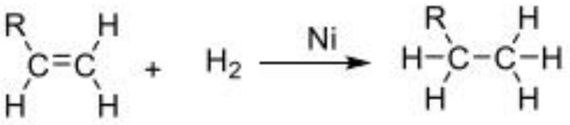
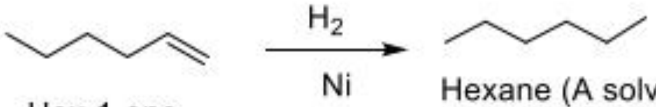
Alkanes:

Catalytic Hydrogenation:

- Catalytic hydrogenation of alkenes or alkynes is a common strategy to alkanes.





Hex-1-ene

Hexane (A solvent)

$$CH_3-C\equiv CH \xrightarrow[Ni]{H_2} CH_3CH_2CH_3$$

Propyne

Propane (A gas)

- Catalytic hydrogenation is the common method for converting unsaturated oils to saturated fats in a process commonly referred to as “hardening of oils”.

Wurtz Reaction:

- Wurtz’s reaction is an organic chemical coupling reaction wherein sodium metal is reacted with two alkyl halides in the environment provided by a solution of dry ether in order to form a higher alkane along with a compound containing sodium and the halogen.

- Apart from sodium, metals like silver, indium, activated copper, zinc, and iron can also be used in the Wurtz reaction in order to obtain alkanes.

- The mechanism of this reaction involves free radicals, allowing for the possibility of side reactions that lead to the formation of alkenes as the product.

- The general form of the Wurtz reaction equation can be written as follows:

$$\mathbf{2R\text{-}X + 2Na \rightarrow R\text{-}R + 2Na^{+}\,X^{-}}$$

- It can be observed from this equation that the two R groups are joined, yielding an alkane with a longer chain along with NaX, where X is a Halogen.

- The mechanism of the Wurtz reaction involves a free radical species denoted by $R^{\bullet}$ which is a part of a halogen-metal exchange. The carbon-carbon bond is formed in a nucleophilic substitution reaction in this reaction mechanism, which can be broken down into the following 3 steps:

Step 1: The transfer of an electron from the metal (sodium in this case) to the halogen leads to the formation of an alkyl halide along with the metal halide.

$$\mathbf{R\text{-}X + Na \rightarrow R^{\bullet} + Na^{+}R^{-}}$$

Step 2: A different sodium atom now donates a single electron to the alkyl radical, leading to the formation of an alkyl anion as shown below.

$$\mathbf{R^{\bullet} + Na \rightarrow R\text{–}Na^{+}}$$

Step 3: The carbon belonging to the alkyl anion having a nucleophilic nature proceeds to displace the halogen in the alkyl halide via an SN2 reaction and form a covalent bond with the carbon which was bonded with the halogen. The reaction detailing this step is given below.

$$\mathbf{R\text{–}Na+ + R\text{-}X \rightarrow R\text{-}R + Na^{+}X^{-}}$$

Limitations of the Wurtz Reaction:

- only symmetric alkanes can be synthesized via this method since a mixture of alkane products are formed when dissimilar alkanes are reacted.

- There exists a side reaction via which an alkene product is formed. Should the alkyl halides be bulky in nature, especially at the halogen end, there is a greater amount of alkene formed.

- Methane cannot be synthesized via the Wurtz reaction since the product of an organic coupling reaction must have at least two carbon atoms.

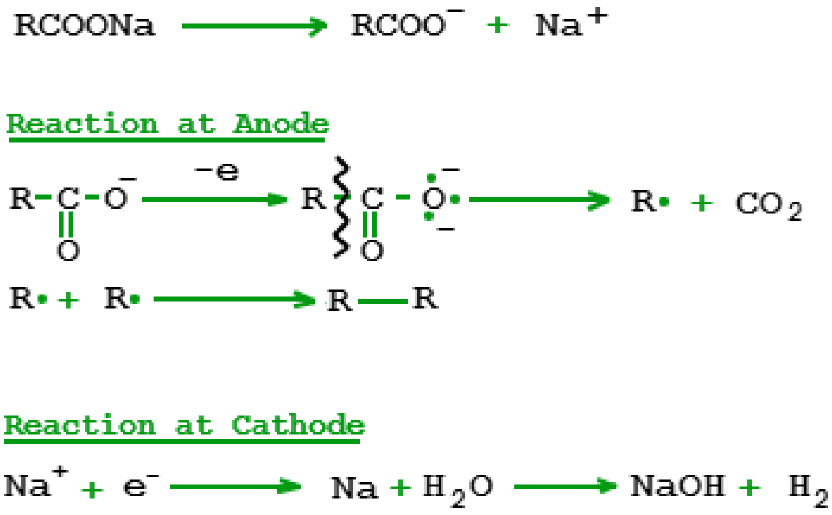
- The Wurtz coupling method generally fails when tertiary alkyl halides are used.

Alkanes from Reduction of Carboxylates - Kolbe's Electrolytic method:

- Sodium or potassium salt of a dicarboxylic acid on electrolysis gives an alkene. An alkene is generated when an aqueous solution of sodium or potassium salt of a dibasic acid (with adjacent carboyxlic groups) is electrolyzed.

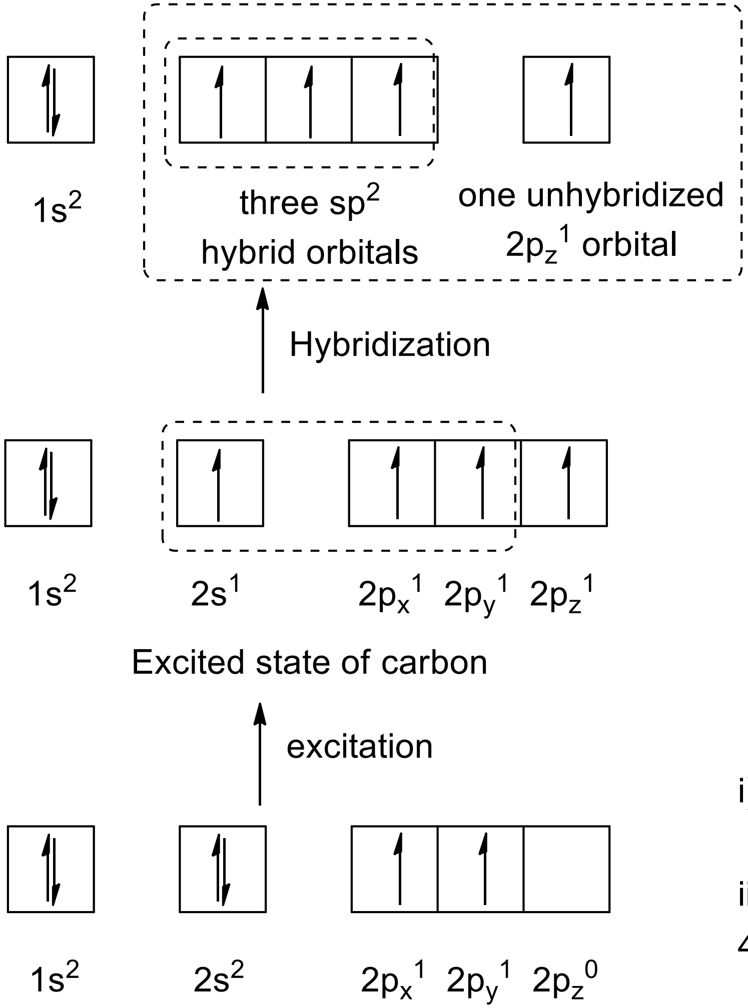
- During this reaction Carbon dioxide is released at anode along with formation of alkanes.

$$2\text{R-COONa (on Electrolysis)} \rightarrow \text{R - R} + 2CO_2 + H_2 + \text{NaOH}$$



Alkenes:

Basic structural features:

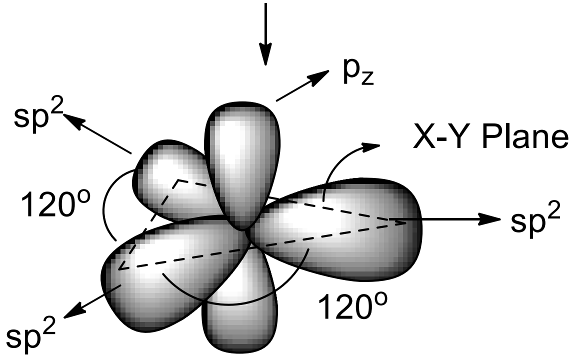


Excited state of carbon

Ground state of carbon

i) 3 equivalent sp^2 hybrid orbitals will equally share the three dimensional space, when they reside on a plane with 120° angle with each other.

ii) Since, p_x and p_y are involved in hybridization, all the three sp^2 orbitals will stay on X-Y plane and the p_z orbital will stay in Z-direction, perpendicular to X-Y plane.

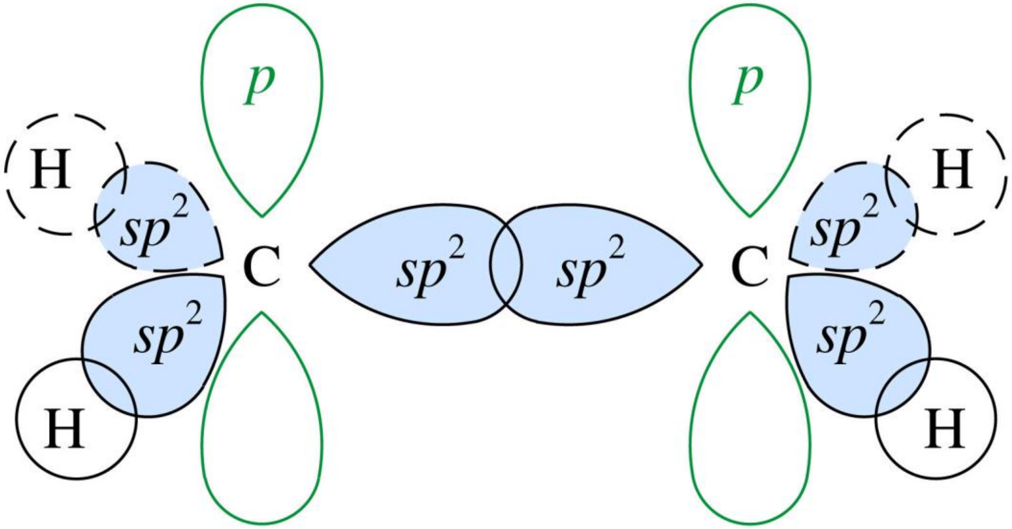


i) In ethylene, each carbon has 3 sp^2 hybrid orbitals, a total of 6.

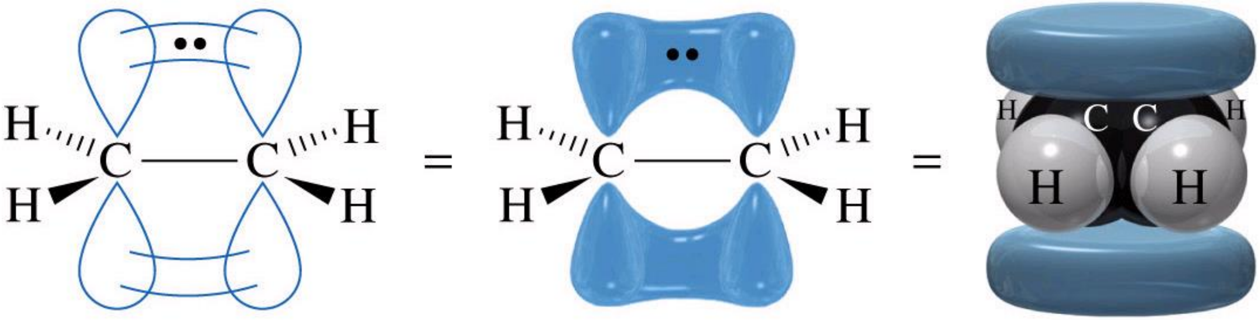
ii) Two of them forms the σ–C-C bond and the remaing four forms 4 σ–C-H bonds.

iii) Two perpendicular p_z orbitals laterally overlaps to form the π-bond.

Ethylene

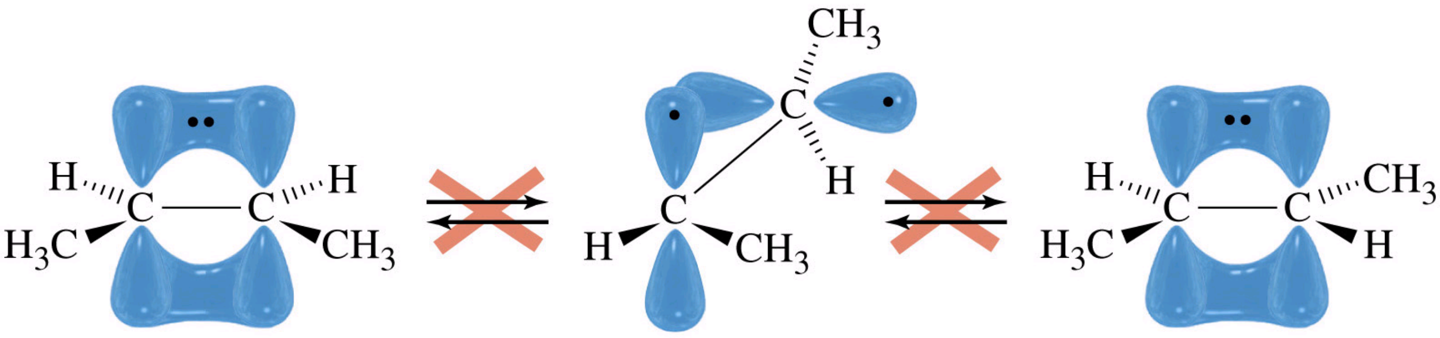


sigma bonding orbitals of ethylene



Of course, in order for such arrangement to be stable, there must be no rotation along the C=C bond, as that would break the C=C π bond.

- The above restriction is the origin of cis-trans geometrical isomerism



cis no overlap with the ends perpendicular trans

- These two stereoisomers of 2-butene do not interconvert at normal temperatures so they are different molecules with different properties and names. Interconversion requires C=C rotation that breaks the π(2p-2p) bond and this process requires a large energy input (about 270 kJ/mol).

- Presence of π-bond also makes $C_{sp2}=C_{sp2}$, a stronger bond than C_{sp3}-C_{sp3} and therefore, C=C bond length is shorter than C-C bond length.

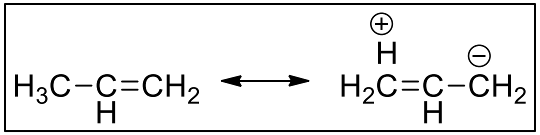
- In fact, presence of sp^2 carbon in a C-C bond, makes it shorter. The reason is, sp^2 carbons have higher s-character (33.3%) than the sp^3 carbons (25%). So, sp^2 orbitals are more compact than sp^3 orbitals. So, whenever sp^2 carbon is involved in forming a C-C bond, involvement of more compact orbital makes the bond shorter. So, we have the following bond length order, $C_{sp2} = C_{sp2} < C_{sp2} – C_{sp3} < C_{sp3} – C_{sp3}$

- Of course, sp-carbons (50% s-character) makes the bond length even shorter.

- **Due to the same reason, C-C bond length in propene is shorter than the C-C bond length in propane,-**

i) C_{sp3}– C_{sp3} of propane is formed by two sp^3 hybrid orbitals, whereas in C_{sp2} – C_{sp3} of propene, one sp^2 hybrid orbital is involved. As, sp^2 hybrid orbital has higher s-character, it is more compact, leading to lower bond length.

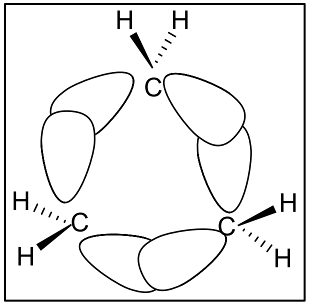
ii) Additionally, alkenes are stabilized by hyperconjugation, as depicted below. It leads to double bond character of the C_{sp2} – C_{sp3} bond, leading to lowering of bond length.



$$H_3C{-}\underset{H}{C}{=}CH_2 \longleftrightarrow \overset{\oplus}{H}\quad H_2C{=}\underset{H}{C}{-}\overset{\ominus}{C}H_2$$

- **Another interesting observation is, C-H bond length in cyclopropane is shorter than the C-H bond length in propane**

In cyclopropane ring, the carbons are sp^3-hybridized. As the angle for a three membered ring should be 60°, such angle leads to ineffective head-on overlap of the sp^3 – orbitals of carbons. In order to have a better overlap, the angle must be broadened. Now, we know that bond angle decreases from 180° to 120° to 109°28′ on going from sp to sp^2 to sp^3 hybridization; i.e. bond angle decreases with increasing p-character. So, in cyclopropane, an adjustment of hybridization takes place, incorporating more p-character in forming the C-C bonds, so that bond angles gets more closer to 60°. The C-C bonds therefore bent away to form “banana bond”. Now. as more p-character is used to make the C-C bonds, more s-character is used to construct C-H bonds, which means, hydrogen is more closer to carbon nucleus, than in C-H bonds of propane. This is why C-H bond length in cyclopropane is shorter than the C-H bond length in propane.

