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PHOTOLYSIS OF BENZYLTRIPHENYLPHOSPHONIUM AND TETRAPHENYLPHOSPHONIUM CHLORIDES

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The ultraviolet irradiation of triarylphosphines has been shown to proceed with scission of a carbon-phosphorus bond and the formation of aryl and diarylphosphinyl radicals; in the presence of halide ions[1] or alcohols,[2] tetraarylphosphonium salts are formed as stable products. In aromatic solvents, radical trapping and dimerization products are observed.[1] As a salient step in the reaction sequence, the photoinitiated reversible steps 1-2 were proposed[1,2]:

$$\mathrm{Ar}^{\bullet} + \mathrm{Ar}_3\mathrm{P} \rightleftharpoons \mathrm{Ar}_4\mathrm{P}^{\bullet} \qquad (1)$$

$$\mathrm{Ar}_4\mathrm{P}^{\bullet} + \mathrm{S}^{\bullet} \rightleftharpoons \mathrm{Ar}_4\mathrm{P}^{+} + \mathrm{S}^{-} \qquad (2)$$

This proposal received partial substantiation from the observation that irradiation of mixtures of triphenylphosphine and benzyltriphenylphosphonium chloride (I) led to the formation of products derived from benzyl radicals as well as the major product, tetraphenylphosphonium chloride (II).[1] In order to test this proposal, the irradiation of I and II in homogeneous media has been examined.

Irradiation of a solution of I in a mixture of benzene and ethanol (65:15 v/v) led to complete consumption of I in 3.5 hours. G.l.c. and mass spectral analysis of the reaction mixture established the presence of the following products (relative amounts): biphenyl (2.5), diphenylmethane (1), bibenzyl (1), diphenylphosphine (3-4) and its oxidation products, and triphenylphosphine (1-2). The mixed phosphines (benzylphenyl, benzyldiphenyl and benzylethylphenyl) were not detected; mass spectral evidence was obtained for the formation of diphenylethylphosphine. No products incorporating chlorine have been detected.

The observed products are consistent with a photochemical degradation of the phosphonium cation by the following sequence: (a) photo-induced one-electron transfer to yield benzyltriphenylphosphoranyl radical[4] (III) and a chlorine atom; decomposition of III to yield either benzyl (b) or phenyl (c) radicals and the corresponding phosphines; (d) coupling of benzyl and phenyl radicals; (e) reaction of benzyl and phenyl radicals with solvent (benzene). The diphenylphosphine probably arises by the photolysis of either triphenylphosphine or benzyldiphenylphosphine by the previously demonstrated route (f,g).[1,2]

$$\text{(a)}\ [C_6H_5CH_2P(C_6H_5)_3]^+\ Cl^- \rightleftharpoons \underset{\text{(III)}}{[C_6H_5CH_2P(C_6H_5)_3]^\bullet} + Cl^\bullet$$

$$\text{(b)}\ \text{III} \rightleftharpoons C_6H_5CH_2^\bullet + (C_6H_5)_3P$$

$$\text{(c)}\ \text{III} \rightleftharpoons C_6H_5^\bullet + C_6H_5CH_2P(C_6H_5)_2$$

$$\text{(d)}\ 2\ C_6H_5^\bullet \longrightarrow C_6H_5\text{-}C_6H_5$$

$$2\ C_6H_5CH_2^\bullet \longrightarrow C_6H_5CH_2CH_2C_6H_5$$

$$\text{(e)}\ C_6H_5^\bullet + C_6H_6 \longrightarrow C_6H_5\text{-}C_6H_5$$

$$C_6H_5CH_2^\bullet + C_6H_6 \longrightarrow C_6H_5CH_2CH_2C_6H_5$$

$$\text{(f)}\ C_6H_5CH_2P(C_6H_5)_2 \longrightarrow C_6H_5CH_2^\bullet + (C_6H_5)_2P^\bullet$$

$$\text{(g)}\ (C_6H_5)_3P \longrightarrow C_6H_5^\bullet + (C_6H_5)_2P^\bullet$$

Steps f and g would provide additional sources of benzyl and phenyl radicals. The failure to detect benzylphosphines among the products indicates that steps b and f must proceed at significantly higher rates than steps c and h.

(h) $C_6H_5CH_2P(C_6H_5)_2 \longrightarrow C_6H_5^{\cdot} + [C_6H_5CH_2PC_6H_5]^{\cdot}$

This behavior would be anticipated on the basis of the relative stabilities of benzyl and phenyl radicals and the relative bond strenghts involved. The remaining product, diphenylethylphosphine, has previously been shown to arise by reaction of triphenylphosphine with ethoxy radicals.

If the sequence postulated above is valid, the photolysis of tetraphenylphosphonium chloride (II) in benzene-ethanol should yield only biphenyl, diphenylphosphine and triphenylphosphine. Irradiation of a solution of II for 2 hours led to the formation of these three products as anticipated; 33% of II was recovered.

These findings confirm the reversible nature of phosphoranyl radical formation in these systems and strongly suggest the occurrence of one-electron transfer processes involving reduction of phosphonium cations. In the previously studied systems, the isolation of phosphonium salts as stable products is undoubtedly due to the insolubility of the salts in the reaction medium.[1,3]

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