[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Reaction of Chloroalkyl Sulfides with Sodium[1]

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The present problem deals with the behavior of several chloroalkyl sulfides with sodium and other metals. Simple alkyl halides are known to react[2] with sodium, giving first the alkylsodium, RNa, then the paraffin, R–R. Some α,ω-dihalides behave similarly, the products of reaction[3] of 1,10-dichlorodecane in ether with sodium being decane, eicosane, triacontane, and so on up to heptacontane, $C_{70}H_{142}$. The only chloroalkyl sulfide whose behavior toward sodium has been reported is 2-chloroethyl sulfide or mustard gas. Like 1,10-dichlorodecane, it also is an α,ω-dihalide, but it is reported to be inert toward sodium either in ether[4] or in refluxing xylene.[5]

Mustard gas was reinvestigated in the present work along with several other chloro sulfides. The list includes sulfides of the general formula $RS(CH_2)_nCl$ wherein R was phenyl, ethyl, *n*-, *s*-, and *t*-butyl, 2-chloroethyl and 3-chloropropyl; and *n* was 1, 2, 3 or 4. These compounds were generally synthesized by reaction of thionyl chloride on the corresponding hydroxy sulfide. Three of the chlorides were new: *s*-butyl 2-chloroethyl sulfide, *t*-butyl 2-chloroethyl sulfide and *n*-butyl 4-chlorobutyl sulfide. The hydroxyalkyl sulfides from which these three compounds were made were new also. They were synthesized from the sodium alkyl sulfide by reaction with either ethylene chlorohydrin or tetramethylene chlorohydrin.

The yield of *t*-butyl 2-chloroethyl sulfide was considerably lower than that for the *n*- and *s*-butyl isomers, pointing to extensive cleavage at the C–S bond. Supporting this statement is the fact that a 25% yield of *t*-butyl chloride was isolated as a by-product.

Reaction of the alkyl (or aryl) 2-chloroethyl sulfides with sodium wire in refluxing toluene was rapid. A purple color formed on the surface of sodium and a gas was evolved, namely, ethylene. The non-volatile reaction products included sodium chloride, sodium alkyl (or aryl) sulfide, and 1,2-bis-(alkylthio)-ethane, $RSCH_2CH_2SR$. None of the 1,4-bis-(alkylthio)-butane, $RSCH_2CH_2CH_2CH_2SR$, was obtained, showing that no Wurtz reaction was involved. The following three equations provide an explanation for the four major products isolated.

$$RSCH_2CH_2Cl + 2Na \longrightarrow RSNa + C_2H_4 + NaCl \quad (1)$$

$$RSNa + RSCH_2CH_2Cl \longrightarrow RSCH_2CH_2SR + NaCl \quad (2)$$

$$RSCH_2CH_2SR + 2Na \longrightarrow 2RSNa + C_2H_4 \quad (3)$$

A transient alkylsodium, $RSCH_2CH_2Na$, may be an intermediate step in equation 1 but, if so, its decomposition into $RSNa + C_2H_4$ took precedence over a tendency for a reaction of the Wurtz type.

The rapidity of these reactions is portrayed graphically in Fig. 1, all experiments being carried out in refluxing toluene. No curve for the *t*-butyl analog is included in Fig. 1, since it was impracticable, because of the vigor of the reaction, to add the sulfide all at once as was done with the others. After the initial rapid spurt of gas, the *t*-butyl compound also gave a slow, prolonged evolution of ethylene.

