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THE FORMATION OF FORMYLMETHYLENETRIPHENYLPHOSPHORANES FROM THE REACTION OF HALONITROALKENES WITH TRIPHENYLPHOSPHINE

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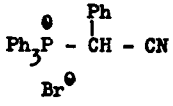
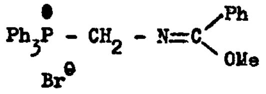
Reaction between triphenylphosphine and 2-bromo-2-nitrostyrene 5e in benzene leads to α-cyanobenzyltriphenylphosphonium bromide 1, while in methanol a different pathway is followed to give the rearranged salt 2.[2] We have now studied the reactions of other substituted β-bromo-β-nitrostyrenes with triphenylphosphine and found that a quite different reaction takes place to give, amongst other products, 1-aryl-1-formylmethylenetriphenylphosphoranes 3. The parent ylid 4 has been recently the subject of a number of partially contradictory nmr studies.[3] Similar studies of compounds 3, which are normally difficult to prepare, have clarified these results[4] and confirmed the work of Snyder and Bestmann.[3b]

1-p-Nitrophenyl-2-bromo-2-nitroethylene 5a reacts with three moles of triphenylphosphine in methanol to give triphenylphosphine oxide, a phosphonium ylid 3a, and a phosphonium salt 6, $C_{36}H_{30}BrNP_2$, m.p. 255-256°; nmr 2.44τ (multiplet) aromatic protons only; m.s. m/e 276; which was identical with an authentic sample of triphenyl(triphenylphosphoranylideneamino)phosphonium bromide.[5]



$$Ph_3\overset{\oplus}{P} - \overset{Ph}{\overset{|}{C}H} - CN \quad Br^{\ominus}$$

1



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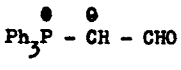
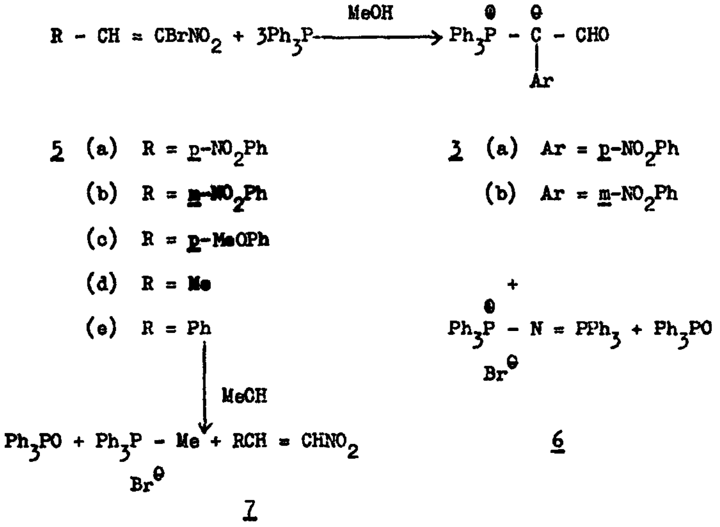


$$Ph_3\overset{\oplus}{P} - \overset{\ominus}{C}H - CHO$$

4



$$R-CH=CBrNO_2 + 3Ph_3P \xrightarrow{MeOH} Ph_3\overset{\oplus}{P}-\underset{Ar}{\overset{\ominus}{C}}-CHO$$

5 (a) R = p-NO_2Ph
(b) R = m-NO_2Ph
(c) R = p-MeOPh
(d) R = Me
(e) R = Ph

3 (a) Ar = p-NO_2Ph
(b) Ar = m-NO_2Ph

$$\underset{Br^{\ominus}}{Ph_3\overset{\oplus}{P}}-N=PPh_3 + Ph_3PO$$

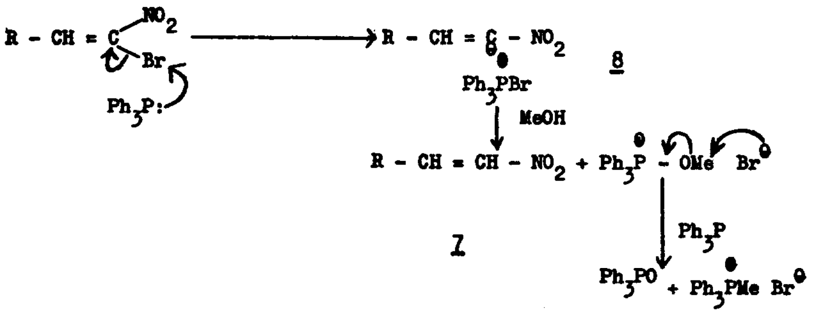
6

$$\xrightarrow{MeOH} Ph_3PO + \underset{Br^{\ominus}}{Ph_3\overset{+}{P}-Me} + RCH=CHNO_2$$

