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Photochemistry of Some Group V Onium Salts. Effect of Magnetic Nuclei on In-Cage Radical Coupling Reactions

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A series of group V arylammonium, arylphosphonium, and arylarsonium salts have been synthesized and their photochemical behavior investigated. Direct irradiation of the onium salts in acetonitrile provided photoproducts that were dependent on the magnitude of the nuclear hyperfine coupling constant of the heteroatom rather than spin-orbit coupling. The ammonium and phosphonium salts provided only out-of-cage coupling products while the arsonium salt provided both in-cage and out-of-cage coupling products.

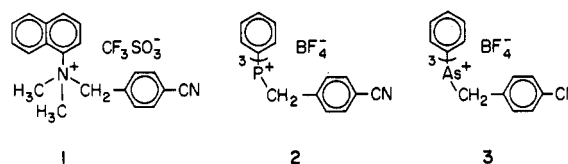
We have recently reported¹ that certain 1-naphthylmethylalkylsulfonium salts undergo a photochemically induced 1,3-sigmatropic rearrangement in which a *p*-cyanobenzyl group, for example, migrates from sulfur to the 2-position of the naphthalene ring. The dihydronaphthalene species produced subsequently loses a proton in the process of aromatization. The quantum yield for the formation of the rearranged product was found to be dependent on the migrating group.¹ A *p*-cyanobenzyl group and phenacyl group formed the rearrangement product in acetonitrile solvent with a quantum yield of 0.18 and 0.10, respectively.

The photoinduced rearrangement appears to take place by way of an intermediate singlet radical-cation/radical pair, which forms from a short-lived singlet excited state. We also believe that the photoinduced sulfur-carbon bond cleavage results from the fact that the σ^* lowest unoccupied molecular orbital (LUMO) is localized on the bond being cleaved.²

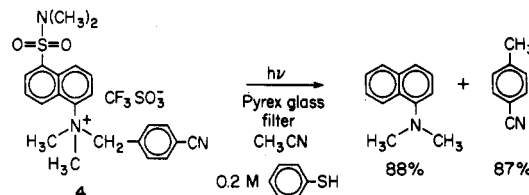
Our objective was to determine if group V onium salts, i.e., ammonium, phosphonium, and arsonium salts, would exhibit photorearrangement of a *p*-cyanobenzyl group from the cationic site, i.e., heteroatom, to an aromatic ring in a manner analogous to sulfonium salts.

Molecular orbital calculations³ have indicated that the ammonium salt 1, phosphonium salt 2, and arsonium salt 3 all exhibit a σ^* LUMO level localized predominantly on the heteroatom and benzylic carbon. We report the photochemical behavior of these three systems in view of the previous discussion.

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Ammonium Salt Photochemistry. Compound 1 was synthesized photochemically from the dansyl derivative 4 in acetonitrile in the presence of benzenethiol to serve as a hydrogen atom donor. Irradiation of 4 produces initially the removal of the sulfonamide group.⁴ Further irradiation produces fragmentation of the benzyl group to provide predominantly out-of-cage reaction products. Simple debenzoylation of 4 was not observed in support of the sequence of photochemical events as indicated above.



The reaction products are consistent with photoinduced homolytic cleavage of the nitrogen-methylene carbon bond in 1 to produce 1-(dimethylamino)naphthylene cation-radical and *p*-cyanobenzyl radical, which reacts with benzenethiol serving as both a one-electron reducing agent

