

TABLE I
 SUBSTITUTED AMMONIUM SALTS OF SULFAMIC ACID

Amine used	Formula	M. p. (uncorr.) °C.	Sulfur, %		Nitrogen, %	
			Calcd.	Found	Calcd.	Found
1 Methylamine ^a	NH ₂ SO ₂ OH·NH ₂ CH ₃	91-92	25.00	25.59	21.9	21.9
2 Dimethylamine ^a	NH ₂ SO ₂ OH·NH(CH ₃) ₂	86-87	22.53	24.15	19.7	19.2
3 Trimethylamine ^a	NH ₂ SO ₂ OH·N(CH ₃) ₃	147.5-149	20.51	20.60	17.9	17.8
4 Ethylamine ^a	NH ₂ SO ₂ OH·NH ₂ CH ₂ CH ₃	65-70	22.53	23.21	19.7	19.3
5 Propylamine	NH ₂ SO ₂ OH·NH ₂ (CH ₂) ₂ CH ₃	67-69	20.51	20.60	18.0	17.6
6 Isopropylamine ^a	NH ₂ SO ₂ OH·NH ₂ CH(CH ₃) ₂	74-75	20.51	21.54	18.0	18.3
7 <i>n</i> -Butylamine	NH ₂ SO ₂ OH·NH ₂ (CH ₂) ₃ CH ₃	107-108	18.82	18.83	16.5	16.1
8 Isobutylamine	NH ₂ SO ₂ OH·NH ₂ C(CH ₃) ₃	138-139	18.82	18.81	16.5	17.1
9 <i>n</i> -Amylamine	NH ₂ SO ₂ OH·NH ₂ (CH ₂) ₄ CH ₃	128-129	17.39	17.65	15.2	15.0
10 Isoamylamine	NH ₂ SO ₂ OH·NH ₂ (CH ₂) ₂ CH(CH ₃) ₂	185	17.39	17.65	15.2	15.1
11 <i>n</i> -Hexylamine	NH ₂ SO ₂ OH·NH ₂ (CH ₂) ₅ CH ₃	109-111	16.16	16.25	14.1	14.3
12 2-Ethylbutylamine	NH ₂ SO ₂ OH·NH ₂ CH ₂ CH(CH ₂ H ₅) ₂	89-90	16.16	16.18	14.1	14.3
13 Ethylenediamine	NH ₂ SO ₂ OH·NH ₂ CH ₂ CH ₂ NH ₂ ·HOSO ₂ NH ₂	156-158	25.19	25.22	22.1	22.0
14 Propylenediamine	NH ₂ SO ₂ OH·NH ₂ CH(CH ₃)CH ₂ NH ₂ ·HOSO ₂ NH ₂	155-156	23.88	24.03	20.9	21.5
15 Cyclohexylamine	NH ₂ SO ₂ OH·NH ₂ C ₆ H ₁₁	157-158	16.33	16.40	14.3	14.3
16 Dicyclohexylamine	NH ₂ SO ₂ OH·NH(C ₆ H ₁₁) ₂	160-162	11.51	11.61	10.1	10.0
17 β -Phenylethylamine	NH ₂ SO ₂ OH·NH ₂ (CH ₂) ₂ C ₆ H ₅	183-184	14.68	14.63	12.8	12.4
18 γ -Phenylpropylamine	NH ₂ SO ₂ OH·NH ₂ (CH ₂) ₃ C ₆ H ₅	104-105	13.79	14.06	12.1	11.8

^a These sulfamates were found to be extremely hygroscopic.

Summary

1. Experimental evidence has been presented to demonstrate that sulfamic acid behaves as a dibasic acid in liquid ammonia.

2. A series of eighteen substituted ammonium

sulfamates has been prepared. Various properties of these compounds, such as melting point, solubilities in common solvents, and hygroscopicity have been determined.

URBANA, ILLINOIS

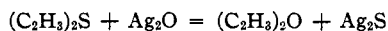
RECEIVED JANUARY 27, 1939

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, MERCK & CO., INC.]

The Reaction of Divinyl Sulfide with Silver Oxide

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The first reference to the preparation of divinyl ether may be found in a paper by Semmler² on the essential oil of the leek, *Allium ursinum* L. When divinyl sulfide derived from this source was treated with dry silver oxide, Semmler obtained a colorless sulfur-free liquid which boiled at 39° and with a molecular weight of 71 as indicated by two vapor density measurements. Without analysis or further characterization he claimed to have prepared divinyl ether (molecular weight 70) for the first time, giving the following equation for the reaction



Recently pure divinyl ether has been synthesized,³ fully characterized, and its boiling point found to be 28.3°, a value confirmed by Miles

and Menzies⁴ and over 10° lower than that reported by Semmler. On theoretical grounds we can find little support for the reaction as formulated by Semmler. It was therefore decided to reinvestigate this reaction.

