

## Stereochemistry of Product Formation in Chlorinolysis of Carbon-Sulphur Bonds

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CHLORINOLYSIS of alkyl aryl sulphides in acetic acid has been shown to occur with the intervention of several kinetically distinguishable sulphonium cation species, which regulate the subsequent product-forming steps at the carbon seat of reaction.<sup>1</sup> The stereochemistry of the solvolytic pathways involved has now been investigated. For this purpose, optically active  $\alpha$ -ethylbenzyl phenyl sulphide was subjected to the same conditions,<sup>1</sup> and the distribution of activity among the products was examined as a function of reaction medium

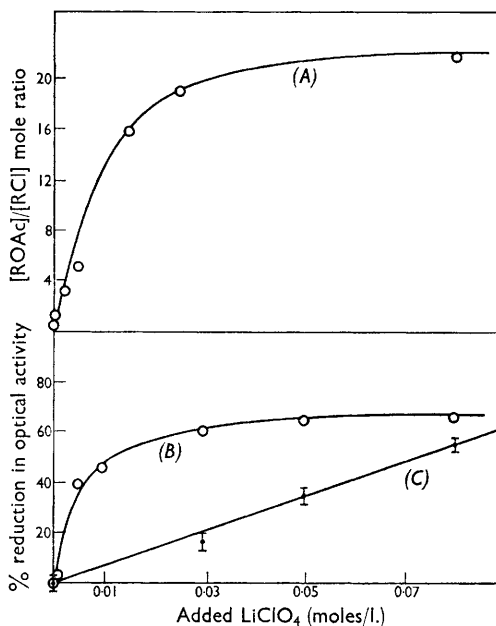
composition. The data when plotted in various ways (Figure) permit several striking inferences.

Firstly, both the optically active alkyl chloride and alkyl acetate products possessed the inverted configuration, but the optical purity of the inverted alkyl chloride was about three times that of the inverted acetate, *i.e.*, 90.5% of an excess of inverted chloride *vs.* 29% acetate.

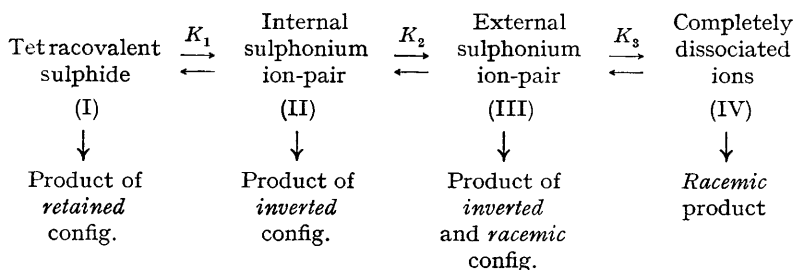
Increasing amounts of added  $\text{LiClO}_4$  induced proportionate increases in the extent (percentage) of racemization of both products; *i.e.*, 0.08M- $\text{LiClO}_4$  reduced the activity of both the chloride and acetate products to about one-third of that found in the absence of  $\text{LiClO}_4$ . A very large amount (0.25M) of  $\text{LiCl}$  (alone) produced no racemization and, indeed, increased the activity of both products very slightly.

A second significant distinction between chloride and acetate product formation is shown by comparison of curves *A* and *B* (Figure), both of which exhibit features reminiscent of the "special salt effect" on solvolysis rate.<sup>1,4</sup> This effect<sup>1</sup> in parallel with a similarly non-linear influence on the optical activity of the alkyl acetate product can be perceived, *i.e.* added  $\text{LiClO}_4$  induces a parallel increase in the amount of alkyl acetate formed and in its racemic character. On the other hand, the optical activity of the alkyl halide appears to decline with an entirely different characteristic (curve *C*) upon addition of  $\text{LiClO}_4$  to the solvolytic medium. This would suggest that the racemization of the acetate and chloride products arises from distinctly different causes. The linear nature of the chloride racemization with added  $\text{LiClO}_4$  would tend to indicate the influence of a normal salt effect.<sup>4</sup>

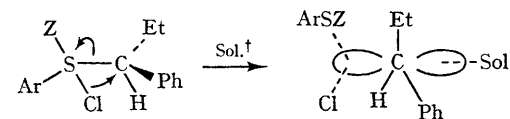
These observations may be readily reconciled with the occurrence of several kinetically distinct entities in the solvolytic reaction.