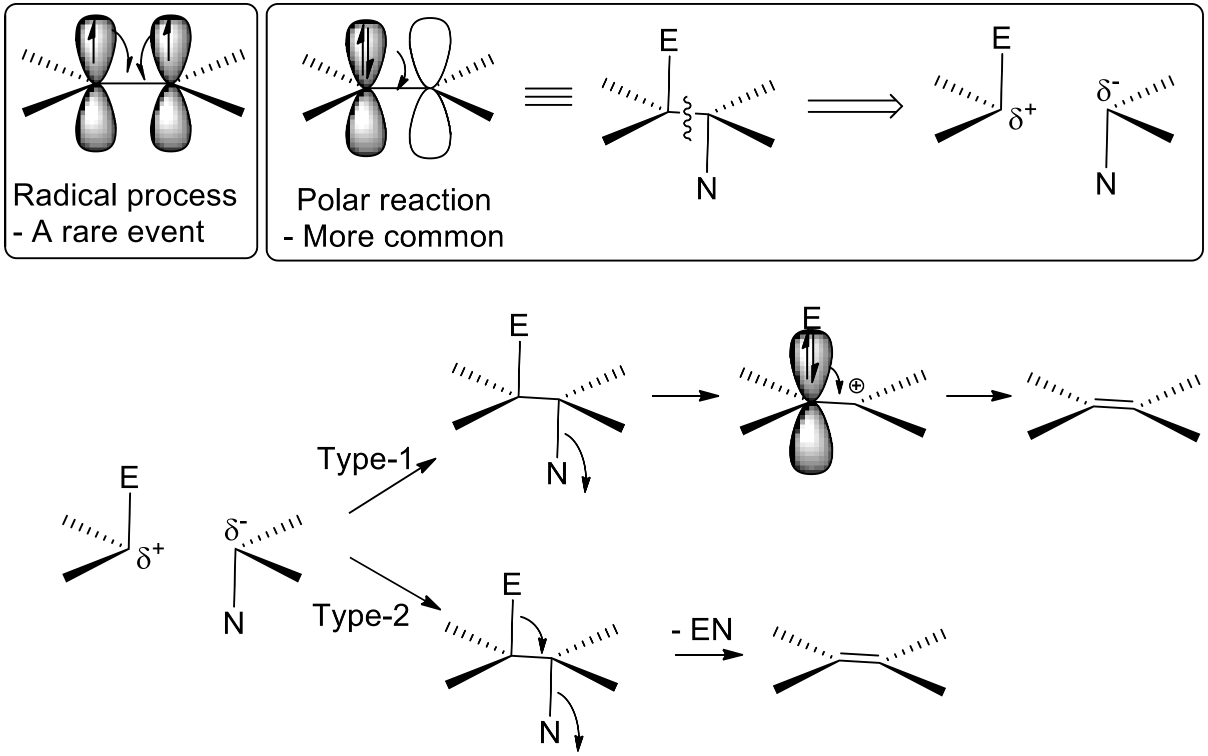


- **Again, shorter C=C bond length in $CF_2=CF_2$ than the C=C bond length in $CH_2=CH_2$ can be explained by considering the difference in degree of s-character of different bonds as follows,-**

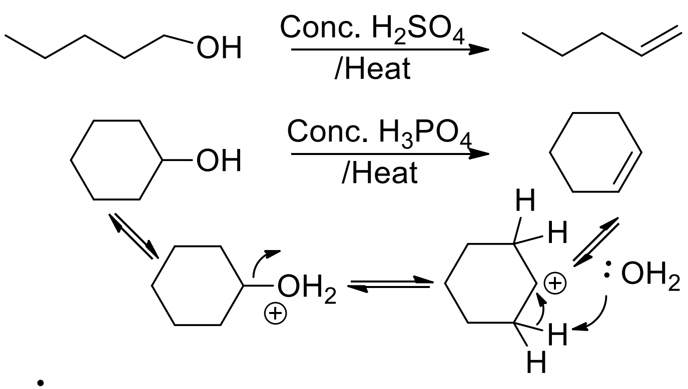
Fluorine being highly electronegative atom, tends to attract the bond pair of C-F bond towards itself. So, according to Bent’s rule, more p-character is utilized in the hybrid orbital of carbon, forming the C-F bond, so that it becomes easier for fluorine to attract the bond pair. This implies, more s-character is utilized to form the C=C bond, leading to shorter C=C bond length in $CF_2=CF_2$ than that in $CH_2=CH_2$.

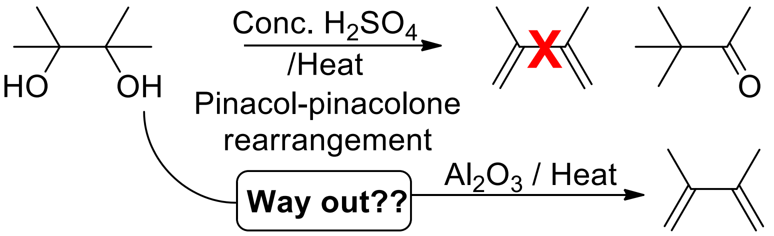
Synthesis of alkenes:

A. We can start from a pre-existing σ-C-C bond, followed by the formation of π-bond i) either by two parallel orbitals, each containing a single electron; i.e. a radical reaction, which is very rare; ii) or, by two parallel orbitals, one of which contains a pair of electron and the other is vacant; i.e. a reaction between $C^{\delta+}$ and $C^{\delta-}$, which is the more accesible.



Type-1 reaction: Dehydration of alcohols:





(Aluminium coordinates with both -OH groups, preventing both carbocation formation and following rearrangement)

Mechanism:

i) Conversion of –OH group in to good leaving group, H_2O, by protonation.

ii) Formation of carbocation by C-O bond breaking.

iii) Elimination of α-hydrogen, to form the double bond.

iv) The rate-determining step is the breaking of C-O bond, i.e. formation of carbocation. So, the alcohol, which gives more stable incipient carbocation in the TS of this step, will react at a faster rate.

For example, dehydration of ethanol, isopropanol and tert-butanol produces 1°, 2° and 3° incipient carbocation in the TS, respectively. This is why, dehydration of ethanol needs conc. H_2SO_4, whereas, that of isopropanol needs 60% H_2SO_4 and tert-butanol needs only 20% H_2SO_4.

1° carbocation , 2° carbocation , 3° carbocation

$\xrightarrow{\hspace{6cm}}$

stability increases

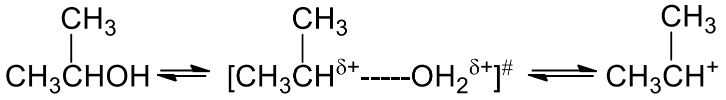
1° alcohol , 2° alcohol , 3° alcohol

$\xrightarrow{\hspace{6cm}}$

Reactivity increases

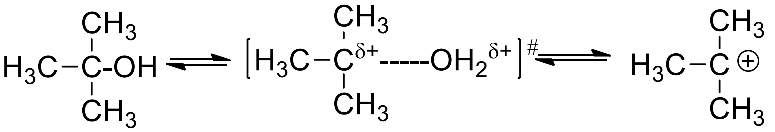
$$CH_3CH_2OH \rightleftharpoons [CH_3CH_2^{\delta+}\text{-----}OH_2^{\delta+}]^{\#} \rightleftharpoons CH_3CH_2^+$$

(1° incipient carbocation, stabilized by 3 hyperconjugative hydrogens and +I effect of 1 methyl group)



$$CH_3\overset{CH_3}{\overset{|}{C}}HOH \rightleftharpoons [CH_3\overset{CH_3}{\overset{|}{C}}H^{\delta+}\text{-----}OH_2^{\delta+}]^{\#} \rightleftharpoons CH_3\overset{CH_3}{\overset{|}{C}}H^+$$

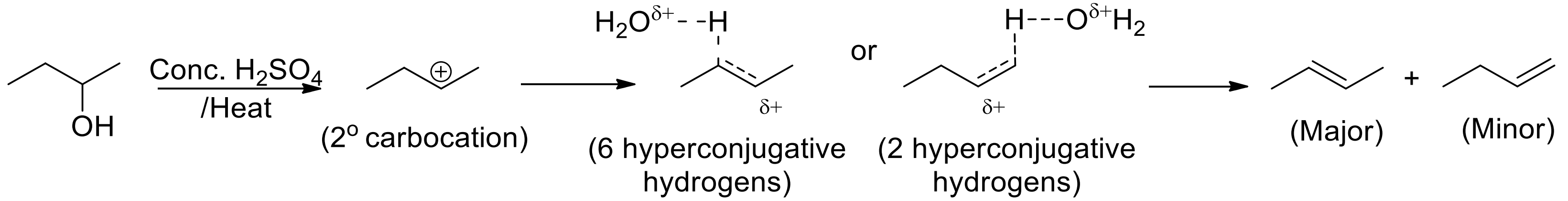
(2° incipient carbocation, stabilized by 6 hyperconjugative hydrogens and +I effect of 2 methyl group)

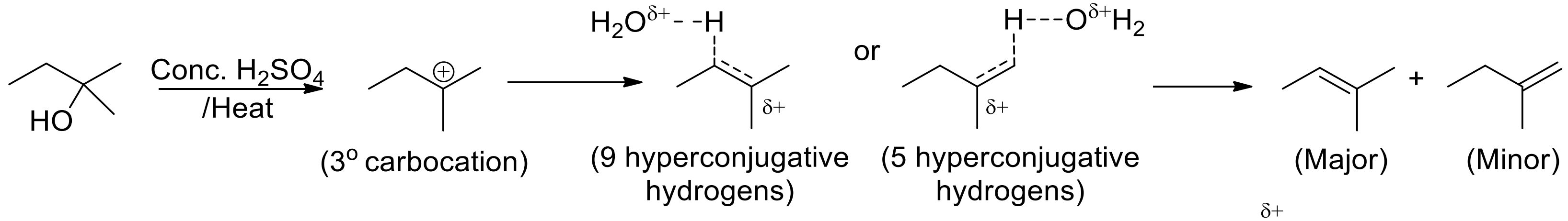


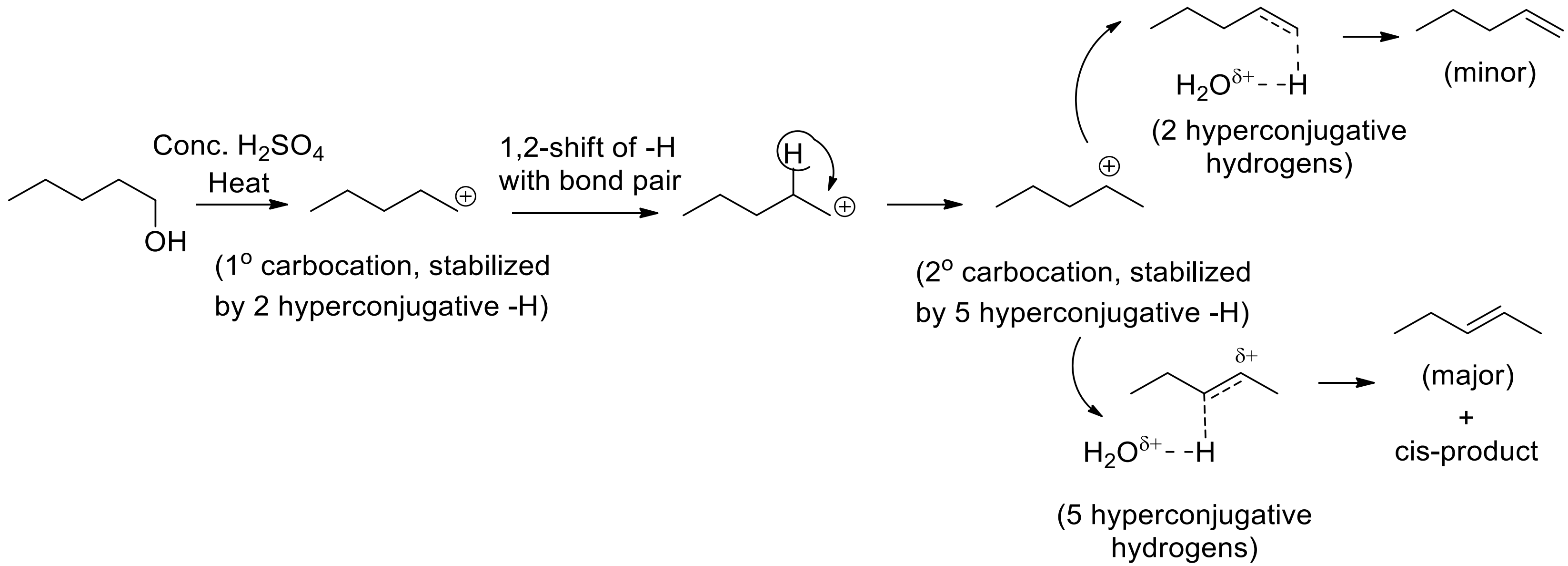
$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}\text{-}OH \rightleftharpoons \left[H_3C-\overset{CH_3}{\underset{CH_3}{C}}{}^{\delta+}\text{-----}OH_2^{\delta+}\right]^{\#} \rightleftharpoons H_3C-\overset{CH_3}{\underset{CH_3}{C}}\oplus$$

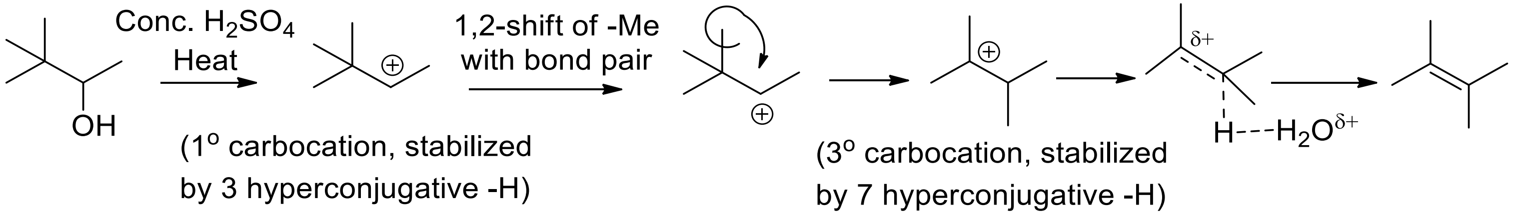
(3° incipient carbocation, stabilized by 9 hyperconjugative hydrogens and +I effect of 3 methyl group)

- The situation becomes complex for alcohols with different types of hydrogens, as the system has a choice now, about which α-hydrogen to be abstracted. Now, the abstraction of hydrogen in step-3, produces the alkene. So, more stable TS in step-3 will produce the major product. Now, the TS of step-3 is an incipient carbocation as well as an incipient alkene. So, more substituted TS is more stabilized by hyperconjugation and +I effect of alkyl sybstitutents. So, more substituted product is the major one. Sometimes, the carbocation can rearrange to more stable carbocation, producing rearranged product.









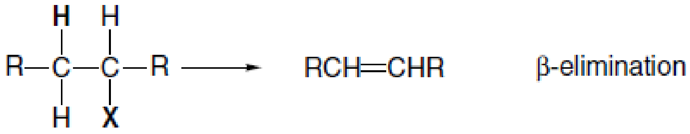
Type-2 reactions: Dehydrohalogenation of Alkyl Halides:

- Elimination reactions involve the removal of another molecule from a reactant.

- According to the structural relationship between the proton and the leaving group, elimination reactions are classified into α-elimination, leading to divalent carbon species called carbenes, and ß-elimination, which leads to formation of carbon-carbon double bonds.

