

CCCXLIII.—*The Influence of the Sulphur Atom on the Reactivity of Adjacent Atoms or Groups. Part III. δ - and ϵ -Chloro-sulphides.*

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THE experiments described in Part I (J., 1927, 477) appeared to indicate that δ -halogenated sulphides would be too unstable for isolation owing to a tendency to produce cyclic sulphonium halides by internal self-addition: $R \cdot S \cdot (CH_2)_4 \cdot X = \left[R \cdot S^+ \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \right] X^-$ (I).

Such a reaction should, however, be slower with a chloro- than with a bromo- or an iodo-sulphide. As it has been found difficult to alkylate aromatic sulphides with alkyl halides (*e.g.*, Kehrman and Duttonhöfer, *Ber.*, 1905, **38**, 4197), self-addition should also occur to a less extent in phenyl alkyl sulphides as compared with purely aliphatic compounds. We therefore undertook the preparation of *phenyl δ -chlorobutyl sulphide*, *phenyl ϵ -chloroamyl sulphide* and, for comparison, *δ -chlorobutyl ethyl* and *ϵ -chloroamyl methyl sulphides* together with the isomeric *γ -chlorodipropyl sulphide*.

The chloro-sulphides were obtained from the corresponding hydroxy-sulphides, the synthesis of which has already been described (this vol., p. 268), and their behaviour is entirely consistent with the considerations advanced above. The aliphatic δ -chlorobutyl ethyl sulphide immediately underwent self-addition to a large extent and consequently could not be distilled without decomposition. The *tetramethylene-ethylsulphonium chloride* formed from it was characterised by preparing its *chloroplatinate*. The remaining chloro-sulphides were all distilled without decomposition, although a pressure of 1 mm. was necessary in the case of phenyl ϵ -chloroamyl sulphide.

Phenyl δ -chlorobutyl sulphide does not suffer hydrolysis when heated in aqueous acetone solution, for no liberation of acid can be detected, yet ionic chlorine appears in increasing quantity. The formation of phenyltetramethylenesulphonium chloride (I; R = Ph; X = Cl) by ring closure appears to be indicated, and this is

confirmed by the isolation from the resulting solution of the corresponding *chloroplatinate* and *chloroaurate*. In the same way phenyl ϵ -chloroamyl sulphide undergoes ring closure, phenylpentamethylenesulphonium chloride being identified by conversion into the *chloroplatinate* and *chloroaurate*, and ϵ -chloroamyl methyl sulphide yields pentamethylenemethylsulphonium chloride, isolated as the *chloroplatinate*.

Quantitative measurements of the progress of these reactions at 70°, 80°, and 90° show that they are of the first order and proceed almost to completion. The velocity coefficients for the closure of the five- and six-membered rings from phenyl δ -chlorobutyl and ϵ -chloroamyl sulphides at 80° are 0.064 and 0.00084, respectively (time in minutes), and the temperature coefficient for 10° is in each case 2.56. The five-membered ring is thus formed 76 times as fast as the six-membered. It is of interest to notice that this ratio is almost identical with that (70 : 1) found by Freundlich and Krestovnikov (*Z. physikal. Chem.*, 1911, **76**, 79) for the ratio of the velocities of formation of the five- and six-membered heterocyclic rings from δ -chlorobutylamine and ϵ -chloroamylamine in presence of alkali. The velocities for these nitrogen compounds, observed at 25°, were greater than those for the chloro-sulphides at 80°, but in view of the identical temperature coefficients in the latter case (and the approximately equal coefficients in the former) the comparison is a valid one and the closeness of the two figures for the ratio of speeds of formation of a five- and a six-membered ring must be more than a coincidence.

In accordance with modern views the relatively slow formation of the six-membered ring is not to be regarded as confirming the presence of a strain in such a ring, for any strain is no doubt eliminated by suitable distortions of the molecule. The ratio of velocities of 76 : 1 is rather an indication of the relative frequency with which the terminal atoms (sulphur and carbon) of a five or a six atom chain approach close enough for reaction in the course of normal molecular contortions involving little or no strain. It would appear at first sight that different reactivities of the chlorine atoms situated in the δ - and ϵ -positions might also be involved in producing the difference under discussion. Any such difference of reactivity of the halogen is, however, according to our view, due almost entirely to the influence of a sulphur atom adjacent in space. Such an effect can only be appreciable at certain moments when the relative position of the atoms is favourable. The relative degree of such an influence through space may therefore be regarded as determined by the statistical steric factor above discussed and need not be considered separately.

