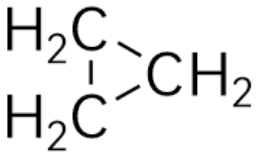
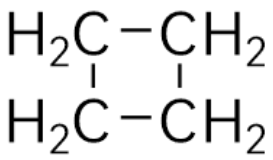
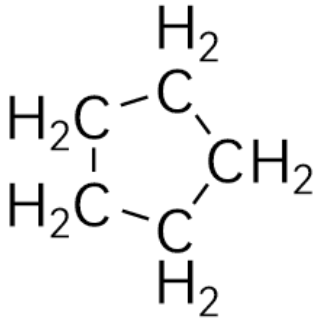
Alicyclics

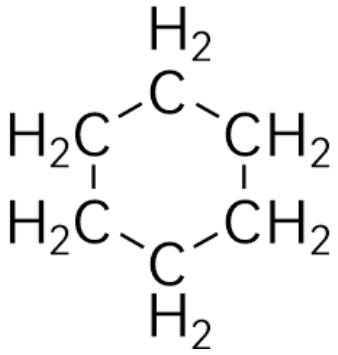
Aliphatic compounds containing rings, cycloalkanes, cycloalkyl halides, cycloalkyl alcohols, cyclic ethers, cycloalkenes, cycloalkadienes, etc.

Cycloalkanes





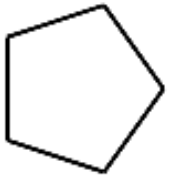


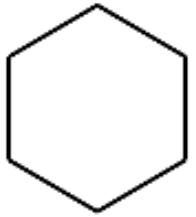


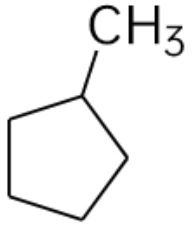
cyclopropane cyclobutane cyclopentane cyclohexane

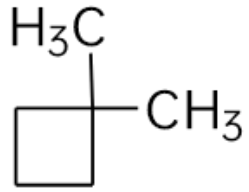






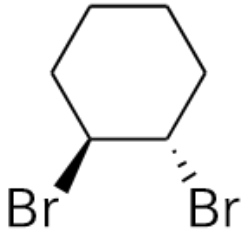


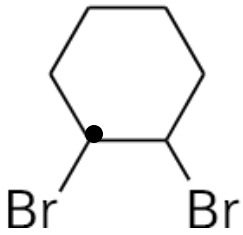


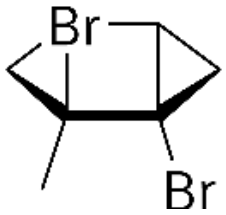


methylcyclopentane

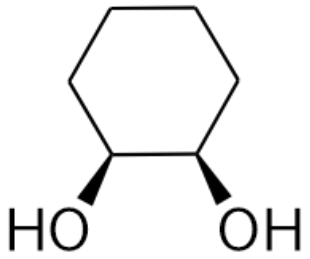
1,1-dimethylcyclobutane

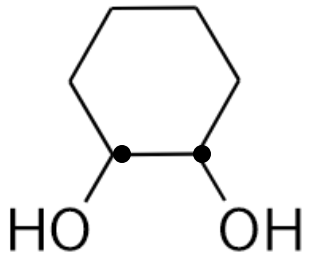


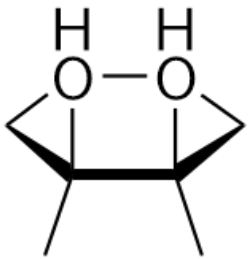




trans-1,2-dibromocyclohexane

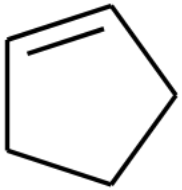


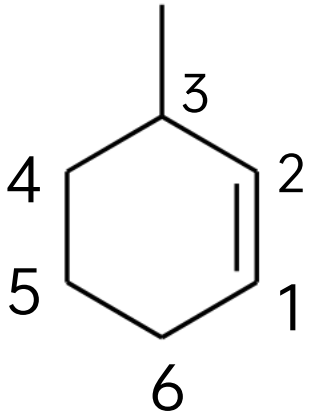




cis-1,2-cyclohexanediol

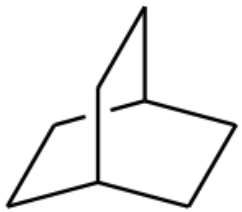
cycloalkenes



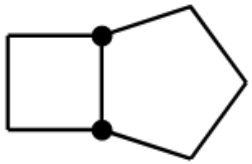




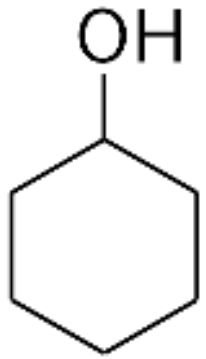
cyclopentene 3-methylcyclohexene 1,3-cyclobutadiene

