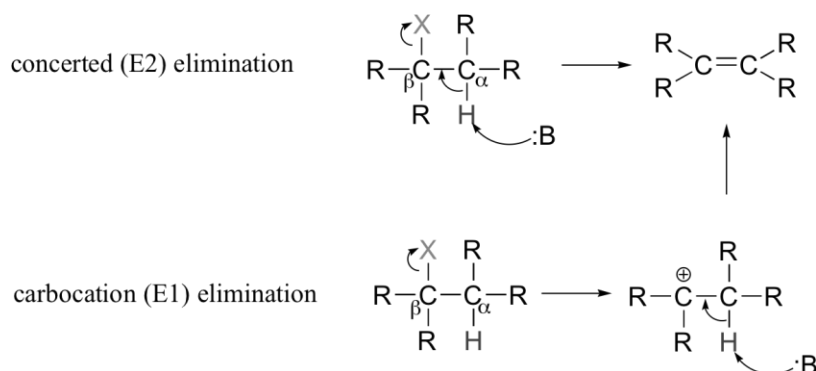


E₁ and E₂ reactions – kinetics, order of reactivity of alkyl halides, rearrangement of carbocations, Saytzeff's orientation and evidences. E₁ versus E₂ reactions, Factors affecting E₁ and E₂ reactions. Ozonolysis, electrophilic addition reactions of alkenes, Markownikoff's orientation, free radical addition reactions of alkenes, Anti Markownikoff's orientation. Stability of conjugated dienes, Diel-Alder, electrophilic addition, free radical addition reactions of conjugated dienes, allylic rearrangement

❖ Elimination reaction

- Elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in either a one or two-step mechanism.
- The one-step mechanism is known as the E₂ reaction, and the two-step mechanism is known as the E₁ reaction.
- In most organic elimination reactions, at least one hydrogen is lost to form the double bond: the unsaturation of the molecule increases. It is also possible that a molecule undergoes reductive elimination, by which the valence of an atom in the molecule decreases by two, though this is more common in inorganic chemistry.
- There are three fundamental events in these elimination reactions:
 - (i) removal of a proton
 - (ii) formation of the CC π bond
 - (iii) breaking of the bond to the leaving group

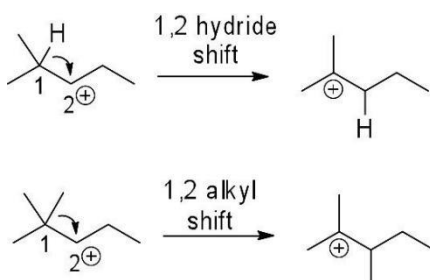


Characteristics of E₁ reaction

1. Unimolecular reaction
2. Two step reaction
3. Carbocation intermediate formed.
4. Reactivity order of RX is $3^\circ > 2^\circ > 1^\circ$
5. No stereospecific.
6. Follow zaitsev rule.
7. Polar protic solvent good because stabilized ionic intermediate.
8. Rate of reaction increases when concentration of substrate increases.
9. Rearrangement may take place.

Characteristics of E₂ reaction

1. Bimolecular reaction.
2. Single step reaction.
3. Hydrogen removes from beta carbon.
4. Trans elimination because low energy consumption.
5. Anti periplanar attack.
6. Polar aprotic solvent best.
7. Phenyl group influence elimination because product alkene further stabilised by resonance.
8. Reactivity order $3^\circ > 2^\circ > 1^\circ$. No steric effect.
9. Strong nucleophile influence elimination.
10. No intermediate formed.

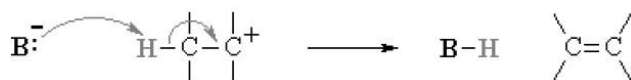


❖ E₁ mechanism

- E₁ indicates a elimination, unimolecular reaction, where rate = k [R-LG]. (R-LG = Substrate)



loss of the leaving group, LG, to generate a carbocation intermediate, then



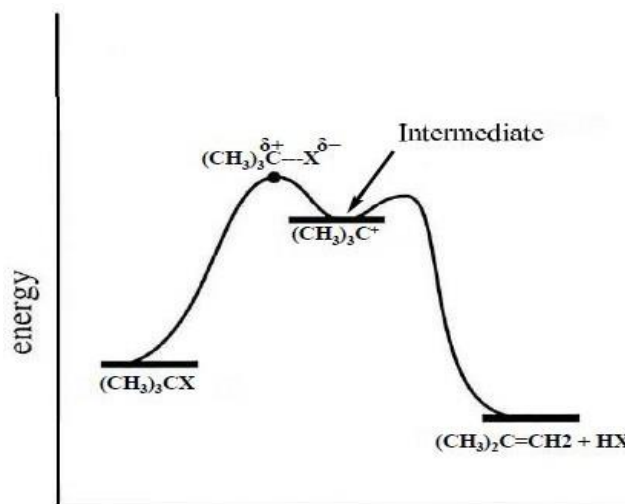
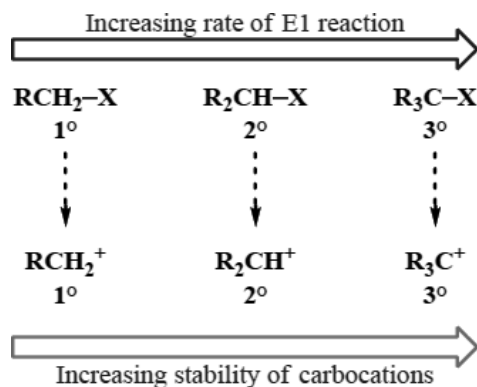
loss of a proton, H⁺, from the carbocation to form the π-bond

• Reaction influence the reaction pathway:

- E₁ mechanistic pathway is most common with:
 - Good leaving groups
 - Stable carbocations
 - Weak bases.
- E₁ Reactions is Non-stereospecific- follows **Zaitsev (Saytseff) Rule**
- Does NOT occur with **primary alkyl halides** (leaving groups)

(i) Effect of R-

- **Reactivity order:** (CH₃)₃C- > (CH₃)₂CH- > CH₃CH₂- > CH₃-
- In an E₁ reaction, the rate determining step is the loss of the leaving group to form the intermediate carbocation. The more stable the carbocation is, the easier it is to form, and the faster the E₁ reaction.
- The rate of an E₁ reaction increases as the number of R groups on the carbon with the leaving group increases.



Energy Profile for an E₁ Reaction

(ii) Leaving Group (LG)

- The only event in the rate determining step of the E₁ is breaking the C-LG bond. Therefore, there is a very strong dependence on the nature of the leaving group, the better the leaving group, the faster the E₁ reaction will be.
- In the acid catalysed reactions of alcohols, the -OH is protonated first to give an oxonium ion, providing the much better leaving group, a water molecule.

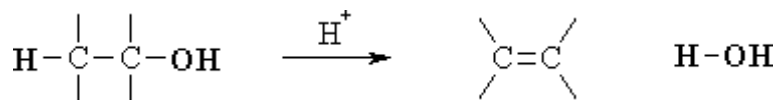
(iii) Base (B)

- Since the base is not involved in the rate determining step, the nature of the base is unimportant in an E₁ reaction.
- Favored by weaker bases such as H₂O and ROH.

(iv) Type of Solvent

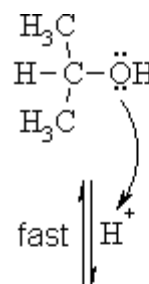
- Favored by polar protic solvents, which can stabilize the ionic intermediates.

• **E₁ Mechanism for Alcohols**



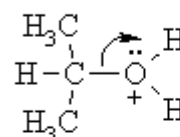
Step 1:

An acid/base reaction. Protonation of the alcoholic oxygen to make a better leaving group. This step is very fast and reversible. The lone pairs on the oxygen make it a Lewis base.



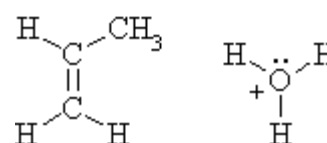
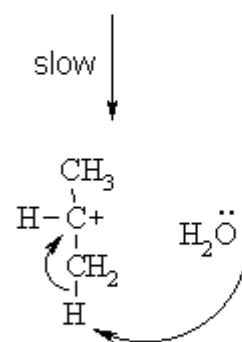
Step 2:

Cleavage of the C-O bond allows the loss of the good leaving group, a neutral water molecule, to give a carbocation intermediate. This is the rate determining step (bond breaking is endothermic)

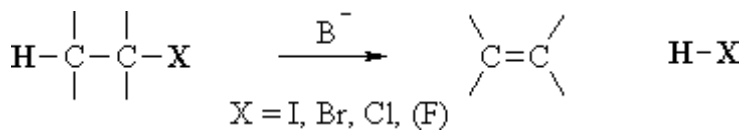


Step 3:

An acid/base reaction. Deprotonation by a base (a water molecule) from a C atom adjacent to the carbocation center leads to the creation of the C=C

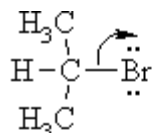


• **E₁ Mechanism for Alkyl Halides**

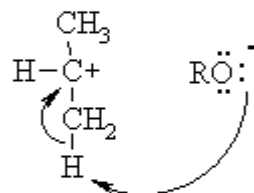


Step 1:

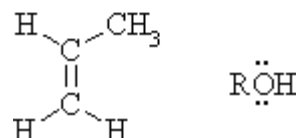
Cleavage of the polarised C-X bond allows the loss of the good leaving group, a halide ion, to give a carbocation intermediate. This is the rate determining step (bond breaking is endothermic)



slow



fast

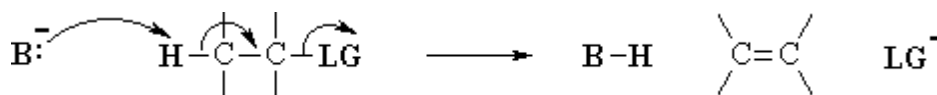


Step 2:

An acid/base reaction. Deprotonation by a base (here an alkoxide ion) from a C atom adjacent to the carbocation center leads to the creation of the C=C

❖ E₂ mechanism

- E₂ indicates an elimination, bimolecular reaction, where rate = k [B][R-LG].
- This implies that the rate determining step involves an interaction between these two species, the **base B**, and the organic **substrate**, R-LG



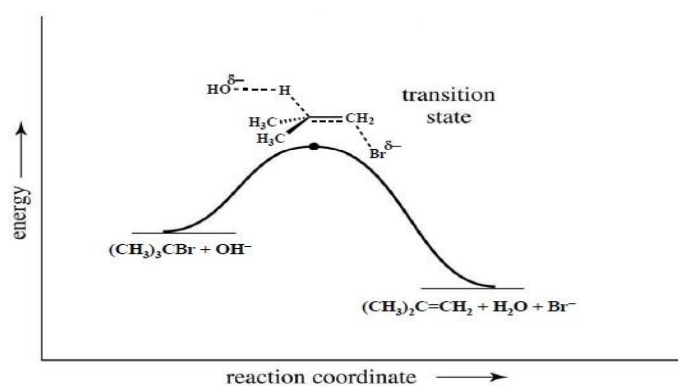
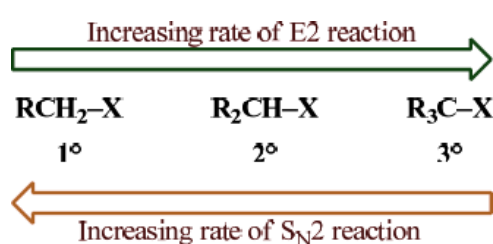
Removal of the proton, H⁺, by the base, loss of the leaving group, LG, and formation of the π-bond

• Reaction influence the reaction pathway:

- **Kinetics** – Second order
- **Mechanism** – Single step
- Stereospecific (Anti-periplanar geometry preferred, Syn-periplanar geometry possible)
- Concerted - all bonds form and break at same time.
- Bimolecular - rate depends on concentration of both base and substrate
- Favoured by strong bases.
- Favoured by polar aprotic solvents.
- Better leaving group leads to faster reaction rates.
- **Identity of R group** – More substituted halides react faster Rate: R₃CX > R₂CHX > RCH₂X

(i) Effects of R-

- Reactivity order: (CH₃)₃C- > (CH₃)₂CH- > CH₃CH₂- > CH₃-
- In an **E₂ reaction**, the reaction transforms **2 sp³ C atoms** into **sp² C atoms**. This moves the substituents further apart decreasing any steric interactions.
- So more highly substituted systems undergo **E₂ eliminations** more rapidly. This is the same reactivity trend as seen in **E₁ reactions**.
- As the number of **R groups** on the carbon with the leaving group increases, the rate of the **E₂ reaction** increases.