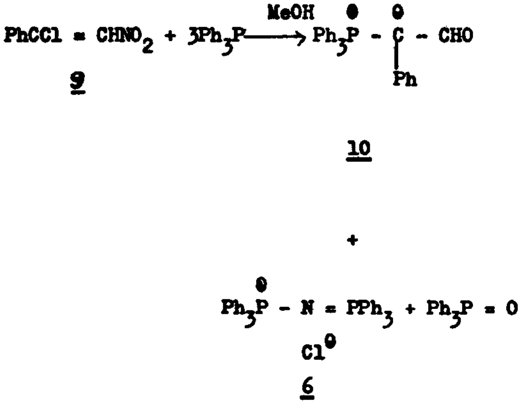
7

The phosphonium ylid 3(a), $C_{26}H_{20}NO_3P$, m.p. 229°, had ir 2,750(w), 1,610(m), 1,570(s), 1305(s) cm^{-1}; m.s. m/e 425 (M^+), 396, 277, 262, 108; nmr ($CDCl_3$ at + 27°) 1.54τ(broad d.) 1H, 2.36τ(m) 19 H.[6] This suggests that 3(a) is 1-p-nitrophenyl-1-formylmethylenetriphenylphosphorane. Further evidence for this structure was obtained by comparison of spectra of a sample of 1-phenyl-1-formylmethylenetriphenylphosphorane prepared from triphenylphosphine and 1-bromo-1-phenylacetaldehyde, followed by base treatment of the phosphonium salt formed. 1-m-Nitrophenyl-2-bromo-2-nitroethylene 5(b) also reacted with triphenylphosphine in methanol to give the salt 6, the phosphonium ylid 3(b) and triphenylphosphine oxide. However, reaction of 1-p-methoxyphenyl-2-bromo-2-nitroethylene 5(c) with triphenylphosphine under similar conditions gave methyltriphenylphosphonium bromide, 1-p-methoxyphenyl-2-nitroethylene 7 (R = p-MeOPh) and triphenylphosphine oxide. 1-Bromo-1-nitroprop-1-ene 5(d) and triphenylphosphine also reacted in methanol by this second pathway to give methyltriphenylphosphonium bromide and phosphine oxide.

The reactions of compounds 5(c) and 5(d) are readily interpreted in terms of initial attack by phosphine on halogen, followed by methanolysis of the ion pair 8 and reaction of triphenylphosphine with the methyl bromide formed.



The formation of the ylids 3(a) and 3(b), together with the salt 6, from 5(a) and 5(b) is more difficult to rationalise, although the pathway followed appears to be controlled by the electron donating, or attracting, ability of the group R in 5. The analogous ylid 10, and the salt 6, are obtained in high yield from the reaction of triphenylphosphine and 1-chloro-2-nitrostyrene 9, but 2-bromo-2-nitrostyrene 5(e) reacts with phosphine to give quite different products.[2]



$$\underset{\underline{9}}{PhCCl = CHNO_2} + 3Ph_3P \xrightarrow{MeOH} Ph_3\overset{\oplus}{P} - \underset{Ph}{\overset{\ominus}{C}} - CHO$$

10

+

$$\underset{Cl^{\ominus}}{Ph_3\overset{\oplus}{P} - N = PPh_3} + Ph_3P = O$$

6

We are presently further investigating the mechanism of these reactions.

References

1. Author to whom correspondence should be addressed.
2. C. J. Devlin and B. J. Walker, Chem.Comm. 917 (1970).
3. (a) M. L. Filleux-Blanchard and G. J. Martin, Compt. rend. ser. C., 1747 (1970).
   (b) J. P. Snyder and H. J. Bestmann, Tetrahedron Letters, 3317 (1970).
   (c) I. F. Wilson and J. C. Tebby, Tetrahedron Letters, 3769 (1970).
4. C. J. Devlin and B. J. Walker, unpublished results.
5. V. R. Appel and A. Hauss, Z. anorg. Chem. 311, 290 (1961).
6. The temperature dependent nmr spectra of compounds 3 and 4 will be described in a forthcoming publication.