The repetition of Semmler's work on the natural sulfide was not possible due to the difficulty of obtaining the oil of *A. ursinum*. Synthetic divinyl sulfide, when treated with dry silver oxide at 30° according to Semmler's procedure, failed to give divinyl ether. In one experiment, when the reaction mixture was heated to reflux the divinyl sulfide, a violent explosion occurred. Moist silver oxide and divinyl sulfide likewise failed to give acetaldehyde and silver as stated by Semmler.

We are indebted to Prof. E. Emmet Reid for suggesting the use of β, β' -dibromodiethyl sulfide

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(2) Semmler, *Ann.*, **241**, 92 (1887).

(3) Rugh and Major, *This Journal*, **53**, 2662 (1931).

(4) Miles and Menzies, *J. Phys. Chem.*, **37**, 425 (1933).

instead of the more dangerous and unpleasant β,β' -dichlorodiethyl sulfide for the preparation of divinyl sulfide.

The hydrolysis of β,β' -dichloroethyl sulfide by alkalis in alcohol was first studied by Helferich and Reid,⁵ who obtained a polymerized vinyl sulfide. Bales and Nickelson⁶ and later Davies and Oxford⁷ describe the preparation of the monomeric divinyl sulfide by this reaction. The latter authors gave 85° for the boiling point and the former 85–86°; our product boiled at 83.5–84.0°. Bales and Nickelson pointed out the wide discrepancy between their value and that obtained by Semmler, who gave a boiling point of 101° for the material obtained from *A. ursinum*.

In reporting this work it may be added that the investigation of the natural oil of *A. ursinum* is not contemplated though such a study might serve to account for the discrepancies here noted.

Experimental

Preparation of Divinyl Sulfide.—The crude β,β' -dibromodiethyl sulfide prepared according to Burrows and Reid⁸ from 244.4 g. of thiodiglycol was melted and added, over a period of an hour, to a solution of 336 g. of potassium hydroxide in 1 liter of alcohol and 150 cc. of water. The heat of reaction necessitated cooling of the flask in addition to the use of a reflux condenser. The bulk of the alcohol was distilled off, the distillate was diluted with five volumes of cold water and the oil which separated was collected and dried over sodium sulfate. The yield of crude product was 64 g. The crude product and the subsequent purer fractions were stored in the ice box with the addition of phenyl- α -naphthylamine to retard polymerization. By distillation through a short column 43.7 g. of material was obtained boiling between 83–86° but mostly between 85–86° at 768 mm. On redistillation the pure material boiled at 83.5–84.0° at 759 mm. Microanalyses were performed by Mr. D. Hayman.

Anal. Calcd. for C_4H_6S : C, 55.75; H, 7.04. Found: C, 55.61, 55.76; H, 6.90, 7.17.

(5) Helferich and Reid, *THIS JOURNAL*, **42**, 1219 (1920).

(6) Bales and Nickelson, *J. Chem. Soc.*, **121**, 2137 (1922); **123**, 2486 (1923).

(7) Davies and Oxford, *ibid.*, 234 (1931).

(8) Burrows and Reid, *THIS JOURNAL*, **56**, 1720 (1934).

Action of Silver Oxide on Divinyl Sulfide

Experiment I.—The silver oxide was prepared according to Semmler by precipitation from silver nitrate with potassium hydroxide, was carefully washed, dried for two days at 100–110° and finally for two hours under oil-pump vacuum. Thirty grams of freshly distilled divinyl sulfide was added to 145 g. of the silver oxide contained in a flask immersed in a bath. The temperature of the bath was gradually raised over a period of two hours to about 90°. During this time no trace of material was condensed in the receiver, which was cooled with ice. At 123° (bath temperature) it was noticed that active refluxing had begun and a few minutes later a violent explosion occurred which completely shattered the apparatus.

Experiment II.—The previous run was duplicated except that the temperature was maintained at about 30° for seventy-one hours. Only a slight mist collected on the walls of the receiver. At the conclusion of the experiment the reaction mixture was extracted with ether and the extract was distilled. Only 6 g. of the material came over between 80 and 86°. Polymerization probably accounted for the remainder of the divinyl sulfide.

Experiment III.—Twenty and one-half grams of divinyl sulfide was added to 100 g. of moist silver oxide and the reaction mixture was held at about 30° for three days. A few drops collected in the receiver. A drop of dilute hydrochloric acid was added to the trace of distillate and the mixture was warmed for a moment. The solution showed no significant darkening after neutralizing with ammonia and testing with Tollens' reagent. The presence of even traces of either acetaldehyde or divinyl ether was thus ruled out. The liquid was probably water which had diffused over from the reaction mixture.

Summary

In our hands the treatment of divinyl sulfide with dry silver oxide at 30° failed to give divinyl ether as claimed by Semmler. Under the same conditions moist silver oxide failed to give acetaldehyde.

When divinyl sulfide was heated to the boiling point in the presence of dry silver oxide, a violent explosion occurred.

An improved method for the preparation of divinyl sulfide from β,β' -dibromodiethyl sulfide is described.

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RECEIVED FEBRUARY 15, 1939