

ALKANE

INTRODUCTION

Alkanes

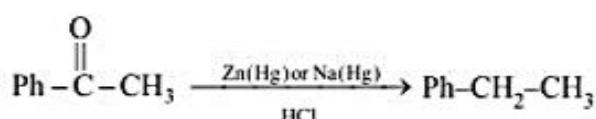
- (i) The alkanes or the paraffins are the saturated hydrocarbons. Many occur naturally, and the chief source of the alkanes is mineral oil or petroleum, which occurs in many parts of the world.
- (ii) These are also called as 'Paraffins' (Parum + Affinis i.e. less reactive).
- (iii) General formula is C_nH_{2n+2} .
- (iv) Hybridisation state of carbon is sp^3 .
- (v) Geometry of carbon is tetrahedral.
- (vi) Bond angle is $109^\circ 28'$.

PREPARATION OF ALKANE

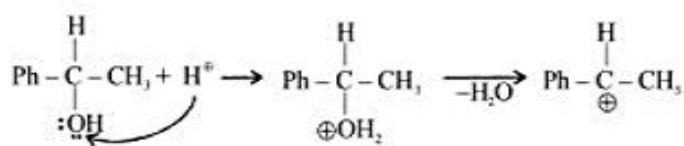
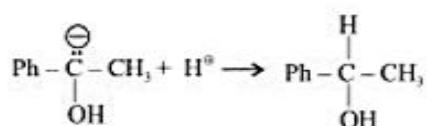
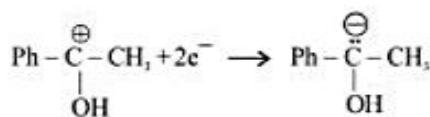
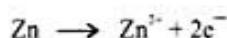
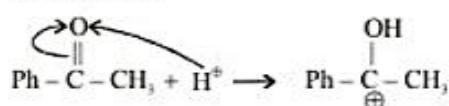
From aldehydes and ketones :

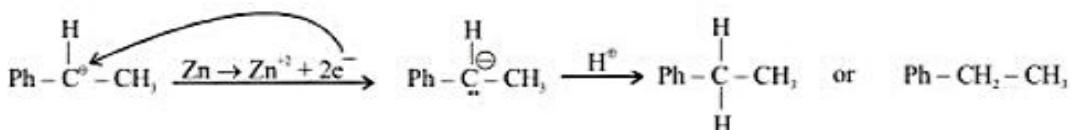
Clemmensen Reduction :

The Clemmensen reduction is most commonly used to convert acylbenzenes to alkylbenzenes, but it also works with other ketones and aldehydes that are not sensitive to acid. The carbonyl compound is heated with an excess of amalgamated zinc (zinc treated with mercury) and hydrochloric acid. The actual reduction occurs by a complex mechanism on the surface of the zinc.



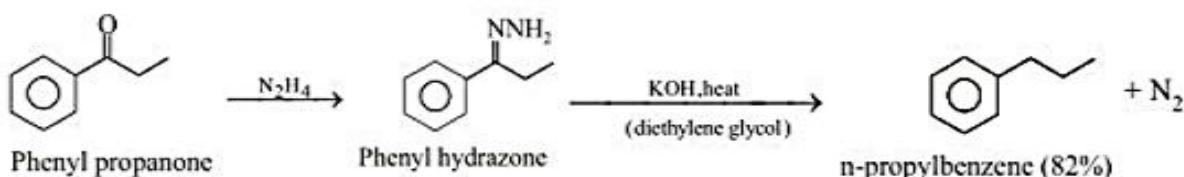
Mechanism



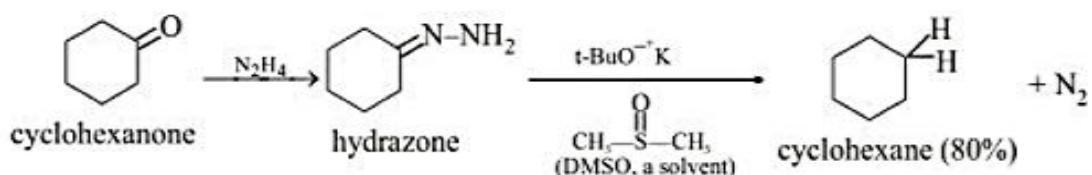
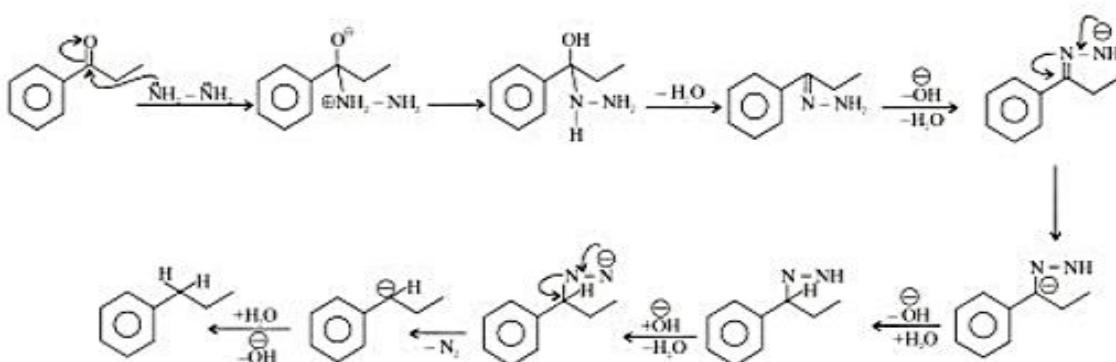


Wolf-Kishner Reduction.

Compounds that cannot survive treatment with hot acid can be deoxygenated using the Wolf-Kishner reduction. The ketone or aldehyde is converted to its hydrazone, which is heated with a strong base such as KOH or potassium t-butoxide.



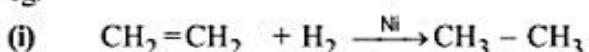
Mechanism



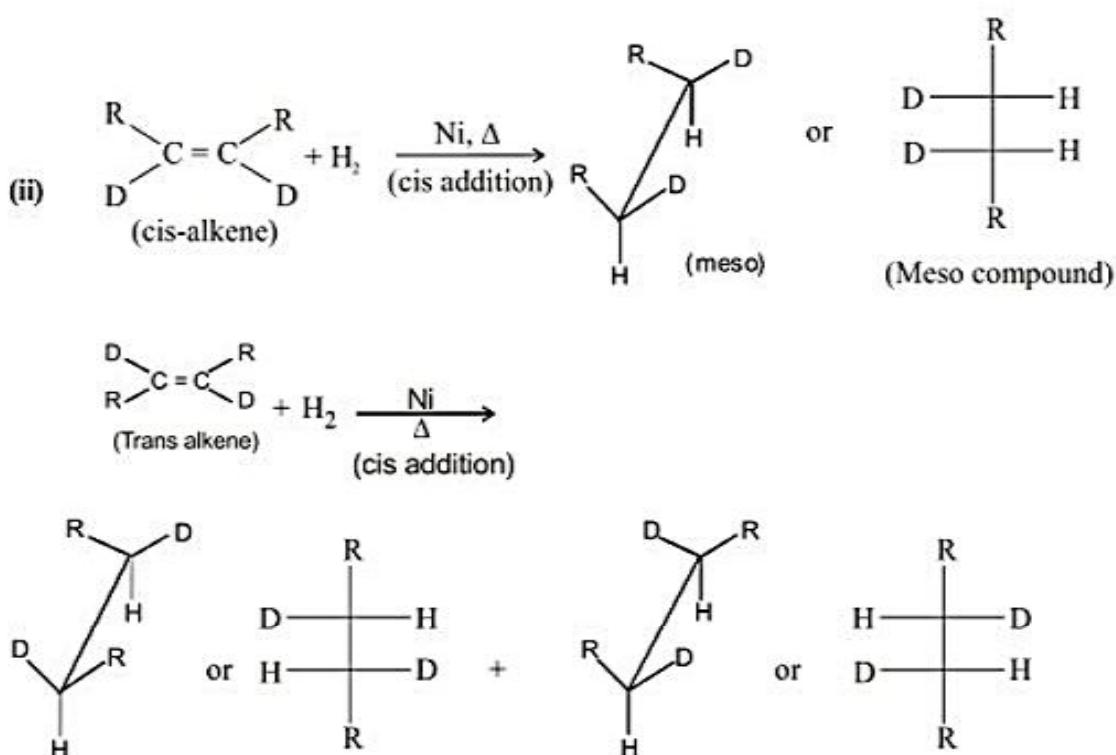
From alkene :

By catalytic hydrogenation : Addition of H_2 on alkene takes place in *cis manner* in the presence of Pt or Ni or Pd to give alkane.

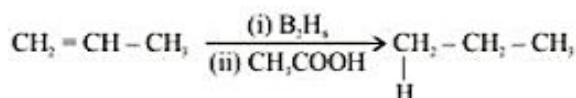
e.g.



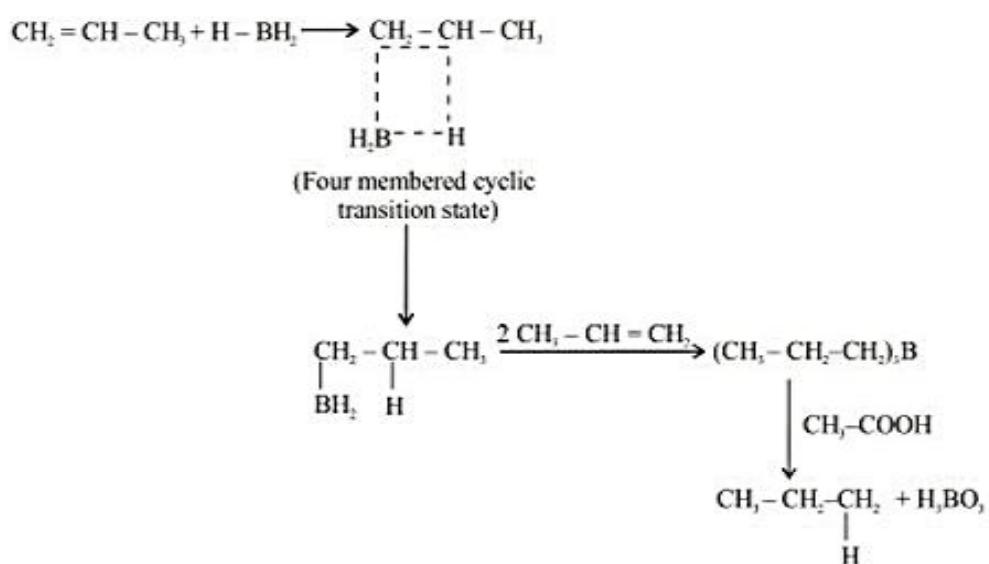
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By hydroboration reduction of alkene

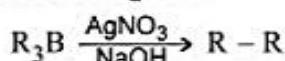


Mechanism

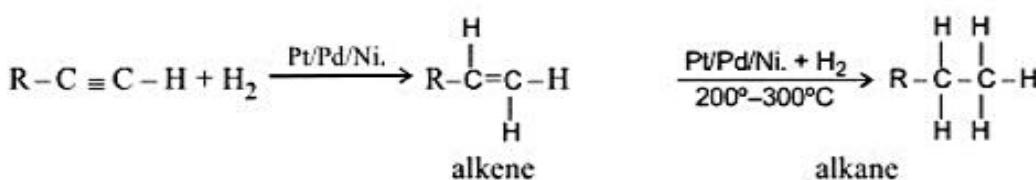


NOTE : Long-chain alkane may be possible by the coupling of alkyl boranes.

If (AgNO₃ + NaOH) is used instead of H₂O/H⁺



From alkyne - by reduction :



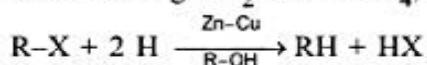
If Ni is used, it is called *Sabatier - Senderen's* reaction (catalytic hydrogenation).

From Alkyl halides :

By reduction :

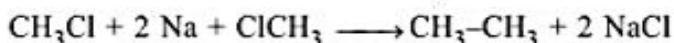
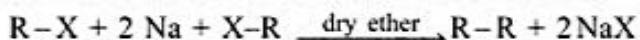
When alkyl halide is reduced with

Zn-Cu couple + ROH or Na + EtOH/ Na- Hg + H₂O or LiAlH₄, then we get respective alkane.



Wurtz reaction :

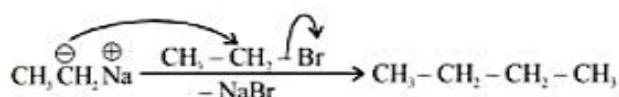
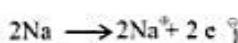
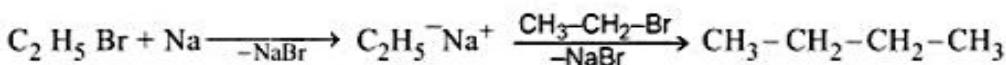
When alkyl halide reacts with Sodium in presence of dry ether then we get higher alkane. Mechanism of the reaction is based on ionic and free radical both.



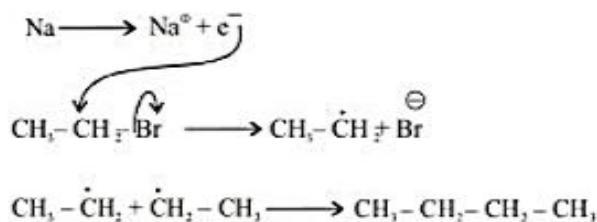
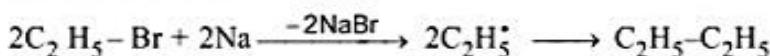
NOTE : * This reaction is not suitable for tertiary alkyl halides

Mechanism : Two mechanism has been suggested for Wurtz reaction.

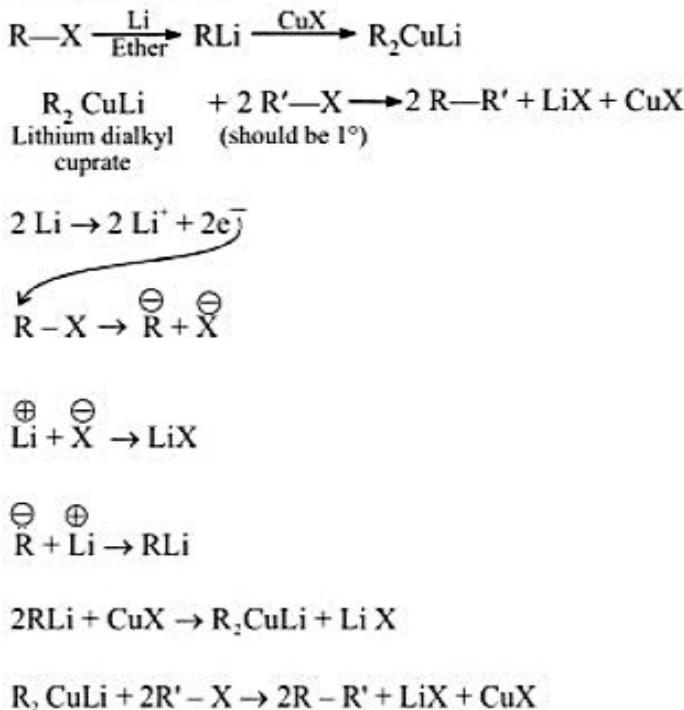
Ionic mechanism



Free radical mechanism



Corey-House Synthesis



This method is better than Wurtz and can be used for preparing symmetrical as well as unsymmetrical alkanes (having an odd number of carbon atoms).

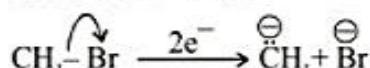
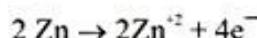
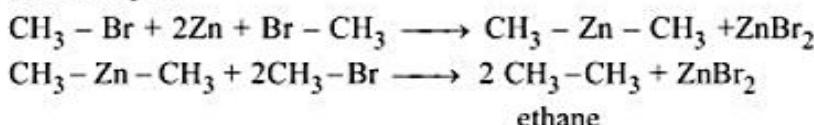
Frankland's reaction :

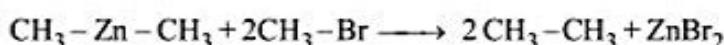
If alkyl halide is treated with Zn dust in closed tube then higher symmetrical alkanes will be formed.



This is known as Frankland's reaction, in this reaction first Frankland's reagent (R-Zn-R , dialkyl Zinc) is formed. Which then react with alkyl halide to give higher alkanes. [Where $\text{R} = \text{CH}_3$]

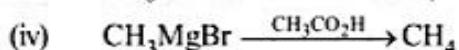
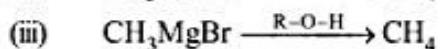
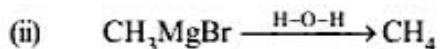
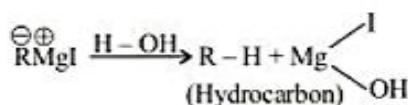
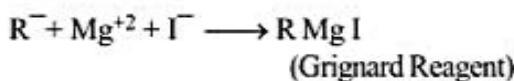
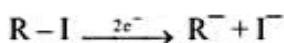
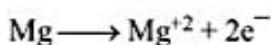
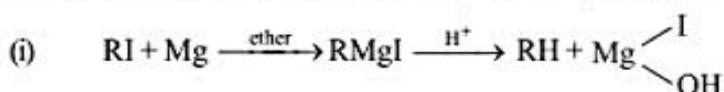
For Example:-





Grignard reagents.

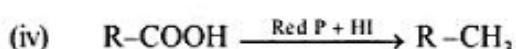
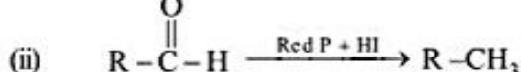
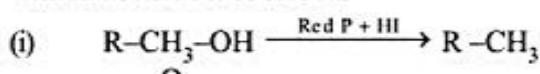
Alkyl halides in ether react with magnesium to form alkyl magnesium halides or Grignard reagents which, on treatment with water or dilute acid, are decomposed to alkanes.



Preparation by Wurtz reaction, Kolbe electrolysis Ullmann reaction, Fitting reaction, Wurtz-Fitting reaction already discussed in free radical reaction.

From Red P + HI :

It is a powerful reducing agent which will convert, aldehyde, ketone, alcohol, carboxylic acid to alkanes with same number of carbon.

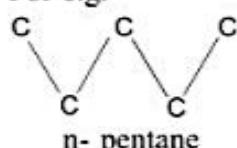


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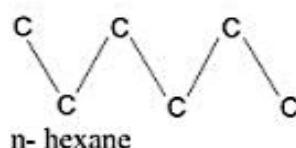
PHYSICAL PROPERTIES

- The first four alkanes (from methane to butane) are colourless and odourless gases. The next thirteen (from pentane to heptadecane) are colourless and odourless liquids. And, the rest of higher alkanes (having 18 carbon atoms or more) are colourless solids at ordinary temperature.
- Alkanes being non-polar molecules, are soluble in non-polar solvents like benzene, ether, and chloroform. However, they are insoluble in polar solvents like water. Their solubility decreases with increase in their molecular weight.
- Melting and boiling points are increases with molecular mass and decreases with No. branches. As far as melting point is concerned the alkane having even carbons has more M.P. than odd carbons, since the intermolecular forces in a crystal depend not only upon the size of the molecules but also upon how well they fit into a crystal lattice.

For e.g.



