

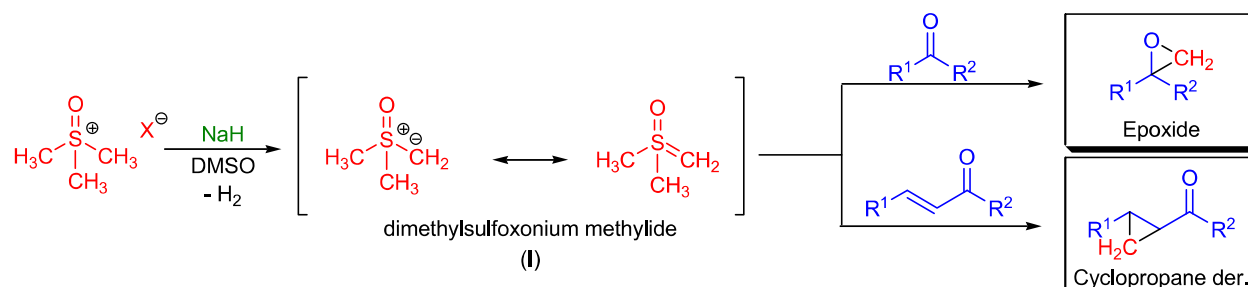
## COREY-CHAYKOVSKY EPOXIDATION AND CYCLOPROPANATION

(References are on page 565)

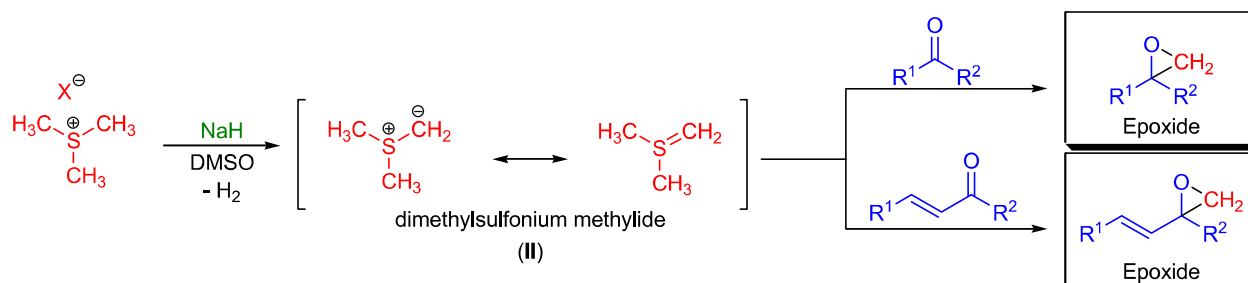
### Importance:

[Seminal Publications<sup>1,2</sup>; Reviews<sup>3-11</sup>; Modifications & Improvements<sup>12-14</sup>; Theoretical Studies<sup>15-17</sup>]

In 1962, E.J. Corey and M. Chaykovsky deprotonated trimethylsulfoxonium halides using powdered sodium hydride under nitrogen at room temperature to form a reactive compound, dimethylsulfoxonium methylide (I).<sup>1</sup> When simple aldehydes and ketones were mixed with I, the formation of epoxides was observed. Likewise, the reaction of dimethylsulfonium methylide (II) with aldehydes and ketones also resulted in epoxide formation.<sup>2</sup> Compounds I and II are both sulfur ylides and are prepared by the deprotonation of the corresponding sulfonium salts. The preparation of epoxides (oxiranes) from aldehydes and ketones using sulfur ylides is known as the *Corey-Chaykovsky epoxidation*. When I is reacted with  $\alpha,\beta$ -unsaturated carbonyl compounds, a conjugate addition takes place to produce a cyclopropane as the major product. This reaction is known as the *Corey-Chaykovsky cyclopropanation*.<sup>1</sup> Sulfur ylide II is more reactive and less stable than I, so it is generated and used at low temperature. The reaction of substituted sulfur ylides with aldehydes is stereoselective, leading predominantly to *trans* epoxides. Asymmetric epoxidations are also possible using chiral sulfides.<sup>12,6</sup> The use of various substituted sulfur ylides allows the transfer of substituted methylene units to carbonyl compounds (isopropylidene or cyclopropylidene fragments) to prepare highly substituted epoxides. Since the S-alkylation of sulfoxides is not a general reaction, it is not practical to obtain the precursor salts in the trialkylsulfoxonium series. This shortcoming limits the corresponding sulfur ylides to the unsubstituted methylide. However, sulfur ylide reagents derived from sulfoximines offer a versatile way to transfer substituted methylene units to carbonyl compounds to prepare oxiranes and cyclopropanes.<sup>12</sup>

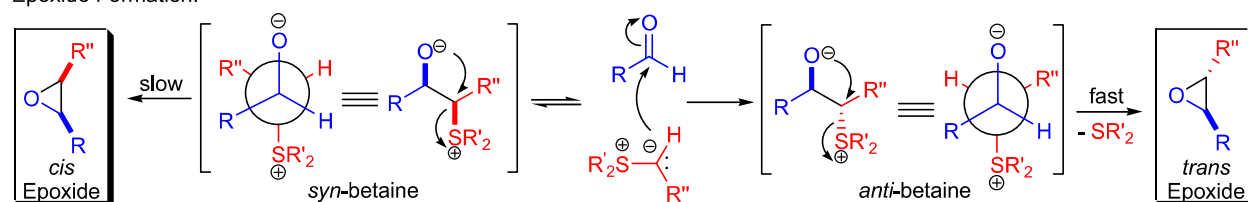


X = Cl, Br, I



### Mechanism: <sup>18-25</sup>

Epoxide Formation:



Cyclopropane Formation:

