present as a contaminant. The essentials of the ^1H NMR spectrum taken in $DCCl_3$ are given in Table II. The electronic spectrum, obtained in 4:1 2-propanol–water, contains bands with maxima (extinction coefficients in parentheses) at 416 nm (2.8×10^3), 295 nm (5.6×10^3), and 248 nm (2.6×10^4). There were also inflections at 355 and 339 nm.

On 14 h of standing at room temperature, crystalline **2a** became sticky. After recrystallization from a methanol–water mixture this material melted at 90 °C and had spectroscopic properties indistinguishable from those of **3a**, described below.

3a was prepared from 0.5 g (1.6 mmol) of **1a** mixed with 20 mL of methanol, in which it is not soluble. With vigorous stirring, 0.4 g (1.9 mmol) of **5** or the mixed reaction produce of **4b** with $NaBH_4$ was added. After 5 min at room temperature no undissolved **1a** remained. The solution was allowed to stand for a further 10 min and then poured into 100 mL of distilled water cooled in an ice bath. Pale yellow crystals separated from solution and were filtered off, washed with more water, and air-dried. The yield was 0.23 g (1.35 mmol, 77%); mp 91–92 °C.

The IR spectrum of **3a** (a thin film of melt) included bands at 2185 and 1645 cm^{-1} in addition to the expected absorptions around 3000 cm^{-1} and in the fingerprint region. The fingerprint region was substantially different from that of **2a**. The electronic spectrum showed maxima at 334 nm (1.2×10^4), 241 nm (8.8×10^3), and 233 nm (1.1×10^4) in 4:1 2-propanol–water. The NMR spectrum of the nonaromatic protons is described in Table II.

3d was prepared by equilibrating a mixture of **2d** and **3d** with **1d**. The mixture was prepared by reducing 1.0 g (3.0 mmol) of **1d** with $NaBH_4$ as described above for **1a**. The mixed reduction product and 0.1 g (0.3 mol) of **1d** were dissolved in a minimum volume of ethanol (~50 mL) and allowed to stand at room temperature for 14 h. The alcohol was then removed under vacuum and the product taken up in CH_2Cl_2. Most of the **1d** was left behind as an insoluble solid. The CH_2Cl_2 was washed with water, the CH_2Cl_2 was removed under vacuum, and the product, **3d**, was purified by recrystallization from an ethanol–water mixture. The yield was 0.56 g (2.3 mmol, 75%); mp 133 °C. The ^1H NMR spectrum, reported in Table II, confirmed its structure.

Compounds **1a–d**, **4a**, **3a**, and **3d** all gave satisfactory elemental analyses for C, H, and N, none differing from the calculated value by more than 0.25%.

The reduction of **4b** with $Na_2S_2O_4$ in D_2O and isolation of the deuterated product was carried out as previously described. The ^2H NMR spectrum was obtained in $DCCl_3$, with a Nicolet NT-300 NMR spectrophotometer operating at 46 MHz and by using 5000 transients and an acquisition time of 0.64 s. Bands were observed at ~3.7 and ~7.7 ppm; positions previously associated with the CH_2 group in the 4-position and the vinylic proton of **5**. Exact band positions were not obtained because no standard was included. No other absorptions were observed. The band at 7.7 ppm had ~8% of the total absorption while that at 3.7 ppm had ~92%.

Other $NaBH_4$ reductions were carried out as described above for **1a**, except that pure water was sometimes used in place of the water–methanol mixture as solvent and slurries of the less soluble quinolinium salts were reduced in place of solutions. Generally the products were not isolated. They were separated from the reaction mixture in which they were produced (10 mL of aqueous or aqueous alcohol solution) by extraction into 1–2 mL of $CDCl_3$. The $CDCl_3$ layer was washed with two 10-mL portions of water, dried, and the H NMR spectrum obtained. The product composition was deduced from the relative intensities of the methyl bands (of methyl derivatives) or the benzylic methylene bands (of benzyl derivatives).

Registry No. **1a**, 46176-64-1; **1b**, 84811-85-8; **1c**, 21979-27-1; **1d**, 85289-84-5; **1e**, 47072-02-6; **2a**, 50741-33-8; **2b**, 85749-92-4; **2c**, 85749-93-5; **2d**, 85749-95-7; **2e**, 85749-96-8; **3a**, 72594-76-4; **3b**, 20224-92-4; **3c**, 85749-94-6; **3d**, 73184-18-6; **3e**, 17260-79-6; **4a**, 49865-82-9; **4b**, 16183-83-8; **5**, 952-92-1; NAD^+, 53-84-9; 3-(aminocarbonyl)-1-benzyl-1,6-dihydropyridine, 2288-38-2; $NaBH_4$, 16940-66-2; $Na_2S_2O_4$, 7775-14-6; 3,5-dichloro-1,2-dihydro-1-methylpyridine, 85749-97-9; 3,5-dichloro-1,4-dihydro-1-methylpyridine, 85749-98-0; 3-(aminocarbonyl)-1,6-dihydro-1-methylpyridine, 23338-78-5.

Photolysis of *p*-Toluenesulfonyl Azide and Its Charge-Transfer Complex with Aniline

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Photolysis of *p*-toluenesulfonyl azide (1) in *p*-xylene and cyclohexane gives primarily the products derived from insertion of (*p*-tolylsulfonyl)nitrene into the solvent. For *p*-xylene, an unstable intermediate product is formed which decomposes in the dark at room temperature to give both the ring-insertion product and the corresponding *p*-toluenesulfonamide (2). Photolysis of the ground-state charge-transfer complex between *p*-toluenesulfonyl azide and aniline gives six products, the major product being the sulfonyl hydrazide 7. Futhermore, formation of the insertion product by reaction with the solvent provides evidence for production of (*p*-tolylsulfonyl)nitrene from the excited charge-transfer complex.

