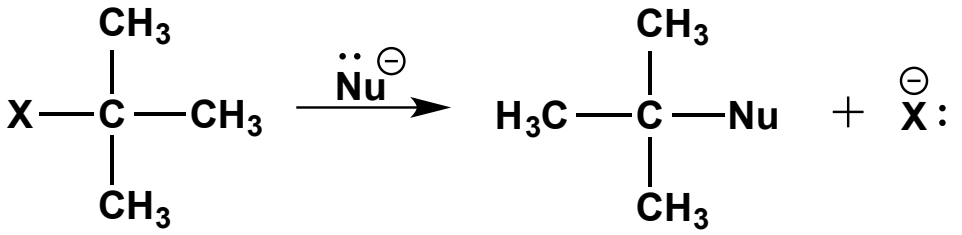
Substitution

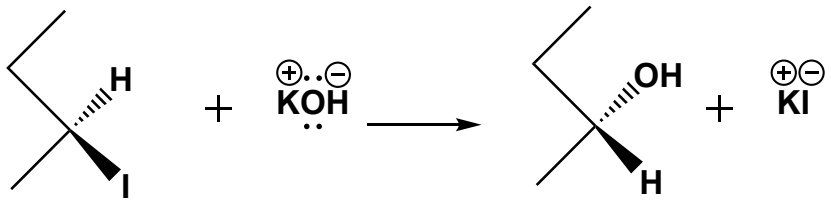


Substitution Reactions (above is S_N1

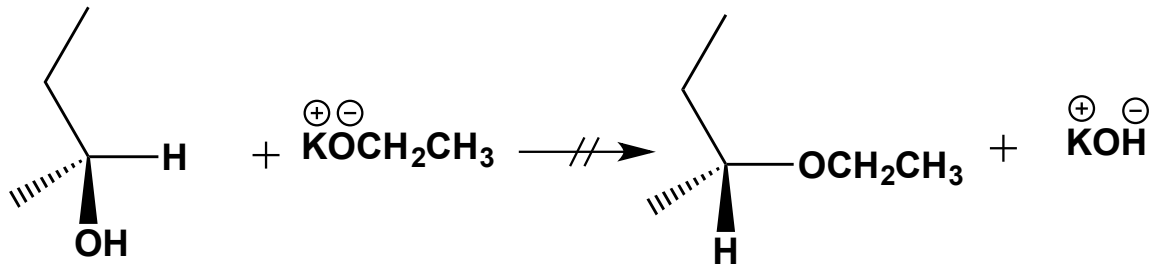
S_N2 Reaction	• **Rate reaction depends on 2 reagents' concentration** • **Concerted** • **Stereospecific**
S_N1 Reaction	• Rate reaction depends on 1 reagent concentration • Stepwise • Carbocation intermediate

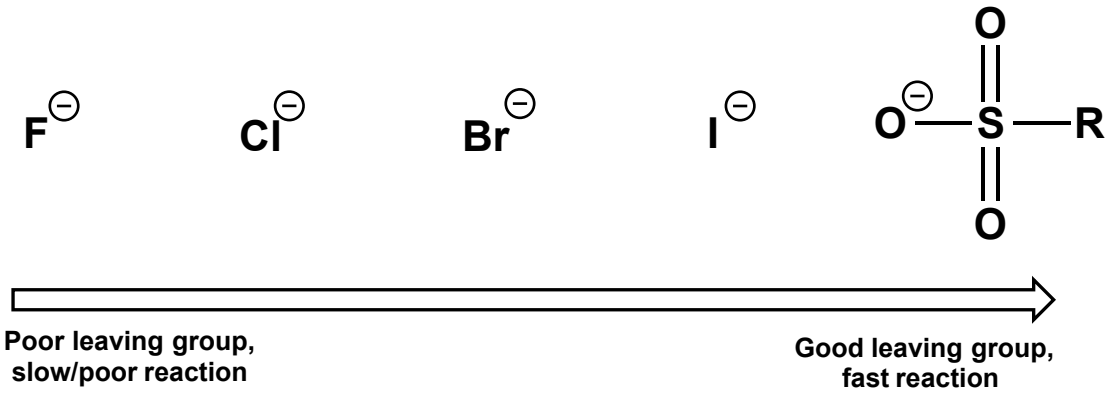
In S_N2 reactions:

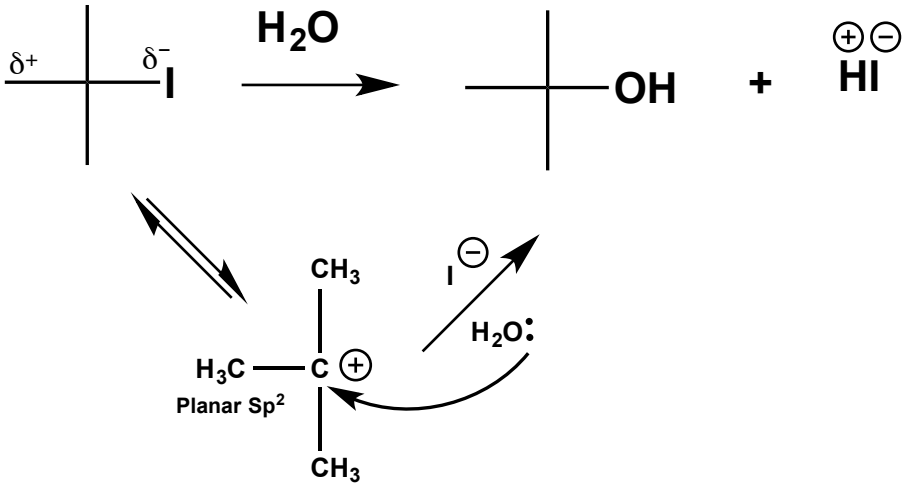
Inversion of configuration

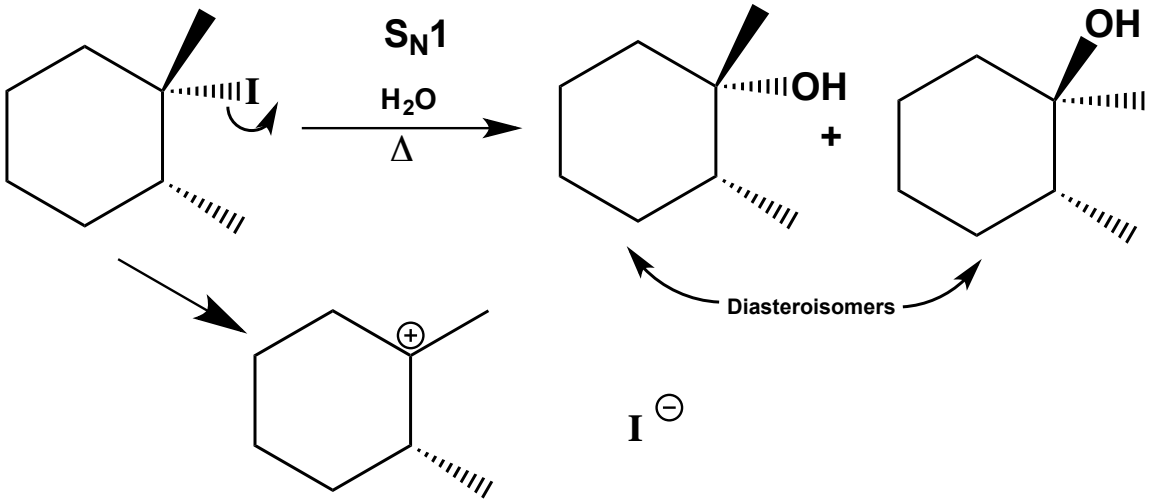


The following reaction **will not occur** in either direction since alkoxides and hydroxides are not good leaving groups

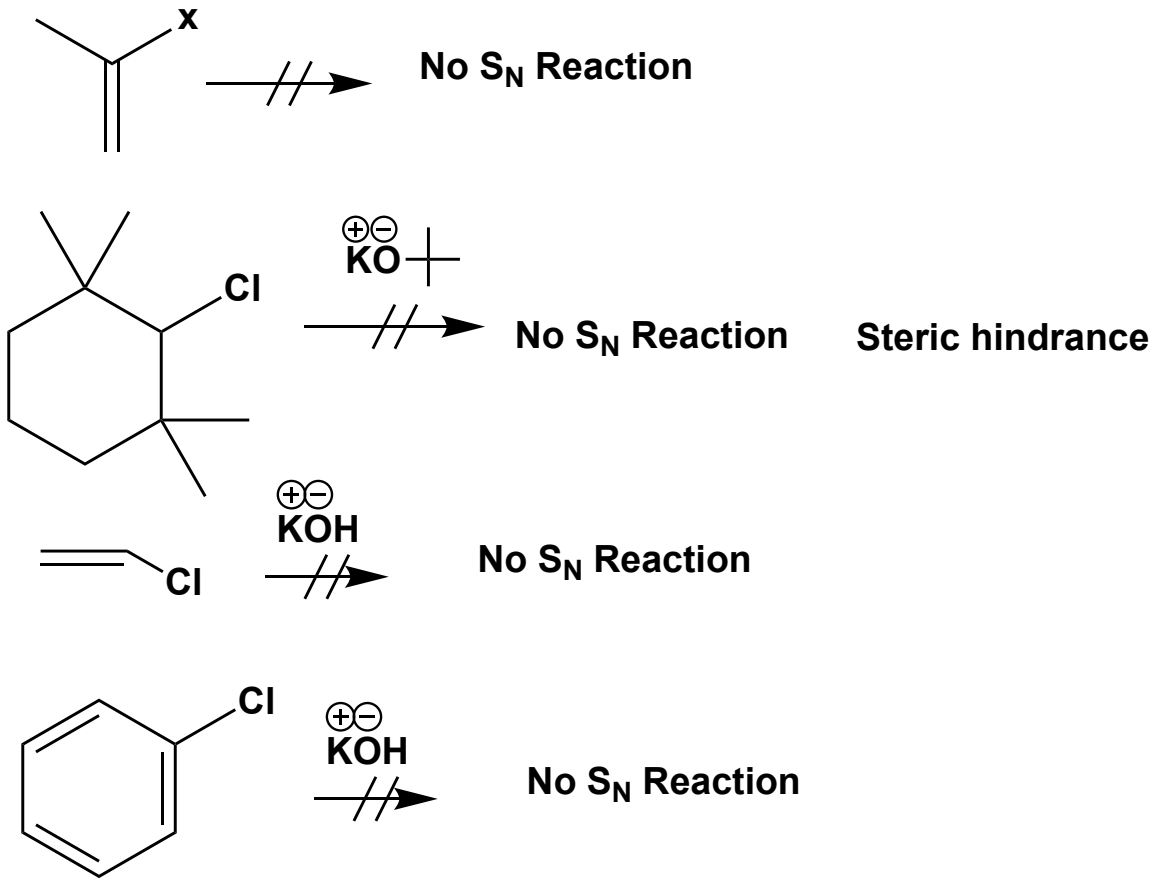



F⊖
Cl⊖
Br⊖
I⊖
O⊖
O
S
O
R
Poor leaving group,
slow/poor reaction
Good leaving group,
fast reaction

