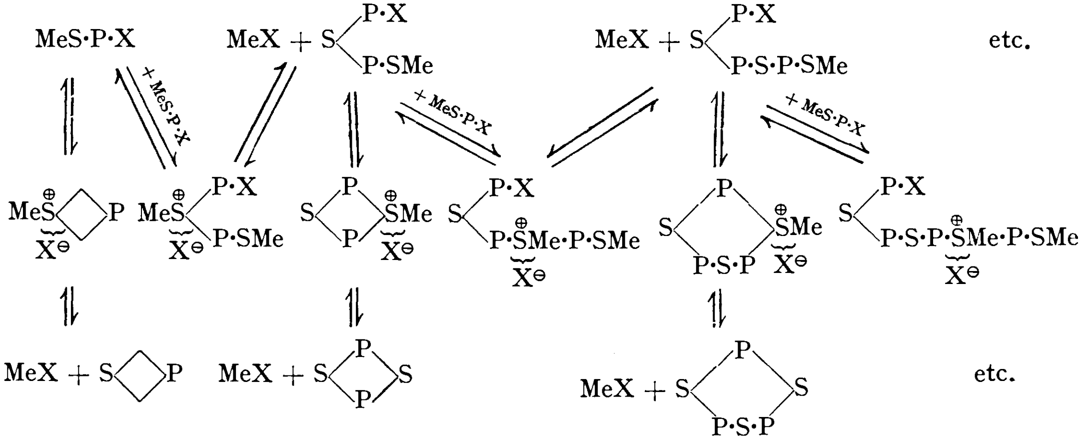
356. *The Formation of Large Ring Monosulphides from Halogenated Sulphides with Extended Carbon Chains.*

By G. M. BENNETT and HERBERT GUDGEON.

Halogenated sulphides have been synthesised in which the halogen and sulphur atoms are separated by chains of seven, eight, nine, ten, twelve, fourteen, sixteen and eighteen carbon atoms, and their behaviour on heating has been examined under various conditions. The products are usually substances of high molecular weight containing two or more atoms of sulphur per molecule, but by the use of highly diluted solutions in suitable solvents the formation of large ring polymethylene sulphides with fifteen, seventeen, and nineteen atoms in the ring has been demonstrated. The conditions necessary are, however, not suitable for a precise study of the velocities of reaction.

IN earlier papers (J., 1927, 477, 1803; 1929, 2567; this vol., p. 813) it has been shown that suitable chloro-sulphides with chlorine and sulphur atoms separated by four, five, and six carbon atoms undergo smooth ring closure at moderate temperatures in solution in aqueous acetone, but the only type of self-addition reaction found in certain other halogenated sulphides is intermolecular. Thus the product from dichlorodiethyl sulphide, after loss of ethylene dichloride, is dithian, a cyclic sulphide containing two sulphur atoms and derived from two molecules of the parent chloro-sulphide. It is evident that



self-addition of two or more molecules of a halogenated sulphide must always be liable to occur, with production of a di- or poly-sulphide, if the conditions of the reaction or the properties of the cyclic monosulphide do not favour the simple first-order reaction which leads to its formation. The foregoing scheme shows the reactions to be expected in the self-addition of a halogenated sulphide such as $MeS{\cdot}[CH_2]_n{\cdot}Cl$ (which is conveniently written as MeS·P·X, where P is a polymethylene chain and X a halogen). All the reactions are readily reversible, and the scheme should be regarded as extending indefinitely towards the right to yield more and more highly complex open-chain and cyclic products.

Recent work on the closure of rings of various types with more than seven ring-members (Ruzicka, *Helv. Chim. Acta*, 1926, **9**, 499, and subsequent papers; Stoll and others, *ibid.*, 1934, **17**, 1283; 1935, **18**, 1087; 1936, **19**, 253, 1079; Ziegler, *Annalen*, 1934, **513**, 43) has shown that the use of highly dilute solutions is the most important factor tending to the formation of a monomeric product, and in some cases good yields of large ring compounds have been obtained. We have now made use of these considerations in a study of the behaviour of halogenated sulphides with long carbon chains.

