Stereochemistry of Photosolvolysis of (−)-1-Phenylethyltrimethylammonium Iodide in Water and in Methanol, and Nucleophile Capture Ratios during Photosolvolysis of Some Benzylammonium Salts

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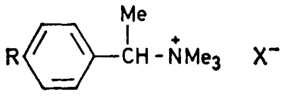
The photosolvolysis of (−)-1-phenylethyltrimethylammonium iodide in water or methanol is characterised by extensive racemisation accompanied by some net configurational inversion, a result similar to that generally observed in thermal solvolysis *via* ion-pairs at chiral secondary centres. Recovered quaternary salt from the photolysis in water is only slightly if at all racemised, while likewise there is no observable epimerisation at nitrogen in recovered benzylammonium salts following photolysis in methanol of suitable derivatives of camphidine, *trans*-decahydroquinoline, and 4-phenylpiperidine. A strong preference for formation of the methyl ether rather than the alcohol is exhibited on either photochemical or thermal solvolysis of 1-*p*-methoxyphenylethyltrimethylammonium iodide in aqueous methanol, but nucleophile capture ratios during photosolvolysis of simple benzyltrimethylammonium salts in this mixed solvent system are much lower.

PHOTOLYSIS of benzylammonium salts and benzyl halides in hydroxylic solvents to give benzyl alcohol or benzyl ethers may plausibly be represented [1] as proceeding *via* intermediate ion-pairs, analogous in this respect to the corresponding thermal reactions. Direct comparisons between the photochemical and the thermal reactions in respect of stereochemistry and nucleophile capture ratios seemed desirable, and some such work, dealing mainly with stereochemical investigations, is reported in this paper.[2]



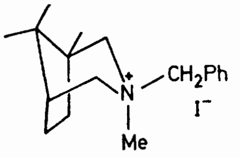
(1)

When 1-phenylethyltrimethylammonium bromide (1; R = H, X = Br) or iodide (1; R = H, X = I) was photolysed in water or in methanol the results (Table 1) were analogous to those obtained [1] from benzyltrimethylammonium halides, the solvolysis products (1-phenylethanol or the methyl ether) being the chief components of the reaction mixtures. Photolysis of 90% optically pure (−)-1-phenylethyltrimethylammonium iodide in water or in methanol gave (+)-1-phenylethanol or (+)-1-phenylethyl methyl ether of 5% and 17% optical purities respectively. Since in this chiral series the primary amine, trimethylammonium salt, alcohol, and methyl ether of the same direction of rotation all have [3,4] the same configuration, it is evident that the photosolvolyses proceed with extensive racemisation but with some net configurational inversion. This type of result is frequently encountered in thermal solvolyses *via* ion-pairs at chiral secondary centres, being observed, for example, in solvolysis of optically active 1-phenylethyl chloride.[5] Our results therefore afford useful stereochemical evidence in support of a mechanism of photosolvolysis which also proceeds *via* ion-pairs.

We were surprised to find that recovered benzylammonium salt from the 70% complete photosolvolysis in water had, without purification, an optical rotation numerically within *ca.* 6% of that of the starting quaternary salt, indicating little (if indeed any) racemisation associated with in-cage return during the solvolysis. Racemisation during return from geminate pairs is often encountered in analogous thermal reactions; indeed, such racemisations are often faster than the solvolyses. In some examples, however, no racemisation is detectable, as is the case for solvolysis of 1-phenylethyl *p*-nitrobenzoate in aqueous acetone.[6] To check for any stereochemical inversion at *nitrogen* during photosolvolysis of benzylammonium salts we photolysed each of the salts (2), (3), (4), and (6) in methanol to about 70% decomposition in every case. None of the epimers [(3), (2), (5), or (7), respectively] could be detected by n.m.r. spectroscopy of the recovered samples. Photolysis of mixed epimeric camphidinium iodides, (2) + (3), resulted in decomposition of the epimers at equal rates, but with mixtures of the decahydroquinolinium, (4) + (5), or 4-phenylpiperidinium salts, (6) + (7), the *N-eq*-benzyl-*N-ax*-methyl salts, (4) and (6), reacted slightly faster than did their *N-ax*-benzyl-*N-eq*-methyl epimers (5) and (7). Application of the appropriate algebra of competitive first-order reactions to the results described in the Experimental section indicates that $k(4)/k(5) \approx k(6)/k(7) \approx 1.2$. This stereochemical differentiation is in interesting contrast to that obtained when such epimeric salts are thermally decomposed by nucleophilic attack: axial benzyl groups are markedly more readily removed in such reactions than are equatorial.[7]