FIGURE



Apparently acetate is formed principally from (III) and (IV) and the majority of the chloride from (I) and (II). As inferred previously,<sup>1</sup> the precursor sulphonium ions (II), (III), and (IV), through transfer of their solvent structure to the developing carbonium ion, create the environment in which both bond-breaking and product-forming steps are completed. Consequently, the stereochemistry of the acetate is controlled predominantly by the ratio of product formed *via* the external ion-pair (III) and the completely separated ion (IV). It would seem that the relative proportions of these intermediates participating in product formation is influenced by the amount of LiClO<sub>4</sub>.



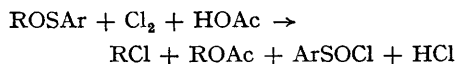
(I) (Z = Cl or OAc)

† Sol = Solvent

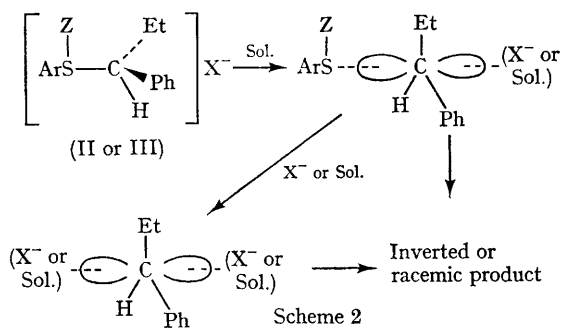
Scheme 1

The components of equilibrium  $K_1$ , *viz.* (I) and (II), are present to the greatest extent in the absence of LiClO<sub>4</sub>, (when the largest [RCl]/[ROAc] ratio is obtained). The transition state leading to product of retained configuration from (I) is visualized as an  $S_Ni$  process<sup>2,3</sup> (see Scheme 1). Here the high degree of inversion in the formation of alkyl halide is indicative of the normal predominance of (II) in the equilibrium  $K_1$ .

This contrasts with the chlorinolysis of thermally stable sulphenate esters. The overall course of these reactions is similar to that of the corresponding reactions of the thioethers:

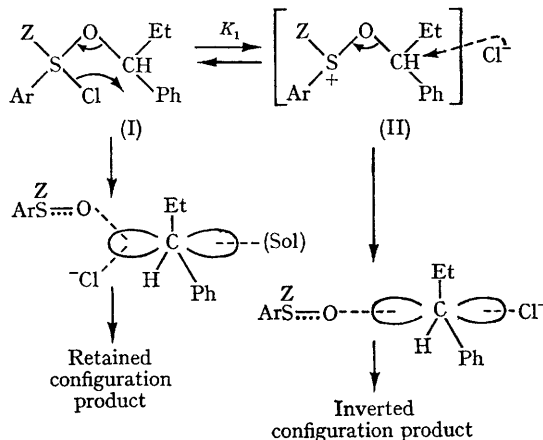


When the 2,4-dinitrophenylsulphenate ester of optically active  $\alpha$ -ethylbenzyl alcohol was chlorinolysed in exactly the same fashion as the analogous sulphide, the alkyl halide and acetate products were again found to be strongly optically active. However, the largest part, by far, of the chloride product was now composed of material of *retained configuration* while the acetate had about the same amount of (excess) inverted configuration. The four-centre transition state of bond-making and -breaking ( $S_Ni$  mechanism) in the tetravalent



Scheme 2

sulphenate ester [see (I) in Scheme 3] is the favoured route leading to RCl as compared to its formation from the intimate ion pair (II), and is apparently responsible for the nearly 80% retained configuration chloride produced in the absence of LiClO<sub>4</sub>.



Scheme 3

The formation of halide and acetate from (II) and (III) is regarded as a conventional  $S_N1$  reaction by analogy to the proposals of Doering and Zeiss.<sup>5</sup> This mechanism accounts for the incomplete racemization in the solvolysis of tertiary alkyl esters as indicated in Scheme 2, where  $X^- = \text{Cl}^-$  or  $\text{ClO}_4^-$  and the brackets denote a solvent structure determined by whether internal or external ion-pairing, or completely separated ions exist.

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<sup>1</sup> H. Kwart, R. W. Body, and D. M. Hoffman, preceding Communication.

<sup>2</sup> E. S. Lewis and C. E. Boozer, *J. Amer. Chem. Soc.*, 1952, **74**, 308; 1953, **75**, 3182.

<sup>3</sup> H. Kwart and R. W. Body, *J. Org. Chem.*, 1965, **30**, 1188.

<sup>4</sup> For a detailed comparison of normal and special salt effects, see S. Winstein, E. Clippinger, A. H. Fainberg, and C. G. Robinson, *J. Amer. Chem. Soc.*, 1954, **76**, 2957.

<sup>5</sup> W. E. Doering and H. H. Zeiss, *J. Amer. Chem. Soc.*, 1953, **75**, 4733.