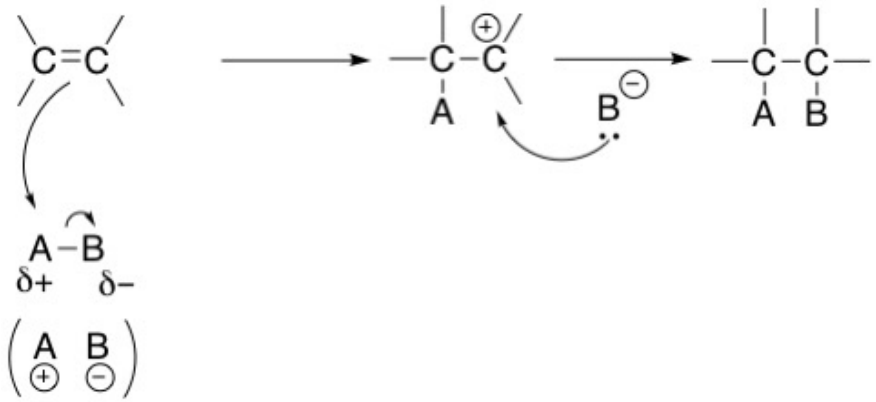
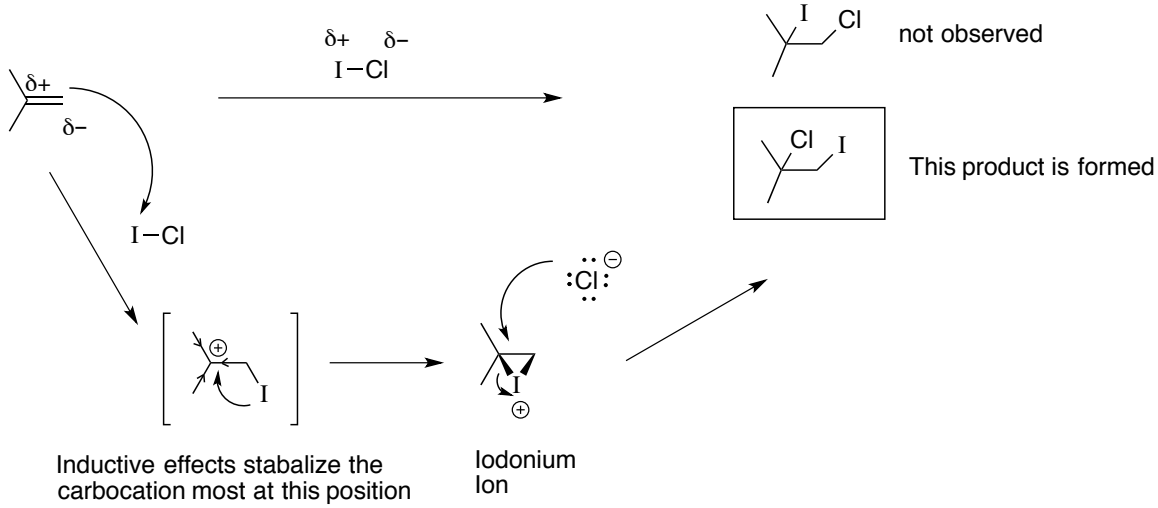
Recall:

Addition Reaction:

General Mechanism

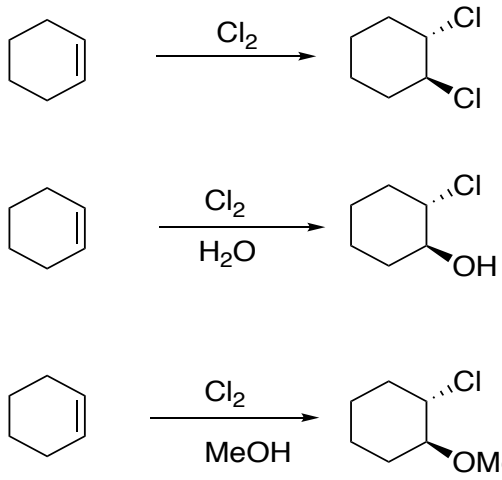


Ex #3) 2-Methylpropene



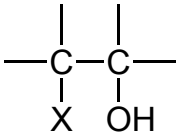
Markovnikov's Rule: In an addition reaction, the positive end of an A–B system (e.g. I–Cl) adds to the least substituted end of the double bond to make the more stable carbocation.

