

Na_2SO_4 , and evaporated under reduced pressure. The residue was extracted with hexane and the hexane solution was eluted from a silicic acid-Celite¹⁰ column by use of a hexane (3 vol)-benzene (7 vol) mixture. Evaporation of the second fraction gave 0.20 g (6%) of white crystalline 1-adamantyl azide: mp 82–83°; ν 3.43, 3.51, 4.80, 6.92, 8.02, 9.49, 11.32, 12.33, 13.67, 14.82 μ ; pmr τ 7.84 (s, 3, γ -H), 8.19 (d, 6, J = 2.6 Hz, β -H), 8.30 (6, δ -H).

Anal. Calcd for $\text{C}_{10}\text{H}_{15}\text{N}_3$: C, 67.76; H, 8.53; N, 23.59. Found: C, 67.56; H, 8.42; N, 23.62.

Evaporation of the first and third fractions gave a trace of 1-adamantyl chloride (identified by infrared spectrum) and 0.3 g of 1-adamantyl azidoformate, mp 42–43°, respectively. A large fourth fraction had an infrared spectrum indicating that it was 1-adamantanol.

Registry No.—1-(1-Adamantyl)-5-methyltetrazole, 24886-62-2; 1-(1-adamantyl)-5-ethyltetrazole, 24940-56-5; 1-(1-adamantyl)-5-propyltetrazole, 24886-63-3; 1-(1-adamantyl)-5-isopropyltetrazole, 24886-64-4; 1-(1-adamantyl)-5-phenyltetrazole, 24886-65-5; 1-(1-adamantyl)-5-vinyltetrazole, 24886-66-6; 1-(1-adamantyl)-5-(α -methylvinyl)tetrazole, 24886-67-7; 1-(1-adamantyl)-5-(*trans*- β -phenylvinyl)tetrazole, 24886-68-8; N-(1-adamantyl)acrylamide, 19026-83-6; N-(1-adamantyl)methacrylamide, 24886-70-2; N-(1-adamantyl)-*trans*-cinnamamide, 24886-71-3; 1-adamantyl azidoformate, 19386-43-7; 1-adamantyl azide, 24886-73-5.

A Reinvestigation of the Mannich Reaction of 4-Nitrophenylacetic Acid and 2,4-Dinitrophenylacetic Acid¹

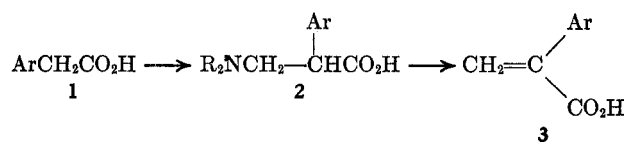
J. HERMAN SCHAUBLE AND ELISABETH HERTZ²

Department of Chemistry, Villanova University, Villanova, Pennsylvania 19085

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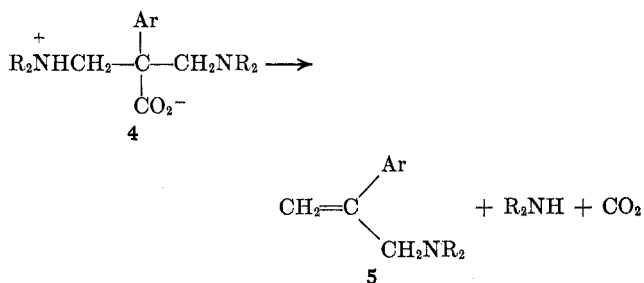
The reaction of 4-nitrophenylacetic acid with piperidine and formaldehyde gives rise to α -(N-piperidinomethyl)-4-nitrostyrene (5) via a slow second Mannich condensation of the intermediate α -(4-nitrophenyl)- β -(N-piperidino)propionic acid (2) and subsequent decarboxylative deamination of 4. 2,4-Dinitrophenylacetic acid also undergoes mono- and bisaminomethylation under Mannich conditions; however, the intermediate amino acids 6 and 7 spontaneously decarboxylate to yield the monoamine 8 and diamine 9. The elimination reactions of 2 have been studied over the pH range of 1–11. In acidic medium, deamination occurs to yield theacrylic acid 3; under basic conditions, decarboxylative deamination predominates to yield 4-nitrostyrene. Above pH 6, 2 also undergoes the retro Mannich reaction.

