Solvolytic and Radical Processes in the Photolysis of Benzylammonium Salts

M. A. RATCLIFF, JR., AND J. K. KOCHI*

Department of Chemistry, Indiana University, Bloomington, Indiana 47401

Received February 8, 1971

Photolysis of various benzylammonium halides with 254-nm light proceeds by concurrent heterolytic and homolytic pathways. In alcohol solutions photolysis produces benzyl ethers and amines, whereas in aprotic media collapse of the ion pair affords benzyl halides. The competing homolytic process generates toluene and an aminocarbonium ion by cage disproportionation of the benzyl radical with its aminium fragment. Bibenzyl formed by dimerization outside the cage is a minor product. No evidence is found for charge transfer processes between the ammonium moiety and its halide counterion. The dichotomy between heterolytic and homolytic paths in the photolysis of benzylammonium salts, benzylsulfonium salts, and benzyl esters are compared. The photolysis of benzylammonium salts are formally related to a variety of other thermal reactions of species containing a quaternary nitrogen center. The importance of ion pairs and cage processes in these photochemical reactions is discussed.

Irradiation of various benzylamines in the π–π^* band with 254-nm light leads to photolysis of the benzyl–nitrogen bond.(1) Photochemistry is largely associated with subsequent reactions involving cage processes of the benzyl radical and the nitrogen-centered radical I (eq 1).

$$\mathrm{PhCH_2NR_2} \longrightarrow \mathrm{PhCH_2\cdot} + \underset{\mathrm{I}}{\cdot\mathrm{NR_2}} \qquad (1)$$

$$\mathrm{R} = \mathrm{H},\ \mathrm{CH_3},\ \mathrm{PhCH_2}$$

Aliphatic amines are also photolyzed under similar conditions probably by involvement of the n–σ^* transition.(2) Partly to offset the latter and partly to examine the chemistry of nitrogen cation radicals, we undertook an examination of the photolysis of various benzylammonium salts. In this study we wish to show that competing homolytic and heterolytic pathways are involved in the photolysis of benzylammonium salts. An analogous dichotomy was reported for the photolysis of benzylsulfonium salts after this work was completed.(3)

Comparisons with the photolysis of phosphonium and other onium salts are also pertinent. Thus, benzyltriphenylphosphonium chloride was irradiated in benzene and ethanol solutions.(4) It was proposed that the products arose from decomposition of the phosphoranyl radical II formed by a reversible electron transfer between chloride ion and the phosphonium ion (eq 2).

$$[\mathrm{PhCH_2PPh_3}]^+\mathrm{Cl}^- \xrightarrow{h\nu} \mathrm{Cl\cdot} + \underset{\mathrm{II}}{[\mathrm{PhCH_2PPh_3}]\cdot} \longrightarrow \text{etc.} \qquad (2)$$

Homolysis of II apparently led to products derived from the coupling of benzyl and phenyl radicals together with di- and triphenylphosphines. No chlorine-containing products were reported. However, phosphorus compounds are particularly susceptible to homolytic displacement (substitution) and other processes may also be involved.(5)

An aqueous solution of dimethylphenacylsulfonium bromide was irradiated through a Pyrex filter to 90% conversion.(6) An initial cleavage of the phenacyl–sulfur bond followed by electron transfer from the bromide ion to the dimethylsulfonium radical was proposed (eq 3). Alternative routes involving nucleophilic substitution or electron transfer between bromide ion and the sulfonium ion in an excited state were ruled out, since the same cationic species, in which the bromide ion was replaced by tetrafluoroborate ion, was photolyzed in alcoholic media with similar results.(3) Others, however, have proposed an initial step in which electron transfer from a halide ion to the triarylsulfonium ion occurred on photolysis in ethanol.(7)

$$[\mathrm{PhCOCH_2S(CH_3)_2}]^+\mathrm{Br}^- \xrightarrow{h\nu} \mathrm{PhCOCH_2\cdot} + \mathrm{(CH_3)_2S\cdot}^+ \xrightarrow{\mathrm{Br}^-} \mathrm{(CH_3)_2S} + \mathrm{Br\cdot},\ \text{etc.} \qquad (3)$$

Similar electron transfer processes were postulated for the photolysis of trimethylanilinium salts (eq 4),

$$[\mathrm{PhN(CH_3)_3}]^+\mathrm{Br}^- \xrightarrow{h\nu} [\mathrm{PhN(CH_3)_3, Br}]^* \longrightarrow \mathrm{Ph\cdot} + \mathrm{(CH_3)_3N} + \mathrm{Br\cdot} \qquad (4)$$

and the highest conversions (90% anisole) were achieved with anisyltrimethylammonium iodide.(8a) An aromatic chromophore attached directly to nitrogen appeared necessary since cyclohexyltrimethylammonium iodide was unchanged on prolonged photolysis and the benzyl analog gave only 10% toluene. No halogen-containing products were reported. On the other hand, sensitized decomposition of these ammonium salts by acetone occurs by transfer of triplet energy to the ion pairs.(8b)

Results and Discussion

A series of primary ($\mathrm{RNH_3^+X^-}$), secondary ($\mathrm{R_2NH_2^+X^-}$), tertiary ($\mathrm{R_3NH^+X^-}$), and quaternary ($\mathrm{R_4N^+X^-}$) ammonium salts were irradiated with 254-nm light from a low-pressure mercury source. All of these salts contained at least one benzyl group in the ammonium moiety and chloride, bromide, or alkoxide as the counterion. Various alcohols and acetonitrile were used as solvents. The ultraviolet absorption spectra of these salts in methanol are shown in Figure 1. No distinction could be made between the bromide and chloride salts in this medium. Figure 1 also shows the

---

(1) M. A. Ratcliff, Jr., and J. K. Kochi, unpublished work.

(2) (a) C. H. Bamford, *J. Chem. Soc.*, 17 (1939); 1504 (1935); (b) H. J. Emeleus and L. J. Jolley, *ibid.*, 928 (1935); (c) P. J. Kozak and H. Gesser, *ibid.*, 448 (1960); (d) J. V. Michael and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **85**, 1228 (1963); R. P. Porter and W. A. Noyes, Jr., *ibid.*, **81**, 2307 (1959); (e) S. G. Hadley and P. H. Volman, *ibid.*, **89**, 1053 (1967).

(3) A. L. Maycock and G. A. Berchtold, *J. Org. Chem.*, **35**, 2532 (1970).

(4) C. E. Griffin and M. L. Kaufman, *Tetrahedron Lett.*, 773 (1965).

(5) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3944 (1969).

(6) T. Laird and H. Williams, *Chem. Commun.*, 561 (1969).

(7) (a) J. Knapczyk and W. McEwen, *J. Amer. Chem. Soc.*, **91**, 145 (1969); (b) *J. Org. Chem.*, **35**, 2539 (1970).

(8) (a) T. D. Walsh and R. C. Long, *J. Amer. Chem. Soc.*, **89**, 3943 (1967); (b) C. Pac and H. Sakurai, *Chem. Commun.*, 20 (1969); *Tetrahedron Lett.*, 1865 (1968); (c) J. D. Mee, D. W. Heseltine, and E. C. Taylor, *J. Amer. Chem. Soc.*, **92**, 5814 (1970).

TABLE I

PRODUCTS DERIVED FROM THE PHOTOLYSIS OF BENZYLAMMONIUM SALTS[a]

Benzylammonium salt	Solvent	Products, mmol			
		$PhCH_3$	$(PhCH_2)_2$	$PhCH_2Cl$	$PhCH_2OCH_2CH_3$
$(PhCH_2)_2N(CH_3)_2^+ Cl^-$	CH_3CN	0.28	0.05[b]	0.12	
$(PhCH_2)_2N(CH_3)_2^+ Cl^-$	CH_3CN	0.37	0.06[b]	0.15 0.05[c]	
$(PhCH_2)_2N(CH_3)_2^+ Cl^-$	EtOH	0.33	0.03[d]	*e*	0.30
$(PhCH_2)_2N(CH_3)_2^+ OEt^-$	EtOH	0.59	0.09[d]	*e*	0.32
$PhCH_2N(CH_3)_3^+ Cl^-$	CH_3CN	0.22	*f*	0.05	
$PhCH_2N(CH_3)_3^+ Cl^-$	EtOH	0.37	*f*	*e*	0.26

[a] Under standard conditions using 10 ml of 0.1 *M* salt solution for 120 min. [b] In addition to 0.02 mmol of benzaldehyde found after hydrolysis. [c] *N*-Benzylacetamide after hydrolysis. [d] Benzaldehyde, <0.01. [e] <0.01. [f] Not determined.

similarity between toluene and the chromophores in the ammonium salts, the molar absorptivities of which are approximately proportional to the number of benzyl groups attached to nitrogen.

