[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

Chemistry of Ethylenimine. IX. Ring-Opening Reactions of 1-*p*-Bromobenzenesulfonyl-2,2-dimethylaziridine[1]

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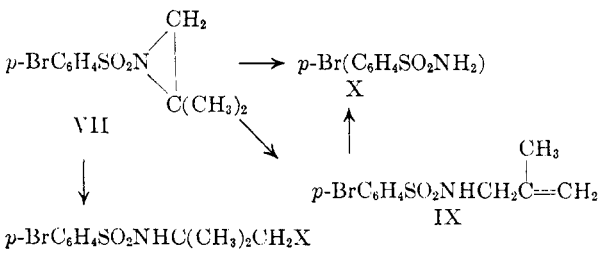
Piperidine and aniline add to 1-(*p*-bromobenzenesulfonyl)-2,2-dimethylaziridine (VII) with cleavage of the nitrogen-primary carbon bond of the aziridine ring. Pyrolysis of VII in toluene at 150° gives a mixture of *p*-bromobenzenesulfonamide (X) and *N*-(β-methallyl)-*p*-bromobenzenesulfonamide (IX). Under the same conditions, IX also yields X. In cold, concentrated sulfuric acid, both VII and IX form X.

Studies of the reactions of 1-acyl-2,2-dimethylaziridines (I) have been reported recently in some detail, and the results are summarized in Fig. 1. On treatment with a typical nucleophilic reagent (*e.g.* sodium iodide in acetone) 1-(*p*-nitrobenzoyl)-2,2-dimethylaziridine (I. R = $-C_6H_4NO_2$) gives the corresponding oxazoline VI, presumably *via* an intermediate V.[3]

Pyrolysis of I (R = $C_6H_4NO_2$ or CH_3), either alone or in an inert solvent, yields the corresponding *N*-(β-methallyl)amides II, which are cyclized on treatment with concentrated sulfuric acid to give oxazolines IV, presumably *via* carbonium ion III.[3,4] Oxazoline IV is obtained directly from I by treatment with sulfuric acid.

The present research was undertaken to determine the extent to which reactions of this type occur in the case of a 1-benzenesulfonyl derivative of 2,2-dimethylaziridine. For this purpose the known[5] 1-(*p*-bromobenzenesulfonyl)-2,2-dimethylaziridine (VII) was prepared by treatment of 2,2-dimethylethylenimine with *p*-bromobenzenesulfonyl chloride and triethylamine in benzene.



VIIIa. X = $N(CH_2)_5$
VIIIb. X = NHC_6H_5

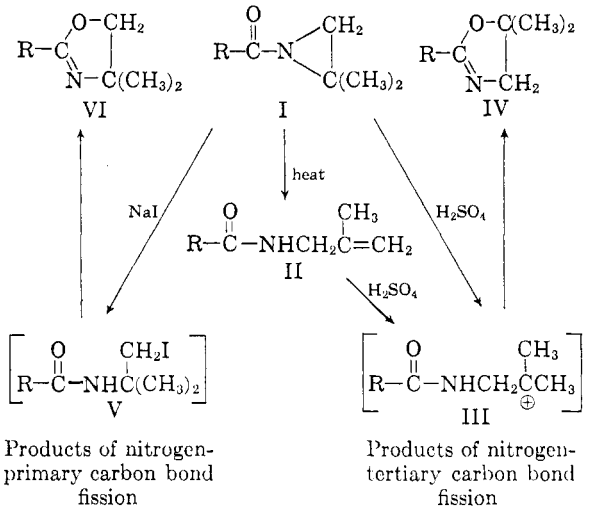


Fig. 1. Summary of the reactions of 1-acyl-2,2-dimethylaziridines. Hypothetical intermediates are in brackets

The mode of reaction of VII with a basic nucleophilic reagent was determined by treatment with piperidine in benzene. In view of the known exchange reactions of arylsulfonamides,[6] it was anticipated that a possible product of the reaction would be the known *N*-(*p*-bromobenzenesulfonyl)-piperidine. However, the only product isolated (in 76% yield) had an elementary composition corresponding to the addition of piperidine to VII. In view of the known reactions of 1-benzenesulfonylaziridine with amines to give *N*-benzenesulfonylethylenediamines,[7] and the preferential attack of nucleophilic reagents at the primary carbon atom of 2,2-dimethylaziridine,[8] the product is formulated as *N*-(1,1-dimethyl-2-piperidylethyl)-*p*-bromobenzenesulfonamide (VIIIa).