Ex #4) Cyclohexene



Chlorohydrin

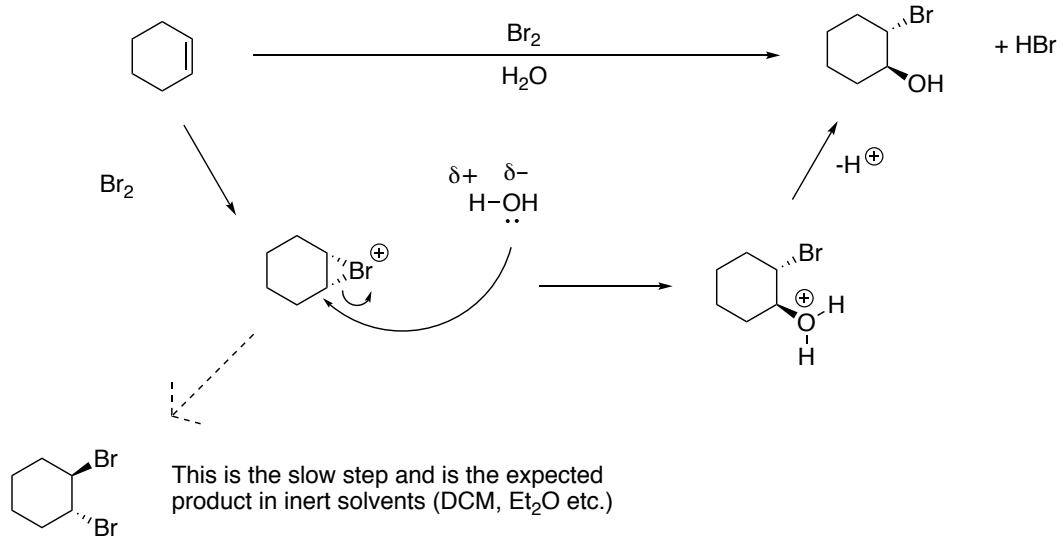
X = halogen



Halohydrin

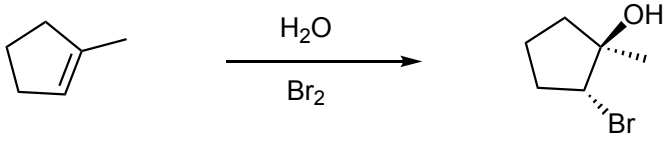
Mechanisms:

#1) Addition of an alcohol functional group (in H_2O)



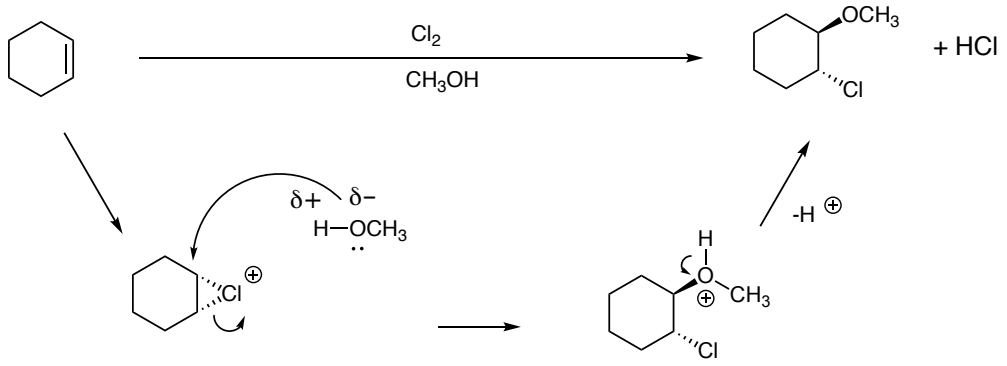
This is the slow step and is the expected product in inert solvents (DCM, Et_2O etc.)