Since the pioneering work of Curtius,[1-3] a large number of papers, summarized in several recent reviews,[4-6] have dealt with the decomposition of arenesulfonyl azides. While most of the reports on sulfonyl azides have been concerned with their thermal decomposition in organic solvents,[7-10] a few have included results of photolysis experiments.[11-17] In general, it has been found that photolysis of arenesulfonyl azides in alcohol solvents yields the corresponding sulfonamide. Thus, Reagan and Nickon[14] found that photolysis of arenesulfonyl azides in either

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(1) Curtius, T. *J. Prakt. Chem.* **1930**, *125*, 303.
(2) Curtius, T. *J. Prakt. Chem.* **1930**, *125*, 323.
(3) Curtius, T. *Z. Angew Chem.* **1913**, *26*, 134.
(4) Abramovitch, R. A.; David, B. A. *Chem. Rev.* **1964**, *64*, 149.
(5) Breslow, D. S. In "Nitrenes"; Lwowski, W., Ed.; Interscience: New York, 1970; p 245.
(6) Abramovitch, R. A.; Kyba, C. P. In "The Chemistry of the Azido Group"; Patai, S., Ed.; Interscience: New York, 1971; p 279.
(7) Sloan, M. F.; Breslow, D. S.; Renfrow, W. B. *Tetrahedron Lett.* **1964**, 2905.

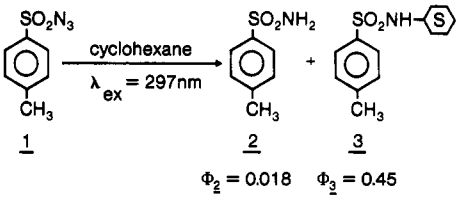
0022-3263/83/1948-2056$01.50/0

anhydrous or aqueous (4% water) 2-propanol gave almost quantitative (>90%) yields of the corresponding unsubstituted sulfonamides. In the case where methanol was the solvent, photolysis of benzenesulfonyl azides gave, in addition to benzenesulfonamide, the hydroxylamine derivative *N*-(phenylsulfonyl)-*O*-methylhydroxylamine.[12] In contrast to these results, photolysis of arenesulfonyl azides in hydrocarbon solvents such as benzene and cyclohexane was reported to give primarily brown precipitates which were not fully characterized.[15] Lwowski et al.[15] did note, however, the presence of some *N*-phenylbenzenesulfonamide and benzenesulfonamide upon photolysis of benzenesulfonyl azide in benzene. In no case have quantum yields been reported for direct photolysis of arenesulfonyl azides in any solvent.

In this paper we report on quantitative investigations of the photolysis of *p*-toluenesulfonyl azide (1) in *p*-xylene and cyclohexane solvents. Quantum yields for product formation are given in both solvents. In *p*-xylene, the existence of an intermediate product that decomposes to form both the corresponding sulfonamide and the ring-insertion product into *p*-xylene was found. Finally, a study of the ground-state charge-transfer (CT) complex formed by 1 and aniline is presented. Photolysis of the ground-state CT complex is a heretofore unexplored method for chemically activating the decomposition of the sulfonyl azide group.

Results and Discussion

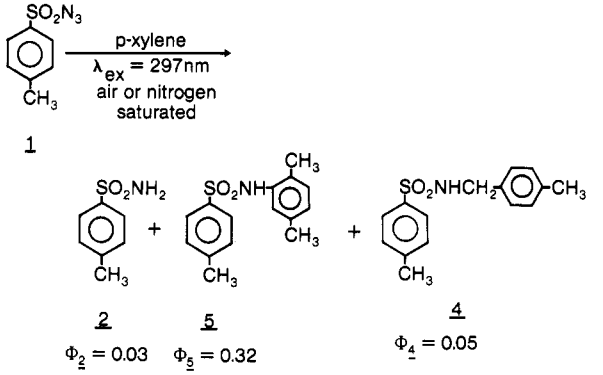
Photolysis of *p*-Toluenesulfonyl Azide in Cyclohexane. As noted in the introduction, previous attempts at photolysis of arenesulfonyl azides in solvents such as benzene or cyclohexane resulted in the formation of brown precipitates which prevented carrying these reactions to high conversions.[15] By using high-pressure liquid chromatography (HPLC) techniques, we have isolated and quantitatively analyzed the products resulting from photolysis of *p*-toluenesulfonyl azide (1) in both cyclohexane and *p*-xylene at low conversions. Thus, photolysis of a 0.047 M solution of 1 in cyclohexane at 297 nm yielded both *p*-toluenesulfonamide (2) and *N*-cyclohexyl-*p*-toluenesulfonamide (3), with quantum yields of 0.018 and 0.45, respectively. The disappearance quantum yield (Φ_D) for 1 is 0.51. The quantum yields were the same in air-saturated or nitrogen-degassed solutions. Presumably for the photolysis of 1, as has been suggested for the thermolysis of 1 in cyclohexane,[8] an intermediate (*p*-tolylsulfonyl)nitrene is formed that can abstract hydrogens from the solvent to give the sulfonamide 2 or react with cyclohexane by inserting into one of the C–H bonds to give the sulfonamide 3 (eq 1). The low value of Φ_2 compared to Φ_3 ($\Phi_3/\Phi_2 = 25$) parallels the low yield reported for 2 (5%) and the high yield for 3 (58%) upon thermolysis of 1 in cyclohexane (yield 3/yield 2 = 12).[8] These results are



