A Possible Azirine Intermediate in the Reaction of Bromonitroalkenes with Triphenylphosphine

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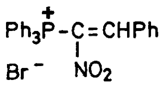
Summary Bromonitroalkenes react with triphenylphosphine in benzene to give α-cyanoalkyltriphenylphosphonium bromides: the same reaction in methanol gives a rearranged product (IV), the formation of which is most easily rationalised *via* an azirine intermediate.

IN an attempt to prepare the presently unknown α-nitrophosphonium salt (I) by an addition–elimination reaction[1] we have investigated the reactions of α-bromonitroalkenes (II) with tervalent phosphorus compounds.

β-Bromo-β-nitrostyrene (II) reacts with 3 mol of triphenylphosphine in dry benzene at room temperature over 24 h to give triphenylphosphine oxide and a phosphonium salt (III), m.p. 255—256°; i.r. (KBr disc) showed no nitro-group; n.m.r. ($CDCl_3$) τ 2·18 (m, 15H), 0·75 [d, *J*(P–C–H) 18 Hz, 1H]; m.s. *m/e* 377. On treatment with dilute aqueous sodium hydroxide at 0° (III) was readily converted into a phosphonium ylide, m.p. 203—204°; i.r. 2145 cm^{-1} (CN); n.m.r. τ 2·20 (m); m.s. *m/e* 377 (100), 337 (4), 262 (23), 183 (75). Refluxing in 5N-aqueous sodium hydroxide for 24 h converted (III) into triphenylphosphine oxide and phenylacetic acid. These results suggest that (III) is α-cyanobenzyltriphenylphosphonium bromide and this was confirmed by its synthesis from triphenylphosphine and α-bromobenzyl cyanide.

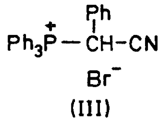


$\mathrm{Ph_3\overset{+}{P}-\underset{NO_2}{C}=CHPh}\quad \mathrm{Br^-}$

(I)

$\mathrm{Ph{-}CH{=}CBrNO_2}$

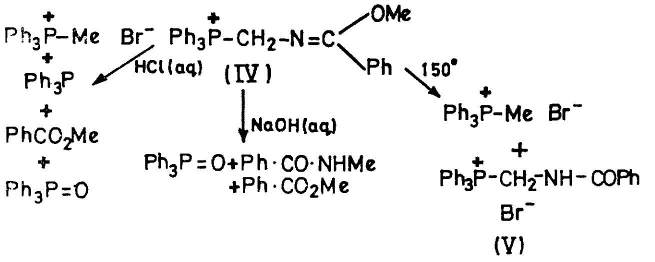
(II)



$\mathrm{Ph_3\overset{+}{P}-\overset{Ph}{C}H-CN}\quad \mathrm{Br^-}$

(III)

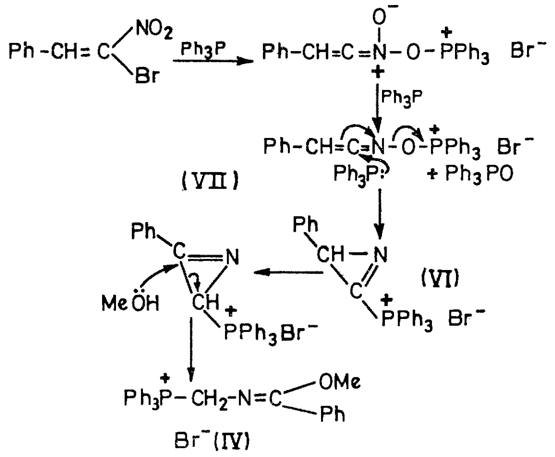
This reaction is closely related to that of α-nitroalkanes with triphenylphosphine [2] and presumably takes place by an analogous mechanism involving initial attack of phosphine on halogen or oxygen. However, when the reaction of (II) with triphenylphosphine is repeated in methanol at room temperature a quite different route is followed to give a phosphonium salt (IV), $C_{27}H_{25}BrNOP$, m.p. 188—190°; i.r. (KBr disc) 2750, 1655 cm^{-1} and no nitro-group; n.m.r. ($CDCl_3$) τ 2·25 (m, 15H), 2·55 (m, 5H), 4·14 [d, J (PH) 8 Hz, 2H], 6·44 (s, 3H); m.s. *m/e* 277(2), 262(100), 183(50), 105(40), 96(50), 94(50). Treatment of the salt (IV) with 5N-aqueous sodium hydroxide solution at room temperature yielded triphenylphosphine oxide, methyl benzoate, and *N*-methylbenzamide in small yield. 5N-Hydrochloric acid converted the salt (IV) into methyltriphenylphosphonium bromide, triphenylphosphine, triphenylphosphine oxide, and methyl benzoate. Pyrolysis of the salt (IV), under vacuum at 150°, yielded a mixture of methyltriphenylphosphonium bromide and a phosphonium salt (V), $C_{26}H_{23}BrNOP$, m.p. 166—167°; i.r. 1670 cm^{-1}; n.m.r. τ 0·04 (br t, 1H), 2·20 (m, 17H), 2·62 (m, 3H), 4·57 [dd, J(1)3, J(2) 6 Hz, 2H]. This information is summarised in Scheme 1.



SCHEME 1

A reasonable structure for phosphonium salt (V) is (benzamidomethyl)triphenylphosphonium bromide and this was confirmed by its synthesis from *N*-(bromomethyl)-benzamide[3] and triphenylphosphine. On the basis of this structure for salt (V) and the hydrolytic and spectral data we suggest that salt (IV) is {[(α-methoxybenzylidene)amino]-methyl}triphenylphosphonium bromide.

The formation of (IV) is most easily rationalised by an intermediate azirine (VI), a possible route to which is summarised in Scheme 2. Support for this mechanism is available from the reactions of α-chloronitroalkanes with triphenylphosphine[4] which appear to proceed *via* an oxime derivative analogous to (VII).



SCHEME 2

We thank Professor C. W. Rees for interesting and profitable discussions.

(*Received, May* 19*th*, 1970; *Com.* 776.)

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