which was treated with 2.0 g of sodium borohydride in 25 ml of 3 *M* sodium hydroxide. Mercury metal was observed after the reduction. The suspension was then saturated with sodium chloride and the product was extracted with 100 ml of ether. The ethereal extract was dried ($MgSO_4$) and the solvent was removed by distillation through a Vigreux column. The mixture contained 2-cyclohexen-1-ol (13%), 3-cyclohexen-1-ol (13%), and a fraction which is believed to be *cis*- and *trans*-2-cyclohexene-1,4-diols (74%).

About 1 g of the reaction mixture was treated with acetic anhydride in pyridine. The resulting acetate mixture was shown to be 2-cyclohexen-1-yl acetate (13%), 3-cyclohexen-1-yl acetate (13%), and a diacetate fraction (74%). The infrared spectrum of the diacetate indicated unsaturation, and its nmr had absorptions at τ 4.25 (d, 2 olefinic hydrogen), 5.0 (m, 2, tertiary hydrogen), 8.03 (m, 6 acetoxymethyl hydrogen), and 8.3 (m, 4 H).

About 0.5 g of the above mixture was hydrogenated in acetic acid under atmospheric pressure using platinum oxide as a catalyst. The mixture contained cyclohexyl acetate (26%) and diacetates. Comparison of the infrared spectrum and nmr spectrum of the diacetate with those of authentic samples of *cis*- and *trans*-1,4-cyclohexanediol diacetates indicated that the diacetate was a mixture of the latter two compounds, perhaps with a different isomeric ratio.

Oxymercuration–Demercuration of 1,4-Cyclohexadiene.—1,4-Cyclohexadiene (2 g, 0.025 mol) was treated with mercuric acetate (8 g, 0.025 mol) in 15 ml of water and 25 ml of THF. The reaction color changed from yellow to clear in 50 sec. The product was isolated as described for oxymercuration–demercuration of 1,3-cyclohexadiene and was shown to be 3-cyclohexen-1-ol (67%) and unidentified diol (33%). The mixture was converted into the corresponding acetates by treatment with acetic anhydride in pyridine.

Registry No.—1, 1700-10-3; 2, 20642-83-5; 11, 111-78-4; 12, 4277-34-3; 14, 1073-07-0; 5,6-epoxycyclooctene, 637-90-1; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1.

The Base-Catalyzed Reaction of Hydrogen Sulfide with α-Chloromethyl Acrylate and α-Chloroacrylonitrile

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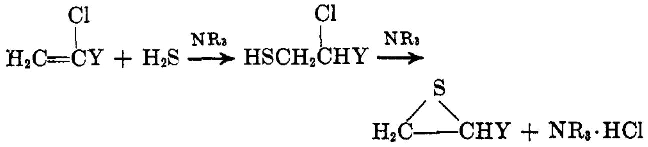
Received November 8, 1968

The amine-catalyzed reaction of hydrogen sulfide with α-chloromethyl acrylate produced β-mercaptomethyl propionate, di(β-carbomethoxyethyl) disulfide, di(β-carbomethoxyethyl) trisulfide, trimethylamine hydrochloride, and sulfur. Analogous products were obtained from α-chloroacrylonitrile. These unexpected products are explained by thiirane intermediates which spontaneously expel sulfur.

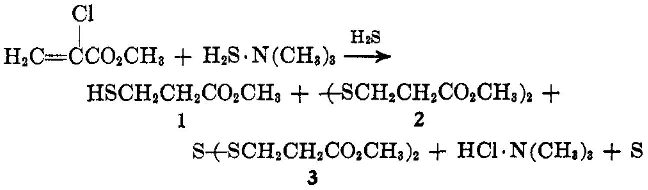
Base-catalyzed Michael addition of hydrogen sulfide to α-chloroacrylates, followed by the well-established internal displacement of the chloride,[1] was considered to be a convenient one-step synthetic route to apparently unknown thiiranes.[2]



$Y = CO_2R, CN$

The occurrence of unexpected products and their mode of formation is the topic of the present paper.

