amount of gas. The reaction flask was then loosely stoppered and refrigerated for 24 hr. The solution was neutralized with 2 *N* potassium hydroxide and concentrated to 20 ml. by boiling. On cooling, a white precipitate formed. Recrystallization from water gave 0.82 g. (44%) of small, colorless needles, m.p. 306–308° sl. dec.

Anal. Calcd. for $C_4H_4N_6$: C, 35.29; H, 2.94; N, 61.77. Found: C, 35.34; H, 3.07; N, 61.73.

The materials in A and B had identical infrared and ultraviolet spectra, and a mixture melting point showed no depression.

Acknowledgment.—The authors are indebted to the Research Service Department, Stamford Research Laboratories, American Cyanamid Company, for microanalyses and aid in the interpretation of infrared, ultraviolet, and nuclear magnetic resonance spectra.

Direction of Ring Opening in the Reaction of Episulfides with Amines[1]

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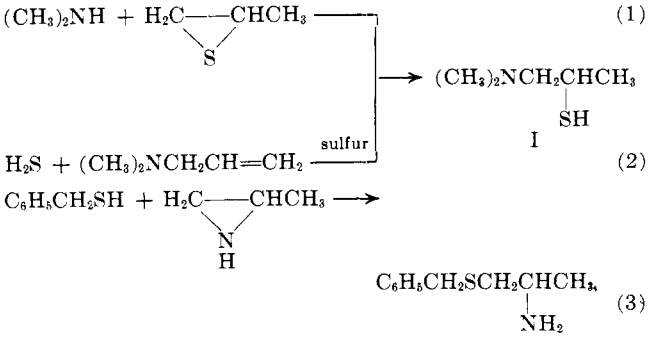
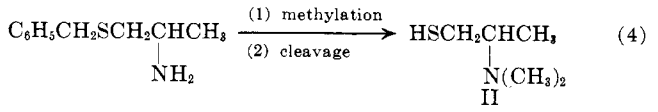
The reaction of isobutylene sulfide with amines has been investigated by Snyder and co-workers[2] who found that displacement occurred at the primary carbon to give tertiary mercaptans as products. Propylene sulfide was used in one instance in their work, but the structure of the product was not investigated. It has also been shown that cleavage of the styrene sulfide ring with secondary amines takes place at the primary carbon atom.[3] In a study of the reaction of propylene sulfide with dimethylamine, however, Hansen[4] concluded that the episulfide ring is opened at the secondary carbon to give 2-dimethylamino-1-propanethiol. Since ring opening reactions of episulfides are of interest in the synthesis of amino mercaptans for evaluation as radioprotectants, we have investigated this reported difference in reactivity of propylene sulfide. Our finding, contrary to that of Hansen's, is that the direction of ring opening in the propylene sulfide–dimethylamine reaction is the same as in the isobutylene sulfide–amine reaction, *i.e.*, the product is 1-dimethylamino-2-propanethiol.

Our approach to establishing the direction of ring opening consisted of comparing the products obtained by the reactions shown in eq. 1, 2, and 4.





Thiolation of dimethylallylamine, in the presence of sulfur to suppress free-radical type addition, gave authentic 1-dimethylamino-2-propanethiol (I). The isomeric addition product, 1-dimethylamino-3-propanethiol, was prepared previously[5] by ultraviolet light-promoted addition of hydrogen sulfide to the hydrochloride of dimethylallylamine. Authentic 2-dimethylamino-1-propanethiol (II) was obtained by opening propylenimine with benzyl mercaptan, methylating the resulting 2-aminopropyl benzyl sulfide, and removing the benzyl group with sodium in liquid ammonia. Meguerian and Clapp[6] have shown that thiophenol opens unsymmetrical ethylenimines in the manner shown in eq. 3. The hydrochloride melting points, the refractive indices, and the boiling points of the products from reactions 1 and 2 were the same. The corresponding properties of II differ significantly from I. These properties, for all three of the dimethylaminopropanethiol isomers, are listed in Table I.

TABLE I

Compound	B.p., °C. (mm.)	$n^{20}D$	Hydrochloride m.p., °C.
$(CH_3)_2NCH_2CHCH_3$ (I)	70 (88)	1.4557	166–167
SH			
$HSCH_2CHCH_3$ (II)	70 (70)	1.4704	120–121
$N(CH_3)_2$			
$HSCH_2CH_2CH_2N(CH_3)_2$[a]	73.5–74.5 (50)	1.4658	105–107

[a] See ref. 5.

The n.m.r. spectra[7] of I obtained by reactions 1 and 2 were identical. A doublet at 1.23 p.p.m. (equivalent to three protons) was characteristic of CH_3 protons in CH_3–CH–SH structures. In the n.m.r. spectrum of II the corresponding doublet was at 1.00 p.p.m., consistent with our observation that nitrogen raises the frequency of nearby protons a smaller degree than does sulfur. Both spectra were dominated by the single strong resonance from the CH_3–N protons at 2.20 p.p.m.