(1)

in marked contrast to the large quantum yield obtained for formation of 2 upon photolysis of 1 in 2-propanol ($\Phi_2 = 0.56$), nearly 30 times larger than in cyclohexane or *p*-xylene. The large yield of 2 in 2-propanol is most likely due to involvement of a chain process as proposed by Reagan and Nickon.[14] The various possibilities for the photolytic decomposition of arenesulfonyl azides in alcohols have been considered by Breslow.[5]

Photolysis of *p*-Toluenesulfonyl Azide in *p*-Xylene. Photolysis of 1 in *p*-xylene afforded three primary products: *p*-toluenesulfonamide (2), *N*-(α-xylyl)-*p*-toluenesulfonamide (4), and *N*-(2,5-dimethylphenyl)-*p*-toluenesulfonamide (5) (isolated by preparative HPLC), whose quantum yields were the same in air-saturated or nitrogen-degassed solutions (eq 2).



(2)

The quantum yield for formation of the sulfonamide 2 in *p*-xylene is small ($\Phi_2 = 0.03$), while the quantum yield for nitrene insertion into the *p*-xylene ring ($\Phi_5 = 0.32$) is much larger, essentially the same trend observed for photolysis in cyclohexane. Surprisingly, the photolysis of 1 in *p*-xylene also gives insertion of the intermediate *p*-toluenesulfonyl nitrene into a carbon–hydrogen bond of one of the methyl groups of *p*-xylene to give product 4, albeit with a lower quantum yield ($\Phi_4 = 0.05$) than for insertion into the carbon–hydrogen bonds on the ring of *p*-xylene or the carbon–hydrogen bonds of the methylene carbons of cyclohexane.[18] Photolysis of 1 in an equimolar solution of cyclohexane and *p*-xylene results in a ratio for the quantum yields of insertion products of 1.0:0.7:0.1 $\Phi_3:\Phi_5:\Phi_4$, essentially the same ratio obtained for the product quantum yields obtained in solutions of *p*-xylene and cyclohexane separately. Apparently, the sulfonylnitrene is indiscriminating with regards to insertion into a ring C–H bond of cyclohexane or *p*-xylene, while insertion into the methyl C–H bonds of *p*-xylene is relatively inefficient.

An observation made concerning the sequence of product formation on photolysis of 1 in *p*-xylene is particularly noteworthy. During HPLC analysis of photolyzed samples of 1 in *p*-xylene it was observed that the yields of products 2 and 5 varied with the time between completion of the photolysis and the start of the HPLC analysis. Delay times of as little as 45 min caused significant increases in the yields of products 2 and 5. A sample of 1 photolyzed for

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(9) Heacock, J. F.; Edmison, M. T. *J. Am. Chem. Soc.* **1960**, *82*, 3460.
(10) Abramovitch, R. A.; Roy, J.; Uma, U. *Can. J. Chem.* **1965**, *43*, 3407.
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(17) McKenna, J. M.; McKenna, J.; Walley, A. R. *J. Chem. Soc., Chem. Comm.* **1974**, 140.

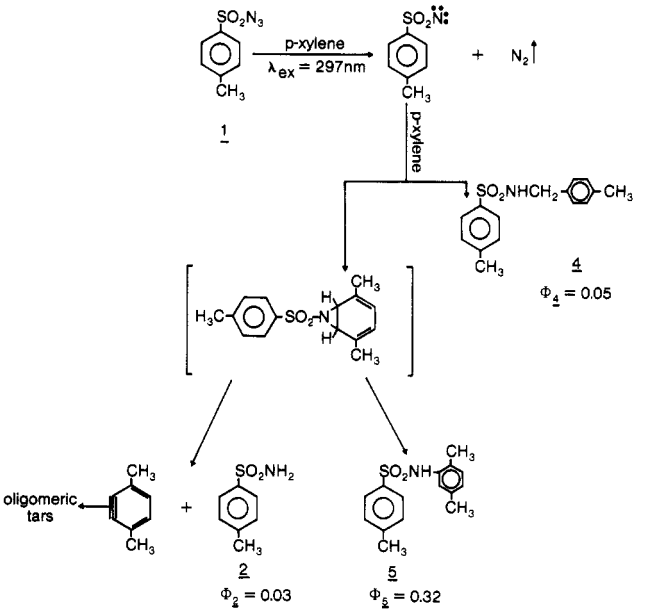
(18) Product 4 is also detected for thermolysis of 1 in *p*-xylene. Details are to be reported in a manuscript currently in preparation.

a short period (5 min) in *p*-xylene and analyzed immediately showed little or none of either the insertion product into *p*-xylene **5** or the unsubstituted sulfonamide **2**; i.e., the quantum yields obtained upon immediate analysis for **2** and **5** are negligible (<0.01). Interestingly, at these short analysis times the quantum yield for formation of product **4** is much larger (Φ_4 = 0.05) than those for **2** and **5**, although it does not increase with time. An unidentified peak (see Experimental Section for details) was also detected by HPLC in samples of **1** analyzed immediately after photolysis. At increasing time increments between the completion of photolysis and the beginning of the HPLC analysis, the unidentified component decreased with a half-life of about 40 min at room temperature while the yields for products **2** and **5** increased concurrently. When the photolyzed solution of **1** was kept in the dark for a few hours, all of the unstable intermediate product was converted into products **2** (Φ_2 = 0.03) and **5** (Φ_5 = 0.32).

