# The Photochemical Reactions of Phenyl Azide with Sulfur Dioxide in Various Solvents

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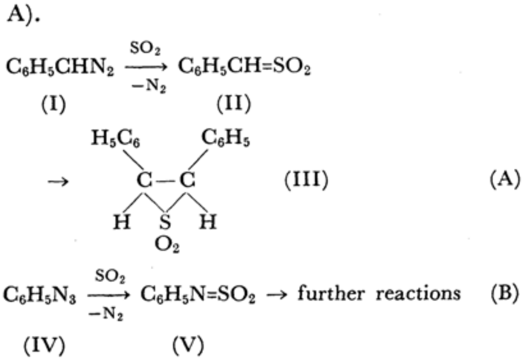
In a previous paper,1) it has been reported that phenyldiazomethane (I) decomposes readily at room temperature by the action of sulfur dioxide in ether, thus producing a *cis*-episulfone (III), *via* phenylsulfene (II) as an intermediate (Scheme 1 A).



$$C_6H_5CHN_2 \xrightarrow[-N_2]{SO_2} C_6H_5CH{=}SO_2$$

$$C_6H_5N_3 \xrightarrow[-N_2]{SO_2} C_6H_5N{=}SO_2 \rightarrow \text{further reactions} \quad (B)$$

Scheme 1.

In the present paper, we will report on the reaction of phenyl azide (IV) with sulfur dioxide. The reaction has been undertaken to see if it results in the formation of phenylazasulfene (V) (Scheme 1 B), analogously to the reaction of I with sulfur dioxide.

Although azasulfene is a new type of intermediate of recent2) interest, only one example2) has been reported. It is shown in Scheme 2.

$$C_6H_5SO_2N_3 \xrightarrow{h\nu} C_6H_5SO_2N: \xrightarrow{\text{Curtius-type rearrangement}}$$

$$C_6H_5N{=}SO_2 \xrightarrow{CH_3OH} C_6H_5NHSO_2OCH_3$$

Scheme 2.

Contrary to the case of I, IV did not react with sulfur dioxide without irradiation. Therefore, the present investigation was carried out under irradiation by a high-pressure mercury lamp.

As has been reported previously, the photolysis of IV in a hydrocarbon solvent in the absence of sulfur dioxide gives3) a small amount of aniline and *N*-alkylaniline, whereas that in benzene gives4) a trace of azobenzene.

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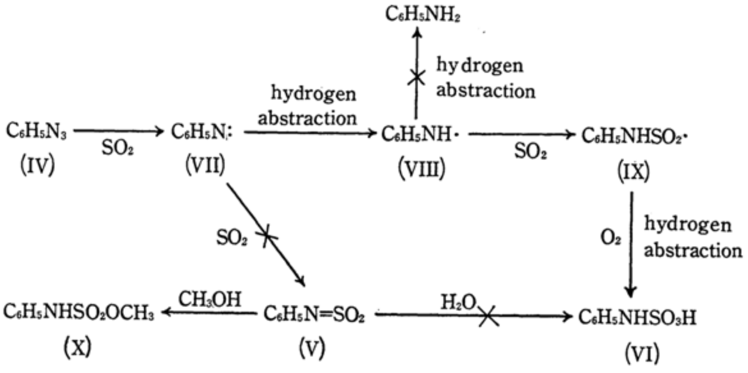
4) W. E. Doering and R. A. Odum, *Tetrahedron*, **22**, 81 (1966).



Scheme 3

## Results and Discussion

When a solution of phenyl azide (IV) in benzene was treated with sulfur dioxide under irradiation, phenylsulfamic acid (VI), benzenesulfanilide (VII), and unchanged phenyl azide were obtained, while azobenzene and aniline were not formed. The photolysis of IV in an ethereal solution containing sulfur dioxide also gave VI. Irradiation in a methanolic solution of IV and sulfur dioxide, afforded, in addition to VI, ammonium sulfate and ammonium bisulfate. On the other hand, the photodecomposition of IV in liquid sulfur dioxide alone failed to yield VI, but produced, in a 7.4% yield, a green solid (XI). The details will be described in the experimental section.

A reasonable account of the formation of VI is given in Scheme 3.

Scheme 3 shows that the formation of VI probably involves the intermediacy of nitrene (VII); the intermediate does not, however, as was expected, react with sulfur dioxide to form azasulfene (V). The nitrene VII abstracts a hydrogen atom from the solvents to produce the anilino radical (VIII), which is followed by sulfonation to form the phenylsulfamoyl radical (IX). The radical (IX) ultimately gives phenylsulfamic acid (VI) by photooxidation5) due to atmospheric oxygen probably present in the reaction system.

Other supporting evidence for the sequence includes the facts that methyl phenylsulfamate (X) is not obtained in a methanolic solution and that VI is not formed in liquid sulfur dioxide alone when a hydrogen source is absent.