α-Chloromethyl Acrylate.—Reaction of equimolar amounts of α-chloromethyl acrylate and trimethylamine–hydrogen sulfide complex dissolved in an excess of liquid hydrogen sulfide at − 78° resulted in five identified products.



$$H_2C{=}\overset{Cl}{C}CO_2CH_3 + H_2S\cdot N(CH_3)_3 \xrightarrow{H_2S} \underset{1}{HSCH_2CH_2CO_2CH_3} + \underset{2}{(SCH_2CH_2CO_2CH_3)_2} + \underset{3}{S(SCH_2CH_2CO_2CH_3)_2} + HCl\cdot N(CH_3)_3 + S$$

The solid products, trimethylamine hydrochloride and sulfur, were isolated in 91 and 22% yield, respectively. These yields are based on molar equivalents of amine or α-chloromethyl acrylate used in the reaction.

Glpc analysis of the liquid product showed three major components, β-mercaptomethyl propionate, 1 (15%), di(β-carbomethoxyethyl) disulfide, 2 (61%), and di(β-carbomethoxyethyl) trisulfide, 3 (19%). In addition, several minor unidentified impurities (5%) were present. A mixture of disulfide 2 and trisulfide 3 was obtained on removal of the volatile impurities and the mercaptan 1 at high vacuum and elevated temperature. Attempts to separate 2 from 3 by fractional distillation failed, owing to substantial sulfur extrusion which converted trisulfide 3 into disulfide 2. A similar situation was experienced with independently synthesized 3. It was also observed that invariably 10–20% disulfide 2 was formed upon glpc analysis of 3. This finding made it necessary to deduce a 7:3 ratio as a more realistic product ratio for compounds 2 and 3 from elemental analysis data and molecular weight determination of the mixture. The presence of minor amounts of polysulfides containing more than three sulfurs, however, cannot be excluded in view of the observed disproportionation of trisulfide 3 during glpc analysis.

The structure elucidation of products 1, 2, and 3 is based on comparison of spectral data and glpc retention times with those of independently synthesized compounds (Scheme I). Amine-catalyzed addition of H_2S to methyl acrylate afforded the β-mercaptomethyl propionate, 1, which was oxidized with dimethyl sulfoxide to the corresponding disulfide 2. Chlorination of this disulfide with sulfuryl chloride resulted in the β-carbomethoxyethanesulfenyl chloride, 4. The compound's nmr spectrum is consistent with its structure; however, positive identification of this thermally labile sulfenyl chloride was achieved through its stable ethylene adduct 5. Reaction of sulfenyl chloride 4 with

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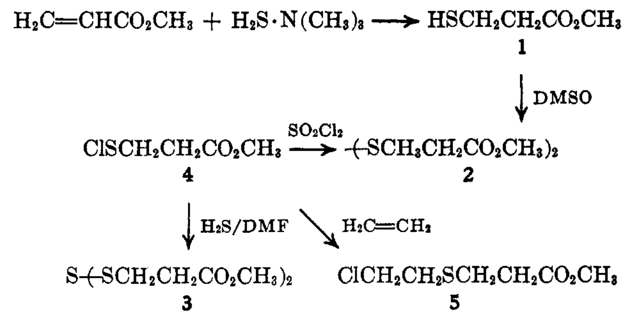
[1] W. Coltof, U. S. Patent 2,183,860 (1939); British Patent 508,932 (1939); Dutch Patent 47,835 (1940).

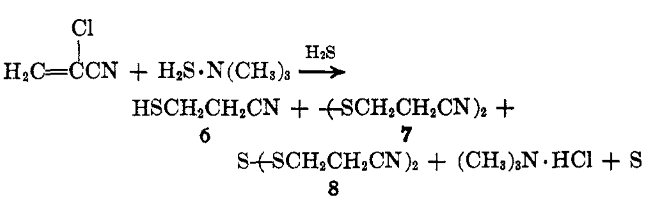
[2] M. Sanders, *Chem. Rev.*, **66**, 297 (1966).

Scheme I



hydrogen sulfide in the presence of dimethylformamide as acid acceptor finally led to the trisulfide **3**.