Although reports due to Mannich and a few later workers indicate that α -methylene functions of certain activated carboxylic acids can undergo condensation to incorporate two $-\text{CH}_2\text{NR}_2$ groups,³ a detailed study of these reactions has not been made. Our interest in this topic arose from an attempt to repeat Mannich's synthesis of α -(4-nitrophenyl)acrylic acid. This procedure involves reaction of the piperidinium salt of 4-nitrophenylacetic acid with formaldehyde in aqueous solution to yield α -(4-nitrophenyl)- β -(N-piperidino)propionic acid (2) which is deaminated by heating in aqueous solution kept neutral by periodic addition of dilute hydrochloric acid.⁴



Ar- = 4-nitrophenyl; R_2N - = piperidyl

In the first step of this sequence, we have isolated a 29% yield of α -(N-piperidinomethyl)-4-nitrostyrene (5) in addition to the β -amino acid 2 (65% yield). This styrene apparently arises by aminomethylation of 2 to yield 4, which then undergoes decarboxylative deamination as shown in the following reaction scheme.



Ar- = 4-nitrophenyl; R_2N - = piperidyl

This conclusion is supported by observation of the β -amino acid 2 as an intermediate in the formation of 5.⁵ Stepwise loss of carbon dioxide and piperidine⁶ is ruled out since 2-(4-nitrophenyl)-1,3-di(N-piperidino)propane was inert under the reaction conditions.

In contrast to the reaction of 4-nitrophenylacetic acid, Mannich and Stein reported that 2,4-dinitrophenylacetic acid reacts with piperidine and formaldehyde to yield only 2-(2,4-dinitrophenyl)-1,3-di(N-piperidino)propane (9).⁴ However, repetition of this reaction in dilute aqueous ethanol solution at 31° resulted in appreciable amounts of the monoamine 8 and 2,4-dinitrotoluene in addition to the diamine 9. Decarboxylation of the piperidinium salt of 2,4-dinitrophenylacetic acid occurred readily under these conditions. Since Kermack and Muir had reported formation of both

(1) Presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(2) Abstracted in part from the M. S. Thesis of E. Hertz, presented to the Department of Chemistry, Villanova University, April 1968.

(3) F. F. Blick, *Org. React.*, **1**, 310 (1942); B. Reichert, "Die Mannich Reaktion," Springer-Verlag, Berlin, 1959, p 41.

(4) C. Mannich and L. Stein, *Ber.*, **58B**, 2659 (1925).

(5) It should be noted that decarboxylative deamination of postulated β -amino acid intermediates under Mannich conditions has been invoked previously, e.g., (a) C. A. Grob and P. W. Schiess, *Angew. Chem. Int. Ed. Engl.*, **6**, 1 (1967), and references cited therein; (b) H. Ulrich and A. A. R. Sayigh, *J. Org. Chem.*, **31**, 4146 (1966).

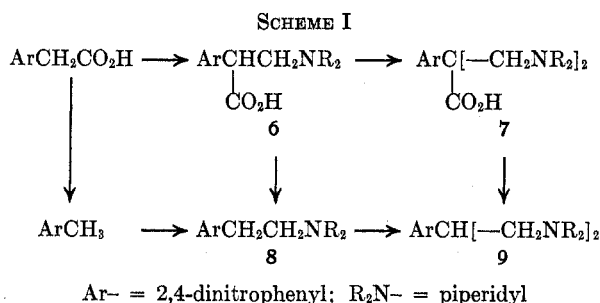
(6) B. B. Thompson, "Some Studies in the Mannich Reaction," Ph.D. Thesis, The University of Mississippi, 1963.

