B Sc SEM VI Chemistry (Hons): DCE
Dynamic Stereochemistry

Dr. Kanika Ghosh
Assistant Professor in Chemistry
B C College, Asansol
Kazi Nazrul University

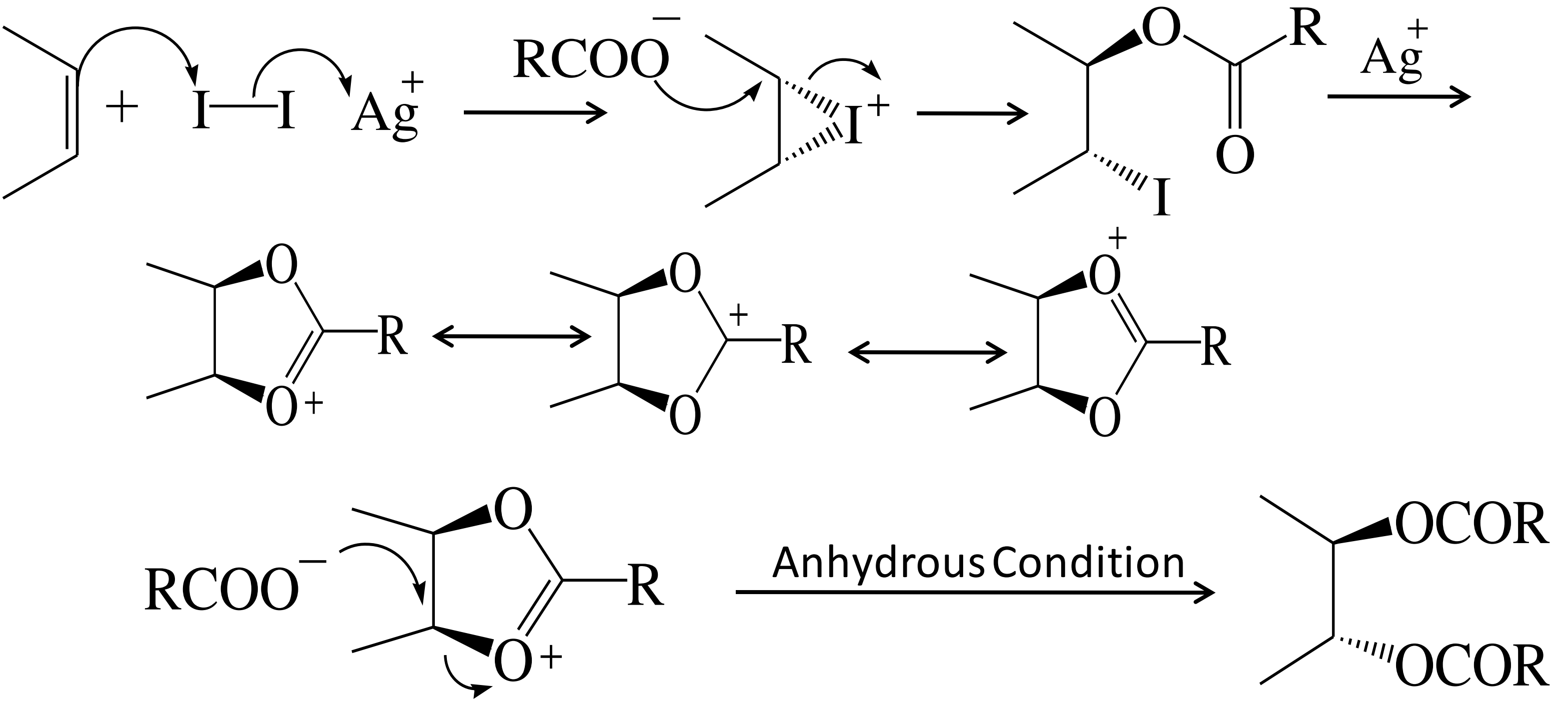
Unit IV: Stereochemical Aspects of a few organic reaction

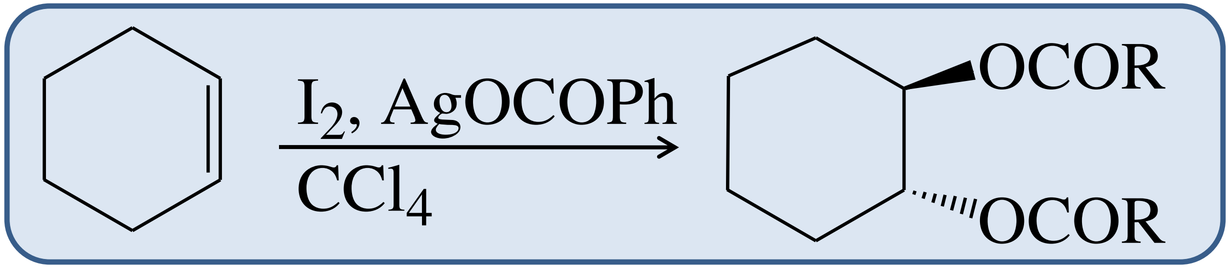
- Prevost and Woodward Hydroxylation
- Hydroxylation by OsO_4
- Catalytic Reduction of Alkenes and Alkynes
- Stereochemical Aspect of few rearrangement reaction
    - Pinacol Rearrangement
    - Beckmann Rearrangement
    - Cope Rearrangement
    - Claisen Rearrangement
- Addition to Alkene

Contact address: ghosh.kanika7@gmail.com

Prevost Hydroxylation

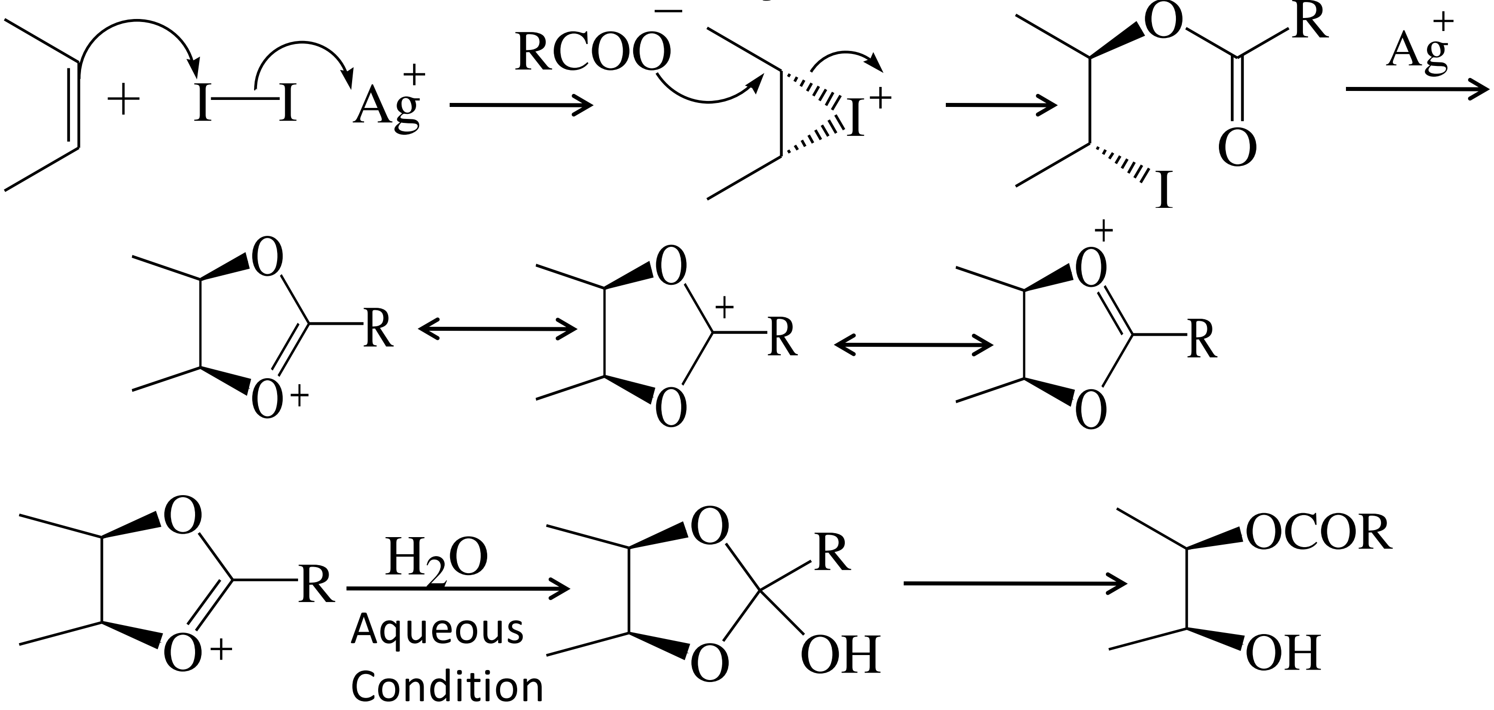
The formation of 1,2-diol products from alkenes can be achieved using Prevost's Reagent -a solution of iodine in carbon tetrachloride together with an equivalent of silver(I) acetate or silver(I) benzoate. The product is **anti**-diol.

