LXIX.—*Production and Reactions of ββ'-Dichlorodiethyl Sulphide.*

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THE most convenient method of preparing ββ'-dichlorodiethyl sulphide, $(CH_2Cl \cdot CH_2)_2S$, furnishes a quantitative yield and consists in treating sulphur monochloride with ethylene (Gibson and Pope, T., 1920, **117**, 271). Under certain conditions (Mann, Pope, and Vernon, T., 1921, **119**, 634), the yield is not quantitative and the technical product is certainly far from pure. Gibson and Pope also showed that the sulphide can be obtained readily by the action of ethylene on sulphur dichloride, but that in this case the yield is only about 30 per cent. of that indicated by theory; the French have founded a technical process of manufacture on this reaction, using carbon tetrachloride as a diluent for the sulphur dichloride.

Many questions connected with the above two reactions are still under discussion, partly because too little experimental data are available for their decision and partly also because the various workers have not defined specifically the nature of the materials which they have used. We have already pointed out the difficulty of obtaining pure sulphur monochloride and it has been shown (Pope and Heycock, Eng. Pat. 142879, 1918) that sulphur dichloride only exists as a definite chemical individual under specific conditions. It seemed therefore desirable to study experimentally the action of the pure sulphur chlorides on ββ'-dichlorodiethyl sulphide and the related reactions between the latter substance and chlorine for the purpose of ascertaining the nature of the by-products which may accompany this organic compound.

It is now shown that on treatment with chlorine ββ'-dichlorodiethyl sulphide yields the corresponding tri-, tetra-, and hexa-chlorodiethyl sulphides, in each of which the further chlorine atoms introduced enter one only of the two ethylene residues of the molecule. This observation has some connexion with Regnault's work (*Ann. Chim. Phys.*, 1839, [ii], **71**, 392), which showed that diethyl ether yields a perchloro-derivative, $(C_2Cl_5)_2O$, on chlorination in sunlight; we have attempted to prepare perchlorodiethyl sulphide by the action of chlorine on ββ'-dichlorodiethyl sulphide in sunlight, but have merely obtained sulphur dichloride and perchloroethane in accordance with the reaction described below. It is interesting to notice that Riche (*Ann. Chim. Phys.*, 1855, [iii], **43**, 283) obtained a tetrachloro-, a hexachloro-, and an octachloro-diethyl sulphide by the chlorination of diethyl sulphide, and that by exhaustive chlorin-

ation in sunlight he obtained perchloroethane and a substance which he thought to be a perchlorodiethyl sulphide. Guthrie (*Quart. J. Chem. Soc.*, 1861, **13**, 35) described a tetrachlorodiethyl sulphide obtained by the action of ethylene on boiling sulphur monochloride, and converted it into a hexachlorodiethyl sulphide by direct chlorination; he presumed thé latter to be identical with a hexachlorodiethyl sulphide which he obtained by the chlorination of diethyl sulphide. The boiling points and densities of the corresponding products now described differ so widely from those of the substances obtained by Riche and Guthrie as to make it improbable that we have been dealing with the same compounds. By the action of sulphur monochloride on ββ'-dichlorodiethyl sulphide we have obtained tri- and tetra-chlorodiethyl sulphide. The same products are formed on treating ββ'-dichlorodiethyl sulphide with sulphur dichloride, and in this case evidence has been also obtained of the formation of β-chloroethylsulphur chloride, $CH_2Cl\cdot CH_2\cdot SCl$.

When ethylene is passed through sulphur dichloride, the ruby-red colour of the latter gives place to an amber-yellow long before two molecular proportions of the hydrocarbon have been absorbed by one of the sulphur chlorides. If the reaction is arrested when the ruby-red colour disappears, a product is obtained from which no ββ'-dichlorodiethyl sulphide can be separated; it yields the tri- and tetra-chlorodiethyl sulphides and the β-chloroethylsulphur chloride together with the sulphur monochloride. It thus appears that the ββ'-dichlorodiethyl sulphide which Gibson and Pope obtained in about a 30 per cent. yield by the action of ethylene on sulphur dichloride is produced from the sulphur monochloride formed during the preliminary decoloration of the sulphur dichloride.

