=Ph) was sought for in spectra run at low temperatures,[3] but was not observed. An analogous β-keto sulphurane[5] also did not give a variable temperature spectrum and o-alkylation gave two isomers which was taken to indicate that there is frequent rotation.

We now have evidence which shows conclusively that β-keto alkylidenephosphanes are fixed in their geometry about the α-β carbon-carbon bond relative to the n.m.r. time scale.

The p.m.r. spectrum of formyl methylenephosphorane (1; Y=Z=H)[6] corresponds to that of a mixture of *cisoid* and *transoid* conformers, the former predominating. No coalescence is observed on raising the temperature to 150°. The variable temperature spectrum previously recorded[2] is attributed to reversible protonation.

Acetyl methylenephosphorane (1; Y=H, Z=Me) gives a p.m.r. spectrum indicating only one conformer in chloroform and benzene. The methyl group appears as a doublet ($^4J_{PH}$ = 1.8 Hz at 60 and 100 MHz) at τ 7.93 p.p.m. in deuteriochloroform. The chemical shift and the magnitude of the coupling constant of the α-proton, (τ 6.33 p.p.m., J_{PCH} = 27 Hz) indicates that the conformer is cisoid. The p.m.r. spectra of the aroyl methylenephosphoranes (1a -c) show two sharp methyl resonances (see Table) which do not coalesce below 150°. In one case, (1a in $CDCl_3$) the two methyl resonances coincide at 7° and 35°, but the signals remain sharp, before and after coincidence. The high field resonances are attributed to the transoid conformer on account of the strong shielding by the triphenylphosphonium group.

Table

P.m.r. spectra of keto alkylidenephosphoranes

	Compound	Solvent	Temperature range	$\tau^{30°}_{Me}$	Rotamer Ratio at 33°		
					cis		trans
1a	Y = CN, Z=mMeC_6H_4	$C_6H_4Cl_2$	+30° to +180°	7.8 7.9	3	:	1
		$CDCl_3$	-35° to +60°	7.65 7.69 (at 10°)	1	:	1
1b	Y=PhCO, Z=mMeC_6H_4	C_6H_6	+30° to +150°	8.0 8.05	3	:	2
1c	Y=p$NO_2C_6H_4CO$, Z=Me	C_6H_6	+30° to +150°	8.14. 8.36	3	;	2

The powerful withdrawing group Y in (1a-c) must reduce the barrier to rotation. Although rotation is not observed, peak intensities do vary with a change in solvent and temperature in accordance with changes in conformer population at a frequency slower than the n.m.r. time scale.

REFERENCES

1. H.I.Zeliger, J.P.Snyder and H.J.Bestmann and references therein, Tetrahedron Letters 2199, (1969)
   M.A. Shaw, J.C.Tebby, R.S.Ward and D.H.Williams, J.Chem.Soc.(C), 2442, (1967)
2. H.J.Bestmann and J.P.Snyder, J.Amer.Chem.Soc., **89**, 3936, (1967)
3. F.J.Randall and A.W.Johnson, Tetrahedron Letters, 2841 (1968)
4. P.Crews, J.Amer.Chem.Soc., **90**, 2961, (1968); H.J.Bestmann, H.G.Liberda, and J.P.Snyder J.Amer. Chem. Soc. **90**. 2963, (1968)
5. S.H.Smallcombe, R.J.Holland, R.H.Fish and M.C.Caserio, Tetrahedron Letters, 5987, (1968)
6. Note added in revision. Since this communication was prepared, a report has appeared by M.L. Filleux-Blanchard and M.G.J.Martin (Comptes rendus 270c 1747 (1970) on the p.m.r. spectrum of the formyl methylenephosphorane (1, Y=Z=H) . Their results are in agreement with our observations.