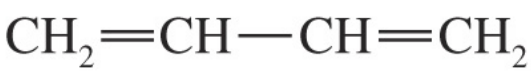
CHAPTER 16

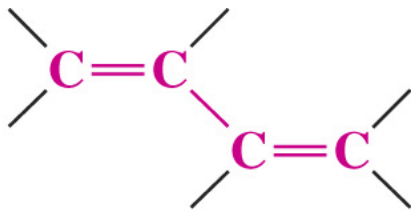
CONJUGATE ADDITION

Conjugated Pi Bonds

- Conjugated double bonds are separated by only one single bond.

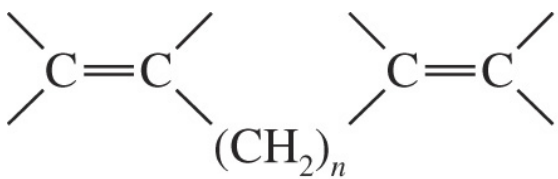


1,3-Butadiene



A conjugated diene

- Isolated double bonds are separated by two or more single bonds.

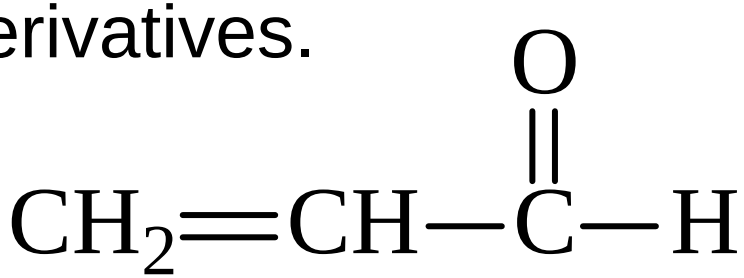


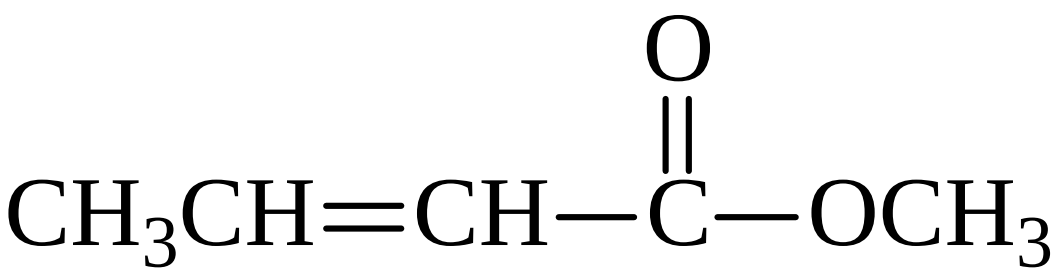
An isolated diene
($n \neq 0$)

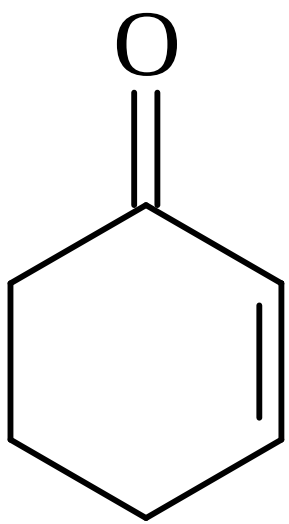
1,4-Pentadiene

Carbonyl Compounds with Conjugated Pi Bonds

A carbon-carbon double bond can also be conjugated pi bond of a carbonyl group in an aldehyde, ketone, carboxylic acid and its derivatives.

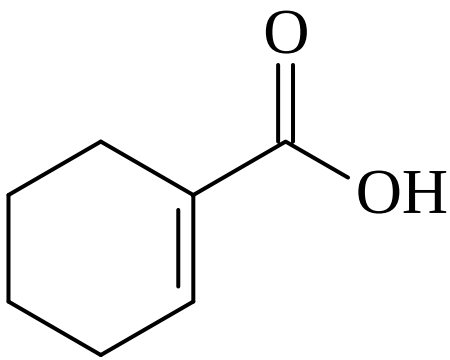




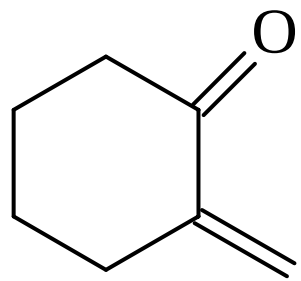


All are Conjugated Pi Bonds

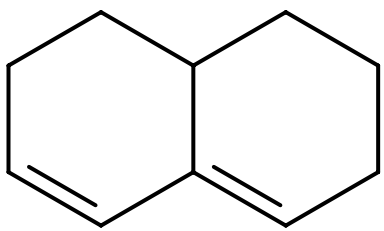
Examples



Conjugated



Conjugated



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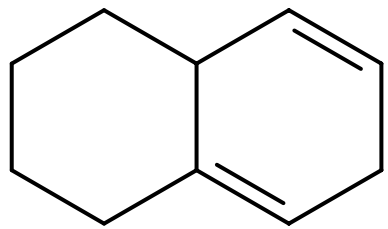
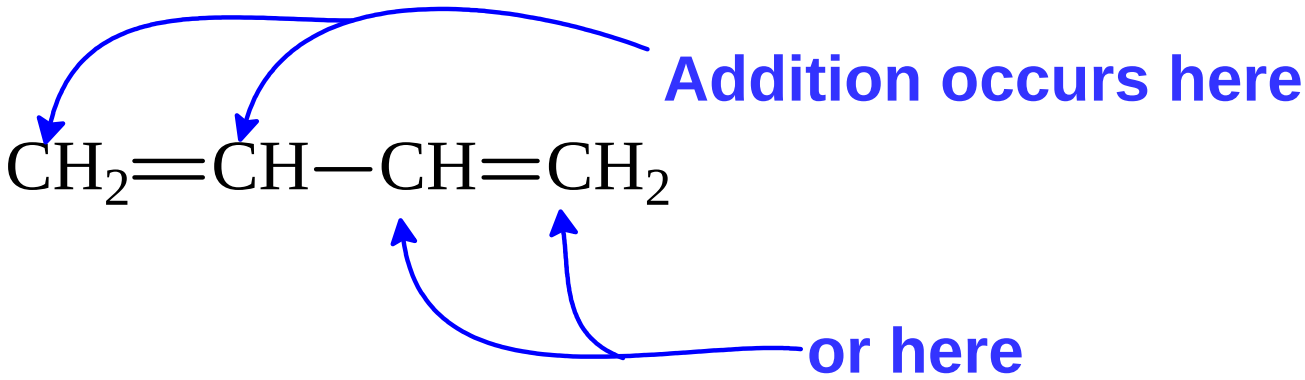
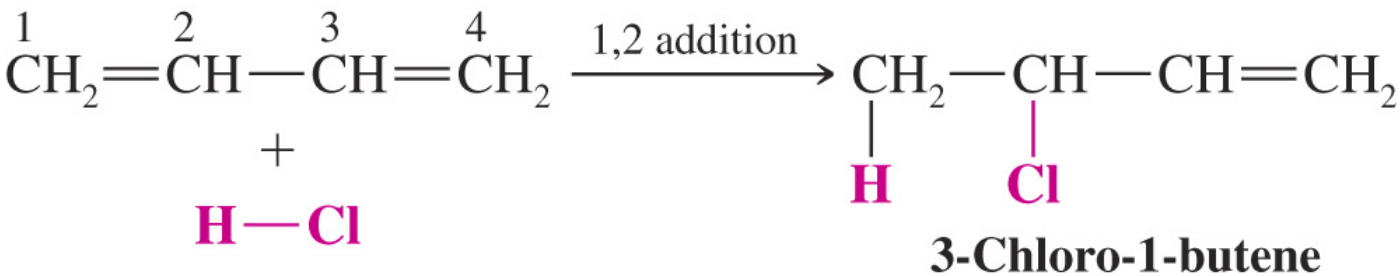


