XXII.—*Observations on the Chlorination Products of ββ′-Dichlorodiethyl Sulphide.*

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In the course of other investigations, it was necessary to prepare the compounds described by Mann and Pope (J., 1922, **121**, 594) as αββ′-trichloro-, αβββ′-tetrachloro-, and ααβββ′-hexachloro-diethyl sulphides, obtained by the chlorination of ββ′-dichlorodiethyl sulphide $(CH_2Cl{\cdot}CH_2)_2S$.

All three compounds as formulated above contain an α-chlorine atom. Now it is a well-known fact that the α-halogen atoms in α-halogen-substituted alkyl ethers are only very loosely attached, and extension of this general statement to include α-halogenated alkyl sulphides would appear to be justifiable from numerous observations recorded in the literature. For example, according to Mann and Pope (J., 1923, **123**, 1172), αα′-dichlorodiethyl sulphide $(CH_3{\cdot}CHCl)_2S$, is considerably less stable than the ββ′-isomeride. Peters and Walker (*Biochem. J.*, 1923, **17**, 272) have found that αα′-dichlorodimethyl sulphide is very readily hydrolysed, and Bales and Nickelson (J., 1922, **121**, 2137; 1923, **123**, 2486) have shown that, in general, α-halogenated ethyl sulphides are unstable and decompose on keeping.

Of the tri-, tetra-, and hexa-chloro-derivatives described by Mann and Pope, the last is considerably hydrolysed by boiling with water for 15 minutes, whereas the first two resist hydrolysis under similar conditions. The general stability characteristic of the compounds described as αββ′-tri- and αβββ′-tetra-chlorodiethyl sulphides was therefore remarkable, and the anomaly appeared to merit further investigation.

The percentage of hydrogen found for these compounds by Mann and Pope (see Table I) is considerably too low for αββ′-trichloro- and αβββ′-tetrachloro-diethyl sulphide, but correct for the hexachloro-compound. ββ′-Dichlorodiethyl sulphide itself gives correct hydrogen analyses, and this fact, coupled with the correct analysis given for the hexachloro-compound, again places the tri- and the tetra-chloro-compound in an anomalous position. Further,

TABLE I

Carbon and Hydrogen Analyses.

			% Found.			
	% Required.		Mann and Pope.		Present authors.	
Compound.	C.	H.	C.	H.	C.	H.
ββ′-Dichlorodiethyl sulphide, $C_4H_8Cl_2S$	30·2	5·0	—	—	30·3	5·0
αββ′-Trichlorodiethyl sulphide, $C_4H_7Cl_3S$	24·8	3·6	25·0	2·6	24·7	2·75
αββ′-Trichlorodiethyl sulphide, less two H atoms, $C_4H_5Cl_3S$	25·1	2·6				
αββ′-Trichlorodiethyl sulphoxide, $C_4H_7OCl_3S$	22·9	3·4	22·8	3·4	—	—
αβββ′-Tetrachlorodiethyl sulphide, $C_4H_6Cl_4S$	21·05	2·6	21·2	1·8	21·4	2·0
αβββ′-Tetrachlorodiethyl sulphide, less two H atoms, $C_4H_4Cl_4S$	21·25	1·8				
αβββ′-Tetrachlorodiethyl sulphoxide, $C_4H_6OCl_4S$	19·7	2·5	19·6	2·5	—	—
ααββββ′-Hexachlorodiethyl sulphide, $C_4H_4Cl_6S$	16·2	1·4	16·3	1·3	16·1	1·5

αββ′-trichloro- and αβββ′-tetrachloro-diethyl sulphoxide give, according to Mann and Pope, hydrogen analyses agreeing with those demanded by theory. These sulphoxides, however, were not prepared from the corresponding sulphides by oxidation, but were obtained from ββ′-dichlorodiethyl sulphoxide, $(CH_2Cl{\cdot}CH_2)_2SO$, by chlorination with hypochlorite solution.

As shown in Table I, we have repeated the carbon and hydrogen analyses of the tri-, tetra-, and hexa-chloro-compounds and have obtained values agreeing with those of Mann and Pope. It would seem, therefore, that the lowness of the observed hydrogen content of the tri- and the tetra-chloro-compound can be explained only on the assumption that these two substances actually do contain less hydrogen, and that they have in fact the empirical formulæ $C_4H_5Cl_3S$ and $C_4H_4Cl_4S$, respectively, instead of the formulæ $C_4H_7Cl_3S$ and $C_4H_6Cl_4S$ assigned to them by Mann and Pope.

