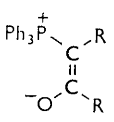
449. *A New Synthesis of Acetylenes. Part II.*[1] *The Reaction of Triphenylphosphine with α-Halogeno-carbonyl Compounds.*

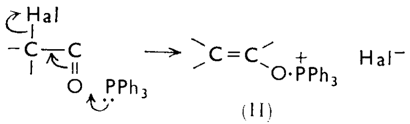
By S. TRIPPETT.

Triphenylphosphine attacks the oxygen of α-halogeno-carbonyl compounds with simultaneous expulsion of halide ion to give, in general, enol phosphonium salts. These are analogous to Rydon reagents and with alcohols give the alkyl halide, triphenylphosphine oxide, and the dehalogenated carbonyl compound. This reaction is related to other anomalous reactions between triphenylphosphine and a variety of halides.

THE pyrolysis of β-ketoalkylidenetriphenylphosphoranes (I) constitutes a general synthesis of the disubstituted acetylenes R·C⋮C·R provided that the acetylenic link is conjugated with an aromatic nucleus or an ester or nitrile group.[1] The simplest preparation of such phosphoranes is from α-halogeno-carbonyl compounds by quaternisation with triphenylphosphine and treatment of the resulting phosphonium salts with aqueous alkali. The reaction of triphenylphosphine with α-halogeno-carbonyl compounds has now been further investigated.

In general, only α-halogeno-carbonyl compounds of the formula $\mathrm{Hal{\cdot}CH_2{\cdot}CO{\cdot}R}$ reacted "normally" with triphenylphosphine to give phosphonium salts $\mathrm{Ph_3P^+{\cdot}CH_2{\cdot}COR\ Hal^-}$, *e.g.*, R = H,[2] Me,[3] Ph.[3] When others, *e.g.*, α-bromodipropyl ketone, 2-bromocyclohexanone, α-chloroacetoacetic ester, were treated with triphenylphosphine with only normal precautions to exclude water, the products were triphenylphosphine oxide and the dehalogenated ketone. Obviously water had entered the reactions and hydrolysed unstable intermediates. These are formulated as enol phosphonium salts (II), formed by attack of the triphenylphosphine on the oxygen of the carbonyl group with simultaneous expulsion of halide ion. Chloral with triphenylphosphine gave a crystalline compound which was extremely hygroscopic and showed no carbonyl absorption in the infrared region in agreement with the formula (II).


(I)



(II)

These enol phosphonium salts bear a formal analogy to Rydon reagents,[4] $\mathrm{(PhO)_3PR^+\ Hal^-}$, that is, they are intermediates in Arbusov reactions in which the second stage of the reaction, S_N2 attack of halide ion on carbon to give alkyl halides, is inhibited

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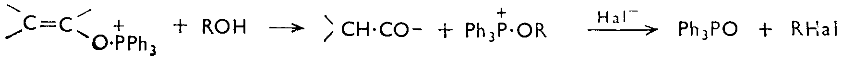
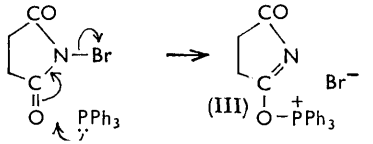
[1] Part I, Gough and Trippett, preceding paper.
[2] Trippett and Walker, *J.*, 1961, 1266.
[3] Michaelis and Kohler, *Ber.*, 1899, **32**, 1566.
[4] Landauer and Rydon, *J.*, 1953, 2224.

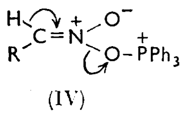
because, in Rydon reagents, this would involve S_N2 attack on the aromatic nucleus and, in the enol phosphonium salts, similar attack on a vinyl system. In agreement with this analogy, the intermediate salts (II), when prepared under anhydrous conditions and then treated ***in situ*** with an alcohol ROH, gave the dehalogenated ketone, triphenylphosphine oxide, and the alkyl halide RHal; *e.g.*, when 3-bromo-2,6-dimethylheptan-4-one and triphenylphosphine were refluxed together in benzene and the solution was then treated with a slight excess of ethanol, 2,6-dimethylheptan-4-one (85%), triphenylphosphine oxide (96%), and ethyl bromide (82%) were isolated. These reactions presumably involve a preliminary ester interchange between phosphonium salt and alcohol to give the ion $RO{\cdot}Ph_3P^+$ which is then attacked by halide ion to give alkyl halide and phosphine oxide.



