# The Mechanism of Photolysis of Some Benzyltrimethylammonium Salts in Water and in Alcohols

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Photolysis of a range of benzyltrimethylammonium and 3,5-dimethoxybenzyltrimethylammonium salts in water or methanol at 253.7 nm gave typically benzyl alcohols (or benzyl methyl ethers), toluenes, bibenzyls and isomers, and di- and tri-methylammonium salts. By detailed sensitisation and quenching experiments it was established that, in the photolysis of benzyltrimethylammonium bromide in aqueous t-butyl alcohol, benzyl t-butyl ether, benzyl alcohol, and some toluene were produced by a singlet pathway and bibenzyl by a triplet pathway. A general mechanistic scheme for all the photolyses studied is thus suggested.

THE photolysis of benzylammonium salts [1] and related phosphonium [2] and sulphonium [3] salts has been studied by previous workers, but not to a stage where a detailed mechanistic scheme for any such system could be proposed with assurance. An interesting feature has been the occurrence of products evidently derived by both ammonium salts in water and in alcohols leading to a particularly clear-cut differentiation between singlet and triplet pathways.[4]

Products from photolysis of benzyl- and 3,5-dimethoxybenzyl-trimethylammonium halides and acetates in methanol and in water at 253.7 nm are shown in

TABLE 1

Photolysis of quaternary ammonium salts at 253.7 nm

| Quaternary salt, $\overset{+}{R N}Me_3\overset{-}{X}$; solvent | Products, with percentage and (where available) quantum yields |
|---|---|
| R = benzyl, $\overset{-}{X}$ = chloride; MeOH | RH (25%) $^a$; ROMe (42%) $^a$; R–R (5%); $RC_6H_4Me$ $^{b,c}$ (12%); ammonium salt residue not examined |
| R = benzyl, $\overset{-}{X}$ = chloride; $H_2O$ | RH (27%); ROH (45%); R–R (10%); $RC_6H_4Me$ $^{b,c}$ (20%); $Me_3\overset{+}{N}H\overset{-}{Cl}$ (77%); $Me_2\overset{+}{N}H_2\overset{-}{Cl}$ (23%) |
| R = benzyl, $\overset{-}{X}$ = bromide; MeOH | RH (27%, 0.17) $^d$; ROMe (33%, 0.19) $^d$; R–R (20%); $RC_6H_4Me$ $^{b,c}$ (20%); $Me_3\overset{+}{N}H\overset{-}{Br}$ (20%); $Me_2\overset{+}{N}H_2\overset{-}{Br}$ (80%) |
| R = benzyl, $\overset{-}{X}$ = bromide; $H_2O$ | RH (34%, 0.18); ROH (35%, 0.20); R–R (15%); $RC_6H_4Me$ $^{b,c}$ (15%); $Me_3\overset{+}{N}H\overset{-}{Br}$ (66%); $Me_2\overset{+}{N}H_2\overset{-}{Br}$ (33%) |
| R = benzyl, $\overset{-}{X}$ = iodide; MeOH | RH (8%, 0.02); ROMe (92%, 0.20); $Me_3\overset{+}{N}H\overset{-}{I}$ (92%); $Me_2\overset{+}{N}H_2\overset{-}{I}$ (5%) |
| R = benzyl, $\overset{-}{X}$ = iodide; $H_2O$ | RH (15%); ROH (50%); R–R (25%); $RC_6H_4Me$ $^{b,c}$ (5%); $Me_3\overset{+}{N}H\overset{-}{I}$ (78%); $Me_2\overset{+}{N}H_2\overset{-}{I}$ (22%) |
| R = benzyl, $\overset{-}{X}$ = acetate; MeOH | RH (20%); ROMe (32%); R–R (5%); $RC_6H_4Me$ $^{b,c}$ (15%); ammonium salt residue not examined |
| R = benzyl, $\overset{-}{X}$ = acetate; $H_2O$ | RH (20%); ROH (35%); R–R (5%); ammonium salt residue not examined |
| R = 3,5-dimethoxybenzyl, $\overset{-}{X}$ = chloride; MeOH | RH (46%); ROMe (12%); R–R (low yield) $^{e,c}$; $Me_3\overset{+}{N}H\overset{-}{Cl}$ (77%); $Me_2\overset{+}{N}H_2\overset{-}{Cl}$ (23%) |
| R = 3,5-dimethoxybenzyl, $\overset{-}{X}$ = bromide; MeOH | RH (55%); ROMe (23%); R–R (low yield) $^{e,c}$; $Me_3\overset{+}{N}H\overset{-}{Br}$ (75%); $Me_2\overset{+}{N}H_2\overset{-}{Br}$ (25%) |
| R = 3,5-dimethoxybenzyl, $\overset{-}{X}$ = iodide; MeOH | RH (52%, 0.17); ROMe (48%, 0.16); $Me_3\overset{+}{N}H\overset{-}{I}$ (73%); $Me_2\overset{+}{N}H_2\overset{-}{I}$ (26%) |
| R = 3,5-dimethoxybenzyl, $\overset{-}{X}$ = iodide; $H_2O$ | RH (31%); ROH (42%); $Me_3\overset{+}{N}H\overset{-}{I}$ (70%); $Me_2\overset{+}{N}H_2\overset{-}{I}$ (30%) |

