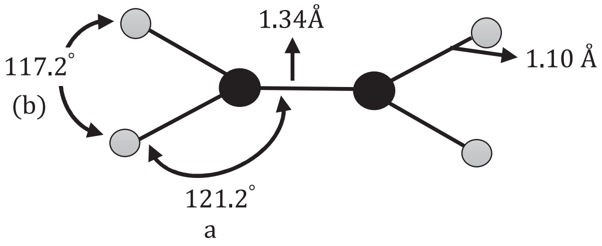
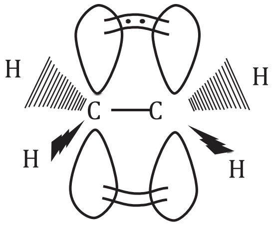
ALKENES

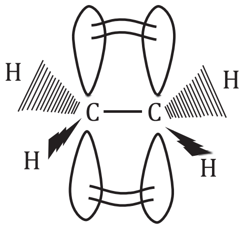
Alkenes are hydrocarbons with carbon-carbon double bonds, Alkenes are sometimes called **olefins**, a term derived from olefiant gas, meaning ‘oil forming gas’. Alkenes are among the most important industrial compounds and many alkenes are also found in plants and many alkenes are also found in plants and animals. Ethylene is the largest-volume industrial organic compound, used to make polyethylene and a variety of other industrial and consumer chemicals. Alkenes polymeries to give many important polymers.

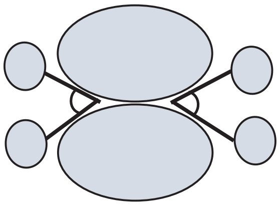
Structure and Bonding in Alkenes

(a) Alkenes are unsaturated hydrocarbons having at least one double bond.
(b) They are represented by general formula (G.F.) C_nH_{2n} (one double bond)
(c) In Ethene $C = C$ bonds length is 1.34 Å
(d) Its bond energy is 146 kcal. mol^{-1}
(e) The hybridization of $(C = C)$ alchemic carbon is sp^2
(f) The π e^- cloud is present above and below the plane of s-bonded skeleton.
(g) They are also known as olefins since ethene, the first member of the homologous series forms oily liquid substance when treated with halogens.
(h) Compounds may exist as conjugated polyenes or as cumulated polyenes or as isolated polyenes





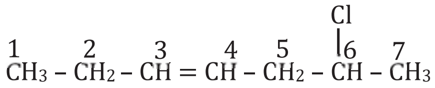
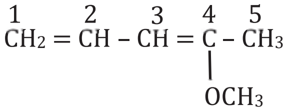
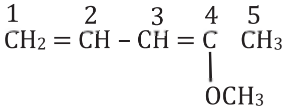
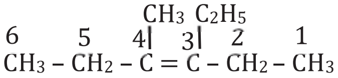
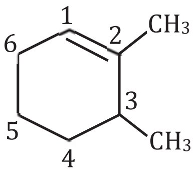
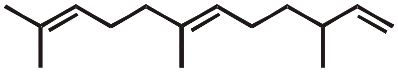




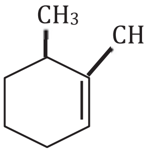
Note: That angle a < b since repulsion due to π electrons (double bond - single bond repulsion < single bond - single bond repulsion according to VSEPR theory.

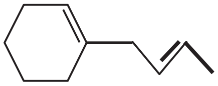
IUPAC Nomenclature Alkenes and Alkatrienes

Sr. No.	Compound	Name	Type
1.	$(CH_3)_2C = CH_2$	2-Methylpropane	Alkene
2.	$CH_3–CH = CH – CH_2 – CH = CH_2$	Hexa-1, 4-diene	Isolated diene
3.	$CH_2 = CH – CH = CH_2$	Buta-1, 3-diene	Conjugated diene
4.	$CH_3 – CH = C = CH – CH_3$	Penta-2, 3-diene	Cumulated diene

5.	 $\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH}=\overset{4}{CH}-\overset{5}{CH_2}-\overset{\overset{Cl}{\vert}}{\overset{6}{CH}}-\overset{7}{CH_3}$	6-Chlorohept-3-ene	Alkene
6.	 $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH}=\underset{\underset{OCH_3}{\vert}}{\overset{4}{C}}-\overset{5}{CH_3}$	4-methoxypenta-1, 3-diene	Conjugated diene
7.	 $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH}=\underset{\underset{OCH_3}{\vert}}{\overset{4}{C}}\quad\overset{5}{CH_3}$	3-Ethynylpenta-1, 4-diene	Isolated diene
8.	 $\overset{6}{CH_3}-\overset{5}{CH_2}-\overset{\overset{CH_3}{4\vert}}{C}=\overset{\overset{C_2H_5}{3\vert}}{C}-\overset{2}{CH_2}-\overset{1}{CH_3}$	3-Ethyl-4-methylhex-3-ene	Alkene
9.		2, 3-Dimethylcyclohex-1-ene	Cycloalkene
10.	$CH_2=C=CH_2$	Propidine	Cumulated diene
11.	$CH_2=C=O$	Ethenone	Alkene
12.		Methylene cyclopentane	Alkene
13.		Cyclopentolate	Alkene
14.		3, 7, 11-trimethyldodeca-1, 6, 10 -triene	Isolated triene

Ex. Write IUPAC names of:

(a) 

(b) 

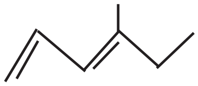
Sol. (a) 2, 3-Dimethylcyclohexene

(b) 1-(2-butenyl) cyclohex-1-ene

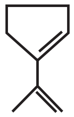
Ex. Give the structure for each of the following

(a) 4-Methyl-1, 3-hexadiene (b) 1-Isopropenylcyclopentene

Sol. (a)



(b)



Isomerism In Alkenes

Alkenes show chain, Ring or functional, Position, Geometrical isomerism and optical isomerism.

Method of Preparation

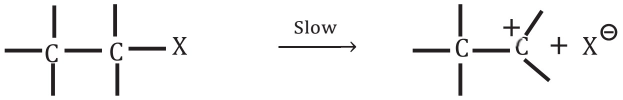
(I) By Elimination Reaction

E-1 Mechanism

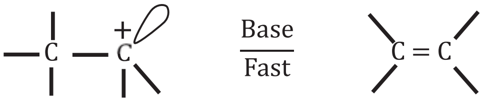
(a) It is called unimolecular elimination reaction

(b) It takes place in two steps.

Ist Step: Departure of leaving group from a molecule to form carbocation.



IInd Step: Carbocation formed above loses a proton to the base and forms the alkene.



(c) **Ist step** of E-1 mechanism is the rate determining step (R.D.S.)

(d) Since in R.D.S. only substrate undergoes covalency change **i.e.,** it follows first order kinetics with respect to substrate

$$\text{Rate} = K\,[\text{substrate}]$$

(e) Since in R.D.S. carbocation is formed as an intermediate to the reactivity order of different substrate follows the stability of order of carbocation formed.

Allylic > Tertiary > Secondary > Primary

(f) Loss of leaving group is the part of R.D.S. therefore the order of reactivity of alkyl halide in elimination reaction is

$$R\text{–}I > R - Br > R - Cl > R - F$$

Above order is parallel to order of leaving group ability

$$I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$$

(g) E-1 mechanism does not show isotopic effect as the loss of hydrogen is not the part of R.D.S.

$$\frac{K_H}{K_D} = 1$$

(h) Since the ionization take place in step I. Therefore, polar solvent favors the E- 1 mechanism.

