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# A Mild Method for Conversion of Epoxides into α-Chloro Ketones

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***Abstract:*** Epoxides on treatment with DMSO, oxalyl chloride, and 10 mole % of methanol in the presence of triethylamine at -60° C are converted to α-chloro ketones in high yield.

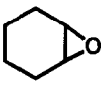
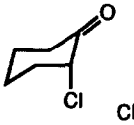
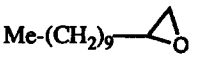
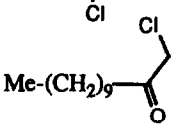
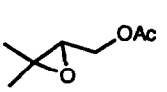
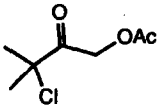
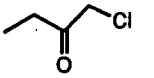
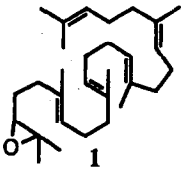
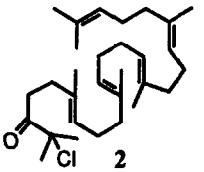
Conversion of α-chloro ketones to optically active epoxides via enantioselective reduction[1] is a very important transformation in organic synthesis. As a part of our programme on enantioselective synthesis of (3*S*)-2,3-oxidosqualene **1**[2], we required to prepare the corresponding α-chloro ketone **2**. Despite the availability of many methods for the synthesis of α-chloro ketones involving the use of olefin[3a], α-halohydrin[2,3b], ketones[3c], and epoxides[3d], there still exists a need for new method, especially for complex and sensitive molecules. In this paper we report a simple and mild method for direct conversion of epoxides to α-chloro ketones through the use of dimethyl sulfoxide, oxalyl chloride, and catalytic amount of methanol in the presence of triethylamine

The reaction of dimethyl sulfoxide and oxalyl chloride at -60° C gives chlorodimethyl sulfonium salt,[4] which readily opens cyclic epoxides to α-chloro alkoxysulfonium salt. But, in the case of acyclic epoxides the reaction is either arbitrary or does not proceed at all. However, we have observed that upon addition of 5-10 mole % of methanol, both the types of epoxides are opened to α-chloro alkoxysulfonium salt, which on treatment with base gives α-chloro carbonyl compounds. In the case of terminal epoxides, 3 to 5 % of α-chloroaldehyde was also obtained. The following is the typical procedure for the conversion of epoxide to α-halo carbonyl compounds:

Oxalyl chloride (2.5 mmol) was added to a solution of DMSO (2.5 mmol) in $CH_2Cl_2$ (10 ml) at -60° C. The reaction mixture was stirred for 5 min and then epoxide (1.0 mmol) and methanol (0.1 mmol) were added. After stirring for 30 min at -60° C, triethylamine (5 mmol) was added and the mixture was stirred for 10 min and then allowed to warm to room temperature (30 min). Usual work-up[4] gave α-chloro ketone[5] in high yield (Table 1).

Further work in the form of mechanism, scope, and application in synthesis in this area is still in progress and will be reported soon.

**Table 1**: Reaction of epoxides with DMSO-ClCOCOCl-MeOH-$Et_3N$ in $CH_2Cl_2$.

| Epoxides | α-Chloro ketones | Isolated Yield (%) |
|---|---|---|
|  |  | 94 |
|  |  | 88 |
|  |  | 90 |
|  |  | 70 |
|  1 |  2 | 55 |

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5. All the compounds were fully characterized by spectral and analytical data.

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