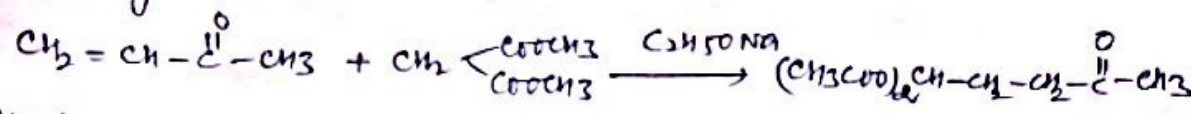
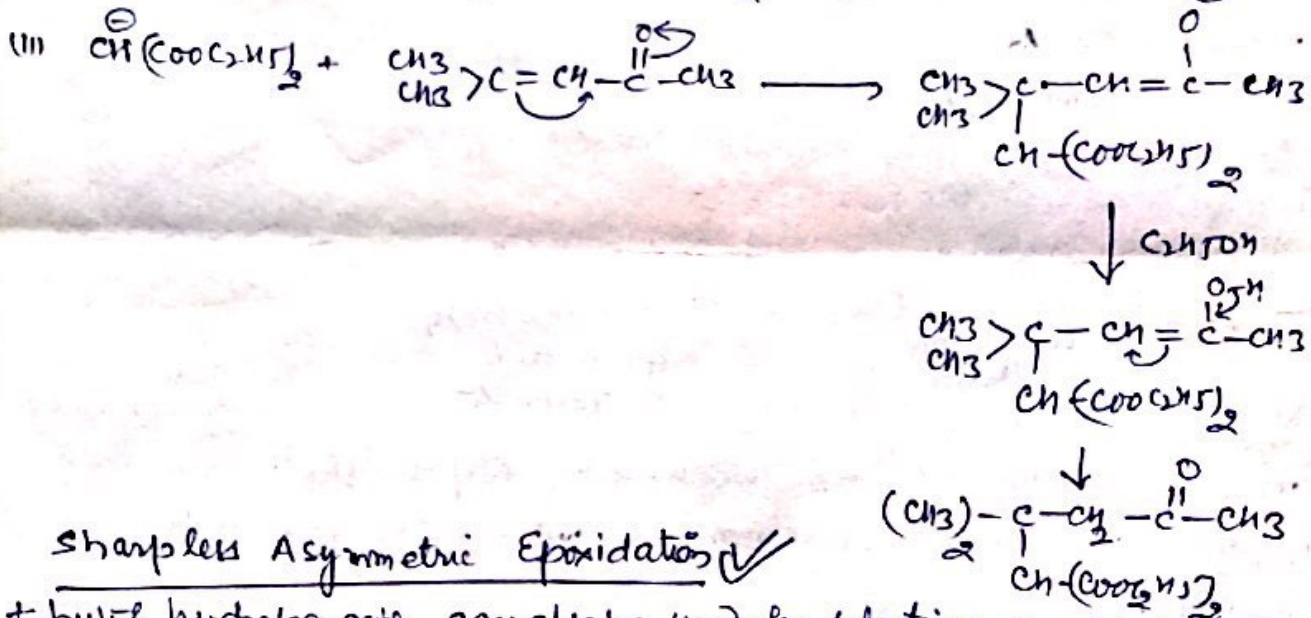
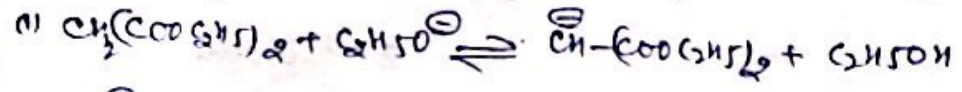


It is the addition reaction between α, β unsaturated carbonyl compound and a compound with active methylene group (malonic ester, aceto acetic ester, cyanoacetic ester etc.) in presence of a base such as sodium ethoxide or secondary amine.



Mech: The enolate derived from malonic ester attacks the β -carbon atom of the unsaturated compound. The resulting carbanion is stabilized by carbonyl, nitro or nitrile group and abstracts a proton from ethanol to give the product and generate ethoxide ion.



