601. *The Reaction of Triphenylphosphine with* 1-*Bromo*-1-*nitroalkanes.*

By S. Trippett and D. M. Walker.

With triphenylphosphine, 1-bromo-1-nitroalkanes and *N*-bromo-amides in general give nitriles, and α-phenylphenacyl chloride gives diphenylacetylene. A common mechanism is suggested for these three reactions.

We showed previously[1] that bromonitromethane and triphenylphosphine smoothly form a phosphonium salt that with aqueous alkali at 0° gives triphenylphosphine oxide and fulminic acid, presumably *via* the phosphorane which can be written as (I). It seemed probable that a similar sequence starting from 1-bromo-1-nitroalkanes would lead to the unknown aliphatic nitrile oxides, and this possibility has been investigated.

1-Bromo-1-nitroethane with triphenylphosphine gave only a 20% yield of the phosphonium bromide. With aqueous alkali at 0°, this gave within one minute a 75% yield of triphenylphosphine oxide, but the expected acetonitrile oxide could not be detected, even by carrying out the reaction in the presence of stilbene with which nitrile oxides condense rapidly to give Δ^2-isoxazolines.[2] In order to increase the molecular weight of the expected nitrile oxide and so make its isolation easier, 1-bromo-1-nitro-octane was treated with triphenylphosphine, but here no quaternary salt was obtained. Instead, two molecules of triphenylphosphine reacted with each molecule of bromonitro-compound to give one molecule each of triphenylphosphine oxide, triphenylphosphine oxide hydrobromide, and octanonitrile. 1-Bromo-1-nitropropane similarly gave propionitrile and no quaternary salt, and it became apparent that the low yield of quaternary salt from 1-bromo-1-nitroethane was due to the intervention of this second reaction leading to a nitrile. The phosphonium salt is not an intermediate in this reaction; 1-nitroethyltriphenylphosphonium bromide was not affected by triphenylphosphine in boiling ethanol.

A possible mechanism for this nitrile formation involves attack of triphenylphosphine on an oxygen of the *aci*-form (II) of a bromonitro-compound with simultaneous expulsion

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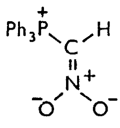
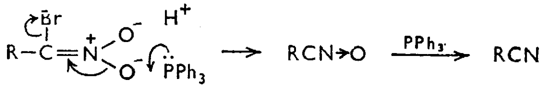
[1] Trippett and Walker, *J.*, 1959, 3874.

[2] Stagno D'Alcontres and Grünager, *Gazzetta*, 1950, **80**, 831.

of bromide ion, leading initially to a nitrile oxide which is then deoxygenated by a second molecule of triphenylphosphine. If this is so, the second step of deoxygenation [3] must be much faster than the first, for when 1-bromo-1-nitro-octane was treated with one mol. of triphenylphosphine half reacted to give the nitrile and half was unchanged. It seemed


(I)



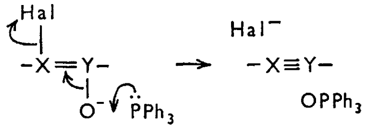
(II)

possible that suitable conjugation might make reduction of the intermediate nitrile oxide more difficult and allow it to be detected, but when bromonitrophenylmethane in ether at 0° was treated with one mol. of triphenylphosphine and the resulting suspension filtered immediately into a solution of maleic anhydride in ether, no Δ^2-isoxazoline was formed. Any benzonitrile oxide would have been detected under these conditions.[4] With two mols. of triphenylphosphine, bromonitrophenylmethane gave benzonitrile.

From the action of silver nitrite on ethyl bromoacetate, Scholl and Schöfer [5] obtained in very low yield a stable crystalline substance, m. p. 111°, to which, on the basis of analysis and molecular-weight determination, they gave the formula $O{\leftarrow}NC{\cdot}CO_2Et$. Although highly improbable, this formulation could not be entirely dismissed, and therefore the reaction of bromonitroacetic ester with triphenylphosphine was investigated. Under a variety of conditions, and with varying molecular proportions of reactants, the only product detected was cyanoformic ester.

While therefore no evidence has been obtained for the intermediate formation of nitrile oxides in the reaction of 1-bromo-1-nitroalkanes with triphenylphosphine, two other reactions have been discovered which fit into the general pattern:

(III)



In the first of these, *N*-bromo-amides (III; X = N, Y = C, Hal = Br; enol form) with triphenylphosphine at room temperature in benzene gave nitriles, *e.g.*, *N*-bromobenzamide gave benzonitrile and *N*-bromophenylacetamide gave phenylacetonitrile. Acylimino-phosphoranes cannot be intermediates, as they form nitriles only when heated to about 200°.[6] In the second reaction, α-phenylphenacyl chloride (CHPhCl·COPh; III; X = Y = C, Hal = Cl; enol form) with triphenylphosphine in boiling benzene gave a 90% yield of diphenylacetylene. Again the expected phosphorane cannot be an intermediate as this gives diphenylacetylene only at 350°.[1] The normal reaction of α-halogeno-ketones with triphenylphosphine is, of course, quaternisation; the direct formation of an acetylene can be expected only in exceptional cases.

