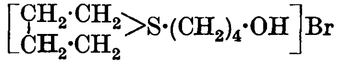
LXX.—*The Influence of the Sulphur Atom on the Reactivity of Adjacent Atoms or Groups. Part I. A Qualitative Comparison of the Reactivities of Chlorine and Hydroxyl in the α-, β-, γ-, and δ-Positions to a Sulphur Atom.*

By GEORGE MACDONALD BENNETT and ALFRED LOUIS HOCK.

THE study of sulphides substituted in the β- and γ-positions having yielded results of great interest (J., 1925, **127**, 2671), we undertook the preparation of a δ-chlorobutyl sulphide. We did not, in fact, succeed in isolating a free δ-chlorobutyl sulphide, owing to the unexpected reactivity of the δ-hydroxy sulphide and to the tendency of the halogenated sulphide to undergo internal salt-formation with production of the tetramethylene sulphide ring. δ-Halogenated butyl sulphides themselves are apparently capable of only a transitory existence. At the same time, the observations made in the course of these experiments provide ample evidence concerning the reactivity of the hydroxyl group in the δ-position.

The method of synthesis proposed was to convert benzyl δ-chlorobutyl ether (see preceding paper) into δδ'-dibenzyloxydibutyl sulphide, $S(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2Ph)_2$, to remove the benzyl groups by means of hydrobromic acid, and subsequently to convert the resulting dihydroxysulphide into the δδ'-dichlorodibutyl sulphide, $S(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl)_2$. In order to test the applicability of the method, and for purposes of comparison, the analogous reactions were first carried out in the γ-substituted propyl series, namely, the conversion of benzyl γ-chloropropyl ether into the sulphide, $S(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2Ph)_2$, and this into the hydroxy-sulphide, $S(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH)_2$, and γγ'-dichlorodipropyl sulphide, of which the last two compounds had been previously described (*loc. cit.*). This series of reactions proceeded very smoothly to give an excellent yield of the expected chloropropyl sulphide. δδ'-Dibenzyloxydibutyl sulphide was readily obtained from benzyl chlorobutyl ether and hydrobromic acid removed the benzyl groups quantitatively at laboratory temperature; but, although the reaction had been conducted in a manner precisely similar to that successfully adopted for the conversion of γγ'-dibenzyloxydipropyl sulphide into the hydroxypropyl sulphide, the second product of this fission was not dihydroxydibutyl sulphide. The substance obtained proved to be *tetrahydrothiophen-δ-hydroxybutylsulphonium bromide*,



$$\left[\begin{matrix}CH_2{\cdot}CH_2\\ |\\ CH_2{\cdot}CH_2\end{matrix}\!\!>S{\cdot}(CH_2)_4{\cdot}OH\right]Br \quad (I)$$

which was characterised as the *picrate*, the *bromoplatinate*, and the *bromoaurate.* Confirmation of the structure of this substance was furnished by its ready decomposition by heat with liberation of tetrahydrothiophen.

Whereas a tendency in a δ-halogenated sulphide to ring-closure by internal salt-formation might have been anticipated from analogy with corresponding nitrogen compounds, the rapid substitution of bromine for hydroxyl, which must have preceded it,* was entirely unexpected.

Reactivity of Hydroxyl or Chlorine in the α-, β-, γ-, *and* δ-*Positions Relative to a Sulphur Atom.*—A valid comparison of the reactivities of two compounds can only be made when the reaction involved is the same and proceeds by the same mechanism in the two cases. The reaction of the type $R{\cdot}S{\cdot}(CH_2)_n{\cdot}OH + HCl \rightleftharpoons R{\cdot}S{\cdot}(CH_2)_nCl + H_2O$ which we propose to consider is at least partially reversible, and it seems legitimate, in comparing sulphides substituted in various positions, to make reference to the behaviour of either the hydroxy- or the chloro-sulphide. The high reactivity of both hydroxyl and chlorine in the β-position and the low reactivity of both in the γ-position support this view, which is moreover justifiable from a consideration of the interpretation of this reactivity in terms of electrons (see below). We now include α- and δ-substituted sulphides, therefore, in the comparison, although the evidence refers in the former case only to a chlorosulphide and in the latter to a hydroxysulphide.