(both methyl group are directed on same side)



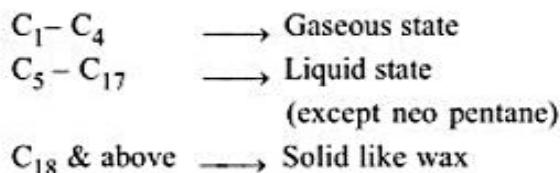
(both methyl group are adversely directed)

Melting point of alkane having odd number of 'c' < alkane with even number of carbom atom.

- Boiling point decreases with the increment of branches.
(n-Pentane is liquid but neo-Pentane is gas due to increase in branching, surface area decrease therefore intermolecular forces & Vander Waals forces of attraction decreases).

- Physical state:

Alkanes

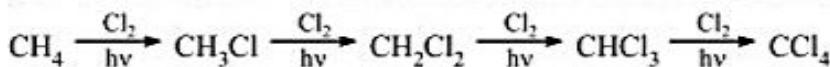


- Alkanes are lighter than water, so it floats over water.

CHEMICAL PROPERTIES

1. Halogenation

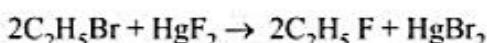
Alkanes react with bromine or chlorine in the presence of sunlight or UV light or in dark at high temperatures ($250^{\circ}\text{C} - 400^{\circ}\text{C}$) forming a mixture of substituted products. For example,



The yield of monohalogenated product can be increased by using substrate (alkane) in excess.

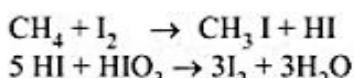
The reactivity of halogens follows the order: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

Direct fluorination is explosive and can be achieved by the action of inorganic fluorides on bromo or iodo derivatives.

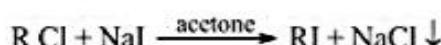


Bromination is slower than chlorination and is carried out at higher temperatures.

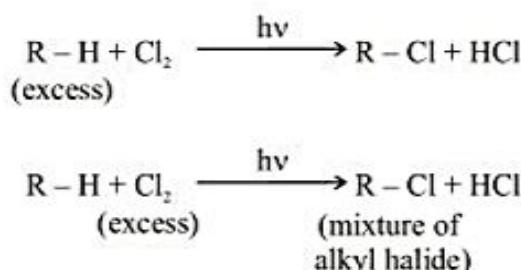
Iodination is reversible and can be carried out sufficiently in the presence of strong oxidising agents like iodic acid (HIO_3) or nitric acid that destroys hydroiodic acid (HI) and shifts the equilibrium towards the right.



Alkyl iodides can be prepared conveniently by **Finkelstein reaction** which involves treating chloro or bromoderivative with NaI in acetone or methanol solution.



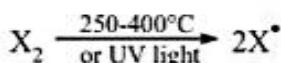
Alkyl chlorides or bromides cannot be prepared by this method of halide exchange because NaCl and NaBr are insoluble in acetone.



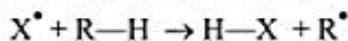
Mechanism of Halogenation :

The mechanism involves the following steps:

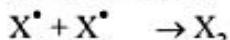
(i) Chain-initiation step



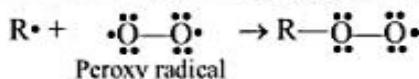
(ii) Chain-propagation step



(iii) Chain-termination step

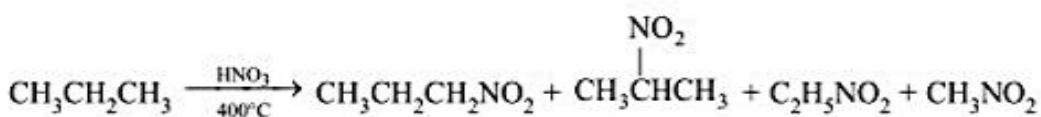


Radical inhibitors stop chain propagation by reacting with free radical intermediates.

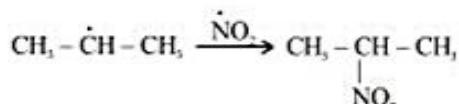
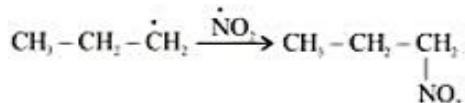
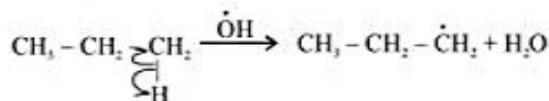
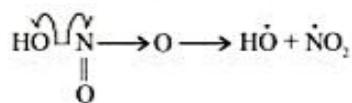


2. Nitration.

Under certain conditions, alkanes react with nitric acid, a hydrogen atom being replaced by a nitro-group, NO_2 . This process is known as nitration. Nitration of the alkanes may be carried out in the vapour phase between 150°C and 475°C , whereupon a complex mixture of mononitroalkanes is obtained.



Mechanism



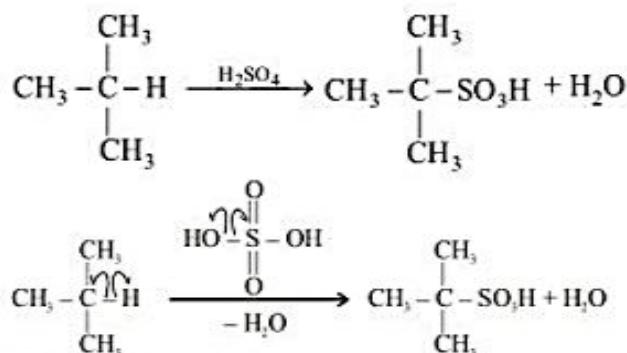
Similarly we deduce other products through some process.

3. Sulphonation.

Sulphonation is the process of replacing a hydrogen atom by a sulphonic acid group, SO_3H . Sulphonation of a normal alkane from hexane onwards may be carried out by treating the alkane with oleum (fuming sulphuric acid). It has been shown that in concentrated sulphuric acid, hydrocarbons containing a tertiary hydrogen atom undergo hydrogen exchange (Ingold et. al. 1936). The mechanism is believed to occur via a carbonium ion:



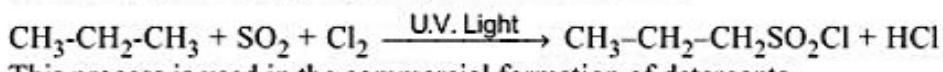
This reaction is of particular interest since optically active hydrocarbons have been racemised in sulphuric acid; e.g., Burwell et. al. (1948) have shown that optically active 3-methylheptane is racemised in sulphuric acid.



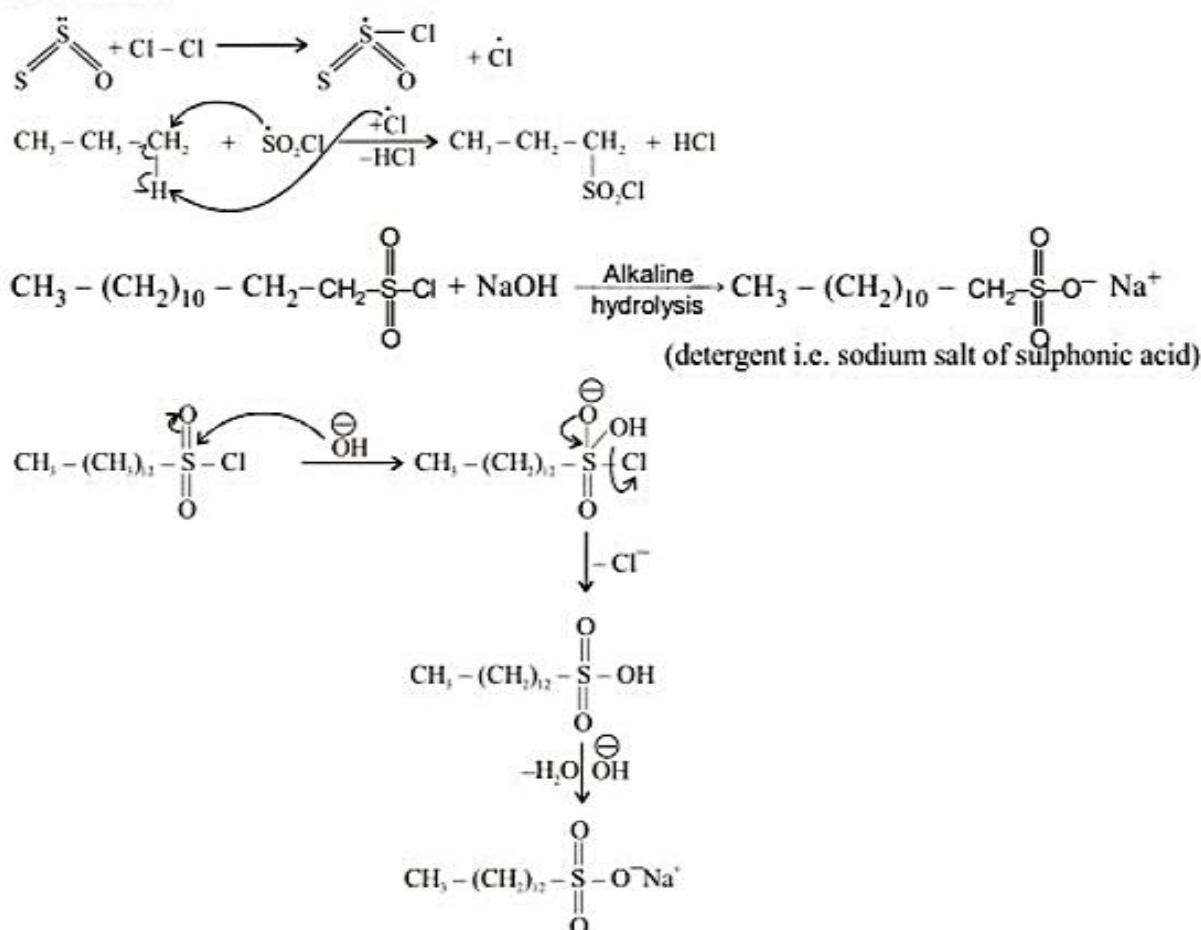
Imp. Rate of sulphonation $3^\circ > 2^\circ > 1^\circ$.

4 Chlorosulphonation/Reaction with SO_2 & Cl_2 :

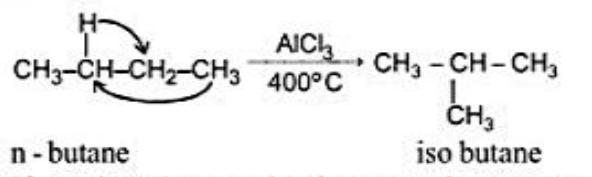
The reaction is also called as Reed's reaction. When propane reacts with SO_2 and Cl_2 in presence of ultraviolet light then propyl sulphonyl chlorides are formed.



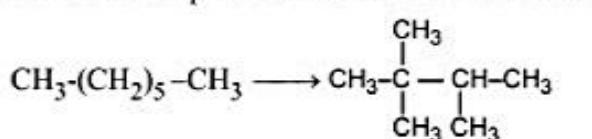
This process is used in the commercial formation of detergents.

Mechanism

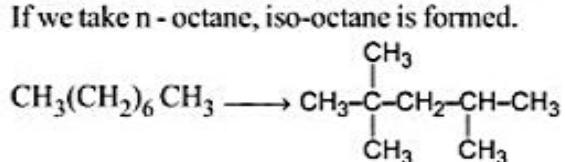
- 5. Isomerization :** Lower alkanes are not isomerised but butane or higher number of alkanes if heated with aluminium chloride at high temperature then they convert into stable isomers by the rearrangement reaction. Isomerisation is also held by heating alkane with- ($\text{AlX}_3 + \text{HX}$; X = Cl, Br, I or $\text{Al}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$) at 200°C .



If we take n- heptane then it converts into most stable form Triptane (trivial name).



If we take n - octane, iso-octane is formed.



n- octane

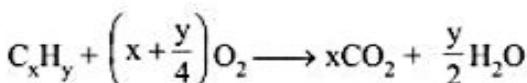
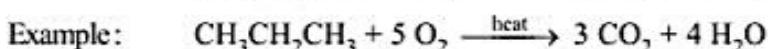
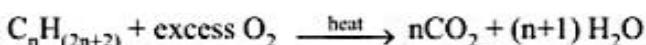
iso-octane

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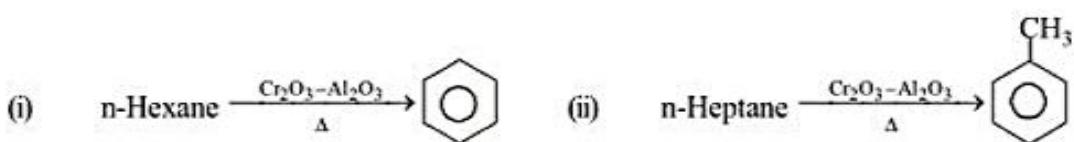
Reaction is used in Petroleum industries, with the help of this reaction, we can convert unbranched alkane to branched alkane (i.e. lower octane number alkane to higher octane number alkane) or bad fuel to good fuel.

6. Combustion :

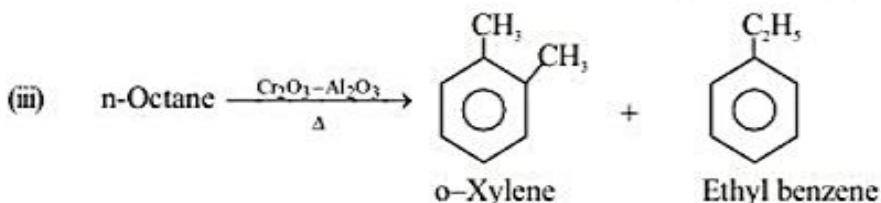
Combustion is a rapid oxidation that takes place at high temperatures, converting alkanes to carbon dioxide and water. Little control over the reaction is possible, except for moderating the temperature and controlling the fuel / air ratio to achieve efficient burning.



7. Aromatization :



For converting aliphatic to aromatic.



MCQ

- Q.1** The Kolbe synthesis of alkane using a sodium salt of butanoic acid gives -
 (A) n-hexane (B) isobutane (C) n-butane (D) propane
- Q.2** Electrolysis of an aqueous solution of sodium butanoate gives main product –
 (A) octane (B) heptane (C) hexane (D) butane
- Q.3** In Wurtz reaction if we take CH_3Cl & C_2H_5Cl then product will be -
 (A) Propane + Ethane (B) Propane
 (C) Propane + Ethane + Butane + Ethene + CH_4 (D) Propane + Butane
- Q.4** Butane cannot be obtained by :
 (A) Action of soda lime on sodium butanoate
 (B) Clemmensen reduction (Zn amalgam in conc. HCl) of butanone
 (C) Action of water on butyl magnesium iodide
 (D) Sabatier Senderens hydrogenation of butene.

- Q.5** The reaction conditions leading to the best yields of C_2H_5Cl are -
 (A) C_2H_6 (Excess) + Cl_2 $\xrightarrow{u.v.\text{light}}$ (B) C_2H_6 + Cl_2 $\xrightarrow{\text{dark room temp.}}$
 (C) C_2H_6 + Cl_2 (Excess) $\xrightarrow{u.v.\text{light}}$ (D) C_2H_6 + Cl_2 $\xrightarrow{u.v.\text{light}}$
- Q.6** $C_2H_6 + SO_2 + Cl_2 \xrightarrow{U.V.\text{Light}}$ product. In this reaction product will be -
 (A) C_2H_4 (B) CH_3CH_2Cl (C) $CH_3CH_2SO_2Cl$ (D) C_2H_2
- Q.7** Which of the following should be subjected to Wurtz reaction to obtain the best yield of n-hexane?
 (A) Ethyl chloride and n-butyl chloride (B) Methyl bromide and n-propyl bromide
 (C) n-Propyl bromide (D) Ethyl bromide and n-butyl bromide
- Q.8** 2-Methylbutane on reacting with bromide in the presence of sunlight gives mainly -
 (A) 1-Bromo-3-methylbutane (B) 2-Bromo-3-methylbutane
 (C) 2-Bromo-2-methylbutane (D) 1-Bromo-2-methylbutane
- Q.9** Which of the following alkyl bromides may be used for the synthesis of 2,3-dimethylbutane by Wurtz reaction?
 (A) n-Propyl bromide (B) Isopropyl bromide (C) Isobutyl bromide (D) s-Butyl bromide

ANSWER KEY

Q.1 A

Q.5 A

Q.9 B

Q.2 C

Q.6 C

Q.3 C

Q.7 C

Q.4 A

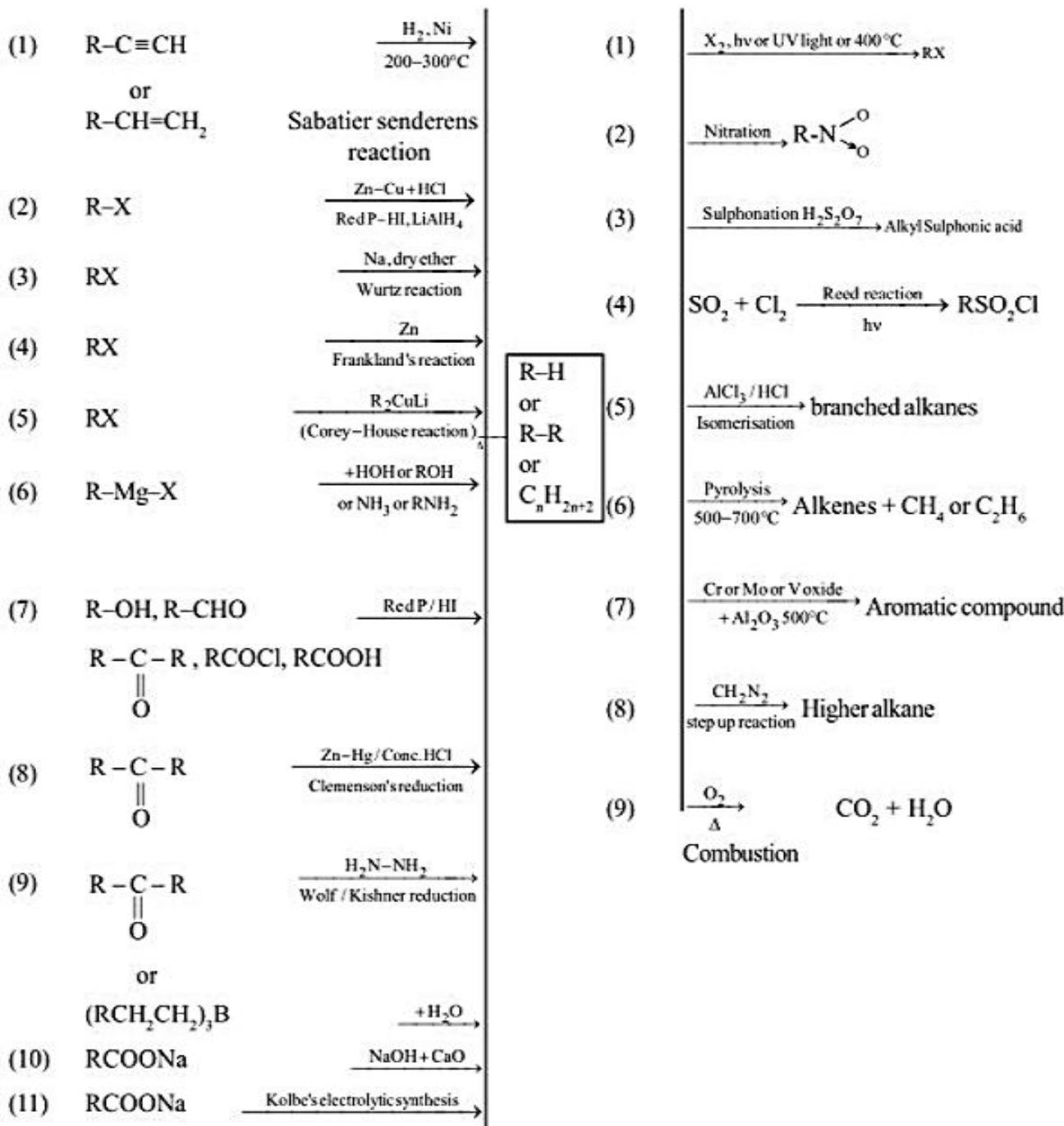
Q.8 C

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REACTION CHART FOR ALKANES

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ALKENE

ALKENE

- (a) General formula : C_nH_{2n} .
- (b) Functional group : in alkenes is $>C=C<$
- (c) The double bond is made up of one sigma and one pi bond.
- (d) The doubly bonded carbon atoms are sp^2 hybridized.
- (e) Geometry of unsaturated 'C' carbon is trigonal planar.
- (f) $C=C$ bond length is 1.34 Å.
- (g) $C-H$ bond length is 1.10 Å.
- (h) $C=C$ bond energy is 143.1 k cal mol⁻¹.
- (i) $C-H$ bond energy is 98.69 k cal mol⁻¹.
- (j) Alkene shows chain, position, ring chain, optical & geometrical isomerism.