Energy Profile for an E₂ Reaction

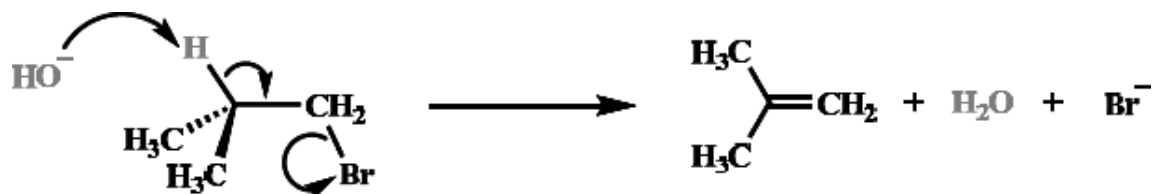
(ii) Leaving Group (LG)

- The **C-LG bond** is broken during the rate determining step, so the rate does depend on the nature of the leaving group.
- However, if a leaving group is too good, then an E₁ reaction may result.
- Rate of reaction follows the order Rate of reaction follows the order, **R-I > R-Br > R-Cl > R-F**

(iii) Base (B)

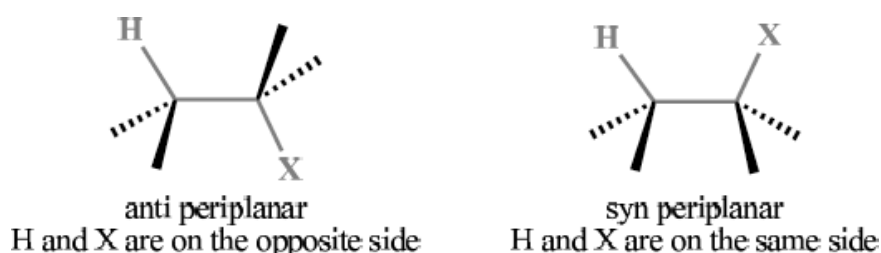
- Stronger bases favor the reaction. Since the base is involved in the rate determining step, the nature of the base is very important in an **E₂ reaction**.
- More reactive bases will favor an **E₂ reaction**.

• E₂ Mechanism

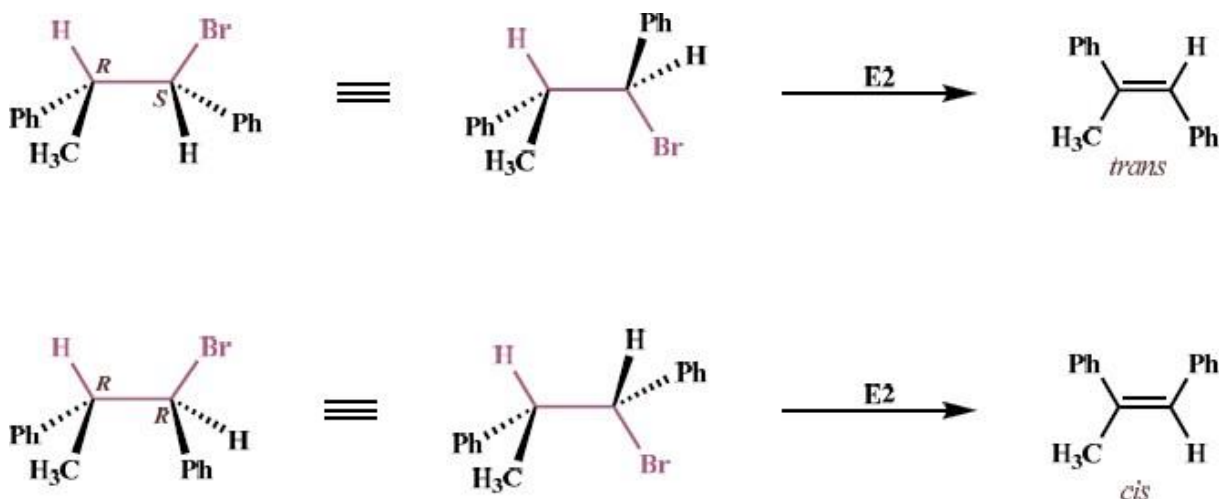


• Stereochemistry of the E₂ Reaction

- The transition state of an E₂ reaction consists of four atoms from the substrate (one hydrogen atom, two carbon atoms, and the leaving group, X) aligned in a plane. There are two ways for the C—H and C—X bonds to be coplanar.



- **E₂ elimination** occurs most often in the anti periplanar geometry. This arrangement allows the molecule to react in the lower energy staggered conformation, and allows the incoming base and leaving group to be further away from each other.
- The anti periplanar geometry also allows direct interaction between the bonding electrons of C — H bond and the antibonding orbital of the C — X bond.
- Diastereomeric starting compounds yield diastereomeric products after an **E₂ reaction**.



❖ Rearrangement of Carbocations

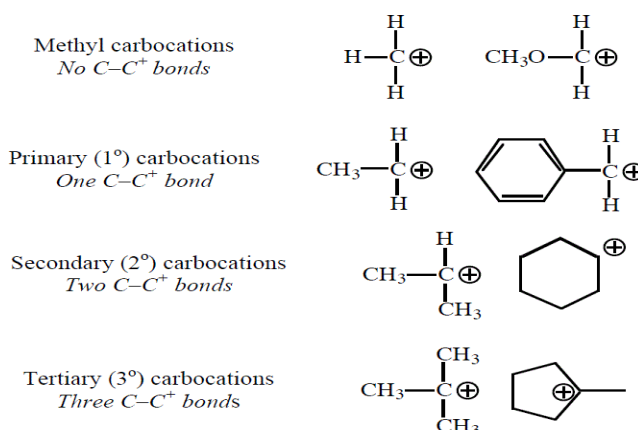
- A carbocation is molecule in which a carbon atom bears three bonds and a positive charge. Carbocations are generally unstable because they do not have eight electrons to satisfy the octet rule. It generate through heterolysis fusion.



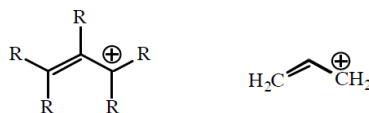
- All carbocations were called carbonium ions. Some carbocations may have two or more positive charges, on the same carbon atom or on different atoms; such as the ethylene dication $\text{C}_2\text{H}_4^{2+}$.
- The charged carbon atom in a carbocation is a "sextet", i.e. it has only six electrons in its outer valence shell instead of the eight valence electrons that ensures maximum stability (octet rule). Therefore, carbocations are often reactive, seeking to fill the octet of valence electrons as well as regain a neutral charge. One could reasonably assume a carbocation to have sp^3 hybridization with an empty sp^3 orbital giving positive charge. However, the reactivity of a carbocation more closely resembles sp^2 hybridization with a trigonal planar molecular geometry. An example is the methyl cation, CH_3^+ .

❖ Carbocation Classification:

- A primary carbocation is one in which there is one carbon group attached to the carbon bearing the positive charge. A secondary carbocation is one in which there are two carbons attached to the carbon bearing the positive charge. Likewise, a tertiary carbocation is one in which there are three carbons attached to the carbon bearing the positive charge.



- If the carbon bearing the positive charge is immediately adjacent to a carbon-carbon double bond, the carbocation is termed an allylic carbocation. The simplest case (all R =H) is called the allyl carbocation.



Generic allylic carbocation The allyl carbocation

- If the carbon bearing the positive charge is immediately adjacent to a benzene ring, the carbocation is termed a benzylic carbocation. The simplest case is called the benzyl carbocation.



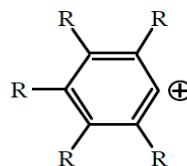
Generic benzylic carbocation The benzyl carbocation

- If the carbon bearing the positive charge is part of an alkene, the carbocation is termed a vinyl carbocation. The simplest case is called the vinyl carbocation. Note that the carbon bearing the positive charge has two attachments and thus adopts sp hybridization and linear geometry.

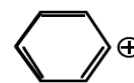


Generic vinylic carbocation The vinyl carbocation

- If the carbon bearing the positive charge is part of a benzene ring, the carbocation is termed an aryl carbocation. The simplest case is called the **phenyl carbocation**.



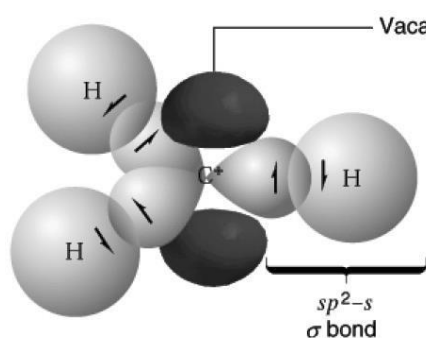
Generic aryl carbocation



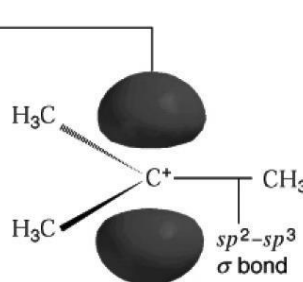
The phenyl carbocation

❖ The structure of carbocations

- The structure of carbocations is trigonal planar



(a)



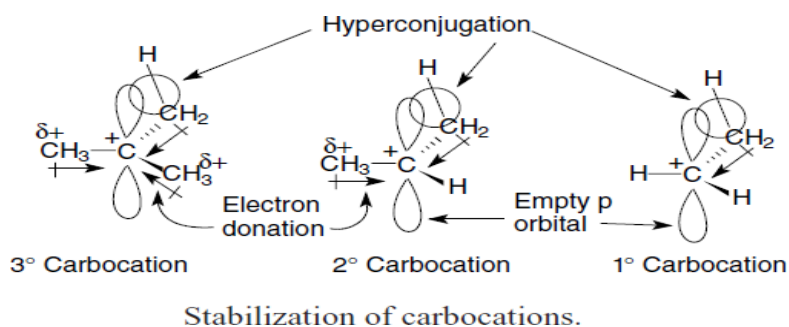
(b)

(a) A stylized orbital structure of the methyl cation. The bonds are sigma (σ) bonds formed by overlap of the carbon atom's three sp^2 orbitals with 1s orbitals of the hydrogen atoms. The **p orbital** is vacant.

