ture of benzyl alcohol and benzaldehyde; 0.73 g. of resinous material was left.

Attempt to Separate 10-Benzylanthrone (XVII) from Reaction Mixture Above.—From the second half of the ethereal solution of the Grignard product, no crystalline material could be separated except anthraquinone, which was obtained in a yield of 10 g.

Catalytic Reduction of Benzalanthrone

10-Benzylanthrone (XVII).—Twenty grams of benzalanthrone in 225 cc. of absolute alcohol was reduced with hydrogen and a palladium catalyst, absorption being rapid. Allowed to stand in the reaction vessel for thirty-six hours, the fluorescence disappeared. The alcohol was removed under diminished pressure, the residue taken up in ether, warmed on water-bath, and let stand for some hours; 2.0 g. of anthraquinone separated, and on adding petroleum ether to the filtered solution, 9 g. of pure 10-benzylanthrone separated in large colorless prisms; recrystallized from ether–petroleum ether, m. p. 91–92°.

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.7; H, 5.68. Found: C, 88.83; H, 5.67.

When a similar run was made and oxygen passed into the filtered solution immediately upon cessation of absorption of hydrogen, 9.5 g. of anthraquinone was obtained and benzyl alcohol, detected as benzaldehyde, was isolated from the residues.

We attempted to prepare the compound listed in Beilstein as 10-benzylanthrone, according to the method of Bach.[9] On treating benzalanthrone dibromide (for which we find m. p. 138° instead of 148° as Bach gives) as described by him, we secured only anthraquinone and benzalanthrone.[7]

Summary

1. The reactions of arylidene and alkylidene anthrones with phenylmagnesium bromide simulate those of α,β-unsaturated ketones with this reagent.

2. 10-Benzylanthranol, like tetraphenylpropenol, gives a crystalline peroxide with atmospheric oxygen.

3. Benzalanthrone reacts with phenylmagnesium bromide, giving an addition product which is under investigation.

(9) Bach, *Ber.*, **23**, 1569 (1890).

GREENCASTLE, IND. RECEIVED JULY 27, 1934

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

Ring Compounds and Polymers from Polymethylene Dihalides and Dimercaptans[1]

BY JACOB R. MEADOW AND E. EMMET REID

Ring compounds containing two sulfur atoms have been reported from this Laboratory.[2] This study has been extended to include (1) the isolation of the sulfide dimercaptans which are byproducts in the preparation of dimercaptans, (2) the preparation of a number of new ring compounds and (3) the decomposition of the polymers.

1. Sulfide Dimercaptans

The high boiling residue when crude ethylene mercaptan is distilled was supposed by Rây[3] to be the disulfide II, but his analyses indicate that his product was impure. By fractionating this residue we have isolated a little II but about ten times as much of the monosulfide mercaptan I. From runs in which a total of 800 g. of ethylene chloride was used we obtained 45 to 55% of ethylene mercaptan, 16% of I and about 1.5% of II along with 5 to 6% of dithiane and 10% of polymers. Besides the usual analyses I was identified by treating it with ethylene chlorohydrin in alkaline solution which converted it into tetraethylene trisulfide glycol, $S(CH_2CH_2SCH_2CH_2OH)_2$, m. p. 91.5°, which had been prepared by Bennett and Whincop[4] from mustard gas and monothioethylene glycol.

The isolation of these sulfide mercaptans is confirmatory evidence for the accepted theory of the building up of sulfide-chain molecules in the reactions of bifunctional compounds. It is probable that even more complicated sulfide mercaptans are present but cannot be isolated on account of their high boiling points and the smallness of the amounts present. As a large excess of sodium hydrosulfide was used all of the products would have —SH terminals which would be less and less evident as the molecular weights increase.

From trimethylene bromide 52% of the calculated amount of trimethylene mercaptan was obtained along with 6% of the sulfide mercaptan III. From dichloroethyl ether and alcoholic potassium hydrosulfide 13% of the oxide mercaptan IV and 5% of the complex mercaptan V were isolated along with 30% of 1,4-thioxane. The

(1) From Ph.D. dissertation of Jacob R. Meadow, Johns Hopkins University, June, 1933.

(2) Tucker and Reid, THIS JOURNAL, **55**, 775 (1933).