A series of methyl ω-halogenoalkyl sulphides was chosen for examination, earlier experiments having shown that self-addition of phenyl chloroalkyl sulphides is too slow, and that such reactions are more rapid with methyl than with ethyl sulphides. The required hydroxy-sulphides were prepared by the action of potassium methyl mercaptide on the chlorohydrins of the respective glycols, the isolation of which has been described (this vol., p. 1679), and from these the following halogenated sulphides have been obtained: methyl 7-chloroheptyl sulphide, methyl 8-chloro-octyl sulphide, methyl 9-chlorononyl sulphide, methyl 10-chlorodecyl sulphide, methyl 12-chlorododecyl sulphide, methyl 14-chlorotetradecyl sulphide, methyl 16-chlorohexadecyl sulphide, and methyl 18-chloro-octadecyl sulphide, together with one bromo-sulphide, namely, methyl 14-bromotetradecyl sulphide.

These substances, when heated alone or in solution, tend to yield, in accordance with expectation, polysulphides of large molecular weight derived from two to five or more molecules of the original substance, methyl halide being lost in the process. In order to examine whether the simple ring closure would take place, these halogenated sulphides were heated for long periods in solution at high dilution. For this purpose it was necessary to use a solvent of as polar a type as possible, since this would accelerate the otherwise slow addition of an alkyl chloride to a sulphide, and also to use as high a temperature as was practicable. The choice of a solvent was difficult. Water does not dissolve the substances, and the temperatures conveniently attainable with the aqueous acetone used in previous experiments were not high enough. Hydroxylic solvents such as butyl alcohol, ethylene glycol and phenol caused alcoholysis, yielding an alkoxy- or phenoxy-sulphide. Acetic acid proved useful, but the reactions at its boiling point were very slow. Subsequently, after many trials, acetophenone was adopted as solvent in spite of the fact that it undergoes self-condensation during the heating.

Simple ring-closure was detected when methyl 14-bromotetradecyl sulphide was heated for long periods in glacial acetic acid at its boiling point. By prolonging the heating the free cyclic sulphide was produced by loss of methyl bromide from the sulphonium salt, and, together with polymeric products, tetradecamethylene sulphide was isolated. Evidence was also obtained that a similar reaction was taking place still more slowly when the corresponding chloro-sulphide was subjected to similar treatment. A more convenient and less tedious method was finally adopted by which the chloro-sulphides were heated at high dilution in boiling acetophenone solution with sodium iodide until no more methyl iodide was evolved. By this means the iodo-sulphide was continuously produced in small quantities, which immediately underwent self-reaction and subsequent loss of methyl iodide. The conditions were chosen, by approximate calculation from known velocities of related reactions, so that the rate of formation of the iodo-sulphide should be of the order of one-thousandth of the velocity of the ring closure, while the degree of dilution should keep reactions of the second order to negligible dimensions. Some production of sulphides of double or treble molecular weight was apparent, but the process did in fact furnish specimens of the monomeric tetradecamethylene sulphide, *hexadecamethylene* *sulphide*, and *octadecamethylene sulphide*, which are nicely crystalline solids of low melting point, the first two of which have a pleasant smell of musk.

It is well known that the odour of musk occurs in cyclic ketones with fourteen to eighteen atoms in the ring. A number of cyclic lactones, anhydrides, and esters have been found, however, to have similar odours provided that the ring size is similar (Hill and Carothers, *J. Amer. Chem. Soc.*, 1933, **55**, 5039) and the number of atoms in the ring seems to be more important than their nature (compare Karrer, " Lehrbuch der org. Chem.," 1937, 757). Hill and Carothers regarded a keto-group as essential, since reduction of the ketones to the alcohols destroys the smell. The occurrence of the musky odour in a simple cyclic sulphide, while further illustrating the importance of ring size, shows the possibility of a wider choice of active groups than had previously been realised.

Although the production of large ring sulphides from long chain halogeno-sulphides has thus been demonstrated, the conditions found necessary are unfortunately not suitable for exact kinetic measurements.

