67. *The Preparation and Reactions of Aliphatic and Alicyclic Ethylene Sulphides.*

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The aliphatic ethylene sulphides often undergo the same ring-opening reactions as do the ethylene oxides, but polymerisation usually prevents the isolation of much of the initial product of ring fission. However, good yields of 2-chlorothiols and 2-chlorothio-esters are obtained by reaction with concentrated hydrochloric acid and acyl chlorides; potassium thioalkoxides and potassium hydrogen sulphide combine readily to form the expected mercapto-sulphides and dithiols; and acetic acid gives a low yield of the 2-mercaptoalkyl acetate.

A characteristic feature of aliphatic ethylene sulphides is the inability of the 3-membered ring to exist with the sulphur atom in the higher-valent state; ring opening always occurs when the preparation of these derivatives is attempted. Sulphoxides and sulphones are not formed, and triethyl- and triphenyl-phosphine and triethyl phosphite remove the sulphur atom to form the ⋮P⁚S compound. Methyl iodide breaks up ethylene sulphides, the larger ones giving good yields of trimethylsulphonium iodide, the smaller ones mixtures of salts containing small amounts of this iodide.

The only survey of ethylene sulphides seems to be in the monograph by A. Schönberg in Ahrens Vorträge, Heft 19, Enke, 1933, on "Thioketone, Thioacetale und Aethylensulfide," where, however, the section (pp. 66 to 72) on ethylene sulphides is almost entirely confined to aromatic derivatives.

It has latterly been realised that ethylene sulphides may have industrial applications, *e.g.*, as synthetic polymers, and during the last eight years the results of some technical studies have been described in patents. The present investigation of aliphatic ethylene sulphides deals partly with their preparation, but is chiefly concerned with their reactions and properties, many of which could not have been deduced, by analogy, from a knowledge of the chemistry of ethylene oxides.

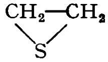
Preparation of Ethylene Sulphides.—The first preparations of authentic ethylene sulphides are due to Delépine (*Bull. Soc. chim.*, 1920, **27**, 740), Delépine and Jaffeux (*ibid.*, 1921, **29**, 136), and Delépine and Eschenbrenner (*ibid.*, 1923, **33**, 703), who obtained small yields by sodium sulphide treatment of ethylene halothiocyanates or dithiocyanates. This process has been applied by Calingaert (*Bull. Soc. chim. Belg.*, 1922, **31**, 109) and by Youtz and Perkins (*J. Amer. Chem. Soc.*, 1929, **51**, 3508) to make tri- and tetra-methylethylene sulphides. A generally better preparative method is the conversion of ethylene oxides into their sulphur analogues by the use of thiourea, first reported by Dachlauer and Jackel (D.R.-P. 636,708) and extended by Culvenor, Davies, and Pausacker (*J.*, 1946, 1050). It is suitable, however, only for those oxides which have no strongly polar group, such as the carbonyl, next to the oxide ring. High yields are claimed by Coltof (U.S.P. 2,183,860, 1939; B.P. 508,932) by treating 2-chloroethylthiols with weakly alkaline buffered solutions to give ethylene sulphides with little of the polymers which earlier workers had found to be the chief product when concentrated alkali was used. A still more recent method doubtless capable of extension is the dehydration by heat of 1 : 2-dithioglycerol to give mercaptopropylene sulphide (Lazier and Signiago, 1946, U.S.P. 2,396,957). The direct production of ethylene, propylene, and *cyclo*hexene sulphides (Jones and Reid, *J. Amer. Chem. Soc.*, 1938, **60**, 2452) by heating the corresponding olefin with ethyl tetrasulphide—which may provide atomic sulphur—unfortunately gives small yields. In the course of the present investigation it has been found that *cyclo*hexene is not converted into its sulphide by being heated at 440° with molecular sulphur in " Pyrex," and from 440° to 630° in silica with and without iron pyrites as catalyst. The direct catalytic method of synthesis, so valuable in the case of ethylene oxide, is obviously restricted where sulphur compounds are concerned.