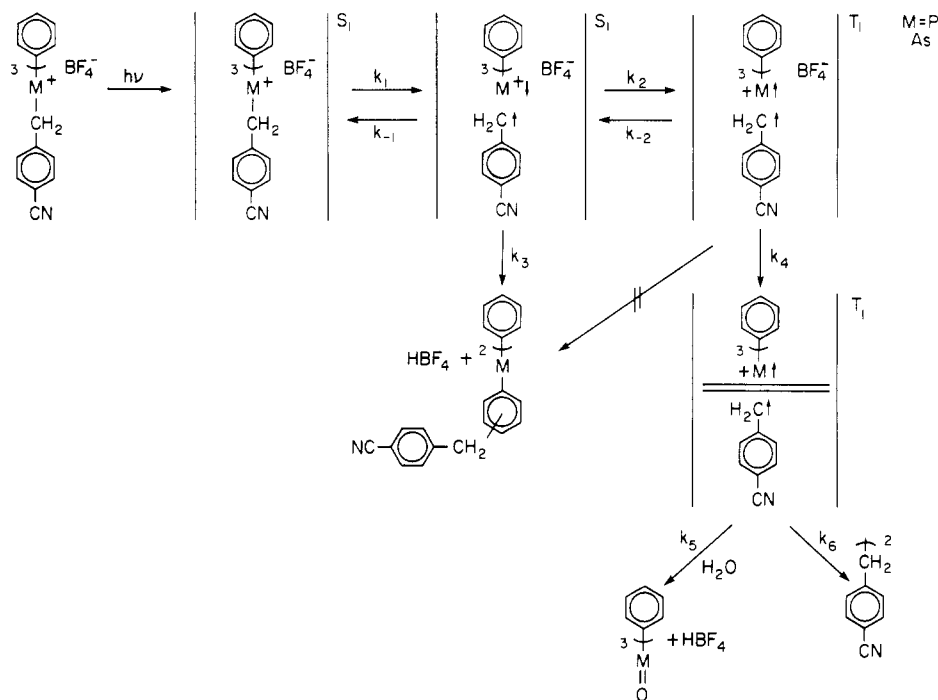
(1) Saeva, F. D.; Morgan, B. P.; Luss, H. R. *J. Org. Chem.* 1985, 50, 4360.

(2) Saeva, F. D.; Morgan, B. P. *J. Am. Chem. Soc.* 1984, 106, 4121.

(3) The MOPAC general-purpose semiempirical molecular-orbital package was used to determine electron spin distributions in the onium salts. Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, 99, 4899.

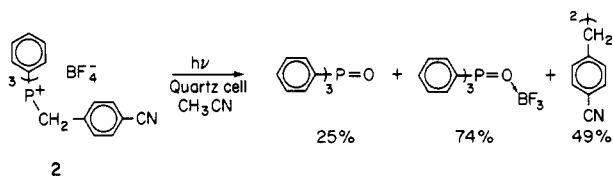
(4) D'Souza, L.; Bhatt, K.; Madaiah, M.; Day, R. A. *Arch. Biochem. Biophys.* 1970, 141, 690.

Scheme I

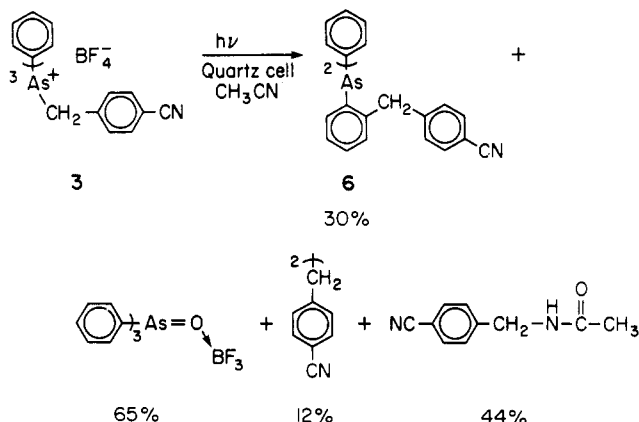


and a hydrogen atom donor.

Phosphonium Salt Photochemistry. Triphenyl(*p*-cyanobenzyl)phosphonium tetrafluoroborate (**2**) was irradiated in acetonitrile solution in a quartz cell. The photoproducts were found to be triphenylphosphine oxide, triphenylphosphine oxide boron trifluoride complex, and the product of dimerization of the *p*-cyanobenzyl radicals, i.e., 4,4'-dicyanobibenzyl (**5**). The products from the photolysis of **2** are derived completely from out-of-cage chemical reactions (see Table I).



Arsonium Salt Photochemistry. The triphenyl(*p*-cyanobenzyl)arsonium tetrafluoroborate salt **3** was photolyzed under experimental conditions identical with that of **2**. In contrast to the photochemistry of **2**, which pro-



vided exclusively out-of-cage products, compound **3** provided predominantly photosolvolysis and in-cage photoproducts.

Table I. Relationship between Atomic Nuclei Hyperfine Coupling Constant and Percent In-Cage Photoproducts

atomic nuclei	hyperfine coupling constant (<i>G</i>) [radical] ^a	% in-cage
³² S	0	100
⁷⁵ As	4.65 [triphenylarsine radical-cation] ^{5a}	56
¹⁴ N	19.3 [dimethylamine radical-cation] ^{5b}	0
³¹ P	306 [triphenylphosphine radical-cation] ⁷	0
¹ H	16.4 [benzyl] ^{5b}	
¹³ C	38.3 [methyl] ^{5b}	

(1% natural abundance)

^aThe specific radical used for the determination of the HCC.

