Hydrocarbon

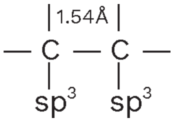
Introduction

The compounds having only C, and H-atoms are known as Hydrocarbon. Natural gas, Petroleum and coal are major sources of Hydrocarbon.

Concept Ladder

Alkanes are saturated acyclic compounds i.e. they have single bonds only.

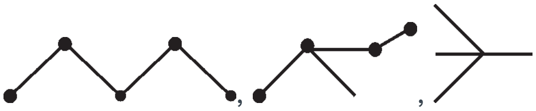
Alkanes



- The general formula of alkanes is $C_n H_{2n+2}$.
- The main sources of alkanes include petroleum, natural gas and coal.
- Alkanes are also termed as paraffins due to their almost inert nature or reduced activity.
- Bond length of C–C is 1.54 Å and that of C–H bond is 1.11 Å.
- Alkanes gives a C–C bond energy of 80 kcal per mole and for C–H bond it is calculated as 97 kcal per mole.
- They are non-polar in nature.
- Alkanes show chain, position, and conformational isomerism.

Rack your Brain

Why alkanes are known as Paraffins?

e.g 

- Liquefied Petroleum Gas (LPG) is composed of propane, butane, and isobutane.

Methods of Preparation of Alkanes

By decarboxylation of sodium salts of fatty acids

When R–COOH heated with Sodalime (4 : 1 Mixture of CaO + NaOH) alkane is formed. Here alkane has one C– atom less than R–COOH as one CO_2 molecule is eliminated.

$$R-COOH \xrightarrow[-H_2O]{NaOH} R-COONa \xrightarrow[NaOH+CaO]{\Delta} R-H + Na_2CO_3$$

R–may be → CH_3, C_2H_5, C_6H_5 etc

$$2HCOONa \xrightarrow[CaO]{\Delta} H_2 + Na_2CO_3$$

Concept Ladder

CaO added, makes sure that the reaction occurs at relatively higher temperature and hence complete decarboxylation occurs.

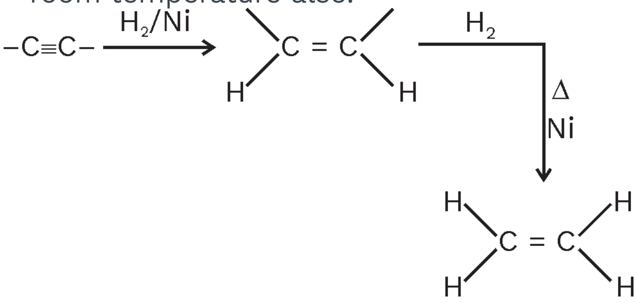
- Here CaO is used to make the reaction more mild and to keep NaOH dry. It also helps in easy fusion.

Rack your Brain

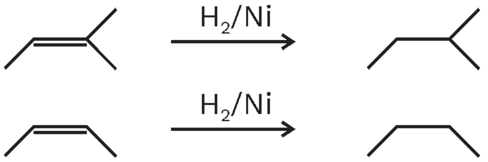
Why we need CaO in the above reaction?

By Sabatier and Senderen Reaction

- Here, catalysts used are Raney Ni [An alloy of Ni–Al] and Pd–Pt (Adam's catalyst).
- Temperature range suited for reaction is 300–400°C.
- In case of Raney Nickel reaction is possible at room temperature also.



For Example : $CH_3-C\equiv CH \xrightarrow[Ni]{H_2} CH_3-CH=CH_2 \xrightarrow[Ni]{H_2} CH_3-CH_2-CH_3$



Concept Ladder

Addition of H_2 to the unsaturated compounds to form alkanes is called reduction.

From the reduction of R–X

- Here, the reducing agent used is usually Zn + NaOH or HCl or Zn–Cu/acid, Na/alcohol. $LiAlH_4$, $NaBH_4$, $(Ph)_3$ SnH etc

$$R-X+H-H \xrightarrow{Zn/HCl} R-H+HX$$

Mechanism

$Zn \rightarrow Zn^{+2} + 2e^-$

$R-X+e^- \rightarrow R^\circ + X^-$

$R:^- + C_2H_5OH \rightarrow R-H+C_2H_5O^-$

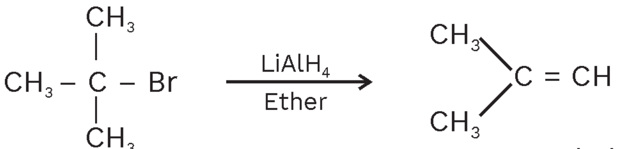
$$R-I+HI \xrightarrow{\Delta, 150^\circ C} R-H+I_2\uparrow$$

$$R-X \xrightarrow[H_2]{\substack{LiAlH \\ or \\ (Ph)_3SnH}} R-H+HX$$

Rack your Brain

How raney Ni is different from Ni?

- Order of Reduction reaction is RI > R – Br > R – Cl > R – F. $LiAlH_4$ is effective in case of 1° and 2° halides while $(Ph)_3SnH$ is effective for all types of halides.



2-Methyl propene

Rack your Brain

Why 3° alkyl halides undergo dehydrohalogenation with $LiAlH_4$?

Using Wurtz Reaction

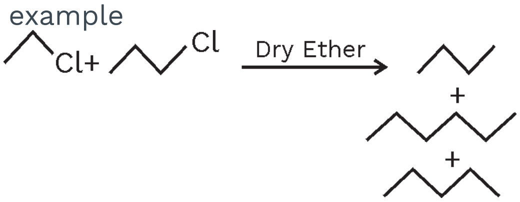
- In case of Wurtz reaction, alkyl halide is treated with sodium metal in presence of dry ether to give alkanes.
- $R - X + 2Na \xrightarrow{\text{Dry ether}} R - R + 2NaX$
- If 'R' group attached is same, then one alkane is formed.

e.g $2CH_3Cl \xrightarrow[\text{Ether}]{2Na} C_2H_6 + 2NaCl$

- If 'R' group attached is different, then it leads to formation of three alkanes.

$R - X + 2Na + X - R' \xrightarrow[-NaX]{\text{Dry ether}} R' - R + R' - R' + R - R'$

For example



The mechanism involved in the reaction is :

$$R - X + \dot{N}a \longrightarrow \dot{R} + NaX$$

$$\dot{R} + \dot{R} \longrightarrow R - R$$

Here disproportion is also possible.

$$C_2H_5^{\bullet} + C_2H_5^{\bullet} \longrightarrow C_2H_4 + C_2H_6$$

- In case of tertiary–halide reaction is not possible as major product is according to dehydro-halogenation which means reaction holds only for a 1° or 2° halide.

Concept Ladder

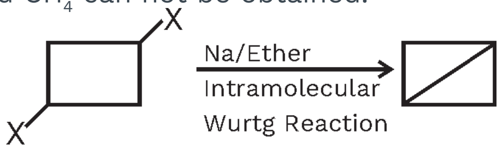
HCl or Zn–Cu/acid – reduction occurs by Transfer of Electrons.

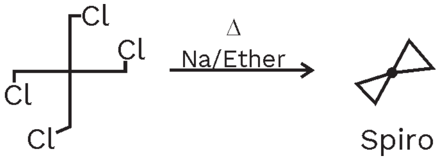
Zn/NaOH – reduction occurs with Nascent Hydrogen

Concept Ladder

Wurtz reaction is used to prepare alkanes containing even number of carbon atoms.

- In place of Na, activated Cu, Ag, Fe can also be used.
- It is good for symmetrical alkanes (C_2H_6, C_4H_{10}) and CH_4 can not be obtained.





Spiro [2, 2] pentane

- In Frankland reaction, alkyl halide is treated with Zn in a closed tube to prepare alkanes.

$$R-X+Zn+X-R \longrightarrow R-R+ZnX_2$$

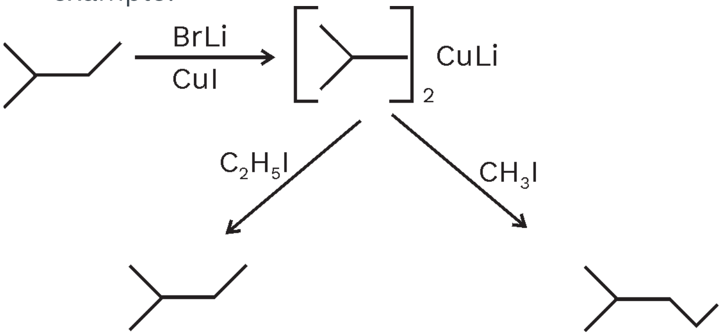
- Rest of process is same as given above in Wurtz reaction.

Corey–house synthesis:

This method is suitable for preparation of alkanes possessing odd number of carbon atoms also (un-symmetrical alkanes).

$$R-X \xrightarrow[\text{Ether} \\ -\text{LiX}]{\text{Li}} R-Li \xrightarrow{\text{CuI}} R_2CuLi \xrightarrow{R'-X} R-R'+R-Cu+LiX$$

The process can be illustrated in following example:



2 methyl butane

Here R–X must be used for better yield.

Kolbe Synthesis

Rack your Brain

Name an alkane which can not be prepared by wurtz reaction?

Previous Year's Question

Which of the following alkane cannot be made in good yield by Wurtz reaction? **[NEET]**

(1) n-Hexane
(2) 2,3-Dimethylbutane
(3) n-Heptane
(4) n-Butane $_2$

Concept Ladder

Corey House reaction is limited to a 1° alkyl halide and the alkyl groups in the Dialkyl Lithium Cuprate may be 1°, 2° or 3°.

$$2R - COONa \xrightarrow{\text{Electrolytic hydrolysis}} \underset{\text{At anode}}{R - R} + 2CO_2^+$$

$$2NaOH + H_2\uparrow$$

Mechanism of Kolbe's electrolysis

$2R{-}COO\ Na \longrightarrow 2R{-}COO^- + 2Na^+$

At Anode :

$2R{-}COO^-{-}2e^- \longrightarrow 2R^\circ + 2CO_2$

$2R{-}COO^\circ \longrightarrow 2R^\circ + 2CO_2$

$R^\circ + R^\circ \longrightarrow R{-}R$

At Cathode :

$2H^+ + 2e^- \longrightarrow d$

e.g

$$\underset{\text{Sodium ecetate}}{2CH_3} - COONa \longrightarrow CH_3 - CH_3 + 2CO_2 + 2NaOH + H_2$$

- pH increases during reaction due to formation of strong bases (NaOH / KOH).
- If two different salts of acid are used, then a mixture of three alkanes will be formed.
- If we take a mixture of sodium acetate and sodium propanoate then ethane, propane, butane will be formed.

$$CH_3 - COONa + C_2H_5COONa \xrightarrow{\text{Electro}} C_2H_6 + C_3H_8 + C_8H_{10} + 2CO_2 + 2NaOH + H_2$$

- The process involves both, ionic as well as free radical mechanism.
- Methane (CH_4) can not be prepared by the method.

Concept Ladder

Sodium or Potassium Salt of monocarboxylic acid is electrolyzed to form alkane.
If n → no. of C-atoms in salt of carboxylic acid,
Then, no. of C-atoms in alkane → 2(n-1)

Rack your Brain

What is Gilman Reagent?

By decomposition of Grignard Reagent

- A compound possessing an active hydrogen atom generally shows this reaction with Grignard reagent.

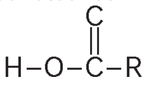
$R{-}MgX + H_2O \rightarrow R{-}H + Mg.X.OH$

Or H_2NR or

Or HOR NH_2etc

Or $HC \equiv CR$

Or H–NH–R



$H{-}O{-}\overset{\overset{\displaystyle C}{\|}}{C}{-}R$ etc.

Concept Ladder

When a Grignard reagent reacts with water, a proton replaces the halogen, and the product is an alkane.

Birch Reduction:

In the process, terminal alkenes are reduced to alkanes.

$$R-CH=CH_2+H_2 \xrightarrow[\text{MeOH}]{\text{Na/Liq.NH}_3} R-CH_2-CH_3$$

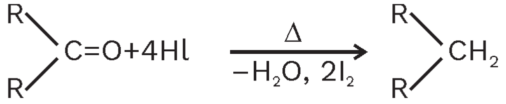
By the reduction of R–OH, R–CHO, R–CO–R, R–COOH

- Here, reagent used is Hydrogen Iodide and red phosphorus at 150°C–200°C.

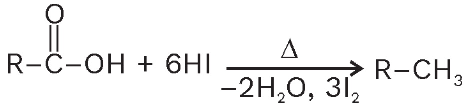
(1) $R-OH+2HI \xrightarrow{\Delta} R-H+H_2O+I_2$

(2) $R-CH=O+4HI \xrightarrow[-H_2O-2I_2]{\Delta} R-CH_3$

(3)



(4)



$$R-\overset{\overset{\large O}{\|}}{C}-OH+6HI \xrightarrow[-2H_2O,\ 3I_2]{\Delta} R-CH_3$$

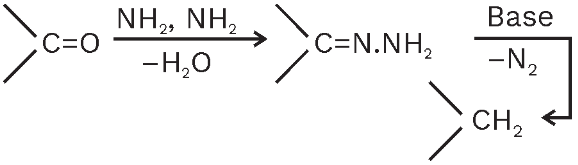
By the hydrolysis of methanides

$Be_2C+4H\cdot OH \rightarrow CH_4+2Be(OH)_2$

$Al_4C_3+12H_2O \rightarrow 3CH_4+4Al(OH)_3$

Wolf–Kishner reduction:

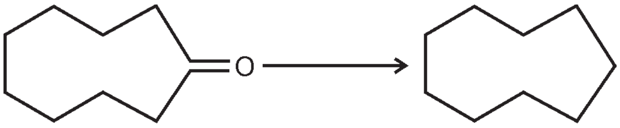
Carbonyl compounds are reduced into alkanes in presence of hydrazine and a base. The bases used are sodamide, C_2H_5ONa.



For example,

(1) $CH_3CHO \xrightarrow[-N_2]{\text{Base}} CH_3-CH=NNH_2 \xrightarrow[-N_2]{\text{Base}} CH_3-CH_3$

(2)



Cyclononane

Concept Ladder

Red P in HI is a reagent that is used to generate Nascent Hydrogen which further helps in reduction.

Previous Year's Question

Hydrocarbon (A) reacts with bromine by substitution to form an alkyl bromide which by Wurtz reaction is converted to gaseous hydrocarbon containing less than four carbon atoms (A) is **[NEET]**

(1) $CH\equiv CH$

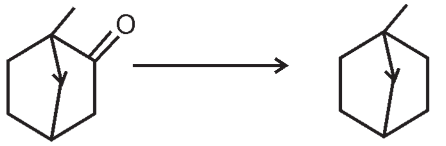
(2) $CH_2=CH_2$

(3) CH_3-CH_3

(4) CH_4

Rack your Brain

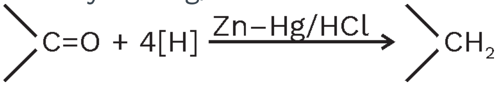
Grignard Reagents are named after which discoverer who also received a Nobel prize in 1912?

(3) 

Camphor Camphane

Clemmensen reduction:

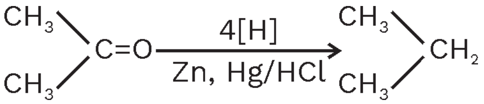
Here, carbonyl compounds are reduced into alkanes by Zn–Hg/HCl as shown below:



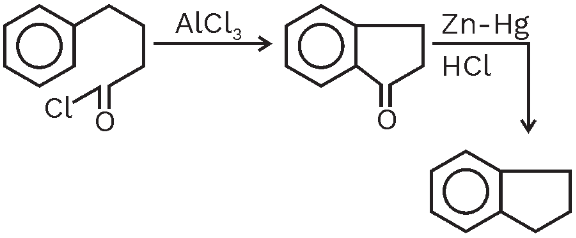
$$>C=O + 4[H] \xrightarrow{Zn-Hg/HCl} >CH_2$$

For example

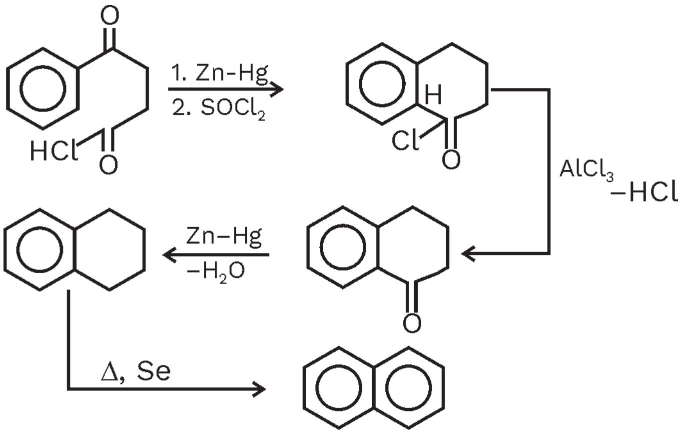
(1) $CH_3-CHO \xrightarrow[Zn.Hg/HCl]{4[H]} CH_3-CH_3$

(2) 

$$\begin{matrix}CH_3\\CH_3\end{matrix}>C=O \xrightarrow[Zn,\ Hg/HCl]{4[H]} \begin{matrix}CH_3\\CH_3\end{matrix}>CH_2$$

(3) 

Indane

(4) 

Napthalene

Rack your Brain

Clemmensen reduction is most recommended for which type of ketones?