TABLE I
pH DEPENDENCE OF THE VARIOUS REACTIONS OF
 α -(4-NITROPHENYL)- β -(N-PIPERIDINO)PROPIONIC ACID IN AQUEOUS SOLUTION

Run	Mol of 2	Mol of HCl	pH range	Temp, °C	Time, hr	% yield of various products				
						Deamination 3	Decarboxylative deamination 10	11	Mannich reaction 1	5
1	0.25	<i>a</i>	11-11 ^b	100	9	0	0	45.9	15.9	12.6
2	0.1	<i>c</i>	11-9	97	3	0	3.1	27.3	22.9	18.7
3	0.05	<i>c</i>	9-9	85	3	1	0.6	17.0	13.1	13.1
4	0.05	0	6-8	100	3	6.3	25.2	20.8	10.6	12.0
5	0.05	<i>d</i>	4-6	100	3	<i>e</i>	23.6	<i>e</i>	<i>e</i>	<i>e</i>
6	0.05	0.0375	3-5	100	3	~1	7.8	30.0	~1	Trace
7	0.05	0.05	1-3.5	100	3	45.7 ^f	0	8.9	~1 ^g	Trace

^a Two equivalents of piperidine (instead of HCl) was added at the beginning of the reaction. ^b Ranges denote the pH at the beginning (at 80°) and at the end of the reaction (except for run 5). ^c One equivalent of piperidine was employed. ^d The pH was kept in the 4-6 range by adding 1 *N* HCl every 5-10 min. ^e Not investigated. ^f Several runs under similar conditions gave 3 in yields of 45.7-60.1%. ^g A 3.3% yield of di(N-piperidino)methane was also obtained from this reaction.

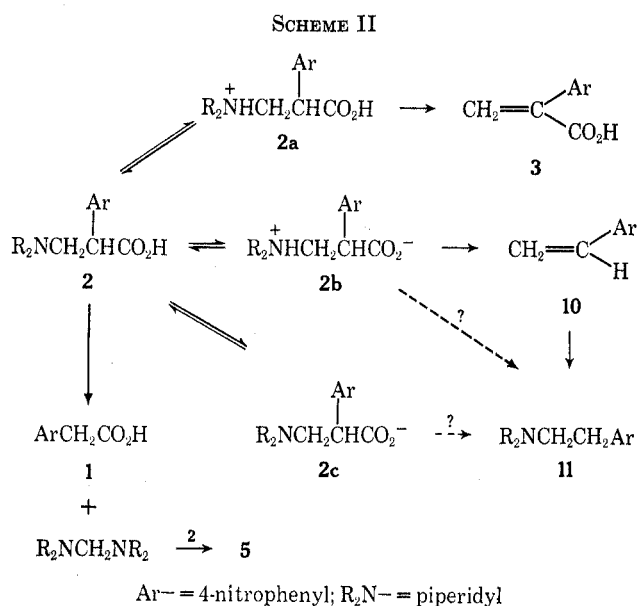
8 and 9 from the reaction of 2,4-dinitrotoluene with piperidine and formaldehyde in refluxing ethanol solution,⁷ it was of interest to determine the relative involvement of the intermediates shown in Scheme I for the Mannich reaction of 2,4-dinitrophenylacetic acid.



Since aminomethylation of the monoamine 8 occurred at a lower rate than the formation of 8 from 2,4-dinitrotoluene in refluxing ethanol solution and since reaction of 2,4-dinitrotoluene with piperidine and formaldehyde was undetectable at 31°, both 2,4-dinitrotoluene and the monoamine 8 can be ruled out as intermediates in the Mannich reaction of 2,4-dinitrophenylacetic acid in dilute solution at room temperature. This implicates intermediate 7 as the source of diamine 9 and the β -amino acid 6 as the precursor to the monoamine 8. Although 8 and 9 may result by decarboxylative deamination of the nonisolable amino acids 6 and 7, followed by reamination of the intermediate 2,4-dinitrostyrene and α -(N-piperidinomethyl)-2,4-dinitrostyrene, the alternate possibility involving decarboxylation of 6 and 7 cannot be eliminated.