METHODS OF PREPARATION OF ALKENES

Elimination reactions

Elimination reactions consist in removing the two groups (generally one being a proton and other is leaving group from one or two carbon atoms of a substrate to form an unsaturated linkage.

Elimination reactions are classified under two general categories.

Types of Elimination reactions

1. α -elimination (1, 1)
2. β -elimination (1, 2)

1. **α -elimination :** When the two atoms or groups are eliminated from the same carbon, the process is called α -elimination.
2. **β -elimination :** When the two groups or atoms are removed from the two adjacent carbon atoms, the process is known as β -elimination.

Some important terms

- (1) **Substrate :** That molecule or ion which undergoes change is called substrate. Substrate may be alkyl halide, alcohol etc.
- (2) **Base :** It is negative ion or neutral molecule which abstract the proton from the substrate.
- (3) **Leaving Group :** It is an ion or molecule which leaves the substrate with a pair of electron. The tendency of leaving group is inversely proportional to basic strength. Leaving group ability of different halide ions follows the sequence
 $I^- > Br^- > Cl^- > F^-$

β -Elimination can occur by three different mechanism

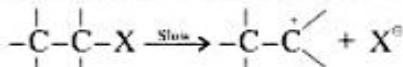
- (1) E-1 mechanism
- (2) E-2 mechanism
- (3) E1 cB mechanism

E-1 MECHANISM

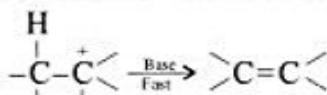
(a) It is called unimolecular elimination reaction.

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

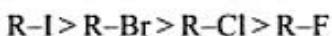
(d) Since in R.D.S. only substrate undergoes covalency change.
i.e. it follows first order kinetics with respect to substrate

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

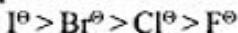
(e) Since in R.D.S. carbocation is formed as an intermediate so the reactivity order of different substrate follows the stability of order of carbocation formed.

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



Above order is parallel to order of leaving group ability



(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.

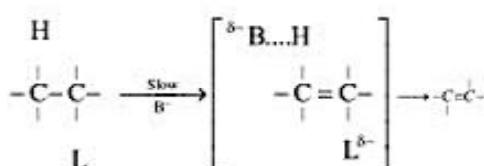
(i) E-1 mechanism involves carbocation as an intermediate so rearrangement of carbocation can take place if possible. More stable carbocation forms the major product in the reaction.

E-2 MECHANISM

(a) It is known as bimolecular elimination mechanism.

(b) It take place in single step.

(c) It involves the formation of transition state



Transition State

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

(e) Rate of reaction depends on the concentration of substrate as well as of base i.e. it follows the second-order kinetics.

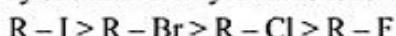
$$\text{Rate} = [\text{Substrate}] [\text{Base}]$$

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

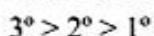
$$\frac{K_H}{K_D} = \frac{7}{1}$$

- (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



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

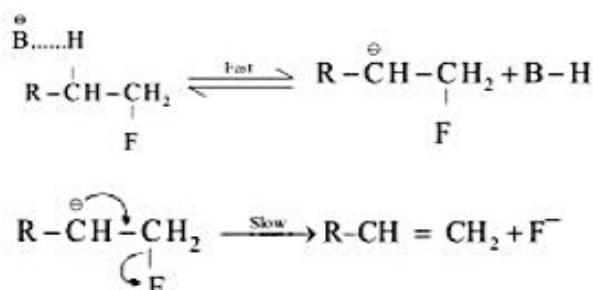
- (i) Non-polar solvent favors the E-2 mechanism.

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

E1 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.

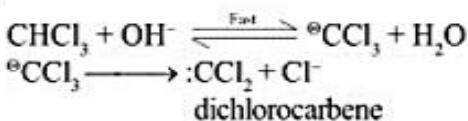


- (b) The overall rate of the reaction is limited to slower second step & hence the rate of reaction depends only on the concentration of carbanion.
(c) Since carbanion is the conjugate base of the alkyl halide and rate of reaction depends on concentration of carbanion hence the mechanism is designated as E1cB mechanism.

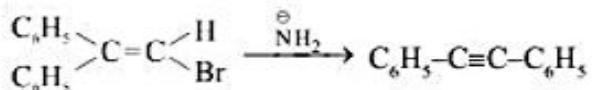
Mechanism of α -Elimination

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

for eq.

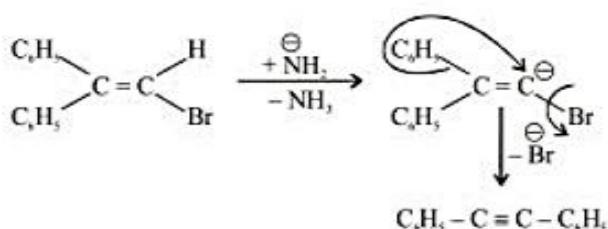


Another example of α -elimination reaction is formation of diphenylacetylene from 2, 2-diphenyl vinyl bromide and sodamide.

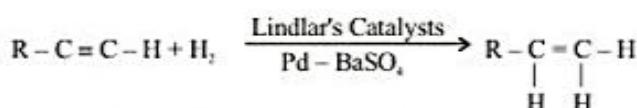


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Mechanism

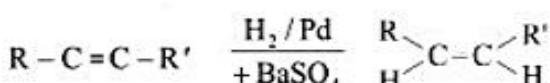


From Alkynes

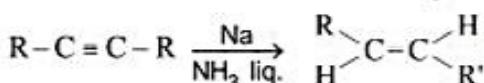


poison of catalyst such as BaSO_4 , CaCO_3 , are used to stop the reaction after the formation of alkene, otherwise alkanes are formed.

- (i) The reaction takes place at the surface of Pd, that is why it is *cis addition* and the product is cis form eg.

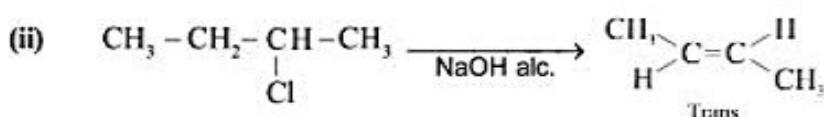
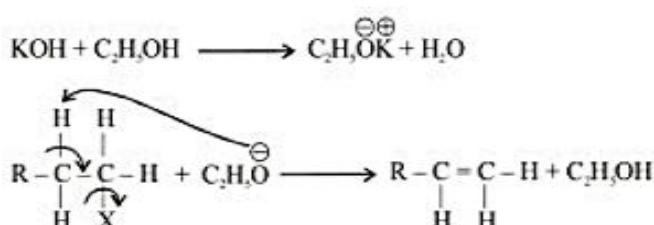
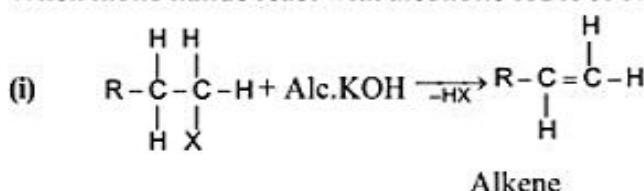


- (ii) Alkyne can be reduced to trans alkene by using $\text{Na} + \text{NH}_3$, or LiAlH_4



From mono halides

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



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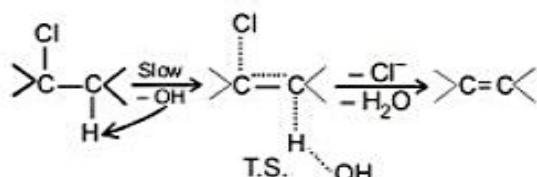
NOTE : $\text{CH}_3\text{---CH}_2\text{CHX---CH}_3 \longrightarrow \text{CH}_3\text{---CH}_2\text{---CH=CH}_2 \longrightarrow \text{CH}_3\text{---CH=CH---CH}_3$

Minor Major

$\text{CH}_3\text{---CH=CH---CH}_3$ (Trans) is the major product because it is more stable as having six ' α ' Hydrogen in the comparison to $\text{CH}_3\text{---CH}_2\text{---CH=CH}_2$ having only two ' α ' hydrogen. This is in accordance with the saytzeff rule.

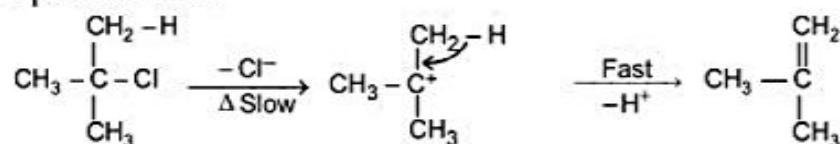
Mechanism : E_2 and E_1 are possible.

E_2 Mechanism :



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

E_1 Mechanism :-

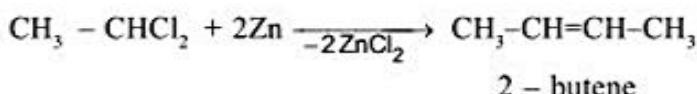
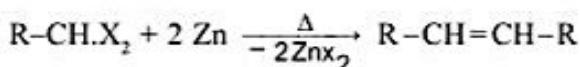


As molecularity of slowest step is one. That is why it is termed as E_1 .

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

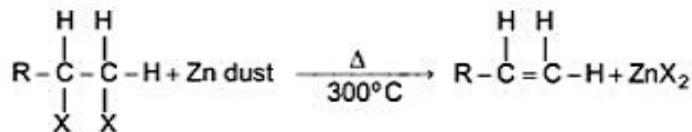


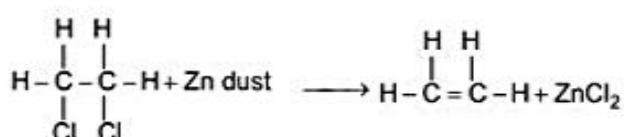
Conclusion – If we take two different types of gemdihalides then we obtain three different types of alkenes.

Note : The above reaction 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 an individual alkene is reduced and it is improper to separate each alkene from the mixture because the difference of boiling points in alkenes is very less.

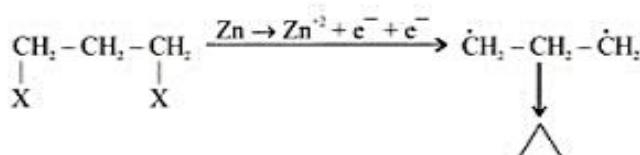
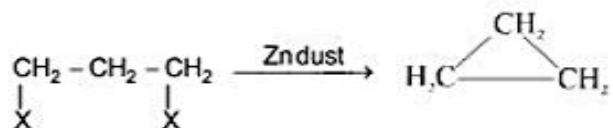
From vicinal dihalides :

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



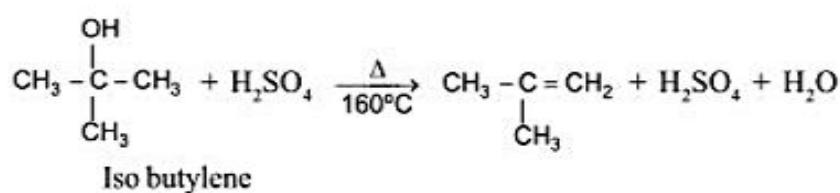
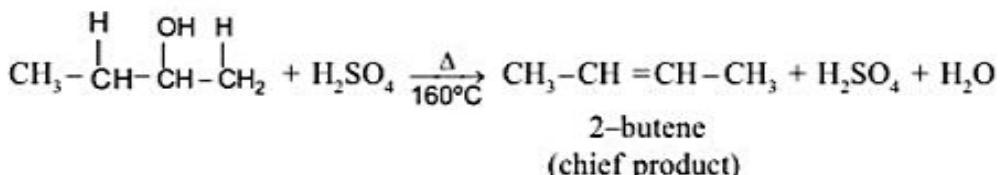
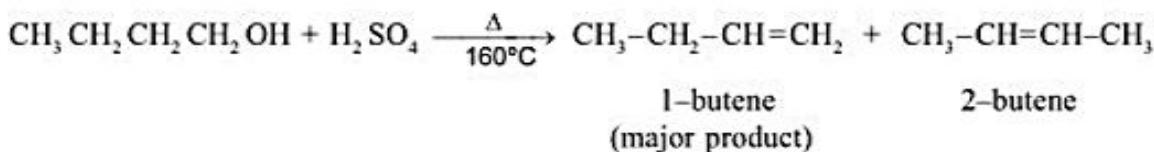
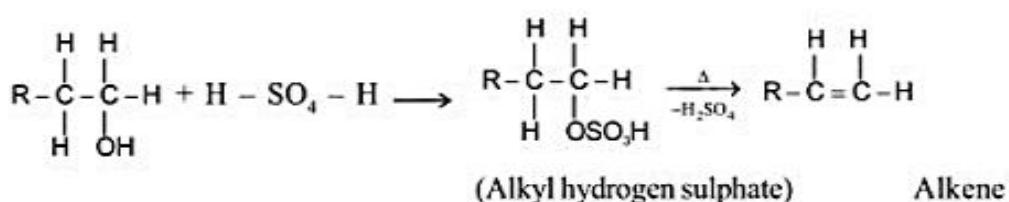


Note : Alkene is not formed from 1,3 dihalides. Cyclo alkanes are formed by dehalogenation of it.
For eg.

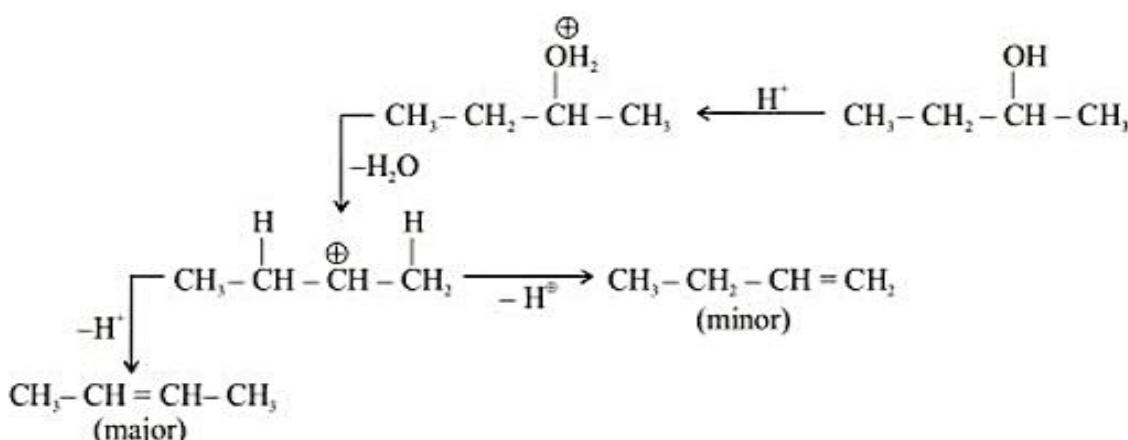


From Alcohols

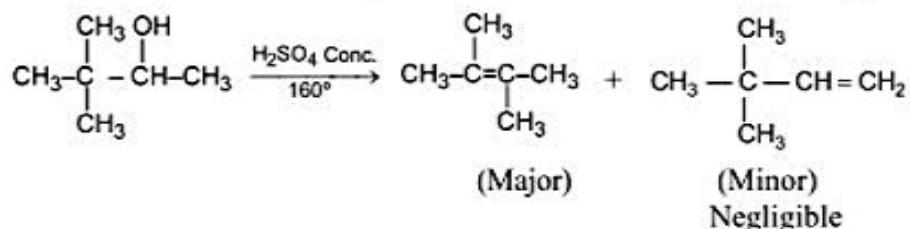
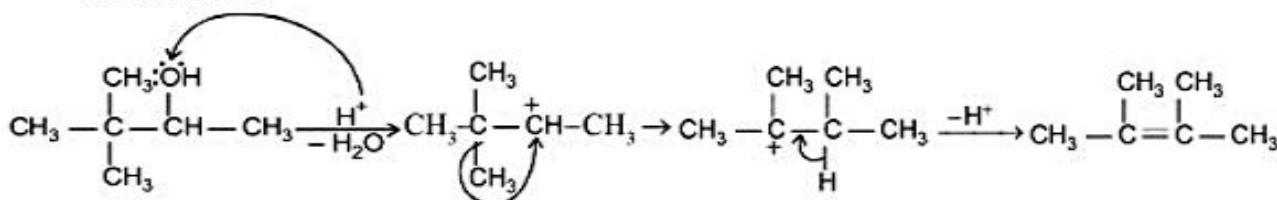
When alcohol is heated with conc. H_2SO_4 at about 160°C , alkenes are formed after dehydration.



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Mechanism :-

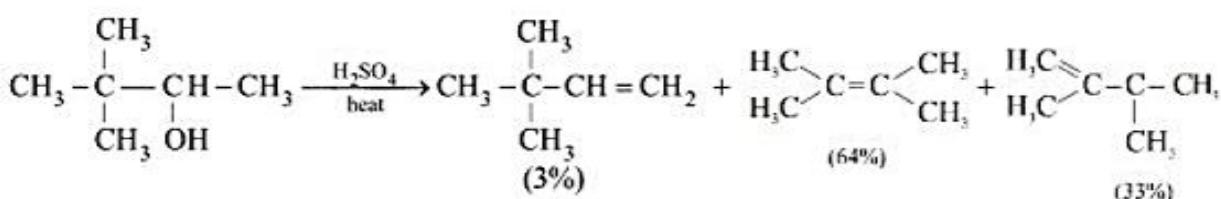
Note : Since the mechanism proceeds via- C^+ ion therefore **rearrangement** is also possible e.g.:

**Mechanism :****Characteristics of dehydration of alcohol**

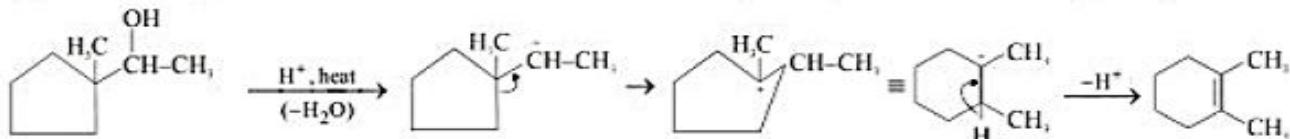
- (1) Since the carbocation is formed as an intermediate in the R.D.S. of dehydration of alcohol The relative reactivity of alcohols decreases in the order.
Tertiary > Secondary > Primary
- (2) Since the R.D.S. is reversible it is necessary to remove the H_2O molecule produced in the reaction. Therefore in experimental condition conc. H_2SO_4 is added in a regular interval.
- (3) For dehydration, different dehydrating agent like Al_2O_3 , ThO_2 can also be employed.
- (4) Rearrangement of carbocation can take place.
- (5) $-\text{OH}$ is not a good leaving group, in alcohols so turn it into a good leaving group, it is converted into $-\text{H}_2\text{O}$ by protonation
- (6) H_2O is a good leaving group.