Our observations for the photolysis of **1** in *p*-xylene are consistent with the proposals of Breslow[5,8] and Abramovitch[10] regarding the reaction of sulfonyl azides with aromatic substrates. They suggested that the initial step for the thermolysis of sulfonyl azides is elimination of nitrogen from the azide to give a sulfonylnitrene, which then reacts with the substrate to form products. Abramovitch[10,11] and others[19] further postulated that addition of the sulfonylnitrene to aromatic molecules proceeds through an aziridine intermediate which decomposes to give a ring-insertion product as well as the corresponding unsubstituted sulfonamide. Our results provide direct evidence for the formation of an intermediate in the photodecomposition of sulfonyl azides in aromatic solvents which decomposes to give both the substituted (product **5**) and unsubstituted (product **2**) sulfonamide. It would be desirable to conclusively identify this intermediate; however, the photochemical and thermal lability of this intermediate severely hinders its isolation and positive identification. Thus, photolysis of **1** leads to a very low steady-state concentration of the intermediate; i.e., no matter how long a solution of **1** is photolyzed the maximum concentration of this species remains constant at an extremely low level (less than 10 μg/mL) with a sulfonyl azide concentration approximately 1000 times larger. As soon as the photolysis is over, the intermediate begins to convert to the final products which themselves are only isolated by preparative HPLC with substantial effort. We attempted to react the photolysate (0.06 M **1** in *p*-xylene photolyzed for 30 min at 297 nm) with the dienophile maleic anhydride (0.1 M). Unfortunately, the Diels–Alder reaction in this case does not compete favorably with the rearrangement process. Furthermore, a Fourier transform infrared spectrum (1000 scans) of a sample of a solution (0.06 M) of **1** in *p*-xylene photolyzed at 297 nm for 30 min (steady-state concentration of the intermediate obtained) showed no peaks in the region (1100–1400 cm^{-1}) expected for an aziridine ring. This is not unreasonable with regards to an aziridine intermediate, however, as IR bands for aziridine rings are not particularly strong and the intermediate is very low in concentration (<10 μg/mL). Work is continuing to try to identify conclusively the structure of the intermediate.

A possible mechanism for the photolysis of **1** in *p*-xylene involving the unstable intermediate (shown here as the aziridine proposed by Abramovitch[10,11]) is given in Scheme I. In the first step, photolysis results in N–N bond cleavage of the azide linkage, eliminating nitrogen and

Scheme I



generating (*p*-tolylsulfonyl)nitrene. The nitrene can then attack *p*-xylene at a methyl carbon–hydrogen bond to give **4** or attack the ring to give the proposed unstable aziridine intermediate. This intermediate can subsequently decompose via two pathways, as shown in Scheme I, to produce products **2** and **5**. According to Abramovitch,[10] formation of **2** should be accompanied by a benzyne structure that rapidly leads to oligomeric tars. Tars are observed in the preparative photolysis of **1** in *p*-xylene. Alternatively, the unstable aziridine intermediate can also collapse to give **5**. Since the quantum yield of **5** is about 11 times that of **2**, it appears that the preferential pathway for decomposition of the intermediate is collapse to the substituted sulfonamide **5** rather than extrusion of unsubstituted sulfonamide **2** with concurrent formation of an unstable benzyne structure.

Photolysis of the Charge-Transfer Complex between 1 and Aniline. During an investigation of the thermal and photochemial reactions of arenesulfonyl azides in a variety of solvents, we found that these azides readily form reactive ground-state charge-transfer (CT) complexes with a number of electron donors including aliphatic and aromatic amines. Formation of CT complexes between arenesulfonyl azides and electron donors provides a means for extending the absorption of light by these systems to wavelengths longer than those absorbed by the sulfonyl azides alone. In this paper we report on the photochemical behavior of the CT complex between **1** and aniline irradiated at 366 nm where neither component of the complex absorbs.

The UV absorption spectra of **1** (0.112 M), aniline (0.704 M), and the CT complex between **1** and aniline at the same concentrations (cyclohexane solution, 1-cm cell) in Figure 1 show that the complex absorbs strongly at 366 nm where neither **1** nor aniline absorbs appreciably. The absorbance of this complex (ϵ_{366} 5 ± 1, K_{eq} = 0.4 ± 0.1) at the same concentrations in a 10-cm path length cell in which the photolysis experiments were conducted was 0.98 while the absorbances of **1** and aniline individually were negligible. Thus, irradiation of this system at 366 nm results in the six products shown in Scheme II, arising exclusively from the CT complex between **1** and aniline. Product quantum yields were calculated for each product by comparison of the HPLC response of the peaks in the photolyzed sample to the response of authentic samples of independently

(19) (a) Ayzangar, N. R.; Photak, M. V.; Purchit, A. K.; Tilak, B. D. *Chem. Ind. (London)* **1979**, 853. (b) Tilney-Bassett, J. F. *J. Chem. Soc.* **1962**, 2517.

