A Novel Ring Closure in the Michaelis–Arbuzov Reaction of Trialkyl Phosphites with Phthaloyl Chloride

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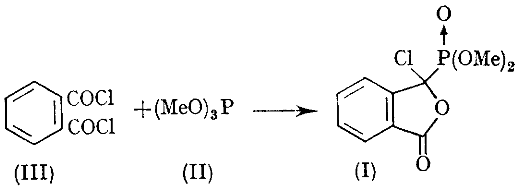
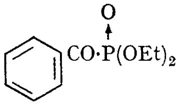
THE formation of a carbon–phosphorus bond *via* reaction of aroyl halides with phosphites has only been examined briefly.[1,2] We report the isolation of a novel phosphorylated heterocycle (I) from the reaction of trimethyl phosphite (II) and phthaloyl chloride (III).

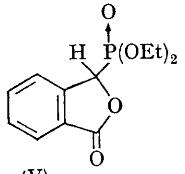
Addition of (III) to (II) (1 : 1 mole ratio) and inverse addition of (II) to (III) (1 : 2 respective mole ratio) gave 64% and 40% yields, respectively, of (I); m.p. 77·5—78·5°. Its ^{31}P n.m.r. spectrum (benzene; 20% w/w) displayed a septet at $-9{\cdot}7$ p.p.m. relative to 80% H_3PO_4 which approximates to that for diethyl dichloromethylphosphonate (neat; $-9{\cdot}3$ p.p.m.)[3] but not that for diethyl benzoylphosphonate (IV) (neat; $+2$ p.p.m.).[4] In addition, an analogue of (I), diethyl phthalidylphosphonate (V), in benzene has a ^{31}P spectrum which displays a multiplet at $-13{\cdot}2$ p.p.m. relative to 85% H_3PO_4.† Rather strong infrared absorption (1803, 1287, 1273, and 1047 cm.$^{-1}$) was found for (I), reminiscent of that observed with dimethyl phthalidylphosphonate (VI) [1787, 1281 (a doublet peak), and 1041 cm.$^{-1}$].[5] Carbonyl group absorptions in dimethyl *o*-substituted aroylphosphonates occur in the range 1675—1650 cm.$^{-1}$.‡

A proton resonance spectrum of (I) revealed a coupling constant of *J*(P–OC–H) 11 c./sec. in several solvents at 60 or 100 Mc./sec. Although

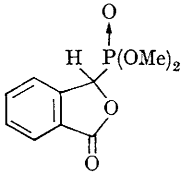




(IV)



(V)



(VI)

dimethyl benzylphosphonate has *J*(P–OC–H) 11 c./sec.,[2] decoupling of the methyl protons from

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‡ The following dimethyl esters of aroylphosphonic acids have been prepared and characterized in our laboratory: Ar = *o*-ClC_6H_4, *o*-$CH_3{\cdot}C_6H_4$, *o*-$C_6H_5{\cdot}C_6H_4$, *o*-$CH_3O{\cdot}C_6H_4$, 1-$C_{10}H_7$.

TABLE. ^1H *n.m.r. absorption for* (I)[a]

Solvent	Temp.	δ, CH_3		Δ	δ, Aromatic H
$HCONMe_2$[b]	22	4·03d[c]	3·85d[c]	0·18	—
CCl_4[b]	22	4·07d	3·68d	0·39	7·98—7·60
C_2Cl_4[e]	27	4·00d	3·59d	0·41	7·93—7·49
C_2Cl_4[e]	100	3·96d	3·58d	0·38	7·98—7·45

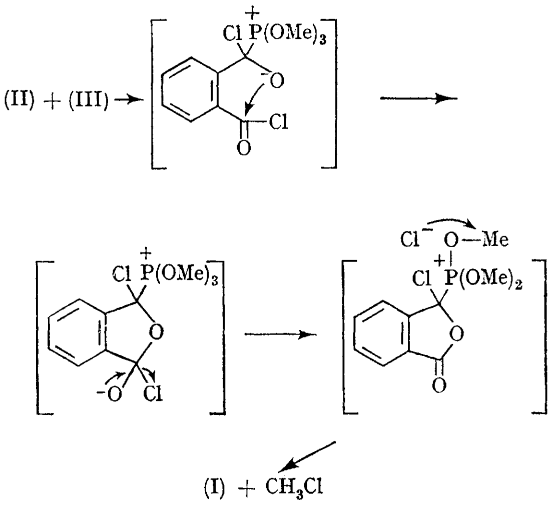
[a] δ-Values downfield from Me_4Si; Δ-separation of methyl signals (p.p.m.); *J*(P–OC–H) 11 c./sec.; d = doublet. [b]Spectrum obtained on a Varian A-60 spectrometer. [c]An apparent triplet resulting from overlapping doublets. [e]Spectrum obtained on a Varian HA-100 spectrometer.

the methylene protons in (V) revealed an approximate *J*(P–OC–H) 8·0 c./sec. (in CCl_4). In view of the width of either nonequivalent[6] triplet for each methyl group in (V), it was not possible to remove all vicinal H–H coupling for an extremely accurate P–H coupling constant in (V).

Inherent asymmetry arising from the asymmetric carbon atom creates nonequivalent environments for the two methyl groups. However, the observed magnitudes for Δ (Table) tentatively suggest a significant population of a molecular conformation having one of the methyl groups nearer to the plane of the magnetically anisotropic benzene ring.[7] In another report,[8] a similar argument has been made with respect to the nonequivalence of the methylene protons of 1-phenylethyl benzyl ether as reflected in changes in Δ with variation in solvent. Although it is possible to envisage two preferred conformations by examination of models, presumably the wagging process of the five-membered ring is also operative. Consequently, it is likely that even assignment of an average conformation is difficult.

Thermal decomposition of (I) occurred at 190° with the formation of phthalic anhydride and dimethoxyphosphorochloridite. The phosphorus compound was converted into dimethyl hydrogen phosphonate by the action of moist ether. Reaction of (II) with triethyl phosphite or tri-n-propyl phosphite gave oils which could not be induced to crystallize. Attempted vacuum-distillation of each gave phthalic anhydride and the respective dialkoxyphosphorochloridite.

A possible pathway for the formation of (I) is depicted. It is presumed that the close proximity of the second aroyl chloride group results in a ring closure step prior to loss of methyl chloride.



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