In the earlier work[2] on reaction of amines with isobutylene sulfide the products were shown to be tertiary mercaptans by a color test and by the ease of formation of sulfenyl iodides. In our investigation the isobutylene sulfide–piperidine reaction was repeated, and the n.m.r. spectrum of the product was consistent with that expected for 1-(1-piperidyl)-2-methyl-2-propanethiol. A single sharp peak, equivalent to six CH_3 protons, was observed at 1.27 p.p.m. The two methylene protons between the quaternary carbon and tertiary nitrogen gave a single sharp peak at 2.28 p.p.m. During the course of the work 1-*n*-octylamino-2-methyl-2-propanethiol and 1-*n*-decylamino-2-methyl-2-propanethiol were

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prepared by reaction of the appropriate amine with isobutylene sulfide. Since these compounds are new to the literature and provide further examples of the isobutylene sulfide–amine reaction, the syntheses are described in the Experimental section.

Experimental[8]

1-Dimethylamino-2-propanethiol (I). A. Addition of Hydrogen Sulfide to Dimethylallylamine.—A mixture of 325 g. (3.8 moles) of dimethylallylamine,[5] 450 g. (13.2 moles) of hydrogen sulfide, and 4 g. of sulfur was heated in an autoclave under autogenous pressure at 85° for 5 hr. Distillation of the reaction mixture under reduced pressure through a 2-ft. column packed with glass helices gave 80–85 g. (18%) of I, b.p. 55° at 47 mm., $n^{20}D$ 1.4558. Analysis of this product by gas–liquid chromatography (Carbowax 20 on Teflon, programmed between 100° and 250°) indicated 100% purity.

B. Reaction of Dimethylamine with Propylene Sulfide.—This reaction, according to the procedure of Hansen,[4] gave a 47% yield of 1-dimethylamino-2-propanethiol, b.p. 70° at 88 mm., $n^{20}D$ 1.4557; lit.[4] (as the other isomer) b.p. 71° at 88 mm., $n^{20}D$ 1.4538. Treatment of the free base with hydrochloric acid, followed by recrystallization of the product from a mixture of 2-propanol and heptane, gave the amine hydrochloride, m.p. 166–167°, lit.[4] (as the other isomer) m.p. 167°.

Anal. Calcd. for $C_5H_{14}ClNS$: C, 38.57; H, 9.06; N, 9.00; S, 20.59. Found: C, 38.61; H, 9.17; N, 8.95; S (as mercaptan), 19.3.

2-(Benzylthio)-1-methylethylamine.—Propylenimine (1 mole, 57 g.) was added slowly to a stirred solution of 124 g. (1 mole) of benzyl mercaptan in 200 ml. of tetrahydrofuran at room temperature. A very slight temperature rise occurred. The solution was allowed to stand at room temperature for 2 days and then was heated under reflux for 3 hr. The volatile materials were removed by distillation from a steam bath, leaving 150 g. of a pale yellow oil. The latter was distilled *in vacuo* through a 15-in. Vigreux column, giving, after a small forecut of unchanged benzyl mercaptan, 100 g. (55%) of the desired amino sulfide, b.p. 78–80° at 0.2 mm., $n^{20}D$ 1.5597.

Anal. Calcd. for $C_{10}H_{15}NS$: C, 66.24; H, 8.34; N, 7.73. Found: C, 66.2; H, 8.3; N, 7.3.

2-(Benzylthio)-*N*,*N*,1-trimethylethylamine.—A solution of 90 g. (0.5 mole) of 2-(benzylthio)-1-methylethylamine in 130 g. (2.5 moles) of 95% formic acid was prepared with cooling; to this was added 115 ml. (1.5 moles) of commercial 37% aqueous formaldehyde. The clear solution was heated on a steam bath until the evolution of carbon dioxide was vigorous (*ca.* 2–3 min.). The heat was removed until the reaction had subsided (*ca.* 10 min.), and then heating was resumed (steam bath) for 10 hr. After cooling, 80 ml. of 12 *N* hydrochloric acid was added, and the solution was stripped at 100° under aspirator pressure. The residue was dissolved in 100 ml. of water, and the solution was made basic by the addition of a solution of 50 g. of sodium hydroxide in 200 ml. of water. The organic layer (oil) was separated, and the aqueous layer was extracted twice with ether. The ether extracts were combined with the oil, and the solution was washed well with water. After drying over potassium carbonate, the ether was distilled. The dark-colored residual oil was distilled under a high vacuum to give the desired amine in an 88% yield (92 g.), b.p. 80° at 0.1 mm., $n^{20}D$ 1.5401.

