Photolysis of Phenacylsulphonium Salts

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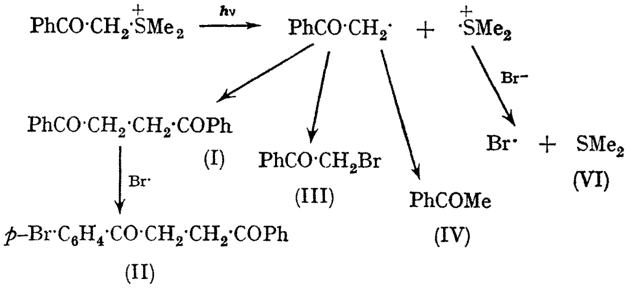
Summary Dimethylphenacylsulphonium bromide undergoes photolysis with homolytic cleavage of the C–S bond.

ALTHOUGH the photolysis of quaternary ammonium[1] and phosphonium[2] salts has been investigated, there has been no report on the photochemistry of sulphonium salts.‡

Photolysis† of a 0·01M solution of dimethylphenacylsulphonium bromide in water led to gradual deposition of an opaque solid on the cooling jacket, evolution of dimethyl sulphide and a decrease in pH. After 7 hr. (90% conversion) the products isolated by preparative layer chromatography were dibenzoylethane (I) (25%), *p*-bromodibenzoylethane (II) (5%), phenacyl bromide (III) (10%), acetophenone (IV) (5%), and benzoic acid (V) (0·2%). There was also much intractable, probably polymeric, product. Products (I), (III), (IV), and (V) were identified by comparison with authentic samples; compound (VI) was isolated as the mercuric chloride complex[3] and a yield of 82% was determined by oxidation to dimethyl sulphone with standard permanganate. Compound (II) was characterised by analysis and spectral properties (i.r., n.m.r., and mass spectrum).

The results are consistent with a radical mechanism. The radicals may arise in several ways: (A) By homolysis of the $\overset{+}{\mathrm{C{-}S}}$ bond leading to a phenacyl radical and a dimethyl sulphide radical ion;[4] (B) By nucleophilic substitution by bromide ion on an excited phenacylsulphonium ion to give excited phenacyl bromide which undergoes homolysis; (C) By a charge-transfer state, analogous to ammonium[1] and phosphonium[2] salts.

Process (C) would be unlikely in dilute aqueous solution and was disproved by irradiation in the presence of a large excess of bromide ion, when no significant change in rate or yield of products was apparent. This experiment also rules out course (B), although it was found that irradiation of phenacyl bromide gave some dibenzoylethane. Irradiation of dimethylphenacyl sulphonium nitrate gave dibenzoylethane (40%) *i.e.* the amount of product derived from the phenacyl moiety is the same for both nitrate and bromide salts, thus indicating mechanism (A).



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No ring-brominated product other than (II) was isolated, nor any phenylacetic acid, which might be expected on the basis of the photolysis of phenacyl halides.[5]

Aqueous solutions of trimethylphenacylammonium bromide and phenacylpyridinium bromide are stable under these conditions of irradiation.[6] Irradiation of the ammonium salt using a quartz filter sleeve instead of Pyrex also failed to cause decomposition. This is consistent with the higher bond strength of the C–N compared with the C–S bond[7] and generally higher reactivity of sulphonium

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† A 100-watt Hanovia U.V. lamp, water-cooled, with a Pyrex filter sleeve was used for all irradiations.

‡ *Note added in proof.* Since submitting this communication, we have noted a report on the photolysis of triaryl sulphonium salts (J. W. Knapezyk and W. E. McEwen, *J. Amer. Chem. Soc.*, 1969, **91**, 145).

compounds compared with quaternary ammonium compounds.[8]

We thank the Sir John Cass College for a Research Assistantship (to T. L.).

(*Received, March 24th*, 1969, *Com.* 405.)

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[1] J. C. Sheehan and R. M. Wilson, *J. Amer. Chem. Soc.*, 1964, **86**, 5277; T. D. Walsh and R. C. Long, *ibid.*, 1967, **89**, 3943; C. Pac and H. Sakurai, *Tetrahedron Letters*, 1968, 1865; *Chem. Comm.*, 1969, 20.

[2] G. E. Griffin and M. L. Kaufmann, *Tetrahedron Letters*, 1965, 773.

[3] F. Challenger, "Aspects of Organic Chemistry of Sulphur", Butterworths, 1959, p. 18.

[4] G. Meissner, *Angew. Chem. Internat. Edn.*, 1966, **5**, 739.

[5] J. C. Anderson and C. B. Reese, *Tetrahedron Letters*, 1962, 1.

[6] A. Fozard and C. K. Bradshaw, *Tetrahedron Letters*, 1966, 3341.

[7] T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, 1958.

[8] G. L. Walcott, M.Sc. Thesis, University of London, 1965.