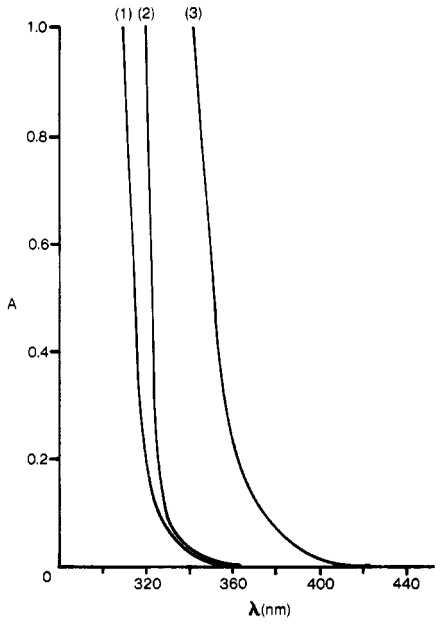
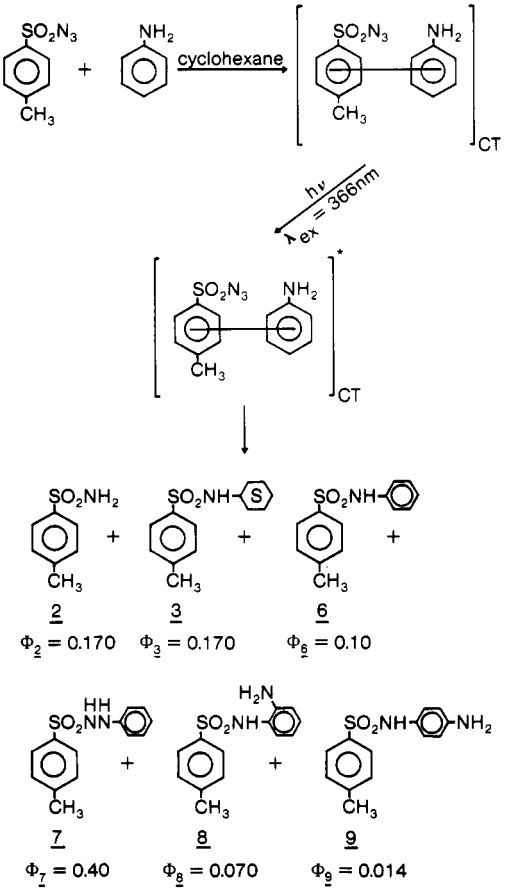


Figure 1. (1) 1 (0.112 M), (2) aniline (0.704 M), and (3) 1 (0.112 M) + aniline (0.704 M) in cyclohexane in a 1-cm cell.

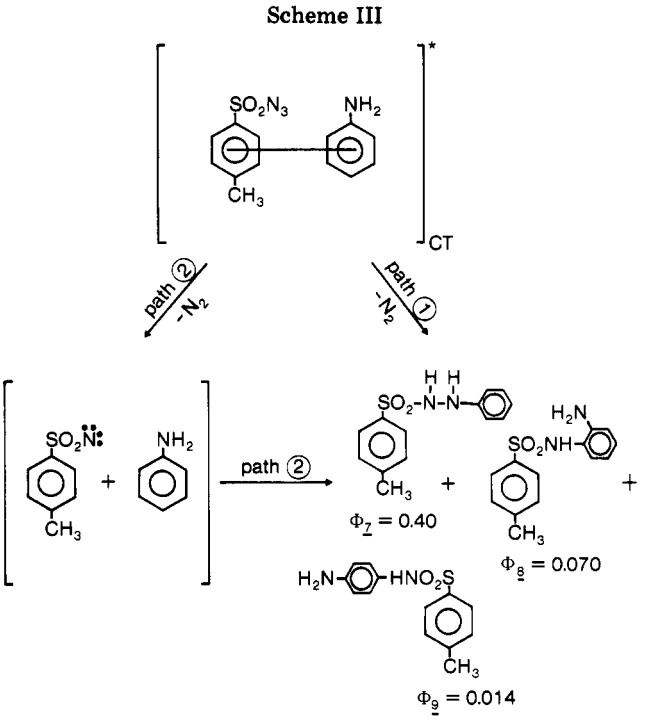
Scheme II



synthesized compounds (see Experimental Section). The sum of the quantum yields for product formation of all the products given in Scheme II (Φ_{total}) is 0.92. The major products for photolysis are almost all accounted for, and only one minor unidentified product peak was detected on HPLC.

Several observations can readily be made concerning the products of photolysis of the CT complex between 1 and aniline (Scheme II). First, while hydrazide 7 has the highest quantum yield of any of the photolysis products,

Scheme III



it has not been reported for the thermolysis of 1 in the presence of aniline.[1,9] This result is understandable as we found that thermolysis (>100 °C) of 7 results in its rapid disappearance, while it decomposes rather slowly (over a period of 2–3 days) at room temperature (dark) even in the presence of aniline and 1. Because the photolysis of the CT complex between 1 and aniline is carried out at room temperature, product 7 can be detected by HPLC before it decomposes to an appreciable extent. Finally, it should be pointed out that a careful HPLC analysis of the thermolysis of 1 in the presence of 0.10 M aniline in *p*-xylene does indeed show a small steady-state concentration of hydrazide 7 remaining constant with thermolysis times up to 8 h.[20]

The hydrazide product 7 and the two sulfonamides 8 and 9 can be envisioned to form either directly from the excited CT complex (path 1, Scheme III) or by decomposition of the complex to give the intermediate (*p*-tolylsulfonyl)nitrene, which then attacks ground-state aniline (path 2, Scheme III). It is possible, within the context of Scheme III, for 7 to form from either the same pathway or from a different pathway than that for products 8 and 9. Regardless of whether path 1 or path 2 leads to product 7, 8, or 9, it is obvious that 7 (Φ_7 = 0.40) is the preferred product, being formed in highest yield. An examination of the quantum yields for formation of sulfonamides 8 and 9 gives a ratio of 5:1 for ortho (8) to para (9) insertion products (Φ_8/Φ_9 = 0.070/0.014 = 5.0). This is interesting since Edmison et al.[9] found that thermolysis of benzenesulfonyl azide in aniline gives a ratio of 1.0:1.3 for the ortho/para insertion products. These contrasting results suggest that the excited CT complex between 1 and aniline has an orientation which, when carried through the reaction by either path 1 or 2, favors the formation of ortho product 8.