(3) Rây, *J. Chem. Soc.*, **117**, 1090 (1920).

(4) Bennett and Whincop, *ibid.*, **119**, 1861 (1921).

properties of these compounds are given in Table I.

TABLE I

SULFIDE AND OXIDE MERCAPTANS

	Mercaptan	M. p., °C.	B. p., °C.	Molecular wt. Calcd.	Molecular wt. Found
I	$HSC_2H_4SC_2H_4$-SH	−12.5	135–136 (10 mm.)	154	158
II	$HSC_2H_4SC_2H_4$-SC_2H_4SH	15–7	168–172 (10 mm.)	214	220
III	$HSC_3H_6SC_3H_6$-SH	− 9 to −8	138–140 (6 mm.)	182	184
IV	$HSC_2H_4OC_2H_4$-SH	−80 (±2)	103–104 (18 mm.)	138	139
V	$HSC_2H_4OC_2H_4$-$SC_2H_4OC_2H_4$-SH	Indefinite	182–185 (8 mm.)	242	249

2. Rings

The rings obtained are given in Table II.

sebacic acid from the polyanhydride, these authors found that on depolymerization a crystalline dimer was formed instead of the 11-ring monomer.

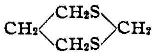
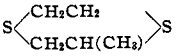
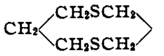
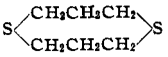
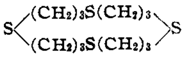
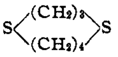
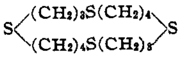
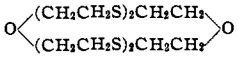
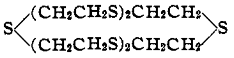
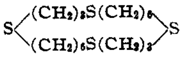
Autenreith and Wolff[7] obtained 1,3-dithiane, VI, from trimethylene mercaptan and formalin as an oil which they were unable to purify. It was later isolated by Gibson.[8] Our yield was 15% with 32% more by decomposition of the polymer.

VIII had been made previously[9] from trimethylene bromide and ethylene mercaptan.

Autenrieth and Wolff[7] obtained IX as an oil which they characterized by its disulfone m. p. 258–259°. We find IX to be accompanied by its dimer X. IX is itself the dimer of trimethylene sulfide from the high boiling fraction of which we isolated it also.

TABLE II

RING COMPOUNDS

	Dimercaptan	Dihalide	Ring formed	Atoms	Yield, %	M. p., °C.	B. p., °C.	Mol. wt. Calcd.	Mol. wt. Found	M. p. of sulfone, °C.
VI	$C_3H_6(SH)_2$	CH_2Cl_2		6	15	53.3	207–208	120	126	307–308 (corr.)
VII	$C_2H_4(SH)_2$	$CH_2BrCHBrCH_3$		6	12.5	20	209–210	134	138	
VIII	$C_3H_6(SH)_2$	$C_2H_4Br_2$		7	8.2	47	221–222	134	140	287–288
IX	$C_3H_6(SH)_2$	$C_3H_6Br_2$		8	4.0	−15	245–246	148	142	257.5–258
X	$C_3H_6(SH)_2$	$C_3H_6Br_2$		16	1.0	46		296	285	
XI	$C_3H_6(SH)_2$	$C_4H_8Br_2$		9	0.6	57.5	260 (subl.)	162	154	185.6 (corr.)
XII	$C_3H_6(SH)_2$	$C_4H_8Br_2$		18	1.8	61		324	336	
XIII	$C_2H_4(SH)_2$	$O(C_2H_4Cl)_2$		18	1.4	125		328	341	265–266
XIV	$S(C_2H_4SH)_2$	$C_2H_4Br_2$		18	1.7	89.6–90		360	354	>330
XV	$C_3H_6(SH)_2$	$C_6H_{12}Br_2$		22	1.1	62		380	386	260–261

The results illustrate the difficulty or perhaps better the improbability of the formation of rings containing 9 to 11 members. In 3 cases where 9-membered rings were expected, the dimeric 18-membered rings were found, accompanied in only one case by a small amount of the 9. Our results agree well with those obtained by workers in other fields. In attempting to prepare the 11-ring lactone of a hydroxydecanoic acid, Lycan and Adams[5] reported a 5% yield of the 22-ring dimeric lactone only. Similar examples are found in the work of Carothers and co-workers.[6] For instance, in attempting to prepare the 11-ring anhydride of

XI, the only nine-membered ring which we were able to find, was difficult to isolate on account of the small amount of it present with its dimer XII.

