ALKENES

structure, preparation and properties

by

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Introduction

- Alkenes are hydrocarbons that contain a carbon-carbon double bond(c=c) in their molecule.
- Molecular formula is C_nH_{2n} where n=number of carbon atoms.
- Alkenes are unsaturated hydrocarbons which contain two hydrogen less than alkanes.
- Alkenes are commonly known as olefins because the lower members form oily products
- Alkenes has physical properties similar to those of alkanes.

Examples-

$H_2C=CH_2$ $H_2C=CH-CH-CH_2$

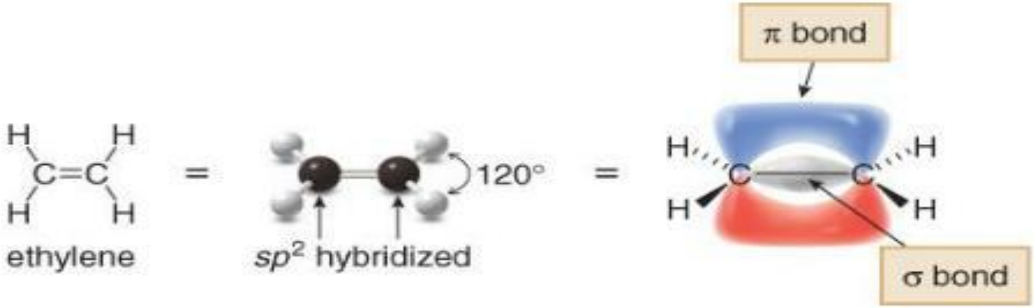
Ethylene 1-Butene

Structure of alkene

Alkenes

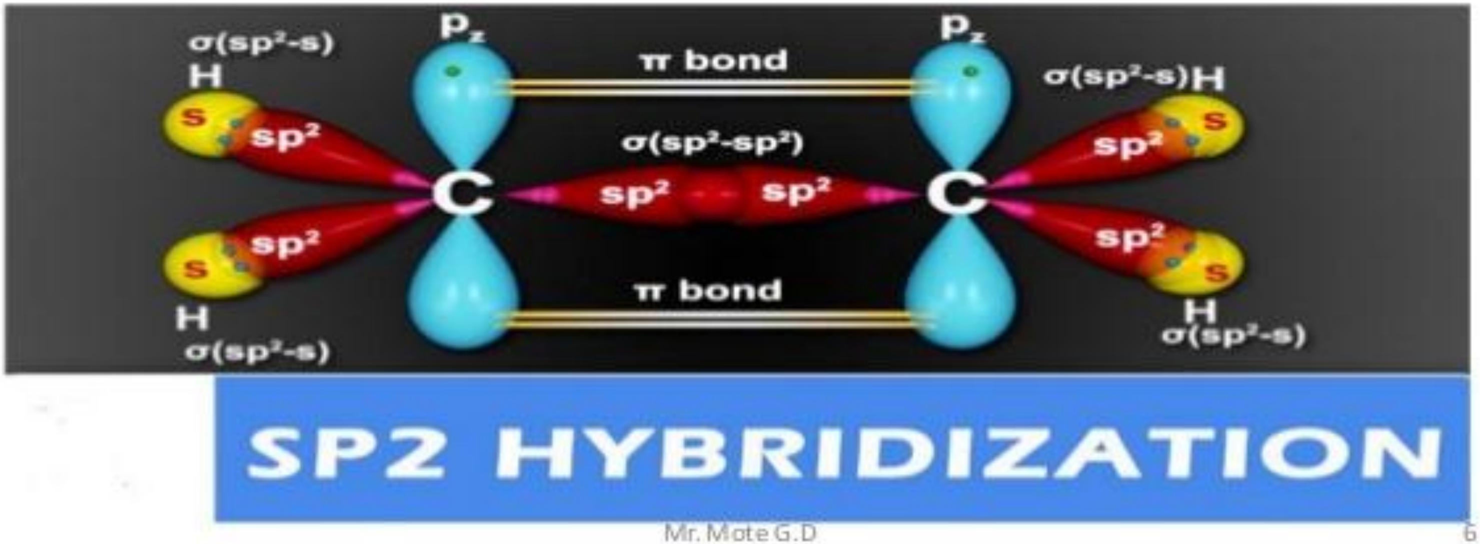
Introduction—Structure and Bonding

- Recall that the double bond consists of a π bond and a σ bond.
- Each carbon is *sp*^{2} hybridized and trigonal planar, with bond angles of approximately 120^0.



SP^2 hybridization

- In ethylene the carbon atoms are sp^2 hybridized, they are attached to each other by a σ bond and a π bond.
- The σ bond results from overlap of one sp^2 hybrid orbital from one with sp^2 hybrid orbital of another carbon.
- The π bond is formed from overlap of unhybridized p orbital's.
- Remaining sp^2 orbital's form σ bond with hydrogen atoms.



Alkenes

Introduction—Structure and Bonding

- Bond dissociation energies of the C—C bonds in ethane (a σ bond only) and ethylene (one σ and one π bond) can be used to estimate the strength of the π component of the double bond.

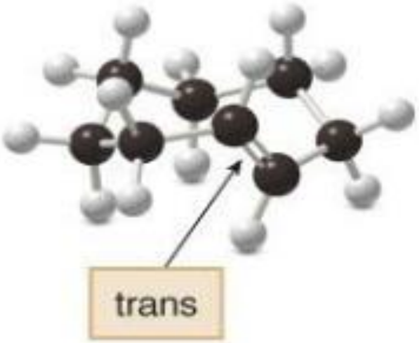
$CH_2{=}CH_2$		$CH_3{-}CH_3$		
152 kcal/mol (σ + π bond)	−	88 kcal/mol (σ bond)	=	64 kcal/mol ↑ **π bond only**

◆ The π bond is much weaker than the σ bond of a C–C double bond, making it much more easily broken. As a result, alkenes undergo many reactions that alkanes do not.

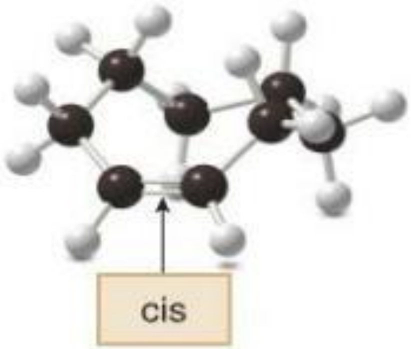
Alkenes

Introduction—Structure and Bonding

- Cycloalkenes having fewer than eight carbon atoms have a cis geometry. A trans cycloalkene must have a carbon chain long enough to connect the ends of the double bond without introducing too much strain.
- *trans*-Cyclooctene is the smallest isolable trans cycloalkene, but it is considerably less stable than *cis*-cyclooctene, making it one of the few alkenes having a higher energy trans isomer.



trans-cyclooctene

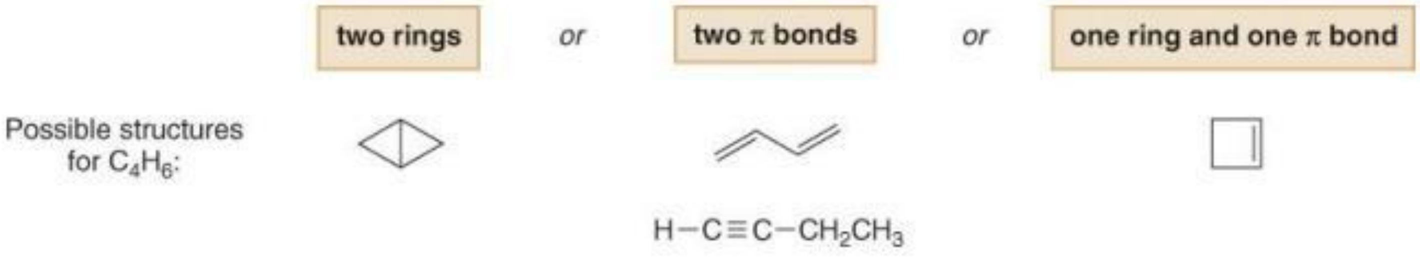


cis-cyclooctene

Alkenes

Calculating Degrees of Unsaturation

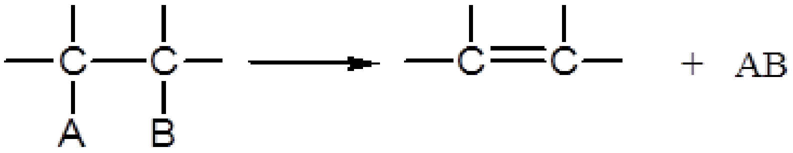
- An acyclic alkene has the general structural formula C_nH_{2n}
- Alkenes are unsaturated hydrocarbons because they have fewer than the maximum number of hydrogen atoms per carbon.
- Cycloalkanes also have the general formula C_nH_{2n}.
- Each π bond or ring removes two hydrogen atoms from a molecule, and this introduces one degree of unsaturation.
- The number of degrees of unsaturation for a given molecular formula can be calculated by comparing the actual number of H atoms in a compound and the maximum number of H atoms possible.
- This procedure gives the total number of rings and/or π bonds in a molecule.



$H-C\equiv C-CH_2CH_3$

PREPARATION OF ALKENES

- Alkenes are prepared by *Elimination* of an atom or group of atoms from adjacent carbons to form *carbon-carbon double bond*.

