Curtius and Lossen Rearrangements. I. The Benzenesulfonyl System[1]

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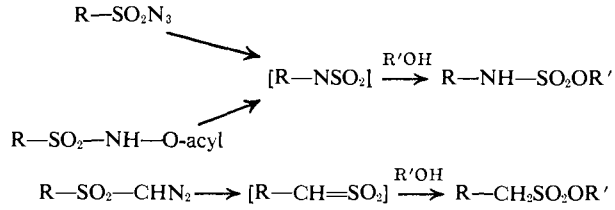
Benzenesulfonyl azide, when thermolyzed in aprotic solvents, gives products containing the unrearranged sequence $ArSO_2N$. Photolysis in alcohols, however, leads to rearrangement and formation of the hitherto unknown phenylsulfamic esters, $ArNHSO_2OR$. N-(p-Nitrobenzenesulfonoxy)benzenesulfonamide (VII) undergoes base-induced decomposition in alcohols and in aniline to give p-nitrobenzenesulfonate ion and the addition products of the alcohol or aniline to the hypothetical intermediate, sulfurylaniline, $ArNSO_2$, in high yields.

Introduction

Rearrangements of the type RSO_2X to $RXSO_2$ have not been reported where X is nitrogen or carbon. Such rearrangements would be analogs of the Curtius or Lossen and the Wolff[2] rearrangements, respectively, with sulfonyl as the migration origin



A reaction tentatively classified as a Hofmann rearrangement of a sulfonamide has been reported.[3] In this case, *o*-hydroxybenzenesulfonamide was treated with bromine and base and yielded tribromoaniline, with loss of the hydroxyl group. Later work by Raffa,[4] using substituted *o*-aminobenzenesulfonamides, indicates that the *ortho* substituent is lost and the new amino group is introduced in *ortho* position to that vacated by the sulfonamido function. Thus, a Hofmann-type rearrangement seems not to be involved here.

The decomposition of arenesulfonyl azides by thermolysis and photolysis has been studied in a variety of media.[5] The reported reaction products always contain the unrearranged sequence RSO_2N. When the substrate R'H was attacked at its C–H bonds the major products were RSO_2NHR' and RSO_2NH_2. The yields frequently were high, *e.g.*, 60% in the thermolysis of benzenesulfonyl azide in methyl benzoate or in a solution of anthracene in dichlorobenzene.[6] In the thermolysis of alkylsulfonyl azides, 80–90% of the azides was accounted for without rearrangement products being found.[7] Thus, rearrangement cannot play a significant role in the above reactions, all of which were conducted under aprotic conditions. Although the photolysis of *p*-toluenesulfonyl azide in methanol has been studied,[8] Horner has kindly informed us that no search for rearrangement products was made in this work.

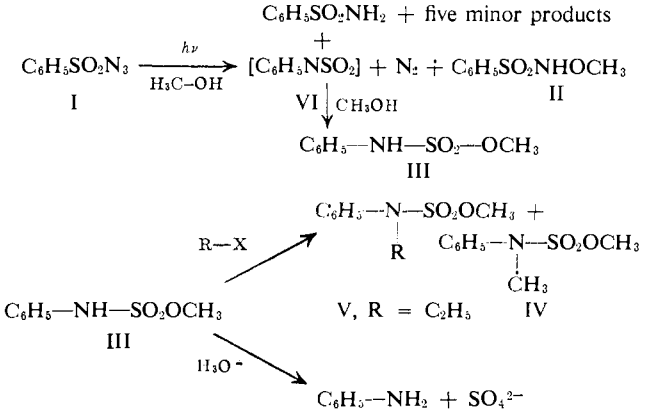
N-Acyloxybenzenesulfonamides have not been investigated extensively, and their rearrangement has not been reported.

We are investigating the mechanism of the Curtius and Lossen rearrangements and their dependence on the mode of decomposition and on the solvation of the rearranging species. As a part of this work, we here report such rearrangements of the benzenesulfonyl system.

Results

Benzenesulfonyl Azide. Pure benzenesulfonyl azide (I), m.p. 10.5–11.5°, does not react with methanol at room temperature. However, when the methanol solution of I was irradiated with the light of a medium-pressure mercury arc, nitrogen was evolved and a dark reaction mixture was produced. This mixture contained a fraction soluble both in ether and in 10% aqueous sodium carbonate solution. This fraction consisted of N-methoxybenzenesulfonamide (II), in an amount corresponding to a 15% yield, and of a liquid isomer of II, in an amount corresponding to a 23% yield, based on azide decomposed. The isomer III upon hydrolysis gave aniline and sulfate ion. Heating to 160° for 20 min. converted III to a glass-like solid, soluble in water and, according to its n.m.r. and infrared spectra, consisting of a mixture of amino- and N-methylaminobenzenesulfonic acids. The solid also contained aniline and N-methylaniline. The infrared spectrum of III shows NH at 3293 and SO_2 bands at 1363 and 1175 $cm.^{-1}$. The n.m.r. spectrum shows five aromatic and three OCH_3 protons. Methylation of III with methyl iodide and potassium methoxide in methanol gave a liquid, the analysis and n.m.r. spectrum of which indicate the structure IV. Alkylation of III with ethyl bromide gave a corresponding ethyl compound V together with the methyl derivative IV, indicating that III itself is a methylating agent. This evidence establishes the structure of III as that of methyl N-phenylsulfamate, apparently formed by a Curtius-type rearrangement of benzenesulfonyl azide (I), followed by addition of methanol to the intermediate sulfurylaniline.

