[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Cyclic and Polymeric Compounds from the Reactions of Ethylene Mercaptan with Polymethylene Halides

BY N. BEVERLEY TUCKER AND E. EMMET REID

Recently there has been much interest in the formation of cyclic and "string" molecules by the interaction of bifunctional compounds. Staudinger and his co-workers[1] have considered such reactions in relation to high polymers while Carothers[2] has elaborated the theory for the reactions of bifunctional compounds in general and with the aid of several co-workers[3] has verified his conclusions by studies of the esters of various α,ω-glycols with α,ω-dibasic acids. The data so obtained are important for an understanding of the formation of rings and for the theories of strainless rings as well as for an understanding of high polymers.

The reactions of dimercaptans with dihalides offer the same possibilities as those of other bifunctional molecules and may be expected to show, in addition, some of the peculiarities of sulfur compounds. The possible reactions can be illustrated with sodium ethylene mercaptide (I) and ethylene bromide (II). Since it is highly improbable that both of the reactive groups of the one molecule will come into contact with both of those of the other molecule simultaneously, it is sufficient to consider only the reactions in which one group of each takes part.

$$NaSCH_2CH_2SNa(I) + BrCH_2CH_2Br(II) \longrightarrow NaSCH_2CH_2SCH_2CH_2Br(III) \quad (1)$$

$$I + III \longrightarrow NaSCH_2CH_2SCH_2CH_2SCH_2CH_2SNa\ (IV) \quad (2)$$

$$II + III \longrightarrow BrCH_2CH_2SCH_2CH_2SCH_2CH_2Br(V) \quad (3)$$

$$IV + II \longrightarrow NaSCH_2CH_2SCH_2CH_2SCH_2CH_2SCH_2CH_2Br(VI) \quad (4)$$

The reaction of I with V also gives VI. In the preparation of ethylene mercaptan both Meyer[4] and Râу[5] have found high boiling liquids, one of which Râу identified as $HSCH_2CH_2SCH_2CH_2SCH_2CH_2SH$(IVa), which corresponds to IV above. The presence of other members of this series has been suggested by V. Meyer.

There is no obvious reason why these processes should not continue indefinitely, since VI may react with I or with II and every product that is formed has reactive groups at both ends. Whether bromine atoms, as in V, or —SNa groups, as in IV, predominate will depend on the relative proportions of the original reactants. It is to be noted that the products are of two kinds, those such as IV and V which have the same kind of groups at both ends and those like III and VI which have different groups

---

(1) Staudinger, *Ber.*, **59**, 3019 (1926); and other articles too numerous to list.

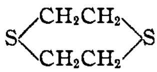
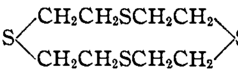
(2) Carothers, THIS JOURNAL, **51**, 2548 (1929); *Chem. Rev.*, **8**, 353 (1931).

(3) THIS JOURNAL, **51**, 2560 (1929); **52**, 314, 711, 3292 (1930); **54**, 1559, 1566, 1569 and 1579 (1932).

(4) Meyer, *Ber.*, **19**, 3259 (1886).

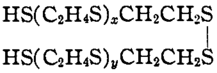
(5) Râу, *J. Ind. Chem. Soc.*, **6**, 865 (1929).

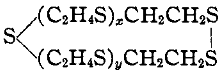
at the two ends and are thus capable of reacting intramolecularly to form ring compounds such as


(VII) and

(VIII)

It is evident that reactions such as these may go on in the preparation of all the polymethylene mercaptans by the usual reactions of the polymethylene bromides on sodium hydrosulfide, since the dimercaptans are present with the dibromides during the course of the reaction. There is here the additional possibility that compounds III, V and VI may react with sodium hydrosulfide which is present in abundance to give a complete series of sulfide–dimercaptans like IV. It is well known that the yields of the polymethylene mercaptans are usually not large and that considerable amounts of amorphous polymeric materials are obtained as by-products.