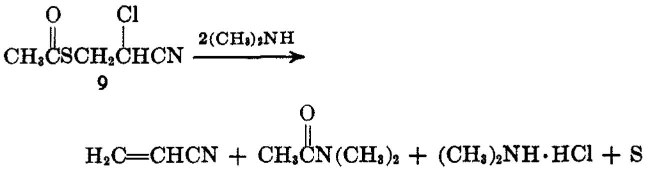
α-Chloroacrylonitrile.—When α-chloroacrylonitrile was allowed to react with an equimolar amount of trimethylamine in excess liquid hydrogen sulfide, products similar to those observed from α-chloromethylacrylate were obtained.



$$\mathrm{H_2C{=}\overset{Cl}{\overset{|}{C}}CN + H_2S\cdot N(CH_3)_3 \xrightarrow{H_2S} \underset{6}{HSCH_2CH_2CN} + \underset{7}{(SCH_2CH_2CN)_2} + \underset{8}{S(SCH_2CH_2CN)_2} + (CH_3)_3N\cdot HCl + S}$$

The solid products, trimethylamine hydrochloride and sulfur, amounted to 91 and 50% yield if based on the molar equivalents of α-chloroacrylonitrile and trimethylamine used in the reaction. Glpc and nmr analysis of the crude, liquid product indicated *ca.* 65% β-mercaptopropionitrile, **6**, accompanied by some higher boiling products. Fractional distillation afforded pure **6** in 46% yield. In analogy to the results from α-chloromethyl acrylate, disulfide **7** and trisulfide **8** are most likely the predominant constituents of the higher-boiling product mixture. The nmr spectrum of the mixture and the relative glpc retention times of its components are consistent with this assumption. However, as with α-chloromethyl acrylate, the concomitant formation of small amounts of higher polysulfides cannot be excluded.

α-Chloro-β-Acetylthiopropionitrile.—The above-described complications experienced during the attempted synthesis of thiiranes from α-chloromethylacrylate or α-chloroacrylonitrile, and the possible unique role of the hydrogen sulfide–amine system, led to an investigation of the aminolysis of α-chloro-β-acetylthiopropionitrile, **9**. Pyridine-catalyzed addition of thiolacetic acid to α-chloroacrylonitrile provided compound **9**. Its reaction with 2 equiv of dimethylamine at −30° resulted in the products shown below.

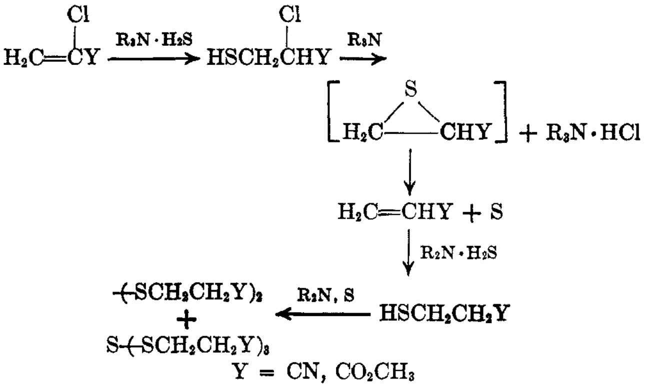


$$\mathrm{\underset{9}{CH_3\overset{O}{\overset{\|}{C}}SCH_2\overset{Cl}{\overset{|}{C}}HCN} \xrightarrow{2(CH_3)_2NH} H_2C{=}CHCN + CH_3\overset{O}{\overset{\|}{C}}N(CH_3)_2 + (CH_3)_2NH\cdot HCl + S}$$

Acrylonitrile and dimethylacetamide were isolated in 70 and 75% yield, respectively. The solid products, dimethylamine hydrochloride and sulfur, amounted to 89% yield each. No cyanoethylenethiirane was found, although some effort was made to detect it as a transient product by nmr analysis of the reaction mixture at temperatures below 0°.

All of the unexpected products obtained during this work are best explained by the intermediacy of the desired thiiranes. Spontaneous expulsion of sulfur from these thiiranes then prompts the formation of methyl acrylate or acrylonitrile, which in turn are transformed under the prevailing reaction conditions into the corresponding thiol, disulfide, and trisulfide (Scheme II).

