LXXIX.—*Observations on the Chlorination Products of ββ'-Dichlorodiethyl Sulphide. Part II.*

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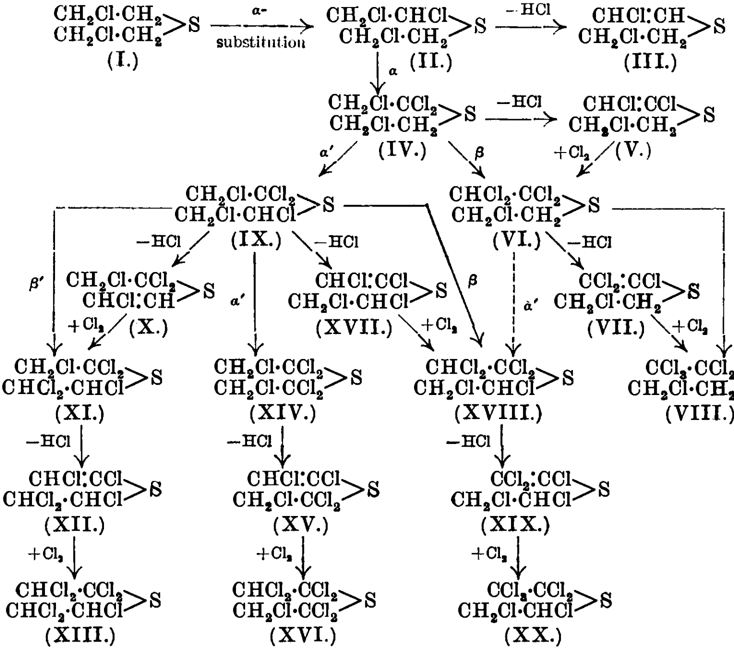
In a previous paper (Mumford and Phillips, J., 1928, 155) the view was advanced that the products of chlorination of ββ'-dichlorodiethyl sulphide described by Mann and Pope (J., 1922, **121**, 594) as αββ'-trichloro- and αβββ'-tetrachloro-diethyl sulphides were αβ-dichloro- and αββ-trichloro-vinyl β-chloroethyl sulphides, respectively. Subsequent to the communication of that paper, but prior to its publication, two papers on the same subject appeared (Lawson and Dawson, *J. Amer. Chem. Soc.*, 1927, **49**, 3119, 3125) in which similar conclusions were reached concerning the unsaturated nature of these compounds.

The present investigation was undertaken primarily to confirm the views previously advanced, but continuation of the work has shown that the chlorination of ββ'-dichlorodiethyl sulphide gives rise, not only to the series of compounds containing an unchanged β-chloroethyl group, as described by Mann and Pope and by Lawson and Dawson, but also to a second series in which chlorination has occurred in both chloroethyl groups. The main result of our work is thus the isolation not only of the tri- and tetra-chlorinated ethyl vinyl sulphides and the hexachlorodiethyl sulphide of the above observers, but also of one, or possibly two, new tetrachlorinated ethyl vinyl sulphides, together with pentachlorinated ethyl vinyl sulphides. hexachlorodiethyl sulphides, and heptachlorodiethyl sulphides derived from them.

Chlorination of ββ'*-Dichlorodiethyl Sulphide* (I).

The experiments now recorded were restricted to the chlorination of ββ'-dichlorodiethyl sulphide with two or more molecules of chlorine, and as far as the production of β-chloroethyl αβ-dichlorovinyl (V) and αββ-trichlorovinyl sulphides (VII) from saturated polychlorodiethyl sulphides is concerned, our results agree with those of Lawson and Dawson. For from the results obtained (Table I), it is evident that ββ'-dichlorodiethyl sulphide, on treatment with chlorine at the ordinary temperature, undergoes substitution, since for every molecule of chlorine used, one molecule of hydrogen chloride is evolved (Expts. 1 and 2). Moreover, each molecule of substitution product so formed breaks down on heating with the evolution of a further molecule of hydrogen chloride.



When one molecule of the dichloro-sulphide reacts with two molecules of chlorine (Expt. 7), the main reaction is the formation of a tetrachlorodiethyl sulphide (IV), which, however, is extremely unstable, and decomposes on attempted distillation, losing a molecular proportion of hydrogen chloride and giving in 90% yield an unsaturated trichloro-sulphide (V). We have not yet had an opportunity of examining the earlier stages of the chlorination process, but from the work of Lawson and Dawson it would appear that this tetrachlorodiethyl sulphide is the di-α-substituted derivative, and that the derived unsaturated trichloro-compound is β-chloroethyl αβ-dichlorovinyl sulphide (V). Confirmation of the existence of the vinyl chain in the latter is afforded by the fact that when the sulphide is treated with chlorine the principal reaction is one of addition, yielding ααββ′-pentachlorodiethyl sulphide (VI), which loses hydrogen chloride on heating to give β-chloroethyl αββ-trichlorovinyl sulphide (VII), in 70% yield (Expts. 13 and 14).

From this, by addition of chlorine, ααβββ′-hexachlorodiethyl sulphide (VIII) is obtained (Expts. 15 and 16), which, as might be expected from its constitution, yields hexachloroethane on further chlorination in the cold, and, like (V) and (VII), gives β-chloroethanesulphonic acid on oxidation (Mann and Pope ; Lawson and Dawson, *locc. cit.*).