The ratio of in-cage to out-of-cage photoproducts for compound **3** was 1.3 after exclusion of the photosolvolysis product.

Mechanistic Rationale. All of the photoproducts observed from 1–3 can be rationalized as occurring through a cation-radical/radical pair, which reacts either within a solvent cage or out-of-cage. This process is heteroatom dependent and is described by Scheme I.

Photolysis of the onium salt provides an excited singlet state species, which undergoes a homolytic bond cleavage reaction to produce a singlet radical-cation/radical pair in a solvent cage. Compounds that do not possess a heteroatom that is magnetically active, i.e., nuclear spin is 0, undergo primarily an in-cage radical coupling to produce a photorearrangement product. Heteroatoms such as N, P, and As possess a nuclear spin that provides a hyperfine interaction that mixes the triplet radical pair spin state with the singlet radical pair spin state to provide an enhancement of the intersystem crossing rate from *S*₁ to *T*₁. Since the triplet contact radical pair is longer lived than the corresponding *S*₁ pair and cannot provide radical coupling, there is time for escape out-of-cage.

The products derived from the photolysis of group V onium salts are strongly influenced by the magnetic properties of the nuclei at the radical sites. The hyperfine coupling constant (HCC), which is a measure of the nuclear

spin interaction with an unpaired electron, of the heteroatom can be related to the percentage of in-cage (or out-of-cage) products. The table provides the HCC⁵ for a series of nuclei of interest along with the percentage of in-cage coupling. Sulfonium salts possessing sulfur (³²S), which does not possess a nuclear spin, provides essentially 100% in-cage coupling products.¹ The ammonium and phosphonium salts, 2 and 3, respectively, provide only out-of-cage products. This is based on the assumption that the rearrangement product is formed only from in-cage coupling. ⁷⁵As, on the other hand, with a modest HCC, provides both in-cage (56%) and out-of-cage (44%) as well as a photosolvolysis product. An increase in heteroatom HCC provides for a decrease in the percent in-cage coupling reaction.

Both spin-orbit coupling (heavy atom effect) and electron-spin nuclear-spin hyperfine interactions can produce a mixing of excited singlet and triplet states to enhance the rate of intersystem crossing. As you proceed down group V from N to P and then to As, spin-orbit coupling should become more important and more out-of-cage coupling should be observed. This is not the case. Also, consistent with the apparent minor role for the spin-orbit coupling mechanism the spin-orbit coupling of group VI S, which is next to P in the periodic table, does not influence the in-cage/out-of-cage ratio. The nuclear hyperfine interaction in the group V onium salts appears to be the dominant mechanism for enhancing intersystem crossing.

Experimental Section

Melting points are uncorrected. Absorption spectra were run on a Perkin-Elmer Model 330 spectrophotometer equipped with a Model 3600 data station and a Model 600 printer. ¹H NMR measurements were run on a GE Nicolet (300 MHz) spectrometer. Photolyses of the onium salts were performed with use of an Oriol 200-W Hg-Xe lamp. Mass spectroscopy, X-ray, and combustion analyses were performed by the Analytical Technology Division of Eastman Kodak Company.

Synthesis. Triphenyl(*p*-cyanobenzyl)phosphonium Tetrafluoroborate (2). Triphenylphosphine (2.6 g, 0.01 mol) and *p*-cyanobenzyl bromide (2.0 g, 0.01 mol) were dissolved in anhydrous diethyl ether (100 mL) and refluxed for 15 h. The crude product as a white precipitate was collected by suction filtration. The ¹H NMR of this material (1.0 g) was consistent with its structure. The methylene protons at δ 4.78 (CD₃CN) were split by phosphorus (15 Hz). This material was dissolved into 20 mL of water to which was added an aqueous solution of NaBF₄ (2.0 g/10 mL of H₂O). The tetrafluoroborate salt crystallized from the aqueous solution and was collected by suction filtration, providing 4.18 g (90% yield). Recrystallization from an acetonitrile/diethyl ether solvent mixture provided the purified product as white crystals: mp 203–204 °C; ¹H NMR (CD₃CN) δ 4.78 (d, 2 H), 7.10–8.20 (m, 19 H, Ar). Anal. Calcd for C₂₆H₂₁PBF₄N: C, 67.12; H 4.55; F, 16.33. Found: C, 67.1; H, 4.6; F, 16.3.