Concept Ladder

The Wolff-Kishner is done under strongly basic conditions using high heat in a polar protic solvent.The Clemmensen is performed in strongly acidic conditions. In both the reactions, reduction of ketone occurs.

Rack your Brain

A hydrazone has how many number of N-atoms?

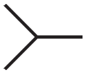
Physical Properties of Alkanes

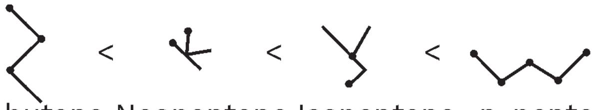
- **Physical state**

  $C_1 - C_4$ ——colourless gases
  $C_5 - C_{17}$——colourless liquids
  C_{18} and above are colourless waxy solids.
- Density ∝ Molecular weight [$CH_4 < C_2H_6 <$]
- All alkanes are lighter than water and their limiting density is 0.8g /cm^3 .
- Cyclo alkanes float on water as they are lighter than water
- Alkanes are insoluble in polar solvents but soluble in non-polar solvents like CCl_4 , ether etc.

  Solubility $\mu \dfrac{1}{\text{Mol.wt}}$

  $CH_4 > C_2H_6 > C_3H_8 > C_4H_{10} >$
- Boiling point ∝ Surface area α Molecular wt. The trend as shown by alkanes in relation to boiling points is as given: normal > iso > neo. when, for each successive member, molecular formula differs by a (–CH_2–) group and subsequently boiling point differs by 20°C – 30°C.

  $CH_4 < C_2H_6 < C_3H_8 <$ 



n-butane Neopentane Isopentane n-pentane

- Melting point (M.P.) of even number alkane > Melting point of odd number alkane, i.e., $C_{15} < C_{16} > C_{17}$
- In case of alkanes with even number of C–atom more than the next alkane having odd number of C–atom as more symmetrical and have closer packing which generally means more stronger Van der Waal forces. It is called alternation or oscillation effect.

Previous Year's Question

Which of the following is used as an antiknocking material? **[AIPMT]**

(1) Glyoxal
(2) Freon
(3) T.E.L.
(4) Ethyl alchol

Concept Ladder

Alkanes with even number have higher M.P than those with odd number of C-atoms. This is known as alteration effect.

Rack your Brain

Why petrol is used to remove grease stains?

Chemical Properties of Alkanes

Alkanes are non-reactive towards bases, acids, oxidizing agents etc. due to non-polar nature of C–C and C–H bonds and the inability to donate or accept electrons.

Halogenation:

Here H–atoms of alkanes are substituted by X–atom ion.

- Reactivity of halogens(X) is $F_2 > Cl_2 > Br_2 > I_2$
- Presence of O_2 suppresses the reaction.
- Replacement of H-atom is easy and follows the trend: 3° > 2° > 1° > methyl.
- Initiation is done by dibenzoyl peroxide, $Pb(Et)_4$. It happens in hν, dark, and at high temperatures in the range of 1250°C – 4000°C.

For example,

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{Final product}}{CCl_4}$$

$$C_6H_6 + Br_2 \xrightarrow[\text{Final product}]{h\nu} C_2H_5Br \xrightarrow{Br_2} C_2Br_6$$

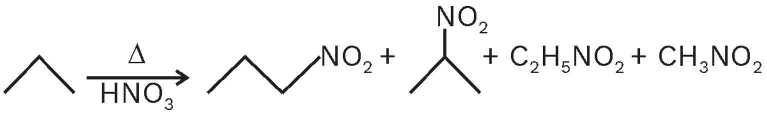
$$2R - X + HgF_2 \longrightarrow 2R - F + HgX_2$$

(X=Br,I)

Nitration

$$R - H + HNO_3 \xrightarrow[\substack{\text{High temp.}\\ 400°C}]{\Delta} R - NO_2 + H_2O$$

- The reaction is used for heptane & hexane.
- In case of lower alkane members, only vapour phase nitration happens as follows:



Sulphonation

$$R - OH + H_2SO_4 \xrightarrow[\substack{\text{Prolonged}\\ \text{heating}}]{\Delta SO_3} R - SO_3H + H_2O$$

- The reaction is given by alkanes having minimum of 6 carbon atoms like in hexane & heptane.

Concept Ladder

Isoination of alkanes is generally not carried out to prepare RI as the reaction is highly endothermic and reversible. But is carried out in the presence of an oxidizing agent, such as HIO_3, HgO and HNO_3, as it removes the HI formed in the reaction.

Concept Ladder

The order of reactivity of different hydrogens for nitration is: 3° > 2° > 1°.

Rack your Brain

What would happen if a direct fluorination of methane takes place?

- Lower members react with SO3 forming sulphonic acids.

$$R-H + SO_3 \xrightarrow[\text{Prolong}]{\Delta} R-SO_3H \quad \text{etc.}$$
$$\hookrightarrow CH_3,\ C_2H_5$$

Rack your Brain

What is vapour phase nitration?

Oxidation reactions

(a) Combustion or complete oxidation

$$(C_6H_{2n+2}) + \frac{(3n+1)}{2}O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

e.g. $C_2H_6 + \frac{7}{2}O_2 \xrightarrow{\Delta} 2CO_2 + 3H_2O + 1538\,KJ$

(b) Incomplete combustion

$$CH_4 + O_2 \xrightarrow{\text{Burn}} \underset{\text{Carbon black}}{C} + 2H_2O$$

- Carbon black is used in printing ink.

$$2CH_4 + 3O_2 \xrightarrow{\text{Burn}} 2CO + 4H_2O$$

(c) Catalytic oxidation

$$CH_4 + [O] \xrightarrow[\text{100 atm 200°C}]{\text{Cu-tube}} CH_3OH$$

$$CH_3-(CH_2)_n-CH_3 \xrightarrow[\text{100°C–160°C}]{O_2} (CH_3)-(CH_2)_n-COOH$$

Mn-Stearate

$$2CH_4 + 3O_2 \xrightarrow{(CH_3COO)_2Mn} 2HCOOH + 2H_2O$$

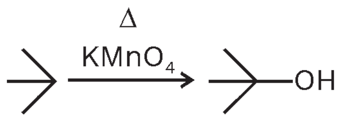
$$2CH_3-CH_3 + 3O_2 \xrightarrow{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$$

Previous Year's Question

The alkane that gives only one monochloro product on chloriantion with Cl¬2 in presence of diffused sunlight is **[NEET]**

(1) 2,2-dimethylbutane
(2) Neopentane
(3) n-pentane
(4) isopentane.

(d) Chemically controlled oxidation is given by alkanes which have tertiary carbon atom.



Isobutane Isobutyl alcohol

Concept Ladder

In presence of $KMnO_4$, iso- butane gives isobutyl alcohol.

Pyrolysis or cracking:

Here, higher alkane breaks into lower alkane, alkene and hydrogen when heated strongly at very high temperatures in absence of air.

$$R-H \xrightarrow[\text{Absence of } O_2]{\Delta} \underset{\text{Lower alkane}}{R-H} + \underset{\text{alkane}}{R=R} + H_2\uparrow$$

It occurs by free radical mechanism. For example.

$$CH_4 \xrightarrow{1000°C} C + 2H_2$$

$$C_2H_6 \xrightarrow[Cr_2O_3+Al_2O_3]{500°C} CH_4 + CH_2 = CH_2 + H_2$$

$$CH_3 - CH_2 - CH_3 \xrightarrow[770-1000K]{\Delta} CH_3 - CH = CH_2 + CH_2 = CH_2 + C_2H_6 + CH_4 + H_2$$

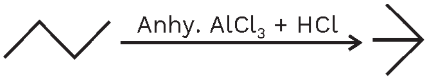
- During pyrolysis C–C bonds break instead of C–H bonds, as bond energy of C–H > C–C.

Isomerization:

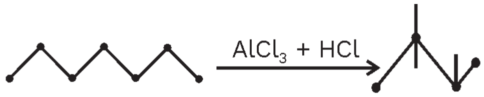
In isomerization, higher alkanes are heated with $AlCl_3$ at high temperatures to convert them into their respective isomers.

Normal Chain isomer

$$\xrightarrow[\text{Anhy.AlCl}_3\text{+HBr,200°C}]{\text{Anhy.AlCl}_3\text{+HCl}} \text{Iso isomer}$$

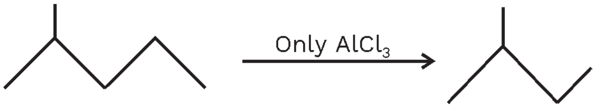


Iso-butane



n-heptane

2, 2, 3 tri methyl butane



2-methyl pentane

2, 3-dimethyl butane

It occurs by 1, 2- hydride or methyl (CH_3) shift.

Concept Ladder

The process of isomerization is good for increasing the octane number.

Aromatization

$$\text{Aliphatic alkanes} \xrightarrow[\substack{\text{10–20 atm 200°C} \\ \text{600°C} \\ \text{Catalyst}}]{\Delta} \text{Aromatic alkanes}$$

For example :

$$\underset{\text{Normal hexane}}{CH_3 - (CH_2)_4 - CH_3} \xrightarrow[Cr_2O_3{-}_2Al_2O_3]{\Delta} C_6H_6 + 4H_2\uparrow$$

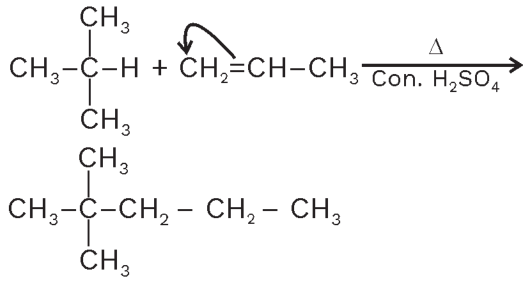
$$\underset{\text{Normal heptane}}{CH_3 - (CH_2)_5 - CH_3} \xrightarrow[Cr_2O_3-Al_2O_3]{\Delta} C_6H_5CH_3 + 4H_2$$

Concept Ladder

This process which involves cyclization, isomerization and dehydrogenation is called aromatization.

Alkylation:

In this, H-atom of an alkyl group is substituted by an alkyl group.



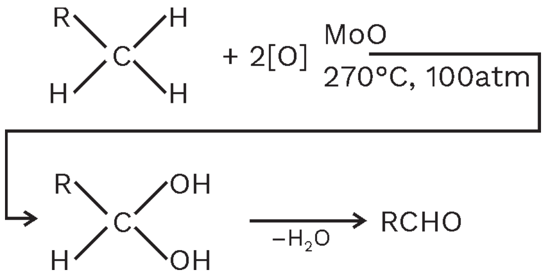
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H + CH_2=CH-CH_3 \xrightarrow[\text{Con. } H_2SO_4]{\Delta} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2-CH_3$$

Eg. 2, 2 Dimethyl pentane

It involves Carbocation formation, and it is useful in increasing octane number of gasoline etc.

Specific reaction

(1)

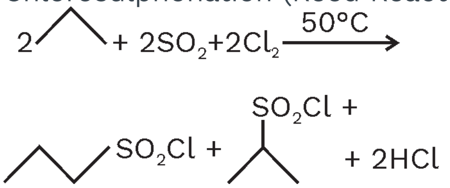


(2) $6CH_4 + 2O_2 \xrightarrow{1500°C} 2CH \equiv CH + 2CO_2 + 10H_2\uparrow$

- $(C_6H_{10}O_5)_n + nH_2O \rightarrow 3n-CH_4 + 3nCO_2$

Cellulose

- Chlorosulphonation (Reed Reaction)



- Cracking, Isomerisation and Aromatization are widely used to increase octane rating of gasoline. Sulphonation, Nitration, Pyrolysis all occur with free radical mechanism.

Concept Ladder

Baeyer's Strain Theory : When ring compounds are formed, the bonds deviate from normal positions which produces a condition of strain in the molecule.

Rack your Brain

What are the drawbacks of Baeyer's Strain Theory?

Previous Year's Question

With respect to the conformers of ethane, which of the following statements is true? **[NEET]**

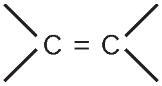
(1) Bond angle changes but bond length remains same.

(2) Both bond angle and bond length change.

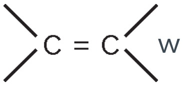
(3) Both bond angle and bond length remain same.

(4) Bond angle remains same but bond length changes. .

Alkenes Or Olefins

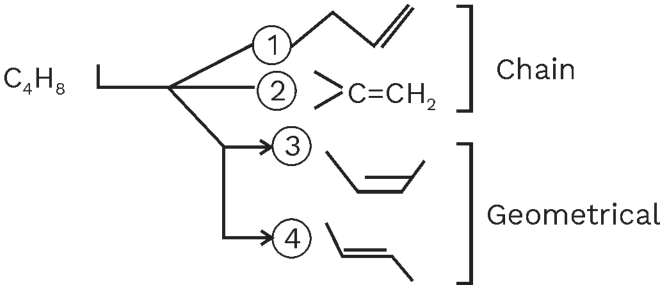


- Alkenes are unsaturated hydrocarbons having

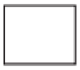


with a general formula C_nH_{2n}

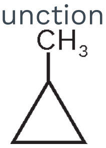
- The word olefin means making oil. Lower members of the group give oily products on halogenation.
- Unsaturated carbon atoms are sp^2 hybridized having a trigonal planar geometry.
- C=C bond has length as 1.34 Å and bond energy is 143.1 kcal per mole.
- Carbon–Hydrogen bond length is 1.1 Å and has bond energy 98.7 kcal per mole.
- Alkenes exhibit chain, ring chain, positional, functional, optical, and geometrical isomerism.



- 3 or 4 with respect to 1 are positional isomers and w.r.t 2 mentioned, are chain isomers.
- All four isomers are functional and ring chain isomers of



and



- Stability $\propto \dfrac{1}{\text{Heat of hydrogenation}}$
- Symmetrical alkenes > unsymmetrical alkene trans alkenes > cis alkenes.

Previous Year's Question

Dihedral angle in staggered form of ethane is **[NEET]**

(1) 0° (2) 120°
(3) 60° (4) 180°.

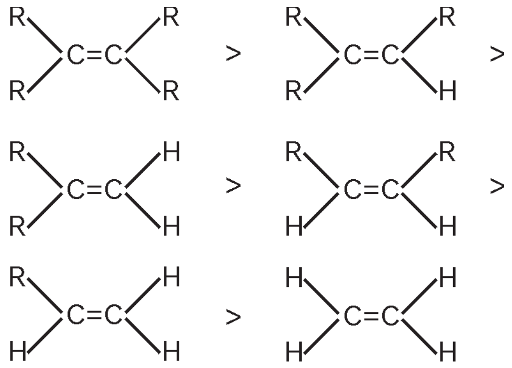
Concept Ladder

The simplest alkene $CH_2=CH_2$ goes by common name Ethylene.

Rack your Brain

Why alkenes are attacked by electrophiles?

Stability in decreasing order

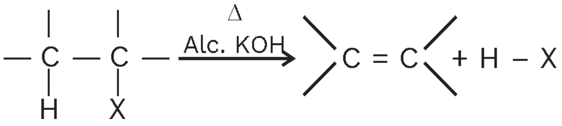


Test of Unsaturation

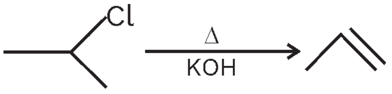
1. Alkenes decolourize Br_2 in CCl_4 or when in water.
2. They also decolourize 1% of alkaline $KMnO_4$ (Baeyer's Reagent).
3. Ozonolysis gives number and location of double bonds in alkene.

