Formation and Cleavage of N-(Benzenesulfonyl)ethylenimines

WALTER J. GENSLER, BARRY A. BROOKS, AND WALTER R. KOEHLER

Department of Chemistry, Boston University, Charles River Campus, Boston, Massachusetts

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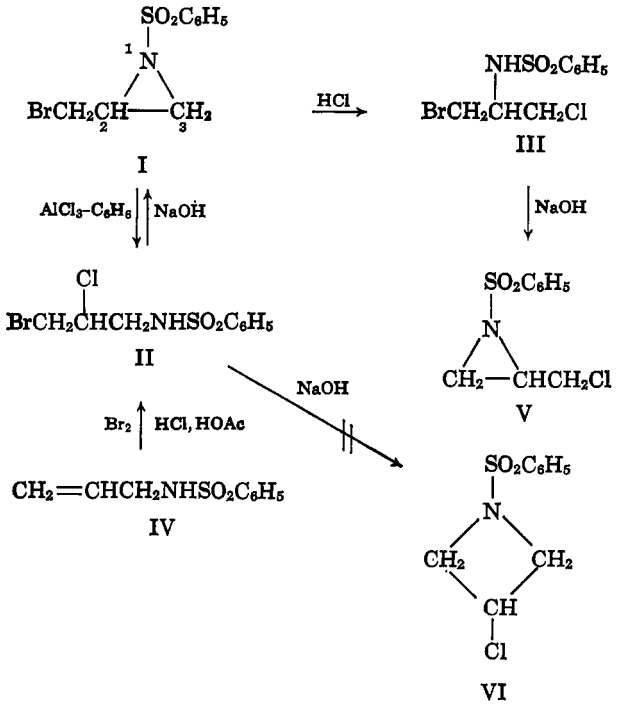
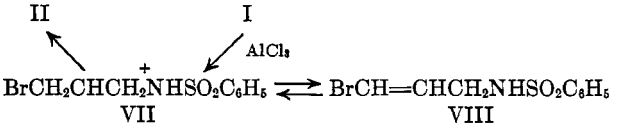
1-Benzenesulfonyl-2-bromomethylethylenimine (I) reacts with benzene in the presence of aluminum chloride to form N-(3,3-diphenylpropyl)benzenesulfonamide.[1] We have also isolated a second product, $C_9H_{11}BrClNO_2S$, which we now have shown to be N-(3-bromo-2-chloropropyl)benzenesulfonamide (II).

The analytical figures for the new material as well as its molecular weight correspond to the values required by N-(bromochloropropyl)benzenesulfonamid. Since the compound (II) cyclizes with alkali to form the starting ethyleneimine I, its structure must be that of either N-(3-bromo-2-chloropropyl)benzenesulfonamide (II) or 1-bromo-2-benzenesulfonamido-3-chloropropane (III). The latter compound, prepared by cleaving the three-membered ring of 1-benzenesulfonamido-2-bromomethylethylenimine (I) with concentrated hydrochloric acid, was found to be different from II. The former compound, prepared by brominating N-allylbenzenesulfonamide (IV) in the presence of hydrochloric acid, proved to be identical with II.



In the Friedel–Crafts mixture, the opening of the 1,2 bond in ethylenimine I to give product II instead of the 1,3 bond to give compound III was unexpected. Presumably aluminum chloride, by coordinating with the sulfonamido group of I, promotes the formation of a secondary carbonium ion (*cf.* VII), which either could combine directly with chloride ion to form II or could lose a proton reversibly to form olefin VIII.

The selective mode of cyclization of the two bromochloro compounds II and III is noteworthy. In 1-bromo-2-benzenesulfonamido-3-chloropropane (III),



both of the two possible cyclization products, I and V, are ethyleneimines. Here, where ring size is the same, the controlling factor is the faster nucleophilic displacement of bromide as compared with chloride, so that the product is 1-benzenesulfonamido-2-chloromethylethylenimine (V). In N-(3-bromo-2-chloropropyl)benzenesulfonamide, the two possible cyclization products are ethylenimine I and azetidine VI. Here, the preference for a three-membered over a four-membered ring is the controlling factor. Despite the unfavorable displacement of chloride from a secondary position relative to the displacement of bromide from a primary position, ethylenimine I is the only product.

Experimental Section[2]

N-(3-Bromo-2-chloropropyl)benzenesulfonamide (II) from 1-Benzenesulfonyl-2-bromomethylethylenimine (I) under Friedel-Crafts Conditions.—A mixture of 3.52 g. (0.0127 mole) of 1-benzenesulfonyl-2-bromomethylethylenimine (I) and 2.55 g. of aluminum chloride with 50 ml. of benzene (reagent grade) was stirred and boiled for 3 hr. A drying tube filled with calcium chloride was fitted to the top of the condenser. The yellow reaction mixture was poured over 100 ml. of ice–water containing 13 ml. of concentrated hydrochloric acid. After several ether extractions, the combined ether layers were washed twice with water, dried with magnesium sulfate, and concentrated *in vacuo*. The viscous residue was dissolved in 15 ml. of methanol, and the solution was cooled. The precipitate was removed and d
The material remaining in solution was recrystallize
small volume of aqueous methanol to give 2.7 g. of N-(3-chloropropyl)benzenesulfonamide (II), m.p. 79.5–82°.
crystallization from aqueous methanol brought the melting point to 82–84°. The analytical sample, from benzene–hexane solvent, showed m.p. 80–82°.