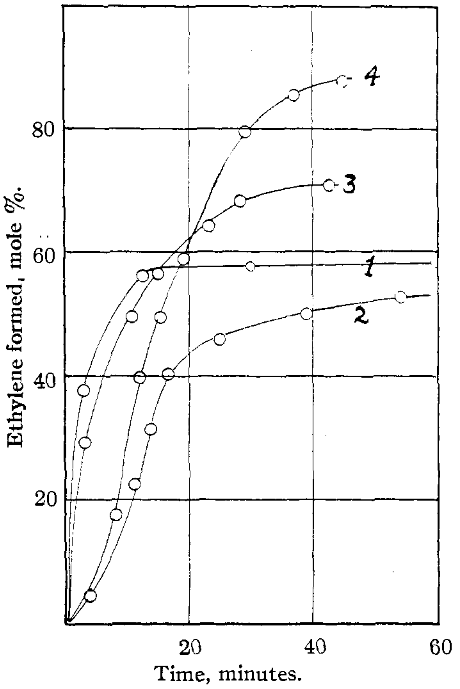

Fig. 1.—Effect of R on the reaction of $RSCH_2CH_2Cl$ with sodium: 1, R, ethyl; 2, R, butyl; 3, R, *s*-butyl; 4, R, phenyl.

All the curves in Fig. 1 depict experiments employing a mole ratio of sodium to the chloro sulfide of about 4:1. Lessening this ratio of 1.5:1 slackened the rate of evolution of ethylene from phenyl 2-chloroethyl sulfide below that of curve 2 for the first thirty-five minutes, passing curve 1 at fifty minutes, finally reaching 71 mole % of ethylene in two hours. This is considerably below the 90% mark reached in one hour when the ratio was 4.3:1.

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(1) This paper consists of a report of work done under contract with the Technical Command, Chemical Corps, Department of the Army.

(2) Morton and Hechenbleikner, THIS JOURNAL, **58**, 1697, 2599 (1936).

(3) Carothers, Hill, Kirby and Jackson, *ibid.*, **52**, 5279 (1930).

(4) Helfrich and Reid, *ibid.*, **42**, 1229 (1920).

(5) Davies, *J. Chem. Soc.*, **117**, 298 (1920).

Support for equation 3 was obtained by treating 1,2-bis-(phenylthio)-ethane with sodium, again in hot toluene. Ethylene was evolved steadily, though slowly; about 27 mole per cent. was collected the first hour and 62% after five hours.

Correlation may be drawn between the formation of ethylene in equation 1 and the last step of the well-known Swallen–Boord synthesis of olefins by reaction of ethyl 2-bromoalkyl ethers with zinc

$$BrCH_2CHROEt + Zn \longrightarrow CH_2{=}CHR + BrZnOEt$$

Zinc dust and zinc amalgam both were found capable of liberating ethylene from phenyl 2-chloroethyl sulfide. Magnesium did not react. As with sodium, the isolated products were ethylene, sodium phenyl sulfide, sodium chloride and 1,2-bis-(phenylthio)-ethane. The yield of ethylene, however, was low. Only 30–37 mole per cent. appeared during the first hour, and only 39–45% after five hours. Thiophenol was not found. This suggests that equation 2 consumed all the thiophenol derivative formed in equation 1, with no cleavage by zinc according to equation 3.

In studying the effect of the distance of halogen from sulfur in $RS(CH_2)_nCl$, butyl chloromethyl sulfide was selected for $n = 1$. This was the only example found where any Wurtz product was obtained, but even here only a trace of 1,2-bis-(butylthio)-ethane was found. The chief product was the mercaptal, bisbutylthiomethane. Lesser quantities of mercaptan and gas appeared also. Butylene was the major gaseous product, ethylene and paraffins being lesser products.

The reaction of 3-chloropropyl compounds with sodium produced cyclopropane, not propylene. Ethyl 3-chloropropyl sulfide, for example, gave rise to sodium chloride, cyclopropane, sodium ethyl sulfide and 1,3-bis-(ethylthio)-propane. Phenyl 3-chloropropyl sulfide yielded cyclopropane, sodium phenyl sulfide and bis-(phenylthio)-propane. There was no formation of Wurtz products. These reaction products are well summarized by an extension of equations 1–3.

The reaction of sodium with phenyl 4-chlorobutyl sulfide was less clear cut. Although the phenyl compound is more stable than the dialkyl analogs,[6] it tends to undergo ring closure, forming a sulfonium chloride. In its reaction with sodium, the chief gas evolved was *n*-butane (not cyclobutane). Appreciable quantities of ethylene and 1-butene were formed also. Other identified products of the reaction were sodium phenyl sulfide, 1,4-bis-(phenylthio)-butane, and sodium chloride. To show that the butane did not arise by hydrogen transfer from an aromatic hydrocarbon, the reaction of butyl 4-chlorobutyl sulfide with sodium in butyl ether also produced butane. This formation of butane resembles the formation of decane[3] from 1,10-dichlorodecane.