The present work on ethylene sulphides makes some statements in the literature seem of questionable value. The preparations of derivatives of ethylene sulphides claimed by Michael (*Ber.*, 1895, **28**, 1633) and Troeger and Hornung (*J. pr. Chem.*, 1897, **56**, 45) are open to doubt from internal evidence. Also we have been unable to repeat the preparation of " αβ-thiocrotonic acid " of Ray and Dey (*J.*, 1917, **111**, 510), and we find that *cyclo*hexene sulphide, b. p. 67—68°/16 mm., can be distilled without difficulty, despite the statement by Mousseron (*Compt. rend.*, 1942, **215**, 201).

Reactions of Ethylene Sulphides.—An outstanding property of ethylene sulphides is the ease, far more pronounced than with ethylene oxides, with which polymers are formed. Delépine and his co-workers were the first to show that lower members of the series gave polymers at ordinary temperatures with water containing traces of acid or alkali.

*cyclo*Hexene sulphide forms polymers in alcohol or aqueous alcohol with hydrazine, hydroxylamine, guanidine, and *o*-aminothiophenol, as well as with other reagents which react normally with ethylene oxides.

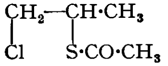
The polymers unavoidably made in the course of the present work vary from viscous distillable liquids to hard non-volatile solids of high molecular weight. The tendency of pure ethylene sulphides to polymerise (which is less pronounced with higher members of the series), according to Coltof and Langedijk (U.S.P. 2,185,660, 1940) can be checked by the presence of hydrogen sulphide and its derivatives, though not by the presence of ordinary antoxidant stabilisers such as quinol. The unit of the polymer from ethylene sulphide itself (I) is probably largely (II).



(I.)

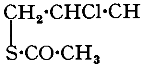
$(CH_2{\cdot}CH_2{\cdot}S)_n$

(II.)



$\begin{array}{ll} CH_2 & CH{\cdot}CH_3 \\ Cl & S{\cdot}CO{\cdot}CH_3 \end{array}$

(III.)



$\begin{array}{l} CH_2{\cdot}CHCl{\cdot}CH_3 \\ S{\cdot}CO{\cdot}CH_3 \end{array}$

(III*a*.)

The polymerisation action of acids can sometimes be controlled by a suitable choice of the conditions of the reaction. An example is the reaction with hydrochloric acid. Delépine (*loc. cit.*), showed that dilute hydrochloric acid instantly polymerised ethylene sulphide to an amorphous powder, whereas the concentrated acid gave a 33% yield of 2-chloroethanethiol. It is now found that excess of concentrated hydrochloric acid at room temperature converts *cyclo*hexene and chloropropylene sulphides into the 2-chlorothiols in 57% and 72% yields respectively, if the reaction mixture is homogenised by mechanical shaking, while polymer is the major product if the reaction is carried out (*a*) at the boiling point, (*b*) by mixing without thorough shaking, or (*c*) by passing hydrogen chloride gas into the sulphide.

Sulphuric acid, dilute or concentrated, appears to exert only a polymerising influence, though this may be due to the instability of the monothioethylene glycol product to acid (cf. Bennett, *J.*, 1922, **121**, 2144). With excess of boiling glacial acetic acid, *cyclo*hexene sulphide gives 2-*mercapto*cyclo*hexyl acetate* and 2-*mercapto*cyclo*hexyl* 2-*acetoxy*cyclo*hexyl sulphide*.