$^a$ Lit.[1]: RH, 27%; ROMe, 54%. $^b$ This isomer of bibenzyl has slightly longer retention times than bibenzyl in g.l.c. separations, and in mass spectra the peak at $m/e$ 91 (presumably benzyl) is only one half the size of the molecular-ion peak at $m/e$ 182; for bibenzyl the relative sizes of these peaks are reversed. Since the response ratio for the compound is not known, a value of 1.00 (relative to the standard anisole) was assigned for the quantitative g.l.c. analyses. $^c$ No authentic specimen available to confirm assigned structure. $^d$ Lit.[1]: $\Phi$ for RH, 0.17; for ROMe, 0.23. $^e$ Tentative identification and quantitative estimation by n.m.r. spectroscopy only, via a peak, presumably for the four methylene protons, at $\tau$ 7.15 in a $CDCl_3$ solution of the photoproducts. The corresponding bibenzyl peak is at $\tau$ 7.10.

heterolytic and homolytic pathways: for example, benzyl ethers, toluene, and bibenzyl were obtained [1] by photolysis of benzylammonium salts in alcoholic solvents. We have been interested in possible mechanistic implications of this dichotomy, and now report a detailed examination of the photolysis of some benzyltrimethyl-

Table 1 together with quantum yields in selected cases. Most of the salts gave, as shown, a reasonable balance of products derived via homolysis and heterolysis, except that benzyltrimethylammonium iodide in methanol yielded a very high proportion of benzyl methyl ether. It is noteworthy that introduction of methoxy-sub-

stituents at *meta*-positions reduced rather than increased the proportion of heterolysis product formed, and also reduced the corresponding quantum yield while increasing that for formation of the toluene. Zimmerman and Sandel observed [5] an opposite result in their study of the photolysis of benzyl acetates in hydroxylic solvents; they interpreted their findings in terms of stabilisation of the benzyl cation in the first excited state by *meta*-methoxylation, and similar experimental results were obtained more recently [3] for photolysis of benzyl-sulphonium salts. With quaternary benzylammonium salts, however, it is evident from our work that in practical terms an iodide anion is more effective in ensuring high yields of heterolysis products than is a *meta*-methoxy-group.

Sensitised photolysis (acetone) of the quaternary bromide was investigated in aqueous t-butyl alcohol after an initial examination of the effect of variation of composition of this mixed solvent on product ratios in the direct photolysis and on quantum yields for product formation. The results are shown in Table 2. It is

TABLE 2

Quantum yields for product formation in direct and acetone-sensitised photolysis of benzyltrimethylammonium bromide in aqueous t-butyl alcohol [a]

| Solvent (vol. %) | $\Phi(T)$ | $\Phi(BA)$ | $\Phi(BTBE)$ | $\Phi(BB)$ | $\Sigma\Phi$ |
|---|---|---|---|---|---|
| Direct irradiations (253.7 nm) | | | | | |
| $H_2O$ (100%) | 0.18 | 0.20 | | 0.04 | 0.42 |
| $H_2O$ (50%), $Bu^tOH$ (50%) | 0.19 | 0.10 | 0.01 | 0.20 | 0.50 |
| $H_2O$ (16%), $Bu^tOH$ (84%) | 0.17 | 0.05 | 0.02 | 0.18 | 0.42 |
| $H_2O$ (10%), $Bu^tOH$ (90%) | 0.17 | 0.04 | 0.03 | 0.22 | 0.46 |
| Sensitised irradiations (1.0M-acetone, 300 nm) [b] | | | | | |
| $H_2O$ (100%) | 0.05 | 0.00 | 0.00 | 0.02 | 0.07 |
| $H_2O$ (50%), $Bu^tOH$ (50%) | 0.06 | 0.00 | 0.00 | 0.20 | 0.26 |
| $H_2O$ (10%), $Bu^tOH$ (90%) | 0.04 | 0.00 | 0.00 | 0.24 | 0.28 |

[a] Abbreviations: T, toluene; BA, benzyl alcohol; BTBE, benzyl t-butyl ether; BB, bibenzyl. [b] In less detailed studies with the quaternary chloride and bromide we have likewise found that no heterolysis products are produced from these salts in the sensitised photolyses.

clear that no heterolysis products are formed by a triplet pathway initiated by sensitisation of the substrate by triplet acetone. Toluene and bibenzyl are produced in both the direct and the sensitised photolyses but the quantum yield for toluene formation in the direct process is so much larger than for the sensitised that one might reasonably conclude that a proportion of the toluene is produced by a singlet pathway in the direct process without the necessity for intersystem crossing.