Experiments on the comparative reactivities of the chlorine atoms

of these δ - and ϵ -chloro-sulphides with respect to the hydrolytic or potassium iodide reactions are not practicable owing to the transformation which these sulphides undergo spontaneously. Evidence as to the relative reactivities of the corresponding hydroxy-sulphides will, however, be submitted in a subsequent communication.

EXPERIMENTAL.

Preparation of Phenyl δ -Chlorobutyl and ϵ -Chloroamyl Sulphides.—The corresponding hydroxy-sulphide, mixed with dimethylaniline (2 mols.) and thionyl chloride (2 mols.) in chloroform, was kept for 2 hours and then heated for 20 minutes on the steam-bath. The chloroform solution was washed thrice with concentrated hydrochloric acid and twice with water, dried over calcium chloride, filtered, and evaporated. The crude chloro-sulphide was then distilled under reduced pressure.

Phenyl δ -chlorobutyl sulphide is a yellow oil, b. p. $155^\circ/12$ mm., $159^\circ/14$ mm. (Found: Cl, 17.3. $C_{10}H_{13}ClS$ requires Cl, 17.7%). The following physical constants were determined: d_4^{20} (vac.) 1.1269; n_D^{20} 1.56321, n_D^{20} 1.56828, n_F^{20} 1.58188; whence $[R_L]_C$ 57.86 (57.17), $[R_L]_D$ 58.28 (57.62), and $[R_L]_F$ 59.42 (58.52).

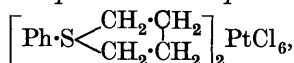
Phenyl ϵ -chloroamyl sulphide is a deep yellow oil which distils with slight decomposition at $174^\circ/14$ mm., but undecomposed at $140^\circ/1$ mm. (Found: Cl, 16.3. $C_{11}H_{15}ClS$ requires Cl, 16.5%). It has d_4^{20} (vac.) 1.1065; n_C^{20} 1.55545, n_D^{20} 1.56040, n_F^{20} 1.57328; whence $[R_L]_C$ 62.32 (61.77), $[R_L]_D$ 62.78 (62.24), and $[R_L]_F$ 63.96 (63.19).

Similar determinations of molecular refraction were made with the two lower homologues for comparison: Phenyl β -chloroethyl sulphide, b. p. $117^\circ/12$ mm., d_4^{20} (vac.) 1.1799, n_C^{20} 1.57813, n_D^{20} 1.58369, n_F^{20} 1.59842; whence $[R_L]_C$ 48.57 (47.97), $[R_L]_D$ 48.95 (48.38), and $[R_L]_F$ 49.95 (49.18). Phenyl γ -chloropropyl sulphide, b. p. $142^\circ/15$ mm., d_4^{20} (vac.) 1.1529, n_C^{20} 1.56953, n_D^{20} 1.57483, n_F^{20} 1.58881; whence $[R_L]_C$ 53.08 (52.57), $[R_L]_D$ 53.49 (53.00), and $[R_L]_F$ 54.55 (53.85). The figures in brackets are values of molecular refractivities calculated from the usual constants. The values determined are throughout high by about 0.3–0.8. Some exaltation may be due to the proximity of the sulphur atom to the nucleus, no sulphide of the type Ar-S-R having been included in the survey by Price and Twiss (J., 1912, **101**, 1259) on which the constants for sulphur are based. If the β -chlorosulphide be taken as a standard, the remaining data show satisfactory agreement.

Conversion of the Phenyl δ -Chlorobutyl and ϵ -Chloroamyl Sulphides into Cyclic Sulphonium Salts.—When a solution of phenyl δ -chlorobutyl sulphide in 50% aqueous acetone was heated at 80° , titration with standard alkali and with silver (Volhard) showed no develop-

ment of acidity, but a steadily increasing chlorion concentration. The nature of the change is shown by the measurements of the velocity of the reaction recorded below, but independent and direct proof was obtained of the formation of a sulphonium salt as follows. A portion of the solution in aqueous acetone, heated at 80° in a sealed tube for several hours, was evaporated on the steam-bath to remove acetone, cooled, and extracted with ether to remove any unchanged oil. The solution now gave precipitates with silver nitrate, sodium picrate, and chloroplatinic and chloroauric acids, of which the last two were isolated and analysed.