(1) Communicated in part: W. Lwowski, R. DeMauriac, T. W. Mattingly, Jr., and E. Scheiffele, *Tetrahedron Letters*, 3285 (1964).
(2) *Cf.* A. M. van Leusen, R. J. Mulder, and J. Strating, *ibid.*, 543 (1964).
(3) L. Raffa, *Farmaco* (Pavia) *Ed. Sci.*, 11, 62 (1956); *Chem. Abstr.*, 50, 15448*h* (1956).
(4) L. Raffa, A. Manzani, and A. Albasini, *Farmaco* (Pavia) *Ed. Sci.*, 19, 35 (1964); *Chem. Abstr.*, 60, 9185*f* (1964).
(5) For a review see R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 64, 149 (1964).
(6) J. F. Heacock and M. T. Edmison, *J. Am. Chem. Soc.*, 82, 3460 (1960); J. F. Tilney-Bassett, *J. Chem. Soc.*, 2517 (1962).
(7) M. F. Sloan, W. B. Renfrow, and D. S. Breslow, *Tetrahedron Letters*, 2905 (1964).
(8) L. Horner and A. Christmann, *Chem. Ber.*, 96, 388 (1963).



N-Methoxybenzenesulfonamide (II) is stable at 160° and can be separated by heating the mixture of II and III and thus converting III into the water-soluble, glass-like solid. The composition of mixtures of II and III can be measured by integrating the two methoxy signals in the n.m.r. spectrum. Both II and III decompose on prolonged irradiation with light of 2537 Å. In accord with this observation, not all the rearranged material in the reaction mixture from the photolysis of I in methanol is present as III. From a typical reaction mixture, III was isolated in 23% yield, but hydrolysis of the crude mixture gave a 28% yield of aniline, weighed as 3,5-dinitrobenzanilide.

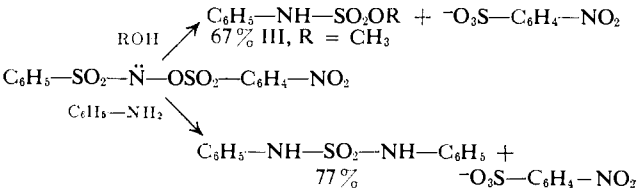
II and III were removed from the ether solution obtained from the original reaction mixture by extraction with a 10% aqueous sodium carbonate solution. Compounds insoluble in the carbonate solution remained in the ether. Most of this material was undecomposed azide I. However, thin layer chromatography showed the presence of six additional components, including benzenesulfonamide, isolated in 4.5% yield. Ammonium benzenesulfonate was found in 8% yield in the ether-insoluble material.

N-p-Nitrobenzenesulfonoxybenzenesulfonamide (VII). In order to attempt a Lossen-type rearrangement on the benzenesulfonyl system, VII was prepared in 60% yield by treating benzenesulfhydroxamic acid with *p*-nitrobenzenesulfonyl chloride and triethylamine in tetrahydrofuran. The structure was confirmed by its infrared spectrum and elemental analysis. The almost colorless crystals, m.p. 179°, have a strong tendency to retain solvent (water, methanol, ether). The bis(*p*-nitrosulfonyl) compound VIII (m.p. 191°) is also formed. VII gives isolable potassium and triethylammonium salts. They are yellowish, crystalline substances which decompose at room temperature within a few days. The potassium salt decomposed explosively at 65°. Decomposition of the pure salts gives the salt of *p*-nitrobenzenesulfonic acid plus tar.

When the potassium salt of VII was suspended in methanol at room temperature, it dissolved over a period of 2 days. Potassium *p*-nitrobenzenesulfonate was isolated from the residue after evaporating the excess methanol. The fraction soluble in ether and in sodium carbonate solution gave methyl N-phenylsulfamate (III) in 67% yield and N-methoxybenzenesulfonamide (II) in 2% yield. From the ether-soluble but carbonate-insoluble fraction, 4–5% yields of benzenesulfonamide were isolated. The triethylammonium salt of VII gave entirely analogous results. This latter salt was soluble in methanol, and the solution was kept at room temperature for 2 days to give III.

Reaction of the potassium and the triethylammonium salts of VII with ethanol gave ethyl N-phenylsulfamate (IX) in 65% yield. The structure of IX was established by its elemental analysis and infrared and n.m.r. spectra. The ethylation of IX with ethyl bromide and potassium ethoxide in ethanol gave the N-ethyl derivative, b.p. 132° (4.3 mm.). Yaguzhinskii[9] reported a boiling point of 135–138° (4.5 mm.).

Reaction of the azide I with aniline led only to solvolysis products. Irradiation of I in dichloromethane, followed by addition of aniline, gave only benzenesulfonamide. However, when the triethylammonium salt of VII was allowed to react with a fivefold excess of a 20% solution of aniline in dichloromethane, N,N′-diphenylsulfamide was isolated in 77% yield. Its identity was shown by mixture melting point and comparison of its infrared spectrum with that of an authentic sample.



The triethylammonium salt of VII is soluble in dichloromethane and some aromatic hydrocarbons. In such solutions, the salt is expected to form ion pairs, with strong hydrogen bonding by the proton of the triethylammonium ion. If hydrogen bonding indeed is required for rearrangement, as discussed below, one would expect at least some rearrangement. We therefore hoped to obtain sulfurylaniline by decomposing the triethylammonium salt of VII in such not nucleophilic media. Products from attack of benzenesulfonylnitrene on solvent also were anticipated. Exploratory reactions in toluene–dichloromethane and in benzene were run, but sulfurylaniline could not be found. Hydrolysis of the reaction mixtures gave aniline, identified as 3,5-dinitrobenzanilide, indicating that rearrangement had taken place. The reaction in toluene did not yield any toluidines, so that attack of the nitrene on toluene could not be demonstrated.