In practically all the chlorinations described in the present paper mixtures of several halogenated products are formed which cannot be resolved by ordinary fractional distillation under diminished pressure; by fractional distillation under 15 mm. pressure through the column which Dufton has recently described (*J. Soc. Chem. Ind.*, 1919, **38**, 45T) the product was in each case separated into its components without great difficulty. The new column is far more efficient than any which we had previously used, and we desire to direct attention to the fact that Dufton has devised a novel piece of apparatus which is of great service to the organic chemist.

Action of Chlorine on ββ'-Dichlorodiethyl Sulphide.

Chlorine is slowly but steadily absorbed when passed through ββ'-dichlorodiethyl sulphide; after a short time hydrogen chloride is evolved and the temperature rises to about 50°. Preliminary experiments in which one, two, three, and four molecules of chlorine

were caused to act on each molecule of the dichlorodiethyl sulphide showed that a single product, the tri-, tetra-, penta-, or hexa-chlorodiethylsulphide, could not be obtained, but that a mixture of several of these substances was always produced. The product boiled with partial decomposition under atmospheric pressure, and when distilled under reduced pressure from a Claisen flask yielded no constant boiling component. On distillation under 15 mm. pressure through a Dufton column 65 cm. in length and of large annular width at the rate of one drop in each three seconds, the mixtures were resolved; after several similar fractional distillations the following three compounds were obtained in a state of purity.

(a) $\alpha\beta\beta'$-Trichlorodiethyl sulphide, $CH_2Cl \cdot CHCl \cdot S \cdot CH_2 \cdot CH_2Cl$, boiling at $106 \cdot 5$—$108°/15$ mm., and of density, $d_{4 \cdot 0°}^{21 \cdot 8°} = 1 \cdot 4219$ (Found : $C = 25 \cdot 0$; $H = 2 \cdot 6$; $Cl = 54 \cdot 84$. $C_4H_7Cl_3S$ requires $C = 24 \cdot 8$; $H = 3 \cdot 6$; $Cl = 55 \cdot 0$ per cent.).

(b) $\alpha\beta\beta\beta'$-Tetrachlorodiethyl sulphide, $CHCl_2 \cdot CHCl \cdot S \cdot CH_2 \cdot CH_2Cl$, boiling at 123—$125°/15$ mm., and of density, $d_{4 \cdot 0°}^{15 \cdot 2°} = 1 \cdot 5441$ (Found : $C = 21 \cdot 2$; $H = 1 \cdot 8$; $Cl = 62 \cdot 1$. $C_4H_6Cl_4S$ requires $C = 21 \cdot 1$; $H = 2 \cdot 6$; $Cl = 62 \cdot 2$ per cent.).

(c) $\alpha\alpha\beta\beta\beta'$-Hexachlorodiethyl sulphide, $CCl_3 \cdot CCl_2 \cdot S \cdot CH_2 \cdot CH_2Cl$, boiling at 160—$161°/15$ mm., and of density, $d_{4 \cdot 0°}^{10 \cdot 6°} = 1 \cdot 6944$ (Found : $C = 16 \cdot 3$; $H = 1 \cdot 3$; $Cl = 71 \cdot 5$. $C_4H_4Cl_6S$ requires $C = 16 \cdot 2$; $H = 1 \cdot 4$; $Cl = 71 \cdot 7$ per cent.).