A clearer picture emerged from an investigation of quenching with piperylene in the direct photolysis of the bromide in aqueous t-butyl alcohol. Formation of benzyl alcohol and benzyl t-butyl ether was unaffected by addition of piperylene (up to 0.15M) in accordance with the deduction made in the last paragraph: it is clear that these heterolysis products are formed ex-

clusively by a singlet pathway. Toluene and bibenzyl were quenched, but quantitatively in a different manner for each hydrocarbon. A Stern–Volmer plot for bibenzyl (Figure 1) was linear, showing that bibenzyl was pro-
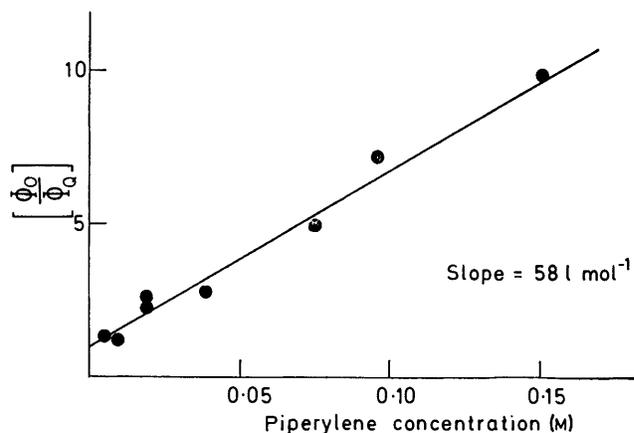


FIGURE 1 Stern–Volmer plot for quenching of bibenzyl in photolysis of benzyltrimethylammonium bromide in water (10 vol. %)–t-butyl alcohol (90 vol. %)

duced exclusively by a triplet pathway. From the Stern–Volmer equation $[\Phi_0/\Phi_Q] = 1 + k\tau[Q]$ the slope is $k\tau$ where $k$ is the (assumed diffusion-controlled) rate constant for quenching and $\tau$ is the triplet lifetime in the absence of quencher. The diffusion-controlled rate constant in the solvent used, a mixture of t-butyl alcohol (90% by volume) and water (10%), is estimated [6] from its viscosity [7] (4.58 × $10^{-2}$ poise) to be 1.41 × $10^9$ l $mol^{-1}$ $s^{-1}$ at 25 °C and the slope of the Stern–Volmer plot (Figure 1) was 48 l $mol^{-1}$. Hence the triplet lifetime is estimated as 4.1 × $10^{-8}$ s. This short lifetime
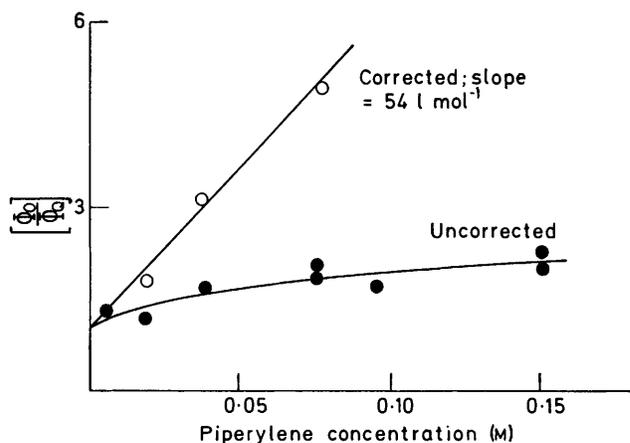


FIGURE 2 Stern–Volmer plots for quenching of toluene in photolysis of benzyltrimethylammonium bromide in water (10 vol. %)–t-butyl alcohol (90 vol. %) uncorrected (points ●) and corrected (points ○) for toluene produced by singlet pathway

accounts for our observation that product quantum yields are insensitive to traces of oxygen. The Stern–Volmer plot for toluene (Figure 2) was curved, indicating that some of this hydrocarbon is indeed produced by a

singlet pathway. Correction of this plot on the basis of roughly 40% of the total unquenched toluene being formed *via* a singlet pathway not subject to quenching by piperylene gave the straight-line plot shown with slope approximately the same as that for the bibenzyl plot. A rather higher figure is suggested from the data in Table 2 but this is also approximate, and the overall conclusion is that about half the toluene is derived by a singlet and half by a triplet pathway. We have no evidence of chemical reaction of the sensitizer or of intermediacy of more than one triplet state.

Fluorescence was observed from benzyltrimethyl-ammonium bromide and iodide in solution in water,

structure was assigned has been previously observed [9] on flash-photolysis of potassium iodide in methanol.