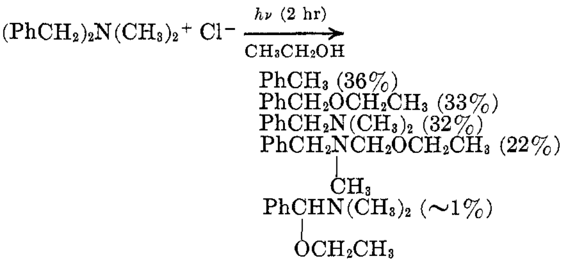
Products and Stoichiometry.—The photolysis of a solution of 0.1 *M* dibenzyldimethylammonium chloride in acetonitrile afforded toluene, bibenzyl, benzyl chloride, and *N*-benzylacetamide. The latter was identified after hydrolysis and no doubt arose *via* the nitrilium salt III[9] (eq 5).

$$PhCH_2^+ + CH_3CN \longrightarrow \underset{\text{III}}{[PhCH_2NCCH_3]^+} \xrightarrow{H_2O} PhCH_2NHCOCH_3 \quad (5)$$

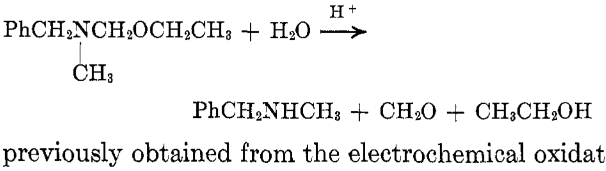
The photolysis of dibenzyldimethylammonium chloride in ethanol afforded the same products, with the exception of *N*-benzylacetamide and benzyl chloride which were largely replaced by benzyl ethyl ether as indicated in Table I. Substituting the chloride counterion with ethoxide had no profound effect on the products obtained.

The photolysis of 0.1 *M* benzyltrimethylammonium chloride in acetonitrile or in ethanol also afforded toluene and bibenzyl, together with benzyl chloride(acetamide) or benzyl ethyl ether, respectively. Benzyl chloride was solvolytically stable to irradiation under these conditions.

Toluene, bibenzyl, benzyl chloride, and benzyl ethyl ether were analyzed by gas chromatography after a separation of the ammonium salts, since the latter were readily pyrolyzed to benzyl chloride and free amine. The amines were separated by column chromatography on basic alumina followed by gas chromatography. A more complete accounting of the products including amines from the photolysis of dibenzyldimethylammonium chloride in ethanol is given in eq 6. The isomeric ethoxybenzyldimethylamines given in eq 6 were difficult to obtain pure and were identified by their hydrolysates (eq 7). Analogous alkoxyamines were

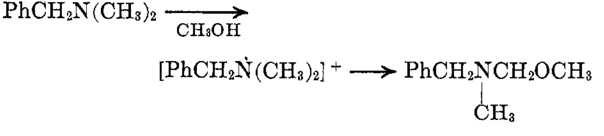


$$(PhCH_2)_2N(CH_3)_2^+ Cl^- \xrightarrow[CH_3CH_2OH]{h\nu\ (2\ hr)} \begin{array}{l} PhCH_3\ (36\%) \\ PhCH_2OCH_2CH_3\ (33\%) \\ PhCH_2N(CH_3)_2\ (32\%) \\ PhCH_2\underset{\underset{CH_3}{|}}{N}CH_2OCH_2CH_3\ (22\%) \\ Ph\underset{\underset{OCH_2CH_3}{|}}{C}HN(CH_3)_2\ ({\sim}1\%) \end{array} \quad (6)$$



$$PhCH_2\underset{\underset{CH_3}{|}}{N}CH_2OCH_2CH_3 + H_2O \xrightarrow{H^+} PhCH_2NHCH_3 + CH_2O + CH_3CH_2OH \quad (7)$$

previously obtained from the electrochemical oxidation of benzyldimethylamine in alcoholic solutions (eq 8),[10]



$$PhCH_2N(CH_3)_2 \xrightarrow[CH_3OH]{\text{elec oxidn}} [PhCH_2\dot{N}(CH_3)_2]^+ \longrightarrow PhCH_2\underset{\underset{CH_3}{|}}{N}CH_2OCH_3 \quad (8)$$

and their behavior coincided with those produced in the photolysis (see Experimental Section).

We infer from these results that two concurrent processes were occurring on photolysis of dibenzyldimethylammonium chloride in alcohol: (1) a route to

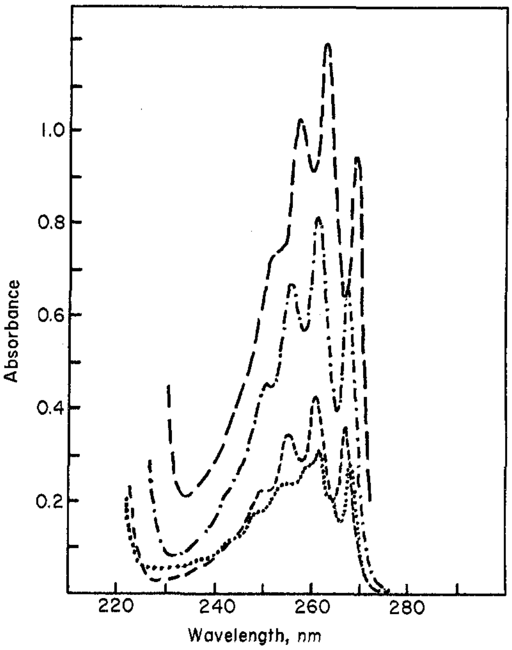


Figure 1.—The ultraviolet spectra of quaternary benzylammonium salts in methanol and their comparison with toluene: benzyltrimethylammonium bromide (1.00 × 10^{-3} *M*), ----; dibenzylammonium chloride (1.01 × 10^{-3} *M*), -·-·-; tribenzylammonium bromide (1.00 × 10^{-3} *M*), — — —; toluene (1.20 × 10^{-3} *M*), ...

---

[9] The capture of carbonium ions as intermediates by acetonitrile has been shown in a number of examples [see, *e.g.*, J. Kochi and A. Bemis, *ibid.*, **90**, 4038 (1968)]. Alkyl radicals, on the other hand, add to carbon [J. R. Shelton and C. W. Uzelmeir, *ibid.*, **88**, 5222 (1966); *cf.* also H. Ohta and K. Tokumaru, *Chem. Commun.*, 1601 (1970)]. *Cf.* J. Ritter and P. Minieri, *J. Amer. Chem. Soc.*, **70**, 4045, 4048 (1948).

[10] N. L. Weinberg and E. A. Brown, *J. Org. Chem.*, **31**, 4058 (1966); *cf.* also S. D. Ross, M. Finkelstein, and R. C. Peterson, *J. Amer. Chem. Soc.*, **92**, 6003 (1970).

benzyl ethers and benzyldimethylamine and (2) a route to toluene and alkoxybenzyldimethylamine. The stoichiometric relationship among these products is given in eq 9, 10. The participation of these two paths in the

$$(PhCH_2)_2N(CH_3)_2{}^+Cl^- \xrightarrow[h\nu]{ROH} \begin{cases} PhCH_2OR + PhCH_2N(CH_3)_2 + HCl & (9) \\ PhCH_3 + PhCH_2N(CH_3)CH_2OR + HCl & (10) \end{cases}$$

photolysis of various benzylammonium salts was most readily and expeditiously compared by examining the formation of the most stable products: (a) benzyl ether and other benzyl derivatives from path 9 and (b) toluene from path 10. The yields of bibenzyl were generally low (Table I) and represented "leakage" from the homolytic pathway.