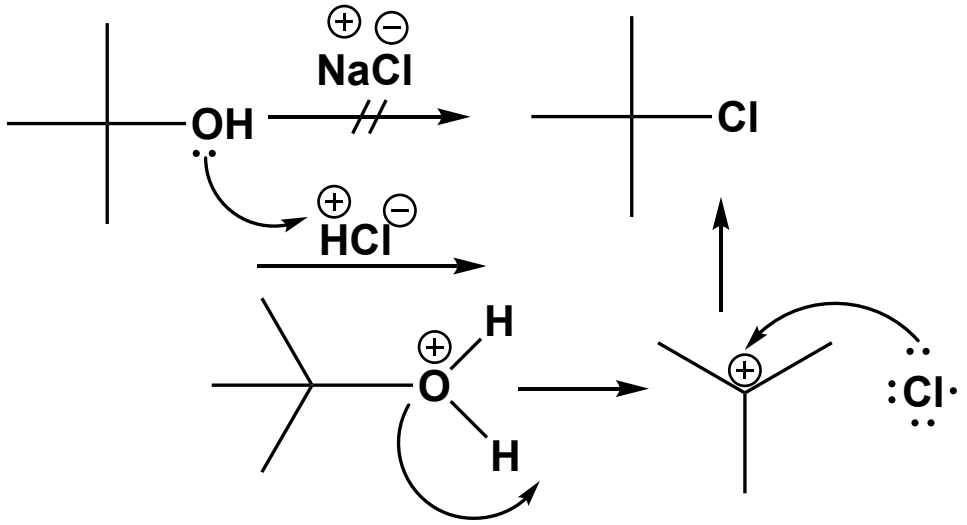

δ+
δ−
I
H2O
OH
+
⊕⊖
HI
CH3
I⊖
H2O:
H3C
C⊕
Planar Sp2
CH3


I
SN1
H2O
Δ
OH
+
OH
Diasteroisomers
I⊖

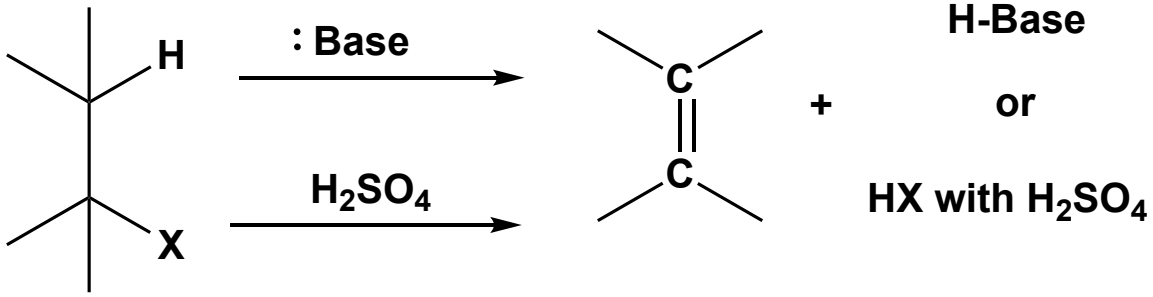
Limitations:



An OH or OR group can be a leaving group only under **acidic** conditions, where it leaves as water or alcohol (ROH) – not under basic conditions

