crystallization from ethanol (Norit) yielded 0.9 g. (0.0032 mole, 32%) of a bright yellow product as plates, m.p. 72–74°.

The diketone was converted to its quinoxaline derivative by refluxing, for an hr., 0.3 g. (0.0011 mole) of it with 0.25 g. (0.0023 mole) of freshly recrystallized *o*-phenylenediamine in 18 ml. of glacial acetic acid. The derivative was isolated by pouring the reaction mixture into 30 ml. of water and cooling to 0°. It was recovered, by filtration, dried, and recrystallized from ethanol (Norit) to give 0.3 g (8.6×10^{-4} mole, 78%) of colorless needles, m.p. 94–95°.

Attempted Intramolecular Acyloin Condensations.—The acyloin condensations were carried out using the apparatus and modifications of the procedures described by Cram[16] and Blomquist.[17] During a 14-hr. period, 42.2 g. (0.1 mole) of 1,6-bis[5′-(β-carbomethoxyethyl)-2′-thienyl]hexane dissolved in 400 ml. of xylene was added to a stirred suspension of 9.5 g. (0.41 g.-atom) of sodium in 300 ml. of refluxing xylene. The reaction mixture was heated for a short period following the addition of the diester, then cooled and a mixture of 100 ml. of glacial acetic acid and 100 ml. of xylene was added which precipitated sodium acetate. A 200-ml. volume of water was added to dissolve the sodium acetate and separate the reaction mixture into two phases, which on filtration yielded 3.8 g. (*ca.* 9%) of a polymeric material.

The aqueous layer was separated and extracted with 100 ml. of xylene. The combined extract and organic layer were washed four times with water and dried. Removal of the solvent yielded a light brown residue which solidified on cooling. Recrystallization of the solid from methanol (Norit) gave 29 g. of the starting diester, m.p. 52–54°. Additional quantities of unchanged diester were obtained from the mother liquors to give a combined weight of 32.8 g. (0.078 mole, 78%) of recovered diester.

Attempted Intramolecular Dieckmann Cyclization of 1,6-Bis[5′-(β-carbomethoxyethyl)-2′-thienyl]hexane.—Using a modification of Leonard's procedure[21] of the intramolecular Dieckmann cyclizations, 250 ml. of dry xylene and 45 g. (0.61 mole) of *t*-butyl alcohol were put in a 3 l. creased flask and 9.3 g. (0.24 g.-atom) of potassium metal (cut in small chunks) were added to the mixture. When the metal had reacted, excess *t*-butyl alcohol was removed and 22 g. (0.05 mole) of the diester dissolved in 200 ml. of xylene was added during 5 hr. The reaction mixture was then heated for a short period, cooled, and 60 ml. of glacial acetic acid and 30 ml. of xylene were added to it, precipitating a white solid. After adding 200 ml. of water to the acidified reaction mixture, 9.1 g. (about 41%) of a polymeric material was collected on filtration of the two phase mixture. The polymer was insoluble in benzene, chloroform, ether, acetone, ethylene dichloride, ethyl acetate, and methylene dichloride and only partially soluble in dimethylformamide.

The xylene layer was separated from the filtrate and the aqueous layer was extracted with 50 ml. of xylene. The extract and xylene layer were combined, washed with water, and dried. Removal of the xylene yielded a brown, oily liquid. This was refluxed with 20 ml. of 3 *N* hydrochloric acid and 5 ml. of ethanol for 12 hr. which caused the evolution of carbon dioxide, observed by precipitation of barium carbonate. The cool hydrolysis mixture was extracted twice with ether in which it was not completely soluble. Removal of the ether left a gummy brown residue which was dissolved in ethyl acetate and decolorized with Norit. The addition of hexane reprecipitated the brown material as an oil which failed to form a crystalline 2,4-dinitrophenylhydrazone.

The ether-insoluble material was dissolved in 50 ml. of methylene dichloride, washed with 25 ml. of water, and dried with anhydrous magnesium sulfate. After removal of the solvent, low pressure distillation (1.0 mm.) of the residue resulted only in its thermal decomposition.

Addition of Hydrogen Sulfide to Unsaturated Amines

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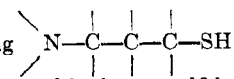
Thiolation of *N*-alkenyl compounds with hydrogen sulfide was investigated as a means of obtaining  structures in connection with the synthesis of potential antiradiation drugs. Irradiating allylamine and hydrogen sulfide gave essentially no thiolation. Heating a mixture of allylamine and hydrogen sulfide, with a free-radical-generating agent, gave a mixture, with Markownikoff addition the predominant reaction. With allylamine hydrochloride and ultraviolet irradiation thiolation resulted, and the mode of addition was directed exclusively to the anti-Markownikoff product, 3-amino-1-propanethiol. Several 3-amino-1-alkanethiols were prepared in this manner. 3-Mercaptopropylformamide and *N*-(3-mercaptopropyl)succinimide were also prepared by this terminal thiolation reaction. The reactivity of *N*-allyl compounds was apparently influenced by electron density at the nitrogen atom, with the observed order of reactivity being imide > amine hydrochloride > amide > dialkylamine hydrochloride > amine acetate ≫ amine. With 3-aminocyclohexene hydrochloride (nonterminal double bond), the products isolated were *cis*- and *trans*-2-aminocyclohexanethiol. Similarly, 1-amino-2-butanethiol was obtained from 1-amino-2-butene hydrochloride. Reaction of *N*-vinyl-2-pyrrolidone with hydrogen sulfide, using ultraviolet light, gave *N*-2-mercaptoethyl-2-pyrrolidone in good yield. *N*-2-Mercaptoethylcaprolactam was prepared in a similar manner.

Compounds containing both amine and thiol groups, and related derivatives, are being investigated extensively as protectants against the harmful effects of ionizing radiation.[1,2] As participants in a program of synthesis of potential antiradiation drugs of this type,[3] an initial task in these laboratories was the preparation of a kilogram lot of high purity 3-amino-1-propanethiol hydrochloride and homologs of the type $H_2NCH(R)CH_2CH_2SH$ (R = alkyl). The parent compound, 3-amino-1-propanethiol, was described in the early literature by

(1) D. R. Kalkwarf, *Nucleonics*, **18**, No. 5, 76 (1960) (review and bibliography).

(2) *Chem. Eng. News*, p. 42, Nov. 23 (1959).

(3) This work was done under Contract DA-49-193-MD-2069 with U. S. Army Medical Research and Development Command.

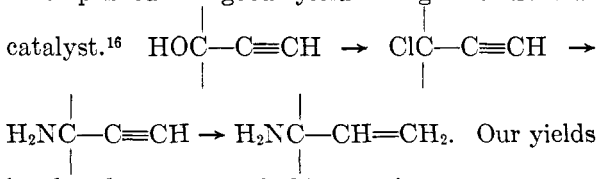
Gabriel.[4,5] Although the compound has been used in more recent investigations,[6,7] preparative difficulties were reported,[8] and apparently in this later work neither the free base nor the hydrochloride was isolated in pure form. No homologous 1,3-aminothiols have been found in the literature.