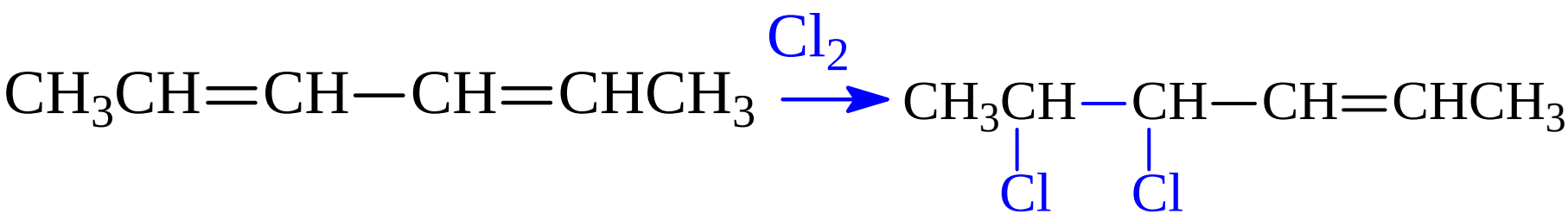
Isolated

1,2-Addition

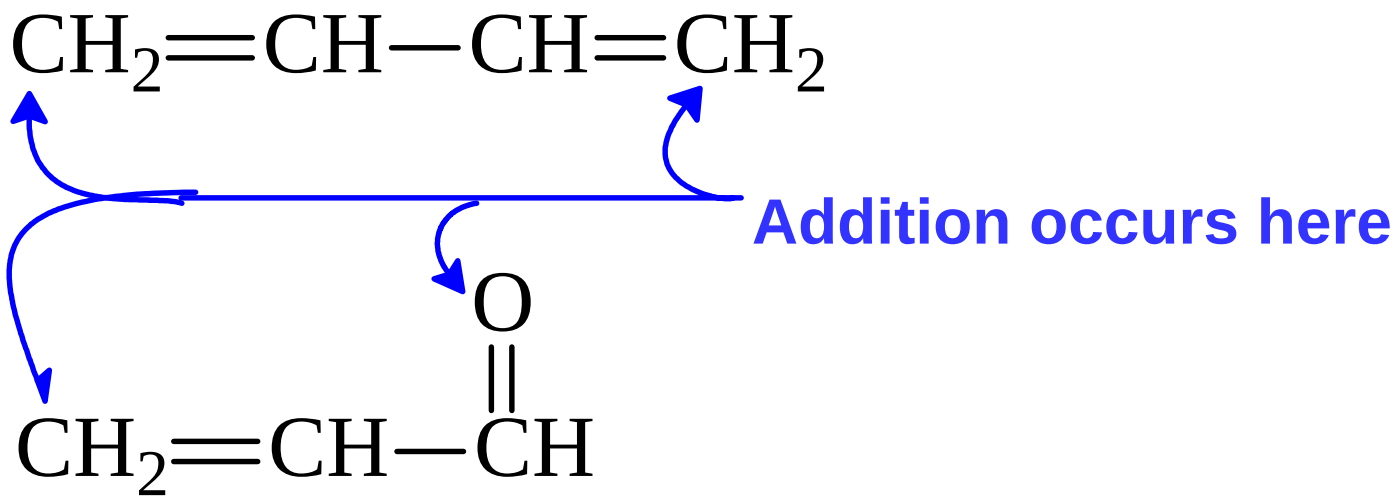


examples

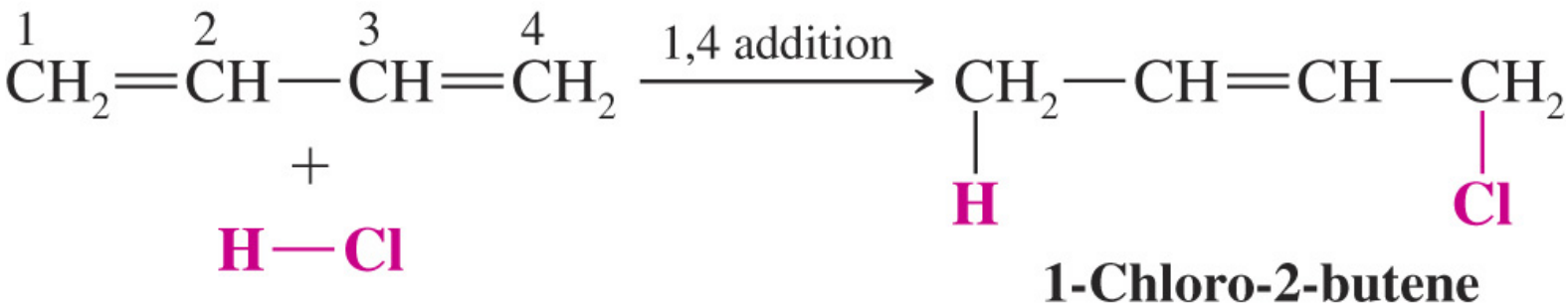




1,4-Addition = Conjugate addition



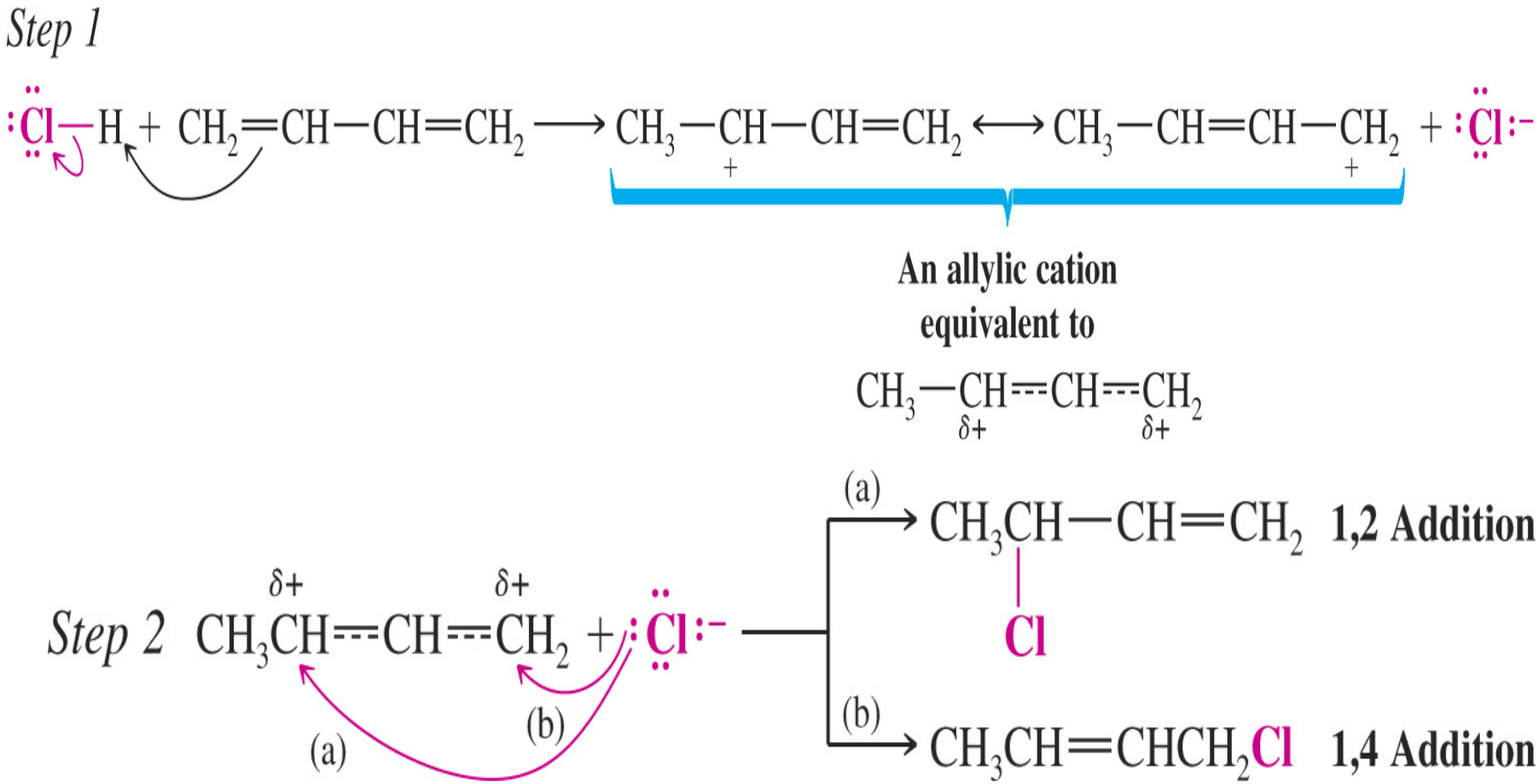
example



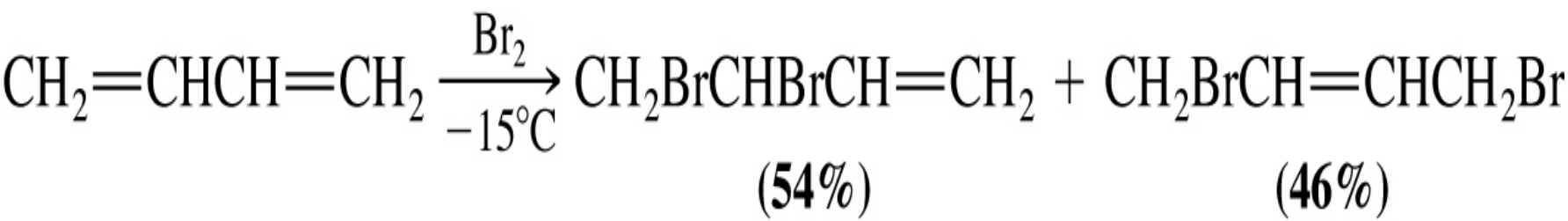
1-Chloro-2-butene

1,2 and 1,4- Addition to Conjugated Dienes

Mechanism

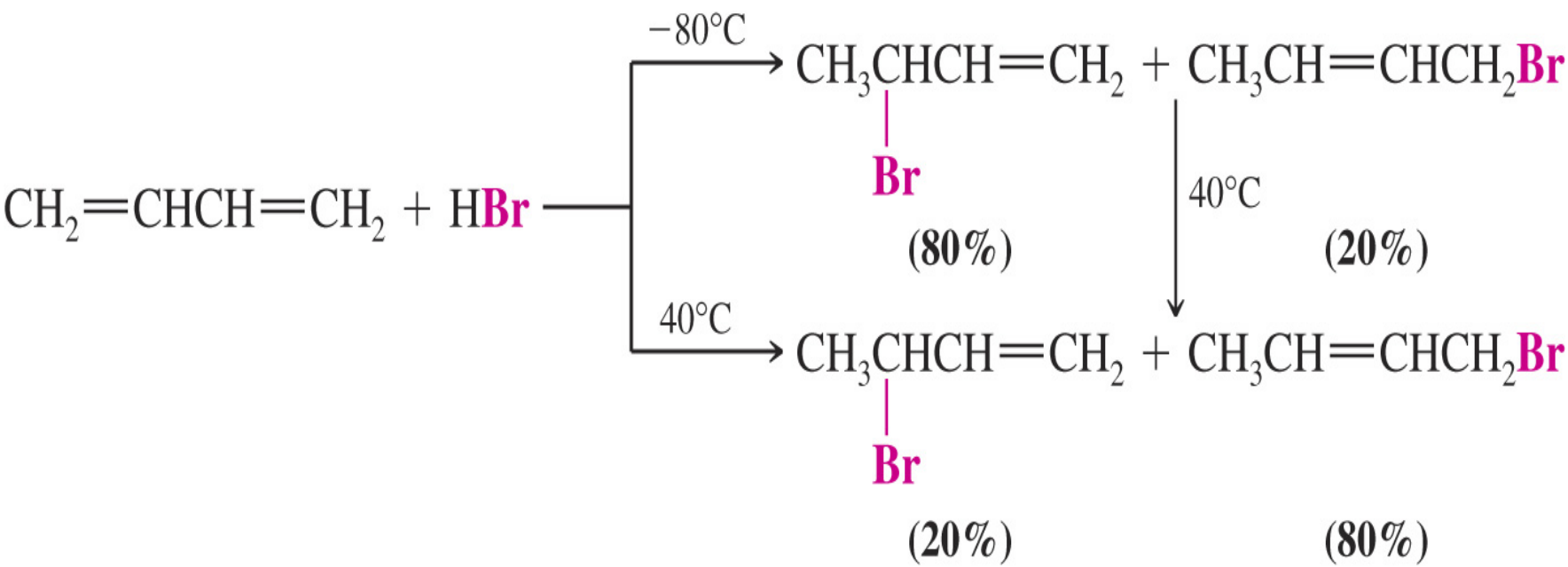


Other electrophilic reagents add to conjugated dienes in similar fashion



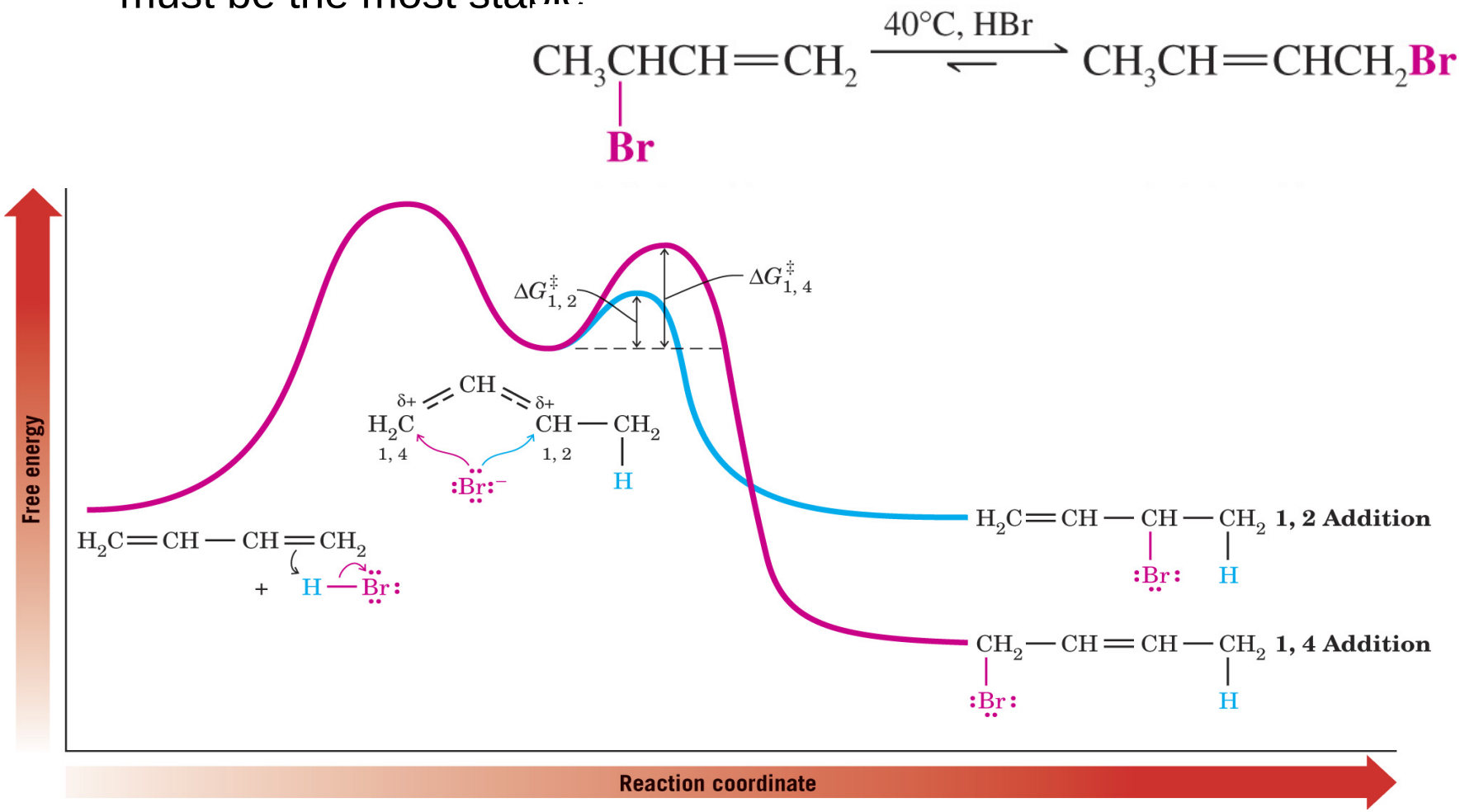
Kinetic Control versus Thermodynamic Control of a Chemical Reaction

In addition of HBr to 1,3-butadiene the temperature of reaction greatly affects the distribution of 1,2 and 1,4 products.