In the course of this study, several alternate, pH-dependent pathways were observed for decomposition of α -(4-nitrophenyl)- β -(N-piperidino)propionic acid (2) in aqueous solution. Although the acrylic acid 3 could be obtained in up to 60% yield under carefully controlled conditions, it was accompanied by 4-nitrostyrene (10), 1-(4-nitrophenyl)-2-(N-piperidino)ethane (11), 4-nitrophenylacetic acid (1), and α -(N-piperidinomethyl)-4-nitrostyrene (5) (Scheme II). The yields of these products as a function of the pH of the reaction medium are listed in Table I.

It should be noted that the yield of α -(4-nitrophenyl)-



acrylic acid (3) decreases with increasing pH while the yield of 4-nitrostyrene (10) follows the opposite trend. Since the isoelectric point for the amino acid 2 occurs at pH 6.0, it is apparent that the protonated species 2a predominating below pH 6, gives rise to the acrylic acid, while the zwitterion 2b predominating above pH 6 is the precursor to 4-nitrostyrene. The sharp decrease in yield of 4-nitrostyrene above pH 8 is largely the result of secondary reaction with piperidine to form the amine 11.⁸ Note that 11 may also arise by decarboxylation of either the anion 2c or the zwitterion 2b.⁹

The formation of 4-nitrophenylacetic acid at high pH is undoubtedly due to a retro Mannich reaction resulting from nucleophilic displacement of the 4-nitrophenylacetate group from the β -amino acid 2 by piperidine.¹⁰ The other product of this reaction, di-(N-piperidino)methane (or species derived therefrom) apparently effects aminomethylation of the amino acid

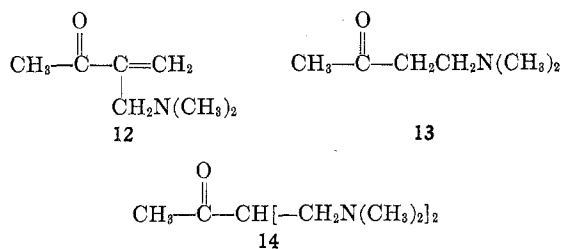
(8) This reaction occurs readily in ethanol solution under similar conditions: W. J. Dale and G. Buell, *J. Org. Chem.*, **21**, 45 (1956).

(9) Ulrich and Sayigh (ref 5b) report that the amine resulting from the reaction of α -(4-nitrophenyl)-*cis*-2,5-dimethoxyinnamic acid with piperidine must form solely by decarboxylation of the β -amino acid intermediate, since the stilbene formed by decarboxylative deamination is inert to reamination.

(10) B. B. Thompson, *J. Pharm. Sci.*, **57**, 715 (1968), and references cited therein.

2,^{10,11} to yield 4, which then undergoes decarboxylative deamination to provide α -(N-piperidinomethyl)-4-nitrostyrene (5).

The variety of reactions accompanying aminomethylation of the nitro-substituted phenylacetic acids prompts extension of this study to other systems. Preliminary results from the reaction of acetoacetic acid with dimethylamine and formaldehyde indicate formation of methyl α -(dimethylaminomethyl)vinyl ketone 12¹² in addition to the monoamine 13 and diamine 14 reported by Mannich and Curtaz.¹³