Heterolytic and Homolytic Pathways.—We propose that these two processes be designated as heterolytic and homolytic in the manner shown in eq 11, 12. The

$$(PhCH_2)_2N(CH_3)_2{}^+ \xrightarrow{h\nu} \begin{cases} \xrightarrow{hetero} PhCH_2{}^+ + PhCH_2N(CH_3)_2 & (11) \\ \xrightarrow{homo} PhCH_2\cdot + PhCH_2\dot{N}(CH_3)_2{}^+ & (12) \end{cases}$$

formation of benzyl ethers and tertiary amines always in equimolar amounts provides support for a heterolytic pathway involving alcoholysis of the benzyl cation. In the aprotic acetonitrile medium, benzyl chloride and *N*-benzylacetamide (after hydrolysis) represent capture of the benzyl cation by the counterion or the solvent (eq 5). The alternative possibility in which benzyl chloride is formed from chlorine atoms and benzyl radicals generated in a charge transfer process (eq 13) is

$$(PhCH_2)_2N(CH_3)_2{}^+ Cl^- \xrightarrow{h\nu} [(PhCH_2)_2N(CH_3)_2\cdot, Cl\cdot] \longrightarrow PhCH_2Cl + PhCH_2N(CH_3)_2 \quad (13)$$

difficult to reconcile with the preferential formation of benzyl ethers when photolysis was carried out in an alcoholic medium. Furthermore, the formation of ether *via* alcoholysis of an immonium ion (eq 14) follow-

$$PhCH_2N(CH_3)CH_2{}^+ + ROH \longrightarrow PhCH_2OR + CH_3N{=}CH_2 + H^+ \quad (14)$$

ing homolysis and disproportionation (*vide infra*) is inconsistent with the observation of similar products in equivalent yields from the photolysis of benzyltrimethylammonium chloride. The close correspondence between the yields of benzyl ether and tertiary amine also does not support a formulation in which the latter is formed by loss of a proton from the radical cation followed by further reactions of the resultant radical with solvent (eq 15).

$$PhCH_2\dot{N}(CH_3)_2{}^+ \xrightarrow{-H^+} PhCH_2N(CH_3)CH_2\cdot \xrightarrow{HS} PhCH_2N(CH_3)_2 + S\cdot, \text{etc.} \quad (15)$$

Additional support for the solvolytic pathway was obtained by carrying out the photolysis of dibenzyldimethylammonium chloride in *tert*-butyl alcohol solutions. The principal solvolytic product was benzyl *tert*-butyl ethers together with small but significant amounts of benzyl chloride (eq 16). Photolysis of

$$(PhCH_2)_2N(CH_3)_2{}^+ Cl^- \xrightarrow[(CH_3)_3COH]{h\nu\ (2\ hr)} \begin{matrix} PhCH_3\ (27\%) \\ PhCH_2N(CH_3)_2\ (13\%) \\ PhCH_2Cl\ (3\%) \\ PhCH_2OC(CH_3)_3\ (9\%) \end{matrix} \quad (16)$$

dibenzyldimethylammonium chloride in a mixture of *tert*-butyl alcohol and ethanol afforded both benzyl ethyl ether and benzyl *tert*-butyl ether (eq 17). The

$$(PhCH_2)_2N(CH_3)_2{}^+ Cl^- \xrightarrow[tert\text{-}BuOH\ (89)]{EtOH\ (24)} \begin{matrix} PhCH_3\ (32\%) \\ PhCH_2N(CH_3)_2\ (20\%) \\ PhCH_2Cl\ (2\%) \\ PhCH_2OCH_2CH_3\ (4.5\%) \\ PhCH_2OC(CH_3)_3\ (10.5\%) \end{matrix} \quad (17)$$

yields of the two ethers, after normalization by the solvent composition, indicated that partitioning of the benzyl cation by *tert*-butyl alcohol was only 0.6 times less favorable than by ethanol. The low selectivity supports a process in which extensive heterolysis of the benzyl–nitrogen bond has occurred prior to solvation (*vide infra*).

The formation of a relatively large amount of toluene from the photolysis of various benzylammonium salts is attributed to a competing homolysis of the benzyl–nitrogen bond during photolysis. We propose that toluene arose by cage disproportionation of the benzyl radical aminium ion pair. Further reaction of the isomeric aminocarbonium ions IV and V with nucleophiles extant in solution led to a mixture of labile amines not readily characterized.[10] Acid-catalyzed hydrolysis of the mixture, however, generated benzylmethylamine from path 18 and benzaldehyde from path 19. From this analysis we deduce that dispro-

$$[PhCH_2\cdot\ PhCH_2\dot{N}(CH_3)_2{}^+] \xrightarrow{h\nu} \begin{cases} PhCH_3 + \underset{IV}{[PhCH_2N(CH_3)CH_2]^+} & (18a) \\ PhCH_3 + \underset{V}{[PhCHN(CH_3)_2]^+} & (19a) \end{cases}$$

$$IV \xrightarrow{ROH} PhCH_2N(CH_3)CH_2OR \quad (18b)$$

$$V \xrightarrow{ROH} PhCH(OR)N(CH_3)_2 \quad (19b)$$

portionation toward the methyl group (eq 18a) far outweighed that to the benzyl group (eq 19a). A similar situation pertained to the same cation radical formed from the electrooxidation of benzyldimethylamine in methanol,[10,11] although the mechanistic interpretations of the results differ.

The cage disproportionation of the radical pair derived by homolysis (eq 18, 19) is supported by scavenger studies involving molecular oxygen and by solvent variations. The photolysis of dibenzyldimethylammonium chloride in ethanol was essentially unaffected by the presence of 10 psig of oxygen (Table II) which shows that benzyl radicals were unavailable to oxygen under these conditions. Furthermore, if toluene were formed by hydrogen abstraction from solvent, its absolute yield should have increased on changing the solvent from *tert*-butyl alcohol to methanol or ethanol consistent with the reactivity of α hydrogens in alcohols. The results were also not largely different in an aprotic

---

[11] P. J. Smith and C. K. Mann, *J. Org. Chem.*, **33**, 316 (1968). See also, *ibid.*, **32**, 1474 (1967); **34**, 1821 (1969); **35**, 2175 (1970).

TABLE II

EFFECTS OF STRUCTURE OF THE BENZYLAMMONIUM SALT ON THE YIELDS OF PRODUCTS[a]

Benzylammonium halide	Solvent (ROH)	Mol %[b] PhCH$_3$	Mol %[b] PhCH$_2$OR	PhCH$_2$OR/PhCH$_3$
$PhCH_2N(CH_3)_3^+ Cl^-$	CH_3OH	27	54	2.0
$PhCH_2N(CH_3)_3^+ Cl^-$	EtOH	37	26	0.7
$(PhCH_2)_2N(CH_3)_2^+ Cl^-$	CH_3OH	29	68	2.3
$(PhCH_2)_2N(CH_3)_2^+ Cl^-$	EtOH	33	30	0.9
$(PhCH_2)_2N(CH_3)_2^+ Cl^-$	EtOH/O_2[c]	34	29	0.85
$(PhCH_2)_3NCH_3^+ Br^-$	CH_3OH	20	69	3.5
$(PhCH_2)_3NCH_3^+ Br^-$	EtOH	15	24	1.6
$PhCH_2N(n\text{-Hex})_3^+ Br^-$	CH_3OH	19	25	1.3
$(PhCH_2)_2NH(CH_3)^+ Cl^-$	CH_3OH	2.5	7	2.8
$(PhCH_2)_3NH^+ Cl^-$	CH_3OH	7	26	3.7
$(PhCH_2)_2NH_2^+ Cl^-$[d]	CH_3OH	e	3	
$PhCH_2NH_3^+ Cl^-$[d]	CH_3OH	e	~1	

[a] Photolysis of 0.1 *M* ammonium halide with 2537-Å light for 2 hr at 30°. [b] Conversion based on moles formed per mole of salt. [c] Run under 10 psi of O_2 after flushing with O_2. [d] Photolysis time, 10 hr. [e] <0.3

TABLE III

QUANTUM YIELDS FOR THE PHOTOCHEMICAL DECOMPOSITION OF BENZYLAMMONIUM SALTS

Benzylammonium salt	Solvent	Φ (ether)	Φ (PhCH$_3$)	Φ (*t*)	Φ (ether)/Φ (PhCH$_3$)
$PhCH_2N(CH_3)_3^+ Cl^-$	EtOH	0.14	0.18	0.32	0.78
$PhCH_2N(CH_3)_3^+ Cl^-$	CH_3OH	0.31	0.19	0.50	1.6
$PhCH_2N(CH_3)_3^+ Br^-$	CH_3OH	0.23	0.17	0.40	1.3
$(PhCH_2)_2N(CH_3)_2^+ Cl^-$	EtOH	0.16	0.21	0.37	0.76
$(PhCH_2)_2N(CH_3)_2^+ EtO^-$	EtOH	0.15	0.18	0.33	0.83
$(PhCH_2)_2N(CH_3)_2^+ Cl^-$	CH_3OH	0.34	0.18	0.52	1.9
$(PhCH_2)_3NCH_3^+ Br^-$	CH_3OH	0.26	0.097	0.36	2.7
$(PhCH_2)_3NH^+ Cl^-$	CH_3OH	0.075	0.019	0.094	3.9

medium such as acetonitrile. Measurements of quantum yields (*vide infra*) also support these conclusions based on product studies.