It has been observed that the high boiling liquids mentioned above are readily oxidized by air to form high molecular weight products. Little is known of these and it may be assumed that some are linear and some cyclic.


$$\begin{array}{l} HS(C_2H_4S)_xCH_2CH_2S \\ \qquad\qquad\qquad\qquad\quad | \\ HS(C_2H_4S)_yCH_2CH_2S \end{array} \quad (IX)$$


(X)

A relatively high proportion of disulfide linkages in the molecule will be evidenced by a high sulfur content.

While rings of any size are possible, from what we know of the arrangement of molecules in space it appears to be very unlikely that the terminal groups will be near enough together for ring closure except when the chains are of certain lengths. It is well known that the reaction of ethylene bromide and sodium sulfide gives 1,4-dithiane along with polymers. Dithiane and polymers are also obtained as by-products in the preparation of ethylene mercaptan. Thus ring closure takes place readily at the stage III to form a six-membered ring. Râу[5,6] has reported a trimeric ring of ethylene sulfide but Bennett and Berry[7] could not get this. Dithiane is the only ring compound that we have isolated from the above reactants. It is quite possible that larger rings of various sizes are mixed with the string molecules in the high molecular weight, insoluble materials that are obtained from such reactions. Mansfeld[8] obtained 1,3,5-trithiane, which is also a six-membered ring, from methylene iodide and sodium sulfide.

From the time of Crafts[9] in 1862 reactions of this type have been studied and many facts have been accumulated but there are many gaps and some discrepancies in the recorded information. The purpose of the present study was to coördinate and extend the earlier observations. It consists of

---

(6) Râу, *J. Chem. Soc.*, **117**, 1090 (1920); **121**, 1279 (1922); **123**, 2174 (1923).

(7) Bennett and Berry, *ibid.*, **127**, 910 (1925).

(8) Mansfeld, *Ber.*, **19**, 697 (1886).

(9) Crafts, *Ann.*, **124**, 112 (1862).

three parts: (1) the isolation of cyclic molecules from reactions between sodium ethylene dimercaptide and the methylene and polymethylene halides up to the hexa-, (2) study of the polymers, particularly those formed in the preparation of ethylene mercaptan, (3) depolymerization or decomposition of some of the more complex compounds.

Ring Formation

The results of our work are given in Table I. In all cases ethylene mercaptan reacted with the dihalide in the presence of alkali. In some cases both the monomeric and the dimeric rings have been obtained while in others only the one or the other. It will be noted that those containing 5, 6 and 7 members are obtained in considerable yields while the monomeric 8 and 9 rings could not be isolated and the 10 was found in only small amount. All of the preparations were made under the conditions found best for 1,4-dithiane. Small yields of dimeric rings of 10, 14, 16 and 18 members were obtained.

The ring No. 1, 1,3-dithiolane was made by Gibson[10] and previously by Baumann and Walter.[11] Gibson gives the sulfone as melting at 224°, which he says checks with the results of previous workers who gave 204–205°. The sulfone from our product melted at 204.5–205°.

TABLE I

RINGS FORMED FROM ETHYLENE MERCAPTAN AND POLYMETHYLENE DIHALIDES

No.	Dihalide	Ring formed	Atoms	Yield, %	M. p., °C.	Molecular wt. Calcd.	Molecular wt. Found
1	CH_2Cl_2	$(CH_2)_2S_2CH_2$	5	26	−51	106	109
2	CH_2Cl_2	$[(CH_2)_2S_2CH_2]_2$	10	0.2	121	212	219
3	$(CH_2)_2Br_2$	$(CH_2)_2S_2(CH_2)_2$	6	46	111	120	118
4	$(CH_2)_3Br_2$	$(CH_2)_2S_2(CH_2)_3$	7	9	47.0	134	140
5	$(CH_2)_3Br_2$	$[(CH_2)_2S_2(CH_2)_3]_2$	14	1	122	268	247
6	$(CH_2)_4Br_2$	$[(CH_2)_2S_2(CH_2)_4]_2$	16	0.2	73	296	290
7	$(CH_2)_5Br_2$	$[(CH_2)_2S_2(CH_2)_5]_2$	18	.15	89	324	319
8	$(CH_2)_6Br_2$	$(CH_2)_2S_2(CH_2)_6$	10	.06	65	176	240

The yield of dithiane was better at room temperature than at the boiling temperature of the alcoholic solution.