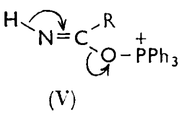
The formation of alkyl halides on treatment with alcohols has been used as a diagnostic test for the presence of enol phosphonium salts. Ethyl trichloroacetate and trichloroacetyl chloride reacted in this abnormal manner with triphenylphosphine, as also did *N*-bromosuccinimide. The last was an exothermic reaction and the product (III) reacted vigorously with ethanol to give ethyl bromide (70%), triphenylphosphine oxide, and succinimide.



(III)



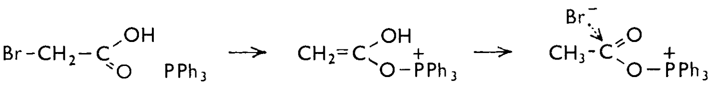
(IV)



(V)

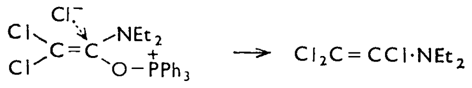
The general mechanism for the formation of enol phosphonium salts from α-halogenocarbonyl compounds can be applied to the reactions of triphenylphosphine with 1-bromo-1-nitroalkanes and with *N*-bromoamides.[5] Here the initially formed phosphonium ions, (IV) and (V) respectively, lose a proton and triphenylphosphine oxide to give the –C⋮N– link. The analogous loss of proton and triphenylphosphine oxide from the enolphosphonium salts (II) to give an acetylene occurred only in the most favourable case, the formation of diphenylacetylene from α-phenylphenacyl chloride and triphenylphosphine.[5]

Denney and Smith [6] recently reported the formation of acetyl bromide and triphenylphosphine oxide in the reaction of bromoacetic acid with triphenylphosphine. This also is accommodated in the above general mechanism, the initial phosphonium ion (VI) rearranging to the ion (VII) which is then attacked by bromide ion to give the observed products.



(VI) (VII)

Speziale and Freeman [7] treated trichloro-*NN*-diethylacetamide with triphenylphosphine and obtained the ethylene (IX), ***via*** the suggested intermediate (VIII). No comparable reactions were observed with our enolphosphonium salts, even on pyrolysis.



(VIII) (IX)

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[5] Trippett and Walker, *J.*, 1960, 2976.
[6] Denney and Smith, *Chem. and Ind.*, 1961, 290.
[7] Speziale and Freeman, *J. Amer. Chem. Soc.*, 1960, **82**, 903.

Enolphosphonium salts are probable intermediates in the reaction of dichlorotriphenylphosphorane with β-diketones in the presence of diethylamine.[1] Addition of ethanol to the anhydrous reaction mixture gave ethyl chloride. By analogy with the action of phosphorus pentachloride on ketones,[8] the initial attack is probably by the cation Ph_3P^+Cl, on oxygen.

EXPERIMENTAL

Known compounds were identified by comparison of their infrared spectra with those of authentic specimens.

Reaction of 3-Bromo-2,6-dimethylheptan-4-one with Triphenylphosphine.—A solution of the bromo-ketone (22 g.) and triphenylphosphine (26 g.) in dry benzene (100 ml.) was refluxed for 1 hr., then cooled, and ethanol (10 ml.) was added. A vigorous reaction occurred. Distillation through an 8″ column packed with gauze rings and fitted with a reflux-ratio head gave ethyl bromide (8·8 g.), b. p. 38—40°. The residue was steam-distilled and the distillate extracted with ether. Removal of solvent and distillation of the residue gave 2,6-dimethylheptan-4-one (12·1 g.), b. p. 165—168°. Filtration of the residue from steam-distillation gave triphenylphosphine oxide (27·5 g.), m. p. and mixed m. p. (from light petroleum, b. p. 100—120°) 156—157°.