It was found by Peters and Walker (*Biochem. J.*, 1923, **17**, 260) that the rate of liberation of acid by hydrolysis in dilute aqueous-alcoholic solution from αα′-dichlorodimethyl sulphide is five times that observed with ββ′-dichlorodiethyl sulphide. Our own experiments, described above, now prove that the hydroxyl group in the δ-position to a sulphur atom has a reactivity with acids of a higher order than that in the γ-position. The reactivities of the hydroxyl group or chlorine atom in these sulphides, with respect to the reactions specified, are therefore related as follows : $\alpha > \beta > \gamma < \delta$.

Interpretation of this Conclusion with Reference to Electronic Theories of Valency.—The markedly higher reactivity of αα′-dichlorodimethyl sulphide and ββ′-dichlorodiethyl sulphide as compared with trimethylene and pentamethylene dichlorides respectively shows that the influence of the sulphur atom is the most important factor involved, any mutual effect of the two chlorine atoms being relatively insignificant.

A high reactivity of the hydroxyl group or of the chlorine atom,

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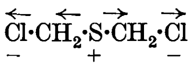
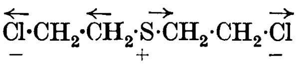
* The only alternative supposition would be the self-addition of the δ-hydroxybutyl sulphide to yield the cyclic sulphonium *base*—a reaction for which we can find no analogy in the chemistry of either sulphur or nitrogen.

with respect to the reaction studied, must depend on an increased negative charge on the oxygen or chlorine atom. Since the carbon chains in these sulphides are saturated, the possibility of an alternating polarity effect need not be considered. The high reactivity of chlorine in the α- and β-positions may be attributed to a general polar effect of the sulphur atom, which, like bivalent oxygen (compare Rây and Robinson, J., 1925, **127**, 1618), tends to repel electrons and thereby increases the negative charge on the chlorine atoms, the effect being greater in the α- than in the β-position owing to the smaller distance of chlorine from sulphur in the former case. In this process, the sulphur atom becomes positively charged to an extent which is presumably increased by the influence of the chlorine atoms in attracting electrons away from it, the reinforcement of the effect of the sulphur atom under the influence of the chlorine atoms being again greatest in the α-chloro-sulphide :

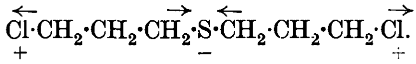


$\underset{-}{\overset{\leftarrow}{\mathrm{Cl}}}\cdot\overset{\leftarrow}{\mathrm{CH_2}}\cdot\underset{+}{\mathrm{S}}\cdot\overset{\rightarrow}{\mathrm{CH_2}}\cdot\underset{-}{\overset{\rightarrow}{\mathrm{Cl}}}$



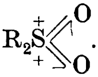
$\underset{-}{\overset{\leftarrow}{\mathrm{Cl}}}\cdot\mathrm{CH_2}\cdot\overset{\leftarrow}{\mathrm{CH_2}}\cdot\underset{+}{\mathrm{S}}\cdot\overset{\rightarrow}{\mathrm{CH_2}}\cdot\mathrm{CH_2}\cdot\underset{-}{\overset{\rightarrow}{\mathrm{Cl}}}$

In the case of the γ-chloro-sulphide, these effects will be further diminished owing to the greater distance between sulphur and chlorine. The sulphur atom is here negative (or at least much less positive), and the chlorine atoms are not made reactive :



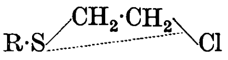
$\underset{+}{\overset{\leftarrow}{\mathrm{Cl}}}\cdot\mathrm{CH_2}\cdot\mathrm{CH_2}\cdot\overset{\rightarrow}{\mathrm{CH_2}}\cdot\underset{-}{\mathrm{S}}\cdot\overset{\leftarrow}{\mathrm{CH_2}}\cdot\mathrm{CH_2}\cdot\mathrm{CH_2}\cdot\underset{+}{\overset{\rightarrow}{\mathrm{Cl}}}.$

