# **102.** *The Decomposition of Chlorosulphinic Esters.*

By Michael P. Balfe and Joseph Kenyon.

In view of a recent contribution by Gerrard (this vol., p. 218) the views put forward by Kenyon and Phillips and their co-workers on the decomposition of semi-aromatic chlorosulphinates are redefined. In the presence of chloride anions—derived either from the hydrochlorides of tertiary bases or by formation of the unstable intermediate addition compounds—the chloride RCl is formed with inversion of configuration. In the absence of tertiary base, the chloride is formed with retention of configuration, probably by the intramolecular mechanism postulated by Hughes, Ingold, and co-workers (J., 1937, 1267).

As we believe that detailed examination of a number of the reactions which have been used in the study of the Walden inversion cannot fail to throw further light on their mechanism, we welcome the studies of Gerrard in one branch of this work. Since, however, it might be inferred from certain of his observations (*loc. cit.*) that some of the conclusions of Kenyon, Phillips, and their co-workers are erroneous, we think it desirable to comment briefly on these points.

It was suggested by Kenyon, Lipscomb, and Phillips (J., 1930, 415) that retention of configuration during the decomposition of ethyl chlorosulphinoxyphenylacetate [$Ph\cdot CH(O\cdot SOCl)\cdot CO_2Et$] in the absence of tertiary base was due to scission into a carbonium anion and chloride kation; later work, however, has shown that retention of configuration during replacement reactions of the type under discussion is unusual—such reactions are commonly accompanied either by inversion of configuration or by racemisation. Accordingly, we now prefer to adopt the view put forward by Hughes, Ingold, and co-workers (J., 1937, 1267) that the reaction proceeds by a molecular rearrangement the steric course of which is controlled by the dimensions of the chlorosulphinate molecule.

In the suggestion of Kenyon, Lipscomb, and Phillips (*loc. cit.*) to explain why inversion occurs when the above-mentioned chlorosulphinate decomposes in presence of pyridine, the structure of the suggested intermediate is less important than the fact (emphasised by Kenyon, Phillips, and Taylor, J., 1931, 382) that its formation liberates chlorine anions which may then take up suitable positions for production of the chloride with inversion of configuration; these anions may also be derived from pyridine hydrochloride, as Gerrard (J., 1939, 99) has suggested. In the absence of a tertiary base, the decomposition occurs with retention of configuration as described above. When the chlorosulphinate is prepared and allowed to decompose in the presence of one molecular proportion of pyridine, which during the decomposition is present as its hydrochloride, it follows that part of the reaction occurs with inversion of configuration (due to interaction with free chloride anion), and part is intramolecular, occurring with retention of configuration, the total product showing inversion of configuration but possessing low rotatory power. In the presence of tertiary base in excess, the concentration of free chloride anions is increased by formation of the above-mentioned intermediate; the inversion reaction is thereby facilitated, and the product possesses the inverted configuration and a comparatively high optical rotatory power. Part of the loss of optical purity in all three types of reaction may also be due to racemisation of carbonium kations which become free before the approach of the entering anion. These observations also apply to the conversion of phenylmethylcarbinol into α-phenyl-α-chloroethane by the action of thionyl chloride (Kenyon, Phillips, and Taylor, *loc. cit.*).

The relevant papers of Kenyon, Phillips, and their co-workers were published some ten years ago, and although, in view of the subsequent development of the subject, in these laboratories and elsewhere, we would now re-word their hypotheses, many of them remain essentially unchanged. Prior to Gerrard's communication (this vol., p. 218) we had thought that the desirable re-wording would be apparent to those interested in the subject, and that their publication was therefore unnecessary.

We conclude that in so far as Gerrard's results bear on the study of the Walden inversion, they agree in principle with the hypotheses put forward by Kenyon, Phillips, and their co-workers.

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