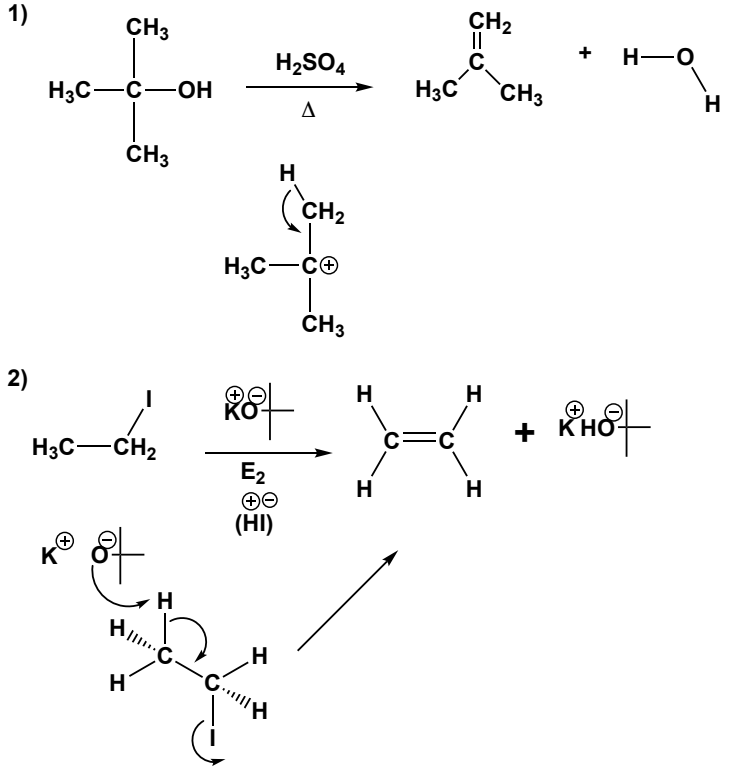


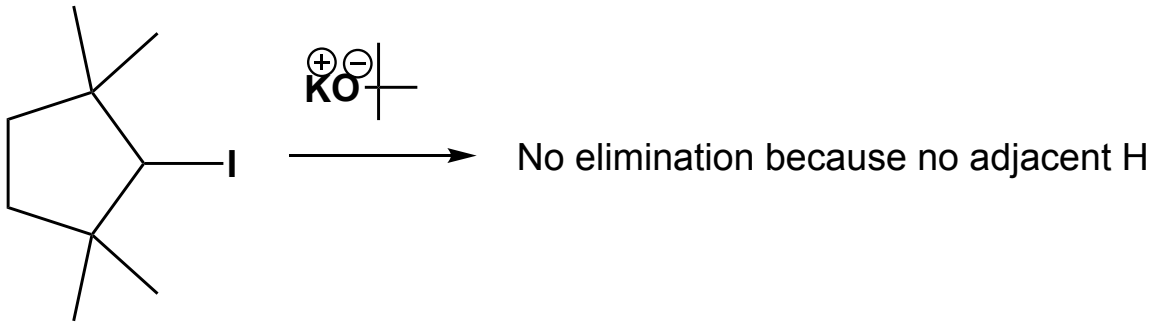
Elimination reactions



E_1	• **Rate reaction depends on 1 reagent concentration** • **Stepwise** • **Carbocation Intermediate**
E_2	• Rate reaction depends on 2 reagents concentration • Concerted • Stereospecific

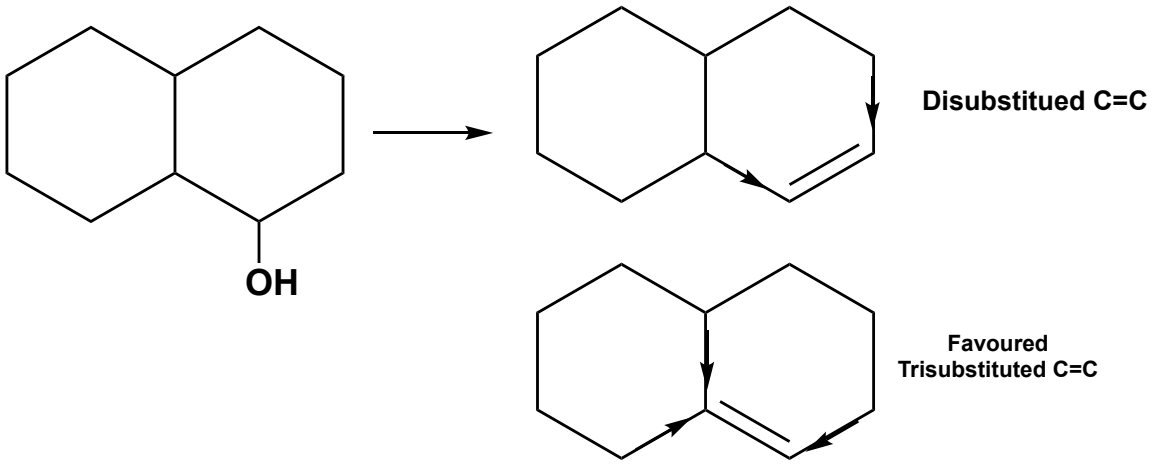
Examples: (Number 1 below is E1)