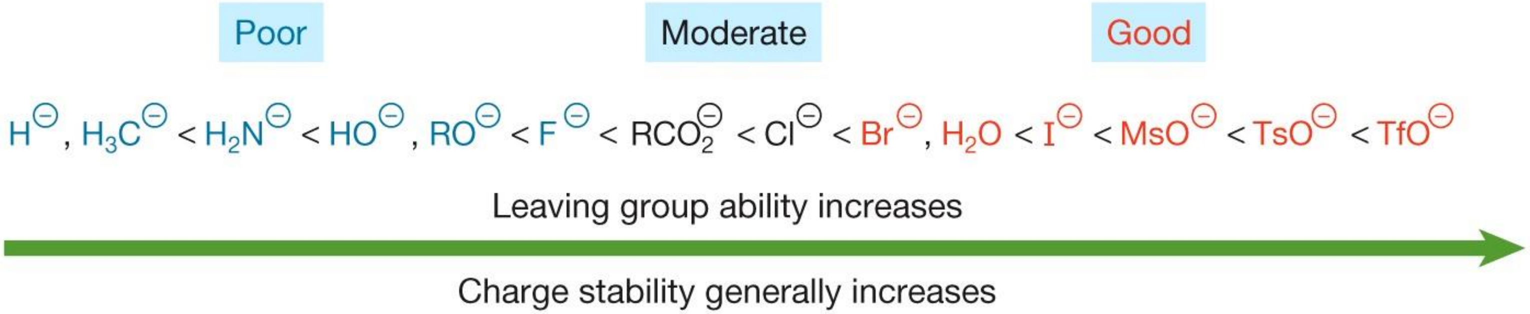
- Besides, there are γ- or other higher degree of eliminations resulting in cyclization; mechanistically they are intramolecular nucleophilic displacements.

- In this course, we will focus mainly on the ß-elimination.



$$R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}-R \longrightarrow RCH{=}CHR$$

β-elimination



Poor Moderate Good

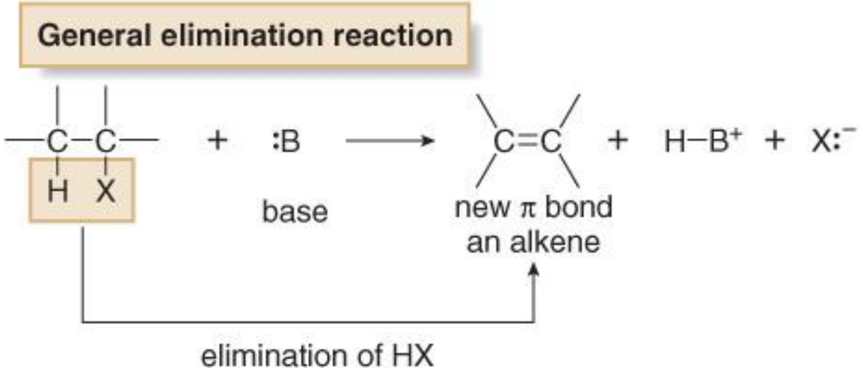
$H^{\ominus}$, $H_3C^{\ominus}$ < $H_2N^{\ominus}$ < $HO^{\ominus}$, $RO^{\ominus}$ < $F^{\ominus}$ < $RCO_2^{\ominus}$ < $Cl^{\ominus}$ < $Br^{\ominus}$, H_2O < $I^{\ominus}$ < $MsO^{\ominus}$ < $TsO^{\ominus}$ < $TfO^{\ominus}$

Leaving group ability increases

Charge stability generally increases

General pattern of a ß-elimination reaction:

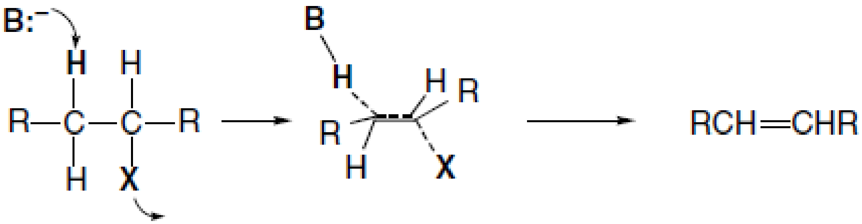
◆ Alkyl halides undergo elimination reactions with Brønsted–Lowry bases. The elements of HX are lost and an alkene is formed.



General elimination reaction

The ß-eliminations can be subdivided on the basis of the mechanisms involved. Three distinct limiting mechanisms are outlined below.

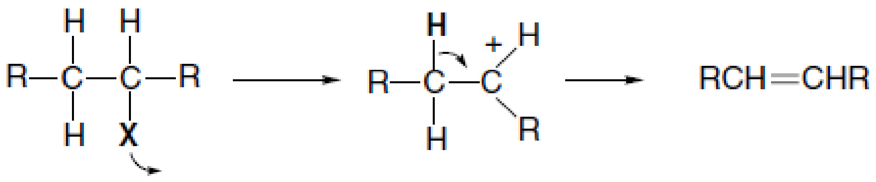
E2 Mechanism (concerted)



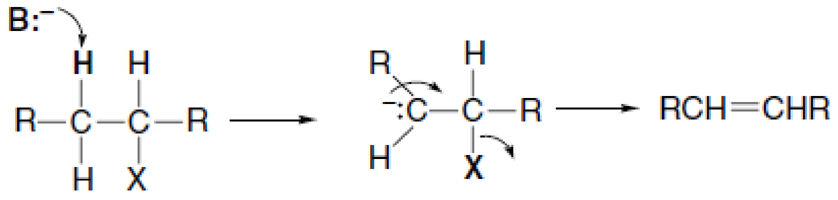
- The E2 mechanism involves a bimolecular TS in which removal of a proton ß to the leaving group is concerted with departure of the leaving group.

- The rate-determining step in the E1 mechanism is the unimolecular ionization of the reactant to form a carbocation intermediate, followed by removal of a ß-proton.

- The E1cb mechanism, also involves two steps: Deprotonation, forming a carbanion intermediate, then expulsion of the leaving group.



E1 Mechanism (carbocation intermediate)

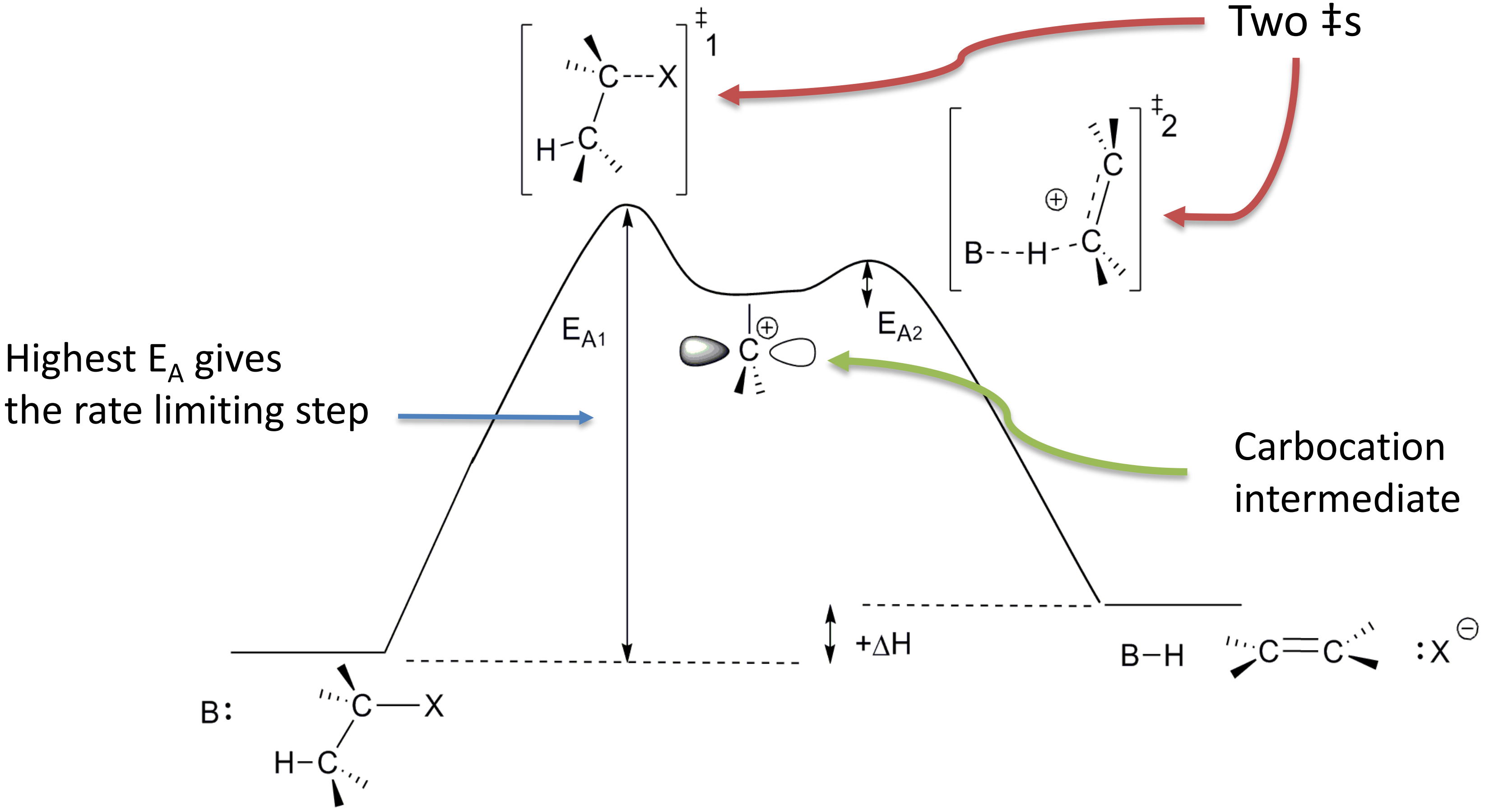


E1cb Mechanism (carbanion intermediate)

E1:

- E1 shows first Order Kinetics: rate = k[RX].

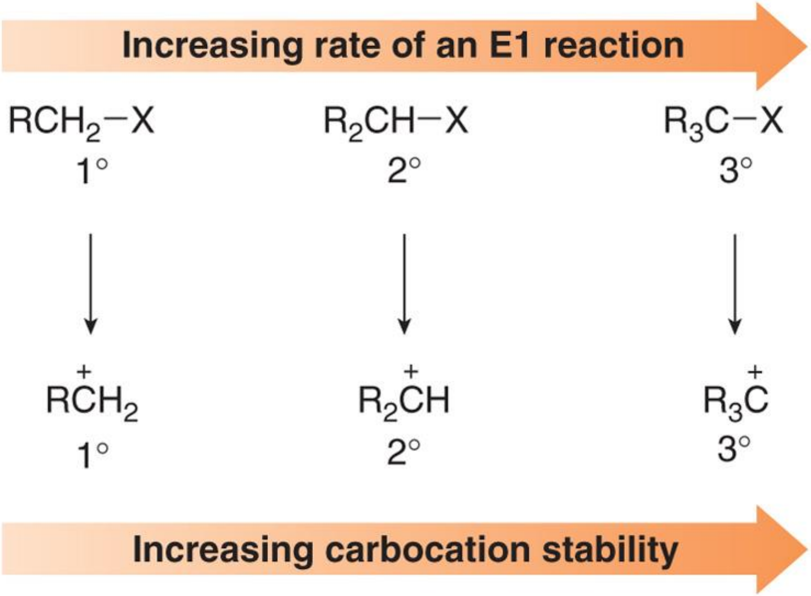
- Ionization is favored by: (1) electron releasing groups that stabilize the positive charge in the carbocation intermediate; (2) readily ionized, i.e., “good,” leaving groups; and (3) solvents that facilitate ionization. The base plays no role in the rate-determining step.



Two ‡s

Highest E_A gives the rate limiting step

Carbocation intermediate



- E1 reactions are most rapid in polar protic solvents.
- Polar protic solvents facilitate the separation of ions in the rate limiting step

Solvent effect on E1:

- Solvents have a profound effect on the rates of E1 reactions. The solvent properties that are most important are polarity and the ability to assist leaving group ionization.

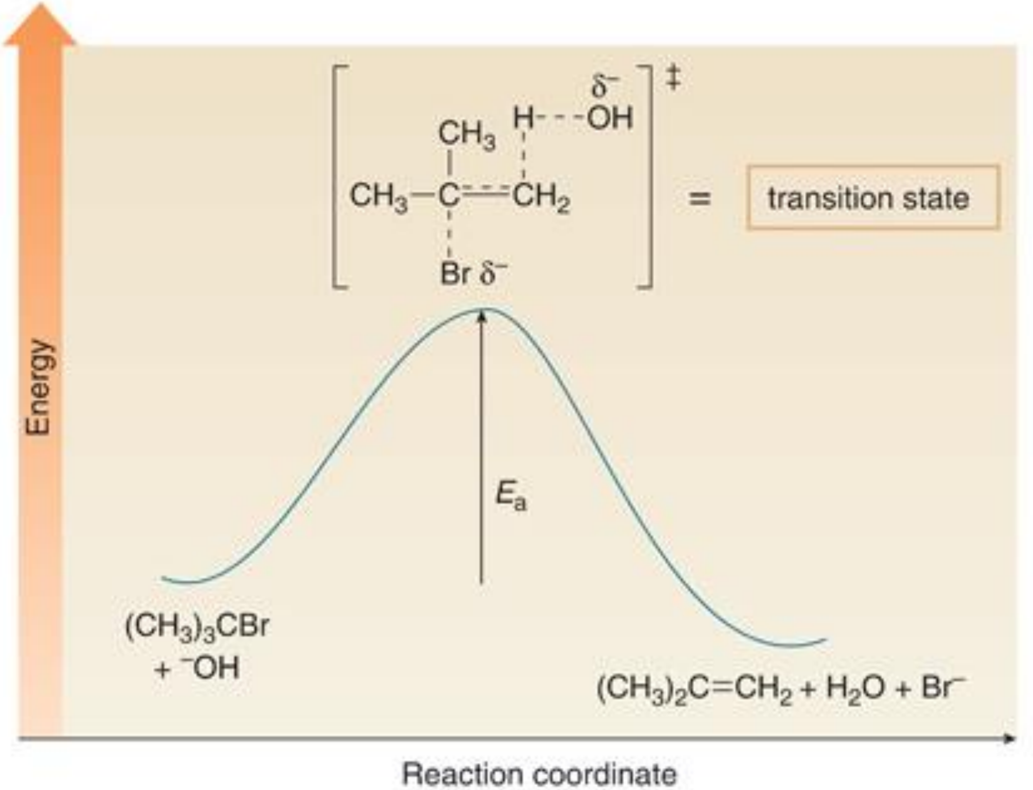
- For t-butyl chloride there are huge differences in the rates in water (log k = −1.54), ethanol (log k = −7.07), and diethyl ether (log k = −12.74).

- Rates of the E1 reaction of 1-methylcyclopentyl bromide range from 1×10^{-3} s^{-1} in methanol to 2×10^{-9} s^{-1} in hexane.

- Polar aprotic solvents such as DMSO ($k = 2\times10^{-4}$ s^{-1}) and acetonitrile ($k = 9\times10^{-5}$ s^{-1} are also conducive for ionization.

E2:

- E2 shows second Order Kinetics: rate = k[RX][base], as base is present in the rate-determining step.
- Here leaving group effect is normally I > Br > Cl >>F because bond-breaking occurs in RDS.
- Kinetic isotope effect for both β-*C-H and leaving group*.
- Kinetic isotope effect for both α- *and β-carbons*.



- An elimination reaction proceeding by an E2 TS will be moved in the E1cb direction by an increase in base strength or by a change to a poorer leaving group. So, more acidic or less hindered hydrogen will be abstracted, giving less-substituted alkene.

- On the other hand, a good leaving group in a highly ionizing solvent will result in an E2 TS that resembles an E1 process, leading to more substituted alkene product.

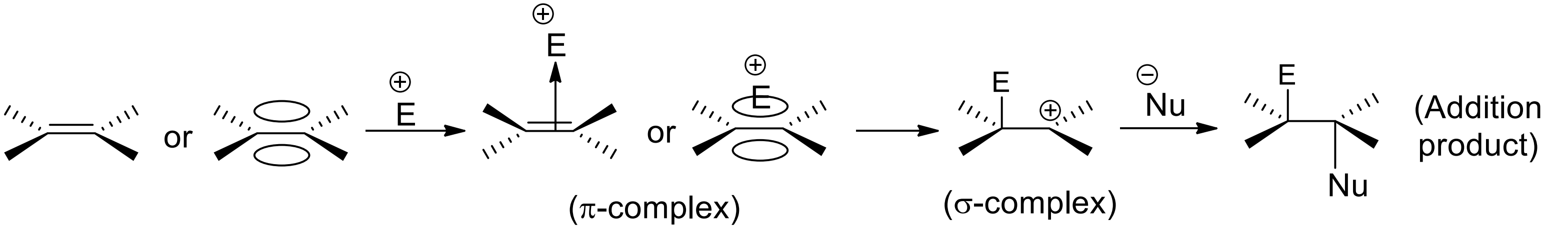
- E1cb shows second order Kinetics: rate = k[RX][base]

- E1cb mechanism is not observed with simple alkyl halides or sulfonates. It is more likely to be involved when the leaving group is ß to a carbonyl, nitro, cyano, sulfinyl, or other carbanion-stabilizing group.