(b) A dashed line-wedge representation of the tert-butyl cation. The bonds between carbon atoms are formed by overlap of sp^3 orbitals of the methyl group with sp^2 orbitals of the central carbon atom.

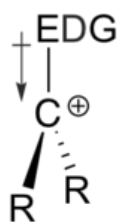
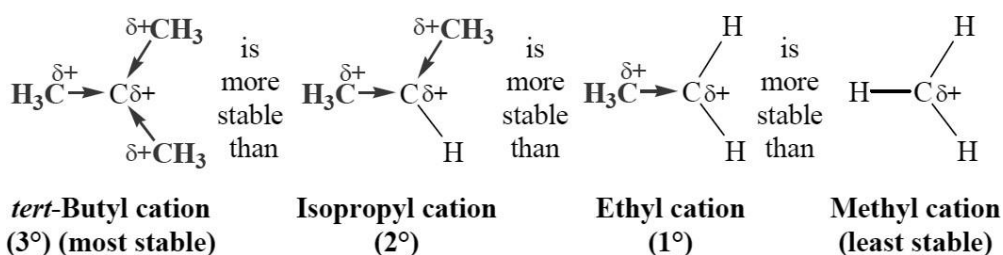
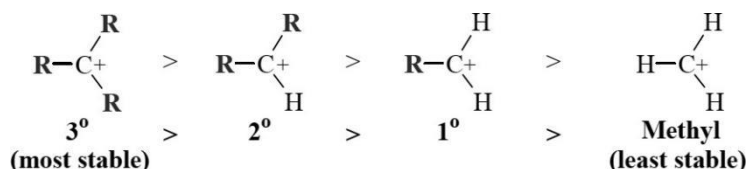
❖ Factors That Stabilize Carbocations

- Three main structural factors that help to stabilize carbocations.
 1. Neighboring carbon atoms.
 2. Neighboring carbon-carbon multiple bonds
 3. Neighboring atoms with lone pairs.
- ✓ The order of stability of alkyl-substituted carbocations to be $3^{\circ} > 2^{\circ} > 1^{\circ}$. One carbon atom of the carbocation is sp^2 hybridized and contains one un-hybridized p -orbital. This p -orbital contains no electrons. The sp^2 hybridized carbon atom has a formal positive charge.

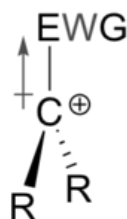


✓ The stability of carbocation through inductive effect:

- Ionic species are more stable if the charge can be delocalized (spread out) throughout the molecule. Alkyl groups (such as $-CH_3$) are electron donating. They donate electrons through a single, σ bond. The donation or withdrawal of electrons through a σ bond is called an *inductive effect*.
- By donating electrons to the electron-deficient sp^2 hybridized carbon atom, the positive charge is delocalized. The full positive charge on the sp^2 hybridized carbon atom is decreased somewhat and a small amount of positive charge is transferred to the alkyl groups, increasing the stability of the carbocation species.
- The **3^o carbocation** has three methyl groups that donate electrons. The **2^o carbocation** has two methyl groups that donate electrons. The **1^o carbocation** has only one methyl group that donates electrons. The greater the number of electron-donating groups, the greater the stability of the carbocation.



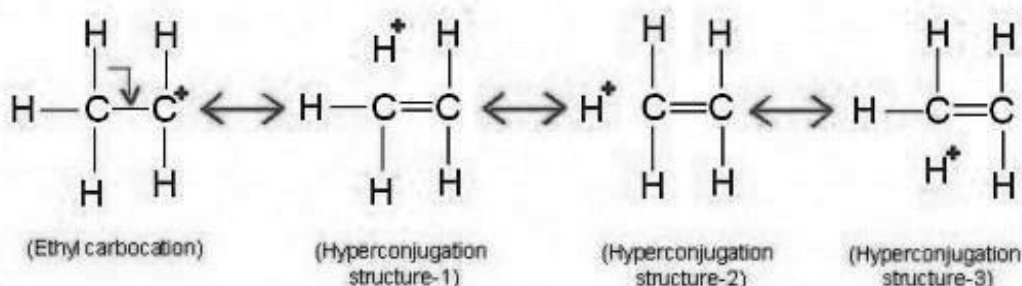
Electron Donating Group:
stabilizes a carbocation



Electron Withdrawing Group:
destabilizes a carbocation

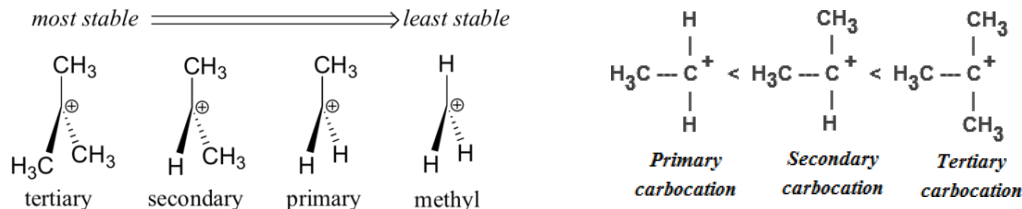
✓ The stability of carbocation through hyperconjugation:

- Hyper conjugation is a special type of resonance in which delocalization of electrons takes place through overlap between sigma bond orbital and pi-bond orbital or p-orbitals.
- The sp^3-s orbitals containing the bonding electrons in the C-H bond adjacent to the sp^2 hybridized carbon atom can overlap with the unhybridized, empty p -orbital on the sp^2 hybridized carbon atom and share the bonding electrons. Sharing electrons in this manner is called *hyperconjugation*.

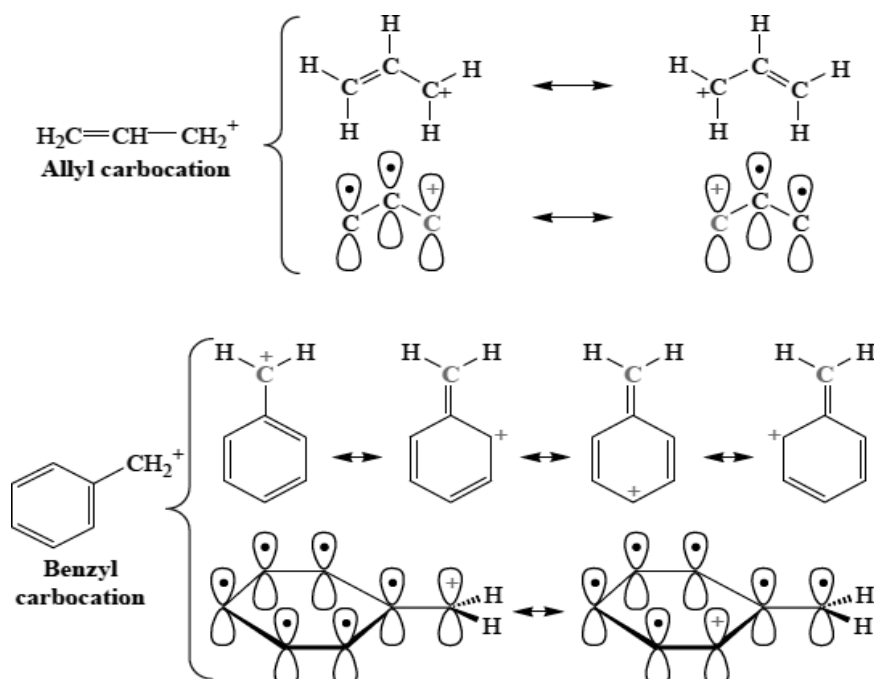


- By donating electrons to the electron-deficient sp^2 hybridized carbon atom, the positive charge is delocalized. The full positive charge on the sp^2 hybridized carbon atom is decreased somewhat and a small amount of positive charge is transferred to the alkyl groups, increasing the stability of the carbocation species.
- The 3^0 carbocation has nine opportunities (there are nine adjacent C-H bonds) for hyperconjugation; while 1^0 carbocation has only three opportunities (there are three adjacent C-H bonds) for hyperconjugation.

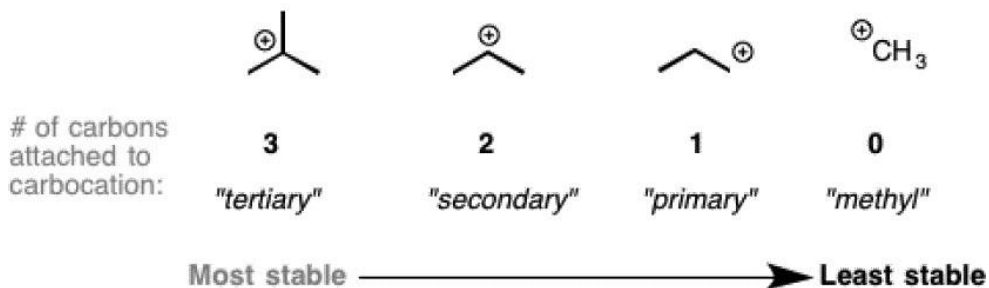
Primary < Secondary < Tertiary carbocation



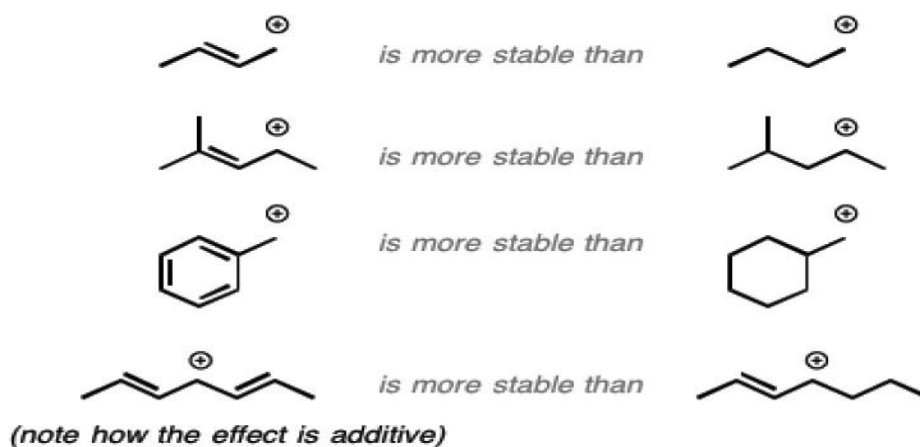
✓ The stability of allylic and benzylic carbocations: delocalization



1. Increasing substitution by carbon stabilizes carbocations



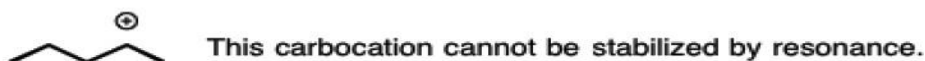
2. Adjacent carbon-carbon π bonds stabilize carbocations



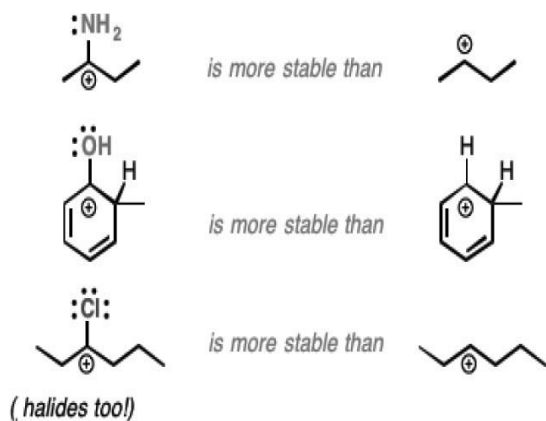
Why? Resonance.