Effects of Alkylation.—A series of benzylammonium salts were photolyzed in alcohol solutions under a given set of standard conditions. The effects of alkylation and the structure of the alkyl groups on the photolysis of these ammonium salts was compared by examining the yields of benzyl ethers and toluene (Table II). In general, quaternary ammonium salts underwent significantly more photolysis than tertiary ammonium salts. Among the latter, higher conversions resulted from tribenzylammonium chloride than from dibenzylmethylammonium chloride. Secondary and primary ammonium salts were rather inert to photolysis under comparable conditions. These salts are also the most extensively hydrogen bonded as ion pairs in solution.[12] However, the relationship is probably more relevant to stabilization of the nitrogen-containing fragments by alkylation, rather than any property intrinsically related to hydrogen bonding. The salutary effects of extensive alkylation on the photolysis of benzylammonium salts no doubt contributed largely toward obtaining good material balances in product studies, since little or no secondary reactions were observed even when the reactions were carried to beyond 80% completion.

For a series of benzylmethylammonium salts the ratios of benzyl ether/toluene increased with the number of benzyl groups, presumably with increasing steric strain. This ratio was also consistently higher in methanol than ethanol. Studies of the quantum yields (*vide infra*) in methanol showed that replacement of chloride by bromide resulted in a slight decrease in the rate of photochemical solvolysis.

Quantum Yields.—Some of the general features observed during the product studies were put on a more quantitative basis by measuring the quantum yields (see Experimental Section) for a variety of benzylammonium salts listed in Table III. These measurements were carried to less than 5% conversion of the benzylammonium salt and gave ratios of benzyl ether/toluene in excellent agreement with those obtained from product studies in which reactions were usually carried to very high conversions. The close agreement between the values obtained by these two methods further substantiates the absence of secondary photochemical processes. For example, if toluene resulted from the secondary decomposition of either benzyl chloride or bromide, the ratios of benzyl ether/toluene would have differed in the product studies from those obtained from the quantum yield studies.

The results in Table IV show that quantum yields for the formation of benzyl methyl ether and toluene from the photolysis of benzyltrimethylammonium chloride in methanol were invariant with the concen-

TABLE IV

EFFECT OF THE CONCENTRATION OF BENZYLTRIMETHYLAMMONIUM CHLORIDE IN METHANOL ON THE QUANTUM YIELD

$PhCH_2N(CH_3)_3^+ Cl^-$, *M*	Φ (PhCH$_3$)	Φ (PhCH$_2$OCH$_3$)	Φ total
0.05	0.16	0.35	0.51
0.10	0.19	0.31	0.50
0.25	0.17	0.32	0.49

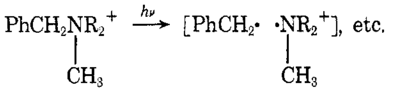
---

(12) (a) M. M. Davis, *Nat. Bur. Stand. (U. S.), Monogr.*, 105 (1968). (b) *Cf.* also *z* values of solvents as a measure of ion pairing [E. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 293 ff]. (c) For solvent effects on electronic states and spectra of molecules, see N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel Dekker, New York, N. Y., 1970, p 374 ff.

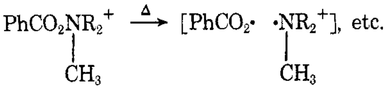
tration of salt. Processes which are kinetically second or higher order were, therefore, unimportant.

Patterns of substitution were not clearly reflected in the rates of formation of toluene. Thus, no appreciable difference was observed between benzyltrimethylammonium and dibenzyldimethylammonium ions in methanol, but the introduction of a third benzyl group resulted in a depression of the toluene rate.

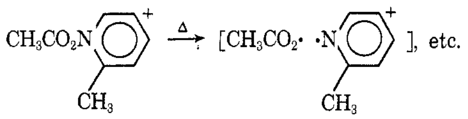
Radical Pairs and Disproportionation.—For a particular benzylammonium ion, the rate of formation of toluene was unaffected by changes in the counterion as well as the solvent. These results are inconsistent with a charge-transfer mechanism similar in type to those previously postulated for phosphonium, sulfonium, and anilinium salts.[4,7,8] Charge transfer should reflect the ease of photoionization of the anion and increase in importance from chloride (and alkoxide) to bromide.[13] The insensitivity to the environment of the quantum yield for toluene formation supports the formulation presented earlier (eq 18, 19) that disproportionation proceeds from a benzyl radical which is intimately associated with the aminium radical. Disproportionation of radical-cation pairs such as that given in eq 20 is analogous to those described in the thermal oxidation of amines with diacyl peroxides (eq 21),[14] the reaction of picoline *N*-oxides with acid anhydrides (eq 22),[15] as well as the Stevens and Meisenheimer rearrangements of quaternary ammonium salts and tertiary amine oxides (eq 23).[16] The investigation of the induced dynamic nuclear polarization of the toluene and amine should provide support for this formulation.[17]



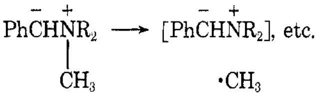
$$\mathrm{PhCH_2\underset{CH_3}{N}R_2{}^+ \xrightarrow{h\nu} [PhCH_2\cdot\ \cdot\underset{CH_3}{N}R_2{}^+],\ etc.} \qquad (20)$$



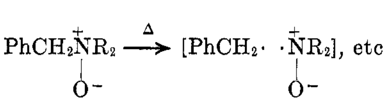
$$\mathrm{PhCO_2\underset{CH_3}{N}R_2{}^+ \xrightarrow{\Delta} [PhCO_2\cdot\ \cdot\underset{CH_3}{N}R_2{}^+],\ etc.} \qquad (21)^{14}$$



(22)[15]



$$\mathrm{Ph\overset{-}{C}H\overset{+}{\underset{CH_3}{N}}R_2 \longrightarrow [Ph\overset{-}{C}H\overset{+}{N}R_2],\ etc. \quad \cdot CH_3} \qquad (23a)^{16}$$



$$\mathrm{PhCH_2\overset{+}{\underset{O^-}{N}}R_2 \xrightarrow{\Delta} [PhCH_2\cdot\ \cdot\overset{+}{\underset{O^-}{N}}R_2],\ etc.} \qquad (23b)^{16}$$

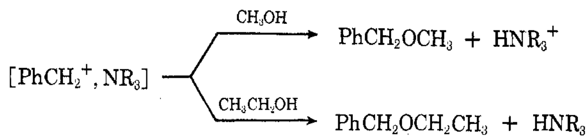
Benzyl Cations and Solvolysis.—The quantum yield for the formation of benzyl ether was markedly dependent on the solvent, in contrast to that observed for toluene. Changing the solvent from ethanol to methanol caused a twofold increase in the rate of formation of benzyl ether for both benzyltrimethylammonium and dibenzyldimethylammonium chlorides. Thus, the ratios of benzyl ether/toluene obtained from product studies of the photolysis of tribenzylammonium salts (Table II) reflect both an increase in the solvolytic product as well as a decrease in the free-radical product. By contrast, the differences in these ratios obtained from benzyltrimethylammonium and dibenzyldimethylammonium salts reflect increases in only the solvoltytic product.

Benzylammonium salts were photolyzed in a medium consisting of various mixtures of two alcohols. The ratios of benzyl ethyl ether/benzyl methyl ether obtained from the photolysis of dibenzyldimethylammonium chloride in mixtures of ethanol and methanol are shown in Figure 2. Since it is likely that benzyl methyl ether and benzyl ethyl ether arise from a common precursor, their relative rates of formation are given by the ratio of their quantum yields. The magnitudes of the slope (Table V) signify that benzyl methyl ether was formed 1.6 times more readily than benzyl ethyl ether and 2.7 times faster than benzyl *tert*-butyl ether. The linearity shown in Figure 2 over a wide range of solvent compositions indicates that the results may be extrapolated to the pure solvents (eq 24, 25).