The chlorine content of the compounds calls for some comment. The compound $C_4H_7Cl_3S$ requires 55·0% of chlorine, $C_4H_6Cl_4S$ 62·2%, $C_4H_5Cl_3S$ 55·6%, and $C_4H_4Cl_4S$ 62·8%. Analyses made by us show that the tri- and the tetra-chloro-compound actually contain 55·6% and 62·8% of chlorine, respectively, and not 55·0% and 62·2% as stated by Mann and Pope. The lower percentages of chlorine are, however, readily and repeatedly obtainable, since, owing to the great stability of the two compounds, it is only by the most protracted heating that the last traces of chlorine can be removed from them when the halogen is being estimated by the Carius method. The tetrachloro-compound gave 62·1% of chlorine after being heated at 300° for 12 hours, 62·4% after 20 hours, and 62·7% after about 60 hours. A concurrent blank experiment showed that this increase was not due to removal of halogen from the glass of the bomb tube itself.

Ultimate analysis thus appears to indicate that the tri- and the tetra-chloro-compound in question contain two hydrogen atoms less than stated by Mann and Pope, and it is suggested that they are the vinyl derivatives (I) $CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}CCl{:}CHCl$ (or $CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}CH{:}CCl_2$) and (II) $CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}CCl{:}CCl_2$ respectively. Compounds of this type, containing an accumulation of halogen atoms around a double bond, should be less readily hydrolysed than the corresponding saturated compounds.

Further support for these constitutions is afforded by the behaviour of the substances towards concentrated sulphuric acid. Both the tri- and the tetra-chloro-compound give deep red colorations, visible at very great dilutions, on treatment with this reagent, whereas the di- and the hexa-chloro-compound give negative results.

The presence of a double bond in the tri- and the tetra-chloro-compound is confirmed by a study of their parachors. From the values given by Sugden (J., 1924, **125**, 1177, 1525, and subsequent papers), for the atomic and structural constants it is evident that the decrease in parachor resulting from the loss of two hydrogen atoms is greater than the increase due to the consequent introduction of a non-polar double bond, or the formation of a three-, four-, or five-membered ring. The observed values of the parachors (Table II) are considerably less than those calculated for the compounds $C_4H_7Cl_3S$ and $C_4H_6Cl_4S$, and are, within the limits of experimental accuracy, identical with those required for the compounds $C_4H_5Cl_3S$ and $C_4H_4Cl_4S$, each containing a non-polar double bond, *i.e.*, for compounds having the structural formulæ (I and II) suggested above. Association does not account for the lowness of the experimental values, for the liquids have normal molecular weights, determined cryoscopically in benzene. Differentiation in this way between the alternative formulæ for the trichloro-compound is not possible, since position isomerism has no effect on the magnitude of the parachor.

TABLE II.

Calculated and Observed Parachors.

The calculated parachors are obtained by the summation of the requisite atomic and structural constants (Sugden, *loc. cit.*), and the observed parachors from the expression $M \times \gamma^{\frac{1}{4}}/D$, where M is the assumed molecular weight, γ the surface tension and D the density, both at the same temperature.

Formula.	[*P*] calc.	*M*.	[*P*] obs.
Trichloro-compound.			
$C_4H_7Cl_3S$	350·0	193·5	341·9
$C_4H_5Cl_3S$ containing :			
(*a*) 5-membered ring	324·3	191·5	338·4
(*b*) 4-membered ring	327·4		
(*c*) 3-membered ring	332·5		
(*d*) non-polar double bond	339·0		
Tetrachloro-compound.			
$C_4H_6Cl_4S$	387·2	228·0	377·4
$C_4H_4Cl_4S$ containing :			
(*a*) 5-membered ring	361·5	226·0	374·1
(*b*) 4-membered ring	364·6		
(*c*) 3-membered ring	369·7		
(*d*) non-polar double bond	376·2		

Finally, the gradation of other physical properties in the series ββ′-dichlorodiethyl sulphide–trichloro-compound–tetrachloro-compound is more in harmony with the present view of the constitutions of the latter two compounds than with that accepted by Mann and Pope. This is particularly evident when a comparison is made with an analogous chlorinated series, such as, for example, that based on ethylene dichloride as parent substance. If the tri- and the tetrachloro-compound are simple substitution derivatives of ββ′-dichlorodiethyl sulphide, the gradation of properties might be expected to correspond approximately with that in the series ethylene dichloride–trichloroethane–*s*-tetrachloroethane. If, on the other hand, the compounds in question are chlorinated but unsaturated derivatives of ββ′-dichlorodiethyl sulphide, the corresponding chlorinated hydrocarbon series would be ethylene dichloride–trichloroethylene–perchloroethylene. From Table III it is immediately apparent that the latter alternative is more in keeping with the facts. The very small increase in boiling point on passing from ββ′-dichlorodiethyl sulphide to the trichloro-derivative (so inappreciable under reduced pressures as to preclude separation of the two compounds by fractional distillation), the diminished increment in molecular volume (*M*/*D*) at 20°, and the decrease in viscosity (η), followed in each case by normal increments on passing to the tetrachloro-compound, all find their parallel in the series ethylene dichloride–trichloroethylene–perchloroethylene, and are in striking contrast with the regular progression in properties characteristic of a simple substitution series such as ethylene dichloride–trichloroethane–*s*-tetrachloroethane.