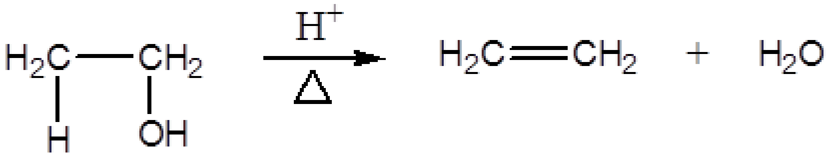


$$-\underset{A}{\underset{|}{\overset{|}{C}}}-\underset{B}{\underset{|}{\overset{|}{C}}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}- \quad + \quad AB$$

(A=H or halogen;
B=OH or halogen)

1) Dehydration of Alcohols

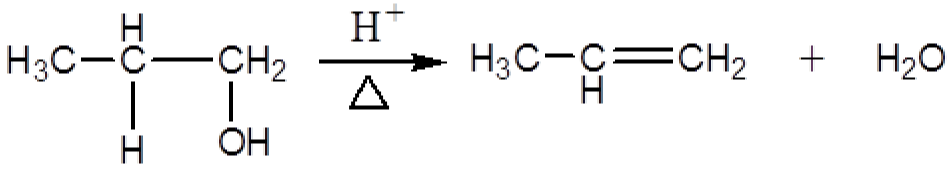
When an alcohol is heated in the presence of a mineral acid catalyst, It readily loses a molecule of water to give an alkene.



$$\underset{H}{\underset{|}{H_2C}}-\underset{OH}{\underset{|}{CH_2}} \xrightarrow[\Delta]{H^+} H_2C=CH_2 \quad + \quad H_2O$$

IUPAC name:	Ethanol	Ethene
Common name:	Ethyl alcohol	Ethylene

The acid catalysts most commonly used are sulfuric acid, H_2S0_4, and phosphoric acid, H_3P0_4.



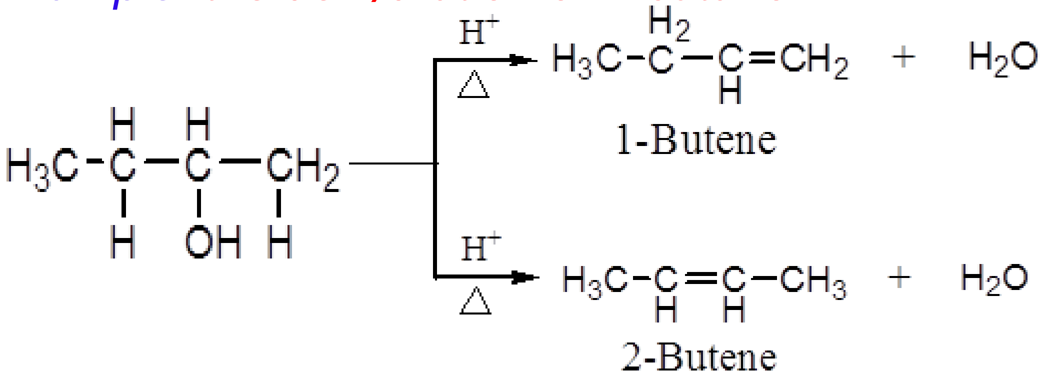
$$H_3C-CH_2-CH_2OH \xrightarrow[\Delta]{H^+} H_3C-CH=CH_2 + H_2O$$

IUPAC name:	1-Propanol	Propene
Common name:	*n*-Propyl alcohol	Propylene

Which Alkene Predominates?; Saytzeff's Rule

The loss of water from adjacent carbon atoms, can give rise to more than one alkene.

Example: the dehydration of 2-butanol.



$$H_3C-CH_2-CH(OH)-CH_3 \xrightarrow[\Delta]{H^+} H_3C-CH_2-CH=CH_2 + H_2O$$

1-Butene

$$H_3C-CH_2-CH(OH)-CH_3 \xrightarrow[\Delta]{H^+} H_3C-CH=CH-CH_3 + H_2O$$

2-Butene

2-butene is the major (with two alkyl substituents attached to C=C)

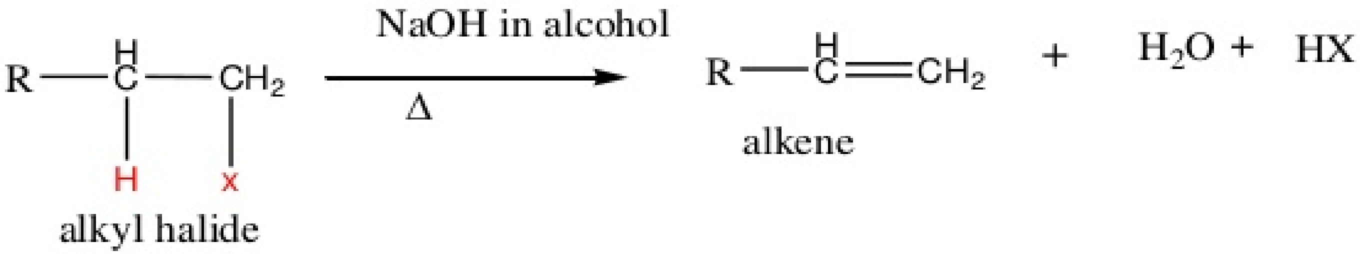
Saytzeff's Rule applies

In every instance in which more than one Alkene can be formed

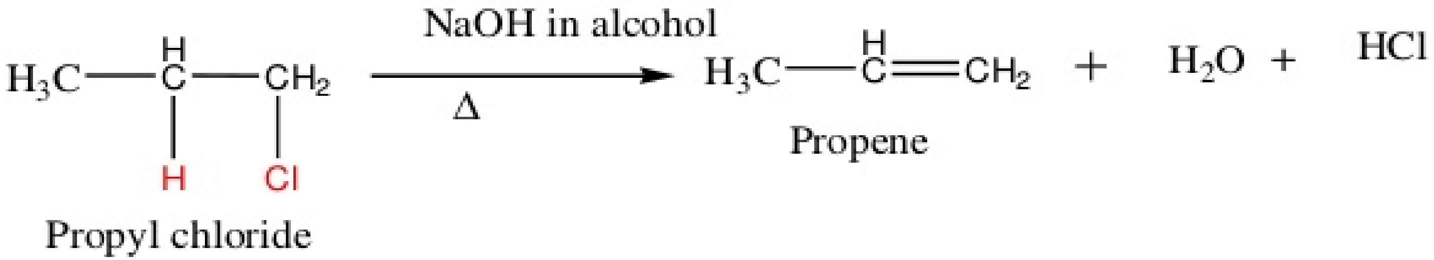
The major product is always the alkene with the most alkyl substituents attached on the double-bonded carbons.

2. Dehydrohalogenation of alkyl halides

- When alkyl halide is heated with alcoholic solution of sodium hydroxide to form alkene and hydrogen halide.



$$R-CH(H)-CH_2(X) \xrightarrow[\Delta]{\text{NaOH in alcohol}} R-CH=CH_2 + H_2O + HX$$



$$H_3C-CH(H)-CH_2(Cl) \xrightarrow[\Delta]{\text{NaOH in alcohol}} H_3C-CH=CH_2 + H_2O + HCl$$

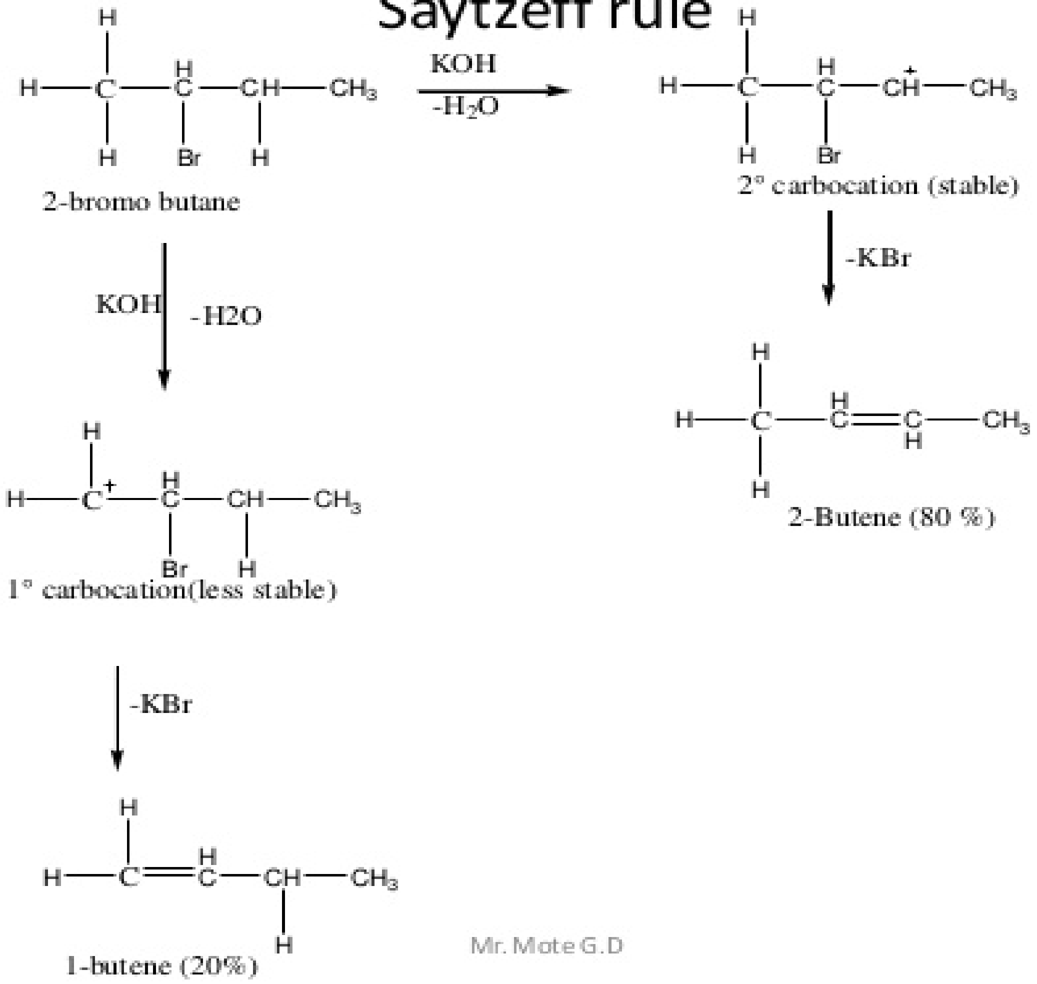
2. Dehydrohalogenation of alkyl halides

Saytzeff rule

- If the dehydrohalogenation of alkyl halide can yield more than one alkene, according to saytzeff rule main product is the most highly substituted alkene.
- E.g. when 2-bromo butane is heated with alcoholic KOH to form 80% 2-butene and 20% 1-butene