In a consideration of methods which might be used for synthesis of the $H_2NCH(R)CH_2CH_2SH$ homologs, it became apparent that the possibilities for directed, anti-Markownikoff addition of hydrogen sulfide to 3-amino-1-alkenes should be investigated. No instance was found in the literature where this particular type of addition reaction has been studied. It has been reported,[9] however, that heating equimolar amounts of diallylamine and hydrogen sulfide gave the cyclic sulfide, 2,6-dimethyl-1,4-thiazine. Presumably, under the influence of the amine group, the reaction proceeded by an ionic or "normal" addition. While it has been established that anti-Markownikoff addition occurs if hydrogen bromide[10] or hydrogen sulfide[11] is added to olefins under conditions favorable for a free radical process, Kharasch and Fuchs[12] found that reaction of hydrogen bromide with diethylallylamine, either in the presence or absence of peroxides, gave a mixture of Markownikoff and anti-Markownikoff products.

When a mixture of allylamine and hydrogen sulfide was subjected to ultraviolet-light irradiation at 30°, no thiolation reaction was detected. When heated at 85–95° under autogenous pressure with azobisisobutyronitrile, a reaction did occur to give a mixture of the two possible thiols, 1-amino-2-propanethiol and 3-amino-1-propanethiol, in a weight ratio of about four to one. Thus, under these conditions Markownikoff addition was the predominant reaction. The melting points of 1-amino-2-propanethiol and its hydrochloride were in reasonable agreement with those reported by Gabriel,[5,13] who prepared the compound by cleavage of 5-methyl-2-mercapto-2-thiazoline. The structure was further confirmed by conversion of the hydrochloride to the known 5-methyl-2-(*p*-nitrophenyl)-2-thiazoline by condensation with *p*-nitrobenzoyl chloride. In the same type of condensation, 3-amino-1-propanethiol hydrochloride was converted to 2-(*p*-nitrophenyl)-4*H*,5,6-dihydro-1,3-thiazine.

The free radical addition of hydrogen sulfide to allylamine would be expected to give the desired 3-amino-1-propanethiol, but since amines are known to be inhibitors of free radical processes, modification which would alter the nature of the amine group was indicated. With allylamine the desired effect was accomplished by using the amine hydrochloride. Irradiation of a mixture of an alcoholic solution of allylamine hydrochloride and excess hydrogen sulfide with ultraviolet light gave only the anti-Markownikoff product, 3-amino-1-propanethiol. As expected, the product contained some of the corresponding sulfide, but there was no evidence for the formation of 1-amino-2-propanethiol or its sulfide. Under the best conditions, allylamine conversions of 85% and mercaptane yields of about 50% were obtained. The acetate salt of allylamine also gave only 3-amino-1-propanethiol, but the yield was less than 10%. During the course of the work, 3-amino-1-propanethiol and the hydrochloride were prepared by three other routes: cleavage of tetrahydro-1,3-thiazine-2-thione with fuming hydrochloric acid, reaction of 3-chloropropylamine with sodium bisulfide, and debenzylation of 3-benzylthiopropylamine. All methods gave the same product. The required kilogram of 3-amino-1-propanethiol was prepared by the debenzylation route prior to our finding that directed addition of hydrogen sulfide to allylamine hydrochloride could be achieved. Tarbell and Cameron[14] used this reaction sequence, $HOCH_2CH_2CH_2NH_2 \rightarrow ClCH_2CH_2CH_2NH_2 \rightarrow C_6H_5CH_2SCH_2CH_2CH_2NH_2 \rightarrow HSCH_2CH_2CH_2NH_2$, but isolated the product as the *S*,*N*-diacetyl derivative. In our work it was found that the benzyl sulfide intermediate could be prepared in high yield more conveniently by using aqueous sodium hydroxide, rather than metallic sodium, to form the sodium mercaptide. The 3-amino-1-propanethiol hydrochloride prepared by this route had a melting point of 79.5–80.5°, compared to the previously reported[4] value of 69°.

The other 3-amino-1-alkanethiols prepared by reaction of hydrogen sulfide with allylic amine hydrochlorides in the presence of ultraviolet light are listed in Table II. Most of the allylic amine intermediates were prepared *via* acetylenic amines obtained from the carbinols by the method of Hennion and Teach.[15] Catalytic hydrogenation of the acetylenic amines to the allylic amines was accomplished in good yield using the Lindlar catalyst.[16]

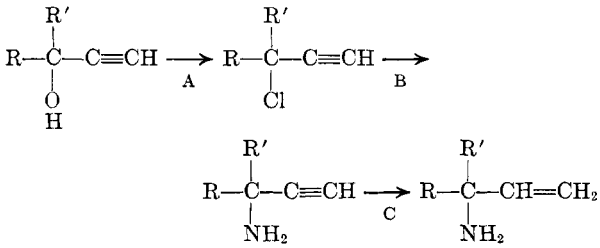


Our yields in the three steps of this reaction sequence are shown in Table I.

(4) S. Gabriel and W. E. Lauer, *Ber.*, **23**, 87 (1890).
(5) S. Gabriel, *ibid.*, **49**, 1110 (1916).
(6) T. Wieland and H. Hornig, *Ann.*, **600**, 12 (1956).
(7) D. G. Doherty, W. T. Burnett, Jr., and R. Shapira, *Radiation Res.*, **7**, 13 (1957).
(8) E. D. Bergmann and A. Kaluszyner, *Rec. trav. chim.*, **78**, 327 (1959).
(9) D. Harman and W. E. Vaughan, *J. Am. Chem. Soc.*, **72**, 631 (1950).
(10) M. S. Kharasch and F. R. Mayo, *ibid.*, **55**, 2468 (1933).
(11) W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, **7**, 472 (1942).
(12) M. S. Kharasch and C. F. Fuchs, *ibid.*, **10**, 159 (1945).
(13) S. Gabriel and E. Leupold, *Ber.*, **31**, 2832 (1898).
(14) D. S. Tarbell and D. P. Cameron, *J. Am. Chem. Soc.*, **78**, 2731 (1956).
(15) G. F. Hennion and E. G. Teach, *ibid.*, **75**, 1653 (1953).
(16) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

TABLE I

ALLYLIC AMINES FROM ACETYLENIC CARBINOLS



R	R′	Yield (%) in step A	B	C	Allylic amines B.p.	$n^{20}D$	M.p., hydrochloride
C_2H_5	H[a]	72	65	83	87.5–88.5	1.4255	196.5–198[b]
C_3H_7	H[c]	62	78	83	113–114.5	1.4285	176–177
C_2H_5	CH_3[d]	63	65	85	101–101.5	1.4270	272 (dec.)