TABLE III.

Comparison of Physical Properties.

Compound.	B. p.	$D_{4^\circ}^{20^\circ}$.	M/D.	Diff.	η_{20°.	Log $\eta \times 10^5$.	Diff.
ββ′-Dichlorodiethyl sulphide series:							
	(15 mm.)						
Dichloro-compound	107°	1·2746	124·7		0·043	3·634	
$(CH_2Cl{\cdot}CH_2)_2S$				+ 9·1			−0·18
Trichloro-compound	107	1·4315	133·8		0·028	3·447	
$C_2H_4Cl{\cdot}S{\cdot}CCl{:}CHCl$				+13·2			+0·144
Tetrachloro-compound	124	1·537	147·0		0·039	3·591	
$C_2H_4Cl{\cdot}S{\cdot}CCl{:}CCl_2$							
Ethylene dichloride series :							
(*a*) Chlorine substitution with unsaturation.							
	(760 mm.)						
Ethylene dichloride	84	1·252	79·0		0·0084	2·924	
$CH_2Cl{\cdot}CH_2Cl$				+10·0			−0·132
Trichloroethylene	88	1·477	89·0		0·006	2·792	
$CCl_2{:}CHCl$				+13·2			+0·162
Perchloroethylene	121	1·623	102·2		0·009	2·954	
$CCl_2{:}CCl_2$							
(*b*) Simple chlorine substitution.							
	(760 mm.)						
Ethylene dichloride	84	1·252	79·0		0·0084	2·924	
$CH_2Cl{\cdot}CH_2Cl$				+13·4			+0·145
Trichloroethane	114	1·443	92·4		0·012	3·079	
$CHCl_2{\cdot}CH_2Cl$				+12·5			+0·151
s-Tetrachloroethane	146	1·600	104·9		0·017	3·230	
$CHCl_2{\cdot}CHCl_2$							

The whole of the evidence indicates that the products of chlorination of ββ′-dichlorodiethyl sulphide described by Mann and Pope as αββ′-tri- and αβββ′-tetra-chlorodiethyl sulphides are in reality di- and tri-chlorovinyl β-chloroethyl sulphides respectively.

It is proposed to attempt the synthesis of the true αββ′-tri- and αβββ′-tetra-chlorodiethyl sulphides by condensing β-chloroethyl mercaptan with mono- and di-chloroacetaldehyde in the presence of hydrogen chloride.

EXPERIMENTAL.

Preparation and Analysis.—The chlorination of ββ′-dichlorodiethyl sulphide and the separation of the products of chlorination were effected in the manner described by Mann and Pope (*loc. cit.*), the tetrachloro-compound being for convenience prepared by the direct chlorination of the trichloro-compound previously obtained. The individual products were subsequently purified by repeated fractional distillation through a Dufton column at 15 mm. pressure and obtained as colourless liquids.

(1) ββ′-*Dichlorodiethyl sulphide*: *M* in benzene, 158; m. p. 14·4°; b. p. 107°/15 mm. (Steinkopf, Herold, and Stöhr, *Ber.*, 1920, **53**, 1007, give 108°/15 mm.) (Found : C, 30·3; H, 5·0; Cl, 44·6. Calc. : C, 30·2; H, 5·0; Cl, 44·6%; *M*, 159).

(2) *Trichloro-compound* : *M* in benzene, 190; b. p. 107°/15 mm. (Mann and Pope, *loc. cit.*, give 106·5—108°/15 mm.) (Found : C, 24·75, 24·7; H, 2·75, 2·75; Cl, 55·5, 55·8. Calc. for $C_4H_5Cl_3S$: C, 25·1; H, 2·6; Cl, 55·6%; *M*, 191·5).

(3) *Tetrachloro-compound* : *M*, in benzene, 225; b. p. 124°/15 mm. (Mann and Pope, *loc. cit.*, give 123—125°/15 mm.) (Found : C, 21·4, 21·45; H, 2·0, 2·05; Cl, 62·6, 62·8. Calc. for $C_4H_4Cl_4S$: C, 21·25; H, 1·8; Cl, 62·8%; *M*, 226).