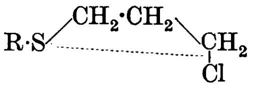
These conclusions are supported by the variations in the chemical behaviour of the sulphur atom itself. Whereas methiodides of α- or β-chloro-sulphides are unknown—although evidence that methyl iodide and ββ′-dichlorodiethyl sulphide combine to some extent was obtained by Helfrich and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1229)—we were able to isolate a crystalline derivative of the sulphonium methiodide derived from γγ′-dichlorodipropyl sulphide (Bennett and Hock, *loc. cit.*). A similar gradation in properties of the sulphur atom in these compounds is evident in the ease and extent of their oxidation either to a sulphoxide or to a sulphone, for the sulphoxide of αα′-dichlorodimethyl sulphide and both the sulphoxide and the sulphone of ββ′-dichlorodiethyl sulphide have been described, whilst we found it impossible to isolate the sulphoxide of the γ-chloro-sulphide, the sulphone being formed in all cases. In both these respects, therefore, involving addition of methyl iodide or of oxygen, the reactivity of the sulphur atom varies in the order $\alpha<\beta<\gamma$. This conclusion is exactly what would be expected as a consequence of the electronic distribution already discussed. The sulphur atom in the α- and to a less extent in the β-chloro-sulphide, being already positively charged, will tend to prevent the addition of methyl iodide. The negative nature of the sulphur atom in the γ-chloro-sulphide, on the other hand, explains its oxidation to a sulphone rather than a sulphoxide, since the production of the former gives to the sulphur atom two positive charges instead of one :

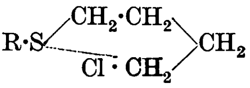


$R_2\overset{+}{\underset{+}{S}}\langle{}^{O}_{O}$.

The high reactivity of the hydroxyl group in the δ-position to the sulphur atom is, however, the most interesting result to be considered, since it furnishes definite evidence that the general polar effect, in this case at least, operates chiefly through space rather than along the chain of carbon atoms. For it is clear that if the effect of the sulphur atom on the chlorine or hydroxyl in the γ-position is only slight, its effect on the δ-hydroxyl group, if transmitted exclusively along the chain, must be negligible. At the same time, the rapid transformation of the corresponding halogenated sulphide into the cyclic sulphonium salt (I) provides experimental proof that a substituent in the δ-position does actually approach close to the sulphur atom in space, and the conclusion appears inevitable that the reactivity of the δ-substituent is due to a direct effect of the sulphur atom on it (or on the electron pair binding it to the terminal carbon atom) :







It appears to have been widely assumed hitherto that the general polar effect is transmitted either exclusively, or at least principally, along the chain of atoms. Allan, Oxford, Robinson, and Smith, for instance (J., 1926, 406, footnote), mention " possibly also an electrical effect exercised across the intervening space rather than through the chain." Our observations appear to place this possibility beyond doubt. It is probable that the general polar effect, like the alternating effect, is more readily transmitted by an unsaturated than by a saturated chain, there being more freedom of movement of electrons in the former. The chain is saturated in the case under discussion, where the effect through space has now been demonstrated, but a similar effect transmitted through space may be anticipated also where the chain is unsaturated.

EXPERIMENTAL.

γγ′-Dibenzyloxydipropyl Sulphide.—Benzyl γ-chloropropyl ether (9·2 g.) was heated for 6 hours with a solution of sodium sulphide (15 g. of $Na_2S,9H_2O$) in 50% aqueous alcohol (20 c.c.), the mixture poured into water, the oil removed in ether, and the solution washed, dried, and evaporated. The pale yellow oil (7·3 g.) left after heating for an hour at 120° under diminished pressure in a current of air was *γγ'-dibenzyloxydipropyl sulphide*, but did not crystallise and was not analysed. This substance reacted readily with fuming hydrobromic acid in the cold. After the mixture had been kept for 24 hours at the ordinary temperature, the acid and the benzyl bromide which had been produced were removed in a current of steam, and all volatile matter was then driven off by heating under diminished pressure. The residue (3·6 g.) was γγ'-dihydroxydipropyl sulphide, since the action of thionyl chloride (6·4 g.) and dimethylaniline (6·4 g.) readily converted it into the corresponding chloropropyl sulphide, b. p. 150—160°/35 mm. (2·8 g.; 77% yield from the benzyl chloropropyl ether).