Heating the 1,2-addition product leads to an equilibrium which favors the 1,4-addition product

– Because equilibrium conditions favor the 1,4-addition product it must be the most stable



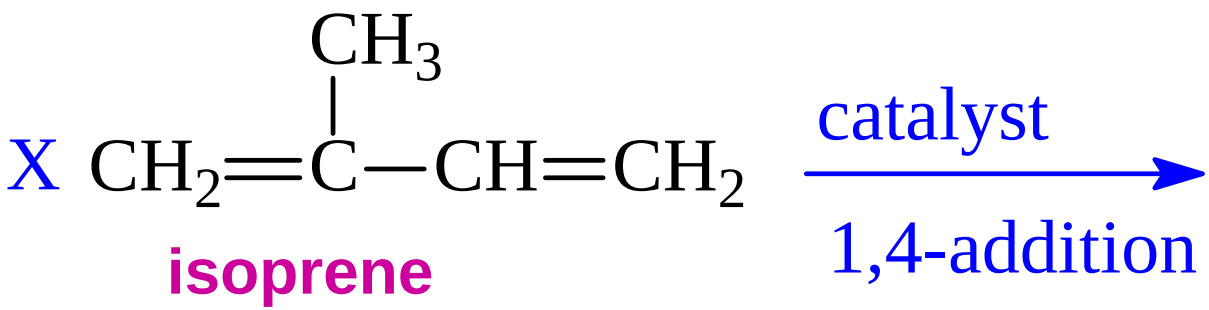
➔**1,2-addition product is formed faster and is the major product at low temperatures due to D*G*‡ of 1,2-addition product is lower than for 1,4-addition product**
The reaction is said to be under kinetic control

➔**At higher temperatures when an equilibrium is established, the most stable product predominates 1,4-addition product is more stable and is the major product at high temperatures**
The reaction is said to be under thermodynamic control

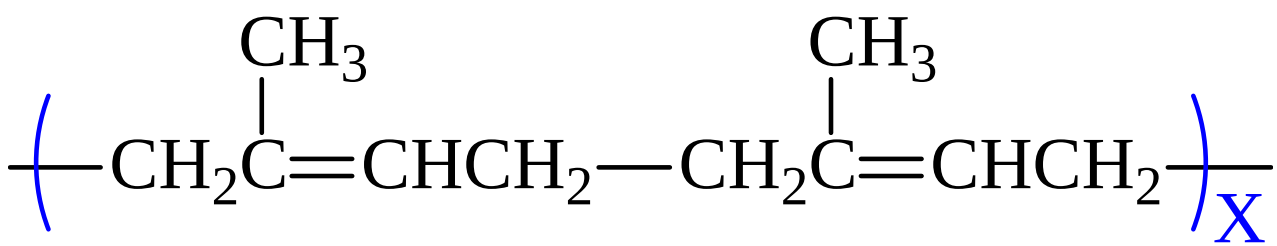
➔**The 1,4 product is most stable because it leads to a disubstituted double bond**