When, however, ββ′-dichlorodiethyl sulphide is treated with more than two molecules of chlorine and the resulting pentachlorodiethyl sulphide is broken down with loss of hydrogen chloride, only on rare occasions is a tetrachlorinated ethyl vinyl sulphide identical with (VII) obtained. More often, an isomeric unsaturated tetrachloro-compound is produced, very similar to (VII) in physical properties but differing markedly from it in rate of hydrolysis. The sulphide (VII), when boiled with water for 15 minutes, is hydrolysed to the extent of 2% only, but with the new unsaturated tetrachloro-compound under similar conditions an apparent chlorine content of 70% is indicated. The compound, however, only contains 62·8% of chlorine, and, as estimation of the chloride formed shows that 59% is due to hydrogen chloride (*i.e.*, about 3·75 atoms of chlorine), it follows that the 70% figure corresponds to the liberation of about 0·75 mol. of acid in excess of that accounted for as hydrogen chloride.

As regards the genesis of this new compound, it would appear that just as ββ′-dichlorodiethyl sulphide in the first two stages is substituted in the α-position to give (IV), so this product, although on rare occasions it is chlorinated in the β-position to give (VI), is normally attacked in the α′-position to give *αα′ββ′-pentachlorodiethyl sulphide* (IX), from which the new tetrachlorinated ethyl vinyl sulphide is derived. It is difficult to predict the course of elimination of hydrogen chloride from (IX), which contains chlorine attached to each carbon atom, but loss of α-chlorine appears more consistent with the facts, and either (X) or (XVII) therefore represents the probable constitution of the second tetrachlorinated ethyl vinyl sulphide; (XVII), however, like the slightly hydrolysable compound (V), contains the chain CHCl:CCl–, and as symmetrical monosubstitution of the other chain could scarcely account for such greatly increased ease of hydrolysis, the new tetrachloro-compound is best formulated as *ααβ-trichloroethyl β-chlorovinyl sulphide* (X). This formulation accounts readily for the high hydrolysis and the development of extra acidity, the α-CCl_2 group, on conversion into a carbonyl group, giving rise to a readily hydrolysable unsaturated thioacetic ester.

Assuming this constitution, the derived series (XI), (XII), and (XIII) can be formulated with a fair degree of certainty. The *αα′ββ′β′-hexachlorodiethyl sulphide* (XI), formed by addition of chlorine to (X), differs from its ααβββ′-isomeride (VIII) in being somewhat more readily hydrolysed, and in breaking down on refluxing to give an unsaturated pentachloro-sulphide. The latter, which evidently differs in type from (X), for even after 2½ hours' boiling with water it develops less than the theoretical quantity of hydrogen chloride with but a little extra acid, appears to be αββ-*trichloroethyl* αβ-*dichlorovinyl sulphide* (XII) derived from (XI) by loss of hydrogen chloride from the $-CCl_2 \cdot CH_2Cl$ chain, the other chain, as found by Lawson and Dawson (*loc. cit.*), being comparatively stable to heat. This, on addition of chlorine, gives αα*α*'ββ*β*'*β*'-*heptachlorodiethyl sulphide* (XIII), the absence of the grouping $CCl_3 \cdot CCl_2 \cdot S$ in which is indicated by the fact that it does not yield hexachloroethane when chlorinated in the cold.

The two unsaturated tetrachloro-compounds, whose very similar boiling points and densities have doubtless led previous observers to assume their identity, are inseparable by fractional distillation, and if, therefore, the two pentachlorodiethyl sulphides (VI) and (IX) should be formed simultaneously during the chlorination of ββ'-dichlorodiethyl sulphide, the derived unsaturated tetrachloro fraction, although distilling as one compound, would be a mixture of the two isomerides and might give any hydrolytic figure between 2% and 70%. As a result of twenty such chlorinations, however, only one instance of low hydrolysis (4·6%) was found, five hydrolysed to the extent of 68—70%, and the remainder gave values between 33% and 66%. The non-production of fractions hydrolysing in the range 5—33% is, we believe, a significant indication that these mixtures do not consist solely of the two isomerides (VII) and (X), but contain in addition a third *tetrachlorinated ethyl vinyl sulphide*, of about 33% hydrolysis, possibly αβ-*dichloroethyl* αβ-*dichlorovinyl sulphide* (XVII), derived from (IX), the parent of (X), by loss of hydrogen chloride from the other chain. This view appears to derive support from the fact that certain of the fractions of intermediate hydrolysis had a slightly lower boiling point and density than a known mixture of (VII) and (X) of the same hydrolysis, and further, that the higher chlorinated products which they gave did not appear to be identical with the corresponding compounds from (VII) and (X). The third isomeride and its derivatives (XVIII), (XIX), and (XX) have not, however, been isolated in a state of purity.

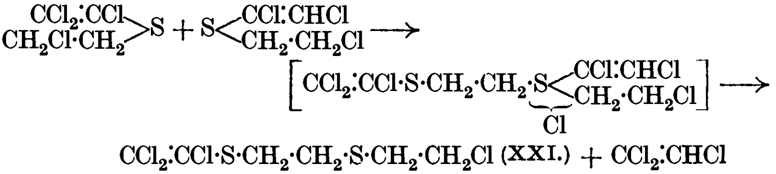
When ββ'-dichlorodiethyl sulphide is treated with more than 3 mols. of chlorine, any or all of the hexachlorodiethyl sulphides given in the scheme may be produced. In general, theααββ'-tetrachlorodiethyl sulphide (IV) is chlorinated in the α'-position to give (IX), from which the hexachloro-compounds (XI), (XIV), and/or (XVIII) are obtained by the subsequent entry of chlorine into the β'-, α'-, or β-position, respectively. It is also possible for ααβββ'-

hexachlorodiethyl sulphide (VIII) to be formed, since (IV) can be chlorinated in the β-position, but in the cases examined here, it does not appear to have been produced in any quantity.