Furthermore, VII reacted with aniline to give *N*-(1,1-dimethyl-2-anilinoethyl)-*p*-bromobenzenesulfonamide (VIIIb) and with pyridine hydrochloride to give *N*-(2-methyl-2-chloropropyl)-*p*-bromobenzenesulfonamide. The latter reaction involves

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(3) H. W. Heine, M. E. Fetter, and E. M. Nicholson, *J. Am. Chem. Soc.*, **81**, 2202 (1959). An alternative mechanism for the isomerization of I to VI involving attack of iodide ion at the carbonyl carbon atom is also suggested by these authors.

(4) P. E. Fanta and A. S. Deutsch, *J. Org. Chem.*, **23**, 72 (1958).

(5) R. Adams and T. L. Cairns, *J. Am. Chem. Soc.*, **61**, 2464 (1939), prepared VII by treatment of *N*-(2-methyl-2-chloropropyl)-*p*-bromobenzenesulfonamide with aqueous sodium hydroxide.

(6) S. Searles and S. Nukina, *Chem. Revs.*, **59**, 1077 (1959).

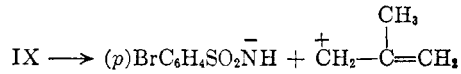
(7) H. Bestian in *Die Methoden der Organischen Chemie (Houben-Weyl)*, ed. by E. Muller, Vol. XI/2, Georg Thieme Verlag, Stuttgart (1958), p. 251.

(8) L. B. Clapp, *J. Am. Chem. Soc.*, **70**, 184 (1948).

cleavage of the nitrogen–tertiary carbon bond of the aziridine ring and probably proceeds *via* a carbonium ion analogous to III.

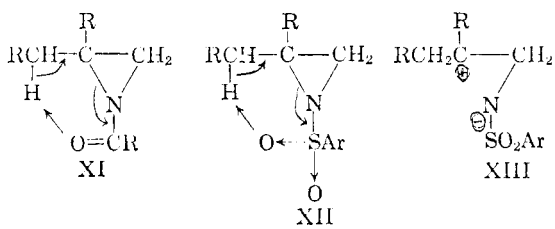
Pyrolysis of VII in toluene solution for sixteen hours at 150° gave a mixture of *p*-bromobenzenesulfonamide (X) (52%) and *N*-(β-methallyl)-*p*-bromobenzenesulfonamide (IX) (15%), which is probably the intermediate in the formation of X, since under the same reaction conditions it gives a 74% yield of X.

Since the cleavage of a sulfonamide under such conditions was thought to be rather unusual,[6,9] *N*-phenyl-*p*-bromobenzenesulfonamide was heated in toluene under the same conditions and was found to be unaffected. The exceptionally facile cleavage of the carbon-nitrogen bond of IX may be ascribed to the stability of the ions produced by the heterolytic cleavage. Completion of the reaction



probably involves participation of the toluene, which may be alkylated by the carbonium ion, and donate a proton to the sulfonamide anion. In the present work the fate of the methallyl group was not established.

Previous papers in this series[4,10] provided evidence that the pyrolytic rearrangement of 1-acyl-2-alkylaziridine derivatives occurs *via* an intramolecular, concerted, and stereospecific transfer of a proton as shown in transition state XI. The analogous transition state for the rearrangement of the corresponding 1-sulfonyl derivative requires an expansion of the sulfur outer valence shell,[11] and is pictured in structure XII. An alternative and more acceptable mechanism is the formation of the zwitterion XIII with consequent release of angular strain, followed by a proton transfer to give the *N*-allylsulfonamide derivative.



In concentrated sulfuric acid at 0–5°, both VII and IX gave excellent yields of X. This result is also in contrast to the corresponding acyl derivatives I and II, which give the oxazoline IV in excellent yield on treatment with cold, concentrated sulfuric acid.[3,4]

(9) On treatment with aluminum chloride in benzene, *N*-cinnamylbenzenesulfonamide gave benzenesulfonamide (40%) as the only crystalline product, W. J. Gensler and J. C. Rockett, *J. Am. Chem. Soc.*, **77**, 3262 (1955).

(10) P. B. Talukdar and P. E. Fanta, *J. Org. Chem.*, **24**, 526 (1959); D. V. Kashelikar and P. E. Fanta, *J. Am. Chem. Soc.*, **82**, 4930 (1960).

(11) G. Cilento, *Chem. Revs.*, **60**, 147 (1960).