[a] 3-Chloro-1-pentyne, b.p. 94–95°, 37.5–38° at 84–85 mm.; $n^{20}D$ 1.4375; reported[21,22] b.p. 40.8–40.9° at 94 mm., $n^{25}D$ 1.4330. 3-Amino-1-pentyne, b.p. 102–103°, 47–48° at 83 mm., $n^{20}D$ 1.4394. [b] 3-Amino-1-pentene hydrochloride. *Anal.* Calcd. for $C_5H_{12}NCl$: C, 49.38; H, 9.95; N, 11.52. Found: C, 49.5; H, 10.1; N, 11.4. [c] 3-Chloro-1-hexyne, b.p. 62.5–63.5° at 100 mm., $n^{20}D$ 1.4415; reported[21,23] b.p. 63° at 97 mm., $n^{25}D$ 1.4366. 3-Amino-1-hexyne, b.p. 68–68.5° at 100 mm., $n^{20}D$ 1.4413; reported[15] b.p. 70–71° at 100 mm., $n^{25}D$ 1.4378. [d] 3-Chloro-3-methyl-1-pentyne, b.p. 55.5–56.5° at 150 mm., $n^{20}D$ 1.4300; reported[23] b.p. 51.9–52.2° at 115 mm., $n^{25}D$ 1.4307. 3-Amino-3-methyl-1-pentyne, b.p. 60–65.5° at 150 mm., $n^{20}D$ 1.4333; reported[15] b.p. 55–56° at 120 mm., $n^{25}D$ 1.4302. 3-Amino-3-methyl-1-pentene reported[24] b.p. 103–104°.

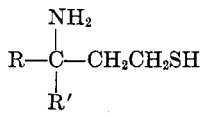
pared by Bergmann[17] by the reaction of hydrogen sulfide with 2,3-dimethylaziridine. Its melting point and boiling point are significantly different from our product. Further confirmation of the 3-amino-1-butanethiol structure was obtained by NMR spectral data which showed the presence of only one methyl group in the compound. With these results it seemed reasonable to assume that the products from the reaction of hydrogen sulfide with the hydrochlorides of 3-amino-1-pentene, 3-amino-1-hexene, and 3-amino-3-methyl-1-pentene were terminal thiols.

The anti-Markownikoff product, 3-dimethylaminopropanethiol, was also obtained when dimethylallylamine hydrochloride was used in the reaction, although the yield was low. Oxidation of the aminothiol gave bis(3-dimethylaminopropyl) disulfide, which was identical with the product obtained by the reaction of bis(3-chloropropyl) disulfide with dimethylamine.

Two allylic amine hydrochlorides were used in which the double bond was not terminal. While this type of system was not investigated thoroughly, only 1-amino-2-alkanethiols were isolated. When a methanolic solution of 3-aminocyclohexene hydrochloride and excess hydrogen sulfide was irradiated, the products isolated (in approximately equal amounts) were the previously known[18–20] *cis*- and *trans*-2-aminocyclohexanethiols. With 1-amino-2-butene hydrochloride, the only pure product isolated was assigned the 1-amino-2-butanethiol structure on the basis of NMR spectral evidence.

TABLE II

3-AMINOALKANETHIOLS BY TERMINAL THIOLATION OF ALLYLIC AMINE HYDROCHLORIDES



R	R′	B.p.	M.p.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
H	H	153	109–110[a]	50	C_3H_9NS	39.51	39.51	9.97	9.94	15.36	15.3	35.17	34.3
CH_3	H	70–74/32 mm.	51–52[b]	57	$C_4H_{11}NS$	45.67	45.5	10.54	10.9	13.31	12.92	30.48	30.0
C_2H_5	H	77/18 mm.	43–45[b]	39	$C_5H_{13}NS$	50.37	50.5	10.99	10.5			26.89	26.2
C_3H_7	H	92–95/15 mm.		36	$C_6H_{15}NS$	54.08	54.21	11.35	11.43			24.06	24.0
C_2H_5	CH_3	99–118/5 mm.		20[c]									
H[d]	H	73.5–74.5/50 mm.		14	$C_5H_{13}NS$	50.37	49.94	10.99	10.97	11.75	11.9		

[a] From toluene; reported[5] m.p. 112–113°. [b] From *n*-pentane. [c] This crude product was converted to the hydrochloride without further purification. [d] Dimethylaminopropanethiol. $n^{20}D$ 1.4658; reported[25] b.p. 40–41° at 12 mm., $n^{20}D$ 1.4666.

In the thiolation reaction using 3-amino-1-butene hydrochloride, the results were the same as with allylamine hydrochloride—*i.e.*, only the terminal thiol, 3-amino-1-butanethiol, was obtained. The isomer which would have resulted from Markownikoff addition, 3-amino-2-butanethiol, has been pre-

The ultraviolet light-promoted addition of hydro-

(17) E. D. Bergmann and A. Kaluszyner, *Rec. trav. chim.*, **78**, 289 (1959).

(18) T. Taguchi and M. Kojima, *J. Am. Chem. Soc.*, **78**, 1464 (1956).

(19) F. Winternitz, M. Mousseron, and D. Dennilauler, *Bull. soc. chim. France*, 1228 (1956).

(20) M. Kojima, *Yakugaku Zasshi*, **79**, 1 (1959); *Chem. Abstr.*, **53**, 10183 (1959).

(21) T. L. Jacobs, W. L. Petty, and E. G. Teach, *J. Am. Chem. Soc.*, **82**, 4094 (1960).

(22) F. C. McGrew and R. Adams, *ibid.*, **59**, 1497 (1937).

(23) G. F. Hennion and K. W. Nelson, *ibid.*, **79**, 2142 (1957).

(24) G. F. Hennison and E. G. Teach, *ibid.*, **75**, 4297 (1953).

(25) K. J.M. Andrews, F. Bergel, and A. L. Morrison, *J. Chem. Soc.*, 2998 (1953).

gen sulfide to an *N*-allylamide and imide was also investigated. With *N*-allylformamide the product was *N*-(3-mercaptopropyl)formamide, although the yield was only 34%. Terminal thiolation was demonstrated by acid hydrolysis of the product, which gave 3-amino-1-propanethiol hydrochloride in nearly quantitative yield. *N*-Allylsuccinimide was considerably more reactive, and *N*-(3-mercaptopropyl)succinimide was obtained as a distilled product in 62% yield.

In general, the yields obtained in terminal thiolation of acid derivatives of allylamine suggested that reactivity was influenced by electron density at the nitrogen atom. Yields were highest in those derivatives where nitrogen electrons were not readily available. When the electron density at the nitrogen was high, the free radical process became more difficult, and in the case of allylamine (free base) no thiolation was detected with ultraviolet light under mild conditions. The observed order of reactivities of the *N*-allyl derivatives, based on yield of thiol (shown in parentheses), was as follows: imide (62%) > amine hydrochloride (50%) > amide (34%) > dimethylamine hydrochloride (14%) > amine acetate (< 10%) >> amine.

Finally, the reaction was extended to the use of *N*-vinyl-2-pyrrolidone and *N*-vinylcaprolactam. With the pyrrolidone, a smooth reaction gave 1-(2-mercaptoethyl)-2-pyrrolidone in 66% yield and the corresponding sulfide, bis[2(2-pyrrolidon-1-yl)-ethyl] sulfide, in 26% yield. The NMR spectrum of the thiol showed the characteristic triplet for mercaptan proton adjacent to a methylene group. With *N*-vinylcaprolactam, the crude yield of reaction product indicated that the reaction proceeded about as well as with the pyrrolidone; however, considerable decomposition occurred during distillation. The yield of distilled *N*-(2-mercaptoethyl)-caprolactam was only 28%, and the sulfide was not isolated as a pure product.