➔**1,2-addition product has a less stable monosubstituted double bond**

1,4-Addition Polymers



isoprene



polyisoprene

Natural rubber = polyisoprene with all cis double bonds

Hard polymer (gutta-percha) = trans polyisoprene

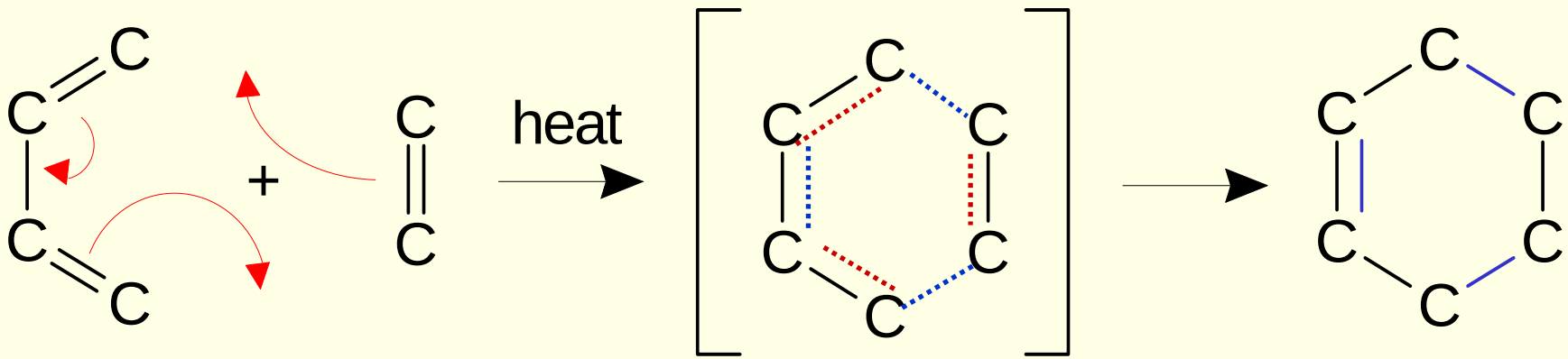
DIELS- ALDER REACTION

The Diels-Alder Reaction

concerted

three pairs of electrons move at one time

ring-forming reaction

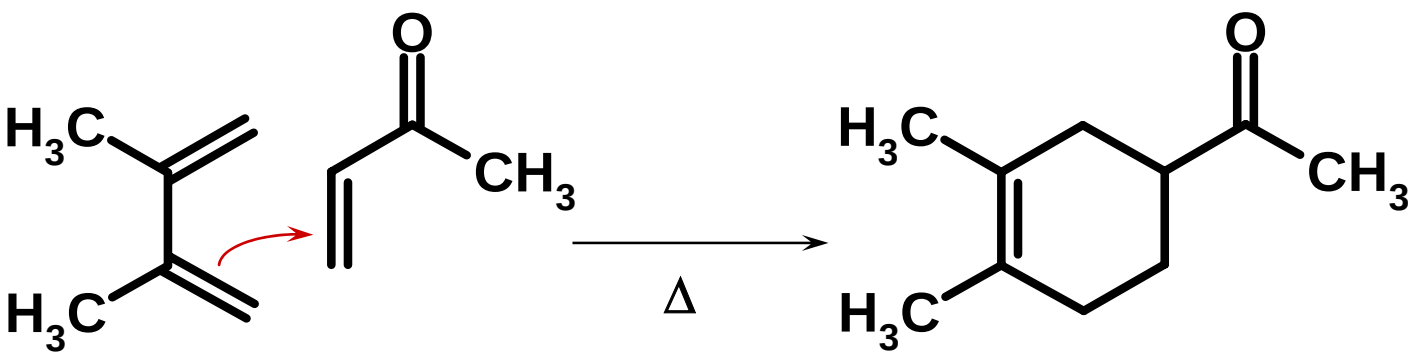


diene + dienophile ⟶ cyclohexene

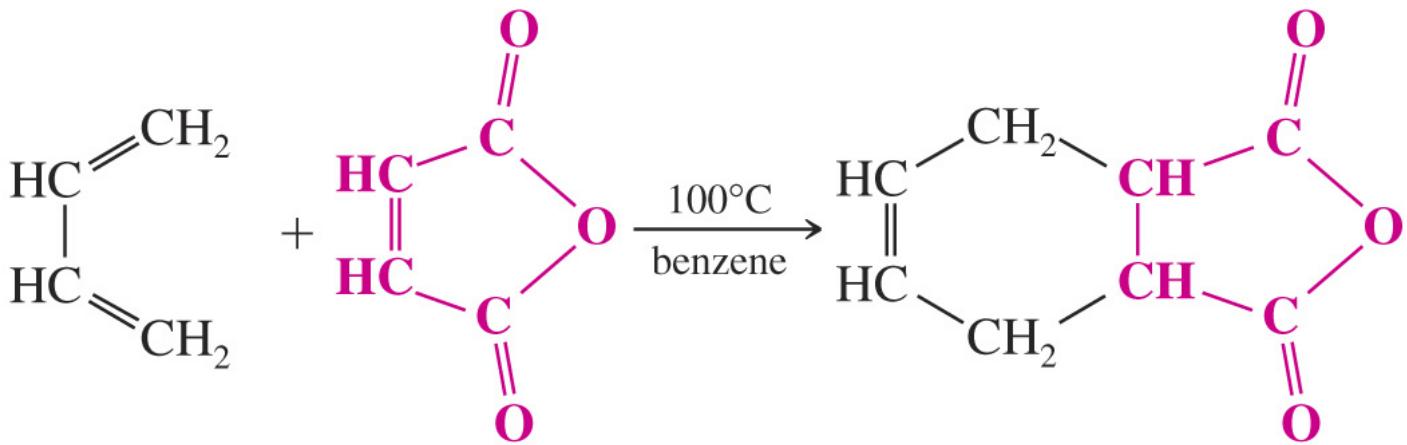
NOTE: ——— ***= gain of bond order***

——— ***= loss of bond order***

EXAMPLES OF DIELS-ALDER REACTION

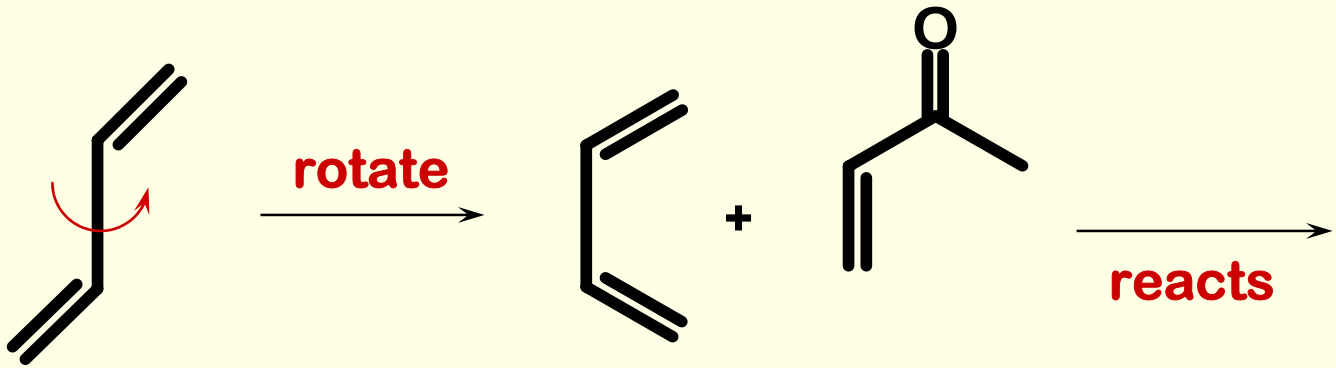


Diene **Dienophile** **A Cyclohexene**



1,3-Butadiene (diene) **Maleic anhydride (dienophile)** **Adduct (100%)**

THE DIENE MUST BE ABLE TO ADOPT THE *S-CIS* CONFORMATION

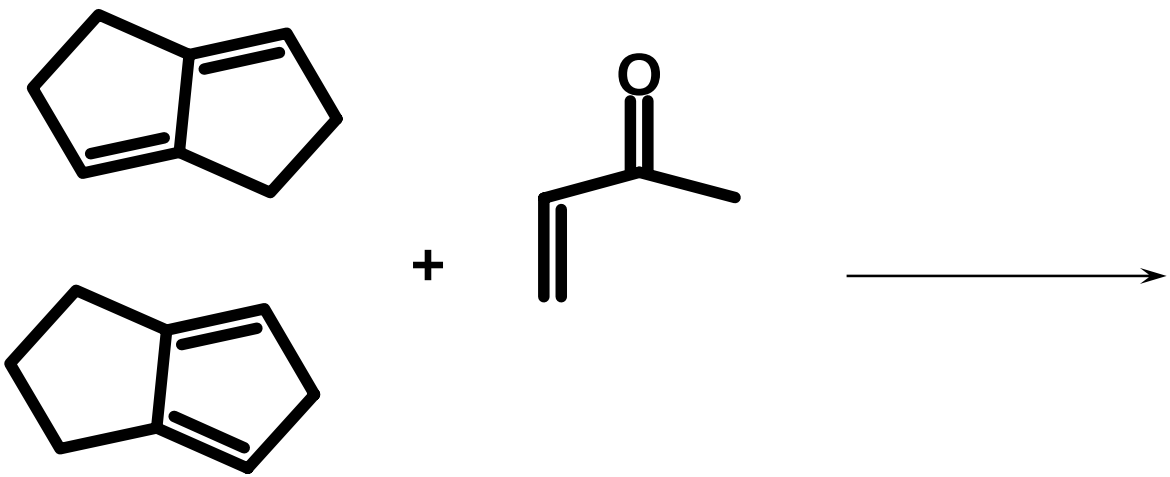


s-trans **conformation**

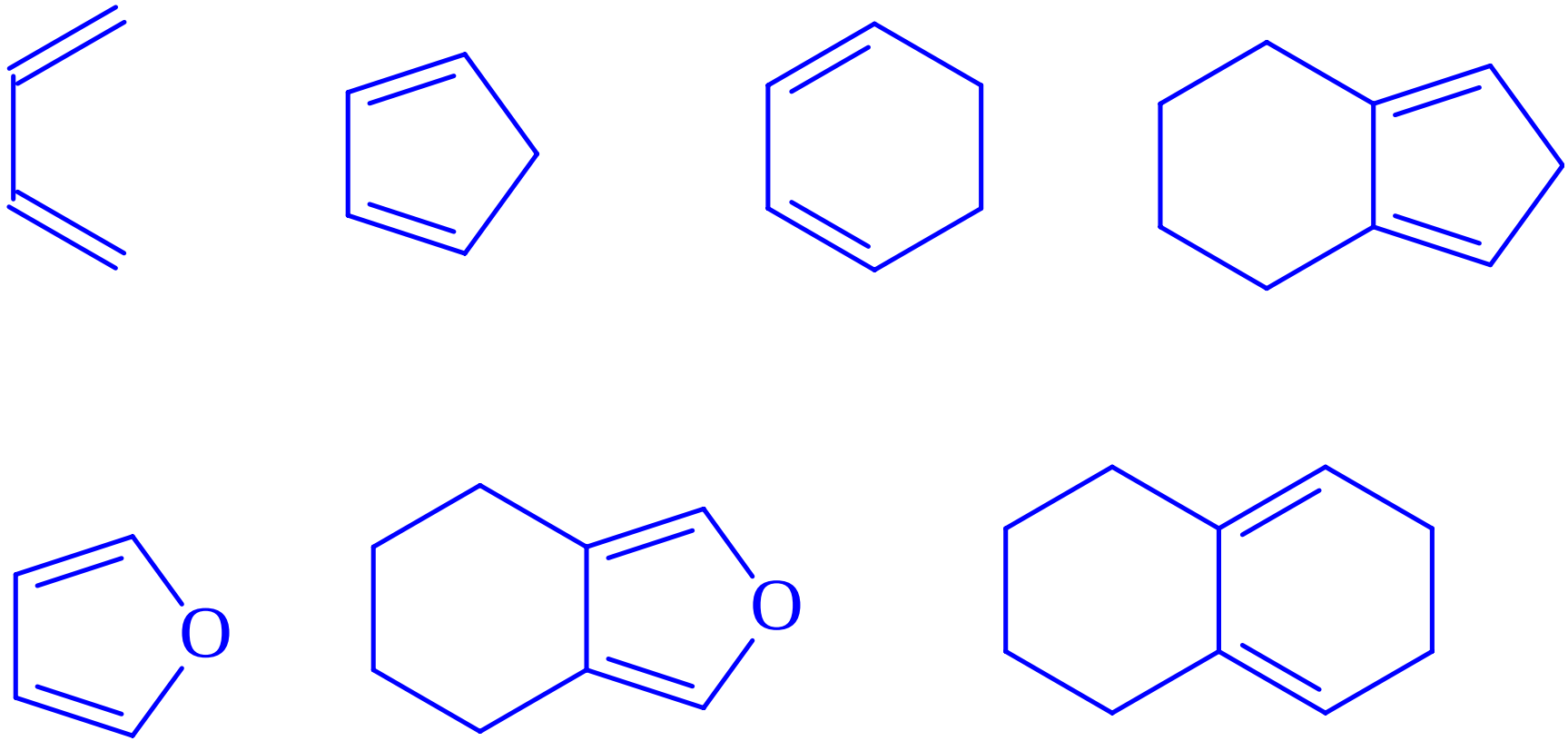
s-cis **conformation**

does not react

reacts normally

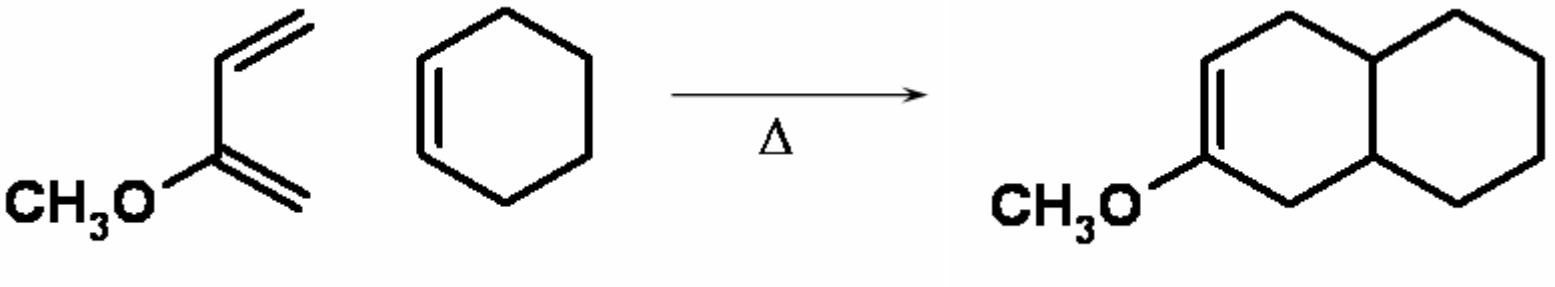


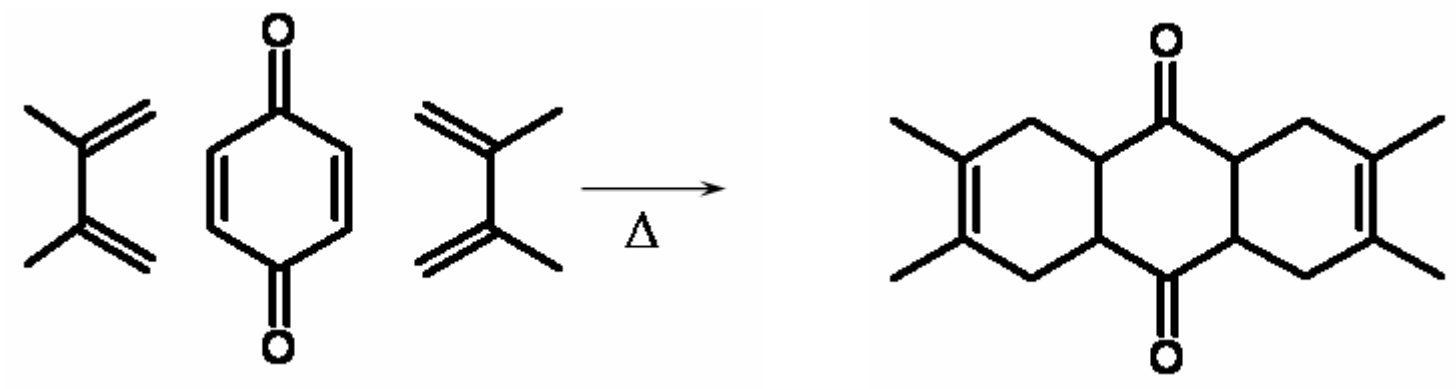
Some s-cis Dienes can be used in Diels –Alder Reaction