Two symmetrical chloroalkyl sulfides were studied also, namely, 2-chloroethyl sulfide and 3-chloropropyl sulfide. This work is of interest in view of the reported non-reaction of sodium and mustard gas. We have confirmed Helfrich and Reid's observation[4] of non-reaction in ethyl ether if strictly anhydrous ether was used, but reaction was initiated by using ether which contained only 0.2% of ethanol. Reaction in benzene, toluene or butyl ether at temperatures of 80–110° was slower than with the alkyl 2-chloroethyl sulfides but so definite that it is difficult to understand the reported non-reaction in hot xylene.[5] About twelve hours was necessary to complete the reaction in hot toluene, whereas it took one week in ethyl ether at 25°.

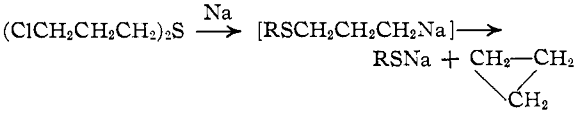
In refluxing toluene, ethylene was evolved to the extent of 148 mole per cent. in twelve hours. The sodium wire assumed a brilliant purple color which did not change color on treatment with alcohol but did change in water to a pale yellow, very insoluble solid melting at 158–160°. It contained no chlorine. Here again, there was no evidence for a product of the Wurtz type. The latter would demand a product with a carbon–sulfur ratio of 4:1, whereas a 2:1 ratio was found.

Equation 1 evidently holds for 2-chloroethyl sulfide as well as for the unsymmetrical analogs. If but one of the chloroethyl groups reacts with sodium, the products would be ethylene and sodium 2-chloroethyl sulfide (A), $ClCH_2CH_2SNa$, whereas if both groups participate, it would lead to sodium sulfide. Actually, some sodium sulfide was formed. The chief solid product, however, was the solid mentioned earlier. It was a polymer with this recurring unit, $(-CH_2CH_2S-)_n$. This might result by reaction of A with itself or with 2-chloroethyl sulfide (equation 2). The extent of equation 3 cannot be estimated but probably some chain-splitting at the C–S bonds occurred.

Oxidation of the polymer by nitric acid yielded a water-soluble polysulfoxide, with apparently a sulfonic acid end group. Oxidation by hydrogen peroxide gave rise to a water-insoluble substance which was believed to be a polysulfone.

Bennett[7] has described a polymer, $(C_2H_4S)_n$, of m. p. 177–180°, made by reaction of 2-hydroxy-1-ethanethiol with hydrochloric acid. Our repetition of Bennett's synthesis yielded a substance of m. p. 158–165°. Apparently, therefore, the polymers from the two sources are similar, although they may not be identical.

3-Chloropropyl sulfide also evolved a gas (cyclopropane) and produced a polymer by reacting with sodium in hot toluene. Gas evolution was complete in less than one hour.



The polymer differed from that from 2-chloroethyl sulfide in melting lower (56°) and in being

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[6] Bennett, Heathcoat and Mosses, *J. Chem. Soc.*, 2567 (1929).

[7] Bennett, *ibid.*, **121**, 2139 (1922).

soluble in hydrocarbon solvents. This polymer contained the recurring unit $(-CH_2CH_2CH_2S-)_n$.

Preliminary experiments with 2-chloroethyl ether (not sulfide) revealed that its reaction with sodium also liberates ethylene. Reaction was faster than with the sulfur analog. When 0.077 mole of this ether reacted with 0.165 mole of sodium wire in boiling toluene there was formed 0.060 mole of ethylene in two hours. A polymeric substance was formed which was soluble in water, alcohol or acetone.

