Stereochemistry of Photosolvolysis of Quaternary Benzylammonium Salts in Hydroxylic Solvents

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Summary The photosolvolysis of optically active 1-phenylethyltrimethylammonium iodide in water or methanol is characterised by extensive racemisation accompanied by some net configurational inversion; the quaternary salt recovered from incomplete reaction in water has fully retained configuration at carbon, while analogous retention at nitrogen is observed in similar experiments in methanol with appropriately chosen related salts.

THE stereochemistry of photosolvolysis of benzyl derivatives has not previously received detailed attention. As part of our mechanistic study[1] of the photolysis of quaternary benzylammonium salts we examined the reactions of optically active 1-phenylethyltrimethylammonium iodide in water and in methanol using 254 nm light.

The chief products from the 90% optically pure (−)-salt[2] were (+)-1-phenylethyl alcohol (22% optical purity[3]) and (+)-1-phenylethyl methyl ether (5% optical purity[3]); these products are stereochemically stable under the photolysis conditions. The known[4] configurational relationships in the 1-phenylethyl series imply that extensive racemisation was in each case associated with net configurational inversion. The parallel with thermal solvolysis *via* intermediate ion-pairs is evident, and the results clearly support the scheme indicated above[1] and exclude product formation by direct reaction of the photoactivated quaternary salt with solvent.

Other photolysis products were phenylethane and 2,3-diphenylbutane (particularly in water), styrene (particularly in methanol), and trimethylammonium iodide.

Of additional interest is the observation that the quarternary salt recovered from the photolysis in water after *ca.* 70% decomposition was unchanged in optical rotatory power, indicating retention of configuration at carbon. To check for analogous retention at nitrogen *N*-methyl benziodides from 4-phenylpiperidine, *trans*-decahydroquinoline, and camphidine[5] were each substantially (*ca.* 70%) photolysed in methanol and the recovered salts were examined. The stereochemically pure epimers, with (predominantly) *ax-N*-methyl were employed and in no case did we observe partial conversion into the diastereoisomeric salt[5] with inverted configuration at nitrogen. A similar result was obtained with the camphidine salt with (predominantly) *eq-N*-methyl. These results stand in strong contrast to the epimerisation (or racemisation) noted in recovered substrates from other photolyses such as type I and type II reactions of chiral ketones;[6] evidently in our work cage-recombination of geminate pairs is either absent or perhaps more likely very rapid.

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

(*Received, 1st April* 1974; *Com.* 378.)

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