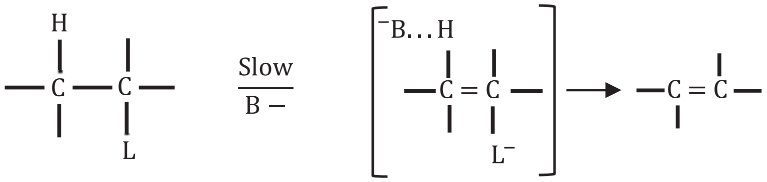
(i) E-1 mechanism involves carbocation as an intermediate so rearrangement of carbocation can take place if possible. More stable carbocation forms the major product in the reaction.

E–2 Mechanism

(a) It is known as bimolecular elimination mechanism.

(b) It takes place in single step.

(c) It involves the formation of transition state



Transition State

(d) Formation of transition state is the rate determination step.

(e) Ratre of reacting depends on the concentration of substrate as well as of base **i.e.,** it follows the second-order kinetics.

$$R = [\text{Substrate}]\,[\text{Base}]$$

(f) E-2 mechanism shows the isotopic effect as the loss of hydrogen is a part of R.D.S.

$$\frac{K_H}{K_D} = \frac{7}{1}$$

(g) E-2 mechanism shows the halogen effect as loss of leaving group is a part of R.D.S.

∴ Reactivity of different alkyl halides follows the sequence

Reactivity order of different substrate follows

$$3° > 2° > 1°$$

(h) The rate of reaction increases with increasing strength and concentration of the base.

(i) Non-polar solvent favors the E-2 mechanism.

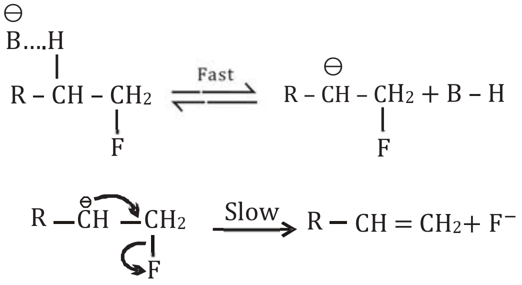
(j) Since E-2 mechanism involves the transition state rearrangement is not possible.

E 1 CB Mechanism

(a) In this mechanism, the reaction take place in two steps.

  (i) The first step involves rapid removal of a proton from the α-carbon (carbon adjacent to the carbon bearing halogen atom) forming a carbanion.

  (ii) The carbanion formed then loses the halides ion in the second-rate determining step.



(b) The overall rate of the reaction is limited to slower second step & hence the rate of reaction depends only on the concentration of carbanion.

(c) Since carbanion is the conjugate base of the alkyl halide and rate of reaction depends on concentrating of carbanion hence the mechanism is designated as E1CB mechanism.

Mechanism of α-Eliminating

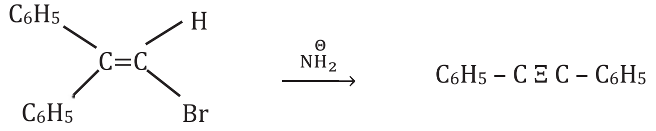
α-elimination does not occur frequently and completes in two stages, the second of which is rate determining.

for eq.

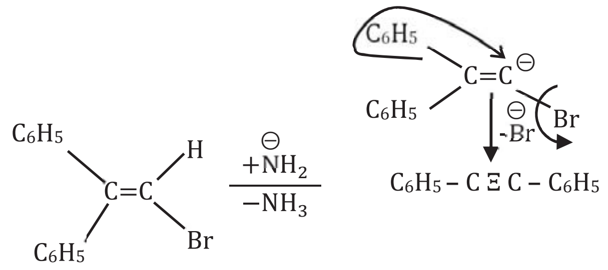
$$CHCl_3 + OH^- \underset{}{\overset{\text{Fast}}{\rightleftharpoons}} \overset{\ominus}{C}Cl_3 + H_2O$$

$$^{\ominus}CCl_3 \rightarrow \underset{\text{Di chlorocarbon}}{:CCl_2} + Cl^-$$

Another example of α-elimination of reaction's formation of diphenylacetylene from 2, 2-diphenyl vinyl bromide and soda lime.



Mechanism



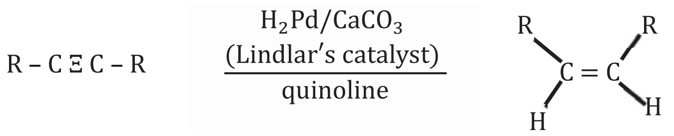
(II) Hydrogenation of Alkyne

By partial reduction of Alkynes

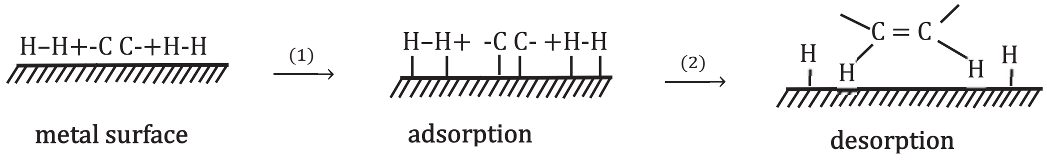
(a) **By catalytic Hydrogenation of Alkynes in presence of poisoned catalyst** (A) Syn Addition of Hydrogen Synthesis of cis-Alkenes: This is performed by

- (i) **Landlar's catalyst:** Metallic palladium deposited on calcium carbonate conditioned with lead acetate and quinoline.
- (ii) P-$_2$ catalyst (Ni_2B nickel boride)

General reaction



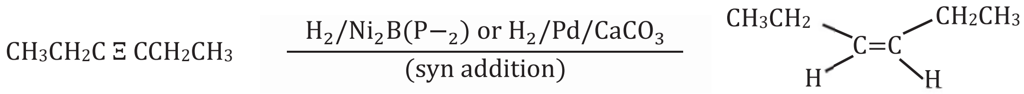
Mechanism of hydrogenation



Steps: The reactant alkyne molecules and hydrogen molecules get adsorbed at the surface of metal catalyst. It is chemical adsorption (chemisorption.)

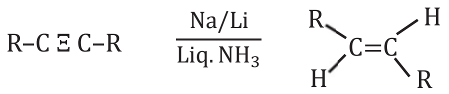
It this state, the reactants lie very close to each other and so the hydrogen atoms start forming bond with carbon. Two hydrogen atoms are added to two triply boned carbon atoms from the same side of π bond and a **cis or syn addition product** is formed. The product alkene now escapes away from the surface of the catalyst. Quinoline occupies the metal surface in hiding further reduction to alkanes **Quinoline** therefore is called catalyst poison and such palladium is called deactivated catalyst or poisoned catalyst.

Ex.