A similar reaction with 2-bromocyclohexanone gave ethyl bromide (52%), cyclohexanone (63%), b. p. 153—155°, and triphenylphosphine oxide (95%), m. p. and mixed m. p. (from benzene–light petroleum) 156—157°.

Reaction of N-*Bromosuccinimide with Triphenylphosphine.*—*N*-Bromosuccinimide (26·7 g.) was added slowly to a cooled solution of triphenylphosphine (39 g.) in dry benzene (100 ml.). A vigorous reaction occurred and a black syrup separated. After 1 hr. at room temperature, ethanol (10 ml.) was added and the solution distilled, to give ethyl bromide (11·5 g.), b. p. 38—40°. Solvent was removed from the residue by steam-distillation. The resulting solid was stirred with dilute aqueous sodium hydroxide, then filtered off, washed with water, and dried, to give triphenylphosphine oxide (42 g.), m. p. and mixed m. p. (from benzene–light petroleum) 156—157°.

When a suspension of *N*-bromosuccinimide (26·7 g.) in benzene (100 ml.) and ethanol (12 ml.) was refluxed, a violent reaction occurred with the evolution of much hydrogen bromide, but no ethyl bromide was formed.

Reaction of Diethyl Bromo-oxaloacetate with Triphenylphosphine.—Diethyl bromo-oxaloacetate (25 g.) was added slowly to a suspension of triphenylphosphine (25 g.) in ethanol (70 ml.), with cooling to keep the temperature below 40°. Distillation then gave a fraction, b. p. 38—45°, which, on being shaken with concentrated sulphuric acid and redistilled, gave ethyl bromide (5·4 g.), b. p. 38—40°. Solvent was removed from the residue and the resulting solid extracted with cold light petroleum (b. p. 40—60°), leaving a residue of triphenylphosphine oxide (27 g.), m. p. and mixed m. p. 155—157°. Distillation of the combined extracts gave diethyl oxaloacetate (12 g.), b. p. 117—120°/16 mm.

Reaction of Ethyl Benzoylchloroacetate with Triphenylphosphine in Propanol.—A solution of ethyl benzoylchloroacetate (25 g.) and triphenylphosphine (26 g.) in propanol (100 ml.) was refluxed for 1 hr., and then distilled under a reflux-ratio head, to give n-propyl chloride (4·6 g.), b. p. 45—47°. Removal of solvent from the residue and extraction of the resulting solid with light petroleum (b. p. 40—60°) left a residue of triphenylphosphine oxide (27 g.), m. p. and mixed m. p. (from light petroleum, b. p. 100—120°) 155—157°. Distillation of the extract gave ethyl benzoylacetate (14 g.), b. p. 139—141°/10 mm.

Reaction of Ethyl α-Chloroacetoacetate with Triphenylphosphine.—A solution of ethyl α-chloroacetoacetate (17 g.) and triphenylphosphine (26 g.) in benzene (100 ml.) was refluxed for 3 hr. and cooled, and ethanol (10 ml.) added. Distillation then gave ethyl chloride (4·1 g.), condensed in a trap cooled in ice–salt. The condensate was immiscible with concentrated sulphuric acid and had b. p. 8—12°. The remaining solution was steam-distilled, leaving a residue of triphenylphosphine oxide (28·5 g.), m. p. 154—156°. Repeated ether-extraction of the distillate gave ethyl acetoacetate (7·1 g.), b. p. 178—181°.

Reaction of Chloral with Triphenylphosphine.—Chloral (10 g.) was slowly added to a cooled solution of triphenylphosphine (20 g.) in benzene (100 ml.). Much heat was evolved and a

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[8] Newman and Wood, *J. Amer. Chem. Soc.*, 1959, **81**, 4300.

syrup separated which slowly crystallised. Ethanol (10 ml.) was then added; the solid dissolved with heat formation. Distillation then gave ethyl chloride (4·2 g.), trapped in an acetone–carbon dioxide bath. On redistillation this had b. p. 10—12°.

In a similar way, ethyl trichloroacetate gave 31%, and trichloroacetyl chloride gave 62%, of ethyl chloride, b. p. 9—12°.

THE UNIVERSITY, LEEDS, 2.

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