1315. *The Reaction of Triphenylphosphine with* 1-*Bromo*-1-*nitroalkanes*

By S. TRIPPETT, B. J. WALKER, and H. HOFFMANN

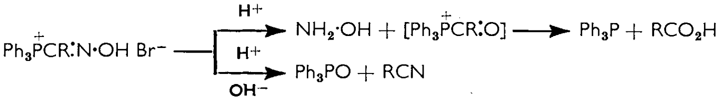
The phosphonium salts obtained from the reaction of triphenylphosphine with 1-bromo-1-nitroalkanes are now shown to be α-hydroxyiminoalkyltriphenylphosphonium bromides.

TRIPHENYLPHOSPHINE reacts with 1-bromo-1-nitroalkanes to give, in general, phosphine oxide, phosphine oxide hydrobromide, and nitrile.[1] However, bromonitromethane, and to a lesser extent 1-bromo-1-nitroethane, give salts which were originally formulated as α-nitroalkylphosphonium bromides.[2] We have reinvestigated these salts, and that now obtained in small yield from 1-bromo-1-nitropropane, and find them to be α-hydroxyiminoalkylphosphonium bromides (I), formed in accord with the equation

$$2Ph_3P + RCHBr{\cdot}NO_2 \longrightarrow Ph_3PO + Ph_3\overset{+}{P}CR{:}N{\cdot}OH\ Br^- \quad \text{(I)}$$

Thus, bromonitromethane with 2 moles of triphenylphosphine in benzene below 5° gives phosphine oxide (91%) and the salt (I; R = H) (75%). Without cooling, no phosphonium salt is obtained.

The hydroxyl groups of the salts (I; R = Me or Et) are apparent in the infrared at ~2750 cm.$^{-1}$, and the n.m.r. spectrum of the salt (I; R = Me) (doublet at 7·8 τ, J = 10 c./sec.) shows the absence of hydrogen on the α-carbon. Alkaline hydrolysis of the salts gives triphenylphosphine oxide and nitrile, whilst acid hydrolysis gives, besides these compounds, triphenylphosphine, hydroxylamine, and carboxylic acid. Increased strength of acid favours hydrolysis to hydroxylamine, which was isolated as benzaldoxime.



Nitroalkanes do not react with triphenylphosphine, and it therefore seems probable that the removal of oxygen in the above quaternisations occurs after formation of an α-nitroalkylphosphonium salt. The present findings mean that so far no α-nitroalkylphosphonium salts have been described.

EXPERIMENTAL

A capillary column (50 m. × 0·5 mm.) coated with polypropylene glycol was used for vapour phase chromtography (v.p.c.).

Hydroxyiminomethyltriphenylphosphonium Bromide.—A solution of bromonitromethane (7 g.) in benzene (15 ml.) was added slowly to a solution of triphenylphosphine (26 g.) in benzene (50 ml.) so that the temperature did not rise above 5°, and the resulting suspension set aside at <5° for 1 hr. Filtration then gave the above *bromide* (15 g.), m. p. (from nitromethane–ethyl acetate) 166° (decomp.) (Found: C, 59·0; H, 4·5; N, 3·6. $C_{19}H_{17}BrNOP$ requires C, 59·05; H, 4·4; N, 3·6%). Evaporation of the filtrate and recrystallisation from ethyl acetate gave triphenylphosphine oxide (12·5 g.), m. p. and mixed m. p. 157—158°.

In a similar way, 1-bromo-1-nitroethane gave *α-hydroxyiminoethyltriphenylphosphonium bromide* (65%), m. p. (from chloroform–ethyl acetate) 153—154° (Found: C, 59·85; H, 4·9; N, 3·5. $C_{20}H_{19}BrNOP$ requires C, 59·9; H, 4·75; N, 3·5%), and triphenylphosphine oxide (80%); 1-bromo-1-nitropropane gave *α-hydroxyiminopropyltriphenylphosphonium bromide* (16%), m. p. 152—154° (Found: C, 60·76; H, 5·2; N, 3·3; P, 7·4. $C_{21}H_{21}BrNOP$ requires C, 60·8; H, 5·1; N, 3·4; P, 7·5%). The filtrate from the last reaction was shown by v.p.c. to contain propionitrile (~60%).

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[1] S. Trippett and D. M. Walker, *J.*, 1960, 2976.

[2] S. Trippett and D. M. Walker, *J.*, 1959, 3874.

Alkaline Hydrolysis.—The salt (I; R = H) (4·92 g.) was dissolved in water (30 ml.) and ethanol (30 ml.), N-sodium hydroxide (13 ml.) added, and the suspension set aside at room temperature for 15 min. Filtration gave triphenylphosphine oxide (3·4 g.), m. p. and mixed m. p. 157—158°. Titration of the filtrate with silver nitrate showed the presence of cyanide ion (28%).

The salts (I; R = Me or Et) dissolved in dilute alkali at room temperature to give stable solutions from which they could be recovered on acidification. Refluxing a solution of the salt (I; R = Me) in 0·5N-sodium hydroxide for 20 min. gave, on cooling and filtration, triphenylphosphine oxide (88%), m. p. and mixed m. p. 157—158°. Analysis of the filtrate by v.p.c. showed the presence of acetonitrile (50%). Similarly the salt (I; R = Et) gave triphenylphosphine oxide and propionitrile (60%).

Acidic Hydrolysis.—A solution of the salt (1—2 g.) in hydrochloric acid (30 ml.) was refluxed for 2—3 hr., the resulting solution analysed directly for nitrile by v.p.c., and then extracted with chloroform. The extract was washed with water, dried, and evaporated, and the residue set aside at room temperature overnight in benzene (10 ml.) containing methyl iodide (2 ml.). Filtration gave methyltriphenylphosphonium iodide, m. p. and mixed m. p. 190—192° (from chloroform–ethyl acetate). Evaporation of the filtrate gave triphenylphosphine oxide, m. p. and mixed m. p. 157—158° (from ethyl acetate). The yields are given in the Table, which relates to 2N-hydrochloric acid except where stated.

R	H		Me	Et	
Ph_3PO	33	12 (12N-HCl)	55	71	trace (12N-HCl)
Ph_3P	57	74 (12N-HCl)	18	trace	67 (12N-HCl)
RCN			30	60	

A solution of the bromide (I; R = H) (6·3 g.) in 12N-hydrochloric acid (15 ml.) was refluxed for 3 hr., cooled, filtered, and made alkaline at 0° by the addition of 5N-sodium hydroxide. Benzaldehyde (2 g.) was then added, the solution set aside at room temperature for 1 hr., and then acidified by the addition of solid carbon dioxide. Ether extraction and distillation of the extract at 110—120°/3 mm. gave a liquid (1·2 g.) whose infrared spectrum was a composite of equal parts of benzaldoxime and benzaldehyde. This was refluxed in acetic anhydride (2 ml.) for 15 min. Analysis by v.p.c. then showed the presence of approximately equal quantities of benzaldehyde and benzonitrile.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, LEICESTER.
(H. H.) INSTITUT FÜR ORGANISCHE CHEMIE DER UNIVERSITÄT,
MAINZ.

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