A small quantity of an oil boiling at about $70°/13$ mm. and possessing a vile and persistent odour was also separated in the distillation of the above crude products; we were unable to collect sufficient of this for identification. These three chlorinated diethyl sulphides are colourless liquids which, like $\beta\beta'$-dichlorodiethyl sulphide, slowly acquire a light green tint when exposed to sunlight; they possess a faint odour similar to the parent dichloro-compound, but are devoid of vesicant properties and have much lower melting points. As the number of chlorine atoms in the molecule increases, the sulphur atom shows increasing reluctance to become quadrivalent. Thus bromine forms no addition compound with the trichlorodiethyl sulphide corresponding with the well-defined dibromide of $\beta\beta'$-dichlorodiethyl sulphide (Gibson and Pope, T., 1920, **117**, 277), but on warming the mixture vigorous reaction occurs with evolution of hydrogen bromide. The trichloro-derivative is not acted on by nitric acid at $0°$, whilst the tetrachloro-compound is precipitated unchanged on addition of water to its solution in nitric acid at 30—$35°$. In each case, warming with nitric acid causes vigorous oxidation and the production of a degradation product having the odour of chloropicrin. Many attempts were made to obtain a pentachlorodiethyl sulphide by acting on the di-, tri-, and tetra-

chloro-compounds with the requisite amount of chlorine, but in each case mixtures were obtained which contained no pentachlorodiethyl sulphide.

When treated with nitric acid, ββ'-dichlorodiethyl sulphide yields the corresponding sulphoxide, and this, as Bennett has shown (T., 1921, **119**, 418), is converted into β-chloroethanesulphonic acid when heated in a sealed tube with fuming nitric acid. The trichloro-, the tetrachloro-, and the hexachloro-diethyl sulphides now described are oxidised to the sulphonic acid by a few hours' heating under a reflux with nitric acid; some product resembling chloropicrin in odour is also formed.   The sulphonic acid is separated as the lead salt and converted into crude ammonium salt, which is readily purified by crystallisation from absolute alcohol. Ammonium β-chloroethanesulphonate is thus obtained in minute needles melting at 198° (corr.), which gave correct analytical results.*

The oxidation to β-chloroethanesulphonic acid shows that all these derivatives contain the group $CH_2Cl \cdot CH_2 \cdot S \cdot$, and indicates that the constitutions are probably those assigned above.

On passing dry chlorine into ββ'-dichlorodiethyl sulphide, allowing the liquid to warm up spontaneously, and finally heating at 100° in the current of chlorine, sulphur dichloride slowly distils over, the absorption ceasing after about twenty-two hours; the product, on distillation, yields a mixture of sulphur monochloride and dichloride followed by an oil boiling at 130—175°.   Above this temperature the distillate solidifies in the condenser, the crystalline substance being identified as perchloroethane, melting at 185°.   The liquid boiling at 130—175° separates sharply, on distillation through a Dufton column, into αββ β-tetrachloroethane, boiling at 129—130° (Kanonnikow, *Diss.*, Kasan, 1880, gives the boiling point as 129·5—130°), and pentachloroethane, boiling at 159—161° (Thorpe, T., 1880, **37**, 192, gives the value 159·1°), whilst a crystalline residue of perchloroethane remains in the distillation flask.   On occasions when the chlorination was less exhaustive, mixtures containing lower chlorinated ethanes were obtained, but these were not further examined.

It thus appears that ααβββ β'-hexachlorodiethyl sulphide is decomposed by the addition of two molecular proportions of chlorine into sulphur dichloride, hexachloroethane, and ethylene dichloride, the last then undergoing further chlorination.

Action of Sulphur Monochloride on ββ'-Dichlorodiethyl Sulphide.

It is known that ββ'-dichlorodiethyl sulphide is fairly resistant to sulphur monochloride, especially in absence of iron (*J. Soc. Chem.*

* Some error has crept into Bennett's analytical results.

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Ind., 1919, **38**, 469R; T., 1921, **119**, 645), but reaction does occur on prolonged contact of the two substances; the nature of the changes induced was therefore studied.