Discussion

Mechanism. Our results show that the photolysis of benzenesulfonyl azide in protic solvents takes a drastically different course from the thermolysis in aprotic media. Unfortunately, photolysis in such aprotic media gave mostly dark, amorphous products, preventing direct comparison of photolysis and thermolysis. Thermolysis in protic solvents is expected to lead to solvolysis in many cases, placing severe limitations on direct comparison of photolysis with thermolysis. The base-induced decomposition of VII in aprotic solvents gave results that are rather different from those reported in the literature[5] for the thermolyses of benzenesulfonyl azide in those solvents. Pending further study, we shall adopt the hypothesis that rearrangement in protic solvent is made possible by hydrogen bonding in the activated complex. That hydrogen bonding is strong in methanol solutions

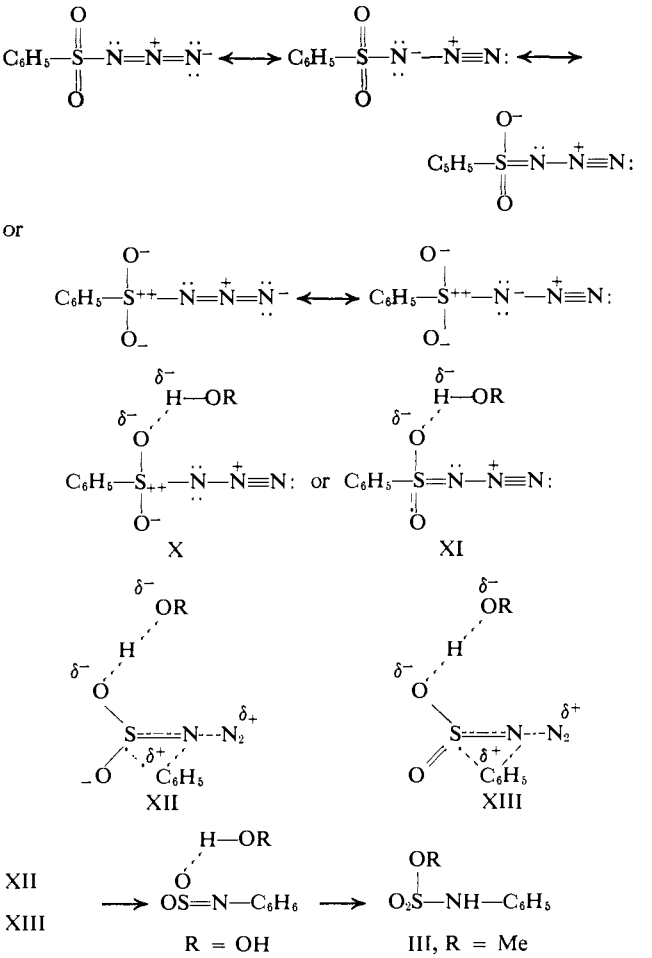
(9) L. S. Yaguzhinskii and A. Ya. Berlin, *Zh. Obshch. Khim.*, 33, 3078 (1963).

of benzenesulfonyl azide is shown by a shift of the antisymmetrical SO_2 stretching vibration of 45 cm.$^{-1}$, relative to the position in carbon tetrachloride solution. (In carbamoyl azides, the C=O stretching frequency shifts about 35 cm.$^{-1}$.) It seems perfectly possible that the rearrangement is concerted and does not involve a distinct nitrene intermediate. We shall discuss the rearrangement in these terms, but assuming the intermediacy of hydrogen-bonded acylnitrenes would not substantially alter our considerations.

CH insertions, such as found in azide decompositions[10,11] in aprotic solvents, are best explained as proceeding through nitrene intermediates. The results we obtained in protic solvents, however, do not require the assumption of nitrenes. The rearrangement might be concerted, the "OH insertion" leading to N-methoxybenzenesulfonamide (II) might involve displacement on nitrogen in the activated, solvated, $ArSO_2N^-X$ (X = N_2^+ or $OSO_2C_6H_4NO_2$). The benzenesulfonamide found could have been formed by dehydrogenation of solvent by excited azide and by radical dissociation of the hydroxylamine derivative VII.

In protic solvents, the nitrene could be formed and rapidly protonated and then rearranged to a protonated sulfurylaniline. Alternatively, concerted rearrangement of solvated (hydrogen-bonded) benzenesulfonyl derivative could give solvated sulfurylaniline directly. Or, by incorporating the solvent in the transition state, the phenylsulfamic ester could be formed without prior formation of either phenylsulfonylnitrene or sulfurylaniline. Hydrogen bonding to oxygen would give increased weight to the resonance contributors X or XI, compared to the analogous, nonhydrogen-bonded structures. However one writes the bonding (in X *vs.* XI) on sulfur, the bond order of the N_α–N_β bond in the azide group is lowered relative to the not hydrogen-bonded sulfonyl azide, and the bond S–N_α assumes a higher bond order. Thus, the hydrogen-bonded species becomes somewhat similar to the rearranging species in the Beckmann and the Schmidt rearrangements.[12] We assume that the transition state is affected by the hydrogen bonding in a manner similar to the ground state, as expressed in XII and XIII. Collapse of the transition state would directly lead to a hydrogen-bonded sulfurylaniline, ready to be attacked by the alcohol and to go to the observed product. Alternatively, either the alcohol molecule that performs the hydrogen bonding or another one could participate in the transition state and the N-phenylsulfamic ester could be formed from the azide in essentially one step. A continuum of mechanisms, having more or less pronounced minima in the energy profile of the reaction, can be envisaged.