Experimental[26]

1-Amino-2-propanethiol. Thermal Reaction of Hydrogen Sulfide with Allylamine.—A mixture of 171 g. (3 moles) of allylamine, 204 g. (6 moles) of hydrogen sulfide, and 6 g. of azobisisobutyronitrile in a stainless-steel rocker-type autoclave was heated at 85–95° for 6 hr. under autogenous (500–590 p.s.i.g.) pressure. At the end of the reaction period the autoclave was vented, and the contents were removed while hot. The mixture was distilled under nitrogen, giving 105 g. (1.15 moles, 38%) of a mixture of aminothiols, b.p. 135–140°, m.p. 54–60°. This mixture of isomers was dissolved in ether and converted to the hydrochlorides with anhydrous hydrogen chloride. Several recrystallizations from chloroform removed the 1,3-isomer and gave pure 1-amino-2-propanethiol hydrochloride, m.p. 91.5–92.5°; reported[13] m.p. 87–88°.

Anal. Calcd. for $C_3H_{10}ClNS$: C, 28.23; H, 7.90; Cl, 27.78; N, 10.98. Found: C, 28.5; H, 8.1; Cl, 27.2; N, 10.95.

The mixture of isomers could also be separated by careful distillation of the free bases. Thus, from a similar reaction with 5 moles of allylamine, 15 moles of hydrogen sulfide, and 7.5 g. of azobisisobutyronitrile was obtained about 190 g. of the mixture of isomers by flash distillation. Redistillation of this through a packed column at a 20:1 reflux ratio gave 100 g. of 1-amino-2-propanethiol, b.p. 134–138°, and 30 g. of 3-amino-1-propanethiol, b.p. 152–158°. The 1-amino-2-propanethiol could be recrystallized from benzene, m.p. 63–64.5°; reported[5] m.p. 65–67°. Analysis of this product (m.p. 63–64.5°) by gas–liquid chromatography (GE Type SE-30 silicone gum rubber on Chromosorb, 110°) indicated 99% purity.

5-Methyl-2-(*p*-nitrophenyl)-2-thiazoline.[27]—A mixture of 1 g. of 1-amino-2-propanethiol hydrochloride and 4 g. of freshly prepared *p*-nitrobenzoyl chloride was heated at 100° until thorough mixing could be effected. The melt was then heated at 195° for 20 min. The reaction mixture was poured into cold water and the water was decanted from the insoluble product. The latter was dissolved in a little acetone and poured into aqueous sodium bicarbonate. The buff-colored solid that formed was recrystallized several times from alcohol to give 1-(*p*-nitrobenzamido)-2-propanethiol *p*-nitrobenzoate, m.p. 177.5–178.5°.

Anal. Calcd. for $C_{17}H_{15}N_3O_6S$: C, 52.43; H, 4.88; N, 10.79; S, 8.24. Found: C, 52.8; H, 4.4; N, 10.4; S, 7.4.

Upon long standing the aqueous sodium bicarbonate filtrate gave a small amount of 5-methyl-2-(*p*-nitrophenyl)-2-thiazoline, m.p. (after two recrystallizations from dilute ethanol) 106–108°; reported[28] m.p. 108–108.5°.

2-(*p*-Nitrophenyl)-4*H*,5,6-dihydro-1,3-thiazine.—A mixture of 0.5 g. of 3-amino-1-propanethiol hydrochloride was heated at 100° with 2.5 g. of freshly prepared *p*-nitrobenzoyl chloride until solution was complete. The melt was then heated at 195° for 20 min. After pouring the hot mixture onto ice, the solid product was dissolved in a little acetone. This solution was poured into aqueous sodium bicarbonate. Recrystallization of the resulting solid product three times from dilute ethanol gave the thiazine, m.p. 141–142°, as small cream-colored needles; reported[28] m.p. 137–138°.

3-Amino-1-propanethiol.—The ultraviolet light–promoted addition of hydrogen sulfide to all the allylic amine hydrochlorides described in this report was carried out in a reactor designed for moderate pressure work. The main part of the reactor was composed of two pieces of concentric tubing, the outer one of a 6-inch section of 3-inch stainless steel pipe and the inner one of 33-mm. quartz tubing. These tubes were sealed together through packing glands on each end. The reaction was carried out in the annular space between the pieces of tubing, and ultraviolet light was transmitted through the quartz tubing by a 450-watt mercury vapor lamp. The reactor was fitted internally with a thermowell and cooling coil. An inlet and outlet were provided for ease in adding and removing the reactants. All the reactions were run at 20–25°, with tap water through the cooling coil, and at autogenous pressure. The reactor was mounted on a horizontal shaker to provide agitation during the radiation period. The reaction of hydrogen sulfide with allylamine hydrochloride will be described in detail as representative for all the allylic amines in this study.

A solution of 142.5 g. (1.5 moles) of allylamine hydrochloride, 102 g. (3 moles) of hydrogen sulfide, 5 ml. of trimethyl phosphite,[29] and 150 g. of isopropyl alcohol was irradiated for 1 hr., keeping the reaction mixture cool by circulation of tap water through the cooling coil. The excess hydrogen sulfide was vented and the reaction mixture was mixed with about 100 ml. of isopropyl alcohol. The isolation and purification steps were conducted under nitrogen. Sodium hydroxide (63 g., a 5% excess) was added to the solution and the mixture was stirred while it was heated to

(26) All melting points are uncorrected.

(27) M. Böse, *Ber.*, **53**, 2000 (1920).

(28) S. H. Babcock and R. Adams, *J. Am. Chem. Soc.*, **59**, 2260 (1937).

(29) In previous work in these laboratories it was found that trialkyl phosphites function as effective promoters in the addition of hydrogen sulfide to unsaturated compounds using ultraviolet light.

boiling. A few small pieces of Dry Ice were added to free any mercaptide, and the mixture was filtered. Distillation of the filtrate yielded 67.5 g. (50%) of 3-amino-1-propanethiol, b.p. 153°, which became an extremely hard crystalline mass upon cooling; recrystallization from toluene afforded an analytical sample, m.p. 109–110°. The higher boiling residue from the distillation, 37.5 g., was not investigated in this run, but contained by-product sulfide (see below).

In a run using a similar but larger capacity reactor and a charge consisting of 15 moles of allylamine hydrochloride, 30 moles of hydrogen sulfide, 1500 g. of isopropyl alcohol, and 50 ml. of trimethyl phosphite, the yield of 3-amino-1-propanethiol was 47%. From this run, bis(3-aminopropyl) sulfide, b.p. 149–150° at 22 mm., $n^{20}D$ 1.5162, was isolated as a colorless oil (18% yield). The infrared spectrum of the latter was superimposable upon that of authentic sulfide prepared from 3-chloropropylamine and sodium bisulfide.

Hydrolysis of Tetrahydro-1,3-thiazine-2-thione.—A solution of 52 g. (0.39 mole) of tetrahydro-1,3-thiazine-2-thione[30] in 300 ml. of concentrated hydrochloric acid was saturated with hydrogen chloride. The solution was heated in a glass-lined autoclave at 170–175° for 2 hr. under autogenous pressure (in excess of 600 p.s.i.g.). After cooling and venting the autoclave (the odor of hydrogen sulfide was strong), the clear yellow reaction solution was removed and evaporated on a rotary evaporator. Cooling the resulting viscous oil gave 50 g. of solid. This was recrystallized twice from isopropyl alcohol to give 3-amino-1-propanethiol hydrochloride, m.p. 78.5–80° (no m.p. depression when mixed with the other samples prepared in this work).