Carefully purified ββ'-dichlorodiethyl sulphide (23·85 grams) was mixed with sulphur monochloride (40·5 grams) free from iron, and the mixture allowed to remain at the ordinary temperature in absence of moisture; hydrogen chloride was slowly evolved and, after seventeen weeks, 9·75 grams of this gas had escaped and crystalline sulphur (5·45 grams) had separated. The yellow liquid (49·2 grams) was distilled, when sulphur monochloride (10·6 grams) came over below 75°/15 mm., followed by an oil (15·9 grams) boiling at 108—126°/15 mm.; much foaming, due to the evolution of hydrogen chloride, occurred during the distillation, and a black, tarry residue, consisting mainly of sulphur, remained. The oil boiling at 108—126° was separated by fractional distillation into trichlorodiethyl sulphide (8·0 grams) and tetrachlorodiethyl sulphide (5·8 grams).

On boiling ββ'-dichlorodiethyl sulphide (1 mol.) with sulphur monochloride (2 mols.) under a reflux, hydrogen chloride is slowly evolved, and after several hours an almost black liquid results; on distillation, a small yield of tetrachlorodiethyl sulphide is obtained (about one-fourth by weight of the original sulphide), whilst a heavy, black tar containing sulphur remains. The same result is obtained on heating the mixture at 100° for ten hours, when the evolution of hydrogen chloride ceases; a similar proportion of tetrachlorodiethyl sulphide and black tar results.

It thus appears that sulphur monochloride acts as a chlorinating agent on ββ'-dichlorodiethyl sulphide, slowly producing therefrom trichloro- and tetrachloro-diethyl sulphide at the ordinary temperature, and tetrachlorodiethyl sulphide in smaller yield at 100° or at the boiling temperature. The foaming which occurs during the distillation is probably due to the removal of hydrogen chloride from ββ'-dichlorodiethyl sulphide dichloride.

Action of Sulphur Dichloride on ββ'-Dichlorodiethyl Sulphide.

On adding sulphur dichloride, prepared by the method of Pope and Heycock, to ββ'-dichlorodiethyl sulphide at 0°, heat is evolved and the red colour of the sulphur dichloride is at once discharged; the liquid becomes yellow, smells of sulphur monochloride, and hydrogen chloride is evolved. As more dichloride is added, the action becomes less vigorous, and ultimately rapid stirring is necessary to discharge the red colour; about four molecular proportions of sulphur dichloride can be added before the red colour becomes persistent for a considerable time, but much of the reagent

is certainly carried away or decomposed by the escape of hydrogen chloride from the agitated liquid. Addition of a trace of iron hastens the action. When the product presenting the persistent red colour is distilled under reduced pressure, sulphur dichloride followed by sulphur monochloride comes over below 75°/15 mm., but distillation is rendered difficult by the evolution of torrents of hydrogen chloride. By distilling small quantities at a time, a further distillate is obtained at 99—116°/14 mm.; this, on further fractionation and analysis, proves to be mainly trichlorodiethyl sulphide and tetrachlorodiethyl sulphide.

On heating the first reaction product at 150—160° under atmospheric pressure, hydrogen chloride is evolved and sulphur monochloride distils; when the dark red residue is distilled under reduced pressure, sulphur monochloride comes over below 75°/18 mm., followed by an orange-coloured fraction at 110—130°/18 mm. Just after condensation this fraction is nearly odourless, but on standing it soon evolves hydrogen chloride and acquires the odour of sulphur monochloride. This change in colour is probably attributable to the presence of β-chloroethylsulphur chloride, $CH_2Cl \cdot CH_2 \cdot SCl$. On treating the fraction with dilute nitric acid in order to oxidise the latter substance to β-chloroethanesulphonic acid, the residual oil, when distilled under reduced pressure through the Dufton column, is resolved into trichloro- and tetrachlorodiethyl sulphides. The tarry residue left in the distillation of the crude product yields sulphur after boiling in benzene solution with animal charcoal.

