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RING CLEAVAGE OF EPOXIDES WITH THIOANISOLE-CHLORINE COMPLEX: A SIMPLE SYNTHESIS OF & CHLOROCARBONYL COMPOUNDS

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The reaction of epoxides (<u>1</u>) with thioanisole-chlorine complex (<u>2</u>) produced (-chlorosulfoxonium intermediates (<u>3a</u> and/or <u>3b</u>), which were quenched with aqNaHCO₃ to afford (-chloroalcohols (<u>4a</u> and/or <u>4b</u>). The intermediate (<u>3a</u> and/or <u>3b</u>) gave (-chlorocarbonyl compounds (<u>5a</u> and/or <u>5b</u>) by treatment with triethylamine.

The ring cleavage of epoxides with various kinds of reagents has been a subject of current interest due to their wide applications in organic synthesis. Ring opening of epoxides with methylsulfide-chlorine complexes developed by Corey et $al_{\cdot}^{1)}$, which transform alcohols to carbonyl compounds, could be one of promising methods applied to epoxide chemistry. Thus we report here a new method for ring cleavage of epoxides and a novel one-step synthesis of α -chlorocarbonyl compounds under mild conditions. The overall synthetic transformation is represented by the scheme I.

The general procedure is described below for the transformation of cyclohexene oxide to 2-chlorocyclohexanol and to 2-chlorocyclohexanone and the results obtained with five different epoxides were summarized in the table I.

To a solution of 2.14g (30.6 mmol) of Cl_2 in 30 ml of CCl_4 was added at -25°C a solution of 3.80g (30.6 mmol) of thioanisole in 15 ml of CH_2Cl_2 under argon. A white precipitate appeared immediately after addition of thioanisole. To the mixture was added a solution of 1.50g (15.3 mmol)of cyclohexene oxide in 20 ml of CH_2Cl_2 . (a) The reaction mixture was poured into large excess of saturated aqNaHCO₃. The organic layer was dried over Na₂SO₄. Removal of dried solvents under reduced pressure produced 2-chlorocyclohexanol almost quantitatively (>98%) after purification by silica gel short column. (b) The reaction mixture was further treated with a solution of 6.18g (61.2 mmol) of triethylamine in 20 ml of CH_2Cl_2 at -25°C to -30°C. The cooling bath was removed and after 5 min 120 ml of Et₂0 was added. The organic layer was washed with 15 ml of 1% aqHCl and dried over MgSO₄. Removal of dried solvents under reduced pressure gave a pale yellow oil which was purified by silica gel short column to give 1.90g (94%) of 2-chlorocyclohexanone. The structures of all products and their ratios were sufficiently analyzed by ir, pmr and mass spectroscopy. Further study on the application of this reaction is in progress. SCHEME I



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- a) Isolated yield after purification on silica gel short column.
- b) The ratio of <u>8a</u> and <u>8b</u> was tentatively estimated from the ratio of <u>N</u>-chlorocarbonyl compounds <u>12a</u> and <u>12b</u>.
- c) The ratio of <u>l0a</u> and <u>l0b</u> was calculated based on area intensities of their methyl signals of pmr spectrum [<u>l0a</u> δ : l.55_{ppm}(3H, s); <u>l0b</u> δ : l.27_{ppm}(3H, s)].
- d) Trans configuration of 2-chlorocyclohexanol $\underline{9}$ was unambiguously comfirmed with pmr peaks of its acetate $\underline{15}$.

Ha (axial):
$$3.86_{ppm}$$
 (ddd, J=4.0, 9.0, 10.0 Hz)
Hb (axial): 4.86_{ppm} (ddd, J=5.0, 9.5, 10.0 Hz)
Hb (axial): 4.86_{ppm} (ddd, J=5.0, 9.5, 10.0 Hz)

- e) Stereochemistry of these two compounds <u>10a</u> and <u>10b</u> was tentatively deduced by followings; a) by analogy of run 4), b) by the fact that only two different compounds were quantitatively obtained.
- f) Under oxidative condition χ -chloroaldehyde C₆H₅CHClCHO expected to be derived from <u>3a</u> was not obtained, but further chlorinated aldehyde C₆H₅CCl₂CHO was obtained in moderate yield.
- g) The ratio was calculated based on area intensities of aldehyde proton $[9.3_{ppm}$ (1H, d)] of <u>12a</u> and chloromethylene proton [3.89_{ppm}(2H, s)] of <u>12b</u>.

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