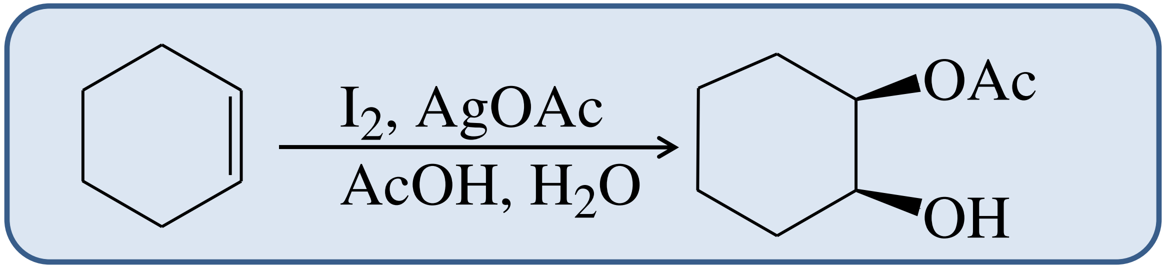




Woodward Hydroxylation

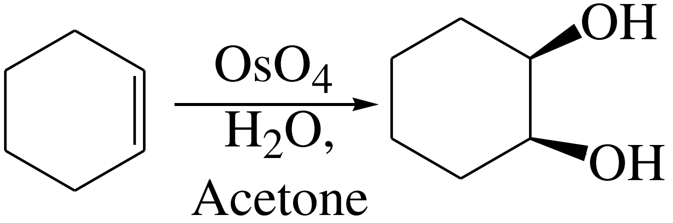
The formation of 1,2-diol products from alkenes can be achieved using Woodward’s Reagent -a solution of iodine in presence of water together with an equivalent of silver(I) acetate or silver(I) benzoate. The product is ***syn***-diol



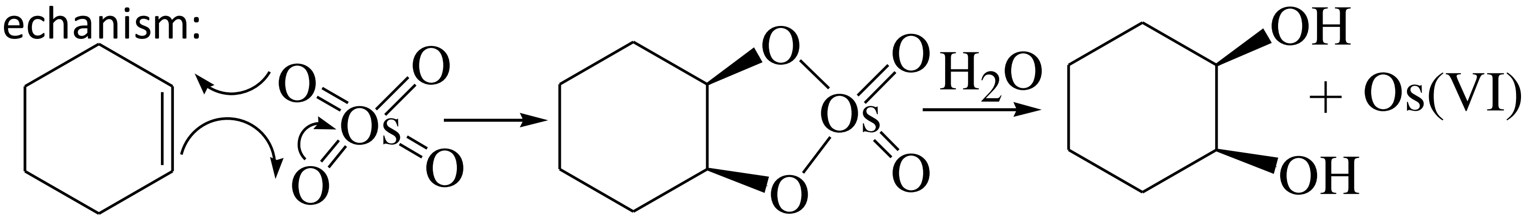


Hydroxylation by OsO_4

OsO_4 carries out a ***syn*** dihydroxylation of the double bond.



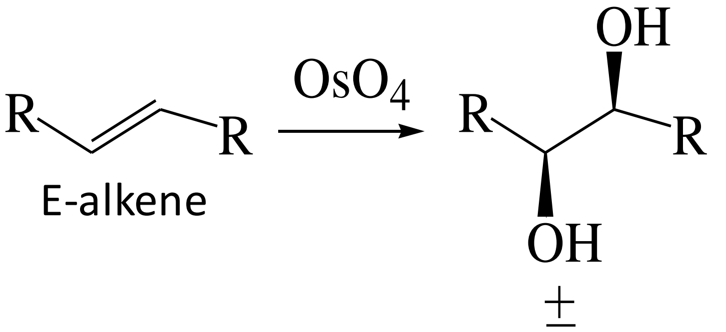
Mechanism:



Osmium tetraoxide:
Os(VIII)

Osmate ester:
Os(VI)

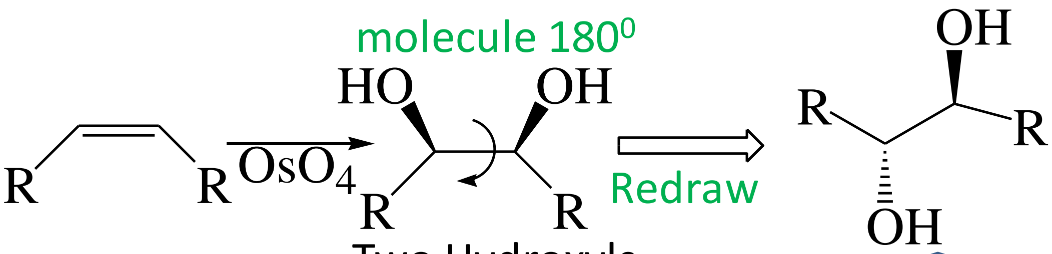
Because OsO_4 adds two hydroxyl groups to an alkene in a syn fashion, the overall product depends on the alkene starting material: it is stereospecific.



E-alkene

Two Hydroxyls added ***syn***

Rotate left half of the molecule 180^0



Z-alkene

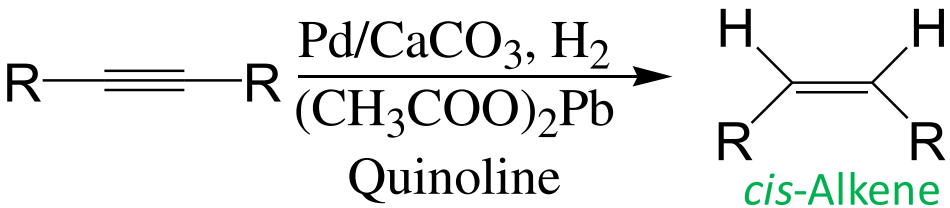
Two Hydroxyls added ***syn***

Redraw

But product is ***anti*** when draw like this

Catalytic Reduction of Alkynes

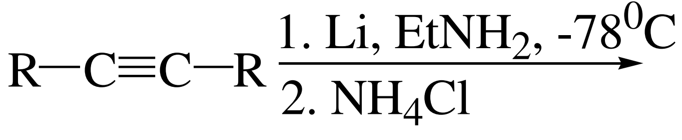
Lindlar's Catalyst produce *cis*-Alkene



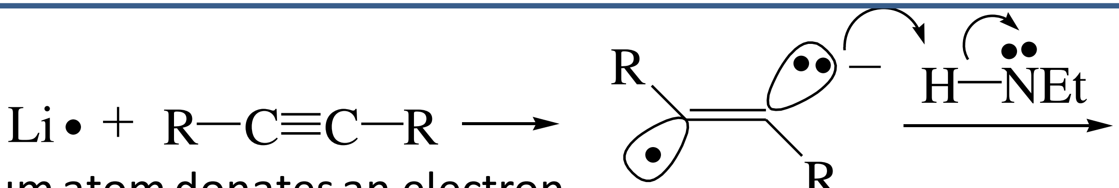
cis-Alkene

Here Lead acetate and quinoline is used as catalytic poison to stop reaction after alkene formation