Experimental Section¹⁴

Mannich Reaction of 4-Nitrophenylacetic Acid.—The crude mixture from reaction of the piperidinium salt of 4-nitrophenylacetic acid with aqueous formaldehyde (1 mol of each, 0.1 mol excess of piperidine) at room temperature⁴ for 4 days was filtered under suction to remove the crystalline 2. The filtrate was extracted with chloroform, and the extract was washed with water, dried (MgSO₄), filtered, and evaporated on the steam bath at aspirator vacuum. The resulting oil was purified by vacuum distillation. After a forerun of di(N-piperidino)methane, bp 62° (0.7 mm) [lit.¹⁵ bp 75–81° (4 mm)], 71.7 g (29.1% yield) of amber α -(N-piperidinomethyl)-4-nitrostyrene (5), bp 144–152° (0.5 mm), was obtained.¹⁶ nmr (CDCl₃) δ 1.4 (m, 6, piperidine ring), 2.4 (m, 4, pip ring), 3.3 (s, -CH₂NR₂), 5.4 and 5.6 (d, J = 2 Hz, H₂C=C), 7.7 and 8.15 (d, d, J = 9 Hz, 4-nitrophenyl).

Anal. Calcd for C₁₄H₁₃N₂O₂: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.02; H, 7.15; N, 11.28.

Reaction of 2 with piperidine and formaldehyde under conditions similar to those just cited also resulted in a mixture of 5 and di(N-piperidino)methane.

Preparation of 2-(4-Nitrophenyl)-1,3-di(N-piperidino)propane.—A mixture of 4.92 g (0.02 mol) of 5 and 10 ml of piperidine was heated under reflux at 120–145° for 20 hr. The remaining piperidine was removed on a rotary evaporator (aspirator vacuum). The crude product was recrystallized 3 times from ethanol to yield 3.4 g (51.5%, not optimum¹⁶) of pale yellow crystals: mp 81.5–83.5°; nmr (CDCl₃) δ 1.45 (m, 12, pip rings), 2.0–2.7 (m, 8, pip rings) overlapping the absorptions for the four -CH₂NR₂ protons, 2.75–3.5 (m, ArCH-) and 7.35 and 8.15 (d, d, J = 8.5 Hz, 4-nitrophenyl).

Anal. Calcd for C₁₉H₂₃N₃O₂: C, 68.85; H, 8.82; N, 12.68. Found: C, 69.06; H, 8.82; N, 12.70.

Aminomethylation of 2,4-Dinitrotoluene.—Reaction of 2,4-dinitrotoluene with piperidine and formaldehyde (equimolar) in refluxing ethanol was carried out according to Kermack and Muir.⁷ Diamine 9 was obtained in 21% yield by successive evaporation and crystallization of the crude ethanol solution. Concentration of the mother liquor gave a red-brown oil which was dissolved in anhydrous ether. Saturation of this solution with HCl resulted in the hydrochloride of 8 which was removed by

suction filtration and triturated with acetone and ether. The light tan powder was obtained in 58.7% yield.

Anal. Calcd for C₁₃H₁₃N₃O₄Cl: C, 49.45; H, 5.75; N, 13.31; Cl, 11.23. Found: C, 49.28; H, 5.82; N, 13.10; Cl, 11.14.

The free amine 8, obtained by treatment of the hydrochloride with dilute KOH solution, exploded at 165° (high vacuum) on attempted distillation. The nmr spectrum of 8 (CDCl₃) has peaks at δ 1.5 (m, 6, pip ring), 2.45 (m, 4, pip ring), 2.7 and 3.2 (t, t, J = 7 Hz, -NCH₂CH₂Ar) plus the three-proton pattern for the 2,4-dinitrophenyl group. The diamine 9 possesses absorptions (CDCl₃) at δ 1.35 (m, 12, pip rings), 2.0–2.7 (m, 8, pip rings), which mask a complex four-proton pattern for the -CH₂-NR₂ protons, and 3.5–4.3 (m, ArCH-) in addition to the expected peaks for the 2,4-dinitrophenyl group.