Rearrangement in Alcohol Dehydration

- (1) Some alcohols undergo dehydration to form alkene having carbon skeleton different from those of the starting alcohol.
- (2) This is due to rearrangement of carbocation formed in the reaction to more stable carbocation.
- (3) An example of alcohol dehydration that is accompanied by rearrangement is.

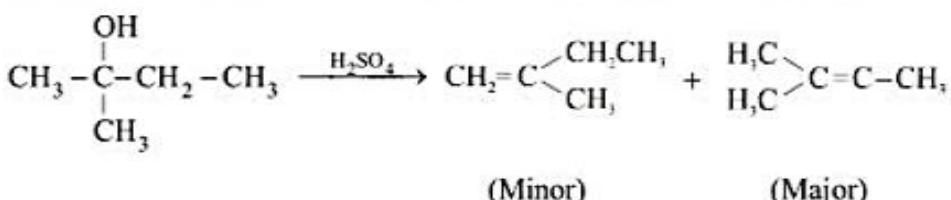


- (4) Percent yield of alkenes formed from rearranged carbocation is greater than the percent yield of alkene obtained from unarranged carbocation.
- (5) Rearrangement of carbocations can also lead to a change in ring size, as the following example shows



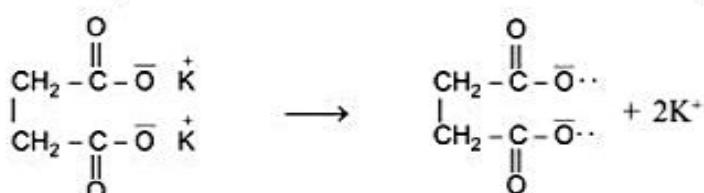
Regioselectivity in alcohol dehydration :

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

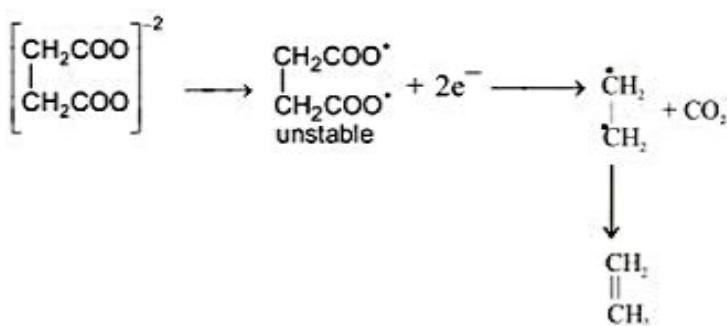


Kolbe's Synthesis

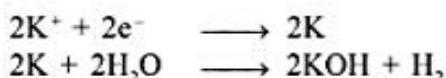
When aqueous solution of K or Na succinate is electrolysed, ethylene is released at anode.



At Anode



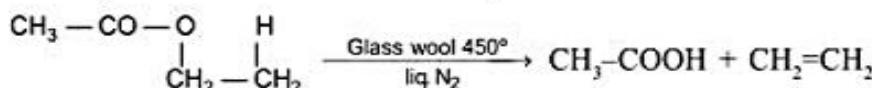
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At Cathode

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

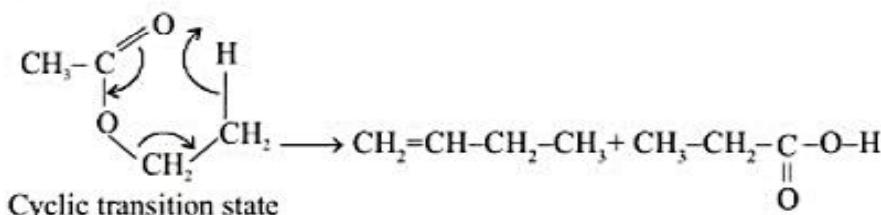
From Esters

When esters are heated in presence of liq. N₂ and glass wool, then alkyl part of ester converts into respective alkene while alkanoate part of ester is converted into respective acid.

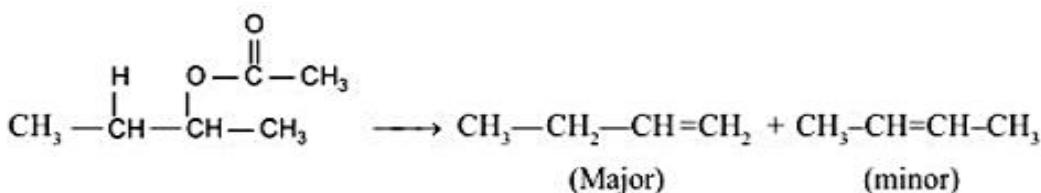


The reaction is called as '**Pyrolysis of Ester**'.

Mechanism : Pyrolysis of Ester is a type of E₁ elimination which proceed via *cyclic T.S.* that is why the product becomes '*cis*'



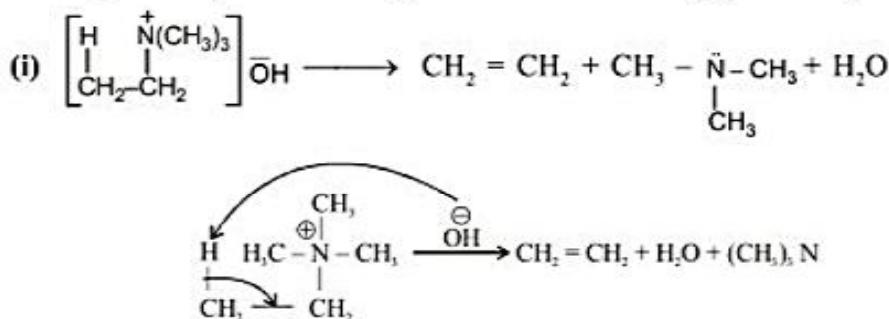
* It is interesting to note that, in this case major product is 1-alkene in the comparison to 2-alkene.



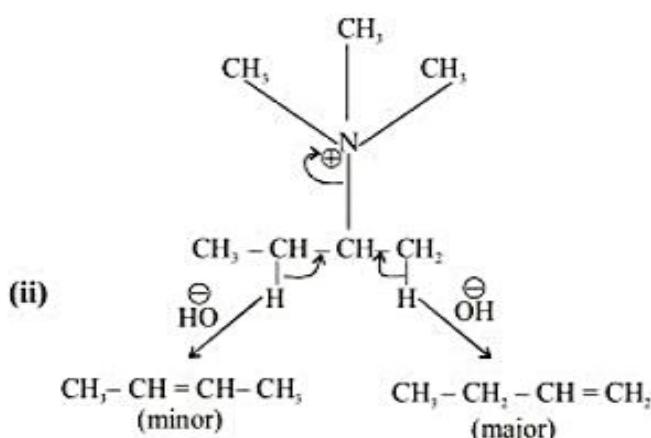
Major product is obtained by reamoval of –H from less hindered carbon.

From quaternary ammonium hydroxide

When quaternary ammonium hydroxide is heated strongly it decomposes to give alkene. e.g.



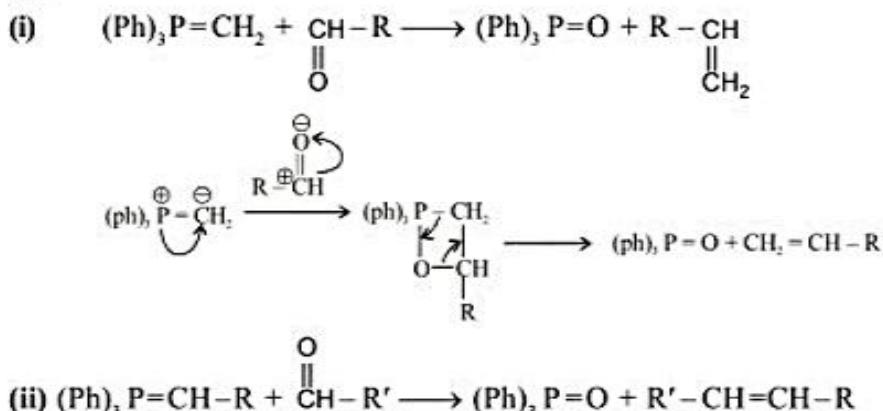
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This elimination is called **Hoffman's elimination**. It is markable that in this reaction more acidic H is preferably eliminated.

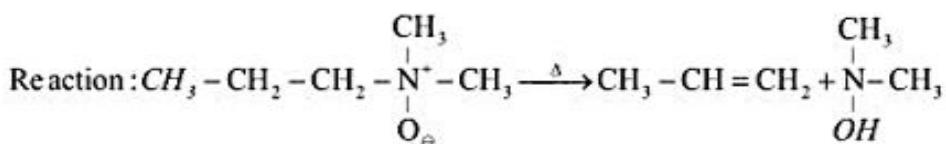
The Wittig reaction

In this reaction methylene triphenyl phosphorane is reacted with carbonyl compound to give alkene.
e.g. :

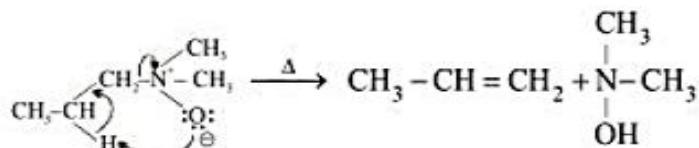


The Cope Elimination :

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



Mechanism :



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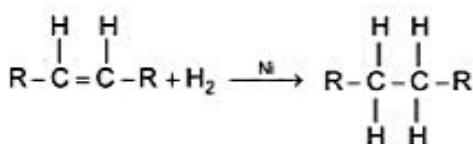
PHYSICAL PROPERTIES

- (i) From C₂–C₄ they are colourless, odourless gases, from C₅–C₁₇ they are colourless liquids, C₁₈ onwards alkenes are solids.
- (ii) Alkenes are practically insoluble in water because they cannot form hydrogen bonds with H₂O molecule. They dissolve freely in organic solvents like benzene, chloroform, CCl₄, petroleum ether, etc. (Like dissolves like)
- (iii) B.P and M.P. decreases with increasing branches in alkene.
- (iv) The melting points of cis isomers are lower than trans isomers because cis isomer is less symmetrical than trans. Thus trans packs more tightly in the crystal lattice and hence has a higher melting point.
- (v) The boiling points of cis isomers are higher than trans isomers because cis–alkenes has greater polarity (Dipole moment) than trans one.
- (vi) These are lighter than water.
- (vii) The increase in branching in carbon chain decreases the boiling point among isomeric alkenes.

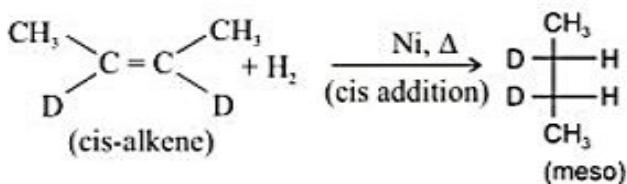
CHEMICAL REACTIONS

The main reactions of alkene are electrophilic addition reaction

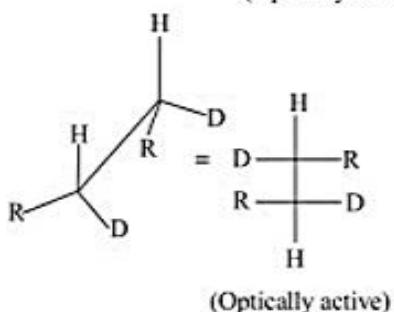
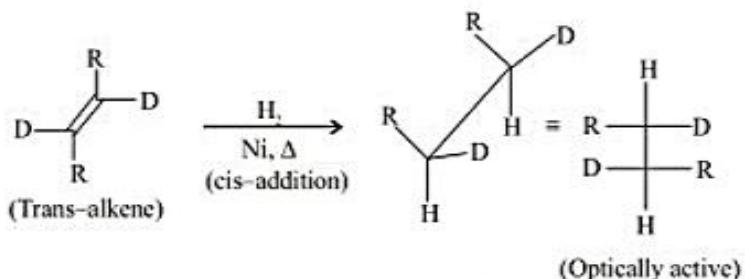
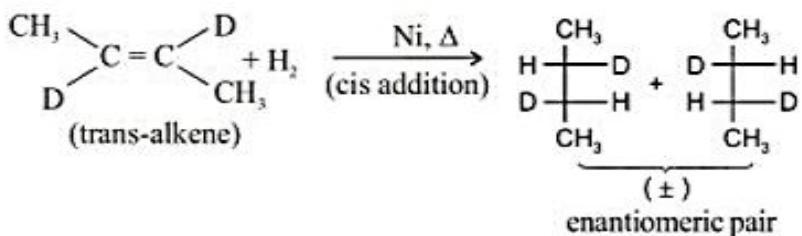
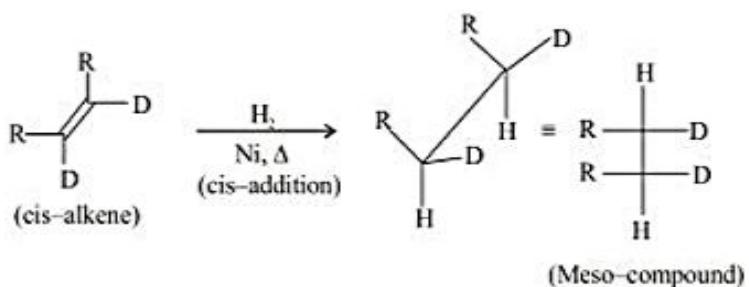
Reaction with Hydrogen –



Mechanism : The reaction takes place at the surface of Ni, therefore the addition is cis addition.
eg :-



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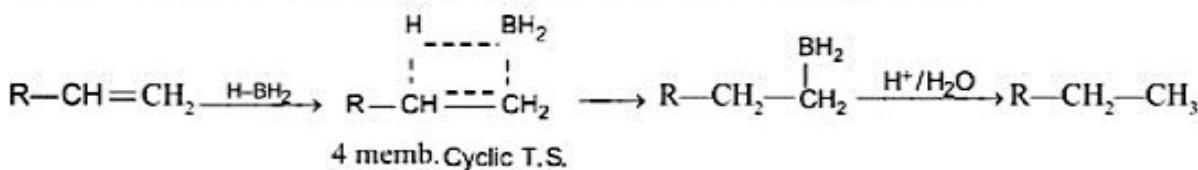


Note : Hydrogenation (catalytic hydrogenation) of alkene is a cis addition and is an exothermic reaction. Thus the heat evolved decreases with increasing stability of alkene.

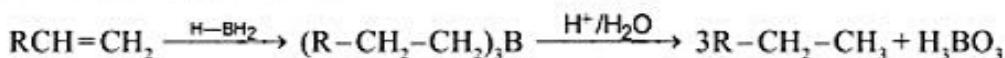
Remember, Stability of alkene depends upon hyperconjugation and type of geometrical isomerism

Reduction of alkene via hydroboration

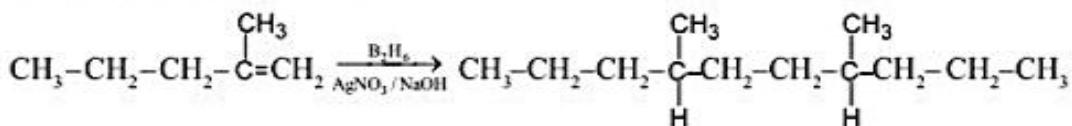
- (i) Alkene can be converted into alkane by hydroboration followed by protolysis



This reaction is also represented as

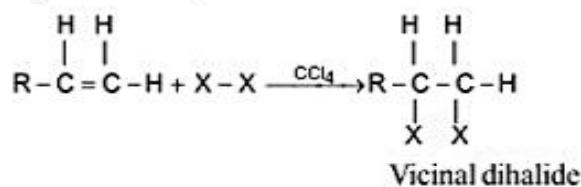


- (ii) Alkene can be converted into alkane by hydroboration followed by treatment with $\text{AgNO}_3 + \text{NaOH}$. This method gives coupling.



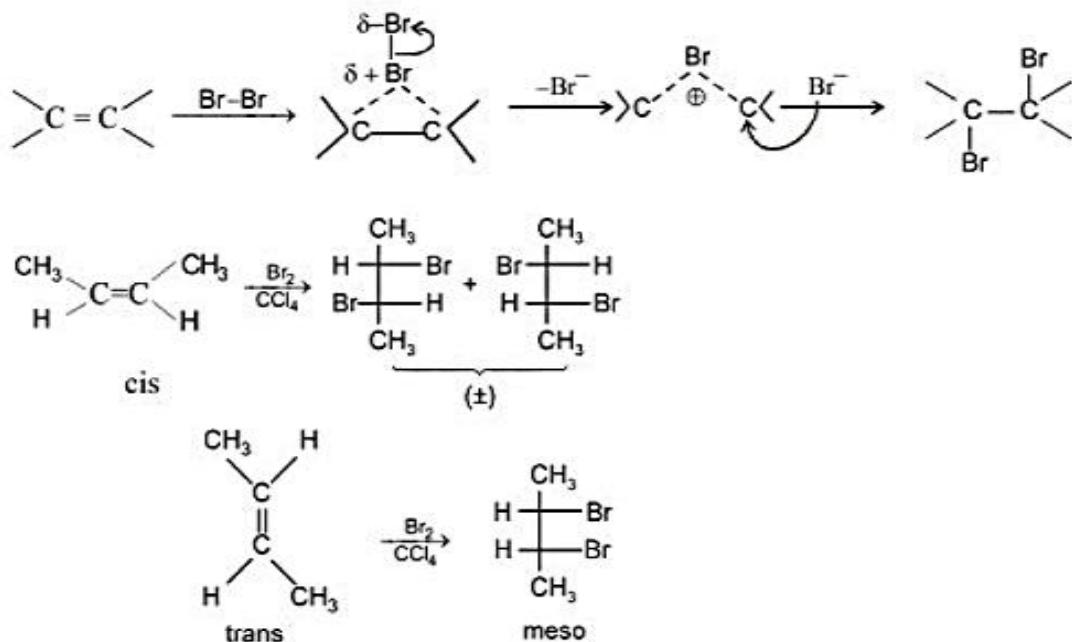
Halogenation –

In presence of polar medium alkene form vicinal dihalide with halogen.



Order of reactivity of halogens is : $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

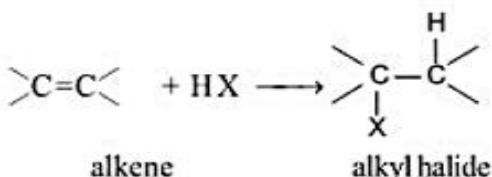
Mechanism : It is an electrophilic addition by molecular attack in which the addition takes place in trans manner.



