(w), 1450 (s), 1425 (m), 1370 (s), 1340–1320 (m), 1275 (w), 1255 (m), 1150 (m), 1125 (m), 1075 (m), 1050 (w), 1040 (w), 975 (s), 890 (m), 870 (s), 840 (m), 820 (m), 780 (w), 760 (w), 705 (w), 680 (m) cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.42; H, 9.52. Found: C, 71.58; H, 9.61.

Oxirane Determination.[10]—To 0.3116 g. of IIa was added 25.0 ml. of 0.2 *N* dry hydrogen chloride in ether. After 2 hr., 50 ml. of neutral ethanol was added and the excess hydrogen chloride was titrated with 0.100 *N* aqueous potassium hydroxide using a Beckman Model B pH meter. A sharp break occurred in the pH *vs.* titrant volume curve at pH 3.2 to 8.2 (midpoint 6.2) corresponding to 2.48 mequiv. of oxirane (1.39 oxirane rings/$C_{10}H_{16}O_2$). Further titration of the sample gave a second pH break at 8 to 10 and corresponded to titration of the total amount of hydrogen chloride introduced. A similar titration of IIb showed 1.26 oxirane rings.

Reaction with Methanol.—To a stirred mixture of 288 g. (9.0 moles) of methanol and 8.5 g. of Amberlyst-15 acidic resin catalyst (Rohm and Haas) was added 190 g. (1.13 moles) of distilled alloocimene dioxide (mixed isomers) during 35 min. at 25–30° with ice bath cooling. After an additional 45 min. at room temperature, the catalyst was filtered off, and washed with two 50-ml. portions of methanol, and the combined filtrate was vacuum stripped to remove the solvent. The residue was pot distilled from 10 g. of potassium hydroxide, giving the dimethoxy product V as a single 186-g. cut, b.p. 137–141° at 5 mm., 77% pure by g.c. Redistillation gave 98% pure V, $n^{20}D$ 1.4667°, d^{20} 1.0215 showing $\bar{\nu}_{\max}^{\text{neat}}$ 3450 (s), 3000–2950–2900 (s), 2800 (m) 2750 (m), 1450–1460 (m, doublet,) 1380 (m), 1290 (w), 1230 (w), 1165 (m), 1105 (s), 1095 (vs) 1040 (w), 990 (m), 952 (m), 920 (w), 875 (w), 828 (w), 750 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{24}O_4$: C, 62.07; H, 10.34. Found: C, 61.92; H, 10.50.

Reaction with Dimethylamine. Monodimethylamino Derivative VII.—To 630 g. (3.75 moles) of alloocimene dioxide (mixed isomers) was added with stirring 539 g. (3.0 moles) of 25% aqueous dimethylamine over a 2.75-hr. period at 45°, slight intermittent heating being required to maintain this temperature. The mixture was stirred an additional 2 hr. at 45°, with increasingly more heat being required. The organic layer (739 g.) was separated and distilled at 3 mm. through a 1.5 × 24 in. column containing stainless steel protruded packing. After a small forerun consisting mainly of water, 274 g. of recovered alloocimene dioxide, b.p. 60–85°, was collected. This was followed by a 276-g. product cut, b.p. 112–123° (61% yield based on unrecovered AOD). The product cut was pot distilled; a center cut, b.p. 114–115° at 5 mm., $n^{20}D$ 1.4674, d^{20} 0.9520, taken for analysis, showed $\bar{\nu}_{\max}^{\text{neat}}$ 3400 (s), 2950–2900–2850–2800–2750 (s), 1650 (w), 1450 (s), 1365 (s), 1320 (m), 1250 (m), 1205 (w), 1160 (m), 1110 (m), 1060 (m), 1020 (m), 970 (s), 925 (w), 910 (w), 868 (m), 820 (w), 750 (w), 700 (w), 680 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{23}NO_2$: C, 67.60; H, 10.79; N, 6.57. Found: C, 67.04; H, 10.77; N, 5.87.

Bisdimethylamino Derivative VIII.—A mixture of 312 g. (1.85 moles) of alloocimene dioxide and 2000 g. (11.1 moles) of 25% aqueous dimethylamine was stirred at room temperature. During the first 2 hr. the temperature gradually rose to 45° and the originally two-phase system became homogeneous. After 3 hr. more, during which time the solution cooled back to 30°, the bulk of the water and excess amine was removed by distillation at atmospheric pressure to a pot temperature of 130° and the remainder stripped away under vacuum. Pot distillation of the residue gave a single product cut (389 g., 82% yield), b.p. 138–144° at 5 mm. Redistillation gave an analytical sample, b.p. 150–153° at 8 mm., $n^{20}D$ 1.4804°, d^{20} 0.9653, which showed $\bar{\nu}_{\max}^{\text{neat}}$ 3400 (s), 2980–2950–2850–2810–2780 (s), 1650 (w), 1450 (s), 1360 (s), 1300 (w), 1250 (w), 1170 (m), 1150 (m), 1100 (w), 1045 (s), 1015 (m), 990 (m), 970–960 (m), 910 (w), 835 (m), 715 (w) cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{30}N_2O_2$: C, 65.11; H, 11.62; N, 10.85. Found: C, 65.16; H, 11.53; N, 10.87.