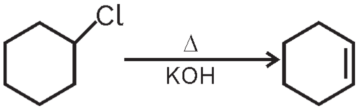
Methods of Preparation of Alkenes

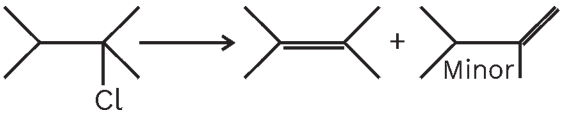
In α, β elimination reactions, By dehydrohalogenation of haloalkanes : Here, reagents used are $C_2H_5O^-$, $(Me)_3COK$, KNH_2, $NaNH_2$, alc. KOH.



For example

(1)


(2)


(3)


Concept Ladder

Ease of dehydrohalogenation 3° > 2° > 1°.
Ease of dehydrohalogenation : Iodides > Bromides >Chlorides

Rack your Brain

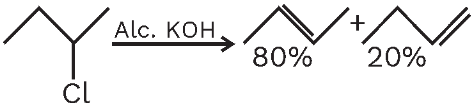
What is Zaitsev rule?

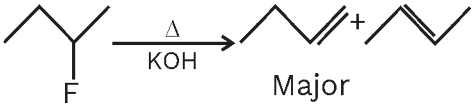
Previous Year's Question

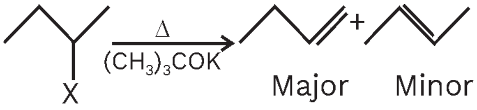
Elimination reaction of 2-Bromo-pentane to form pent-2-ene is:
(a) β-Elimination reaction
(b) follows Zaitsev rule
(c) Dehydrohalogenation reaction
(d) Dehydration reaction

[NEET]

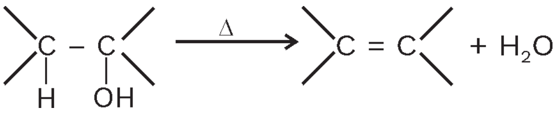
(1) (a), (c), (d)
(2) (b), (c), (d)
(3) (a), (b), (d)
(4) (a), (b), (c).

(4) 

(5) 

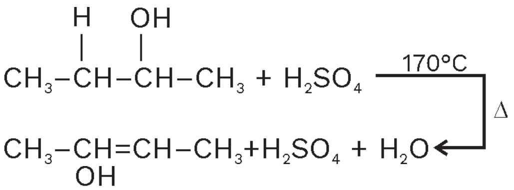
(6) 

Major Product in eq. No. V, VI are according to Hoffmann Rule. By dehydration of alcohol: Here dehydrating agents are H_2SO_4 at 170° C, H_3PO_4 at 200° C, P_2O_5, $ZnCl_2$ at 350° C, BF_3, dry HCl, $KHSO_4$.

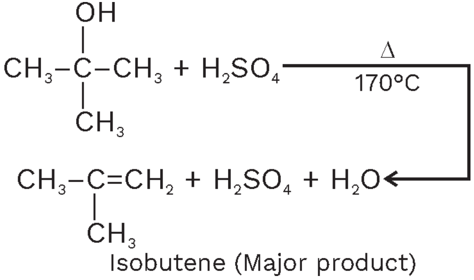


For example :

(1) $CH_3CH_2OH \xrightarrow[170°C]{\Delta, Conc. H_2SO_4} CH_2 = CH_2 + H_2O$

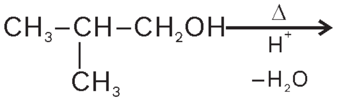
(2) 

$$CH_3-\overset{\overset{H}{|}}{C}H-\overset{\overset{OH}{|}}{C}H-CH_3 + H_2SO_4 \xrightarrow[\Delta]{170°C} CH_3-CH=CH-CH_3+H_2SO_4 + H_2O$$

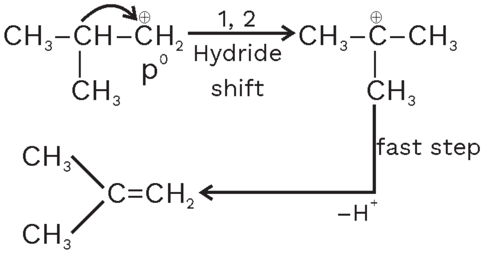
(3) 

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 + H_2SO_4 \xrightarrow[170°C]{\Delta} CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + H_2SO_4 + H_2O$$

Isobutene (Major product)



$$CH_3-\underset{\underset{CH_3}{|}}{C}H-CH_2OH \xrightarrow[H^+ \; -H_2O]{\Delta}$$

(4) 

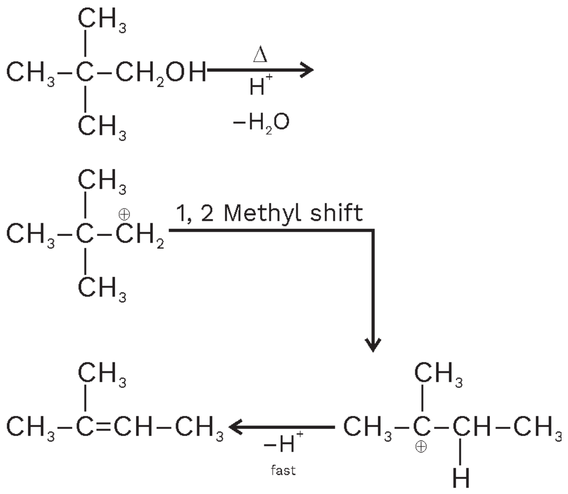
$$CH_3-\underset{\underset{CH_3}{|}}{C}H-\overset{\oplus}{C}H_2 \; p^0 \xrightarrow[\text{Hydride shift}]{1, 2} CH_3-\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}-CH_3 \xrightarrow[-H^+]{\text{fast step}} (CH_3)_2C=CH_2$$

Concept Ladder

Ease of dehydration of alcohols 3° > 2° > 1°

Rack your Brain

What is a β-elimination reaction?



(5)

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH \xrightarrow[-H_2O]{\Delta,\ H^+} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2 \xrightarrow{\text{1, 2 Methyl shift}} CH_3-\underset{\oplus}{\overset{CH_3}{C}}-\underset{H}{CH}-CH_3 \xrightarrow[\text{fast}]{-H^+} CH_3-\overset{CH_3}{C}=CH-CH_3$$

From dehalogenation of dihalogen derivative

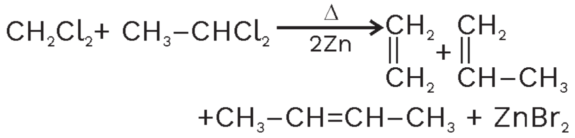
From gem dihalides: When gem dihalides are heated with Zn dust and alcohols alkenes are formed.

$$R-CHX_2+2Zn+x_2CH-R \xrightarrow[-2ZnX_2]{\Delta} R-CH=CH-R$$

For example :

$$CH_3-CHCl_2+2Zn+Cl_2CH-CH_3 \xrightarrow[-ZnCl_2]{\Delta} \underset{\text{But 2-ene}}{CH_3-CH=CH-CH_3}$$

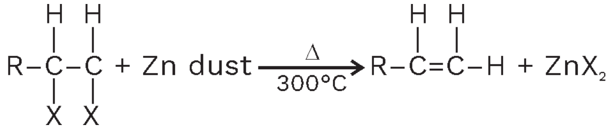
- If we consider two different types of gem dihalides, we obtain 3 different types of alkenes in the reaction.



$$CH_2Cl_2+CH_3-CHCl_2 \xrightarrow[2Zn]{\Delta} \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + \begin{matrix}CH_2\\ \|\\ CH-CH_3\end{matrix} + CH_3-CH=CH-CH_3 + ZnBr_2$$

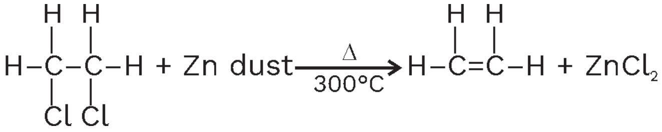
From vicinal dihalides

When vicinal dihalides are heated with Zinc dust, alkene having same number of carbon atoms is obtained.

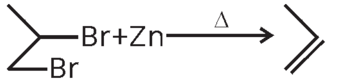


$$R-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}+\text{Zn dust} \xrightarrow[300°C]{\Delta} R-\overset{H}{C}=\overset{H}{C}-H+ZnX_2$$

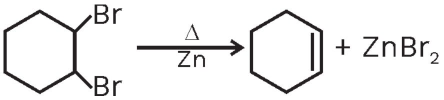
For example

(1) 

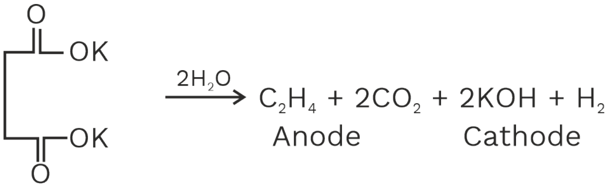
$$H-\underset{Cl}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}-H + \text{Zn dust} \xrightarrow[300°C]{\Delta} H-\overset{H}{C}=\overset{H}{C}-H + ZnCl_2$$

(2) 

1, 2-dibromopropane Propene

(3) 

By Kolbe's electrolytic reaction

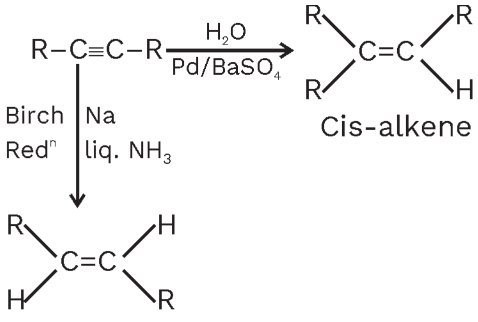


Potassium succinate

By partial reduction of alkynes

$$R-C \equiv CH + H_2 \xrightarrow[\text{catalyst}]{\text{Lindlar}} R-CH=CH_2$$

- Lindlar's catalyst is $CaCO_3$ poisoned with sulphur or Pd-$BaSO_4$ or quinoline. It is generally used to prevent excessive reduction. It is basically Syn-addition and gives cis alkene while with Li/NH_3 or Na addition it is Anti.



Cis-alkene

trans-alkene

Rack your Brain

What do you mean by syn and anti addition?

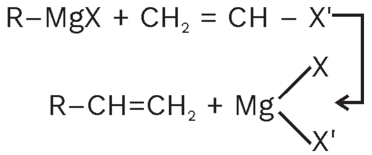
Concept Ladder

Electrolysis of Dicarboxylic acid gives alkenes.

Rack your Brain

Why K^+ ion remains in the solution?

From Grignard reagent



From other organometallic compound

$$CH_2 = CH-Cl + CuR_2 \xrightarrow{Alc.KOH} R-CH = CH_2 + R-Cu-Cl$$

Here, R may be CH_3, C_6H_6 etc.

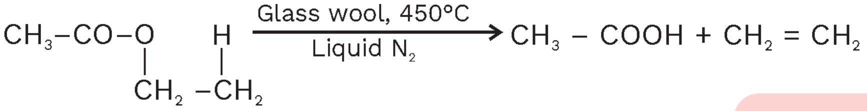
By heating tetra alkyl ammonium halide or hydroxide

$$(C_2H_5)_4N.OH \xrightarrow{\Delta} C_2H_4 + H_2O + (C_2H_5)_3N$$

Concept Ladder

Wittig reaction won its inventor, Georg Wittig, the 1979 Nobel Prize in Chemistry.

Using esters by pyrolysis: When esters are heated in presence of liquid nitrogen (N_2) and glass wool, alkyl part of ester converts into respective alkene, while alkanoate part of ester converts into respective acid.



$$CH_3-CO-O(CH_2-CH_2)H \xrightarrow[\text{Liquid } N_2]{\text{Glass wool, 450°C}} CH_3-COOH + CH_2 = CH_2$$

Wittig reaction: Here, methylene triphenyl phosphorane or phosphorus ylide is treated with a carbonyl compound to prepare an alkene.

Rack your Brain

In order to extend the number of C-atoms in the product alkene, which reaction should be used?

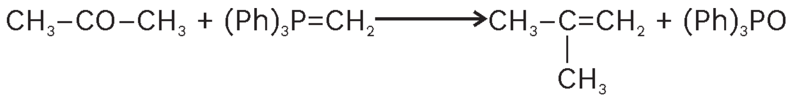
For example :

(1)

$$CH_3-CHO + (Ph)_3P=CH_2 \longrightarrow CH_3-CH=CH_2+(Ph)_3PO$$

Acetaldehyde Propene

(2)



$$CH_3-CO-CH_3 + (Ph)_3P=CH_2 \longrightarrow CH_3-C(CH_3)=CH_2 + (Ph)_3PO$$

Acetone Isobutene

Physical Properties of Alkenes

- Alkenes are odourless, colourless and also lighter than water.

- Alkenes are soluble in organic solvents but insoluble in water.

Physical state

C_1 to C_4	colourless gases
C_5 to C_{16}	colourless liquids
C_{17} and higher	colourless waxy solids

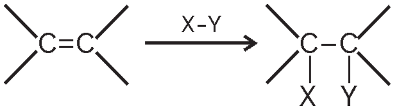
Boiling Point of an alkene is more than that of corresponding alkene because of more polarizability of π electrons.

- Cis -alkenes have higher values of B.P., dipole moment, reactivity, heat of hydrogenation and refractive index than corresponding trans alkenes.
- Trans-alkenes have higher melting point(M.P.) than corresponding cis alkenes. This is because of compact packing of the crystal lattice.

Chemical Properties of Alkenes

Addition reactions of alkenes: As alkenes have pi bonds so they are very reactive, as electrons are easily available when required.

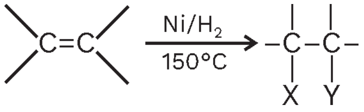
It means carbon-carbon double bond behaves as source of electrons on which electrophiles can easily attack.



Alkenes give electrophilic addition reaction generally with HX, H_2 , X_2 , $H–OSO_3H$, H–OH.

Reaction with H_2

- The reaction occurs on surface of catalysts like Ni, Pd or Pt in a cis-syn addition manner.



- Reducing agents like Wilkinson catalyst $[RhCl(Ph)_3P]$ and $PtCl_2$, $NaBH_4$ can also be used.

Concept Ladder

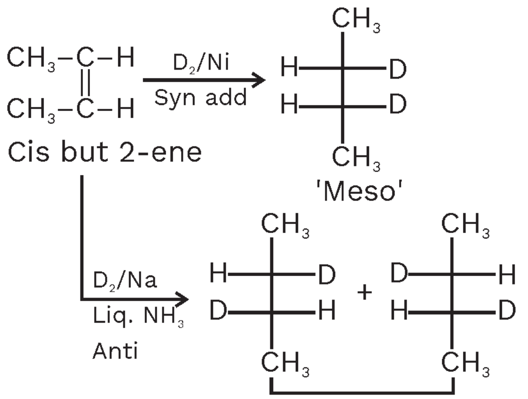
The solubility in non-polar solvents are in the following order: alkanes > alkenes > alkynes.

Rack your Brain

Hexene will float or sink in water?

Concept Ladder

Heat of hydrogenation is the the energy released when one mole of alkenes is hydrogenated with H_2 is called the heat of hydrogenation. More negative the heat of hydrogenation of an alkene, less stable is the alkene.

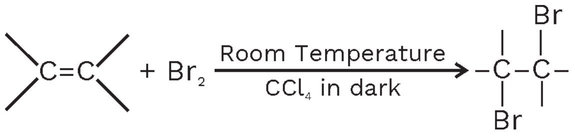


Racemic mixture

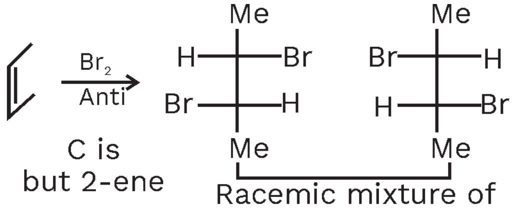
In case of trans 2-butene, nature of product is totally opposite to cis 2-butene.

Reaction with X_2 :

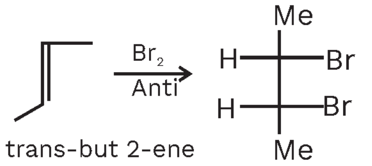
It usually involves trans-addition (Stereospecific)



Here, colour of Br_2/H_2O disappears.

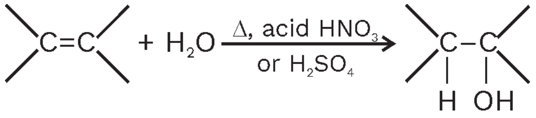


Racemic mixture of 2, 3 dibromo butane



Meso 2, 3 dibromo butane

Reaction with H_2O



Rack your Brain

What is Sabatier and Senderen's reduction?