Since 1-phenylethyltrimethylammonium iodide is thermally quite stable in aqueous or alcoholic solution, the most direct comparisons between the outcome of thermal and photochemical solvolyses cannot be made for this substrate. However, introduction of a *p*-methoxy-group into such quaternary salts leads to an increased ease of thermal solvolysis,[8] presumably because of the effect of the substituent on the stability of an intermediate carbonium ion (or ion-pair). To provide a direct comparison between the thermal and photochemical solvolyses of 1-*p*-methoxyphenylethyltrimethylammonium iodide (1; R = OMe, X = I) we sought to measure the nucleophile capture ratios, k(MeOH)/

$k(H_2O)$ for each process when the salt reacted in aqueous methanolic solution. Even when the water content of the solvent was over two-fold in excess of the methanol (0.31 mol fraction MeOH) we detected only 1-*p*-methoxyphenylethyl methyl ether, and none of the corresponding alcohol, in reaction mixtures from either the photochemical or the thermal solvolyses. The ether is formed in at least 90% yield, and it may thus be calculated that the capture ratio, $k(\text{MeOH})/k(H_2O)$ is at least 20 for the mixed solvent used. It is satisfactory to get this degree of correspondence between the thermal and photochemical reactions, which provides further evidence in favour of an intermediate ion-pair in the photosolvolysis.



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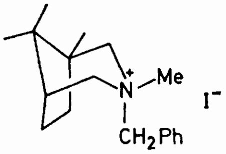

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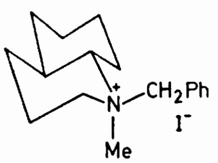

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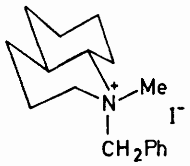

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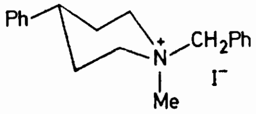

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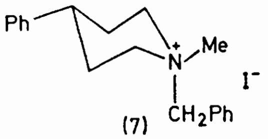

(7)

The large value of the capture ratio (relatively high selectivity) is probably related to stabilisation of the ion-pair by the *p*-methoxy-group. The corresponding capture ratios for photolysis of the simple benzyltrimethylammonium salts in aqueous methanol were shown to be much lower [$k(\text{MeOH})/k(H_2O) = 1.8$ for chloride and bromide, 1.45 for the iodide, with solvent of 0.31 mol fraction MeOH] but here the much less stable and less-selective * ion-pairs are inaccessible by thermal reactions.

EXPERIMENTAL

Instrumentation.—This was as described in the previous Paper.[1] Optical rotations were measured at room temperature on a Perkin-Elmer 141 polarimeter.

Photolysis Substrates and Products.—Some were commercially available; others were synthesised by standard procedures and had the expected physical and spectroscopic properties.

Reduction of acetophenone with sodium borohydride in ethanol gave 1-phenylethanol, which was converted into 1-phenylethyl bromide by treatment with constant-boiling hydrobromic acid. The bromide gave 1-phenylethyl methyl ether with refluxing methanol in the presence of solid potassium carbonate, while with ethanolic trimethylamine it yielded 1-*phenylethyltrimethylammonium bromide* (1; R = H; X = Br), m.p. (MeOH–Et_2O) 203—204 °C (Found: C, 53.8; H, 7.4; Br, 32.6; N, 5.5. $C_{11}H_{18}BrN$ requires C, 54.1; H, 7.4; Br, 32.7; N, 5.7%), τ ($CDCl_3$) 2.3—2.6 (5 H, m, Ar), 6.65 [9 H, s, $N(CH_3)_3$], 8.17 (3 H, d, J 7 Hz, C-CH_3).

p-Methoxyacetophenone was likewise converted into 1-*p*-methoxyphenylethanol,[10] while reduction of the ketoxime gave 1-*p*-methoxyphenylethylamine, converted with methyl iodide and potassium carbonate into 1-p-*methoxyphenylethyltrimethylammonium iodide* (1; R = OMe; X = I), m.p. (MeOH–Et_2O) 162 °C (Found: C, 44.7; H, 6.2; N, 4.4. $C_{12}H_{20}INO$ requires C, 44.9; H, 6.3; N, 4.4%), τ ($CDCl_3$) 2.39, 3.06 (4 H, AB, J 10 Hz, Ar), 6.19 (3 H, s, OCH_3), 6.68 [9 H, s, $N(CH_3)_3$], and 8.18 (3 H, d, J 8 Hz, C-CH_3).