Note : For suitable condition

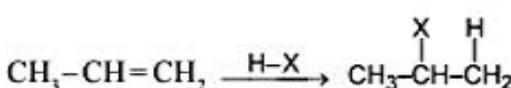
- (i) Cis addition on cis form results meso
- (ii) Cis addition on trans form results (\pm)
- (iii) Trans addition on cis form results (\pm)
- (iv) Trans addition on trans form results meso.

Reaction with HX (Hydrohalogenation) –

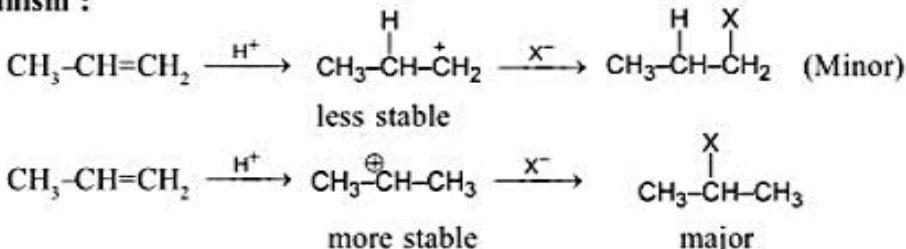


Markovnikoff's Rule

When an unsaturated unsymmetrical hydrocarbon reacts with HX then halogen goes on that unsaturated carbon which has minimum number of hydrogen atom. Mechanism of the reaction is based on $-\text{C}^+$.



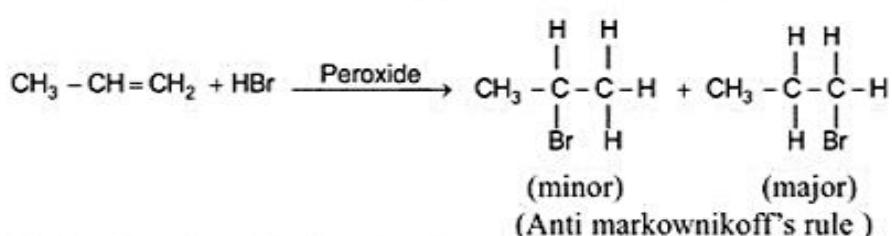
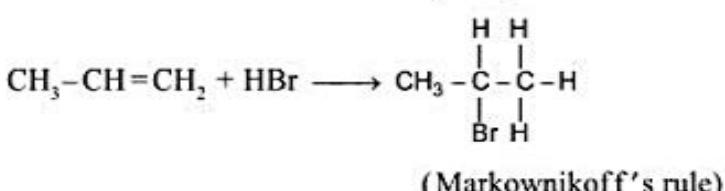
Mechanism :



- (i) Formation of Carbocation is Rate determining step.
- (ii) Rearrangement of carbocation to more stable carbocation can occur to form a more stable product.
- (iii) Regiochemistry - Markownikoff's Addition of HX.
- (iv) Reactivity order of different hydrogen halide towards addition
 $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

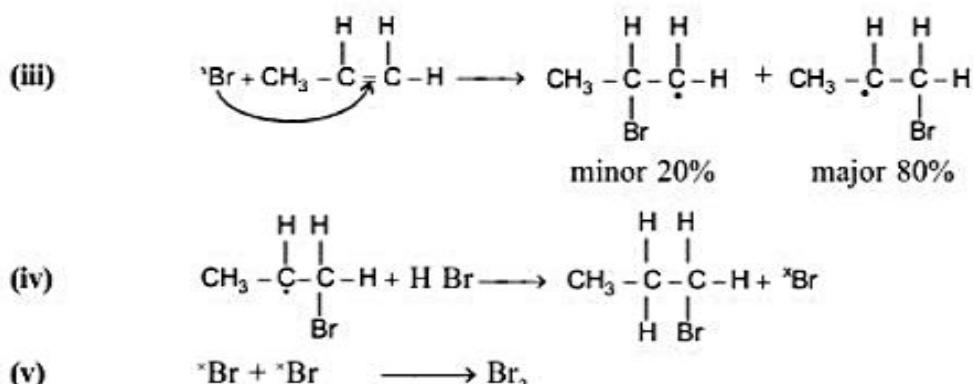
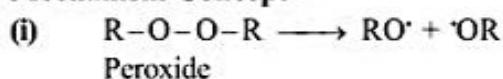
Anti Markownikoff's Principle / Kharasch Effect / Peroxide Effect –

To understand antimarkownikoff's principle let us consider the following reactions



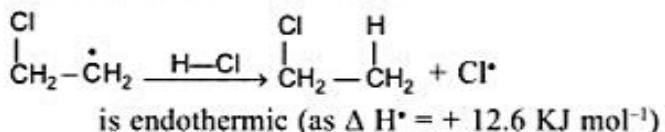
It is based on free radical mechanism.

(a) Mechanism Concept -

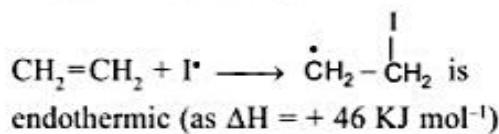


Note : It is interesting to note that anti markovnikov addition in the presence of peroxide is not applicable for HCl and HI

(i) In the case of H – Cl, the step



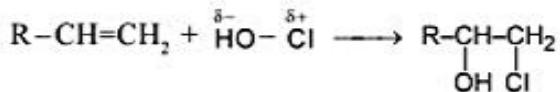
(ii) In the case of H – I, the step



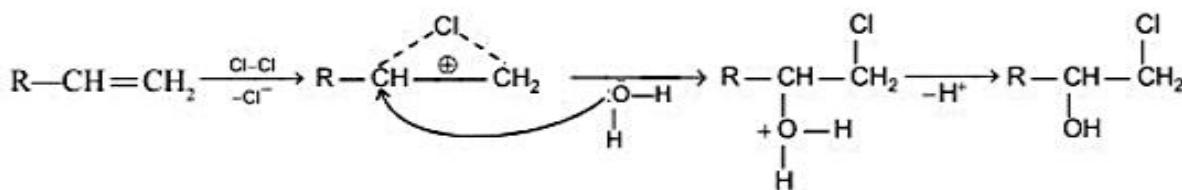
But in the case of HBr both of the steps are exothermic, which results spontaneous reaction.

* $\text{CCl}_4, \text{CBrCl}_3$ etc. can also be added to alkene in anti markovnikov manner.

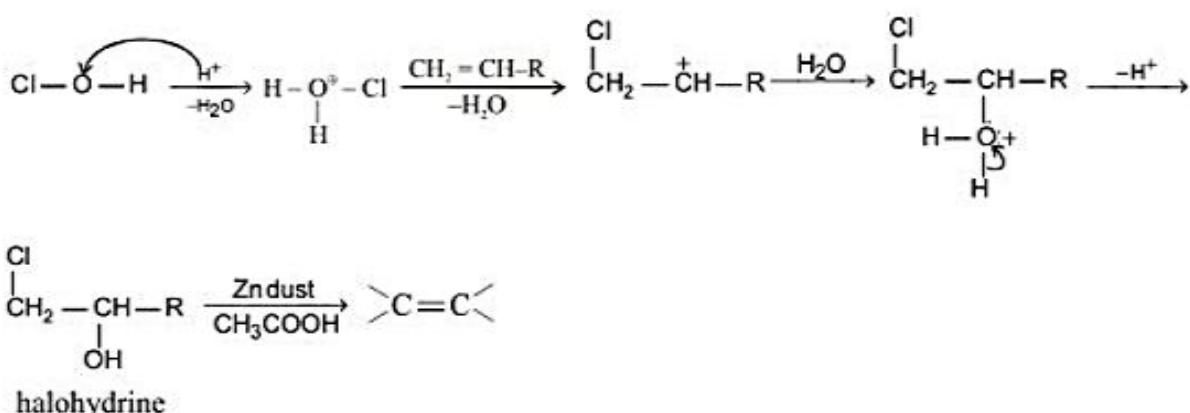
Reaction with Hypohalous Acid -



(i) When chlorine water or bromine water is used.

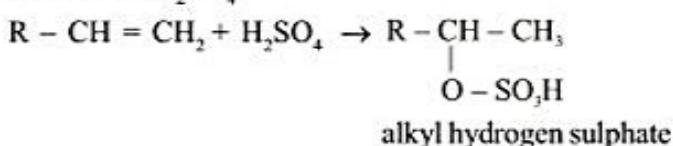


(ii) When aq. solution of HOCl is added in the presence of strong acid.

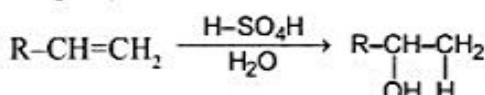


Reaction with H_2SO_4 -

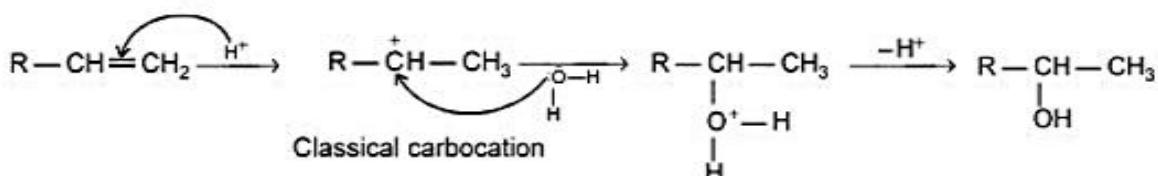
(a) With conc. H_2SO_4



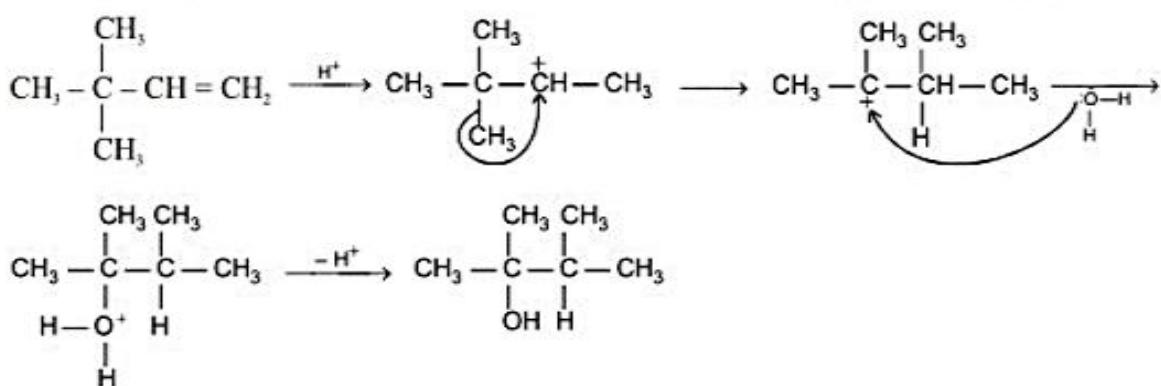
(b) With dil. H_2SO_4



Mechanism:

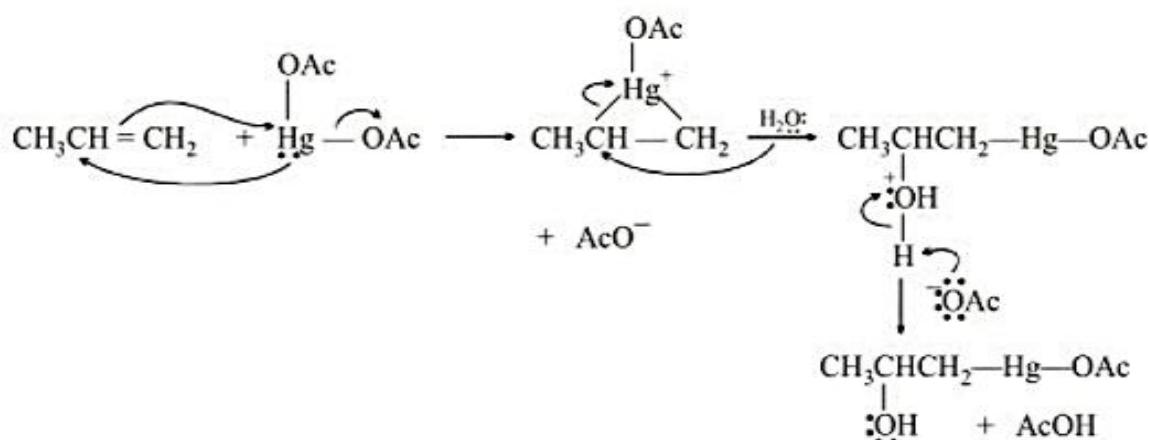


- * The hydration of alkene is not stereoselective, as in the case of HCl addition. This fact can be explained on the basis of classical carbon cation formation.
- * Since hydration proceeds via carbocation intermediate therefore rearrangement is always probable.

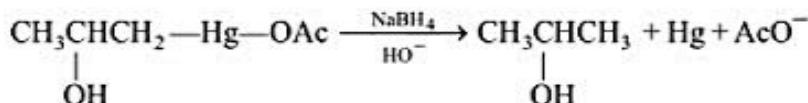


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- * Rearrangement, however, may be avoided by treatment of alkene by *oxymercuration-demercuration* method

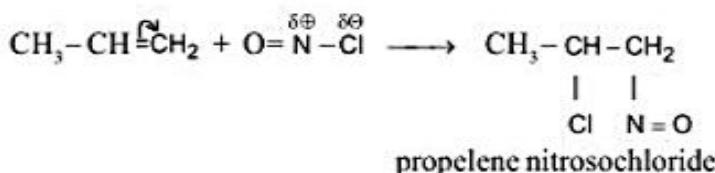
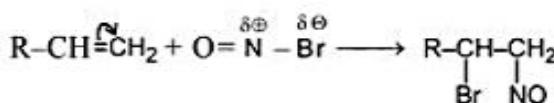
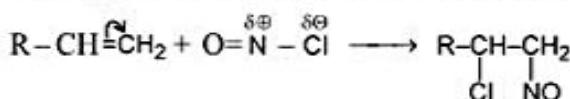


Sodium borohydride (NaBH_4) converts the carbon-mercury bond into a carbon-hydrogen bond. Because the reaction results in the loss of mercury, it is called demercuration.



Addition of Nitrosyl halide –

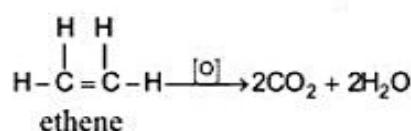
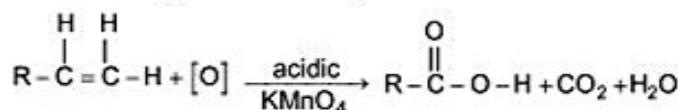
Alkene with nitrosyl bromide or nitrosyl chloride (**Tilden reagent**) react according to Markovnikoff's rule to give alkene nitrosobromide and alkene nitrosochloride respectively.

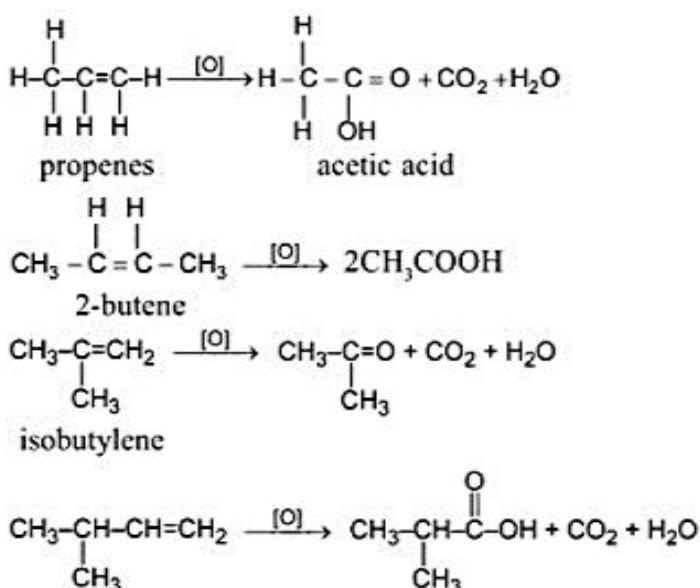


Oxidation

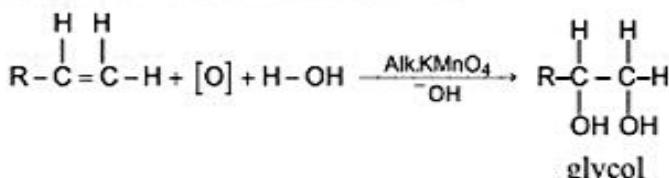
Oxidation is completed by the following ways.

With Acidic KMnO_4 / Hot KMnO_4

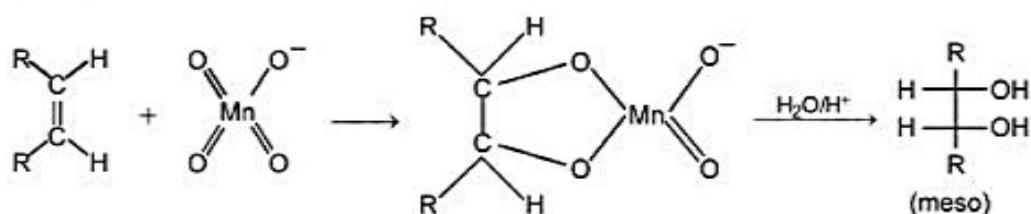




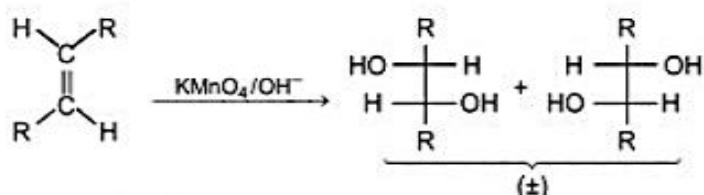
With alkaline KMnO_4 / Bayer's reagent



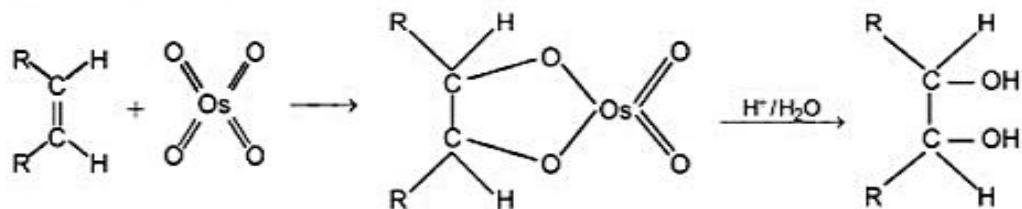
Mechanism: Hydroxylation by alkaline KMnO_4 (Bayer's reagent) is cis addition and the mechanism is cyclic.



