Acknowledgment. We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Cancer Institute of the National Institutes of Health for support of this work.

References and Notes

(1) O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4842 (1968).
(2) R. A. Lewis and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7009 (1969).
(3) K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969).
(4) A. Nudelman and D. J. Cram, *J. Am. Chem. Soc.*, **90**, 3869 (1968).
(5) H. P. Benschop, D. H. J. M. Platenburg, F. H. Meppelder, and H. J. Boter, *Chem. Commun.*, 33 (1970).
(6) R. A. Lewis, O. Korpiun, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4847 (1968).
(7) K. E. DeBruin and J. R. Petersen, *J. Org. Chem.*, **37**, 2272 (1972).
(8) K. E. DeBruin and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7393 (1969).
(9) A. Herriott, *J. Am. Chem. Soc.*, **93**, 3304 (1971).
(10) N. J. De'ath, K. Ellis, D. J. H. Smith, and S. Trippett, *Chem. Commun.*, 714 (1971); D. M. Johnson, Ph.D. Thesis, Colorado State University, 1974.
(11) K. E. DeBruin and D. M. Johnson, *J. Am. Chem. Soc.*, **95**, 4675 (1973).
(12) See, for comparison, S. Hirsl-Starcevic, Z. Majerski, and D. E. Sunko, *J. Am. Chem. Soc.*, **96**, 3659 (1974).
(13) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952).
(14) D. D. Roberts and W. Hendrickson, *J. Org. Chem.*, **34**, 2415 (1969).
(15) This result may suggest that the tosylate leaving group is protonated by solvent trifluoroacetic acid and leaves as a neutral molecule.

Gas Phase Thermolysis of Sulfonyl Azides

W. B. Renfrow* and Manoharran Devadoss

Department of Chemistry, Oberlin College, Oberlin, Ohio 44074

Received January 2, 1975

Prior information about the gas phase thermolysis of a sulfonyl azide is restricted to a report by Reichle,[1] who obtained azobenzene (17%) and tar from benzenesulfonyl azide (1) at 625° and 0.5 Torr.

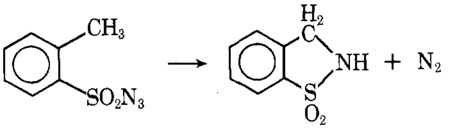
It was of interest to us to determine whether or not gas phase thermolysis of 1 in the presence of benzene would produce products obtainable from the same reactants in the liquid phase. The liquid phase thermolysis of sulfonyl azides has been studied extensively.[2] Thermolysis of 1 in benzene solution produces[3] nitrogen gas, *N*-phenylbenzenesulfonamide (2), benzenesulfonamide (3), and tar. A sulfonylnitrene, $C_6H_5SO_2N$, is generally considered[2] to be an intermediate in these reactions. In agreement with the earlier work, we have isolated from liquid phase thermolysis a 64% yield of 2 and 6% yield of 3.

$$\underset{\mathbf{1}}{PhSO_2N_3} + PhH \longrightarrow \underset{\mathbf{2}}{PhSO_2NHPh} + \underset{\mathbf{3}}{PhSO_2NH_2} + N_2 + \text{tar}$$

Products and yields from gas phase thermolysis of 1 in the presence/absence of benzene were as follows: sulfur dioxide, 65/71%; azobenzene, 32/27%; 3, 2/2%; diphenylamine, 1/3%; and biphenyl, 2/1%. Fluorescent material, probably a mixture of *N*-phenylbiphenylamines and triphenylamine, was formed in about 1% yield in the absence of benzene and in less amount in the presence of benzene. No insertion product into benzene (2) could be detected among the products formed in the presence of benzene.

Phenylnitrene (C_6H_5N) is a likely intermediate in the gas phase thermolysis of 1 because azobenzene is also the major organic product (72%) from gas phase thermolysis of phenyl azide.[4] Phenylnitrene could be formed by a Curtius-type rearrangement[5] of benzenesulfonylnitrene, followed by loss of sulfur dioxide. Decomposition products in the reaction zone of the hot tube probably include phenyl radicals, hydrogen atoms, singlet and triplet forms of benzenesulfonylnitrene, and phenylnitrene. Aniline was not detected among the products. The fact that the yield of diphenylamine was greater in the absence than in the presence of benzene is evidence against an insertion reaction of phenynitrene into benzene.

