

An analytical sample was obtained by crystallization of the crude material from benzene followed by 3 recrystallizations from ethyl acetate. It softened at 150° and melted at 192.5–194.0°.

A mixed melting point of 2-quinoxalinoformamide and 2-acetamidoquinoxaline (m.p. 192.6–193.8°)<sup>12</sup> showed a sharp depression.

*3',4'-Dichloroformanilide.* Acetic formic anhydride was prepared from acetic anhydride (40.8 ml.) and 98% formic acid (17.2 ml.). This mixture was cooled in an ice bath to 12°. A gradual addition of 3,4-dichloroaniline (32.4 g., 0.2 mole) was made so that the temperature did not rise above 40°. The dark red solution was held at room temperature (35°) for five hours after which ether (100 ml.) was added. The following day the dark purple solution was extracted with 2 × 100 ml. of water. The ether layer was

evaporated on the steam bath to furnish 36.7 g. (96.5%) of crude material, m.p. 94–103°. A hot benzene (150 ml.) solution of the crude product was treated with Nuchar C. The filtrate was cooled for several hours prior to collecting the product by filtration. A cold benzene wash was applied to the gray solid. The purified 3',4'-dichloroformanilide weighed 30.4 g. It sintered at 99° and melted at 110–112°. Recrystallization from a large volume of carbon tetrachloride furnished off-white crystals with no change in melting point. The product is soluble in chloroform and cyclohexene but insoluble in petroleum ether or cyclohexane. Possibly a reduction in the quantity of acetic formic anhydride to slightly over one mole would give a satisfactory result for this type of preparation.

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[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER COMPANY]

## Preparation of Ethenesulfonamide<sup>1</sup>

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Received September 30, 1957

Ethenesulfonamide has been prepared in moderate yields by heating 2-sulfamylethylamines and their salts.

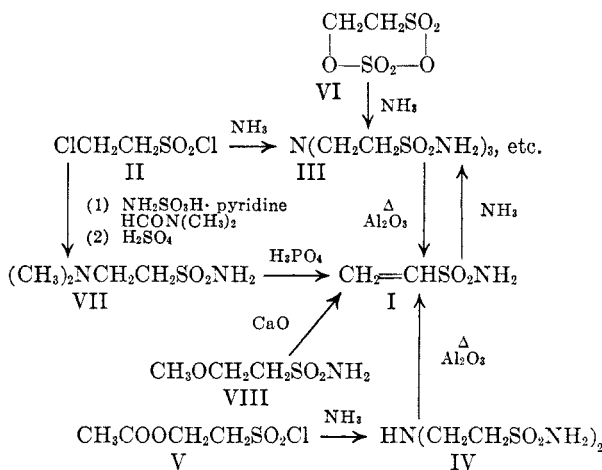
The literature records three different sets of properties for ethenesulfonamide (I).<sup>2–9</sup> None of these are those that would be predicted from the prop-

erties of the closely related ethanesulfonamide.<sup>10,11</sup> These discrepancies prompted a reinvestigation of the preparation of I.

Ethenesulfonamide has now been prepared in 53% yield by heating with alumina a mixture obtained by ammonolysis of 2-chloroethanesulfonyl chloride (II). After crystallization from ether it melted at 24° and was soluble in ethanol, water, ethyl acetate, and acetone but insoluble in benzene and hexane. Ammonia added readily to I to form tris(2-sulfamylethyl)amine (III) and thiophenol added to I to form 2-phenylthioethanesulfonamide. No Diels-Alder reaction occurred with anthracene on heating with I at 100° for 72 hr.

The formation of I on heating is believed to occur by elimination of ammonia from the mixture of 2-sulfamylethylamines obtained by ammonolysis of II.<sup>12</sup> The preparation of I (in 35% yield) from bis-(2-sulfamylethyl)amine (IV) under the same conditions lends support to this view. Heating the hydrochloride of IV also gave I in 30% yield. The sample of IV used was prepared by ammonolysis of 2-acetoxyethanesulfonyl chloride (V).