Acetyl chloride combines readily with ethylene sulphides at ordinary temperatures to give excellent yields of the 2-chloro-thiolacetates. In this way *cyclo*hexene sulphide gives 2-*chloro*cyclo*hexyl thiolacetate*. The question whether the *chloropropyl thiolacetate* from propylene sulphide, and the *dichloropropyl thiolacetate* from chloropropylene sulphide are derivatives of *iso*propylthiol (as III) or of *n*-propylthiol (as III*a*) is under investigation. Benzoyl chloride reacts more slowly than acetyl chloride with propylene sulphide, and gives a high yield of a 2-*chloropropyl thiolbenzoate*. Aldermann, Brubaker, and Hanford (U.S.P. 2,212,141, 1940) have already converted ethylene sulphide itself into 2-chloroethyl thiolacetate and 2-acetoxyethyl thiolacetate, by the action of acetyl chloride, and of acetic anhydride with pyridine, respectively. We find that the ethylene sulphides used (chiefly propylene and *cyclo*hexene sulphides) merely form polymers with the following halogen compounds: benzoyl fluoride, picryl chloride, 3 : 5-dinitrobenzoyl chloride, triphenylmethyl chloride, and toluene-*p*-sulphonyl chloride and fluoride.

*cyclo*Hexene sulphide is polymerised by aqueous alkali and by excess of concentrated aqueous ammonia, but reacts with methylaniline to form 2-*methylanilino*cyclo*hexylthiol*. The nature of the product and also the catalytic effect on the reaction of hydroxy-compounds such as ethanol, clearly bring out the analogy between ethylene oxides and sulphides. Reppe and Nicolai (D.R.-P. 631,016; "Friedländer," XXIII, 244) describe the reaction of ethylene and propylene sulphides at high temperatures with primary and secondary amines, and the expected 2-aminothiol is the chief product. Organometallic compounds also seem to react in the expected way; thus ethylene sulphide and diethylaminelithium give 2-diethylaminoethylthiol (Gilman and Woods, *J. Amer. Chem. Soc.*, 1945, **67**, 1843).

It has recently been shown (Culvenor, Davies, and Heath, preceding paper) that ethylene oxides are remarkably reactive with soluble metallic derivatives of R•SH, and ethylene sulphides are now found to be similarly reactive. Potassium hydrogen sulphide converts *cyclo*hexene and propylene sulphides into the corresponding dithiols, while from chloropropylene sulphide is obtained a small amount of trithioglycerol. Simple alkali thioalkoxides also combine with *cyclo*hexene sulphide, and in this way are obtained *ethyl* and tert.-*butyl* 2-*mercapto*cyclo*hexyl sulphides*; in each case considerable amounts of higher condensed products were formed.

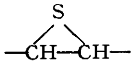
It is now seen that the powerful polymerising action of sodium hydroxide or other strongly alkaline reagents (NaX) is due to the conversion of a molecule of ethylene sulphide into $NaS{\cdot}CH_2{\cdot}CH_2X$, which then opens another sulphide ring to form $NaS{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2X$, a long chain then being rapidly formed. Such polymerisation with alkaline reagents can be prevented when the reagent (*e.g.*, potassium xanthate) is so constituted that the condensation product with one molecule of ethylene sulphide can yield a stable cyclic compound such as trithiocarbonate (Culvenor, Davies, and Pausacker, *loc. cit.*).

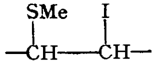
Some very recent technical applications of ethylene sulphides are noteworthy. Barr and Speakman (*J. Soc. Dyers and Col.*, 1944, **60**, 238) and Blackburn and Phillips (*ibid.*, 1945, **61**, 203) describe the modification of wool fibres with ethylene sulphide, and Lazier and Signiago (*loc. cit.*) combine mercaptopropylene sulphide with both natural and synthetic polymers. From the foregoing account of ethylene sulphides it is clear that they may be capable of reacting with the amino- or thiol groups in natural proteins such as wool, or with the hydroxy-groups (causing polymerisation) in cellulose fibres.