Experimental Part

Preparation of Chloro Sulfides.—These compounds were prepared as described in the literature: 2-chloroethyl sulfide,[9] ethyl 3-chloropropyl sulfide,[8] butyl chloromethyl sulfide,[11] phenyl 3-chloropropyl sulfide,[14] phenyl 4-chlorobutyl sulfide,[6] 3-chloropropyl sulfide.[12] Supplementary information as shown was obtained for ethyl 2-chloroethyl sulfide[15] (60% yield, b. p. 69-73° (37 mm.)), butyl 2-chloroethyl sulfide[10] (74% yield, b. p. 98-100° (26 mm.)), phenyl 2-chloroethyl sulfide[13] (97% yield, b. p. 127-129° (6 mm.)).

Alkyl Hydroxyalkyl Sulfides.—Sodium was dissolved in a sevenfold weight of absolute alcohol. An equivalent portion of mercaptan (RSH: R = *s*-Bu, *t*-Bu, *n*-Bu) was added, followed by gradual addition of 1.1 equivalents of the chlorohydrin ($ClCH_2CH_2OH$ or $Cl(CH_2)_4OH$). After refluxing up to one hour, the solution was filtered and distilled. These products were obtained:

I. ***s*-Butyl 2-hydroxyethyl sulfide**, yield 44%, b. p. 105-108° (42 mm.).

II. ***t*-Butyl 2-hydroxyethyl sulfide**, yield 85%, b. p. 111-114° (45 mm.).

Anal. Calcd. for $C_6H_{14}OS$: C, 53.50; H, 10.58. Found: C, 53.73; H, 10.46.

III. **Butyl 4-hydroxybutyl sulfide**, yield 60%, b. p. 129-130° (6 mm.).

Anal. Calcd. for $C_8H_{18}OS$: C, 59.26; H, 11.18. Found: C, 60.02; H, 11.15.

Halogenation.—A small excess of thionyl chloride was added to the above hydroxy compounds. It was added directly, dropwise, to I and II. The product from I was distilled after thirty minutes of refluxing; yield 58%, b. p. 98-100° (40 mm.). That from II was allowed to stand overnight, distilled, and redistilled; yield, 30%, b. p. 85-88° (32 mm.). There was much higher boiling residue. Eight grams of *t*-butyl chloride from 39 g. of II was found in the cold trap.

III was diluted with 1.6 volumes each of carbon tetrachloride and dimethylaniline before addition of thionyl chloride; after refluxing the mixture for thirty minutes, it was acidified (hydrochloric acid) and the non-aqueous layer distilled. A 20% yield of crude butyl 4-chlorobutyl sulfide was collected at 120-124° (10 mm.). Purity was only 70% by halogen analysis. This instability compares with that of ethyl 4-chlorobutyl sulfide,[6] which immediately isomerized to the sulfonium chloride and could not be distilled without decomposition. When our hydroxy sulfide was treated with concd. hydrochloric acid as in the synthesis of mustard gas, reaction was rapid. There was formed a water-soluble sulfonium chloride which gave a characteristic yellow precipitate with picric acid.

Anal. Butyl 2-chloroethyl sulfides. *s*-Butyl. Calcd. for $C_6H_{13}ClS$: C, 47.20; H, 8.51. Found: C, 46.26; H, 8.72. *t*-Butyl. Found: C, 47.12; H, 8.95.

Reaction of Chloro Sulfides.—The reaction of the various chloro sulfides with sodium (or zinc) was carried out in a closed system consisting of a reaction flask (100-ml.) attached to a reflux condenser at the top of which was a dropping funnel and a delivery tube leading to a 10-ml. trap at −78°. In turn, this trap was connected to an Orsat gas analyzer. The cold trap was omitted in the experiments involving the 3-chloropropyl and 4-chlorobutyl compounds. The gas evolved was collected over mercury. A controlled rate of heating of the reaction flask by an electrically controlled oil-bath permitted an accurate measurement of the gas evolved. The volume of gas was plotted against time to indicate the speed of the reaction. Whenever the off gas had a volume larger than 100 ml., it was flushed into a collection bulb over water and retained for analytical purposes.