Our flash-photolysis results are clearly of little value in development of a detailed mechanism for photolysis of the benzyltrimethylammonium salts, but the studies on product-ratios, quantum-yields, sensitisation and quenching together with the stereochemical and other evidence on intermediacy of ion-pairs described in the following paper [10] do permit formulation of the reaction Scheme shown. The essential features of this Scheme are perhaps self-explanatory, but some aspects require comment. Intersystem crossing between loose singlet and triplet radical pairs might also take place, although this
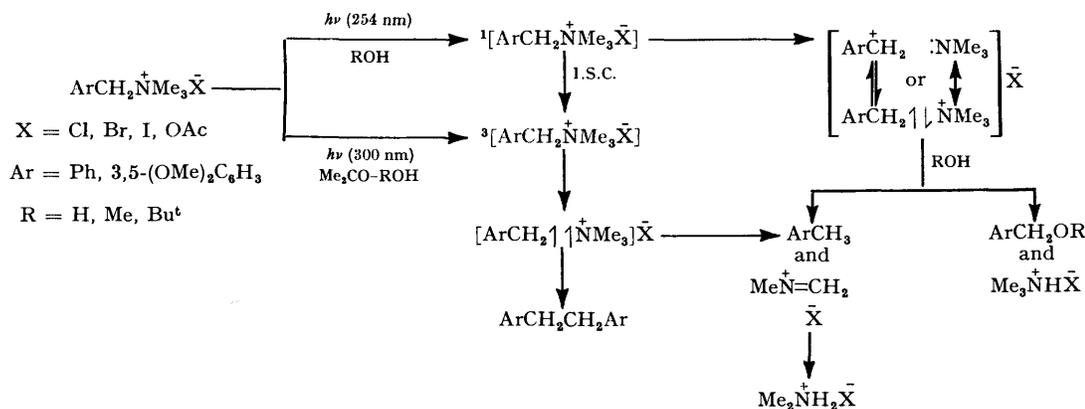
SCHEME

methanol, or t-butyl alcohol at room temperature. The spectra, obtained on excitation at 250 nm, were independent of solvent and gegen-ion chosen and showed a single structureless peak with $\lambda_{max.}$ 295 nm and $O$–$O$ band at 255 nm (112 kcal mol$^{-1}$). Phosphorescence was also observed for these salts in 2 : 1 ethanol–methanol glasses at $-170$ °C. Again, the spectra were independent of gegen-ion; $\lambda_{max.}$ was 390 nm and the $O$–$O$ band was at 350 nm (82 kcal mol$^{-1}$). The phosphorescence was markedly quenched, as expected, by addition of 0.2M-piperylene.

Flash-photolysis studies with benzyltrimethylammonium bromide and iodide in methanol produced a species observable over *ca.* 120 μs with $\lambda_{max.}$ 302 and 313 nm. The u.v. spectrum and decay period agree with published characteristics for the benzyl radical,[8] which has been produced in a range of solvents by pulse radiolysis or flash photolysis of benzyl chloride or sodium phenylacetate. Since photolysis of the quaternary iodide in methanol yields no observable bibenzyl, however (Table 1), it seems that the species produced in our flash experiments may nevertheless not be the free benzyl radical. We could not study the decay kinetics accurately using the photographic recording method, and it is also possible therefore that more than one species with similar absorption spectra may have been present. Another product, from the iodide but not the bromide, had a broad absorption band from 325 to 500 nm and a lifetime observable over *ca.* 50 μs. This is probably $I_2^-$; a transient with similar characteristics to which this

feature is not represented. In the case of photolysis of the ammonium salts no special significance attaches to this particular possibility whereas with benzyl halides and acetate (accompanying paper [11]) the analogous intersystem crossing appears to be a key component of the overall reaction pathway for the triplet substrate. Whether a tight singlet radical-pair and the corresponding intimate cation-base geminate pair derived from the quaternary cation are separate species or not is a question [12] we leave open, as indicated by the alternative equilibrium or resonance symbols. For simplicity, any successive additional geminate pairs with differing degrees of solvation are omitted from the Scheme. The available evidence (including that in the following paper [10]) does not exclude part return of photolytic geminate pairs to quaternary cation. We have no evidence of formation of toluene by any mechanism other than the homolytic pathways indicated in the Scheme.

The particularly high yield of benzyl methyl ether from photolysis of benzyltrimethylammonium iodide in methanol is explained by the low quantum yields for products derived *via* the radical route for this reaction. The iodide anion may be acting as a more efficient triplet quencher than chloride or bromide in solution, although from the phosphorescence results it evidently does not do so in a frozen glass. The chemical shift of the methylene proton signal in the n.m.r. spectrum of a solution of benzyltrimethylammonium iodide in [$^2H_4$]-methanol was more sensitive to temperature than was the case for the spectrum of the bromide, a result which

could possibly be related to a higher degree of ion-pairing in the former salts, which would thus provide a better opportunity for internal triplet quenching by the anion.

Benzyltrimethylammonium iodide in methanol was found to be a useful chemical actinometer, and was so used in some of our work after calibration against the usual ferrioxalate solution. We recommend it for use with light of wavelength 253.7 nm ($\Phi$ for formation of benzyl methyl ether = 0.20 at 25 °C) on the following grounds. (a) For reasonably fast working there is no need to protect from daylight or normal artificial light. (b) There is no particular need to remove oxygen rigorously from the actinometer sample prior to irradiation. (c) The quantum yield for product formation is unaffected by considerable variations in initial concentrations (we recommend $10^{-1}$M) or percentage decomposition (up to 10%). (d) The products from the reaction are readily determined both qualitatively and quantitatively by g.l.c. analysis as described in the Experimental section.

We initiated our work in this area as the result of an unsuccessful attempt to freeze the conformational equilibria in biased $N$-methylpiperidines by reaction with the photo-generated 3,5-dimethoxybenzyl carbonium ion to yield mixtures of diastereoisomeric quaternary salts, and thus determine the conformational equilibrium constants. Zimmerman and Sandel obtained[5] only the heterolysis product, 3,5-dimethoxybenzyl alcohol, when 3,5-dimethoxybenzyl acetate was photolysed in 50% aqueous dioxan. When we subjected the acetate to photolysis in cyclohexane in the presence of piperidine we obtained products from both heterolytic and homolytic pathways, isolating 1-(3,5-dimethoxybenzyl)piperidine and another product, apparently the 2-substituted isomer, which may readily be formulated as being derived by a radical route.[13] However, in an analogous experiment with 1-methylpiperidine no quaternary salt was obtained. Subsequently it was shown that a mixture of diastereoisomeric 4-t-butyl-1-(3,5-dimethoxybenzyl)-1-methylpiperidinium acetates was rapidly photolysed in aqueous solution, yielding 3,5-dimethoxybenzyl alcohol and 3,5-dimethoxytoluene, and it seems that such quaternary salts may also be decomposed under the conditions described above for their attempted preparation. In the experiment with piperidine, the protonated dimethoxybenzyl salt formed initially presumably loses its proton by equilibration with the excess of piperidine present; otherwise it too would be expected[1] slowly to undergo further photolysis.

EXPERIMENTAL

*Instrumentation.*—Photolyses and quantum-yield determinations were carried out in a Rayonet photochemical reactor fitted with a ' merry-go-round ' attachment MGR-100 and either 2 537 or 3 000 Å lamps as appropriate. G.l.c. analyses were performed in a Perkin–Elmer gas chromatograph, model F 11, using either OV 17 ($2\frac{1}{2}$%) on Chromasorb G-AW-DMCS, 80—100 mesh, in a 6-ft × $\frac{1}{8}$-in glass column, or Poropack Q, 80—100 mesh, in a 2-ft × $\frac{1}{8}$-in glass column with preconditioning for 12 h at 210 °C; the carrier gas was

nitrogen with flow rate of 40 ml per min, and a flame-ionisation detector was employed. Mass spectra were taken on an A.E.I. MS-12 instrument fitted with a Pye 104 gas chromatograph interfaced to the mass spectrometer *via* a Watson-Biemann molecular separator. N.m.r. spectra were taken on Varian HA-100 or Perkin-Elmer R 12A or R 34 spectrometers, using tetramethylsilane as an internal ($CDCl_3$ solution) or external ($D_2O$) standard. The flash-photolysis equipment was constructed in this Department, having xenon flashlamps for both the main (200—2 000 J) and spectroscopic (25—200 J) flashes; spectra were recorded photographically. Phosphorescence and fluorescence spectra were taken on an Aminco-Bowman spectrophotofluorometer.

*Photolysis Substrates and Products.*—Some were commercially available, but most of the quaternary salts and authentic specimens for comparison with photolysis products were made by standard procedures. In the case of known compounds, the properties of our samples agreed with literature values. All compounds had the spectroscopic characteristics expected from their structures. Elemental analyses of new compounds and of some others of particular importance are given in Table 3.

*Temperature Dependence of Some N.M.R. Spectra.*—Solutions of benzyltrimethylammonium bromide and iodide (0.125M in [$^2H_4$]methanol) were examined between +30 and −50 °C. The chemical shift of the $N$-methyl group in each salt showed hardly any temperature variation relative to that of the internal standard or to that from a trace of methyl-protonated solvent. However, the benzyl-methylene proton signal of the iodide solution shifted 12 Hz downfield (at 100 MHz) on cooling over the temperature range; the corresponding shift for the bromide was only 4 Hz.

*Photolysis of Quaternary Ammonium Salts: General Procedures.*—Solutions of quaternary salts ($10^{-3}$—$10^{-4}$ mol) in the appropriate solvents (10 ml) in Pyrex (300 nm photolysis) or silica (253.7 nm) tubes stoppered with plastic septa were deoxygenated by passage of nitrogen or argon for 20—30 min and then submitted to photolysis in the Rayonet reactor. Decomposition of substrate to a suitable extent (>50%) usually required 1—2 h. The reactor temperature was *ca.* 30 °C; in earlier experiments with water-cooling (18—20 °C) of the reaction tubes no appreciable differences in results were noted. Anisole (1.91 × 10$^{-4}$ mol) was added as a calibrant to the total reaction mixture by a standardised 20 μl pipette, dimethoxybenzyl acetate or bibenzyl being used instead for mixtures containing higher-boiling components (column temperature 140 °C upwards). Subsequent work-up depended on the solvent used. (a) Aliquots of methanol solutions were taken directly for g.l.c. and g.l.c.–m.s. analysis; the remainder of the methanol was then evaporated and the residue was triturated with ether to isolate ammonium salt mixtures for analysis by n.m.r.; residues containing higher proportions of biphenyls were dissolved in chloroform and the salts precipitated with ether. (b) When the photolysis had been carried out in water the ether-soluble components were extracted with ether, the extract was dried ($MgSO_4$) and concentrated by part distillation of solvent through a fractionating column; aliquots of the concentrate were used for g.l.c. and g.l.c.–m.s. analysis, while ammonium salt mixtures were isolated by evaporation of the aqueous phase. (c) Aqueous methanol and butanol solutions were shaken with water and ether and each phase examined appropriately as indicated above.