Concept Ladder

Order of reactivity is $F_2 > Cl_2 > Br_2 > I_2$ (because the $E_{activation}$ order is $F_2 < Cl_2 < Br_2 < I_2$)

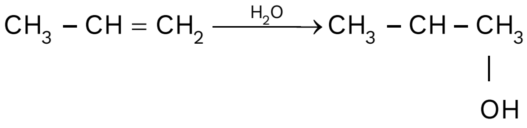
Previous Year's Question

The compound that will react most readily with gaseous bromine has the formula

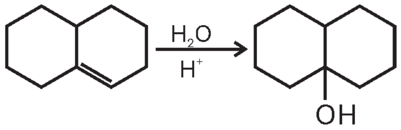
[NEET]

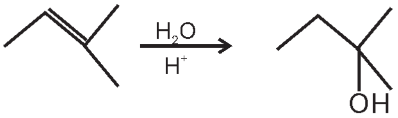
(1) C_3H_6
(2) C_2H_2
(3) C_4H_{10}
(4) C_2H_4

For example :

(1) 

$CH_3-CH=CH_2 \xrightarrow{H_2O} CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$

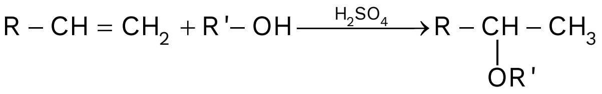
(2) 



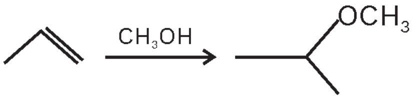
2-Methyl butan 2-ol

In all these addition occur according to Markwonikoff's Rule (Regioselective by nature).

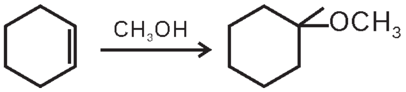
Reaction with R–OH



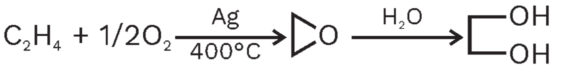
$R-CH=CH_2 + R'-OH \xrightarrow{H_2SO_4} R-\underset{OR'}{\underset{|}{CH}}-CH_3$



2-Methoxy propane

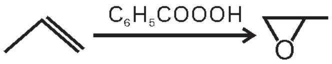


Addition of O_2 to alkenes



Oxirane

Epoxyethane or oxirane



1, 2 Epoxy propane

Rack your Brain

Tell whether the product will be anti or meso.

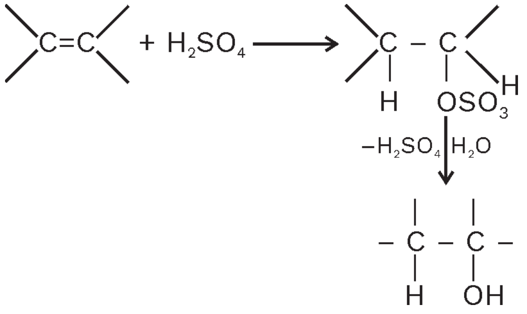
Concept Ladder

According to Markwonikoff's Rule acidic hydrogen attaches itself to the carbon having a greater number of hydrogen substituents whereas the halide group attaches itself to the carbon atom which has a greater number of alkyl substituents.

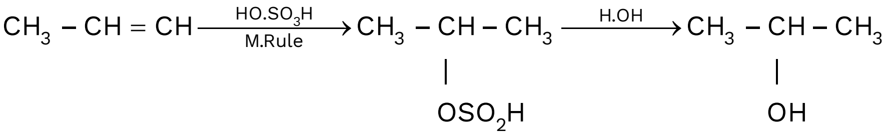
Rack your Brain

What is indirect hydration alkenes?

Reaction with H_2SO_4

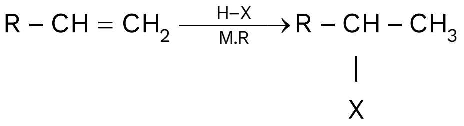


For example :



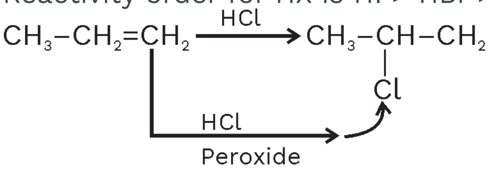
$$CH_3-CH=CH \xrightarrow[M.Rule]{HO.SO_3H} CH_3-\underset{OSO_2H}{\underset{|}{CH}}-CH_3 \xrightarrow{H.OH} CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$$

Addition with HX

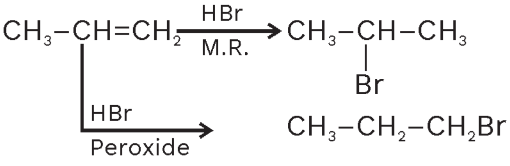


$$R-CH=CH_2 \xrightarrow[M.R]{H-X} R-\underset{X}{\underset{|}{CH}}-CH_3$$

Reactivity order for HX is HI > HBr > HCl > HF.



use only Markwonikoff's Rule



Anti M.R.

No Anti M.R is followed for HF, HCl and HI. [See in G.O.C II]

Addition with hypohalous acid (HXO or X^+OH^-)

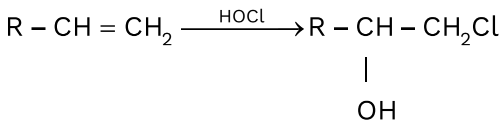
In addition reaction, with HXO alkenes give halohydrins according to Markonikov's Rule and here attacking reagent is X^+ (Halonium ion).

Rack your Brain

Why addition of sulphuric acid to alkene is known as indirect hydration of alkenes?

Concept Ladder

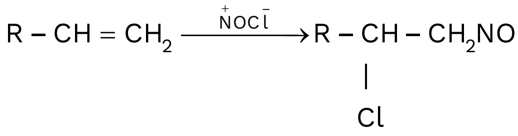
Epoxides are three-atom cyclic systems in which one of the atoms is oxygen. The simplest epoxide is epoxyethane (ethylene oxide).



$$R-CH=CH_2 \xrightarrow{HOCl} R-\underset{OH}{\underset{|}{CH}}-CH_2Cl$$

R may be $-CH_3$, $-C_2H_5$, $-C_6H_5$ etc.

⇒ With NOCl addition occurs as follows :



$$R-CH=CH_2 \xrightarrow{\overset{+}{N}O\overset{-}{Cl}} R-\underset{Cl}{\underset{|}{CH}}-CH_2NO$$

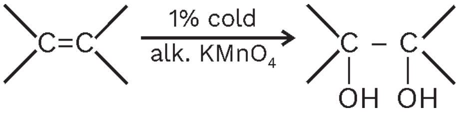
Concept Ladder

According to Markovnikov's Rule, the major product is formed by the most stable carbocation.

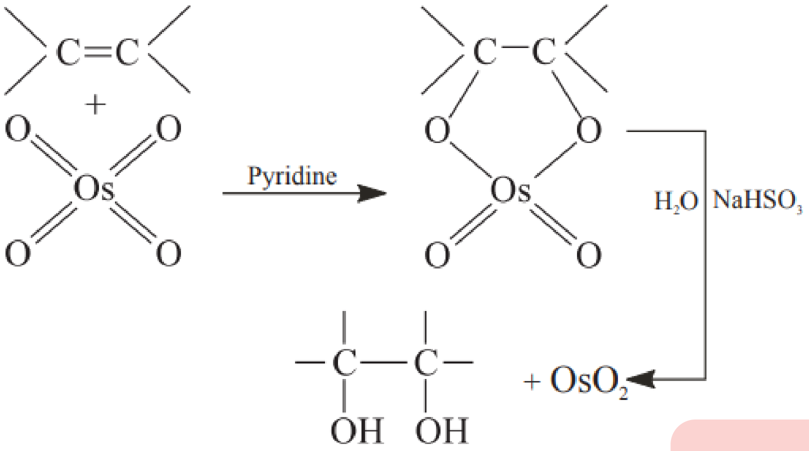
Oxydation or hydroxylation

- Here, hydroxylation occurs by using OsO_4, pyridine or $NaHSO_3/H_2O$, 1% alkaline $KMnO_4$ (Baeyer's reagent).
- On hydroxylation, all of these reagents give syn addition.

  For example,



- With OsO_4, pyridine, $NaHSO_3/H_2O$



Cis 1, 2 di–O1s

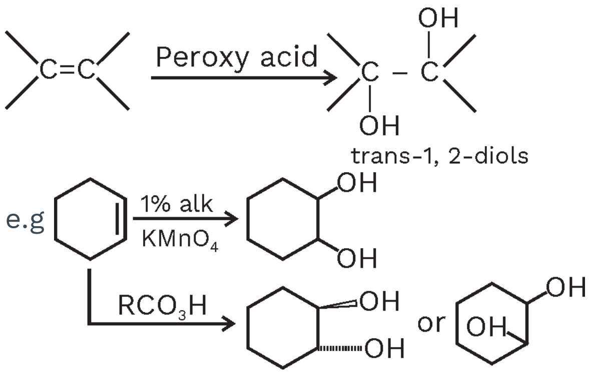
- Anti-hydroxylation is not so common and is shown as follows:

Rack your Brain

Why peroxide effect is observed with HBr only?

Rack your Brain

The most reactive HOX is _____.



- **Stereochemistry of hydroxylation**

cis alkene + cis mode reagent $\xrightarrow[\text{or } OSO_4/NaHSO]{1\%alk.KMO_4}$ meso product

trans alkene + cis mode ⟶ reagent racemic mixture

cis alkene + trans mode reagent $\xrightarrow[H-COOOH]{C_6H_5-\overset{\overset{O}{\|}}{C}-O-OH \text{ or}}$ racemic mixture

trans alkene + trans mode reagent ⟶ meso product

Rack your Brain

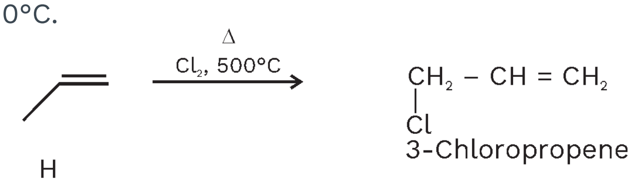
What is Baeyer's Reagent?

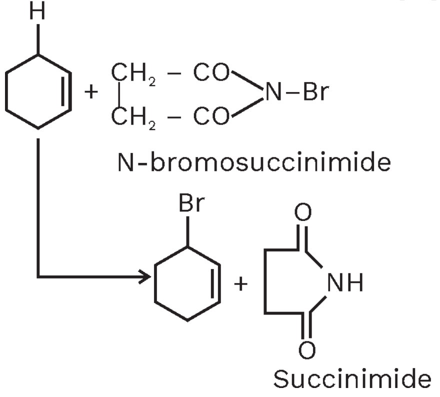
Concept Ladder

Hydoxylation – Addition of -OH groups.

Substitution reaction:

Alkenes undergo substitution only at allylic position and at high temperature of 450°C–500°C.





Concept Ladder

The relative rate of abstraction of hydrogen: 3° allylic > 2° allylic > 1° allylic > 3° > 2° > 1° > methyl > vinylic

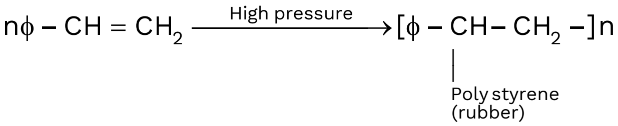
Isomerization

Polymerization

General catalyst used for polymerization of olefins is Zeigler-Natta catalyst[$TiCl_4 + (Et)_3 Al$].

$$nH_2C = CH_2 \xrightarrow[\text{High temperature}]{\Delta} [-CH_2-CH_2-]n$$

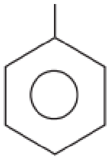
Polythene



$$n\phi - CH = CH_2 \xrightarrow{\text{High pressure}} [\phi - CH - CH_2 -]n$$

Poly styrene (rubber)

Where $\phi = C_6H_5$ or

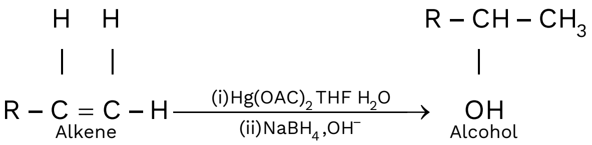


$$nCF_2 = CF_2 \text{ [illegible] } [-CF_2-CF_2-]n$$

Tetra fluro ethylene Teflon(PTFE)

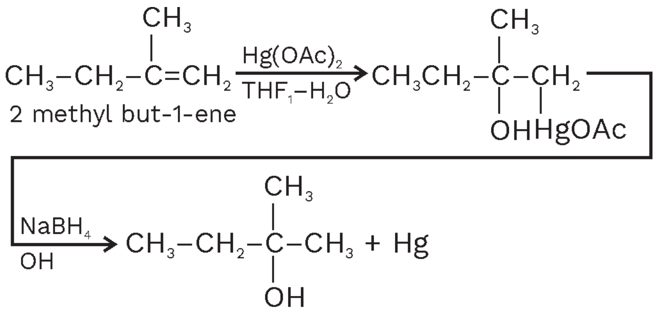
Oxymercuration–demercuration

It involves synthesis of ethers or alcohol from alkenes in accordance with Markovnikov's rule as given below:



$$\underset{\text{Alkene}}{R-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H} \xrightarrow[\text{(ii)}NaBH_4, OH^-]{\text{(i)}Hg(OAC)_2\text{ THF }H_2O} \underset{\text{Alcohol}}{\underset{OH}{\underset{|}{R-CH-CH_3}}}$$

For example :



$$\underset{\text{2 methyl but-1-ene}}{CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}=CH_2} \xrightarrow[THF_1-H_2O]{Hg(OAc)_2} CH_3CH_2-\underset{OH}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\underset{HgOAc}{\underset{|}{CH_2}}$$

$$\xrightarrow[OH]{NaBH_4} CH_3-CH_2-\underset{OH}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3 + Hg$$

2 methyl butan-2-01

Concept Ladder

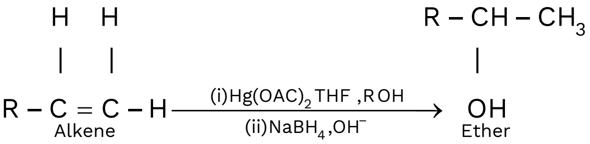
Polymerization is a process through which a large number of monomer molecules react together to form a polymer.

Concept Ladder

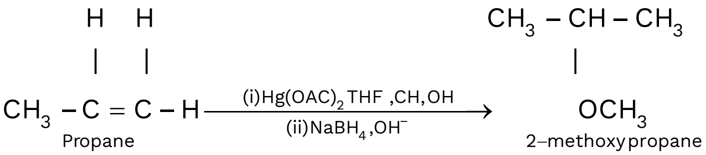
Shifting of double bond (centre of the chain) or migration of methyl group takes place when heated at 770–970K or when heated with a catalyst $Al_2(SO_4)_3$ at 470–570K

Rack your Brain

On what factors does the ratio of isomers depend?

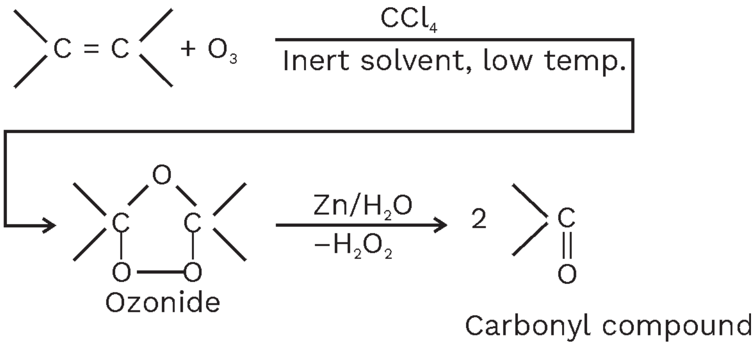


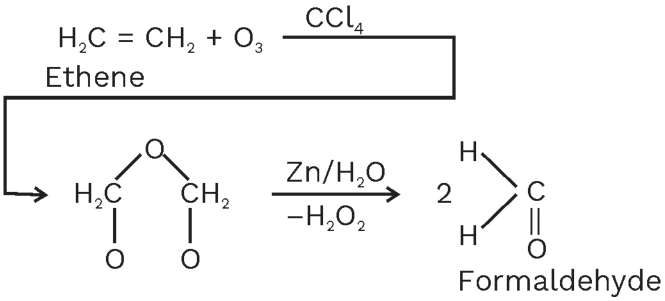
$$\underset{\text{Alkene}}{R-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H} \xrightarrow[\text{(ii)}NaBH_4,OH^-]{\text{(i)}Hg(OAC)_2\,THF\,,ROH} \underset{\text{Ether}}{R-\underset{OH}{\underset{|}{CH}}-CH_3}$$



$$\underset{\text{Propane}}{CH_3-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H} \xrightarrow[\text{(ii)}NaBH_4,OH^-]{\text{(i)}Hg(OAC)_2\,THF\,,CH_3OH} \underset{\text{2–methoxypropane}}{CH_3-\underset{OCH_3}{\underset{|}{CH}}-CH_3}$$

- Here no rearrangement takes place and oxidation number of Hg becomes zero.
- It is an important reaction to find number of double bonds present in alkenes and location.





- If Zn is not used, carbonyl compounds get oxidized into acids.

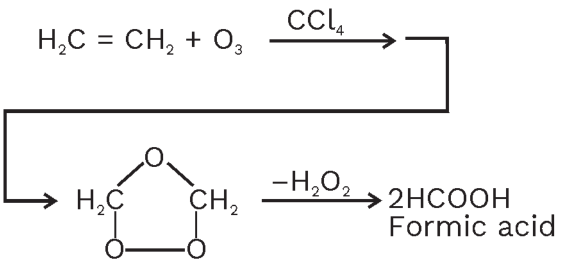
Rack your Brain

Fire Resistant Polymer is?

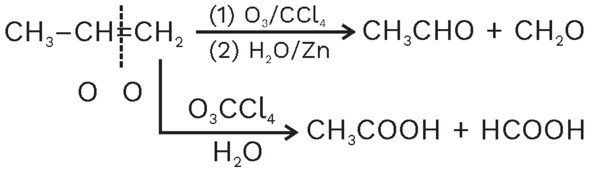
Concept Ladder

There is no stereochemical control in this reaction because the addition of the mercuric ion and the hydrogen in the demercuration step occurs both as syn and anti orientation. As a result, the new stereogenic center forms in R and S configuration leading to a racemic mixture.

For example

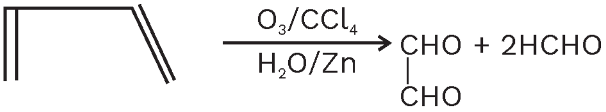


$$H_2C = CH_2 + O_3 \xrightarrow{CCl_4} \text{ozonide} \xrightarrow{-H_2O_2} 2HCOOH$$

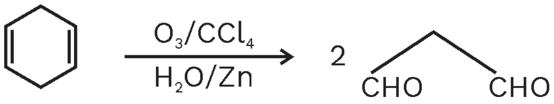


$$CH_3{-}CH{=}CH_2 \xrightarrow[(2)\ H_2O/Zn]{(1)\ O_3/CCl_4} CH_3CHO + CH_2O$$

$$\xrightarrow[H_2O]{O_3CCl_4} CH_3COOH + HCOOH$$

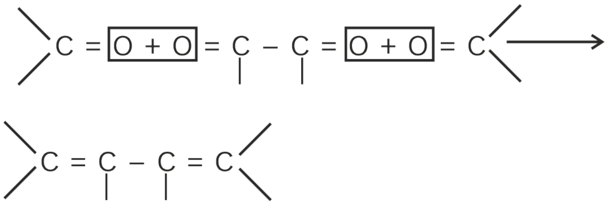


$$\xrightarrow[H_2O/Zn]{O_3/CCl_4} \text{CHO–CHO} + 2HCHO$$



$$\xrightarrow[H_2O/Zn]{O_3/CCl_4} 2\ \text{OHC–CH}_2\text{–CHO}$$

When alkene is to be decided by ozonolysis products, following is done.



$$>C = \boxed{O + O} = C - C = \boxed{O + O} = C< \longrightarrow$$

$$>C = C - C = C<$$

e.g., An alkene after ozonolysis gives one molecule each of HCHO, CH_3CHO and CHO–CHO.

$$CH_3 - CH = \boxed{O + O} = CH - CH = \boxed{O + O} = CH_2$$

$$\downarrow$$

$$CH_3 - CH = CH - CH = CH_2$$

Penta 1, 3 diene

$$R - CH = CH_2 \xrightarrow{CHCl_3} R - CH_2 - CH_2 \,.\, CCl_3$$

$$\xrightarrow{CCl_4} R - \underset{\displaystyle Cl}{\underset{|}{CH}} - CH_2 \,.\, CCl_3$$

Rack your Brain

For the formation of two ethanal molecules after ozonolysis, the alkene is?

Concept Ladder

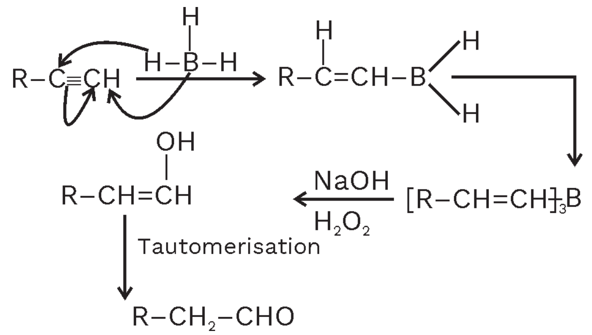
With Polyhalogen compounds like CHX_3, CCl_4 addition occurs according to Anti Markwonikoff's rule.

Hydroboration oxidation

It is used to prepare alcohols following anti-Markovnikov's rule.

$$\underset{\text{Alkene}}{R-CH=CH}\xrightarrow[H_2O_2-NaOH]{B_2H_6}R-CH_2-CH_2-OH$$

Mechanism



This is shown in the following examples:

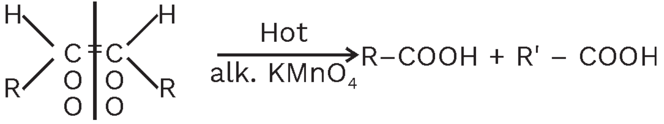
$$\underset{\text{Ethene}}{H_2C=CH_2}\xrightarrow[H_2O_2-NaOH]{B_2H_6}\underset{\text{Ethanol}}{H_3C-CH_2-OH}$$

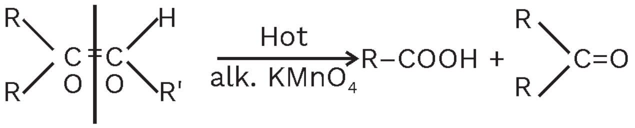
For example,

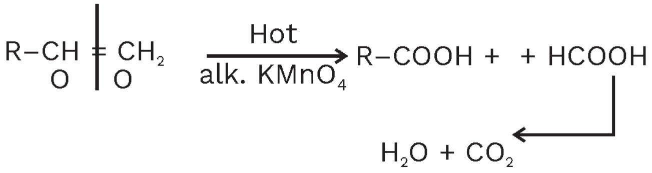
$$\underset{\text{Propane}}{H_3C-CH=CH_2}\xrightarrow[H_2O_2-NaOH]{B_2H_6}\underset{\text{Propan-1-ol}}{H_3C-CH_2-CH_2-OH}$$

Oxidative cleavage by Hot alk. $KMnO_4$

Alkenes on oxidative cleavage by hot alkaline $KMnO_4$ gives carboxylic acids, ketones etc.





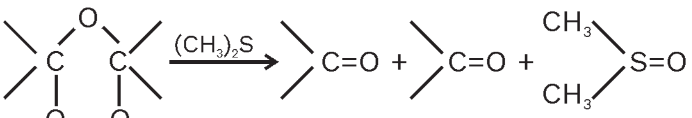


HCOOH further decomposes or oxidises into CO_2 and water.

- Ozonide can also be reduced by using $(CH_3)_2S$ as follows:

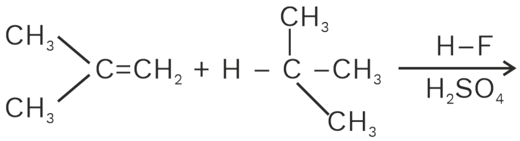
Concept Ladder

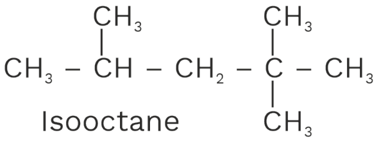
The hydroboration oxidation reaction is a reaction which is employed for the conversion of alkenes into alcohols that are neutral. This is done via a two-step process which includes a hydroboration step and an oxidation step.



Dimethyl suophoxide
(D.M.S.O.)

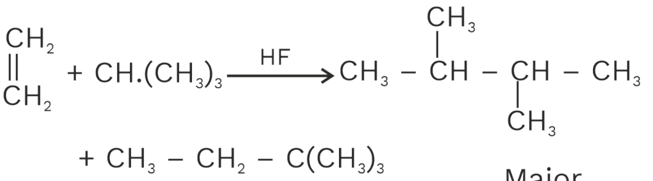
Alkylation of alkenes





$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

Isooctane



$$\underset{CH_2}{\overset{CH_2}{\|}} + CH.(CH_3)_3 \xrightarrow{HF} CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3 + CH_3-CH_2-C(CH_3)_3$$

Minor Major

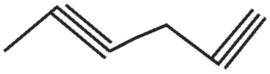
The reactions occur with Carbocation formation and 1,2, shift of H– or $-CH_3$ group.

Alkynes

$$\overset{sp}{-C} \equiv \overset{sp}{C-}$$

- Alkynes have a general formula of (C_nH_{2n-2}). For example,

$CH\equiv CH$	Ethyne
$CH_3-C\equiv CH$	Propyne
$CH_3-C\equiv C-CH_3$	Butyne-2



Hexa 1, 4 di-yne

- Alkynes show chain, positional, functional isomerism (with alkadienes).

 and  (Position Isomers)

Rack your Brain

A single mole of hydroborane can undergo reaction with alkenes in a quantity of how many moles?

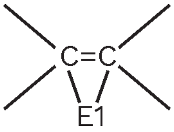
Concept Ladder

With terminal alkenes, one of the products is always formic acid which further decomposes to $CO_2 + H_2O$.

Rack your Brain

What is the role of DMSO?

- All the terminal alkynes have weakly acidic nature and acidic nature decreases in following order:
  $R{-}C{\equiv}H > R{-}CH{=}CH_2 > R{-}CH_3$
- $CH{\equiv}CH > CH_3{-}C{\equiv}CH > CH_3{-}CH_2{-}C{\equiv}CH > \ldots..$
- C_2H_2 is a linear compound, which is poisonous and has garlic like smell due to the presence of impurities of AsH_3, PH_3, H_2S.
- C_2H_2 acts as a dibasic acid with very strong bases like NH_2^-, CH_3^-.
- Alkynes are generally less reactive to electrophilic addition because greater activation energy is needed as formation of a less stable cyclic reaction intermediate species takes place.



Concept Ladder

Alkylation is the addition of alkene to alkane in the presence of H_2SO_4 or HF at 273 K.

Test of Terminal Alkynes

- Terminal alkynes on reaction with with ammonical silver nitrate ($AgNO_3$) give a white precipitate of $R{-}C{\equiv}CAg$.
- Alkynes give a red precipitate of $R{-}C{\equiv}C.Cu$ with ammonical CuCl.

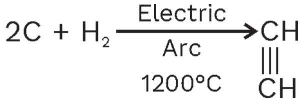
Preparation of Alkynes

Using carbides: Carbides on hydrolysis give alkynes as follows

$$CaO + 3C \xrightarrow[-CO]{1800-2100^\circ C} CaC_2 \xrightarrow{2H_2O} C_2H_2 + Ca(OH)_2$$

$$Mg_2C_3 \xrightarrow{4H_2O} CH_3 - C \equiv CH = 2Mg(OH)_2$$

Berthelot's synthesis



$$2C + H_2 \xrightarrow[\text{Arc} \; 1200^\circ C]{\text{Electric}} \begin{array}{c} CH \\ ||| \\ CH \end{array}$$

From CH_4

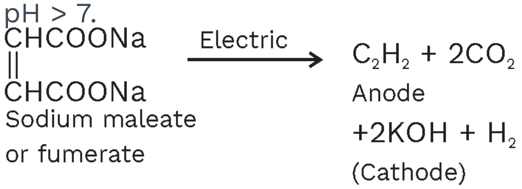
$$2C_2H_4 \xrightarrow[1200^\circ C]{\text{Elecarc}} C_2H_2 + 3H_2$$

$$6CH_4 + O_2 \xrightarrow{1500^\circ C} 2C_2H_2 + 2CO + 10H_2$$

By heating CHX_3 with silver powder

$$CHX_3 + 6Ag + X_3CH \xrightarrow{\Delta} HC \equiv CH + 6AgX$$

Kolbe's method: Sodium or potassium maleate or fumerate on their aqueous salt electrolysis gives acetylene at anode. Here, solution is basic and pH > 7.



$$\begin{matrix} CHCOONa \\ \| \\ CHCOONa \end{matrix} \xrightarrow{\text{Electric}} \underset{\text{Anode}}{C_2H_2 + 2CO_2} \; \underset{\text{(Cathode)}}{+2KOH + H_2}$$

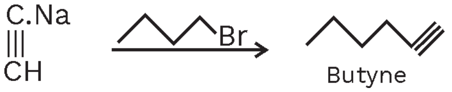
Sodium maleate or fumerate

By alkylation of acetylene or terminal alkynes

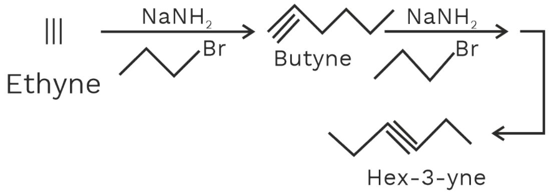
$$R-C\equiv CH \xrightarrow{NaNH_2} R-C\equiv CNa \xrightarrow{R'X} R-C\equiv R' + NaX$$

for example

(1)



(2)

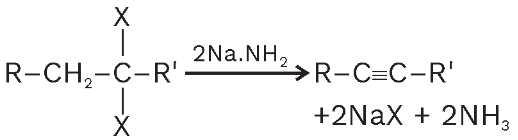


$$CH_3-C\equiv CH \xrightarrow[-NH_3]{NaNH_2} CH_3-C\equiv C^-Na^+ \xrightarrow{CH_3Cl} CH_3-C\equiv C-CH_3$$

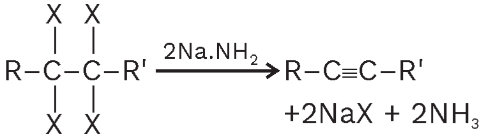
$$\xrightarrow[-NaCl]{C_2H_5Cl} CH_3-C\equiv C-CH_2-CH_3$$

Pent 2-Yne

By elimination reaction: Here, dihalides undergo α, β-elimination reaction with $NaNH_2$ or alc. KOH to give alkynes.



$$R-CH_2-\underset{X}{\overset{X}{C}}-R' \xrightarrow{2Na.NH_2} R-C\equiv C-R' + 2NaX + 2NH_3$$



$$R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-R' \xrightarrow{2Na.NH_2} R-C\equiv C-R' + 2NaX + 2NH_3$$

Concept Ladder

Each carbon atom of alkyne is sp-hybridized. Carbon-carbon triple bond consists of one strong σ-bond and two weak π-bonds

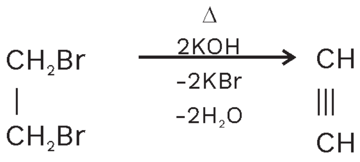
Rack your Brain

Can alkynes show geometrical isomerism?

Concept Ladder

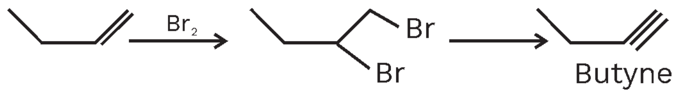
Acetylene reacts explosively with air, therefore it is replaced by oil gas.