1-Phenylethylamine (from acetophenone oxime) was resolved by the procedure described by Ault [11] and the base, $[\alpha]_D$ −37.1° (neat; lit.,[12] −40.3°) was converted into (−)-1-phenylethyltrimethylammonium iodide (1; R = H; X = I) m.p. 157—158 °C, $[\alpha]_D$ −17.7° (*c*, 1.5 in MeOH){lit.,[13] m.p. 157—157.5 °C, $[\alpha]_D$ +19.6° (*c*, 2.5 in EtOH) for the pure enantiomer}. The corresponding racemic salt was also prepared for preliminary photolysis experiments.

Epimeric *N*-benzyl-*N*-methylcamphidinium iodides, (2) and (3), have been described previously [14] and likewise [15] *N*-*eq*-benzyl-*N*-*ax*-methyl-4-phenylpiperidinium iodide (6), *N*-*eq*-benzyl-*N*-*ax*-methyl-*trans*-decahydroquinolinium iodide (4), m.p. 213 °C, was obtained by fractional crystallisation ($CHCl_3$–AcMe) of the mixture of epimeric salts produced [14] by the reaction of *N*-benzyl-*trans*-decahydroquinoline with methyl iodide, the progress of the separation being followed by the n.m.r. spectra [τ ($CDCl_3$) 4.98 (2 H, s, NCH_2Ph), 6.86 (3 H, s, NCH_3) for *N*-*eq*-benzyl-*N*-*ax*-Me salt (4) and 5.25, 5.57 (2 H, AB, J 13 Hz, NCH_2Ph), 6.80 (3 H, s, N-CH_3) for *N*-*ax*-benzyl-*N*-*eq*-methyl salt (5)].

General Procedures for Photolysis.—These were as described in a previous paper [1] of this series, product analysis being effected, as before, by g.l.c. and g.l.c.–m.s. Retention times and mass-spectroscopic data are given in Table 2. All photolyses were at 253.7 nm.

Photolysis of 1-*Phenylethyltrimethylammonium Salts.*—For initial experience with 1-phenylethyltrimethylammonium salts the racemic bromide and the racemic iodide were photolysed in methanol and in water. Results are given in Table 1.

(−)-1-Phenylethyltrimethylammonium iodide (1; R = H, X = I) $[\alpha]_D$ −17.7° (MeOH; 90% optically pure) was photolysed in methanol and the major ether-soluble component was isolated by preparative g.l.c. and identified by retention-time and fragmentation pattern (Table 2) as 1-phenylethyl methyl ether, an authentic sample of which was available for comparison. This product had $[\alpha]_D$ +6.2° (*c*, 1.5 in MeOH) corresponding to *ca.* 5% optical purity if the specific rotation of the optically pure compound is assumed to be approximately the same neat ($[\alpha]_D$ +128.3°, ref. 4) and in methanol solution.

The (−)-salt was also photolysed in water and the chief ether-soluble product was purified by chromatography on neutral alumina (Brockman activity 1); it was eluted with

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* For a recent discussion on application of the reactivity-selectivity principle in such reactions, and leading references see ref. 9.

benzene–ether (9 : 1) and identified as 1-phenylethanol by retention time and fragmentation pattern (Table 1) and comparison in relation to these criteria with an authentic specimen. The product had $[\alpha]_D$ +7.9° (*c*, 1.8 in MeOH) corresponding to *ca.* 17% optical purity: the optically pure (−)-compound [16] has $[\alpha]_D$ −45.5° in methanol. The alcohol, $[\alpha]_D$ +7.9°, retained this specific rotation on further prolonged exposure (16 h) to 254-nm light in methanol or in suspension in aqueous methanol.

