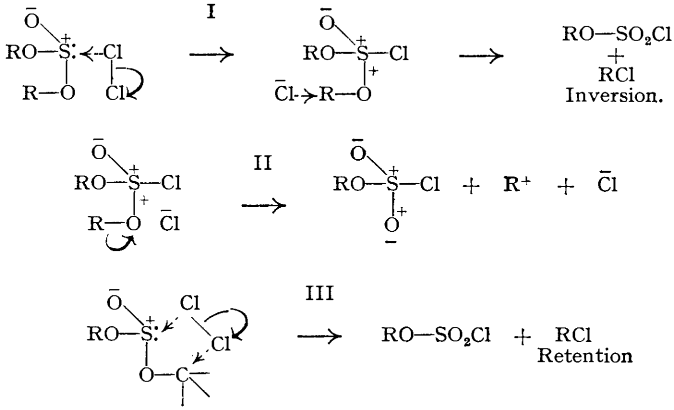
566. *Interaction of Halogens with (+)-Di-2-octyl Sulphite.*

By Arthur H. J. Cross and William Gerrard.

Chlorine readily interacted with the sulphite, R_2SO_3, of (+)-octan-2-ol, forming (—)-2-chloro-octane, accompanied by considerable loss in rotatory power, and the chlorosulphonate, $RO{\cdot}SO_2Cl$, whose interaction with pyridine resulted in the formation of pyridine–sulphur trioxide, and (—)-2-chloro-octane of the same rotatory power as the specimen obtained in the primary interaction. Similar observations were made when bromine was used instead of chlorine. It has previously been shown (Gerrard and Philip, *Research*, 1948, **1**, 477) that (—)-2-chloro-octane and (—)-2-bromo-octane were obtained with inversion and very little loss in optical activity by the respective interaction of the halogen and the phosphite, $(RO)_3P$. The spontaneous decomposition of the chlorosulphonate appears to be complex.

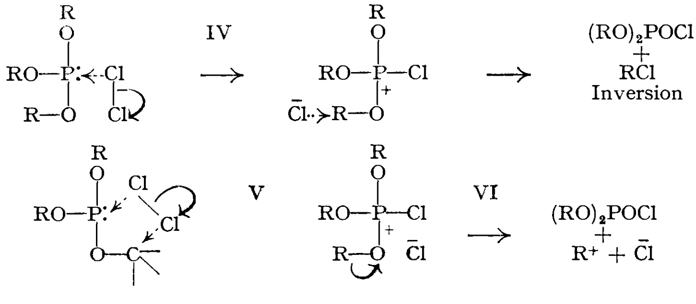
Whereas pyridine hydrochloride was quantitatively precipitated and the sulphite, (R′O)(RO)SO, was formed when *n*-butyl chlorosulphinate, $RO{\cdot}SOCl$, was added to an ethereal solution of ethyl lactate and pyridine, pyridine " sulphate " was precipitated and *n*-butyl chloride was formed instead of the expected mixed sulphate, $(RO)(R'O)SO_2$, when the sulphonate, $RO{\cdot}SO_2Cl$, was used in place of the sulphinate (Gerrard, *J.*, 1940, 218). Baumgartin (*Ber.*, 1926, **59**, 1166) had previously obtained pyridine–sulphur trioxide, C_5H_5N,SO_3, in 85% yield, by the interaction of ethyl chlorosulphonate and pyridine. Gerrard extended the methods of Bushong (*Amer. Chem. J.*, 1903, **30**, 212) and Levaillant (*Ann. Chim.*, 1936, **6**, 461) for the preparation of alkyl chlorosulphonates to the hydroxy-ester, ethyl lactate. The chlorosulphonate of the last compound, when mixed with pyridine, afforded pyridine–sulphur trioxide, unaccompanied by chloride ion, and the chloride, RCl, in 85% yield. Alkyl chlorosulphinates, RO·SOCl (Gerrard, *J.*, **1936**, 688) behaved somewhat differently: the pyridine distributed itself between (*a*) the sulphur atom (thereby forming the alkyl chloride in less than 50% yield, together with presumably unstable pyridine–sulphur dioxide), and (*b*) the alkyl group (thereby forming the quaternary compound, $RN\overset{+}{C}_5H_5O\overset{-}{S}OCl$, in considerable yield).

