The Mechanism of Photolysis of Benzyl Halides and Benzyl Acetate in Alcohols

By **David C. Appleton, Brian Brocklehurst, James McKenna,*** **Jean M. McKenna, Stephen Thackeray** and **Andrew R. Walley,** Chemistry Department, The University, Sheffield S3 7HF

The photolysis of benzyl chloride, bromide, iodide, and acetate, and 3,5-dimethoxybenzyl bromide and acetate in methanol and t-butyl alcohol have been examined, and also 3,5-dimethoxybenzyl chloride in ethanol. Solvolysis products and products derived by non-ionic mechanisms are obtained by either direct photolysis at 254 nm or acetone-sensitised photolysis at 300 nm. The mechanisms of the reactions are discussed.

In a previous paper[1] we discussed the mechanism of photolysis of benzyltrimethylammonium salts in hydroxylic solvents. In this paper[2] we describe a corresponding study with covalent benzyl derivatives (halides and acetates) in alcoholic solvents; this has disclosed interesting differences between these substrates and the ammonium salts, particularly in relation to acetone-sensitised photolysis.

TABLE 1

Photolysis of benzyl halides and acetates at 253.7 nm (direct photolyses) or 300 nm (acetone-sensitised photolyses)

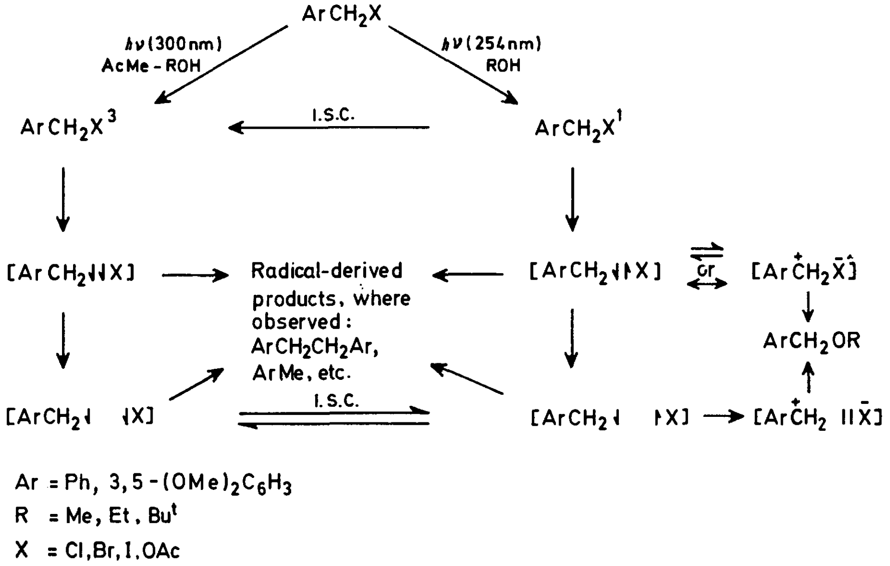
Compound; solvent	Products with percentage yields and/or quantum yields for formation
Benzyl chloride; methanol	$PhCH_2OMe$ (26%); $PhCH_2CH_2Ph$ (23%); $PhCH_2CH_2OH$ (37%); PhMe (trace)
Benzyl chloride; methanol–acetone [a]	$PhCH_2OMe$ (45%); $PhCH_2CH_2Ph$ (2%); $PhCH_2CH_2OH$ (15%); PhMe (trace); other unidentified products
Benzyl chloride; ethanol	$PhCH_2OEt$ (25%); $PhCH_2CH_2Ph$ (14%); $PhCH_2CHOHCH_3$ (29%); [b,c] PhMe (5%)
Benzyl chloride; t-butyl alcohol	$PhCH_2OBu^t$ (0.12); $PhCH_2CH_2Ph$ (0.05); $PhCH_2CH_2CMe_2OH$ [b]
Benzyl chloride: t-butyl alcohol–acetone	$PhCH_2OBu^t$ (0.20); $PhCH_2CH_2Ph$ (0.03); $PhCH_2CH_2CMe_2OH$; [b] $PhCH_2CH_2COMe$ [b]
Benzyl bromide; methanol	$PhCH_2OMe$ (64%); $PhCH_2CH_2Ph$ (26%); PhMe (minimal trace)
Benzyl bromide; t-butyl alcohol	$PhCH_2OBu^t$ (0.23); $PhCH_2CH_2Ph$ (0.01)
Benzyl bromide; t-butyl alcohol–acetone	$PhCH_2OBu^t$ (0.12); $PhCH_2CH_2Ph$ not observed
Benzyl iodide; methanol	$PhCH_2OMe$ (*ca.* 100%; 0.52)
Benzyl iodide; t-butyl alcohol	$PhCH_2OBu^t$ (0.20)
Benzyl acetate; methanol	$PhCH_2OMe$ (33%); $PhCH_2CH_2Ph$ (10%); PhMe (trace)
Benzyl acetate; t-butyl alcohol	$PhCH_2OBu^t$ (<0.01); $PhCH_2CH_2Ph$ (<0.01); PhMe (<0.01); $PhCH_2CH_3$ (0.02)
Benzyl acetate; t-butyl alcohol–acetone	$PhCH_2OBu^t$ (<0.01); $PhCH_2CH_2Ph$ (<0.01)
3,5-Dimethoxybenzyl bromide; methanol	3,5-$(MeO)_2C_6H_3CH_2OMe$ (95%); 3,5-$(MeO)_2C_6H_3Me$ (trace)
3,5-Dimethoxybenzyl bromide; t-butyl alcohol	3,5-$(MeO)_2C_6H_3CH_2OBu^t$ (0.17); 3,5-$(MeO)_2C_6H_3Me$ not observed
3,5-Dimethoxybenzyl acetate; methanol	3,5-$(MeO)_2C_6H_3CH_2OMe$ (42%); 3,5-$(MeO)_2C_6H_3Me$ (trace); 3,5-$(MeO)_2C_6H_3CH_2Me$ (trace); [b] $(MeO)_2C_6H_3CH_2CH_2C_6H_3(OMe)_2$ uncertain [c]
3,5-Dimethoxybenzyl acetate; t-butyl alcohol	3,5-$(MeO)_2C_6H_3CH_2OBu^t$ (0.03); 3,5-$(MeO)_2C_6H_3CH_2Me$ (0.16); [b,c] $(MeO)_2C_6H_3$-$CH_2CH_2C_6H_3(OMe)_2$ uncertain [d]