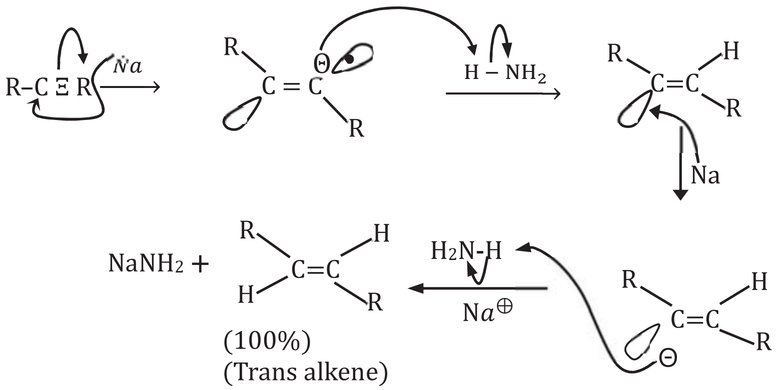
(Z)-3-Hexene
Cis-3-Hexene
(97%)

(b) **Birch Reduction:** (Anti addition of hydrogen: synthesis of trans-alkenes)

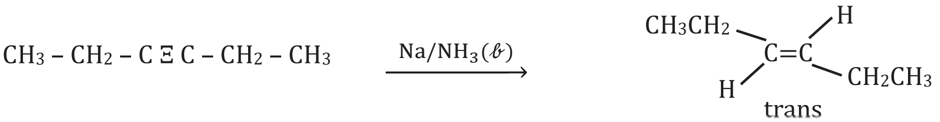


General Reaction

Mechanism: Reagents Na (or Li, K) + liq $NH_3 \rightarrow Na^+ + e^-$ (solvated electron)



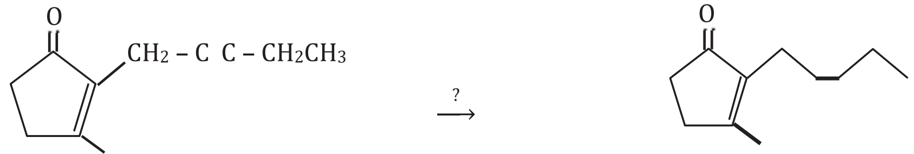
Ex.



trans
Hex-3-ene

Note: This process of reduction is not eligible when terminal alkynes are taken (R–C≡CH) because terminal alkynes form sodium salt with Na metal.

Ex. Identify the reagent for following synthesis.



(A)

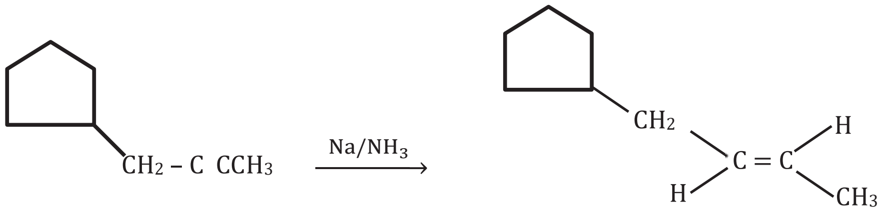
cis — jasmone

Sol. H_2/Landlar's catalyst

$A \xrightarrow[\text{Lindlar's catalyst}]{H}$ cis – Jasmone

Ex. Identify the product in the following reaction:

Sol.

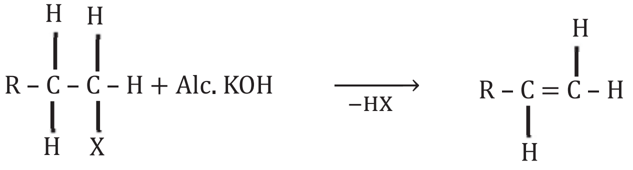


(III) From Alkyl Halides

From Mono Halides

When mono halide reacts with alcoholic KOH or NaOH then respective alkenes are formed

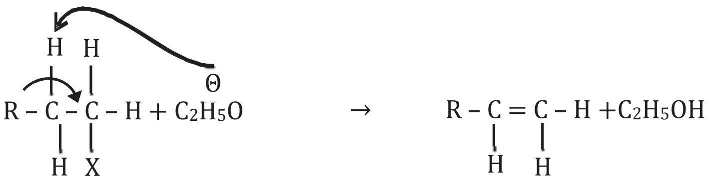
(i)



$$R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}-H + \text{Alc. KOH} \xrightarrow[-HX]{} R-\underset{H}{C}=\overset{H}{C}-H$$

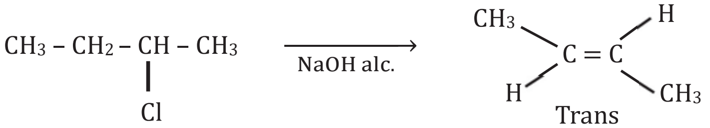
Alkene

$$KOH + C_2H_5OH \rightarrow C_2H_3\overset{\ominus\oplus}{OK} + H_2O$$



$$R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}-H + C_2H_5\overset{\ominus}{O} \rightarrow R-\underset{H}{C}=\underset{H}{C}-H + C_2H_5OH$$

(ii)



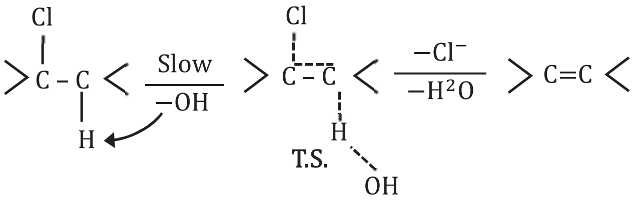
$$CH_3-CH_2-\underset{Cl}{CH}-CH_3 \xrightarrow[\text{NaOH alc.}]{}$$

Trans

This is in accordance with the say Zeff rule.

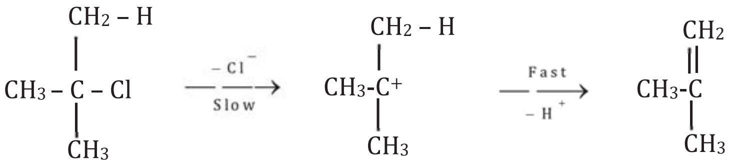
Mechanism: E_2 and E_1 are possible.

E_2 Mechanism



As molecularity of slowest step is two i.e., E_2 mechanism.

E_1 Mechanism



$$CH_3-\underset{CH_3}{\overset{CH_2-H}{C}}-Cl \xrightarrow[Slow]{-Cl^-} CH_3\text{-}\underset{CH_3}{\overset{CH_2-H}{C^+}} \xrightarrow[-H^+]{Fast} CH_3\text{-}\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}}$$

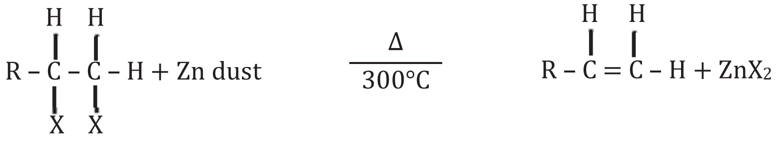
As molecularity of slowest step in one. That is why it is termed as E_1.

Remember: Possibility of E_1 increases with increasing stability of carbo cation. Similarly, possibility of E_2 increases with decreasing stability of expected carbocation.