Reaction of Sodium Bisulfide with 3-Chloropropylamine.—A solution of 80 g. (2 moles) of sodium hydroxide in 400 ml. of methanol was saturated with hydrogen sulfide. Over a period of 30 min., this solution was treated, under nitrogen with stirring at 50–60°, with a solution of 130 g. (1 mole) of 3-chloropropylamine hydrochloride[31] in 130 ml. of methanol. After cooling, the mixture was diluted with 300 ml. of ether. The salts were filtered under nitrogen and washed with ether. The filtrate was distilled, giving 34 g. (46%) of 3-amino-1-propanethiol, b.p. 156°, m.p. 97–105°; hydrochloride (from isopropyl alcohol–ether mixture) m.p. 76–78° (no m.p. depression when mixed with the hydrochlorides obtained by the other methods in this report). The higher boiling distillation residue from two runs was combined and distilled to give bis(3-aminopropyl) sulfide, b.p. 146° at 14 mm., $n^{20}D$ 1.5120.

3-Benzylthiopropylamine.—A solution of 496 g. (4 moles) of benzyl mercaptan in 1200 ml. of methanol under nitrogen was treated with 352 g. (8.8 moles) of sodium hydroxide. The resulting mixture was stirred while 650 g. (4 moles) of 3-chloropropylamine hydrochloride,[31] assumed to be 80% pure, was added in small portions. The resulting solution, after being heated under reflux for 30 min. with stirring, was diluted with 2 l. of water. The mixture was extracted with 500 ml. of chloroform. The chloroform solution was distilled through a packed column, giving 609 g. (84%) of 3-benzylthiopropylamine, b.p. 112° at 0.4 mm., $n^{20}D$ 1.5668; reported[14] b.p. 97° at 0.1–0.07 mm., $n^{25}D$ 1.5645. A small sample of the free amine in chloroform was converted to the hydrochloride by introduction of anhydrous hydrogen chloride; recrystallized from benzene for analysis, m.p. 76–77°.

Anal. Calcd. for $C_{10}H_{16}NSCl$: C, 55.15; H, 7.4; N, 6.4; S, 14.7. Found: C, 55.0; H, 7.7; N, 6.5; S, 14.7.

3-Amino-1-propanethiol Hydrochloride. By Debenzylation of 3-Benzylthiopropylamine.—A solution of 410 g. (2.26 moles) of 3-benzylthiopropylamine in 3 l. of liquid ammonia was treated with stirring with 5–7 g. pieces of sodium until the blue color persisted for 50 min.; about 83 g. (3.6 g.-atoms) of sodium was required. Ammonium chloride (198 g., 3.7 moles) was added to the mixture, and the ammonia was evaporated on a steam bath while 1500 ml. of 1-propanol was added slowly. When the internal temperature reached about 25°, the mixture was placed under nitrogen for the remainder of the procedure. The mixture was heated to 80° and then cooled in an ice bath. Anhydrous hydrogen chloride was added until the vapors were acidic, and the mixture was again heated to 80°. After filtering the hot solution and washing the solid with 100 ml. of 1-propanol, the filtrate was evaporated on a rotary evaporator until an oil appeared. The mixture was cooled rapidly in an ice bath until crystals appeared. About 800 ml. of ether was added and the mixture was shaken vigorously until crystallization was complete. The product was filtered and washed with ether and pentane to give, after drying *in vacuo* at 35°, 265 g. (64%) of crude 3-amino-1-propanethiol hydrochloride, m.p. 73–76°. 1,2-Diphenylethane, m.p. 51–52°, was obtained upon concentration of the mother liquor.

For purification, the combined product from 4 runs (1035 g.) was dissolved under nitrogen in 1250 ml. of 1-butanol at 60°. The hot solution was filtered and cooled slowly to crystallize. The recrystallization was repeated from 1-butanol containing a little anhydrous hydrogen chloride. The product was filtered and washed twice with 200 ml. of 1:1 1-butanol–ether and then with ether alone to give pure 3-amino-1-propanethiol hydrochloride, m.p. 79.5–80.5°; reported[4] m.p. 69°. There was no depression of the m.p. when mixed with samples of the product prepared by the other methods described in this report, but the m.p. was depressed when mixed with 1-amino-2-propanethiol hydrochloride.

Anal. Calcd. for $C_3H_{10}ClNS$: C, 28.23; H, 7.9; N, 10.98; S, 25.1. Found: C, 28.4; H, 8.1; N, 10.95; S, 24.5.

Synthesis of Allylic Amines.—Yields and properties of the intermediates obtained in the acetylenic carbinol route[15] to allylic Amines are given in Table I. 1-Pentyne-3-ol was prepared by reaction of sodium acetylide with propionaldehyde; yield, 52%; b.p. 120–122°, 55° at 40 mm., $n^{20}D$ 1.4318; reported[21,22,32] b.p. 121–124°, 52.4–52.6° at 35 mm., $n^{25}D$ 1.4320, 1.4330. The other two acetylenic carbinols were otherwise available.[33] The aminoalkynes were selectively hydrogenated[34,35] to the allylic amines in pentane solutions with 50 p.s.i.g. hydrogen and using about 10% by weight of the Lindlar[16] catalyst (5% palladium on calcium carbonate). The physical properties of the amines and hydrochlorides are shown in Table I.

3-Amino-1-butene was prepared from 3-chloro-1-butene in an overall yield of about 40% by the method of Roberts and Mazur[36]; b.p. 61.5–62°, $n^{20}D$ 1.4130; reported[36,37] b.p. 62–64°, $n^{20}D$ 1.4150, $n^{25}D$ 1.4090, 1.4104. The free amine was converted to the hydrochloride, m.p. 126–127°.

Dimethylallylamine was prepared in 67% yield by adding dropwise 1070 g. (8.85 moles) of allyl bromide to a cold solution of 1500 ml. of anhydrous dimethylamine in 1500 ml. of *n*-heptane; b.p. 60–63°. The product was converted to the hydrochloride before use by dissolving the amine in concentrated hydrochloric acid and evaporating to dryness.

Synthesis of 3-Amino-1-alkanethiols.—The reactions of the allylic amine hydrochlorides with hydrogen sulfide were carried out in the ultraviolet light reactor previously described. The experimental conditions were essentially the same as those outlined for allylamine hydrochloride. The

(30) F. H. Hammer and R. J. Rathbone, *J. Chem. Soc.*, 243 (1943).

(31) Prepared in nearly quantitative yield by the action of thionyl chloride upon a heptane suspension of 3-aminopropanol hydrochloride; m.p. of product 144–146°.

(32) N. J. Leonard and J. A. Adamcik, *J. Am. Chem. Soc.*, **81**, 595 (1959).

(33) Samples of 1-hexyne-3-ol and 3-methyl-1-pentyne-3-ol were kindly supplied by Air Reduction Chemical Company.

(34) G. F. Hennion and R. S. Hanzel, *J. Am. Chem. Soc.*, **82**, 4908 (1960).

(35) G. F. Hennion, W. A. Schroeder, R. P. Lu, and W. B. Scanlon, *J. Org. Chem.*, **21**, 1142 (1956).