In a separate experiment a sample of (−)-phenylethyltrimethylammonium iodide of $[\alpha]_D$ −15.7° was photolysed in water to 70% decomposition, as shown by n.m.r. examination of a D_2O solution of the water-soluble residue after removal of ether-soluble products. A methanol solution of this residue was refluxed with solid potassium carbonate under a flow of nitrogen for 3 h to decompose trimethylamine hydriodide (see Table 2), the solvent was removed, the residue was triturated with ether, and the quaternary salt was extracted with chloroform and filtered from potassium salts. The residue from the chloroform, $[\alpha]_D$ −14.7°, was somewhat discoloured, but the n.m.r. spectrum was identical with that of the starting quaternary salt.

Photolysis of 4-*Phenylpiperidinium,* trans-*Decahydroquinolinium, and Camphidinium Salts.*—Solutions of the following pure salts in methanol were photolysed, and the products and undecomposed reactants examined, by the previously described [1] procedure: *N*-*eq*-benzyl-*N*-*ax*-methyl-4-phenylpiperidinium iodide (6), *N*-*eq*-benzyl-*N*-*ax*-methyl-*trans*-decahydroquinolinium iodide (4), *N*-*eq*-benzyl-*N*-*ax*-methylcamphidinium iodide (2), and *N*-*ax*-benzyl-*N*-*eq*-methylcamphidinium iodide (3). In each case the photolysis was carried to *ca.* 70% completion. Toluene and benzyl methyl ether were produced, the latter predominating, but the chief interest was in the undecomposed reactant. No evidence of epimerisation at nitrogen to give the diastereoisomeric salt was obtained from the n.m.r. spectra of the total salt fractions from reaction mixtures. In each of the three systems studied, the diastereoisomeric *N*-methyl-*N*-benzyl salts have characteristically different n.m.r. spectra (see above and refs. 17 and 18) which makes possible the easy identification of one diastereoisomer in presence of the other.

TABLE 1

Photolysis of 1-phenylethyltrimethylammonium salts at 253.7 nm

Anion; solvent	Products (R = PhCHMe) and percentage yields
Bromide; MeOH	R–H (10%); ROMe (86%); R–R (trace); styrene (trace); $Me_3\overset{+}{N}H\overset{-}{Br}$ (100%)
Bromide; H_2O	RH (14%); ROH (62%); R–R (trace); $Me_3\overset{+}{N}H\overset{-}{Br}$ (95%); $Me_2\overset{+}{N}H_2\overset{-}{Br}$ (trace)
Iodide; MeOH	RH (trace); ROMe (84%); R–R (trace); styrene (10%); $Me_3\overset{+}{N}H\overset{-}{I}$ (95%); $Me_2\overset{+}{N}H_2\overset{-}{I}$ (trace)
Iodide; H_2O	RH (5%); ROH (60%); R–R (5%); styrene (trace); $Me_3\overset{+}{N}H\overset{-}{I}$ (100%)

When a mixture of the epimeric *N*-methyl-*N*-benzylcamphidinium iodides [(1) and (2), 50% of each] was photolysed to 55% completion the recovered salt mixture had the epimers in unchanged proportions. However, the recovered mixture of unchanged epimers on 63% decomposition of a mixture of *N*-*eq*-benzyl-*N*-*ax*-methyl- (6) and *N*-*ax*-benzyl-*N*-*eq*-methyl-4-phenyl-piperidinium iodide (7) indicated preferential decomposition of the former salt [initial ratio, salt (6) : salt (7), 3.74 : 1; recovered, 3.08 : 1]. A similar observation was made on partial decomposition of a mixture of the corresponding epimeric *trans*-decahydroquinolinium iodides (77% decomposition; initial ratio, salt 4 : salt, 5 1.09 : 1; recovered, 0.83 : 1). These results may be analysed using the equation:

$$k_A/k_B = \frac{\ln[(Q_0)_A/(Q_t)_A]}{\ln[(Q_0)_B/(Q_t)_B]}$$

where *k*, Q_0, and Q_t are the rate constant, the quantity at zero time, and the quantity at time *t* for salts A and B in a mixture undergoing photolysis. Appropriate relative values for these quantities may readily be derived from the experimental results by simple proportion. It may thus be calculated that $k(6)/k(7) = 1.23$ and $k(4)/k(5) = 1.20$.