[a] Acetone *ca.* 1.3M for the sensitised photolyses. [b] Postulated from the fragmentation patterns (Table 2). [c] Response ratio of 1.00 (relative to standard anisole) assigned for quantitative g.l.c. analyses. [d] This compound is difficult to identify by g.l.c. (streaks on column) and for the reaction mixtures in this paper (*cf.* ref. 1) was also difficult to identify with reasonable assurance by n.m.r.

The results are summarised in Table 1. All the substrates were photolysed with 254-nm light in methanol and in t-butyl alcohol, the latter solvent being usually chosen for measurement of quantum yields. Some of the photolyses were also run at 300 nm with acetone as a sensitiser. The direct photolysis of benzyl chloride in ethanol was also examined.

As in the case of the ammonium salts,[1] both ionic and non-ionic mechanisms are evidently involved, the former leading to solvolysis products and the latter to the other observed products, derived from reactions of benzyl (or chlorine) radicals. However, solvolysis products arise in both direct and sensitised reactions, and in this respect benzyl halides and acetates clearly differ markedly from benzyltrimethylammonium salts, which yield solvolysis products only on direct photolysis. Any satisfactory mechanistic interpretation of the results must take this important difference into account. We return to this aspect later, but first note several other points of interest.

2-Phenylethanol and analogous compounds derived from reaction of radicals (initially presumably chlorine radicals) with the alcoholic solvents were prominent products in the photolysis of benzyl chloride but not of any of the other substrates examined in this or in the previous paper.[1] Little toluene (or 3,5-dimethoxytoluene) was obtained from the covalent substrates, in contrast to the results observed for the ammonium salts. The bibenzyl isomer, believed to be a methyldiphenylmethane, which was a commonly observed product in the ammonium-salt photolyses was not observed from the halides or acetates in either direct or sensitised reactions. Curiously, however, this product did appear when we attempted to use piperylene as a quencher in the photolysis of benzyl chloride in methanol. Traces of four other products, apparently (mass spectra; Table 2) isomeric benzylpiperylenes, were also produced; all five compounds also appeared in analogous work with benzyl bromide in methanol or t-butyl alcohol, but with the bromide quite large yields of benzylpiperylenes were produced and very little methyldiphenylmethane. No similar observations or other difficulties have previously[1] been encountered in quenching investigations with benzyltrimethylammonium bromide in aqueous t-butyl alcohol. Fortunately, the obvious absence of the possibility of any clear-cut multiplicity differentiation as between formation of solvolysis and other products in the photolysis of the covalent halides and acetates, evidenced by the results summarised in Table 1, reduced the importance of the quenching experiments for photolysis of these substrates. Good linear Stern–Volmer plots were hardly expected, although those obtained for benzyl t-butyl ether and bibenzyl in the photolysis of benzyl chloride in t-butyl alcohol did not deviate far from linearity, and in these examples there was no evidence of chemical reaction of the quencher. Interestingly, the plot for the ether had a slope only about one-eighth of that for bibenzyl.