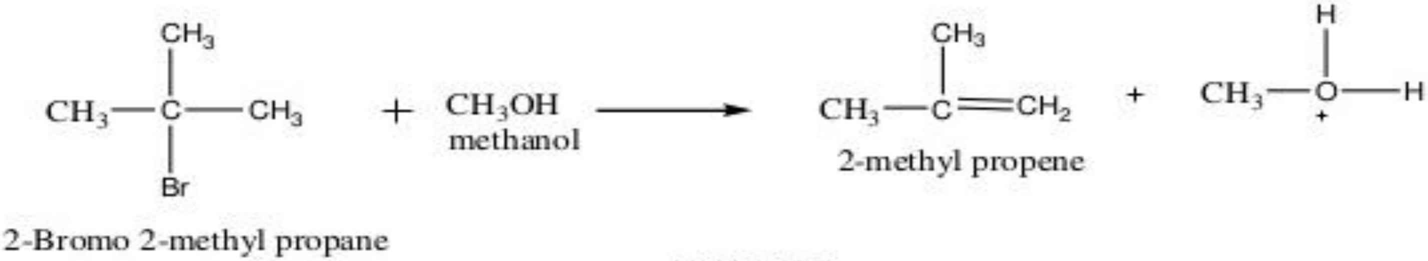
2. Dehydrohalogenation of alkyl halides

Saytzeff rule

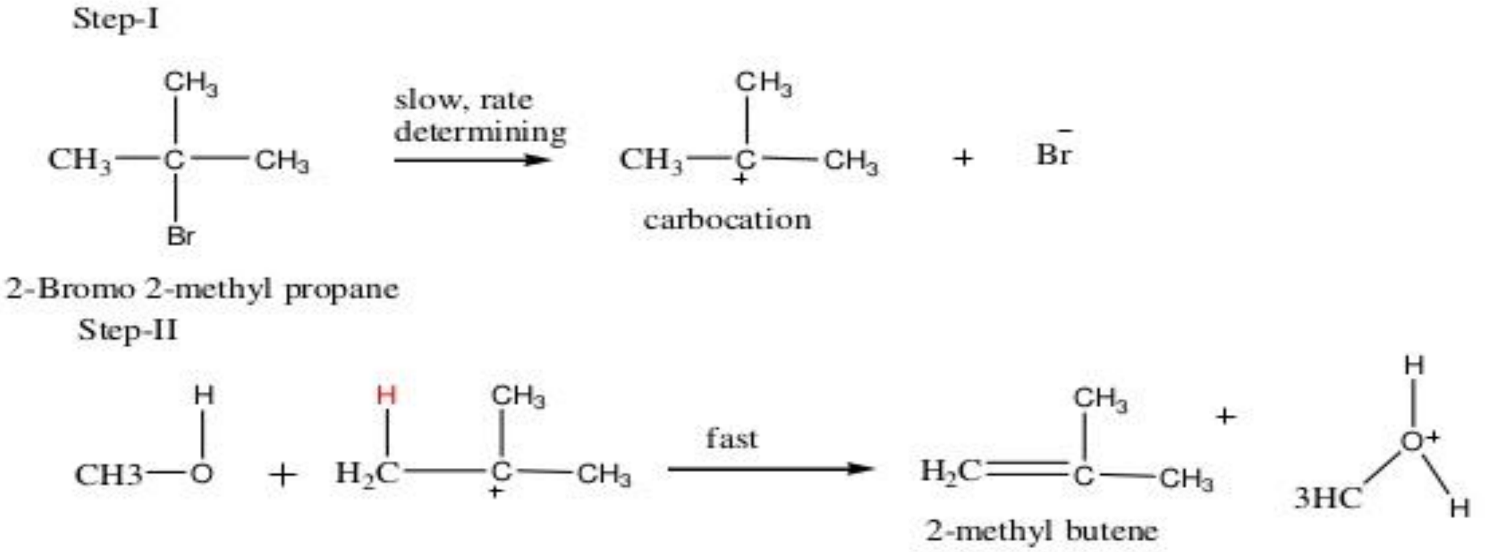


2. Dehydrohalogenation of alkyl halides (ß-Elimination reaction)

- E1 Mechanism: in this mechanism, breaking of the C-X bond is complete before any reaction occurs with base to lose hydrogen and before the carbon-carbon double bond is formed.
- This mechanism is designated E1, E- elimination 1- unimolecular
- E.g. reaction of 2-bromo -2- methyl propane to form 2-methyl propene which follows two step mechanism via carbocation intermediate.

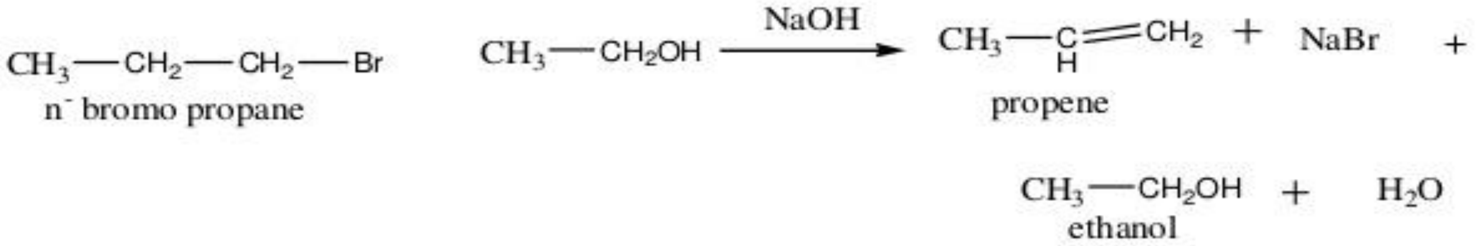


E 1 Mechanism



2. Dehydrohalogenation of alkyl halides (ß-Elimination reaction)

- E2 Mechanism: this a concerted process, E stands for elimination 2- stands for bimolecular because the base removes a ß- hydrogen at the same time the C-X bond is broken to form alkyl ion.
- The rate law for the rate determining step is dependent on both the alkyl halide and base.
- Rate: k[alkyl halide][base], if base is strong then E2 mechanism is operated.



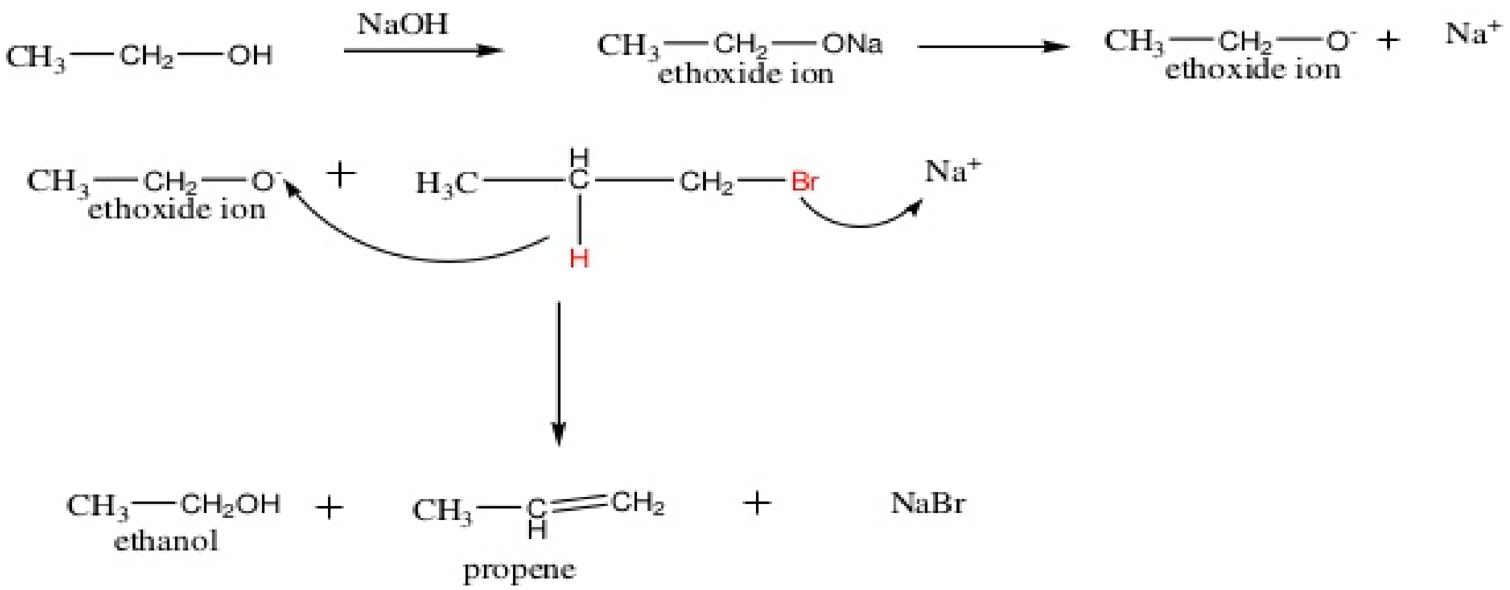
$$CH_3-CH_2-CH_2-Br \quad CH_3-CH_2OH \xrightarrow{NaOH} CH_3-\underset{H}{C}=CH_2 + NaBr + CH_3-CH_2OH + H_2O$$