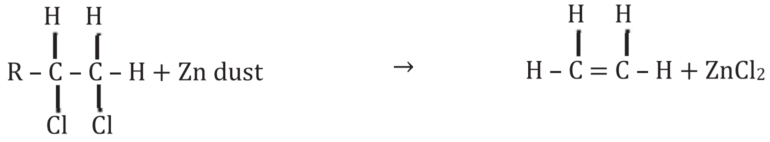
From Dihalides

From vicinal dihalides

When vicinal dihalides are heated with Zn dust, alkene of same no. of carbon is obtained.



$$R-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-H + Zn\ dust \xrightarrow[300°C]{\Delta} R-\overset{H}{C}=\overset{H}{C}-H + ZnX_2$$



$$R-\underset{Cl}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-H + Zn\ dust \rightarrow H-\overset{H}{C}=\overset{H}{C}-H + ZnCl_2$$

From gem dihalides: When gem dihalides is heated with Na in ether then higher alkenes are formed.

$$R–CH.X_2 + 2Zn \xrightarrow[-2\ Zn\ \ _2]{\Delta} R – CH = CH – R$$

$$CH_3 – CHCl_2 + 2Zn \xrightarrow[-2\ ZnCl_2]{} CH_3 – CH – CH – CH_3$$

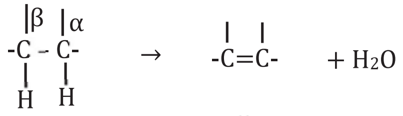
2 - butene

Conclusion – If we take two different types of gems dihalides then we obtain three different types of alkenes.

Note: The above react in is used in the formation of symmetrical alkenes only because if we take two different types of halides then mixture of alkenes is obtained so the yield of are individual alkene is reduced and is improper to separate each alkene from the mixture because the difference of boiling points in alkenes is very less.

(IV) From Alcohols:

Alkenes can be prepared from monohydric alcohols or alkanols by the loss of H_2O and the reaction is known as **dehydration reaction.**



$$\underset{H}{\overset{|\beta}{-\underset{|}{C}}}-\underset{H}{\overset{|\alpha}{\underset{|}{C}-}} \rightarrow \overset{|\ \ |}{-C=C-} + H_2O$$

Alcohol Alkene

The dehydration can be carried with **Al_2O_3** or with **mineral acid** upon heating.

(a) **Dehydration with Al_2O_3:** Ethene is prepared by heating ethanol with Al_2O_3 at 620 K.

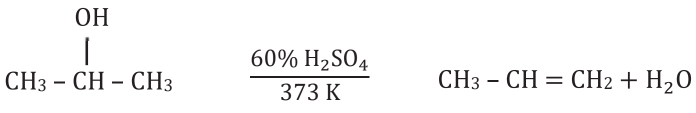
$$CH_3-CH_2-OH \xrightarrow[620\ K]{Al_2O_3} CH_2=CH_2+H_2O$$

Ethanol Ethene

(b) **Dehydration with mineral acid:** Alcohols upon heating with conc. H_2SO_4 form alkenes and the reaction is called **acidic dehydration.**

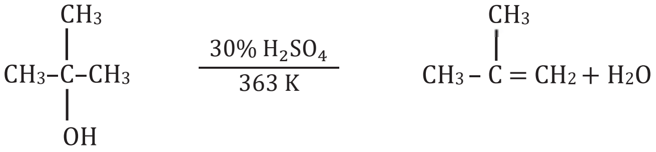
$$CH_3-CH_2-OH \xrightarrow[440\ K]{95\%H_2SO_4} CH_2=CH_2+H_2O$$

Ethanol Ethene



$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[373\ K]{60\%\ H_2SO_4} CH_3-CH=CH_2+H_2O$$

Propan-2-ol Propene



$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow[363\ K]{30\%\ H_2SO_4} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2+H_2O$$

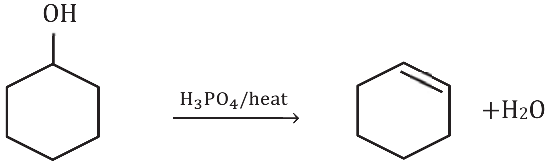
2-Methylpropan-2-ol 2-Methylpropene

From the above reactions, it is clear that the order of acidic dehydration in different alcohols is

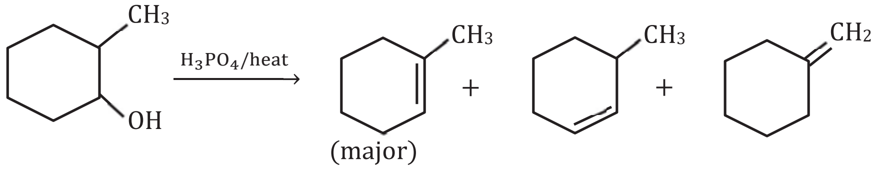
Tertiary > Secondary > Primary

Cycloalkenes can be prepared in the same way be the dehydration of cycloalkanols.

Ex.



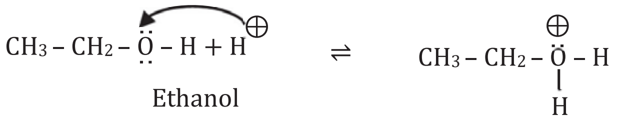
Cyclohexanol Cyclohexene



Regioselectivity of β elimination is governed by Zaitsev's Rule.

Mechanism of Reaction: The acidic dehydration of alcohol proceeds through the formation of a carbocation intermediate and is explained as follows:

Step - I: Alcohol being a Lewis base accepts a proton (H^+) from the acid in a reversible step as follows.

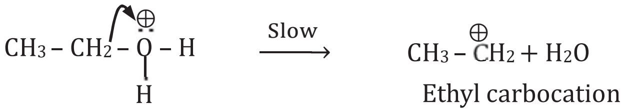


$$CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H+\overset{\oplus}{H} \rightleftharpoons CH_3-CH_2-\overset{\oplus}{\underset{\underset{H}{|}}{\ddot{O}}}-H$$

Ethanol

(From acid)
Protonated ethanol

Step - II: Due to presence of positive change on electronegative oxygen, its electron accepting tendency increases. As a result, C – O bond becomes weak and cleaves as follows:
This is a slow and is regarded as rate determining step.



$$CH_3-CH_2-\overset{\oplus}{\underset{\underset{H}{|}}{\ddot{O}}}-H \xrightarrow{\text{Slow}} CH_3-\overset{\oplus}{C}H_2+H_2O$$

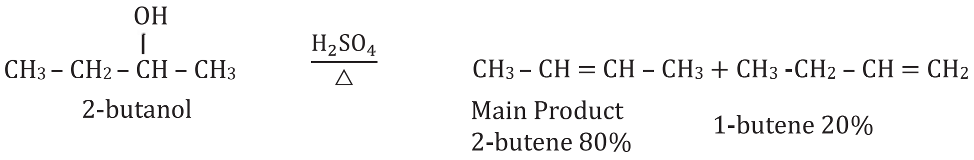
Ethyl carbocation

Step - III: Carbocation is unstable in nature and loses a H^+ and changes into ethane in a fast step as follows:

$$H-CH_2-\overset{\oplus}{C}H_2 \xrightarrow{\text{Fast}} \underset{\text{Ethene}}{CH_2}=CH_2+H^+$$

Note: Dehydration of secondary and tart alcohol is best carried out by using dil. H_2SO_4. Since alkenes produced from those alcohols have a tendency to form polymers under the influence of concentrated acid.