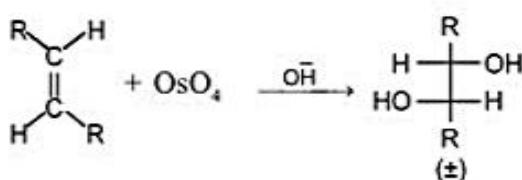
Similarly



Hydroxylation by OsO_4 :

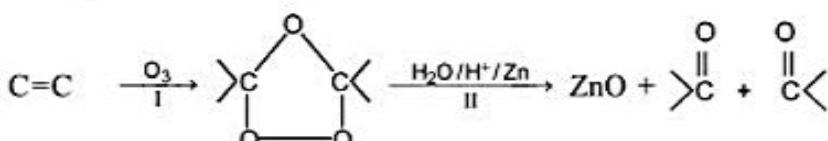


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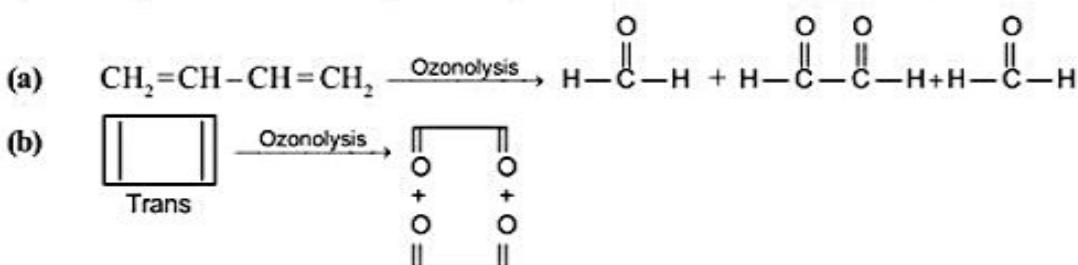
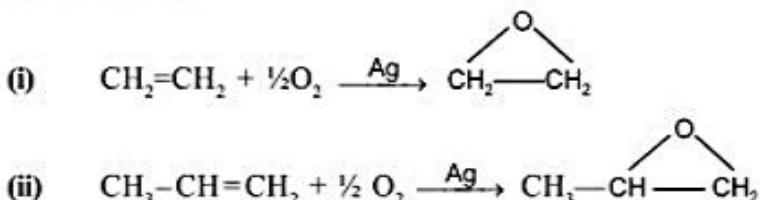
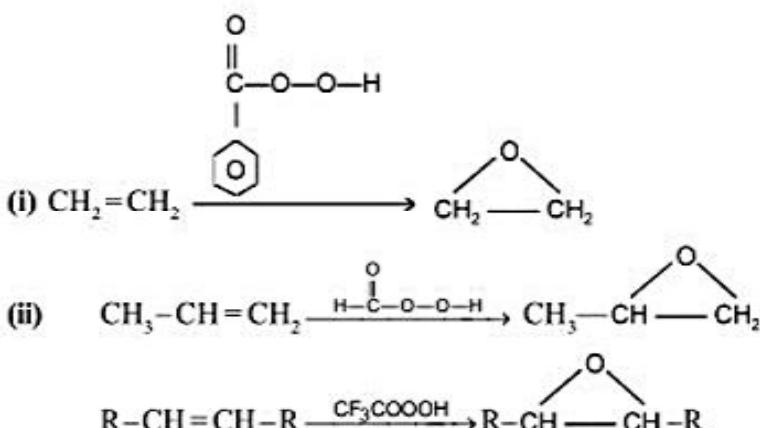
**Ozonolysis :-**

This is the two step reaction

- (i) Ozonide formation
- (ii) decomposition of ozonide (reductive hydrolysis)
eg:-



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

**Epoxidation by O_2/Ag** **Epoxidation by per acid**

Hydroboration

Alkene with borane hydride form an important compound called trialkyl borane.



- (a) Trialkyl borane is an important compound because it gives respective alkane on acidic hydrolysis.

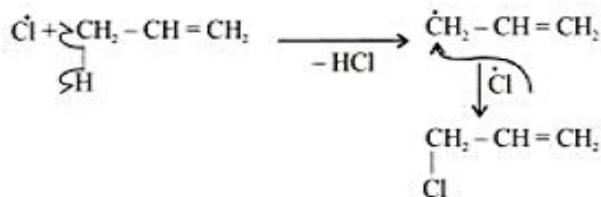
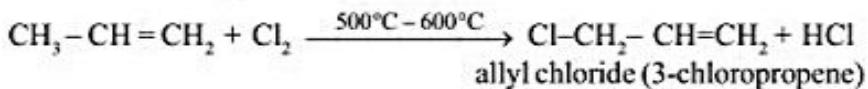
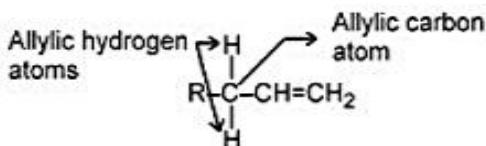
$$(R-CH_2CH_2)_3B + 3 H_2O \xrightarrow{HCl} 3 R-CH_2-CH_3 + B(OH)_3$$
- (b) It gives respective alcohol on alkaline hydrolysis

$$(R-CH_2CH_2)_3B + 3 H_2O_2 + 3NaOH \longrightarrow 3 R CH_2 CH_2 OH + B(OH)_3$$
- (c) It gives 1° amine on alkaline hydrolysis with chloramine

$$(R-CH_2CH_2)_3B + 3 NH_2Cl + 3NaOH \longrightarrow 3R-CH_2CH_2NH_2 + 3NaCl + H_3BO_3$$
- (d) $(R-CH_2CH_2)_3B \xrightarrow[\text{NaOH}]{\text{AgNO}_3} 3R-CH_2-CH_2-CH_2-CH_2-R$
- (e) In the overall hydroboration-oxidation reaction, three moles of alkene react with one mole of BH_3 to form three moles of alcohol.
- (f) Because carbocation intermediates are not formed in the reaction carbocation rearrangement do not occur.
- (g) Regiochemistry Anti-markownikoff's Addition of water.
- (h) Alkyl boranes undergo coupling by means of silver nitrate in the presence of $NaOH$ at $25^\circ C$. Higher alkanes are the products of this reaction.

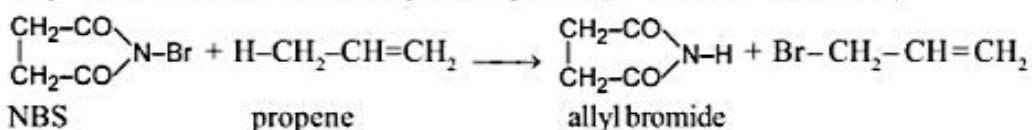
Allylic substitution reaction –

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



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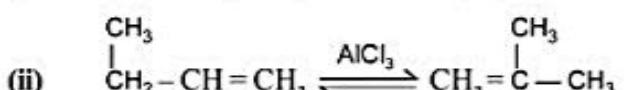
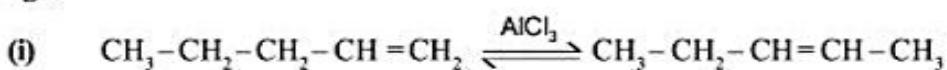
- (b) Allylic bromination can be easily done by NBS (N-bromo succinamide)



Isomerisation :-

Alkenes isomerises when heated at high temperature or at lower temperature in the presence of various catalysts as AlCl_3 ,

eg :-



the mechanism proceeds through carbocation

MCQ

- Q.1 $\text{R}-\text{CH}=\text{CH}_2 \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{Na/NH}_3(\text{l})} \text{RCH}_2\text{CH}_3$ is called

- (A) Clemmensen's reduction (B) Fisher-Spier reduction
 (C) Birch reduction (D) Arndt-Eistert reduction

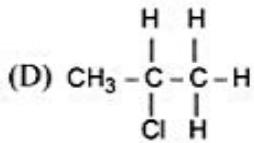
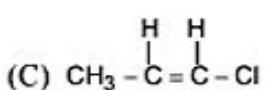
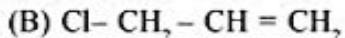
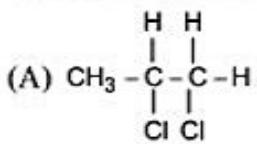
- Q.2 What would be the product when 2-pentene reacts with HBr -

- (A) 2-bromo pentane (B) 3-bromo pentane (C) Both A and B (D) 1-bromo pentane

- Q.3 What would be the product when ethene is oxidised with ozone and forms ozonide which is hydrolysed in the presence of Zn and acetic acid?

- (A) $\begin{matrix} \text{H}-\text{C}-\text{H} \\ || \\ \text{O} \end{matrix}$ (B) CH_3OH (C) $\begin{matrix} \text{H}-\text{C}-\text{OH} \\ || \\ \text{O} \end{matrix}$ (D) $\begin{matrix} \text{H}-\text{C}-\text{C}-\text{H} \\ || \quad || \\ \text{O} \quad \text{O} \end{matrix}$

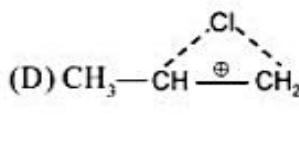
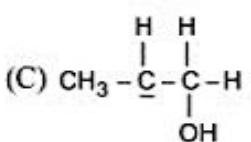
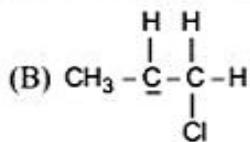
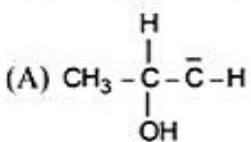
- Q.4 What would be the product when propene reacts with chlorine in presence of CCl_4



- Q.5 Propene on reaction with methylene iodide in presence of Zn-Cu couple gives :

- (A) Cyclopropane (B) Cyclopropane
 (C) Methyl Cyclopropane (D) Cyclobutene

Q.6 Propene + HOCl \rightarrow A \rightarrow Final product. In the above reaction A will be



Q.7 In hydroboration it is evident that in the overall reaction a molecule of a water has been added to propene and the addition is :

- (A) According to markownikoff's rule (B) Contrary to Markownikoff's rule
 (C) Not concerned with markownikoff's rule (D) None of above

Q.8 NBS react with 1-butene to give –

- (A) 3-bromobutene-1 (B) 1,2-dibromobutane (C) 1-bromobutene (D) 1,2-dibromobutene-1

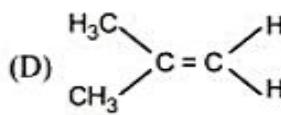
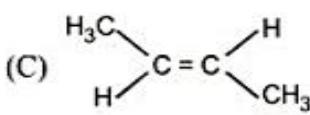
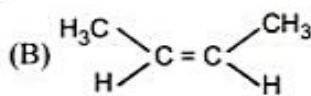
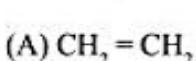
Q.9 Isobutane reacts with the following to form isoctane :

- (A) Isobutylene (B) n-Butene (C) n-Pentene (D) Isopentene

Q.10 Reaction of alkene and peracid gives oxirane. This reaction is named as –

- (A) Peroxidation (B) Oxidation (C) Priles chaeiv (D) None

Q.11 The compound which reacts with HBr obeying Markownikov's rule is -



Q.12 Alkene and alkyne gives following types of polymerisation –

- (A) Addition (B) Condensation (C) Substitution (D) Replacement

Q.13 Cyclic osmium ester of alkene after reacting with aqueous solution of sodium bisulphite gives –

- (A) Diol (B) Cis-diol (C) Trans-diol (D) Salt

Q.14 The minimum number of C atoms required to be present in an optically active alkene are:

- (A) 4 (B) 6 (C) 8 (D) 10

Q.15 Chloroethane reacts with alcoholic KOH to form –

- (A) Propyl chloride (B) Ethyl chloride (C) Ethene (D) None

Q.16 The synthesis of ethene from electrolysis of an aqueous solution of potassium succinate is known as:

- (A) Faradays electrolysis (B) Kolbe - Schmidt reaction
 (C) Hoffmann's rearrangement (D) Kolbe's electrolytic Synthesis

- Q.17 $\begin{array}{c} \text{H} \\ | \\ \text{CH}_2 - \text{CH}_2 \\ | \\ \text{Cl} \end{array} \xrightarrow[\text{alk.}]{\text{NaOH}} \text{CH}_2 = \text{CH}_2$. Most probable mechanism for this reaction is -
 (A) E1 (B) E2 (C) E1CB (D) α elimination

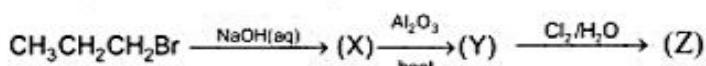
- Q.18 $\text{RCH} = \text{CH}_2$ can be obtained by :

- (A) $\text{R}-\overset{\text{O}}{\underset{\downarrow}{\text{C}}}-\text{H}$ and $(\text{C}_6\text{H}_5)_3\text{P} = \text{CH}_2$ (B) By heating $\text{RCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$
 (C) By heating $\text{RCH}_2\text{CH}_2\text{OCOCH}_3$ (D) All of these

- Q.19 If we take ethylidene chloride and isopropylidene chloride with zinc dust then product will be -

- (A) 2-butene
 (B) 2-butene + 2,3-dimethyl-2-butene
 (C) 2-methyl-2-butene
 (D) 2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene

- Q.20 Identify 'Z' in the following reaction series,



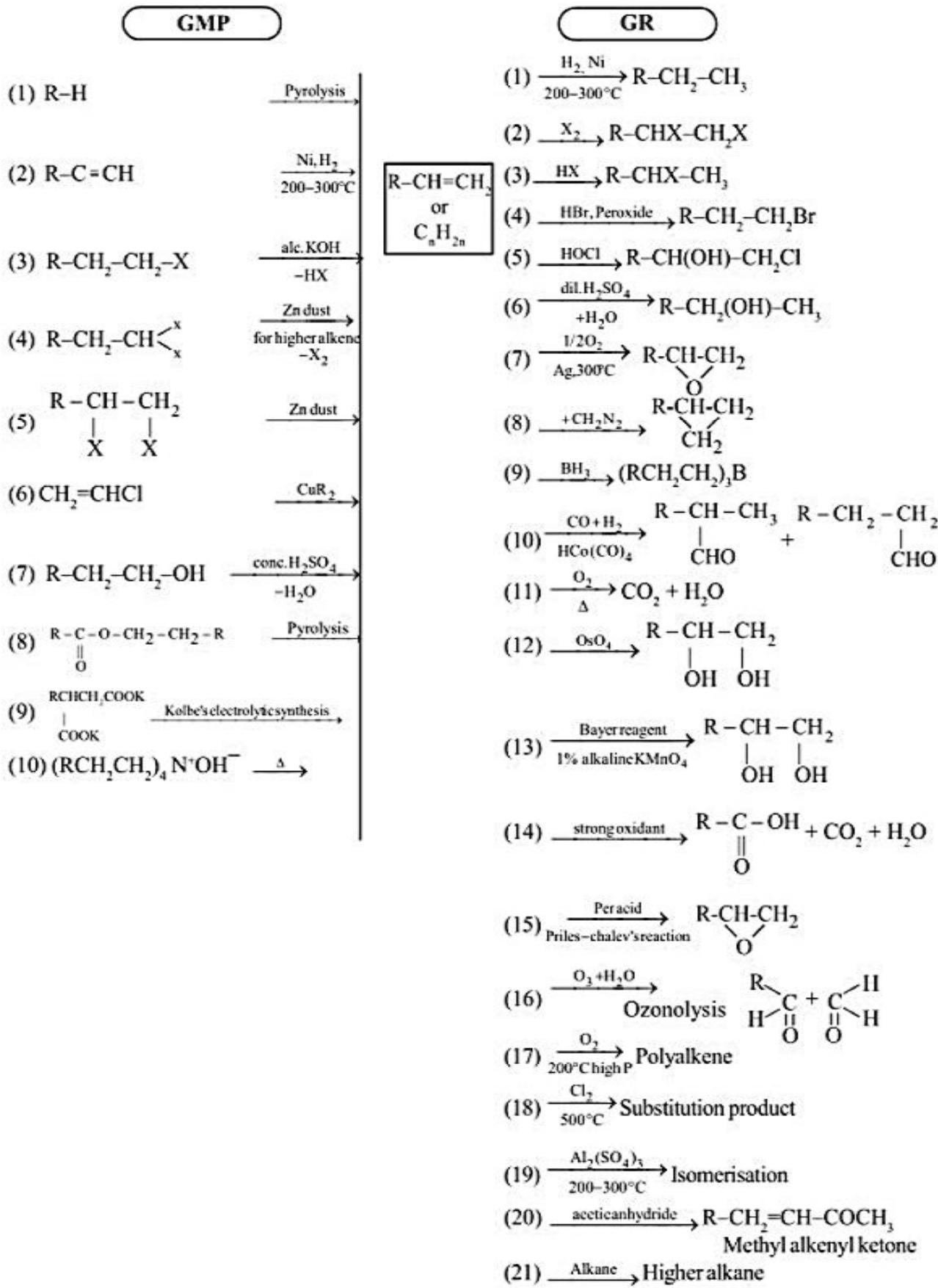
- (A) Mixture of $\begin{array}{c} \text{CH}_3 - \underset{\text{Cl}}{\text{CH}} - \text{CH}_2 \text{ and } \text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \underset{\text{Cl}}{\text{CH}_2} \end{array}$
 (B) $\begin{array}{c} \text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 \end{array}$
 (C) $\begin{array}{c} \text{CH}_3 - \underset{\text{Cl}}{\text{CH}} - \underset{\text{OH}}{\text{CH}_2} \end{array}$ (D) $\begin{array}{c} \text{CH}_3 - \underset{\text{Cl}}{\text{CH}} - \text{CH}_2 \end{array}$

ANSWERS KEY

Q.1 C	Q.2 C	Q.3 A	Q.4 A
Q.5 C	Q.6 D	Q.7 B	Q.8 A
Q.9 A	Q.10 C	Q.11 D	Q.12 A
Q.13 B	Q.14 B	Q.15 C	Q.16 D
Q.17 B	Q.18 D	Q.19 D	Q.20 B

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REACTION CHART FOR ALKENES



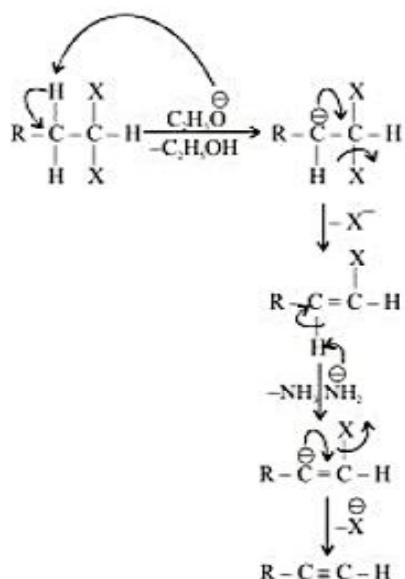
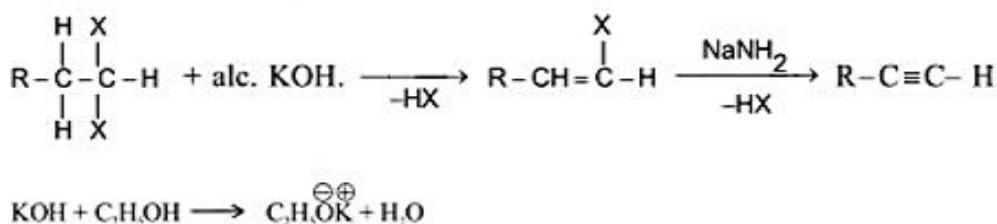
ALKYNE

GENERAL INTRODUCTION

- (1) The chemistry of the carbon–carbon triple bond is similar to that of the double bond. In this chapter, we see that alkynes undergo most of the reactions of alkenes, especially the additions and the oxidations. We also consider reactions that are specific to alkynes : some that depend on the unique characteristics of the $\text{C} \equiv \text{C}$ triple bond, and others that depend on the unusual acidity of the acetylenic C– bond.
- (2) Alkynes are hydrocarbons that contain carbon–carbon triple bonds. Alkynes are also called acetylenes because they are derivatives of acetylene, the simplest alkyne.
- (3) Bond angle in alkyne is 180° .
- (4) Their general formula is $\text{C}_n\text{H}_{2n-2}$
- (5) C–C triple bond length is 1.20 \AA .
- (6) C–H bond length is 1.08 \AA .