TABLE V

RELATIVE RATES OF FORMATION OF ETHERS FROM THE PHOTOLYSIS THE BENZYLAMMONIUM SALTS IN ALCOHOLS

Benzylammonium salt	*k* (MeOH)/ *k* (EtOH)	*k* (MeOH)/ *k* (*tert*-BuOH)
$(\mathrm{PhCH_2})_2\mathrm{N(CH_3)_2}^+\ \mathrm{Cl}^-$	1.60	2.70
$\mathrm{PhCH_2N(CH_3)_3}^+\ \mathrm{Cl}^-$	1.60	



$$\mathrm{[PhCH_2{}^+, NR_3] \xrightarrow{CH_3OH} PhCH_2OCH_3 + HNR_3{}^+} \qquad (24)$$

$$\mathrm{[PhCH_2{}^+, NR_3] \xrightarrow{CH_3CH_2OH} PhCH_2OCH_2CH_3 + HNR_3{}^+} \qquad (25)$$

If the Grunwald–Winstein equation[18] can be applied to this system, the relative rates of ether formation are expressed by eq 26. The value of $m = 0.2$

$$\log k\,(\mathrm{CH_3OH}) - \log k\,(\mathrm{CH_3CH_2OH}) = m(-1.02 + 2.03) \qquad (26)$$

implies that the photochemical reaction leading to benzyl ether is relatively insensitive to the solvating power of the medium. Although nucleophilic substitution reactions of the $\mathrm{S_N2}$ type usually show this behavior, the low solvent selectivity can be explained in an alternative manner. As seen in Tables II and

---

[13] (a) C. Czapski, J. Ogdan, and M. Ottolenghi, *Chem. Phys. Lett.*, **3**, 383 (1969); (b) L. E. Orgel, *Quart. Rev., Chem. Soc.*, **8**, 422 (1954); (c) H. L. Friedman, *J. Chem. Phys.*, **21**, 319 (1953); (d) E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).

[14] (a) L. Horner and B. Anders, *Chem. Ber.*, **95**, 2470 (1962); (b) C. Walling and N. Indictor, *J. Amer. Chem. Soc.*, **80**, 5814 (1958); (c) T. Sato and T. Otsu, *Chem. Ind. (London)*, 125 (1970).

[15] (a) V. J. Traynelis and R. F. Martello, *J. Amer. Chem. Soc.*, **80**, 6590 (1958); **82**, 2744 (1960); also **87**, 5710 (1965). (b) S. Oae, T. Kitao, and Y. Kitaska, *ibid.*, **84**, 3359 (1962); *Tetrahedron*, **20**, 2685 (1964); *Tetrahedron Lett.*, 917 (1968), and related papers. (c) T. Cohen and J. H. Fager, *J. Amer. Chem. Soc.*, **87**, 5701 (1965); also **89**, 4968 (1969). (d) T. Koenig, *ibid.*, **88**, 4045 (1966); *Tetrahedron Lett.*, 2751 (1967); 3127 (1965); *J. Org. Chem.*, **33**, 1530 (1968); **35**, 500 (1970). (e) H. Iwamura, M. Iwamura, T. Nishida, and S. Saot, *J. Amer. Chem. Soc.*, **92**, 7475 (1970).

[16] (a) V. Schöllkopf, U. Ludwig, M. Patsch, and W. Franken, *Justus Liebigs Ann. Chem.*, **703**, 77 (1967); *Chem. Ber.*, **101**, 2224 (1968); see also U. Schöllkopf and I. Hoppe, *Tetrahedron Lett.*, 4527 (1970), 3415 (1969); (b) J. P. Lorand, R. W. Grant, P. A. Samuel, E. O'Connell, and J. Zero, *ibid.*, 4087 (1969); (c) A. R. Lepley, P. M. Cook, and G. F. Willard, *J. Amer. Chem. Soc.*, **92**, 1101 (1970); *Chem. Commun.*, 1460 (1969); (d) S. H. Pine, B. A. Catto, and F. G. Yamagishi, *J. Org. Chem.*, **35**, 3663 (1970); (e) N. Castagnoli, J. C. Craig, A. P. Melikian, and S. K. Roy, *Tetrahedron*, **26**, 4319 (1970); D. G. Morris, *Chem. Commun.*, 221 (1971); A. R. Lepley and A. G. Guimanini, *J. Org. Chem.*, **36**, 1217 (1971).

[17] G. L. Closs and D. R. Paulson, *J. Amer. Chem. Soc.*, **92**, 7231 (1970); G. L. Closs and A. D. Trifunac, *ibid.*, **92**, 2183, 7221 (1970).

[18] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951).

III, increasing the steric bulk around nitrogen by substituting benzyl for methyl groups did not depress the yield of ether as would be expected in an SN2 process. A slight increase, in fact, was observed. At the opposte extreme, photolysis of the benzyl–nitrogen bond could produce a benzyl cation and a neutral amine separated by a molecular diameter or more due to the absorbed energy in excess of that required for bond breaking.[19] The benzyl cation formed under these conditions should be relatively free of the influence of its uncharged partner and problems associated with ion pairing usually important in solvolysis of benzyl derivatives are minimal. A completely free carbonium ion is not necessarily implied, however, since the amine fragment may still perturb the ion. The low *m* values then reflect the low selectivity of the benzyl cation toward nucleophiles rather than an SN2 attack on a photoexcited state of the benzylammonium ion.

Ion Pairs.—As mentioned earlier the formation of benzyl halides during photolysis of benzylammonium halides in acetonitrile solutions is also interpreted as arising *via* benzyl cations. Benzylammonium chlorides exist partially as ion pairs in acetonitrile[20] and the high yield of benzyl chloride relative to *N*-benzylacetamide (Table I) probably reflects the extent to which the benzyl cation collapses with the counterion or the solvent; *e.g.*, see eq 27, 28.

$$[\mathrm{PhCH_2NR_3^+\ Cl^-}] \xrightarrow{h\nu} \mathrm{PhCH_2Cl + NR_3} \qquad (27)$$

$$\Big\downarrow\!\Big\uparrow K_A$$

$$\mathrm{PhCH_2NR_3^+ + Cl^-} \xrightarrow[\mathrm{CH_3CN}]{h\nu} \mathrm{PhCH_2NCCH_3^+ + NR_3 + Cl^-},\ \text{etc.} \qquad (28)$$

The formation of contact ion pairs alone (eq 29),

$$\mathrm{R_4N^+ + X^-} \overset{K_A}{\rightleftharpoons} \mathrm{R_4N^+X^-} \qquad (29)$$

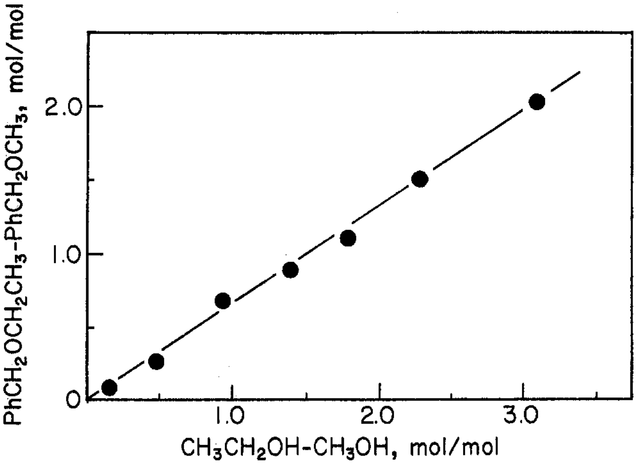


Figure 2.—Relative rates of formation of benzyl ethyl ether and benzyl methyl ether from the photolysis of dibenzyldimethylammonium chloride in ethanol–methanol mixtures.

TABLE VI
ASSOCIATION CONSTANTS FOR SOME QUATERNARY AMMONIUM HALIDES

Ammonium salt	Solvent	K_A	Temp, °C	Ref
$(n\text{-Bu})_4N^+I^-$	Dioxane–H_2O	5.1	25	*a*
$Me_4N^+Br^-$	H_2O	1.38		*b*
$Me_4N^+I^-$	H_2O	1.78		*b*
$Me_4N^+Cl^-$	MeOH	7	25	*c*
$Me_4N^+Br^-$	MeOH	14	25	*c*
$Et_4N^+Br^-$	MeOH	10	25	*c*
$(n\text{-Bu})_4N^+Br^-$	MeOH	3	25	*c*
$Me_4N^+I^-$	MeOH	18	25	*c*
$(n\text{-Bu})_4N^+I^-$	MeOH	16	25	*c*
$Me_4N^+Cl^-$	EtOH	141	25	*d*
$Me_4N^+Br^-$	EtOH	164	25	*d*
$Et_4N^+Br^-$	EtOH	96	25	*e*
$Et_4N^+I^-$	EtOH	130	25	*e, f*
$Me_4N^+Br^-$	CH_3CN	46	25	*g*
$(n\text{-Bu})_4N^+Br^-$	CH_3CN	2	25	*g*
$Me_4N^+I^-$	CH_3CN	19	25	*g*
$(n\text{-Bu})_4N^+I^-$	CH_3CN	3	25	*g*
$(n\text{-Bu})_4N^+Cl^-$	Acetone	438	25	*h*
$(n\text{-Bu})_4N^+Br^-$	Acetone	303	25	*i, j*
$(n\text{-Bu})_4N^+I^-$	Acetone	154	25	*i*
$(n\text{-Bu})_4N^+Cl^-$	*n*-BuOH	620	25	*k*
$(n\text{-Bu})_4N^+Br^-$	*n*-BuOH	860	25	*k*
$(n\text{-Bu})_4N^+I^-$	*n*-BuOH	1180	25	*k*