Properties of alkenes:

- π-bond of an alkene is composed of loosely-bound electron cloud and therefore reaction on alkenes initiates on the π-bond, generally by an electrophile and results in net addition across the double bond. Such reactions are known as "**electrophilic addition**", as they are initiated by electrophiles.

- Mechanistically, the electrophile (E) initially gets attracted by the π-electron cloud and sits there, forming a π-complex. It eventually turns into a σ-complex, when the π-bond breaks and finally, the σ-complex gets attacked by a nucleophile (Nu) to form the E-Nu addition product.

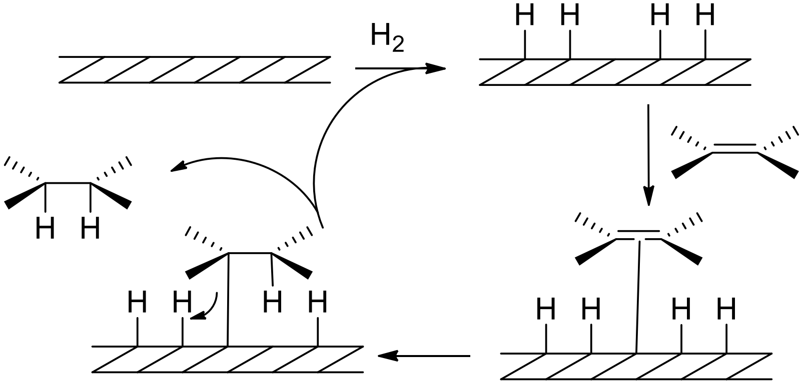


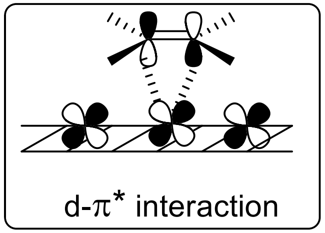
- Since, two σ-bonds were produced, at the expense of one π-bond, ΔH is < 0 and the electrophilic addition reaction on alkene is energetically favorable. However, in this reaction ΔS is also < 0, i.e. entropically unfavorable, as two molecules combine together to produce one addition product.

1. Hydrogenation: Mechanism:

- Metals, such as Ni, Pd, Pt etc., in presence of H_2 reduces alkenes in cis-manner into an alkane.

- The most commonly used reagent is Raney Nickel, which is prepared by dissolving 50:50 Ni-Al alloy in NaOH.

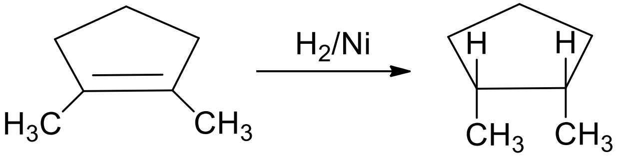




During dissolution, $NaAlO_2$ and H_2 areproduced and the H_2 gets adsorbed by Ni-surface. When alkene is added, through d-π^* interaction, the alkene interacts with the Ni-surface and hydrogen adds to it from one face, i.e. adds up in cis-fashion. When, Pd/Pt is used, alkene reacts in same fashion.

Stereochemistry of hydrogenation:

- Ni/Pd/Pt-catalysed hydrogenation occurs in cis-fashion and is proved by configuration of the product.



- A cis-product. So, hydrogens were added in cis-manner.

Energetics of hydrogenation:

1 x C=C bond energy = 147.6 Kcal/mole

1 x H-H bond energy = 104.2 Kcal/mole

So, energy required to break these bonds

= (147.6+104.2) = 251.8 Kcal/mole

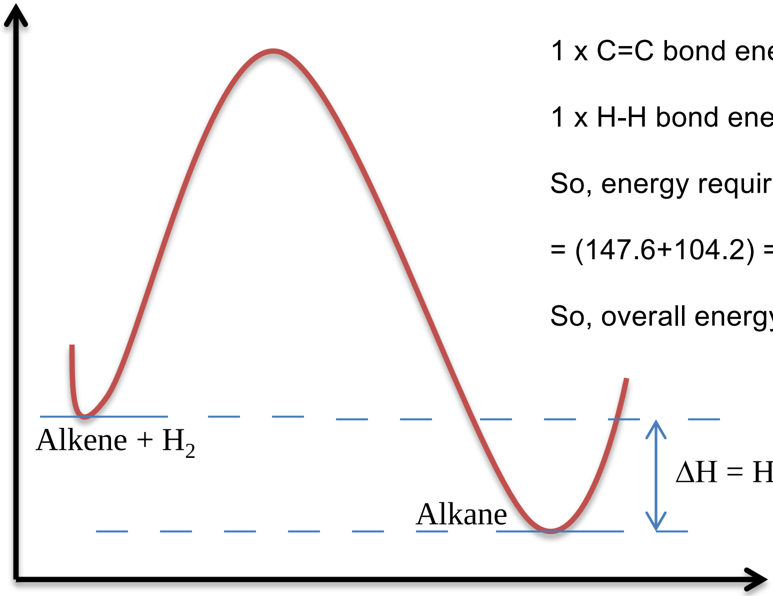
1 x C-C bond energy = 83.3 Kcal/mole

2 x C-H bond energy = 2 x 99.4 = 198.8 Kcal/mole

So, energy released, on formation of these bonds

= - (83.3 +198.8) = - 282.1 Kcal/mole

So, overall energy released = (251.8 - 282.1) = - 30.3 Kcal/mole



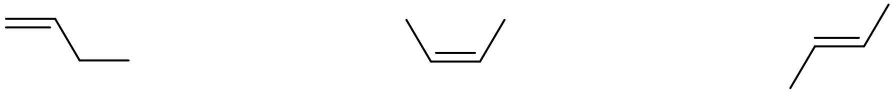
ΔH = Heat of hydrogenation = Energy released during hydrogenation

- Now, heat of hydrogenation = measure of stability of the alkene. Because, higher the stability of alkene, lower is its position in the energy profile diagram = lower is the difference in energy between alkene and alkane = lower is the heat of hydrogenation.

- Heat of hydrogenations of 1-butene, *cis*-2-butene and *trans*-2-butene were found to be -30.3, -28.6 and -27.6 Kcal/mole, respectively.

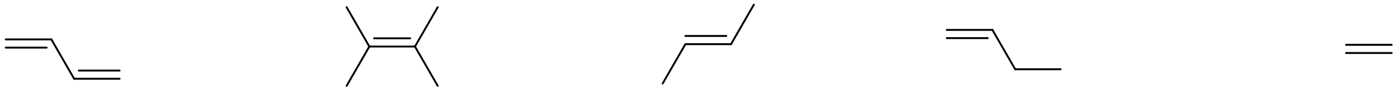
- This result is in accordance with our idea that, more substituted alkenes (*cis*-2-butene and *trans*-2-butene) are more stable than less substituted alkenes (1-butene), due to hyperconjugation.

- Also, cis-alkenes are less stable than trans alkene, which is expected due to steric crowding of cis-groups in cis-alkene.



$\Delta H_{hydrogenation}$ -30.3 Kcal/mole -28.6 Kcal/mole -27.6 Kcal/mole

- It is also interesting to note that, on going down the following series of alkenes, the heat of hydrogenation increases. This is expected because, conjugation provides more space for electron delocalization and therefore imposes more stabilization than hyperconjugation. Since, butadiene is a conjugated system, it is expected to be most stable.



Conjugated system

12 hyperconjugative hydrogens

6 hyperconjugative hydrogens

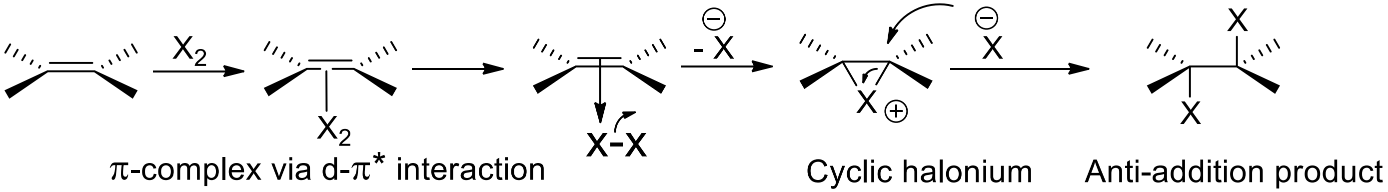
2 hyperconjugative hydrogens

no hyperconjugative hydrogens

$\Delta H_{hydrogenation}$ increases, i.e alkene stability decreases

2. **Halogenation**: Mechanism:

- Chlorine/bromine in presence of CCl_4, adds across the alkene double bond in trans-fashion, to produce vicinal-dihalides.

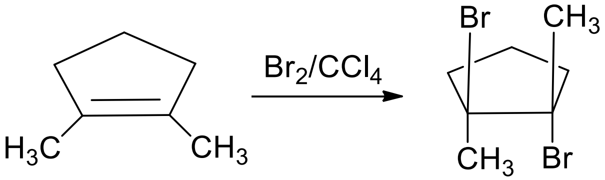


- Halogen "*d*-orbital" and alkene π*-orbitals, having similar symmetry, interacts with each other and forms a π-complex, which rearranges into a cyclic halonium ion.

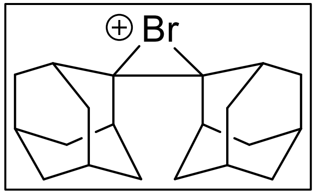
- In order to release the ring strain, the three-membered cyclic halonium ion easily gets attacked from backside in S_N2-manner by the halide, produced during halonium ion formation.

Evidence:

- Such anti-addition is evident by the configuration of bromination product of the following alkene.



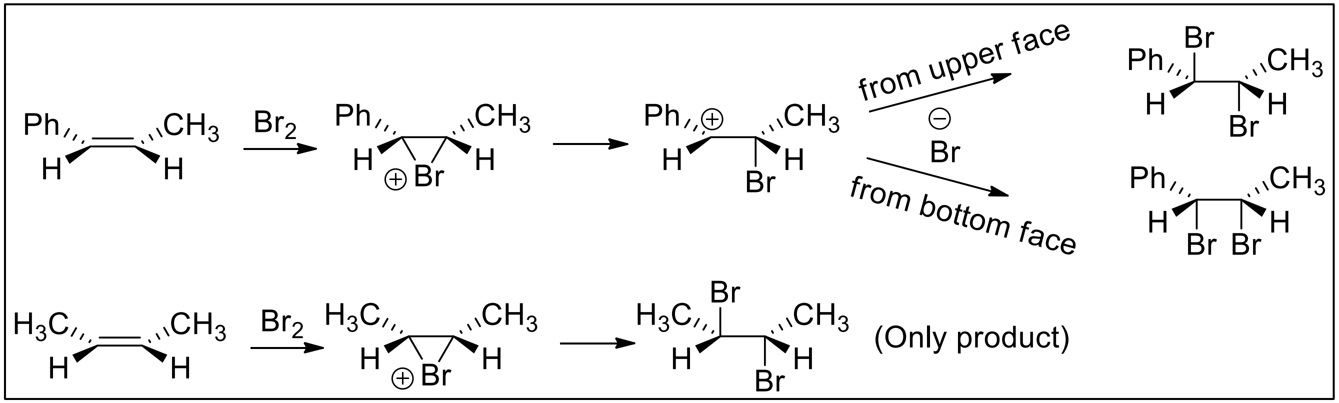
- A trans-product. So, bromines were added in trans-manner.



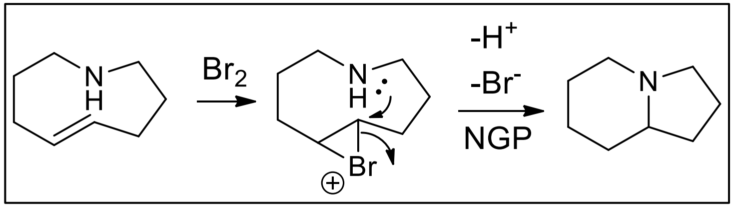
- Also, when backside attack is blocked, cyclic brominum could be isolated. For example, cage-like structure in following system has hindered the backside attack and allowed the isolation of the cyclic bromonium ion.
- However, chlorine being a more reactive substrate, it's addition is less selective than bromination.

Examples:

- Selective anti-bromine addition is basically the result of backside attack on intermediate bromonium ion. But, substrates like 1-phenylpropene takes a different course. Here cyclic bromonium can transform in to a classical carbocation, due to the high stability of benzylic carbocations, before the bromoniums could be quenched by the bromide. Now, carbocations being planar, are capable of being attacked by the bromide from both the faces, producing both syn- and anti-dibromides. So, overall we get ~ 70% anti-selectivety. However, 2-butuenes can't can't produce such highly stable carbocations and therefore follows the cyclic bromonium pathway only, giving 100% anti-selectivity.



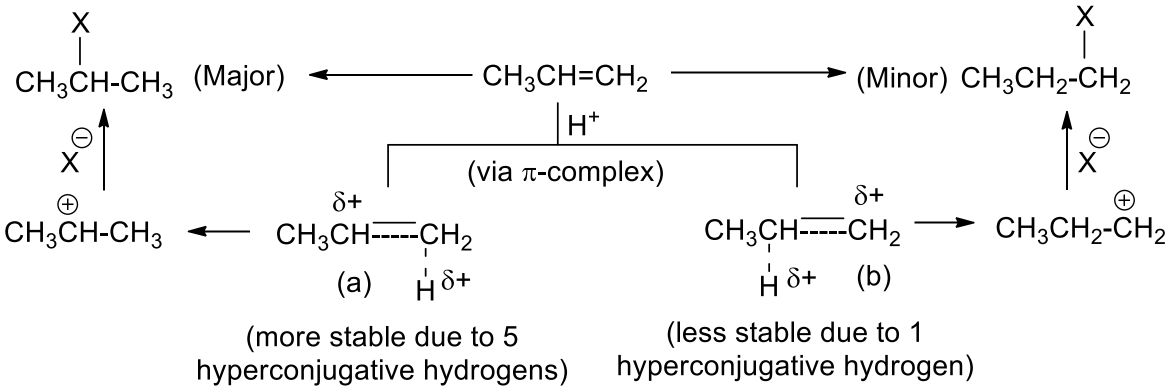
- Another interesting example is the NGP of ring nitrogen to quench the bromonium into a monobromide

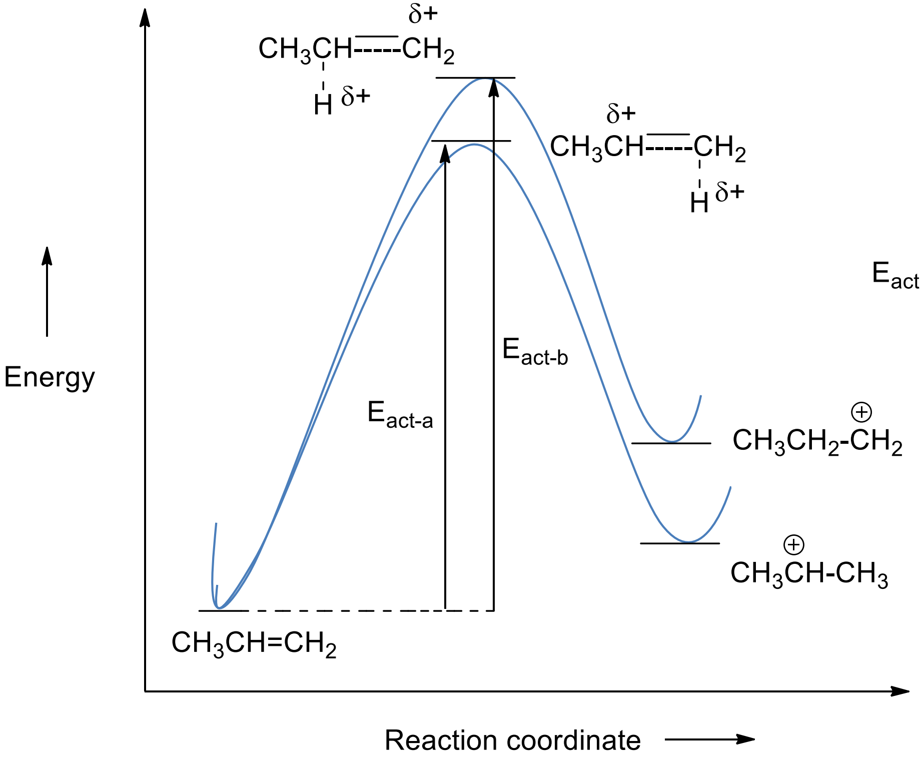


3. H-X addition:

- Alkenes, being a source of loosely bound pi-cloud, is a soft-reaction site and prefers soft electrophiles. So, HX addition reaction is generally performed by passing HX gas or by adding HX in AcOH, in abence of water. Because, HX produces hard electrophile H^+, which prefers hard oxygen center of water. But, in water-free condition, it has no choice but to attack soft alkene.