Dissolving metal reduction of an alkyne (**Birch Reduction**)



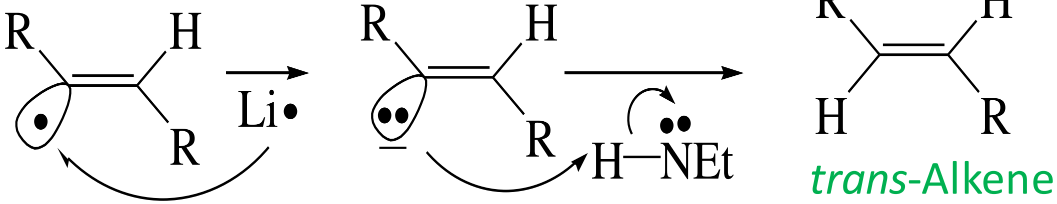
trans-Alkene



Vinylic Radical

A lithium atom donates an electron to the π bond of the alkyne

Radical anion



trans-Alkene

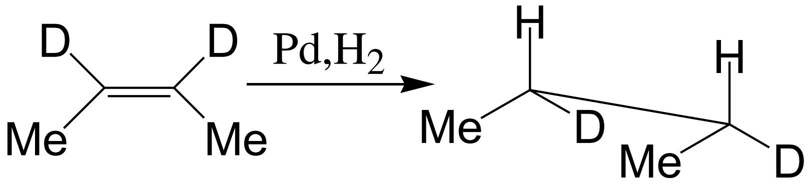
Vinylic Radical

Second lithium atom donates an electron to vinylic radical

Catalytic Reduction of Alkenes

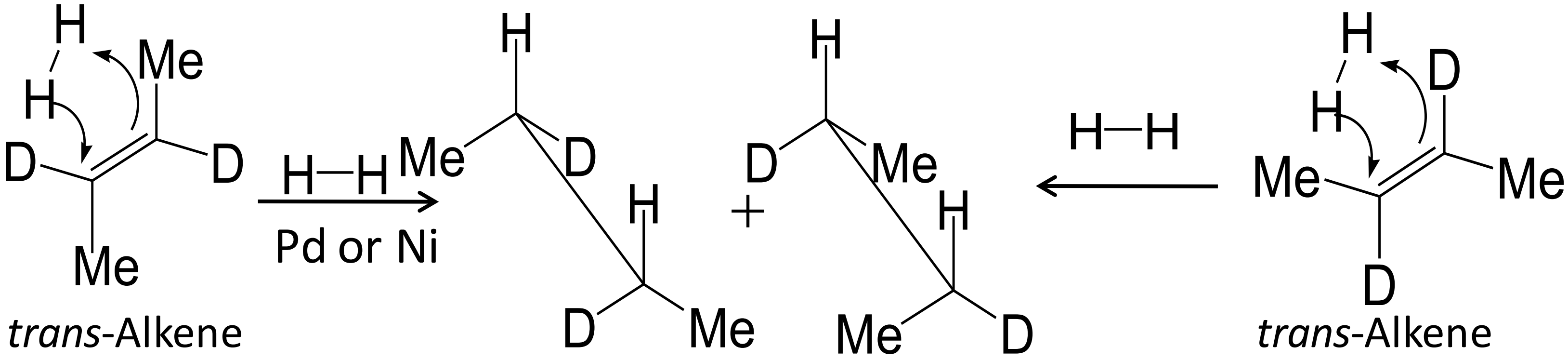
cis-Alkene $\xrightarrow[\textbf{\textit{syn}}\text{ addition}]{H_2}$ Meso compound

trans-Alkene $\xrightarrow[\textbf{\textit{syn}}\text{ addition}]{H_2}$ Threo (±)



cis-Alkene

Meso compound



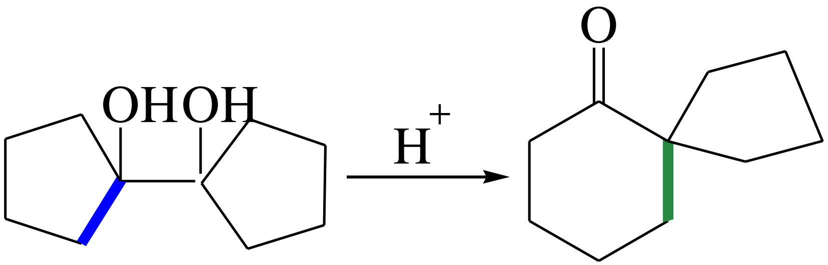
trans-Alkene

trans-Alkene

Threo (±)

Pinacol Rearrangement

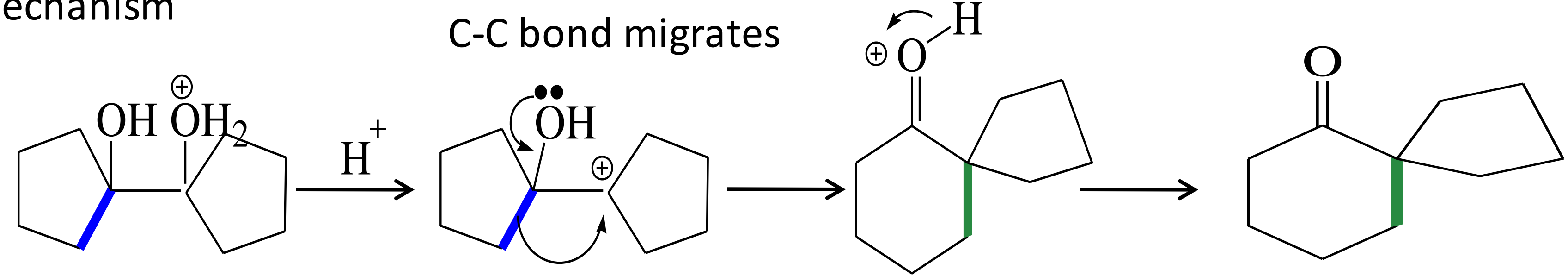
When 1,2-Diol pinacol is treated with acid, a rearrangement takes place.



Blue bond breaks

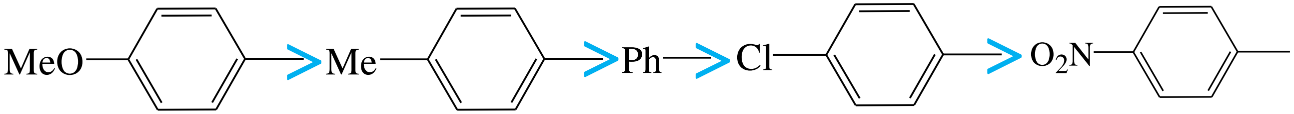
Green bond forms

Mechanism



Migratory Aptitude: In general the migratory aptitude is Aryl>Alkyl

Among Aryl grs:

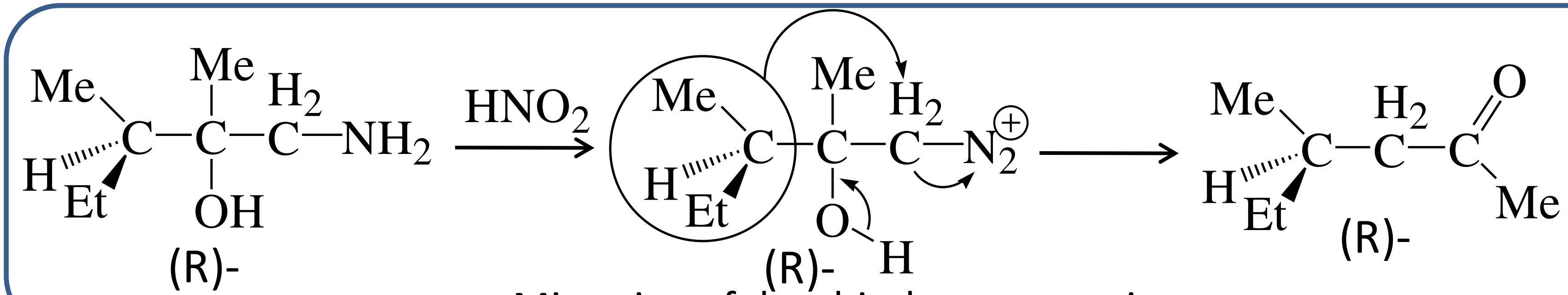


etc

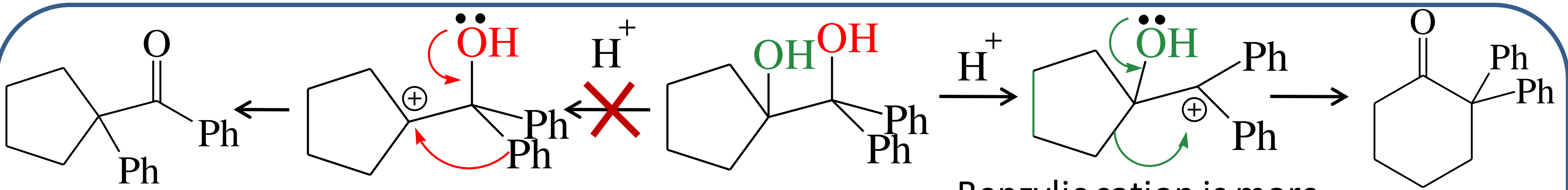
Among alkyl grs: $3^0 > 2^0 > 1^0$

Migratory aptitude of hydrogen is seen to be greater than an aryl group; may be to developed more stable carbocation.

If the migratory group is a chiral one, the configaration of this group will be retained in this Rearrangement;



Migration of the chiral gr. as an anion



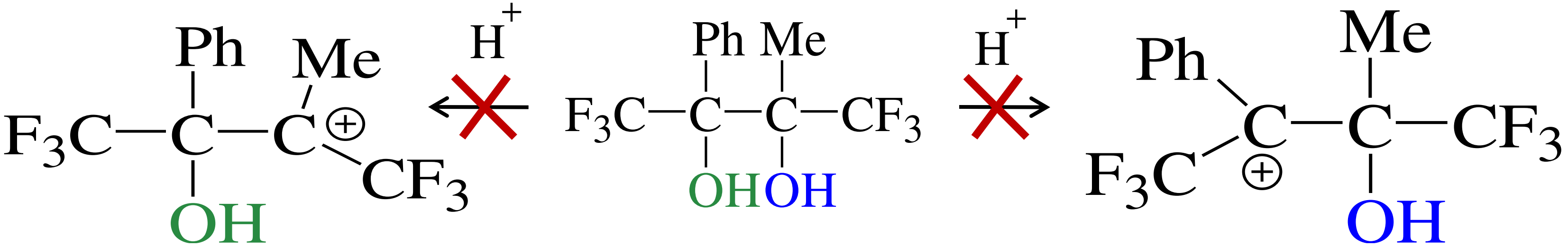
This product is not formed

Starting Material

Benzylic cation is more stable and is formed faster

This product is formed

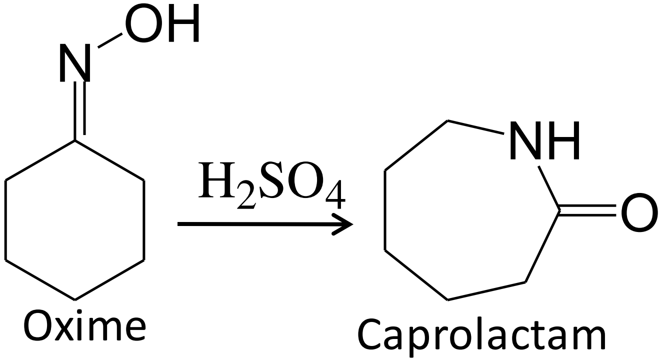
This product is formed because the red OH group leaves more readily than the green as the carbocation stabilized by two phenyl groups forms more readily than the carbocation stabilized by two alkyl groups.

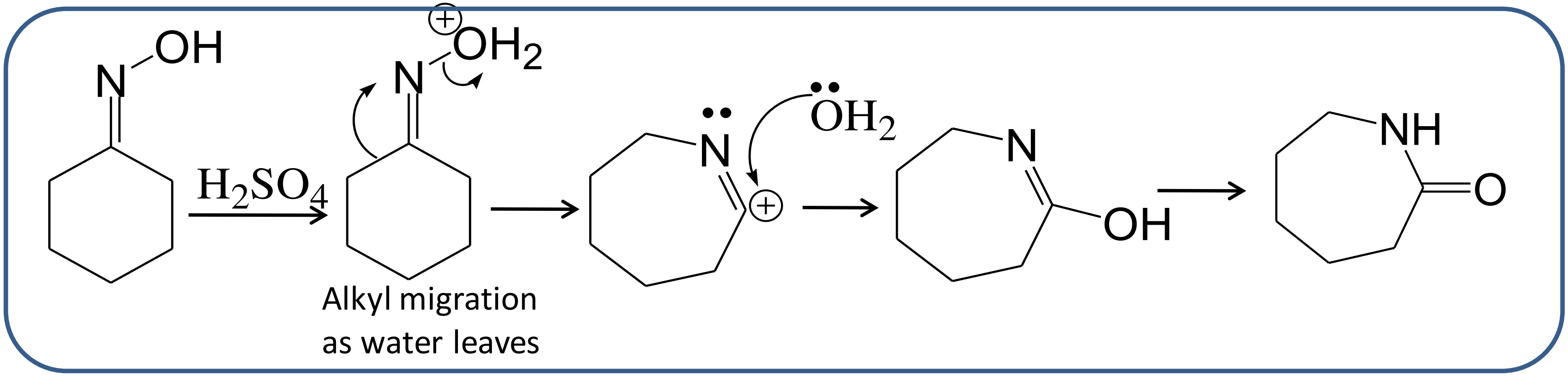


The formed carbocation is unstable due to $-CF_3$ group; This pinacol does not undergoes rearrangement reaction in presence of acid

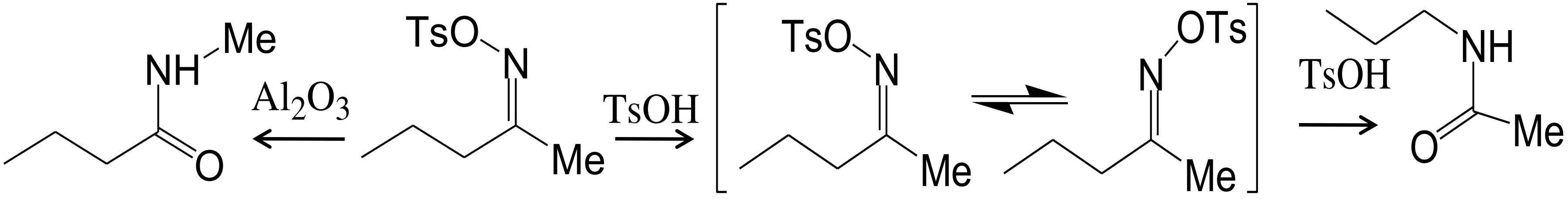
Beckmann Rearrangement

The mechanism of the Beckmann rearrangement Follows the same pattern as a pinacol: Acid converts the oxime OH into a leaving group, and an alkyl group migrates to nitrogen as water departs. The product cation is then trapped by water to give any amide.