The ring No. 4 was prepared from trimethylene mercaptan and ethylene bromide but not isolated by Autenrieth and Wolff,[12] who gave 282° as the melting point of its sulfone, which agrees with ours. Ring No. 5 has not been isolated previously.

Rings Nos. 6, 7 and 8 were obtained only in minute yields and on this account the statements about them are to be regarded as preliminary only. They separate in crystals when the ether extracts of the accompanying polymers are evaporated to small volume. They were recrystallized from

---

(10) Gibson, *J. Chem. Soc.*, **1930**, 13.

(11) Baumann and Walter, *Ber.*, **26**, 1129 (1893).

(12) Autenrieth and Wolff, *ibid.*, **32** (1899).

ether and alcohol. It is noteworthy that the monomeric 8 and 9 membered rings were not obtained.

Polymers

In the preparation of all of the ring compounds of Table I, large amounts of polymers were obtained. In appearance they are all much alike, white, fluffy and apparently amorphous. Their sulfur content is in all cases within 1% of that of the rings which they accompany. This suggests chains made up of the unit $—(CH_2)_2—S—(CH_2)_n—S—$. In case the bromide is in excess one or both of the terminal groups may be bromine atoms as seems to have been the case in the polymers studied by Râу and Bose-Râу.[13]

Bennett and Hill[14] suggest $—CH{=}CH_2$ and $—CH_2OH$ as possible end groups. It seems more likely that $—OC_2H_5$ may be formed occasionally by the reaction of the bromide with sodium ethylate, a trace of which must be present in the reaction mixture.

All of these polymers are mixtures which can be roughly separated into fractions by partial solution in solvents such as ether, benzene and chloroform. The solubility in chloroform increases as the number of carbons in the polymethylene bromide goes up.

The mixture of polymers obtained in the preparation of ethylene mercaptan was studied more extensively on account of its availability. Indications as to the nature of these are obtained from a consideration of the products intermediate between the ethylene mercaptan and the solids. Steam distillation of the ethylene mercaptan leaves a quantity of heavy oil a part of which is slightly volatile with steam. A quantity of this oil was collected and fractionated but sharp cuts could not be obtained. A portion boiling at 120–140° at 30 mm. from which dithiane crystallized showed an average molecular weight of 154 corresponding to $HSC_2H_4SC_2H_4SH$. Iodine titration gave the high equivalent weight of 132, which was probably due to the presence of dithiane. This oil on standing for several days precipitated an amorphous white solid entirely similar to the original polymeric part. An iodine titration of the remaining oil gave an equivalent weight of 151, showing that it had suffered oxidation. In a portion of the original oil that had been steam distilled a white solid appeared after a time. This was filtered off and freed from dithiane by washing with ether and showed a molecular weight of 1300. It was no longer volatile with steam. It must have been formed by spontaneous oxidation.

The solid polymers from several preparations were united and separated roughly into fractions by successive extractions with solvents. The properties of these are shown in Table II.

No. 5 was titrated with iodine and gave 2950 and 3000 as equivalent

---

(13) Râу and Bose-Râу, *J. Indian Chem. Soc.*, **3**, 75 (1928).

(14) Bennett and Hill, *J. Chem. Soc.*, 1803 (1927).

TABLE II

PROPERTIES OF THE FRACTIONS OF THE POLYMERS

No.	Solvent	Wt.	Softens at °C.	Melts at °C.	S, %		Mol. wt.	
1	Ether	...	..	30–40				
2	Benzene	2.6	..	80–83	59.5	59.7	1330	1380
3	Hot benzene	8.0	74	79–81	65.8	64.1	1750	1690
4	Hot benzene	1.4	58	67–72	64.2	64.7	1530	1350
5	Hot chloroform	13.0	70	80–81	63.0	62.6	2880	
6	Hot benzene	4.5	66	79–84	63.0	62.6	2325	2660
7	Hot benzene	3.5	67	80–82	61.8	61.3	1366	1388
8	Hot xylene	4.0	65	88–91	62.0			
9	Hot nitrobenzene	2.4	86	118–121	64.2			