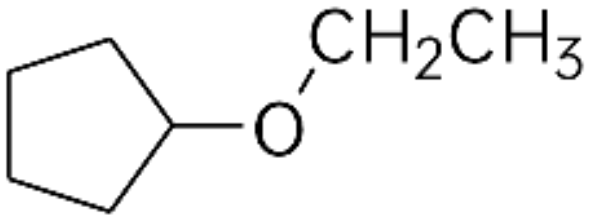


bicyclo[2.2.2]octane



bicyclo[3.2.0]heptane





cyclohexanol

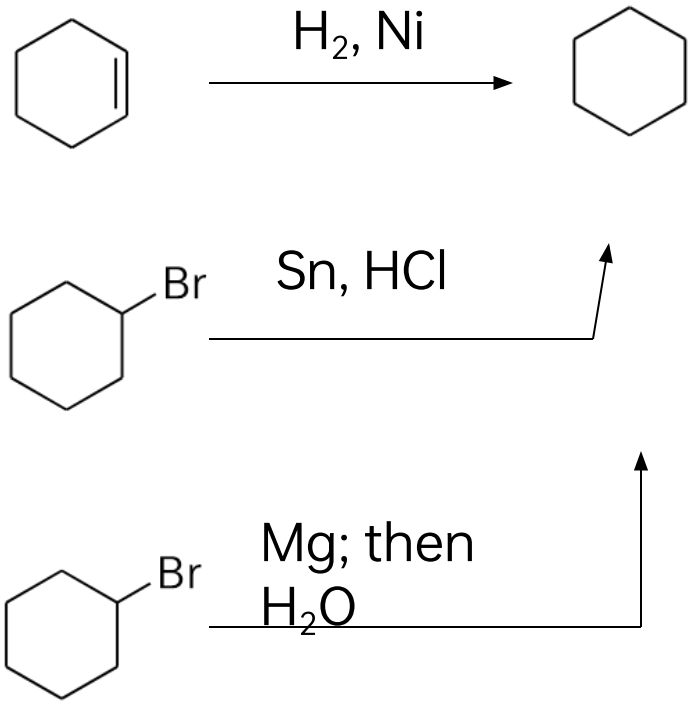
cyclohexyl alcohol

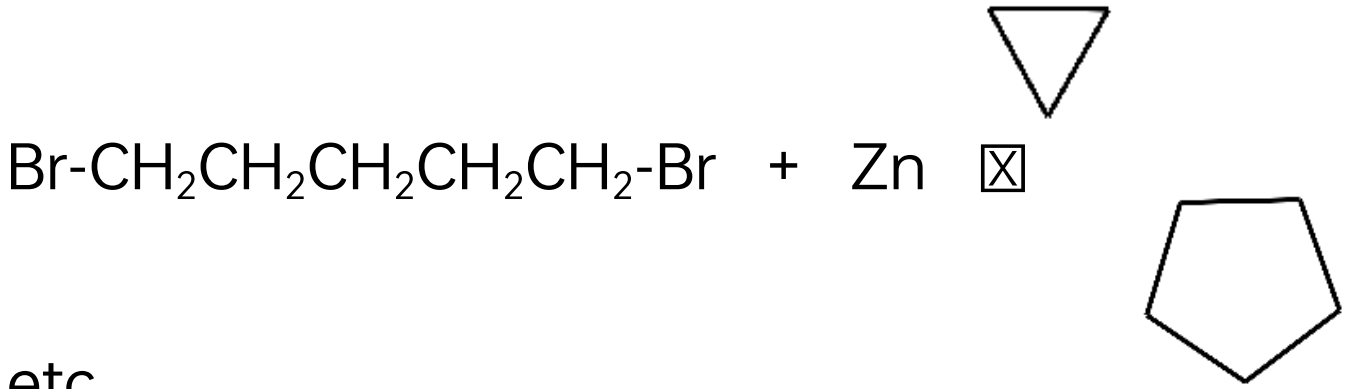
ethyl cyclopentyl ether

Cycloalkanes, syntheses:

A. Modification of a ring compound:
    1. reduction of cycloalkene
    2. reduction of cyclic halide
        a) hydrolysis of Grignard reagent
        b) active metal & acid
    3. Corey House
B. Ring closures