Acknowledgment.—The authors wish to express sincere appreciation to Dr. Leon Mandell, Emory University, for his aid in the determination and interpretation of n.m.r. spectra.

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Unsymmetrical Disulfides from an Amino Bunte Salt

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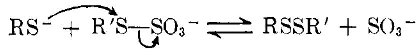
The reaction of Bunte salts (alkyl thiosulfates) with mercaptans has been used with varying success in the synthesis of unsymmetrical disulfides.[1-4] The reaction apparently proceeds *via* an SN2 attack of mercaptide ion on the sulfur atom attached to the alkyl group in the Bunte salt.[5] There is no instance reported in the literature, however, in which a Bunte salt bearing an amino group was used for the synthesis of a mixed disulfide. It was of interest, therefore, to see if 2-aminoethanethiosulfuric acid could be used to prepare an unsymmetrical disulfide containing the cysteamine (mercaptoethylamine) moiety.



$$RS^- + R'S{-}SO_3^- \rightleftharpoons RSSR' + SO_3^{-2}$$

Using the method of Swan,[3] 2-aminoethanethiosulfuric acid was combined with 1 equiv. of a mercaptan in both aqueous and aqueous ethanolic media. A stream of nitrogen was bubbled into the solution to remove the sulfur dioxide anticipated as a by-product. The reaction failed to proceed at room temperature. On prolonged heating a very slight evolution of sulfur dioxide was detected, but nearly all the starting Bunte salt was recovered unchanged on work-up of the reaction mixture.

$$H_2NCH_2CH_2SSO_3H + RSH \longrightarrow H_2NCH_2CH_2SSR + SO_2 + H_2O$$

The reaction of sodium 2-aminoethanethiosulfate with a sodium mercaptide in water by the method of Footner and Smiles[1] proceeded with a slow uptake of the thiol. The use of methanol as the solvent for the above reaction markedly increased the rate of the reaction. A prompt precipitation of sodium sulfite occurred and the mercaptan was consumed in less than 5 min. The insolubility of sodium sulfite in methanol presumably served to drive the reaction to completion. Performance of the reaction at 0°, rather than at room or elevated temperatures, improved yields. Reactions run at −10° or below were too slow to be useful. The mixed disulfides were isolated and purified as hydrochloride salts (Table I).

$$RS^- + H_2NCH_2CH_2SSO_3^- \rightleftharpoons H_2NCH_2CH_2SSR + SO_3^{-2}$$

Yields of unsymmetrical disulfides were rarely greater than 60% due to the formation of considerable quantities of symmetrical disulfides. The ease with which mixed disulfides disproporionate into symmetrical disulfides has been observed by Schöberl and Bauer.[2]

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[1] H. B. Footner and S. Smiles, *J. Chem. Soc.*, **127**, 2887 (1925).

[2] A. Schöberl and G. Bauer, *Angew. Chem.*, **69**, 478 (1957).

[3] J. M. Swan, *Nature*, **180**, 643 (1957).

[4] B. Milligan and J. M. Swan, *J. Chem. Soc.*, 6008 (1963).

[5] O. Foss, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, p. 83.

TABLE I

$RSSCH_2CH_2NH_2 \cdot HCl$

R	M.p., °C.	Yield, %	Recryst. solvent	Calcd., % C	H	N	S	Found, % C	H	N	S
n-Butyl	96–97	40.5	Ethanol	35.71	7.99	6.94	31.78	35.66	8.30	6.89	31.85
n-Hexyl	112–115	42.4	Carbon tetrachloride	41.80	8.77	6.10	27.90	41.68	9.01	5.57	27.84
n-Octyl	112–114	49.0	2-Propanol–acetonitrile	46.57	9.38	5.43	24.87	46.83	9.55	5.42	24.75
n-Decyl	111–112	68.4	Ethanol	50.90	9.87	4.90	22.43	50.52	9.81	5.41	22.43
Phenyl	137–138	63.2	Acetonitrile	43.32	5.46	6.32	28.92	42.84	5.47	6.44	29.26
Benzyl	150–151	50.9	2-Propanol	45.84	5.98	5.94	27.20	45.82	6.21	6.07	27.21

They found that in alkaline or strongly acidic solutions, at elevated temperatures especially, mixed disulfides disproportionate rapidly. Because of the possibility

$$2H_2NCH_2CH_2SSR \rightleftharpoons RSSR + H_2NCH_2CH_2SSCH_2CH_2NH_2$$

that the cystamine [bis(2-aminoethyl) disulfide] dihydrochloride isolated from each reaction mixture may have originated, not only by disproportionation of the mixed disulfide, but by the alkaline decomposition of 2-aminoethanethiosulfuric acid, the stability of the latter compound was determined under experimental conditions. The amino Bunte salt (1 equiv.) was stirred in a nitrogen atmosphere for 5 hr. with 1.75 equiv. of sodium hydroxide in methanol at 0°. Only a trace of sodium sulfite (<0.1% of theory) was formed indicating slight amino Bunte salt decomposition. The quantity was insufficient, however, to account for the amount of cystamine obtained in the mixed disulfide syntheses.