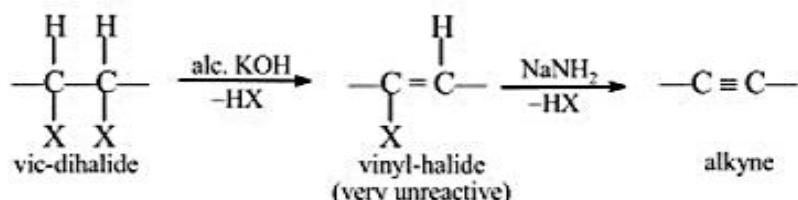
Methods of Preparation

From Gem Dihalides (Dehydrohalogenation):



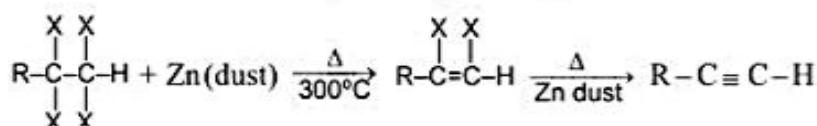
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From vicinal dihalides :



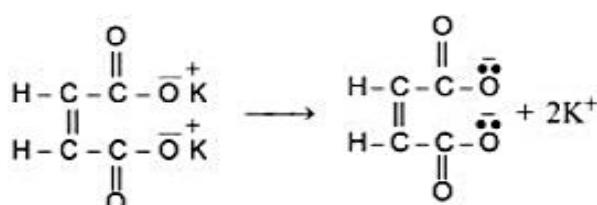
The elimination of one molecule of hydrogen halide yields vinyl halide which is very unreactive. Under mild conditions, the dehydrohalogenation stops at vinylic halide stage but more vigorous conditions—like the use of a stronger base like amide ion (NH_2^-)—are required for alkyne formation.

From Tetrahaloalkanes (Dehalogenation) :



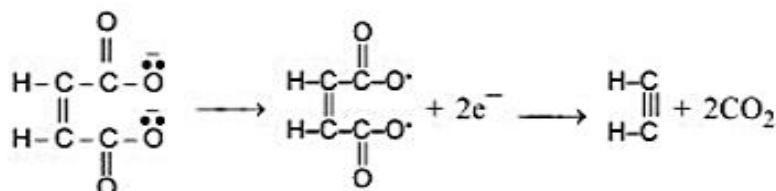
In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends then the product cyclo alkene is obtained.

From Kolbe's Synthesis :

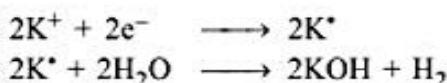


Potassium Malaete

At Anode :

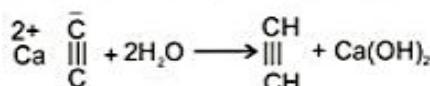


At Cathode :

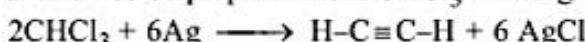


Laboratory method of preparation of Acetylene :

- (a) In laboratory acetylene is prepared by hydrolysis of calcium carbide.

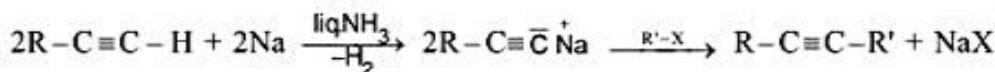
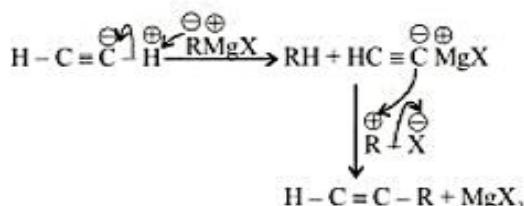
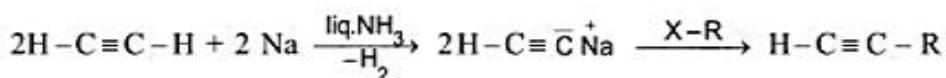


- (b) It can also be prepared from CHCl_3 with Ag dust.

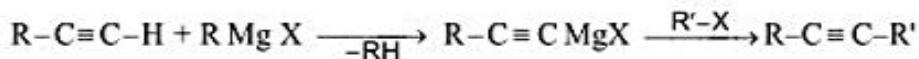
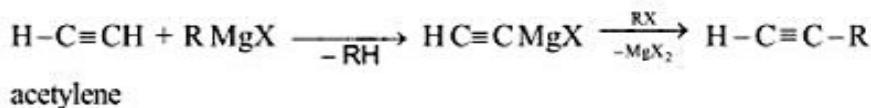


From Alkynes : (To form higher Alkynes)

With Na : When acetylene or 1- alkyne react with Na in presence of liq. NH₃ then an intermediate compound sodium acetylid or sodium alkynide is formed which gives higher alkyne with alkyl halide.



With Grignard reagent : When acetyline or 1- alkyne react with GR then alkane and unsaturated GR is formed which further react with alkyl halide and form higher alkyne.



PHYSICAL PROPERTIES

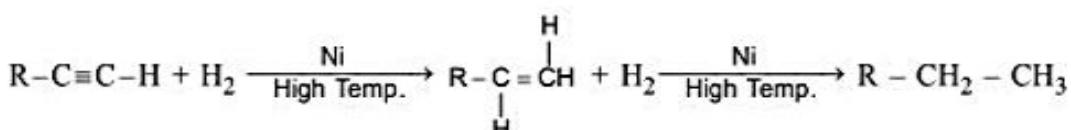
- (a) Alkynes are colourless, odourless and tasteless.
- (b) Lower alkynes are partially soluble in H₂O. (It is due to its polarisibility).
- (c) Higher alkynes are insoluble in water due to more % of covalent character.
- (d) Completely soluble in organic solvents.
- (e) Melting point and boiling point increases with molecular mass and decreases with number of branches.
- (f) Upto C₄ alkynes are gaseous. C₅-C₁₁ are liquid, C₁₂ & above are solids.
- (g) Pure acetylene is odourless and impure acetylene has odour like garlic. It is due to impurities of Arsene (AsH₃) & Phosphine (PH₃).

- (h) Acetylene & 1- alkyne are acidic in nature. It is due to greater electronegativity of sp hybridised 'C'.
- (i) Acetylene has two acidic hydrogen atoms. It can neutralise two equivalents of base at the same time. So it is also called as dibasic acid. But the base should be very stronger as -NH_2 or -CH_3 etc.

CHEMICAL PROPERTIES

The chemical behaviour of alkynes is similar to that of alkenes. Alkynes form addition products with two or four univalent atoms or groups. They are generally less reactive than alkenes towards electrophilic addition reactions even though π electron density is higher in alkynes. This is because on moving from alkene to alkyne, the C—H bond has more of s character (33% in alkenes as compared to 50% in alkynes). Therefore, the π -electrons are more firmly held by carbon nuclei in alkynes and are thus less reactive to an electrophile.

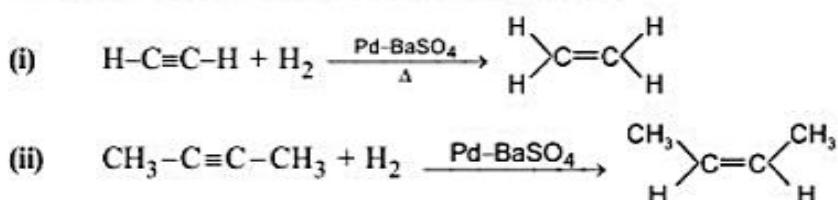
Hydrogenation



The above reaction is called as **Sabatier Senderson's reaction**.

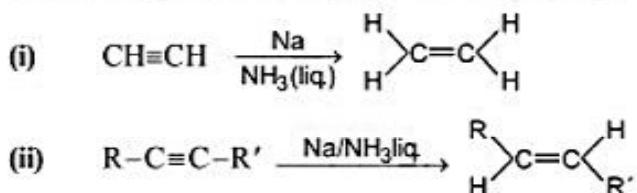
Hydrogenation in the presence of Lindlar's Catalyst :

Addition up to alkene takes place in cis manner.

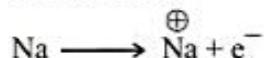


Hydrogenation by Na + NH₃ (liq.) :

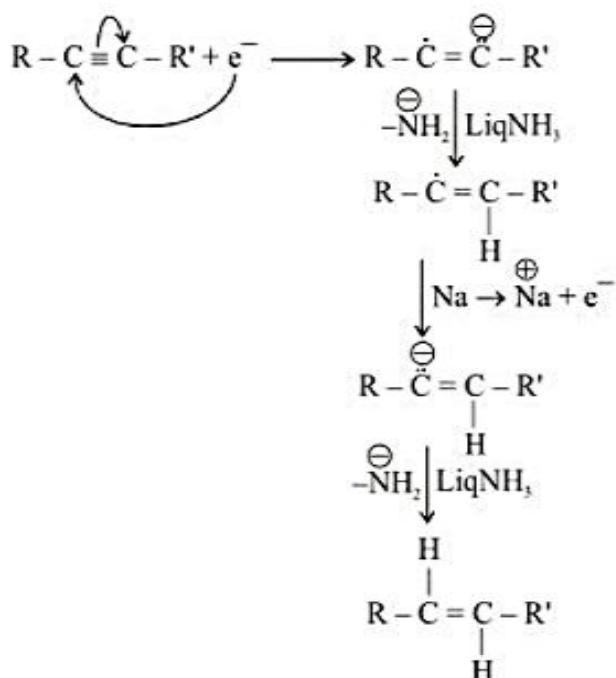
Addition upto alkene takes place in trans manner



Mechanism :

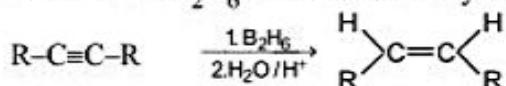


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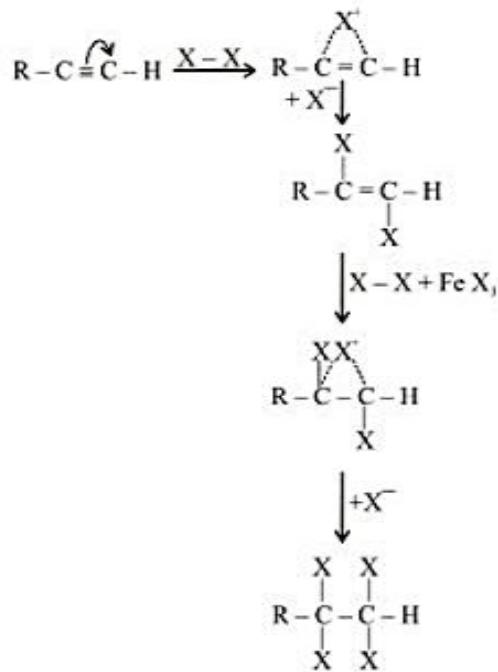
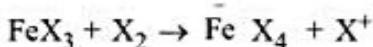
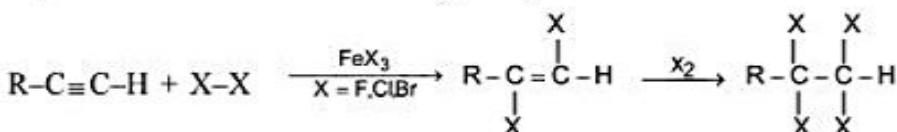
Reduction with the help of B_2H_6 :

Alkyne is first reacted with B_2H_6 and is followed by acidic hydrolysis, cis alkene is obtained.

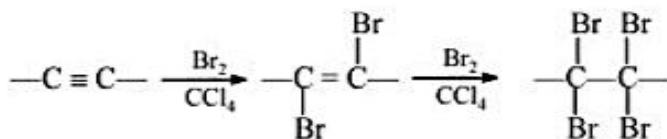


Halogenation :

In presence of Lewis acid as a catalyst alkyne form tetrahaloderivative with halogen.



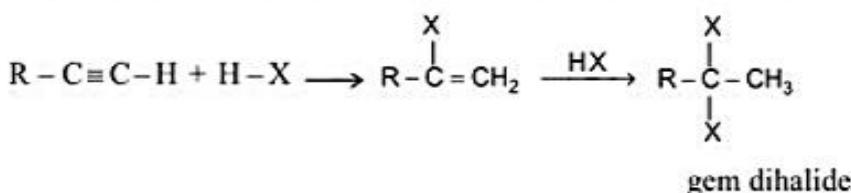
Example :



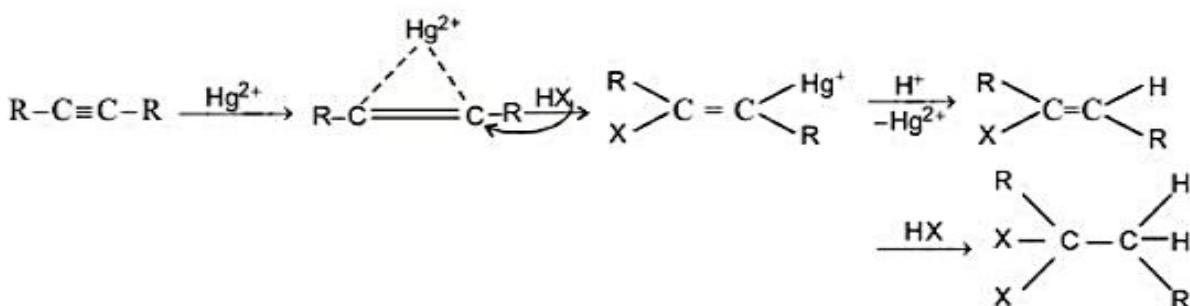
Alkynes add two molecules of Br_2 in CCl_4 and decoloration of bromine water is used to detect the presence of a double or triple bond.

Reaction with HX (Hydrohalogenation) :

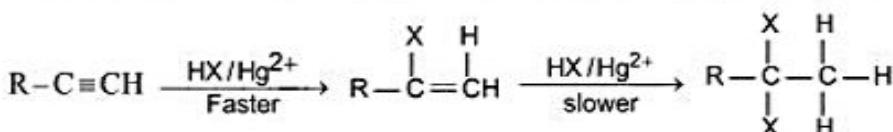
Alkyne form gem dihalide with HX because reaction follows Markownikoff's 1st and IIInd rule both.



Mechanism : The reaction takes place in the presence of Hg^{2+} ion.

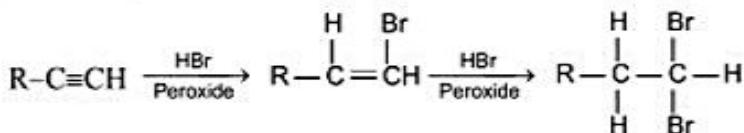


Note : (i) First step is faster than the second step among addition of two HX on alkyne.

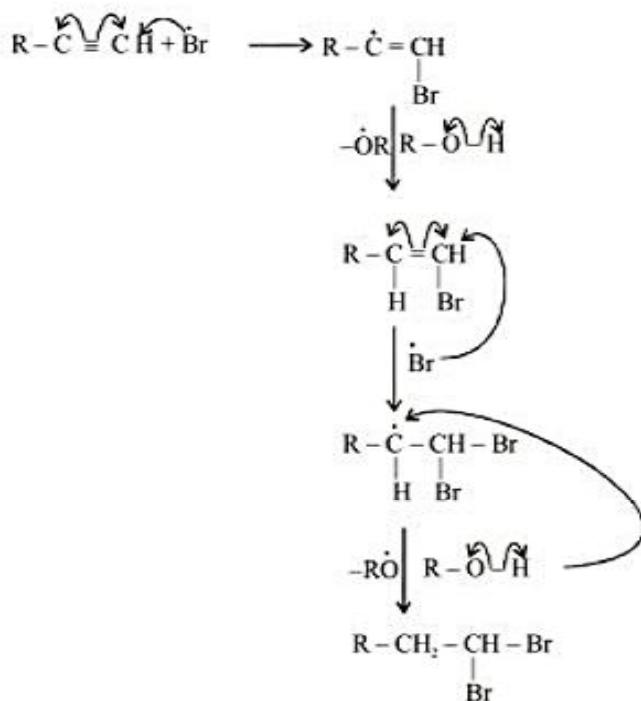
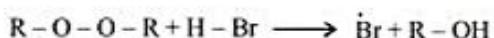


Slower rate of addition of 2nd molecule is caused by lower electron cloud density on $\text{C}=\text{C}$, due to - I effect of 'Cl'.

(ii) peroxide give same effect as in alkene

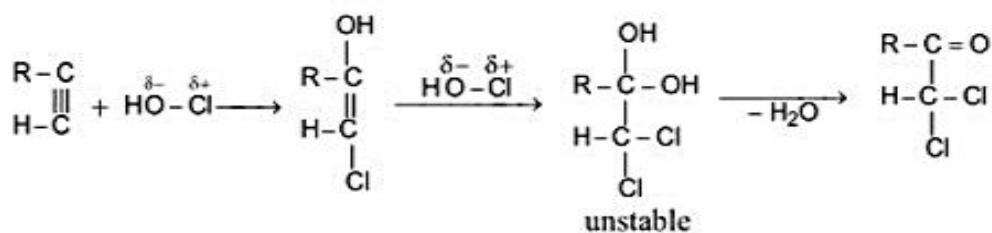


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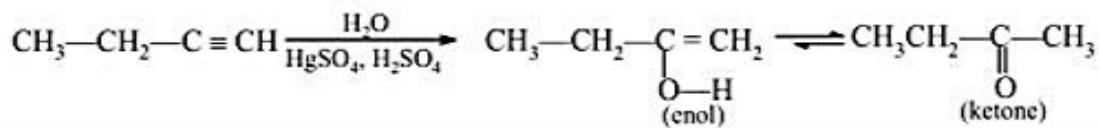
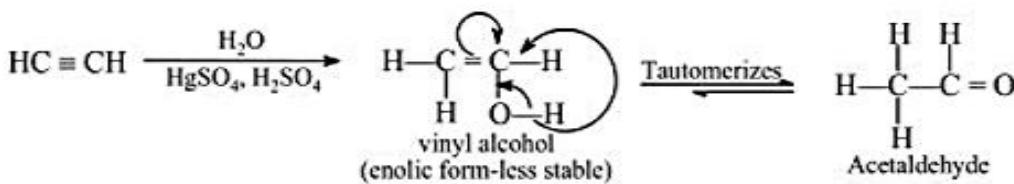


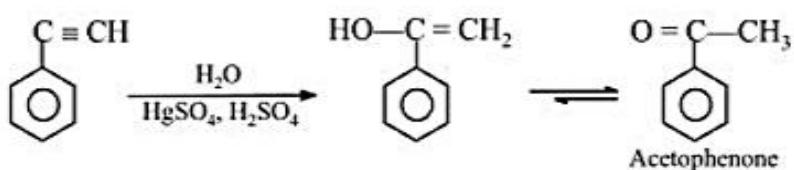
Reaction with Hypochlorous acid or Chlorine water :

Hypochlorous acid is broken into $\text{HO}^{\ddagger}\text{Cl}^{\ddagger}$ & ions & give product. according to markonicoff's rule.