Consideration of the results described, which are typical of many others obtained, leads to the conclusion that the chief reactions concerned in the action of sulphur dichloride on ββ′-dichlorodiethyl sulphide are the following :

1. $(CH_2Cl \cdot CH_2)_2S + 2SCl_2 = CH_2Cl \cdot CHCl \cdot S \cdot CH_2 \cdot CH_2Cl + S_2Cl_2 + HCl.$
2. $(CH_2Cl \cdot CH_2)_2S + S_2Cl_2 = CH_2Cl \cdot CHCl \cdot S \cdot CH_2 \cdot CH_2Cl + 2S + HCl.$

With these is coupled the further chlorination to tetrachlorodiethyl sulphide.

Whilst the above represent the principal reactions of sulphur dichloride with ββ′-dichlorodiethyl sulphide, evidence has been obtained, as is noted above, that a certain proportion of β-chloroethylsulphur chloride is also formed. This substance could only result from the reaction expressed by equation 3, namely :

3. $(CH_2Cl \cdot CH_2)_2S + SCl_2 = 2CH_2Cl \cdot CH_2 \cdot SCl,$

and it appears that reaction 3 is reversible under appropriate temperature conditions, yielding ββ′-dichlorodiethyl sulphide, which,

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in presence of sulphur dichloride, yields trichlorodiethyl sulphide in accordance with equations 1 and 2. We are still occupied with the preparation in a pure state of β-chloroethylsulphur chloride and with the study of its properties. The production of β-chloroethylsulphur chloride seems to be proved by numerous experiments, of which the following may be quoted as typical.

Sulphur dichloride (305·8 grams) was gradually added during four hours, with constant stirring, to ββ′-dichlorodiethyl sulphide (71·3 grams), the temperature being maintained at 0°. Concentrated nitric acid (293 c.c., d 1·42) was then slowly added with cooling, when vigorous oxidation took place intermittently; after standing over-night, the mixture was run into water, the separated oil (54·0 grams) washed with water and very dilute sodium bicarbonate solution, dried, and distilled at atmospheric pressure. After repeated fractional distillation a colourless oil, which fumed slightly in the air and boiled at 198—204° under atmospheric pressure and at 93—97°/17 mm., was obtained. On analysis, this proved to be the β-chloroethanesulphonyl chloride, $CH_2Cl \cdot CH_2 \cdot SO_2Cl$, described by Kolbe (*J. Chem. Soc.*, 1862, **15**, 97) as boiling at about 200° and by James (T., 1883, **43**, 42) as boiling at 200—205° (Found : Cl = 43·74; S = 19·33. Calc., Cl = 43·50; S = 19·67 per cent.). When this oil was repeatedly evaporated with the diluted nitric acid solution, the liquid treated with lead carbonate, and the filtrate evaporated, *lead β-chloroethanesulphonate* was obtained as a white powder (Found : C = 9·7; H = 1·4; Pb = 42·18. $C_2H_4O_3ClSPb$ requires C = 9·7; H = 1·6; Pb = 41·9 per cent.).

A further secondary reaction seems to accompany the action of sulphur dichloride on ββ′-dichlorodiethyl sulphide and results in the formation of diethylene disulphide. On agitating the crude product of the action of sulphur dichloride on ββ′-dichlorodiethyl sulphide with a paste of chalk and water in order to hydrolyse the chlorides of sulphur, extracting with ether, evaporating the ether extract, and treating the residue with nitric acid at 0° until no further oxidation occurs, the residual heavy oil, after washing and drying, gives on distillation the sulphonyl chloride boiling at 95—98°/16 mm., and a residue which yields a solid condensate when distilled under atmospheric pressure. This solid material crystallises from alcohol and is diethylene disulphide (Found : C=39·6 ; H=6·6. Calc., C = 39·9; H = 6·7 per cent.); it gives the characteristic blood-red coloration with nitric acid, and the quantity of pure product (1·5 grams) obtained from highly purified ββ′-dichlorodiethyl sulphide (54 grams) melting at 14° is so large as to preclude its having been present in the original materials.