#2) Example

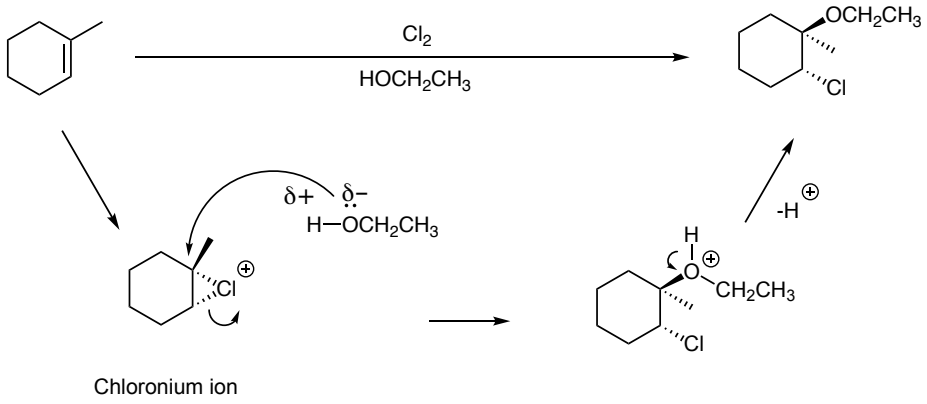


Markovnikov addition

#3) Addition of an ether functional group (in CH_3OH)

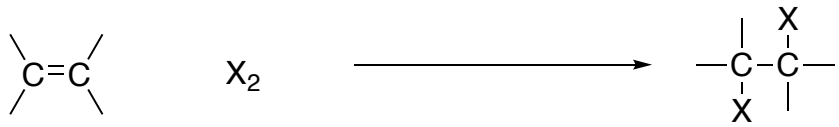


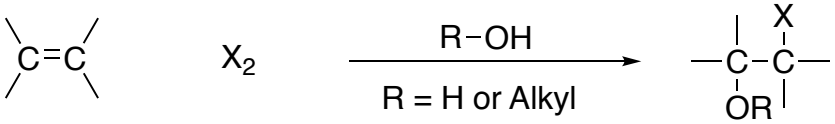
#4) Example



Chloronium ion

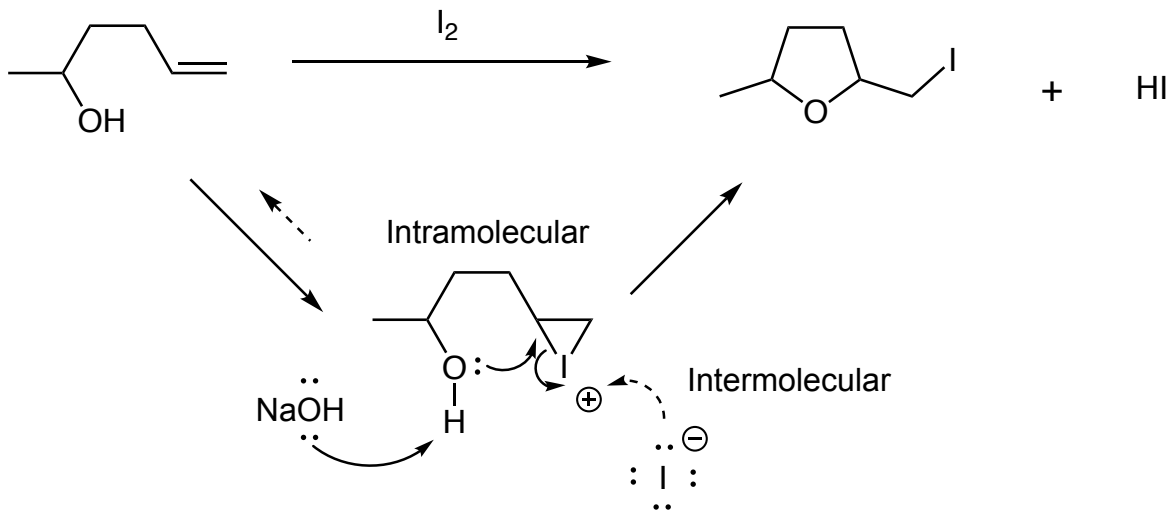
Summary:





Will add in Markovnikov fashion

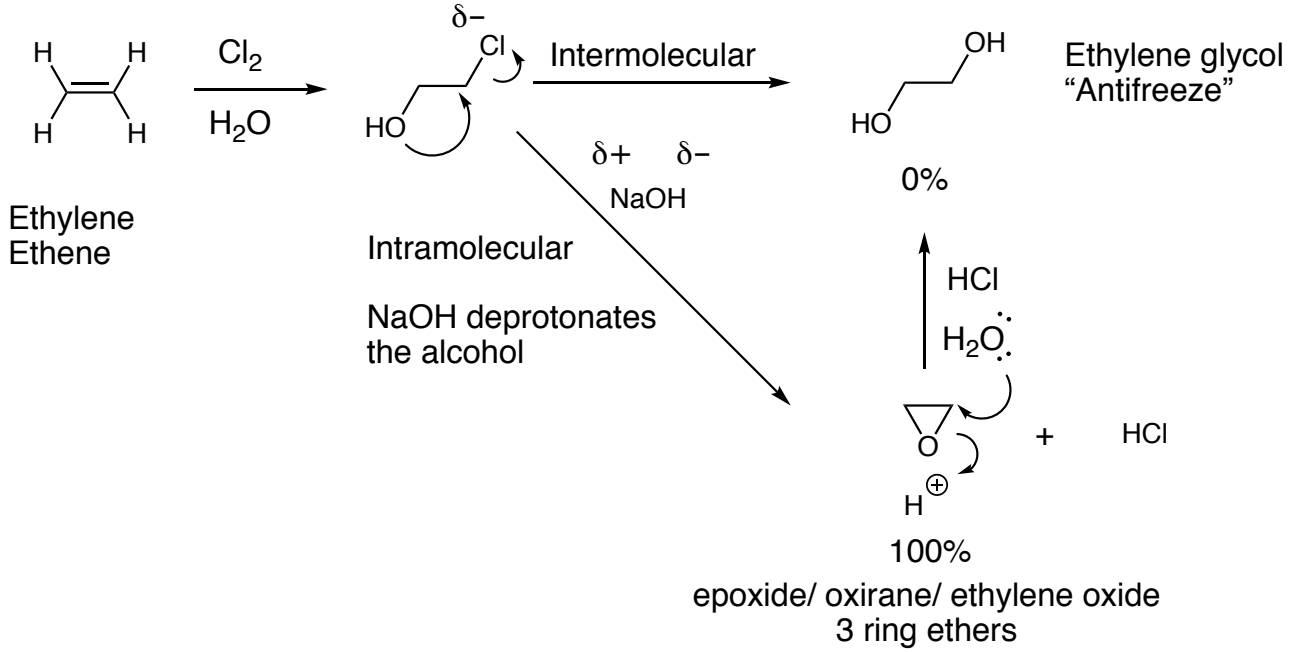
Ex #5)



In the above example, the intramolecular reaction (meaning within the same molecule) occurs much much FASTER than the intermolecular reaction (between two or more molecules). This means that the –OH group will attack the iodonium ion much faster than the I^- group because it is an intramolecular reaction.

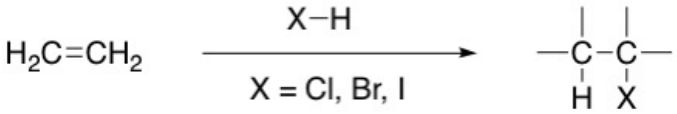
Intramolecular reaction almost always beats intermolecular reactions.

Ex #6)



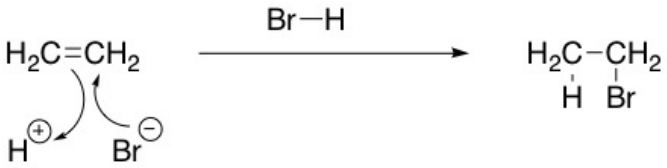
Addition Reactions

Hydrogen Halide (H-X)