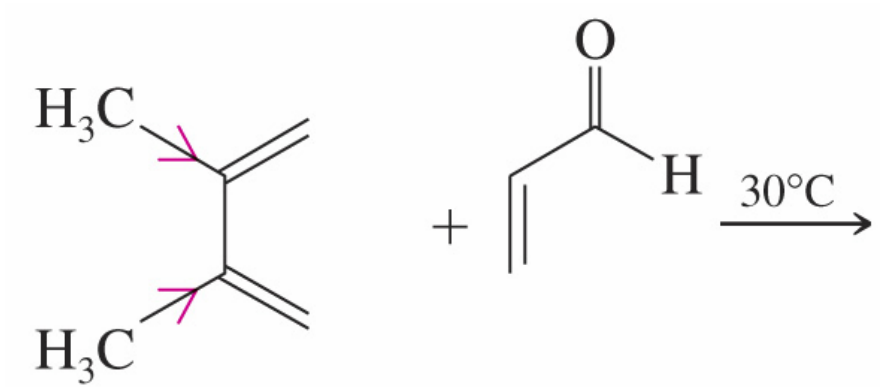


All are s-cis

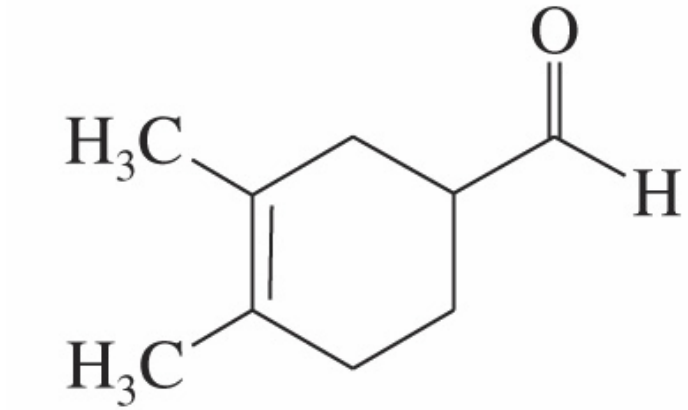
MORE DIELS-ALDER REACTIONS

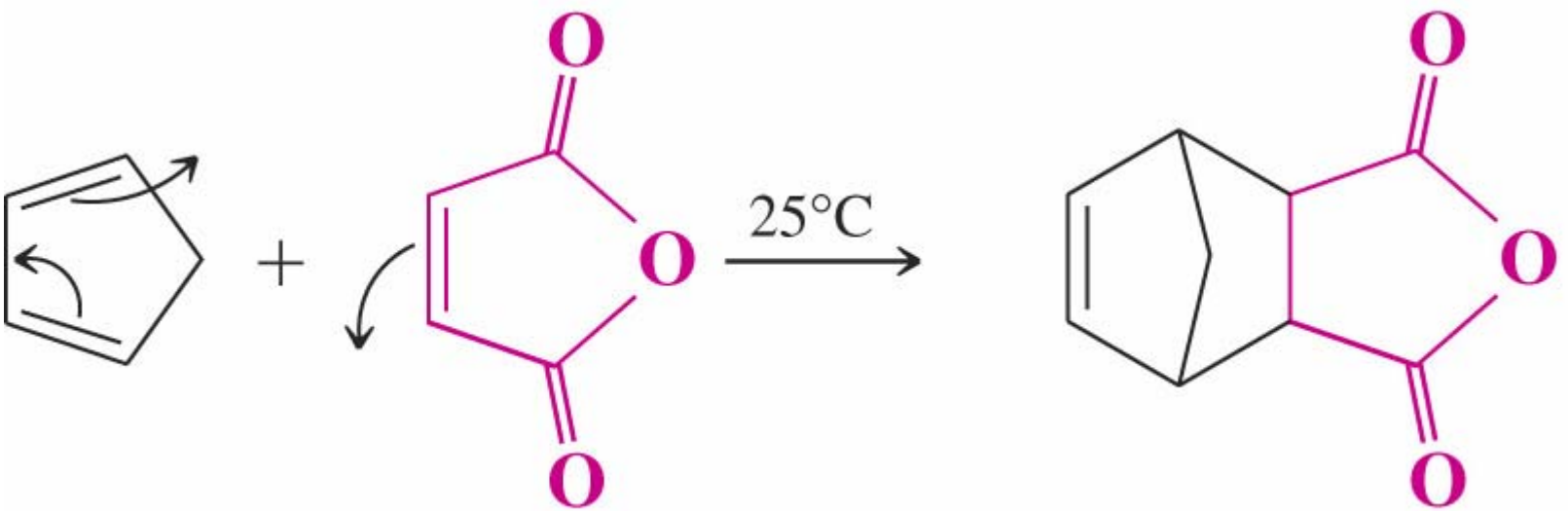


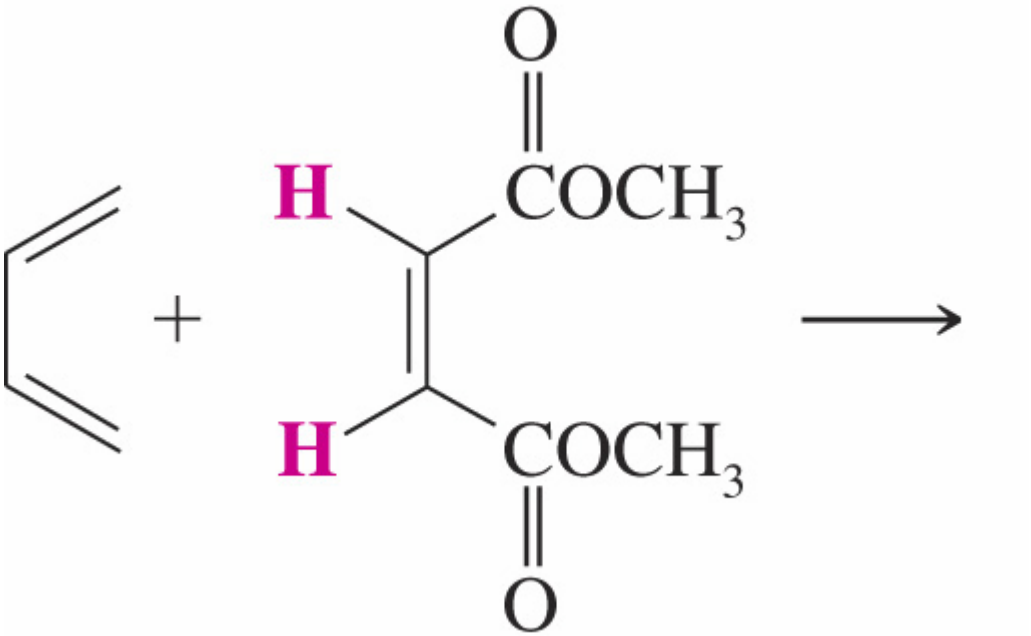




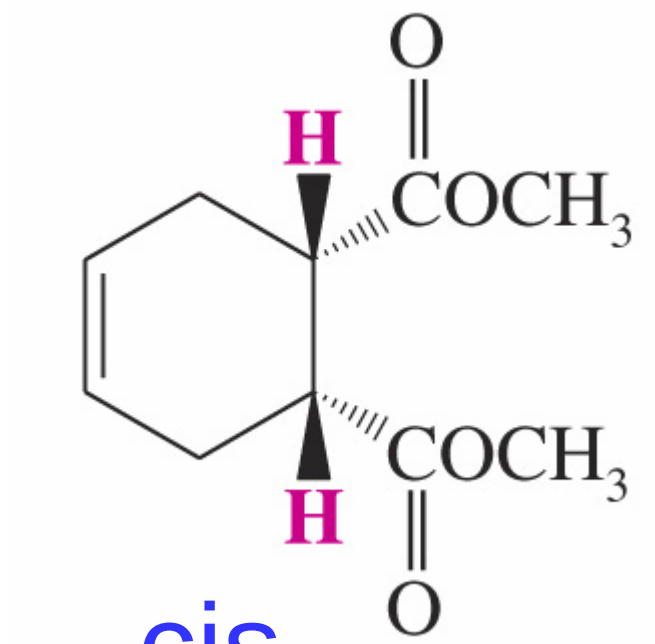
2,3-Dimethyl-1,3-butadiene **Propenal**



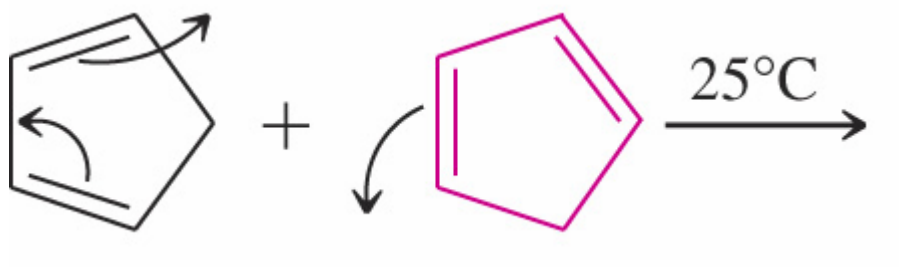


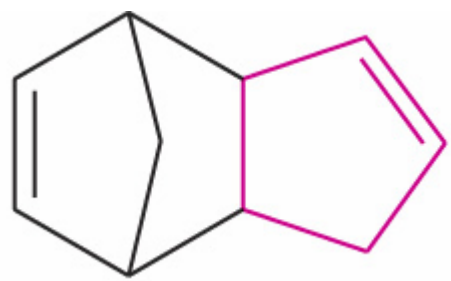


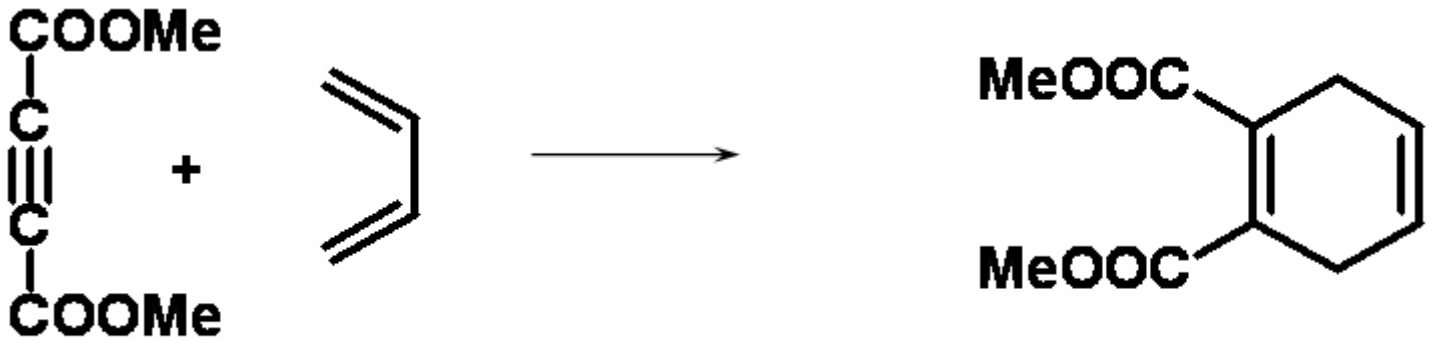
cis



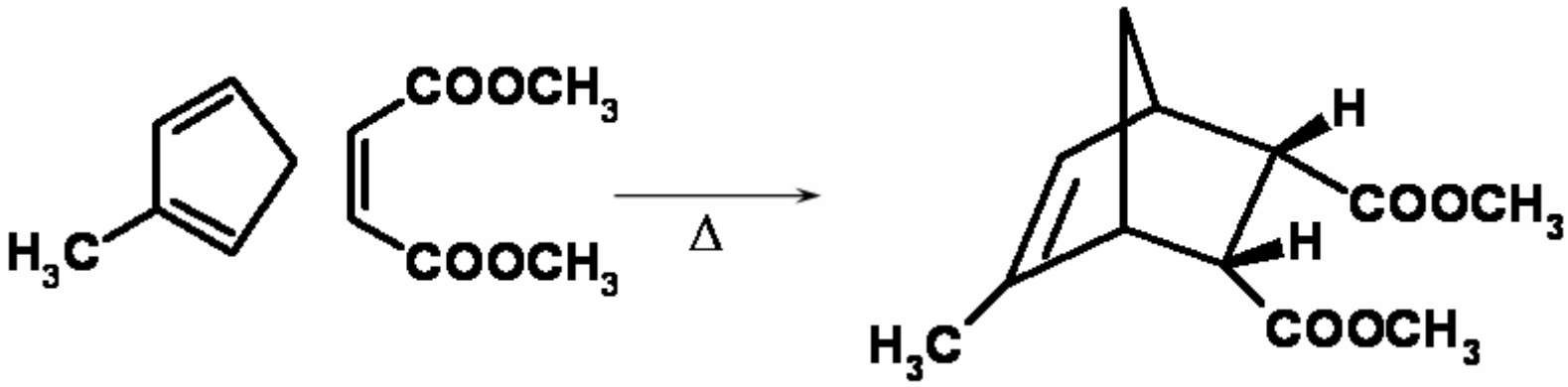
cis

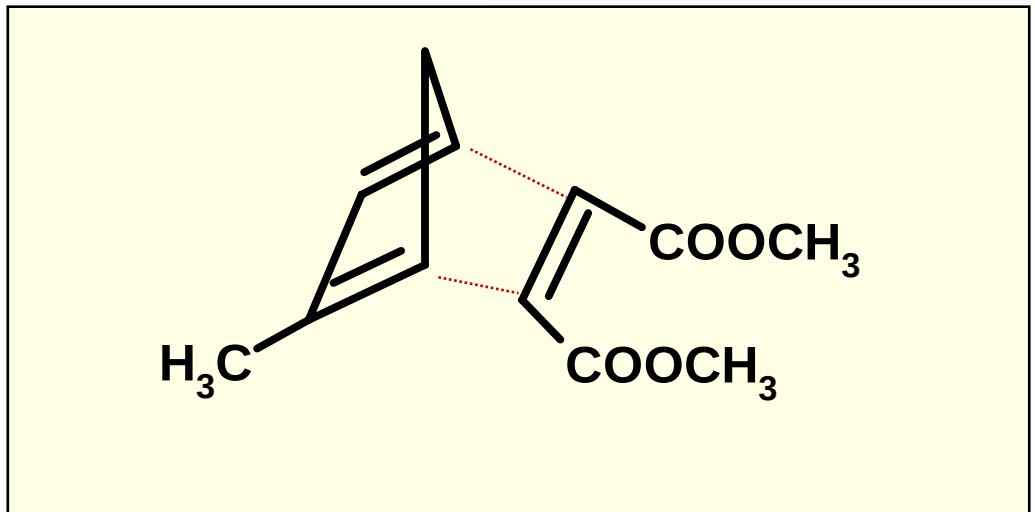






If the dienophile is an alkyne a cyclohexadiene is formed.