An examination of the chloro-sulphides with seven, eight, nine, ten and twelve carbon atoms in the chain, under the conditions which were found to be most favourable for the formation of the larger rings, showed in all cases that polymeric sulphides were formed, but in no case could the simple ring sulphide be detected. This is in agreement with the observations of Ziegler (*loc. cit.*) and of Spanagel and Carothers (*J. Amer. Chem. Soc.*, 1935, **57**, 929) that rings of from eight (or nine) to thirteen members are less easily obtainable than larger ones owing, presumably, to some difficulty in packing the atoms of the chain suitably for ring closure. In a reaction such as that now studied, the isolation of the less easily formed ring compounds was not to be expected, since any sulphonium salt formed would always be liable to dissociate very readily, so that the slightly congested " transition rings " (of eight to thirteen members) would tend to reverse the initial reaction. The regenerated chloro-sulphide would again be divided between the uni- and the bi-molecular reaction, and even if a small amount of the monomeric cyclic sulphonium salt were at first formed, it might all eventually be converted into polymeric substances. The polymeric rings are all so large as to fall outside the " transition range " and so will be stable and not very liable to become reconverted into simpler substances.

The only compounds having large rings with sulphur as a member which had been described before we undertook these experiments contained more than one atom of sulphur per molecule. Autenrieth and his co-workers (*Ber.*, 1908, **41**, 4250; 1909, **42**, 4346, 4357) isolated cyclic mercaptols of acetone with dithiopentamethylene glycol and with dithio-*p*- and -*m*-xylylene glycols, the rings being of sixteen and eighteen members and each substance having four atoms of sulphur per molecule. More recently Tucker and Reid (*J. Amer. Chem. Soc.*, 1933, **55**, 775) found small quantities of cyclic tetrasulphides, with ten, fourteen, sixteen and eighteen atoms in the ring, among the products of the condensation of dithioethylene glycol and various polymethylene dibromides.

After this work had been completed the isolation of three cyclic monosulphides, having thirteen, fourteen, and fifteen members in the ring, was described by Müller and Schütz (*Ber.*, 1938, **71**, 692). These substances were prepared by the direct action of alcoholic sodium sulphide on the polymethylene dibromides.

EXPERIMENTAL.

Preparation of the Chloro-sulphides.—The requisite hydroxy-sulphide was in each case obtained in good yield by condensing the particular chlorohydrin with potassium methyl mercaptide in aqueous alcoholic solution and purifying the product by crystallisation or distillation, or both. For their conversion into the chloro-sulphides the action of thionyl chloride alone was found to be more satisfactory than in presence of a base (compare Clark and Streight, *Trans. Roy. Soc. Canada*, 1929, **23**, 77). The chloro-sulphides showed signs of decomposition when distilled at about 20 mm., so lower pressures were used. It is therefore unlikely that the bromo- or iodo-sulphides could be distilled with safety. The chloro-sulphides all yielded mercuric chloride addition compounds. These tend to give slightly high values for mercury on analysis even after repeated crystallisation (or perhaps because of this) : the method of analysis was not at fault, since entirely satisfactory values were obtained with mercuric chloride under exactly similar conditions.