(36) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(37) D. Semenow, Ch.-H. Shih, and W. G. Young, *ibid.*, **80**, 5472 (1958).

thiolations were conducted in isopropyl alcohol as a solvent where solubility permitted. Otherwise (with aminopentene and -hexene) methanol was used. The yields and physical constants of the product aminothiols are listed in Table II. The hydrochlorides (Table III) were prepared by adding anhydrous hydrogen chloride to a pentane solution of the free base (except that isopropyl alcohol was used for 3-dimethylaminopropanethiol). In general, it was found best to carefully purify the free base prior to conversion to the hydrochloride.

Bis(3-dimethylaminopropyl) Disulfide.—A mixture of 274 g. (2 moles) of bis(3-chloropropyl) disulfide[38] and 750 ml. of anhydrous dimethylamine was heated in an autoclave over a 90-min. period to 120°, and then held at that temperature for another 30 min. After cooling, the product was removed and mixed with 500 ml. of water and 1 l. of ether. Sodium hydroxide (110 g., 2.75 moles) was added in small portions, with stirring, and the phases were separated. After washing with water, the ether solution was distilled to give 225 g. (77%) of bis(3-dimethylaminopropyl) disulfide, b.p. 105° at 0.35 mm., $n^{20}D$ 1.5023.

Anal. Calcd. for $C_{10}H_{24}N_2S_2$: C, 50.80; H, 10.23; N, 11.85; S, 27.12. Found: C, 50.85; H, 10.91; N, 12.1; S, 27.4.

A small sample was converted to the dihydrochloride, m.p. 212–213°[39] (from isopropyl alcohol) and in admixture with the disulfide prepared by the oxidation of 3-dimethylaminopropanethiol hydrochloride from the addition of hydrogen sulfide to dimethylallylamine.

***N*-(2-Cyclohexenyl)phthalimide.**—A mixture of 190 g. (1.63 moles) of 3-chlorocyclohexene[40] and 305 g. (1.65 moles) of potassium phthalimide in 600 ml. of dimethylformamide was stirred at 90° for 2 hr., then under reflux for another 2 hr. The hot mixture was poured onto 1 kg. of crushed ice. The solid was filtered and washed with 500 ml. of 1 *N* sodium hydroxide, 1 l. of water, 1 l. of 1 *N* hydrochloric acid, and again with 1 l. of water. The light-yellow powder was air-dried to give 327 g. (88%) of *N*-(2-cyclohexenyl)phthalimide m.p. 112–113°. Recrystallization from ethanol gave a product with m.p. 114–115°; reported[41,42] m.p. 114.5°.

3-Aminocyclohexene.—A mixture of 485 g. (2.13 moles) of the phthalimide, 135 g. (2.3 moles) of 85% hydrazine hydrate, and 750 ml. of ethanol was heated under reflux for 22 hr. The cooled mixture was stirred vigorously while 210 ml. of concentrated hydrochloric acid, 100 ml. of alcohol, and 200 ml. of hot water were added. After heating to about 60° the mixture was filtered and the solid cake was washed three times with hot water. The filtrate was concentrated under aspirator pressure to about 500 ml. and then refiltered. The clear filtrate was cooled in an ice bath and made basic by the addition of 80 g. of sodium hydroxide in 200 ml. of water. The resulting solution was extracted continuously with ether for several hours. After drying the ethereal solution over potassium hydroxide, the ether was distilled. Distillation of the residue through a 15-in. Vigreux column gave 153 g. (73%) of 3-aminocyclohexene, b.p. 138–139°, $n^{20}D$ 1.4845; reported[43] b.p. 139–140°, $n^{25}D$ 1.4816–1.4822. The amine was converted to the hydrochloride, m.p. 163–164° (from methanol–ether or chloroform–carbon tetrachloride mixtures).

Anal. Calcd. for $C_6H_{12}ClN$: C, 53.92; H, 9.05; N, 10.48. Found: C, 54.0; H, 9.4; N, 10.6.

***cis*- and *trans*-2-Aminocyclohexanethiol.**—A solution of 155 g. (1.16 moles) of the hydrochloride, 116 g. of methanol, 78 g. (2.3 moles) of hydrogen sulfide, and 4 ml. of trimethyl

TABLE III

HYDROCHLORIDES OF 3-AMINO-1-ALKANETHIOLS

$$\begin{matrix} & & NH_2\cdot HCl \\ & & | \\ R- & C & -CH_2CH_2SH \\ & | & \\ & R' & \end{matrix}$$

R	R′	M.p.	Recrystallization solvent	Formula	Carbon, % Calc.	Carbon, % Found	Hydrogen, % Calc.	Hydrogen, % Found	Nitrogen, % Calc.	Nitrogen, % Found	Sulfur, % Calc.	Sulfur, % Found	Chlorine, % Calc.	Chlorine, % Found
H	H	79.5–80.5	1-Butanol	$C_3H_{10}ClNS$	28.23	28.4	7.90	8.1	10.98	10.95	25.1	24.5		
CH_3	H	75.5–77	*n*-Pentane	$C_4H_{12}ClNS$	33.9	34.1	8.55	9.0	9.89	9.8	22.63	22.9	25.02	25.1
C_2H_5	H	164–165	2-Propanol	$C_5H_{14}ClNS$	38.57	38.8	9.06	9.2	9.00	9.0	20.59	20.45	22.78	23.4
C_3H_7	H	184–185	$CHCl_3$-ether	$C_6H_{16}ClNS$	42.46	42.74	9.50	9.76	8.25	8.2	18.89	18.78	20.84	21.1
C_3H_5	CH_3	272 (dec.)	Acetonitrile	$C_6H_{16}ClNS$	42.46	43.0	9.50	9.0	8.25	9.1	18.89	18.2		
H[a]	H	105–107	2-Propanol	$C_5H_{14}ClNS$	38.57	38.56	9.06	9.3			20.6	20.8		

[a] Dimethylaminopropanethiol hydrochloride.

(38) J. M. Stewart and C. H. Burnside, *ibid.*, **75**, 243 (1953).

(39) F. Yu. Rachinskii *et al.*, *Zh. Obshch. Khim.*, **28**, 2998 (1958); *Chem. Abstr.*, **53**, 9045 (1959), report m. p. 188°.

(40) C. A. Grob, H. Kny, and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

(41) A. Fono, *Chem. Ind.* (London), 414 (1958).

(42) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **23**, 325 (1958).

(43) L. Goodman, S. Winstein, and R. Boschan, *J. Am. Chem. Soc.*, **80**, 4312 (1958).

phosphite was irradiated for 2.5 hr. with a 450-watt mercury vapor lamp. The reaction mixture was vented into a 500 ml. three-necked flask. All subsequent operations were carried out under nitrogen. The reaction solution was treated with 50 g. (1.25 moles) of sodium hydroxide in 300 ml. of water. After stirring until solution of the salts was complete, 100 ml. of benzene was added. The benzene layer was separated and the aqueous layer was extracted twice more with a mixture of 50 ml. of benzene and 25 ml. of isopropyl alcohol. The extracts were combined and distilled through an 18-in. glass helice-packed column, keeping the pot temperature below 100°. The residue was then flashed through a Vigreux column under reduced pressure, keeping the pot temperature below 110°. Unchanged aminocyclohexene (30–40 g.) was collected and a white solid appeared in the column head. The column was washed down with hot benzene into the residual oil, and the resulting benzene solution was evaporated under aspirator pressure, keeping the temperature as cool as possible. The residue was sublimed and distilled through a short Vigreux column under high vacuum to a pot temperature of 170°, giving 49 g. of white solid. This was dissolved in 100 ml. of benzene. Cooling the solution gave fine white crystals of *cis*-2-aminocyclohexanethiol, m.p. 117–118°. This isomer was essentially insoluble in cold benzene, and sublimed rather than distilling, both characteristics distinguishing it from the *trans* isomer. Other runs gave crystals, m.p. 119–120° and 121–122°.