Similar mechanisms can be written for the rearrangement of a hydrogen-bonded sulfonylnitrene. The Lossen-type rearrangement of VII can be accommodated by essentially the same mechanisms, substituting *p*-nitrobenzenesulfonate ion for nitrogen as the leaving group, and, in one case, aniline as the hydrogen-bonding species.



Other mechanisms come to mind, but the hypothesis advanced above correlates the behavior of three types of azides: alkyl azidoformates, carbamoyl azides, and sulfonyl azides. Considerations based on bond strengths are unable to do this: rearrangement of carbamoyl azides can be estimated to be roughly 75 kcal./mole more endothermic than rearrangement in the benzenesulfonyl system, yet both systems behave in much the same manner. The protic solvents used here are more polar than the aprotic ones, and the Curtius rearrangement is known to proceed faster in more polar solvents. One could thus base an explanation for the observed rearrangements on solvent polarity. However, such an explanation does not hold for alkyl azidoformates, which rearrange in methanol,[1] but not in acetonitrile,[13] a solvent of similar polarity.

Hydrogen bonding to N_α rather than to the oxygen of the sulfonyl (and carbonyl) group does not seem to be important in the ground state, as shown by the shifts in the infrared spectra. We assume that it also is unimportant in the transition state. Some hydrogen bonding to N_α is to be expected, however, and could be important in the formation of the N-methoxybenzenesulfonamide (II). This would explain the disparity in yields of II from I and from VII—in the anion of VII, hydrogen bonding to N_α would promote reprotonation and thus deactivate the reactive species.

N-Phenylsulfamic esters have long been regarded as too strong alkylating agents to be isolable. They were supposed to alkylate themselves at the nitrogen to give

(10) T. Curtius, *Z. angew. Chem.*, **26**, 134 (1913).
(11) M. F. Sloan, T. J. Prosser, N. R. Newburg, and D. S. Breslow, *Tetrahedron Letters*, 2945 (1964)
(12) *Cf.* P. A. S. Smith and E. P. Antoniades, *Tetrahedron*, **9**, 210 (1960).
(13) W. Lwowski, A. Hartenstein, C. deVita, and R. L. Smick, *Tetrahedron Letters*, 2497 (1964).

N-aryl-N-alkylsulfamic acids and products derived from the latter.[9,14] This is unlikely, since one N-unsubstituted sulfamic ester is known, as well as some mono-N-alkyl and many N-dialkyl and diaryl sulfamic esters. Their rearrangement to the corresponding betaines $R_3N^+SO_3^-$ has been studied, most recently by Orchin and Ziegler.[15] Ethyl N-phenylsulfamate seems to have been obtained recently[16] by treating imino-sulfur oxydifluoride with sodium ethoxide. The compound was not quite pure and its N–H absorption in the infrared spectrum was given as 3.3 μ (3030 cm.$^{-1}$) whereas our ethyl ester absorbs at 3290 cm.$^{-1}$. There might be a typographical error in Cramer's paper.

We find the N-monophenylsulfamic esters to be relatively stable, but not distillable. They are not particularly strong alkylating agents and are stable at room temperature.

Experimental Section

General. Irradiations were carried out in fused silica vessels in a Rayonet photochemical reactor[17] containing 16 medium-pressure mercury lamps, 84% of whose emission is at 2537 Å.

Infrared spectra were recorded with a Perkin-Elmer Model 421 spectrometer, n.m.r. spectra with an A-60 spectrometer from Varian Associates.

For thin layer chromatography, silica gel GF_{254} from E. Merck, A.G., Darmstadt, was used. The solvent system A consisted of *n*-heptane, chloroform, and acetone in the ratio 2:2:1; solvent system B of chloroform and ethanol in the ratio 99:1.

Benzenesulfonyl azide (*I*) was prepared by a modification of the method of Zalkow and Oehlschlager.[18] Acetone was used as the solvent and the ether solution was washed with a 10% sodium carbonate solution and water before isolation of the azide. The product was crystallized from *n*-heptane–cyclohexane at $-30°$ and melted at $+10.5$–$11.5°$; infrared spectrum in (CCl_4): N_3 at 2128, SO_2 at 1385 and 1170 cm.$^{-1}$; infrared spectrum in CH_3OH: N_3 at 2133, SO_{2as} at 1340 cm.$^{-1}$.

N-Methoxybenzenesulfonamide (*II*) was prepared by adding benzenesulfonyl chloride to an excess of methoxyamine, in a manner analogous to the preparation of N-methoxy-*p*-toluenesulfonamide,[8] yield 88%; m.p. 79° after recrystallization from chloroform–cyclohexane, R_f 0.44 (system A); infrared spectrum (in KBr): NH at τ 3240, SO_2 at 1333 and 1165 cm.$^{-1}$; n.m.r. spectrum: CH_3 singlet at τ 6.19 (3), aromatic CH at 2.75 (5).

Anal. Calcd. for $C_7H_9NO_3S$ (187.24): C, 44.92; H, 4.85; N, 7.48; S, 17.12. Found: C, 44.94; H, 4.74; N, 7.45; S, 17.09.

II forms colorless needles and is soluble in chloroform but only slightly in carbon tetrachloride. It is extracted from its ether or chloroform solutions by aqueous sodium carbonate, but not by sodium bicarbonate solution.

