Synthesis and Tautomerism of 1-Methylphospholan-3-one 1-Oxide

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WE have devised a method for preparing 1-methylphospholan-3-one 1-oxide, the first known ketoderivative of the phospholan family. This compound exhibited a pronounced preference for the enol form when in the solid state or in concentrated solutions. While the phosphoryl group is well-known to assist in stabilizing a negative charge on an adjacent carbon,¹ this appears to be the first instance where a significant degree of stabilization of the enol function is imparted by this group. This effect was specifically sought for in an acyclic β -keto-phosphonate $[(EtO), PO \cdot CH, COMe]^2$ it was found that the mole fraction of enol could not have exceeded about 0.001.†

The product of the cycloaddition³ of chloroprene and methylphosphonous dichloride was hydrolyzed by addition to ice; after 12 hr., the solution was neutralized with sodium carbonate. The product was a 9:1 mixture (by gas chromatography) of 2and 3-phospholen oxides [(IIa) and (IIb)], having m.p. 58.5-61.5°, b.p. 87-90° at 0.075 mm., and displaying two C=C stretching bands $(1626 \text{ and } 1590 \text{ cm}.^{-1})$. The composition of the mixture is determined by the length of exposure to the acid medium before neutralization, shorter times leading to a higher 3-isomer content. The chlorine atom of (IIa) proved to be readily displaced by methoxide ion, owing to the conjugative and/or inductive effect of the phosphoryl group,⁴ yielding enol ether (III) in 58% yield (b.p. $96^{\circ}/0.15$ mm.). Its n.m.r. spectrum consisted of a vinyl-H doublet (J 17 c./sec.) at δ 5.15; OCH₃ singlet at δ 3.78; complex multiplet at δ 2.85—1.75; and a P-CH₃ doublet (J 13 c./sec.) at δ 1.62. Heating a water solution of (III) containing a trace of hydrochloric acid caused hydrolysis to ketone (IV) (53%, m.p. 89—91°), a highly water-soluble solid, analysis correct for C₅H₉O₂P.



In dilute chloroform solution, the i.r. spectrum was that expected for ketone structure (IV); there was a strong carbonyl band at 1730 cm^{-1} , and no appreciable OH or C=C absorption. In a Nujol mull, the spectrum was entirely different; the carbonyl peak was very weak, and there was a broad band at $2440-2275 \text{ cm}^{-1}$ attributable to hydrogen-bonded OH, as well as a very strong

[†] Among α-cyano-derivatives of β-keto-phosphonates, the enol content is considerable (M. Kirilov and G. Petrov, Monatsh., 1968, 99, 166). This has been attributed to the conjugative effect of the cyano-group on the enol, although the phosphoryl group may assist in enol stabilization by hydrogen-bonding.

peak in the C=C region (1558 cm.⁻¹). Similarly a KBr pellet of (IV) of high concentration had a spectrum resembling that in Nujol, but the spectrum of a pellet of low concentration resembled that in dilute chloroform solution.

These spectral effects suggest the tautomeric equilibrium:



In high concentration, enol (V) predominates; in low concentration, ketone (IV) predominates.

The i.r. spectrum of enol (V) resembles that for cyclopentane-1,3-dione,⁵ which also shows a broad OH band around 2500 cm.⁻¹ and a band attributable to C=C at 1587 cm.⁻¹. The broad OH band has been noted for other β -diketones,⁶ and for cyclic compounds has been attributed to dimeric hydrogen-bonded forms similar to those from carboxylic acids. For (V), dimeric structure (VI) can be written, although polymeric forms should also be considered.



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The tautomerism of (IV) is also evident in its n.m.r. spectra. Its ³¹P spectrum (3·4 molal solution in chloroform) has two signals, -51.0 and -60.5 p.p.m. (H₃PO₄ reference). The latter signal (about 25% of total area) is attributed to enol (V) [cf. -58.5 for enol ether (III)]. The ¹H n.m.r. spectrum of the same solution shows a vinyl proton doublet (J 22 c./sec.) at δ 5.07, and two P-CH_s doublets (δ 1.82, J 13.5 c./sec.; δ 1.67, J 13.5 c./sec.). Since the area ratio of vinyl to total P-CH₃ signals is approximately 1:12, 20% of enol (V) is present, in accord with the ³¹P assignment. On dilution, the vinyl signal and one P-CH₃ doublet disappear as the equilibrium shifts to the keto-side.

The phosphoryl group may be considered to contribute to the stability of the enol by two effects. It is a very good acceptor in hydrogen bonding, a factor of significance in stabilization of enols of dicarbonyl compounds. Also, some stabilization should result from d-p resonance with the enolic double bond.⁴ The operation of such an effect among phospholen oxides has already been suggested by the greater thermodynamic stability of 2-phospholen oxides relative to the 3-isomers.7

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Notice

The Editor regrets that the two Communications entitled 'Stereospecificity in the thermal- and photo-additions of trans-stilbene to tetrachloro-p-benzoquinone. Importance of charge-correlation factors in cycloadditions which involve donor-acceptor pairs' and 'Photochemical and thermal cylcoadditions of cis-stilbene and tolan (diphenylacetylene) to tetrachloro-p-benzoquinone. Photodecarboxylation of an α -diketone', by D. Bryce-Smith and A. Gilbert, which appeared in Issue No. 21, pp. 1318–1320, were incorrectly printed and should be disregarded. The correct versions will be published shortly.