EXPERIMENTAL

Nitriles were identified by comparison of their infrared spectra with those of authentic materials.

1-*Nitroethyltriphenylphosphonium Bromide*.—A solution of 1-bromo-1-nitroethane (7·7 g.) in benzene (20 ml.) was added slowly to triphenylphosphine (13 g.) in benzene (150 ml.) at 0° and the suspension set aside at 0° overnight. Filtration then gave the above *phosphonium bromide*

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[3] Horner and Oediger, *Chem. Ber.*, 1958, **91**, 437.

[4] Quilico, Stagno D'Alcontres, and Grünager, *Gazzetta*, 1950, **80**, 479.

[5] Scholl and Schöfer, *Ber.*, 1901, **34**, 870.

[6] Staudinger and Hauser, *Helv. Chim. Acta*, 1921, **4**, 861.

(4·3 g.), m. p. (from nitromethane) 103° (decomp.) (Found: N, 3·3. $C_{20}H_{19}BrNO_2P$ requires N, 3·4%). It was unchanged by triphenylphosphine in refluxing ethanol. The mother-liquors deposited triphenylphosphine oxide hydrobromide, m. p. 145—148°, which fumed in moist air and on crystallisation from ethanol–water gave triphenylphosphine oxide, m. p. 154—155°.

Reaction of 1-*Bromo*-1-*nitroalkanes with Triphenylphosphine.*—A solution of 1-bromo-1-nitrooctane (4·76 g.) in benzene (5 ml.) was added to triphenylphosphine (11·5 g.) in benzene (30 ml.) at room temperature, and the suspension set aside at room temperature overnight. Filtration then gave triphenylphosphine oxide hydrobromide (5·0 g.). The filtrate was evaporated *in vacuo*, and the crystalline residue stirred with light petroleum (80 ml.) and filtered, to give triphenylphosphine oxide (6·7 g.). The filtrate was evaporated and the residue distilled under reduced pressure to give octanonitrile (1·8 g., 72%), b. p. 90—92°/13 mm.

The reaction can also be carried out in ether; the triphenylphosphine oxide then separates with the hydrobromide.

In a similar way, 1-bromo-1-nitropropane gave propiononitrile (63%), b. p. 98°, bromonitroacetic ester gave cyanoformic ester (50%), b. p. 115—116°, and bromonitrophenylmethane gave benzonitrile (75%), b. p. 185—188°.

1-*Bromo*-1-*nitroalkanes.*—The only satisfactory way of preparing these in a pure condition was by addition of the finely powdered dry sodium or ammonium salt of the corresponding nitro-compound to bromine in carbon disulphide or carbon tetrachloride at 0°. In this way were obtained 1-bromo-1-nitroethane (65%), b. p. 73°/50 mm., 1-bromo-1-nitropropane (67%), b. p. 56°/14 mm., 1-*bromo*-1-*nitro-octane* (70%), b. p. 79—80°/0·45 mm. (Found: N, 5·8. $C_8H_{16}BrNO_2$ requires N, 5·9%), bromonitrophenylmethane (42%), b. p. 75°/0·4 mm., and bromonitroacetic ester (71%), b. p. 54—55°/0·1 mm. Yields are overall from nitro-compounds.

Reaction of N-*Bromo-amides with Triphenylphosphine.*—A solution of triphenylphosphine (5·2 g.) in benzene (50 ml.) was added to a suspension of *N*-bromobenzamide (4·0 g.) in benzene (50 ml.) at room temperature. After 15 min., the solution was decanted from the semi-solid phosphine oxide hydrobromide and washed with water, dried, and evaporated. Extraction of the residue with ether (5 + 5 ml.) and distillation of the extract gave benzonitrile (1·0 g.), b. p. 63—65°/9 mm.

In a similar way, *N*-bromophenylacetamide gave phenylacetonitrile (60%), b. p. 99—100°/10 mm.

Reaction of α-Phenylphenacyl Chloride with Triphenylphosphine.—Triphenylphosphine (13·1 g.) and α-phenylphenacyl chloride (11·3 g.) were refluxed in dry benzene (150 ml.) for 20 hr., hydrogen chloride being evolved. After evaporation, extraction of the residue with hot light petroleum (b. p. 60—80°) and cooling gave triphenylphosphine oxide (11 g., 84%), m. p. and mixed m. p. 154—155°. The mother-liquors on distillation gave diphenylacetylene (7·8 g., 90%), b. p. 130—132°/0·45 mm., m. p. (from aqueous ethanol) 58·5—59·5°, having the recorded ultraviolet spectrum.[7]

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[7] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," J. Wiley & Sons, New York, 1951.