Anal. Calcd. for $C_{12}H_{19}NS$: C, 68.84; H, 9.15; N, 6.69. Found: C, 68.72; H, 9.20; N, 6.4.

2-Dimethylamino-1-propanethiol (II).—A solution of 75 g. (0.36 mole) of 2-(benzylthio)-*N*,*N*,1-trimethylethylamine in *ca.* 1000 ml. of liquid ammonia was prepared. To this, small pieces of sodium were added with stirring until the resulting blue coloration persisted for an hour; about 15 g. of sodium was required. Ammonium chloride (*ca.* 50 g.) was added, and the ammonia was evaporated. The residue was mixed with 300 ml. of 2-propanol under nitrogen, and the mixture was heated to boiling. After cooling in an ice bath, the mixture was filtered under nitrogen; the solids were washed twice with ether. The ether and alcoholic filtrate were combined and the solvents were removed. The residue was distilled through a short Vigreux column under reduced pressure giving 19 g. (45%) of the desired aminothiol, b.p. 70° at 70 mm., $n^{20}D$ 1.4704; lit.[4] (as the other isomer) b.p. 78.5° at 70 mm., $n^{20}D$ 1.4684. Conversion of the product to the hydrochloride gave, from a mixture of 2-propanol and heptane, small white crystals, m.p. 120–121°, lit.[4] (as the other isomer) m.p. 114–115°.

Anal. Calcd. for $C_5H_{14}ClNS$: C, 38.57; H, 9.06; N, 9.00; S, 20.59. Found: C, 38.6; H, 9.3; N, 8.9; S (as mercaptan), 19.1.

1-(1-Piperidyl)-2-methyl-2-propanethiol.—A solution of 44 g. (0.5 mole) of isobutylene sulfide[2] and 42.5 g. (0.5 mole) of piperidine was heated on a steam bath for 20 hr. Fractional distillation of the product gave a 71% yield of 1-(1-piperidyl)-2-methyl-2-propanethiol, b.p. 54.5° at 2.5 mm., $n^{20}D$ 1.4842; lit.[2] b.p. 47° at 2.5 mm., $n^{20}D$ 1.4840.

Anal. Calcd. for $C_9H_{19}NS$: C, 62.37; H, 11.05; N, 8.08; S, 18.5. Found: C, 62.31; H, 11.09; N, 7.8; S (as mercaptan), 17.6.

The hydrochloride (from 2-propanol) melted at 193–194°, lit.[2] m.p. 198–199°.

1-*n*-Octylamino-2-methyl-2-propanethiol.—A solution of 84.3 g. (0.57 mole) of *n*-octylamine in 180 ml. of benzene and 20 ml. of ethanol was heated under reflux, while a solution of 24.4 g. (0.28 mole) of isobutylene sulfide in 90 ml. of benzene and 10 ml. of ethanol was added dropwise over a period of 3 hr. After heating overnight, the reaction solution was fractionally distilled to give a 43% yield of the desired aminothiol, b.p. 105–108° at 0.25 mm., $n^{20}D$ 1.4620. Treating a methanolic solution of the free base with concentrated hydrochloric acid, stripping the solution to dryness, and recrystallizing the residue from tetrahydrofuran gave 1-*n*-octylamino-2-methyl-2-propanethiol hydrochloride, m.p. 163–164.5°.

Anal. Calcd. for $C_{12}H_{28}ClNS$: C, 56.77; H, 11.11; N, 5.52; S, 12.63. Found: C, 56.8; H, 11.3; N, 5.8; S (as mercaptan), 12.93.

1-*n*-Decylamino-2-methyl-2-propanethiol.—A solution of 89 g. (0.57 mole) of *n*-decylamine and 25 g. (0.28 mole) of isobutylene sulfide was heated 20 hr. on a steam bath. The reaction solution was fractionally distilled through a 60-cm. column packed with glass helices to give a 66% yield of the desired aminothiol, b.p. 121° at 1 mm., $n^{20}D$ 1.4642. This was converted to the hydrochloride in the same manner as described above for the *n*-octyl homolog, m.p. 151–153°.

Anal. Calcd. for $C_{14}H_{32}ClNS$: C, 59.65; H, 11.44; N, 4.97; S, 11.37. Found: C, 59.65; H, 11.3; N, 5.4; S (as mercaptan), 11.7.

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(8) All melting points are uncorrected.

Novel Complexes of Metallocenes with π-Acceptors

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The objective of this study was to investigate the possibility of preparing charge transfer complexes of metallocenes, where either the π-cyclopentadienyl ring as in I or the coordinated metal as in II might act as an electron donor to a π-acceptor, such as *p*-chloroanil or *sym*-trinitrobenzene. Though much work has been done on the synthesis of metallocinium salts of aromatic acids, such as the ferrocinium and nickelocinium picrates,[2,3]

(1) To whom all inquiries should be addressed.

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