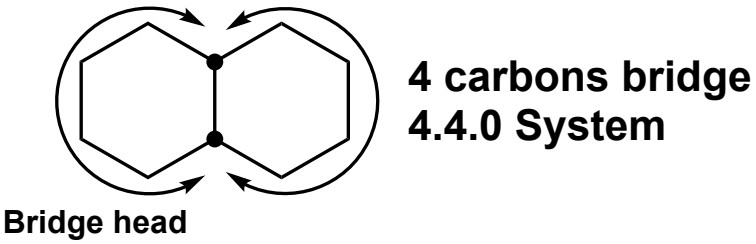
Zaitsev' Rule = Saytzeff Rule

Zaitsev's or Saytzeff's rule is an empirical rule used to predict regioselectivity of 1,2-elimination reactions occurring via the E1 or E2 mechanisms. It states that in a regioselective E1 or E2 reaction the major product is the more stable alkene, (i.e., the alkene with the more highly substituted double bond).



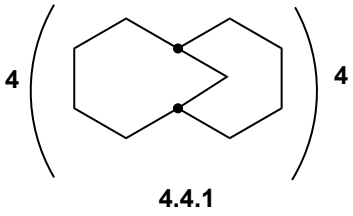
Limitation Bret's rule

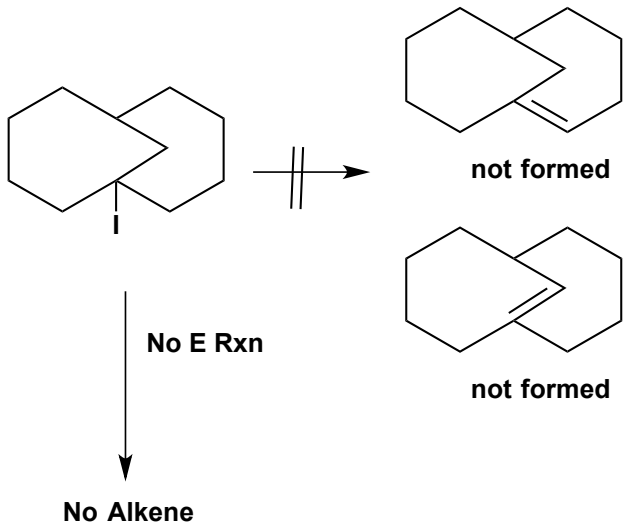
No C=C can be formed to a bridge head if all bridges are >0 and small size rings



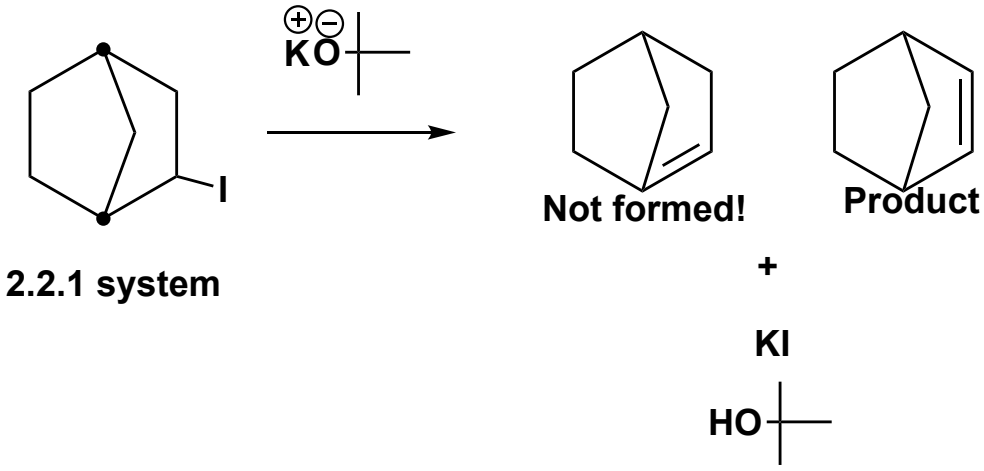
Example:

1)



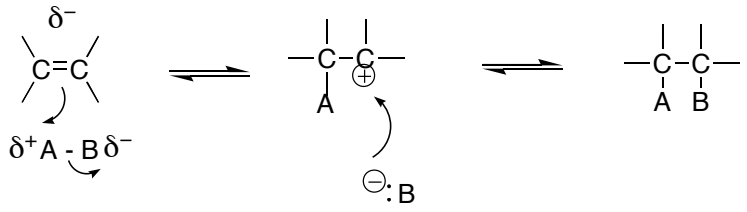


2) Below is an E2 reaction



LECTURE OUTLINE 4

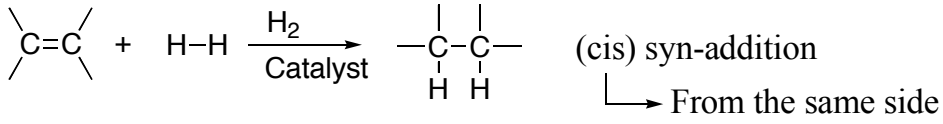
Reaction of Alkenes: Addition Reactions



Reverse is called an elimination reaction

Hydrogenation:

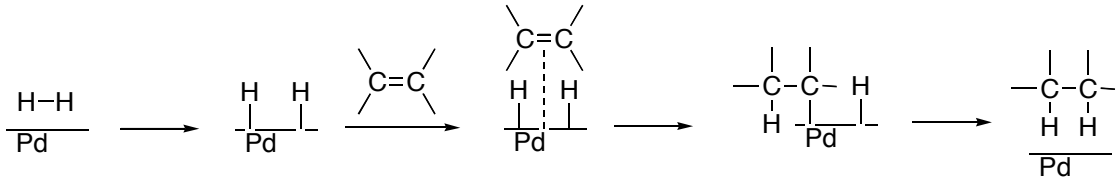
- Addition of H_2
- Requires a catalyst
- Stereospecific reaction (cis or syn addition)



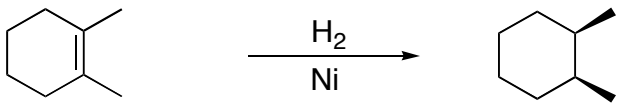
Catalyst is one of Ni (Nickel), Pd(Palladium), Pt(Platinum)

Catalyst: Lowers the activation energy of a reaction (transition state) but is not permanently transformed

Mechanism



Hydrogenation with these catalyst proceeds with syn addition (from the same side), giving the cis-product.