Another source of mixtures containing 2-sulfamylethylamines was the reaction of ammonia



(1) Presented in part at the Delaware Chemical Symposium, University of Delaware, February 19, 1955.

(2) J. W. James, *J. prakt. Chem.*, **34**, 348 (1886).

(3) E. P. Kohler, *Am. Chem. J.*, **19**, 744 (1897).

(4) P. W. Clutterbuck and J. B. Cohen, *J. Chem. Soc.*, **121**, 120 (1922).

(5) H. F. Park and R. I. Longley, Jr., U.S. Patent 2,710,882 (1955).

(6) H. F. Park, U.S. Patent 2,700,055 (1955).

(7) H. F. Park, U.S. Patent 2,715,142 (1955).

(8) H. F. Park, U.S. Patent 2,709,707 (1955).

(9) Two patents report the use but not the preparation or properties of I: V. R. Grassie, U.S. Patent 2,580,351 (1951) and J. B. Dickey and H. W. Coover, U.S. Patent 2,533,207 (1950).

(10) I. Kolker and A. Lapworth, *J. Chem. Soc.*, **127**, 314 (1928).

(11) A. P. N. Franchimont, *Koninkl. Akad. Wetenschap. Amsterdam*, **22**, 285 (1913); *Chem. Zentr.*, **84**, II, 1960 (1913).

(12) H. W. Coover and N. H. Shearer, Jr. [U.S. Patent 2,719,178 (1955)] report the preparation of *N,N*-dimethylmethacrylamide by passing its dimethylamine adduct over alumina at 550°.

with carbyl sulfate (VI).<sup>13</sup> Pyrolysis of this mixture with alumina gave a 15% yield of I.

Another 2-sulfamylethylamine, 2-dimethylaminoethanesulfonamide (VII), was obtained unexpectedly (in 31% yield) when II was treated with sulfamic acid in pyridine-dimethylformamide. No I was obtained when the reaction was carried out without the dimethylformamide. That the dimethylamino group and not an unsubstituted amino group was present in the 2 position was shown by formation of a methiodide involving the addition of only one methyl group. Heating the phosphate of VII gave I in 36% yield whereas heating the quaternary hydroxide corresponding to the methiodide gave none at all.

Several other approaches to the preparation of I were examined briefly. Heating 2-methoxyethanesulfonamide (VIII) with calcium oxide apparently gave I in 40% yield but mixed with unchanged starting material from which it could not be readily separated. 1-Chloroethanesulfonamide<sup>14</sup> was not dehydrochlorinated on boiling with pyridine for 5 days. Boiling with quinoline for 3 hr. gave only a tar. When II was treated at  $-60^{\circ}$  with pyridine and one mole of ammonia or with two moles of ammonia, the products resembled those made at higher temperatures.<sup>2</sup> Ammonium carbamate with II at  $-10$  to  $0^{\circ}$  gave no I.

Sodium<sup>15</sup> and  $\alpha, \alpha'$ -azodiisobutyronitrile catalyzed polymerization of I to polymers of low molecular weight.

#### EXPERIMENTAL<sup>16</sup>

All melting points are corrected. A trace (0.5–1.0%) of *N*-phenyl-2-naphthylamine, as a polymerization inhibitor, was included in all distillations of I. The yields given have been determined by quantitative hydrogenation in aqueous solution with palladium-charcoal catalyst and are believed to be accurate to  $\pm 3\%$ . In several instances yields of I were also determined by isolation of its thiophenol adduct, a typical procedure being given under the heating of bis(2-sulfamylethyl)amine.