Resonance allows for the positive charge to be distributed over multiple carbons, which is a stabilizing influence.

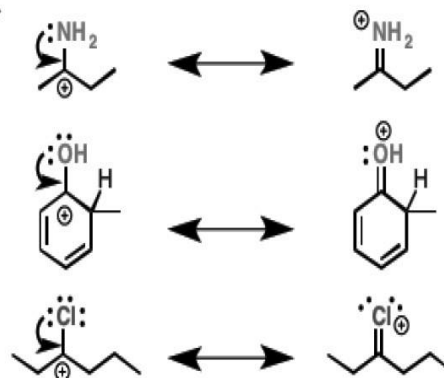


3. Adjacent atoms with lone pairs stabilize carbocations



Why? Resonance (again)

Donation of a lone pair by the atom allows for formation of a new π bond, which is a stabilizing influence



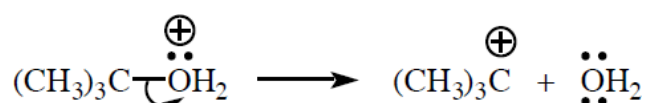
Even though Cl is fairly electronegative the lone pair can still form a π bond!

❖ Carbocation Formation

- ✓ Even though carbocations can be found in many organic reaction mechanisms, most carbocations are formed by one of only two basic mechanism steps: ionization of a carbon - leaving group bond or electrophilic addition to a π bond.

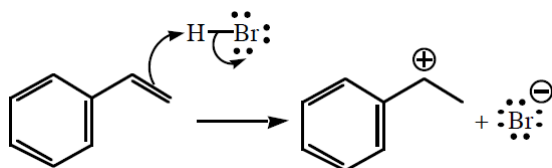
1. Ionization of a Carbon - Leaving Group Bond

- When a bond between a carbon atom and a leaving group ionizes, the leaving group accepts the pair of electrons that used to be shared in the covalent bond.
- This may leave the carbon atom with an open octet, resulting in a carbocation.
- The ionization is indicated with a curved arrow starting at the bond and pointing to the leaving group atom that accepts the electron pair.
- Better leaving groups or formation of a more stable carbocation result in lower activation energy and faster ionization.
- Carbocation formation by ionization of a leaving group occurs in many organic reactions such as the S_N1 and $E1$ mechanisms.



2. Electrophilic Addition to a π Bond

- When an electrophile attacks a π bond, the π electron pair may form a new σ bond to the electron-deficient atom of the electrophile. (Not all additions to π bonds involve electrophiles or carbocations.)
- The other π bond carbon no longer shares the π electron pair, resulting in a carbocation.
- Electrophilic addition to a π bond occurs in many reactions of alkenes, alkynes and benzene rings. Note every addition reaction forms a carbocation, for example, catalytic hydrogenation or ozonolysis.

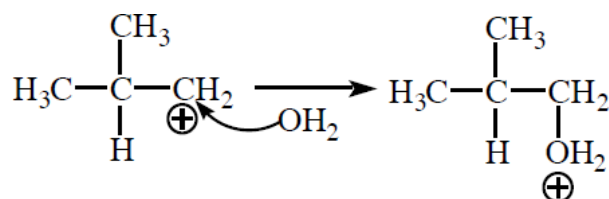


❖ Three Fates of a Carbocation

- Generally, carbocations are unstable due to their open octets and positive charges. Thus, their reactions will be strongly influenced by filling the octet of the carbon bearing the positive charge, or at least making this positive charge more stable.
- There are three common mechanism pathways (or fates) by which carbocations may achieve this stability. These fates are (a) capture a nucleophile; (b) loses a proton to form a π bond, and (c) rearrange.

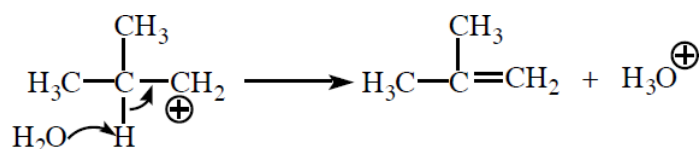
1. Capture a nucleophile

- The carbocation is electrophilic because it has a positive charge and (in most cases) a carbon atom with an open octet.
- The positive charge is neutralized when an electron pair is accepted and a new covalent bond is formed. By definition, a species that donates a pair of electrons to form a new covalent bond is a nucleophile. Because carbocations are very reactive, even weak nucleophiles such as water can be captured with ease.



2. Lose a proton to form a π bond

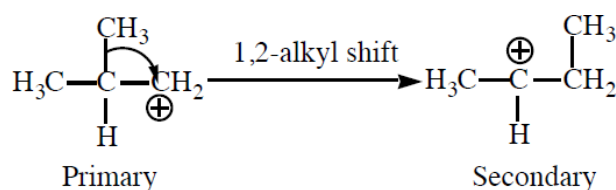
- ✓ Accepting an electron pair from an adjacent bond to a hydrogen atom neutralizes the positive charge or fills the open octet and forms a **new π bond**. (The carbocation carbon now has four bonds and a full octet, so its formal charge is zero.)
- ✓ The hydrogen atom must be removed by a base, but because carbocations are generally very reactive species and very strongly driven to dispose of the positive charge even a weak base such as water or iodide ion can accomplish this deprotonation.
- ✓ When carbocation deprotonation can lead to more than one product, the more stable product is major.



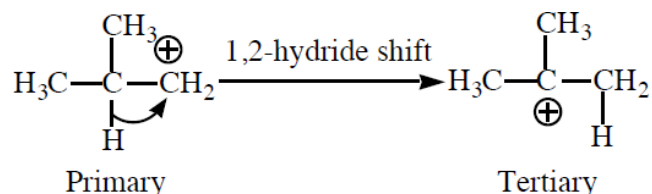
3. Rearrangement

- The bonding electrons of a carbocation may shift between adjacent atoms to form a more stable carbocation.
- For example, rearrangement will occur if a secondary carbocation can be formed from a primary carbocation because a secondary carbocation is more stable than the primary carbocation.
- There can be two types of rearrangements.

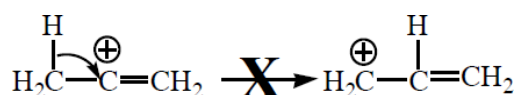
(i) Shift of an alkyl group is called a 1,2-alkyl shift.



(ii) Shift of a hydrogen atom is called a 1,2-hydride shift. Hydride ion = H^-



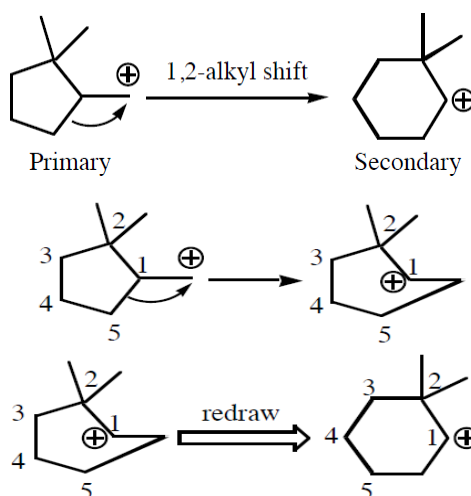
- Of these two examples, hydride shift leads to a tertiary carbocation whereas alkyl shift leads to a secondary carbocation. Because a tertiary carbocation is more stable than a secondary carbocation, the hydride shift is favored in preference to the alkyl shift.
- Any C-H or C-C bond adjacent to a carbocation may shift (including C-C bonds that are part of a ring), but only C-C and C-H bonds can migrate during carbocation rearrangement.
- **Vinyl carbocations** generally do not rearrange, even if they can become more stable. For example, the rearrangement shown below does not occur, even though a secondary carbocation would rearrange to become a more stable allylic carbocation (primary with resonance).



(This resistance to rearrangement is probably due to orbital alignment restrictions during the rearrangement transition state.)

❖ Rearrangement Causing a Change in Ring Size

- Rearrangement may lead to a change in ring size. For example



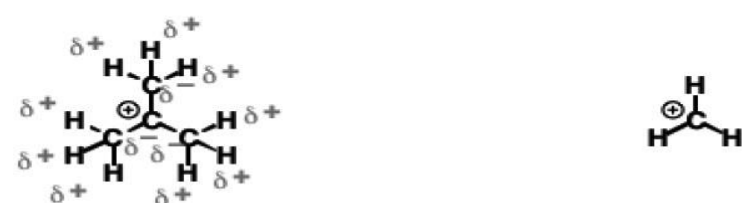
In this case, the C₁-C₅ bond shifts, taking a pair of electrons from C₁, leaving C₁ with an open octet and a positive formal charge. The former carbocation carbon gained an electron pair, so its formal charge becomes one unit more negative (+1 to zero). The five-membered ring has expanded to a six-membered ring.

❖ Three Factors that Destabilize Carbocations

1. The effect of substitution

Carbocations are destabilized as alkyl groups are replaced by hydrogen

The "inductive effect" explanation



Electronegativity of C = 2.5
Electronegativity of H = 2.2

Carbons are slightly electron rich and can donate these electrons to the carbocation

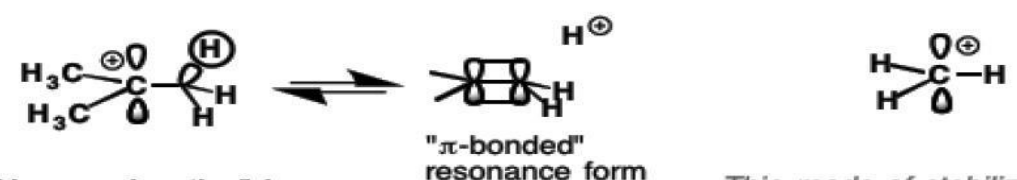
Each alkyl group added to a carbocation will increase stability

Hydrogens do not have excess electron density to donate

Adjacent hydrogens do not stabilize carbocations

The "hyperconjugation" explanation for carbocation stabilization

π -bond / "no bond" resonance



" π -bonded" resonance form

"Hyperconjugation" is a stabilizing interaction between the orbitals of the C-H bond and the empty p-orbital of the carbocation

This mode of stabilization is not possible when H is the substituent

2. Neighboring electron withdrawing groups (without lone pairs)

Carbocations are destabilized by neighboring electron-withdrawing groups

H-C-H
⊕

vs.

EWG
⊕

Examples of electron withdrawing groups:

Two factors: 1) Contain an atom more electronegative than C
2) No atom with a lone pair is directly attached to the carbocation!

The key "destabilizing interaction" is two adjacent positive charges or partial positive charges.

EWG
⊕

e.g.

δ^- O δ^+ C R
⊕

δ^- O δ^+ N δ^+ C
⊕

δ^- F δ^+ C δ^- F
⊕

The whole basis of this is electronegativity: that is, inductive effects.

Note that resonance is *not* stabilizing in these instances because the resonance isomer would have an incomplete octet on an atom more electronegative than carbon.