weights. Bromine was not detected in any of the fractions. Fraction No. 1 was waxy. It is to be noted that all of the fractions show a higher sulfur content than the unit $—CH_2CH_2S—$, which has 53.3%. The molecular weight and composition of No. 5 would be accounted for by $(C_2H_4S)_{38}S_{18}$, indicating a large number of disulfide linkages. This approximates $(—CH_2CH_2SCH_2CH_2S—S)_{18}$, an oxidation product of $HSCH_2CH_2SCH_2CH_2SH$.

On account of the amorphous character of the polymers, x-ray inspection[15] did not show much but powder diagrams of all of the fractions showed the spacing —C—C—S—. Nos. 2, 4 and 9 were photographed with a larger camera and Nos. 4 and 9 gave a line corresponding to —C—C—S—S—.

Depolymerization

Apparently these polymers show no reaction corresponding to the ester interchange found by Carothers.[16] Dithiane heated for two days in a sealed tube to 180–190° was unchanged. The polymers heated for several hours in a molecular still under high vacuum showed no decomposition. In some cases there was a slight sublimation of low molecular weight material which was probably present originally.

Bennett[17] has shown that ethylene sulfide polymers give dithiane on heating with ethylene bromide. The reaction involves the formation of a sulfonium bromide since ionic bromine appears. We have extended this reaction to all of our polymers and have obtained dithiane from all of them. The yields are given in Table III. The same polymers heated with trimethylene bromide do not yield any isolable ring compounds though ionic bromine is formed. This is curious considering the fact that the ring $(CH_2)_2S_2(CH_2)_3$ is readily obtained from ethylene mercaptan and trimethylene bromide. These facts are further evidence of the unique properties of six-membered rings.

(15) For which our thanks are due to Mr. D. A. Wilson.

(16) Carothers, THIS JOURNAL, 54, 761 (1932).

(17) Bennett, *J. Chem. Soc.*, 1803 (1927).

TABLE III

YIELDS OF DITHIANE FROM POLYMERS WITH ETHYLENE BROMIDE

Polymer	Percentage of weight	Percentage of calcd.
$[\text{—}CH_2S(CH_2)_2S\text{—}]_x$	51	43
$[\text{—}(CH_2)_2S(CH_2)_2S\text{—}]_x$	65	65
No. 2 Table II	28	32
No. 9 Table II	24	31
$[\text{—}(CH_2)_2S(CH_2)_3S\text{—}]_x$	25	28
$[\text{—}(CH_2)_2S(CH_2)_6S\text{—}]_x$	21	31

To get further light on this reaction by applying it to a compound of known structure, dibutyl dithioglycol ether, $C_4H_9SCH_2CH_2SC_4H_9$, was prepared and heated with ethylene bromide. A 48% yield of dithiane was obtained but a similar experiment using trimethylene bromide gave no definite results.

It was found that some of the polymers give dithiane when heated in a current of hydrogen chloride. The results of this treatment are given in Table IV.

TABLE IV

YIELDS OF DITHIANE FROM POLYMERS WITH HYDROGEN CHLORIDE

Polymer	Percentage of weight	Percentage of calcd.
$[\text{—}(CH_2)_2S(CH_2)_2S\text{—}]_x$	40	40
$[\text{—}(CH_2)_2S(CH_2)_3S\text{—}]_x$	18	40
$[\text{—}(CH_2)_2S(CH_2)_6S\text{—}]_x$	14	41

The polymer $[\text{—}CH_2S(CH_2)_2S\text{—}]_x$ gave a 30% yield of the corresponding monomeric ring, 1,3-dithiolane.