*Ethanesulfonamide* (I) from 2-chloroethanesulfonyl chloride (II). Ammonia was passed into a stirred solution of II (15.5 g.) in dioxane (150 ml.) at  $10^{\circ}$  until no further solid precipitated. The ice bath was removed and the passage of ammonia continued while the mixture warmed up to room temperature. The solid, after removal by filtration, was extracted with hot dimethylformamide. The combination of filtrate and extract was taken to dryness *in vacuo* leaving a 12.7-g. residue. A 6.7-g. portion was ground in a mortar with alumina (10 g.), then heated in a small distilling flask at 0.1 mm. with a free flame until no more liquid distilled, alumina frequently being carried over with the distillate. The residue from an acetone extract of the material in the

(13) Although it is not possible to stop the reaction with ammonia at I, reaction with aniline gives good yields of the unsaturated sulfonanilide; F. Ebel, U.S. Patent 2,666,788 (1954).

(14) R. L. Shriner and A. H. Land, *J. Org. Chem.*, **6**, 888 (1941).

(15) D. S. Breslow, G. E. Hulse, and A. S. Matlack, *J. Am. Chem. Soc.*, **79**, 3760 (1957).

(16) Analyses were carried out by the Analytical Division of the Hercules Research Center.

condenser and receiver (3.5 g.) absorbed 1.23% of its weight of hydrogen (theory 1.87%). Redistillation gave 2.8 g., b.p.  $114^{\circ}$  at 0.1 mm., which absorbed 1.51% hydrogen. The samples then were 66% and 81% pure, respectively, the yield of ethanesulfonamide being 53% (based on the unsaturation in the initial product). The product was taken up in a small amount of ether, cooled to  $-10^{\circ}$ , and seeded; seed crystals being obtained by cooling the 81% pure sample in Dry Ice. The crystals were removed by filtration in a cold room at  $0-3^{\circ}$ . After two more crystallizations large colorless prisms, m.p.  $24^{\circ}$ , were obtained. A fourth crystallization (giving 1.0 g.) did not raise the melting point.

*Anal.* Calcd. for  $C_2H_5NO_2S$ : C, 22.42; H, 4.70; N, 13.08; hydrogen uptake, 1.87. Found: C, 22.52; H, 4.75; N, 13.5; hydrogen uptake, 1.85.

*Derivatives of ethanesulfonamide* (I). I (1.00 g.) was dissolved in water (2 ml.) containing ammonia (0.053 g.). After standing overnight at room temperature it was taken to dryness. The residue of tris(2-sulfamylethyl)amine (III) was crystallized from aqueous ethanol and then twice from acetone-water-ether to give crystals melting at  $182^{\circ}$ .

*Anal.* Calcd. for  $C_6H_{18}N_4O_6S_3$ : C, 21.29; H, 5.36; N, 16.56. Found: C, 21.38; H, 4.92; N, 16.74.

The addition of two drops of Triton B (25% methanolic solution) to a solution of I (0.50 g.) and thiophenol (0.51 g.) in dioxane (10 ml.) produced a mildly exothermic reaction. After standing 3 days at room temperature the mixture was neutralized with acetic acid and the solvent removed *in vacuo*. After three crystallizations from ethyl acetate the thiophenol adduct (colorless plates) melted at  $109-110^{\circ}$ .

*Anal.* Calcd. for  $C_8H_{11}NO_2S_2$ : C, 44.21; H, 5.10; N, 6.45. Found: C, 44.09; H, 5.01; N, 6.62.

*Preparation and heating of bis(2-sulfamylethyl)amine* (IV) and its salts. 2-Acetoxyethanesulfonylchloride<sup>17</sup> (247 g.) was added dropwise to concentrated aqueous ammonia (1 liter) cooled in an ice bath. After standing at  $25^{\circ}$  for 3 days it was evaporated to dryness *in vacuo*. The residue was extracted successively with chloroform, absolute ethanol, and dimethylformamide. Removal of solvent from the last extract followed by crystallization from aqueous ethanol gave a material, 27 g. (8%), m.p.  $160^{\circ}$ , which was apparently a hydrate of bis(2-sulfamylethyl)amine. A second crystallization raised the melting point to  $179.0-179.5^{\circ}$ . It was analyzed as the hydrochloride, m.p.  $177^{\circ}$ .

