Photolysis of Benzyl Halides and Benzyl Acetate in Alcohols

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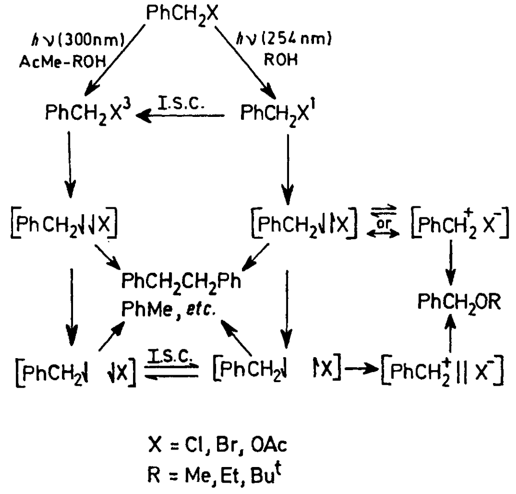
Summary Solvolysis products and products derived by non-ionic mechanisms are obtained by either direct or sensitised photolysis of benzyl halides or benzyl acetate in alcohols; the sensitised solvolysis pathway appears to be facilitated by the solvation energies of ion-pair intermediates in relation to those of precursor radical-pairs.

In earlier work[1] we found that direct photolysis of benzyltrimethylammonium salts in hydroxylic solvents gave solvolysis products apparently derived *via* ion-pair intermediates together with toluene and bibenzyl produced *via* radical-pairs; only the latter products were obtained on sensitised photolysis. By contrast Cristol and Greenwald[2] identified only bibenzyl and 2-phenylethanol in the products of direct photolysis (254 nm) of benzyl chloride in methanol; no benzyl methyl ether was reported from this reaction, but it was the sole product identified on sensitised (acetophenone; 300 nm) photolysis. Similar results were reported for other alcoholic solvents and other sensitisers, including acetone and benzonitrile. We now report that benzyl halides and benzyl acetate give solvolysis products and products derived *via* non-ionic pathways on either direct or sensitised photolysis in alcoholic solvents.

Benzyl chloride in methanol on irradiation through silica at 254 nm gave benzyl methyl ether (26% of decomposed halide), bibenzyl (23%), 2-phenylethanol (37%) and a trace of toluene; analogous results were obtained in ethanol.† In methanol containing 10% (v/v) acetone, irradiation through Pyrex at 300 nm yielded benzyl methyl ether (45%), bibenzyl (2%), 2-phenylethanol (15%), a trace of toluene, and various unidentified products apparently (mass spectra) derived from reactions of benzyl radicals. Either direct or sensitised photolysis of benzyl chloride in t-butyl alcohol gave benzyl t-butyl ether, bibenzyl, and unidentified products, the quantum yields for ether formation being 0·12 for the direct and 0·20 for the sensitised reaction. The same products were obtained from benzyl bromide or benzyl acetate in this solvent; in the case of the bromide the quantum yield for ether formation was higher in the direct (0·23) than in the sensitised (0·12) reaction, but a similar comparison was impossible for the acetate because of the very low relevant quantum yields (<0·01). Benzyl iodide gave the corresponding ethers exclusively on direct photolysis in methanol (Φ 0·52) or t-butyl alcohol (Φ 0·20) but the acetone-sensitised reactions could not be explored because of high end-absorption of the substrate at *ca.* 300 nm

We propose that the mechanistic scheme already suggested[1] for photolysis of benzylammonium salts applies also to the reactions described above with one very important difference: a route from triplet substrates to solvolysis products is evidently required for benzyl halides and acetate, but not for the ammonium salts. The key steps appear to be the interconversion of loose triplet and singlet radical pairs[3] (see Scheme) followed by electron transfer in the singlet pair to give a solvent-separated ion-pair. The last step will involve an activation barrier associated with solvent reorganisation, but the barrier height may nevertheless be quite low for the strongly exothermic reaction, the polar solvent markedly favouring the ion-pair. Such a favouring influence would be absent for an analogous process in a loose singlet radical-pair derived from the ammonium salt, where the coulombic distinction between radical-pair and ion-pair is removed [equation (1)].



Scheme

$$[\overset{+}{\mathrm{PhCH_2}}\upharpoonleft\ \downharpoonright\overset{-}{\mathrm{NMe_3X}}] \not\rightarrow [\overset{+}{\mathrm{PhCH_2}}\,\|\,\overset{-}{\mathrm{NMe_3X}}] \qquad (1)$$

A more detailed interpretation of the results would have to include comment on the interesting and somewhat unexpected pattern of quantum yields noted above, but we are unable to provide this convincingly on presently available evidence.

Nucleophilic capture ratios in mixed alcohols have already[2] been employed to demonstrate the identity or close similarity of ion-pairs produced by sensitised photolysis and by thermal heterolysis of benzyl chloride. We find that direct photolysis (254 nm) of the chloride or bromide in aqueous methanol at 25 °C and thermal solvolysis of the chloride (25 °C) and bromide (80 °C) all result in capture ratios $[k(\mathrm{MeOH})/k(\mathrm{H_2O})]$ in the range 3—4. A corresponding comparison is less readily made for benzyl ammon-

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† Because of the obvious discrepancies in the literature (ref. 2 and *cf.* also M. A. Ratcliff, Jr. and J. K. Kochi, *J. Org. Chem.*, 1971 **36**, 3112; V. B. Ivanov, V. L. Ivanov, and M. G. Kuz'min, *J. Org. Chem. U.S.S.R.*, 1973, **9**, 345) we made particularly rigorous checks for thermal solvolysis in all our experiments, and we identified products by g.l.c. on two different columns and mass spectrometry; these analytical procedures were checked with authentic specimens.

ium salts, but the iodide $p\text{-MeOC}_6\text{H}_4\text{CHMe}\overset{+}{\text{N}}\text{Me}_3\text{I}^-$ underwent heterolysis[4] at 120 °C in aqueous methanol (molar ratio H_2O : MeOH 2·2 : 1) to give the corresponding benzyl methyl ether as the sole identified product accounting for >90% of decomposed salt; an identical result, corresponding to a similarly very high capture ratio $[k(\text{MeOH})/k(\text{H}_2\text{O}) > 20]$, was obtained on direct photolysis (254 nm) of the iodide in the same solvent mixture at 20 °C.

We thank the S.R.C. for support.

(*Received*, 18*th November* 1976; *Com.* 1273.)

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[1] D. C. Appleton, D. C. Bull, R. S. Givens, V. Lillis, J. McKenna, J. M. McKenna, and A. R. Walley, *J.C.S. Chem. Comm.*, 1974, 473.

[2] S. J. Cristol and B. E. Greenwald, *Tetrahedron Letters*, 1976, 2105.

[3] See, for example, R. G. Lawler and H. R. Ward in 'Determination of Organic Structures by Physical Methods,' eds. F. C. Nachod and J. J. Zuckerman, Academic Press, New York, 1973, pp. 99—150, where the mechanism of such interconversions and their importance in the development of nuclear polarisation effects are discussed.

[4] *Cf.* G. Norcross and H. T. Openshaw, *J. Chem. Soc.*, 1949, 1174.