(4) ααβββ′-*Hexachlorodiethyl sulphide* : *M*, in benzene, 297; b. p. 160°/15 mm. (Mann and Pope, *loc. cit.*, give 160—161°/15 mm.) (Found : C, 16·1; H, 1·5; Cl, 71·6. Calc. for $C_4H_4Cl_6S$: C, 16·2; H, 1·4; Cl, 71·7%; *M*, 297).

The chlorine values for the tri- and the tetra-chloro-compound, respectively, were obtained after 12 and 60 hours' heating at 300°.

Hydrolysis.—A comparison of the rates of hydrolysis was made by refluxing approximately 0·12 g. of each of the substances with 50 c.c. of water for 15 minutes and rapidly titrating the liberated acid with standard bartya solution (Found : Cl, 43·6, 3·6, 2·6, and 17·25% for the di-, tri-, tetra-, and hexa-chloro-compound, respectively).

Densities.—The densities of ββ′-dichlorodiethyl sulphide and of the tri- and the tetra-chloro-compound were determined at 20° and 25° with a calibrated density bottle of approximately 5 c.c. capacity. The values obtained are in good agreement with those recorded in the literature (Mann and Pope, *loc. cit.*; Wilkinson and Wernlund, *J. Amer. Chem. Soc.*, 1920, **42**, 1382) : ββ′-dichlorodiethyl sulphide, $D_{4^\circ}^{20^\circ}$ 1·2746, $D_{4^\circ}^{25^\circ}$ 1·2693 ; trichloro-compound, $D_{4^\circ}^{20^\circ}$ 1·4315, $D_{4^\circ}^{25^\circ}$ 1·4255 ; tetrachloro-compound, $D_{4^\circ}^{20^\circ}$ 1·537, $D_{4^\circ}^{25^\circ}$ 1·531.

The densities and boiling points of the chlorinated hydrocarbons quoted for comparison in Table III are taken from the International Critical Tables, Vol. I (National Research Council, U.S.A., 1926).

Surface Tensions.—The surface tensions of the compounds were measured by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 860; 1924, **125**, 27). The bubblers employed were calibrated as described in the reference quoted, their constants being :

Apparatus	1	2	3	4	5	6	7
K_1	0·01325	0·01403	0·01339	0·01981	0·01475	0·01055	0·02664
R_2 (cm.)	0·1219	0·1215	0·1110	0·1071	0·1215	0·1433	0·0796
$K_2 = 0{\cdot}69\ R_2g$	82·51	82·24	75·14	72·5	82·24	96·97	53·88

The surface tension (γ) is obtained from the equation $\gamma = K_1(P + K_2D)$, and the parachor calculated from the expression $M\gamma^{\frac{1}{4}}/(D - d)$, where P is the difference in the pressures required to liberate bubbles from the two tubes, expressed in dynes/cm.^{2}, D and d are the densities of the liquid and vapour respectively at the temperature of measurement in g./c.c., and M is the molecular weight.

Trichloro-compound (M = 191·5).

Temp.	App. No.	P.	K_2D.	γ.	Parachor.
20°	4	1963	104	40·9	338·3
25	7	1430	76	40·1	338·1
25	2	2656	117	40·3	338·5
25	6	3669	138	40·2	338·3
30	3	2871	107	39·9	339·1
					Mean 338·4

Tetrachloro-compound (M = 226).

20	6	3799	149	41·7	373·6
20	5	2735	126	42·2	374·8
20	1	3041	127	42·0	374·3
25	6	3752	149	41·2	374·0
25	5	2668	126	41·2	374·0
					Mean 374·1

Viscosities.—The viscosities of ββ′-dichlorodiethyl sulphide and of the tri- and the tetra-chloro-compound were determined at 20° in an Ostwald viscometer by the method of Scarpa (*Gazzetta,* 1910, **40**, ii, 261). The instrument was calibrated with water, and the calibration checked by means of purified benzene and carbon tetrachloride.

The viscosities of trichloroethylene, trichloroethane, and *s*-tetrachloroethane were similarly determined. Those given in Table III for ethylene dichloride and perchloroethylene are the values obtained by Thorpe and Rodger and quoted in Landolt–Börnstein–Roth "Tabellen" (4 Auflage, 1912).

Summary.

Analytical, chemical, and physical data are given in support of the view that the products of chlorination of ββ′-dichlorodiethyl sulphide described by Mann and Pope (J., 1922, **121**, 594) as αββ′-tri- and αβββ′-tetra-chlorodiethyl sulphides are in reality dichloro- and trichloro-vinyl β-chloroethyl sulphides, respectively.

Sir W. J. Pope and Dr. F. G. Mann have read the manuscript of this paper and concur in the general conclusion that their tri- and tetra-chlorodiethyl sulphides are really substituted vinyl ethyl sulphides, but adhere to the disposition of the chlorine atoms which they previously suggested.

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