Product 6 is probably formed directly from the excited CT complex through a nucleophilic displacement of the azide leaving group by aniline. Breslow[21] similarly concluded that a nucleophilic displacement process was re-

(20) Hoyle, C. E.; Christie, P. A., unpublished results.
(21) Breslow, D. S., ref 5, p 276.

sponsible for certain of the anilide products obtained by Curtius[1] and Edmison[9] for the thermolysis of arenesulfonyl azides in the presence of aniline. The quantum efficiency for formation of **2** from photolysis of the CT complex (Φ_2 = 0.170) is much larger than for direct photolysis of **1** in cyclohexane (Φ_2 = 0.018) or *p*-xylene (0.03). This can be explained on the basis of the more readily abstractable hydrogens in aniline than those of *p*-xylene or cyclohexane.[22] Finally, **3** is formed in an appreciable yield, indicating that, indeed, the excited CT complex between **1** and aniline decomposes, at least in part, to give (*p*-tolylsulfonyl)nitrene (the first part of path 2, Scheme III) which diffuses into the solvent to react with cyclohexane to produce **3**.

Conclusions

Photolysis of *p*-toluenesulfonyl azide (**1**) in cyclohexane and *p*-xylene gives primarily the products formed by insertion of (*p*-tolylsulfonyl)nitrene into the solvent. In *p*-xylene, a single unstable intermediate was detected which leads upon decomposition to both the ring-insertion product **5** and the unsubstituted sulfonamide **2**. The presence of this intermediate, although not conclusively identified, supports the proposal of Abramovitch[10,11] that sulfonylnitrenes react with aromatic solvents by a two-step process with formation and subsequent rearrangement of an aziridine intermediate.

The ground-state charge-transfer complex between **1** and aniline has been photolyzed to give six products, the primary product being the sulfonyl hydrazide **7** which was previously unreported for the thermolysis of **1** in aniline. Formation of the insertion product **3** into cyclohexane provides evidence for formation of (*p*-tolylsulfonyl)nitrene directly from the excited CT complex. Thus, photolysis of the CT complex between **1** and aniline is a unique method for chemically activating sulfonyl azides to give a number of products and provides a rationale for the excellent success of aromatic amines and other electron donors as sensitizers for photoresist polymers bearing pendant arenesulfonyl azide chromophores.[23] Work is continuing in our laboratory on the photolysis of other ground-state CT complexes between sulfonyl azides and various electron donors. Results of quenching and sensitization studies to determine the spin multiplicity of (*p*-tolylsulfonyl)nitrenes leading to products will be reported in a separate paper.

Experimental Section

Uncorrected melting points were determined on a Thomas-Hoover capillary melting point apparatus. NMR spectra were taken on a 90-MHz JEOL Model FX90Q spectrometer. The high-pressure liquid chromatography was carried out for both quantitative and preparative analysis on a Waters Associates (Milford, MA) liquid chromatograph with a Laboratory Data Control (Riviera Beach, FL) variable-wavelength Spectro Monitor I detector. A U6K universal (Water Associates) injector valve and two Model 6000 high-pressure pumps plus a Model 660 solvent programmer (with several standard solvent gradients) made up the HPLC system. UV absorbances were measured on a Perkin-Elmer 552 spectrophotometer.

Materials. All solvents were spectrograde and were purchased from Burdick and Jackson. Sodium azide (Alfa, 99%), *p*-toluenesulfonyl chloride (Aldrich, 98%), and *p*-toluenesulfonamide (**2**, Aldrich) were used as received. *p*-Toluenesulfonyl azide (**1**) was prepared by the method of Breslow,[8] and its purity was established by HPLC. Aniline (Aldrich Chemical Co.) was purified by refluxing and distillation from tin(II) chloride.

Preparation of Substituted Sulfonamides 3–9. The following sulfonamides were prepared by literature procedures involving reaction of *p*-toluenesulfonyl chloride with the appropriate amine (or hydrazine): *N*-cyclohexyl-*p*-toluenesulfonamide (**3**),[24] *N*-*p*-xylyl-*p*-toluenesulfonamide (**4**),[25] *N*-(2,5-dimethylphenyl)-*p*-toluenesulfonamide (**5**),[26] *N*-phenyl-*p*-toluenesulfonamide (**6**),[27] *N*-phenyl-*p*-toluenesulfonyl hydrazide (**7**),[28] *N*-(2-aminophenyl)-*p*-toluenesulfonamide (**8**),[29] *N*-(4-aminophenyl)-*p*-toluenesulfonamide (**9**).[30] The melting points of these compounds were in agreement with literature values, and spectral data supported the assigned structures.

Photolysis Equipment. Preparative photolysis was carried out on a Rayonet Model RPR-100 (Southern New England Radiation Corp.) with eight irradiation lamps of the appropriate wavelength range. The sample solutions were placed in quartz tubes.

Quantitative photolysis was performed on either a Schoeffel lamp system or a Hanovia lamp system.[31] The Schoeffel system was comprised of a LDS 255-HR DC regulated power supply, a 151-N/2 housing with quartz optics, and a 450-W Osram medium-pressure short-arc mercury lamp. The Hanovia system was comprised of a 450-W Hanovia power supply, a 450-W medium-pressure long-arc mercury lamp from Hanovia, and a homemade housing with a 2.5-in. opening. Both systems were directed along an optical bench holding an electronic shutter (Burke & James) with an automatic timer (Cole-Parmer) for accurate measurement (±0.1 s) of photolysis time, a mounting for 2 in. × 2 in. filters, and the sample cell. The sample cell was either a 1 cm × 1 cm × 3.5 cm quartz cell or a 10-cm path length (25-mL capacity) Pyrex cell. The photon intensity was measured either by standard actinometry or with a calibrated photodiode. The photodiode was a PT-171C quartz wide-eye from Illumination Industries. The intensity (photon flux) was read on an Illumination Industries Model 745 radiometer. The PT-171C photodiode/745 radiometer combination was calibrated with both a standard lamp source and ferrioxalate actinometry.