Anal. Calcd. for $C_9H_{11}BrClNO_2S$: C, 34.57; H, 3.55; Br + Cl, 36.90; mol. wt., 313. Found: C, 35.0; H, 3.6; Br + Cl, 36.4; mol. wt. (Rast), 303.

A mixture of product II with the same material, m.p. 82-83.5°, prepared as described below from N-allyl-benzenesulfonamide (IV), melted at 81–83°. The identity of the two samples of II was confirmed by their identical infrared absorption spectra. A mixture of product II with the starting material I, m.p. 86–88°, melted at 66–85°. A mixture of product II with 1-bromo-2-benzenesulfonamido-3-chloropropane (III), m.p. 85.5–87°, melted over a 20° range (60–80°). Also, comparison of the infrared absorption spectra of product II and compound III showed that the two were different.

N-(3-Bromo-2-chloropropyl)benzenesulfonamide (II) gave no precipitate with alcoholic silver nitrate at 80° or with sodium iodide at room temperature. At 50°, the latter test solution became brown and deposited a solid.

N-(3-Bromo-2-chloropropyl)benzenesulfonamide (II) from N-allylbenzenesulfonamide (IV).—A solution of bromine (8.1 g., 0.050 mole) in 100 ml. of glacial acetic acid was added over a period of 2 hr. to a stirred, ice cold mixture of N-allylbenzenesulfonamide[3] (IV, 10 g., 0.050 mole) in 100 ml. of glacial acetic

(1) W. J. Gensler and J. C. Rockett, *J. Am. Chem. Soc.*, **77**, 3262 (1955); W. J. Gensler and W. R. Koehler, *J. Org. Chem.*, **27**, 2754 (1962).

(2) Melting points are uncorrected. Analyses were performed by C. K. Fitz, Needham Heights, Mass., and by S. M. Nagy, Microanalytical Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.

(3) W. J. Gensler, *J. Am. Chem. Soc.*, **70**, 1843 (1948). In the present work, the colorless, crystalline allyl compound IV melted without distillation or recrystallization at 37–38.5° and was used without further purification.

acid plus 50 ml. of concentrated hydrochloric acid. Warming the reaction mixture under reduced pressure removed some of the solvent and any bromine that remained. The mixture, diluted by the slow addition of water, was allowed to stand in the refrigerator for 1 day. The dried, off-white, crystalline precipitate (II) weighed 12 g. and melted at 80–84°. Two crystallizations from aqueous methanol gave pure N-(3-bromo-2-chloropropyl)benzenesulfonamide (II), m.p. 82–83.5°.

Anal. Calcd. for $C_9H_{11}BrClNO_2S$: C, 34.57; H, 3.55; N, 4.48. Found: C, 34.56; H, 3.65; N, 4.48.

1-Benzenesulfonyl-2-bromomethylenimine (I) from N-(3-Bromo-2-chloropropyl)benzenesulfonamide (II).—Although compound II dissolved in 5% aqueous sodium hydroxide, the solution soon became cloudy and deposited a crystalline precipitate. After 2 hr., the mixture was filtered, and the solid was washed with water and dried *in vacuo* over calcium chloride. This material, 1-benzenesulfonyl-2-bromomethylethylenimine (I), melted sharply without further purification at 84.5–85.5°. When mixed with authentic material, m.p. 86–88°, the cyclized product showed m.p. 85–86.5°. Comparison of infrared spectra confirmed the identity of the cyclized material as 1-benzenesulfonyl-2-bromomethylethylenimine (I) but also indicated the presence of trace amounts of impurities.

1-Bromo-2-benzenesulfonamido-3-chloropropane (III) from 1-Benzenesulfonyl-2-bromomethylethylenimine (I) and Hydrochloric Acid.—A mixture of 2.0 g. (7.2 mmoles) of 1-benzenesulfonyl-2-bromomethylethylenimine (I) and 22 ml. of 37% hydrochloric acid was stirred and heated on the steam bath under a condenser for 3.5 hr. After addition of 62 ml. of water, the reaction mixture was cooled in ice. The collected precipitate, dissolved in methanol, was first filtered through decolorizing carbon and then crystallized twice from aqueous methanol. The pure white, crystalline 1-bromo-2-benzenesulfonamido-3-chloropropane (III), m.p. 85.5–87°, weighed 1.7 g. (68%). Two additional crystallizations did not change the melting point.

Anal. Calcd. for $C_9H_{11}BrClNO_2S$: C, 34.58; H, 3.45; N, 4.48. Found: C, 34.34; H, 3.45; N, 4.41.

A mixture of product III with the starting material I melted at 65–85°.