δδ'-Dibenzyloxydibutyl Sulphide.—Benzyl δ-chlorobutyl ether (see preceding paper) (9·2 g.) was subjected to the action of aqueous-alcoholic sodium sulphide solution precisely as described above for the corresponding chloropropyl ether, and was thus converted into *δδ'-dibenzyloxydibutyl sulphide* (8 g.), a pale yellow oil which could not be distilled and did not solidify.

Action of Hydrobromic Acid on δδ'-Dibenzyloxydibutyl Sulphide.—Dibenzyloxydibutyl sulphide (8 g.) was covered with 48% hydrobromic acid, hydrogen bromide passed into the cooled mixture to saturation, and the whole kept at the ordinary temperature for 24 hours. A current of steam was passed to remove volatile products, and a heavy oil (7·4 g.) was then collected, b. p. 190—205°, d 1·46, identified as benzyl bromide (b. p. 198°, d^{15° 1·43; calculated yield, 7·9 g.). The residual aqueous solution was evaporated several times, and with addition of more water, under diminished pressure in order to remove free acid, and finally dried in a current of air under diminished pressure at 100°. The residue left after these operations had been completed was a viscous material readily soluble in cold water, but insoluble in ether or benzene, and by analogy with the corresponding product derived in a similar way from dibenzyloxydipropyl sulphide it was at first assumed to be dihydroxydibutyl sulphide. Yet the action of phenylcarbimide in benzene and of *p*-nitrobenzoyl chloride at 130° yielded no crystalline derivative, diphenylcarbamide and *p*-nitrobenzoic anhydride (m. p. 181°, not depressed by admixture of an authentic specimen) being produced respectively, whereas the dihydroxydipropyl sulphide reacts readily with phenylcarbimide (compare Bennett and Hock, J., 1925, **127**, 2673) and it is readily converted, when heated at 130° for 1 hour with *p*-nitrobenzoyl chloride (2 mols.), into *di*-p-*nitrobenzoyloxydipropyl sulphide*, pale yellow needles,

m. p. 104—105°, from benzene–light petroleum (Found: N, 6·4. $C_{20}H_{20}O_8N_2S$ requires N, 6·3%). The residue was also subjected to the action of thionyl chloride (2 mols.) in presence of dimethylaniline and alternatively of pyridine (2 mols.), but no insoluble dichloro-compound was obtained. A closer examination of the substance then showed it to be *tetrahydrothiophen-δ-hydroxybutylsulphonium bromide* (I). Attempts to induce crystallisation or to purify it by precipitation of its solution in ethyl alcohol by ether were unsuccessful. The aqueous solution contained ionic bromine in quantity, and when shaken with freshly-precipitated silver oxide yielded a caustic solution which liberated ammonia from ammonium chloride. With aqueous sodium picrate, a *picrate* was produced which solidified in contact with ethyl alcohol and crystallised in yellow needles, m. p. 189—190°. Heated at 250° with nitric acid and silver nitrate in a sealed tube, it yielded no silver bromide. Owing to an unexpected transformation of the sulphonium bromide on keeping for several weeks (see p. 483), no analysis of this picrate could be made.