[a] R. M. Fuoss, *J. Amer. Chem. Soc.*, **79**, 3304 (1957). [b] B. J. Levien, *Aust. J. Chem.*, **18**, 1161 (1965). [c] R. L. Kay, C. Zawoyski, and D. F. Evans, *J. Phys. Chem.*, **69**, 4208 (1965). [d] T. H. Mead, O. L. Hughes, and H. Hartley, *J. Chem. Soc.*, 1207 (1933). [e] M. Barak and H. Hartley, *Z. Phys. Chem. (Leipzig)*, **165**, 273 (1933). [f] T. A. Grover and P. G. Sears, *J. Phys. Chem.*, **60**, 330 (1956). [g] D. F. Evans, C. Zawoyski, and R. L. Kay, *ibid.*, **69**, 3878 (1965). [h] M. J. McDowell and C. A. Kraus, *J. Amer. Chem. Soc.*, **73**, 3293 (1951). [i] M. B. Reynolds and C. A. Kraus, *ibid.*, **70**, 1709 (1948). [j] D. F. Evans and P. Gardam, *J. Phys. Chem.*, **72**, 3281 (1968). [k] D. F. Evans and P. Gardam, *ibid.*, **73**, 158 (1969).

however, cannot account for the relative yields of benzyl halides since the association constants K_A for a variety of quaternary ammonium halides listed in Table VI are actually *higher* in alcohols than in acetonitrile. Conductance studies show that these salts behave differently in hydrogen bonding solvents such as water, alcohols, and amides than in aprotic media such as acetonitrile, nitroalkanes, and acetone.[21] The most significant difference between these two classes of solvents is that the degree of association increases with decreasing crystallographic size of the ions in acetonitrile in harmony with expectations based on coulombic interactions. In alcohols, however, larger ions (particularly anions) show larger association constants, the variation of which decreases with increasing alkyl chain in the alcohol. The difference has been explained by a multistep association process, especially in hydrogen bonding solvents, involving solvent separated ion pairs VI and contact ion pairs VII (*e.g.*,[21] see eq 30) in

$$\mathrm{R_4N^+ + X^-\,(ROH)_n} \overset{K_1}{\rightleftharpoons} \underset{\mathrm{VI}}{\mathrm{R_4N^+(ROH)_nX^-}} \overset{K_2}{\rightleftharpoons} \underset{\mathrm{VII}}{\mathrm{R_4N^+X^-(ROH)_{n-1}}} + \mathrm{ROH} \qquad (30)$$

which the measured association constant K_A is given by $K_1(1 + K_2)$.

The absence of benzyl halides from the photolysis of benzylammonium halides in methanol and ethanol despite the rather large values of the association constants can then be attributed to the dominance of the solvent separated species VI which afford benzyl ethers rather than benzyl halides. The latter is in accord with the

---

[19] D. Booth and R. M. Noyes, Jr., *J. Amer. Chem. Soc.*, **82**, 1868 (1960); R. M. Noyes, Jr., *Z. Elektrochem.*, **64**, 153 (1960).

[20] D. F. Evans, C. Zawoyski, and R. C. McKay, *J. Phys. Chem.*, **69**, 3878 (1965).

[21] D. F. Evans and P. Gardam, *ibid.*, **72**, 3281 (1968); **73**, 158 (1969). J. Thomas and D. F. Evans, *ibid.*, **74**, 3812 (1970).

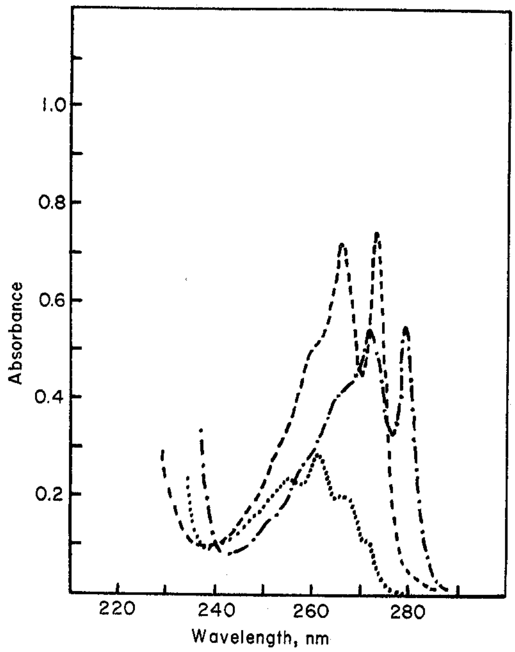


Figure 3.—Ultraviolet absorption spectra of substituted benzyltrimethylammonium chlorides in methanol: ....., *p*-methyl (1.01 × 10^{-3} *M*); –·–·–, *m*-cyano (1.00 × 10^{3} *M*); -----, *m*-methyl (1.06 × 10^{-3} *M*).

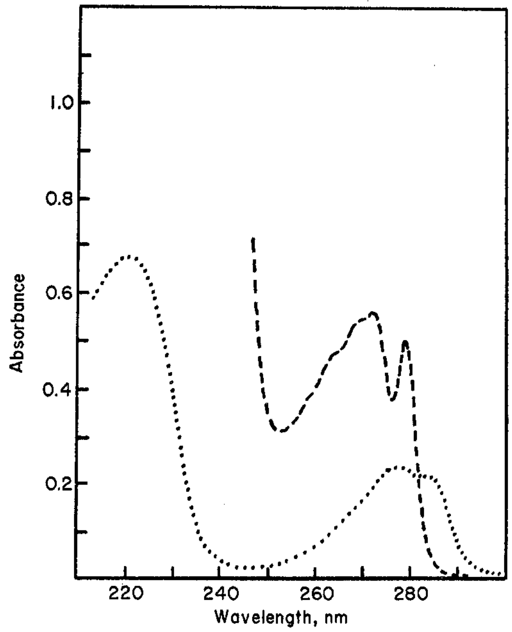


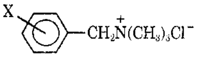
Figure 4.—Ultraviolet absorption spectra of methoxybenzyltrimethylammonium chlorides in methanol: ...., meta (1.07 × 10^{-4} *M*); ---- para (5.1 × 10^{-4} *M*).

lower quantum yields observed for the formation of benzyl ether from the photolysis of benzyltrimethylammonium bromide compared to the chloride (Table III). Unfortunately the quantum yields for the formation of benzyl halides were not measured under the same conditions. The increased importance of benzyl chloride relative to benzyl ether in *tert*-butyl alcohol (eq 16) compared to ethanol (eq 6) is also consistent with the higher concentration of ion pairs in the less polar medium.[22] Other factors being unchanged, such a formulation would predict that the relative amounts of benzyl halide–*N*-benzylacetamide in acetonitrile would decrease in the sequence $I^- < Br^- < Cl^-$ provided that the association constants for the ammonium salts also increased in the same sequence.[20]

Effects of Nuclear Substitution.—The aromatic nucleus was substituted by methyl, methoxy, and cyano groups to provide a variation in the electronic effects (Figures 3 and 4). The photolysis of a series of substituted benzylammonium salts listed in Table VII was examined, and the quantum yields for the formation of the corresponding toluenes and benzyl ethers were determined. The overall quantum yield for the formation of products was increased by meta substitution according to the electron donating ability of the substituents $CH_3O > CH_3 > H \gg CN$. However, the increase was due largely to the contribution from the homolytic route. The decrease in the quantum yield for the *m*-cyano compound was expected, although the magnitude was greater than anticipated based on the bathochromic shifts observed in the ultraviolet spectrum of the aralkylammonium salts (Figure 3). Para substitution, by contrast, had little effect on the quantum yields for overall product formation. The small decrease which was observed was associated with a decrease in the free-radical product.

TABLE VII

EFFECT OF AROMATIC SUBSTITUTION ON THE QUANTUM YIELDS[a]



X	Registry no.	Φ ($XC_6H_4CH_3$)	Φ (XC_6H_4-CH_2OCH_3)	Φ (*t*)
H		0.19	0.31	0.50
p-CH_3	4519-36-2	0.11	0.31	0.42
p-CH_3O	31280-95-2	0.15	0.30	0.45
m-CH_3	31280-96-3	0.24	0.39	0.63
m-CH_3O	31280-97-4	0.32	0.38	0.70
m-NC	31280-98-5	~0.005	~0.005	

[a] In methanol, 0.1 *M* salt.

Photolysis of Benzyl Derivatives. A Comparison.—The photolysis of benzylammonium salts can be compared with previous studies involving benzylsulfonium salts and benzyl esters, all of which proceed *via* heterolytic as well as homolytic routes. Zimmerman and Sandel[23] studied substituted benzyl acetates and found that a *m*-methoxy group increased the quantum yield for solvolysis tenfold relative to the *p*-methoxy analog. The latter is consistent with a benzyl cation as a model since a LCAO–MO treatment indicated that the electron density at the meta position is decreased in the first excited state. The quantum yield for the free-radical products was not measured. However, from the data obtained in preparative runs, there appears to be a corresponding drop in the quantum yield for homolysis when the methoxy group was relocated from the para to the meta position. Photolysis of *p*-methoxybenzyl acetate, thus, afforded mainly products from a homolytic scission whereas at the other extreme only solvolytic products were identified from the photolysis of 3,5-dimethoxybenzyl acetate.

Maycock and Berchtold[8] also found that a *m*-methoxy substituent enhanced the amount of benzyl ether formed from the photolysis of benzyldimethylsulfonium

---

[22] T. L. Broadwater and R. L. McKay, *J. Phys. Chem.*, **74**, 3802 (1970).

[23] H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963).

tetrafluoroborates in alcohol. No quantum yields were measured and photolysis was usually carried to sufficiently high conversions to cause further reactions to obscure the primary photochemical products.

Methoxytoluenes were not observed from the photolysis of *m*- and *p*-methoxybenzyl acetates in aqueous dioxane or ethanol, although other products indicated the presence of benzylic radicals.[23] Similarly, no toluene was observed from the photolysis of benzyldimethylsulfonium salt in methanol, isopropyl alcohol, or even acetonitrile.[3] A small yield of *m*-methoxytoluene was obtained when the *m*-methoxy salt was photolyzed in methanol, an observation contrary to the trend established in the photolysis of methoxybenzyl acetates.[23]

The absence of toluenes in the photolysis of benzyl acetates is consistent with our formulation of disproportionation as the route to toluene. The cage pair would consist of a benzyl and an acetoxyl radical incapable of disproportionation, and recombination or attack on solvent represents the only available recourse for reaction. The formation of relatively high yields of bibenzyls from coupling is also in accord with this formulation as it is in the photolysis of benzylsulfonium salts. However, in the latter case disproportionation is formally possible, but it apparently did not occur except when a *m*-methoxy substituent was present. The low yields of bibenzyls observed during photolysis of benzylammonium salts also indicate that cage disproportionation of nitrogen cation radicals (eq 18, 19) is more efficient than that of the sulfur analogs (eq 31).

$$[PhCH_2\cdot\ \cdot S(CH_3)_2{}^+] \longrightarrow PhCH_3 + [CH_3SCH_2]^+,\ \text{etc.} \quad (31)$$

The competition between heterolytic and homolytic pathways, thus, is clearly established in the photolysis of a variety of benzyl derivatives.[3,23-25] However, polar effects on the relative and absolute rates of both processes differ appreciably among these derivatives. They are significantly less important in the photolysis of benzylammonium salts than they are with benzyl acetates. In the photolysis of benzylammonium salts the competition between heterolysis and homolysis is not based primarily on the relative ease of formation of the electronically excited benzyl cation as it appears to be with benzyl acetates. In this system the homolytic pathway shows greater changes as a result of perturbation by polar groups than does the heterolytic route.[26] Quantitative interpretation of these differences among various benzyl derivatives must take into account a number of other factors. Thus, the reassociation of the fragments (cage recombination) produced by photochemical heterolysis or homolysis is an important variable which would affect the significance of apparent quantum yields measured in solution.[27] Moreover, an almost complete ignorance at this juncture of the relative importance of different excited states of the chromophore involved makes further discussion unfruitful. Photosensitization and induced nuclear polarization studies may help to distinguish between excited states of different multiplicities. The resolution of these questions is vital to a further understanding of this problem.

Experimental Section

Preparation of Materials. Benzylammonium Salts.—Amine hydrochlorides were prepared by passing hydrogen chloride gas through an ethereal solution of the amine. The precipitate was filtered, washed with ether, and recrystallized from either ethanol or acetonitrile. Quarternary ammonium salts were prepared by refluxing equimolar amounts of the tertiary amine and benzyl bromide or chloride in dioxane or tetrahydrofuran. The salt was filtered and recrystallized from either benzene or an ethanol–cyclohexane mixture. Benzyltrimethylammonium salts containing ring substituents were prepared by passing trimethylamine gas through an ethanolic solution of the appropriately substituted benzyl halide. Ethanol was removed by rotary evaporation leaving, in most instances, a thick oil. The oil was taken up in a small volume of acetonitrile and ether was added until the solution remained cloudy with stirring. This mixture was left in a freezer overnight whereupon an amorphous powder precipitated. The salt was filtered, dried in a vacuum oven at 60° for 12 hr, and stored in a desiccator. Satisfactory elemental analyses were obtained for the following ammonium halides: *N*,*N*,*N*-tri-*n*-hexyl-*N*-benzylammonium bromide, *N*,*N*,*N*-trimethyl-*N*-benzylammonium bromide, *N*-methyl-*N*,*N*,*N*-tribenzylammonium bromide, *N*,*N*,*N*-tribenzylammonium bromide, *N*,*N*,*N*-trimethyl-*N*-*m*-xylylammonium bromide, *N*,*N*,*N*-trimethyl-*N*-*p*-xylylammonium bromide, *N*,*N*,*N*-trimethyl-*N*-*m*-cyanobenzylammonium chloride.

The nmr spectra of all the ammonium salts were taken in D_2O using TMSP [sodium γ-(trimethylsilyl)propyl sulfonate] as an internal standard. Chemical shifts and coupling constants also followed the pattern expected for these compounds.

Ethers.—Authentic ethers were prepared for a comparison of their retention times on gas chromatography with products from the photolysis of ammonium salts. In general, the corresponding benzyl chloride or bromide was added to a 10% excess of sodium alkoxide in the alcohol as solvent. For the *tert*-butyl ether, the potassium salt was used. Precipitation of the alkali halide in many instances was immediate. After being stirred for 15 min, the mixture was poured into a large excess of water and extracted with pentane. The pentane layer was dried over sodium sulfate and the pentane removed by rotary evaporation. The ethers prepared in this manner were pure by nmr analysis and by gas chromatography. The *m*- and *p*-methoxybenzyl methyl ethers were prepared by refluxing the corresponding alcohols in a large volume of methanol with a catalytic amount of *p*-toluenesulfonic acid.

***N*-Benzyl-*N*-methylaminomethylethyl Ether, $PhCH_2N(CH_3)CH_2OCH_2CH_3$.**—To a solution of 24.2 g of benzylmethylamine and 15 g of absolute ethanol, cooled in an ice bath, was added 6 g of paraformaldehyde. The solution was stirred with cooling for 2 hr and at room temperature for 10 hr. Solid potassium carbonate (excess) was added and the mixture stirred for 24 hr after which it was filtered through Celite and distilled *in vacuo*.

The fraction boiling at 67–70° (0.3 mm) was retained:[28] nmr ($CDCl_3$ *vs.* TMS) methyl triplet (δ 1.138), *N*-methyl singlet (3.2), *O*-methylene quartet (2.31), benzyl methylene singlet (3.66), *N*-methylene singlet (3.99), aromatic (7.19); ir 7.4 (m), 8.5 (m), 8.9 (m), 9.15 (m), 9.4 (m), 9.5 (m), 9.8 (m), 10.3 (s), 13.5 (s), 14.4 μ (s).

An alcoholic solution (1 ml) containing 34.43 mg/ml (0.19 mmol) of the amino ether was hydrolyzed in 5 ml of H_2O containing 9 mequiv of sulfuric acid. After 15 min, 5 ml of a 2 *N* potassium hydroxide solution was added and the mixture extracted with 5 ml of ether. Gas chromatographic analysis of the ether extract indicated 22.2 mg (0.185 mmol) of benzylmethylamine. The same technique was used to determine the amount of amine resulting from hydrolysis of a portion of the photolysis solution. When the amino ether, in ethanol, was hydrolyzed

---

[24] *Cf.* also (a) R. Grinter and E. Heilbronner, *Tetrahedron Lett.*, 771 (1961); (b) D. A. DeBie and E. Havinga, *Tetrahedron*, **21**, 2359 (1965); E. Havinga, R. O. de Jongh, and M. E. Kronenberg, *Helv. Chim. Acta*, **50**, 2550 (1967); G. Frater and E. Havinga, *Tetrahedron Lett.*, 4603 (1969).