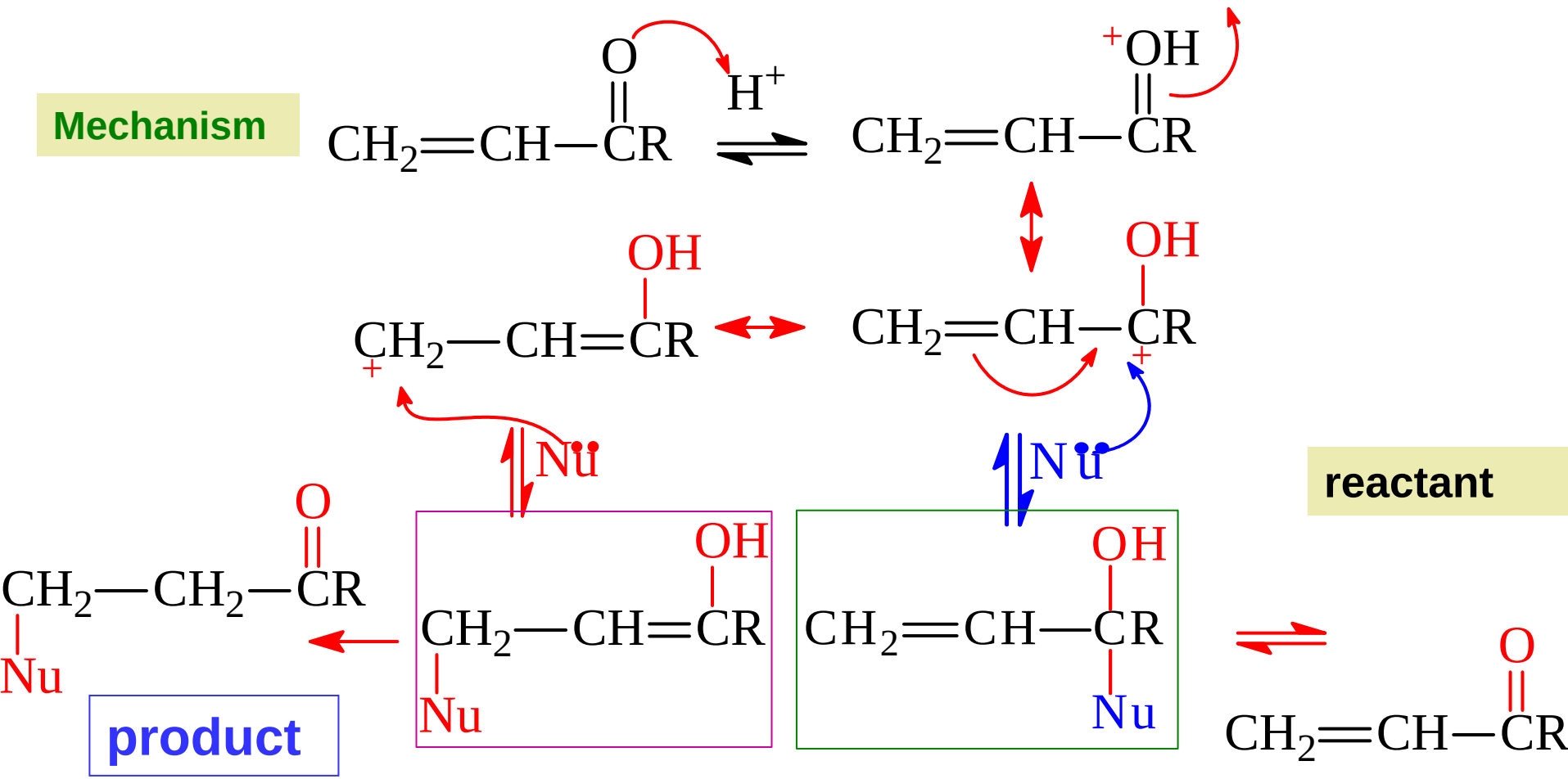




1- Electrophilic 1,4-Addition to α,β-Unsaturated Carbonyl Compounds

Weak Nu: catalyzed by H^+

Mechanism

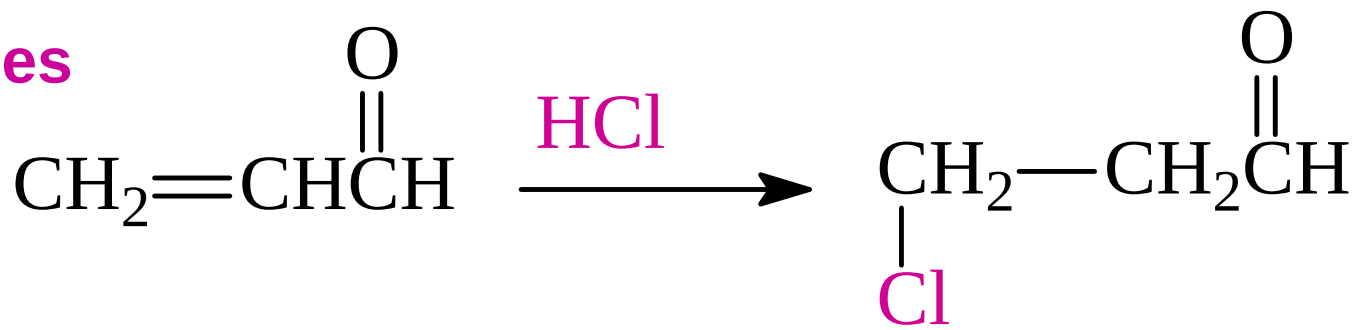


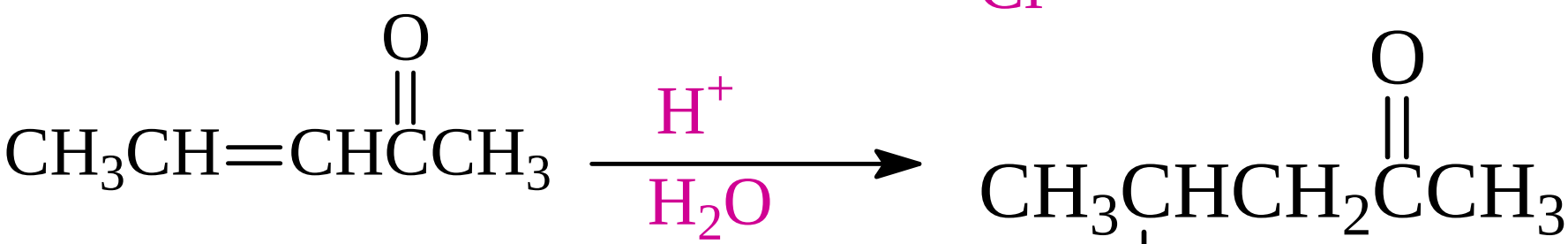
reactant

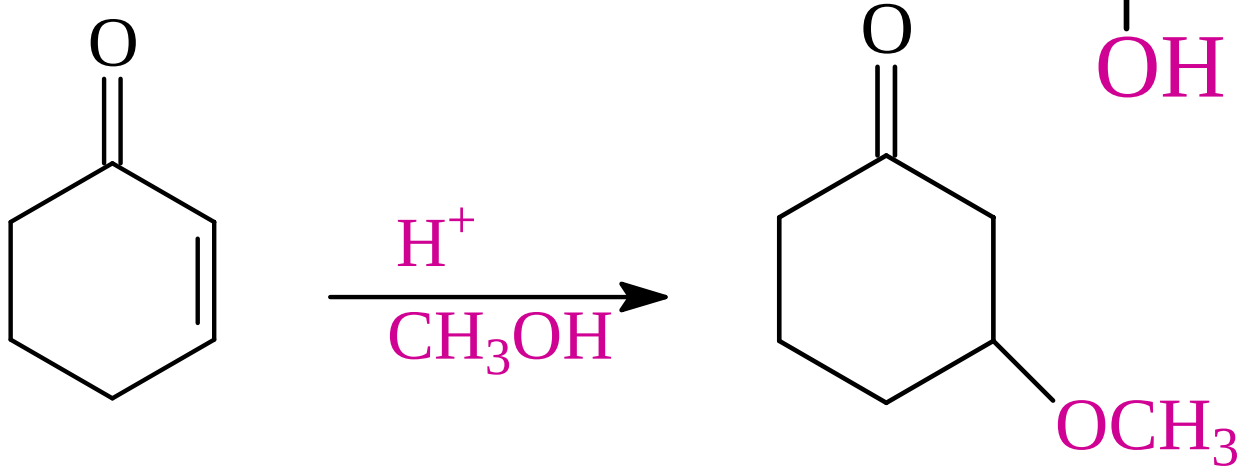
product

- **Under acid condition ➔ Nu: attacks the β-carbon**

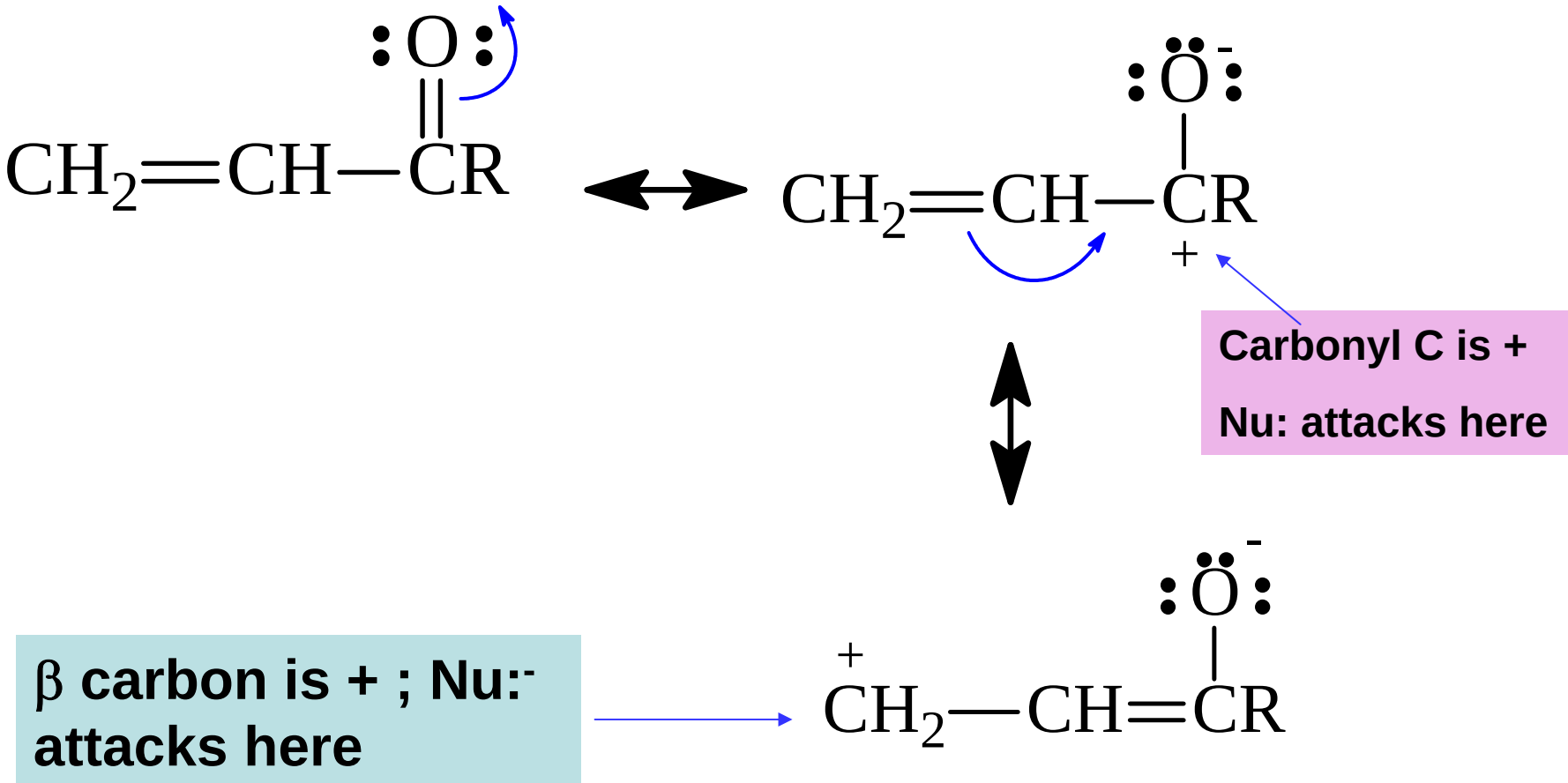
Examples



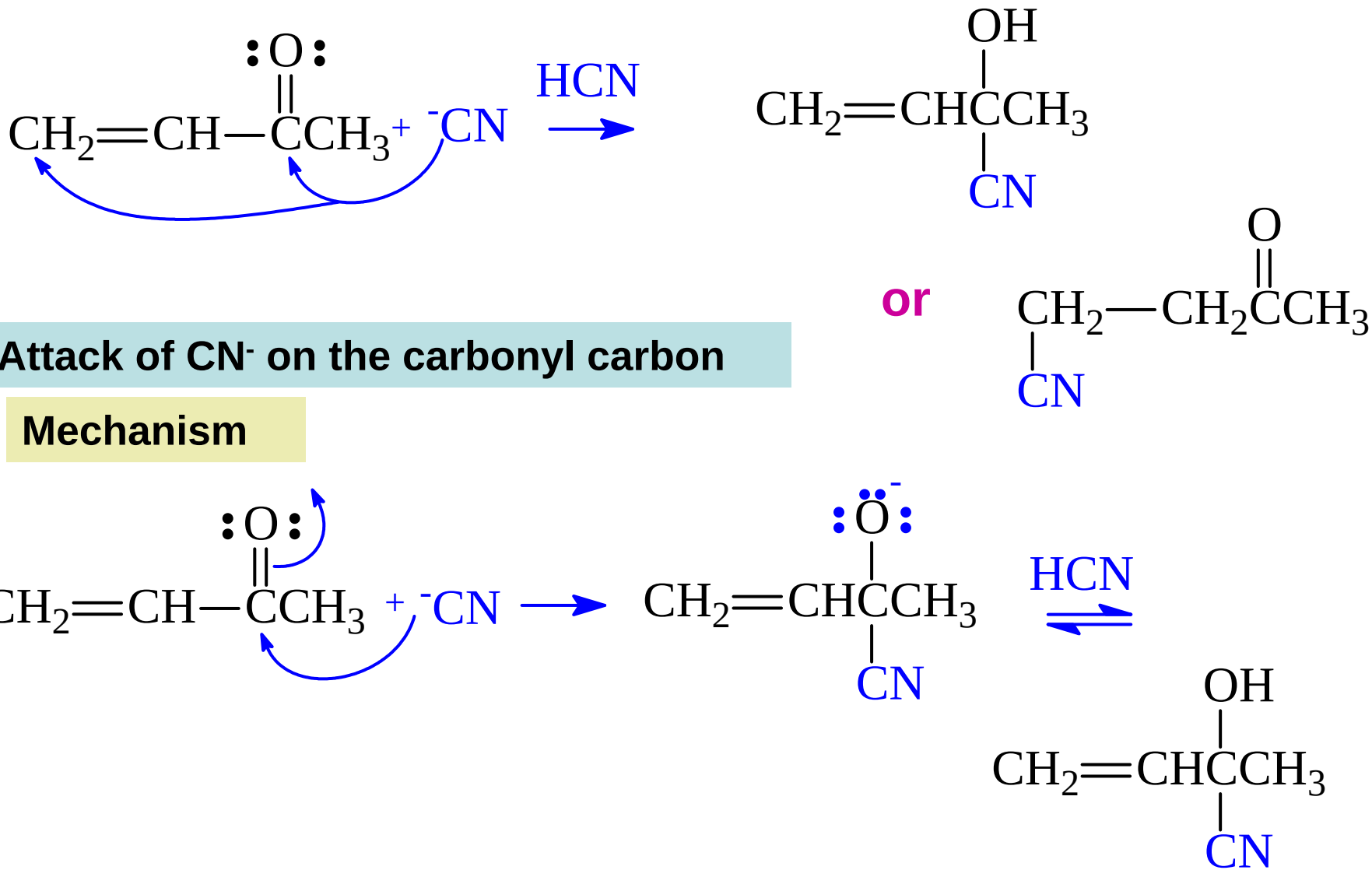




2- Nucleophilic Addition to α,β unsaturated carbonyl compounds

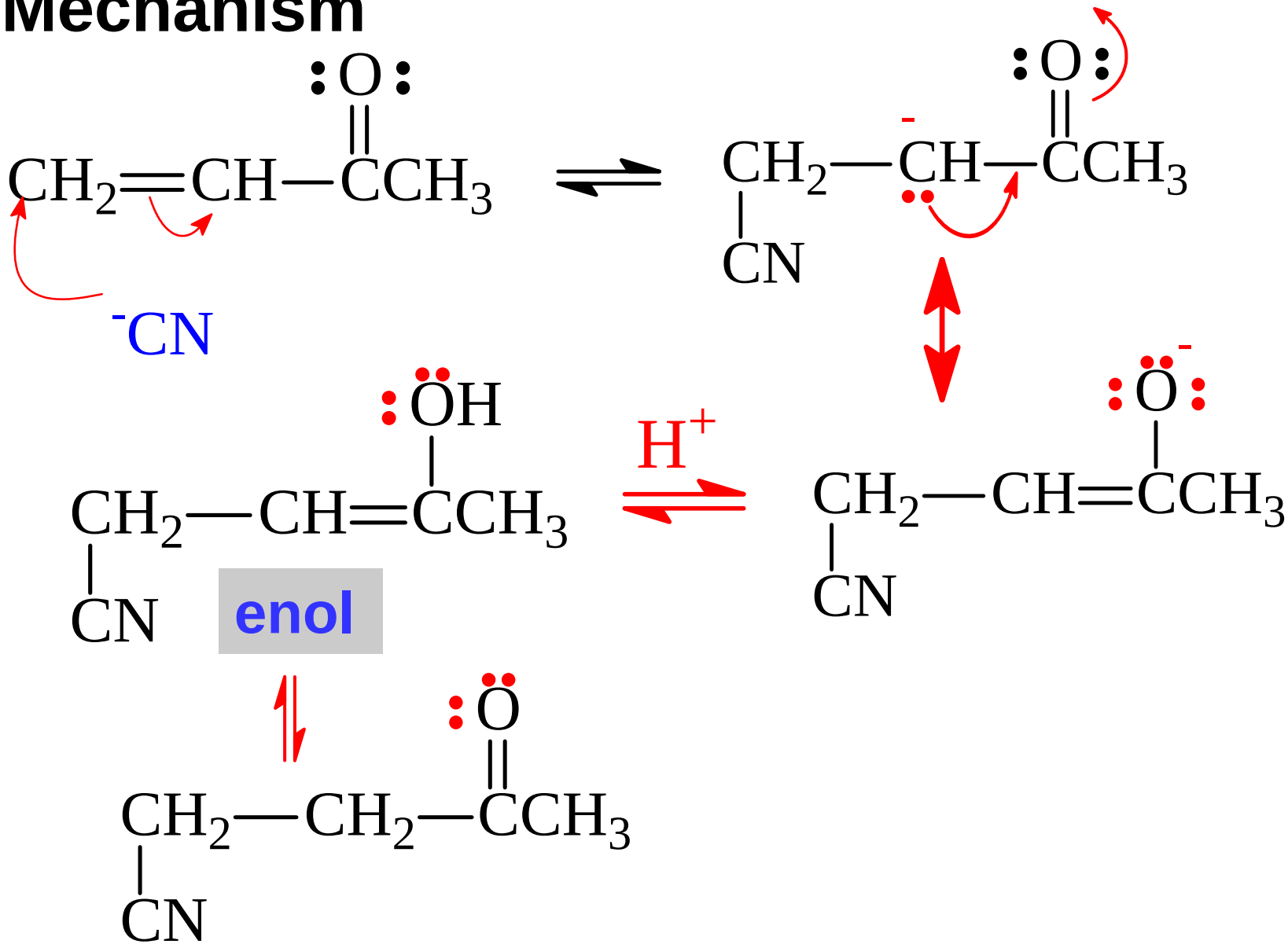