Methyl 7-*hydroxyheptyl sulphide*, a colourless oil, b. p. 133—134°/10 mm. (Found: S, 19·6. $C_8H_{18}OS$ requires S, 19·8%), yielded *methyl* 7-*chloroheptyl sulphide* as a straw-coloured oil, b. p. 100—102°/3 mm. (Found: Cl, 19·8; S, 17·5. $C_8H_{17}ClS$ requires Cl, 19·6; S, 17·7%). The liquid had $d_{4^\circ}^{20^\circ}$ 0·9969, $n_D^{20^\circ}$ 1·4831, whence $[R]_D$ 51·77 (Calc., 51·98). The *mercurichloride* formed white crystals, m. p. 60—61° (Found: Hg, 45·1. $C_8H_{17}Cl_3SHg$ requires Hg, 44·4%). *Methyl* 8-*hydroxyoctyl sulphide*, a colourless liquid, b. p. 135—138°/10 mm., which solidified and crystallised from light petroleum in silvery plates, m. p. 12° (Found: S, 18·0. $C_9H_{20}OS$ requires S, 18·2%), furnished *methyl* 8-*chloro-octyl sulphide*, b. p. 113—116°/3 mm. (Found: Cl, 18·5; S, 16·3. $C_9H_{19}ClS$ requires Cl, 18·2; S, 16·5%), having $d_{4^\circ}^{20^\circ}$ 0·9849, $n_D^{20^\circ}$ 1·4821, $[R]_D$ 56·37 (calc., 56·60). The *mercurichloride* had m. p. 75° (Found: Hg, 43·5. $C_9H_{19}Cl_3SHg$ requires Hg, 43·0%). *Methyl* 9-*hydroxynonyl sulphide* formed white plates, b. p. 138—142°/9 mm., m. p. 22°, from light petroleum (Found: S, 16·6. $C_{10}H_{22}OS$ requires S, 16·8%), and was converted into *methyl* 9-*chlorononyl sulphide*, an almost colourless oil, b. p. 118—124°/2 mm. (Found: Cl, 17·1; S, 15·2. $C_{10}H_{21}ClS$ requires Cl, 17·0; S, 15·4%), $d_{4^\circ}^{20^\circ}$ 0·9725, $n_D^{20^\circ}$ 1·4811, $[R]_D$ 61·09 (calc., 61·22). The *mercurichloride* had m. p. 60—62° (Found: Hg, 42·2. $C_{10}H_{21}Cl_3SHg$ requires Hg, 41·8%). *Methyl* 10-*hydroxydecyl sulphide*, a colourless oil, b. p. 170—172°/13 mm., which crystallised in white plates, m. p. 25°, from light petroleum (Found: S, 15·5. $C_{11}H_{24}OS$ requires S, 15·7%), was converted by thionyl chloride into *methyl* 10-*chlorodecyl sulphide*, an oil, b. p. 128—131°/1 mm. (Found: Cl, 16·0; S, 14·3. $C_{11}H_{23}ClS$ requires Cl, 15·9; S, 14·4%), having $d_{4^\circ}^{20^\circ}$ 0·9641, $n_D^{20^\circ}$ 1·4802, $[R]_D$ 65·66 (calc., 65·84). The *mercurichloride* had m. p. 75—78° after several recrystallisations from alcohol (Found: Hg, 41·8. $C_{11}H_{23}Cl_3SHg$ requires Hg, 40·6%). *Methyl* 12-*hydroxydodecyl sulphide* crystallised from ligroin in white plates, m. p. 49° (Found: S, 13·8. $C_{13}H_{28}OS$ requires S, 13·8%), and yielded the crude chloro-sulphide by the action of thionyl chloride (4 mols. in boiling benzene). The product was isolated as the *mercurichloride*, deposited from alcohol as a brown oil which solidified and was several times crystallised from the same solvent, forming white crystals, m. p. 62—64° (Found: Hg, 39·1. $C_{13}H_{27}Cl_3SHg$ requires Hg, 38·4%) (yield, 70%). This was decomposed in hot alcoholic solution by hydrogen sulphide, the organic material recovered in ether, and the solution washed with aqueous sodium carbonate and with water, dried over sodium sulphate, and evaporated. The residue was quickly distilled at 140°/1 mm.; *methyl* 12-*chlorododecyl sulphide* thus obtained solidified in a freezing mixture and had m. p. 3—4° (Found: Cl, 14·2; S, 13·0. $C_{13}H_{27}ClS$ requires Cl, 14·2; S, 12·8%), $d_{4^\circ}^{20^\circ}$ 0·9497; $n_D^{20^\circ}$ 1·4789, $[R]_D$ 74·84 (calc., 75·07). In a similar way *methyl* 14-*hydroxytetradecyl sulphide*, crystallising in white plates, m. p. 38°, from light petroleum (Found: S, 12·3. $C_{15}H_{32}OS$ requires S, 12·3%), was converted into a chloro-sulphide, isolated as its *mercurichloride*, white crystals, m. p. 66° (Found: Hg, 36·4. $C_{15}H_{31}Cl_3SHg$ requires Hg, 35·8%), from which *methyl* 14-*chlorotetradecyl sulphide* was recovered as a pale oil, b. p. 155°/1 mm., m. p. 13—14° (Found: Cl, 12·6; S, 11·3. $C_{15}H_{31}ClS$ requires Cl, 12·7; S, 11·5%), having $d_{4^\circ}^{20^\circ}$ 0·9389, $n_D^{20^\circ}$ 1·4780, $[R]_D$ 84·07 (calc., 84·31). *Methyl* 16-*hydroxyhexadecyl sulphide*, white plates, m. p. 54—56° (Found: S, 10·9. $C_{17}H_{36}OS$ requires S, 11·1%), gave *methyl* 16-*chlorohexadecyl sulphide*, isolated through its *mercurichloride*, m. p. 72—76° (Found: Hg, 35·9. $C_{17}H_{35}Cl_3SHg$ requires Hg, 34·8%), as an oil which could not be distilled without decomposition. It was freed from volatile matter by heating at 100° in a stream of dry air, after which it solidified and melted at 22° (Found: Cl, 11·3; S, 10·7. $C_{17}H_{33}ClS$ requires Cl, 11·6; S, 10·5%). The super-cooled liquid had $d_{4^\circ}^{20^\circ}$ 0·9294, $n_D^{20^\circ}$ 1·4773, $[R]_D$ 92·9 (calc., 93·5). *Methyl* 18-*hydroxyoctadecyl sulphide*, separating from light petroleum in colourless crystals, m. p. 62° (Found: S, 9·9. $C_{19}H_{42}OS$ requires S, 10·1%), furnished *methyl* 18-*chloro-octadecyl sulphide*, isolated first as the *mercurichloride*, m. p. 91—94° (Found: Hg, 34·6. $C_{19}H_{39}Cl_3SHg$ requires Hg, 33·0%). The chloro-sulphide, when recovered, solidified and was twice recrystallised from ethyl alcohol, forming colourless crystals, of m. p. 31° (Found: Cl, 10·8; S, 9·5. $C_{19}H_{39}ClS$ requires Cl, 10·6; S, 9·7%).