Scheme II



The possibility of sulfur expulsion in its atomic form has been considered. However, attempts to trap it as episulfide by having an olefin present during the reaction failed.

Facile loss of sulfur by some electronegatively substituted thiiranes with the formation of olefins has been previously reported.[3-6] Examples which show some resemblance to our cases are a tetrasubstituted thiirane bearing two geminal cyano groups[5] and a trisubstituted thiirane with an ethyl carboxylate group.[6] The unusual structural complexity of these thiiranes, however, did not allow an *a priori* assessment of the influence of cyano or carboxylate substituents on their stability. This is particularly true, since in at least one instance a stable thiirane with a carboxylate substituent is known.[2]

The formation of disulfide 2, trisulfide **3**, and possibly small amounts of higher polysulfides from methyl acrylate is a consequence of base-catalyzed addition of hydrogen sulfide to form mercaptan **1** and subsequent oxidation of equimolar amounts of either methyl acrylate or β-mercaptomethyl propionate and sulfur in liquid hydrogen sulfide–trimethylamine. In both cases, product distributions of **1**, **2**, and **3** were found to be identical with that obtained from β-chloromethyl acrylate. Base-catalyzed oxidation of mercaptans by sulfur to polysulfides is well established[7,8] and has been recently investigated in detail.[9]

Experimental Section

Materials.—The α-chloroacrylonitrile from Columbia Organic Chemicals Company and α-chloromethyl acrylate and methyl acrylate from Borden Chemical Company were purified by fractional distillation prior to their use. All other reagents were used in the highest purity grade commercially available.

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[3] D. S. Tarbell and D. P. Harnisch, *Chem. Rev.*, **49**, 21 (1951).

[4] W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, **30**, 1378 (1965).

[5] W. J. Middleton, *ibid.*, **31**, 3731 (1966).

[6] A. Schönberg and E. Frese, *Chem. Ber.*, **96**, 2420 (1963).

[7] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, p 387.

[8] W. A. Pryor, "Mechanism of Sulfur Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 9.

[9] B. D. Vineyard, *J. Org. Chem.*, **32**, 3833 (1967).

Methods of Analysis.—Nmr spectra were recorded on a Varian Model A-60 resonance spectrometer using tetramethylsilane as an internal standard.

Gas–liquid partition chromatography was done on an Aerograph 1520 programmed temperature gas chromatograph with a 5 ft × 0.125 in. o.d. column. The packing consisted of 3% Dowfax 9N40 (an ethylene oxide–*p*-nonylphenol polyether of a 40:1 molar ratio) on 60–80 mesh Gas Chrom W. Operating conditions were as follows: detector, 270°; injector, 190°; flow rate, 50 ml/min.; column heating rate, 4°/min.; starting temperature, 50°; final temperature, 200°.

Reaction of Hydrogen Sulfide with α-Chloromethyl Acrylate in the Presence of Trimethylamine.—Trimethylamine (12 g, 0.204 mol) in 68 g (2 mol) of hydrogen sulfide were condensed at −78° into a heavy-wall Pyrex tube equipped with a Teflon valve. The tube was sealed and allowed to warm to ambient temperature, which caused the solid amine–hydrogen sulfide complex to dissolve in the excess hydrogen sulfide. After cooling this solution again to −78°, the α-chloromethyl acrylate (24.1 g, 0.2 mol) was slowly added. Mixing of the contents was accomplished by inverting the tube several times. The sealed tube was subsequently allowed to stand at ambient temperature for 30 min. The unreacted gases were then slowly released and the semisolid residue was suspended in ether. Filtration afforded 19 g of solid. Treatment of this solid with water followed by filtration yielded 1.4 g of elemental sulfur. Removal of the water from the filtrate resulted in 17.4 g (0.182 mol) of trimethylamine hydrochloride, mp 269–274° dec.