A typical example for the reaction of butyl 2-chloroethyl sulfide with sodium indicates the general technique. A mixture of 50 ml. of dry toluene and 2.3 g. of sodium wire was refluxed until there was no volume change in the gas collection bulb (five minutes). As long as the refluxing was gentle, the sodium remained as a molten wire presenting a large surface. When 7.023 g. of butyl 2-chloroethyl sulfide was drawn into the reaction flask and washed in with three 1-ml. portions of toluene without the admission of air, a reaction started immediately and a gas (ethylene) was evolved at a moderate rate. A faint fleeting blue color developed on the surface of the sodium wire. Over a period of ninety-nine minutes 580 ml. (S. T. P.) of a gas was collected at a measured rate. The last portion of the evolved gas was identified as ethylene by its absorption in 15% fuming sulfuric acid but not in 88%; reaction of 100 cc. of gas with liquid bromine produced 1 ml. of ethylene bromide, b. p. 128-130°, $n^{23}\text{D}$ 1.5358 (lit. b. p. 131°, $n^{20}\text{D}$ 1.5379).

The toluene in the reaction flask was decanted from the solid as quantitatively as possible, the excess sodium destroyed with ethanol and combined with a water extract of the toluene. This aqueous solution of chloride and mercaptide ion was diluted volumetrically and aliquots titrated for quantitative data. In the chloride analysis an aliquot was warmed for ten minutes with 30% hydrogen peroxide to destroy the mercaptan, the solution acidified with nitric acid, zinc oxide added as a buffer, and the aliquot titrated with standard silver nitrate using dichlorofluorescein as indicator. Another aliquot was acidified with hydrochloric acid and titrated with standard iodine solution to determine the mercaptan content. The toluene layer was evaporated to 10 ml. on a steam-bath then in an oil-bath at 150°. The remaining crude material was shown to be bis-(butylthio)-ethane by its boiling point (160-161° at 20 mm.) and by oxidation in glacial acetic acid with 30% hydrogen peroxide to the disulfone, m. p. 179°; lit. m. p. 180°.

Table I indicates the products isolated by reactions carried out in refluxing toluene with a variety of chloro sulfides.

Identification of Gaseous Products. Ethylene.—This gas was uncondensed in the −78° trap. When diluted with an equal volume of air, it was insoluble in 88% sulfuric acid but dissolved completely after three passes into fuming (15%) sulfuric acid. It dissolved readily in liquid bromine, forming ethylene bromide; b. p. 129-130°, $n^{20}\text{D}$ 1.5374.

Cyclopropane.—A molecular weight determination on a sample of the gas gave a value of 42, which corresponds to C_3H_6. That it was cyclopropane and not propylene was confirmed by its reactivity toward sulfuric acid and its sluggishness toward bromine. When the gas was diluted with an equal volume of air, it dissolved rapidly in 88% sulfuric acid. Practically the entire sample dissolved in the first pass. Propylene, in contrast, requires several passes for complete solution. After twelve passes through 76% sulfuric acid, this gas was 92% absorbed, whereas a 1:1 propylene-air mixture was only 56% absorbed.

Cyclopropane also is known to react sluggishly with

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[8] Dawson, THIS JOURNAL, **55**, 2070 (1933).

[9] Clarke, *J. Chem. Soc.*, **101**, 1585 (1912).

[10] Whitner and Reid, THIS JOURNAL, **43**, 636 (1921).

[11] Walter, Goodson and Fosbinder, *ibid.*, **67**, 655 (1945).

[12] Bennett and Hock, *J. Chem. Soc.*, **127**, 2671 (1925).

[13] Steinkopf, Herold and Stöhr, *Ber.*, **53**, 1012 (1920).

[14] Kirner and Richter, THIS JOURNAL, **51**, 3413 (1929).

[15] Demuth and Meyer, *Ann.*, **240**, 310 (1887).

