Isolation of Cyclohexene Oxide from the Chromyl Chloride Oxidation of Cyclohexene

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Summary Oxidation of cyclohexene with chromyl chloride gives, among other products, cyclohexene oxide in low yield.

Although it has been postulated that epoxide type intermediates occur in the chromyl chloride oxidation of olefins,[1] as yet, no epoxide has been isolated. Epoxides have been isolated from oxidations by chromium trioxide[2] and chromyl acetate[3] suggesting that they also occur in the case of chromyl chloride. However under the normal work-up conditions, either aqueous acid or aqueous bisulphite, epoxides usually decompose. We report that the decomposition of the chromyl chloride–cyclohexene complex, suspended in methylene chloride, with cold 5% aqueous sodium bicarbonate allowed the isolation of cyclohexene oxide in a yield of 1·5%. Other products isolated from the reaction (based on recovered cyclohexene) were cyclohexanone (5%), 2-chlorocyclohexanone (7·5%), *cis*-2-chlorocyclohexanol (20%), *trans*-2-chlorocyclohexanol (30%), cyclohex-2-en-1-ol (5%), cyclohex-2-en-1-one (10%), and polymeric material (22%). With a large excess of cyclohexene and a very short reaction time, the amount of epoxide increased to 3·5% of the reaction products while the cyclohexanone decreased to 1·6%. No significant changes were observed in the yields of the other products. Thus the epoxide is mainly converted into the ketone presumably by Lewis acid catalysis.[4]

That the epoxide did not arise from the *trans*-chlorohydrin was demonstrated by subjecting authentic *trans*-chlorohydrin to similar work-up conditions. No detectable amount of epoxide was formed by treating *trans*-2-chlorocyclohexanol with 5% sodium bicarbonate at room temperature for several hours. If the chromyl chloride–cyclohexene complex is decomposed in water or aqueous bisulphite, no epoxide is detected.

Our results are similar to those of Stairs *et al.*[5] but we have isolated three additional products, the epoxide, the chloroketone and the allylic alcohol. Attempts to isolate the epoxides of styrene and α-pinene were unsuccessful, these epoxides being exceedingly unstable under reaction conditions.

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