TABLE 3

Some photolysis substrates and products [a]

| Compound | M.p. or b.p./mmHg (° C); lit. value | Found (%) C | H | N | Br or I | Formula | Calc. (%) C | H | N | Br or I |
|---|---|---|---|---|---|---|---|---|---|---|
| Benzyltrimethylammonium iodide | 182; lit.,[b] 178—179 | 43.25 | 5.6 | 5.25 | | $C_{10}H_{16}IN$ | 43.35 | 5.8 | 5.05 | |
| 3,5-*Dimethoxybenzyltrimethyl-ammonium bromide* | 193—195 | 49.9 | 6.65 | 4.75 | 27.65 | $C_{12}H_{20}BrNO_2$ | 49.65 | 6.95 | 4.8 | 27.55 |
| 3,5-*Dimethoxybenzyltrimethyl-ammonium iodide* | 209—210 | 42.7 | 5.95 | 4.35 | 37.45 | $C_{12}H_{20}INO_2$ | 42.75 | 5.95 | 4.15 | 37.65 |
| 3,5-*Dimethoxybenzylmethyl ether* | 138 [c]/12 mmHg | 65.65 | 7.85 | | | $C_{10}H_{14}O_3$ | 65.9 | 7.75 | | |
| N-(3,5-Dimethoxybenzyl)piperidine hydrochloride | 182—183; lit.,[d] 185.5—187 | 61.6 | 8.05 | 4.6 | | $C_{14}H_{22}ClNO_2$ | 61.85 | 8.15 | 5.15 | |

[a] New compounds italicised. [b] G. M. Coppinger, *J. Amer. Chem. Soc.*, 1954, **76**, 1372. [c] B.p. [d] K. Hejno and Z. Arnold, *Chem. Listy*, 1953, **47**, 601.

Response ratios in the g.l.c. analyses were determined relative to anisole, 3,5-dimethoxybenzyl acetate, or bibenzyl as appropriate. Typical retention times for one column and fragmentation patterns of products from photolyses are given in Table 4. The work-up procedures, the retention times and the fragmentation patterns were checked with authentic specimens of all compounds identified, except for the two examples noted in Table 1. Confirmatory evidence of identities of reaction products and of approximate relative proportions was also obtained from the n.m.r. spectra of the methanol or ether solutions.

N.m.r. analysis of $D_2O$ solutions served for determination of the composition of the ammonium salt residues (hydrohalides of di- and tri-methylamine plus undecomposed reactant) obtained from quaternary ammonium halides as described above. Again the method was checked and calibrated with authentic samples which were also taken through the whole work-up procedure; some care was found necessary to avoid sublimation of dimethylamine hydrochloride during this processing. N-Methyl peaks ($\tau$; total salt concentration ca. 0.5M) in the spectra of the hydrohalide salts were as follows: $\overset{+}{N}HMe_3\overset{-}{Cl}$, 7.00; $\overset{+}{N}H_2Me_2\overset{-}{Cl}$, 7.19; $\overset{+}{N}HMe_3\overset{-}{Br}$, 7.06; $\overset{+}{N}H_2Me_2\overset{-}{Br}$, 7.25; $\overset{+}{N}HMe_3\overset{-}{I}$, 7.09; $\overset{+}{N}H_2Me_2\overset{-}{I}$, 7.29. The N-methyl peaks for unchanged quaternary salts lay ca. 0.2 p.p.m. downfield from the trimethylammonium hydrohalide having the same anion (range ca. $\tau$ 6.8—6.9). Absolute peak positions are sensitive to salt concentrations.

Thermal blanks (showing no reaction) were carried out for all photochemical reactions studied. The stability of the products of these reactions under the photolysis conditions was also checked; no decomposition occurred except, to a negligible extent, in the case of 3,5-dimethoxybenzyl alcohol and the corresponding methyl ether. Prolonged photolysis of these compounds in methanol led slowly to formation of 3,5-dimethoxytoluene and other products. The temperature of the injection ports of the g.l.c. instruments was always kept low enough to avoid thermal decomposition of any ammonium salts present in the samples.

Quantum yields were determined at <10% decomposition using the standard ferrioxalate procedure,[14] or by employment of benzyltrimethylammonium iodide in methanol as a secondary actinometer, as discussed above.