XIII and XIV are dimers of nine-membered rings that could not be found.

Rây[10] reported trimethylene trisulfide which should be identical with XIV but his compound melted at 113°, which is suspiciously near the melting point of dithiane with which it was identified by Bennett and Berry.[11] We are sure that this is correct.

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[5] Lycan and Adams, THIS JOURNAL, **51**, 3450 (1929).

[6] Carothers and Hill, *ibid.*, **54**, 1569 (1932).

[7] Autenrieth and Wolff, *Ber.*, **32**, 1368 (1899).

[8] Gibson, *J. Chem. Soc.*, 13 (1930).

[9] Tucker and Reid, THIS JOURNAL, **55**, 775 (1933).

[10] Rây, *J. Chem. Soc.*, **117**, 1090 (1920).

[11] Bennett and Berry, *ibid.*, **127**, 910 (1928).

None of the expected eleven-membered ring corresponding to the dimer XV could be isolated.

3. Depolymerization

The polymers which were obtained along with the above-mentioned ring compounds and some from reactants that did not give rings are listed in Table III with their decomposition products. Polymer E was from mustard gas sulfone and sodium ethylene mercaptide. Determinations on these polymers in chloroform, benzene and camphor gave figures ranging from 1500 to 3000 for their average molecular weights. By partial solution in, or by partial precipitation from, such solvents as benzene, chloroform and ethylene chloride the polymers can be separated into higher and lower molecular weight fractions but such separations were not pushed as our chief interest was in their decomposition products.

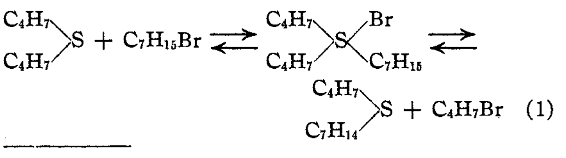
The decomposition of these polymers was effected by heating either in a current of dry hydrogen chloride for two or three hours or for a longer time in the molecular still at 175–200°, keeping the pressure as low as possible.

TABLE III

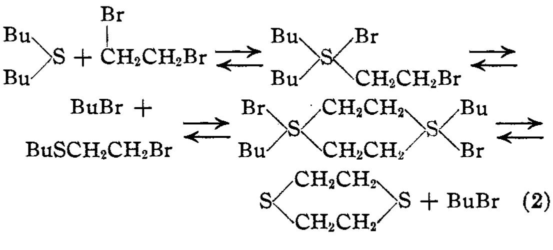
DECOMPOSITION OF SULFIDE POLYMERS

Polymer	Structural unit	Products of decomposition
A	$-C_2H_4SC_2H_4S-$	1,4-Dithiane, 40–60%
B	$-C_2H_4SCH_2S-$	1,3-Dithiolane, 30%
C	$-C_2H_4SC_3H_6S-$	VII 5–10% and 1,4-dithiane, 5–10%
D	$-C_3H_6SC_3H_6S-$	Nothing definite
E	$-C_2H_4SO_2C_2H_4SC_2H_4S-$	Monosulfone of dithiane, 20% and 1,4-dithiane, 10–15%
F	$-C_2H_4SC_2H_4SC_2H_4O-$	1,4-Thioxane, 15–20% and 1,4-dithiane, 5–10%
G	$-C_3H_6SCH_2S-$	1,3-Dithiane, 30–40%
H	$-C_2H_4SC_6H_{12}S-$	1,4-Dithiane, 10%
I	$-C_3H_6SC_4H_8S-$	Tetramethylene sulfide, 10%
J	$-C_3H_6SC_5H_{10}S-$	Pentamethylene sulfide, 15–20%

These polymers do not break down into monomeric rings unless halogen is present. This fact supports Bennett's idea of inter- and intramolecular sulfonium addition.[12] To test this several simple cases have been studied. A definite exchange of radicals was effected when *n*-butyl sulfide and heptyl bromide were heated together, butyl bromide, butyl sulfide, heptyl bromide and butyl heptyl sulfide being obtained in approximately equal amounts.