The extensive disproportionation of the unsymmetrical disulfides in the strongly alkaline reaction mixture necessitated rapid isolation at a low temperature. Recrystallization of the hydrochloride salts from water also induced disproportionation but the use of organic solvents seemed to avoid this difficulty.

The reaction of the selenium Bunte salt, 2-aminoethaneselenosulfuric acid, with a mercaptide under the conditions described here for the formation of unsymmetrical disulfides resulted in the synthesis of the selenosulfide. These results will be described in a separate communication.

Experimental[6]

2-Aminoethyl Alkyl (or Aryl) Disulfide Hydrochlorides.—To a solution of 3.0 g. (0.075 mole) of sodium hydroxide in 60 ml. of methanol, through which nitrogen was bubbled, was added 7.08 g. (0.045 mole) of 2-aminoethanethiosulfuric acid.[7] When solution was complete, the flask was immersed in an ice–water bath and the temperature was lowered to *ca.* 0°. The mercaptan (0.03 mole), previously distilled under nitrogen, was added to the solution, causing a slightly exothermic reaction and an almost immediate precipitation of sodium sulfite. After the addition of the mercaptan, aliquots of the mixture were centrifuged and the supernatant liquid was tested for the presence of unreacted mercaptan with sodium nitroprusside. When the test became weakly positive or negative, the time varying from 2 to 5 min. after the addition of the mercaptan, the reaction mixture was suction filtered through Whatman No. 50 filter paper. The cloudy filtrate, kept at 0–10°, was neutralized with ethanolic hydrogen chloride. The solid which formed, most of which was cystamine dihydrochloride, m.p. 210–215° dec., was removed by filtration and the filtrate was evaporated to dryness under reduced pressure at 50° using a rotary evaporator. The white, waxy residue was recrystallized several times to obtain an analytical sample.

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Preparation of N-Perchlorylpiperidine

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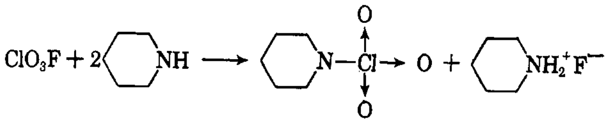
Perchloryl fluoride reacts with aqueous or anhydrous ammonia to produce a mixture of NH_4F and NH_4NHClO_3[1,2] from which salts of the unstable dibasic acid NH_2ClO_3 may be prepared by precipitation reactions in aqueous solution.

At the time of this work perchloryl fluoride was not known to form derivatives with amines other than ammonia. In general, perchloryl fluoride either reacts explosively with pure amines or produces complex mixtures of oxidation products. Reactions in aqueous or alcoholic solution are moderated but are characterized also by complex oxidation products of the organic base.[3]

In view of the above it was surprising to discover that aqueous piperidine will react with a fast flow of ClO_3F gas to form a light oily layer, identified as N-perchlorylpiperidine, on the surface of the aqueous solution. Piperidinium fluoride was found as a second product.

N-perchlorylpiperidine is the first known member of a new class of organic compounds and is the first liquid covalent perchlorylamide prepared to date.



Experimental

A rapidly stirred solution of 8.0 g. (0.094 mole) of piperidine in 250 ml. of water was treated with a fast flow of perchloryl fluoride gas (170 cc./min.) introduced through a fritted-glass dispersion tube below the surface of the solution. The aqueous solution clouded immediately and remained so during the 20-min. reaction time. The perchloryl fluoride flow was stopped, and the solution was purged with nitrogen for 10 min. The aqueous solution was extracted with ether and the ether extract was washed with three 50-ml. portions of 10% HCl. The ethereal solution was dried over magnesium sulfate and evaporated at room temperature under reduced pressure to give 5.2 g. (0.031 mole) of N-perchlorylpiperidine (66% yield based on the above equation).

N-perchlorylpiperidine is a *dangerously sensitive* material. It explodes on heating and on contact with anhydrous piperidine. A sample of the oil exploded with violence on storage in an outside bunker as a possible result of exposure to the heat of the sun or

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[6] Microanalyses were performed by Mr. Joseph Alicino, Metuchen, N. J. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected.

[7] H. Bretschneider, *Monatsh.*, **81**, 372 (1950).

[1] A. Engelbrecht and H. Atzwanger, *J. Inorg. Nucl. Chem.*, **2**, 348 (1956).

[2] H. C. Mandell and G. Barth-Wehrenalp, *ibid.*, **12**, 90 (1959).

[3] Unpublished observations at this laboratory.