The ether-soluble portion of the products, a pale yellow oil (18.6 g), showed the following product distribution on glpc analysis: 15% β-mercaptomethyl propionate (7), 61% di(β-carbomethoxyethyl)disulfide (2), and 19% di(β-carbomethoxyethyl)trisulfide (3). A 5% total of several minor impurities remained unidentified. Product identification is based on comparison of glc retention times with authentic samples. Heating of this product to 100° (0.1 mm) for 1 hr removed essentially all of the β-mercaptomethyl propionate and the impurities; glpc analysis now indicated products 2 and 3 in a 4:1 ratio. Elemental analysis data, however, are more consistent with a 7:3 ratio. This is explained by the apparent sulfur extrusion, *i.e.*, formation of 2, observed during glpc analysis of independently synthesized **3**.

Anal. Calcd for a mixture of 70% $C_8H_{14}O_4S_2$ and 30% $C_8H_{14}O_4S_3$: C, 39.48; H, 5.71; S, 29.51; mol wt, 248. Found: C, 39.61; H, 5.82; S, 29.74; mol wt, 255.

Di(β-carbomethoxyethyl) Disulfide (2).—Hydrogen sulfide (102 g, 3 mol) and trimethylamine (10 g, 0.17 mol) were condensed into a Pyrex tube and mixed as described above. Methyl acrylate (43 g, 0.5 mol) was then slowly added at −78°. After completion of the addition, the contents of the sealed tube were allowed to gradually reach room temperature. The excess hydrogen sulfide and the trimethylamine were then slowly released. Fractional distillation of the residual product afforded 49.55 g (82% yield) of β-mercaptomethyl propionate (1), bp 73° (24 mm).

A solution of 24 g (0.2 mol) of 1 in *ca.* 20 ml of dimethyl sulfoxide (DMSO) was heated for 10 hr at 100°. The excess DMSO was then extracted with water. Distillation of the dried ($MgSO_4$) residue afforded 18.8 g (80% yield) of di(β-carbomethoxyethyl) disulfide (2): bp 118–120° (10^{-4} mm); nmr ($CDCl_3$) δ 2.55–31 (m, 4, $SCH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}$) and 3.69 (s, 3, OCH_3).

Anal. Calcd for $C_8H_{14}O_4S_2$: C, 40.32; H, 5.92; S, 26.91. Found: C, 40.16; H, 5.82; S, 26.68.

β-Carbomethoxyethanesulfenyl Chloride (4).—To a solution of 11.9 g (0.05 mol) of disulfide 2 in 50 ml of methylene chloride, 6.75 g (0.05 mol) of sulfuryl chloride was slowly added at −50°. Removal of the solvent and SO_2 at 0° (10 mm) afforded 15.2 g (98% yield) of a tan oil whose nmr spectrum is consistent with that of **4**: nmr ($CDCl_3$) δ 2.65–3.00 (m, 2, $CH_2C{=}O$), 3.27–3.55 (m, 2, SCH_2), and 3.70 (s, 3, OCH_3).

The sulfenyl chloride decomposed on attempted distillation, and was, therefore, further identified through its stable ethylene adduct **5**. Ethylene was blown through a solution of **4** in methylene chloride at −30°. Removal of the solvent and distillation resulted in adduct **5**: bp 76–78° (0.1 mm); nmr ($CDCl_3$) δ 2.42–3.03 (m, 6, $CH_2SCH_2CH_2C{=}O$), 3.50–3.82 (m, 2, CH_2Cl), and 3.68 (s, 3, OCH_3).

Anal. Calcd for $C_6H_{11}O_2SCl$: C, 39.45; H, 6.07; S, 17.55. Found: C, 39.75; H, 6.04; S, 17.19.

Di(β-carbomethoxyethyl) Trisulfide (3).—Hydrogen sulfide was slowly introduced into a solution of 6.18 g (0.04 mol) of sulfenyl chloride **4** and 8 g of dimethylformamide in 50 ml of methylacetate at −20°. The completion of the reaction was indicated by the disappearance of the typical orange color of sulfenyl chloride **4**. The solvent was then removed, ether was added, and the ethereal solution was washed with 5% aqueous sodium bicarbonate followed by water. Drying over magnesium sulfate and removal of the ether afforded 9.4 g (87% yield) of essentially pure trisulfide **3**: nmr ($CDCl_3$) δ 2.60–3.30 (m, 4, $SCH_2CH_2C{=}O$) and 3.69 (s, 3, OCH_3).