SCHEME

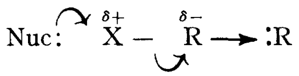
Although it is tempting to speculate, some of the detailed results described in the previous paragraph cannot be explained convincingly in any simple manner on available evidence, nor can the rather curious pattern of quantum yields (Table 1), with the value for formation of benzyl t-butyl ether from benzyl chloride, for example, being higher in the sensitised than in the direct reaction. The low yields of toluenes, by comparison with results from photolysis of the ammonium salts, is intelligible, since with the salts geminate pairs of benzyl and trimethylammonium-cation radicals provide a ready source of toluenes. The greater variety of products evidently derived from benzyl radicals in the photolysis of the halides and acetates may also be partly related to the absence of this particularly easy route for reaction of benzyl radicals.

Our interpretation of the general mechanistic features for direct and sensitised photolyses is indicated in the Scheme. This resembles that given in the previous paper[1] for photolysis of benzyltrimethylammonium salts, with the very imporant difference that for the halides and acetates a route from triplet substrates to solvolysis products is evidently required. We believe that the most likely such route involves interconversion (see Scheme) of loose singlet and triplet radical pairs, followed by electron transfer in the singlet pair to give a solvent-separated ion pair. From studies of the C.I.D.N.P. and related effects[3] it is known that interconversion between singlet and triplet states of a radical pair where the partners are already adequately separated can occur at a rate comparable to that of the final separation of the partners; this is due to electron-nuclear hyperfine interaction, while spin-orbit relaxation may also contribute when one of the partners is a halogen atom. Spin interconversions of the same type could arise in geminate radical pairs derived from the ammonium salts, but further conversion of the singlet pair into a solvent-separated ion pair is likely to be less favourable in this case. In the photolysis pathway for the halides and acetates, the polar geminate pair will be favoured energetically over the radical pair in the polar solvent, and the exothermicity of the electron-transfer step may therefore substantially offset the barrier due to solvent reorganisation. The singlet pair from the ammonium salt, however, $(\mathrm{PhCH_2}\upharpoonright\ \downharpoonleft\overset{+}{\mathrm{N}}\mathrm{Me_3}\overset{-}{\mathrm{X}})$ is *also* an ion pair, so the coulombic driving force for interconversion to $(\mathrm{Ph}\overset{+}{\mathrm{C}}\mathrm{H_2}\ \mathrm{NMe_3}\overset{-}{\mathrm{X}})$ in the polar solvent will be relatively small, and apparently inadequate in this case to offset the energy of solvent-reorganisation.

As in the previous paper,[1] we leave open the question of whether tight singlet radical pairs and the corresponding ion pairs are contributors to resonance-hybridised species[4] from which radical and solvolysis products are derived, or whether we have separate species formed consecutively. Other workers in related investigations[5] prefer to postulate consecutive formation of radical and (by electron transfer) ion pairs. If this does occur we believe that the transfer would perhaps be more likely to take place in looser geminate systems, in line with the suggestions made above for the triplet-derived species.*

Additional preliminary evidence of intermediacy of ion pairs in photolysis of benzyl halides has been derived[2] from consideration of nucleophile capture ratios (*cf.* refs. 6 and 7).