Relative Reactivity of 2,4-Dinitrophenylacetic Acid and 2,4-Dinitrotoluene with Piperidine and Formaldehyde.—A solution of 5.6 g of 2,4-dinitrophenylacetic acid and 2.12 g of piperidine (0.025 mol of each) in 450 ml of 95% ethanol at 31.5° was mixed with a solution of 3.65 ml (0.05 mol) of 37.7% formaldehyde and 2.12 g (0.025 mol) of piperidine in 20 ml of 95% ethanol at the same temperature (constant-temperature bath). After 6 hr the mixture was poured into 1500 ml of water and extracted with chloroform. The extract was reserved. The basic aqueous fraction was neutralized with dilute HCl and extracted with chloroform. This extract was dried (MgSO₄), filtered, and evaporated to yield 0.41 g (7.25%) of 2,4-dinitrophenylacetic acid. The reserved chloroform extract which contained monoamine 8, diamine 9, and 2,4-dinitrotoluene was shaken with dilute HCl to remove the amines. The chloroform layer was then washed with water, dried (MgSO₄), and evaporated to yield 0.58 g (12.7%) of 2,4-dinitrotoluene. The acidic aqueous layer was neutralized with KOH pellets and extracted with ether. The extract was dried (MgSO₄) and evaporated. Crystallization of the crude product from ethanol yielded 3.35 g (35.5%) of diamine 9 and 1.18 g (16.9%) of red-brown oil, identified by nmr as quite pure monoamine 8.¹⁷

A similar run conducted with 2,4-dinitrotoluene and 0.025 mol of acetic acid in place of 2,4-dinitrophenylacetic acid resulted in 87% recovery of 2,4-dinitrotoluene. The only amine isolated was di(N-piperidino)methane. The same results were obtained when acetic acid was omitted.

Decarboxylation of 2,4-dinitrophenylacetic acid with piperidine in the absence of formaldehyde was examined under similar conditions. When the reaction mixture was poured into water, 0.69 g (24.4% yield) of 2,4-dinitrotoluene was isolated (~0.3 g was probably lost owing to solubility in water-ethanol).

Elimination Reactions of α -(4-Nitrophenyl)- β -(N-piperidino)propionic Acid (2). **General Procedure for Reactions Listed in Table I.**—The indicated amount of 2 plus 10 ml of water/0.01 mol of 2 was placed in a three-necked round-bottom flask fitted with a heating mantle, magnetic stirrer, and reflux condenser. The pH was controlled by addition of 1 N HCl or piperidine. The reaction mixture was then heated at the specified temperature for the time indicated. After cooling and basifying with dilute KOH solution, 4-nitrostyrene and the amines were removed by ether extraction. Treatment of this extract with dilute HCl resulted in an ether solution of 4-nitrostyrene and an aqueous solution of the amine hydrochlorides. The free amines were isolated from aqueous solution by treatment with KOH solution, followed by ether extraction. The extract was washed with water, dried (MgSO₄), and evaporated *in vacuo*. The yields of amines were conveniently determined by nmr analysis of the crude mixtures. Crystalline α -(4-nitrophenyl)acrylic acid (3) and/or 4-nitrophenylacetic acid (1) were obtained by acidifying the initial basic aqueous fraction to pH 1 with concentrated HCl and cooling overnight. The yields were determined by nmr.

The optimum yield of 3 was achieved under the conditions indicated in run 7. The reaction time of 3 hr was optimum. When 2 equiv of HCl was employed or when the reaction was scaled up to 0.2 mol, the yield dropped sharply. Crude 3, isolated by acidifying the reaction mixture to pH 1 with concentrated HCl and cooling overnight, contained no 4-nitrophenylacetic acid. After recrystallization from acetone-methylene chloride (decolorizing carbon), 3 was collected and dried *in vacuo*:

(17) When 2,4-dinitrophenylacetic acid was treated with piperidine and formaldehyde (0.03:0.06:0.06 mol ratio) in 200 ml of ethanol for 2 days at room temperature, a 66% yield of 9, a 14% yield of 8, and a trace of 2,4-dinitrotoluene were realized.