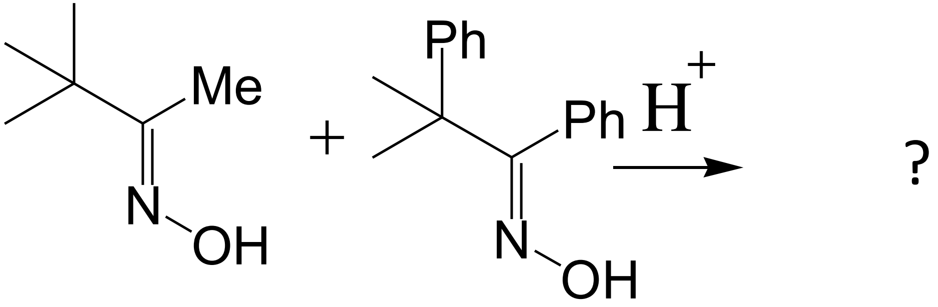


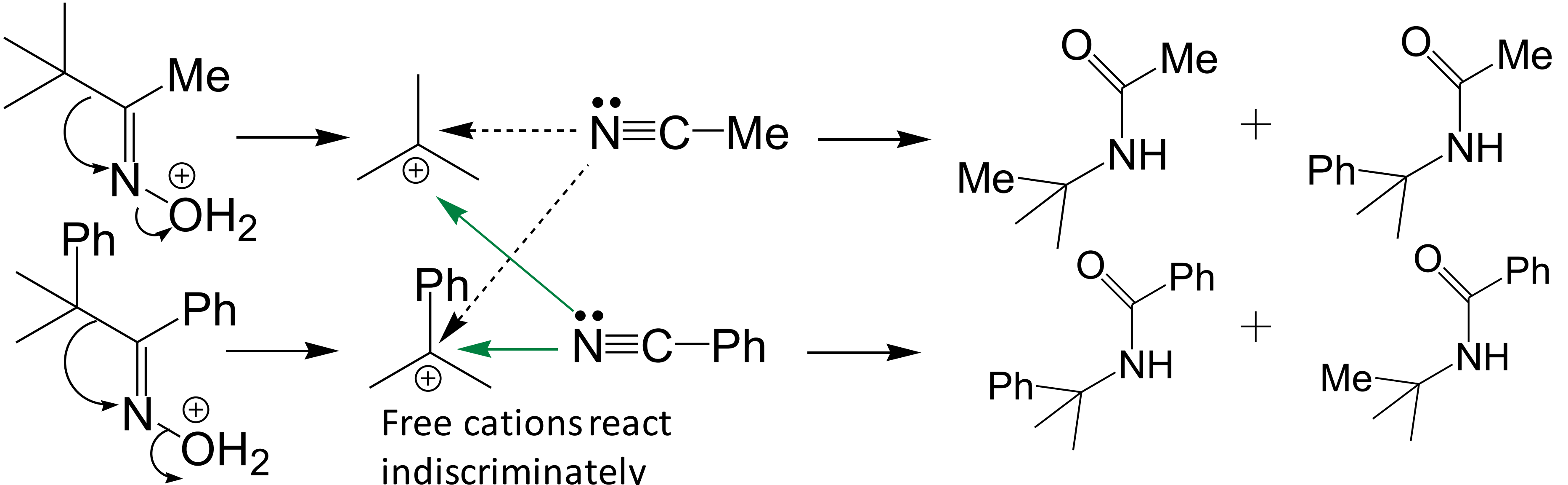


Which group migrates? **The group** in the starting material that has **migrated trans to the OH in starting material**



Intercoversion faster than rearrangement





Free cations react indiscriminately

C-C bond fragmentation gives stable tertiary carbon

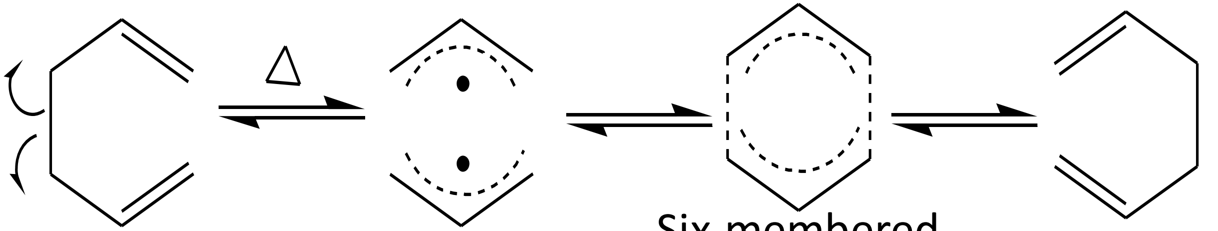
Expected Product

Crossover product

Migrating groups have to provide some degree of cation stabilization. But if they stabilises a cation too well there is good chance that fragmentation will occur and the migrating group will be lost as a carbocation.

Cope Rearrangement

Cope rearrangement is done thermally. It is [3,3] sigmatropic rearrangement

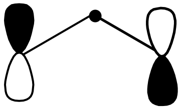


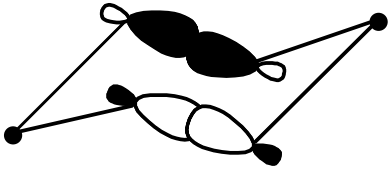
Two allyl radicals

Six-membered Cyclic T.S.

HOMO of allyl radical is $\Psi_2 \Rightarrow C_2$ symmetry

HOMO of allyl radical is C_2 symmetry





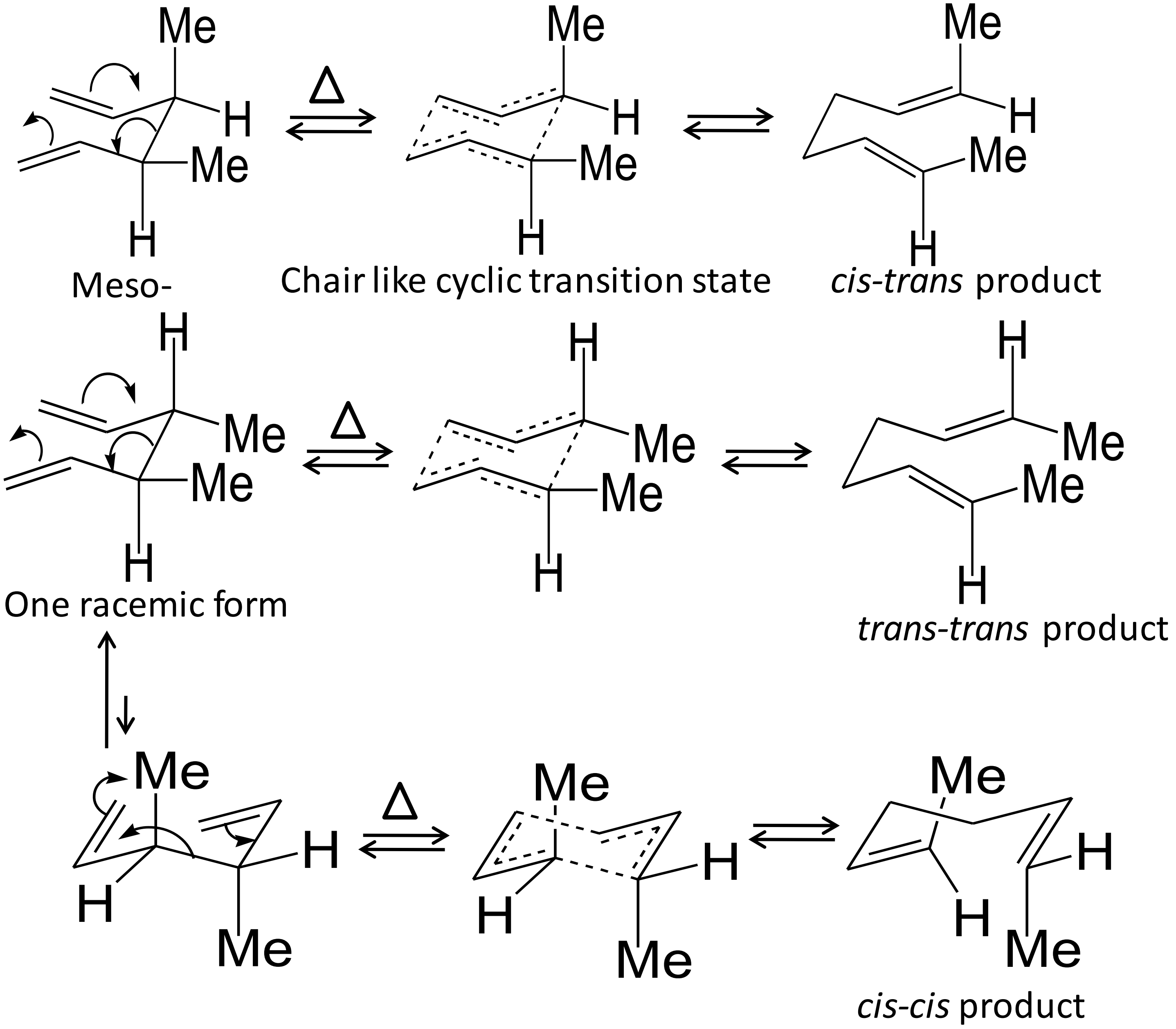
Six-membered chair like transition state

