# Thermal Rearrangement of 2-Chloro-1-(chloromethyl)ethyl Acetate

By R. Garth Pews* and Ralph A. Davis

(Halogens Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640)

Summary 2-Chloro-1-(chloromethyl)ethyl acetate (1a) and 2,3-dichloropropyl acetate (2a) equilibrate under thermal conditions by an unprecedented intermolecular pathway, i.e., solvent-separated ion pairs.
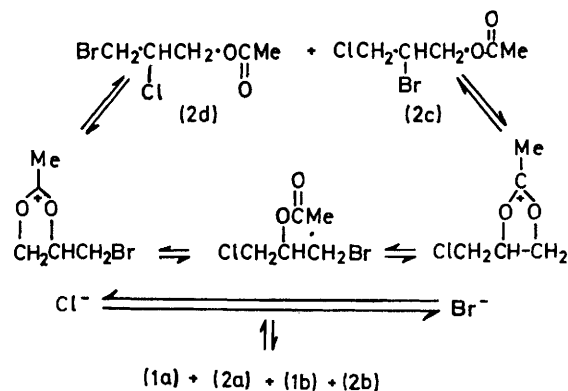
THE rearrangement of halohydrin esters in cyclic systems, i.e., the diaxial → diequatorial rearrangement has been studied extensively.[1] We report a halohydrin acetate rearrangement in the acyclic series.

$$XCH_2CHCH_2Y \rightleftharpoons XCH_2CHCH_2OCOMe$$
$$\underset{OCOMe}{|} \qquad\qquad \underset{Y}{|}$$
$$(1) \qquad\qquad\qquad (2)$$
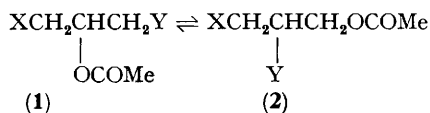
a;	X = Y = Cl
b;	X = Y = Br
c;	X = Cl, Y = Br
(2d);	X = Br, Y = Cl

The dichloro-acetate (1a) rearranges when heated at 180° to an equilibrium mixture of (1a) (37%) and (2a) (63%) in 9 h. The corresponding dibromides (1b) and (2b) equilibrate in less than 30 min at 180°. Equilibration of the bromochloro-acetate (1c) gave not only the expected isomeric 1,2-bromochloro-acetates (2c) and (2d) but also the corresponding dichloro-acetates (1a) and (2a), and dibromo-acetates (1b) and (2b). The rearrangement product of (1c) was assumed to be a mixture of the isomeric acetates (2c) and (2d).

SCHEME

Elimination of acetyl chloride and formation of an equilibrium between acetyl halide and the epihalohydrin was excluded as a possible mechanism. Thermolysis of (2b) in the presence of excess of epichlorohydrin at 180° for 30 min produced only the equilibrium mixture of (1b) and (2b) with no detectable amounts (< 1·0%) of the bromochloro-acetates (1c), (2c), and (2d). We suggest that the bromochloro-acetate (2c) rearranges via an acetoxonium ion with concomitant scrambling of the solvent separated gegenions as in the Scheme.

[1] V. Hach, J. Org. Chem., 1971, 36, 2568; C. A. Grob and S. Winstein, Helv. Chim. Acta, 1952, 35, 782; D. H. R. Barton and J. F. King, J. Chem. Soc., 1958, 4398; J. F. King and R. G. Pews, Canad. J. Chem., 1965, 43, 847.