For Example :



$$\begin{matrix}CH_2Br \\ | \\ CH_2Br\end{matrix} \xrightarrow[-2KBr,\ -2H_2O]{\Delta,\ 2KOH} \begin{matrix}CH \\ ||| \\ CH\end{matrix}$$

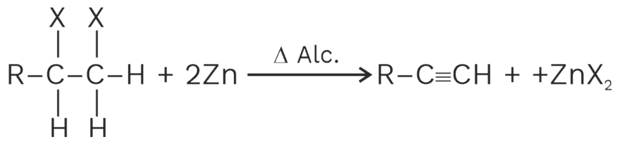
$$CH_3-CH_2-CHCl_2 \xrightarrow[2KOH]{\Delta} CH_3-C\equiv CH + 2KCl + 2H_2O$$



Concept Ladder

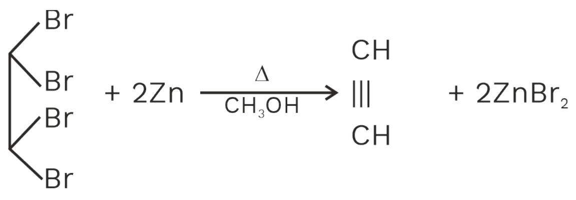
The most frequent application of these procedures are in the preparation of terminal alkynes.

From tetrahalogen compounds



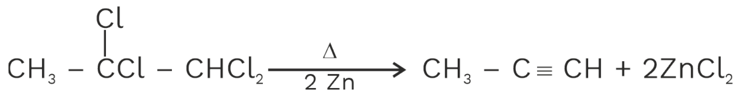
$$R-\underset{H}{\overset{X}{C}}-\underset{H}{\overset{X}{C}}-H + 2Zn \xrightarrow{\Delta\ Alc.} R-C\equiv CH + +ZnX_2$$

For example,



Rack your Brain

Do we get different products for geminal and vicinal dihalides?



$$CH_3-\overset{Cl}{CCl}-CHCl_2 \xrightarrow[2\ Zn]{\Delta} CH_3-C\equiv CH + 2ZnCl_2$$

Physical Properties

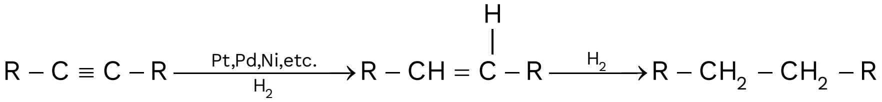
- Acetylene is colourless gas having garlic like smell and boiling point of −84°C. It is poisonous and lighter than air.
- Alkynes having more than 3 carbon atoms are liquid while those with more than 14 carbon atoms are solids.
- They are lighter than water.
- Alkynes have higher B.P., M.P. than corresponding alkanes, alkenes because of more close packed arrangement (Linear Structure) and stronger interaction.

Concept Ladder

Decreasing solubility in H_2O:
Alkynes > Alkenes > Alkanes
Alkynes are slightly more soluble in H_2O because they are somewhat more polar.

Chemical Properties

Hydrogenation

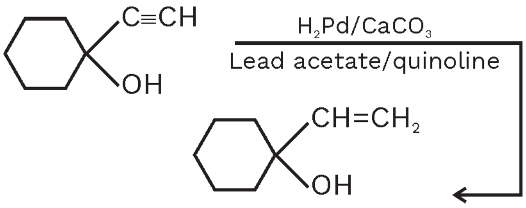


$$R-C\equiv C-R \xrightarrow[H_2]{Pt,Pd,Ni,etc.} R-CH=\overset{H}{\overset{|}{C}}-R \xrightarrow{H_2} R-CH_2-CH_2-R$$

$$CH\equiv CH \xrightarrow[Ni]{H_2} CH_2=CH_2 \xrightarrow[Ni]{H_2} CH_3-CH_3$$

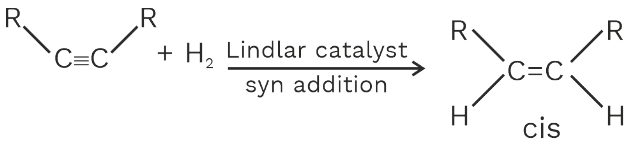
$$CH_3-C\equiv CH \xrightarrow[Ni]{H_2} CH_3-CH=CH_2 \xrightarrow[Ni]{H_2} CH_3-CH_2-CH_3$$

- Lindlar's catalyst ($PdCO_3/BaCO_3$) poisoned with quinoline or lead acetate is generally used for selective hydrogenation in preparation of alkene only.



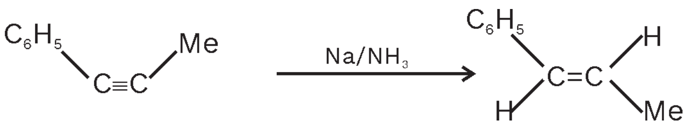
1-vinyl cyclo hexanol

Stereochemistry of the reaction



- Nickel boride (P-2) gives syn-addition.
- When Na/NH_3 is used, hydrogenation is anti-addition.

For example,



Rack your Brain

Why alkynes are less stable than her isomeric diene?

Concept Ladder

The reaction takes place on the surface of Pt or Pd. Since the addition is twice, it is hard to see the syn addition.

Previous Year's Question

In the following reaction

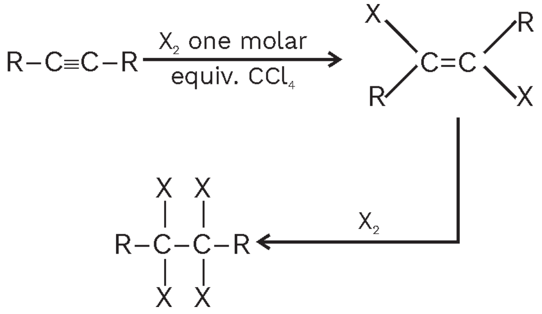
$$H_3C-C\equiv CH \xrightarrow[893\ K]{\text{red hot iron tube}} A$$

The number of sigma (σ) bonds present in the product A, is

[NEET]

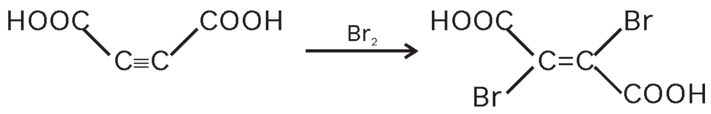
(1) 21 (2) 18 (3) 9 (4) 24

Reaction with Halogen



In this, addition is anti and reactivity order for Halogens is $Cl_2 > Br_2 > I_2$

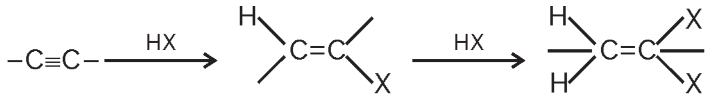
For example,



$$CH \equiv CH \xrightarrow{Cl_2} CHCl = CHCl \xrightarrow{Cl_2} \underset{\text{Westrone}}{CHCl_2 - CHCl_2} \xrightarrow{BaCl_2} \underset{\text{Westrosol}}{CCl_2 = CHCl}$$

Westrone and westrosol both are good industrial solvents for oils, fat and waxes.

Addition of HX to alkynes: Addition takes place according to Markonikov's rule and anti-Markovnikov's rule.

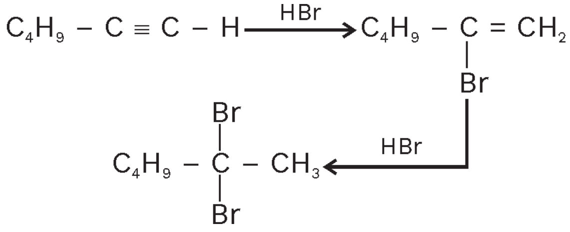


Gemdi halide

Reactivity order is HI > HBr > HCl

For example,

$$CH_3 - C \equiv CH \xrightarrow{HCl} CH_3 - CCl_2 - CH_3$$



$$C_4H_9 - C \equiv C - H \xrightarrow{HBr} C_4H_9 - \underset{Br}{\underset{|}{C}} = CH_2 \xrightarrow{HBr} C_4H_9 - \overset{Br}{\overset{|}{\underset{Br}{\underset{|}{C}}}} - CH_3$$

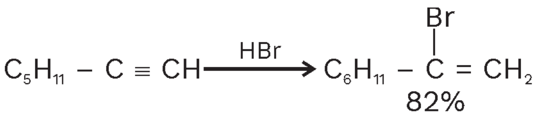
If we use CH_3COBr/alumina, the rate of reaction increases.

Rack your Brain

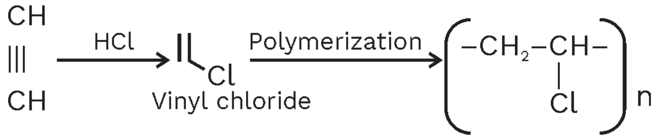
What is the mechanism followed by addition of HX to alkyne?

Concept Ladder

Addition of HX to alkyne yields vinyl halides and alkylidene dihalides.

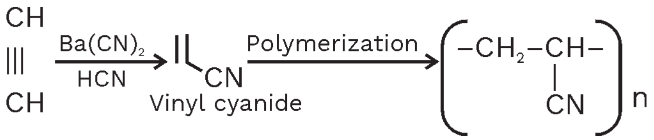


$$C_5H_{11}-C\equiv CH\xrightarrow{HBr}C_6H_{11}-\underset{82\%}{\overset{\overset{Br}{|}}{C}}=CH_2$$



Poly vinyl chloride (PVC)

Reaction with HCN

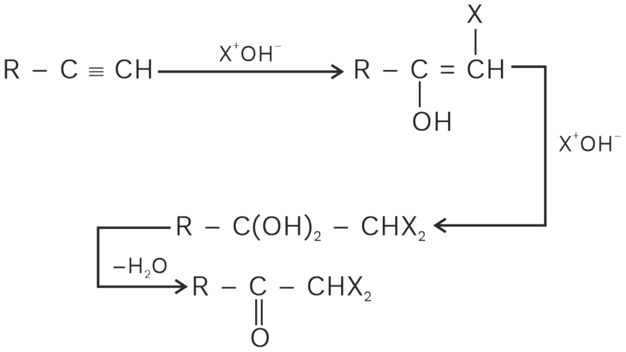


Orlon or acrylonitrile (synthetic fber) or poly vinyl cyanide

Concept Ladder

Unsymmeterical non-terminal alkynes give mixture of two isomeric ketones.

Reaction with HOX:
Addition occurs according to Markonikov's rule and here X^+ is attacking reagent.



$$R-C\equiv CH\xrightarrow{X^+OH^-}R-\underset{\underset{OH}{|}}{C}=\overset{\overset{X}{|}}{CH}\xrightarrow{X^+OH^-}R-C(OH)_2-CHX_2\xrightarrow{-H_2O}R-\underset{\underset{O}{\|}}{C}-CHX_2$$

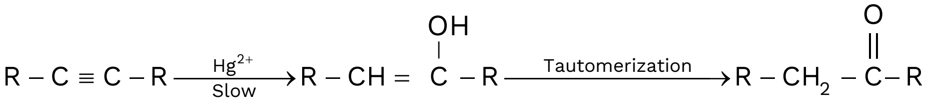
Rack your Brain

What is the role of $HgSO_4$ in the hydration of alkynes?

For example,

$$CH\equiv CH\xrightarrow{HOCl}CHOH=CHCl\xrightarrow{HOCl}CH(OH)_2-CHCl_2\xrightarrow{-H_2O}\underset{\text{Dichloroacetaldehyde}}{CHO-CHCl_2}$$

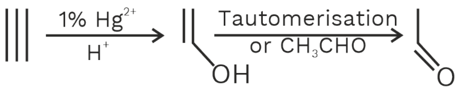
Hydration of alkynes : Alkynes give Carbonyl Compounds on hydration by 1% $HgSO_4$ and di/ H_2SO_4 as follows.



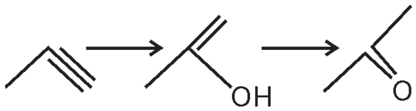
$$R-C\equiv C-R\xrightarrow[\text{Slow}]{Hg^{2+}}R-CH=\overset{\overset{OH}{|}}{C}-R\xrightarrow{\text{Tautomerization}}R-CH_2-\overset{\overset{O}{\|}}{C}-R$$

It is called kucherov reaction.
This is shown in following examples:

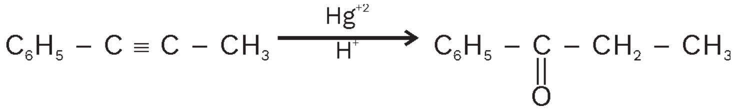
(1)



(2)

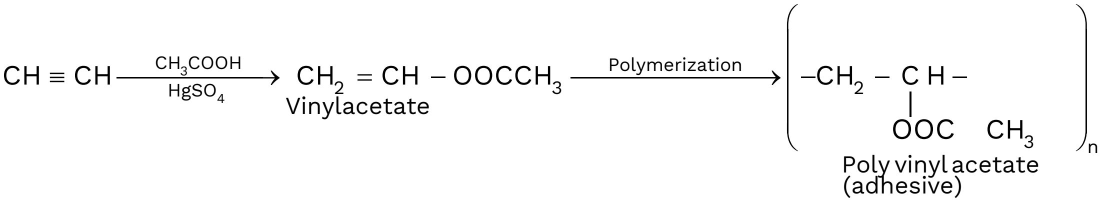


(3)



$$C_6H_5 - C \equiv C - CH_3 \xrightarrow[H^+]{Hg^{+2}} C_6H_5 - \underset{\underset{O}{\|}}{C} - CH_2 - CH_3$$

Reaction with Alcohol



$$CH \equiv CH \xrightarrow[HgSO_4]{CH_3COOH} \underset{\text{Vinylacetate}}{CH_2 = CH - OOCCH_3} \xrightarrow{\text{Polymerization}} \left(-CH_2 - \underset{\underset{OOC\quad CH_3}{|}}{CH} - \right)_n$$

Poly vinyl acetate
(adhesive)

Reaction with AsCl$_3$

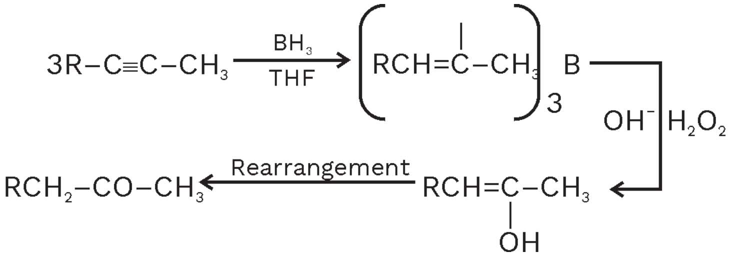
$$CH \equiv CH \xrightarrow{AsCl_3} CHCl = CHAsCl_2$$

Lewis site or Lewis gas
(War gas)
(β–chlorovinyl dichloroarsine)

Lewisite (β-chloro vinyl dichloro arsine) is a poisonous gas which on inhalation causes sudden death. The antidote for it is British anti-Lewisite (BAL).

CH_2-SH
|
$CH-SH$ 3-Hydroxy propan 1, 2di-thiol
|
CH_2-OH

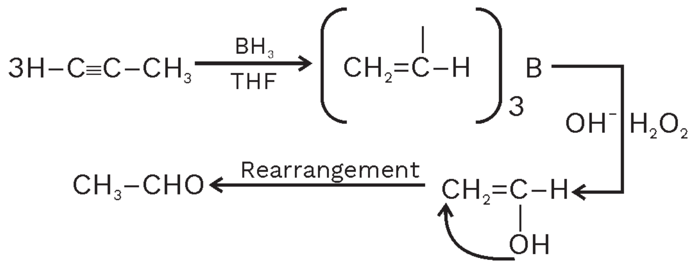
Hydroboration: Used for preparation of ketones from alkynes except from ethyne which gives acetaldehyde.



$$3R-C\equiv C-CH_3 \xrightarrow[THF]{BH_3} \left(RCH=\overset{|}{C}-CH_3 \right)_3 B \xrightarrow{OH^- \; H_2O_2} RCH=\underset{\underset{OH}{|}}{C}-CH_3 \xrightarrow{\text{Rearrangement}} RCH_2-CO-CH_3$$

Concept Ladder

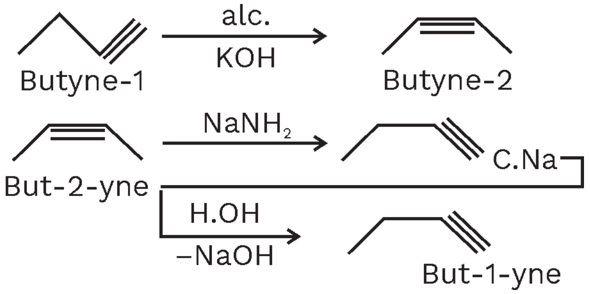
The terminal alkynes can also undergo hydroboration. This proceeds in an anti-Markovnikov way as well.



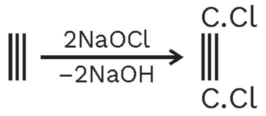
Rack your Brain

Why alkenes are converted into neutral alcohols and alkynes are converted into aldehydes using the hydroboration method?