Preparation of a Bromo-sulphide.—Methyl 14-hydroxytetradecyl sulphide (5 g.) was warmed for ½ hour with phosphorus pentabromide (10 g.) in benzene (100 c.c.). After addition of a little water and evaporation of the benzene, the product was taken up in ether and the solution washed. Precipitation with alcoholic mercuric chloride gave the *mercurichloride*, which separated from alcohol in white crystals, m. p. 69—70° (Found: Hg, 34·3. $C_{15}H_{31}Cl_2BrSHg$ requires Hg, 33·7%). The *bromo-sulphide* was recovered as usual and freed from solvents in a vacuum at 40° (Found: Br, 24·6. $C_{15}H_{31}BrS$ requires Br, 24·7%). The yield of this substance was only 35% of that calculated: it is probable that water-soluble sulphonium salts and polymeric material account for much of the defect.

Preliminary Experiments on Heating the Chloro-sulphides in Various Solvents.—Methyl 10-chlorodecyl sulphide (1 g.) was heated in boiling acetic acid (1 l., 100%, prepared by the method of Orton and Bradfield, J., 1927, 983) for 1 week. The residue from the evaporation of the solvent was taken up in ether and water, and the ethereal solution, after washing with sodium carbonate solution, yielded the bulk of the original substance unchanged (1 g. of crude oil contained Cl, 14·6%). It gave a mercurichloride, m. p. 75°, and the sulphide recovered from this was, after distillation, almost pure, having Cl, 15·1%. The aqueous solution left, on evaporation, some crystalline material, which melted with decomposition on heating, but was insufficient for further examination (0·01 g.).