Interaction of Ethylene and Sulphur Dichloride.

It has previously been shown (Gibson and Pope, T., 1920, **117**, 271) that on saturating sulphur dichloride with ethylene and distilling the product under reduced pressure a fraction is obtained which contains about 90 per cent. of ββ'-dichlorodiethyl sulphide and weighs about half as much as the sulphur dichloride used ; this corresponds with a yield of about 30 per cent. of that which should be obtained in accordance with equation 4.

4. $2CH_2:CH_2 + SCl_2 = (CH_2Cl\cdot CH_2)_2S.$
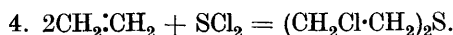
On treating ethylene with sulphur dichloride, although not to completion, Guthrie (*Quart. Journ. Chem. Soc.*, 1860, **12**, 116) obtained the unstable β-chloroethylsulphur chloride, and Conant, Hartshorn, and Richardson (*J. Amer. Chem. Soc.*, 1920, **42**, 590) concluded that they obtained the same substance by the action of sulphur dichloride on an excess of ethylene. For the purpose of elucidating the reaction between ethylene and sulphur dichloride we have carried out a number of experiments.

On passing a current of dry ethylene through strongly agitated sulphur dichloride maintained at 0°, the ruby-red colour of the dichloride changes to straw-yellow long before the proportion of ethylene absorbed attains that indicated in equation 4. When the product, obtained by passing in ethylene until the ruby-red colour is on the point of disappearing, is distilled under diminished pressure, a little sulphur dichloride comes over, followed by a considerable quantity of sulphur monochloride, both below 80°/15 mm.; much foaming, with evolution of hydrogen chloride, then occurs, and a fraction having the orange colour of β-chloroethylsulphur chloride distils at 95—130°/15 mm., and, lastly, a small fraction boiling at 150—160°/15 mm. A black tar remains in the distilling flask and this, as also the fraction distilling at 150—160°/15 mm., is instantly oxidised by nitric acid, giving β-chloroethanesulphonic acid. On agitating the fraction boiling at 95—130°/15 mm. with dilute nitric acid, to convert the β-chloroethylsulphur chloride into the sulphonic acid, a pale green oil remains, which is separable, by repeated fractionation through a Dufton column under reduced pressure, into about two parts of the trichlorodiethyl sulphide and one part of the tetrachlorodiethyl sulphide described above.

No evidence has been obtained of the presence of ββ'-dichlorodiethyl sulphide in the product which results from treating sulphur dichloride with ethylene up to the stage at which the dichloride itself disappears; the method of examining the product should have led to the detection of dichlorodiethyl sulphide, had this been present, because the chlorides of sulphur were distilled off rapidly

below 80°.   During the distillation, little evolution of hydrogen chloride takes place before the sulphur chlorides have been volatilised and it thus appears that sulphur monochloride is present in the product before distillation.

The results obtained are in accordance with the view that several reactions occur simultaneously, namely, that indicated by Guthrie (5), followed by the conversion of β-chloroethylsulphur chloride into trichlorodiethyl sulphide, hydrogen chloride, and sulphur monochloride in accordance with 1 and 3.

The results obtained suggest that two reactions, represented by equations 5 and 6, occur simultaneously when ethylene is brought into contact with sulphur dichloride at 0°, namely :