(14) W. Traube, H. Zander, and H. Gaffron, *Ber.*, **57**, 1045 (1924); W. Traube, *Angew. Chem.*, **38**, 441 (1925); A. Dorlars in "Methoden der Organischen Chemie," Vol. XI/2, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, Germany, 1958, p. 704

(15) P. F. Ziegler, Thesis, University of Cincinnati, 1963.

(16) R. Cramer and D. D. Coffman, *J. Org. Chem.*, **26**, 4010 (1961).

(17) A product of the Southern New England Ultraviolet Co., Middletown, Conn.

(18) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963).

Acid Treatment of II. II (360 mg.) was heated to reflux in a mixture of 10 ml. of ethanol and 10 ml. of concentrated hydrochloric acid for 10 min. Concentrating the solution *in vacuo* gave 280 mg. of crystalline, unchanged starting material.

Irradiation of Benzenesulfonyl Azide (*I*) *in Methanol.* I (10 g., 55 mmoles) in 350 ml. of methanol was irradiated until 600 ml. of nitrogen (26 mmoles) had been evolved. The brownish solution was evaporated *in vacuo* to give 9.8 g. of a brown oil. Digestion with ether left 1.8 g. of a sirup (a). The ether extract was washed with 5% aqueous sodium bicarbonate solution and extracted three times with 10% aqueous sodium carbonate. The ether phase was dried and evaporated to give 5.4 g. of a brown oil (b), consisting largely of benzenesulfonyl azide. The combined sodium carbonate extracts were layered with ether and acidified by adding, with shaking, saturated aqueous potassium bisulfate solution. The dried ether phase gave 2.26 g. of an oily residue (c).

Treatment of sirup a with 5 ml. of acetone gave 400 mg. (8%) of ammonium benzenesulfonate, identified by comparison of its infrared spectrum with that of authentic material.

The oil c was stirred with 7 ml. of carbon tetrachloride, and the insoluble residue was crystallized from ethanol–water containing some hydrochloric acid and recrystallized from chloroform–cyclohexane; 370 mg. of colorless needles were obtained, m.p. 79°. The infrared spectrum and an undepressed mixture melting point showed the material to be N-methoxybenzenesulfonamide (II). This method of isolating II involves large losses. The amount of II formed can be determined by taking quantitative n.m.r. spectra of the oil c, which typically consisted of II and III in a ratio of 4:6.

Methyl Phenylsulfamate, $MeOSO_2NHC_6H_5$ (*III*). The carbon tetrachloride extract of oil c was concentrated *in vacuo* and decanted from some oily precipitate. Upon evaporation, 800 mg. of a slightly yellow liquid was obtained, R_f 0.44 (system A). III was purified by chromatography on a thick layer of silica gel; infrared spectrum (in CCl_4): NH at 3293, phenyl at 1603 (strong), SO_2 at 1363 and 1175 cm.$^{-1}$; n.m.r. spectrum: OCH_3 at τ 6.19 (3), aromatic CH at 2.75 (5).

Anal. Calcd. for $C_7H_9NO_3S$: C, 44.92; H, 4.85; N, 7.48; S, 17.12. Found: C, 44.87; H, 5.00; N, 7.44; S, 17.30.

Hydrolysis of III. III (70 mg., 0.37 mmole) was dissolved in 15 ml. of 5% aqueous sodium carbonate and kept at 100° for 10 min. Concentrated hydrochloric acid and barium chloride solution were added while the solution was still hot. Barium sulfate (81 mg., 0.35 mmole) was collected. The filtrate was treated with sodium carbonate and shaken with ether containing 200 mg. of 3,5-dinitrobenzoyl chloride and 1 ml. of pyridine. From the ether phase, 71 mg. (0.25 mmole) of 3,5-dinitrobenzanilide, m.p. 235°, was obtained and identified by comparison of its infrared spectrum with that of an authentic sample. R_f (system B) was 0.3. N-Methyl-3,5-dinitrobenzanilide (R_f 0.6) could not be detected on the thin layer chromatogram.

Alkaline hydrolysis of III was attempted by dissolving 60 mg. in 10 ml. of 1 *N* sodium hydroxide solution and heating to reflux for 10 min. After cooling, the

solution was layered with ether and acidified with aqueous potassium bisulfate solution while shaking. The ether phase yielded 45 mg. of unchanged starting material.

Methyl N-Methylphenylsulfamate (IV). Methylation of III. III (823 mg., 4.4 mmoles) was dissolved in 20 ml. of methanol containing 4.4 mmoles of potassium methoxide, and 10 ml. of methyl iodide was added. After heating to reflux for 30 min. and evaporating *in vacuo*, the viscous residue was extracted with ether, the extract washed with sodium carbonate solution, dried, and evaporated *in vacuo*. Oily IV (285 mg., 30%) was obtained. Carrying out the reaction at 75° for 20 min. gave a lower yield; infrared spectrum (in CCl_4): SO_2 at 1376 and 1186 $cm.^{-1}$; n.m.r. spectrum: aromatic CH at τ 2.66 (5) and OCH_3 at 6.25 (3).

Anal. Calcd. for $C_8H_{11}NO_3S$: C, 47.75; H, 5.50; N, 6.95; S, 15.93. Found: C, 47.89; H, 5.50; N, 6.86; S, 16.09.