With 2-methylbenzenesulfonyl azide (4), the intramolecular insertion product, benzylsultam (5), was obtained in 21% yield from gas phase thermolysis in the absence of benzene and in 13% yield with benzene present. This result is readily explained in terms of a sulfonylnitrene intermediate which inserts into the adjacent methyl group. No 2,2′-dimethylazobenzene was found among the products from gaseous 4.

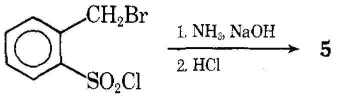


4 5

The main product from gas phase thermolysis of 4 was a clear yellow gum. On TLC the gum gave a yellow band and several bands which fluoresced under 350-nm light. Attempts to obtain identifiable pure substances from the yellow and fluorescent bands were unsuccessful because of spontaneous conversion to nonvolatile, presumably polymeric products. Smolinsky[4] obtained a polymeric product from gas phase thermolysis of 2,6-dimethylazidobenzene and suggested that a quinoid compound was a likely intermediate. The same type of intermediate is probably formed from 4.

Liquid phase thermolysis of 4 in benzene gave the insertion product into the solvent, *N*-phenyl-2-methylbenzenesulfonamide (63%), and 2-methylbenzenesulfonamide (8%). No 5 was found. The stereochemical restriction which allows intermolecular C–H insertion to predominate over intramolecular insertion in the liquid phase thermolysis of 4 is obscure. Some sulfonyl azides that can either cyclize or insert into solvent have been studied by Abramovitch and coworkers,[5,6] who found a range of behaviors.

A preparation of 5 in very low yield from *N*,*N*-dichloro-2-methylbenzenesulfonamide has been reported,[7] and 5 has been obtained as a reduction product of saccharin used as a brightener in electroplating.[8] We have prepared 5 in 50% yield from 2-bromomethylbenzenesulfonyl chloride (6). Ammonia and sodium hydroxide react with 6 to produce a salt of 5 which is converted to 5 by acidification.



6

Experimental Section

Mass spectra were obtained with a Hitachi Perkin-Elmer RMS-4 at 70 eV. Preparative TLC was performed using E. Merck No. 7747 silica gel PF-254 in 1-mm layers on 20 × 20 cm glass plates. Ratios of solvent mixtures are v/v. Bands of sorbent from TLC plates were placed in small columns and eluted with chloroform–methanol (9:1) to remove products. Development of TLC plates carrying azobenzene was done in the dark to avoid photochemical cis–trans interconversion[9]. Only *trans*-azobenzene was isolated. In calculating percentage yields all products are considered to have resulted exclusively from sulfonyl azides.

2-Methylbenzenesulfonyl chloride was purified by partial crystallization from its melt until a product was obtained containing less than 0.5% of the 4-methyl isomer by ^1H NMR analysis. Benzenesulfonyl azide (1), bp 61° (0.05 Torr), and 2-methylbenzenesulfonyl azide (4), bp 70° (0.05 Torr), were prepared[10] from the corresponding sulfonyl chlorides and sodium azide in aqueous acetone.

Gas Phase Pyrolyses.[4] Reactions were carried out in a vertical tube, 12 mm i.d., of which a 120-mm length was maintained at 360 ± 5° by an external electric heater. A mercury thermometer with the bulb in the center of the reaction zone was used to measure temperature. A loose plug of Pyrex glass wool (0.15 g) was inserted immediately beneath the thermometer bulb. The tube was cleaned and the glass wool replaced after each run.

Samples entered the reaction zone through a side arm and short portion of the top of the reaction tube maintained at 110°. The side arm was attached to a vertical 8-mm i.d. tube surrounded by a water bath. A volume of about 0.5 ml could be held at the bottom of the 8-mm tube below the side arm. Pure sulfonyl azides (about 100 mg) were placed in the bottom of the 8-mm tube, a stream of nitrogen or benzene vapor regulated by a capillary was passed over the surface, and the water bath was maintained at a temperature (70–100°) selected to give a desired time (100–5 min) for complete distillation. An alternative method was routinely used for introducing sulfonyl azides plus benzene that avoided distilling the potentially explosive[11] pure azides: a solution of the sulfonyl azide in benzene was introduced through a fine capillary into the bottom of the 8-mm tube with the bath near the temperature of boiling water. Pressure in the system increased with rate of throughput and was usually in the range 0.05–0.2 Torr.