A characteristic unsuspected property of the ethylene sulphide ring is its inability to exist in a stable condition when the sulphur atom has a higher valency than two. The only authentic instances of such compounds are the very unstable tetraphenylethylene sulphone of Staudinger and Pfenninger (*Ber.*, 1916, **49**, 1946) and the equally unstable diphenyldiethylethylene sulphones of Vargha and Kovacs (*Ber.*, 1942, **75**, 794). All these were prepared from sulphur dioxide and the corresponding substituted diazomethane. The instability of these sulphones contrast with the stability of the sulphones, formed by direct oxidation, of 3 : 4-diphenyl- and tetraphenyl-thiophens (Hinsberg, *Ber.*, 1915, **48**, 1612). The present investigations show that whereas thiophens do not form higher-valent sulphur derivatives other than sulphones, the sulphur in aliphatic ethylene sulphides is most prone to become higher-valent, but the three-membered ring undergoes fission in the process. Thus thiophen and ethylene sulphides are anomalous, though for different reasons.

*cyclo*Hexene and 4-methyl*cyclo*hexene sulphides slowly react at ordinary temperature with a slight excess of methyl iodide to form, in about 50% yield, trimethylsulphonium iodide (VII). This is also formed from chloropropylene sulphide and propylene sulphide, in the latter case only when a large excess of methyl iodide is used. The reaction with ethylene sulphide has been studied by Delépine (*Bull. Soc. chim.*, 1920, **27**, 743), who isolated a salt of the approximate composition $(C_2H_4S)_3,CH_3I$. The anlysis did not agree with this or any other formula, and the product is undoubtedly a mixture. These statements apply equally to Delépine and Jaffeux's product (*loc. cit.*) from propylene sulphide and methyl iodide.

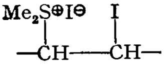
Trimethylsulphonium iodide is formed less easily from low-molecular ethylene sulphides than from higher ones. It is known that the iodine in higher aliphatic iodides is generally less reactive than in lower ones, and consequently, when *cyclo*hexene sulphide is used, the derived iodide (IV) will be inert compared with methyl iodide. Hence (VII) will be ultimately formed;





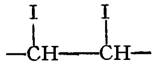
$-\overset{SMe}{CH}-\overset{I}{CH}-$

(IV.)



$-\overset{Me_2S^{\oplus}I^{\ominus}}{CH}-\overset{I}{CH}-$

(V.)



$-\overset{I}{CH}-\overset{I}{CH}-$

(VI.)

+ Me_3SI

(VII.)

but when, say, propylene sulphide is used with only a small excess of methyl iodide, the selective action of the latter on (IV) will not be so pronounced, because it will now be in competition with the moderately reactive methyl iodopropyl sulphide (as IV). This could react with itself, or with unchanged propylene sulphide, and so form a complex mixture of salts (see p. 287). This effect would be diminished by increasing the proportion of methyl iodide, and, in fact, (VII) can be isolated only when a large excess (20 to 30 mols.) of methyl iodide is used. The above considerations explain why Delépine (*loc. cit.*) obtained a mixture of salts from ethylene and propylene sulphides and methyl iodide.

The formation of trimethylsulphonium iodide from the interaction of thioethers and methyl iodide is described by Ray and Levine (*J. Org. Chem.*, 1937—1938, **2**, 267), and further references to this type of fission are Farmer and Shipley (*J. Polymer Sci.*, 1946, **1**, 293; *J.*, 1947, 1531) and Naylor (*J.*, 1947, 1107). It is abundantly clear from the present investigation that, when a thio-compound and methyl iodide form a simple addition compound, :SMeI, this clearly indicates that the original thio-compound was not an ethylene sulphide. Thus the product, $C_{10}H_{16}S$, from pinene and sulphur is unlikely to have the ethylene sulphide ring assumed by Budnikoff and Schilow (*Ber.*, 1922, **55**, 3850) because they show that methyl iodide forms $C_{10}H_{16}S$,MeI. Similarly, the methyl iodide method of examining the sulphur linkage in vulcanised rubber (Westlake, *Chem. Reviews*, 1946, **39**, 233; Selker and Kemp, *Ind. Eng. Chem.*, 1944, **36**, 22) now requires reconsideration in view of the possibility of the presence of ethylene sulphide groups.