(11) W. L. Nobles and N. D. Potti, *J. Pharm. Sci.*, **57**, 1097 (1968).

(12) H. J. Spinelli, unpublished results, this laboratory.

(13) C. Mannich and K. Curtaz, *Arch. Pharm. (Weinheim)*, **264**, 741 (1926).

(14) The nmr spectra were obtained with a Varian A-60 spectrometer using TMS as the internal standard. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were obtained with a liquid bath and are uncorrected.

(15) A. Binz and L. H. Pence, *J. Amer. Chem. Soc.*, **61**, 3134 (1939).

(16) Caution: The above reaction mixture and α -(N-piperidinomethyl)-4-nitrostyrene are severe vesicants.

mp 174.5–177° (lit.⁴ mp 176–177°; nmr (d_6 -acetone) 6.2 and 6.6 (s, s, $H_2C=C$) and 7.8 and 8.25 (d, d, $J = 9$ Hz, 4-nitrophenyl) as well as absorption for the acidic hydrogen.

Registry No.—1, 104-03-0; 2, 13797-13-2; 5, 24886-58-6; 8, 24886-59-7; 8 HCl, 24886-60-0; 2,4-dinitro-

phenylacetic acid, 643-43-6; 2-(4-nitrophenyl)-1,3-di-(N-piperidino)propane, 24886-61-1.

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Photochemical Reactions of Phenacyl- and Benzylsulfonium Salts¹

ALAN L. MAYCOCK² AND GLENN A. BERCHTOLD

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Phenacylsulfonium tetrafluoroborates (1, 5, 7, 9, and 11) on irradiation afford products resulting from homolytic cleavage of the phenacyl carbon-sulfur bond. Benzylsulfonium tetrafluoroborates (13, 22, 24, 29, and 32) on irradiation afford products resulting from both homolytic and heterolytic cleavage of the benzyl carbon-sulfur bond where the heterolytic cleavage is the major pathway. β -Keto sulfonium fluoroborates (44 and 46) on irradiation in methanol are converted to polymeric products. Syntheses are described for all photochemical products previously unreported.

The photolysis of dimethylphenacylsulfonium bromide in water was recently reported.³ Irradiation of the salt in methanol for 1 hr in these laboratories also produced acetophenone (51%) and phenacyl bromide (<5%) but no significant amount of *p*-bromodibenzoyl ethane which was reported to be the major product (25%) on irradiation in water.³ Furthermore, irradiation of phenacyl bromide in methanol under similar conditions for 1 hr produced acetophenone (41%) indicating that acetophenone must arise in part, if not completely, from phenacyl bromide as an intermediate.⁴ In view of this involvement of bromide ion in the photolysis, the tetrafluoroborate salt of dimethylphenacylsulfonium ion and other aroylsulfonium ions was irradiated in order to prevent anion involvement whether the cleavage of the carbon-sulfur bond was heterolytic or homolytic. The nonpolymeric products formed are listed in Table I.

Acetophenone (2) was the sole product from photolysis of 1 in methanol, but the coupling product 3 was observed in *t*-butyl alcohol and acetonitrile and the rearrangement product 4 was observed in low yield in *t*-butyl alcohol. In similar fashion 5, 7, and 9, on irradiation in methanol, were converted to 6, 8, and 10, respectively. Tetrafluoroborate salt 11 follows a similar reaction course in methanol and water.

The presence of the phenacyl dimer 3 in solvents other than methanol is in line with the increased difficulty of abstraction of a hydrogen atom by a radical from the other solvents.⁵ An excited-state solvolysis of the sulfonium salts in methanol to form the corresponding α -methoxy ketone can not be discarded since α -methoxyacetophenone rapidly photolyzed in meth-

anol to form 2.⁶ On the other hand, α -hydroxyacetophenone gave no monomeric products on irradiation in water and thus would not appear to be an intermediate in the irradiation of 1 or 11 in water. This would appear to eliminate an excited-state solvolysis as the reaction pathway of the BF_4^- salts in water.