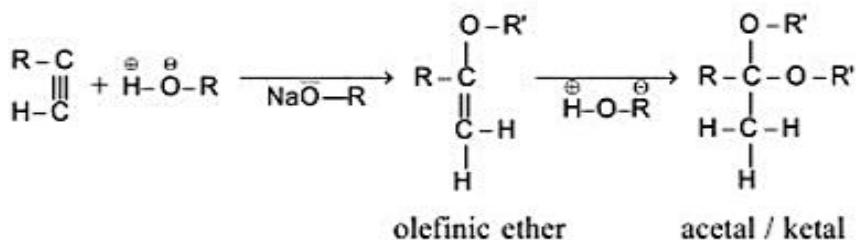


Hydration : Addition of water to alkynes is carried out in the presence of acid and mercuric sulphate.



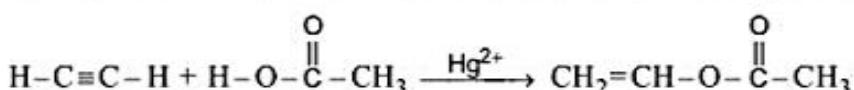


Addition of alcohol



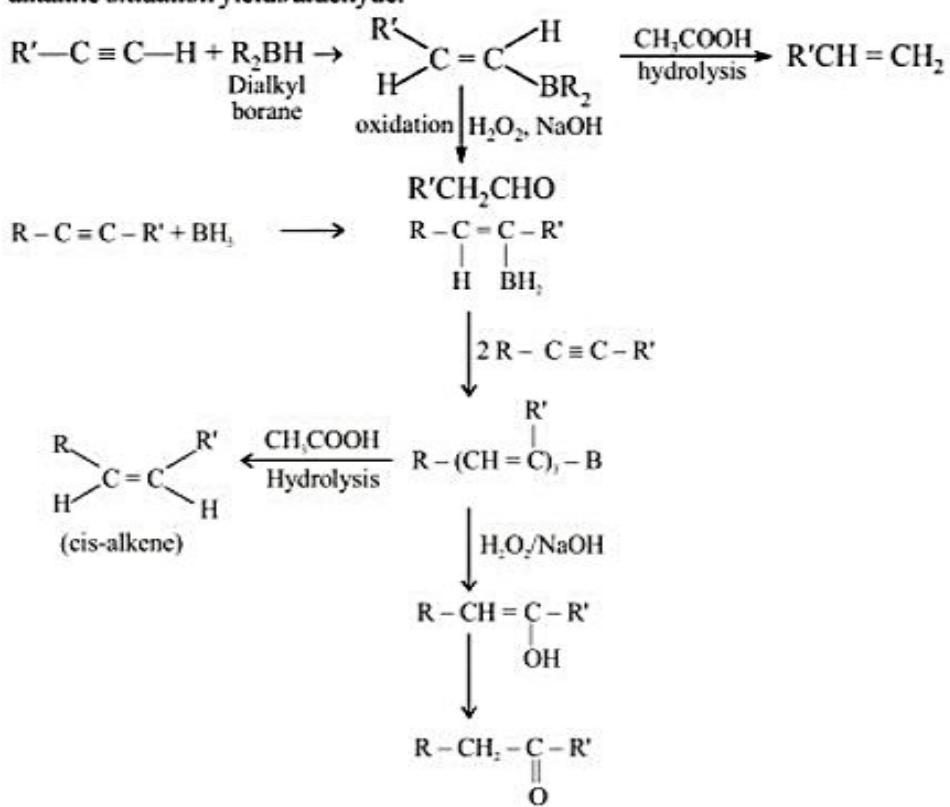
Addition of carboxylic acid :

In the presence of Hg^{2+} unioxylation of carboxylic acid takes place.

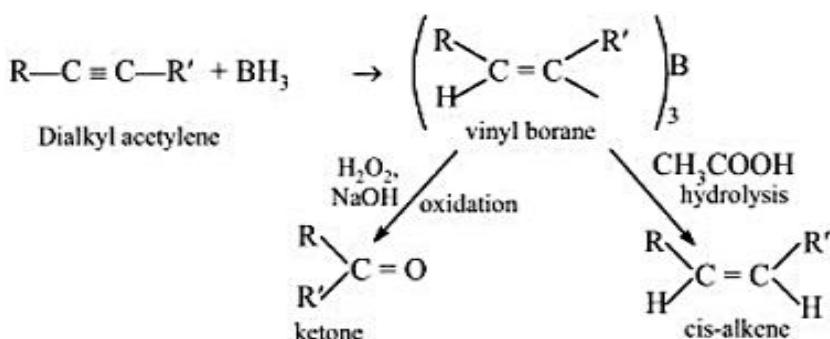


Addition of Boron Hydride (Hydroboration) :

- (i) With mono-alkyl acetylene, R_2BH gives an intermediate which on hydrolysis gives alkene but on alkaline oxidation yields aldehyde.

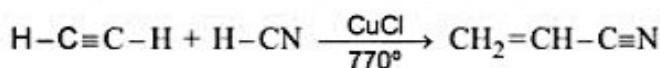


- (ii) With dialkyl acetylenes, the product of hydrolysis is cis-alkene and that of oxidation is a ketone.



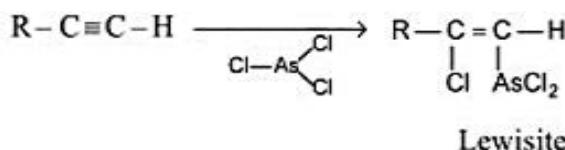
Addition of HCN :

Addition takes place in the presence of CuCl



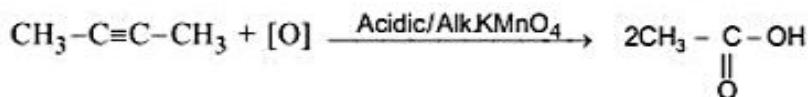
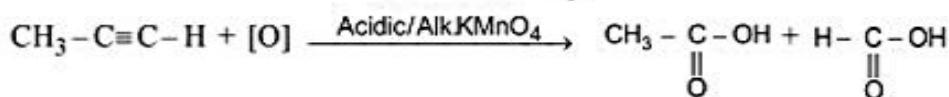
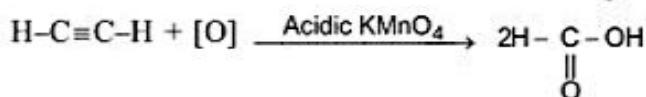
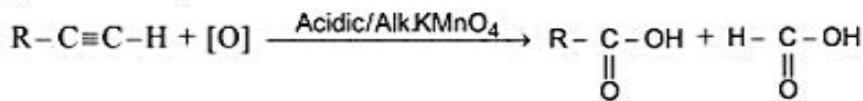
Addition of AsCl₃ :

Lewisite is obtained

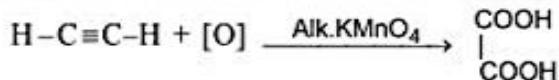


Oxidation :

With acidic or alkaline KMnO₄ alkyne break into two parts from triply bonded carbon and every part forms respective acid.

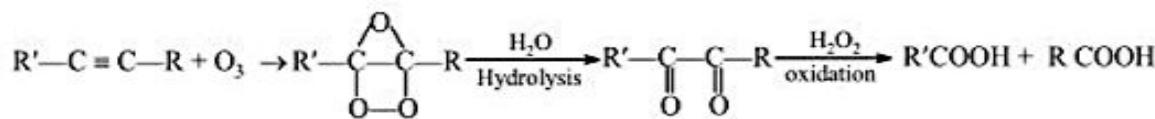


Exception : Acetylene forms oxalic acid with alkaline KMnO₄ exceptionally.



Ozonolysis

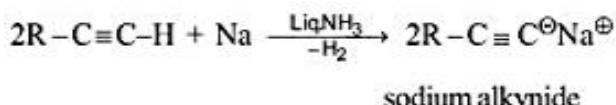
The ozonolysis of alkynes yields a mixture of carboxylic acids.



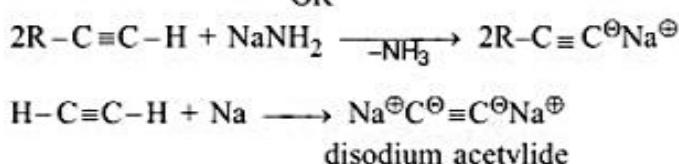
Acidic nature of 1-Alkyne or Acetylene

In 1- alkyne or acetylene, the H which is linked with sp hybridised carbon is called as acidic or active H. It can easily be substituted by metal or alkaline species. Hence 1- alkyne or acetylene are acidic in nature. eg.

Reaction with Na :



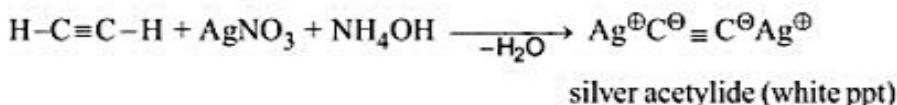
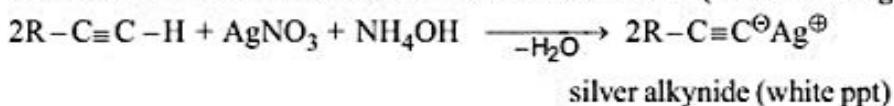
OR



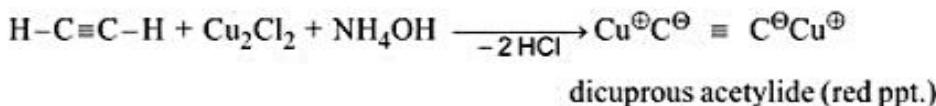
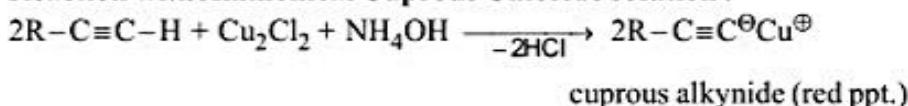
Note : Where this alkynide is treat with alkyl halide higher alkyne is obtained.



Reaction with Ammonical Silver Nitrate solution : (Tollen's Reagent)



Reaction with Ammonical Cuprous Chloride solution :

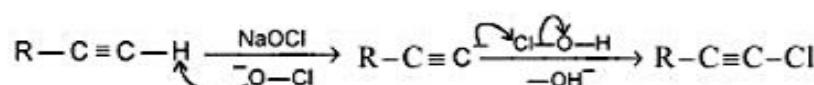


Reaction with NaOCl :

Acidic hydrogen is substituted by 'Cl'

- (i) $H-C\equiv C-H \xrightarrow{NaOCl} Cl-C\equiv C-Cl$
- (ii) $R-C\equiv C-H \xrightarrow{NaOCl} R-C\equiv C-Cl$

Mechanism :

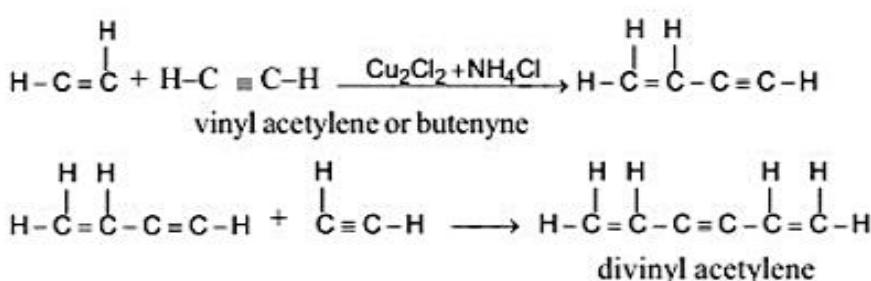


Polymerisation Reactions : Alkyne mainly shows addition polymerisation reactions.
Dimerisation and Cyclization

(a) **Dimerisation :**

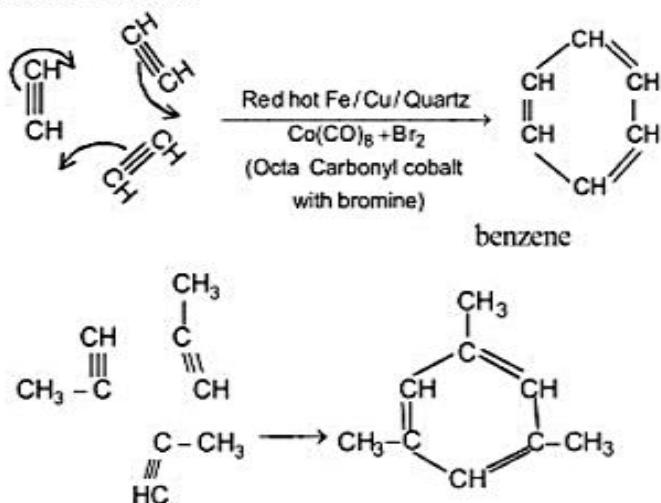
Two mole acetylene reacts with Cu_2Cl_2 & NH_4Cl and forms vinyl acetylene.

Note : If acetylene would be in excess then product would be divinyl acetylene and the reaction is called *trimerisation*.



(b) **Trimerisation :**

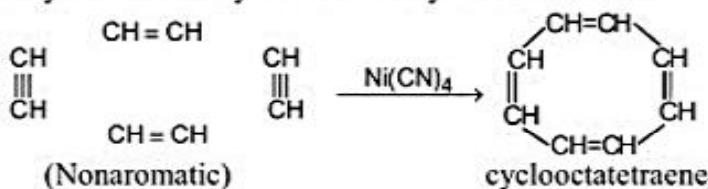
If three mole of acetylene is passed into red hot iron or Cu or quartz tube, then a cyclic trimer is formed which is called benzene.



mesitylene (having 3-1°, 3-2° & 3-3° carbons)

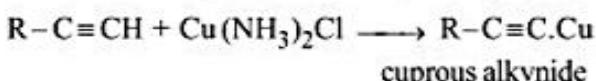
Important : Mesitylene can also be obtained from acetone by condensation polymerisation.

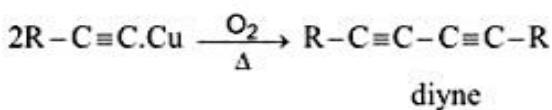
(c) **Tetramerisation :** According to the name four moles of acetylene are heated with nickel tetra cyanide, then acetylene forms a cyclic tetramer cyclo octa tetraene.



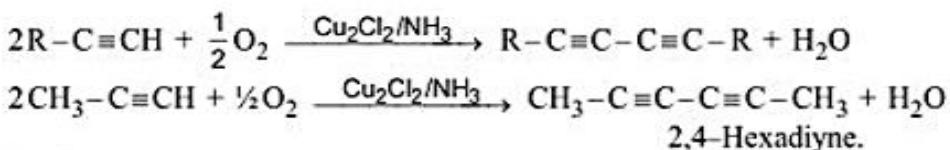
Coupling:-

- (a) Alkyne form respective cuprous alkynide with ammonical cuprous chloride solution. When cuprous alkynide is reacted with potassium ferri cyanide $[\text{K}_3\text{Fe}(\text{CN})_6]$ they converted into conjugated diyne.



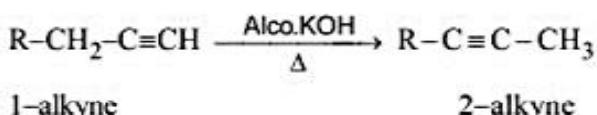


- (b) Coupling is also done easily by 1-alkyne in the presence of Cu_2Cl_2 (cuprous compound) and amine (ie. pyridine + air) cuprous alkynide is formed (this coupling is known as oxidative coupling or glaser coupling)

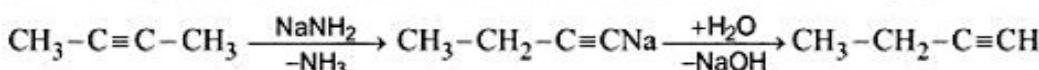


Isomerisation :-

- (a) When 1-alkyne is treated with alcoholic KOH 2-alkyne is formed.



- (b) When 2-alkyne is treated with sodamide then it is converted into 1-alkyne.



MCQ

- Q.1** What happens when 2- butyne reacts with H_2 in presence of Nickle Boride or lindlar's catalyst ($Pd/CaCO_3-PbO$) -
- (A) $\begin{matrix} CH_3-C-H \\ || \\ CH_3-C-H \end{matrix}$ (B) $\begin{matrix} CH_3-C-H \\ || \\ H-C-CH_3 \end{matrix}$
- (C) $CH_3-CH_2-CH_2-CH_3$ (D) $\begin{matrix} CH_2=CH \\ | \\ CH=CH_2 \end{matrix}$
- Q.2** What will be the product of chlorine water and acetylene -
- (A) Dichloro propanol (B) Dichloroethanal
- (C) Propanol (D) 2-Chloro ethanol
- Q.3** Product formed by the oxidation of acetylene in the presence of alkaline $KMnO_4$
- (A) Glyoxal (B) Oxyrane (C) $CO_2 + H_2O$ (D) Oxalic acid
- Q.4** Acetylene on treating with HI gives -
- (A) 1,1-Diodoethane (B) Ethylene (C) Iodoethane (D) Ethane
- Q.5** Acetylene and ethylene react with alk $KMnO_4$ to give -
- (A) Oxalic acid and formic acid (B) Acetic acid and ethylene glycol
- (C) Ethyl alcohol and ethylene glycol (D) None

- Q.6** When 2-butyne reacts with sodamide in an inert solvent in the presence of dilute HCl, the product formed is
 (A) n-Butane (B) 2-Butene (C) 1-Butyne (D) 1-Propyne
- Q.7** Which of the following can not react with ammonical silver nitrate-
 (A) Acetylene (B) Hexyne-1 (C) Phenyl acetaldehyde (D) hept-4-yne-2-ene
- Q.8** The hydrocarbon that reacts with ammonical cuprous chloride is-
 (A) Essentially aromatic (B) Ethane (C) Ethyne (D) Ethene
- Q.9** The product of reaction $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} + \text{HC}\equiv\text{CCH}_3 \rightarrow$ is
 (A) $\text{CH}_3\text{CH}_2\text{CH}_3$
 (B) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3$
 (C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 (D) $\text{CH}_3\text{CH}_2\text{CHO}$
- Q.10** 1-butyne can be distinguished from 2-butyne by using
 (A) bromine water (Br_2 in CCl_4)
 (B) cold alk. KMnO_4 (Baeyer's Reagent)
 (C) ammoniacal solution of silver (Tollen's Reagent)
 (D) diethyl ether
- Q.11** What is the chief product of reaction between β -butylene chloride and alc. KOH/NaNH_2
 (A) 1,2-butadiene (B) 1,3-butadiene (C) 2-butyne (D) 1-butyne
- Q.12** Chloroform is heated with Ag powder in laboratory what will be the product -
 (A) Acetylene (B) Ag_2O (C) CH_2Cl_2 (D) CH_4
- Q.13** Ethylene dibromide on treating with alcoholic KOH gives-
 (A) C_2H_6 (B) CH_4 (C) C_2H_4 (D) C_2H_2
- Q.14** Treatment of an alkyne with H_2 in presence of palladised coke results in the formation of-
 (A) Alkane (B) Alkane vigourously (C) Trans-alkene (D) cis-alkene

ANSWER KEY

Q.1 A	Q.2 B	Q.3 D	Q.4 A
Q.5 A	Q.6 C	Q.7 D	Q.8 C
Q.9 A	Q.10 C	Q.11 C	Q.12 A
Q.13 D	Q.14 D		

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REACTION CHART FOR ALKYNES