The results described may be compared with those from other authors. Zimmerman and Sandel, in a pioneering paper,[8] discussed the increased yields of solvolysis *vis-a-vis* radical products associated with *meta*-methoxylation in photolysis of (mostly) benzyl acetates in aqueous dioxan. Our observations are in accord, but the particular efficacy of benzyl iodide in giving high yields of solvolysis products is even more evident, a result which recalls that obtained[1] for photolysis of benzyltrimethylammonium iodide. Recently, the literature of photolysis of benzyl chloride has been confused and contradictory. It has been stated[9] that this compound is solvolytically stable to irradiation in ethanol; alternatively it has been said[10] to undergo solvolysis in aqueous methanol giving benzyl alcohol, with a quantum yield of unity. In other work,[7] only bibenzyl and 2-phenylethanol were identified 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. Evidently these claims, taken together, present a conflicting picture, and there is also some disparity between each of them and our own results. It is difficult to comment on the lack of agreement, particularly since the published papers do not always include full experimental details, although there are some evident differences in methodology—one group,[10] for example, used a combination of i.r. spectroscopy and titration for qualitative and quantitative analysis of photolysis products, in contrast to the commoner g.l.c. method. A more recent paper[11] describes results in line with our own: benzyl chloride on direct photolysis in aqueous methanol yielded, *inter alia*, benzyl alcohol and benzyl methyl ether. Apart from work with benzyl halides there has been increasing interest paid recently to photolysis of alkyl and cycloalkyl halides, particularly by Kropp and his co-workers.[5] In line with our own observations, iodides were especially prone to undergo solvolysis, sometimes, as in the norbornane system, with concomitant Wagner–Meerwein rearrangements. A particularly interesting feature of this work[5] was deuterium incorporation from CH_3OD into reduction products from some halides, and intermediacy of anions derived by nucleophile attack on n,σ^* excited states was suggested:



$$\mathrm{Nuc{:}}\ \overset{\delta+}{\mathrm{X}} - \overset{\delta-}{\mathrm{R}} \longrightarrow \mathrm{:R}$$

We have not yet checked for similar deuterium incorporation into toluenes in our own work; if this were found, an additional route to these hydrocarbons would be added to the radical route shown in the Scheme.

EXPERIMENTAL

Instrumentation.—This was as described in a previous paper.[1]

Photolysis Substrates and Products.—Most were commercially available but some were synthesised by conventional procedures; the products were often identical to those obtained by photolysis of ammonium salts (previous paper).[1] All were purified by standard methods and had physical, including spectroscopic, properties in agreement with literature values and with expectation from structure. 3,5-Dimethoxybenzyl bromide, obtained by heating the alcohol with constant-boiling hydrobromic acid for 30 min at 60 °C, had m.p. 71 °C after sublimation (lit.,[12] m.p. 71—72 °C from light petroleum) (Found: C, 46.95; H, 5.1. Calc. for $C_9H_{11}BrO_2$: C, 46.75; H, 4.8%), $\tau(CDCl_3)$ 3.4—3.6 (3 H, m, Ar), 5.55 (2 H, s, CH_2), and 6.20 (6 H, s, OCH_3). 3,5-Dimethoxybenzyl acetate was obtained by the method of Zimmerman and Sandel[8] and had b.p. 121 °C at 0.4 mmHg (lit.,[8] b.p. 121.5 °C at 0.4 mmHg), $\tau(CDCl_3)$ 3.4—3.5 (3 H, m, Ar) 4.91 (2 H, s, CH_2), 6.20 (6 H, s, OCH_3), and 7.90 (3 H, s, $OCOCH_3$).

Procedures for Photolysis.—The general procedure was similar to that given previously,[1] the solutions after photolysis being used directly after addition of the calibrant (and sometimes being diluted with ether) for g.l.c. and g.l.c.–m.s. analyses. Detailed results have been given in Table 1 while retention times from the g.l.c. analyses and mass spectroscopic data are given in Table 2. Identification of the most important products from the photolyses was confirmed, as in the previous Paper, by comparison with the behaviour of authentic specimens in the g.l.c. and g.l.c.–m.s. analyses; in other cases, noted in

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* After this paper had been prepared for publication, a paper by Cristol and his co-workers became available, which dealt with the photolysis of some complex polycyclic halides (S. J. Cristol, D. P. Stull, and R. D. Daussin, *J. Amer. Chem. Soc.*, 1978, **100**, 6674). These authors state that '. . . McKenna and his co-workers have extended the Kropp hypothesis to benzyltrimethylammonium ion, benzyl chloride, and benzyl acetate, although without evidence to distinguish seriatim from simultaneous processes . . .'; the reference to Kropp's work appears to relate to his suggestion of successive formation of radical- and ion-pairs in photolysis of certain organic halides (as noted above; ref. 5). In fact we have felt (ref. 2 and also 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) and continue to feel, unable to distinguish the tight singlet radical pairs and intimate ion pairs with certainty as separate species. For loose singlet radical pairs derived from benzyl halides and acetates, but *quite specifically not* for those derived from quaternary benzylammonium salts, we suggested[2] partial conversion into solvent-separated ion pairs as part of a mechanistic Scheme, and we made this suggestion in order to provide a reasonable interpretation of the experimental observation of triplet solvolysis of the former substrates but not of the latter. Our views have been developed primarily from the work of Walling and his collaborators, which we quoted (*cf.* ref. 4 above), and from earlier theoretical views by one of us dealing with related aspects of the chemistry of geminate pairs (B. Brocklehurst, *Nature*, 1969, **221**, 921).

