Methyltrineopentyloxyphosphonium Iodide: A Crystalline Michaelis-Arbuzov Intermediate and its Mode of Decomposition

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Summary Methyltrineopentyloxyphosphonium iodide is obtained as a stable, crystalline intermediate, by the interaction of trineopentyl phosphite and iodomethane at room temperature; in solution the intermediate decomposes by a first-order reaction to yield neopentyl iodide, without rearrangement.

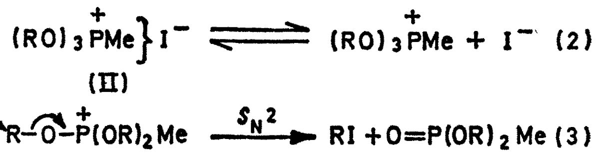
THE Michaelis–Arbuzov reaction provides one of the most important routes for the preparations of alkyl phosphonates and has been extensively studied and reviewed.[1] A quasi-phosphonium intermediate (I) [equation (1)] is thought to be formed, although no such adduct from a trialkyl phosphite has proved sufficiently stable for isolation. Viscous "intermediates" were reported from the reactions of

$$(R^1O)_3P + R^2X \rightarrow \underset{(I)}{[(R^1O)_3PR^2X]} \rightarrow (R^1O)_2P(O)R^2 + R^1X \qquad (1)$$

trialkyl phosphites with $\alpha\beta$-dihalogenoalkyl ethers, or with the methyl ester or nitrile of $\alpha\beta$-dihalogenopropionic acids, but were not characterized.[1] Spectroscopic evidence for an intermediate in the bromination of $P(OCH_2)_3CMe$ has, however, recently been published.[2] Triaryl phosphites form stable adducts on heating with alkyl halides because of the extremely slow rate of nucleophilic attack by halide ion on the benzene ring;[1] crystalline intermediates have also been obtained from alkyl iodides and a number of alkylphosphonous or dialkylphosphinous esters.[3]

We now report the isolation of methyltrineopentyloxyphosphonium iodide as the first stable, crystalline Michaelis–Arbuzov intermediate to be obtained from a trialkyl phosphite. On mixing equimolar amounts of trineopentyl phosphite and iodomethane at room temperature the product slowly crystallizes, and yields white needles after washing with anhydrous ether; m.p. 86° (sealed tube), ^{31}P δ -54 p.p.m. (m) (relative to 85% H_3PO_4), τ 8·96 (Me_3C, s), 7·27 (Me–P, d, J_{PH} 16·75 Hz), 5·69 (CH_2, d, J_{POCH} 4·9 Hz; elemental analysis is consistent with $C_{16}H_{36}IO_3P$. The conditions are critical, since the compound is unstable in solution and decomposes to dineopentyl methylphosphonate and neopentyl iodide in a matter of hours. Excess of iodomethane, in which the adduct is soluble, should therefore be avoided. As a crystalline product, it is indefinitely stable in a dessicator or under anhydrous ether, but is susceptible to hydrolysis by atmospheric moisture and to discolouration by light. The ^{31}P n.m.r. spectrum is consistent with the phosphonium structure $[(Me_3CCH_2O)_3PMe]^+I^-$, rather than with that of a phosphorane.[4]

The relative rates of formation and decomposition of the intermediate are clearly of importance in determining whether or not isolation is possible. The steric resistance of the neopentyl group to S_N2 attack (the mechanism of dealkylation indicated by work with optically active tri-2-octyl phosphite[5]) is thus particularly favourable to the build-up of sufficient concentration of the intermediate to allow crystallization to occur. In solution in chloroform, the decomposition of the intermediate was shown to follow first-order kinetics up to at least 85% reaction (k_1 $1·1 \times 10^{-4}\,s^{-1}$ at 33·5°). This result, together with the n.m.r. data above, is consistent with the decomposition of an intermediate whose structure is that of an undissociated ion-pair (II) [equations (2) and (3)].



The exclusive operation of the S_N2 mode of dealkylation was confirmed by the complete absence of rearrangement in the alkyl iodide obtained. No olefinic by-product was detected.

Kinetic measurements were made by following the disappearance of the methylene ^1H n.m.r. doublet of the intermediate.

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