A. Modification of a cyclic compound:

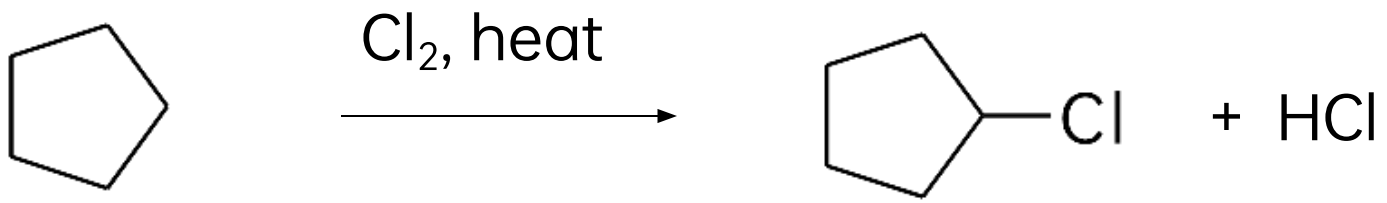


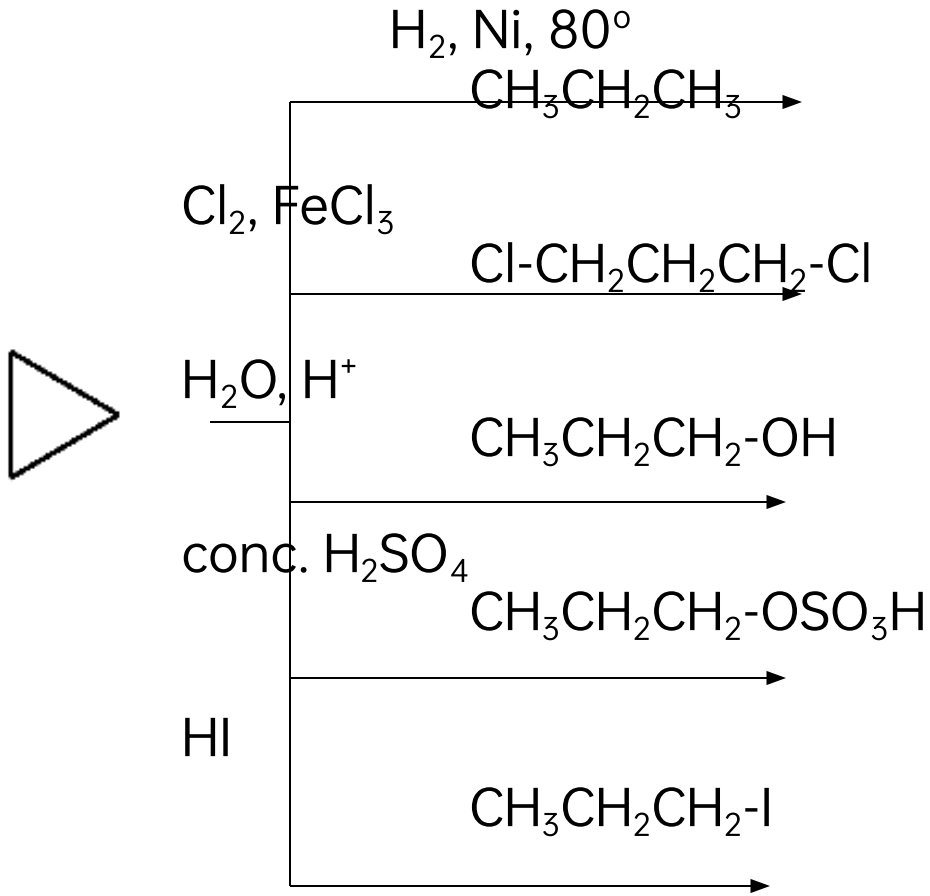


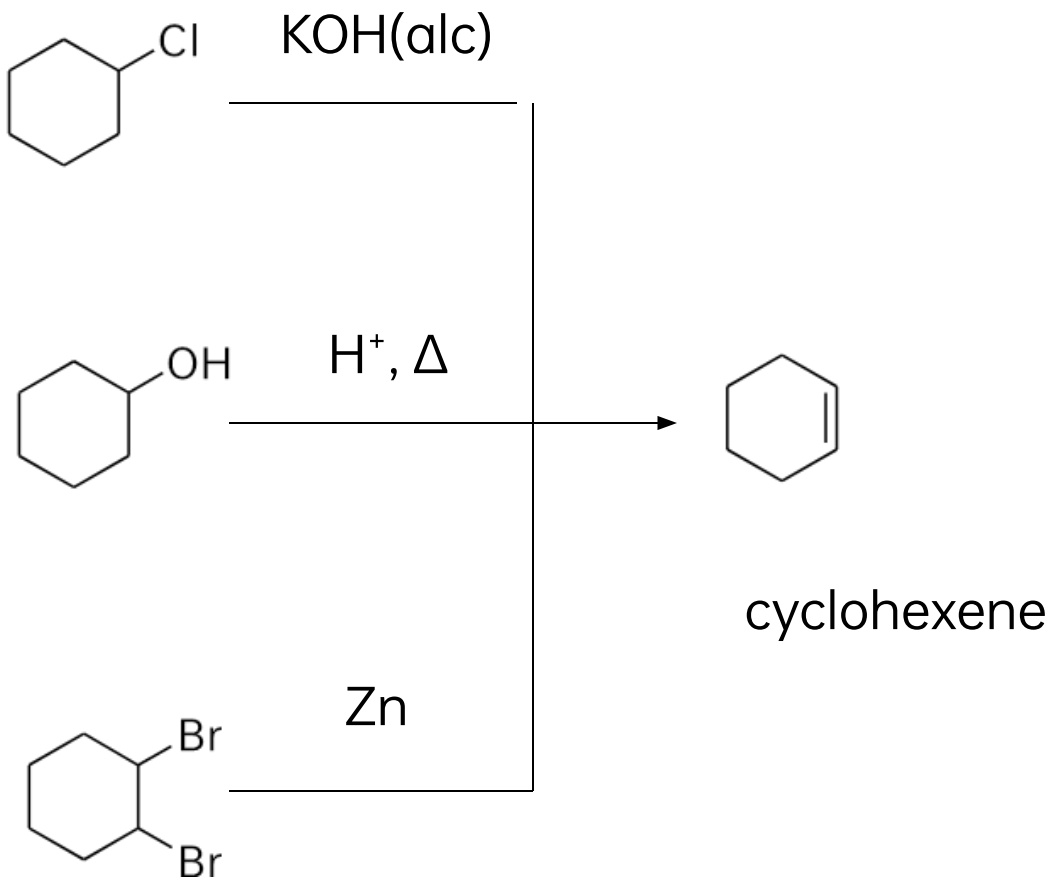
etc.

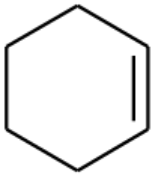
cycloalkanes, reactions:

1. halogenation

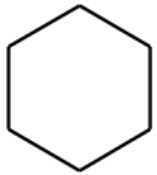


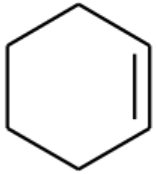

H2, Ni, 80°
CH3CH2CH3
Cl2, FeCl3
Cl-CH2CH2CH2-Cl
H2O, H+
CH3CH2CH2-OH
conc. H2SO4
CH3CH2CH2-OSO3H
HI
CH3CH2CH2-I


Cl
KOH(alc)
OH
H+, Δ
cyclohexene
Zn
Br
Br

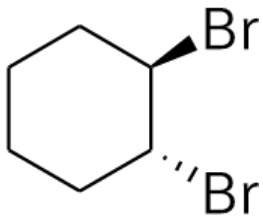


H_2,
Pt

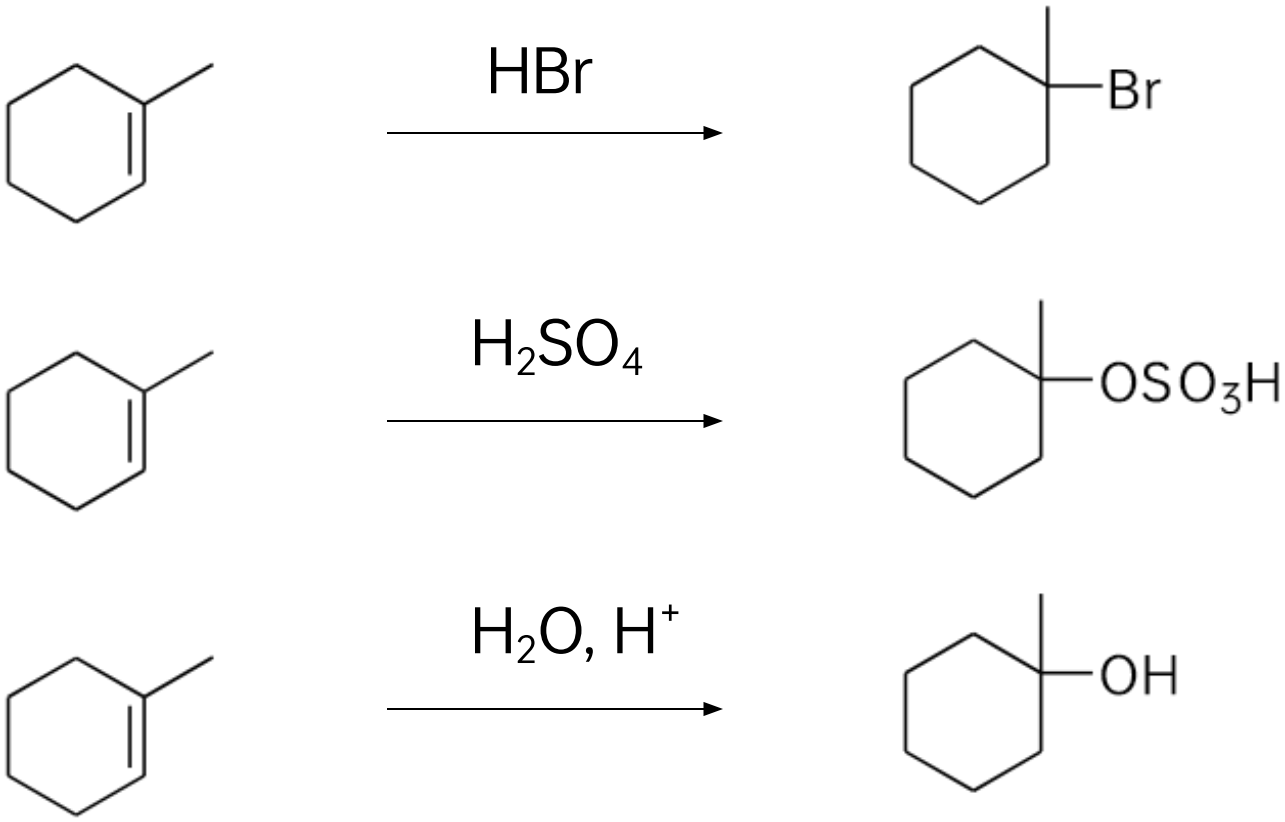




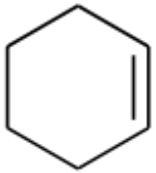
Br_2, CCl_4



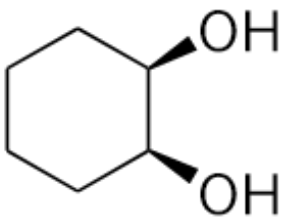
trans-1,2-dibromocyclohexane



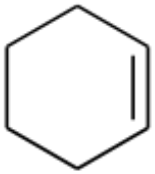
Markovnikov orientation



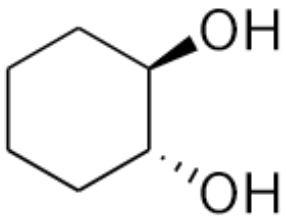
$KMnO_4$



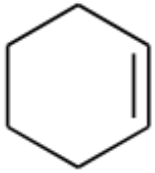
cis-1,2-cyclohexanediol



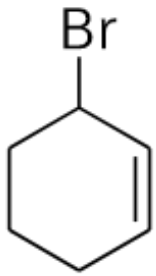
HCO_3H

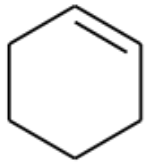


trans-1,2-cyclohexanedio



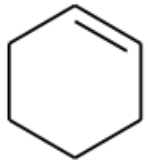
Br_2, heat





O_3 H_2O,Zn

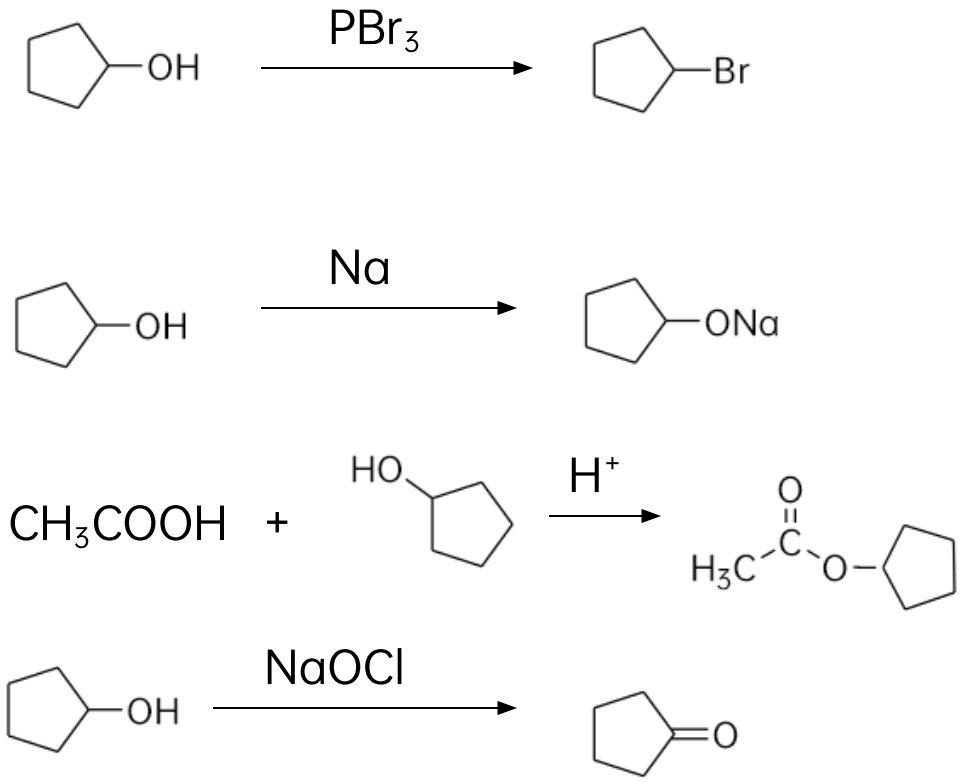
$O{=}CHCH_2CH_2CH_2CH_2CH{=}O$

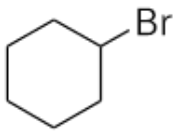


$KMnO_4$, heat

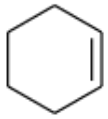
$HO_2CCH_2CH_2CH_2CH_2CO_2H$

cyclic alcohols, halides, ethers <u>as expected</u>:

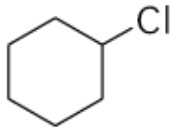




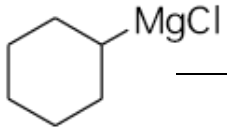
NaOH



2° alkyl halide => E2

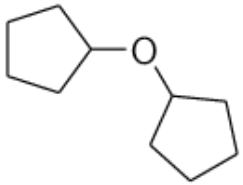


Mg



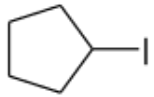
H_2O

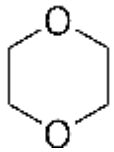




conc. HI, ~~heat~~

2





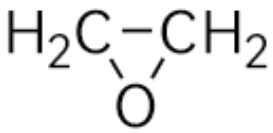
conc. HBr, heat

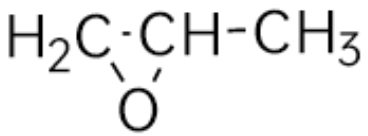
2 Br-CH_2CH_2-Br

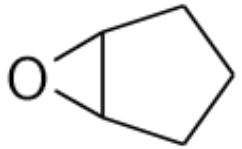
1,4-dioxane

Alicyclic compounds are chemically like their open chain analogs. The exceptions are for small ring compounds where angle strain may give rise to reactions that are not typical of other molecules.