In Expt. 35 the hexachlorodiethyl sulphide and the derived pentachlorinated ethyl vinyl sulphide approximated closely in properties to (XI) and (XII) respectively, but in other cases the products were evidently non-homogeneous. In Expt. 36, the hexachloro fraction was not examined, but the derived pentachloro fraction, though distilling as a homogeneous substance, exhibited differences in density in its various sub-fractions; the less dense fractions resembled (XIX) in properties and, like it, furnished a heptachlorodiethyl sulphide which gave hexachloroethane on further chlorination in the cold. The unsaturated tetra- and pentachloro fractions obtained in this experiment were accompanied by considerable quantities of low-boiling degradation products, presumably formed by the destructive chlorination of one or other of the polychloroethyl sulphides present. As these low-boiling fractions consisted almost exclusively of *as*-tetrachloroethane and *trichloroethyl sulphur chloride* in the approximate molecular ratio 2 : 1, they would appear to be derived from a hexachlorodiethyl sulphide of the constitution (XI) or (XIV), preferably the latter, which could evidently be chlorinated further to give either trichloroethyl sulphur chloride and *as*-tetrachloroethane, or sulphur dichloride and the chlorinated ethane. The excess of the latter would thus be accounted for, since the sulphur dichloride would not have been collected under the conditions of the experiment owing to its higher volatility. The tetrachloroethane could not, in this instance, be produced by the further chlorination of ethylene dichloride (compare Mann and Pope, *loc. cit.*), for the chlorination was carried out at about 20° in the absence of direct sunlight, and, further, neither penta- nor hexachloroethane was simultaneously formed.

There would thus appear to be reason for believing that no one hexachlorodiethyl sulphide is exclusively formed by the direct chlorination of ββ′-dichlorodiethyl sulphide, but that the product may be either (XI), (XIV), or (XVIII), or some mixture of these.

In Expt. 17, in which the tri- and tetra-chloro-compounds of Mann and Pope were the chief products, the higher-boiling fractions, on being kept, deposited a small amount of a solid, $C_6H_8Cl_4S_2$, m. p. 70·5°. This, however, is not a simple chlorination product, but is considered to arise during distillation by interaction of some of the chlorinated ethyl vinyl sulphides with the intermediate formation of a sulphonium chloride. Its exact constitution has not been determined, but it appears probable that it is a β-(*β-chloroethyl-thiol*) *ethyl trichlorovinyl sulphide* (XXI) formed by some such scheme as the following (compare Bell, Bennett, and Hock, J., 1927, 1803):



$$\begin{array}{l}\mathrm{CCl_2{:}CCl}\\ \mathrm{CH_2Cl{\cdot}CH_2}\end{array}\!\!>\!\mathrm{S} + \mathrm{S}\!<\!\!\begin{array}{l}\mathrm{CCl{:}CHCl}\\ \mathrm{CH_2{\cdot}CH_2Cl}\end{array}\longrightarrow$$

$$\left[\mathrm{CCl_2{:}CCl{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}}\underset{\mathrm{Cl}}{\underbrace{\mathrm{S}}}\!<\!\!\begin{array}{l}\mathrm{CCl{:}CHCl}\\ \mathrm{CH_2{\cdot}CH_2Cl}\end{array}\right]\longrightarrow$$

$$\mathrm{CCl_2{:}CCl{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl}\ \text{(XXI.)} + \mathrm{CCl_2{:}CHCl}$$

On the above hypothesis it is possible for a compound $C_6H_8Cl_4S_2$ to be formed in many ways, but in this case the most probable components are those suggested.

EXPERIMENTAL.

I. *Quantitative Chlorination Experiments.*

In experiments 1 to 6 (Table I) a carbon tetrachloride solution of the liquid to be chlorinated was placed in a boiling tube (A), attached to a small reflux condenser. A solution of the requisite amount of chlorine in carbon tetrachloride was placed in an adjoining vessel (B), and the two vessels were so connected that by aspirating dry carbon dioxide-free air through the apparatus the chlorine was slowly transferred *via* a capillary jet into the liquid in the reaction vessel (A). The hydrogen chloride evolved during the chlorination was collected in bubblers containing standard alkali and subsequently estimated by titration. Towards the end of the experiment (B) was gently heated to expel the last traces of chlorine, and the pressure in the apparatus reduced to about 150 mm. to ensure complete removal of hydrogen chloride.

In the second stage of the reaction (B) was removed, and the pressure in the apparatus further reduced, first to 60 mm., to expel the carbon tetrachloride, and subsequently to 15—20 mm., at which pressure the liquid was gently refluxed for some 20 minutes, the hydrogen chloride evolved during the process being collected and estimated as before. The heating was repeated until no further evolution of hydrogen chloride occurred.

Finally, the contents of the reaction vessel were fractionated through a small column. The product was, in general, a mixture of two liquids only, and more or less quantitative separation was therefore possible. Individual products were identified by boiling point and density, the composition of the middle runnings, invariably obtained in small quantity, being approximately estimated from its density.

In the larger-scale experiments (Nos. 7—16, Table I), chlorine was bubbled through the liquid at room temperature until the increase in weight of the latter indicated that the desired stage of chlorination

TABLE I.

Quantitative Chlorination Experiments.