[25] See also (a) J. C. Sheehan and R. M. Wilson, *J. Amer. Chem. Soc.*, **86**, 5277 (1964); (b) Y. Ogata and K. Takagi, *J. Org. Chem.*, **35**, 1642 (1970); (c) K. E. Steeler and R. L. Letsinger, *ibid.*, **35**, 308 (1970).

[26] For polar effects in the formation of benzyl radical, see (a) P. D. Bartlett and C. Ruchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960); (b) C. Walling and B. Jackson, *ibid.*, **82**, 6113 (1960); (c) R. E. Pearson and J. C. Martin, *ibid.*, **85**, 354 (1963).

[27] Finally no distinction can be made on the basis of these experiments as to whether a radical pair of the type described by Walling, *et al.* [C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnou, *ibid.*, **92**, 4927 (1970)], for peroxide decomposition actually precedes the heterolytic and homolytic pathways.

[28] H. Böhme and H. Ellenberg, *Chem. Ber.*, **92**, 2976 (1959).

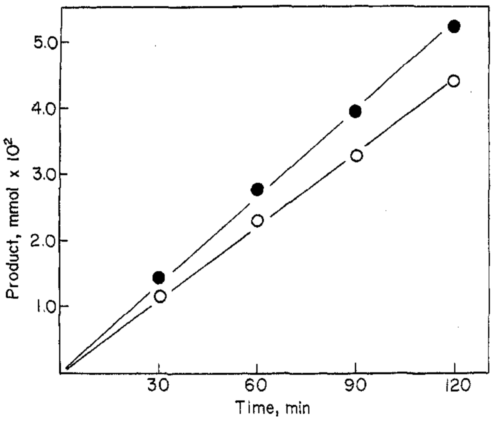


Figure 5.—The determination of the quantum yield of formation of (●) *m*-methoxybenzyl methyl ether and (○) *m*-methoxytoluene from the photolysis of *m*-methoxybenzyltrimethylammonium chloride in methanol.

with a catalytic amount of hydrogen chloride in the presence of 5,5-dimethylcyclohexane-1,3-dione, the dimedone derivative was formed.[29] The nmr spectrum of the compound prepared in this manner was compared with an authentic specimen obtained by reacting aqueous formaldehyde. When a portion of the photolysate was treated in a similar manner, the dimedone derivative was formed, as indicated by its nmr spectrum, but it was not analyzed quantitatively.

Product Analysis.—All quantitative analyses were performed by gas chromatography on a Varian Aerograph Model 1200 gas chromatograph equipped with a flame ionization detector. Products were identified by comparing their retention times with those of authentic samples on at least two columns whose separation characteristics differed. Analyses were performed by the internal standard method with a marker chosen, where possible, which had a similar functional group and a retention time close to that of the compound being analyzed.

Photolysis Studies.—Samples of ammonium salts were weighed into 10-ml volumetric flasks and diluted to volume with the appropriate solvent. The solution was then transferred to a cylindrical quartz tube (15 × 1.5 cm) and degassed by passing a slow stream of nitrogen through the solution for 10 min. The tube was sealed with a rubber septum. The photolyses were carried out in a Rayonet RPR-100 photochemical reactor (The Southern New England Ultraviolet Co.) using sixteen 253-nm lamps and rotated with a Rayonet MGR-100 merry-go-round.

Quantum Yield Measurements.—Aliquots (3.0 ml) of standard solutions were transferred to 10 × 1 cm quartz tubes and degassed as above. The solutions were photolyzed in a merry-go-round apparatus (F. G. Moses, Co., Wilmington, Delaware). A helix coil low-pressure Hg lamp (Mr. Charles Shott, University of Alberta), operating on 100 mA from a 5000-V transformer, was placed in the center of the apparatus. More than 97% of the light was centered about a sharp band at 254 nm. A shutter was arranged so that photolysis was allowed only after the lamp was warmed. A constant temperature of 32° was maintained in the reactor. Chloroacetic acid was used for actinometry and a value of 0.370 chosen as the quantum yield for chloride formation at 32°.[30] The flux of light through each slit was found to be $7.22 \pm 0.08 \times 10^{-5}$ einsteins hr^{-1} by this method (average of 20 separate runs). The formation of each product was followed periodically up to 5% conversion as shown in Figure 5 for the photolysis of *m*-methoxybenzyltrimethylammonium chloride in methanol. The quantum yield (moles einstein^{-1}) was obtained by dividing the slope (mole hour^{-1}) by the flux (einsteins hour^{-1}).

Registry No.—$PhCH_2N(CH_3)_3^+\ Br^-$, 5350-41-4; $(PhCH_2)_2N(CH_3)_2^+\ Cl^-$, 100-94-7; $(PhCH_2)_3NCH_3^+\ Br^-$, 31246-85-2; $PhCH_2N(CH_3)_3^+\ Cl^-$, 56-93-9; $(PhCH_2)_2N(CH_3)_2^+\ EtO^-$, 31280-85-0; $(PhCH_2)_3NH^+\ Cl^-$, 7673-07-6; $PhCH_2N(n\text{-}Hex)_3^+\ Br^-$, 31280-89-4; $(PhCH_2)_2NH(CH_3)^+\ Cl^-$, 5441-24-7; $(PhCH_2)_2NH_2^+\ Cl^-$, 20455-68-9; $PhCH_2NH_3^+\ Cl^-$, 3287-99-8; $PhCH_2N(CH_3)CH_2OCH_2CH_3$, 31280-93-0; benzyl ethyl ether, 539-30-0; benzyl methyl ether, 538-86-3; *m*-methoxybenzyl methyl ether, 1515-82-8; *m*-methoxytoluene, 100-84-5.

Acknowledgment.—We wish to thank the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, and the Edgewood Arsenal, U. S. Army, for generous financial support and the Miles Chemical Co. for samples of some benzylammonium salts.

---

[29] A. I. Vogel, "Practical Organic Chemistry," Wiley, New York, N. Y., 1956, p 332.

[30] R. N. Smith, P. A. Leighton, and W. G. Leighton, *J. Amer. Chem. Soc.*, **61**, 2299 (1939).

Syntheses of (3-Aminoalkyl)silicon Compounds

JOHN L. SPEIER,* C. A. ROTH, AND JOHN W. RYAN[1]

Silicone Research Department, Dow Corning Corporation, Midland, Michigan 48640

Received March 16, 1971

The syntheses and chemical properties of some 54 compounds are described, all having structural units including ≡SiCCCN= with either methyl, phenyl, siloxy, alkoxy, or amino groups on silicon and H, alkyl, or phenyl groups on nitrogen. Thirteen of the compounds are novel substituted heterocyclic 1-aza-2-silacyclopentanes and one is a 1-aza-2-silacyclohexane.

During the course of some years we have had occasion in these laboratories to prepare large numbers of 3-silylalkylamino compounds. Nearly all of these amines had either methyl, alkoxy, or siloxy groups attached to silicon and hydrogen, alkyl, aryl, or other groups attached to nitrogen.

Only a few compounds of this kind were previously known. Some examples are 3-trimethylsilylpropylamine (**2**)[2a] which was first made by reduction of 3-trimethylsilylpropionitrile with lithium aluminum hydride[2b] and later by hydrogenation of the same intermediate.[3] Comparable hydrogenation of 2-cyanoethylalkoxysilanes has also been described.[3a,4]

Examples of the alkylation of amines or ammonia with 3-silylalkyl chlorides are also known.[3b,5]

In this paper many structures of this kind, including

---

[1] Many of the experiments in this paper were carried out by G. K. Menzie (deceased).

[2] (a) Throughout this paper the numbers in parentheses, (**2**), refer to compounds as listed in Table II. (b) L. H. Sommer and J. Rockett, *J. Amer. Chem. Soc.*, **73**, 5130 (1951).

[3] (a) L. Kh. Friedlin, A. D. Petrov, T. A. Sladkova, and V. M. Vdouin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1878 (1960); (b) K. Shiina, H. Inui, Z. Ota, and M. Kumada, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **63**, 168 (1960).

[4] V. B. Jex and D. L. Bailey, U. S. Patent 2,930,809 (1960).

[5] J. L. Speier, U. S. Patent 2,971,864 (1961); U. S. Patent 3,146,250 (1964).