Products were collected in a trap cooled by liquid nitrogen. At the conclusion of a run and after the vacuum was broken a tube containing 0.100 *N* sodium hydroxide was attached to the trap containing products. Nitrogen was passed through the reaction tube and trap and bubbled through the standard base while the reactor tube cooled and the trap warmed to room temperature. The base was titrated to a phenolphthalein end point with hydrochloric acid. Confirmation that the volatile acid was sulfur dioxide was provided by further titration with 0.100 *N* iodine solution. Milliequivalents of base and of iodine consumed were practically the same.

Benzene was added to the trap to bring the liquid volume to about 2 ml and refluxed into the formerly heated reaction tube. Azobenzene and unreacted sulfonyl azide dissolved while tar or gum and benzenesulfonamide deposited beyond the hot zone of the reactor did not dissolve. The benzene solution was assayed for unchanged azide by measuring the intensity of absorption at 2150 cm^{-1}, after which the benzene was evaporated. Tar and sulfonamide remaining in the reaction tube were dissolved in refluxing chloroform–methanol (4:1), the residue from the benzene solution was added, and the solution was streaked onto a TLC plate. The plate was developed in benzene–ethyl acetate (3:1). R_f values for products isolated at this stage follow: benzenesulfonamides and **5**, 0.3–0.4; benzenesulfonanilides, 0.65–0.75. Materials with R_f greater than 0.8 were eluted, streaked onto a fresh TLC plate, and developed with benzene–hexane (1:1). R_f values of products isolated at this stage follow: sulfonyl azides, 0.3; diphenylamine, 0.5; *trans*-azobenzene, 0.7; a fluorescent substance of uncertain structure, 0.8; biphenyl, 0.9. Diphenylamine was the only substance of known structure which fluoresced under 350-nm light. All products of known structures gave dark bands under 254-nm light.

The ir spectra of products isolated from TLC plates were often the same as the spectra of authentic materials, and yields reported were determined at this stage unless otherwise specified. Solid products were further purified by distillation (0.02 Torr) and crystallization, and melting points were compared with those of authentic samples.

Benzenesulfonyl azide (**1**, 121 mg) plus benzene (1.25 g) pyrolyzed in the gas phase during 45 min gave unchanged **1** (15 mg by ir, 11 mg isolated), *trans*-azobenzene (17 mg, 32%), **3** (2 mg, 2%), diphenylamine (0.5 mg, 1%), biphenyl (1 mg, 2%), and sulfur dioxide (0.38 mmol, 65%). A small fluorescent band between azobenzene and biphenyl gave insufficient material for characterization. In the absence of benzene **1** (98 mg) pyrolyzed during 15 min gave no unchanged **1**, *trans*-azobenzene (12.6 mg, 27%), **3** (1.6 mg, 2%), diphenylamine (1.5 mg, 3.5%), biphenyl (0.4 mg, 1%), and sulfur dioxide (0.39 mmol, 71%). A fluorescent band between azobenzene and biphenyl gave on elution 1 mg of brown oil. The mass spectrum of the oil was as follows: *m/e* (rel intensity) 245 (100), 77 (55), 51 (40), 154 (33), 244 (33), 167 (29).

2-Methylbenzenesulfonyl azide (**4**, 104 mg) pyrolyzed alone in the gas phase during 10 min gave no unchanged **4**, 18.5 mg (21%) of **5** after sublimation to clean up the ir spectrum, and sulfur dioxide (0.33 mmol, 62%). Pyrolysis of **4** (95 mg) plus benzene (900 mg) during 100 min gave 4 mg of unchanged **4** and 10 mg (13%) of **5** after sublimation. The first TLC plate from each run showed a yellow band and five fluorescent bands under 350-nm lights. Attempts to purify the yellow and fluorescent materials by further chromatography or distillation led to chromatographically immobile and nonvolatile products.

Liquid Phase Thermolyses. The reactants in glass tubes were frozen, and the tubes were evacuated, sealed, and heated at 145–155° for 8 hr. From **1** (125 mg) in benzene (1.23 g) there was obtained 0.1 mg of unchanged **1**, 102 mg (64%) of **2**, and 6.5 mg (6%) of **3**. From **4** (113 mg) in benzene (1.13 g) there was obtained 89.5 mg (63%) of *N*-phenyl-2-methylbenzenesulfonamide and 8 mg (8%) of 2-methylbenzenesulfonamide.