Epoxides:





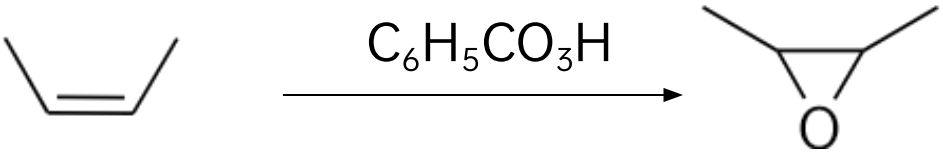


ethylene oxide
oxide
(oxirane)

propylene oxide
(methyloxirane)

cyclopentene

Synthesis:

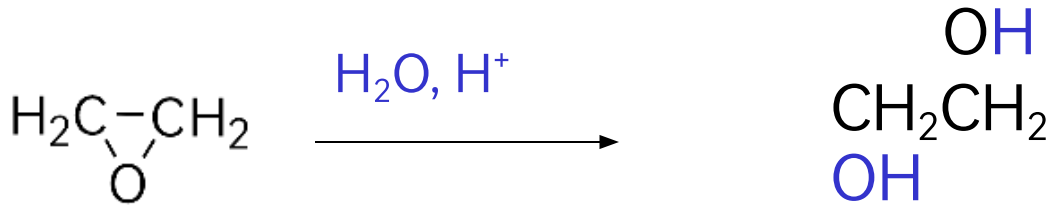


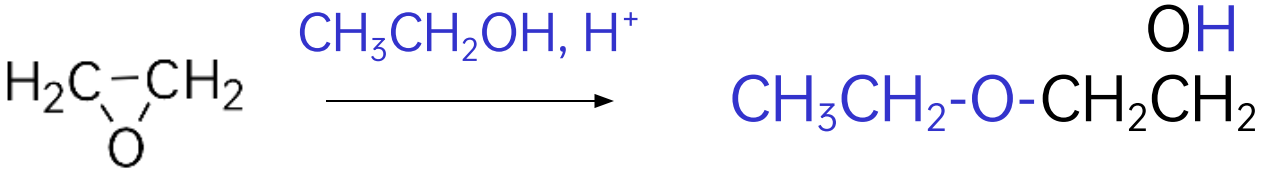
cis-2-butene

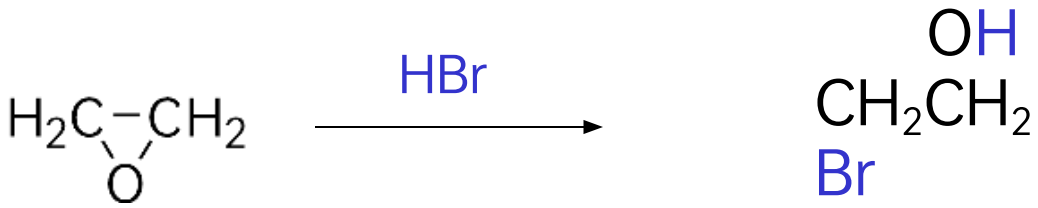
β-butylene oxide

epoxides, reactions:

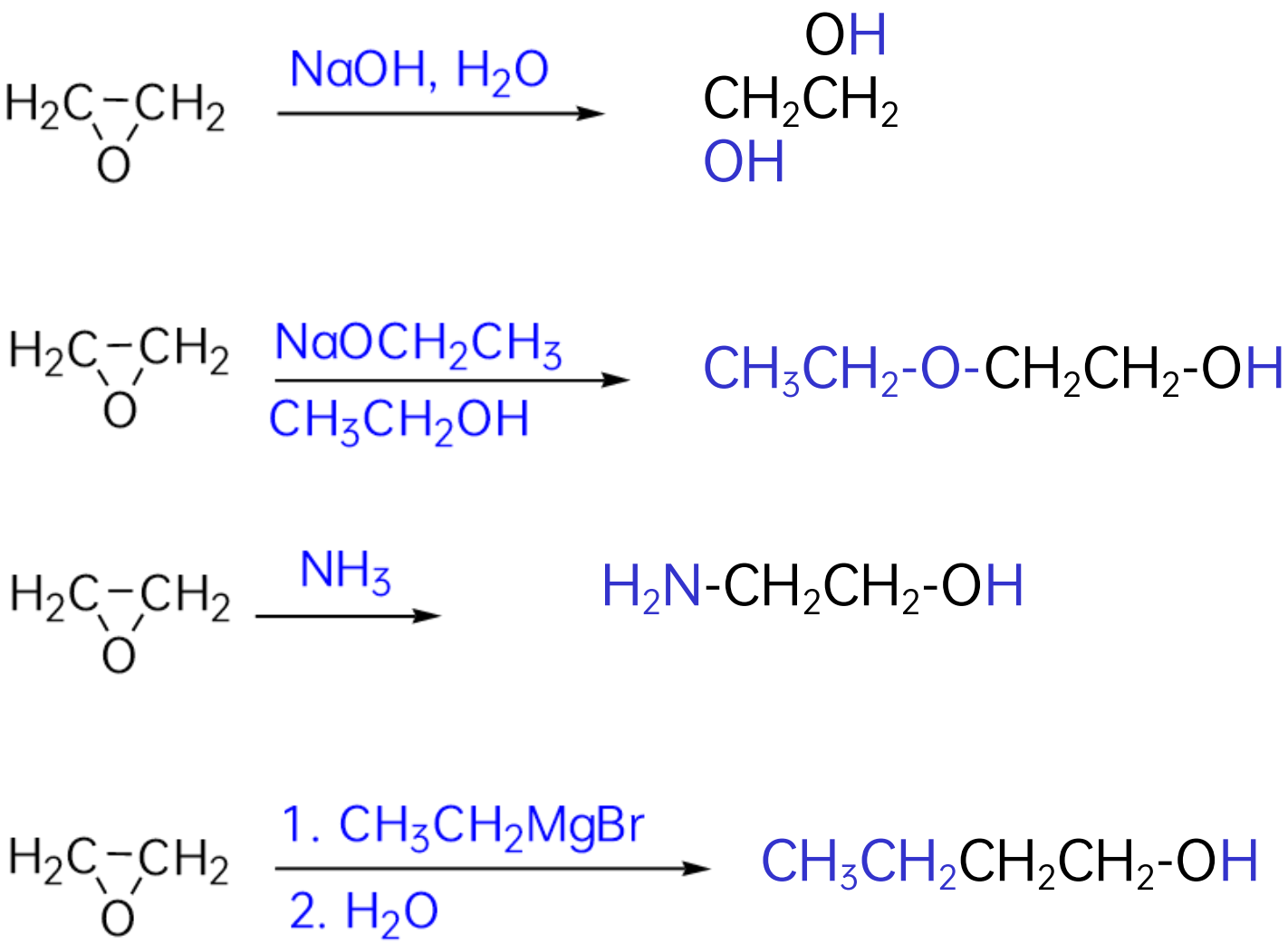
1) acid catalyzed addition



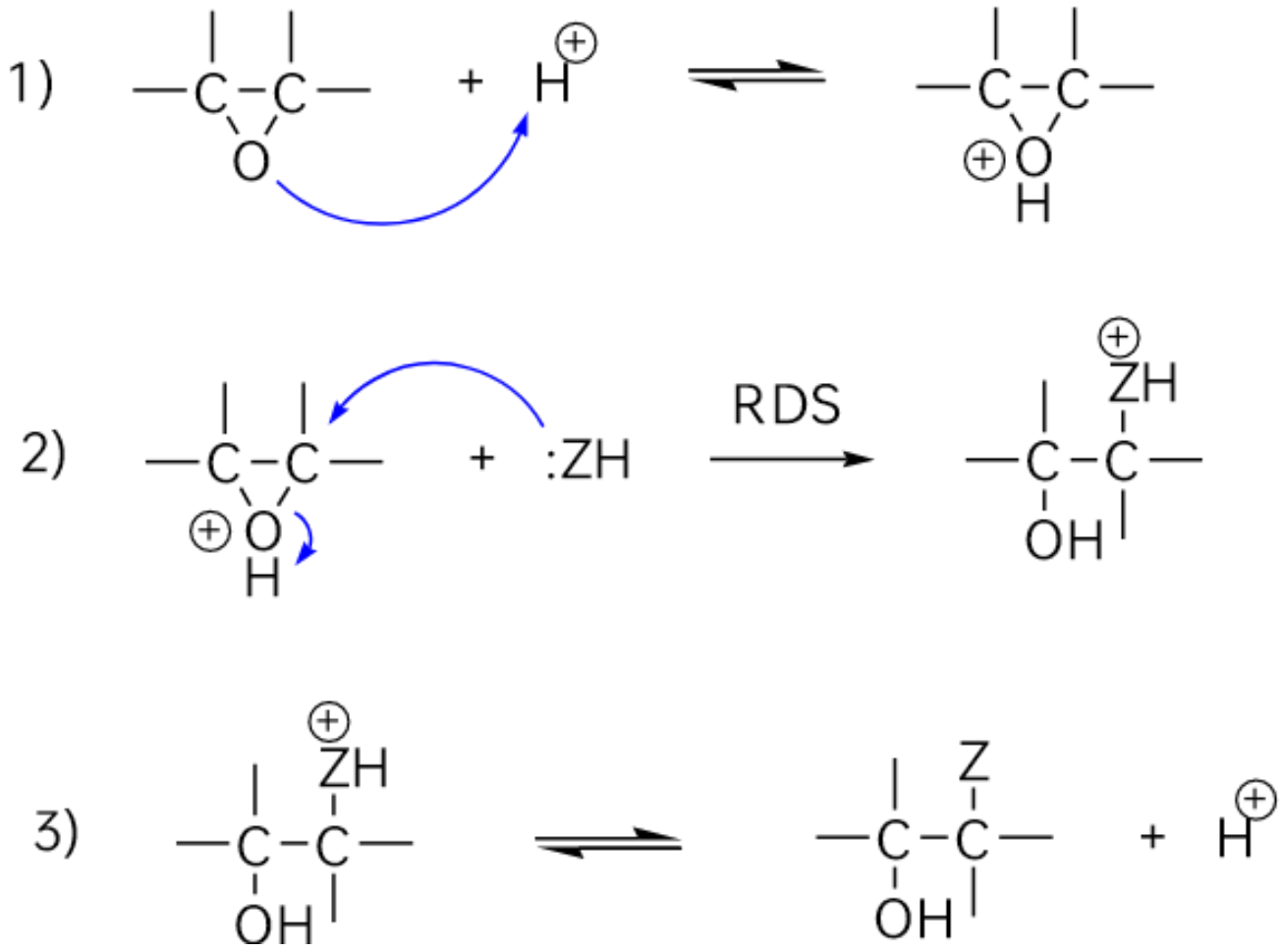




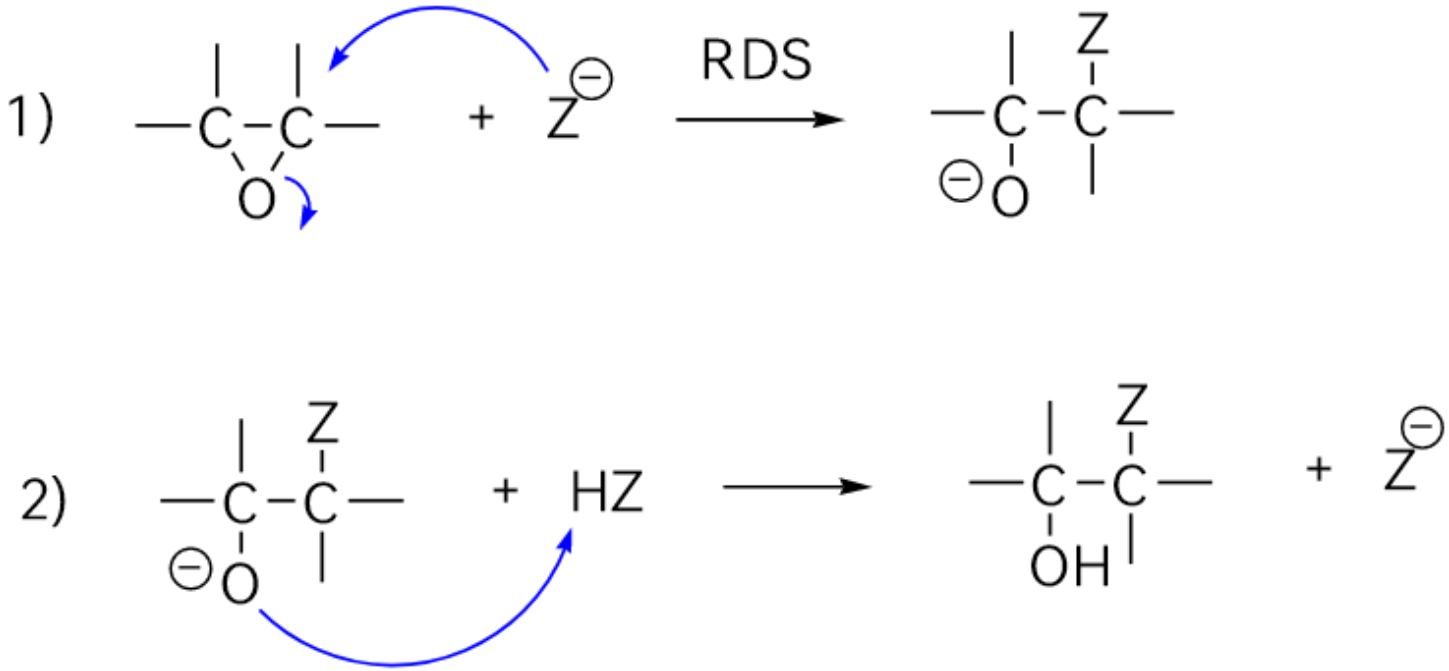
2. Base catalyzed addition



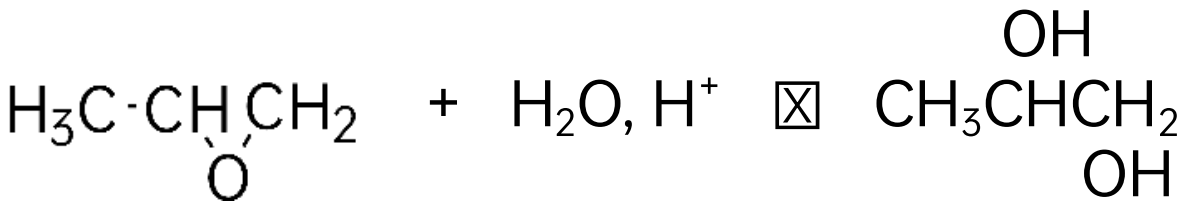
mechanism for acid catalyzed addition to an epoxide