The reaction between methyl iodide and ethylene sulphides has a very limited analogy in the ethylene oxide series, where the conditions have to be drastic to bring about any reaction at all. The oxide ring can be opened; *e.g.*, methyl iodide with epichlorohydrin at 190° for 5 hours gives $CH_2Cl{\cdot}CHI{\cdot}CH_2{\cdot}OMe$ (Paul, *Ber.*, 1888, **21**, 2971), and with *cyclo*hexene oxide at 150—160° for 48 hours gives 2-iodo*cyclo*hexyl methyl ether (Bedos, *Compt. rend.*, 1926, **183**, 563).

Ethylene sulphides react at ordinary temperatures with chloramine-T to form opaque, thick liquids but no sulphilimine. Ethylene, propylene, chloropropylene, *iso*butylene, and *cyclo*hexene sulphides at ordinary temperatures lose their sulphur to triethylphosphine, the crystalline triethylphosphine sulphide being isolated. Similarly triphenylphosphine sulphide and triethyl thiophosphate are formed by interaction of *cyclo*hexene sulphide with triphenylphosphine and triethyl phosphite respectively. *cyclo*Hexene and propylene sulphides give viscous liquids with methyl sulphate, and the former reacts with chlorine in carbon tetrachloride to form 1 : 2-dichloro*cyclo*hexane, together with polymeric material. Hydrogen peroxide reacts very readily with ethylene sulphides (the explosive "peroxide" of acetone is formed when acetone is used as solvent), but sulphoxides or sulphones cannot be isolated by the use of either aqueous peroxide or permanganate. Delépine and Eschenbrenner (*loc. cit.*) have shown that oxidation of ethylene sulphide with concentrated nitric acid leads to sulphoacetic acid, $SO_3H{\cdot}CH_2{\cdot}CO_2H$, and other more condensed acids of which the acid

$$SO_3H{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H$$

was characterised.

An instantaneous reaction is given with aqueous mercuric salts, but as the precipitates cannot be purified they have little theoretical implication. All the above experiments, carried out with the object of making derivatives of ethylene sulphides in which the higher valency of sulphur is invoked, can be explained by the fission of the ethylene sulphide ring.

EXPERIMENTAL.

Opening of Ethylene Sulphides by Hydroxy-compounds.—At ordinary temperatures, ethylene sulphides are fairly stable to neutral water and alcohols. However, ethylene sulphides instantly produce nitrogen when treated with aqueous sodium azide and iodine, showing that at least a trace of a thiol is immediately formed (Feigl, "Spot Tests," Nordemann, 1937, p. 241; *Z. anal. Chem.*, 1928, **74**, 369). Propylene sulphide, heated with 2 mols. of water at 100° for 17 hours in a sealed tube, forms a mixture of products, some of which can be distilled at high temperatures. The same conditions with absolute ethyl alcohol give similar though more fragrant products, and in both experiments a considerable gas pressure is produced.

2-*Chloro*cyclo*hexylthiol*, b. p. 83°/20 mm., $n_D^{20^\circ}$ 1·5015, is obtained when *cyclo*hexene sulphide (10 g.) is shaken continuously with concentrated hydrochloric acid (100 ml.) for twelve hours, and the product extracted with chloroform, washed once with water, dried, and distilled. Yield, 7·5 g.; 57% (Found: C, 48·2; H, 7·4. $C_6H_{11}ClS$ requires C, 47·8; H, 7·3%). The oil liberates carbon dioxide very slowly from sodium hydrogen carbonate solution, and is converted into *cyclo*hexene trithiocarbonate by potassium xanthate. Similarly, a *dichloropropylthiol*, b. p. 81°/33 mm. (9·6 g.; 72% yield), of which the structure is under investigation, is formed when chloropropylene sulphide (10 g.) and concentrated hydrochloric acid (120 ml.) are shaken for 12 hours and worked up as above (Found: S, 22·4. $C_3H_6Cl_2S$ requires S, 22·1%).