(1)

When *n*-butyl sulfide was heated with ethylene bromide a large quantity of 1,4-dithiane was produced and butyl bromide was identified among the products


(2)

Di-*n*-amyl methylene sulfide $C_5H_{11}SCH_2SC_5H_{11}$, heated with ethylene bromide gave 1,3-dithiolane along with amyl bromide.

Only rings containing 5, 6 or 7 atoms have so far been obtained by depolymerization. Polymers in which the structural units contain 8, 9 or 10 atoms, two of which are sulfur (such as $-C_2H_6-S-C_7H_8-S-$) give rings containing one sulfur atom provided this can have at least five members. Depolymerization of the polymeric by-products may double or even triple the yield obtainable of the ring compounds as in the preparation of 1,3-dithiolane, 1,3-dithiane and even of 1,4-dithiane.

Experimental

The highs from a number of preparations of ethylene mercaptan were united and fractionated at 10 mm. Two fairly distinct fractions, I, b. p. 135–136°, and II, b. p. 168–172°, were obtained: I, *d* 0/4 1.2352, *d* 25/4 1.2187. S calcd. for $C_4H_{10}S_3$, 62.4; found, 62.8 and 63.0%. Mol. wt. calcd. 154, found 158 in camphor and 150–160 in naphthalene. Silver salt, calcd. Ag, 58.7; found 58.9 and 59.1%. II could not be obtained in pure condition as there seemed to be some decomposition during distillation even at 10 mm. It melted at 15–17°, mol. wt. in camphor 220, calcd. 214. Silver salt contained 48.8% of Ag instead of calcd. 50.3%.

Trimethylene bromide was added slowly to a 20% excess of alcoholic KSH solution at room temperature. After standing the mixture was poured into several volumes of water and the oil separated, dried and fractionated. The yield of trimethylene mercaptan of b. p. 66–68° at 18 mm. was 52%, m. p. $-79 \pm 2°$, n^{20}_{D} 1.5403, *d* 0/4 1.1009, *d* 25/4 1.0896. From the residue from the above III was obtained in about 6% yield, b. p. 138–140° at 6 mm., m. p. −9 to −8°, n^{20}_{D} 1.5740, *d* 0/4 1.1612, *d* 25/4 1.1456. *Anal.* S found 52.2, calcd. 52.7%; for silver salt Ag found 54.45, calcd. 54.6%.

Dimercapto-diethyl ether IV was obtained from β,β'-dichloroethyl ether and alcoholic KSH. At 0° the yield was 16% but only 12% at room temperature. Fractionation of the crude oil gave IV, b. p. 103–104° at 18 mm., m. p. $-80 \pm 2°$, n^{20}_{D} 1.5339, *d* 0/4 1.1854 and *d* 25/4 1.1648.

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[12] Bennett, Bell and Hock, *J. Chem. Soc.*, 1803 (1927).

Anal. Silver salt: Ag found 61.55, calcd. 61.4%. Fractionation of the residue from the above gave V, b. p. 182–185° at 8 mm., mol. wt. in camphor 249, calcd. 242. *Anal.* Silver salt: Ag found 47.8; calcd. 47.37%.

1,3-Dithiane VI.—An excess of methylene chloride was added to 27 g. of trimethylene mercaptan in 500 cc. of absolute alcohol containing an equivalent amount of sodium ethylate. The reaction was completed at room temperature and the mixture poured into water and the solid high polymer filtered off. Extraction of the filtrate with ether gave a mixture of VI and low polymer from which VI sublimed readily in the molecular still at 80–90°, m. p. 53.3°, b. p. 207–208° (micro method), mol. wt. in camphor 126. An additional amount of VI was obtained from the high polymer by heating in a current of dry hydrogen chloride. The sulfone was obtained by oxidation of VI in 50 parts of acetic acid with perhydrol.

2-Methyl-1,4-dithiane VII was similarly obtained from propylene bromide and the sodium salt of ethylene mercaptan, mol. wt. in borneol 140, S found 48.05, calcd. 47.76%.