Example



Attack of CN^- on the β carbon -

Mechanism



Which of the two addition reactions occurs?

A mixture of products results but the major product depends on the nature of nucleophiles

1. **Stronger bases attack *1,2*** (at C=O).

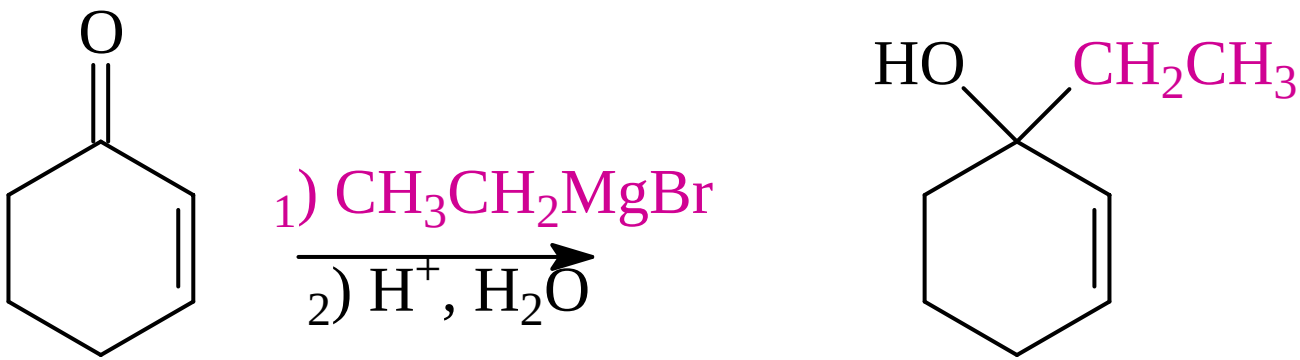
   eg. $LiAlH_4$, $NaBH_4$, RMgX

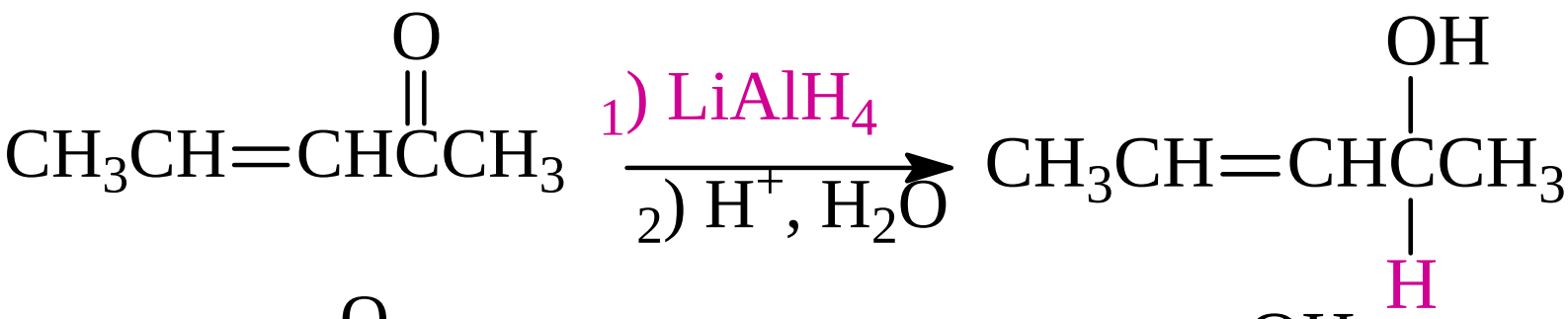
2. **Weaker bases attack *1,4*** (at C=C)

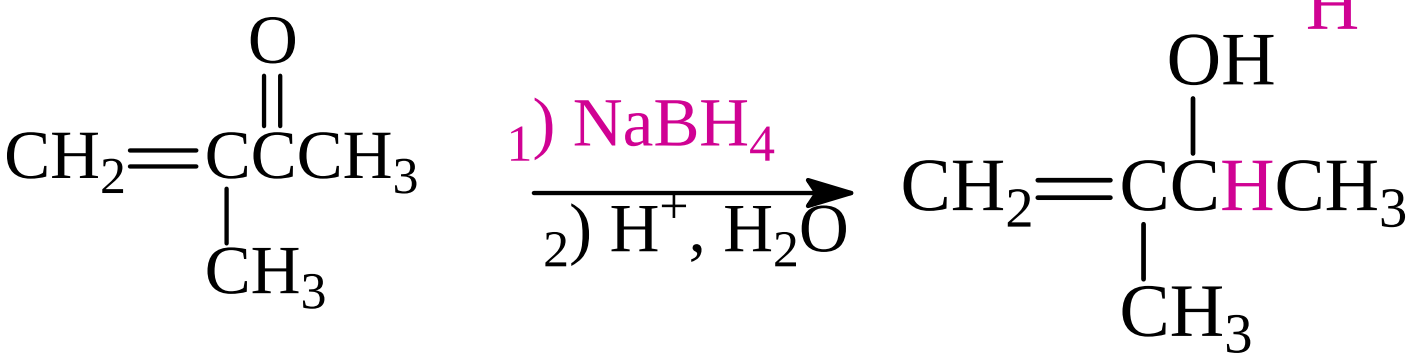
   e.g. CN^-, NH_3, RNH_2

3. **Cuprates (R_2CuLi) attack *1,4*** (at C=C).