Acetic Acid and cyclo*Hexene Sulphide*.—*cyclo*Hexene sulphide (5 g.) and glacial acetic acid (15 ml.) are rapidly mixed in the cold and added as quickly as possible to boiling glacial acetic acid (20 ml.) through the condenser. The addition is regulated so that the mixture remains boiling, and, when complete, the refluxing is continued for 45 minutes. Fractionation of the product gives, after a small low fraction, 2-*mercapto*cyclo*hexyl acetate* (2 g., 26%), b. p. 109°/15 mm. (Found: C, 55·6; H, 8·33. $C_8H_{14}O_2S$ requires C, 55·2; H, 8·05%), and 2-*mercapto*cyclo*hexyl* 2-*acetoxy*cyclo*hexyl sulphide* (3 g., 48%), b. p. 165°/0·7 mm. (Found: C, 57·9; H, 8·5. $C_{14}H_{24}O_2S_2$ requires C, 58·3; H, 8·3%), with very little higher-boiling residue. The low fractions redistilled four times gave each time a pink distillate, which became colourless after 30 minutes.

To ensure that the oil of b. p. 109°/15 mm. was not the diacetyl derivative, the latter compound was made by acetylation of 2-mercapto*cyclo*hexanol (Culvenor, Davies, and Heath, *loc. cit.*). 2-Mercapto*cyclo*hexanol (5 g.) was dropped slowly into acetyl chloride (7·5 g., 50% excess) with cooling, and the mixture heated for 2 hours at 50° under reflux. Distillation yielded 2-*mercapto*cyclo*hexanol diacetate* (7·6 g., 93%), b. p. 145°/19 mm. (Found: S, 15·0. $C_{10}H_{16}O_3S$ requires S, 14·81%).

Addition of Potassium Hydrogen Sulphide to Sulphides.—The sulphide (0·2 mol.) is added with shaking to potassium hydrogen sulphide prepared by saturating a solution of potassium hydroxide (1·1 g.) in alcohol (12 ml.) with hydrogen sulphide at 0°. After 24 hours, the mixture is diluted with water, acidified, and extracted with chloroform. Propylene sulphide gives propylenedithiol (0·5 g.), b. p. 72—74°/55 mm., *cyclo*hexene sulphide gives *cyclo*hexenedithiol (1·1 g., 38%), b. p. 97°/15 mm. (Culvenor and Davies, *Australian J. of Scientific Research*, 1948, **1**, 236), while from chloropropylene sulphide and excess of potassium hydrogen sulphide is obtained a small amount of trithioglycerol, b. p. 112—120°/14 mm., identified by conversion into the trimethyl ether trisulphone, m. p. 203° (Rheinboldt and Tetsch, *Ber.*, 1937, **70**, 675).

Addition of Thioalkoxides to Ethylene Sulphides.—Free thiols do not easily open the ethylene sulphide ring; *e.g.*, *cyclo*hexene sulphide and ethylthiol, after being heated in a sealed tube at 120° for 6 hours, are recovered unchanged except for a very small amount of non-distillable oil. In the presence of a mol. of alkali, however, reaction occurs readily. *cyclo*Hexene sulphide (5·5 g.) is added with shaking to a solution prepared by adding the thiol in small excess to alcoholic potassium hydroxide (2·8 g.) in alcohol (15 ml.). The mixture is cooled till no more heat is evolved, then left overnight and worked up as in the potassium hydrogen sulphide reaction. Ethylthiol gives in this way 2-*mercapto*cyclo*hexyl ethyl sulphide* (4·7 g., 55%), b. p. 124°/20 mm. (Found: C, 54·4; H, 8·9. $C_8H_{16}S_2$ requires C, 54·5; H, 9·16%), and 2-*mercapto*cyclo*hexyl* 2-*ethylthio*cyclo*hexyl sulphide* (1·8 g., 30%), b. p. 152°/0·25 mm. (Found: C, 57·6; H, 9·1. $C_{14}H_{26}S_3$ requires C, 57·9; H, 9·03%). *tert.*-Butylthiol gives 2-*mercapto*cyclo*hexyl* tert.-*butyl sulphide* (2·5 g., 25%), b. p. 133°/12 mm. (Found: C, 58·5; H, 9·8. $C_{10}H_{20}S_2$ requires C, 58·8; H, 9·8%), and 2-*mercapto*cyclo*hexyl* 2-tert.-*butylthio*cyclo*hexyl sulphide* (2·0 g., 25%), b. p. 187—188°/1 mm. (Found: C, 59·9; H, 9·3. $C_{16}H_{30}S_3$ requires C, 60·4; H, 9·4%). Polymeric material is formed in all these reactions, and this is the only product when mercaptobenzthiazole is used.

