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PHOTOLYSIS OF TRIARYLPHOSPHINES

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In an extension of earlier studies of the photoinitiated reactions of organophosphorus compounds,[1] we observed that the UV-initiated reaction of benzyl chloride with triphenylphosphine (I) led to the formation of tetraphenylphosphonium chloride (II) rather than the anticipated benzyltriphenylphosphonium chloride (III). It was also observed that UV-irradiation of mixtures of I or tris-p-tolylphosphine (IV) and phosphonium salts (II, III, n-butyltriphenylphosphonium halide) led specifically to the formation of II and tetrakis-p-tolylphosphonium halide (V), respectively. In each case a variety of free radical products arising from homolysis of carbon-phosphorus bonds in the salt were also observed.[2]

These findings suggested that I and IV undergo a photoinitiated homolysis to produce aryl radicals in a process independent of the photolysis of the phosphonium salts. This process has now been confirmed by a study of the photolysis of I and IV in simpler reaction systems. A parallel and independent study of the photolysis of I in alcohol and dioxane solutions was carried out simultaneously by Horner[3]; the results of this study are in agreement with those of Horner regarding primary photochemical processes.

Irradiation[4] of a benzene-ethanol solution (65:15 v/v) of I in the presence of one equivalent of lithium chloride led to the isolation of

II, indicating that in the previously studied photolyses, II and III served only as sources of halide ion. Similar results were obtained in the presence of potassium iodide. Diphenylphosphine (VI) and biphenyl (VII) were also detected.

Irradiation of I alone in benzene for one hour gave VI and VII as major products. In the absence of oxygen, the yields of VI and VII were approximately equal (20%); in the presence of oxygen, the yield of biphenyl (VII) was reduced below equivalence and extensive conversion of I to its oxide was observed. Longer irradiation periods did not appreciably increase the extent of decomposition of I. Tetraphenylbiphosphine and terphenyls were also detected. Analogous results were obtained with naphthalene as solvent. Irradiation of a benzene solution of tris-p-tolylphosphine (IV) led to the formation of 4-methylbiphenyl, 4,4'-dimethylbiphenyl and di-p-tolylphosphine (VIII). The unsymmetrical phosphine, diphenyl-p-tolylphosphine, gave biphenyl, 4-methylbiphenyl, VI, VIII and di-p-tolylphenylphosphine. The relative yields of the biaryls and the diarylphosphines indicated a higher percentage of phenyl-phosphorus bond cleavage than statistically predicted.

These experimental observations are consistent with an initial homolysis of an aryl-phosphorus bond and the following sequence:

$$Ar_3P \longrightarrow Ar^{\cdot} + Ar_2P^{\cdot}$$

$$Ar_2P^{\cdot} + C_6H_6 \longrightarrow Ar_2PH + C_6H_5^{\cdot}$$

$$Ar^{\cdot} + C_6H_6 \text{ or } C_6H_5^{\cdot} \longrightarrow Ar\text{-}C_6H_5$$

$$2\ Ar^{\cdot} \longrightarrow Ar\text{-}Ar$$

$$2\ Ar_2P^{\cdot} \longrightarrow Ar_2P\text{-}PAr_2$$

In those reactions leading to the formation of salts, the attack of aryl radicals on triarylphosphine to produce a tetraarylphosphoranyl radical is proposed.[5] A one-electron transfer process would then produce the cation.

$$Ar^{\cdot} + Ar_3P \rightleftharpoons Ar_4P^{\cdot}$$

$$Ar_4P^{\cdot} + Ar_2P^{\cdot}\ (\text{or } Ar^{\cdot}) \rightleftharpoons Ar_4P^{+} + Ar_2P^{-}\ (\text{or } Ar^{-})$$

In the absence of halide ion, the phosphonium cation is most probably generated but is not stabilized in aromatic solvents and its formation is reversed; in alcoholic solvents, formation of a phosphonium alkoxide provides stabilization.[3] The photochemical dissocation of phosphonium cations and phosphoranyl radicals is supported by the studies of Horner[3] and by studies of the photolysis of the cations.[2]

In the presence of alcohols, a different course of reaction is observed. Irradiation of a solution of I in benzene-ethanol yielded diphenylphosphine and ethyldiphenylphosphine as major products; tetraphenylbiphosphine and terphenyls were observed as minor products. Walling[6] has shown that trialkylphosphites are attacked by alkoxy radicals to produce phosphates and alkyl radicals. A similar formation of ethyl radicals would be anticipated in this system. Attack of ethyl radical on I would yield ethyltriphenylphosphoranyl radical which could (in the absence of a stabilizing halide ion) dissociate to either phenyl radical and ethyldiphenylphosphine or to the initial reactants.

$$C_2H_5^{\cdot} + (C_6H_5)_3P \rightleftharpoons [C_2H_5P(C_6H_5)_3]^{\cdot}$$

$$[C_2H_5P(C_6H_5)_3]^{\cdot} \rightleftharpoons C_2H_5P(C_6H_5)_2 + C_6H_5^{\cdot}$$

Diphenylphosphine failed to undergo photolysis in benzene. In contrast, Horner[2] has observed extensive carbon-phosphorus bond cleavage for this phosphine in alcoholic solvents.

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3. L. Horner and J. Dörges, *Tetrahedron Letters*, this issue. We are deeply indebted to Professor Horner for communicating the results of his studies prior to publication.

4. Irradiations were carried out at 25° with an internal source Hanovia Model L679A 450 watt lamp using quartz apparatus. Solutions of 2 g. of phosphine in 80 ml. of solvent were employed.

5. For other examples of the radical arylation of I, see L. Horner and H. Hoffmann, *Chem. Ber.*, **91**, 45, 50 (1958) and reference 1a. For other examples of the formation of phosphoranyl radicals, see: G. Kamai and Z. Kharrasova, *Zhur. Obshchei Khim.*, **27**, 953 (1957); C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **79**, 5326 (1957); F. Ramirez and N. McKelvie, *ibid*, **79**, 5829 (1957).

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