			Quantities (g.-mols.).							
								Products of distillation.		
No.	Liquid chlorinated.	Molecular ratio, chlorine/liquid.	Liquid.	Chlorine.		HCl evolved during chlorination.	HCl evolved during heating.	Unsat. tri-chloro-compound.	Unsat. tetra-chloro-compound.	Hexa-chloro-compound.
	Small-scale experiments :									
1	$\beta\beta'$-Dichlorodiethyl sulphide	2·24	0·081	0·180		0·187	0·082	0·058	0·018	—
2	,, ,, ...	2·40	0·081	0·195		0·180	0·084	0·045	0·030	—
3	β-Chloroethyl $\alpha\beta$-dichlorovinyl sulphide...	0·29	0·056	0·016		0·0025	0·0145	0·038	0·015	—
4	,, ,, ,, ...	0·47	0·075	0·035		0·007	0·027	0·038	0·032	—
5	β-Chloroethyl $\alpha\beta\beta$-trichlorovinyl sulphide	0·32	0·068	0·022		Negligible	Negligible	—	0·044	0·02
6	,, ,, ,,	0·48	0·055	0·026		,,	,,	—	0·026	0·026
	Large-scale experiments :									
7	$\beta\beta'$-Dichlorodiethyl sulphide	2·10	2·00	4·20	not measured	Continuous	1·75	1·80	Some	—
8	,, ,, ...	2·16	1·18	2·55		,,	1·04	0·90	0·15	—
9	,, ,, ...	2·37	0·77	1·83		,,	0·76	0·45	0·27	—
10	,, ,, ...	3·10	1·00	3·10		,,	0·90	Some	0·85	Some
11	,, ,, ...	3·40	1·20	4·20		,,	0·65	—	0·55	0·50
12	,, ,, ...	4·10	0·40	1·65		,,	Not measured	—	0·15	0·08 *
13	β-Chloroethyl $\alpha\beta$-dichlorovinyl sulphide...	1·03	0·133	0·14		Slight	0·11	—	0·10	Some
14	,, ,, ,, ...	1·00	0·360	0·36		,,	0·34	—	0·29	—
15	β-Chloroethyl $\alpha\beta\beta$-trichlorovinyl sulphide	0·53	0·340	0·18		Nil	Negligible	—	0·165	0·165
16	,, ,, ,,	1·00	0·200	0·20		,,	,,	—	—	0·180

* Quantities of degradation products.

had been reached. Subsequently the product was gently refluxed under reduced pressure to constant weight, the loss in weight being taken as an approximate measure of the hydrogen chloride evolved during the heating process, and finally the product was fractionated as before.

The results of these quantitative chlorinations are in Table I, in which the quantities of reactants and products of reaction are expressed in gram-molecules.

II. *Examination of the Products of Chlorination.*

The compounds examined, prepared in a manner analogous to that employed in the larger-scale quantitative chlorinations, were purified by repeated fractional distillation through a 60 cm. column under reduced pressure. Densities and viscosities were determined as previously described (J., 1928, 155), and refractive indices with an Abbé refractometer. Rates of hydrolysis, for purposes of comparison, were roughly estimated by refluxing about 0·1 g. of the different substances with 50 c.c. of water for 15 minutes, and for 150 minutes, followed by rapid titration with baryta. The values given below are, in most instances, the mean of at least three such determinations, and are expressed in terms of % Cl split off.

(a) *Chlorination of ββ'-Dichlorodiethyl Sulphide with Two Molecules of Chlorine.*—The unstable ααββ'-tetrachlorodiethyl sulphide (IV) obtained in an impure condition by treating ββ'-dichlorodiethyl sulphide with two molecules of chlorine (Expt. 7), when cleared of dissolved hydrogen chloride by the passage of dry carbon dioxide-free air under reduced pressure, had $d_{4^\circ}^{20^\circ}$ 1·53. On heating to 90—100° even under 2 mm. pressure, it decomposed with evolution of hydrogen chloride and gave β-chloroethyl αβ-dichlorovinyl sulphide (V) in 80—90% yield. The latter, after two fractionations, was a colourless mobile liquid, b. p. 107°/15 mm., $d_{4^\circ}^{20^\circ}$ 1·4315, $d_{4^\circ}^{25^\circ}$ 1·4255, η^{20° 0·028 dyne/cm.^{2}, and $n_D^{20^\circ}$ 1·5562 (Found: C, 24·8; H, 2·6; Cl, 55·7; *M*, cryoscopic in benzene, 190. Calc. for $C_4H_5Cl_3S$: C, 25·1; H, 2·6; Cl, 55·6%; *M*, 191·5). Hydrolysis: 15 minutes, 4; 150 minutes, 12·5% Cl. Oxidation with nitric acid gave β-chloroethanesulphonic acid, identified as the ammonium salt, m. p. 198°.

(b) *Chlorination of β-Chloroethyl αβ-Dichlorovinyl Sulphide* (V).—By adding chlorine (1 mol.) to the above unsaturated trichloro-compound (Expts. 13, 14), ααβββ'-pentachlorodiethyl sulphide (VI) was obtained as an unstable yellow liquid which, on heating, lost hydrogen chloride and gave β-chloroethyl αββ-trichlorovinyl sulphide (VII) in 70—80% yield. The latter, after three fractionations, had b. p. 122—124°/15 mm., $d_{4^\circ}^{20^\circ}$ 1·5425, $d_{4^\circ}^{25^\circ}$ 1·5361, η^{20° 0·039 dyne/cm.^{2}, and $n_D^{20°}$ 1·5700 (Found : C, 21·4; H, 1·9; Cl, 62·8; *M*, cryoscopic in benzene, 225. Calc. for $C_4H_4Cl_4S$: C, 21·25; H, 1·8; Cl, 62·8%; *M*, 226). Hydrolysis : 15 minutes, 2; 150 minutes, 10% Cl. On oxidation with nitric acid it gave β-chloroethanesulphonic acid. The lower density given previously (*loc. cit.*) was that of a sample of the tetrachloro-compound obtained directly from ββ′-dichlorodiethyl sulphide [compare (d) below].