Phenyltetramethylenesulphonium chloroplatinate,



forms a yellow precipitate insoluble in water (Found : Pt, 25.9. $\text{C}_{20}\text{H}_{26}\text{Cl}_6\text{S}_2\text{Pt}$ requires Pt, 26.4%). For comparison, chloroplatinic acid was added to the original chloro-sulphide in acetone; a red oil separated which could not be induced to crystallise. The corresponding *chloroaurate*, $(\text{Ph} \cdot \text{S} < \text{C}_4\text{H}_8)\text{AuCl}_4$, formed a brown-yellow precipitate sparingly soluble in water but readily soluble in acetone (Found : Au, 38.8. $\text{C}_{10}\text{H}_{13}\text{Cl}_4\text{SAu}$ requires Au, 39.1%).

Similar observations were made with phenyl ϵ -chloroamyl sulphide, which is converted by heating in aqueous acetone into phenylpentamethylenesulphonium chloride. The *chloroplatinate* was obtained as a yellow precipitate insoluble in water (Found : Pt, 25.4. $\text{C}_{22}\text{H}_{30}\text{Cl}_6\text{S}_2\text{Pt}$ requires Pt, 25.5%), and the *chloroaurate* as a dark yellow precipitate insoluble in water but soluble in acetone, from which it was recrystallised (Found : Au, 37.8. $\text{C}_{11}\text{H}_{15}\text{Cl}_4\text{SAu}$ requires Au, 38.1%).

Aliphatic δ - and ϵ -Chloro-sulphides.— δ -Hydroxybutyl ethyl sulphide, after having been mixed with thionyl chloride and dimethylaniline, and the product worked up in the usual manner, yielded an oil which decomposed on distillation under diminished pressure. The liquid of b. p. 97—104°/20 mm. (decomp.) contained the required *chloro-sulphide* (Found : Cl, 17.2, 17.6. $\text{C}_6\text{H}_{13}\text{ClS}$ requires Cl, 23.2%). It was of a deep yellow colour, had the characteristic odour of chloro-sulphides, and, when kept, deposited crystals of the sulphonium chloride described below. Loss of ethyl chloride from a cyclic sulphonium salt in the distillation would account for the uncertain boiling point and the low chlorine content. The low yield (10—15%) also pointed to loss of material either by dissociation or by dissolution in the water used for washing.

The preparation was repeated, the reagents being mixed drop by drop at 40—50° and then poured at once into dilute hydrochloric acid. The chloroform layer was quickly separated, washed twice

with small amounts of dilute hydrochloric acid and once with water, and dried over sodium sulphate and the solvent was evaporated in a current of air under diminished pressure. The dark yellow oil (yield, 50%) usually set to a sludge of crystals at the end of the evaporation. This product already consisted largely of the cyclic sulphonium salt (Found in the crude oil: Cl, 16.1%). The solid *tetramethylene-ethylsulphonium chloride* was not obtained pure in quantity, but a little, drained on porous earthenware, formed pale yellow crystals, m. p. 130—135°. It is soluble in water and in chloroform but sparingly soluble in ether. The aqueous solution gave a copious precipitate with silver nitrate. This solution was obtained in quantity from the crude chloro-sulphide and from it the *chloroplatinate*, $\left[\text{Et} \cdot \text{S} \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \right\rangle_2 \right] \text{PtCl}_6$, was obtained as a yellow crystalline precipitate (Found: Pt, 30.2. $\text{C}_{12}\text{H}_{26}\text{Cl}_6\text{S}_2\text{Pt}$ requires Pt, 30.4%).

Titration of the ionic chlorine in an aqueous-acetone solution of the crude "chloro-sulphide" above described showed that its high content of chlorion did not increase when the solution was heated to 80°. δ -Chlorobutyl ethyl sulphide therefore suffers ring-closure very rapidly at laboratory temperature. It may be supposed, however, that when it is heated the sulphonium salt dissociates in the two possible ways, so that part loses ethyl chloride and part distils as the open-chain chloro-sulphide.