2-Bromomethylbenzenesulfonyl Chloride (**6**). A solution of 2-methylbenzenesulfonyl chloride (7.7 g) in 50 ml of carbon tetrachloride was cooled and irradiated with a 450-W mercury lamp while a solution of bromine (7.4 g) in carbon tetrachloride (50 ml) was run in during 30 min. A fraction (8.2 g), bp 95–110° (0.1 Torr), crystallized and was recrystallized from petroleum ether to yield 3.6 g of **6**: mp 58–60° (lit.[12] mp 48–55°); mass spectrum *m/e* (rel intensity) 268 (100), 270 (130), 272 (37).

Benzylsultam (**5**). Solutions of **6** (270 mg) in 10 ml of dimethoxyethane and of 2.5 *N* sodium hydroxide (1.5 ml) and 15 *N* ammonia (0.3 ml) in 10 ml of dimethoxyethane were cooled in an ice bath. The first solution was poured with good mixing into the second. The solution was swirled for 10 min in the ice bath and allowed to stand overnight at room temperature. The solvent was removed, the residue was dissolved in 3 ml of water, and the solution was acidified with 0.5 ml of 12 *N* hydrochloric acid. The precipitate was extracted into 5 ml of dichloromethane, washed twice with water, dried ($MgSO_4$), concentrated, and streaked onto a TLC plate. The plate was developed with benzene–ethyl acetate (3:1). The band of R_f 0.4 was eluted with chloroform–methanol (9:1), sublimed at 0.02 Torr, and the sublimate crystallized from carbon tetrachloride–95% ethanol (5:1). The yield of **5** was 90 mg (53%): mp 111–113° (lit.[7] mp 113°); ir 3220, 1270, 1150, 742 cm^{-1}; mass spectrum *m/e* (rel intensity) 169 (100), 78 (96), 77 (76), 104 (72), 149 (62), 168 (55); ^{1}H NMR δ 4.47 and 4.56 (s, 2, CH_2 not equivalent), 5.3 (broad, 1, NH), 7.2–7.9 (m, 4, ArH).

Acknowledgment. We thank Professor R. A. Abramovitch for his advice and for supplying manuscripts of his unpublished works.

Registry No.—**1**, 938-10-3; **4**, 13222-19-0; **5**, 936-16-3; **6**, 34981-56-1; 2-methylbenzenesulfonyl chloride, 133-59-5; benzenesulfonyl chloride, 98-09-9; sodium azide, 12136-89-9.

References and Notes

(1) W. T. Reichle, *Inorg. Chem.*, **3**, 402 (1964).

(2) The following references review the relevant material: (a) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1965); (b) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes and Arynes", Thomas Nelson & Son, London, 1969; (c) W. Lwowski, Ed., "Nitrenes", Interscience, New York, N.Y., 1970.

(3) T. Curtius, *J. Prakt. Chem.*, **125**, 303 (1930).

(4) G. Smolinsky, *J. Org. Chem.*, **26**, 4108 (1961).

(5) R. A. Abramovitch and W. D. Holcomb, *Chem. Commun.*, 1298 (1969).

(6) R. A. Abramovitch, C. I. Azogu, and I. T. McMaster, *J. Am. Chem. Soc.*, **91**, 1219 (1969).

(7) J. Koetschet and P. Koetschet, *Helv. Chim. Acta*, **12**, 669 (1929).

(8) (a) D. Mockute, G. Adamonyte, A. Bodnevas, and J. Matulis, *Liet. TSR Mokslu Akad. Darb., Ser. B*, 23 (1968); (b) I. Dubsky and P. Kozak, *Metalloberflaeche-Angew. Elektrochem.*, **27**, 217 (1973).

(9) J. F. Janssen, *J. Chem. Educ.*, **46**, 117 (1969).

(10) J. E. Leffler and Y. Tsuno, *J. Org. Chem.*, **28**, 902 (1963).

(11) (a) O. C. Dermer and M. T. Edmison, *J. Am. Chem. Soc.*, **77**, 70 (1955); (b) G. P. Balabanov and Yu. I. Dergunov, *Zh. Prikl. Khim.* (*Leningrad*), **41**, 2578 (1968).

(12) L. A. Levy, *J. Heterocycl. Chem.*, **8**, 873 (1971).