n⁻ bromo propane

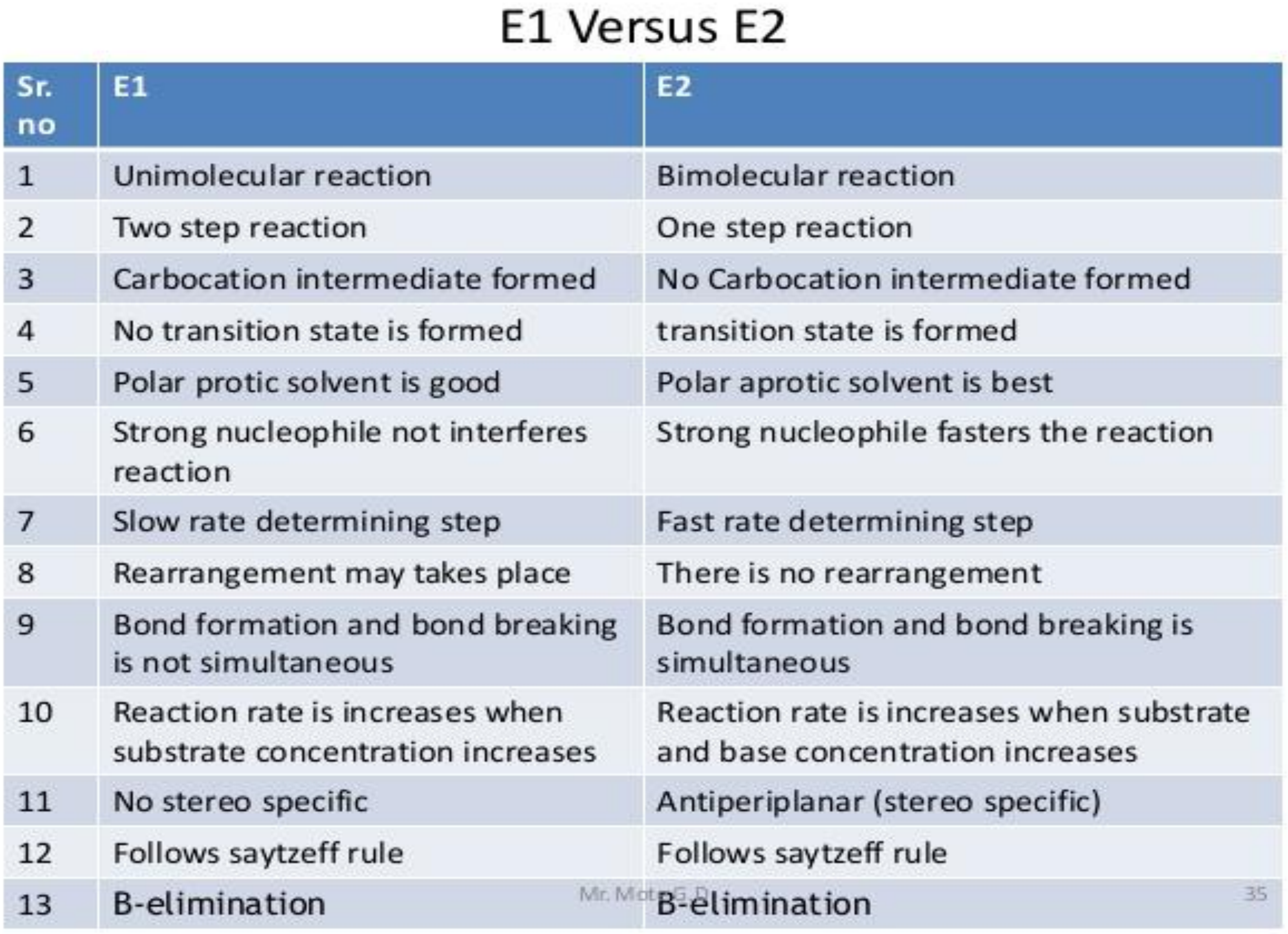
propene

ethanol

E 2 Mechanism



1. In this mechanism, proton transfer to the base, formation of carbon-carbon double bond Ejection of bromide ion occurs simultaneously, that is all bond forming and breaking occur at the same time.
2. Product is formed according to saytzeff rule.



E1 Versus E2

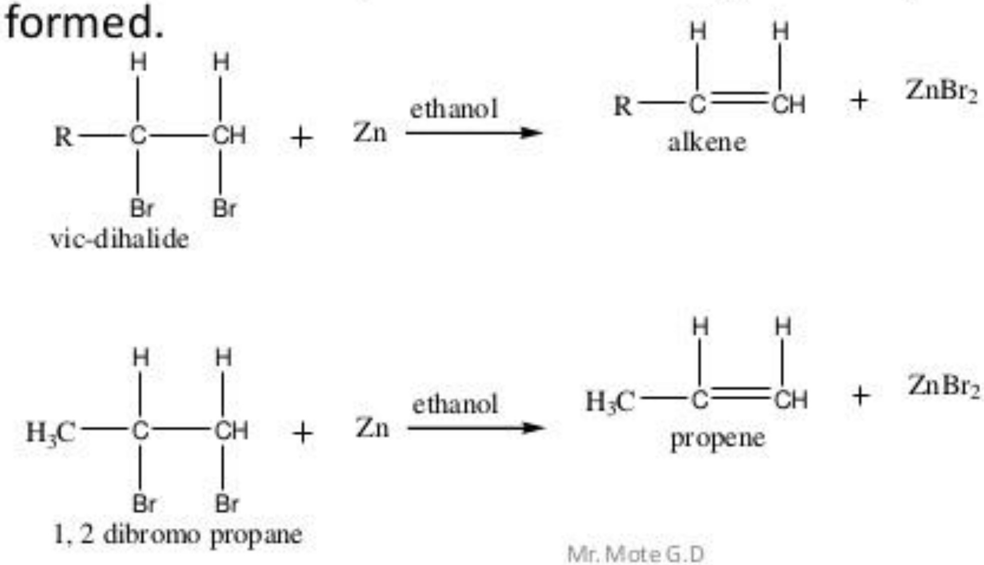
Sr. no	E1	E2
1	Unimolecular reaction	Bimolecular reaction
2	Two step reaction	One step reaction
3	Carbocation intermediate formed	No Carbocation intermediate formed
4	No transition state is formed	transition state is formed
5	Polar protic solvent is good	Polar aprotic solvent is best
6	Strong nucleophile not interferes reaction	Strong nucleophile fasters the reaction
7	Slow rate determining step	Fast rate determining step
8	Rearrangement may takes place	There is no rearrangement
9	Bond formation and bond breaking is not simultaneous	Bond formation and bond breaking is simultaneous
10	Reaction rate is increases when substrate concentration increases	Reaction rate is increases when substrate and base concentration increases
11	No stereo specific	Antiperiplanar (stereo specific)
12	Follows saytzeff rule	Follows saytzeff rule
13	B-elimination	B-elimination

Factor affecting on E1 and E2

Sr. no	E1	E2
1	Good leaving group- alcohol	Better leaving groups faster the reaction
2	Reactivity order: 3°>2°>1°	Reactivity order: 3°>2°>1°
3	Stable carbocation-tertiary carbocation	
4	Weak bases-Water or Alcohol	Favored by strong base
5	Polar protic solvents	Polar aprotic solvents
6	Only substrate concentration fasters the reaction	substrate concentration as well as strong base fasters the reaction
7	First order kinetics	Second order kinetics
8		
9		
10		
11		
12		

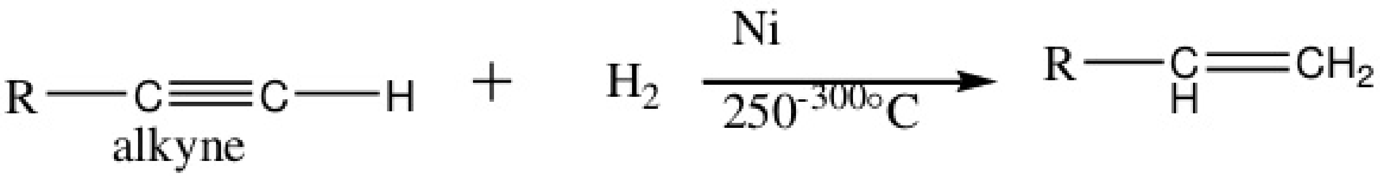
3. Dehalogenation of vicinal dihalide

- *Dehalogenazion involves the removal of a molecule (X—X)from a reactant molecule.*
- *A compound having two halogen atoms on* adjacent carbon atoms called a vicinal dihalide (or vic .dihalide).
- The treatment of vic-dihalides with zinc dust using ethyl alcohol as solvent, results in dehalogenation, and an alkene is formed.