Isomerization



Substituion



$$R - C \equiv CH \xrightarrow[2NaOH]{NaOCl} R - C \equiv C - Cl$$

Concept Ladder

Alkynes are oxidatively cleaved in alkaline or acidic conditions at higher temperature.

Combustion

$$C_nH_{(2n-2)} + \frac{3(n-1)}{2}O_2 \xrightarrow{\Delta} nCO_2 + (n-1)H_2O$$

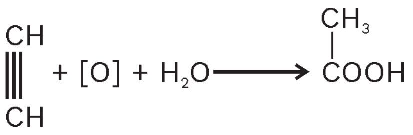
for Example

$$C_2H_2 + \frac{5}{2}O_2 \xrightarrow{\Delta} 2CO_2 + H_2O$$

$$C_3H_4 + 4O_2 \xrightarrow{\Delta} 3CO_2 + 2H_2O$$

Oxidation

(a) By $K_2Cr_7O_7/H_2SO_4$

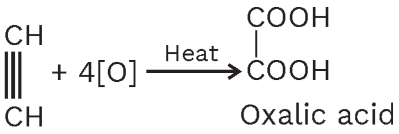


$$\begin{array}{c}CH\\ \|\|\\ CH\end{array} + [O] + H_2O \longrightarrow \begin{array}{c}CH_3\\ |\\ COOH\end{array}$$

Rack your Brain

Name a reagent which can oxidise alkenes but not alkynes.

(b) By alkaline $KMnO_4$

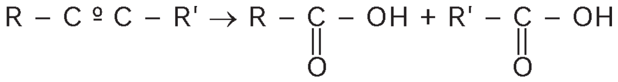


$$\begin{matrix} CH \\ ||| \\ CH \end{matrix} + 4[O] \xrightarrow{Heat} \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

Oxalic acid

(c) With hot alkaline or acidic $KMnO_4$

In this, oxidative cleavage occurs to give acids.



$$R - C \text{ º } C - R' \rightarrow R - \underset{\underset{O}{||}}{C} - OH + R' - \underset{\underset{O}{||}}{C} - OH$$

- If triple bond is at corner, formic acid is formed, which oxidizes into CO_2 and water.

For example,

$$CH_3 - C \equiv CH \xrightarrow{\text{Hot alk.}KMnO_4} CH_3COOH + HCOOH \xrightarrow{(O)} H_2O + CO_2$$

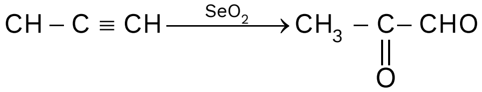
$$CH_3 - C \equiv C - CH_3 \xrightarrow{\text{Hot alk.}KMnO_4} 2CH_3COOH$$

(d) With selenium dioxide

$$R - C \equiv CH + 2[O] \xrightarrow{SeO_2} R - CO - CHO$$

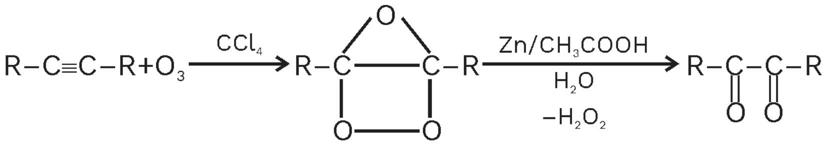
For example,

$$CH \equiv CH \xrightarrow{SeO_2} \underset{\text{Glyoxal}}{CHO - CHO}$$



$$CH - C \equiv CH \xrightarrow{SeO_2} CH_3 - \underset{\underset{O}{||}}{C} - CHO$$

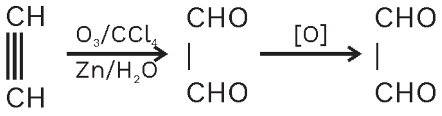
Ozonolysis



Ozonide

- If decomposition is carried out by H_2O_2 and Zn/CH_3COOH is not used then dicarbonyl compounds formed undergo further oxidation to give acids.

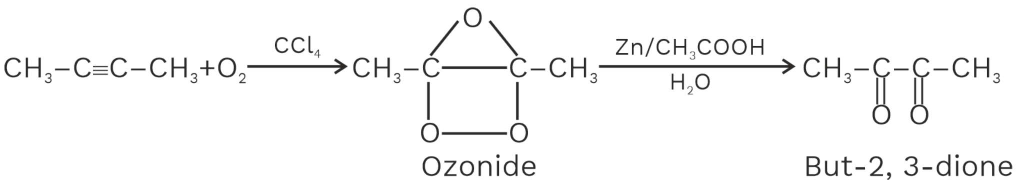
  For example,



$$\begin{matrix} CH \\ ||| \\ CH \end{matrix} \xrightarrow[Zn/H_2O]{O_3/CCl_4} \begin{matrix} CHO \\ | \\ CHO \end{matrix} \xrightarrow{[O]} \begin{matrix} CHO \\ | \\ CHO \end{matrix}$$

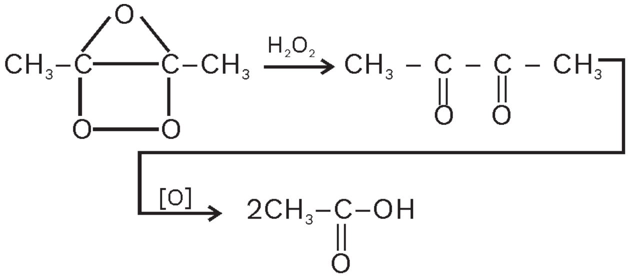
Concept Ladder

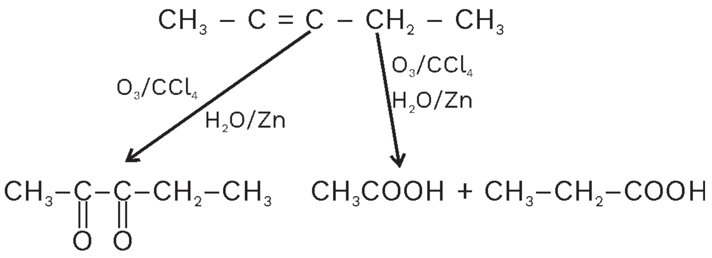
Terminal alkynes give HCOOH as one of the products which is further oxidized to CO_2.



Ozonide

But-2, 3-dione

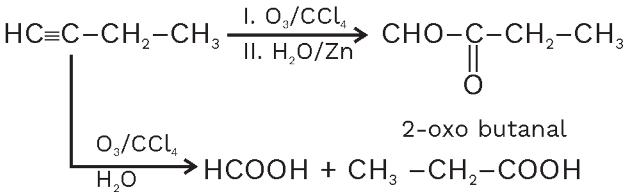




$$CH_3-C=C-CH_2-CH_3 \xrightarrow[H_2O/Zn]{O_3/CCl_4} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$$

$$CH_3-C=C-CH_2-CH_3 \xrightarrow[H_2O/Zn]{O_3/CCl_4} CH_3COOH + CH_3-CH_2-COOH$$

Pentan 2, 3 di-one



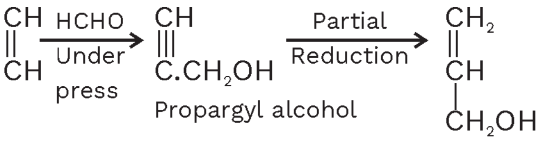
$$HC\equiv C-CH_2-CH_3 \xrightarrow[II.\ H_2O/Zn]{I.\ O_3/CCl_4} CHO-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$$

2-oxo butanal

- $$HC\equiv C-CH_2-CH_3 \xrightarrow[H_2O]{O_3/CCl_4} HCOOH + CH_3-CH_2-COOH$$

In this, formic acid does not further oxidise into CO_2 and H_2O as in case of oxidative cleavage by hot. $KMnO_4$.

Reaction with HCHO

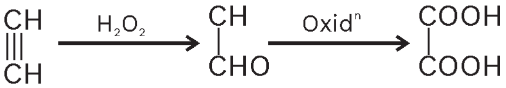


$$CH\equiv CH \xrightarrow[\text{Under press}]{HCHO} CH\equiv C.CH_2OH \xrightarrow[\text{Reduction}]{\text{Partial}} CH_2=CH-CH_2OH$$

Propargyl alcohol

Alkyl alcohol (prop 2-en-ol)

With H_2O_2

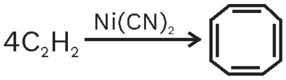


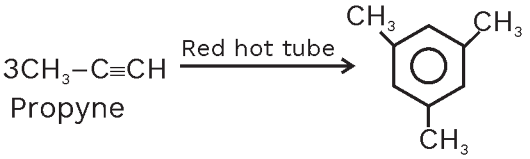
Glyoxal

Polymerization

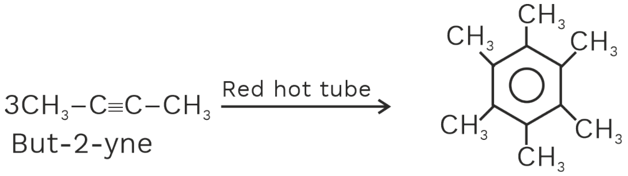
Cyclic polymerization: In this, alkynes polymerize to produce aromatic compounds as follows:

$$\underset{\text{Ethyne}}{3C_2H_2} \xrightarrow{\text{Redhot tube}} \underset{\text{Benzene}}{C_6H_6}$$

- 

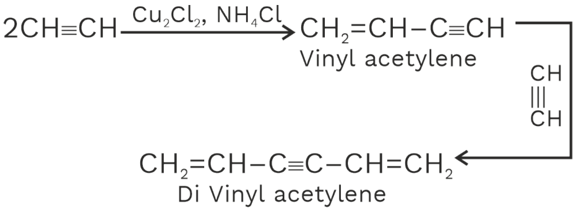
- 

Propyne
Mesitylene

- 

But-2-yne
hexamethyl benzene

Linear polymerization



$$CH_2 = CH - C \equiv CH \xrightarrow{HCl} CH_2 = CH - CHCl = CH_2$$

Chloroprene
or
2–chloro–buta–1,3–diene

- Addition of HCl takes place at triple bonded carbon atom instead of double bonded carbon atom, because of formation of a more stable conjugated diene product which is resonance stabilised.

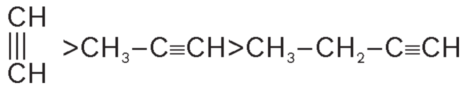
Previous Year's Question

The pair of electrons in the given carbanion, , is present in which of the following orbitals?

[NEET]

(1) sp^2 (2) sp (3) 2p (4) sp^3

Acidic Nature of terminal alkynes: They are very less acidic in nature and it decreases in them with increase of no. of C–atoms. It is confirmed by following reactions:



$$\begin{matrix}CH\\ |||\\ CH\end{matrix} > CH_3-C\equiv CH > CH_3-CH_2-C\equiv CH$$

With ammonical silver nitrate: Here, terminal alkynes react with it as follows:

Concept Ladder

Metal acetylides can be used to distinguish terminal alkynes from non-terminal alkynes or alkenes.

$$R-C\equiv CH+\underset{\text{Solution in nitric acid}}{Ag(NH_3)_2^+}+OH^- \longrightarrow \underset{\text{White PPT}}{R-C\equiv C.Ag}+H_2O+2NH_3$$

For example,

$$CH\equiv CH+2AgNO_3+2NH_4OH \longrightarrow \underset{\text{Whiteppt. of silver Acetilide}}{AgC\equiv CAg}+2NH_4NO_3+2H_2O$$

With ammonical cuprous chloride

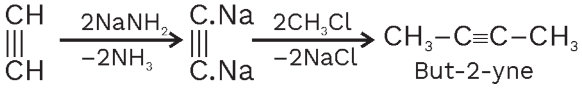
$$R-C\equiv CH+Cu(NH_3)_2^+ + OH^- \longrightarrow \underset{\text{Red PPT}}{R-C\equiv C.Cu}\downarrow +H_2O+2NH_3$$

for example,

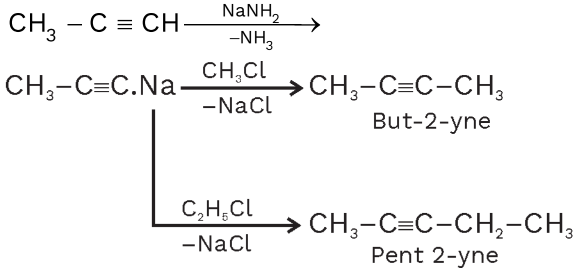
$$CH\equiv CH+Cu_2Cl_2+2NH_4OH \longrightarrow \underset{\substack{\text{Cuprous Acetilide}\\ \text{Red PPT}}}{Cu.C\equiv C.Cu}+2NH_4Cl+2H_2O$$

Replacement of terminal H-atom from terminal alkynes

$$R-C\equiv CH \xrightarrow[\text{Liq.}NH_3]{NaNH_2} R-C\equiv C.Na \xrightarrow{R'-CH_2X} R-C\equiv C-CH_2R'$$



$$\begin{matrix}CH\\ |||\\ CH\end{matrix} \xrightarrow[-2NH_3]{2NaNH_2} \begin{matrix}C.Na\\ |||\\ C.Na\end{matrix} \xrightarrow[-2NaCl]{2CH_3Cl} \underset{\text{But-2-yne}}{CH_3-C\equiv C-CH_3}$$



$$CH_3-C\equiv CH \xrightarrow[-NH_3]{NaNH_2}$$

$$CH_3-C\equiv C.Na \xrightarrow[-NaCl]{CH_3Cl} \underset{\text{But-2-yne}}{CH_3-C\equiv C-CH_3}$$

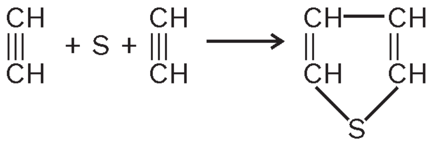
$$CH_3-C\equiv C.Na \xrightarrow[-NaCl]{C_2H_5Cl} \underset{\text{Pent 2-yne}}{CH_3-C\equiv C-CH_2-CH_3}$$

Rack your Brain

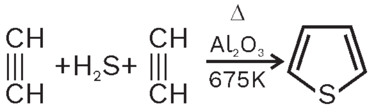
What are Alkynyl Grignard reagents?

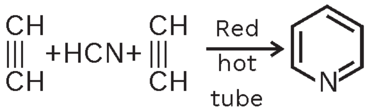
Formation of heterocyclic compounds

- When C_2H_2 is passed over iron pyrite at 300°C, it reacts with sulphur atom of iron pyrite to give thiophene.



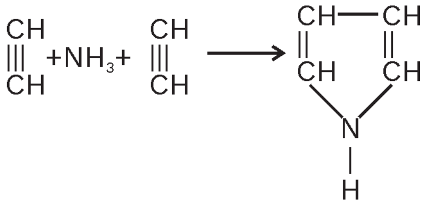
Thio phene





Pyridine

- Ethyne on reaction with ammonia gives pyrrole.

- 

Pyrole

Reaction with Nitrogen

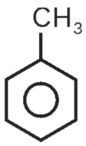
$$CH \equiv CH + N_2 \xrightarrow{\text{electric arc}} 2HCN$$

Aromatic Hydrocarbons

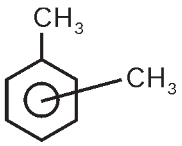
Aromatic word has been derived from Greek word Aroma which generally means pleasant smell. Benzene and compounds which resemble benzene in chemical properties are known as Benzenoid compounds or Aromatic compounds.

Aromatic hydrocarbons or Arenes have a general formula C_nH_{2n6y} (By represents No. of benzene Rings). and n > 6. main sources are coaltar coal, Petroleum etc.

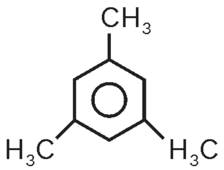
Benzene



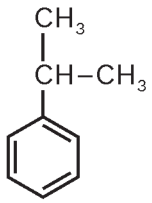
Toluenes



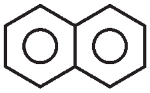
Xylene



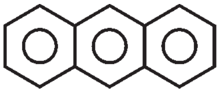
Mesitylene



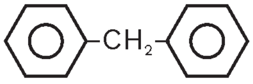
Cumene
(Isopropyl benzene)



Napthalene



Anthracene



Diphenyl Methane

Aromaticity and Hunckel (4n + 2)Rule

Aromaticity is defned as "An aromatic compound having a reasonably planar cyclic structure, with $(4n + 2)\pi$ electron clouds and having unusual stablity because of delocalisation of π electron.