(c) *Chlorination of* β-*Chloroethyl* αββ-*Trichlorovinyl Sulphide* (VII).—From the above unsaturated tetrachloro-compound, by addition of one molecule of chlorine (Expt. 16), ααβββ′-hexachlorodiethyl sulphide (VIII) was obtained in 90% yield as a stable viscid fluid which, after purification, had b. p. 158—159°/15 mm., $d_{4°}^{20°}$ 1·6849, $d_{4°}^{25°}$ 1·6794, $\eta^{20°}$ 0·254 dyne/cm.², and $n_D^{20°}$ 1·5683 (Found : C, 16·25; H, 1·4; Cl, 71·7; *M*, cryoscopic in benzene, 297. Calc. for $C_4H_4Cl_6S$: C, 16·2; H, 1·4; Cl, 71·7%; *M*, 297). Hydrolysis : 15 minutes, 14; 150 minutes, 33% Cl. On further chlorination, even in the cold, hexachloroethane, m. p. 186—187°, was obtained. When the hexachloro-sulphide was heated at 200°/100—120 mm. for 4 hours, an unstable yellow oil slowly distilled, in too small quantity, however, for identification. The residue, on fractionation, yielded 40% of unchanged hexachlorodiethyl sulphide, but no definite lower-boiling fraction could be isolated.

(d) *Chlorination of* ββ′-*Dichlorodiethyl Sulphide with Three Molecules of Chlorine.*—When ββ′-dichlorodiethyl sulphide was treated with three molecules of chlorine (Expt. 10), the *pentachlorodiethyl sulphide* obtained (Found : Cl, 66·5. $C_4H_5Cl_5S$ requires Cl, 67·6%), when freed from dissolved hydrogen chloride, had $d_{4°}^{20°}$ 1·57. Like that described in (b), however, it lost hydrogen chloride on heating to give an unsaturated tetrachloro-compound in 75% yield.

An unsaturated tetrachloro fraction was always obtained when ββ′-dichlorodiethyl sulphide was chlorinated with more than two molecules of chlorine, and the product subsequently decomposed by heating, but out of twenty such chlorinations (Table II), in one case only (Expt. 17) did this fraction appear to be identical with the β-chloroethyl αββ-trichlorovinyl sulphide described in (b) above. In this one instance, 3·86 mols. of the sulphide were treated with about 8·88 mols. of chlorine in diffused daylight, and the β-chloroethyl αβ-dichlorovinyl sulphide (2·3 mols.), b. p. 79·2°/3 mm., obtained on fractionation was accompanied by an unsaturated tetrachloro-sulphide (0·8 mol.), b. p. 87·5—88·5°/2·6 mm., having $d_{4°}^{20°}$ 1·542, and a 15-minute hydrolysis of 4·5% Cl (Found : C, 21·2; H, 1·8; Cl, 62·5%). This was slightly impure β-chloroethyl αββ-trichlorovinyl sulphide. The higher-boiling fractions (b. p. 157—167°/2·5—3 mm.) obtained in this experiment deposited, on standing, a white solid,

TABLE II.

Formation of Unsaturated Tetrachloro-sulphides by the Chlorination of ββ′-*Dichlorodiethyl Sulphide.*

Expt. No.	Molecular ratio, chlorine/ββ′-dichloro-diethyl sulphide.	Rate of increase of wt. during chlorination (g. per min.).	Pressure during de-composition (mm.).	15-Min.-hydrolysis of unsat. tetrachloro fraction obtained.	Other products obtained.
17	2·30	—	—	4	Unsaturated trichloro-compound
18	2·41	0·74	30	33	
19	2·46	1·00	40—50	39	
20	2·85	0·48	40—50	43	
21	3·00	1·00	80	68	None
22	3·00	1·00	40—50	49	
23	3·00	1·00	30—40	33	
24	3·00	1·00	30—40	34	
25	3·00	0·62	30	50	
26	3·02	1·00	30	39	
27	3·02	1·00	30	38	
28	3·02	1·50	30	53	
29	3·03	0·05	120	69	
30	3·04	0·80	100	69	
31	3·06	1·60	20	54	
32	3·06	1·60	80—90	59	
33	3·30	0·60	80	65	Hexachloro-compounds
34	3·60	0·70	50—60	56	
35	4·08	0·30	80	70	Hexachloro-compounds and degradation products
36	4·12	—	—	69	

crystallising from alcohol in long flat needles, m. p. 70·5°, apparently a β-(β-*chloroethyl-thiol*)*ethyl trichlorovinyl sulphide* (XXI) (Found : C, 25·2; H, 2·8; Cl, 49·6; S, 22·3; *M*, cryoscopic in benzene, 271—286. $C_6H_8Cl_4S_2$ requires C, 25·2; H, 2·8; Cl, 49·6; S, 22·4%; *M*, 286).