Thermal Decomposition of III. In an attempted distillation, 1.2 g. of III was heated to 165° at 0.2 mm. After cooling, the material formed a glass, insoluble in ether but almost completely soluble in water, with pH 1.5. Barium chloride solution did not precipitate any barium sulfate. Part of the solution was treated with 3,5-dinitrobenzoyl chloride. The mixture of aniline derivatives so formed was separated by thin layer chromatography using system B. 3,5-Dinitrobenzanilide and N-methyl-3,5-dinitrobenzanilide were obtained and identified by comparison of their infrared spectra with those of authentic samples. To another part of the acidic aqueous solution, acetone was added and a precipitate was obtained. Its infrared spectrum was similar to that of *p*-aminobenzenesulfonic acid, but the n.m.r. spectrum showed signals indicating the presence of four types of NCH_3 or OCH_3 groups. The thermal reaction of III can be used to separate II from the mixtures obtained from the photolysis of I in methanol. A mixture of 40% II and 60% III (1.68 g.) (composition determined by comparison of the CH_3 signals in the n.m.r. spectrum) was heated to 160° for 20 min. and the resulting glass was treated with water to leave 590 mg. of II, identified by its infrared spectrum and melting point.

Benzenesulfonamide from the Irradiation of I in Methanol. The oil b (2 g.) was chromatographed on a 4.5 × 50 cm. silica gel column and eluted with chloroform–cyclohexane (2:1). Three hundred fractions were collected. Fractions 233–250 contained 80 mg. of benzenesulfonamide, identified by its infrared spectrum (4.5% yield). Undecomposed I was obtained from fractions 55–70 (2.3 g.).

Chromatography of the Ether-Soluble Products of the Irradiation of I. I (10 g., 55 mmoles) was irradiated in 350 ml. of methanol until 30 mmoles of nitrogen was evolved. The ether-soluble components (see above) were chromatographed as above and 310 fractions were collected. I (2.3 g.), 0.4 g. of an unidentified unstable liquid, 1.26 g. (22%) of II, and 0.210 g. of benzenesulfonamide were obtained.

Hydrolysis of the Sodium Carbonate Extract from the Irradiation of I. A sodium carbonate extract was obtained, as above, from the photolysis in methanol of 15 mmoles of I. It was acidified with concentrated hydrochloric acid and kept at 100° for 15 min., then treated with 3,5-dinitrobenzoyl chloride to give a 28% yield of 3,5-dinitrobenzoylaniline, m.p. 235°.

Irradiation of I in Cyclohexane. I (10 g.) in 350 ml. of cyclohexane was irradiated. The solution turned brown and a brown precipitate formed on the walls of the tube preventing light from entering, so that the photolysis came to a halt.

Irradiation of I in Benzene. I (1 g.) in 100 ml. of benzene was irradiated. The solution quickly turned brown and nitrogen evolution became very slow. After 5 hr., the solution contained mainly undecomposed I, a dark, amorphous material, and some benzenesulfonylaniline and benzenesulfonamide, as identified by comparison of their infrared spectra with those of authentic samples.

N-p-Nitrobenzenesulfonoxybenzenesulfonamide (VII). To a stirred solution of 6.92 g. (40 mmoles) of N-hydroxybenzenesulfonamide[19] in 140 ml. of tetrahydrofuran, kept at 10°, was added in portions 8.86 g. (40 mmoles) of *p*-nitrobenzenesulfonyl chloride in 60 ml. of tetrahydrofuran, and dropwise 3.7 g. (36 mmoles) of triethylamine in 30 ml. of tetrahydrofuran over 2 hr. An excess of amine was never present in the reaction mixture. The mixture was stirred for another hour at room temperature, the precipitate of triethylammonium chloride was filtered off, and the filtrate was evaporated *in vacuo*. The oily residue was extracted with ether and the extracts were kept at 0° for 2 days, producing 7.1 g. of slightly yellow crystals. An additional 2.1 g. was obtained by treating the oily residue from the reaction (after the ether extraction) with water and crystallizing the water-insoluble fraction from tetrahydrofuran–ether–cyclohexane. Recrystallization of the crude VII gave pure material: m.p. 179°; R_f 0.35 (system A), easily soluble in methanol and tetrahydrofuran, less soluble in ether; yield 58%; infrared spectrum: NH at 3450 (broad), CH at 3117, 2983, 2785, aromatic ring at 1610, NO_2 and SO_2 at 1385–1340, SO_2 at 1190–1160 $cm.^{-1}$.

Anal. Calcd. for $C_{12}H_{10}N_2S_2O_7$: C, 40.22; H, 2.81; N, 7.81; S, 17.89. Found: C, 40.25; H, 2.83; N, 8.00; S, 18.02.

N-p-Nitrobenzenesulfonyl-N-p-nitrobenzenesulfonoxybenzenesulfonamide (VIII). Evaporation of the mother liquors of the ether extracts from the preparation of VII, and treatment of the residue with methanol, produced a crystalline material, little soluble in methanol. Recrystallized from tetrahydrofuran–cyclohexane it had m.p. 191°, R_f 0.63 (system A); the infrared spectrum did not show NH; yield 3.5%.

Anal. Calcd. for $C_{18}H_{13}N_3O_{11}S_3$: C, 39.77; H, 2.41; N, 7.73; S, 17.69. Found: C, 39.84; H, 2.51; N, 7.84; S, 17.76.

Potassium Salt of VII. VII (1.7 g., 3 mmoles) was dissolved in 20 ml. of methanol and filtered. Methanol (5 ml.), containing 3 mmoles of potassium methoxide, was added with cooling. After 1 hr., 1.1 g. (92%) of yellow crystalline salt was collected, m.p. 130° dec. Samples of this potassium salt decomposed within 2 weeks at room temperature. When 500 mg. was heated to 65–60° at 1.0 mm. it decomposed explosively, leaving a dark brown solid.