Say Zeff Rule: When two possible alkenes are obtained by the elimination reaction than that alkene will be in good yield, containing maximum number of alkyl group on double bonded C-atoms.



$$CH_3-CH_2-\overset{\overset{OH}{|}}{C}H-CH_3 \xrightarrow[\triangle]{H_2SO_4} CH_3-CH=CH-CH_3+CH_3-CH_2-CH=CH_2$$

2-butanol

Main Product
2-butene 80%

1-butene 20%

$$CH_3-CH_2-CH_2-CH_2\text{-}OH \xrightarrow{H_2SO_4} CH_3-CH=CH-CH_3+CH_3CH_2CH=CH_2$$

1-butanol

2-butene 80%
Main product

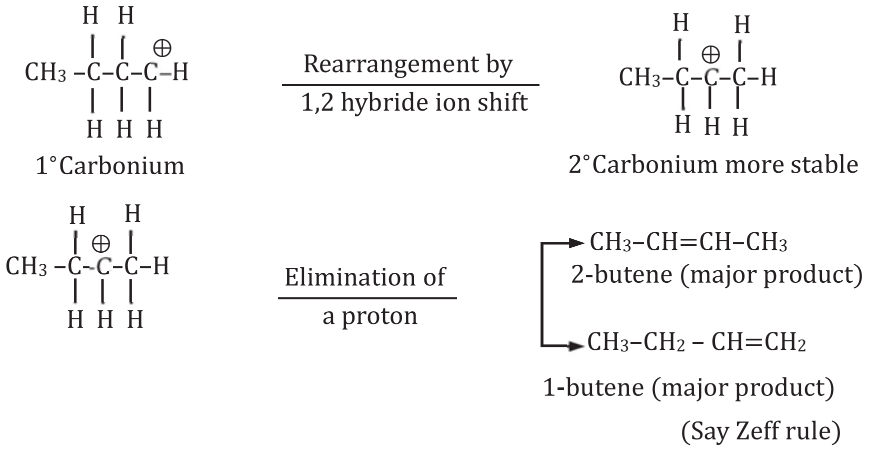
1-butene 20%

Mechanism: Acid catalyzed dehydration of alkanols proceeds via the formation of more stable carbonium ion.

$$CH_3CH_2CH_2-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H+\overset{\oplus}{H} \rightarrow CH_3CH_2CH_2\overset{\oplus}{O}H_2$$

$$CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2-H+\overset{\oplus}{H} \rightarrow CH_3CH_2CH_2-\overset{\oplus}{C}H_2+H_2O$$

Primary Carbonium ion



$$CH_3-CH_2-CH_2-\overset{\oplus}{C}H_2 \xrightarrow[\text{1,2 hybride ion shift}]{\text{Rearrangement by}} CH_3-CH_2-\overset{\oplus}{C}H-CH_3$$

1°Carbonium 2°Carbonium more stable

$$CH_3-CH_2-\overset{\oplus}{C}H-CH_3 \xrightarrow[\text{a proton}]{\text{Elimination of}} \begin{cases} CH_3-CH=CH-CH_3 \\ CH_3-CH_2-CH=CH_2 \end{cases}$$

2-butene (major product)

1-butene (major product)

(Say Zeff rule)

Characteristic of dehydration of alcohol

(1) Since the carbocation is formed s an intermediate in the R.D.S. of dehydration of alcohol The relative reactivity of alcohols decreases in the order.

Tertiary > Secondary > Primary

(2) Since the R.D.S. is reversible it is necessary to remove the H_2O molecule produced in the reaction.

Therefore, in experimented condition conc. H_2SO_4 is added in a regular interval.

(3) For dehydration, different dehydrating agent like Al_2O_3, ThO_2 ca also be employed.

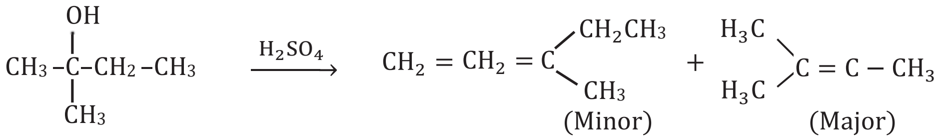
(4) Rearrangement of carbocation can take place.

(5) –OH, is not a good leaving group. in alcohols so turn it into a good leaving group, it is converted into H_2O by protonation.

(6) H_2O is a good leaving group.

Regioselectivity in alcohol dehydration

1. In alcohols such as 2-methyl-2-butanol, dehydration can occur in two different directions to give alkenes that are constitution isomers.
2. More substituted alkene forms the major product and is called Say Zeff alkene or Zaitsev alkene.
3. Less substituted forms the minor product and is called Hofmann's alkene.



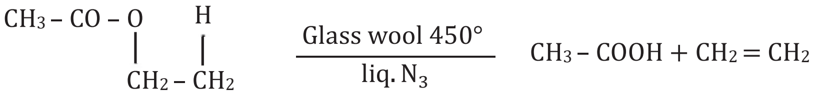
$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-CH_3 \xrightarrow{H_2SO_4} CH_2=CH_2=C(CH_2CH_3)(CH_3) + (H_3C)_2C=C-CH_3$$

(Minor) (Major)

(V) From Esters

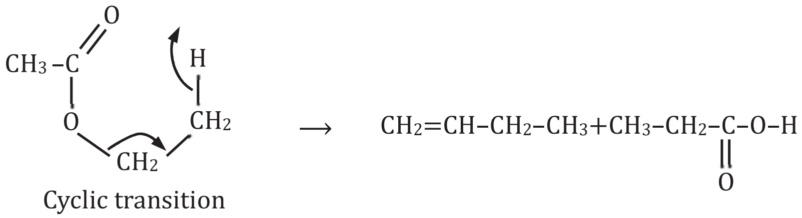
When esters are heated in presence of liq. N_2 and glass wool, then alkyl part of ester converts into respective alkene while alkenoate part of ester is converted into respective acid.

The reaction is called as '**Pyrolysis of Ester**.'



$$CH_3-CO-O-CH_2-CH_2-H \xrightarrow[\text{liq. } N_3]{\text{Glass wool } 450°} CH_3-COOH + CH_2=CH_2$$

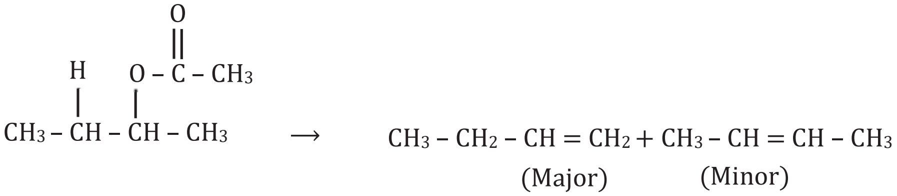
Mechanism: Pyrolysis of Ester is a type of E_1 elimination which proceed via cyclic T.S. that is why the product becomes ‘cis.



$$CH_2=CH-CH_2-CH_3+CH_3-CH_2-\underset{\underset{O}{||}}{C}-O-H$$

Cyclic transition

It is interesting to note that, in this case major produce is 1-alkene in the comparison to 2-alkene.

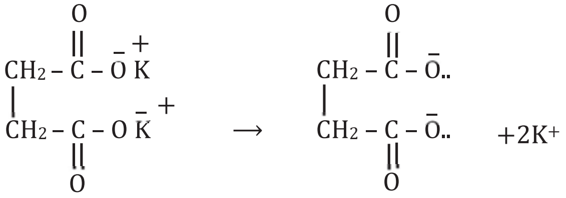


$$CH_3-\overset{\overset{H}{|}}{C}H-\overset{\overset{O-\overset{\overset{O}{||}}{C}-CH_3}{|}}{C}H-CH_3 \longrightarrow \underset{(Major)}{CH_3-CH_2-CH=CH_2} + \underset{(Minor)}{CH_3-CH=CH-CH_3}$$

Major product is obtained by removal of –H from less hindered carbon.