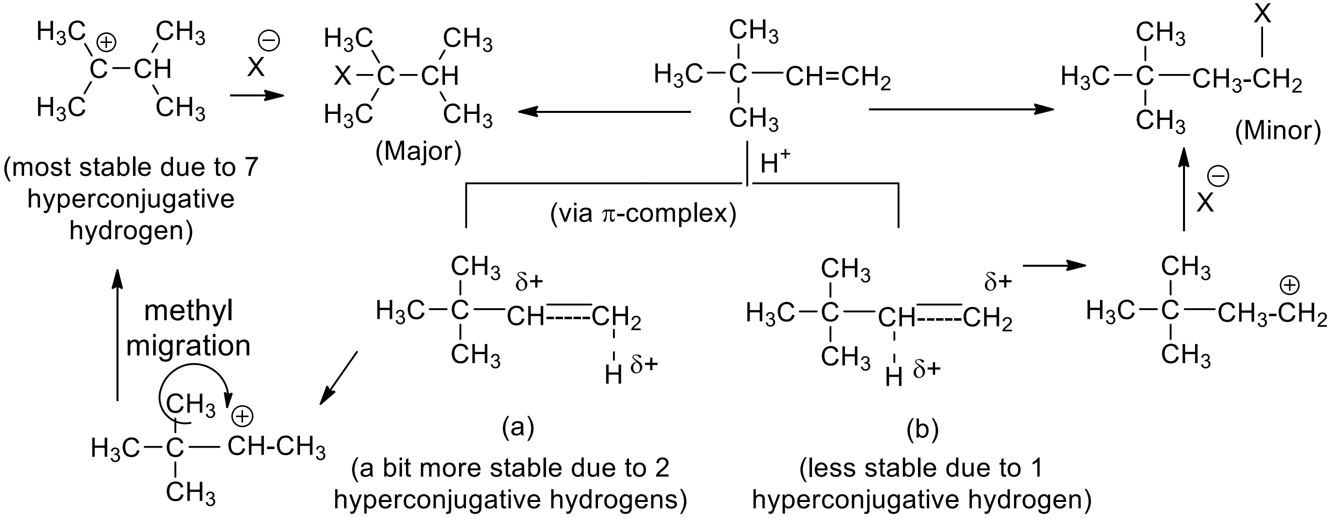
- The reaction proceeds through carbocation intermediate and the carbocation formation step is the r.d.s. This is why unsymmetrical alkenes may lead to two incipient carbocations, but the more stable one. i.e., the more substituted one prevails and produces the corresponding halide. This is in accordance with **“Markownikoff’s rule”..**

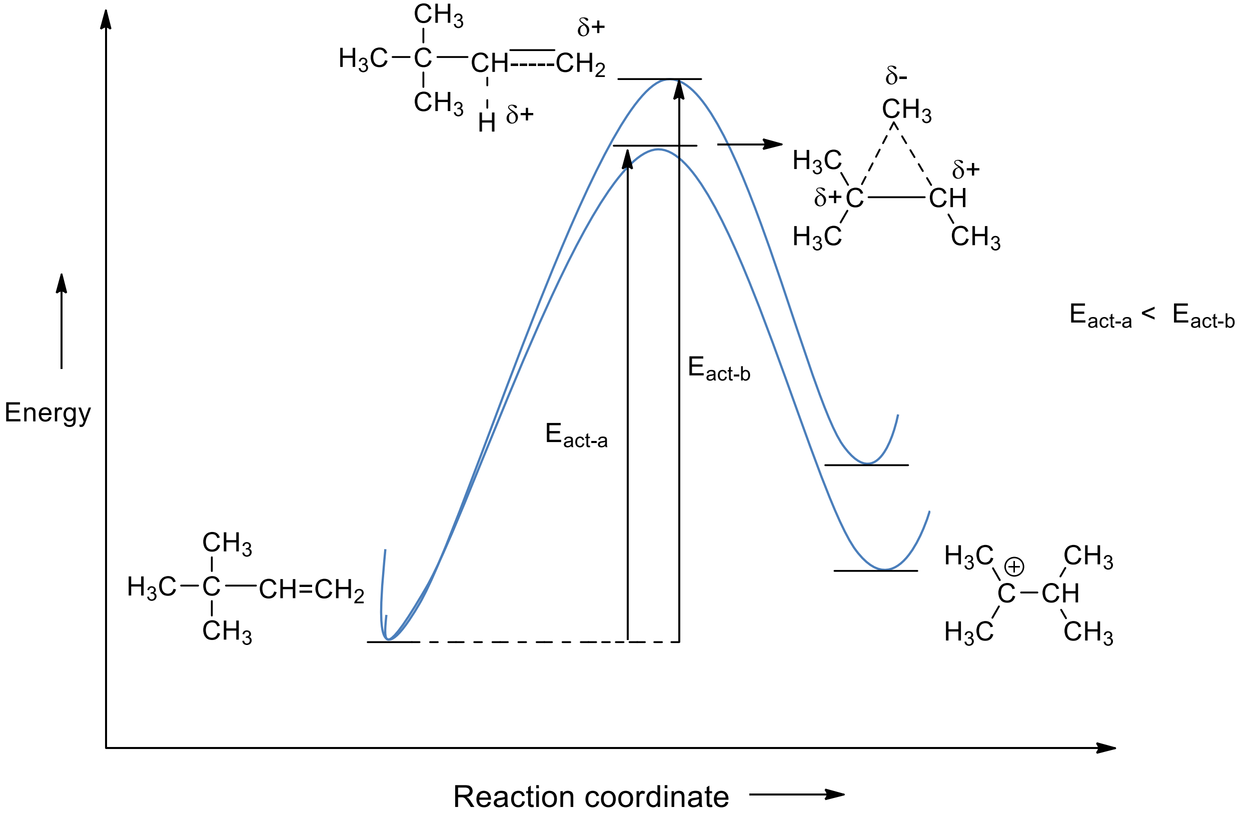




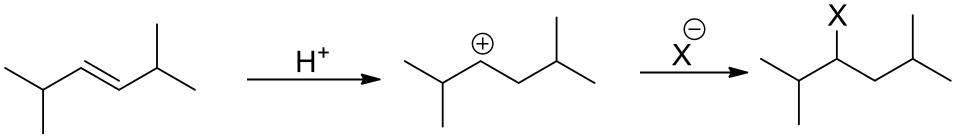
- However, sometimes rearrangements also occur to produce more stable incepient carbocations, leading to rearranged halide products.

- Now, more substituted alkene will form more substituted and therefore more stabilized carbocation. We also know that, both alkene and carbocation are stabilized by hyperconjugation, but the extent of stabilization is more in carbocations. So, energy difference between incipient carbocations will be even more than that between ground state alkenes. So, more substituted alkenes are generally more reactive.



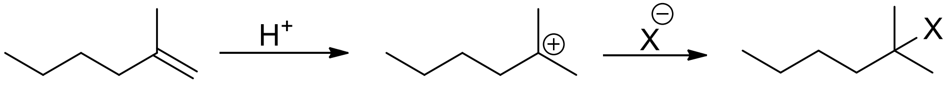


- However, in the above argument, substitution must be present at the alkene double bond and not on any other part of the alkene. Because, following is an interesting example, where a more branched but less stabilized and less reactive alkene is often misinterpreted as more substituted alkene, which apparently defies the earlier statement, which is not the fact.



more branched, and less stabilized by 2 hyperconjugative -H, but not more substituted

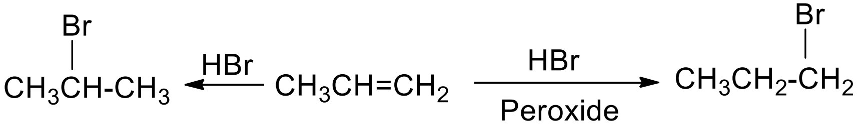
less stable, with 3 hyperconjugative -H



less branched, and more stabilized by 5 hyperconjugative -H, but not less substituted

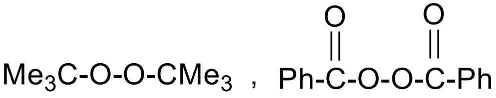
more stable, with 8 hyperconjugative -H

- HBr, under normal condition also follows the Markownikoff's addition rule. However, in presence of peroxides (as low as 0.01 mole), the opposite regioselectivity is seen, known as peroxide effect / anti-markownikoff's addition / Kharash addition. This is because, in presence of peroxide, HBr addition proceeds through radical pathway as follows. Of course, attack of Br-radical, leading to the formation of alkyl-radical is the r.d.s., and proceeds with preferential formation of more stabilized and therefore more substituted radical, which explains the anti-markownikoff's addition



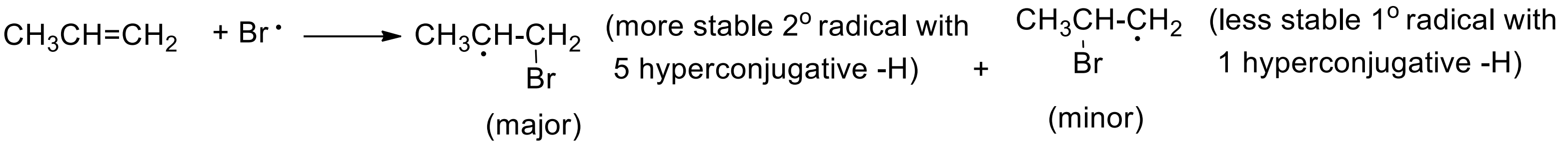
$$CH_3\overset{\overset{Br}{|}}{C}H\text{-}CH_3 \xleftarrow{HBr} CH_3CH{=}CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3CH_2\text{-}\overset{\overset{Br}{|}}{C}H_2$$

Some commonly used peroxides:



$$Me_3C\text{-}O\text{-}O\text{-}CMe_3\ ,\ Ph\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}Ph$$

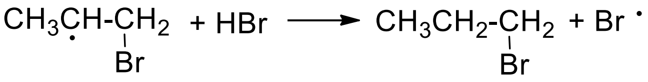
Chain initiation: $RO\text{-}OR \xrightarrow{\text{Heat or } h\nu} RO\cdot$ $\quad RO\cdot + HBr \longrightarrow ROH + Br\cdot$



Chain propagation: $CH_3CH{=}CH_2 + Br\cdot \longrightarrow CH_3\underset{\cdot}{C}H\text{-}\underset{\overset{|}{Br}}{CH_2}$ (more stable 2^o radical with 5 hyperconjugative -H) + $CH_3\underset{\overset{|}{Br}}{CH}\text{-}\underset{\cdot}{C}H_2$ (less stable 1^o radical with 1 hyperconjugative -H)

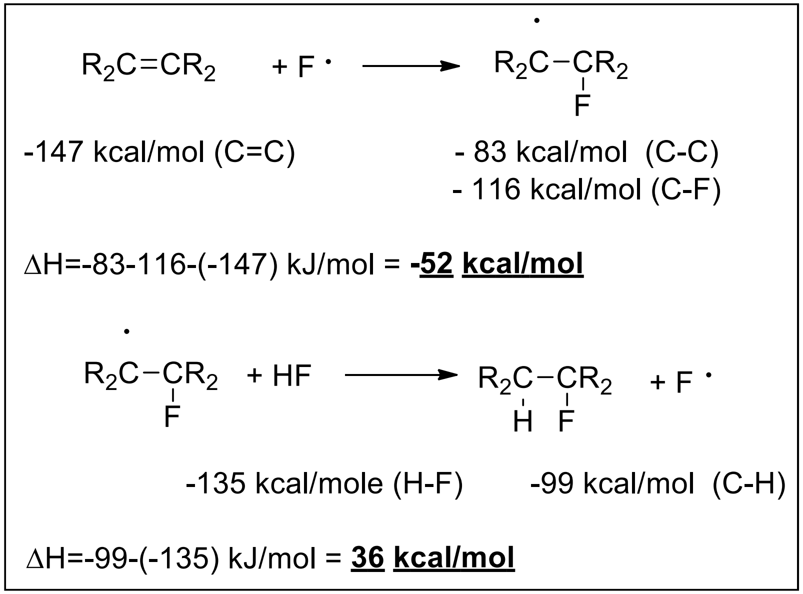
(major)

(minor)



$$CH_3\underset{\cdot}{C}H\text{-}\underset{\overset{|}{Br}}{CH_2} + HBr \longrightarrow CH_3CH_2\text{-}\underset{\overset{|}{Br}}{CH_2} + Br\cdot$$

- Note that, only in case of HBr, both the steps of chain propagation are energetically favorable, as obvious from the following enthalpy changes of both the steps of HF / HCl / HBr / HI-addition.



$$R_2C{=}CR_2 + F^{\bullet} \longrightarrow R_2\overset{\bullet}{C}-\underset{F}{CR_2}$$

-147 kcal/mol (C=C)

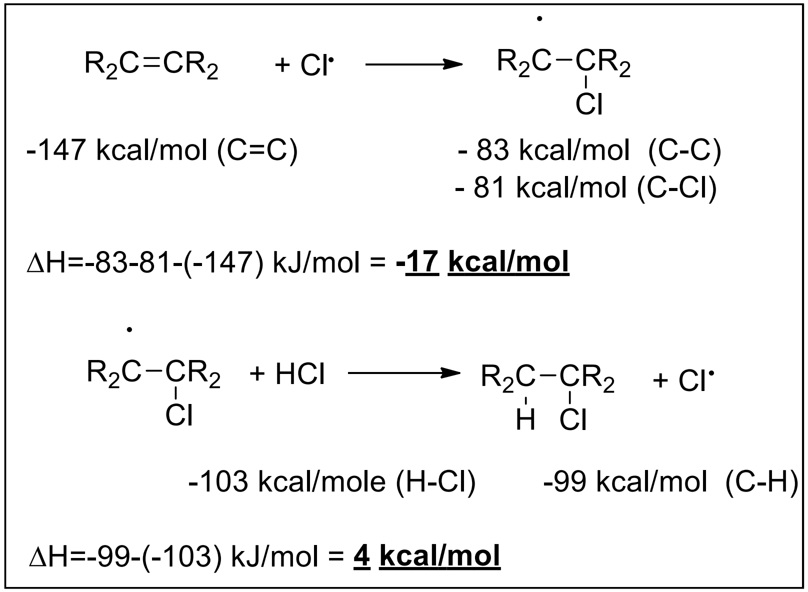
- 83 kcal/mol (C-C)
- 116 kcal/mol (C-F)

ΔH=-83-116-(-147) kJ/mol = **-52 kcal/mol**

$$R_2\overset{\bullet}{C}-\underset{F}{CR_2} + HF \longrightarrow R_2\underset{H}{C}-\underset{F}{CR_2} + F^{\bullet}$$

-135 kcal/mole (H-F)   -99 kcal/mol (C-H)

ΔH=-99-(-135) kJ/mol = **36 kcal/mol**



$$R_2C{=}CR_2 + Cl^{\bullet} \longrightarrow R_2\overset{\bullet}{C}-\underset{Cl}{CR_2}$$

-147 kcal/mol (C=C)