TABLE I

CHLOROALKYL SULFIDES AND METALS

Sulfide	Mole	Metal, g.		Time, min.	Products isolated, moles				
					Gas		RSNa	Cl^-	$RS(CH_2)_nSR$
Ethyl 2-chloroethyl	0.0231	Sodium	1.2	60	Ethylene	0.0135	0.0034	0.0231	0.0047
Butyl 2-chloroethyl	.0460	Sodium	2.3	99	Ethylene	.0258	.0084	.0460	.0204
s-Butyl 2-chloroethyl	.0200	Sodium	1.5	43	Ethylene	.0141	.0084	.0200	.0058
t-Butyl 2-chloroethyl	.0336	Sodium	1.8	90	Ethylene	.0204	.0067	.0336	.0120
Phenyl 2-chloroethyl	.0197	Sodium	2.0	72	Ethylene	.0179	.0175	.0197	....
Phenyl 2-chloroethyl	.0197	Sodium	0.7	105	Ethylene	.0139	.0089	.0196	.0049
Butyl chloromethyl	.0480	Sodium	4.0	30	Ethylene	.0010	.0032	.0483	.016[a]
					Butene	.0025			
					Saturates	.0019			
Ethyl 3-chloropropyl	.0450	Sodium	3.1	35	Cyclopropane	.0293	.023	.044	.012
Phenyl 3-chloropropyl	.0228	Sodium	2.3	63	Cyclopropane	.0135	.0158	.0230	.0038
Phenyl 4-chlorobutyl	.0186	Sodium	2.0	85	Ethylene	.0009	.0089	.0190	.0057
					Butene	.0012			
					Butane	.0039			
Phenyl 2-chloroethyl	.015	Zinc	4.2	300	Ethylene	.0061	None	.0146	....
Phenyl 2-chloroethyl	.0393	Zinc amalgam	10.0	65	Ethylene	.0154	None	.0391	-
2-Chloroethyl	.0035	Sodium	1.8	720	Ethylene	.0052	....	....	[b]
3-Chloropropyl	.0094	Sodium	1.6	30	Cyclopropane	.0093	....	....	[c]

[a] Also found 0.0004 mole of bis-(butylthio)-ethane and 0.2 g. of high boiling hydrocarbon. [b] Mostly bis-(phenylthio)-ethane but also an unidentified solid. [c] Polymers.

bromine. This gas reacted slowly with bromine even when irradiated. The dibromide formed could not have been propylene bromide (b. p. 141°), since it boiled above 150°. 1,3-Dibromopropene boils at 167°. The quantity of dibromide at hand was not purified rigorously.

1-Butene from Butyl Chloromethyl Sulfide.—The gas which collected in the −78° trap boiled at −5.0 to −4.0° (745 mm.). A Siwoloboff micro method[16] was used in this determination, on an 80-cc. sample of material. The gas also was absorbed in 88% sulfuric acid and was absorbed readily by bromine to yield 1,2-dibromobutane.

Butane from Phenyl 4-Chlorobutyl Sulfide.—This gas was unabsorbed in fuming sulfuric acid. Its boiling point was −1.0 to −0.6° by the Siwoloboff micro method. The H:C ratio was determined by combustion analysis to be 0.206. That calculated for C_4H_{10} is 0.208, and for C_4H_8 is 0.166, thus confirming its identity as butane, not cyclobutane.

2-Chloroethyl Sulfide and Sodium.—When 1.8 g. of sodium wire and 40 ml. of toluene was heated to gentle boiling, the sodium formed a pliable, molten wire. A 0.5518-g. sample of 2-chloroethyl sulfide was introduced and rinsed into the flask with two 10-ml. portions of dry toluene. The sodium turned blue. About 115 cc. (S. T. P.) of ethylene was collected in twelve hours.

Similarly, from 18 g. of the sulfide, 10 g. of sodium wire and 150 ml. of butyl ether kept at 80° for eight hours, there was collected 1996 cc. (S. T. P.) of ethylene.

The solid product from these reactions was processed by decanting the solvent, adding alcohol if an excess of sodium was used, then washing with water. Alcohol did not change the blue color, but water decolorized it to pale yellow; m. p. 158–160°.