Methyl chlorodecyl sulphide was heated for 1 week in boiling tetrachloroethane (2 l. to 1 g. of solute). There was no water-soluble product. When the solution was fractionally distilled, a portion of the chloro-sulphide was recovered unchanged (Found : Cl, 15·6. Calc. : Cl, 15·9%) and a non-volatile residue (0·5 g.) was left, containing sulphur, but almost free from chlorine. This was polymeric material, from which no definite substance was isolated. A *substance*, b. p. 90°/10 mm., was also separated during the distillation, which crystallised and sublimed very readily and after recrystallisation from ethyl alcohol formed a white crystalline mass, m. p. 104—106°, with a musty odour. Its composition is that of a nonachloro*cyclo*hexane (Found : C, 18·3; H, 1·5; Cl, 79·1. $C_6H_3Cl_9$ requires C, 18·3; H, 0·76; Cl, 80·9%). This compound was not examined further, but it seems probable that it may have been formed by the loss of 3 mols. of hydrogen chloride between 3 mols. of tetrachloroethane, which should give the hexachloride of *s*-trichlorobenzene. The hexachloride of 1 : 2 : 4-trichlorobenzene is described as having m. p. 96° and a musty smell (Willgerodt, *J. pr. Chem.*, 1887, **35**, 415).

The same chloro-sulphide was heated in boiling ethylene glycol (1 l. to 1 g.) continuously for 4 days. The product was extracted in ether, and the solution washed and evaporated. The residual oil contained sulphur but no chlorine, and, after purification through the mercurichloride, m. p. *ca.* 60°, *methyl* 10-(β-*hydroxyethoxy*)*decyl sulphide* was obtained as a pale yellow oil (Found : C, 62·6; H, 11·3; S, 12·7. $C_{13}H_{28}O_2S$ requires C, 62·8; H, 11·4; S, 12·9%).

When methyl 14-chlorotetradecyl sulphide was heated for 17 days in boiling tetrachloroethane (1·5 l. for 1·1 g.), the material was badly charred and no mercurichloride or other pure product was isolated. The same sulphide was heated in boiling ethylene glycol (2·5 l. to 1 g.) for 17 days. By extraction with ether a brown waxy solid (0·3 g.) was obtained, containing sulphur but no chlorine, from which no pure substance was isolated and which may have been a mixture of products of interaction with the glycol and of cyclisation or polymerisation.

Methyl chlorotetradecyl sulphide (2·1 g.) was heated with potassium iodide (1·25 g.) in boiling butyl alcohol (500 c.c., carefully dried) for 90 hours, and the solution washed with water and evaporated under diminished pressure. The waxy brown residue contained sulphur and no halogen and had an intense smell like that of celery. After five crystallisations from ethyl alcohol *methyl* 14-*butoxytetradecyl sulphide*, m. p. 60—68°, was almost free from impurity (Found : S, 10·1. $C_{19}H_{40}OS$ requires S, 10·1%).

Similarly this chloro-sulphide (1·4 g.) was heated with sodium iodide in boiling phenol (500 c.c.) for 4 hours, the solvent evaporated, and the residue extracted with ether. The brown solid, after being twice crystallised from ethyl alcohol, was *methyl* 14-*phenoxytetradecyl sulphide*, m. p. 46—50° (Found : S, 9·3. $C_{21}H_{36}OS$ requires S, 9·5%).