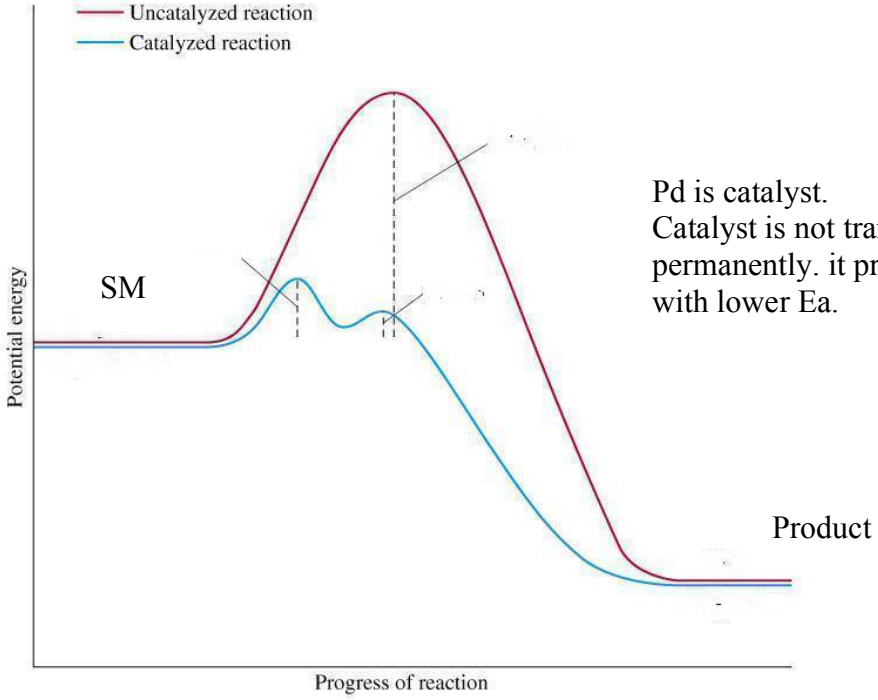


1,2-dimethylcyclohexene *cis*-1,2-dimethylcyclohexane

The starting material and products are achiral because of an internal mirror plane of symmetry.

These two products are identical.
Achiral, but with stereogenic centres
--> meso compounds

Energy Diagram for the Reaction



Pd is catalyst.
Catalyst is not transformed permanently. it provides a path with lower Ea.

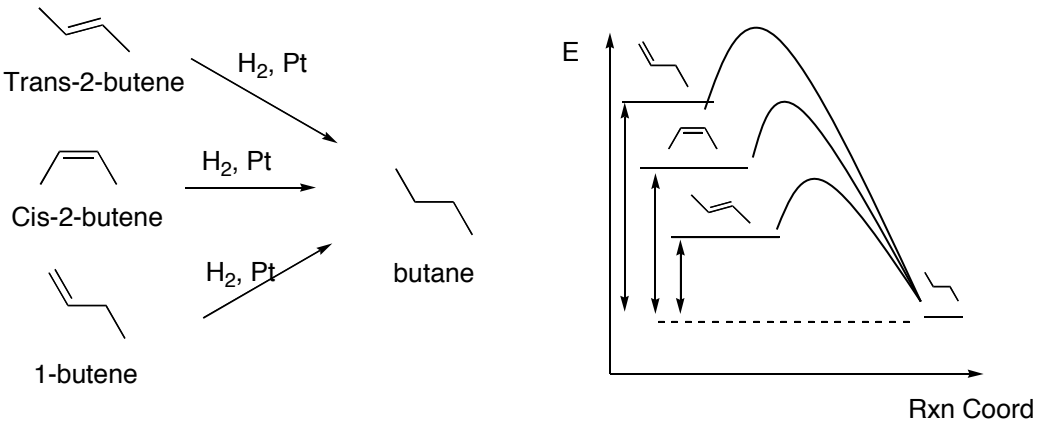
SM : alkene and H_2

Product : alkane (after hydrogenation)

Example: How to determine thermodynamic stability of alkenes

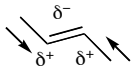
cis-2-butene and trans-2-butene are diastereomers with different physical properties

1-butene is a structural isomer of both cis-2-butene and trans-2-butene

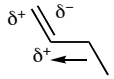


All of the above reactions are exothermic.

trans-2-butene is most stable (smallest amount of energy released)



more alkyl substitution gives increased electron donation, making the alkene more stable and less reactive



trans more stable than cis due to sterics

cis-2-butene has intermediate stability (disubstituted double bond but sterically more crowded

1-butene is least stable (monosubstituted double bond - largest amount of energy released)