1-Benzenesulfonyl-2-chloromethylethylenimine (V) from 1-Bromo-2-benzenesulfonamido-3-chloropropane (III).—A solution of 1.0 g. (3.2 mmoles) of 1-bromo-2-benzenesulfonamido-3-chloropropane in 10 ml. of 95% ethanol containing 50 ml. of 0.094 *N* aqueous sodium hydroxide was diluted with 25 ml. of water and was allowed to stand at 0°. The crystalline precipitate, obtained in near quantitative yield, was crystallized from aqueous methanol to give 0.75 g. (85%) of 1-benzenesulfonyl-2-chloromethylethylenimine (V), m.p. 83.5–84.5°. The melting point was not changed by two additional crystallizations. A mixture melting point with starting material II, m.p. 85.5–87°, was depressed to 70–85°.

Anal. Calcd. for $C_9H_{10}ClNO_2S$: C, 46.64; H, 4.34; Cl, 15.30; N, 6.05. Found: C, 46.65; H, 4.29; Cl, 15.27; N, 6.07.

A Convenient Synthesis of Dimethyl and Diethyl Diazomalonate

ENGELBERT CIGANEK

Contribution No. 1122 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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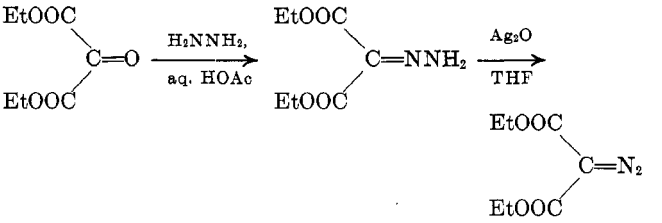
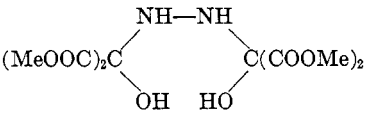
The finding[1] that two cyano groups in the 7-position stabilize the norcaradiene skeleton led us to investigate the effect of other electron-withdrawing groups on the position of the norcaradiene–cycloheptatriene equilibrium.[2] To that purpose we attempted to prepare the adducts of benzene to dialkoxycarbonylcarbenes, generated by thermolysis of photolysis of the corresponding dialkyl diazomalonates. Although these attempts were abortive because of the failure of the carbenes to add to benzene, we wish to report here convenient syntheses for two precursors, dimethyl and diethyl diazomalonate.

Diethyl diazomalonate has been prepared by diazotization of diethyl aminomalonate,[3] but the product obtained by this method is grossly contaminated by ethyl diazoacetate[4] and has to be purified by repeated distillation and recrystallization. Similarly, diethyl diazomalonate obtained[5] by the reaction of ethyl diazoacetate with phosgene followed by addition of ethanol is contaminated by chlorine-containing by-products.[6] We have found that the diazo ester may be prepared in 67% over-all yield and in a high state of purity from commercially available diethyl mesoxalate. Treatment of the latter in aqueous acetic acid



solution with hydrazine gave diethyl mesoxalate hydrazone in 75% yield. Oxidation of the hydrazone with silver oxide in tetrahydrofuran produced gas chromatographically pure diethyl diazomalonate in 89% yield. Diethyl mesoxalate hydrazone has been described previously,[7] and the fact that it is readily oxidized to diethyl diazomalonate has also been mentioned.[8] When dimethyl mesoxalate was treated with hydrazine under the conditions described for the diethyl analog, mainly the hydrazine derivative **1**[9] and only a small



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amount of the desired dimethyl mesoxalate hydrazone were obtained. Since dimethyl mesoxalate is not commercially available, this approach was abandoned in favor of one involving transesterification of diethyl mesoxalate hydrazone with methanol and hydrochloric acid. Yields of dimethyl mesoxalate hydrazone were only moderate (25%), but the procedure could be scaled up to a molar scale without any difficulties. Oxidation of the hydrazone with silver oxide in tetrahydrofuran furnished dimethyl diazomalonate in 89% yield.

Complete thermolysis of diethyl and dimethyl diazomalonate in benzene required a temperature of 150°. The products were complex mixtures, the analyses and molecular weight determinations of which indicated that they were mostly dimers of the dialkoxycarbonylcarbenes. Similar mixtures were obtained

(1) E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652 (1965).
(2) E. Ciganek, *ibid.*, **87**, 1149 (1965).
(3) H. Lindemann, A. Wolter, and R. Groger, *Ber.*, **63**, 702 (1930).
(4) W. v. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **83**, 1989 (1961).
(5) H. Staudinger, J. Becker, and H. Hirzel, *Ber.*, **49**, 1978 (1916).
(6) See ref. 5, footnote 1 on p. 1984.
(7) H. Staudinger and L. Hammett, *Helv. Chim. Acta*, **4**, 217 (1921).
(8) J. Neresheimer, Doctoral Dissertation, Munich, 1908.
(9) R. S. Curtiss and P. T. Tarnowski, *J. Am. Chem. Soc.*, **30**, 1264 (1908).