In the discussion of the experiments now to be described, R = 2-octyl, *n*-C_6H_{13}·CHMe·. The (—)-sulphite, $(RO)_2SO$, [from (+)-ROH] reacted readily with chlorine at —10° and afforded the (—)-chloride, RCl, α_D^{18} —20·3°, and the chlorosulphonate, RO·SO_2Cl, which reacted with pyridine to give pyridine–sulphur trioxide and the (—)-chloride, RCl, having the same rotatory power as the chloride primarily formed. It may be assumed that the configuration of R in the sulphite and in the chlorosulphonate is the same as in the alcohol from which these compounds are made by reactions not likely to disturb the bond between R and O of R—O—H. It therefore appears that the chlorine atom became attached to the asymmetric carbon atom by at least two processes, one predominating and producing inversion, the other resulting in retention of configuration and thereby reducing the rotatory power. The annexed schemes are suggested.



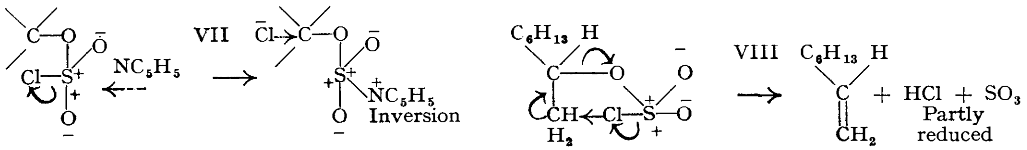
The inverted chloride, RCl, is probably due to mechanism I, and the loss in rotatory power due either to II, in which a planar carbonium ion is formed, or to III, in which a broadside approach of the chlorine molecule is postulated, or to the operation of both mechanisms. Disposition of the atoms in space is somewhat arbitrarily assumed in III, but the disposition depicted is not unlikely.

Gerrard and Philip (*loc. cit.*) obtained the (—)-chloride, without significant loss of activity, by the ready interaction of chlorine and tri-2-octyl phosphite, $(RO)_3P$ [from (+)-ROH]. The suggested mechanism is formulated in IV:



The broadside mechanism V, and the carbonium-ion mechanism VI, evidently have low probability. That II is more probable than VI is acceptable, in consideration of the lower electron density on the sulphur atom.

Pyridine may function as depicted in VII, the partial loss in activity being due either to the formation of a carbonium cation, or to an intramolecular mechanism similar to VIII, but with the chlorine atom approaching the asymmetric carbon atom. The primary reaction mixture obtained by the interaction of sulphite and chlorine undergoes some decomposition on storage, one mode of decomposition being shown in VIII. The decomposition of the distillation residue



(from the washed ethereal solution of the primary mixture) did not appear to involve the elimination of hydrogen chloride; the water-soluble matter afforded sulphuric acid, but no chloride ion.

EXPERIMENTAL.

Materials.—Octan-2-ol was resolved by the method of Kenyon (*J.*, 1922, **121**, 2540). (−)-Di-2-octyl sulphite was obtained from (+)-octan-2-ol as described by Gerrard (*loc. cit.*). Rotatory powers are recorded for $l = 1$ dm.

Interaction of Chlorine and Sulphite.—Into the (−)-sulphite, R_2SO_3, (4·54 g.), α_D^{18} −8·4° [from (+)-ROH, α_D^{18} +3·95°], chlorine was slowly passed at −10°. After 30 minutes the mixture suddenly became green, when the theoretical increase in weight in accordance with the equation, $R_2SO_3 + Cl_2 \rightarrow RCl + RO{\cdot}SO_2Cl$, was achieved. The mixture was dissolved in ether and washed with 10 separate portions of dilute aqueous sodium carbonate, with the intention of hydrolysing the chlorosulphonate and extracting the half-ester. A final washing with distilled water afforded an aqueous layer free from chloride ion. Distillation of the dried ethereal solution led to the isolation of (−)-chloride (2·03 g.; calc., 2·20 g.), b. p. 70·3°/18 mm., α_D^{20} −10·04° (α_D^{20} −20·3° for fully active ROH), and a dark brown residue (1·82 g.) which decomposed, evolving octene and sulphur dioxide, when distillation was attempted.

The aqueous washings of the ethereal solution contained 0·315 g. of chloride ion, whereas the weight calculated for complete hydrolysis of the chlorosulphonate was 0·526 g. It thus appears that the chlorosulphonate is but slowly hydrolysed to the acid, $RO{\cdot}SO_2{\cdot}OH$, under these conditions.