Two HOMOs of two allyl radicals come in overlap following supra-supra interaction

The reaction is stereo-specific and proceeds through formation of a **chair like six membered cyclic transition state**

Meso (Compound A) $\xrightleftharpoons{\Delta}$ *cis-trans* product (Compound B)

Racimate (Compound A) $\xrightleftharpoons{\Delta}$ *trans-trans* product (Compound B); 90%
cis-cis Product (Compound B); 10%



Meso-

Chair like cyclic transition state

cis-trans product

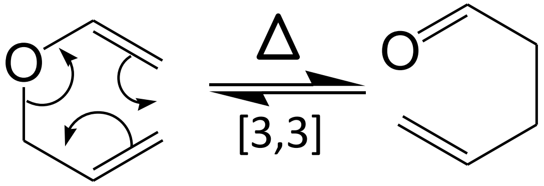
One racemic form

trans-trans product

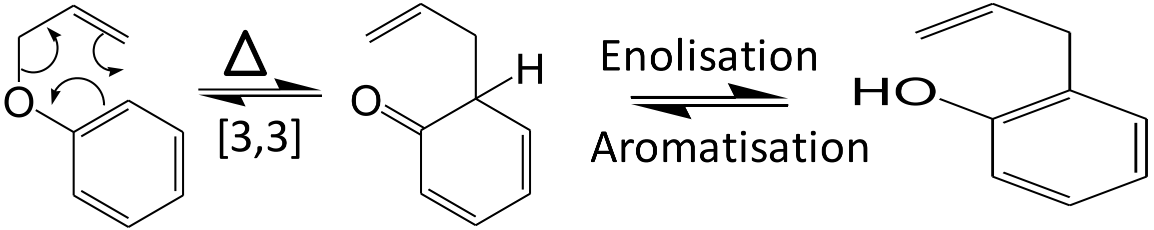
cis-cis product

Claisen Rearrangement

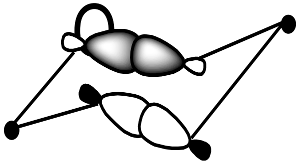
Claisen rearrangement is also done thermally. It is [3,3] sigmatropic rearrangement
But here substrate is allyl-Vinyl esters and allyl-aryl esters.



Allyl-Vinyl ester



Allyl-Aryl ester

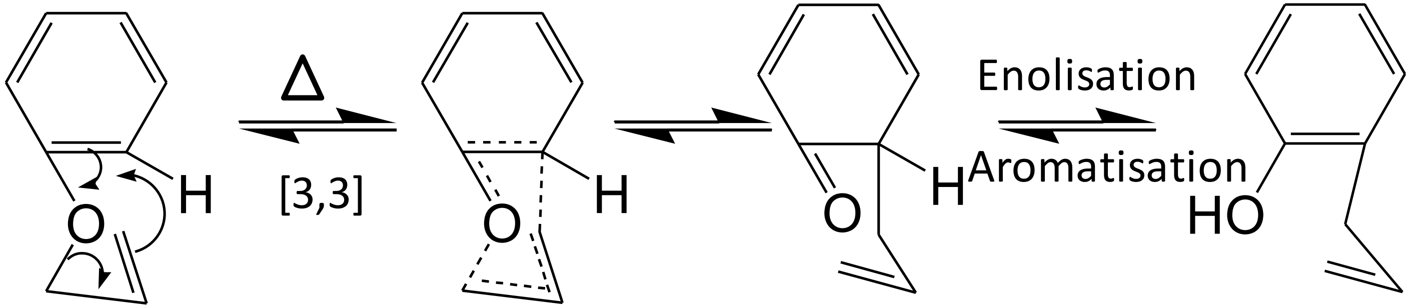


HOMO of allyl radical is $\Psi_2 \Rightarrow C_2$ symmetry

HOMO of oxygen containing allyl radical is $\Psi_2 \Rightarrow C_2$ symmetry

Two HOMOs of allyl and oxygen containing allyl radical come in overlap following supra-supra interaction

The reaction is stereo-specific and proceeds through formation of a **chair like six membered cyclic transition state**



Allyl-Aryl ester   Six membered chair like TS

Addition to Alkene

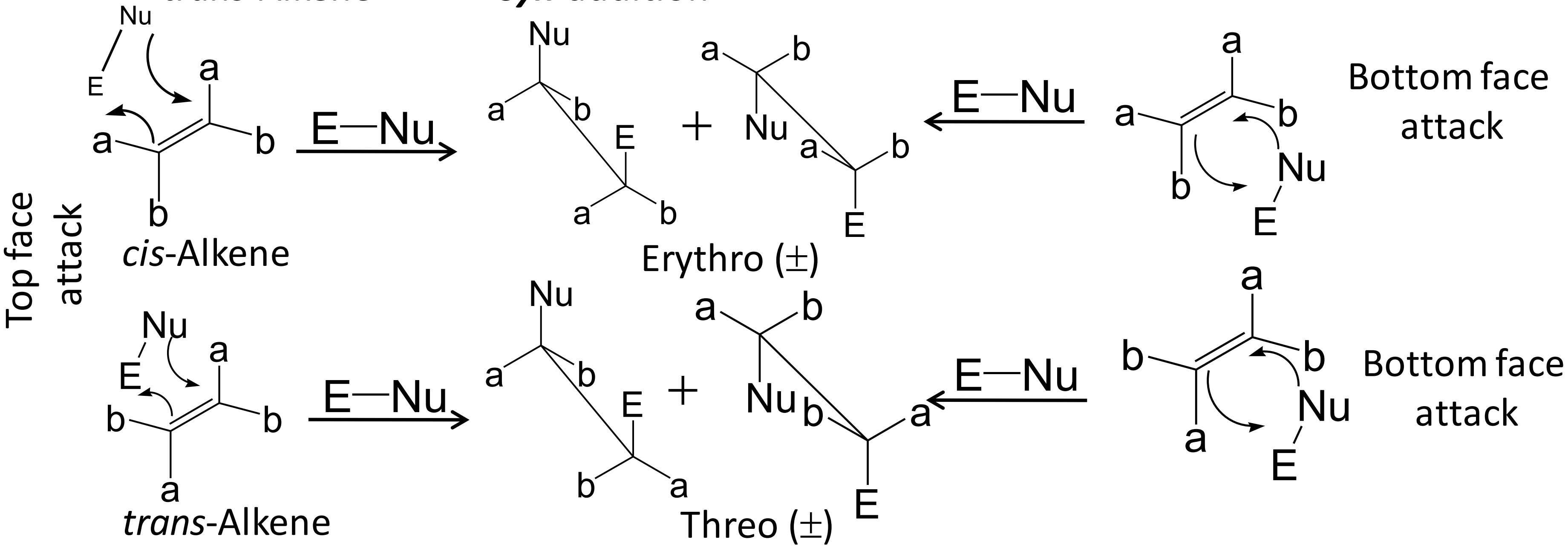
Stereochemistry of addition reaction

Stereochemistry of a addition reactions depends on whether both electrofile (E^+) and the nucleophile (Nu^-) will join themselves to the two double bonded carbons from the same side (syn addition) of the double bond or from the opposite sides (Anti addition).