*Flash-photolysis Studies.*—Solutions of benzyltrimethylammonium bromide or iodide (20 mg) in methanol (100 ml) containing ethanolic trimethylamine (33%; 0.5 ml) contained in quartz photolysis cells were deoxygenated on a vacuum line (5 × 10⁻⁵ mmHg) using the freeze-thaw technique. The output from the xenon flashlamps (used at energies of 800—1 600 J) was suitably filtered (aqueous cobalt/nickel sulphate and chlorine gas filters) to transmit only light <300 nm, and the absorption spectra of products

TABLE 4

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

| | |
|---|---|
| Anisole (standard) | 1.3 min/120 °C |
| 3-5-Dimethoxybenzyl acetate (standard) | 38 min/140 °C |
| Benzyl alcohol | 3 min/120 °C; 108 ($M^{+\cdot}$), 107 ($M^{+\cdot}$ — H·), 91 ($C_7H_7^+$; $M^{+\cdot}$ — OH·), 79 ($M^{+\cdot}$ — CHO·), 77 ($M^{+\cdot}$ — $CH_3O\cdot$) |
| Benzyl methyl ether | 1.6 min/120 °C; 122 ($M^{+\cdot}$), 121 [a] ($M^{+\cdot}$ — H·), 91 ($C_7H_7^+$; $M^{+\cdot}$ — $CH_3O\cdot$), 65 ($C_5H_5^+$; $M^{+\cdot}$ — $C_3H_5\cdot$) |
| Benzyl t-butyl ether | 3.2 min/140 °C; 164 ($M^{+\cdot}$), 149 ($M^{+\cdot}$ — $CH_3\cdot$), 108 ($M^{+\cdot}$ — $C_4H_8$), 107 ($M^{+\cdot}$ — $C_4H_9\cdot$), 91 ($C_7H_7^+$; $M^{+\cdot}$ — $C_4H_9O\cdot$), 57 ($C_4H_9^+$; $M^{+\cdot}$ — $C_7H_7O\cdot$) |
| Toluene | 0.7 min/120 °C; 92 ($M^{+\cdot}$), 91 ($C_7H_7^+$; $M^{+\cdot}$ — H·), 65 ($C_5H_5^+$; $M^{+\cdot}$ — $C_2H_3\cdot$) |
| Bibenzyl | 14 min [b]/120—160 °C; 182 ($C_{14}H_{14}^{+\cdot}$; $M^{+\cdot}$), 91 [c] ($C_7H_7^+$), 65 ($C_5H_5^+$; $M^{+\cdot}$ — $C_9H_9\cdot$) |
| Postulated methyl diphenylmethane [c] | 15 min [b]/120—160 °C; 182 ($C_{14}H_{14}^{+\cdot}$; $M^{+\cdot}$), 167 ($M^{+\cdot}$ — $CH_3\cdot$), 91 [c] ($C_7H_7^+$), 65 ($C_5H_5^+$; $M^{+\cdot}$ — $C_9H_9\cdot$) |
| 3,5-Dimethoxybenzyl alcohol | 23 min/140 °C; 168 ($M^{+\cdot}$), 151 ($M^{+\cdot}$ — OH·), 139 ($M^{+\cdot}$ — CHO·) |
| 3,5-Dimethoxybenzyl methyl ether | 14 min/140 °C; 182 ($M^{+\cdot}$), 152 ($M^{+\cdot}$ — $CH_2O$), 151 ($M^{+\cdot}$ — $CH_3O\cdot$), 150 ($M^{+\cdot}$ — $CH_4O$) |
| 3,5-Dimethoxybenzyl t-butyl ether | 33 min/140 °C; 224 ($M^{+\cdot}$), 151 ($M^{+\cdot}$ — $C_4H_9O\cdot$), 121 ($M^{+\cdot}$ — $C_5H_{11}O_2\cdot$) |
| 3,5-Dimethoxytoluene | 5 min/140 °C; 152 ($M^{+\cdot}$), 137 ($M^{+\cdot}$ — $CH_3\cdot$), 123 ($M^{+\cdot}$ — CHO·) |
| 1-(3,5-Dimethoxybenzyl)piperidine | 7.5 min/200 °C; 235 ($M^{+\cdot}$), 234 ($M^{+\cdot}$ — H·), 152 ($M^{+\cdot}$ — $C_5H_9N$), 98 ($C_6H_{12}N^+$: $M^{+\cdot}$ — $C_8H_9O_2\cdot$), 84 ($C_5H_{10}N^+$; $M^{+\cdot}$ — $C_9H_{11}O_2\cdot$) |
| Postulated 2-(3,5-dimethoxybenzyl)-piperidine | 11 min/200 °C; mass spectrum identical to that of 1-isomer |

[a] This peak is very small if the sample is injected directly into the mass spectrometer rather than *via* the g.l.c. analysis attachment. [b] First 4 min at 120 °C, then temp. raised to 160 °C; total elapsed times from injection to peak centre given. All retention times quoted, and particularly these, are indicative of quality of results and of course meaningful in a relative rather than in an absolute sense. In some analyses an automatic temperature programmer was employed. [c] See Table 1, especially footnote b.

were photographed (spectroscopic flash, 150 J) after various delay times from 2 μs upwards. In the absence of tri-methylamine the photolysis solutions became slightly yellow during the experiments (halogen?) and photographic recording was made difficult.