*Anal.* Calcd. for  $C_4H_{14}ClN_2O_4S$ : C, 17.94; H, 5.27; N, 15.69. Found: C, 18.23; H, 5.25; N, 15.32.

Heating the hydrate of IV (2.0 g.) with alumina (3.0 g.) (as described in the preparation of I from II) gave a liquid (0.8 g.) which after redistillation (0.7 g.) absorbed 1.69% hydrogen, corresponding to ethanesulfonamide of 90% purity, a yield of 35%. A portion (0.52 g.) was treated with thiophenol to give the adduct (first crop 1.51 g., m.p.  $106-108^{\circ}$ , after two crystallizations from ethyl acetate,  $109-110^{\circ}$ ; second crop, 0.53 g., m.p.  $97-101^{\circ}$ ). This showed the product to be about 85% ethanesulfonamide.

Heating the hydrochloride (0.76 g., at 0.1 mm.) gave a liquid (0.39 g.) which after redistillation (0.21 g.) absorbed 1.68% hydrogen, corresponding to 90% purity. The isolation of the thiophenol adduct indicated 78% purity. Based on hydrogenation the yield of ethanesulfonamide was 30%.

*Ethanesulfonamide* (I) from carbyl sulfate (VI). VI<sup>18</sup> (23 g.) was added in small portions to liquid ammonia (150 ml.) cooled in Dry Ice. The excess ammonia was removed with a water aspirator before the mixture warmed to room temperature. A sample of the product (2.7 g.) was dissolved in a solution of sodium carbonate (2.0 g.) in water. After standing overnight at room temperature it was taken to dryness *in vacuo* and the residue extracted with acetone in a Soxhlet extractor. The residue left after removing the solvent from the extract (0.61 g.) was crystallized three times from ace-

(17) R. Anschutz, *Ann.*, **415**, 97 (1918).

(18) D. S. Breslow and R. R. Hough, *J. Am. Chem. Soc.*, **79**, 5000 (1957).

tone-water-ether to give crystals melting at 182–183°. A mixed melting point with authentic tris(2-sulfamylethyl)-amine showed no depression.

A second sample of the carbyl sulfate-ammonia product (5.3 g.) was heated with alumina (6 g.) (as described under the preparation of I from II) to give 0.67 g. liquid which on redistillation gave 0.53 g. that was 71% ethenesulfonamide as indicated by isolation of the thiophenol adduct, corresponding to a 15% yield of I.

*2-Dimethylaminoethanesulfonamide* (VII). A solution of II<sup>19</sup> (60 g.) in dimethylformamide (200 ml.) was added dropwise at 25° to a stirred suspension prepared by adding pyridine (100 ml.) to sulfamic acid (35.7 g.) in dimethylformamide (750 ml.). After standing overnight the solvent was removed *in vacuo*. The residue was treated with aqueous sodium carbonate and again evaporated to dryness. Evaporation of a methanol extract of this residue left a viscous liquid (85 g.). Sulfuric acid (19 g.) in water (500 ml.) was allowed to stand with 57 g. of it for 4 hr. at 25°, then the solution was neutralized with sodium carbonate and evaporated to dryness. This residue was extracted repeatedly with acetone. The hydrolysis procedure was now repeated on the residue with sulfuric acid (10 g.). The combined acetone extracts were evaporated to dryness and the residue crystallized from benzene to give 2-dimethylaminoethanesulfonamide (11.6 g., m.p. 94.5–96.5°, 31%). Colorless plates, m.p. 95.5–97.0°, were obtained by recrystallization from benzene.

*Anal.* Calcd. for C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S: C, 31.56; H, 7.94; N, 18.41. Found: C, 31.51; H, 7.78; N, 18.31.