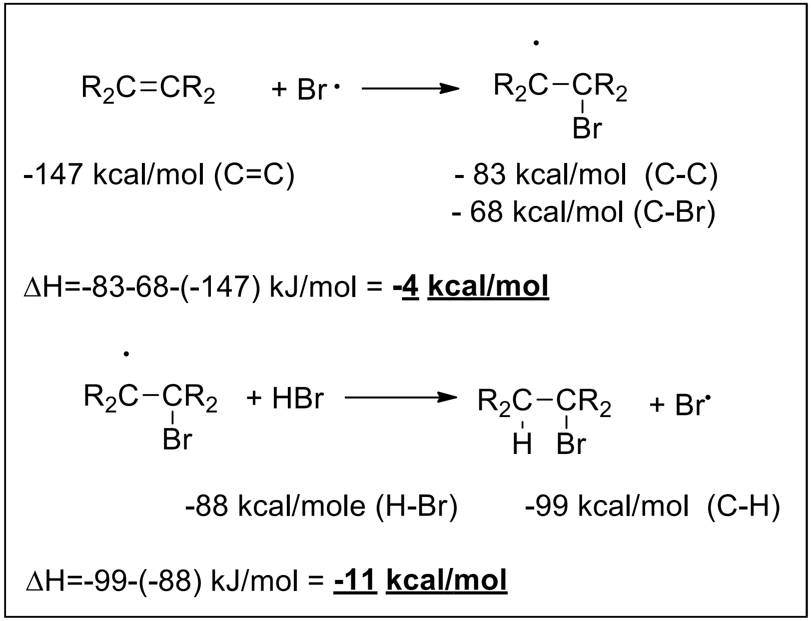
- 83 kcal/mol (C-C)
- 81 kcal/mol (C-Cl)

ΔH=-83-81-(-147) kJ/mol = **-17 kcal/mol**

$$R_2\overset{\bullet}{C}-\underset{Cl}{CR_2} + HCl \longrightarrow R_2\underset{H}{C}-\underset{Cl}{CR_2} + Cl^{\bullet}$$

-103 kcal/mole (H-Cl)   -99 kcal/mol (C-H)

ΔH=-99-(-103) kJ/mol = **4 kcal/mol**



$$R_2C{=}CR_2 + Br^{\bullet} \longrightarrow R_2\overset{\bullet}{C}-\underset{Br}{CR_2}$$

-147 kcal/mol (C=C)

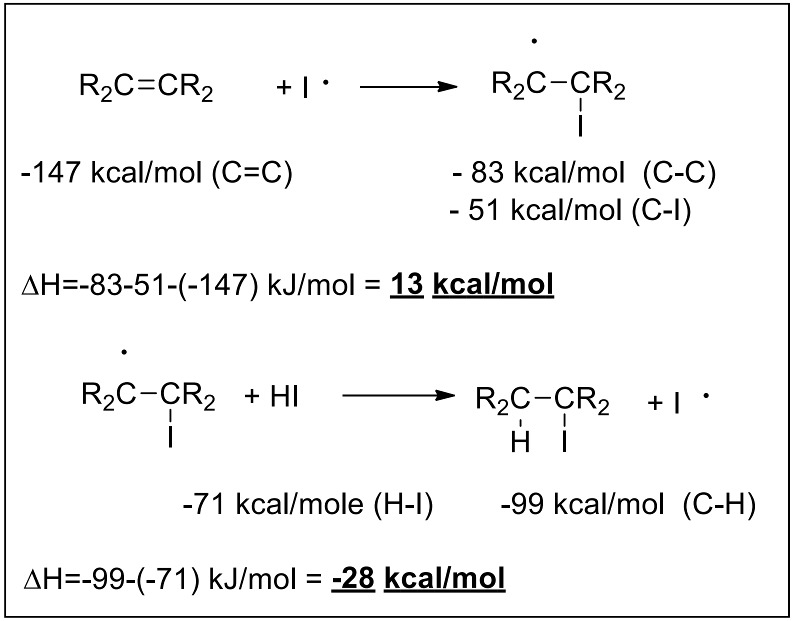
- 83 kcal/mol (C-C)
- 68 kcal/mol (C-Br)

ΔH=-83-68-(-147) kJ/mol = **-4 kcal/mol**

$$R_2\overset{\bullet}{C}-\underset{Br}{CR_2} + HBr \longrightarrow R_2\underset{H}{C}-\underset{Br}{CR_2} + Br^{\bullet}$$

-88 kcal/mole (H-Br)   -99 kcal/mol (C-H)

ΔH=-99-(-88) kJ/mol = **-11 kcal/mol**



$$R_2C{=}CR_2 + I^{\bullet} \longrightarrow R_2\overset{\bullet}{C}-\underset{I}{CR_2}$$

-147 kcal/mol (C=C)

- 83 kcal/mol (C-C)
- 51 kcal/mol (C-I)

ΔH=-83-51-(-147) kJ/mol = **13 kcal/mol**

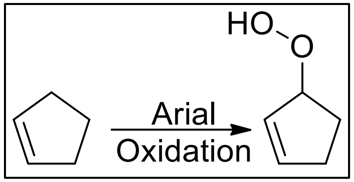
$$R_2\overset{\bullet}{C}-\underset{I}{CR_2} + HI \longrightarrow R_2\underset{H}{C}-\underset{I}{CR_2} + I^{\bullet}$$

-71 kcal/mole (H-I)   -99 kcal/mol (C-H)

ΔH=-99-(-71) kJ/mol = **-28 kcal/mol**

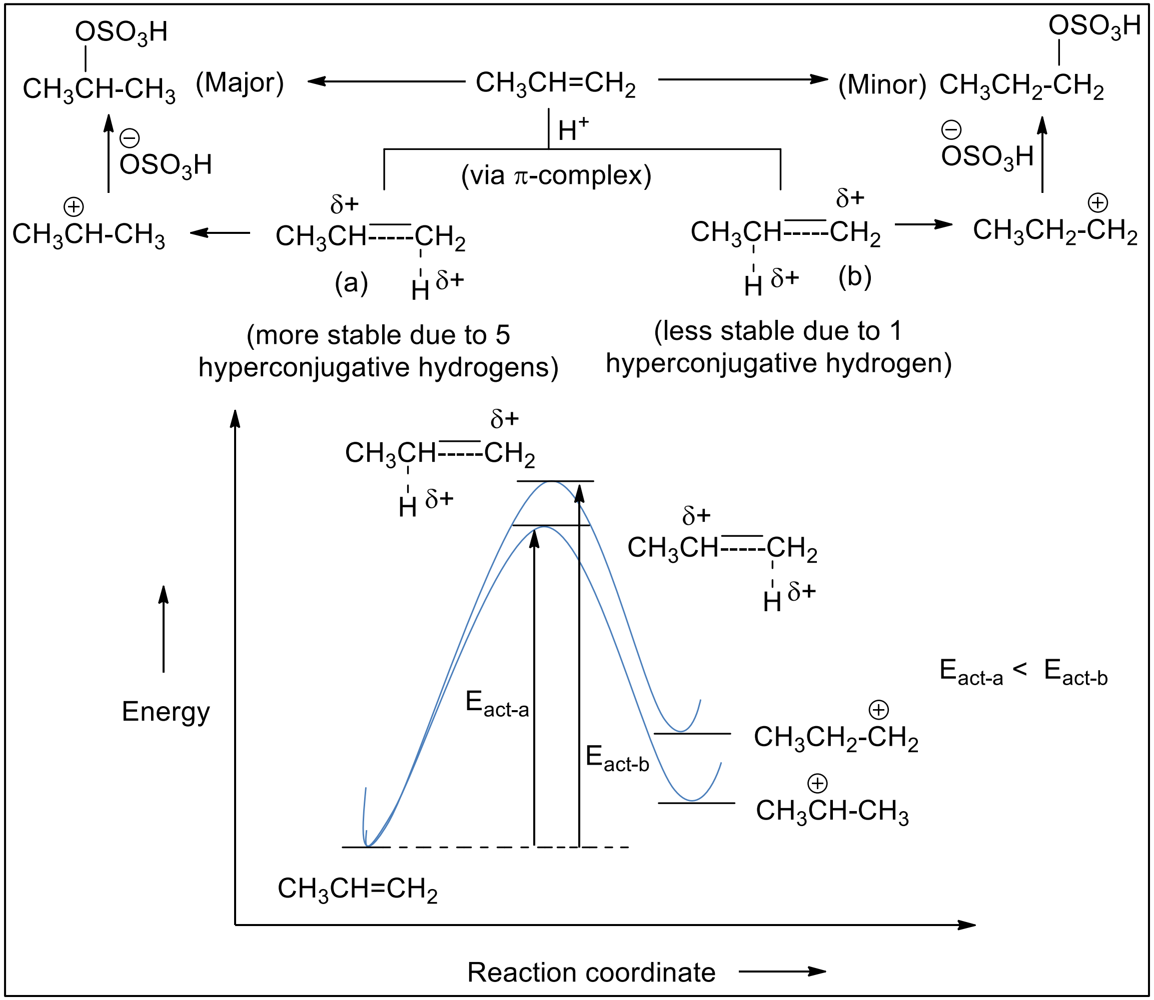
- However, the second step of HCl addition is only weakly unfavorable enthalpically. Now, in the second step of the chain propagation, HCl is consumed. So, introduction of more HCl in the system will drive the equilibrium towards right. So, under high HCl concentration, HCl also shows peroxide effect.

- Sometimes, even in absence of peroxide, anti-markownikoff's addition takes place. This is because, alkenes get aerially oxidized to alkene peroxides, which trigger the anti-markownikoff's addition



4. **Hydration of alkenes:**

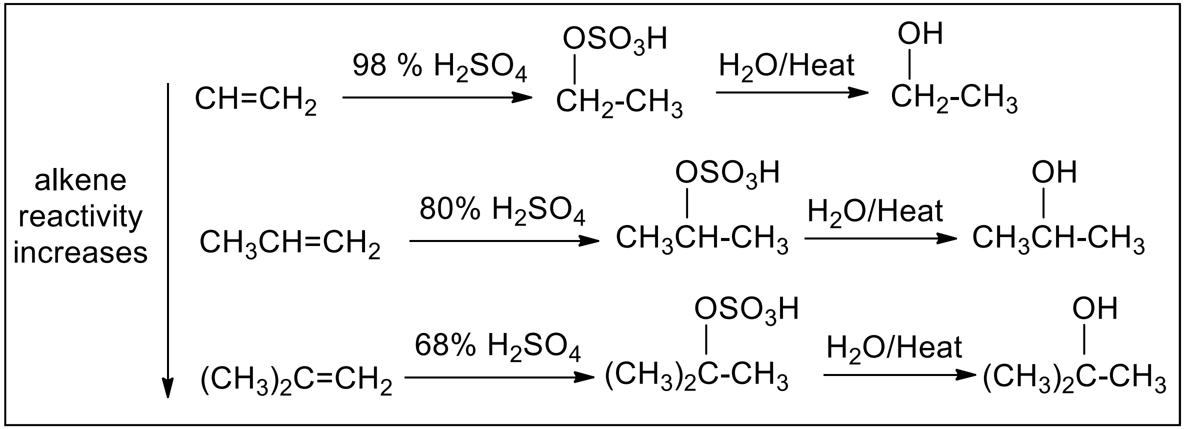
i) H_2SO_4 treatment and acidic water treatment:



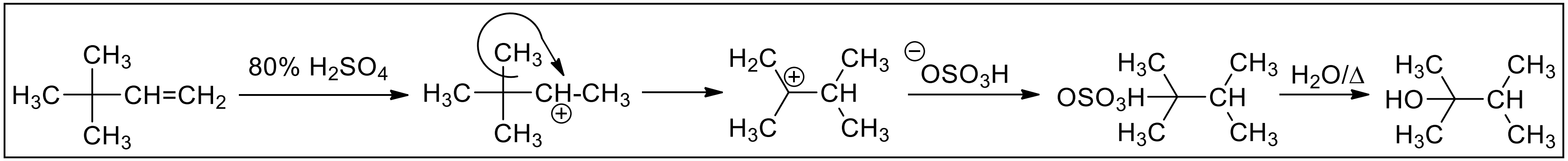
- Addition of H_2SO_4, to give alkyl hydrogen sulphates, by treatment with conc. H_2SO_4, can be considered as addition of H-X (H-HSO_4) and proceeds through carbocation intermediate. Therefore, rearrangements are often observed, if more stable carbocation could be formed.

- The alkyl hydrogen sulphates being soluble in both H_2SO_4 and water, this reaction is used to remove alkene impurity from alkanes and to separate alkane-alkene mixture, by passing through conc. H_2SO_4. After separating them, the alkene can also be reproduced by heating the alkyl hydrogen sulphate.

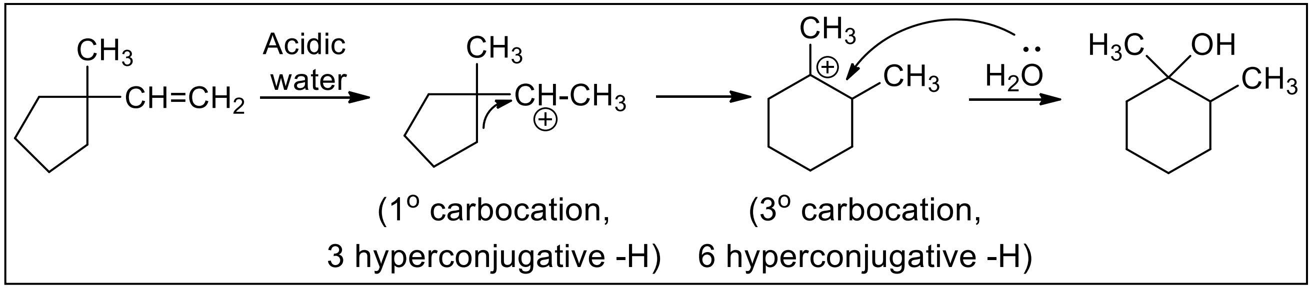
- The alkyl hydrogen sulphates, on heating with water, gives an alcohol. So, overall a hydration process accross the alkene double bond takes place, to form an internal alcohol.

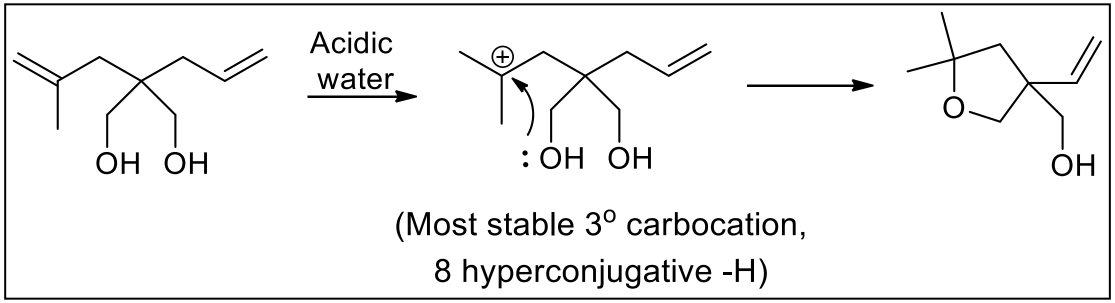


- Of course, more substituted alkenes react more rapidly, as obvious from the decreasing concentration of required H_2SO_4 , in the above series of reactions with different alkenes. Therefore, simple acidic waters can also hydrate an alkene, but could only be observed with highly substituted/stabilized alkenes.



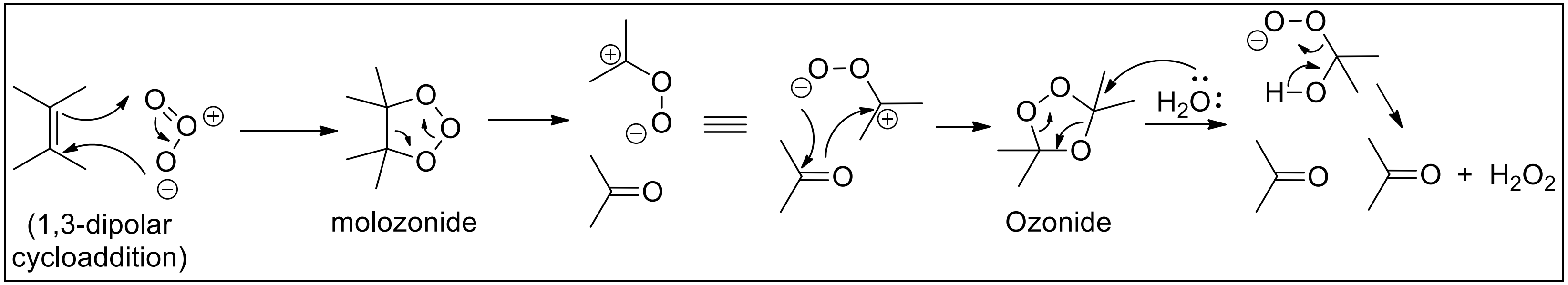
- Also, alkenes capable of forming stable carbocations, by rearrangement, also reacts with H_2SO_4 and acidic water and sometimes produces ring-expanded or ring-closed products too.



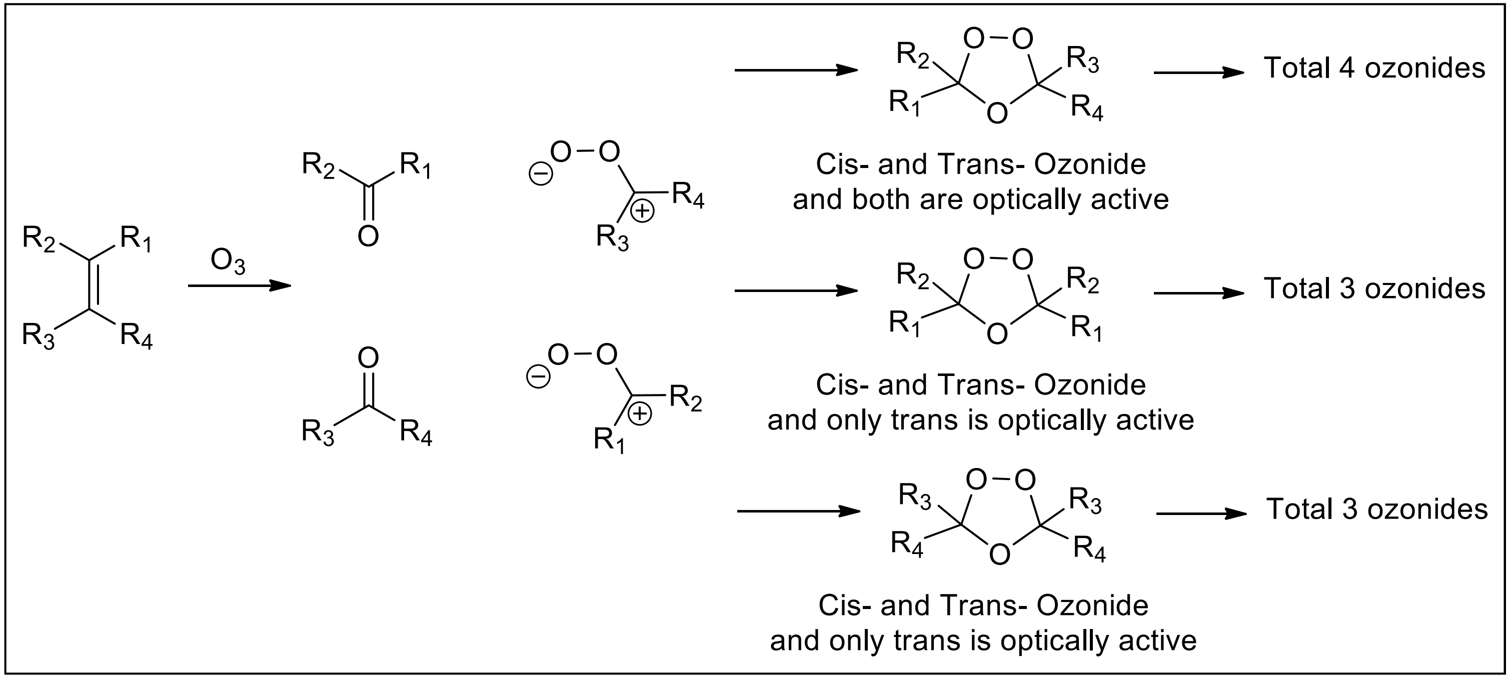


5. **Ozonolysis:**

- Ozone, in an inert solvent (such as CCl_4, $CHCl_3$, CH_2Cl_2 etc.) reacts with alkene to give an ozonide, through a 1,3-dipolar cycloaddition, which on hydrolysis, produces carbonyl compounds and H_2O_2. The process is known as ***ozonolysis***.



- Note that, in general there is a possibility of formation of 10 types of ozonides, during the reaction of ozone with an alkene having a generalised structure $R_1R_2C{=}CR_3R_4$.



Total 4 ozonides

Cis- and Trans- Ozonide and both are optically active

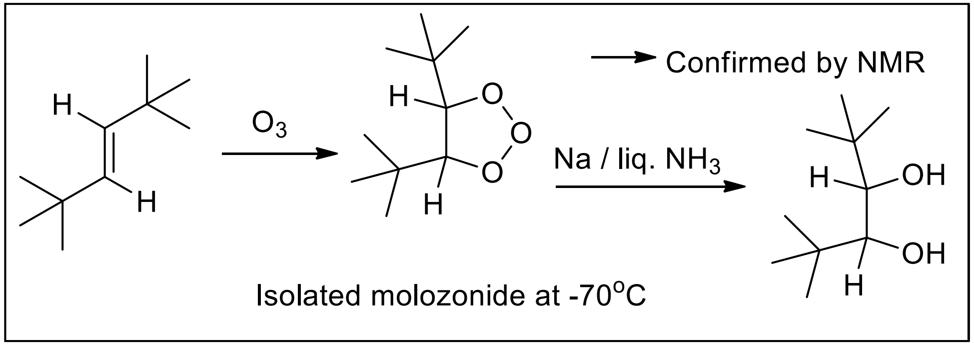
Total 3 ozonides

Cis- and Trans- Ozonide and only trans is optically active

Total 3 ozonides

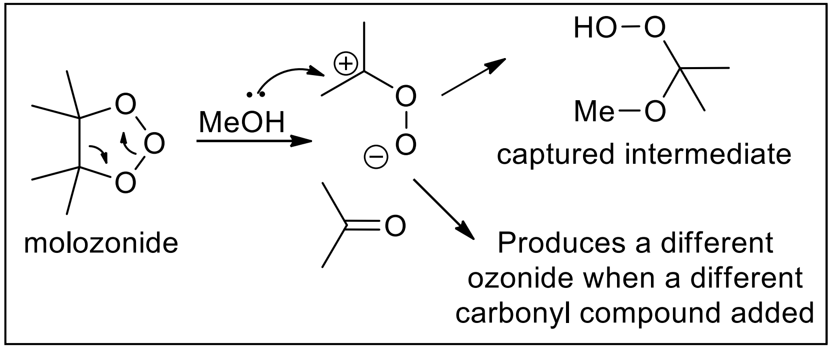
Cis- and Trans- Ozonide and only trans is optically active

- The mechanism is proved by, i) isolation of a crowded ozonide, ii) a solvent-captured intermediate by using MeOH, iii) formation of a different ozonide by external addition of a different carbonyl compound.



Confirmed by NMR

Isolated molozonide at -70°C



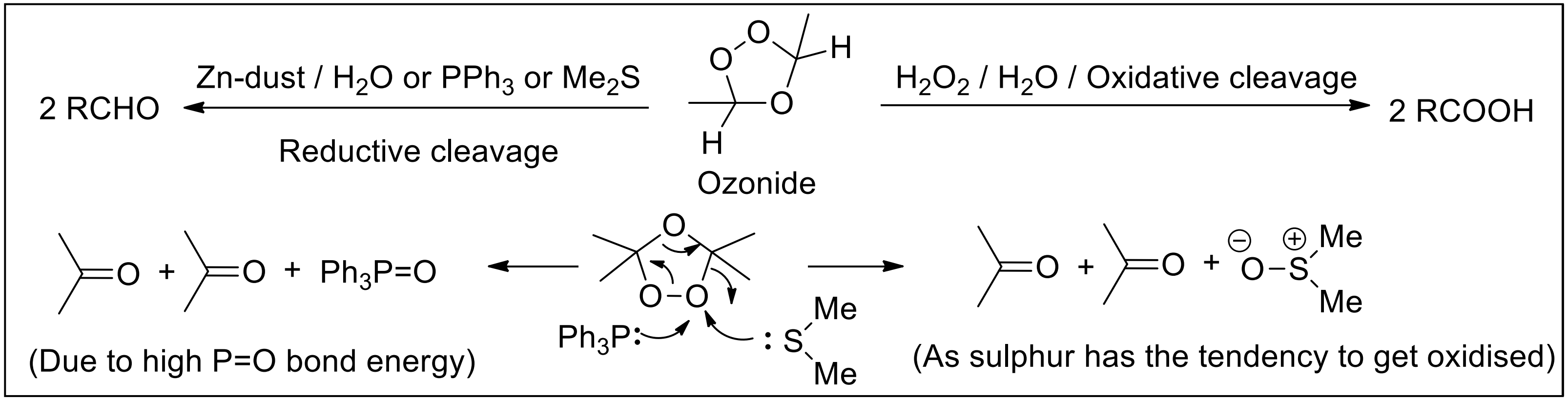
molozonide

captured intermediate

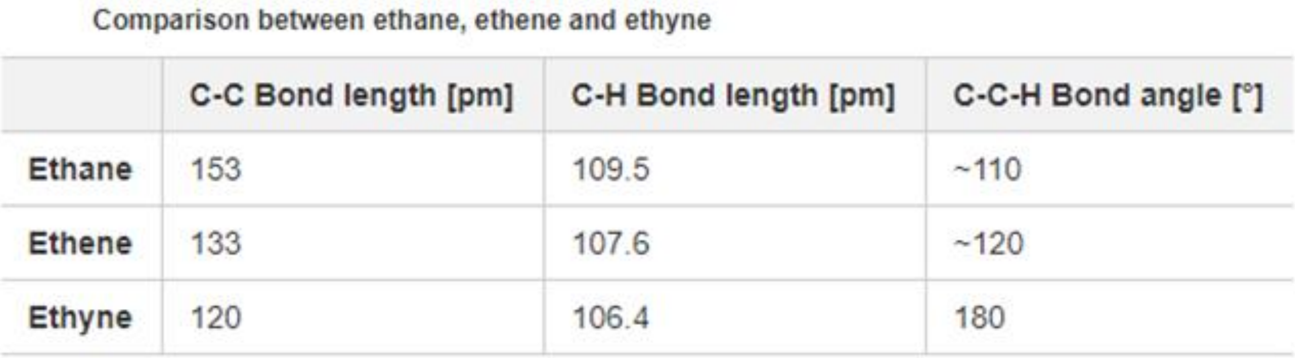
Produces a different ozonide when a different carbonyl compound added

- If product(s) is aldehyde, the produced H_2O_2 oxidizes it to carboxylic acid. To avoid this, Zn-dust is used, which decomposes H_2O_2.

- Sometimes Me_2S or PPh_3 is also used for reductive cleavage of ozonide and when carboxylic acid is needed, H_2O_2 is deliberately added from outside.

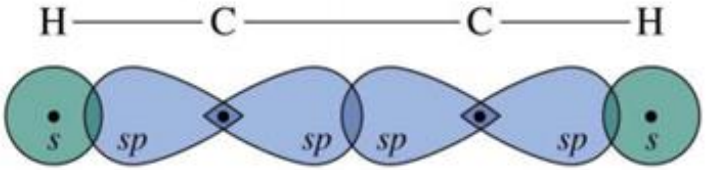


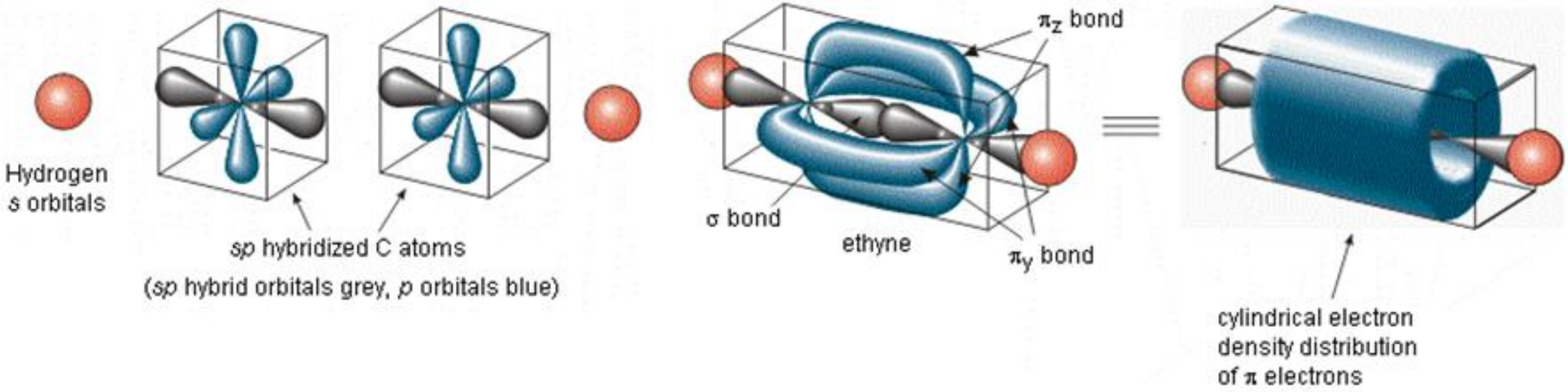
Basic structural details of alkynes:



Comparison between ethane, ethene and ethyne

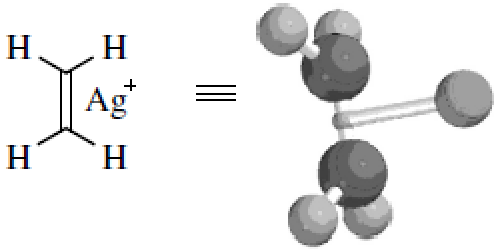
	C-C Bond length [pm]	C-H Bond length [pm]	C-C-H Bond angle [°]
Ethane	153	109.5	~110
Ethene	133	107.6	~120
Ethyne	120	106.4	180



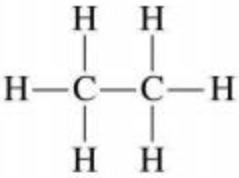
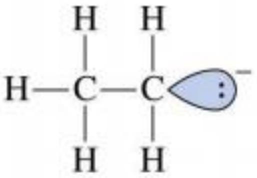
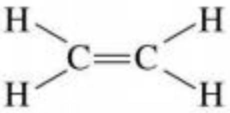
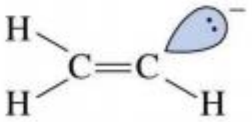
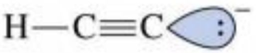


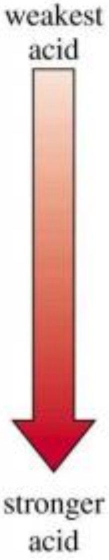
- More s character, so shorter length.
- Three bonding overlaps, so shorter.
- Higher s-character, so higher bond angle.

- Due to the presence of loosely bound pi-electron cloud in alkynes, they easily form Electron Donor–Acceptor (EDA) complexes with metal ions, such as Ag^+, Hg^{2+} etc.



- Terminal alkynes, R-C≡C-H, are more acidic than other hydrocarbons. Acetylene → acetylide can be done by NH_2^- , but not by OH^- or RO^- .
- Upon deprotonation, 1-alkynes do not form resonance-stabilized carbanions, but it is more stabilized than the carbanions from alkenes and alkanes, as the negative charge is contained in an Sp-orbital. More s character, so pair of electrons in anion is held more closely to the nucleus. Less charge separation, so more stable. So, alkynes are more acidic than alkanes and alkenes.

Compound	Conjugate Base	Hybridization	*s* Character	pK_a
		sp^3	25%	50
		sp^2	33%	44
$:NH_3$	$:\ddot{N}H_2^-$	(ammonia)		35
H—C≡C—H		*sp*	50%	25
R—OH	$R-\ddot{O}:^-$	(alcohols)		16–18



Methods of Preparation of Alkynes

Acetylene itself is formed from the reaction of the inorganic compound calcium carbide with water.

$CaC_2 + 2\,H_2O \rightarrow Ca(OH)_2 + HC\equiv CH$

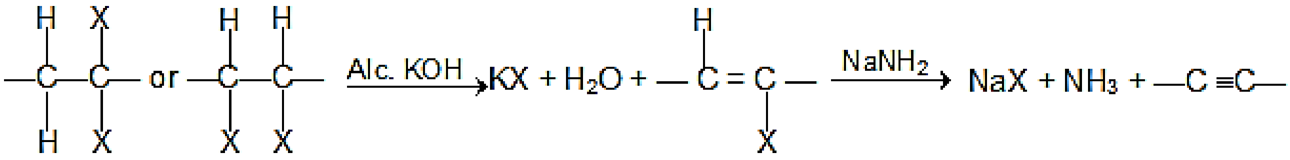
This method was once an important industrial process for the manufacture of acetylene. However, the method has now been replaced by a process in which methane is pyrolyzed in a flow system with short contact time.

$$2CH_4 \xrightarrow[0.01-0.1\ \text{sec.}]{1500^\circ C} HC\equiv CH + 3\,H_2$$

This reaction is endothermic at ordinary temperatures, but is thermodynamically favored at high temperatures.