Anal. Calcd. for $C_6H_{13}NS$: S, 24.4. Found (by mercaptan titration): S, 25.2.

Introducing hydrogen chloride into a methanol solution of the free base gave the hydrochloride, m.p. 258–261° after recrystallization from methanol–ether; reported[18,19] m.p. 245–247°, 238–241°.

Anal. Calcd. for $C_6H_{14}ClNS$: C, 42.97; H, 8.41; Cl, 21.14; N, 8.35; S, 19.12. Found: C, 42.77; H, 8.44; Cl, 21.7; N, 8.35; S, 19.75.

Schotten-Baumann benzoylation of the free base gave a mixture of bis(*cis*-2-benzamidocyclohexyl) disulfide, m.p. 219–220° (from chloroform–methanol) and *cis*-2-benzamidocyclohexyl thiolbenzoate, m.p. 150.5–151.5° (from benzene); reported[19,20] m.p. 203–206° and 147–148°, respectively.

Anal. Calcd. for $C_{26}H_{32}N_2O_2S_2$ (disulfide): C, 66.63; H, 6.88; N, 5.98; S, 13.69. Found: C, 67.35, H, 7.25; N, 5.93; S, 13.6.

Anal. Calcd. for $C_{20}H_{21}NO_2S$ (*N*,*S*-dibenzoyl): C, 70.76; H, 6.24; N, 4.13; S, 9.45. Found: C, 71.04; H, 6.59; N, 4.2; S, 8.95.

After crystallization of the *cis*-aminothiol from the benzene solution above, the mother liquor was evaporated. The residue was distilled under reduced pressure to give *trans*-2-aminocyclohexanethiol, b.p. 129–131° at 60 mm. and 108–109° at 30 mm., solidifying to a white solid, m.p. 80°; reported[44,45] m.p. 79–80° and 79–81°. The free base was converted to the hydrochloride, m.p. 226–227° (from methanol); reported[18] m.p. 225°.

Anal. Calcd. for $C_6H_{14}ClNS$: C, 42.97; H, 8.41; Cl, 21.14; N, 8.35; S, 19.12. Found: C, 43.06; H, 8.56; Cl, 21.5; N, 8.54; S, 19.72.

Schotten-Baumann benzoylation of this isomer gave a mixture of *trans*-2-benzamidocyclohexyl thiolbenzoate, m.p. 153–155° (from methanol), and *trans*-2-benzamidocyclohexanethiol, m.p. 163–165° (from benzene); reported[18,20,44] m.p. 155–157° and 161–162°, respectively.

Addition of Hydrogen Sulfide to Crotylamine Hydrochloride.—A mixture of 96.3 g. (0.9 mole) of crotylamine hydrochloride,[36] 68 g. of hydrogen sulfide, 3 ml. of trimethyl phosphite, and 100 g. of methanol was irradiated under autogenous pressure with a 450-watt mercury vapor lamp for 150 min. The reaction mixture was treated as other allylic amines to give a total of 23 g. (24%) of 1-amino-2-butanethiol, b.p. 83–87° at 52 mm. A center cut was recrystallized once from a mixture of pentane and toluene, and then from ether at a low temperature to give the pure aminothiol, m.p. 65–66.5°. This material (9.4 g.) was dissolved in ether and converted to the hydrochloride by introduction of hydrogen chloride. The product, m.p. 139–146° (11 g.) was recrystallized twice from chloroform to give 6.3 g. of 1-amino-2-butanethiol hydrochloride, m.p. 154–157°.

Anal. Calcd. for $C_4H_{12}ClNS$: C, 33.90; H, 8.55; N, 9.89. Found: C, 34.1; H, 8.8; N, 10.55.

The NMR spectrum of the hydrochloride was determined with a Varian V-4300c, 60-Mc. high resolution spectrometer. The sample was examined as a solution in deuterium oxide with benzene as an external standard. The methyl group resonance occurred as a triplet, indicating an adjacent methylene group and confirming the structure $CH_3CH_2CH(SH)CH_2NH_3^+ Cl^-$. The alternate 3-mercapto structure would give only a doublet for the methyl resonance.

3-Mercaptopropylformamide.—A mixture of 163 g. (1.92 moles) of allylformamide,[46] 136 g. (4 moles) of hydrogen sulfide, and 6 ml. of trimethyl phosphite was irradiated for 2 hr. under autogenous pressure with a 450-watt mercury vapor lamp. The product, which was not too stable to heat, was purified by three distillations on a short-path column. The second distillation gave 75 g. (34%) of crude product, b.p. 120–134° at less than 3 mm. (with some decomposition). Redistillation gave 22.5 g. of a center cut of pure 3-mercaptopropylformamide,[5] b.p. 100–103° at 1 mm., $n^{20}D$ 1.5190.

Anal. Calcd. for C_6H_9NOS: C, 40.31; H, 7.61; N, 11.75; S, 26.90. Found: C, 40.48; H, 8.17; N, 11.54; S, 26.85.

Hydrolysis of a sample of the product by heating overnight with concentrated hydrochloric acid gave a nearly quantitative yield of 3-amino-1-propanethiol hydrochloride, as shown by mixed m.p. determination with authentic material.

***N*-3-Mercaptopropylsuccinimide.**—A mixture of 86 g. (0.62 mole) of *N*-allylsuccinimide,[47] 42 g. (1.2 moles) of hydrogen sulfide, and 3 ml. of trimethyl phosphite was irradiated for 1 hr. under autogenous pressure with a 100-watt mercury vapor lamp. Distillation of the product gave *N*-3-mercaptopropylsuccinimide, b.p. 137° at 0.35 mm., $n^{20}D$ 1.5330, in a 62% yield.

Anal. Calcd. for $C_7H_{11}NO_2S$: C, 48.53; H, 6.40; N, 8.09; S, 18.51. Found: C, 48.61; H, 6.45; N, 8.2; S, 18.1.

1-(2-Mercaptoethyl)-2-pyrrolidone.—A mixture of 180 g. (1.62 moles) of *N*-vinyl-2-pyrrolidone, 112 g. (3.3 moles) of hydrogen sulfide, and 5 ml. of trimethyl phosphite was irradiated under autogenous pressure with a 100-watt mercury vapor lamp for 90 min. Distillation of the product gave 1-(2-mercaptoethyl)-2-pyrrolidone, b.p. 99° at 0.3 mm., $n^{20}D$ 1.5278, in a 66% yield; reported[48] b.p. 118–119° at 2 mm., $n^{20}D$ 1.5300.

Anal. Calcd. for $C_6H_{11}NOS$: C, 49.62; H, 7.63; N, 9.65; S, 22.08. Found: C, 49.3; H, 7.8; N, 9.35; S, 21.6.