6 e⁻ on C

↔ X ↔

6 e⁻ on O

Forbidden resonance form - the more electronegative atom must have a full octet

3. Hybridization

- The trend here is pretty simple: the stability of a carbocation decreases as it moves from sp^3 to sp^2 to sp .

Carbocations are destabilized as hybridization goes from $sp^3 \Rightarrow sp^2 \Rightarrow sp$

sp^3
most stable

>

sp^2

>

sp
least stable

Think of this as the *opposite* of the effect of hybridization on carbanions

most stable

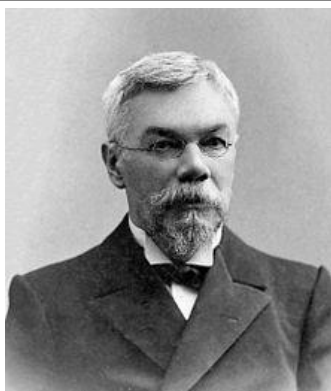
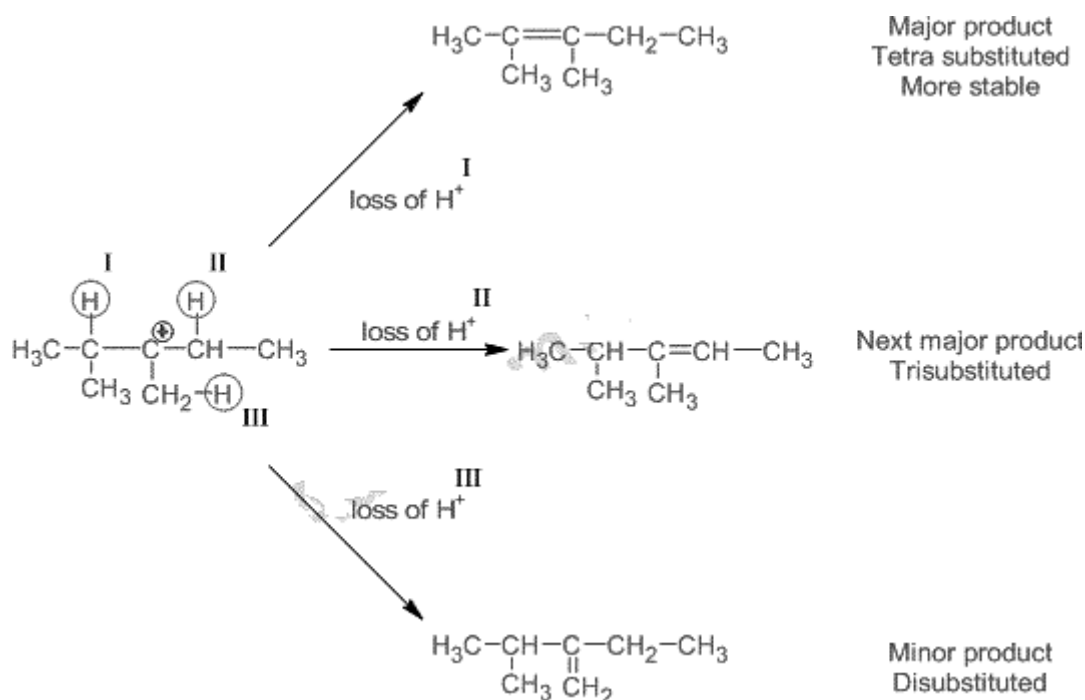
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>

least stable

❖ Saytzeffs Rule

- **Saytzeffs rule** (or Zaitsev's rule, Saytzev rule) is an empirical rule for predicting the favored alkene product(s) in elimination reactions.
- This reaction predicted by Russian chemist *Sir Alexander Zaitsev*.
- **Saytzeffs rule** states that when alternative exist hydrogen is preferentially eliminated from the carbon atom with fewer number of hydrogen atoms.
- **Saytzeff Rule** implies that base-induced **eliminations (E₂)** will lead predominantly to the olefin in which the double bond is more highly substituted, i.e. that the product distribution will be controlled by thermodynamics.



Sir Aleksander Mikhaylovich Zaitsev, also spelled as Saytzeff and Saytzev (2 July 1841 – 1 September 1910), was a Russian chemist from Kazan. He worked on organic compounds and proposed Zaitsev's rule, which predicts the product composition of an elimination reaction.

A neutron walks into a restaurant and orders a couple of sodas. As she is about to leave, she asks the waiter how much she owes. The waiter replies, "For you, No Charge!"

Teacher: Describe hydrogen

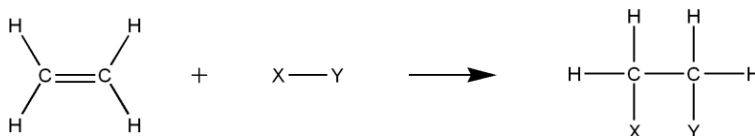
Student: It is a prostitute element

Teacher: Who taught you that?

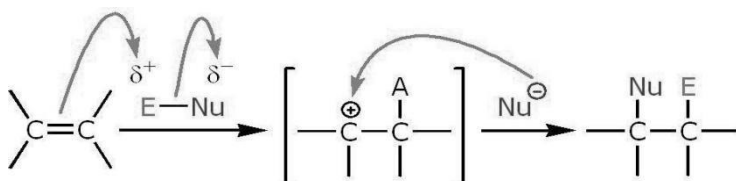
Student: You said it does not belong to a particular group and it reacts with almost all the elements in the periodic table.

❖ Electrophilic Addition Reactions of Alkenes

- Electrophilic addition reaction is an addition reaction where, in a chemical compound, a π bond is broken and two new σ bonds are formed.
- The substrate of an electrophilic addition reaction must have a double bond or triple bond.

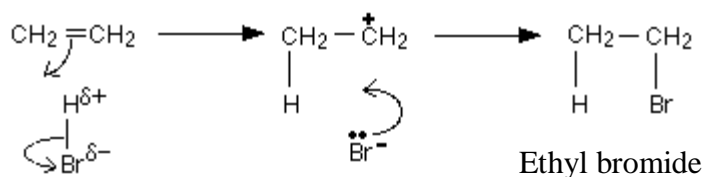


- Electrophilic addition to alkenes takes the following general form:

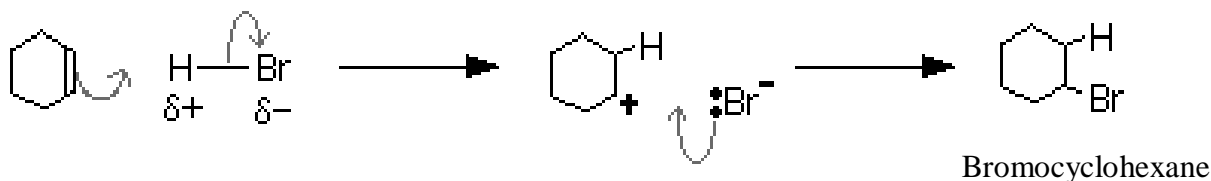


• Electrophilic addition reaction between symmetrical alkenes and the hydrogen halides

- *The reactions of electrophilic addition with ethene and HBr:*



- *The reactions of electrophilic addition with cyclohexene and HBr:*



- *Electrophilic addition reactions involving the other hydrogen halides*

- Hydrogen chloride and the other hydrogen halides add on in exactly the same way. For example, hydrogen chloride adds to ethene to make Chloroethane: $\text{CH}_2=\text{CH}_2 + \text{HCl} \longrightarrow \text{CH}_3\text{CH}_2\text{Cl}$

- The only difference is in how fast the reactions happen with the different hydrogen halides. The rate of reaction increases as you go from HF to HCl to HBr to HI.

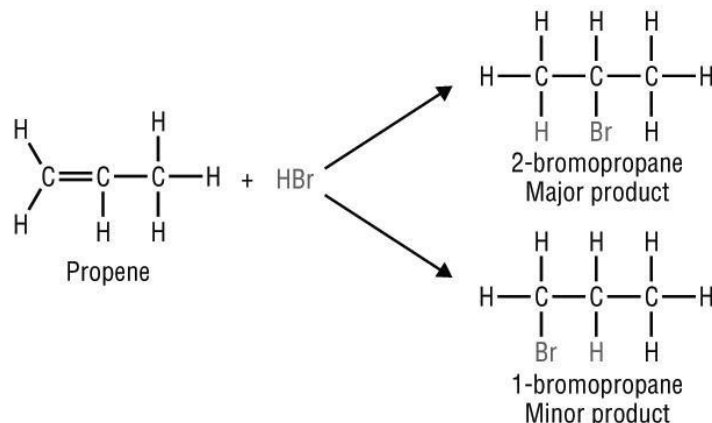
HF	slowest reaction
HCl	
HBr	
HI	fastest reaction

- The reason for this is that as the halogen atoms get bigger, the strength of the hydrogen-halogen bond falls. Bond strengths (measured in **kilojoules per mole**) are:

H-F	568
H-Cl	432
H-Br	366
H-I	298

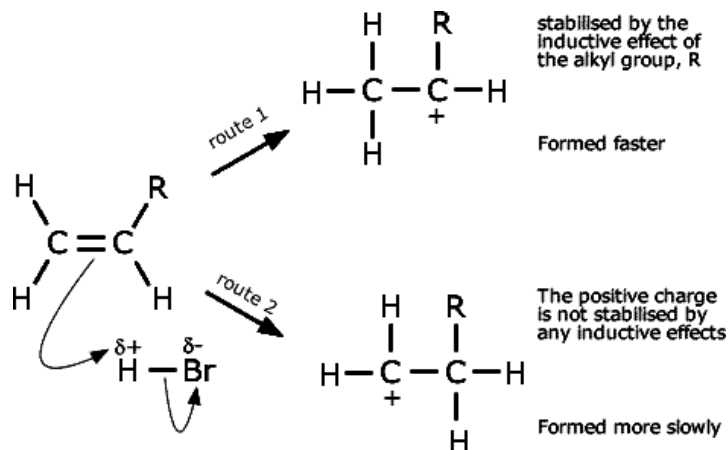
• Electrophilic addition reaction between unsymmetrical alkenes and the hydrogen halides

- The reactions of electrophilic addition with Propene and HBr:



- **Markownikoff's rule:**

- The rule states that with the addition of a protic acid HX to an asymmetric alkene, the acid hydrogen (H) becomes attached to the carbon with more hydrogen substituents, and the halide (X) group becomes attached to the carbon with more alkyl substituents. Alternatively, the rule can be stated that the hydrogen atom is added to the carbon with the greatest number of hydrogen atoms while the X component is added to the carbon with the least number of hydrogen atoms