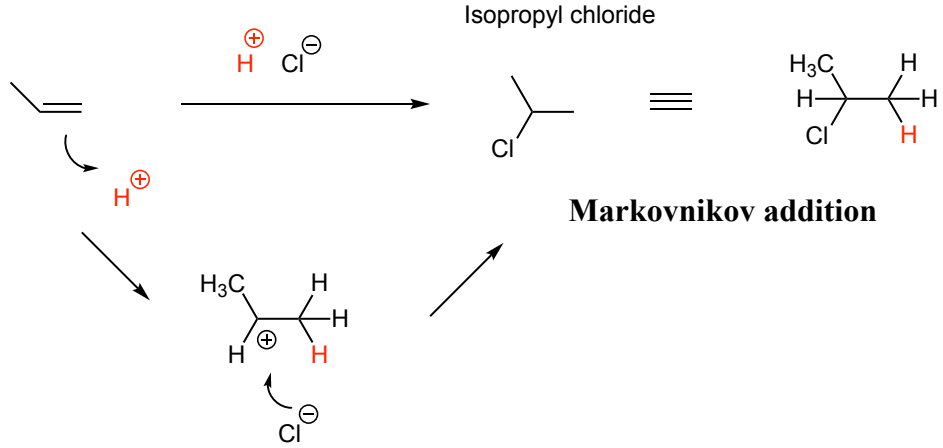


Reaction generally leads to syn/cis addition

Example 1: Ethylene

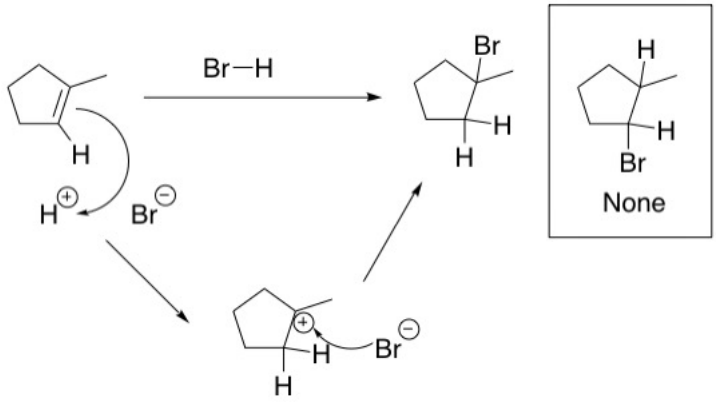


Example 2: Propylene (Propene)



Markovnikov addition

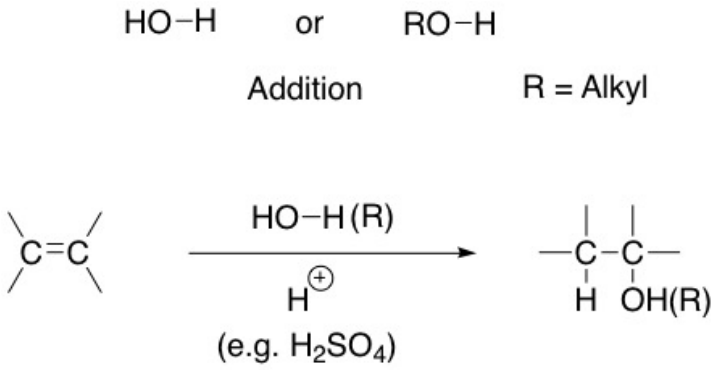
Example 3: 1-Methylcyclopent-1-ene



-Markovnikov addition

RECALL: Carbocation stability $3^o > 2^o > 1^o > CH_3^+$

Hydration and alcohol or ether formation

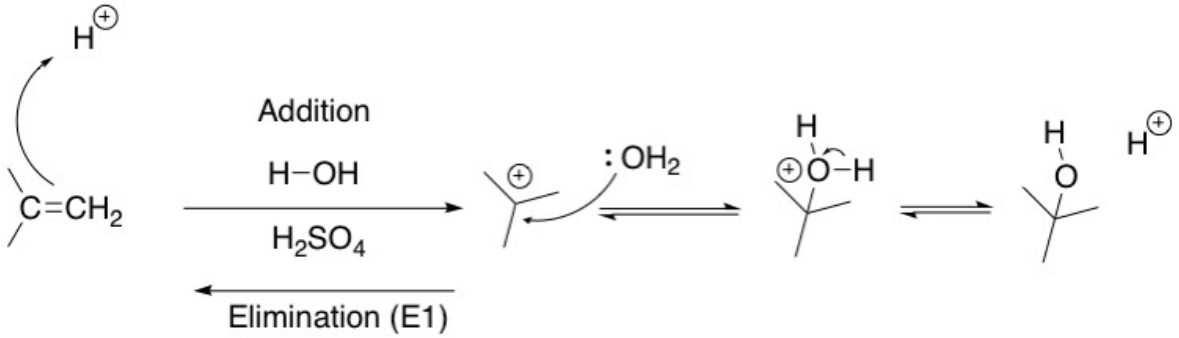


Not Stereospecific

Examples

Hydration (Water Addition)