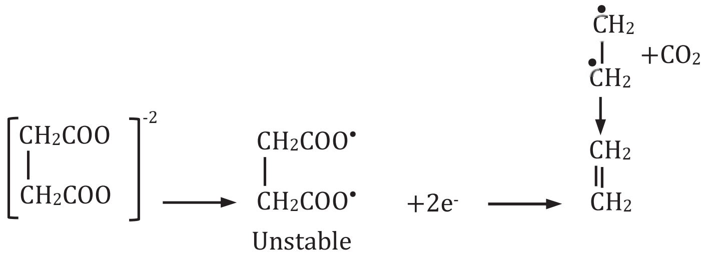
(VI) Kolbe’s Synthesis

When aqueous solution of K or Na succinate is electrolysed, ethylene is released at anode.



$$\begin{array}{l} CH_2-\overset{\overset{O}{||}}{C}-\overset{-}{O}\overset{+}{K} \\ | \\ CH_2-\underset{\underset{O}{||}}{C}-\overset{-}{O}\overset{+}{K} \end{array} \longrightarrow \begin{array}{l} CH_2-\overset{\overset{O}{||}}{C}-\overset{-}{O}{:} \\ | \\ CH_2-\underset{\underset{O}{||}}{C}-\overset{-}{O}{:} \end{array} +2K^+$$

At Anode



$$\begin{bmatrix} CH_2COO \\ | \\ CH_2COO \end{bmatrix}^{-2} \longrightarrow \begin{array}{c} CH_2COO^{\bullet} \\ | \\ CH_2COO^{\bullet} \end{array} +2e^- \longrightarrow \begin{array}{c} \dot{C}H_2 \\ | \\ \dot{C}H_2 \end{array} +CO_2 \longrightarrow \begin{array}{c} CH_2 \\ || \\ CH_2 \end{array}$$

Unstable

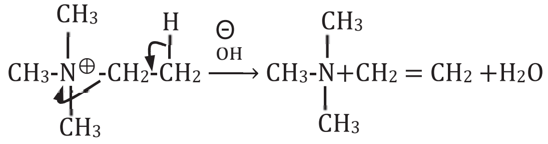
At Cathode

$$2K^+ + 2e^- \longrightarrow 2K$$

$$2K + 2H_2O \longrightarrow 2KOH + H_2$$

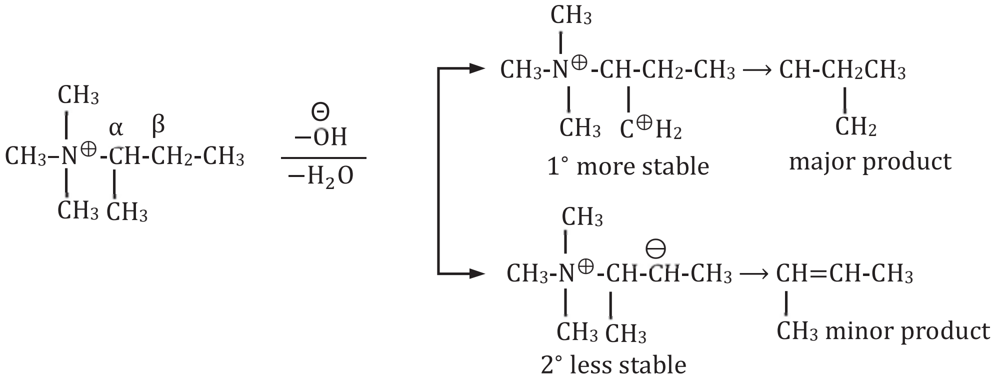
Note: If we use methyl succinic acid as reactant then propylene is formed.

(VII) From Quaternary Ammonium Hydroxide



$$CH_3-\underset{CH_3}{\overset{CH_3}{N^{\oplus}}}-CH_2-\overset{H}{CH_2} \xrightarrow{\overset{\ominus}{O}H} CH_3-\underset{CH_3}{\overset{CH_3}{N}}+CH_2=CH_2+H_2O$$

Ex.



$$CH_3-\underset{CH_3}{\overset{CH_3}{N^{\oplus}}}-\underset{CH_3}{\overset{\alpha}{CH}}-\overset{\beta}{CH_2}-CH_3 \xrightarrow[-H_2O]{-\overset{\ominus}{O}H}$$

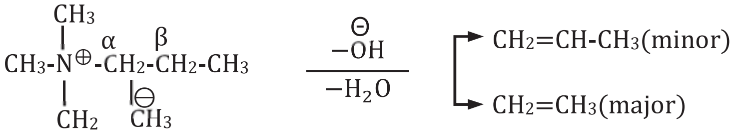
$$CH_3-\underset{CH_3}{\overset{CH_3}{N^{\oplus}}}-\underset{C^{\oplus}H_2}{CH}-CH_2-CH_3 \longrightarrow \underset{CH_2}{CH}-CH_2CH_3$$

1° more stable major product

$$CH_3-\underset{CH_3}{\overset{CH_3}{N^{\oplus}}}-\underset{CH_3}{CH}-\overset{\ominus}{CH}-CH_3 \longrightarrow \underset{CH_3}{CH}=CH-CH_3$$

2° less stable minor product

Ex.



$$CH_3-\underset{CH_2}{\overset{CH_3}{N^{\oplus}}}-\overset{\alpha}{CH_2}-\underset{\ominus\,CH_3}{\overset{\beta}{CH_2}}-CH_2-CH_3 \xrightarrow[-H_2O]{-\overset{\ominus}{O}H} \begin{cases} CH_2=CH-CH_3(\text{minor}) \\ CH_2=CH_3(\text{major}) \end{cases}$$

(a) In this reaction β-hydrogen of tetra-alkyl ammonium ion is attached by a base and alkene is formed.

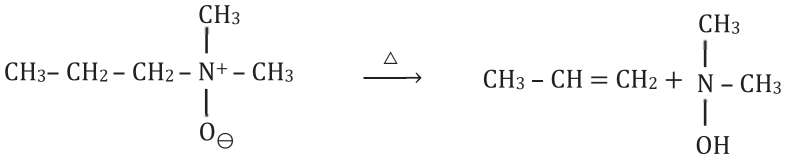
(b) In this reaction intermediate is carbanion. So, yield of product depends on stability of carbanion.

(c) In this reaction Hoffmann's Rule is followed.

(VIII) The Cope Elimination

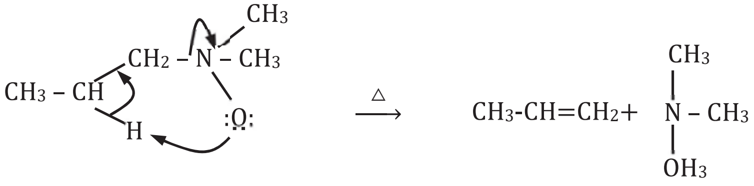
Tertiary amine oxide undergoes the elimination of a dialkylhydroxylamine when they heated. This reaction is called the Cope elimination.