(*p*-Cyanobenzyl)triphenylarsonium Tetrafluoroborate (3). Triphenylarsine (10.0 g, 33 mmol) and *p*-cyanobenzyl bromide (6.47 g, 33 mmol) were dissolved in nitromethane (50 mL). The solution was refluxed for 2 h and cooled to room temperature. The product, which precipitated from solution (10.75 g, 65% yield) as the bromide salt, was collected by suction filtration. To the bromide salt dissolved in a minimum amount of water (100 mL) was added an aqueous solution of sodium tetrafluoroborate. The product, which precipitated (10.1 g, 64% yield) from solution, was collected by suction filtration, dried, and recrystallized from acetonitrile/ether: mp 203–204 °C; ¹H NMR (CD₃CN) δ 4.79 (s, 2 H), 7.4–8.0 (s, 19 H, Ar); FDMS, *m/e* 422.

***N*-[5-[(Dimethylamino)sulfonyl]naphth-1-yl]-*N,N*-dimethyl-*N*-(*p*-cyanobenzyl)ammonium Trifluoromethanesulfonate (4).** *N*-[5-[(Dimethylamino)sulfonyl]naphth-1-yl]-*N,N*-dimethylamine (5.0 g, 17 mmol) and *p*-cyanobenzyl bromide (3.4 g, 17 mmol) were dissolved in 25 mL of methylene chloride. Silver trifluoromethanesulfonate (4.4 g, 17 mmol) was added to the reaction mixture and stirred for 2 h. The reaction mixture was filtered into anhydrous diethyl ether (200 mL), and the product was obtained as an oil. The ether was decanted, and acetonitrile (~5 mL) was added. Crystallization of the crude product was accomplished by clouding with diethyl ether and cooling to ~ -10 °C in a freezer. The product (1.0 g), which crystallized as white crystals, was collected by suction filtration; mp 196–198 °C; ¹H NMR (CD₃CN) δ 5.43 (s, 2 H) 3.81 (s, 6 H) 2.85 (s, 6 H), aromatic 6.88–8.92 (m, 6 H); FDMS, *m/e* 380.

***N*-[5-[(Dimethylamino)sulfonyl]naphth-1-yl]-*N,N*-dimethylamine.** A solution of *N,N*-dimethylamine (5.0 mL, 75 mmol) in anhydrous diethyl ether (20 mL) was added slowly to a solution of dansyl chloride (5-(dimethylamino)-1-naphthalenesulfonyl chloride, Kodak 990) (10.0 g, 37 mmol) in anhydrous diethyl ether (100 mL). The reaction mixture was stirred for 1 h and extracted twice with 100-mL portions of 10% HCl. The extract was neutralized with NaOH, and the crystallized product was collected by suction filtration. The yield was 7.0 g of light yellow crystals obtained after recrystallization from MeOH: mp 100–101 °C; ¹H NMR (CD₃CN) δ 2.62 (s, 6 H), 2.53 (s, 6 H), 6.85–8.33 (m, 6 H, Ar); FDMS, *m/e* 278.

Photochemistry. The onium salts were photolyzed with a 200-W Hg-Xe lamp (Oriol Corp.) in either a quartz or Pyrex cell, depending on their electronic absorption properties. In a typical photolysis experiment, 5.0 g of the onium salt was dissolved in 50 mL of acetonitrile, previously dried over CaH, and the solution was purged with argon before and during the photolysis. Samples were periodically analyzed by ¹H NMR spectroscopy and TLC to determine the extent of reaction. Once the reaction was considered complete, the acetonitrile solution was flash evaporated and taken up into a minimum of methylene chloride. The material insoluble in methylene chloride, triphenylphosphine oxide, e.g., was separated from soluble compounds at this time. The methylene chloride solution was then added to 200 mL of anhydrous ether to separate the starting material from the diethyl ether soluble products. The material insoluble in ether was then analyzed by ¹H NMR spectroscopy. Recrystallization from CH₃CN/Et₂O provided the recovered starting sulfonium salts and the triphenylphosphine (arsine) tetrafluoroborate complex. The ether-soluble fraction was dried over Na₂SO₄, filtered, and flash evaporated prior to ¹H analyses and column chromatography to provide the rearrangement products and the bibenzyl derivative.

The photoproducts were compared to known materials that were commercially available, i.e., 1-(dimethylamino)naphthalene, toluenitrile, triphenylphosphine oxide, triphenylarsine oxide, or synthesized by known synthetic pathways, i.e., boron trifluoride complexes of the oxides of triphenylphosphine and triphenylarsine. Compound 6 was characterized by mass spectroscopy, ¹H NMR spectroscopy, and combustion analysis.

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