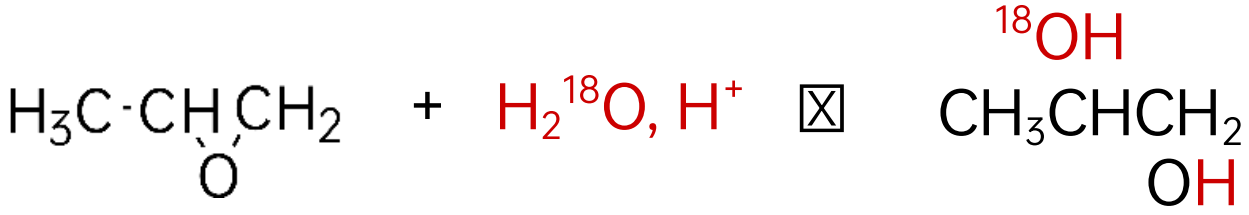
mechanism for base-catalyzed addition to an epoxide:

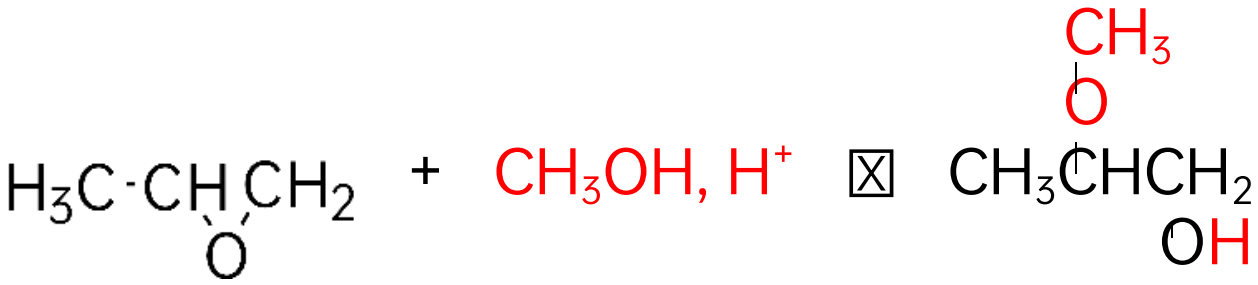


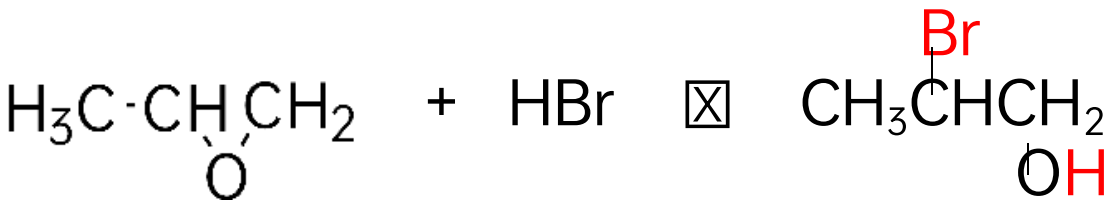
acid catalyzed addition to <u>unsymmetric</u> epoxides?