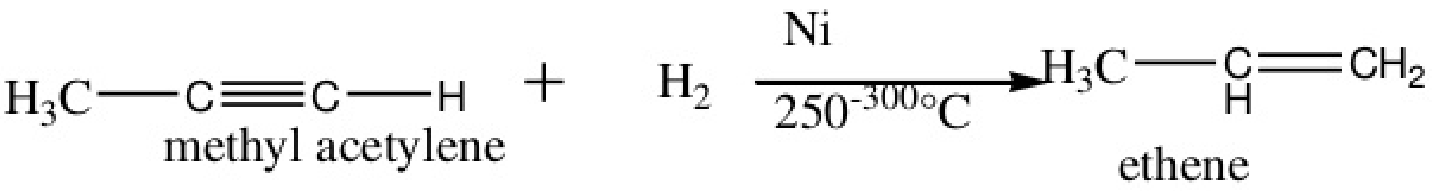


4. Controlled hydrogenation of alkyne

1. Alkynes undergoes hydrogenation in the nickel or palladium or platinum to form alkenes



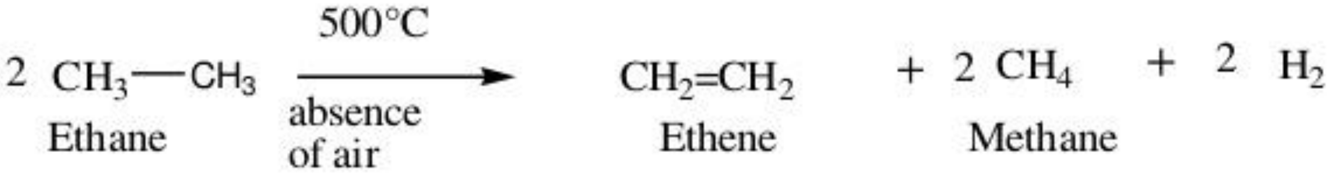
$$R-C\equiv C-H + H_2 \xrightarrow[250\text{-}300^\circ C]{Ni} R-\underset{H}{C}=CH_2$$



$$H_3C-C\equiv C-H + H_2 \xrightarrow[250\text{-}300^\circ C]{Ni} H_3C-\underset{H}{C}=CH_2$$

5. Pyrolysis (Cracking)

- The decomposition of a compound by heat is called pyrolysis.
- This process when applied to alkane is known as cracking.
- Larger alkanes are broken into a mixture lower molecular weight alkanes, alkenes and hydrogen



$$2\ \underset{\text{Ethane}}{CH_3{-}CH_3} \xrightarrow[\text{absence of air}]{500^{\circ}C} \underset{\text{Ethene}}{CH_2{=}CH_2} + \underset{\text{Methane}}{2\ CH_4} + 2\ H_2$$

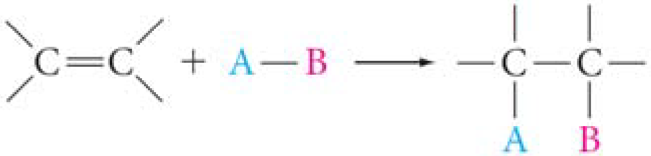
reactions of alkenes

1. Addition of hydrogen halides.
2. Addition hypohalous acids.
3. Addition of sulphuric acid.
4. Addition of water.
5. Addition halogens.
6. Addition of hydrogen
7. Catalytic oxidation
8. Oxidation with potassium permanganate
9. Ozonolysis
10. Polymerization.
11. Oxymercuration-demercuration of alkenes

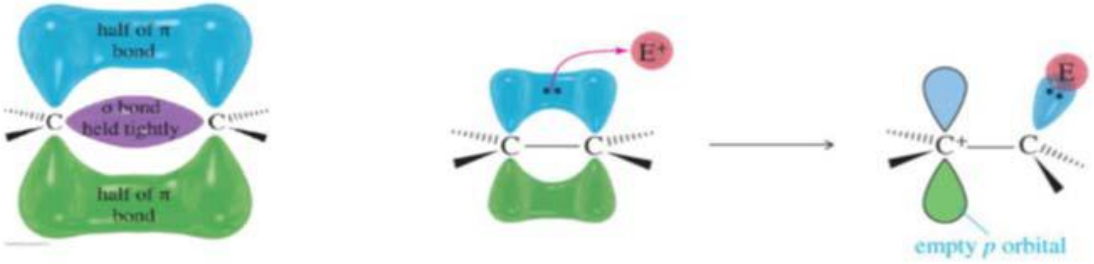
REACTIONS OF ALKENES

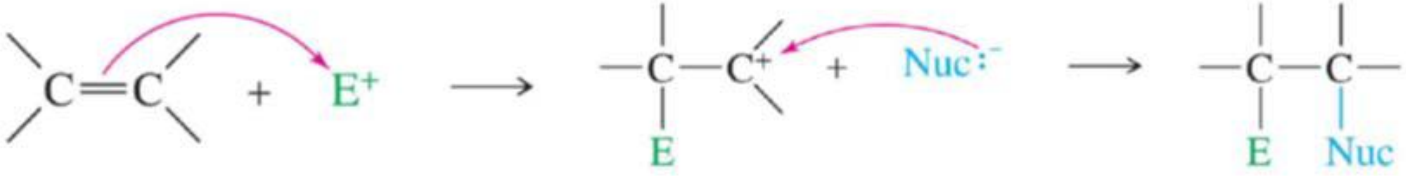
The chemistry of alkenes can be divided into two general types of reactions:

(1) Electrophilic Addition Reactions



- The pi bond is localized above and below the C-C sigma bond.
- The pi electrons are relatively far away from the nuclei and are therefore loosely bound.





The double bond acts as a nucleophile (attacks the electrophile).

Addition of Symmetric and Unsymmetric Reagents to Symmetric Alkenes.

1. Addition of Hydrogen: Catalytic Hydrogenation
2. Addition of Halogens: Halogenation

Addition of Unsymmetric Reagents to Unsymmetric Alkenes; Markovnikov's Rule.

1. Addition of Hydrogen Halides
2. Addition of Sulfuric Acid
3. Addition of Water: Hydration
4. Addition of HOX: Halohydrin Formation

(2) Oxidation Reactions

1. Ozonolysis
2. Oxidation Using $KMnO_4$

- Reagents and alkenes can be classified as either symmetric or unsymmetric with respect to addition reactions.

- But if *both* the reagent *and* the alkene are *unsymmetric*, two products are possible.
- If a reagent and/or an alkene is symmetric, only one addition product is possible.

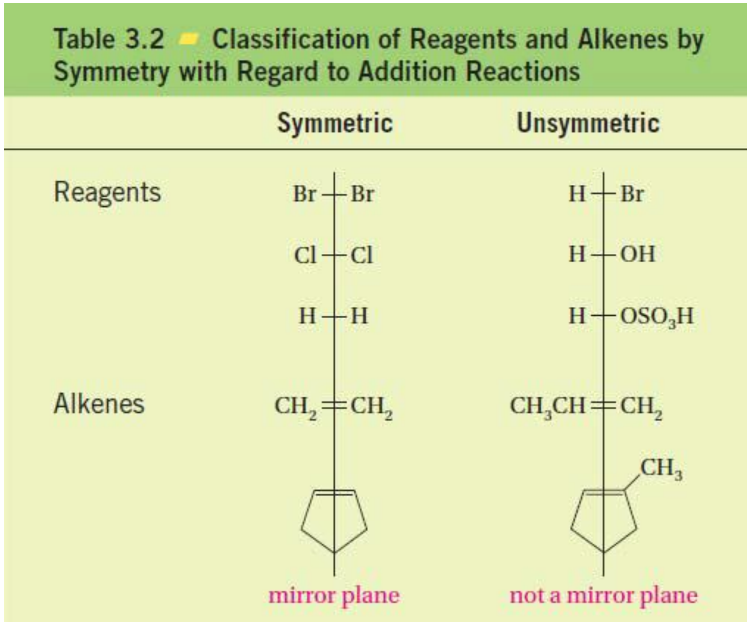
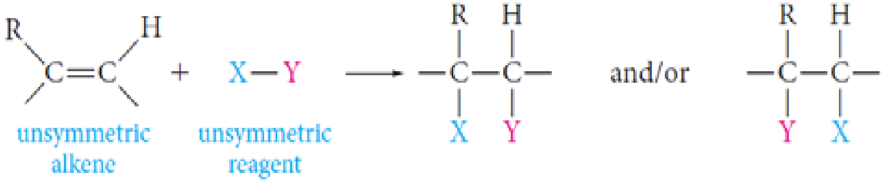


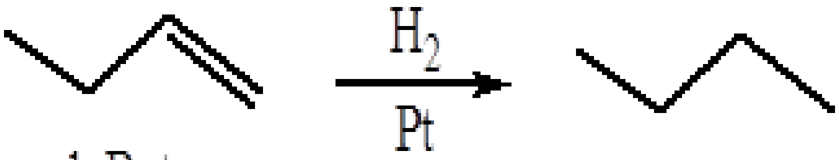
Table 3.2 Classification of Reagents and Alkenes by Symmetry with Regard to Addition Reactions

	Symmetric	Unsymmetric
Reagents	Br—Br	H—Br
	Cl—Cl	H—OH
	H—H	H—OSO_3H
Alkenes	$CH_2{=}CH_2$	$CH_3CH{=}CH_2$
	mirror plane	not a mirror plane



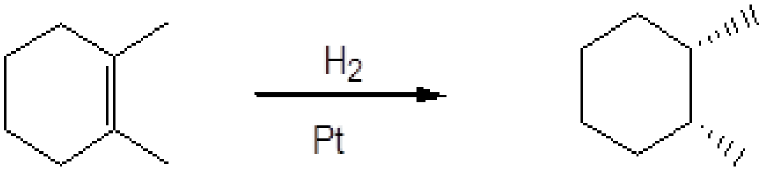
1. Addition of Hydrogen: Hydrogenation

Addition of a mole of hydrogen to carbon-carbon double bond of Alkenes in the presence of suitable catalysts to give an Alkane.