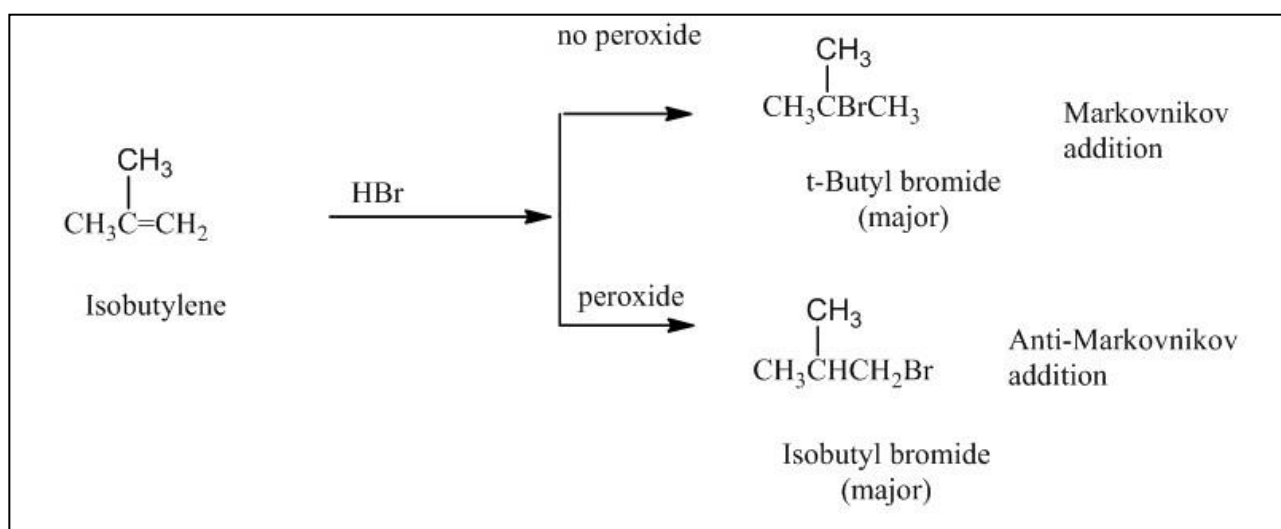
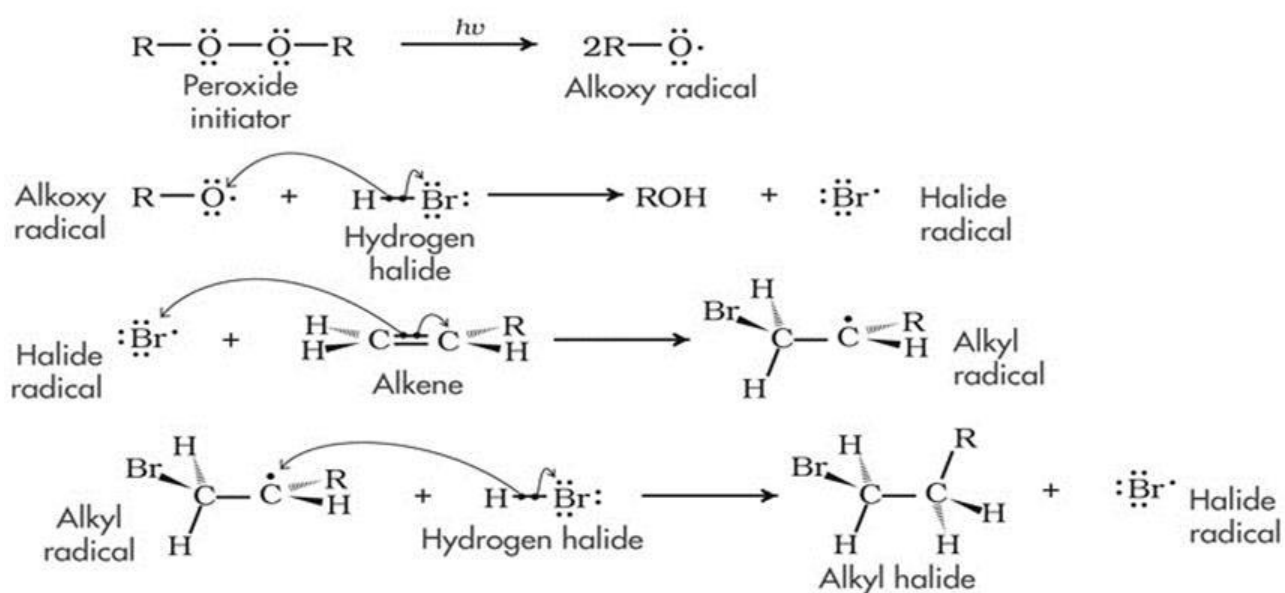


✓ Reason:

- The top one has two alkyl groups (the CH₃ and the R group) that can push electrons towards it, stabilizing the positive charge.
- It will form quite easily.
- The bottom carbocation only has one alkyl group to stabilise it so forms less well.
- So, since the first carbocation forms in preference the Hydrogen atom on the H-Br will mostly end up on the left-hand Carbon atom in the alkene - and will only sometimes end up on the middle one.
- And the Br atom is more likely to end up in the middle rather than on the left-hand Carbon atom.
- Alkyl groups pushing electrons is known as the Alkyl Inductive Effect.

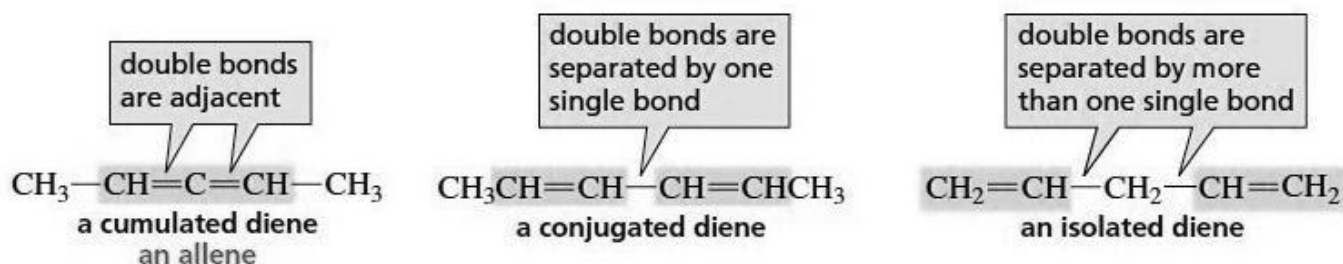
- **Anti- Markownikoff's rule (free radical addition reactions of alkenes)**

- In an addition reaction of a generic electrophile HX to an alkene or alkyne, the hydrogen atom of HX becomes bonded to the carbon atom that had the least number of hydrogen atoms in the starting alkene or alkyne.
- In the presence of Peroxide for H-Br, the reaction will always yield the **Anti-Markovnikov product**.
- Anti Markovnikov addition reaction is found to follow a free radical mechanism. The peroxide compound involved helps in the generation of free radicals.
 - Generation of free radical through homolytic cleavage of peroxide compound.
 - Attack of generated free radical on hydrogen halide to form halide radical through homolysis
 - Attack of generated halide radical on alkene molecule to form alkyl radical through homolysis.
 - Attack of generated alkyl radical on hydrogen halide to form alkyl halide through homolytic cleavage of hydrogen halide bond.



❖ Diene

- An unsaturated hydrocarbon containing two double bonds between carbon atoms.
- Dienes can be divided into three classes, depending on the relative location of the double bonds:
 - Cumulated dienes** have the double bonds sharing a common atom as in a group of compounds called allenes.
 - Conjugated dienes** have conjugated double bonds separated by one single bond.
 - Unconjugated dienes** have the double bonds separated by two or more single bonds. They are usually less stable than isomeric conjugated dienes. This can also be known as an **isolated dienes**.

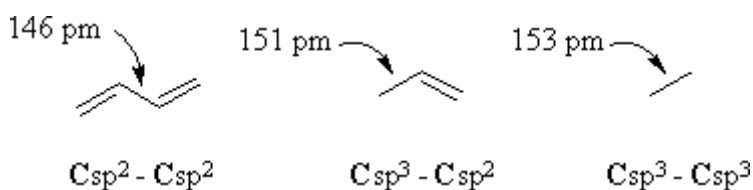


• Isolated Dienes

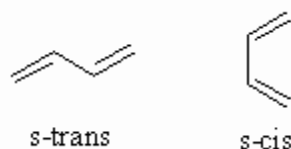
- ✓ The bonding in isolated dienes is the same as that in alkenes.

• Conjugated Dienes

- ✓ The **C-C single bond** between conjugated double bonds is shorter than a typical alkane C-C.
- ✓ This is due to the difference in the hybridisation of the **C atoms** involved (check the % s character) and the conjugation of the **two π bonds**.

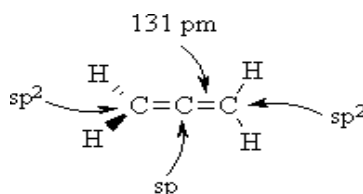


- ✓ Two conformations of conjugated dienes are important, **s-cis** and **s-trans**, as for 1,3-butadiene.
- ✓ The "s" refers to rotation about a σ bond.
- ✓ **Stability of conjugated dienes:** The **s-trans** conformation of 1,3-butadiene is about 12 kJ/mol (2.8 kcal/mol) more stable than the **s-cis** due to the unfavourable steric interaction of substituents at C_1 and C_4 .



• Cumulated Dienes

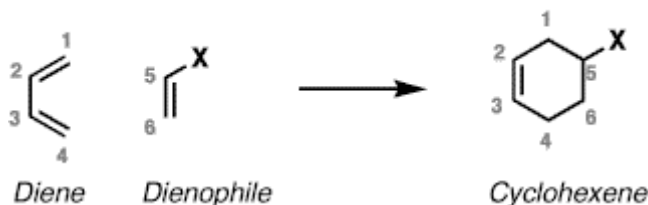
- ✓ Like the triple bond unit of an alkyne, the $\text{C}=\text{C}=\text{C}$ unit of allenes are linear.
- ✓ The central **sp hybridised C** atom.
- ✓ The $\text{C}=\text{C}$ bonds in allenes are slightly shorter (131 pm) than those in a typical alkene $\text{C}=\text{C}$ (134 pm)
- ✓ Allenes are non-planar. Note the perpendicular nature of the **C-H bonds**.



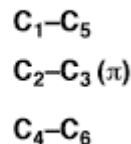
❖ Diels-Alder Reaction

- The Diels Alder reaction converts a **diene** (an unsaturated hydrocarbon containing two double bonds between carbon atoms.) and an alkene (**usually electron-poor, called a —dienophile**) into a six-membered ring containing an alkene (cyclohexene).

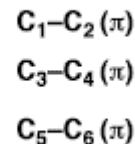
The Diels Alder Reaction



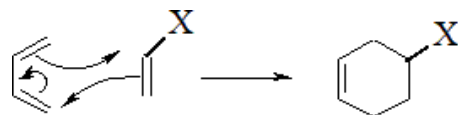
Bonds Formed



Bonds Broken



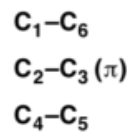
Mechanism



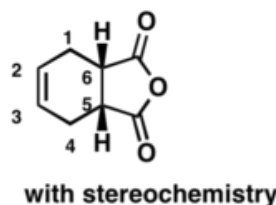
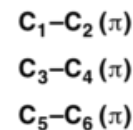
Diels-Alder reaction of a cyclic dienophile



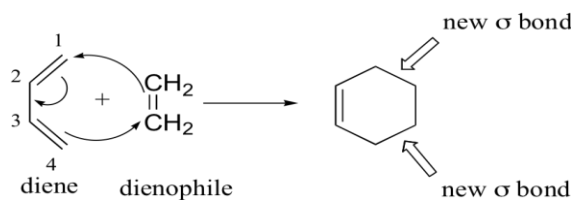
Bonds Formed



Bonds Broken

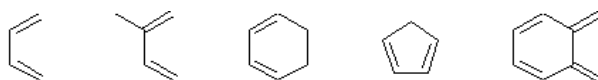


- Diels Alder reaction usually thermodynamically favourable due to the conversion of **2 π -bonds** into **2 new stronger σ -bonds**.