When **E≠Nu** and the addition is **syn**

cis-Alkene $\xrightarrow{\textbf{\textit{syn}}\text{ addition}}$ Erythro (±)

trans-Alkene $\xrightarrow{\textbf{\textit{syn}}\text{ addition}}$ Threo (±)



Top face attack

cis-Alkene

Erythro (±)

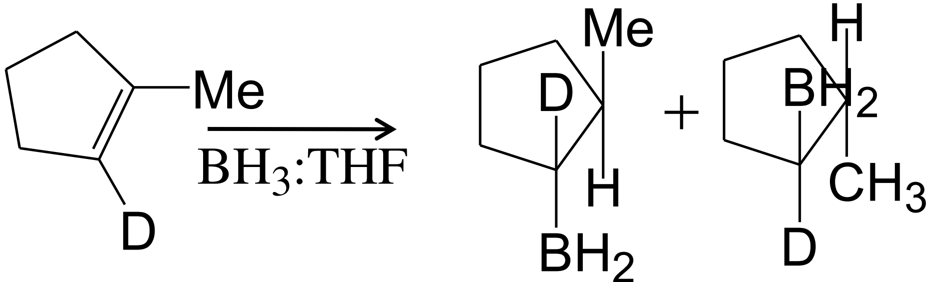
Bottom face attack

trans-Alkene

Threo (±)

Bottom face attack

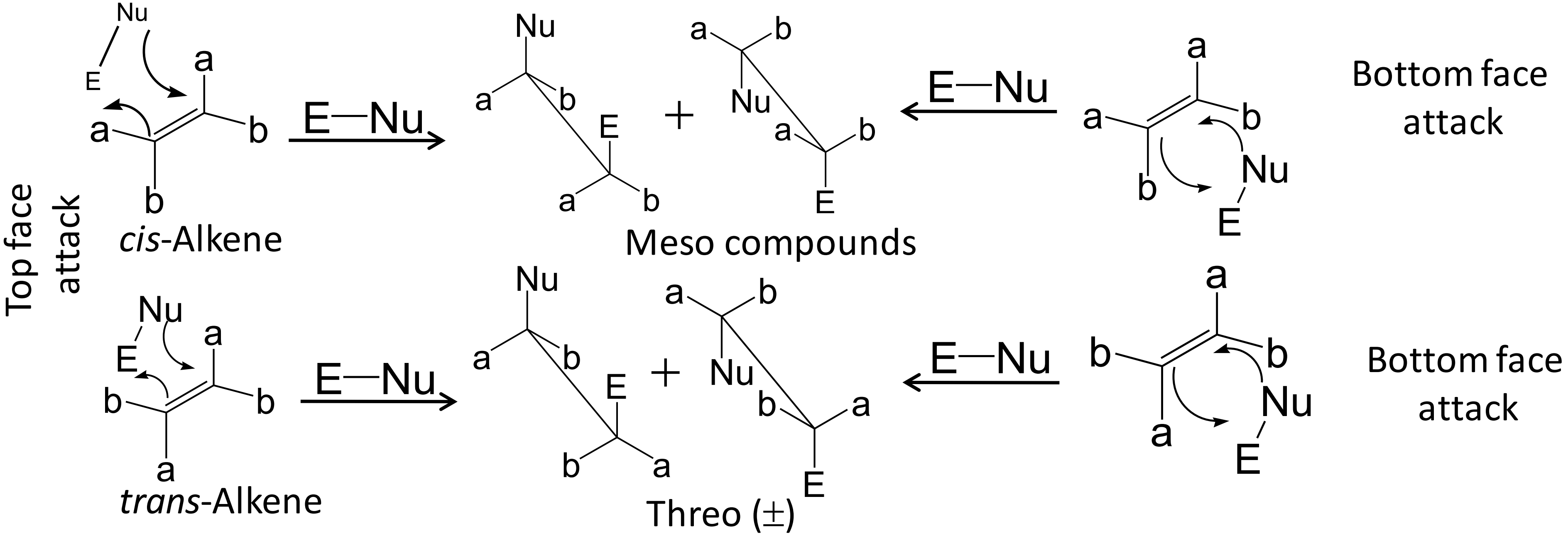
For eample: Addition of BH_3



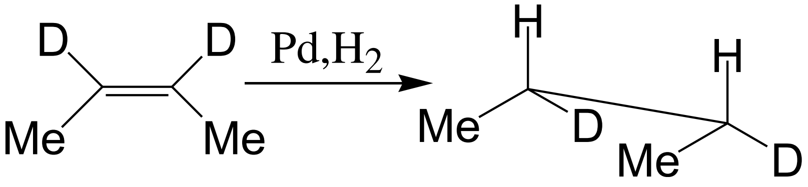
When **E=Nu** and the addition is **syn**

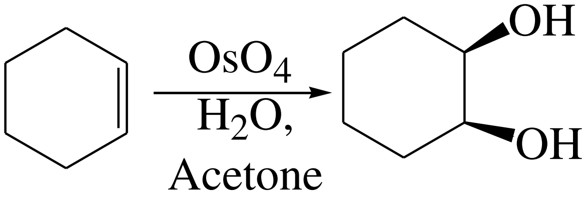
cis-Alkene ⟹ ***syn*** addition ⟹ Meso compound

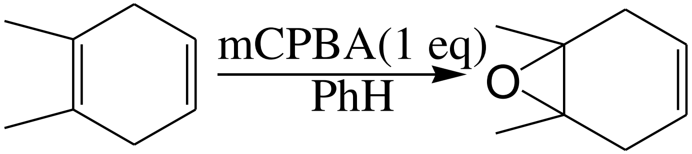
trans-Alkene ⟹ ***syn*** addition ⟹ Threo (±)



For eample: Addition of H_2; Hydroxylation with OsO_4; Epoxidation







All starting materials are cis-alkene, so
All products are meso.

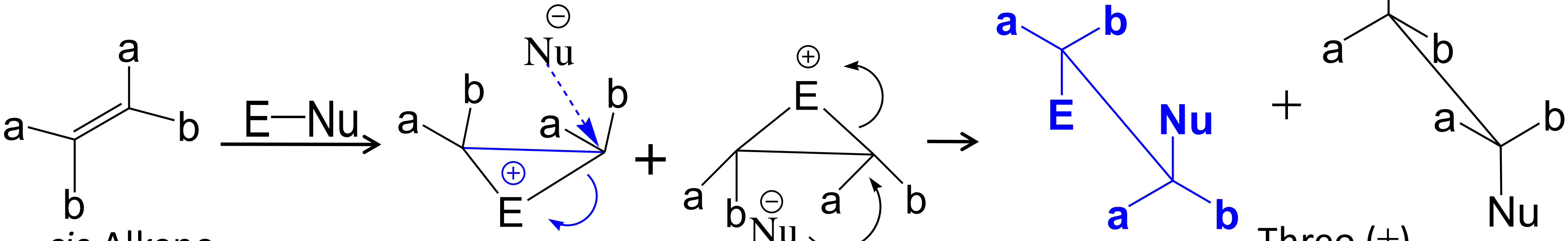
This reaction is regeoselective one too because epoxidation occurs selectively on more substituted double bond

If the electrofile forms a cyclic cation as an intermediate, the nucleophile has no other alternative but to attack the intermediate from the opposite side and the addition is **stereospecific and anti**.