1-Butene

Butane

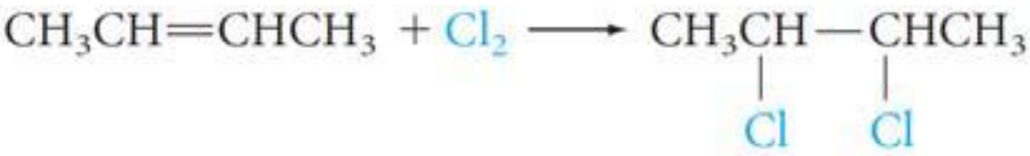


1,2-Dimethylcyclohexene

cis-1,2-Dimethylcyclohexane

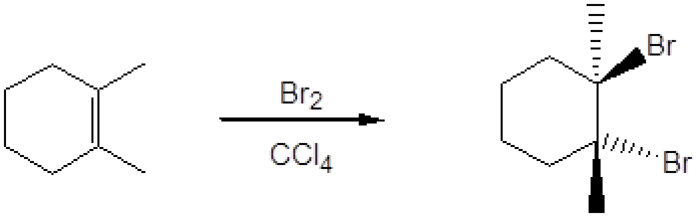
2. Addition of Halogen: Halogenation

When an alkene is treated at room temperature with a solution of bromine or chlorine in carbon tetrachloride to give the corresponding vicinal dihalide (two halogens attached to adjacent carbons)



$$CH_3CH{=}CHCH_3 + Cl_2 \longrightarrow CH_3\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}CH_3$$

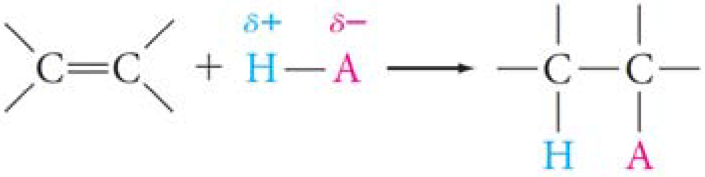
2-butene 2,3-dichlorobutane



1,2-Dimethylcyclohexene *trans*-1,2-Dibromocyclohexane

3. Addition of Acids

- A variety of acids add to the double bond of alkenes.
  - *The hydrogen ion (or proton) adds to one carbon of the double bond, and the remainder of the acid becomes connected to the other carbon.*



- Acids that add in this way are the hydrogen halides (H-F, H-Cl, H-Br, H-I), sulfuric acid (H-OSO_3H) and water (H-OH).

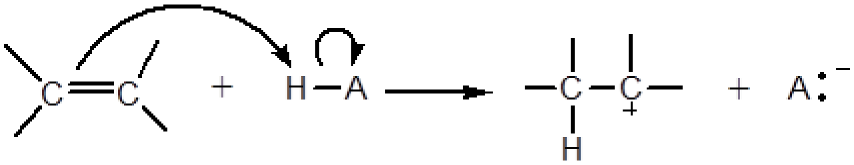
Note that

-Any electron-deficient species is called an electrophile.

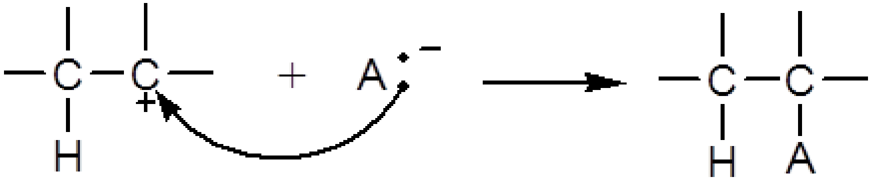
- Any electron-rich species is called a nucleophile.

- The addition of H—A to an alkene is believed to be a two-step process.

Step 1. The hydrogen ion (the electrophile) attacks the pi-electrons of the alkene, forming a C—H bond and a carbocation.



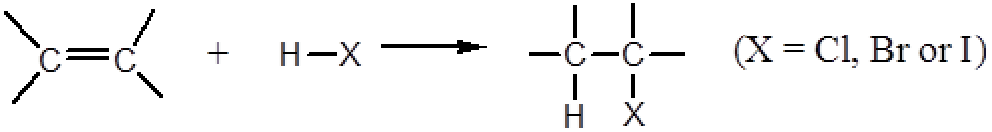
Step 2. The negatively charged species A: - (a nucleophile) attacks the carbocation and forms a new C—A bond.



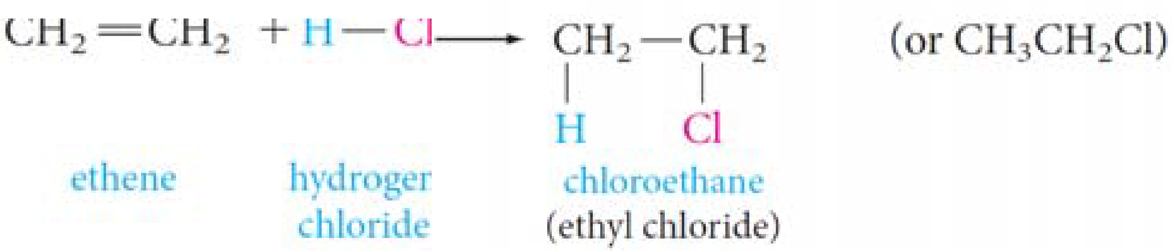
4. Addition of Hydrogen Halide

Alkenes react with hydrogen chloride, HC1, hydrogen bromide, HBr and hydrogen iodide, HI, to form alkyl halides, RX.

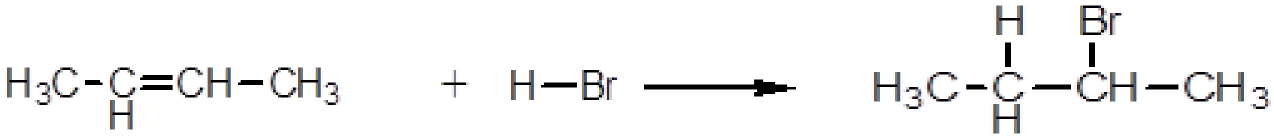
General equation



(X = Cl, Br or I)



$CH_2{=}CH_2 + H{-}Cl \longrightarrow CH_2(H){-}CH_2(Cl)$ (or CH_3CH_2Cl)



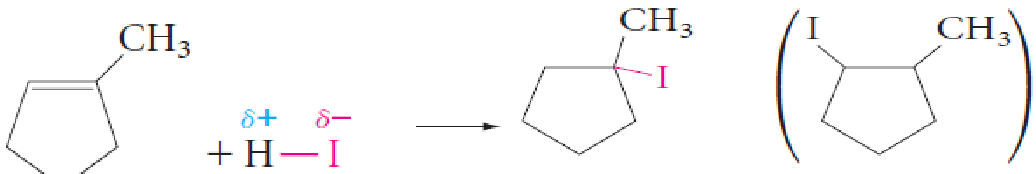
$$H_3C-CH=CH-CH_3 + H-Br \longrightarrow H_3C-CH_2-CHBr-CH_3$$

2-Butene
(a symmetrical alkene)

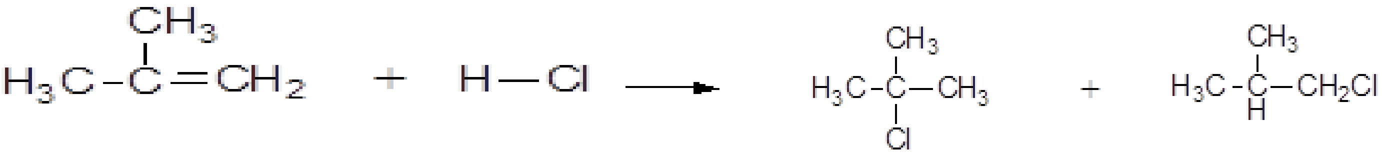
2-Bromobutane
(only one product possible)

Markovnikov’s Rule

In electrophilic addition of H—X *to Unsymmetrical Alkenes the hydrogen of the hydrogen halide adds to the double-bonded carbon that bears the greater number of hydrogen atoms and the negative halide ion adds to the other double-bonded carbon.*



not observed



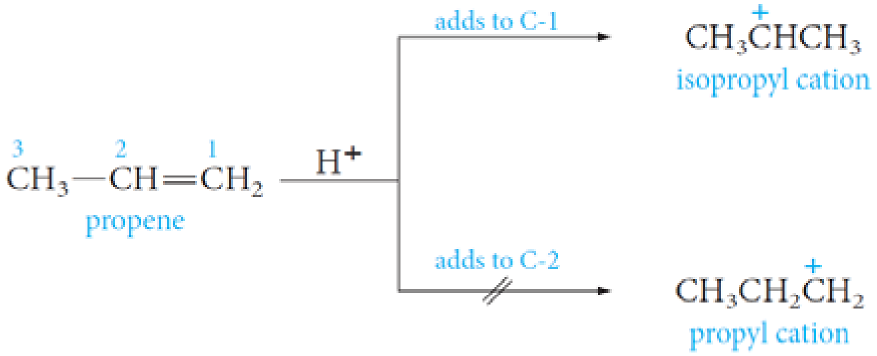
$$(CH_3)_2C=CH_2 + H-Cl \longrightarrow (CH_3)_3C-Cl + (CH_3)_2CH-CH_2Cl$$

2-Chloro-2-methylpropane
(major product)

1-Chloro-2-methylpropane
(minor product)

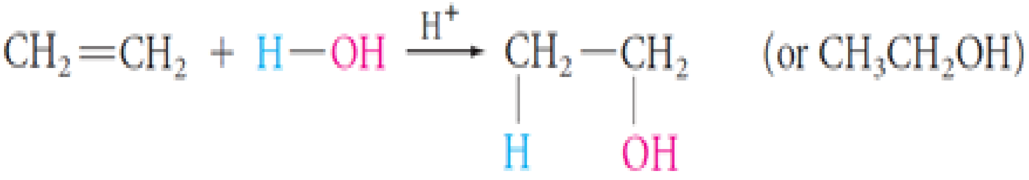
Explanation for Markovnikov’s Rule

Example; the addition of HBr to propene



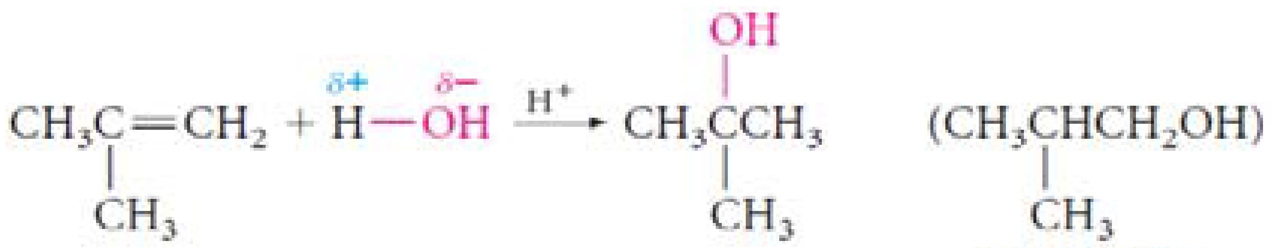
5.Addition of Water: Hydration

If an acid catalyst is present, water (as H-OH) adds to alkenes and the product is alcohol.