- ## Laboratory Methods of Preparation of Alkynes:

1. Dehydrohalogenation of vic-Dihalides or gem-Dihalides



$$-\overset{H}{\underset{H}{C}}-\overset{X}{\underset{X}{C}}-\ \text{or}\ -\overset{H}{\underset{X}{C}}-\overset{H}{\underset{X}{C}}- \xrightarrow{\text{Alc. KOH}} KX + H_2O + -\overset{H}{C}=\underset{X}{C}- \xrightarrow{NaNH_2} NaX + NH_3 + -C\equiv C-$$

A gem-dihalide A vic - dihalide A vinyl halide

2. Dehalogenation of vic-Tetrahalogen Compounds

$$\underset{\text{2,2,3,3-Tetrabromobutane}}{CH_3-CBr_2-CBr_2-CH_3} + 2Zn \xrightarrow[\text{heat}]{\text{EtOH}} \underset{\text{2-butyne}}{CH_3-C\equiv C-CH_3} + 2ZnBr_2$$

This reaction has the drawback that the halogen compound is itself prepared by halogen addition to alkynes.

Reactions:

Forming Acetylide Ions: $CH_3{-}C{\equiv}C{-}H + NaNH_2 \longrightarrow CH_3{-}C{\equiv}C{:}^{-}\,Na^{+} + NH_3$

- Terminal alkynes form a precipitate with Ag(I) or Cu(I) salts.
- Internal alkynes do not react.
- Two uses: i) Qualitative test for terminal alkyne
  ii) Separation of a mixture of terminal and internal alkynes.

$$CH_3{-}C{\equiv}C{-}CH_3 \xrightarrow{Cu'} \text{No reaction}$$

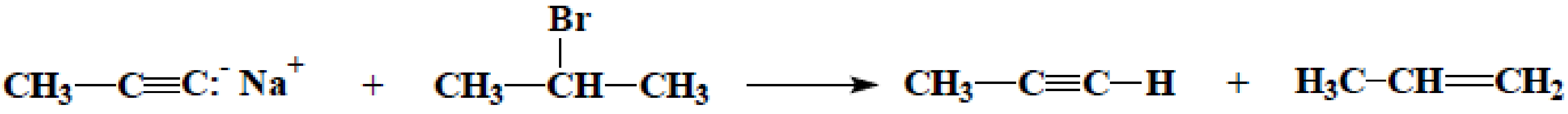
$$+$$

$$CH_3{-}CH_2{-}C{\equiv}C{-}H \xrightarrow{Cu^{+}} CH_3{-}CH_2{-}C{\equiv}C{-}Cu\downarrow$$

red-brown precipitate

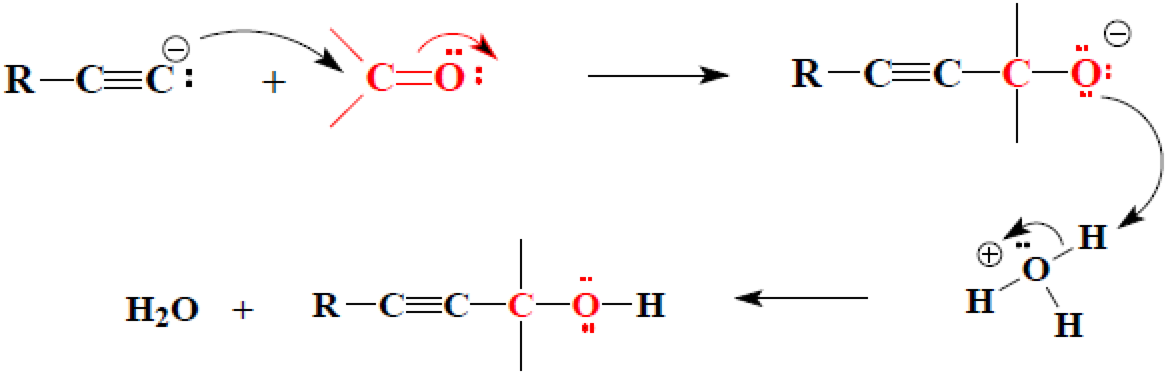
- Acetylide ions are good nucleophiles.
- S_N2 reaction with 1° alkyl halides lengthens the alkyne chain.
- Acetylide ions can also remove H^+.
- If back-side approach is hindered, elimination reaction happens via E2.

$$CH_3{-}C{\equiv}C{:}^{-}\,Na^{+} + CH_3CH_2{-}Br \longrightarrow CH_3{-}C{\equiv}C{-}CH_2{-}CH_3 + NaBr$$



$$CH_3{-}C{\equiv}C{:}^{-}\,Na^{+} + CH_3{-}\underset{}{\overset{Br}{\overset{|}{C}}}H{-}CH_3 \longrightarrow CH_3{-}C{\equiv}C{-}H + H_3C{-}CH{=}CH_2$$

- Acetylide ion adds to a carbonyl group to yield an alkynol. Both aldehyde and ketone participates in this reaction.



Addition Reactions:

- Similar to addition to alkenes
- Pi bond becomes two sigma bonds.
- Usually exothermic
- One or two molecules may add.

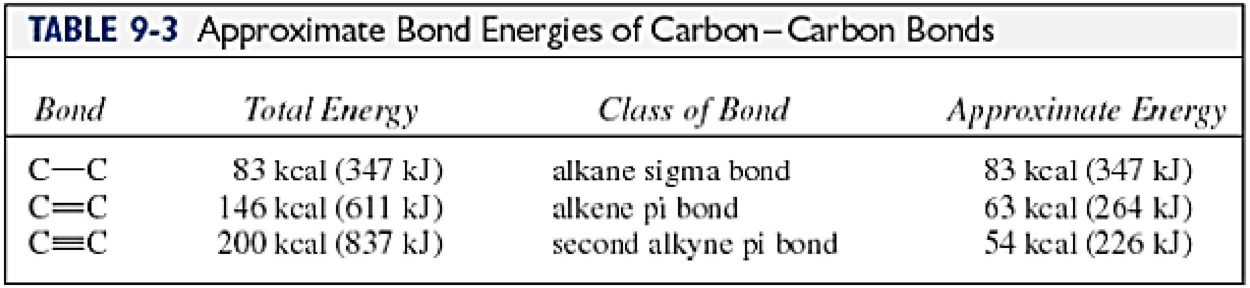


TABLE 9-3 Approximate Bond Energies of Carbon–Carbon Bonds

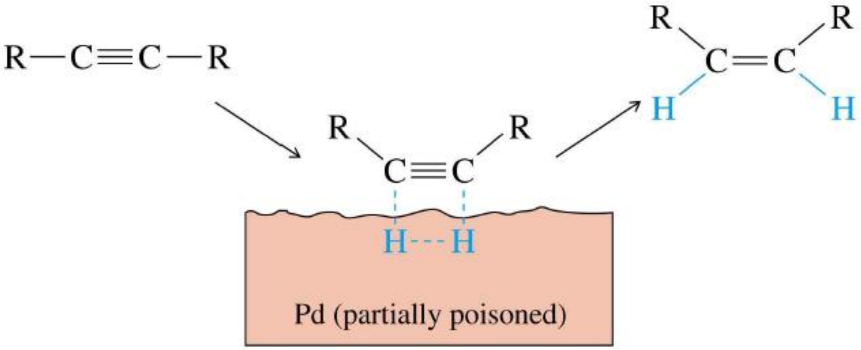
Bond	*Total Energy*	*Class of Bond*	*Approximate Energy*
C—C	83 kcal (347 kJ)	alkane sigma bond	83 kcal (347 kJ)
C=C	146 kcal (611 kJ)	alkene pi bond	63 kcal (264 kJ)
C≡C	200 kcal (837 kJ)	second alkyne pi bond	54 kcal (226 kJ)

Addition of Hydrogen: Three reactions:

- Add lots of H_2 with metal catalyst (Pd, Pt, or Ni) to reduce alkyne to alkane, completely saturated.
- Use a special catalyst, Lindlar's catalyst to convert an alkyne to a **cis**-alkene.
- React the alkyne with sodium in liquid ammonia to form a **trans**-alkene.

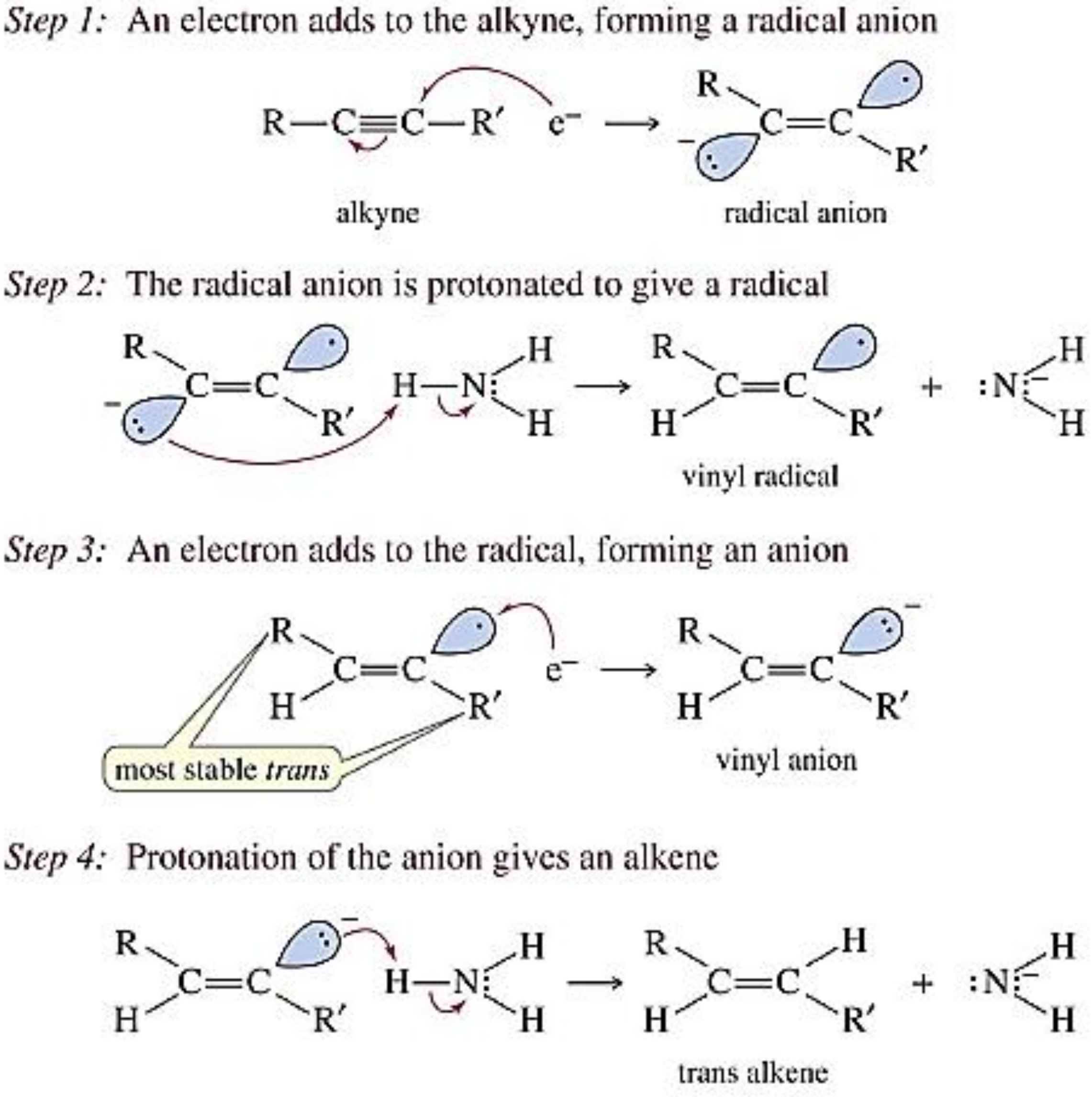
Lindlar's Catalyst: Powdered $BaSO_4$ coated with Pd, poisoned with quinoline.

- H_2 adds syn, so **cis**-alkene is formed



Na in Liquid Ammonia: $NH_3 + Na \longrightarrow NH_3{\cdot}e^- + Na^+$

- As sodium metal dissolves in the ammonia, it loses an electron.
- The electron is solvated by the ammonia, creating a deep blue solution.



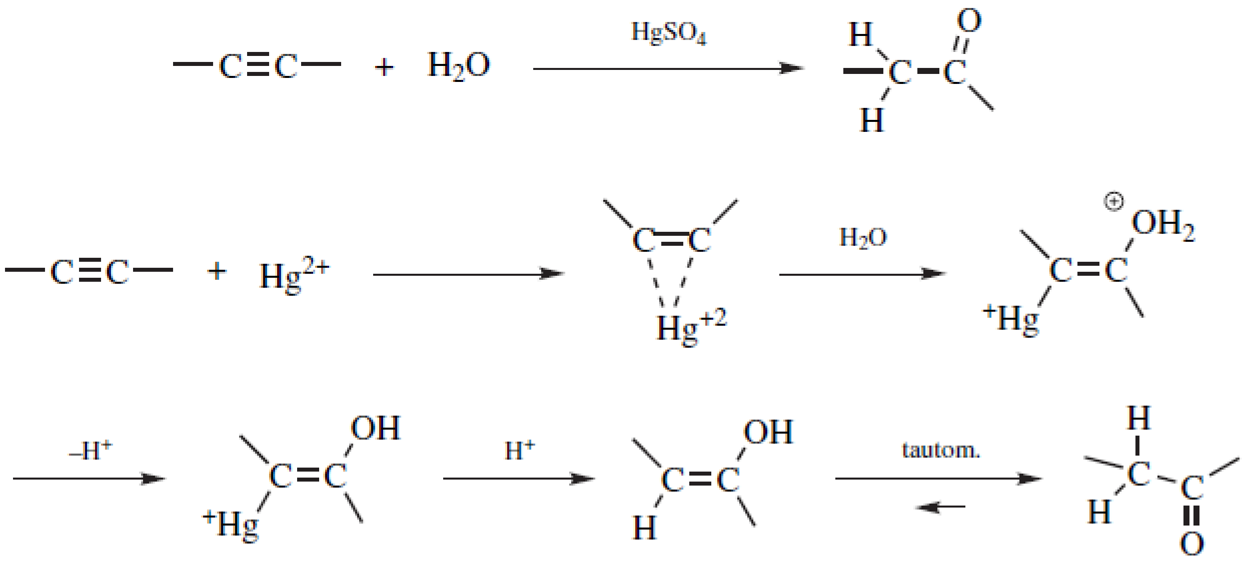
Step 1: An electron adds to the alkyne, forming a radical anion

Step 2: The radical anion is protonated to give a radical

Step 3: An electron adds to the radical, forming an anion

Step 4: Protonation of the anion gives an alkene

Hydration of Triple Bonds:



- The hydration of triple bonds is generally carried out with mercuric ion salts (often the sulfate or acetate) or Mercuric oxide in the presence of an acid.

- The first step of the mechanism is formation of a mercury-complex (soft-soft interaction between Hg^{2+} and alkynes).

- Water then attacks in an S_N2-type process and loses a proton to give an alkenyl-mercury intermediate, which upon hydrolysis gives the enol, which tautomerizes to the product.

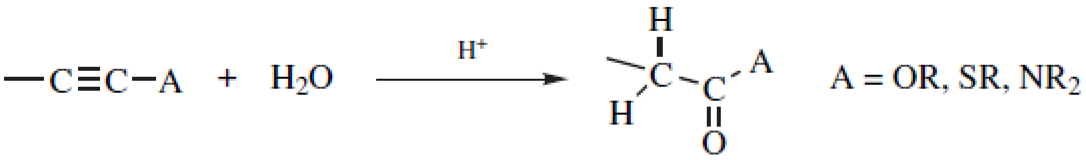
- Intermediacy of enol was confirmed by spectral analysis, when phenylacetylene was hydrated photolytically.

- The addition follows Markovnikov’s rule. So, only acetylene give an aldehyde. All other triple-bond compounds give ketones.

- With alkynes of the form RCCH, methyl ketones are formed almost exclusively, but with RCCR$'$ both possible products are usually obtained.

- The presence of certain functionality can influence the regioselectivity of hydration. 1-Seleno alkynes, such as PhSe-CC-Ph, react with tosic acid in dichloromethane to give a seleno ester PhSeC(O)CH$_2$Ph, after treatment with water.

- Carboxylic esters, thiol esters, and amides can be made, respectively, by acid-catalyzed hydration of acetylenic ethers, thioethers and ynamines, without a mercuric.



- It’s an ordinary electrophilic addition, with rate-determining protonation as the first step.

- Simple alkynes can also be converted to ketones by heating with formic acid, without a catalyst.