Experimental

Ethylene mercaptan was prepared by heating for one and a half hours in an autoclave at about 100° with stirring, ethylene chloride and a 10% excess of aqueous sodium hydrosulfide made by saturating crystalline sodium sulfide, $Na_2S\cdot 9H_2O$, with hydrogen sulfide. The pressure developed was about 2.5 atm. The product was acidified with sulfuric acid and the mercaptan distilled out with steam. The crude mercaptan was dried and fractionated in a column still, b. p. 146–146.5°. It melted at −41 to −41.4° and had n^{25}_{D} 1.5558. The yields were 55 to 65%.

Trimethylene and pentamethylene bromides were purchased from the Eastman Kodak Co. The tetra- and hexamethylene bromides were prepared from the corresponding glycols which were obtained by the Beauveault and Blanc reduction of the butyl esters of succinic and adipic acids.

The condensations of ethylene mercaptan with the polymethylene bromides were all carried out in the same way: 0.25 mole of the mercaptan was dissolved in 500 cc. of absolute alcohol in which 12 g. of sodium had been dissolved and 0.25 mole of the bromide added slowly at room temperature. The separation of sodium bromide began immediately but the mixture was boiled for one-half hour and poured into water. Ether was added and the whole filtered. The solid material was dried and extracted for twelve hours with ether. The two ether solutions were united and dried over calcium chloride and evaporated to get the monomeric and dimeric ring compounds.

1,3-Dithiolane.—The evaporation of the ether solution obtained as above left 10 g. of oil which was distilled, 7 g. going over between 178 and 182° or 26%. This was fractionated through a small column and gave 5 g. boiling at 179–180°. This had n_D^{25} 1.5983 and solidified at −51 to −52°; molecular weight in borneol, 108, 110; calcd., 106. The residue from the distillation was a heavy oil from which needles separated after three weeks standing. These were picked out, dried on filter paper and recrystallized twice from ether and once from alcohol; yield, 50 mg., 0.2%, m. p. 121°, mol. wt. calcd. 212; found 220; sulfur calcd., $C_6H_{12}S_4$, 60.3; found, 63.3.

Dithiane.—The experimental conditions given above were chosen after a number of experiments on the condensation of ethylene mercaptan with ethylene bromide. Where the reaction was run at the boiling temperature the ratio of polymer to dithiane was 2:1 but at room temperature the yield of dithiane was 46% to 51 of polymer. At 0° the ratio was even more favorable to dithiane but the reaction was incomplete.

Ethylene-trimethylene Disulfide.—On evaporation of the ether extracts some amorphous material separated and later small colorless apparently cubic crystals, weight 0.15 g. These were unaffected by alkali, gave no test for halogen, melted at 121–122°; m. w. calcd. for $C_{10}H_{20}S_4$, 268; found, 247; sulfur calcd., 47.8; found, 48.1. Complete evaporation of the ether left a yellow semi-crystalline mass from which flakes were obtained by sublimation on the water-bath, yield 3.2 g. or 9%. These melted at 47.0–47.5° and contained 47.4, 48.0% of sulfur; calcd. for $C_5H_{10}S_2$, 47.8; m. w. 140; calcd., 134. The sulfone was obtained by oxidation of 0.3 g. suspended in 20 cc. of water by the addition of potassium permanganate and acid, m. p. 281–282°.

Ethylene-tetramethylene Disulfide.—This was prepared in a slightly different way. A slight excess of 50% caustic soda was added dropwise to a solution of 11 g. of the dibromide and 5 g. of the mercaptan in 150 cc. of alcohol. The mixture was heated for thirty minutes, poured into water and extracted with ether. Crystals separate from the ether.

Ethylene-pentamethylene Disulfide.—This was obtained in the same way as the above.

Ethylene-hexamethylene Disulfide.—In this case the ether solution deposited amorphous material along with a small amount of crystals. These were picked out and recrystallized from ether.

Summary

Ethylene mercaptan has reacted with methylene chloride and the polymethylene bromides up to the hexa-. Cyclic compounds have been obtained in all cases along with amorphous materials having high molecular weights.

All of the polymers give dithiane when heated with ethylene bromide. The most of them give the same material when heated in a current of dry hydrogen chloride.

BALTIMORE, MARYLAND

RECEIVED AUGUST 9, 1932
PUBLISHED FEBRUARY 9, 1933