Sharpless Asymmetric Epoxidation ✓

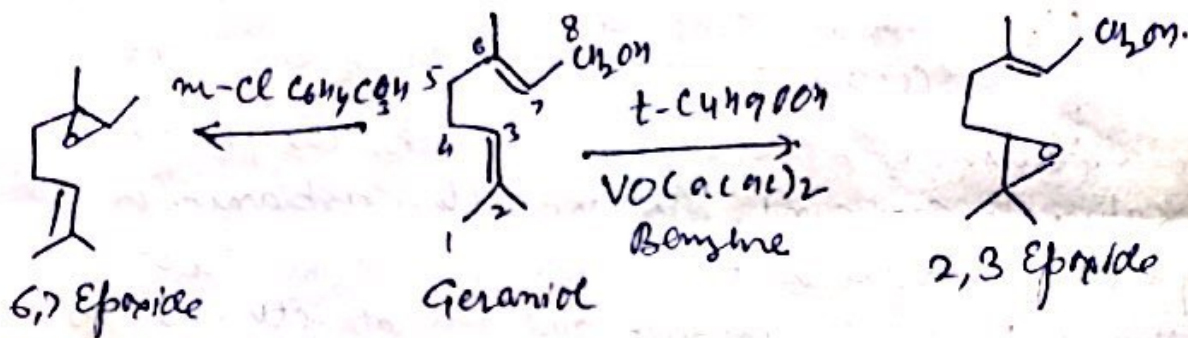
t-butyl hydroperoxide can also be used for selective epoxidation which is not easily possible by other reagents. In fact this reagent shows remarkable selectivity towards the double bond of allylic alcohols.

The epoxidation of alkenes with hydroperoxide gives racemic products mostly. However by using chiral ligands, chiral epoxides can be obtained. This epoxidation was discovered by Sharpless in 1980 and so is known as Sharpless Asymmetric Epoxidation.

It involves the use of *t*-butyl hydroperoxide using a titanium complex as catalyst. $[\text{Ti}(\text{O}i\text{Pr})_4]$

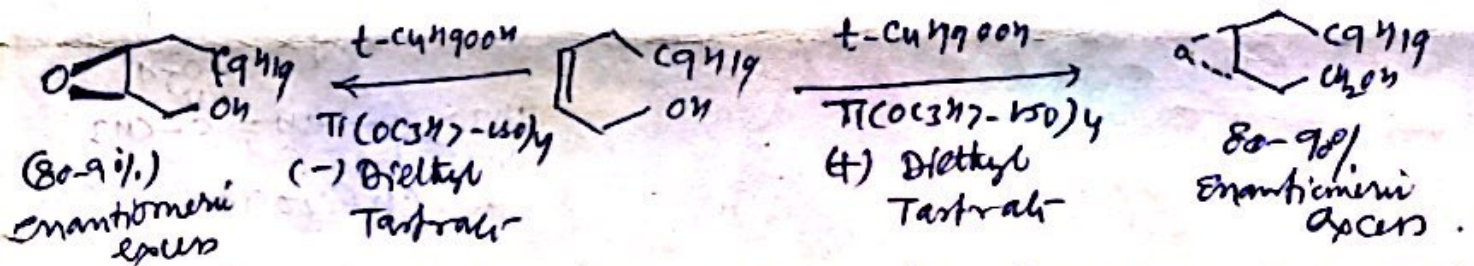
The oxidation of allylic alcohols with *t*-butyl hydroperoxide

in presence of either (+) or (-) diethyl tartrate and Titanium tetrachloride yields the corresponding asymmetric Epoxide in high optical yield. This method is more stereoselective than any other method used for this reaction. (2)



This reaction of Geraniol with *t*-butyl hydroperoxide in presence of catalytic amount of vanadium acetyl acetonate gives exclusively 2,3 Epoxide. While with per oxy acids epoxidation occurs at the other double bond.

An example of highly enantioselective epoxidation of allylic alcohols can be cited here as -



This epoxidation has been used as a key step in the synthesis of terpenes, carbohydrates, pheromones and macrocyclic natural products.