The isolation of 12 from the photolysis of 11 rules out a Norrish type II process for the formation of 2⁷ since the $C_3H_7CH=S^+C_4H_9$ formed in such a process would be converted to $C_3H_7CH(OR)CHSC_4H_9$ ($R = CH_3$ in methanol, $R = H$ in water).

The data from irradiation of the BF_4^- salts are most consistent with a radical pathway involving initial homolytic cleavage to the phenacyl radical^{8,9} and the dialkylsulfonium cation radical.^{10–12} Diarylsulfonium cation radicals are probably involved in the photolytic decomposition of triarylsulfonium salts.¹⁴ The dimethylsulfonium cation radical formed from photolysis of 1 (in *t*-butyl alcohol) may lose H^+ to form $\cdot CH_2CSH_2$

(6) R. B. LaCount and C. E. Griffin, *Tetrahedron Lett.*, 1549 (1965), report that photolysis of α -methoxyacetophenone in benzene gives 3-phenyl-3-oxethanol (10% yield). P. Yates and A. G. Szabo, *ibid.*, 485 (1965), report obtaining the same product (29% yield) in benzene on irradiation for 12 hr. A detailed study of the photochemistry of α -alkoxyacetophenones has appeared recently: F. D. Lewis and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 311 (1970).

(7) This assumes 2 and 12 are formed in the same reaction process.

(8) The study by R. L. Huang and P. Williams, *J. Chem. Soc.*, 2637 (1958), indicates that phenacyl radicals are probably more reactive than benzyl radicals.

(9) Acetophenone, one of the products of the photolytic decomposition of dimethylsulfonium phenacylide [B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 138 (1967)] and diazoacetophenone [D. O. Cowan, *et al.*, *J. Org. Chem.*, **29**, 1922 (1964)] in alcohols, presumably arose *via* phenacyl radicals formed from hydrogen atom abstraction by benzoyl carbene.

(10) Cation radicals of this type have been produced by the oxidation of aryl sulfides in concentrated H_2SO_4 :¹¹ H. J. Shine, *et al.*, *J. Org. Chem.*, **32**, 1901 (1966), and references cited therein; A. Zweig, *et al.*, *Tetrahedron Lett.*, 1821 (1963).

(11) Reviews on the formation of sulfur cation radicals have appeared: (a) U. Schmidt, in "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience Publishers, New York, N. Y., 1967, p 75; (b) H. J. Shine, in ref 11a, p 93.

(12) Although the anodic oxidation of dialkyl sulfides is reported to produce a single wave representing removal of two electrons,¹³ Zweig, *et al.*, (ref 10) cite convincing evidence for formation of the cation radical from dithiohydroquinone dimethyl ether by electrochemical oxidation.

(13) M. M. Nicholson, *J. Amer. Chem. Soc.*, **76**, 2539 (1954); V. Drushel and J. F. Miller, *Anal. Chem.*, **29**, 1456 (1957).

(14) J. W. Knapezyk and W. E. McEwen, *J. Amer. Chem. Soc.*, **91**, 145 (1969).

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(2) National Institutes of Health Predoctoral Fellow, 1965–1968.

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

(4) Irradiation of phenacyl chloride in ethanol affords only acetophenone (53%); J. C. Anderson and C. B. Reese, *Tetrahedron Lett.*, 1 (1962).

(5) (a) V. K. Schwetlich, R. Karland and J. Jentzsch, *J. Prakt. Chem.*, **22**, 113 (1963), report the rate of hydrogen atom abstraction by *t*-butoxy radicals to decrease in the following order: $CH_3OH > CH_3CN > (CH_3)_2OH$. (b) Water is known to be a poor hydrogen atom donor: A. Becket and G. Porter, *Trans. Faraday Soc.*, **59**, 2039 (1963).