*Experiments with Piperidines.*—A solution of piperidine (1.67 g) and 3,5-dimethoxybenzyl acetate (0.3 g) in cyclo-hexane (30 ml) was irradiated for 24 h at 30 °C with light of >260 nm (aqueous KI filter). A crystalline deposit (piperidine acetate) was filtered off, the filtrate was shaken with excess of aqueous hydrochloric acid, and the acid layer was extracted several times with ether and con-centrated to a small volume. The bases were liberated with alkali, extracted into ether, and after removal of the solvent were analysed by g.l.c., n.m.r., and m.s. Two products were present with somewhat different retention times and in approximately equal proportions (assuming similar response ratios). One base was identical in retention time and frag-mentation pattern (Table 4) with an authentic specimen of 1-(3,5-dimethoxybenzyl)piperidine (hydrochloride: Table 3) and the n.m.r. spectrum of an isolated sample also accorded (as hydrochloride) with that of the authentic specimen: $\tau$ (CDCl$_3$) 3.05—3.6 (3 H, m, Ar), 5.70 (2 H, s, CH$_2$), and 6.15 (6 H, s, OCH$_3$). The fragmentation pattern of the other base was virtually identical in all respects (including relative intensities) with that of the first, and it is evidently an isomer, presumably 2-(3,5-dimethoxybenzyl)-piperidine. Most of the dimethoxybenzyl acetate was converted into dimethoxybenzylpiperidines, as shown by quantitative u.v. spectrophotometry of the basic extract at 280 nm.

In a similar experiment with 1-methylpiperidine, some base containing the 3,5-dimethoxybenzyl chromophore ($\lambda_{max.}$ 280 nm in ether), presumably 1-methyl-2-(3,5-di-methoxybenzyl)piperidine, was obtained but none of the water-soluble 1-methyl-1-(3,5-dimethoxybenzyl)piperidin-ium acetate. An authentic sample of this compound, pre-pared *via* the bromide, and a sample of mixed *cis-* and *trans-*4-t-butyl-1-methyl-1-(3,5-dimethoxybenzyl)piperidinium

acetates (*ca.* 1 : 1 ratio, $\overset{+}{\text{N}}$-CH$_3$ signals at $\tau$ 6.85 and 6.90 in CDCl$_3$) also prepared from the *N*-methyl base [15] *via* the mixed bromides, were in each case rapidly photolysed in aqueous solution when irradiated with light of wavelength >260 nm. Examination of the products by the standard procedure outlined above showed formation of 3,5-di-methoxytoluene and 3,5-dimethoxybenzyl alcohol.

REFERENCES

[1] M. A. Ratcliff, jun., and J. K. Kochi, *J. Org. Chem.*, 1971, **36**, 3112.
[2] C. E. Griffin and M. L. Kaufman, *Tetrahedron Letters*, 1965, 773.
[3] A. L. Maycock and G. A. Berchtold, *J. Org. Chem.*, 1970, **35**, 2532.
[4] Preliminary communication: 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.
[5] H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, 1963, **85**, 915.
[6] C. A. Parker, ' Photoluminescence of Solutions,' Elsevier, Amsterdam, 1968, pp. 74—75.
[7] J. Timmermans, ' The Physico-chemical Constants of Binary Systems in Concentrated Solutions,' Wiley–Interscience, New York, 1960, vol. 4, p. 236.
[8] R. L. McCarthy and A. McLachlan, *Trans. Faraday Soc.*, 1960, **56**, 1187; T. O. Meiggs, L. I. Grossweiner, and S. I. Miller, *J. Amer. Chem. Soc.*, 1972, **94**, 7981, 7986.
[9] F. H. C. Edgecombe and R. G. W. Norrish, *Proc. Roy. Soc.*, 1959, **A253**, 154.
[10] V. Lillis, J. McKenna, J. M. McKenna, M. J. Smith, P. S. Taylor, and I. H. Williams, following paper.
[11] D. C. Appleton, B. Brocklehurst, J. McKenna, J. M. Mc-Kenna, S. Thackeray, and A. R. Walley, *J.C.S. Perkin II*, 1980, 87.
[12] *Cf.* C. Walling, H. P. Waits, J. Milovanovic, and C. J. Pappiaonnou, *J. Amer. Chem. Soc.*, 1970, **92**, 4927.
[13] *Cf.* R. C. Cookson, J. Hudec, and N. A. Mirza, *Chem. Comm.*, 1967, 824.
[14] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518.
[15] H. O. House, B. A. Tefertiller, and C. G. Pitt, *J. Org. Chem.*, 1966, **31**, 1073.