Quantitative HPLC Analysis. All quantitative measurements were made by comparison of the HPLC peak heights of the products in photolyzed samples (25-μL injections) with the peak heights of standard solutions (known concentrations) and authentic samples synthesized by an independent method. The following analytical columns and conditions will be referred to in describing the quantitative analysis for the samples in this work. **Conditions A**: 25 cm × 4.6 mm Amino Hi-Chrom reversible column (Regis Chemical); 1.2 cm^3/min flow rate; eluent A is 1% 2-propanol/isooctane, and B is 50% 2-propanol/isooctane; A for 23 min then A → 75% B with standard gradient (no. 6, 60 min) Spectromonitor at 240 nm. **Conditions B**: 25 cm × 4.6 mm Nitrile Hi-Chrom reversible column (Regis Chemical); 1.2 cm^3/min flow rate; eluent A is 1% 2-propanol/isooctane, and B is 50% 2-propanol/isooctane; A for 23 min then A → 75% B with standard gradient (no. 6, 60 min) Spectromonitor at 240 nm. **Conditions C**: 25 cm × 4.6 mm Nitrile Hi-Chrom reversible column (Regis Chemical); 1.2 cm^3/min flow rate; eluent A is isooctane, and B is 6% 2-propanol/chloroform; 10% B/A for 10 min and then 10% B/A → 70% B with standard gradient (no. 6, 60 min) Spectromonitor at 260 nm. **Conditions D**: 25 cm × 4.6 mm Nitrile Hi-Chrom reversible column (Regis Chemical); 1.2 cm^3/min flow rate; eluent A is isooctane and B is 20% 2-propanol/isooctane with 20% B → 100% standard gradient (no. 7, 15 min) Spectromonitor at 240 nm. Many other column/solvent gradient combinations were run for the product separations of the photolyzed samples described in this work.

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Photolysis of p-Toluenesulfonyl Azide (1) in Cyclohexane. For preparative photolysis, a nitrogen-degassed solution of 0.46 g of 1 in 50 mL of cyclohexane was photolyzed in a Rayonet reactor at ~300 nm (eight RPR 3000-Å lamps) for 2 h. After the solid portion (brown precipitate) was filtered, the resultant liquid was concentrated to dryness with a rotary evaporator. The dried sample was then dissolved in 6% 2-propanol/chloroform, and preparative HPLC was used to isolate products. Two 200-mg preparative separations were performed by using a 50 cm × 9.4 mm M-9 μ-Partisil semipreparative column by Whatman (4.8 cm^3/min) with a standard gradient, having eluent A = isooctane and B = 6% 2-propanol/chloroform (10% B → 100% B). Fractions 5 (15.0–18.0 min) and 6 (18.0–21.0 min) were combined to give about 10 mg of a white solid with a ^1H NMR identical with that of an authentic independently synthesized sample of 3.

For quantitative measurements, which were run in both air and nitrogen-degassed solutions, 3-mL aliquots of a 0.047 M solution ($A_{297nm} > 2.5$) of 1 in cyclohexane (1-cm quartz cell) were photolyzed at 297 nm (Schoeffel system, Baird Atomic 297-nm band-pass filter) for periods of 5, 10, 20, and 40 min. Quantitative yields of products were obtained by comparison of the peak heights (HPLC) of the photolyzed samples with the peak heights of standards of known concentrations of authentic samples of 2 and 3 which were independently synthesized: conditions A, t_R (retention time) for 2 is 52.7 min, t_R for 3 is 33.8 min; conditions B, t_R for 2 is 45.1 min, t_R for 3 is 28.9 min; conditions C, t_R for 2 is 37.6 min, t_R for 3 is 20.6 min; conditions D, t_R for 2 is 18.2 min, t_R for 3 is 9.9 min. Light intensity measurements, obtained by standard ferrioxalate actinometry (2.95×10^{15} photons/s in a 3-mL volume), were used to calculate quantum yields for 2 and 3 from the quantitative HPLC yields. The quantum yields for 2 and 3 were invariant with photolysis time (5, 10, 20, 40 min).

Photolysis of p-Toluenesulfonyl Azide (1) in p-Xylene. For preparative photolysis a nitrogen-degassed solution of 0.75 g of 1 in 50-mL of p-xylene was photolyzed in a Rayonet reactor at ~300 nm (eight RPR 3000-Å lamps) for 1.75 h. A brown precipitate which was found to be soluble in methanol was filtered off. The liquid portion was evaporated to about 2 mL, and preparative HPLC was used to isolate products as follows. Several 250-mg samples were separated on the first run on a 50 cm × 9.4 mm M-9 μ-Partisil semipreparative column by Whatman (4.8 cm^3/min) by using a standard gradient with eluent A = isooctane and B = 6% 2-propanol/chloroform (gradient of 5% B → 25% B). Fraction 7 (23.5–25.0 min) gave 16 mg of a white solid identified as 5 by comparison with the ^1H NMR spectrum of an authentic sample independently synthesized.