The lower reactivity of IV with sulfur dioxide compared with that of I may be interpreted in terms of the difference in nucleophilicity between N $(-\underline{\overline{N}}=N=\overline{N}|)$ and C $(-\underline{\overline{C}}H-N\equiv N|)$ toward the S atom of sulfur dioxide.

The production of ammonium sulfate or ammonium bisulfate in a methanolic system indicates that the C–N bond of IV cleaves to form hydrogen azide ($HN_3$), which then undergoes photodecomposition to give ammonia.6) The ammonia thus formed reacts with sulfur dioxide and water to yield ammonium sulfate or ammonium bisulfate.

## Experimental

**Apparatus.** A vessel equipped with a 300-watt high-pressure mercury lamp described previously7) was used for irradiation.

**The Photochemical Reaction.** *A Typical Experiment.* A solution of 250 m*l* of liquid sulfur dioxide and 8.3 g of freshly-prepared IV8) in 500 m*l* of benzene was irradiated at 0—−10°C for 29 hr under a nitrogen atmosphere. The brown solid which precipitated from the reaction mixture was recrystallized from ethanol to give 0.76 g of white plates (VI), mp above 300°C. The mother liquor, after the sulfur dioxide had been removed, was chromatographed over silica gel. Elution with benzene gave unchanged phenyl azide, while elution with ether yielded a trace of benzenesulfanilide (VII). Azobenzene, aniline, and biphenyl were not obtained.

**The Identification of the Products.** *Phenylsulfamic Acid* ($C_6H_5NH_2^+SO_3^-$,9) VI). The infrared spectrum (Nujol mull) of VI exhibited characteristic peaks at 2000—2500 ($NH_2^+$); 1600 and 1500 (phenyl); 1140 and 1020 ($SO_3$), and 740 and 680 cm$^{-1}$ (monosubstituted benzene). VI displayed absorption peaks in the ultraviolet spectrum at $\lambda_{max}^{CH_3OH}$ 237 ($\varepsilon$, $5.48\times10^3$) and 288 m$\mu$ ($9.80\times10^2$). These spectra were identical with those of authentic phenylsulfamic acid prepared by a method similar to that described by Traube.10)

*Benzenesulfanilide* ($C_6H_5SO_2NHC_6H_5$, VII). The infrared spectrum (1150, 1300, and 1325 cm$^{-1}$ due to

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5) Y. Ogata, Y. Izawa and J. Tsuda, *ibid.*, **21**, 1349 (1965).

6) B. A. Thrush, *Proc. Roy. Soc.*, **A235**, 143 (1956).

7) T. Nagai, K. Terauchi and N. Tokura, This Bulletin, **39**, 868 (1966).

8) R. O. Lindsay and C. F. H. Allen, "Organic Syntheses," Coll. Vol. 3, p. 710 (1955).

9) A. M. Vuagnat and E. L. Wagner, *J. Chem. Phys.*, **26**, 79 (1957).

10) W. Traube, *Ber.*, **23**, 1654 (1890).

$SO_2$ and 3150 cm$^{-1}$ due to NH) coincided with that of authentic⁽¹¹⁾ benzenesulfanilide prepared by the reaction of aniline with benzenesulfonyl chloride.

*Ammonium Sulfate* ($(NH_4)_2SO_4$) *and Ammonium Bisulfate* ($(NH_4)HSO_4$). These were obtained as a 1 : 1 mixture, and their identity confirmed by the coincidence of their infrared spectra with those of respective authentic specimen⁽¹²⁾ and by elemental analyses.

Found: H, 5.28; N, 16.63; S, 25.65%. Calcd for $H_{13}N_3S_2O_8$: H, 5.24; N, 16.68; S. 26.06%.

*A Green Solid (XI).* XI was soluble in an aqueous solution of sodium hydroxide and dimethyl sulfoxide. The treatment of XI with silver nitrate gave a white precipitate ($Ag_2SO_3$), indicating the presence of the $SO_3H$ group. The infrared spectrum of XI (KBr disk) indicated bands at 1500 and 1600 (phenyl); 1180 and 1030 ($-SO_3H$), and 830 cm$^{-1}$ (*p*-di-substituted benzene). The UV spectra of XI (68 mg/*l* dimethyl sulfoxide) displayed absorptions at 317 (absorbance 3.1), 440 (0.68), and 585 m$\mu$ (broad, 0.53). Moreover XI showed only bands due to aromatic protons in the NMR spectrum at 2.5—3.0 $\tau$ (multiplet). The molecular-weight determination and the elemental analysis indicate that XI may be a dimeric product and not a hydrogenated product such as VI, though its structure is not clear.

Found: C, 52.30; H, 3.91; S, 11.01%. Mol wt (MW), 307. Calcd for $C_{12}H_{10}N_2SO_4$; C, 51.80; H, 3.60; S, 11.51%; MW, 278.

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11) M. Ascher and V. Meyer, *ibid.*, **4**, 326 (1871).

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