Several conditions were studied using ether as solvent. A typical run involved refluxing a mixture of 63 g. of 2-chloroethyl sulfide (14 g. recovered), 350 g. of absolute ether, 0.5 g. of ethanol and 20.5 g. of sodium sand for six days. The ethylene was not collected. After decanting the ether, water was added thereby turning the blue solid yellow. It was rinsed thoroughly with acetone, and dried; m. p. 158–160°; yield, 4.2 g. It contained no ash and was insoluble in all the common solvents to less than 0.1% at 100°. These solvents included alcohols, ethers, esters, hydrocarbons, alkyl or aryl chlorides, ketones, nitriles, aniline, nitromethane, nitrobenzene, but was soluble at 170° in aniline, nitrobenzene or camphor.

Anal. Calcd. for $(C_2H_4S)_n$: C, 39.96; H, 6.70; S, 53.33. Found: C, 40.31; H, 6.67; S, 52.35.

Oxidation by Nitric Acid.—A mixture of 3 ml. of concentrated nitric acid and 0.8 g. of this solid was heated on a steam-bath for twenty minutes. Oxides of nitrogen were evolved vigorously at first. Excess nitric acid was removed by adding alcohol. Alcohol caused separation of a yellow precipitate. It was dissolved in 10 ml. of hot water, and reprecipitated by 10 ml. of hot acetone; yield, 0.6 g., m. p. 168–169°. After drying at 100° (30 mm.), it was analyzed.

Anal. Calcd. for $(C_2H_4SO)_n$: C, 31.6; H, 5.28; S, 42.1. Found: C, 31.56; H, 5.27; S, 35.33; neut. equiv., 420, 475, 487.

A terminal sulfonic acid group is suggested by the neutral equivalent. The compound reacted in aqueous solution with aniline to form a salt, m. p. 180–181° dec., precipitated by acetone.

Oxidation by Hydrogen Peroxide.—No solution occurred when 1.17 g. of the solid (m. p. 158–160°), 10 g. of glacial acetic acid and 10 ml. of 30% hydrogen peroxide were heated together for a few minutes but the solid changed to 1.34 g. of a substance of m. p. 312°. It was insoluble in water, alcohol, furfural, acetone or benzene.

Anal. Calcd. for $(C_2H_4SO_2)_n$: C, 26.2; H, 4.35; S, 34.8. Found: C, 26.14; H, 4.94; S, 31.92.

3-Chloropropyl Sulfide.—Butyl ether or toluene were used as solvents. In a typical run, 3.6 g. of sodium wire, 50 ml. of toluene and 4.2 g. of 3-chloropropyl sulfide were heated to gentle refluxing for thirty minutes. The products included 390 cc. (S. T. P.) of cyclopropane, and 0.75 g. of a water-insoluble, benzene-soluble, halogen-free solid of m. p. 55–61°. It was purified by dissolving in chloroform, adding acetone, and partially evaporating; m. p. 56–57°.

Anal. Calcd. for $(C_3H_6S)_x$: C, 48.65; H, 8.10. Found: C, 48.69; H, 8.10; mol. wt. (ebullioscopically in benzene), 2020.

1,2-Bis-(phenylthio)-ethane.—A solution of 0.760 g. of this compound in 10 ml. of toluene was added to a boiling mixture of 50 ml. of toluene and 1.4 g. of sodium wire. The ethylene evolved during three and one-half hours was 41 cc. (S. T. P.). From the reaction flask, 0.21 g. of the

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[16] Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1938, p. 51.

starting material was recovered, and 0.42 g. of thiophenol was identified by titration with iodine. Thus one mole of ethylene was formed for each two of thiophenol.

Acknowledgments.—Combustion microanalyses for C, H or N were performed by Margaret Ledyard, Patricia Craig, Margaret Hines and Jean Gibbs. Assistance given by Lawrence Buckles of the Chemical Corps eased many of the difficulties.

Summary

The reaction of chloroalkyl sulfides with sodium in inert solvents has been shown to be a general reaction. Examples were studied where n in the formula $RS(CH_2)_nCl$ represented 1, 2, 3 and 4. Ethylene is evolved when $n = 2$, cyclopropane when $n = 3$, and n-butane together with ethylene and butene when $n = 4$. Mixed gases were formed also when $n = 1$. Mercaptans and bis-(alkylthio)-alkanes, $RS(CH_2)_nSR$ were formed but practically none of the products which would have been predicted by the Wurtz reaction. 2-Chloroethyl ether also evolves ethylene in reaction with sodium.