Fraction 8 (25.0–27.1 min) and fraction 9 (27.1–31.5 min) were combined and run on the same Partisil semipreparative column as above but with eluent A = isooctane and B = ethyl acetate (20% B/A) and no gradient. Fraction 2 (10.0–16.0 min) from this run was 1 mg of a pure white solid identified as 4 by comparison of its ^1H NMR spectrum with that of an authentic sample independently synthesized.

Fraction 11 (42.0–58.0 min) of the first preparative run was also run a second time on the same Partisil column with eluent A = isooctane and B = ethyl acetate (35% B/A) and no gradient. Fraction 2 (10.0–17.0 min) of this run yielded 2 mg of a white solid identified as 2 by comparison of its ^1H NMR spectrum with that of an authentic sample.

For quantitative measurements, which were run in both air-saturated and nitrogen-degassed solutions, 3-mL aliquots of a 0.060 M solution ($A > 2.5$) of 1 in p-xylene (1-cm path length quartz cell) were photolyzed at 297 nm (Schoeffel system, Baird Atomic 297-nm band-pass filter) for various times from 5 to 40 min. Due to interference from absorbing products, quantitative results were obtained for the short photolysis time (5 min). Quantitative yields of products were obtained by comparison of the peak heights (HPLC) of the photolyzed sample with peak heights of standards of known concentrations of authentic samples of 2, 4, and 5 which were independently synthesized: conditions A, t_R for 2 is 52.7 min, t_R for 4 is 38.6 min, t_R for 5 is 33.8 min; conditions B, t_R for 2 is 45.1 min, t_R for 4 is 33.6, t_R for 5 is 22.4 min; conditions C, t_R for 2 is 37.6 min, t_R for 4 is 21.8 min, t_R for 5 is 17.0 min; conditions D, t_R for 2 is 18.2 min, t_R for 4 is 11.0, t_R for 5 is 9.0 min. Light intensity measurements, obtained by standard ferrioxalate actinometry (2.95×10^{15} photons/s in a 3-mL volume) were used to calculate quantum yields for 2, 4, and 5 from the quantitative HPLC yields. An unidentified product with t_R = 8.5 min on column B was obtained for photolyzed samples (5-min photolysis time) analyzed on the HPLC immediately after photolysis. Subsequent HPLC analysis at increasing time delays after the photolysis showed a loss in the peak at 8.2 min with a concurrent increase in 2 and 5. The quantum yields quoted in the text for 2 and 5 were determined after a several-hour delay between the photolysis and the analysis on the HPLC to ensure that all of the unidentified intermediate had been converted to 2 and 5.

Photolysis of p-Toluenesulfonyl Azide (1) in 2-Propanol. For preparative photolysis a nitrogen-degassed solution of 0.649 g of 1 dissolved in 50-mL of 2-propanol was photolyzed in a Rayonet reactor at ~300 nm (eight RPR 3000-Å lamps) for 2 h. According to HPLC analysis, all of 1 was gone. The clear photolyzed solution was rotary evaporated to dryness and the solid dissolved in 1,1,2-trichlorotrifluoroethane. The solution, after suction filtration to remove insoluble material, was rotary evaporated, giving a white solid product (0.3 g) identified as 2 by melting point and ^1H NMR.

For quantitative measurements, a 3-mL aliquot of a 0.041 M solution ($A > 2.5$) of 1 in 2-propanol (1-cm path length quartz cell) was photolyzed at 297 nm (Schoeffel system, Baird Atomic 297-nm band-pass filter) for 25 min. Quantitative yields of products were obtained by comparison of the peak heights (HPLC) of the photolyzed sample with peak heights of standards of known concentrations of authentic samples of 2: conditions A, t_R for 2 is 52.7 min; conditions B, t_R for 2 is 45.1 min; conditions C, t_R for 2 is 37.6 min; conditions D, t_R for 2 is 18.2 min. In this case, the quantum yield was obtained by comparison with the results for a similarly treated sample of 1 in cyclohexane (determined as described earlier).

Photolysis of CT Complex between p-Toluenesulfonyl Azide (1) and Aniline. A solution of 25 mL of 0.112 M 1 and 0.704 M aniline (A = 0.98 at 366 nm) was photolyzed for 5400 s at 366 min in a 10-cm path length cell by using the previously described Hanovia lamp system. The sample solution cell was mounted horizontally about 0.75 m from the source where the beam divergence was minimized. A Corning 366-nm filter combination was used. The number of photons entering the sample at 366 nm (2.7×10^{15} photons/s) were calculated by using the PT-171C quartz wide-eye photodiode/745 radiometer combination calibrated as described previously. Quantitative yields of products were obtained by comparison of the peak heights (HPLC) of the photolyzed sample with peak heights of standards of known concentration of authentic samples of 2, 3, and 6–9 which were independently synthesized: conditions A, t_R for 2 is 52.7 min, t_R for 3 is 33.8 min, t_R for 6 is 49.7 min, t_R for 7 is 48.5 min, t_R for 8 is 72.6 min, t_R for 9 is 70.9 min; conditions B, t_R for 2 is 45.3 min, t_R for 3 is 28.9 min, t_R for 6 is 34.1 min, t_R for 7 is 39.9 min, t_R for 8 is 45.7 min, t_R for 9 is 65.3 min; conditions C, t_R for 2 is 37.6 min, t_R for 3 is 20.6 min, t_R for 6 is 24.5 min, t_R for 7 is 28.3 min, t_R for 8 is 34.6 min, t_R for 9 is 44.8 min. The light intensity meaurements and quantitative yields from the HPLC analysis were used to calculate quantum yields for 2, 3, and 6–9.

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