When **E≠Nu** and the addition is **Anti**

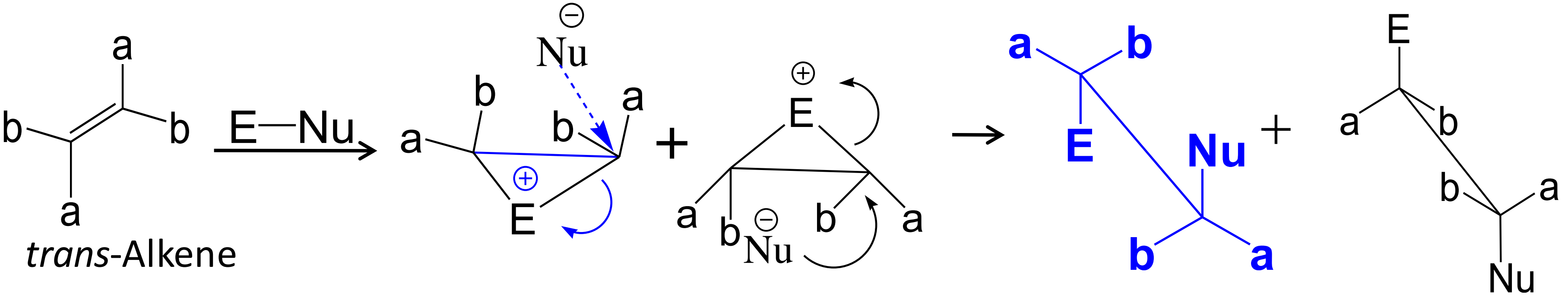
cis-Alkene ⇒ ***anti*** addition ⇒ Threo (±)

trans-Alkene ⇒ ***anti*** addition ⇒ Erythro (±)



cis-Alkene

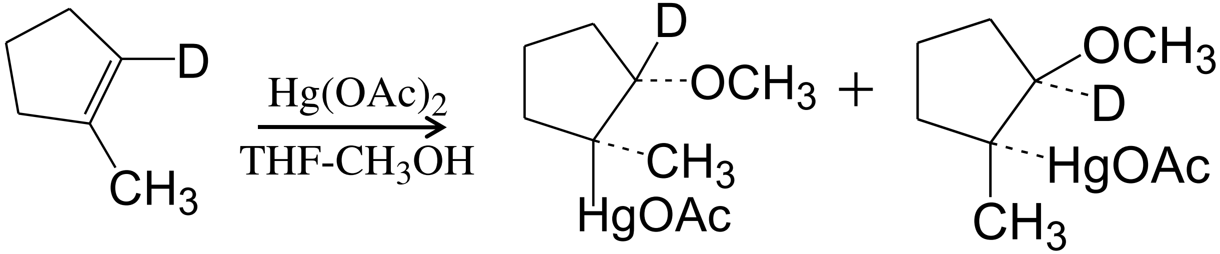
Threo (±)



trans-Alkene

Erythro (±)

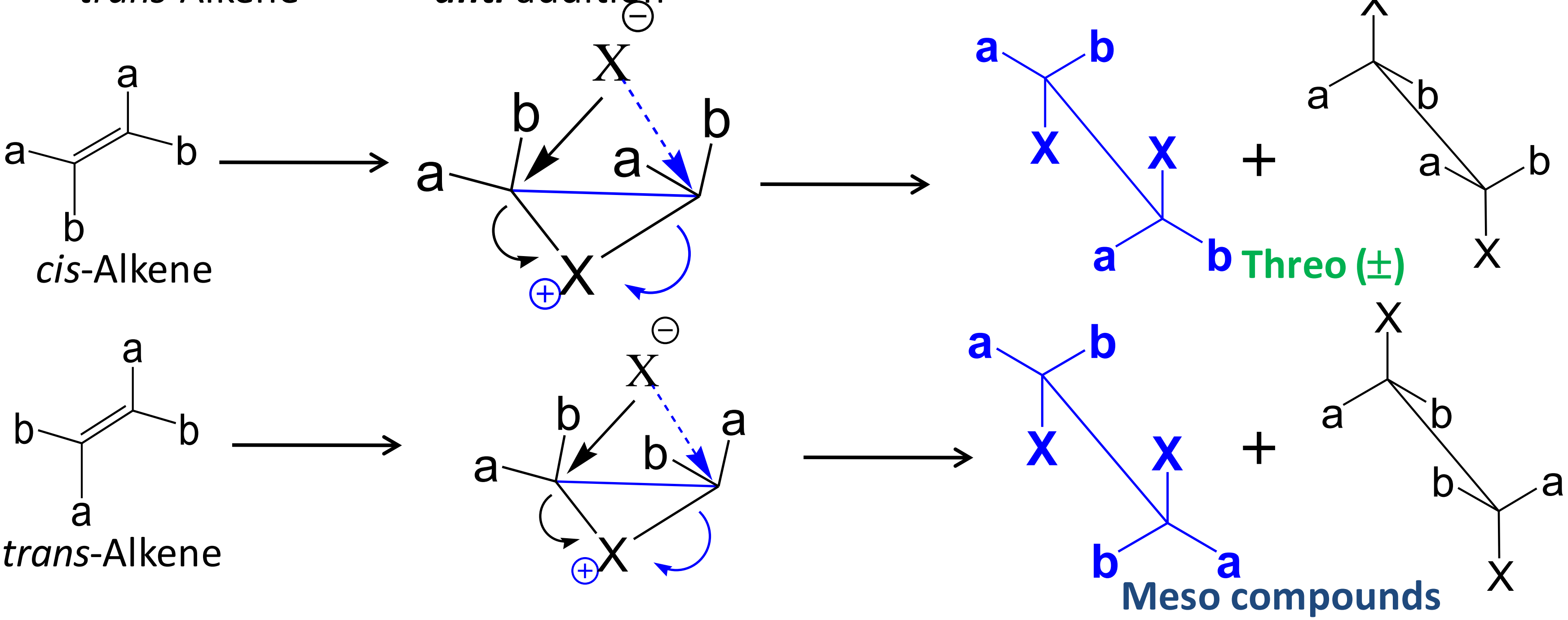
For eample: Oxymercuration, Br_2 in water etc



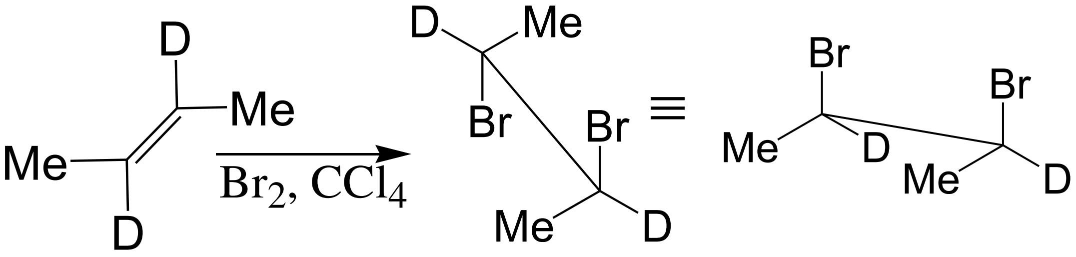
When **E=Nu** and the addition is **anti**

cis-Alkene → ***anti*** addition → **Threo (±)**

trans-Alkene → ***anti*** addition → **Meso compound**



For eample: Addition of I_2, Br_2; Epoxidation followed by acid or base hydrolysis



All starting materials are *trans*-alkene, so product is meso.