(19) O. Piloty, *Ber.*, **29**, 1559 (1896).

Triethylammonium Salt of VII. VII (3.58 g., 10 mmoles) was dissolved in 20 ml. of benzene and just enough tetrahydrofuran to give a homogeneous solution. Triethylamine (1.01 g., 10 mmoles) was added with cooling and scratching and the mixture was kept at 5° for 30 min. Slightly yellow, crystalline, triethylammonium salt of VII (4.3 g., 93%) was collected and washed with a little cold benzene. The salt decomposes at room temperature within 2 days; infrared spectrum; ammonium NH from 2800 to 2300, C–H at 3120 and 2990, aromatic ring at 1610, NO_2 at 1535 cm.$^{-1}$.

Methyl Phenylsulfamate (III) from VII. The freshly prepared triethylammonium salt of VII (3.2 g., 70 mmoles) was dissolved in 70 ml. of methanol and kept at 28° for 2 days. The solvent was evaporated *in vacuo* and the oily residue was treated with 30 ml. of ether with scratching. Colorless, crystalline triethylammonium *p*-nitrobenzenesulfonate (2.1 g., 98%) was collected and identified by its melting point of 121° and comparison of the infrared spectrum with that of an authentic sample. The ether solution was washed with 5% aqueous sodium bicarbonate solution, then extracted with 10% aqueous sodium carbonate. The sodium carbonate extracts were layered with ether and acidified, while shaking with aqueous potassium bisulfate. The ether extract was concentrated *in vacuo* to leave 890 mg. of a nearly colorless oil. Its infrared spectrum was identical with that of III, but the n.m.r. spectrum showed a trace of impurity, yield 69%. Treatment with a quantity of carbon tetrachloride insufficient to dissolve all the oil, followed by evaporation of the solvent, gave pure III.

The impurity in the crude product was separated by heating to reflux 250 mg. of the crude material in 7 ml. of ethanol and 3 ml. of concentrated hydrochloric acid for 15 min. The solution was neutralized, the ethanol was evaporated *in vacuo*, and the residue was acidified with potassium bisulfate, then extracted with ether. From the ether extract, 5 mg. (1.3%) of II was obtained and identified by its infrared spectrum.

Benzenesulfonamide (50 mg., 4.5%) was obtained from the ether solution after extraction with sodium carbonate (see above) and from the sodium bicarbonate extract. It was identified by its infrared spectrum.

Ethyl Phenylsulfamate (IX, $C_6H_5NHSO_2OC_2H_5$). The freshly prepared triethylammonium salt of VII (3 g., 6.53 mmoles) was dissolved in a mixture of 50 ml. of ethanol and 50 ml. of dichloromethane. After 3 days at room temperature, the reaction mixture was worked up as described for the methyl ester III (above). Ethyl phenylsulfamate (850 mg., 65%) was obtained as an almost colorless liquid, R_f 0.5 (system A): infrared spectrum: NH at 3290, aromatic ring at 1600, SO_2 at 1370 and 1163 cm.$^{-1}$; n.m.r. spectrum: NH at τ 2.4 (0.92), aromatic CH at 2.8 (5.0), CH_2 at 5.8 (2.0), CH_3 at 8.7 (3.07).

Anal. Calcd. for $C_8H_{11}NO_3S$: C, 47.75; H, 5.50; N, 6.95; S, 15.93. Found: C, 47.70; H, 5.48; N, 7.11; S, 15.99.

Ethyl N-Ethylphenylsulfamate. IX (950 mg., 4.73 mmoles) was dissolved in 40 ml. of ethanol containing 4.73 mmoles of potassium ethoxide. Ethyl bromide (15 ml.) was added and the mixture was kept at 75° for 20 min., then evaporated and the residue extracted with ether. The extract was washed with sodium carbonate solution, dried, and evaporated to leave 650 mg. of an oil, b.p. 132° (4.3 mm.). Yaguzhinskii[9] reported b.p. 135–138° (4.5 mm.) The infrared spectrum showed no NH, aromatic ring at 1590, SO_2 at 1360 and 1175 cm.$^{-1}$. The yield was 60%; n.m.r. spectrum: aromatic CH at τ 2.65 (5), N–CH_2 at 5.85 (2), OCH_2 at 6.33 (2), CH_3 at 8.70 and 8.90 (6).

Anal. Calcd. for $C_{10}H_{15}NO_3S$: C, 52.40; H, 6.60; N, 6.11. Found: C, 52.28; H, 6.45; N, 6.09.

The ether-insoluble residue from the ethylation contained some potassium N-phenylsulfamate, as indicated by the infrared spectrum.

Ethylation of III. III (550 mg., 2.9 mmoles) was dissolved in 50 ml. of ethanol containing 2.9 mmoles of potassium ethoxide. Ethyl bromide (10 ml.) was added and the mixture was kept at 80° for 20 min., then evaporated *in vacuo*, and the residue was treated with carbon tetrachloride. A colorless solid (370 mg.) remained. It contained potassium N-phenylsulfamate, as shown by its infrared spectrum. The carbon tetrachloride solution was evaporated *in vacuo* to give 400 mg. of a slightly yellow liquid, shown by n.m.r. to consist of a 3:1 mixture of methyl N-ethyl- and N-methyl phenylsulfamate. Apparently, the methyl N-phenylsulfamate (III) can compete as an alkylating agent, with the large excess of ethyl bromide used.