On five other occasions (Expts. 21, 29, 30, 35, and 36) when ββ′-dichlorodiethyl sulphide was treated with 3—4 molecules of chlorine, the unsaturated tetrachloro fraction obtained on distillation appeared to be ααβ-*trichloroethyl* β-*chlorovinyl sulphide* (X). This, after three fractionations, was a colourless mobile liquid, b. p. 122—123°/15 mm., $d_{4^\circ}^{20^\circ}$ 1·5404, $d_{4^\circ}^{25^\circ}$ 1·5342, η^{20° 0·057 dyne/cm.², and $n_D^{20^\circ}$ 1·5661 (Found : C, 21·3; H, 1·9; Cl, 63·0; *M*, cryoscopic in benzene, 227. $C_4H_4Cl_4S$ requires C, 21·25; H, 1·8; Cl, 62·8%; *M*, 226). When it was boiled with water for 15 minutes, or for 150 minutes, acid equivalent to 70% Cl was liberated, but of this, 58—59% only was found by Volhard estimation to be due to hydrochloric acid.

By reason of their identical boiling points, the two isomeric unsaturated tetrachloro-sulphides, when admixed, could not be separated by fractionation, all portions of the distillate being hydrolytically and otherwise identical. The density and other physical properties of such mixtures are approximately linear functions of the composition, a known mixture of the two in about equal proportion (actually 53% of VII to 47% of X) having $d_{4°}^{25°}$ 1·5346, $\eta^{20°}$ 0·047 dyne/cm.^{2}, and $n_D^{20°}$ 1·5679, as compared with values calculated on an additive basis of 1·5352, 0·047, and 1·5681, respectively. By careful fractionation of this mixture, first and last fractions were obtained having 15-minute hydrolyses of 31 and 34% Cl, respectively, that of the original mixture being 33% Cl (Calc.: on an additive basis, 33% Cl).

In the other fourteen cases examined (see Table II), some of the unsaturated tetrachloro fractions obtained, all of which had 15-minute hydrolyses between 33 and 65% Cl, differed slightly in properties from such known mixtures, and appeared to contain a third isomeride, possibly *αβ-dichloroethyl αβ-dichlorovinyl sulphide* (XVII), having a 15-minute hydrolysis of about 33% Cl. The latter apparently formed the chief constituent of the unsaturated tetrachloro fractions obtained in Expts. 18, 23, and 24, these, after repeated fractionation, yielding a colourless liquid, b. p. 120—121°/15 mm., $d_{4°}^{15·2°}$ 1·544 (Mann and Pope, *loc. cit.*, give $d_{4°}^{15·2°}$ 1·5441 for their so-called αββ β'-tetrachlorodiethyl sulphide), $d_{4°}^{20°}$ 1·5378, $d_{4°}^{25°}$ 1·5315, $\eta^{20°}$ 0·046 dyne/cm.^{2}, and $n_D^{20°}$ 1·5673 (Found: C, 21·4; H, 1·9; Cl, 62·7. $C_4H_4Cl_4S$ requires C, 21·25; H, 1·8; Cl, 62·8%). Hydrolysis: 15 minutes, 33% Cl. The boiling point and density of this substance are, it will be observed, slightly but definitely lower than those of either of the other two isomerides.

Some of these unsaturated tetrachloro fractions of intermediate hydrolysis yielded hexachloroethane on chlorination beyond the hexachloro-stage, indicating the presence in them of β-chloroethyl αββ-trichlorovinyl sulphide [compare (c) above], but the amount appeared to be relatively small.

The rate at which the chlorination of ββ'-dichlorodiethyl sulphide was carried out did not, apparently, influence the course of the reaction to any great extent, but from the data in Table II it would appear that production of unsaturated tetrachloro fractions having intermediate hydrolysis was favoured by the employment of comparatively low pressures during the preliminary decomposition process, fractions rich in ααβ-trichloroethyl β-chlorovinyl sulphide, and hence having high hydrolysis, being, in general, obtained when pressures of 80—120 mm. were used.

(e) *Chlorination of ααβ-Trichloroethyl β-Chlorovinyl Sulphide* (X).—When ααβ-trichloroethyl β-chlorovinyl sulphide was treated with chlorine (1 mol.) in the cold, slight evolution of hydrogen chloride occurred, but the main reaction was one of addition, *ααα'ββ'β'-hexa-*

chlorodiethyl sulphide (XI) being obtained in 70—75% yield. This, after two fractionations, was a colourless oily liquid, b. p. 159—160°/15 mm., $d_{4^\circ}^{20^\circ}$ 1·6841, $d_{4^\circ}^{25^\circ}$ 1·6783, η^{20° 0·294 dyne/cm.^{2}, and $n_D^{20^\circ}$ 1·5681 (Found : C, 16·2 ; H, 1·3 ; Cl, 71·7 ; *M*, cryoscopic in benzene, 296. $C_4H_4Cl_6S$ requires C, 16·2 ; H, 1·4 ; Cl, 71·7% ; *M*, 297). Hydrolysis : 15 minutes, 31 ; 150 minutes, 55% Cl.

On heating at 200°/100—120 mm. for 3—4 hours, this hexachloro-sulphide, unlike its ααβββ′-isomeride [compare (c) above], lost hydrogen chloride and gave an unsaturated pentachloro-derivative, αββ-*trichloroethyl* αβ-*dichlorovinyl sulphide* (XII), in 65—70% yield. The latter after three fractionations was a colourless liquid, b. p. 134—135°/15 mm., $d_{4^\circ}^{20^\circ}$ 1·6293, $d_{4^\circ}^{25^\circ}$ 1·6236, η^{20° 0·065 dyne/cm.^{2}, and $n_D^{20^\circ}$ 1·5778 (Found : C, 18·5 ; H, 1·35 ; Cl, 68·2 ; *M*, cryoscopic in benzene, 260. $C_4H_3Cl_5S$ requires C, 18·4 ; H, 1·2 ; Cl, 68·1% ; *M*, 260). Hydrolysis : 15 minutes, 32·5 ; 150 minutes, 66% Cl ; of the latter, however, only 59% was found by Volhard estimation to be due to hydrochloric acid.