Anal. Calcd for $C_8H_{14}O_4S_3$: C, 35.54; H, 5.22; S, 35.58. Found: C, 35.29; H, 5.12; S, 35.87.

During an attempt to distil trisulfide **3** at 114–134° (10^{-4} mm), sulfur extrusion was observed which resulted in a distillate containing *ca.* 40% of disulfide **2**. A similar, although less extensive, degradation of **3** apparently occurs during glpc analysis. Undistilled trisulfide **3**, whose elemental analysis is in good agreement with its structure, showed invariably 10–20% of disulfide **2** with our glc conditions.

Reaction of Hydrogen Sulfide with α-Chloroacrylonitrile in the Presence of Trimethylamine.—The α-chloroacrylonitrile (17.5 g, 0.2 mol) was allowed to react with 60 g (1.76 mol) of hydrogen sulfide and 11.8 g (0.2 mol) of trimethylamine. Reaction conditions and work-up were identical with those described above for the analogous reaction with α-chloromethyl acrylate. Trimethylamine hydrochloride (17.4 g, 1.82 mol), 3.2 g of sulfur, and 15.8 g of a yellow oil were isolated. Glpc and nmr analysis of this crude product indicated *ca.* 65% β-mercaptopropionitrile, **6**, accompanied by some higher boiling products, most likely the corresponding di- and trisulfides **7** and **8**.

Distillation afforded 8 g (46% yield) of pure β-mercaptopropionitrile, bp 55–56° (6 mm), which was identified by comparison of glpc retention time and spectral data with those of an authentic sample.

α-Chloro-β-acetylthiopropionitrile (9).—The α-chloroacrylonitrile (35.00 g, 0.4 mol) was slowly added to 33.44 g (0.44 mol) of thiolacetic acid containing 3.16 g (0.04 mol) of pyridine. The reaction temperature was kept between −5 and 0° during the addition. The reaction mixture was then allowed to warm to ambient temperature. After 30 min at ambient temperature, 500 ml of ether was added and the ethereal solution was washed with 5% aqueous sodium bicarbonate solution followed by water. Drying and removal of the ether afforded 59.2 g (91% yield) of α-chloro-β-acetylthiopropionitrile (9): nmr ($CDCl_3$) δ 2.41 (s, 3, CH_3O), 3.53 (ABX spin system, pair of overlapping quartets, 2, CH_2S), 4.80 (dd, 1 CH(Cl)CN).

Anal. Calcd for C_5H_6ClNOS: C, 36.70; H, 3.70; S, 19.60. Found: C, 36.91; H, 3.57; S, 20.21.

Reaction of Dimethylamine with α-Chloro-β-acetylthiopropionitrile (9).—Dimethylamine (4.5 g, 0.1 mol) was slowly introduced into a solution of 8.2 g (0.05 mol) of α-chloro-β-acetylthiopropionitrile in 10 ml of methylene chloride at −30°. After completion of the addition, the reaction mixture was allowed to warm to 0°. The solvent and volatile products were then condensed *in vacuo* into a Dry Ice cooled trap. Nmr analysis of this condensate showed acrylonitrile and very small amounts of dimethylamine and dimethylacetamide to be present in the solvent. Fractional distillation yielded 1.86 g (70% yield) of pure acrylonitrile.

The residue from the initial low-temperature transfer was taken up in ether and the insoluble material was filtered off. Removal of the ether from the filtrate afforded 3.26 g (75% of dimethylacetamide. Treatment of the ether-insoluble material with water and subsequent filtration yielded 1.43 g (89%) of elemental sulfur. Removal of the water from the filtrate and recrystallization of the solid residue from methanol resulted in 3.6 g (89%) of dimethylamine hydrochloride, mp 168–170°.

Registry No.—Hydrogen sulfide, 7783-06-4; α-chloromethyl acrylate, 80-63-7; α-chloroacrylonitrile, 920-37-6; **2**, 15441-06-2; **3**, 20707-94-2; **5**, 20707-95-3; **9**, 20707-96-4.

Acknowledgment.—The author gratefully acknowledges Mr. W. C. Whitlock for his excellent technical assistance.