Reaction:



$$CH_3-CH_2-CH_2-\underset{O^{\ominus}}{\overset{CH_3}{N^+}}-CH_3 \xrightarrow{\triangle} CH_3-CH=CH_2+\underset{OH}{\overset{CH_3}{N}}-CH_3$$

Mechanism:

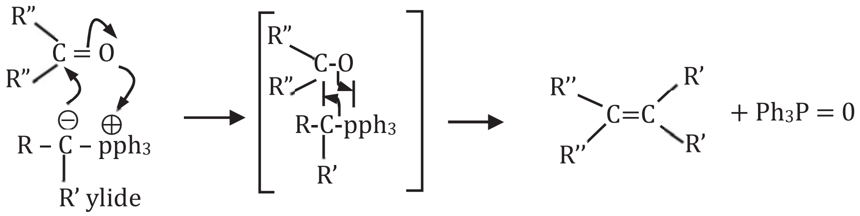


$$CH_3-\underset{H}{CH}-CH_2-\underset{:\ddot{O}:}{\overset{CH_3}{N}}-CH_3 \xrightarrow{\triangle} CH_3\text{-}CH=CH_2+\underset{OH_3}{\overset{CH_3}{N}}-CH_3$$

(IX) Witting Reaction

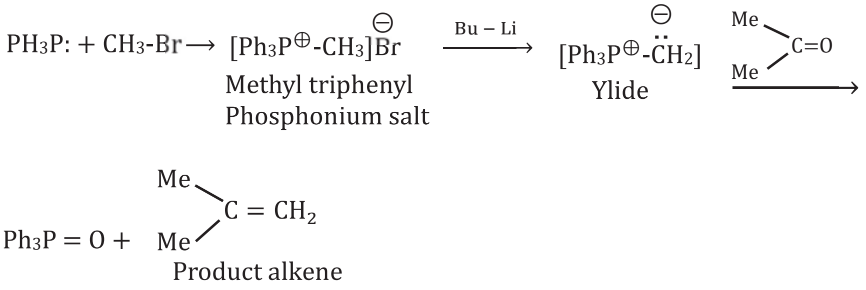
The aldehydes and ketones are converted into alkenes by using a special class of compounds called phosphorus ylides, also called Witting reagents.

The Triphenyl group of phosphorane has a strong tendency to pull oxygen atom of the aldehyde or ketone via a cyclic transition state forming an alkene.



(R, R', R'' and R''' may be hydrogen or any alkyl group)

Ex.



Physical and Chemical Properties of Alkenes

Physical Properties of Alkenes / Hydrocarbon

S.No.	Physical Properties	Homologues Series	Isomers
1.	Physical state	$C_1 - C_3$ gases $C_4 - C_{20}$ liquids $> C_{20}$: solids	
2.	Dipole moment (μ)	-	cis > trans
3.	Polarity	-	cis > trans (Fro $C_{ab} = C_{ab}$ type of alkenes)
4.	Melting point	increases with M.W.	trans > cis (due to more packing capacity)
5.	Boiling point	increases with M.W.	cis > trans # branching decreases B.P. C | C-C=C<C-C=C-C Polarity increases, boiling point increases
6.	Solubility	Practically insoluble in water but fairly soluble in nonpolar solvents like benzene petroleum ether, etc.	cis > trans Polarity increases, solubility in polar solvents increases.

7.	Stability Waals		trans > cis (cis isomers has more Vander repulsion)

Chemical Properties of Alkenes

Alkenes are more reactive than alkane this is because –

(a) The π electrons of double bond are located much far from the carbon nuclei and are thus less firmly bound to them.

(b) π bond is weaker than σ bond and more easily broken.

The reactivity order for alkenes –

$$CH_2{=}CH_2 > R{-}CH{=}CH_2 > R_2C{=}CH_2 \approx RCH{=}CHR > R_2C{=}CHR > R_2C = CR_2$$

(Trans < Cis)

The reactivity order of alkenes has been delt in terms of heat of hydrogenation of alkene, more is the heat of hydrogenation ($\Delta H = -ve$), more is the reactivity, the reactivity of alkene is however also related to

(i) Steric hinderence
(ii) Hyperconjugation
(iii)Heat of Combustion.

All four butanes may be compared, since all give the same products on combustion viz. $4CO_2 + 4H_2O$.

Alkenes give the following type of reactions:

(1) Electrophilic addition reaction
(2) Oxidation reaction
(3) Ozonolysis
(4) Substitution reaction
(5) Polymerization reaction
(6) Isomerisation

(1) Electrophilic Addition Reactions

The double bond in alkenes readily undergoes addition reactions with electrophiles, such as hydrogen halides (e.g., HCl, HBr), water (hydration), and halogens (e.g., bromine, chlorine). In these reactions, the pi bond of the alkene is broken, and new bonds are formed to the carbon atoms of the double bond, resulting in the addition of the electrophile across the double bond.

(2) Oxidation reaction

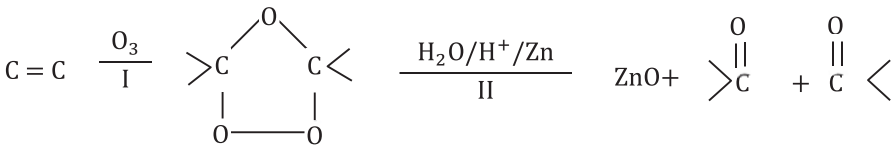
Alkenes can undergo various oxidation reactions, particularly if the double bond is in a position where it can be oxidized.

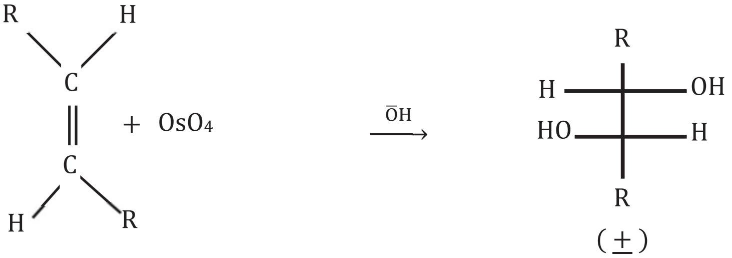
For example, ozonolysis breaks the double bond, forming carbonyl compounds. Other oxidation reactions may lead to the formation of diols or epoxides, depending on the conditions and reagents used.

(3) Ozonolysis

This is the two-step reaction

(i) Ozonide formation
(ii) decomposition of ozonide (reductive hydrolysis)

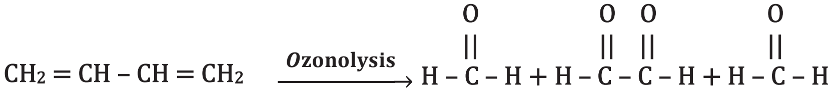




Remember: Ozonolysis gives oxidative cleavage of alkene to form two carbonyl group for each >C=C<. Whether it is in acyclic or cyclic or in aromatic compound.