5. $2CH_2{:}CH_2 + SCl_2 = (CH_2Cl{\cdot}CH_2)_2S$
6. $CH_2{:}CH_2 + SCl_2 = CH_2Cl{\cdot}CH_2{\cdot}SCl,$
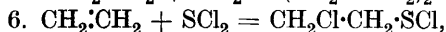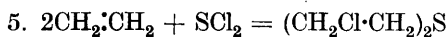
and that at the low temperature reaction 5 is followed by that represented by equation 1, already shown to occur ; after the sulphur chlorides have been distilled off, the product of reaction 6 decomposes in part in accordance with the reversal of reaction 3.   A complication is introduced by further chlorination of trichlorodiethyl sulphide to give the tetrachloro-derivative.   After the sulphur dichloride has disappeared, further absorption of ethylene occurs by the sulphur monochloride produced ; if this follows the completion of reactions 5, 6, 1, and 2, the yield of ββ′-dichlorodiethyl sulphide should be 25 per cent. of that which would be obtained if reaction 5 proceeded alone.   It has been shown, however, that some tetrachlorodiethyl sulphide is produced by further chlorination ;   the occurrence of this as a subsidiary reaction would increase the 25 per cent. yield ; and, as has been noted, the total yield obtained by Gibson and Pope was about 30 per cent. of that possible from equation 5.

It has been stated by Conant and his colleagues (loc. cit.), that chlorination of the ββ′-dichlorodiethyl sulphide first formed can be prevented and a fairly pure sample of the latter obtained by treating dilute solutions of sulphur dichloride in carbon tetrachloride with ethylene.

Although the tri-, tetra-, and hexa-chlorodiethyl sulphides now described are more readily oxidised to the β-chloroethanesulphonic acid than is the dichloro-derivative, it was not found possible to prepare the corresponding sulphoxides and sulphones by the customary methods of oxidation.   The sulphoxides of the tri- and tetra-chloro-compounds were obtained by the action of alkaline hypochlorite solutions on ββ′-dichlorodiethyl sulphoxide ;   the hexachlorodiethyl sulphoxide could not be obtained, and it appears

that the facility with which the sulphoxide is formed diminishes as the number of chlorine atoms in the molecule increases.

αββ'-*Trichlorodiethyl Sulphoxide*, $CH_2Cl \cdot CHCl \cdot SO \cdot CH_2 \cdot CH_2Cl$.

ββ'-Dichlorodiethyl sulphoxide (50 grams) is mixed with sodium hydrogen carbonate (80 grams) and stirred up with sodium hypochlorite solution (500 c.c. containing 15 per cent. of available chlorine); vigorous action soon sets in and carbon dioxide is evolved. The mixture is cooled at 20° and filtered after two hours, the filtrate and residue extracted with chloroform, and the chloroform solution evaporated. The residual oil (32 grams) deposits crystalline ββ'-dichlorodiethyl sulphoxide (15 grams) and, after filtration of the latter, the oil is extracted with hot 30 per cent. alcohol; after heating on the water-bath and cooling, the remaining oil crystallises. The crystalline deposit is purified by crystallisation from carbon tetrachloride and proves to be αββ'-*trichlorodiethyl sulphoxide* (6 grams), which crystallises in long, colourless needles melting at 69° (Found : C = 22·8; H = 3·40; Cl = 50·82. $C_4H_7OCl_3S$ requires C = 22·9; H = 3·37; Cl = 50·77 per cent.). The compound is freely soluble in benzene, chloroform, or alcohol, less soluble in ether, and nearly insoluble in cold water or carbon tetrachloride.

αβββ'-*Tetrachlorodiethyl Sulphoxide*, $CHCl_2 \cdot CHCl \cdot SO \cdot CH_2 \cdot CH_2Cl$.

The previous preparation is carried out so far as the cooling after the initial reaction with hypochlorite, and a large excess of hypochlorite solution is then added; after remaining over-night, the sludge is filtered by the aid of the pump, all oily products being drained away as completely as possible. The residue is washed with dilute hydrochloric acid, and the almost dry filter cake extracted with alcohol; on evaporating the alcoholic extract, a crystalline residue of the crude tetrachloro-compound is obtained, which is purified by crystallisation from boiling water. The substance separates from water in long, white needles melting at 121°; it is very soluble in alcohol or chloroform, less so in ether, and nearly insoluble in cold water (Found : C = 19·6; H = 2·5; Cl = 58·1. $C_4H_6OCl_4S$ requires C = 19·7; H = 2·5; Cl = 58·1 per cent.).

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