Trimethylene sulfide was prepared from 100 g. of trimethylene bromide with an excess of sodium sulfide (from sodium ethylate and hydrogen sulfide) in 800 cc. of absolute alcohol. Fractionation of the crude sulfide gave a 33% yield, m. p. −64 ± 1°, b. p. 93.6°, *d* 0/4 1.0371, *d* 25/41 0.0163 and n_D^{20} 1.5072. These properties agree fairly well with those reported by Trokhimovski.[13] From the residue 2% of its dimer IX was obtained.

Di-trimethylene-1,5-disulfide IX besides being found in the above was prepared from trimethylene mercaptan and bromide. It was separated from low polymer and its dimer by sublimation in the molecular still, keeping the bath at 90°, m. p. −15°, b. p. 245–246° (micro method) n_D^{20} 1.5747, *d* 0/4 1.1579, *d* 25/0 1.1476, mol. wt. in naphthalene 142. *Anal.* S found 43.33 and 43.02; calcd. 43.25%. The sulfone was obtained by oxidation with 30% hydrogen peroxide in acetic acid. The dimer of this X was sublimed from the still residue by raising the temperature to 170°, m. p. 46°, mol. wt. in camphor 285.

XI was obtained in 0.25 g. (0.6%) yield from 52 g. of tetramethylene bromide and 27 g. of trimethylene mercaptan. It was purified by sublimation below 100°, needles 2 cm. long, m. p. 57.5–58°, mol. wt. in naphthalene 154; S found 39.88, calcd. 39.51%. By raising the temperature of the still to 175° the dimer XII was obtained m. p. 61–62°, mol. wt. in camphor 336; S found 39.18, calcd. 39.51%. A mixture of XI and XII melted around 44°.

The dimeric ring XIII was obtained in two ways, from dimercapto-ethyl ether with ethylene bromide and from dichloroethyl ether with ethylene mercaptan, mol. wt. in borneol 341, in camphor 316; S found 38.56, calcd. 39.02%. No reactive groups could be detected.

The dimeric ring XIV from the sulfide mercaptan III and ethylene bromide showed mol. wt. 354 in borneol and 368 in camphor; S found 52.91, calcd. 53.33%.

The 22-membered dimeric ring XV was obtained from hexamethylene bromide and trimethylene mercaptan, m. p. 62°, mol. wt. found 386, minimum sublimation temperature 170°; S found 33.31, calcd. 33.68%.

Summary

Sulfide di-mercaptans have been identified as by-products in the preparation of simple dimercaptans.

Rings, some monomeric and some dimeric, have been obtained by the reaction of a polymethylene halide with a polymethylene mercaptan and along with these high molecular weight polymers.

Exchange of radicals between an alkyl sulfide and an alkyl halide has been effected. This reaction has been used to break down polymers.

BALTIMORE, MD. RECEIVED JULY 30, 1934

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[13] Trokhimovski, *J. Russ. Phys.-Chem. Soc.*, **48**, 880 (1916).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Studies in the Chlorophyll Series. XIII. Nuclear Isomerism of the Porphyrins[1]

BY EMMA M. DIETZ AND TYRRELL H. WERNER

In paper IX of this series Conant and Bailey[2] reported the conversion of a simply constituted chlorin, chlorin *f*, to the corresponding porphyrin, isorhodoporphyrin, by the removal of two hydrogen atoms with potassium ferricyanide. The measurements of low temperature absorption spectra by Conant and Kamerling[3] similarly pointed to the view that porphyrins contain conjugated unsaturated systems which are partially hydrogenated in the chlorins. Conant therefore reiterated his former hypothesis that the fundamental nucleus of chlorophyll *a*, of the related phaeophorbides and of the chlorins is that of a reduced porphyrin ring, more specifically a reduced isorhodoporphyrin ring. This would lead to the assumption that the drastic alkali degradation of chlorophyll which produces rhodoporphyrin, but never isorhodoporphyrin, causes an isomerization as well as a dehydrogenation of the original chlorophyll nucleus.

This isomerism of rhodo- and isorhodoporphyrins is discussed at some length in paper IX. Verdoporphyrin is a second but much less stable

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[1] This problem was suggested by President James B. Conant, to whom we are indebted for advice during its investigation.

[2] THIS JOURNAL, **55**, 798 (1933).

[3] *Ibid.*, **53**, 3522 (1931).