Formation of a Cyclic Monosulphide with a 15-*Membered Ring.*—Methyl bromotetradecyl sulphide (1·5 g.) was heated for 24 hours in boiling dry acetic acid (3 l.), the solution evaporated, and the product extracted with ether and water. From the ethereal solution, almost the whole of the sulphide was recovered unchanged, giving the mercurichloride, m. p. 67—69°, not depressed by addition of the original mercurichloride, and yielding a bromo-sulphide which, recovered without distillation, was almost pure (Found : Br, 23·2. Calc. : Br, 24·6%). The aqueous extract yielded, on evaporation, a white crystalline deliquescent solid (0·1 g.), which was evidently a sulphonium salt, since it contained sulphur and ionic bromine. It gave a crystalline platinichloride, but not enough for analysis. The bromo-sulphide recovered as described above was therefore heated in boiling acetic acid (2·5 l.) for 1 week, and the products examined as before. Owing, no doubt, to the tendency for the sulphonium salt to dissociate and for methyl bromide to escape, no water-soluble substance was now found, but from the ether a halogen-free brown oil (0·5 g.) was obtained which partly solidified. After two crystallisations from ethyl alcohol the *polymeric tetradecamethylene sulphide* was an almost colourless solid (Found : C, 72·6; H, 12·2; S, 14·0; *M*, 542. $C_{14}H_{28}S$ requires C, 73·5; H, 12·3; S, 14·1; *M*, 228). Addition of mercuric chloride to the alcoholic mother-liquors furnished a beautifully crystalline mercurichloride of the *monomeric tetradecamethylene sulphide*. This substance crystallised from alcohol in oblique-ended needles with a high double refraction and a straight extinction, m. p. 167° after preliminary softening (yield, 0·2 g.) (Found : Hg, 47·2%). The sulphide was liberated and, after crystallisation from light petroleum, it formed colourless elongated plates with an extinction angle of 33° and m. p. 71°. The substance had a distinct smell of musk [Found : C, 73·5; H, 11·9; S, 14·6%; *M* (in camphor), 249, 241].

Methyl chlorotetradecyl sulphide was heated similarly for 24 days in boiling dry acetic acid. A small quantity of a water-soluble sulphonium chloride was obtained (0·1 g.) but was not sufficient for purification and analysis. The ethereal extract gave chiefly the original chloro-sulphide and a small amount of a crystalline substance (0·02 g.) containing sulphur but not chlorine, m. p. 115—118°, which could not be further investigated. The mother-liquors from the precipitation of these sulphides with mercuric chloride deposited, on standing, some fine white needles of the mercurichloride of monomeric tetradecamethylene sulphide.

This cyclic sulphide was produced most readily by the use of sodium iodide with acetophenone as solvent. The chloro-sulphide (2 g.) was boiled with its own weight of dry sodium iodide in pure dry acetophenone (500 c.c.) for 2 hours, and the solution concentrated to about 20 c.c. under diminished pressure. Water extracted nothing. The ethereal extract was fractionated. After removal of a little acetophenone, the main sulphur-containing portion of the material (1·5 g.) distilled up to 170°/3 mm., followed by some distillate free from sulphur, which was presumably a self-condensation product of the solvent. The distilled sulphides gave with mercuric chloride in alcohol the mercurichloride of tetradecamethylene sulphide (0·4 g.), m. p. 167°. The residue in the distillation flask used in the fractionation contained sulphur but hardly any halogen. It was a black solid which softened readily on warming and could be drawn out into long elastic fibres. These resembled the fibres, described by Carothers and Hill (*J. Amer. Chem. Soc.*, 1932, **54**, 1579), given by synthetic linear " condensation polymers." Subsequent experiments showed that the period of heating in the above case was not long enough to drive off all the methyl halide. The addition reactions were therefore not complete and, after the acetophenone had been evaporated, the concentrated solution of iodo-sulphide would undergo rapid self-reaction with production of highly polymerised substances, which would show just these properties. In later experiments the heating was continued until the evolution of methyl iodide had ceased. No highly polymerised products then resulted.

The evolution of methyl iodide in this process was confirmed by passing the vapour into dimethylaniline, crystals of phenyltrimethylammonium iodide, m. p. 210—211°, being produced.

In another operation the chloro-sulphide, dissolved in acetophenone, was run into a solution of the iodide in more of the solvent kept at the b. p., but under these conditions polymerisation was increased and the yield of monomeric product was smaller.

