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PHOTOCHEMICAL TRANSFORMATIONS. XVI. SINGLET AND TRIPLET PHOTOREACTIONS OF BENZYL CHLORIDE IN PROTIC SOLVENTS[1]

Stanley J. Cristol* and Brian E. Greenwald
Department of Chemistry, University of Colorado
Boulder, Colorado 80309

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Some time ago, Zimmerman and his coworkers reported[2] that a variety of appropriately substituted benzyl chlorides and acetates suffered hydrolysis in aqueous dioxan when subjected to direct irradiation. Shortly afterwards, Jeger and Schaffner and their coworkers reported[3] that α-p-toluenesulfonoxy ketones also solvolyzed upon direct irradiation (not, however, on triplet sensitization) and demonstrated the carbenium-ion character of the intermediates. Benzyldimethylsulfonium ion, as the fluoborate, and related compounds were irradiated at 254 nm in methanol, t-butyl alcohol and acetonitrile by Maycock and Berchtold,[4] who found that solvolysis products predominated over radical products. Similar results were seen in the direct irradiation of benzyltrimethylammonium, dibenzyldimethylammonium, and tribenzylmethylammonium halides at 254 nm by Ratcliff and Kochi.[5] These authors showed,by competitive capture rates of various alcohols, that the photosolvolyses involved benzyl cations (photochemical S_N1) rather than concerted (S_N2) displacement reactions.

More recently, McKenna and his coworkers[6] looked at the mechanisms of the photoreactions of benzyltrimethylammonium bromide and iodide in more detail. They observed that acetone-sensitized photoreaction led only to homolytic cleavage of the carbon-nitrogen bond, ultimately giving products derived from benzyl radicals. On the other hand, direct irradiation gave solvolysis products (benzyl alcohol and benzyl t-butyl ether) from irradiation in aqueous t-butyl alcohol, as well as some bibenzyl and toluene, from the bromide salt, and more than 90% yield of benzyl methyl ether from the iodide salt in methanol. They concluded that the radical reaction involved the triplet state of the benzyltrimethylammonium salt, while the heterolytic reaction involved the singlet state. We wish now to report our results on photoreactions of benzyl chloride (1), where precisely opposite results obtain--direct irradiation gives products from benzyl radicals and chlorine atoms and photosensitization with acetone or acetophenone leads to products from benzyl cations.

$PhCH_2Cl$

1

$PhCH_2OR$

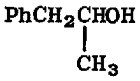
2

$PhCH_2CH_2Ph$

3

$PhCH_2CH_2OH$

4



$PhCH_2CH(OH)CH_3$

5

Although, as noted above, certain benzyl or substituted benzyl derivatives give solvolysis products upon direct irradiation, when 1 was irradiated in methanol in a Rayonet photoreactor with 254 nm light, the halide was consumed rapidly, but no benzyl methyl ether (2-OMe) was found. Instead, the products were bibenzyl (3) and 2-phenylethanol (4) in a ratio of 1:2. These are obviously the end products of a primary photolytic homolysis of 1 into benzyl radicals and chlorine atoms. If the chlorine atom abstracts a hydrogen atom from methanol, an hydroxymethyl radical would result. Combination of this with a benzyl radical gives 4, while combination of two benzyl radicals gives 3. Similar results were observed in ethanol, leading to 3 and to 5.

On the other hand, quite different results were seen with triplet sensitizers. Thus, with 10% acetone in ethanol or in isopropyl alcohol, solutions of 1 were converted to the corresponding ethers 2, when irradiated in Pyrex tubes with an Hanovia 450-W type L lamp. 1 in ethanol was converted to 2-OEt with 0.1 M benzonitrile as sensitizer. Solvolysis also occurred in acetic acid and in formic acid to the corresponding esters when 10% acetone was present. Dark reactions in all of these cases were negligible.

With 0.4 M acetophenone and 0.4 M 1, solvolysis occurred readily upon irradiation with 300 nm light in methanol, ethanol, isopropyl alcohol and formic and acetic acids.

Under the conditions used, the sole volatile products noted were the solvolysis products. Thus the triplet state of 1 in each of the solvents gives, within our ability to measure, only the ethers 2 from 1 in methanol, ethanol and 2-propanol and only the esters (benzyl acetate or formate) from 1 in acetic or formic acid. No radical products (toluene, 3, 4 or 5) were noted.[7] Further evidence of the triplet nature of the process may be noted from the fact that about 0.002 M piperylene quenches one half of the 2-OMe formation rate. Chemical yields were close to quantitative in preparative experiments.

The benzyl cations produced in the photosolvolysis have properties similar to those produced from benzyl chloride and silver ion, as measured by capture ratios for different alcohols. Thus, cations produced from photosolvolyzed benzyl chloride (acetophenone sensitization) in methanol-isopropyl alcoholmixtures have a capture ratio (k_{MeOH}/k_{i-PrOH}) of 2.5 ± 0.7 over a range of 4-75% methanol, compared with a similar ratio of 2.4 ± 0.2 for the silver-ion promoted reaction. These data and those of Kochi[5] suggest that the benzyl ions produced in the two photochemical processes (one sensitized and one not) are close to "normal" in behavior--that is, they are in the electronic ground state, and probably thermally equilibrated as well, at the time of coordination with solvent.

Why the nature of the leaving group has such a great bearing upon the effect of multiplicity on the reaction course remains to be understood. Experiments to test whether this dichotomy is general or not, and to test whether structural changes in the benzylic group, as well as in the leaving group, are important, are necessary for understanding these phenomena.

Some of these, as well as studies of solvent effects and quantum yield measurements, are in progress.

Analyses of reaction mixtures were performed by gas chromatography using 15% diethylene glycol succinate on Chromosorb W, 100-200 mesh, columns and flame ionization detection.

ACKNOWLEDGEMENT

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