By the action of thionyl chloride in the usual manner ϵ -hydroxy-amyl methyl sulphide was converted into ϵ -*chloroamyl methyl sulphide* (yield, 75%), an almost colourless oil of characteristic chloro-sulphide odour, b. p. 94°/15 mm. (Found: Cl, 23.3, 23.5. $\text{C}_6\text{H}_{13}\text{ClS}$ requires Cl, 23.2%). The density and refractive index were determined on a freshly prepared specimen: d_4^{20} (vac.) 1.0300, n_D^{20} 1.48597, whence $[R_L]_D$ 42.53 (calc., 42.74).

This substance undergoes ring closure when heated in aqueous-acetone solution to give pentamethylenemethylsulphonium chloride, of which the *chloroplatinate*, $\left[\text{MeS} \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \right\rangle_2 \text{CH}_2 \right] \text{PtCl}_6$, was isolated as an orange-coloured crystalline precipitate insoluble in water (Found: Pt, 30.8. $\text{C}_{12}\text{H}_{26}\text{Cl}_6\text{S}_2\text{Pt}$ requires Pt, 30.4%).

γ -*Chlorodipropyl sulphide* was prepared for comparison by the same method from the corresponding hydroxy-sulphide. It is a colourless oil of unpleasant odour, b. p. 87°/16 mm. (yield, 85%) (Found: Cl, 23.3. $\text{C}_6\text{H}_{13}\text{ClS}$ requires Cl, 23.2%). It has d_4^{20} (vac.) 1.0267 and n_D^{20} 1.47779, whence $[R_L]_C = 42.07$ (calc., 42.41). When heated in aqueous acetone at 150°, this chloro-sulphide is slowly hydrolysed with liberation of hydrochloric acid.

Kinetics of the Formation of Cyclic Sulphonium Salts from δ - and ϵ -Chloro-sulphides.—The formation of the sulphonium salts from phenyl δ -chlorobutyl and ϵ -chloroamyl sulphides and ϵ -chloroamyl methyl sulphide was followed by titration, the Volhard method with $N/100$ -solutions being used. The chloro-sulphide was dissolved to a determined concentration in 50% aqueous acetone and sealed up in a number of glass tubes. These were heated at the required temperature by complete immersion in a vigorously stirred thermostatic bath (controlled to less than 0.1° ; thermometer recently standardised) and removed at suitable intervals, and the contents titrated. The coefficient has been calculated from the formula

$$k = 1/(t_2 - t_1) \cdot \log_e(b - x_1)/(b - x_2),$$

where b represents the amount of substance which has reacted at equilibrium and x_1 and x_2 are the amounts converted at times t_1 and t_2 , measured in minutes. The value of b was found either by assuming the equality of two values of k or from the titration at $t = \infty$, the two methods giving results in good agreement.

Phenyl δ -chlorobutyl sulphide in 50% acetone-water at 70.0° .

t (mins.).	C.c. $N/100$ -AgNO ₃ .	k .	t (mins.).	C.c. $N/100$ -AgNO ₃ .	k .
15	7.03	—	75	20.00	0.0236
30	12.45	0.0254	90	21.51	0.0249
45	16.18	0.0255	∞	24.15	—
60	18.11	0.0232			Mean 0.0245

The complete results obtained with three chloro-sulphides are given in the following table.

Sulphide.	Temp.	$k \times 10^4$ (limits).	$k \times 10^4$ (mean).	b (expressed as % converted).
Phenyl δ -chlorobutyl	70°	232—255	245	96.6
	80	610—670	630	93.6
	80	590—710	650	93.6
	90	1250—1880	1610	93.2
Phenyl ϵ -chloroamyl	80	7.55—9.70	8.3	100*
	80	7.50—10.4	8.5	100*
	90	19.9—22.0	21.5	100*
Methyl ϵ -chloroamyl	80	153—164	160	—

* By extrapolation only.

Temperature coefficient of k per 10° for phenyl δ -chlorobutyl sulphide: 70 — 80° , 2.61; 80 — 90° , 2.52; mean, 2.56: for phenyl ϵ -chloroamyl sulphide, 80 — 90° , 2.56.

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