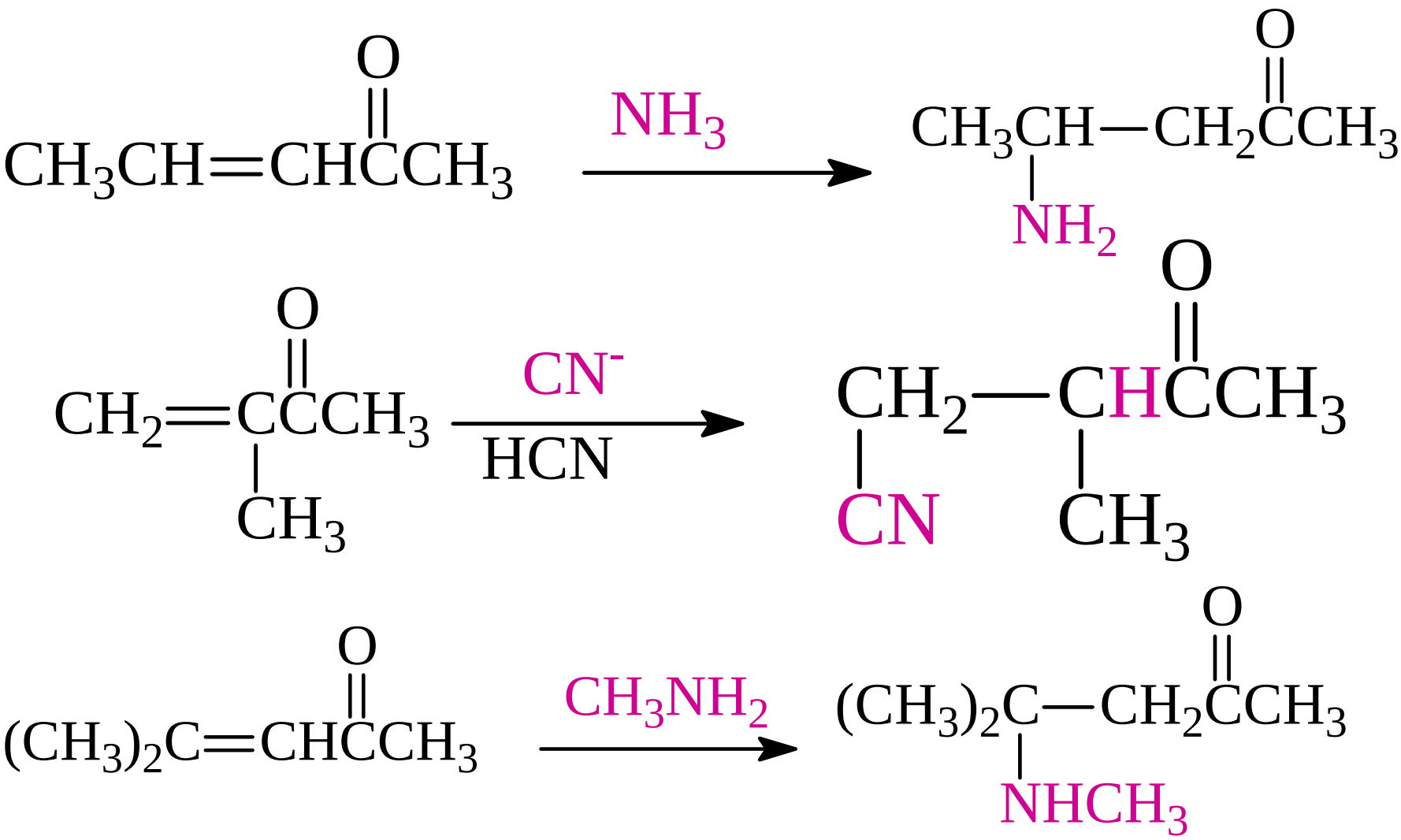
Stronger bases attack *1,2* (at C=O)



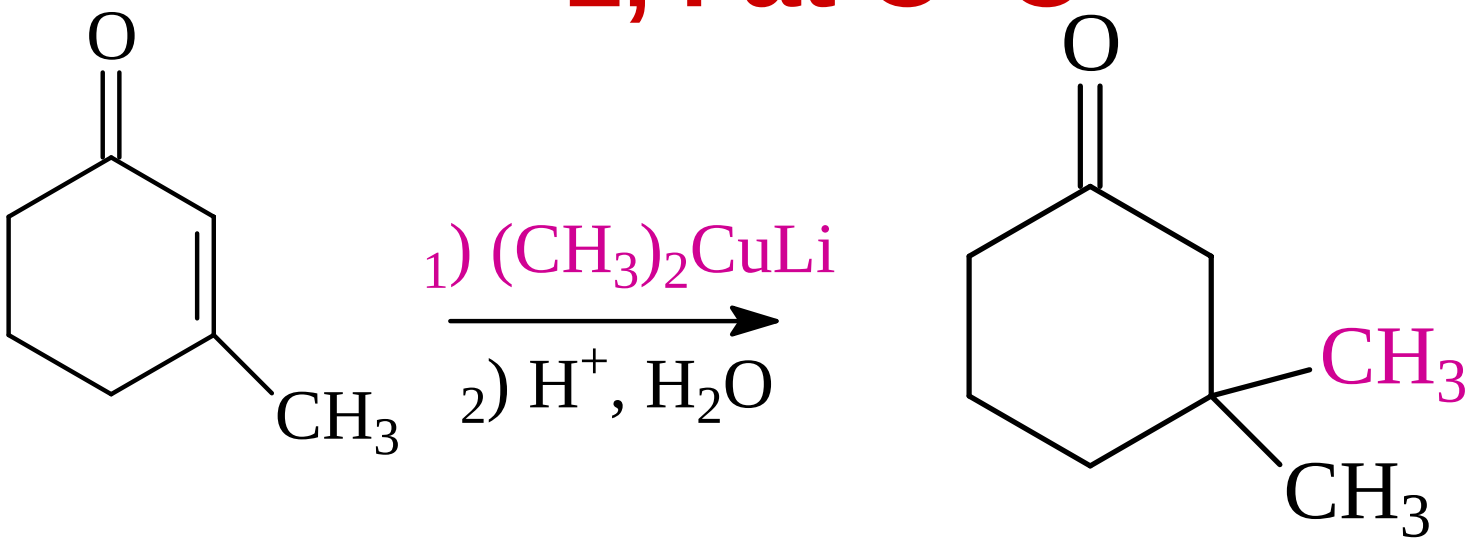


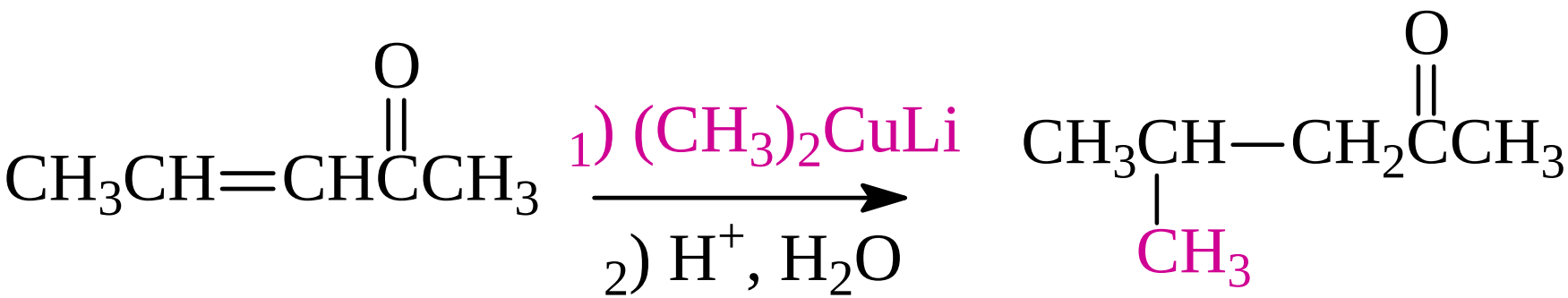


Weaker bases attack *1,4* (at C=C)



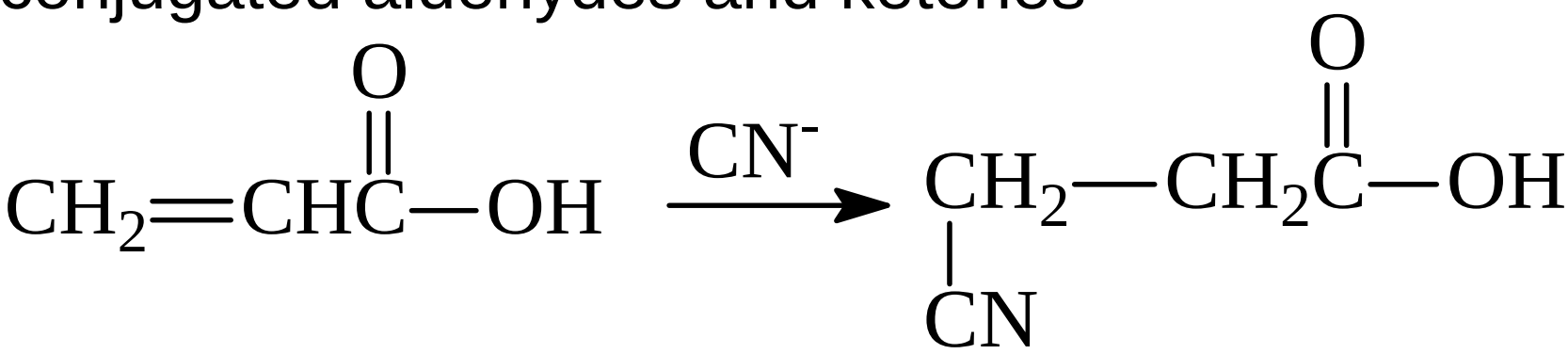
Lithium dialkylcuprates attack 1,4 at C=C

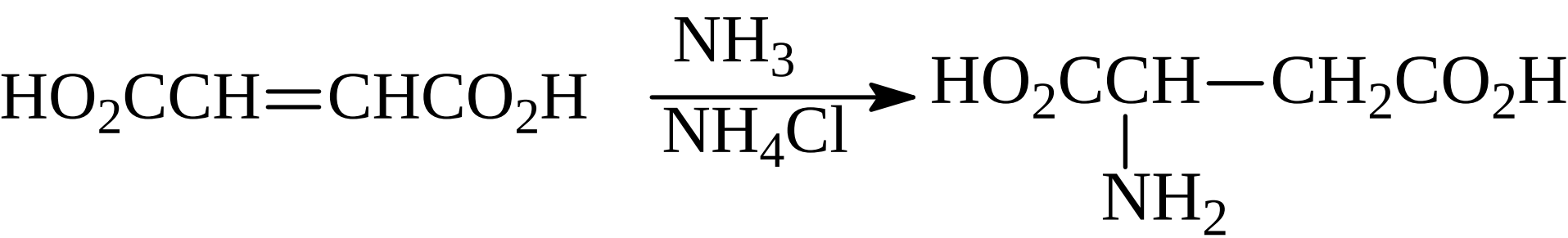




α,β- Unsaturated carboxylic acid

- A conjugated carboxylic acid behaves like conjugated aldehydes and ketones





Examples