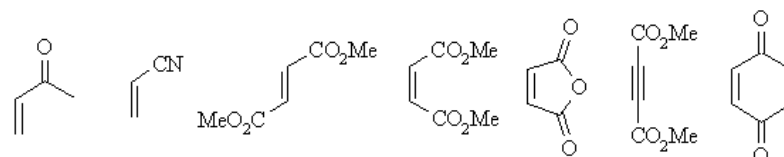


- The normal Diels-Alder reaction is favoured by **electron withdrawing groups on the electrophilic dienophile** and by **electron donating groups on the nucleophilic diene**.

Dienes



Dienophiles

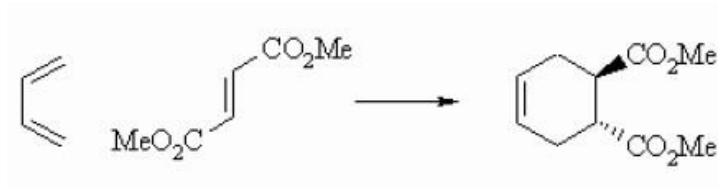


- The Diels-Alder reaction is stereospecific

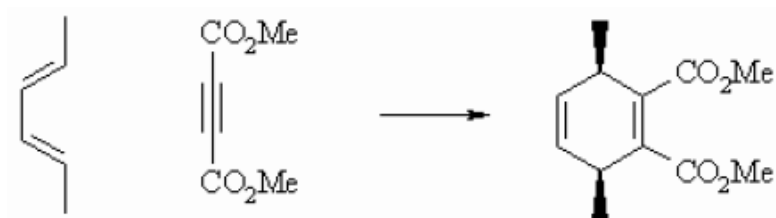
a *cis*-dienophile gives *cis* substituents in the product



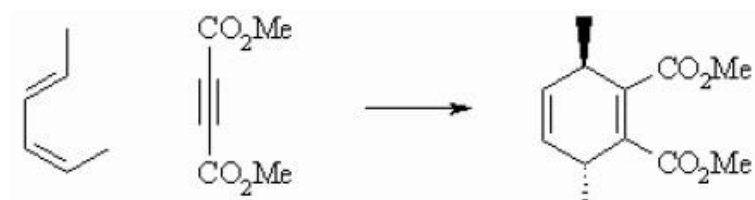
a *trans*-dienophile gives *trans*-substituents in the product.



If the **diene** substituents have the same stereochemistry (here they are both E), then both **diene** substituents end up on the same face of the product.

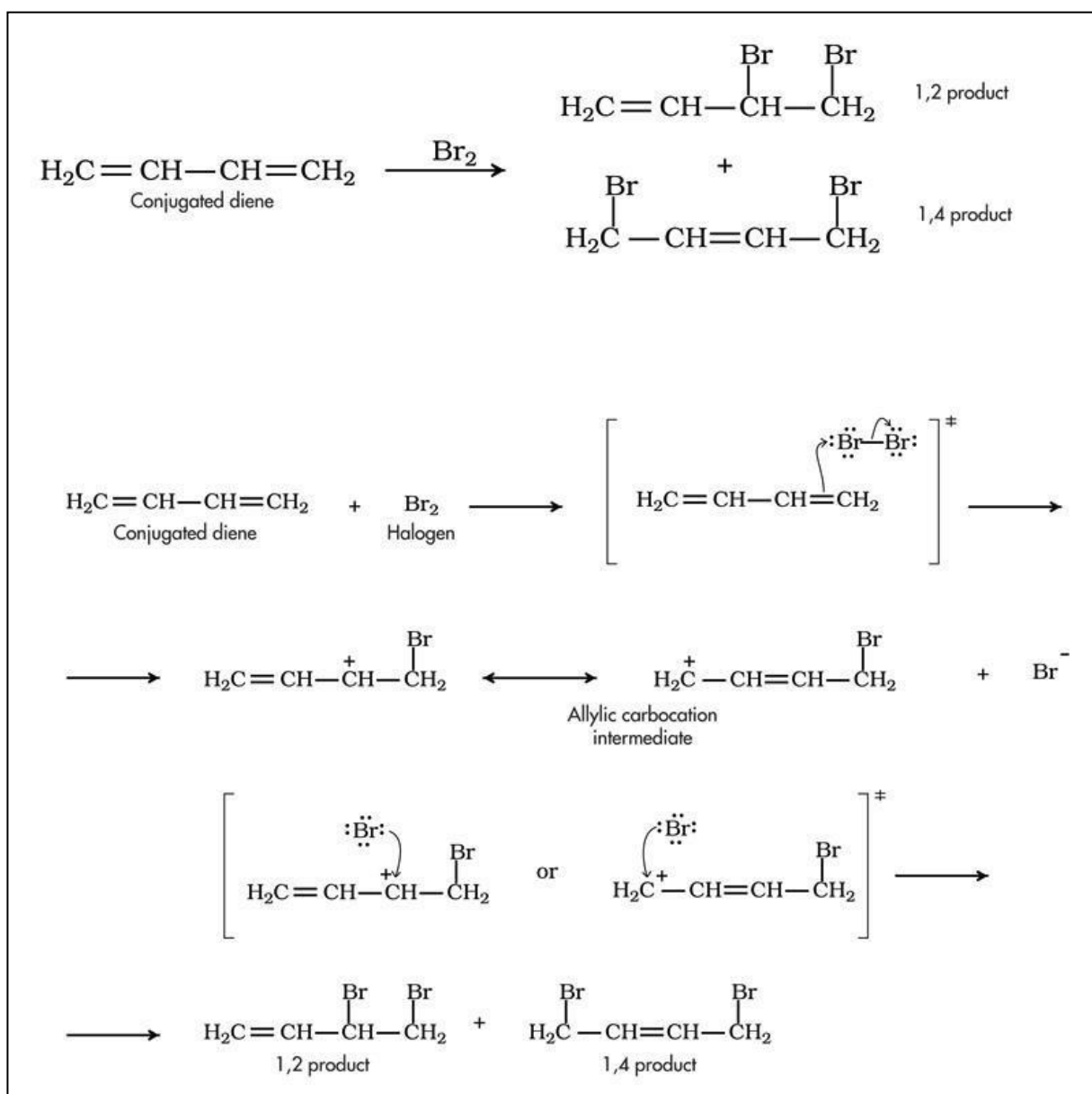
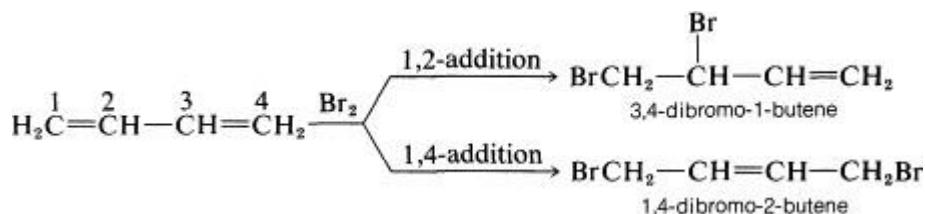


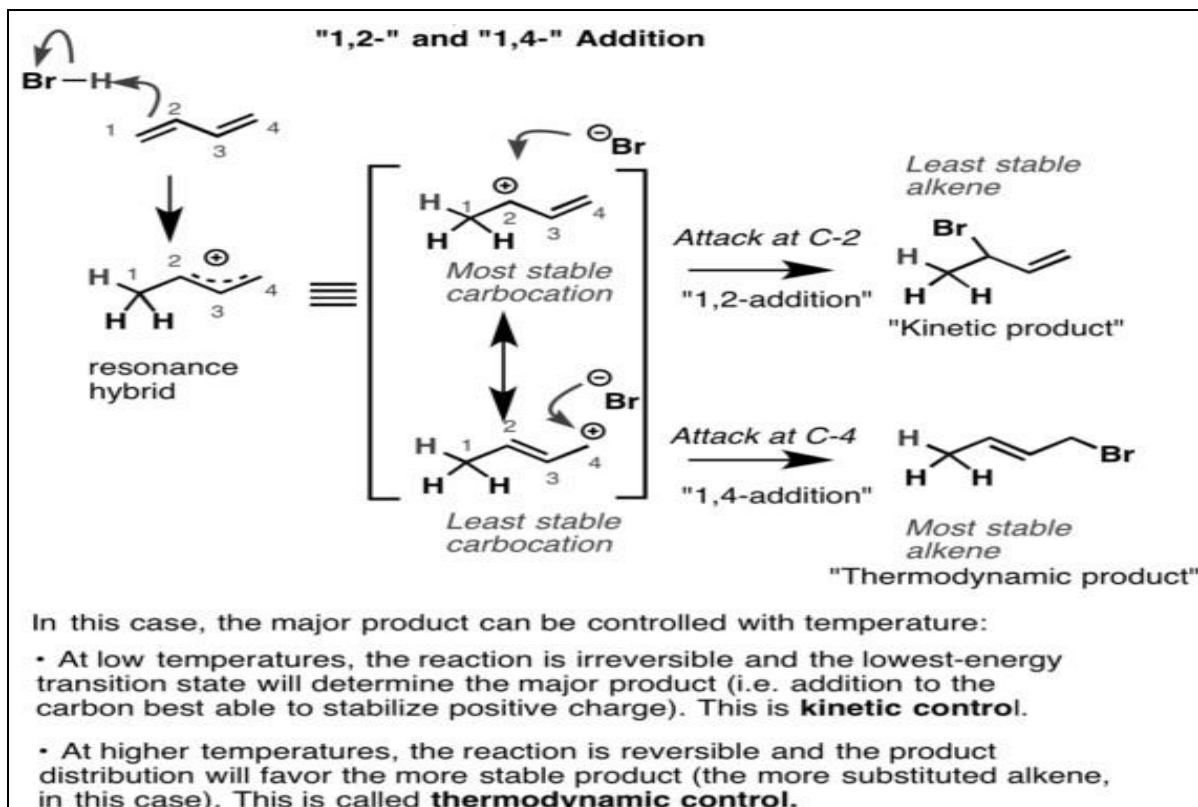
If the **diene** substituents have opposite stereochemistry (here one is E and one Z), then the **diene** substituents end up on opposite faces of the product.