Polymers were important products from the reactions involving 2-chloroethyl sulfide and 3-chloropropyl sulfide. The statements in the literature regarding the non-reactivity of mustard gas towards sodium need revision.

Zinc and zinc amalgam also cause liberation of ethylene from the 2-chloroalkyl sulfides.

EVANSTON, ILLINOIS RECEIVED APRIL 16, 1949

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORIES OF THE UNIVERSITY OF FLORIDA]

Dimercaptols of Acetonylacetone. II[1]

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With four exceptions, the normal dimercaptols of acetonylacetone, methyl through n-dodecyl, have been recorded.[2,3] The present paper describes the properties of the remaining four: n-amyl, n-heptyl, n-nonyl, and n-undecyl, as well as the preparation and properties of the sulfone and the mercuric chloride addition product derived from each member of the series.

The four dimercaptols were prepared in approximately 75% yield by the interaction of acetonylacetone and the mercaptan under the influence of hydrogen chloride according to the directions previously described.[3] The properties and analyses of the products are shown in Table I, and the melting points of the series are plotted in Fig. 1. Two observations should be made with regard to the series: Lengthening of four chains has the same effect as the lengthening of one chain in an ordinary homologous series, and a reversal of alternation of melting point occurs at the nonyl dimercaptol.

TABLE I

MELTING POINTS AND ANALYSES OF THE DIMERCAPTOLS, $CH_3C(SR)_2CH_2CH_2C(SR)_2CH_3$

Mercaptol	M. p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Amyl[a]	6.5	$C_{26}H_{54}S_4$	63.09	62.90	11.00	11.00
n-Heptyl	31	$C_{34}H_{70}S_4$	67.26	67.26	11.62	11.64
n-Nonyl	50	$C_{42}H_{86}S_4$	69.16	69.05	11.88	11.56
n-Undecyl	61	$C_{50}H_{102}S_4$	72.20	71.83	12.37	12.27

[a] d^{25}_4 0.9572. n^{25}_D 1.5098. Calcd. M_D, 154.2. Found: M_D 154.6.

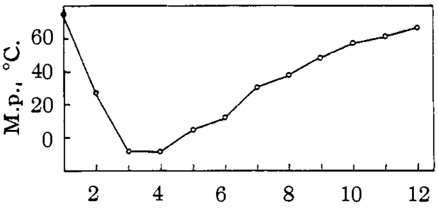

Fig. 1.—Melting points of the mercaptols plotted against the number of carbons in the alkyls.

Early attempts at the preparation of the sulfones were directed at the preparation of the sulfoxides as intermediates, but bromine oxidation failed to yield crystalline products. Hence the sulfones were prepared directly by use of permanganate or by acetic anhydride-catalyzed perhydrol oxidation. Yields of the sulfones were uniform and approximated 30%. The melting points and analyses of the sulfones are shown in Table II; the graph of the melting points in Fig. 2.

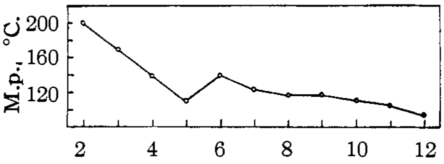

Fig. 2.—Melting points of the sulfones plotted against the number of carbons in the alkyls.

The mercuric chloride addition products were readily obtained by mixing diethylcarbitol solutions of the mercaptol and of mercuric chloride in molecular proportions 1:8, respectively.

The constitution of the mercuric chloride addition product is a function of the chain length. Maximum addition of eight mercuric chloride molecules per molecule of dimercaptol occurs with the

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(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Oak Ridge, Tenn., June 11, 1949.

(2) Posner, *Ber.*, **33**, 2983–2993 (1900).

(3) Rietz, Chapman and Fernandez, THIS JOURNAL, **70**, 3486 (1948).