Further distillation of the residue gave 26% of bis[2(2-pyrrolidon-1-yl)ethyl] sulfide, b.p. 200–230° at 1 mm., m.p. 59–60° (from ethyl acetate).[49]

Anal. Calcd. for $C_{12}H_{20}N_2O_2S$: C, 56.25; H, 7.81; N, 10.93; S, 12.51. Found: C, 56.4; H, 7.8; N, 10.8; S, 12.13.

***N*-(2-Mercaptoethyl)caprolactam.**—A mixture of 210 g. (1.5 moles) of *N*-vinylcaprolactam, 154 g. (4.5 moles) of hydrogen sulfide, and 5 ml. of trimethyl phosphite was ir-

(44) T. Taguchi, M. Kojima, and T. Muro, *J. Am. Chem. Soc.*, **81**, 4322 (1959).

(45) F. Winternitz, M. Mousseron, and R. Dennilauler, *Bull. soc. chim. France*, 382 (1956).

(46) G. C. Clayton, *Ber.*, **28**, 1665 (1895).

(47) L. Szekeres, *Gazz. chim. ital.*, **79**, 56 (1949); *Chem. Abstr.*, **43**, 7921 (1949).

(48) M. F. Shostakovskii, E. S. Shapiro, and F. P. Sidel'kovskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 68 (1958); *Chem. Abstr.*, **52**, 9070 (1958); *Chem. Zentr.*, 1854 (1960).

radiated under autogenous pressure with a 100-watt mercury vapor lamp for 90 min. An initial distillation of the product under high vacuum was made on a short-path column, since there was a marked tendency for decomposition. Redistillation of this crude material through a 24-in. Vigreux column gave 74 g. (28%) of *N*-2-mercaptoethylcaprolactam, b.p. 128–129° at 0.7 mm., $n^{20}D$ 1.5315.[49]

Anal. Calcd. for $C_8H_{15}NOS$: C, 55.45; H, 8.73; N, 8.08; S, 18.51. Found: C, 55.7; H, 8.9; N, 7.9; S, 17.0.

(49) Shostakovskii *et al.* (ref. 48) have reported that the reaction of hydrogen sulfide with the appropriate *N*-vinyllactam in the presence of azobisisobutyronitrile gave bis[2-(2-pyrrolidon-1-yl) ethyl]sulfide (m.p. 101.5°), *N*-2-mercaptoethylcaprolactam (b.p. 113–114° at 2.5 mm., $n^{20}D$ 1.5254), and the sulfide of the latter (m.p. 83°).

Preparation of Sulfonic Acids from Unsaturated Compounds[1]

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Sulfonic acids have been prepared in good yield from a series of 1-olefins and also from oleic and 10-hendecenoic acids by free radical addition of thiolacetic acid to form thiolacetates, followed by hydrogen peroxide–acetic acid oxidation. This reaction sequence permits the preparation of isomer-free terminal sulfonic acids from 1-olefins. A method of purifying 1-olefins by a partial, selective epoxidation procedure has also been described. It has been shown for the first time that methyl esters are obtained in high yield by reaction of sulfonic acids with diazomethane. Reaction paths for the oxidation of thiolacetates to sulfonic acids are discussed.

Sulfonic acids are a well known class of compounds whose preparation and properties have been thoroughly studied.[3,4] Surprisingly, there is no general synthesis of sulfonic acids that does not involve isolation of a salt (Pb^{+2}, Ba^{+2}, Ca^{+2}), followed by a precipitation of the cation with a suitable anion (SO_4^{-2}, Cl^-) or by ion exchange.

As an adjunct to other work in our laboratory, isomer-free terminal sulfonic acids were prepared from 1-olefins by a new preparative route. This procedure involved the free-radical addition of thiolacetic acid to the desired 1-olefin to give a terminal thiolacetate,[5] followed by oxidation with hydrogen peroxide (92–93%) and acetic acid directly to the terminal alkanesulfonic acid in high overall yield, as illustrated:

$$\mathrm{R{-}CH{=}CH_2} \xrightarrow[2.\ H_2O_2\text{-}CH_3CO_2H]{1.\ CH_3COSH} \mathrm{R{-}CH_2CH_2SO_3H}$$

[R = Straight-chain and branched-chain alkyl and $HO_2C{-}(CH_2)_8{-}$]

The reaction sequence was also applied to several nonterminal unsaturated compounds, such as cyclopentene, cyclohexene, and methyl oleate with equally good results, but in the last case a mixture of isomeric sulfonic acids is obtained because the unsaturated compound is not symmetric.

Experimental

Purification of 1-Olefins.—Advantage was taken of the much faster rate of epoxidation of an internal double bond compared with that of a terminal double bond to perform a selective, partial epoxidation.

Commercial peracetic acid (30% in acetic acid) was added dropwise in a 1:1 mole ratio to a commercial sample of terminal olefin which contained some nonterminal olefin. The stirred reaction mixture was maintained at 25–30° for 2.5 to 6 hr., depending upon the olefin and amount of nonterminal isomer. Good temperature control was important to moderate the exothermic reaction of the peracetic acid with the olefin and the subsequent neutralization of the reaction mixture with base.

Water (1–2 l.) was added to the reaction flask to halt the reaction, and cold base (6 *N* NaOH) was then added dropwise to the reaction mixture over a period of 0.5 to 0.75 hr. until it was weakly basic, the temperature being kept between 20 to 25° throughout. As neutrality was approached, foaming occurred which was broken by agitation. (Care must be taken to avoid too rapid addition of base which sends the temperature out of control and causes unreacted peracetic acid to react vigorously with 1-olefin.)

The organic layer was separated with no attempt to break any emulsion present, and it was washed with saturated salt solution until neutral. Excess base was then neutralized to decrease foaming that occurs during subsequent steam distillation, and the mixture was then added to water (2–3 l.) and steam distilled until either the water being co-distilled with the olefin brought the latter over yellow or the organic phase stopped codistilling (as was the case with the short-chain olefins). The steam distillation separated the unoxidized 1-olefin from emulsion and from most of the products of epoxidation (epoxide, glycol, hydroxyacetate, and polymer). The organic layer in the steam distillate was separated and dried successively with sodium sulfate and calcium sulfate. The olefin was then analyzed for oxirane content (hydrobromic acid–acetic acid).[6] In most cases, after epoxidation, washing and steam distillation, the olefin contained less than 2% epoxide. This amount of epoxide was removed by fractional distillation of the 1-olefin. A visual inspection of the pot residue after fractional distillation of the olefins always revealed a white gelatinous material which is believed to be polymer formed from the epoxide. Oxirane analyses of the fractionally distilled olefins showed them to be oxirane-free.

(1) Paper VI in the series "Organic Sulfur Derivatives." Paper V is *J. Org. Chem.*, **23**, 1525 (1958).

(2) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(3) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, 1944, p. 94 *et. seq.*

(4) M. Quaedvlieg, "Methoden der Organischen Chemie," Vol. IX, 4th Ed., G. Thieme Verlag, Stuttgart, 1955, pp. 347–405.

(5) See N. H. Koenig and D. Swern, *J. Am. Chem. Soc.*, **79**, 362, 4235 (1957), for leading references to earlier literature.

(6) A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).