The hydrochloride was prepared by dissolving the compound in a slight excess of 1*N* hydrochloric acid followed by evaporation to dryness under reduced pressure. Two recrystallizations from 95% ethanol gave a colorless solid melting at 177.5–178.5°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>2</sub>S: C, 25.46; H, 6.94; N, 14.85. Found: C, 25.68; H, 6.95; N, 14.68.

VII was converted to its methiodide by heating under reflux overnight with excess iodomethane. The product (m.p. 190.0–193.0°, 100% yield) was removed by filtration. After two recrystallizations from aqueous ethanol it melted at 196.5–197.0°.

*Anal.* Calcd. for C<sub>5</sub>H<sub>15</sub>IN<sub>2</sub>O<sub>2</sub>S: C, 20.41; H, 5.14. Found: C, 20.47; H, 5.36.

VII (1.03 g.) was treated with phosphoric acid (0.27 g. in 3 ml. of water). The residue from evaporation gave on heating at 0.1 mm. a liquid (0.63 g.) which contained 41% ethenesulfonamide, determined by isolation of the thiophenol adduct, a 36% yield.

*2-Methoxyethanesulfonamide* (IX). Sodium isethionate (1000 g.) was converted to sodium 2-bromoethanesulfonate

by the method of Rumpf.<sup>20</sup> The product (1134 g.) was heated for 18 hr. with a boiling solution of sodium (80 g.) in methanol, then the sodium bromide removed by hot filtration. The solvent was removed and the residue taken up in phosphorus oxychloride. Phosphorus pentachloride (1450 g.) was added in portions with cooling. After completion of the addition, the mixture was heated for 2 hr. at 100°. The cooled mixture was extracted with dry ether and the extract distilled to give 354 g. (42%) of the sulfonyl chloride, b.p. 100–105° at 18 mm. Ammonia was passed into a chloroform solution of the product at 5–10° until no further formation of precipitate occurred. After removal of the chloroform by distillation, the product was separated from most of the ammonium chloride by extraction with dimethylformamide. Two distillations gave the sulfonamide (169 g.), b.p. 135° at 0.3 mm., 55% yield, based on the sulfonyl chloride.

*Anal.* Calcd. for C<sub>3</sub>H<sub>7</sub>NO<sub>2</sub>S: S, 23.0. Found: S, 23.2.

This sulfonamide (10.4 g.) was dropped through 15 cm. of 6-mesh calcium oxide (topped with 0.5 cm. of glass beads) at 270° (0.3 mm.) over a period of 65 min. The acetone-soluble portion of the product (5.0 g.) was distilled to give a light yellow oil (4.0 g.), b.p. 118° at 0.06 mm. It contained 11.8% nitrogen (theory for ethenesulfonamide 13.1%, for 2-methoxyethanesulfonamide 10.1%) and took up 0.89% hydrogen (theory for ethenesulfonamide 1.87%). It gave solid adducts with both ammonia and 2,2'-thiodiethanethiol<sup>21</sup> (with Triton B). These facts suggest the production of ethenesulfonamide in 40% yield (based on material actually consumed in the reaction). At lower temperatures no demethanolation occurred; at higher temperatures tar formation predominated. Increased contact time gave a greater degree of unsaturation (up to 78%) at the expense of yield of pyrolyzate. The substitution of alumina for calcium oxide gave similar results.

*Polymerization of ethenesulfonamide* (I). A solution of  $\alpha,\alpha'$ -azodiisobutyronitrile (0.01 g.) in I (1.00 g.) was covered with nitrogen and heated overnight at 60°. The product was soluble in hot water (but insoluble in cold) and insoluble in acetone and ethyl acetate. It was triturated with acetone, taken up in dimethylformamide, and precipitated by pouring into acetone. The brittle solid (0.3 g., after drying) did not melt on ignition. A 1% solution in dimethylformamide had a specific viscosity of 0.172.

*Acknowledgment.* The author is indebted to Dr. G. E. Hulse for many helpful suggestions during the course of this work.

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(19) A. A. Goldberg, *J. Chem. Soc.*, 464 (1945).