TABLE 2

Retention times (OV 17) and fragmentation patterns for photolysis products [a]

Anisole (standard)	2.1 min/100 °C; 1.3 min/120 °C
1-Phenylethanol	5.1 min/100 °C; 122 ($M^{+\cdot}$), 107 ($M^{+\cdot} - CH_3\cdot$), 104 ($C_8H_8^{+\cdot}$; $M^{+\cdot} - H_2O$), 77 ($C_6H_5^+$; $M^{+\cdot} - C_2H_5O\cdot$)
1-Phenylethyl methyl ether	3.2 min/100 °C; 136 ($M^{+\cdot}$, 135 ($M^{+\cdot} - H\cdot$), 121 ($M^{+\cdot} - CH_3\cdot$), 105 ($M^{+\cdot} - CH_3O\cdot$), 91 ($C_7H_7^+$; $M^{+\cdot} - C_2H_5O\cdot$), 77 ($C_6H_5^+$; $M^{+\cdot} - C_3H_7O\cdot$)
2,3-Diphenylbutane	5 min/160 °C; 210 ($C_{16}H_{18}^{+\cdot}$; $M^{+\cdot}$), 105 ($C_8H_9^+$; $M^{+\cdot} - C_8H_9\cdot$)
Styrene	1.7 min/100 °C; 104 ($M^{+\cdot}$), 103 ($M^{+\cdot} - H\cdot$), 77 ($C_6H_5^+$; $M^{+\cdot} - C_2H_3\cdot$)
1-*p*-Methoxyphenylethanol	19 min/120 °C; 152 ($M^{+\cdot}$), 137 ($M^{+\cdot} - CH_3\cdot$), 134 ($M^{+\cdot} - H_2O$), 119 ($M^{+\cdot} - CH_3\cdot - H_2O$)
1-*p*-Methoxyphenylethyl methyl ether [b]	14 min/120 °C: 166 ($M^{+\cdot}$), 151 ($M^{+\cdot} - CH_3\cdot$), 134 ($M^{+\cdot} - CH_4O$), 119 ($M^{+\cdot} - C_2H_7O\cdot$)

[a] Data for some products already given in preceding paper.[1]

[b] We found it impossible to prepare an analytically pure sample of this photolysis product, or of an authentic specimen of the (apparently novel) ether, as samples with satisfactory n.m.r. spectra [$\tau(CDCl_3)$ 2.80, 3.14 (4 H, AB, *J* 11 Hz, Ar), 5.78 (1 H, q, Me-C–*H*), 6.23 (3 H, s, Ar-OC*H*$_3$), 6.85 (3 H, s, MeCHOC*H*$_3$), and 8.61 (3 H, d, *J* 6 Hz, H–C–C*H*$_3$] partially decomposed during final purification by distillation or preparative g.l.c. giving *p*-methoxystyrene, itself identified by m.s. and n.m.r. Found (P.C.M.U., Aldermaston) for the ether: $M^{+\cdot}$, 166.0990. $C_{10}H_{14}O_2$ requires $M^{+\cdot}$, 166.0994.

Photolysis and Thermal Solvolysis of 1-p-*Methoxyphenylethyltrimethylammonium Iodide in Aqueous Methanol.*—The quaternary iodide (23 mg, 8.3 × 10^{-5} mol) was photolysed in aqueous methanol (0.31 mol fraction MeOH, 10 ml) the standard procedure being used for photolysis and for product analysis by g.l.c. and g.l.c.–m.s. (Table 2). A similar solution was subjected to thermal solvolysis by heating in a sealed tube at 120 °C for 3 days, and the products were analysed in the same way. No 1-*p*-methoxyphenylethanol was identified in either reaction mixture; an authentic specimen of this alcohol was available and was readily detected by the procedure employed. 1-*p*-Methoxyphenylethyl methyl ether (>90% of decomposed salt) was the sole identified product (m.s.; Table 2) of each reaction. Traces of unidentified products were also present.

For comparison with the above photochemical result, benzyltrimethylammonium chloride, bromide, and iodide were each photolysed in the same solvent (aqueous methanol; 0.31 mol fraction MeOH). Benzyl alcohol and benzyl methyl ether were present in each reaction mixture in ratios (alcohol : ether) of 1.2 : 1 (chloride), 1.2 : 1 (bromide), and 1.5 : 1 (iodide).

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