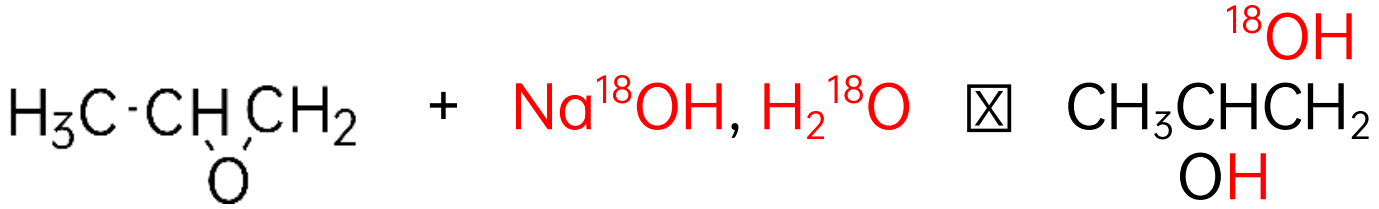
which oxygen in the product came from the water?

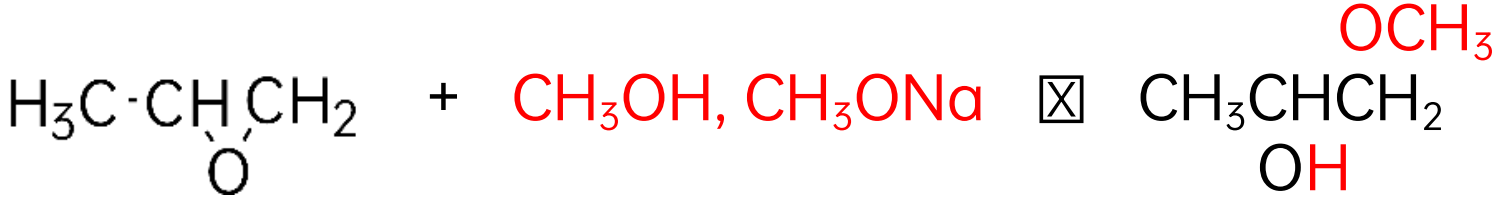


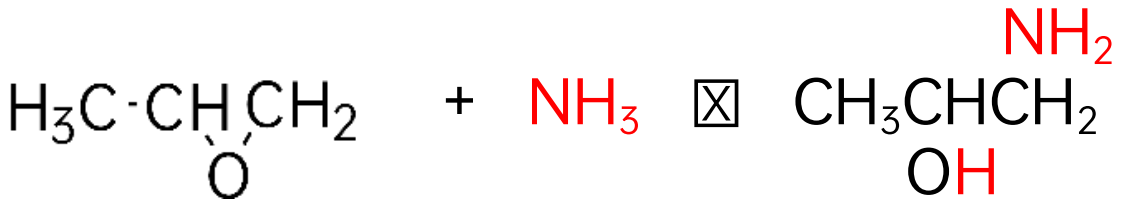




Base?


H3C·CH CH2
O
+
Na18OH, H218O
CH3CHCH2
18OH
OH

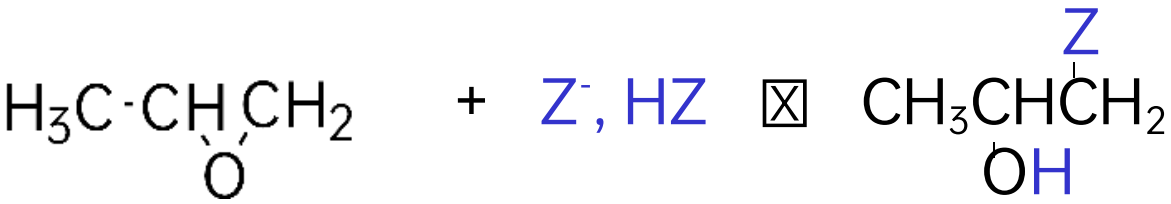

H3C·CH CH2
O
+
CH3OH, CH3ONa
CH3CHCH2
OCH3
OH


H3C·CH CH2
O
+
NH3
CH3CHCH2
NH2
OH

Acid:

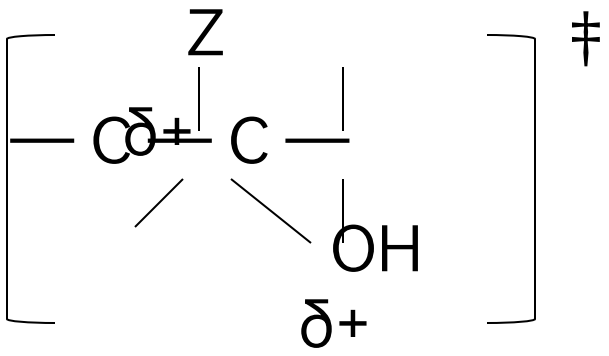


Base:



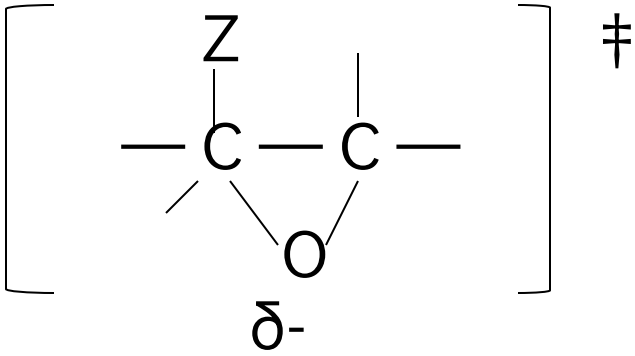
"variable transition state"

acid:



Bond breaking is occurring faster than bond making, making the carbon slightly positive. C δ+ : 3° > 2° > 1°

base:



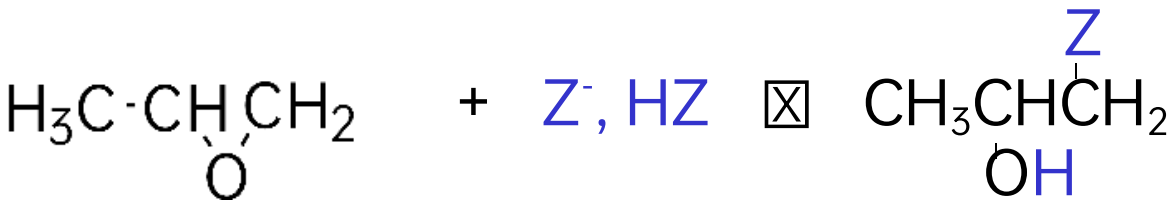
Bond breaking is occurring at the same time as bond breaking, there is no charge on the carbon. Steric factors are most important: 1° > 2° > 3°

Acid:



Cδ+: Z to 2° carbon

Base:



steric factors: Z to 1° carbon