Acyl Chlorides and Ethylene Sulphides.—Addition is effected by mixing the sulphide and acyl chloride in equimolecular amounts with cooling when necessary. After being left overnight, the product is distilled. Propylene sulphide and acetyl chloride give a *chloropropyl thiolacetate*, b. p. 84·5°/21 mm. (Found: C, 39·0; H, 5·5. C_5H_9OClS requires C, 39·5; H, 5·9%); propylene sulphide and benzoyl chloride give a *chloropropyl thiolbenzoate*, b. p. 117°/0·2 mm. (Found C, 56·15; H, 5·05. $C_{10}H_{11}OClS$ requires C, 56·1; H, 5·3%). *cyclo*Hexene sulphide and acetyl chloride give 2-*chloro*cyclo*hexyl thiolacetate*, b. p. 110°/20 mm. (Found: Cl, 18·5. $C_8H_{13}OClS$ requires Cl, 18·4%); and chloropropylene sulphide and acetyl chloride combine with very little heat evolution to form a *dichloropropyl thiolacetate*, b. p. 115°/18 mm., $n_D^{20^\circ}$ 1·5157 (Found: C, 32·0; H, 4·28. $C_5H_8OCl_2S$ requires C, 32·1; H, 4·28%).

2-*Methylanilino*cyclo*hexylthiol* (2 g.; 50% yield), a yellow oil, b. p. 175°/16 mm., is formed when *cyclo*hexene sulphide (2 g.) and methylaniline (2 g.) are refluxed in 80% alcohol (15 ml.) for 8 hours, poured into water, and extracted with ether (Found: S, 14·7. $C_{13}H_{19}NS$ requires S, 14·5%). It is not obtained when the reactants are heated at 100° for 24 hours without a solvent.

Reaction of Ethylene Sulphides with Methyl Iodide.—cyclo*Hexene sulphide*. *cyclo*Hexene sulphide (1·1 g.) is mixed with dry methyl iodide (1·5 g.) and left at room temperature. After 48 hours the dark brown solid containing iodide is filtered off, washed with dry acetone, and recrystallised from absolute alcohol to give white needles of trimethylsulphonium iodide, m. p. 215°. If excess of methyl iodide (5 g.) be used, after 2 weeks the yield of trimethylsulphonium iodide is 1 g. (50%) (Found: I, 62·8; S, 15·2. Calc. for C_3H_9SI: I, 62·3; S, 15·6%). The iodide gave no m. p. depression on admixture with an authentic specimen. No success met attempts to isolate the unknown 1 : 2-di-iodo*cyclo*hexane from the reaction mixture. Similarly 4-methyl*cyclo*hexane sulphide (1·2 g.) gave 1·0 g. of trimethylsulphonium iodide.

Chloropropylene sulphide. Chloropropylene sulphide (1·1 g.) is refluxed with excess (5 g.) of dry methyl iodide. Trimethylsulphonium iodide slowly crystallises from the reaction mixture and is obtained pure by the procedure above. The reaction occurs also at room temperature, but is much slower than that of *cyclo*hexene sulphide.