EXPERIMENTAL[12]

1-(p-Bromobenzenesulfonyl)-2,2-dimethylaziridine. (VII). A solution of 7.11 g. of 2,2-dimethylethylenimine and 10.12 g. of triethylamine in 50 ml. of benzene was stirred at 0–5° while a solution of 25.55 g. of *p*-bromobenzenesulfonyl chloride in 75 ml. of benzene was added dropwise. After stirring for an additional 90 min., the reaction mixture was filtered, and the filtrate was distilled in vacuum to remove benzene. The crude, crystalline residue (m.p. 70–75°) was recrystallized successively from ethyl acetate–petroleum ether (b.p. 40–60°) and petroleum ether, giving 22.0 g. (76%) of white, cubic crystalline product, m.p. 81.5–82.5° (lit.[5] m.p. 79.5–81.5°).

Anal. Calcd. for $C_{10}H_{12}NSO_2Br$: C, 41.39; H, 4.17; N, 4.83. Found: C, 41.57; H, 4.41; N, 5.20.

N-(1,1-Dimethyl-2-piperidylethyl)-p-bromobenzenesulfonamide (VIIIa). A solution of 2.9 g. of VII and 0.86 g. of piperidine in 60 ml. of benzene was refluxed for 90 min. The solvent was removed in vacuum and the crystalline residue was recrystallized from ethanol, giving 2 6 g. of white, crystalline product, m.p. 106–107.5°, NH band in the infrared absorption spectrum.

Anal. Calcd. for $C_{15}H_{23}N_2SO_2Br$: C, 48.00; H, 6.18; N, 7.47. Found: C, 48.18; H, 6.10; N, 7.29.

N-(1,1-Dimethyl-2-anilinoethyl)-p-bromobenzenesulfonamide (VIIIb). A solution of 1.45 g. of VII and 0.47 g. of aniline in 25 ml. of benzene was refluxed for 24 hr. The solvent was removed in vacuum and the residue was recrystallized from ethanol, giving 1.39 g. (73%) of white, crystalline solid, m.p. 143.5–144.5°.

Anal. Calcd. for $C_{16}H_{19}N_2SO_2Br$; C, 50.13; H, 5.00; N, 7.31. Found: C, 50.01; H, 5.07; N, 7.22.

N-(2-methyl-2-chloropropyl)-p-bromobenzenesulfonamide. A solution of VII and pyridine hydrochloride (not especially dried) in chloroform was refluxed for 2 hr. Removal of the solvent in vacuum and two successive recrystallizations of the residue from ethanol gave colorless needles, m.p. 127.5–130° (lit.[5] m.p. 123–128°).

Anal. Calcd. for $C_{10}H_{13}NSO_2BrCl$: C, 36.77; H, 4.01; N, 4.29. Found: C, 37.34; H, 4.21; N, 4.26.

Pyrolysis of VII *in toluene.* A solution of 2.0 g. of VII in 35 ml. of toluene was heated in a glass liner in a steel bomb at 150 ± 5° for 16 hr. Cooling gave a precipitate of 0.85 g. (52%) of tan *p*-bromobenzene-sulfonamide (X), m.p. 165–168°. Identity of the product was confirmed by a mixed melting point with authentic X which had m.p. 166.5–167.5°. The brown toluene mother-liquor was reduced to a sirup which was taken up in petroleum ether and cooled, giving 0.30 g. (15%) of white *N*-(β-methallyl)-*p*-bromobenzenesulfonamide (IX), m.p. 74°. Identity of this product was confirmed by a melting point with authentic IX, m.p. 74–75° (lit.[5] m.p. 74–76°).

Pyrolysis of IX *in toluene.* A solution of 0.5 g. of IX in 20 ml. of toluene was heated in a glass liner in a steel bomb at 150 ± 5° for 16 hr. Cooling, filtration, and concentration of the mother liquors gave a total of 0.30 g. (74%) of *p*-bromobenzenesulfonamide, identified by mixed melting point.

Attempted pyrolysis of N-phenyl-p-bromobenzenesulfonamide in toluene. A solution of 1.0 g. of the amide, m.p. 119–120° (lit. m.p. 119°) in 25 ml. of toluene was treated as described in the previous experiments. Upon removal of the solvent in vacuum, unchanged starting material was obtained.

Reaction of VII *or* IX *with cold, concentrated sulfuric acid.* Either VII or IX (0.5 g.) was stirred with 10 ml. of concd. sulfuric acid at 0–5° for 4 hr. The solution was poured on 50 g. of ice and neutralized with concentrated aqueous sodium hydroxide solution, giving 88–98% of crude, colorless *p*-bromobenzenesulfonamide, identified by melting point and mixed melting point.

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(12) Melting points are corrected. Analyses are by Micro-Tech Laboratories, Skokie, Ill.