Formation of Cyclic Monosulphides with 17- *and* 19-*Membered Rings.*—Methyl 16-chlorohexadecyl sulphide (1·1 g.) was boiled with sodium iodide (1 g.) in acetophenone (500 c.c.) until methyl iodide ceased to be evolved. The solvent was evaporated, the residue extracted with ether, and the concentrate from the latter solvent taken up in hot alcohol and left overnight. A dark brown, sticky substance (0·5 g.), which was deposited from solution, was recrystallised from alcohol; it then had m. p. 60—75° and showed no fibrous properties near the m. p. This substance contained no halogen and was a *polymeric hexadecamethylene sulphide* [Found : S, 12·1; *M* (in camphor), 585. $C_{16}H_{32}S$ requires S, 12·5%; *M*, 256].

Addition of mercuric chloride to the alcoholic mother-liquors, from which the crude polymeric material had been deposited, threw down a fine crystalline precipitate of a mercurichloride (*ca.* 0·4 g.). The material from three such preparations was recrystallised, and the sulphide liberated (0·4 g.) and purified by one distillation and two crystallisations from ethyl alcohol, in which it was very soluble. *Hexadecamethylene sulphide* was thus obtained as a solid, m. p. 61°, having a faint smell of musk. The crystals were in small acute-angled rhombs with high double refraction, or in spear-headed needles with an extinction angle of 5°. Fused on a microscope slide, it crystallised in large plates of variable oblique extinction showing a low birefringence (Found : C, 74·7; H, 12·5; S, 12·1; *M*, 281. $C_{16}H_{32}S$ requires C, 74·9; H, 12·6; S, 12·5%; *M*, 256). The mercurichloride had m. p. 164—166°.

Methyl 18-chloro-octadecyl sulphide was heated with iodide in an exactly similar manner in acetophenone, and the products isolated as before. The crude *polymeric sulphide*, after crystallisation from alcohol, had m. p. 60—77° and was probably a mixture of di- and tripolymers (Found : S, 10·9; *M*, 650. $C_{18}H_{36}S$ requires S, 11·3%; *M*, 284). The concentrated mother-liquors yielded a mercurichloride, which was recrystallised from alcohol and decomposed to recover the sulphide (0·4 g.). This was once distilled and crystallised from alcohol. *Octadecamethylene sulphide*, so obtained, had b. p. 186°/16 mm., m. p. 74°. When fused on a slide, it crystallised in plates showing a high birefringence and a variable oblique extinction (Found :

C, 75·8; H, 12·8; S, 11·4; *M*, 258. $C_{18}H_{36}S$ requires C, 76·0; H, 12·8; S, 11·3%; *M*, 284). 10% of the possible yield of pure sulphide was isolated. The mercurichloride crystallised from alcohol in white needles, m. p. 121—125°.

Behaviour of Chloro-sulphides with 7-, 8-, 9-, 10- *and* 12-*Carbon Chains*.—Methyl chloroheptyl, octyl, nonyl, decyl, and dodecyl sulphides were each heated with sodium iodide in dilute acetophenone solution, as had proved most favourable to production of the larger rings. No monomeric product was detected in any case, although both the reaction mixture and the volatile products were carefully examined. No water-soluble material was found. The mercuric chloride precipitates were gummy and sometimes unworkable. In each case a dark brown solid polymeric product was obtained, containing sulphur but no halogen, which decomposed when distillation was attempted. Their molecular complexity was between twice and thrice that of a monomeric ring sulphide (Found for polymeride from the chloroheptyl sulphide: *M*, 291. $C_7H_{14}S$ requires *M*, 130).

Methyl chlorodecyl and chlorododecyl sulphides were also heated alone without solvent at 250° for 8 hours. Each gave a dark solid, which was only sparingly soluble in alcohol, contained sulphur but not halogen, and was more highly polymerised than those formed in solution (Found: for polymeride from methyl chlorodecyl sulphide, *M*, 680; from chlorododecyl sulphide, *M*, 825. $C_{10}H_{20}S$ and $C_{12}H_{24}S$ require *M*, 172 and 200 respectively).

The authors thank the Department of Scientific and Industrial Research for a grant.

THE UNIVERSITY, SHEFFIELD.

[*Received, September* 24*th*, 1938.]