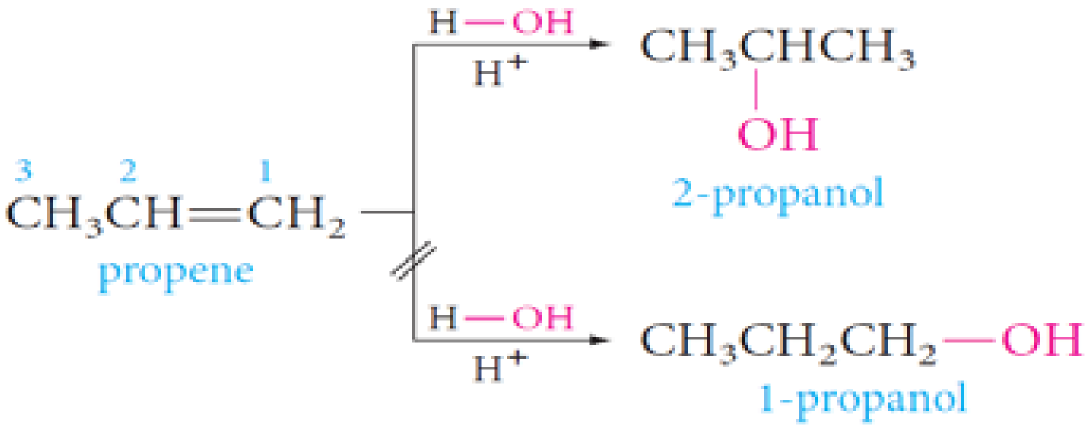
$$CH_2{=}CH_2 + H{-}OH \xrightarrow{H^+} \underset{H}{CH_2}{-}\underset{OH}{CH_2} \quad (\text{or } CH_3CH_2OH)$$

ethanol



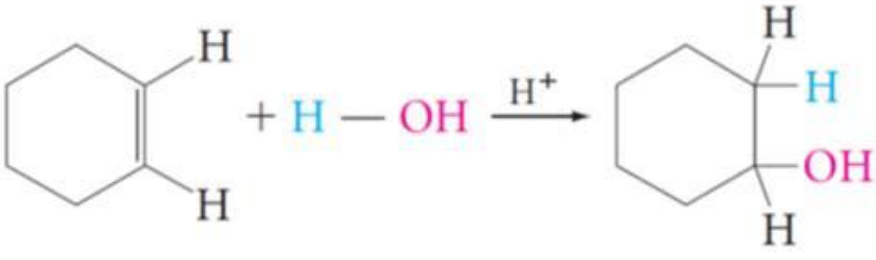
$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 + \overset{\delta+}{H}{-}\overset{\delta-}{OH} \xrightarrow{H^+} CH_3\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}CH_3 \qquad (CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH)$$

not observed



$$\overset{3}{CH_3}\overset{2}{CH}{=}\overset{1}{CH_2} \xrightarrow[H^+]{H-OH} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$$

$$\overset{3}{CH_3}\overset{2}{CH}{=}\overset{1}{CH_2} \not\xrightarrow[H^+]{H-OH} CH_3CH_2CH_2{-}OH$$

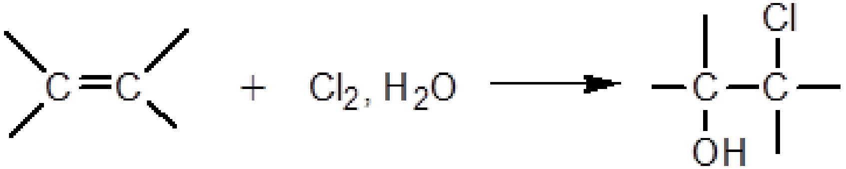


cyclohexene
bp 83.0°C

cyclohexanol
bp 161.1°C

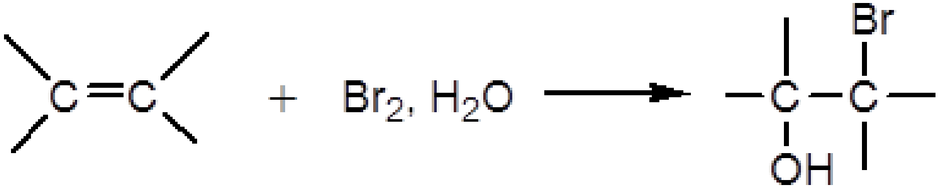
6.Addition of HOX: Halohydrin Formation

- When an alkene is treated with aqueous chlorine or aqueous bromine, the addition product is a halohydrin.
- When Cl_2 is used, the product is a chlorohydrin.



A chlorohydrin

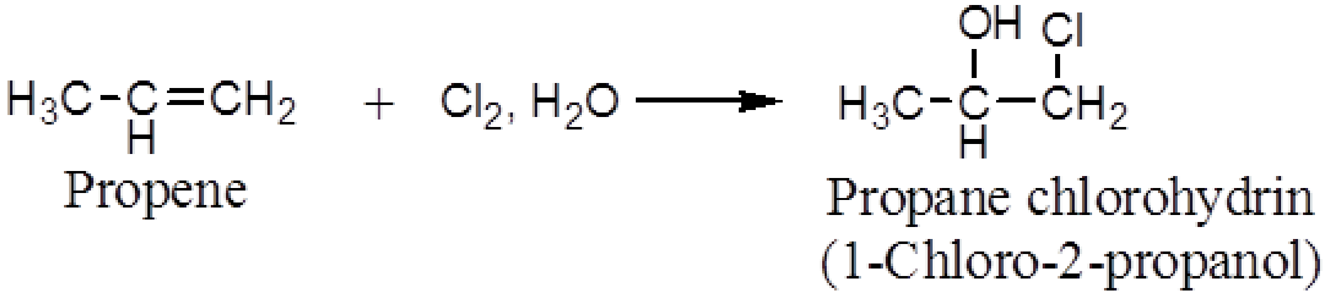
- When Br_2 is used, the product is a bromohydrin.



A bromohydrin

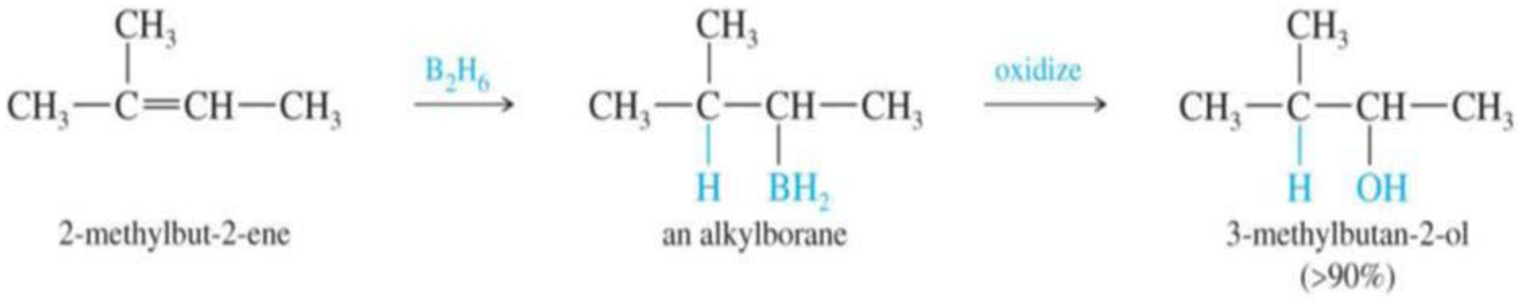
- The reaction proceeds as if hypochlorous acid, HO—Cl, or hypobromous acid,HO—Br, were the adding reagent.
- The nucleopbile is hydroxide ion, OH^-.
- The electrophile is chloronium ion, Cl^+, or bromoniumion, Br^+.

- Addition of HOX also follows Markovnikov's rule.

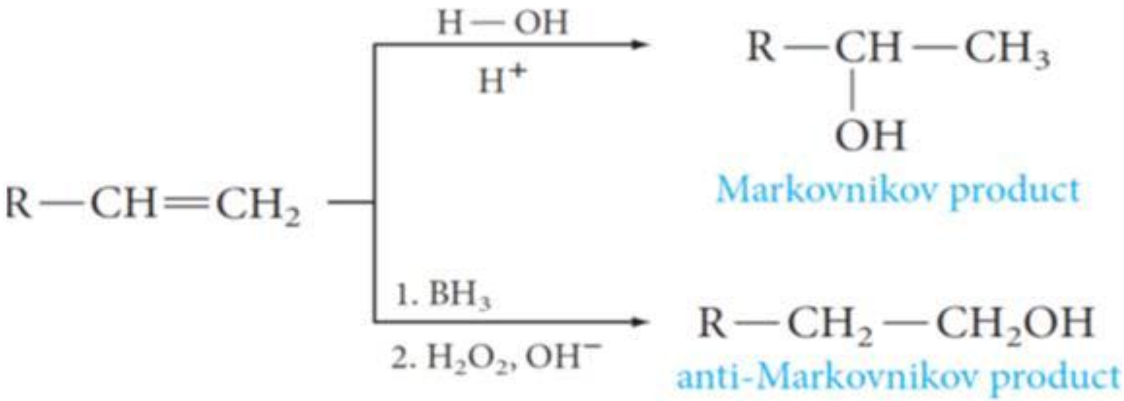


7.Hydroboration of Alkenes

- There is also a way to obtain anti-Markovnikov oriented alcohols: hydroboration.