❖ Electrophilic addition reactions of conjugated dienes

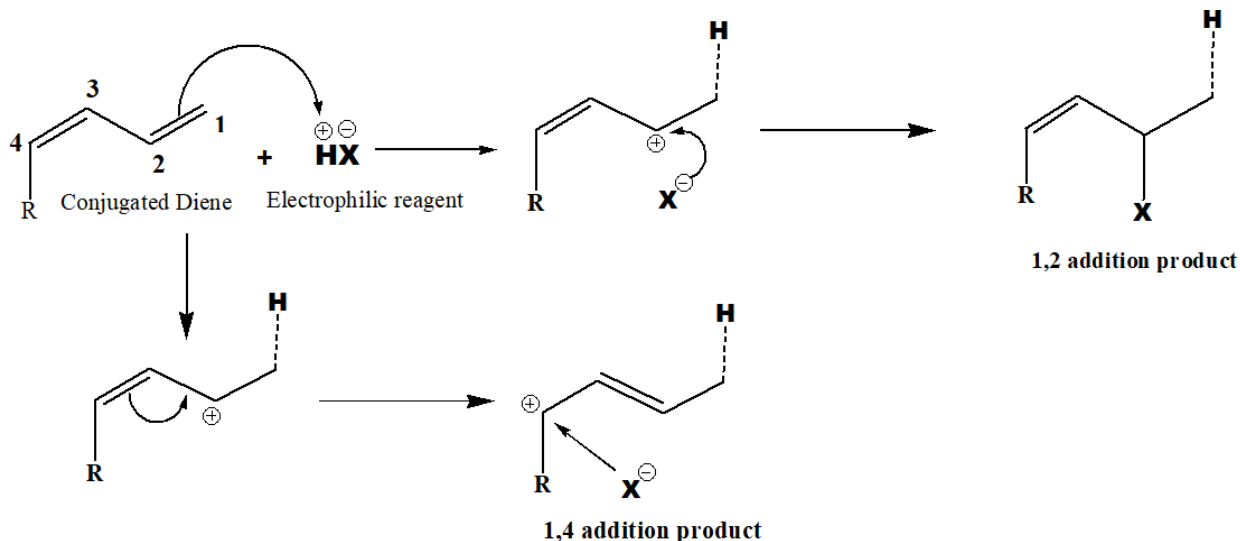
- Dienes with electrophilic reagents like halo acids give electrophilic addition reaction.
- Conjugated dienes undergo addition reactions in a similar manner to simple alkenes, but two modes of addition are possible.
- Consider the reaction of **1,3-butadiene**.





• Which is the major product formed predominantly 1,2 or 1,4?

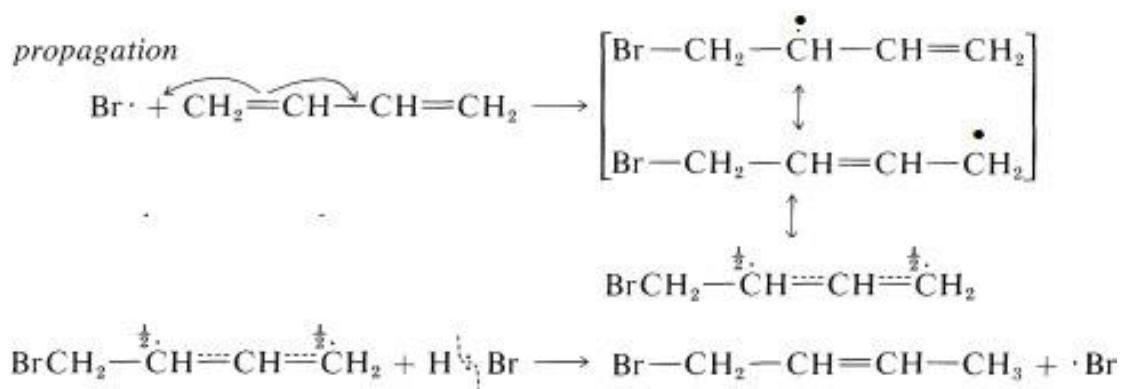
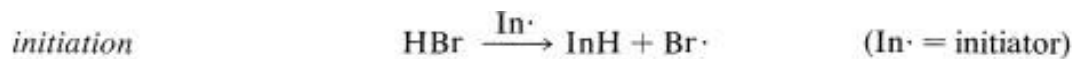
- The formation of product will depend on
 - (i) **Stability of carbocation:** The addition of proton occurs as per the **Markovnikov rule**; the stable carbocation will be formed at the more substituted carbon atom.
 - (ii) **Rate of reaction:**
 - The energy of activation for the formation of 1,2 product is lower and hence formed faster. However, equilibrium is less favored.
 - 1,4 product require higher activation energy but favors equilibrium.
 - (iv) **Reaction temperature:**
 - Kinetic product is product which appears first in reaction but the stable product is the thermodynamic product.
 - 1,2 product is formed first at lower temperature but rearranges to 1,4 product at high temperature or on standing for some time even at low temperature.
 - (v) **Reagent:** Use of milder condition gives mixture of products, use of excess of reagent result in 1,4 product.





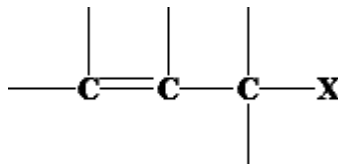
❖ Free radical addition reactions of conjugated dienes

- Conjugated dienes also undergo addition reactions by radical-chain mechanisms. Here, the addition product almost always is the 1,4 adduct. Thus radical addition of hydrogen bromide to 1,3-butadiene gives 1-bromo-2-butene.



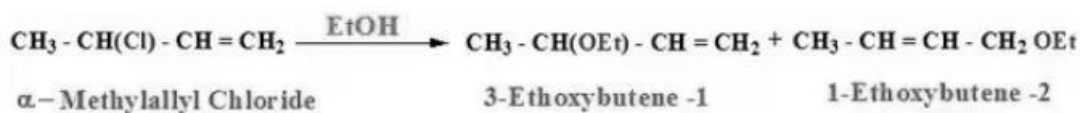
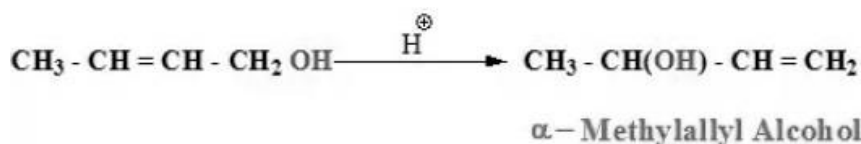
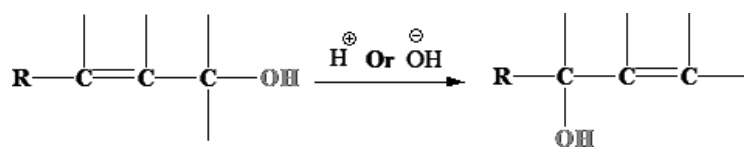
❖ Allylic Rearrangement

- Allylic compounds are those which have a functional group on a carbon atom α to an olefinic bond, e.g.,

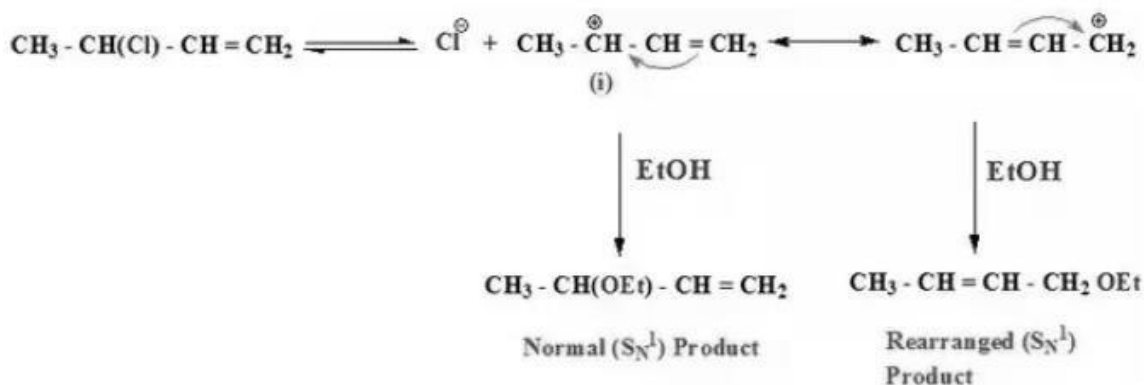


Alkenes are also called Olefins because they form oily liquids on reaction with chlorine gas. An alkene consists of atleast one double bond. This double bond is known as the **olefinic bond**.

- The double bond (and the functional group) in these compounds undergo acid or base catalyzed migration to form a new compound.



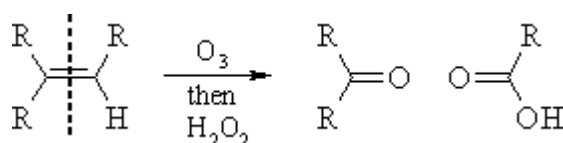
- **Mechanism:** Allylic rearrangement is observed generally in nucleophilic substitution reactions which may be $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ type.



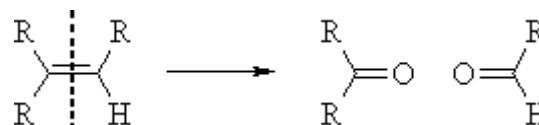
❖ Ozonolysis

- Ozonolysis is an organic reaction where the unsaturated bonds of alkenes, alkynes, or azo compounds are cleaved with ozone.
- Alkenes and alkynes form organic compounds in which the multiple carbon-carbon bond has been replaced by a carbonyl group while **azo** compounds form **nitrosamines**.
- **Reaction type:** Electrophilic Addition.
- **Reagents:** ozone followed by :
 - o a reducing work-up, either Zn in acetic acid or dimethyl sulfide, (CH₃)₂S
 - o an oxidising work-up, usually H₂O₂ (under these conditions, carboxylic acids are obtained instead of aldehydes)

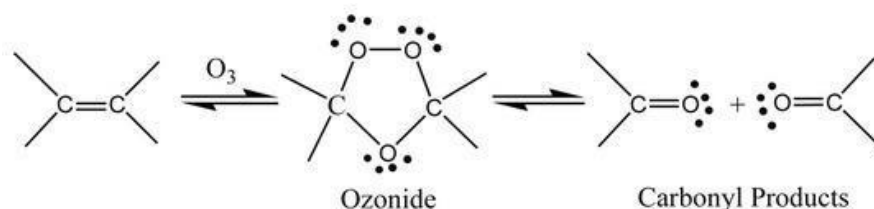
OXIDATIVE work-up



REDUCTIVE work-up

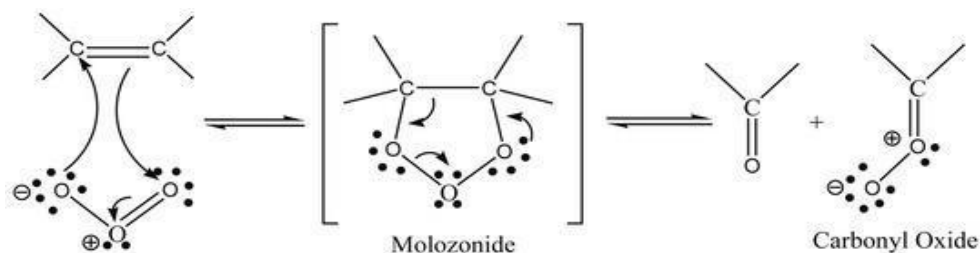


• Reaction:



• Reaction Mechanism:

- **Step 1:** The first step in the mechanism of ozonolysis is the initial **electrophilic addition** of **ozone** to the **Carbon-Carbon double bond**, which then forms the **molozone intermediate**. Due to the unstable **molozone** molecule, it continues further with the reaction and breaks apart to form a carbonyl and a carbonyl oxide molecule.



- **Step 2:** The carbonyl and the **carbonyl oxide (zwitterions)** rearranges itself and reforms to create the **stable ozonide intermediate**. A reductive workup could then be performed to convert the **ozonide** molecule into the **desired carbonyl products**.