Propylene sulphide. Propylene sulphide, left at room temperature with a moderate excess of dry methyl iodide, deposits a white, unstable, crystalline salt which decomposes in the range 70—90°. This material soon decomposes if left in the air, and although it can be recrystallised from absolute alcohol by working quickly, or by solution in absolute alcohol and precipitation with dry ether, consistent analyses are not obtained. A series of products gave (Parr bomb process with Na_2O_2) I from 41·2% to 68·5%, and S, on one sample only, 7·7%. Delépine (*loc. cit.*) found I, 47·7%. The simple addition formula C_3H_6S,CH_3I, requiring I, 58·8; S, 14·8%, as well as more complex addition formulæ, are clearly untenable. If the reaction time is prolonged no crystalline material is obtained, the darkening is more pronounced, and, if the reaction mixture is tightly stoppered, a considerable gas pressure develops.

Propylene sulphide and a large excess of methyl iodide. If propylene sulphide is added in small lots (0·5 g.) daily to dry methyl iodide (140 g., about 20 mols.), after three or four additions a salt crystallises out which is much more stable. After the product has been washed with acetone and recrystallised from absolute alcohol three or four times, pure trimethylsulphonium iodide, m. p. 215°, is obtained, identified as above.

Ethylene sulphide. On being kept at room temperature with a moderate excess of methyl iodide, ethylene sulphide gives a mixture of salts decomposing about 60° (Found : S, 11·0%. Delépine gives I, 37·9%. Neither result agrees with the simple addition formula, C_2H_4S,MeI requiring I, 62·9 ; S, 15·8%, or with other possible addition formulæ).

Ethylene Sulphides and Tervalent Phosphorus Compounds.—Ethylene, chloropropylene, propylene, and *cyclo*hexene sulphides when mixed with a slight excess of triethyl phosphine and left at room temperature for 2 days, deposit needles of triethylphosphine sulphide, m. p. 90°. In the case of ethylene and propylene sulphide, cooling is necessary to avoid polymerisation, while for *iso*butylene sulphide the main product is amorphous, but, by solution in toluene and careful evaporation, some triethylphosphine sulphide can be obtained.

Triethyl phosphite (3 g.) and *cyclo*hexene sulphide (2 g.) are kept at room temperature a week, heated on the water-bath for an hour, and fractionated under reduced pressure. Triethyl thiophosphate, b. p. 104°/20 mm., is obtained as the main fraction; this is identical with a sample obtained by the method of Strecker and Spitaler (*Ber.*, 1926, **59**, 1772), who record b. p. 95·5°/12 mm.

*cyclo*Hexene sulphide (1·5 g.) and triphenylphosphine (2·6 g.) are mixed in carbon disulphide or chloroform (10 ml.); after 3 days the solvent is removed and the white solid residue recrystallised from absolute alcohol to give white needles of triphenylphosphine sulphide, m. p. 158°. This gave no m. p. depression on admixture with a sample of the sulphide prepared by the method of Michaelis *et al.* (*Ber.*, 1882, **15**, 803; *Annalen*, 1885, **229**, 307).

Reaction of cyclo*Hexene Sulphide and Chlorine.*—*cyclo*Hexene sulphide diluted with an equal volume of carbon tetrachloride is added drop by drop with cooling to a slight excess of a chlorine–carbon tetrachloride solution. After the mixture has been left overnight and distilled, a fraction, b. p. 82°/18 mm., is obtained, containing chlorine but no sulphur, and with $n_D^{18°}$ 1·4893, as well as a large amount of polymeric material which will not distil. This lower fraction on being kept with potassium hydroxide and *o*-aminothiophenol gives hexahydrophenthiazine, m. p. 81° (Culvenor, Davies, and Heath, *loc. cit.*), and hence is concluded to be 1 : 2-dichloro*cyclo*hexane which has $n_D^{16°}$ 1·4886, b. p. 187—190°/760 mm.

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