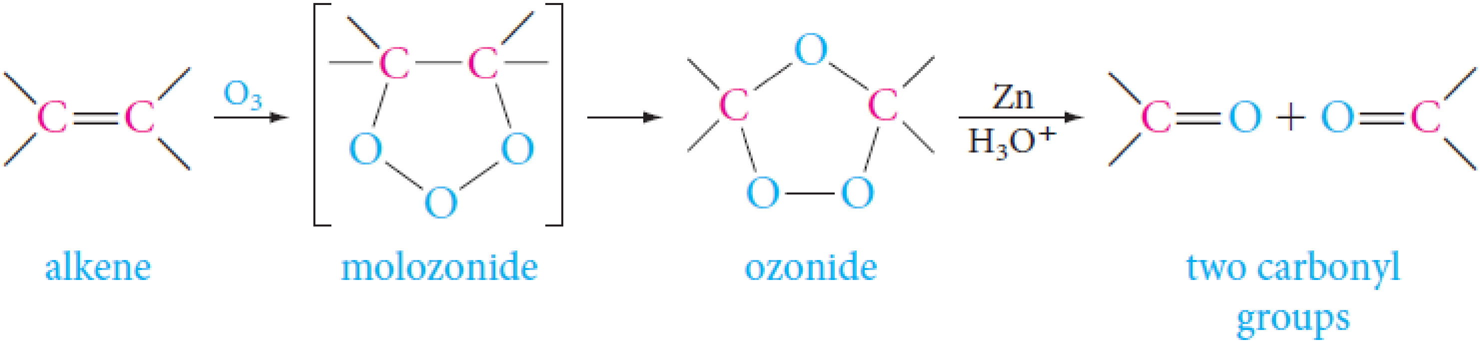
- One great advantage of this hydroboration-oxidation sequence is that it provides a route to alcohols that cannot be obtained by the acid-catalyzed hydration of alkenes.



OXIDATION REACTIONS

1. Ozonolysis

- The first product, a molozonide, is formed by cycloaddition of the oxygen at each end of the ozone molecule to the carbon–carbon double bond.
- This product then rearranges rapidly to an ozonide (explosive if isolated).
- They are usually treated directly with a reducing agent, commonly zinc and aqueous acid,to give carbonyl compounds as the isolated products.



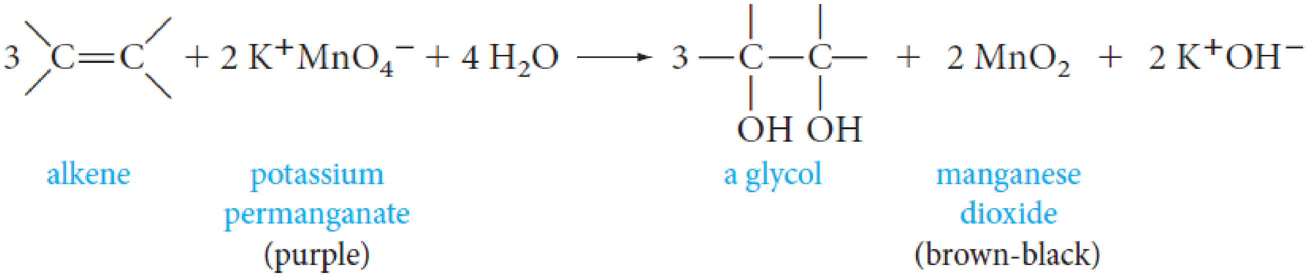
- Ozonolysis can be used to locate the position of a double bond.
- For example, ozonolysis of 1-butene gives two different aldehydes, whereas 2-butene gives a single aldehyde.

$$\underset{\text{1-butene}}{CH_2{=}CHCH_2CH_3} \xrightarrow[\text{2. Zn, H}^+]{\text{1. O}_3} \underset{\text{formaldehyde}}{CH_2{=}O} \quad \underset{\text{propanal}}{O{=}CHCH_2CH_3}$$

$$\underset{\text{2-butene}}{CH_3CH{=}CHCH_3} \xrightarrow[\text{2. Zn, H}^+]{\text{1. O}_3} \underset{\text{ethanal}}{2\,CH_3CH{=}O}$$

2. Oxidation Using $KMnO_4$

Alkenes react with alkaline potassium permanganate to form glycols (compounds with two adjacent hydroxyl groups).



$$3\,\underset{\text{alkene}}{{>}C{=}C{<}} + 2\,\underset{\substack{\text{potassium}\\ \text{permanganate}\\ \text{(purple)}}}{K^+MnO_4^-} + 4\,H_2O \longrightarrow 3\,\underset{\text{a glycol}}{-\overset{|}{\underset{\underset{OH}{|}}{C}}-\overset{|}{\underset{\underset{OH}{|}}{C}}-} + \underset{\substack{\text{manganese}\\ \text{dioxide}\\ \text{(brown-black)}}}{2\,MnO_2} + 2\,K^+OH^-$$

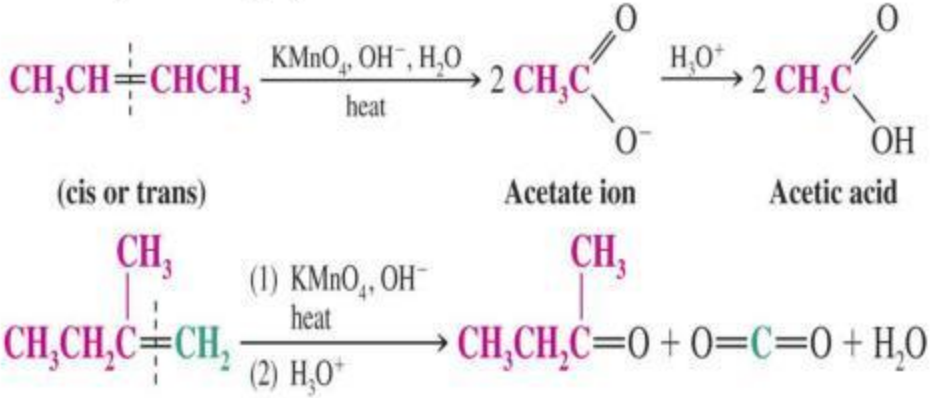
Anti-markovnikov rule

- the $H^+$of HX goes to the double bonded carbon that has already least number of hydrogen's. in presence of peroxide is known as anti- markovnikov.
- E.g. propylene reacts with HBr in the presence of a by a free radical mechanism.

Sr.no	Markovnikov	Antimarkovnikov
1	H of goes to double bonded carbon atom which has greatest number of hydrogen atom	H of goes to double bonded carbon atom which has least number of hydrogen atom
2.	Initially hydrogen goes to carbon to carbocation	Initially halogen goes to carbon atom which has greatest number of hydrogen atom
3.	Secondary carbocation intermediate formed	Secondary free radical intermediate formed
4.	Peroxide effect is not considered	Peroxide effect is considered
5.	Electrophilic addition reaction	Free radical addition reaction

Oxidative Cleavage of Alkenes

- Reaction of an alkene with hot $KMnO_4$ results in cleavage of the double bond and formation of highly oxidized carbons
  - Unsubstituted carbons become CO_2, monosubstituted carbons become carboxylates and disubstituted carbons



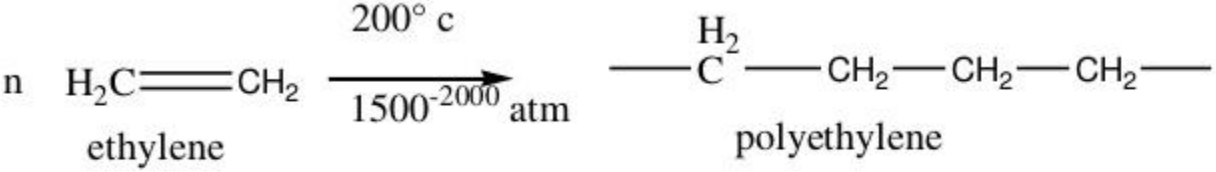
$$CH_3CH{=}CHCH_3 \xrightarrow[\text{heat}]{KMnO_4,\ OH^-,\ H_2O} 2\ CH_3C(=O)O^- \xrightarrow{H_3O^+} 2\ CH_3C(=O)OH$$

$$CH_3CH_2C(CH_3){=}CH_2 \xrightarrow[\text{(2) } H_3O^+]{\text{(1) } KMnO_4,\ OH^-\text{, heat}} CH_3CH_2C(CH_3){=}O + O{=}C{=}O + H_2O$$

- This be used as a chemical test for alkenes in which the purple color of the $KMnO_4$ disappears and forms brown MnO_2 residue if alkene (or alkyne) is present

10. Polymerization

- Two or more alkene joins together to form new compound which has several identical units, that reaction is called as polymerization.
- Addition of alkene together without any loss of atoms that polymerization is called addition polymerization.



$$n\ H_2C{=}CH_2 \xrightarrow[1500^{-2000}\ \text{atm}]{200^\circ\ \text{c}} -\overset{H_2}{C}-CH_2-CH_2-CH_2-$$

11. Oxymercuration-demercuration of alkenes

- Mercuric acetate and water add to alkenes called as oxymercuration
- Reduction of oxymercuration product in presence of sodium borohydride to form alcohol called as demercuration