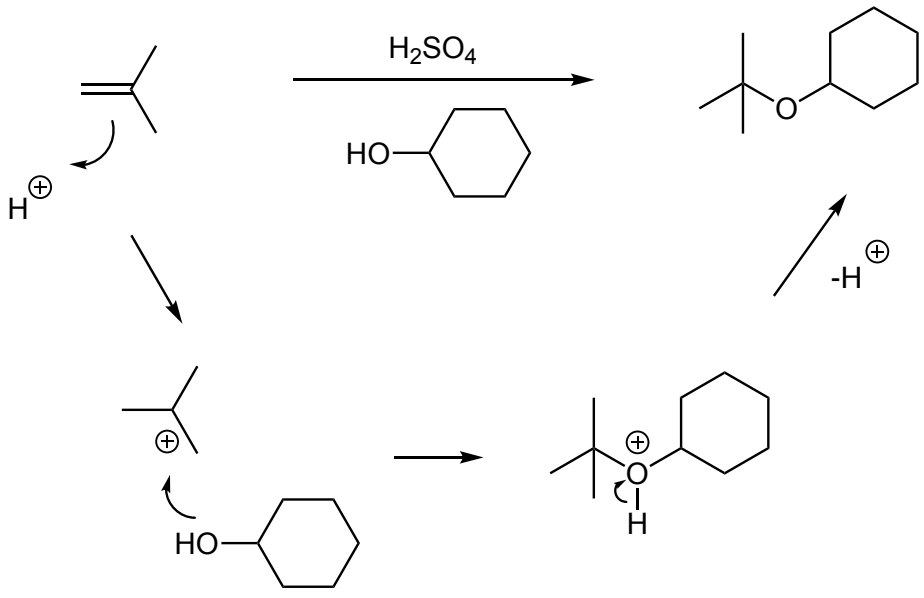
Ex #1)



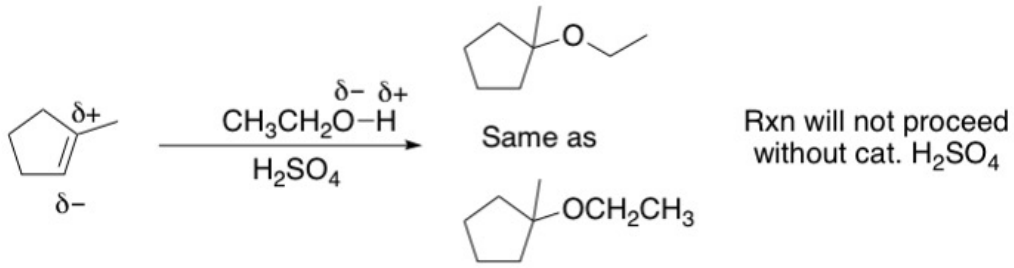
H_2SO_4 (H^+) is a catalyst, meaning that it is not transformed or used up in the reaction but is present to lower the activation energy.

Ether formation

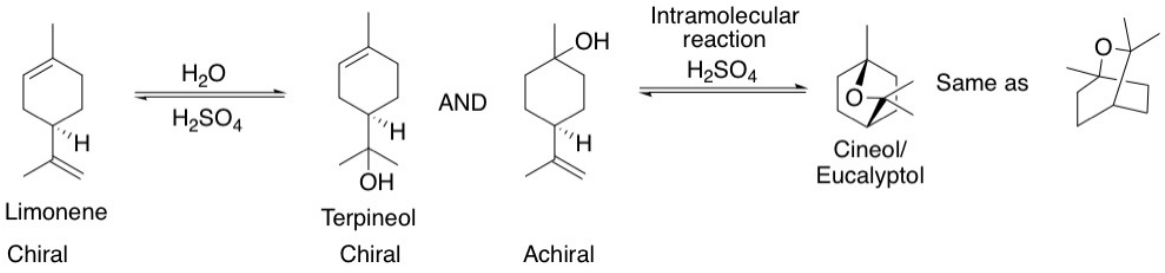
Ex #1)



Ex #2)


δ+
δ−
δ− δ+
CH3CH2O−H
H2SO4
O
Same as
OCH2CH3
Rxn will not proceed
without cat. H2SO4

Ex #3)


H
H2O
H2SO4
H
OH
AND
OH
H
Intramolecular
reaction
H2SO4
O
Same as
O
Limonene
Chiral
Terpineol
Chiral
Achiral
Cineol/
Eucalyptol