By the addition of one molecule of chlorine in the cold to this unsaturated pentachloro-compound, and fractionation of the product, αα′ββ′β′-*heptachlorodiethyl sulphide* (XIII) was obtained in 60—70% yield as a colourless viscid liquid, b. p. 170—172°/15 mm., $d_{4^\circ}^{20^\circ}$ 1·7473, $d_{4^\circ}^{25^\circ}$ 1·7415, η^{20° 0·427 dyne/cm.^{2}, and $n_D^{20^\circ}$ 1·5741 (Found : C, 14·5 ; H, 0·9 ; Cl, 74·8 ; *M*, cryoscopic in benzene, 329. $C_4H_3Cl_7S$ requires C, 14·5 ; H, 0·9 ; Cl, 74·9% ; *M*, 331). Hydrolysis : 15 minutes, 4 ; 150 minutes, 32% Cl. No hexachloroethane was obtained when this heptachloro-sulphide was further chlorinated in the cold.

All the above compounds, and also the unsaturated tetrachloro-sulphide from which they were derived, appeared to evolve hydrogen sulphide during hydrolysis.

(f) *Chlorination of Unsaturated Tetrachloro Fractions of Intermediate Hydrolysis.*—By the addition of one molecule of chlorine to unsaturated tetrachloro fractions of intermediate hydrolysis [see (d) above], and repeated fractionation of the product, a saturated hexachloro-sulphide, presumably mainly ααα′ββ′-*hexachlorodiethyl sulphide* (XVIII), was obtained in 70% yield ; b. p. 157—159°/15 mm., $d_{4^\circ}^{20^\circ}$ 1·6825, $d_{4^\circ}^{25^\circ}$ 1·6763, η^{20° 0·273 dyne/cm.^{2}, and $n_D^{20^\circ}$ 1·5681 (Found : C, 16·5 ; H, 1·3 ; Cl, 71·6. $C_4H_4Cl_6S$ requires C, 16·2 ; H, 1·4 ; Cl, 71·7%). Hydrolysis : 15 minutes, 25 ; 150 minutes, 56% Cl.

This, when heated at 200°/100—110 mm. for 3 hours, lost hydrogen chloride to form an unsaturated pentachloro-sulphide, possibly αβ-*dichloroethyl* αββ-*trichlorovinyl sulphide* (XIX), in 60% yield, which, after three fractionations, had b. p. 133—134°/15 mm.,

$d_{4^\circ}^{20^\circ}$ 1·6190, $d_{4^\circ}^{25^\circ}$ 1·6131, η^{20° 0·063 dyne/cm.^{2}, and $n_D^{20^\circ}$ 1·5770 (Found : C, 18·3; H, 1·4; Cl, 67·6. $C_4H_3Cl_5S$ requires C, 18·4; H, 1·2; Cl, 68·1%). Hydrolysis : 15 minutes, 32; 150 minutes, 66% Cl. Of the latter, 60% was found by Volhard estimation to be due to hydrochloric acid.

When this unsaturated pentachloro-sulphide was treated with chlorine (1 mol.) in the cold, hydrogen chloride was evolved continuously, but only the addition product could be separated on fractionation (yield, 50%). This, apparently *αα′ββββ′-heptachlorodiethyl sulphide* (XX), was obtained in too small quantity to permit of adequate purification, but after one further fractionation through a small column, it had b. p. 132—134°/*ca.* 2 mm., $d_{4^\circ}^{20^\circ}$ 1·743, $d_{4^\circ}^{25^\circ}$ 1·737, η^{20° 0·382 dyne/cm.^{2}, and $n_D^{20^\circ}$ 1·5741 (Found : C, 14·4; H, 1·0; Cl, 74·5. $C_4H_3Cl_7S$ requires C, 14·5; H, 0·9; Cl, 74·9%). Hydrolysis : 15 minutes, 8% Cl. On further chlorination in the cold hexachloroethane was obtained.

All these compounds, like those described in (d) and (e) above, evolved during hydrolysis a vapour having an odour like that of hydrogen sulphide.

(g) *Chlorination of ββ′-Dichlorodiethyl Sulphide with Four Molecules of Chlorine.*—The complete conversion of ββ′-dichlorodiethyl sulphide into hexachloro-sulphides by treatment with chlorine (4 mols.) in the cold was not found possible, maximum yields being obtained when about 3·5 mols. of chlorine were used (compare Expt. 11). Chlorination beyond this point resulted in partial destruction of the hexachloro-sulphides already formed, low-boiling chlorinated hydrocarbons and other degradation products being obtained on subsequent distillation, together with a residual tetrachloro fraction (compare Expts. 12, 35, and 36).

By reason of the number of isomerides possible and of the extreme difficulty of separating them, no attempt was made to isolate and identify the hexachlorodiethyl sulphides obtained in these experiments, investigation of the products of the reaction being restricted to an examination of the accompanying degradation products, and of the unsaturated pentachloro-compounds resulting from the decomposition of the hexachloro fractions.