In a second experiment with the same sulphite (5·55 g.) the ethereal solution of the reaction mixture was washed with 4 portions of N-sodium hydroxide (distilled water then extracted no chloride ion), and from the dried ethereal solution the (−)-chloride (2·65 g.), b. p. 69°/20 mm., α_D^{20} −10·0° (for fully active ROH, α_D^{20} −20·1°), n_D^{20} 1·4291 (Found: Cl, 23·82. Calc. for $C_8H_{17}Cl$: Cl, 23·9%), and a residue (1·98 g). were obtained. The residue was coloured by carbonised matter and had an odour of sulphur dioxide (Found, for a filtered specimen: Cl, 15·3; S, 13·96. $C_8H_{17}O_3ClS$ requires Cl, 15·5; S, 14·0%).

In another experiment the residue (4·95 g. from 14·3 g. of sulphite) obtained as just described formed two layers after being kept for 4 days. The upper layer was dark brown and miscible with ether; the lower layer, blackened by small particles, was miscible with water. It is remarkable that the aqueous solution was acid and rich in sulphate ion (see later), but contained no chloride ion. After the last traces of ether had been removed from the dried ethereal solution by heating it for 10 minutes at 100°, a further separation of dark brown water-soluble liquid occurred. Therefore, the heating was continued at 100° for 24 hours, and the final mixture was treated with water and extracted with ether. The total aqueous extracts contained 1·26 g. of sulphuric acid, but no chloride ion. The ethereal solution afforded a mixture [3·09 g. (Found: Cl, 8·0%); α_D^{20} −3·2°] of octene and 2-chloro-octane, and a residue (0·5 g.) (Found: Cl, 27·7%).

In other experiments the residues described in the foregoing paragraph, when set aside at room temperature for several months, likewise separated into two layers, the water-soluble layer affording no chloride ion.

Interaction of the Chlorosulphonate and Pyridine.—The product from the interaction of chlorine and sulphite [5·27 g.; α_D^{18} −13·59°; from (+)-ROH, α_D^{18} +6·49°] was dissolved in ether and treated with pyridine (1·38 g.) at −10°. A white precipitate formed immediately, and, after 30 minutes at 0°, was separated and kept in a vacuum-desiccator for 48 hours. It then weighed 2·70 g. (Found: SO_3, 50·2. Calc. for C_5H_5N,SO_3: SO_3, 50·3%). From the washed and dried ethereal solution, the (−)-chloride (4·69 g.; calc., 5·12 g.), b. p. 70°/21 mm., α_D^{21} −16·6° (α_D^{21} −20·4°, for fully active alcohol), was obtained.

Decomposition of the Chlorosulphonate.—The reaction mixture from the sulphite [17·91 g., from (+)-ROH, α_D^{20} +8·0°] and chlorine was divided into two parts. One (7·92 g.) was washed with a solution of sodium hydroxide and dried as described. Distillation afforded the chloride (2·95 g.), b. p. 70°/21 mm., α_D^{21} −20·2°, n_D^{20} 1·4270 (Found: Cl, 23·8%), and a residue (0·96 g.). The other part (14·4 g.) was set aside at 15° in a vessel connected to an absorption vessel containing a solution of sodium hydroxide. Signs of decomposition were apparent after 2 hours, and a gas was evolved. After 48 hours, a slow stream of nitrogen was passed through the mixture for 1 hour. The absorption liquid then contained Cl, 0·933 g., and SO_2, 0·161 g. 6·15 G. of there action mixture were dissolved in ether and washed as described. From the dried solution, the chloride (2·15 g.), b. p. 72—73°/23 mm., α_D^{23} −17·0° (Found: Cl, 23·9%), and a residue (2·07 g.) (Found: Cl, 14·2%) were obtained. It is clear that the yield of chloride has not been increased by the decomposition of the chlorosulphonate; but nevertheless the chloride has suffered some racemisation.

Interaction of Sulphite and Bromine.—Into the sulphite (10·32 g.; from ROH, α_D^{20} +8·0°) bromine vapour was passed at −10°. Air was then passed to remove unchanged bromine, and the mixture was divided into 2 parts. One part (9·0 g.) was dissolved in ether and washed as described. Of the 1·54 g. of bromide ion available from the hydrolysis of the bromosulphonate, only 0·83 g. was actually extracted. From the dried ethereal solution, the bromide, RBr (3·04 g.), b. p. 82·5—84°/17 mm., α_D^{21} −18·2°, n_D^{20} 1·4520, and a residue (3·45 g.) were obtained.

The other part (6·37 g.) of the mixture was dissolved in ether and treated with pyridine (1·10 g.). From the ethereal solution, the bromide (2·84 g.), b. p. 83—84°/17 mm., α_D^{20} $-18·4°$, n_D^{20} 1·4518, was obtained.

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