

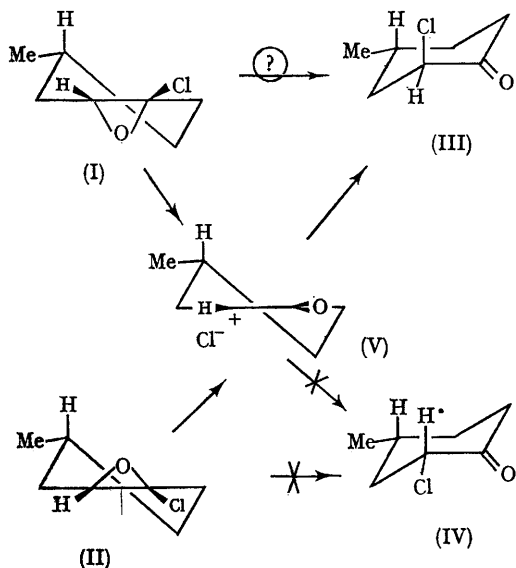
## An $\alpha$ -Ketocarbenium Ion-Chloride Ion Pair in the Thermal Rearrangement of 1-Chloro-*cis*- and -*trans*-4-methylcyclohexene Oxide<sup>1</sup>

By RICHARD N. McDONALD and THEODORE E. TABOR

(Department of Chemistry, Kansas State University, Manhattan, Kansas 66502)

EPOXIDATION of 1-chloro-4-methylcyclohexene produces a mixture of 1-chloro-*cis*- and -*trans*-4-methylcyclohexene oxide [(I) and (II), respectively].<sup>2</sup> Thermal rearrangement of this mixture under reduced pressure (10 mm.) yields nearly exclusive initial formation of *trans*-2-chloro-4-methylcyclohexanone (III) with the *cis*-isomer (IV) arising during later stages of rearrangement by the known equilibration of (III) and (IV).<sup>3</sup> To demonstrate that there is no significant difference

in the rates of rearrangement of the isomeric  $\alpha$ -chloro-epoxides (I) and (II), the n.m.r. spectra were taken of successive fractions of the  $\alpha$ -chloro-epoxide mixture during a very slow distillation in which partial rearrangement occurred. These spectra showed essentially no change in the composition of the  $\alpha$ -chloro-epoxide mixture. Vapour-phase-chromatographic analysis of the pot residue showed only the presence of (III) along with some unrearranged epoxide.



Our interpretation of these results involves the intermediacy of the  $\alpha$ -ketocarbonium ion-chloride ion pair (V). Preferential *axial* carbon-chlorine bond formation would be favoured stereoelectronically and lead to (III), the product of kinetic control. In the presence of trace amounts of hydrogen chloride (III) could then isomerize to (IV), the product of thermodynamic control. This argument is somewhat similar to the observation that *axial*  $\alpha$ -bromo-ketones are predominantly produced in the bromination of a number of oxosteroids under kinetically controlled conditions.<sup>4</sup>

This interpretation rules out a chloronium ion as the method of chlorine migration in the rearrangement of (II). Such a mechanism for chlorine transfer in the rearrangement of (I) to (III) cannot as yet be definitely eliminated, but it appears most likely that (V) is also involved here.

(Received, August 15th, 1966; Com. 600.)

<sup>1</sup> Paper IV in the series "Molecular Rearrangements".

<sup>2</sup> This is rationalized from the nature of the reaction, and the n.m.r. spectrum of the product exhibiting two methyl doublets at  $\tau$  9.10 and 9.18, and the expected multiplicity for the epoxide ring proton.

<sup>3</sup> E. Campaigne and R. D. Lake, *J. Org. Chem.*, 1959, **24**, 478; M. Godchot and P. Bedos, *Compt. rend.*, 1925, **180**, 295.

<sup>4</sup> E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, pp. 241-242 and references therein.