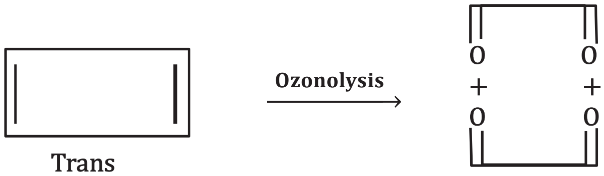
e.g.: -

(a)



$$CH_2 = CH - CH = CH_2 \xrightarrow{Ozonolysis} H-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H$$

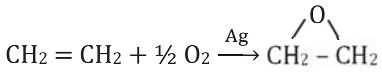
(b)



Trans

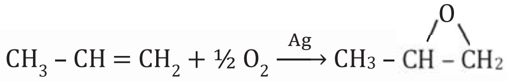
Epoxidation by O_2/Ag

(i)



$$CH_2 = CH_2 + ½ O_2 \xrightarrow{Ag} \overset{O}{CH_2 - CH_2}$$

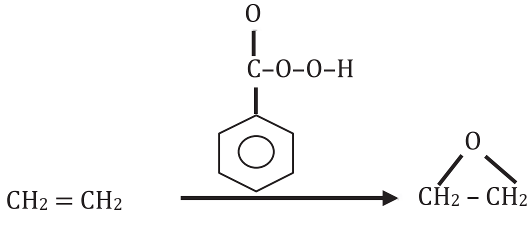
(ii)



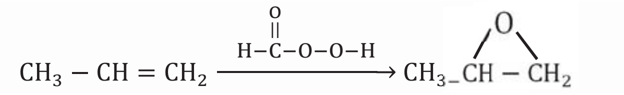
$$CH_3 - CH = CH_2 + ½ O_2 \xrightarrow{Ag} CH_3 - \overset{O}{CH - CH_2}$$

Epoxidation by per acid

(i)



(ii)

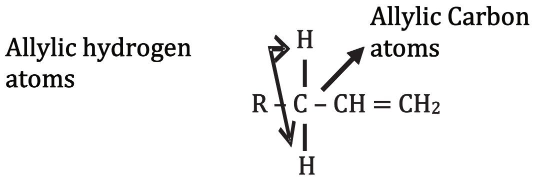


$$CH_3-CH=CH_2 \xrightarrow{H-\overset{O}{\overset{\|}{C}}-O-O-H} CH_3-\underset{\ \ \ O\ \ \ }{CH-CH_2}$$

$$R-CH=CH-R \xrightarrow{CF_3COOOH} R-CH-CH-R$$

(4) Substitution Reaction

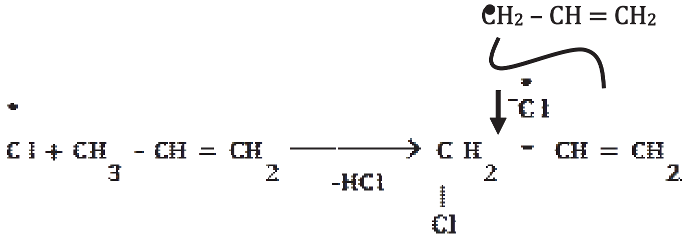
(a) Except ethene other higher alkene having alkyl hydrogen when treated with chlorine or bromine 'α' H is substituted.



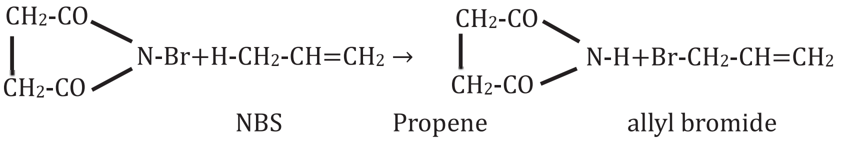
$$CH_3-CH=CH_2+Cl_2 \xrightarrow{500^{\circ}C\ -600^{\circ}C} Cl-CH_2-CH=CH_2+HCl$$

allyl chloride (3-chloropropene)

$$Cl-Cl \overset{\Delta}{\longrightarrow} 2Cl^{\cdot}$$



(b) Allylic bromination can be easily done by NBS (N-bromo succinimide)



(5) Polymerization Reaction

Polymerization is a chemical reaction in which small molecules, called monomers, join together to form a larger molecule, called a polymer. Polymerization can occur through various mechanisms, including addition polymerization and condensation polymerization. Here, I'll focus on addition polymerization, which is commonly associated with alkenes.

In addition, polymerization, monomers with carbon-carbon double bonds (alkenes) undergo a chain reaction to form a long-chain polymer.

The process typically involves the following steps:

Initiation: The polymerization reaction begins with the initiation step, where a free radical initiator generates reactive species, such as free radicals. This can be initiated by heat, light, or a chemical initiator.

For example, in the polymerization of ethylene to form polyethylene, a peroxide initiator may be used to generate free radicals.

Propagation: In this step, the generated free radical attacks a double bond in a monomer molecule, causing the monomer to lose a radical and form a new radical on one end. This newly formed radical can then react with another monomer molecule, continuing the chain reaction. As a result, the polymer chain grows with each monomer addition.

Termination: Eventually, the polymerization reaction terminates when two growing polymer chains combine or when a radical reacts with a terminating agent. Termination reactions can lead to the formation of polymer chains with different end groups or lengths.

The overall result of addition polymerization is the formation of a polymer with a repeating unit derived from the monomer.

For example, the addition polymerization of ethylene produces polyethylene, which has a repeating unit of ($-CH_2-CH_2-$).

(6) Isomerisation

Alkenes isomerase when heated at high temperature or at lower temperature in the presence of various catalysts as $AlCl_3$.

Ex.

(i) $$CH_3-CH_2-CH_2-CH=CH_2 \overset{AlCl_3}{\rightleftharpoons} CH_3-CH_2-CH=CH-CH_3$$

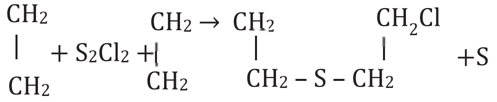
(ii)

$$\overset{\overset{CH_3}{|}}{CH_2}-CH=CH_2 \xrightleftharpoons{AlCl_3} CH_2=\overset{\overset{CH_3}{|}}{C}-CH_3$$

the mechanism proceeds through carbocation

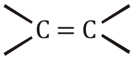
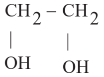
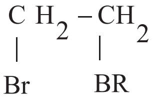
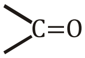
Uses

(a) In plastic formation.
(b) In oxy ethylene welding
(c) As food preservatives and ripening fruits.
(d) As general anaesthetic (C_2H_4 with8 10% O_2)
(e) In preparation of mustard gas



$$\begin{matrix}CH_2\\|\\CH_2\end{matrix} + S_2Cl_2 + \begin{matrix}CH_2\\|\\CH_2\end{matrix} \rightarrow \overset{\overset{CH_2}{|}}{CH_2}-S-\overset{\overset{CH_2Cl}{|}}{CH_2} + S$$

2,2'or (β, β')trichloro diethyl-sulphide
(mustard gas)

Functional Group	Reagent	Observation	Reaction	Remarks
(1) Bayer's Reagent alk. dil. cold $KMnO_4$	Pink colour Disappears 	$CH_2=CH_2+H_2O+O$	$\xrightarrow{alk.KMnO_4}$  $\underset{OH}{CH_2}-\underset{OH}{CH_2}$	Dihydroxylation
(2) Br_2/H_2O	Red colour decolorizes	$Br_2+CH_2=CH_2 \rightarrow$	 $\underset{Br}{CH_2}-\underset{BR}{CH_2}$ White ppt.	Debromination
(3) O_3 (ozone)	 Compounds	$CH_2=CH_2+O_3$	$\xrightarrow{Zn/H_2O}$	Ozonolysis