TABLE 2

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

Anisole (standard)	2.1 min/100 °C; 1.3 min/120 °C
3,5-Dimethoxybenzyl acetate (standard)	38 min/140 °C
Benzyl chloride; bromide; iodide; acetate; 3,5-dimethoxybenzyl bromide	2.3 min/120 °C; 3.8 min/120 °C; 6.6 min/120 °C; 5.5 min/120 °C; 2.8 min/140 °C
2-Phenylethanol	4.6 min/120 °C; 122 ($M^{+\cdot}$); 92 ($C_7H_8^{+\cdot}$; $M^{+\cdot} - CH_2O$), 91 ($C_7H_7^+$; $M^{+\cdot} - CH_3O\cdot$), 65 ($C_5H_5^+$; $M^{+\cdot} - C_3H_5O\cdot$)
2-Methyl-4-phenylbutan-2-ol, $PhCH_2CH_2CMe_2OH$	7.5 min [c]/140 °C; $M^{+\cdot}$ not observed, 149 ($M^{+\cdot} - CH_3\cdot$), 146 ($M^{+\cdot} - H_2O$), 131 ($M^{+\cdot} - H_2O - CH_3\cdot$), 105 ($M^{+\cdot} - C_3H_7O\cdot$), 91 ($C_7H_7^+$; $M^{+\cdot} - C_4H_9O\cdot$), 77 ($C_6H_5^+$; $M^{+\cdot} - C_5H_{11}O\cdot$), 59 ($M^{+\cdot} - C_8H_9\cdot$)
Benzylacetone	9 min/140 °C; 148 ($M^{+\cdot}$), 133 ($M^{+\cdot} - CH_3\cdot$), 105 ($M^{+\cdot} - CH_3CO\cdot$), 91 ($C_7H_7^+$; $M^{+\cdot} - CH_3COCH_2\cdot$), 43 ($M^{+\cdot} - C_8H_9\cdot$)
3,5-Dimethoxyphenylethane	7 min/140 °C; 166 ($M^{+\cdot}$), 151 ($M^{+\cdot} - CH_3\cdot$), 121 ($M^{+\cdot} - C_2H_5O\cdot$)
3-Phenylpropan-2-ol, $PhCH_2CHOHMe$	3.7 min/100 °C; 136 ($M^{+\cdot}$), 134 ($M^{+\cdot} - H_2$), 92 ($M^{+\cdot} - C_2H_4O$), 91 ($C_7H_7^+$; $M^{+\cdot} - C_2H_5O\cdot$)
Benzyl ethyl ether	1.8 min/100 °C; 136 ($M^{+\cdot}$), 135 [d] ($M^{+\cdot} - H\cdot$), 107 ($M^{+\cdot} - C_2H_5\cdot$), 92 ($M^{+\cdot} - C_2H_4O$), 91 $C_7H_7^+$; $M^{+\cdot} - C_2H_5O\cdot$), 65 ($C_5H_5^+$; $M^{+\cdot} - C_4H_7O\cdot$)
Phenylethane	1.2 min/100 °C; 106 ($M^{+\cdot}$), 91 ($C_7H_7^+$; $M^{+\cdot} - CH_3\cdot$), 65 ($C_5H_5^+$; $M^{+\cdot} - C_3H_6\cdot$)
Four isomeric benzyl piperylenes [e]	158 ($C_{12}H_{14}^{+\cdot}$; $M^{+\cdot}$), 143 ($M^{+\cdot} - CH_3\cdot$), 91 ($C_7H_7^+$; $M^{+\cdot} - C_5H_7\cdot$)

[a] Data for some products already given in Table 4 of ref. 1. [b] Undecomposed volatile reactants also identified by g.l.c.–m.s. [c] Response probably from olefin formed by dehydration of tertiary alcohol; *cf.* m.s. results. [d] This peak is very small if sample is injected directly into the mass spectrometer rather than *via* the g.l.c. attachment. [e] Four peaks preceded bibenzyl in (usually) temperature-programmed runs. M.s. differed only in relative intensities of peaks for different isomers.

Table 1, tentative structures or partial structures were assigned on the basis of the observed fragmentation patterns.

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