Precipitation of the aqueous acetone or alcoholic solution of the sulphonium bromide with mercuric bromide under various conditions gave white solids of m. p. 110—135° and 150—200°, which did not seem to be definite chemical individuals and were not further examined. The *bromoplatinate* is a buff, microcrystalline powder insoluble in water and most organic solvents but readily soluble in glycerol-α-dichlorohydrin, and decomposes without melting at 165—170° (Found: Pt, 19·4, 19·2; Br, 49·7. $C_{16}H_{34}O_2Br_6S_2Pt$ requires Pt, 19·6; Br, 48·1%). The *bromoaurate* was precipitated from aqueous solution as a viscous mass which then solidified to a reddish-purple solid; after being washed with water and ether, and dried at the ordinary temperature, it melted with decomposition at 65—70° (Found: Au, 28·9; Br, 48·4. $C_8H_{17}OBr_4SAu$ requires Au, 29·1; Br, 47·3%).

When the dibenzyloxydibutyl sulphide (2 g.) and saturated hydrobromic acid (3·5 g.) were heated together in a sealed tube at 120—150° for 6 hours, the products were identical with those obtained when the reaction occurred at the ordinary temperature. The picrate, m. p. 190°, was readily obtained pure and shown to be identical with the picrate described above, and it was again found to be free from bromine.

Decomposition of Tetrahydrothiophen-δ-hydroxybutylsulphonium Bromide by Heat.—When the crude sulphonium bromide was heated, it decomposed readily, the products being almost entirely of a volatile nature. Some two-thirds of the distillate collected during the operation had b. p. 110—135°, and the remainder had b. p.

140—185°. The former fraction, which had an unpleasant odour, was separated from a little water and dried, and was then identified as tetrahydrothiophen (tetramethylene sulphide) by the preparation of its methiodide, m. p. 195—197° (decomp.) (Found : I, 54·4. Calc. : I, 55·1%) (v. Braun and Trümpler, *Ber.*, 1910, **43**, 547, give the b. p. of tetrahydrothiophen as 119° and the m. p. of the methiodide as 185—190°), its mercurichloride, m. p. 125—128° (decomp.) [Grischkevitch-Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 901, gives 124·5—125·5° (decomp.) : recrystallisation of this mercurichloride raised the m. p. to 127—133° (decomp.), but the smell of the parent sulphide was evident in the mother-liquor], and the *bromoplatinate*, an orange-red solid darkening at 230° and decomposing at 236—238° (Found : Pt, 28·5 ; Br, 45·8. $C_8H_{10}Br_4S_2Pt$ requires Pt, 28·2 ; Br, 46·2%).

Tetrahydrothiophen-δ-bromobutylsulphonium Bromide.—It was found that this substance had been unexpectedly produced from a sample of the δ-hydroxybutylsulphonium bromide which, without having been completely freed from hydrobromic acid, had been left for several weeks in a desiccator. When this was converted into its picrate, the oily substance would not crystallise on inoculation with the picrate of m. p. 190°, but it finally solidified at 0° and after eight crystallisations from ethyl alcohol, *tetrahydrothiophen-δ-bromobutylsulphonium picrate* was obtained as bright yellow needles, m. p. 92—96°, quite distinct from the picrate of m. p. 190° described above (Found : C, 36·7 ; H, 4·3 ; Br, 16·6. $C_{14}H_{18}O_7N_3BrS$ requires C, 37·2 ; H, 4·0 ; Br, 17·7%). This picrate decomposed when kept for a few days at the ordinary temperature (compare the decomposition of dimethyl-β-hydroxyethylsulphonium iodide, Renshaw, Bacon, and Roblyer, *J. Amer. Chem. Soc.*, 1926, **48**, 517). Its production is not easily accounted for in view of the fact that it was not formed in the experiment described above where the reaction was conducted in a sealed tube at 100°. It is conceivable, however, that its isolation in this case may be due to the partial dissociation of the hydroxybutylsulphonium bromide, the conversion of the δ-bromobutyl alcohol liberated into αδ-dibromobutane, and recombination of the latter with the tetrahydrothiophen to yield a bromobutylsulphonium salt.

We wish once more to express our thanks to the West Riding County Council for a scholarship which has enabled one of us (A. L. H.) to take part in the investigation recorded in this and the preceding paper, and to the Chemical Society for a grant which has defrayed some of the expense involved.

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