In Expt. 35, the hexachloro-sulphide obtained (Found : C, 16·1; H, 1·5; Cl, 71·6%) had b. p. 158—159°/15 mm., $d_{4^\circ}^{25^\circ}$ 1·6787, and η^{20° 0·284 dyne/cm.^{2}, and decomposed, on being heated at 200°/100 mm. for 4 hours, to give an unsaturated pentachloro-sulphide having b. p. 133—134°/15 mm., $d_{4^\circ}^{25^\circ}$ 1·6237, η^{20° 0·067 dyne/cm.^{2}, $n_D^{20^\circ}$ 1·5783, and 15-minute hydrolysis of 33% Cl (Found : C, 18·3; H, 1·3; Cl, 67·8%). These values approximate closely to those found for αα′ββ′β′-hexachlorodiethyl sulphide (XI) and its decomposition product, αββ-trichloroethyl αβ-dichlorovinyl sulphide (XII), respectively [compare (e) above].

In Expt. 36, in which 5·37 mols. of ββ′-dichlorodiethyl sulphide were treated with 22·12 mols. of chlorine, the product, after decomposition by heating and subsequent fractionation, yielded 0·6 mol. of αααβ-tetrachloroethane, b. p. 35—36°/20 mm. or 129—129·7°/760 mm. (Found : C, 14·7 ; H, 1·2 ; Cl, 84·5. Calc. for $C_2H_2Cl_4$: C, 14·3 ; H, 1·2 ; Cl, 84·5%), together with 0·26 mol. of an unstable yellow liquid, b. p. 53·8°/3·5 mm., which appeared to be impure *trichloroethyl sulphur chloride* (Found : C, 13·4 ; H, 1·1 ; Cl, 69·1 ; S, 15·0 ; *M*, cryoscopic in benzene, 191. $C_2H_2Cl_4S$ requires C, 12·0 ; H, 1·0 ; Cl, 71·0 ; S, 16·0% ; *M*, 200).

Owing to the comparatively high pressure employed, the hexachlorodiethyl sulphide formed in this experiment underwent more or less complete decomposition during the preliminary heating process. The unsaturated pentachloro-sulphide derived from it, and occurring in the distillate, appeared to consist chiefly of αβ-dichloroethyl αββ-trichlorovinyl sulphide (XIX), the middle portion, after purification, having b. p. 133·5—134°/15 mm., $d_{4°}^{20°}$ 1·6183, $d_{4°}^{25°}$ 1·6125, $\eta^{20°}$ 0·069 dyne/cm.², and $n_D^{20°}$ 1·5750 (Found : C, 18·55 ; H, 1·15 ; Cl, 67·7. $C_4H_3Cl_5S$ requires C, 18·4 ; H, 1·2 ; Cl, 68·1%). Hydrolysis : 15 minutes, 31 ; 150 minutes, 66% Cl ; 63% of the latter being actually due to hydrochloric acid. When this portion was treated with one molecule of chlorine, absorption took place, accompanied by evolution of hydrogen chloride, and the product, on fractionation, yielded a *heptachlorodiethyl sulphide*, b. p. 144—146°/5·5 mm., $d_{4°}^{20°}$ 1·7373, $d_{4°}^{25°}$ 1·7325, $\eta^{20°}$ 0·379 dyne/cm.², $n_D^{20°}$ 1·5739 (Found : C, 14·4 ; H, 1·0 ; Cl, 74·8. $C_4H_3Cl_7S$ requires C, 14·5 ; H, 0·9 ; Cl, 74·9%), and hydrolysis : 15 minutes, 5 ; 150 minutes, 30% Cl, which yielded hexachloroethane on further chlorination.

The higher-boiling portion of the pentachloro fraction obtained in this experiment appeared to contain a heavier isomeride, possibly (XII) or (XV) or both. It had b. p. 134—134·5°/15 mm., $d_{4°}^{20°}$ 1·6248, $d_{4°}^{25°}$ 1·6195, and $\eta^{20°}$ 0·069 dyne/cm.² (Found : C, 18·4 ; H, 1·2 ; Cl, 67·5 ; S, 12·4. $C_4H_3Cl_5S$ requires C, 18·4 ; H, 1·2 ; Cl, 68·1 ; S, 12·3%). Hydrolysis, 15 minutes, 36% Cl. Both fractions evolved a vapour resembling hydrogen sulphide during hydrolysis.

In none of the cases examined was ααβββ′-hexachlorodiethyl sulphide (VIII) formed in appreciable quantity by the treatment of ββ′-dichlorodiethyl sulphide with four molecules of chlorine, hexachloroethane being absent from the degradation products. *as*-Tetrachloroethane and yellow oils resembling trichloroethyl sulphur chloride were of frequent occurrence in the latter, and the accompanying unsaturated tetrachloro fractions consisted for the most part of ααβ-trichloroethyl β-chlorovinyl sulphide (X).

Summary.

An extended study of the chlorination of ββ'-dichlorodiethyl sulphide with two and more mols. of chlorine has confirmed the view, advanced previously (J., 1928, 155) and independently of the work of Lawson and Dawson (*J. Amer. Chem. Soc.*, 1927, **49**, 3119, 3125), that the αββ'-trichloro- and αβββ'-tetrachloro-diethyl sulphides of Mann and Pope (J., 1922, **131**, 594) are β-chloroethyl αβ-dichlorovinyl and αββ-trichlorovinyl sulphides, respectively, and that the formation of chloroethyl chlorovinyl sulphides is in all cases due to the loss of hydrogen chloride from saturated polychlorodiethyl sulphides, which are the first, but less stable products of chlorination. Further, contrary to previous views, chlorination is not confined to one chain, as is proved by the isolation from amongst the products of direct chlorination of ββ'-dichlorodiethyl sulphide of new tetra- and penta-chlorinated ethyl vinyl sulphides and hexachlorodiethyl sulphides. The pentachlorinated ethyl vinyl sulphides furnish heptachlorodiethyl sulphides on further addition of chlorine. A mechanism of the course of chlorination is suggested.

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