N,N′-Diphenylsulfamide. The triethylammonium salt of VII (3.1 g., 6.7 mmoles) was dissolved in a mixture of 15 ml. of dichloromethane and 3 ml. of aniline and kept at room temperature for 2 days. The solution was evaporated *in vacuo* and the residue was digested with ether, leaving 2.0 g. of triethylammonium *p*-nitrobenzenesulfonate. The ether solution was washed with aqueous potassium bisulfate and evaporated, and the residue was crystallized by adding cyclohexane. The product, recrystallized from chloroform–cyclohexane, melted at 112°. A mixture melting point with authentic N,N′-diphenylsulfamide showed no depression and the infrared spectra were identical, yield 1.3 g. (77%).

Reaction of the Triethylammonium Salt of VII in Toluene–Dichloromethane. The triethylammonium salt of VII (2 g.) was dissolved in a mixture of 70 ml. of dichloromethane and 70 ml. of toluene. Triethylamine (5 ml.) was added and the mixture was allowed to stand for 10 days at room temperature. The solvents were evaporated and the semisolid residue was treated with ether. The ether solution was extracted with a saturated solution of potassium hydrogen sulfate. A thin layer chromatogram (system A) of the residue in the ether phase did not show N-tolylbenzenesulfonamide or benzenesulfonamide. The n.m.r. spectrum of the residue in the ether phase did not show a CH_3 signal attributable to a tolyl group. The aqueous acid extract was neutralized and then extracted with ether. The material that went into the ether was treated with 3,5-dinitrobenzoyl chloride. By thin layer chromatography, 3,5-dinitrobenzanilide was isolated. It was identified by its infrared spectrum. No 3,5-dinitrobenztoluidides could be detected.

Reaction of VII with Triethylamine in Benzene. VII (570 mg., 1.59 mmoles) was suspended in 20 ml. of

benzene and 160 mg. (1.59 mmoles) of triethylamine was added, rendering the solution homogeneous. A precipitate began to appear after 30 min. After 3 hr., triethylammonium *p*-nitrobenzenesulfonate began to crystallize; after 3 days crystals of dianilinium sulfate also separated. After 5 days, the benzene layer was decanted and the residue was washed with benzene and dissolved in acetone. N-Phenylbenzenesulfonamide was not detected.

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Epoxidation Studies. III. The Peracid Oxidation of Substituted Benzoylimines[1-3]

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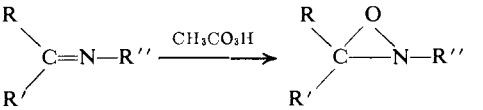
N,N-Dibenzoylamines have been identified as the major product of reaction of several monoarylimines of benzil with peracids. Data are presented demonstrating that 3-benzoyloxaziranes function as transient intermediates. The kinetics of the rearrangement of the relatively stable 2-cyclohexyl-3-phenyl-3-benzoyloxazirane to N-cyclohexyldibenzamide was studied. The rate was found to follow first-order kinetics. From these results we conclude that the mechanism of the rearrangement involves attack of the electron pair of nitrogen of the oxazirane ring on the neighboring benzoyl group. A study of the peracid epoxidation of the related class of N-benzoylimines was also carried out. It was found that substituted phenols and dibenzamide were the major products. A mechanism involving initial epoxidation is proposed to account for the results.

The oxidation of ketones to esters by means of peracids was first described in 1899 by Baeyer and Villiger[4] and has proved useful in a variety of both synthetic and degradative studies. The early work has been reviewed in several places[5,6] and a treatment of applications and experimental techniques is available.[7] The application of this reaction to α,β-unsaturated ketones may lead either to cleavage toward or away from the carbon–carbon double bond. Still another possibility for this class of compounds is the preferential attack at the olefinic linkage leading to an α,β-epoxy ketone. Examples of the formation of all three types of compounds are available in the literature.[8,9]

The epoxidation of the related class of benzoylimines has not yet been reported. The present investigation had its origin in our interest in determining which (if either) type of behavior would be observed in this related reaction. In particular, we were interested in the possible stability of the unknown 2- and 3-benzoyloxaziranes. Such compounds are three-membered carbon–nitrogen–oxygen ring analogs of α,β-epoxy ketones. In view of the many polar rearrangements exhibited by the latter class of compounds, we considered that an investigation to determine whether 2- and 3-acyloxaziranes would undergo related transformations was desirable. In this paper we present evidence that shows still a third type of behavior is possible in the benzoylimine–peracid system.

Results and Discussion

The reaction initially examined was the treatment of monophenyl- (I) mono-*p*-methoxyphenyl- (II), and monocyclohexylbenzilimine (III) with anhydrous peracetic acid in methylene chloride. At the time, it was hoped that the reaction would proceed in a fashion analogous to the preparation of a wide variety of aliphatic oxaziranes.[10] Emmons had previously demon-



strated that the conversion of imines to oxaziranes is a reasonably selective oxidation and may be carried out in the presence of functional groups which normally react with peracids.[11] It was hoped, furthermore, that the stability and reactivity of the oxazirane ring would be influenced by the benzoyl group present in the molecule.

The desired monoimines of benzil (I–III) were readily available from the corresponding amines on reaction with benzil at elevated temperatures. Yields of the benzoylimines prepared by this method were of the order of 75–85%.

Reaction of the monoanil of benzil[12] (I) with anhydrous peracetic acid in methylene chloride at 0° afforded in excellent yield a product whose structure was

(1) This work was presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.
(2) For preliminary reports of this work see (a) A. Padwa, *Tetrahedron Letters*, No. 30, 2001 (1964); (b) *ibid.*, No. 14, 879 (1965).
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