According to Huckels Rule,

Any compound can be aromatic when:

(1) It has a cyclic planar structure (Necessary for complete delocalisation of πe^-)

e.g.,

(2) It has a conjugate system.

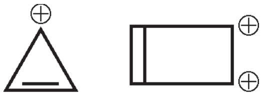
(3) It has high value of resonance energy.

(4) It has number of π electrons according to (4n + 2) rule that is, 2, 6, 10, 14, etc. (where n = Number of cyclic planar ring).

In case any compound has πe^- according to 4n rule it is Anti aromatic.

e.g., (1) When n = 0, No. of πe^- = 2

e.g.,



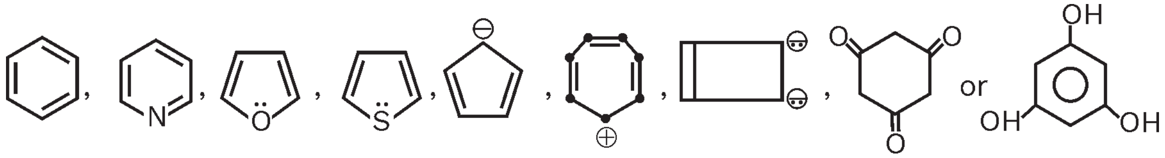
e.g., (2) When n = 1, No. of πe^- = 6

Concept Ladder

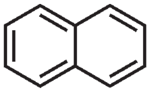
Aromatic Compounds which don't contain benzene ring are called non-benezeniods.

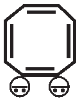
Rack your Brain

Which acts as a moth repellant?



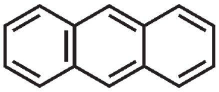
e.g., When n = 2, No. of πe^- = 10



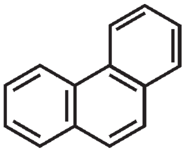


Napthalene

It has $10\pi e^-$ so it is also aromatic.
When n = 3, No. of πe^- = 14

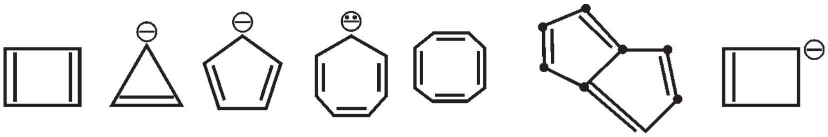


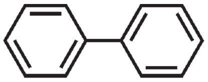
Anthracene



Phenanthrene

Anti Aromatic compounds having 4, 8 πe^-.





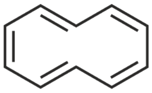
and

are also

$12\pi e^-$ $18\pi e^-$

Aromatic in nature because each benzene ring has $6\pi e^-$ which are involved in making resonance. Few non-planar molecules which are non aromatic are given below.

Cyclooctatetraene



Cyclodecapentane
(10) Annulene

Benzene

- Benzene is structurally depicted as shown below:

- Benzene was discovered by Faraday in 1825.
- The structure of benzene was given by Kekule in 1865

Rack your Brain

What are annulenes? Are they aromatic Nature?

Methods of Preparation of Benzene

From light oil fraction : Light oil fraction of coal-tar consists benzene, xylene, toluene. This mixture on fractional distillation produces benzene as one of the product.

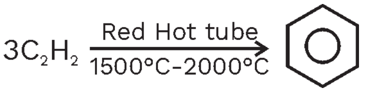
From petroleum :

$$h-\text{Hexane}\xrightarrow[\text{HighPressure},\,-4H_2]{CrO_3,Al_2O_3,600°C}\text{Benzene}$$

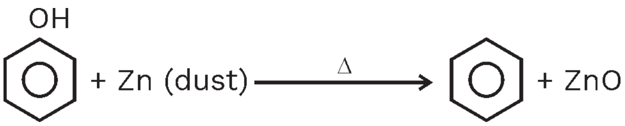
Concept Ladder

Preparation of benzene on large is done using light oil fraction and by petroleum.

Using acetylene : On passing acetylene through red hot tube polymerizes into benzene.



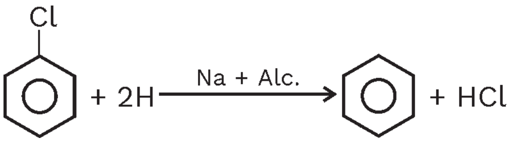
Using phenol : Phenol on distillation with Zn dust gives benzene.



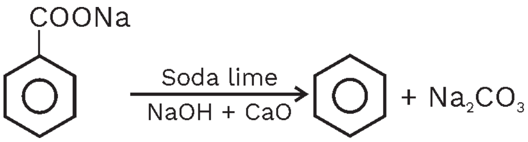
Rack your Brain

Who first isolated benzene?

Using chlorobenzene : Chlorobenzene or halobenzene on reduction with alcoholic Na or Ni–Al alloy gives benzene.



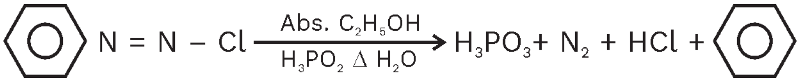
Using benzoic acid : Chlorobenzene or halobenzene on reduction with alcoholic Na or Ni– Al alloy gives benzene.



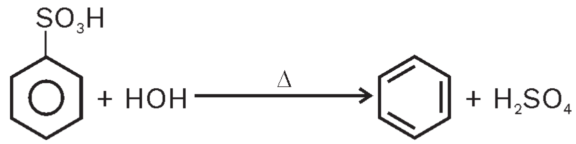
Concept Ladder

The different methods are of small scale production of benzene.

Using benzene diazonium chloride : Benzene diazonium chloride on reaction with hypo phophorus acid produces benzene.



Using benzene sulphonic acid : Benzene sulphonic acid on treatment with steam produces benzene.



Physical Properties

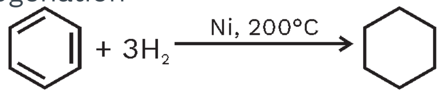
- It is highly inflammable.
- Freezing point of benzene is 5.5°C.
- Its boiling point is 80°C.
- It is immiscible in water.
- A good solvent for resin, rubber and fat.
- Benzene is lighter than water.
- It is colourless volatile, liquid.

Chemical Properties

Benzene has three alternative double bonds, still, it doesn't show usual addition reactions or test of unsaturation with bromine water or Baeyer's reagent. It gives electrophilic substitution reaction due to phenomenon of resonance or complete delocalization of six π electrons.

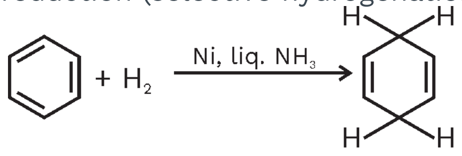
Addition reaction

Hydrogenation



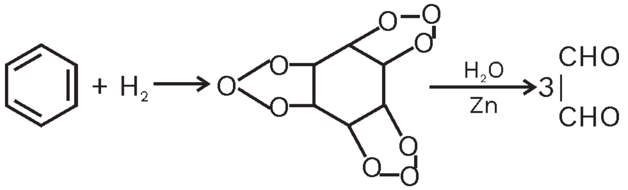
Cyclohexane

Birch reduction (selective hydrogenation)



1, 4-dihydrobenzene

Ozonolysis: Benzene on ozonolysis produces glyoxal as shown:



Benzene triozonide

Concept Ladder

All aromatic compounds are non-polar in nature.

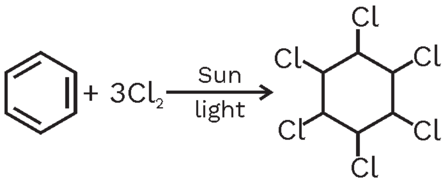
Rack your Brain

Which isomer -o, -m or -p; will have maximum melting point?

Concept Ladder

Aromatic compounds are less reactive than alkenes and alkynes due to the delocalisation of electrons.

With chlorine: C_6H_6 on chlorination in presence of sunlight produces gammexane or 666 or γ-Lindane, which is a famous insecticide.

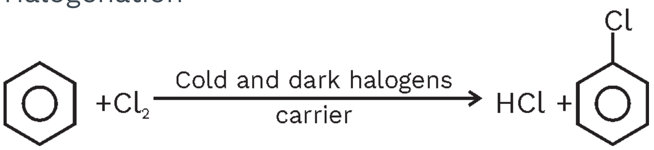


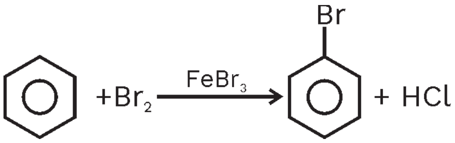
$C_6H_6Cl_6$

Benzene hexa chloride (BHC) or Gammexene

Electrophilic substitution reaction

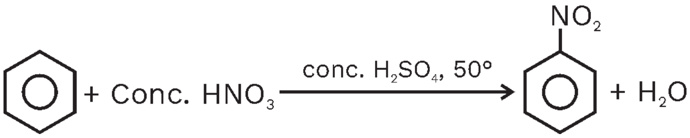
Halogenation

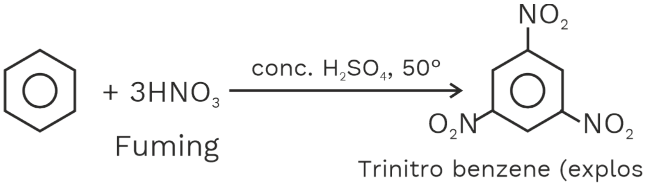




- Iodination of benzene is a very slow reversible process, Hence, it is carried out in presence of oxidants like HIO_3 or HgO to keep a check HI formation.

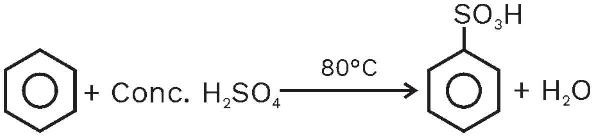
Nitration





Trinitro benzene (explosive)

Sulphonation



Rack your Brain

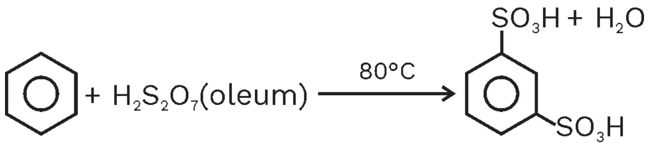
Anisole has higher b.p. than benzne. Why?

Concept Ladder

In the presence of sunlight and and absence of halogen carriers, benzene show addition reactions.

Rack your Brain

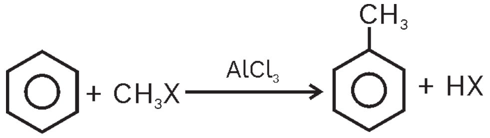
Why benzene doesn't undergo addition reactions readily?

- 

m-benzene disulphonic acid

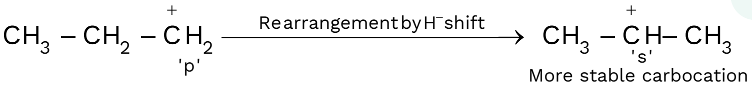
Friedel–Crafts reaction: In this,alkylation or acylation reaction takes place in presence of catalysts like BF_3, $ZnCl_2$, anhyd. $AlCl_3$, $FeCl_3$, or $SnCl_4$.

- Alkylation: alkyl halide in presence of anhyd. $AlCl_3$; alcohol alkene in presence of conc. H_2SO_4 can be used.



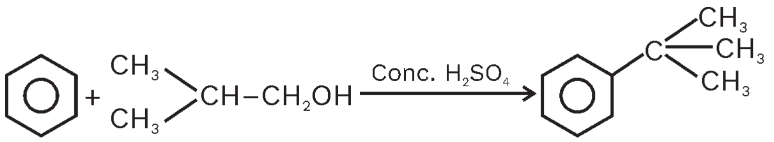
Toluene

- In this, one time rearrangement of carbocation is possible as shown in the reaction below:

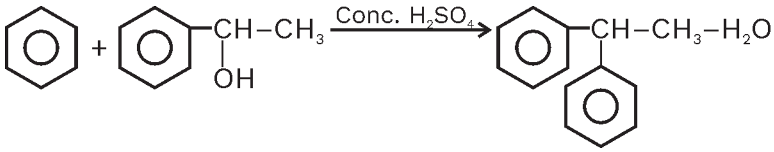


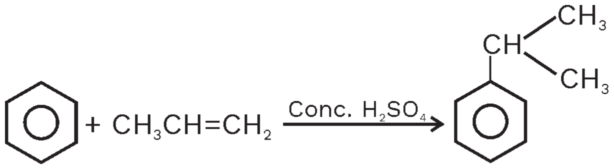
$$CH_3-CH_2-\underset{'p'}{\overset{+}{C}}H_2 \xrightarrow{\text{Rearrangement by } H^- \text{shift}} CH_3-\underset{'s'}{\overset{+}{C}}H-CH_3$$

More stable carbocation

- 

Tertiary butyl benzene

- 

- 

Acylation:

Acid anhydrides or acid halides can be used with anhyd. $AlCl_3$.

Concept Ladder

Halogenation occurs in the presence of lewis acids but in the absence of sunlight to from aryl halides.

Previous Year's Question

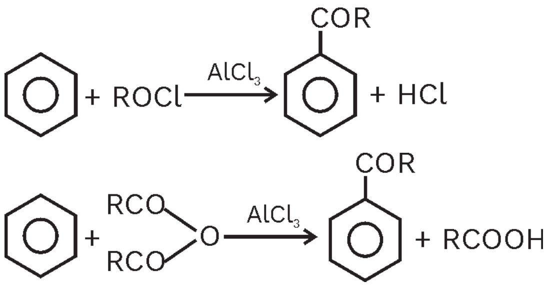
Which of the following compounds will not undergo Friedel-Crafts reaction easily?

[NEET]

(1) Nitrobenzene
(2) Toluene
(3) Cumene
(4) Xylene

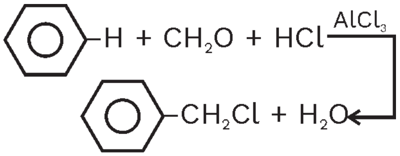
Rack your Brain

What are Halogen Carriers?

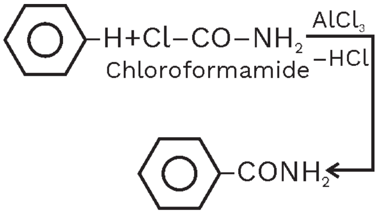


Where, R may be CH_3COCl, C_6H_5COCl.

Chloromethylation

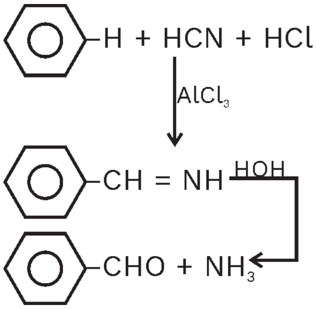


Chloromethyl benzene

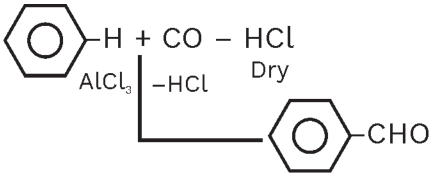


Benzamide

Gatterman aldehyde reaction



Gattermann Koch or formylation



Benzaldehyde

- In Friedel–Crafts reaction, electrophiles are R^+, RC^+O, $C^+H{=}NH$, C^+OCl, C^+ONH_2, C^+O.

Previous Year's Question

Which of the following can be used as the halide component for Friedel-Crafts reaction?

[NEET]

(1) Chlorobenzene
(2) Bromobenzene
(3) Chloroethene
(4) Isopropyl chloride

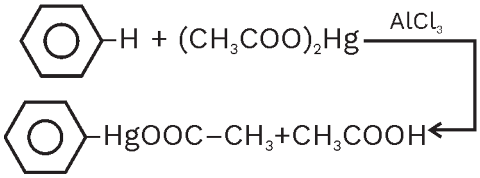
Concept Ladder

Nitration and sulphonation both occur by the formation of the α-complex.

Rack your Brain

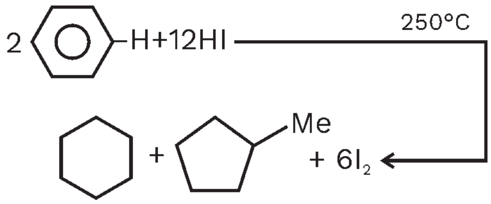
What are the attacking electrophiles in nitration and sulphonation of benzene?

Mercuration



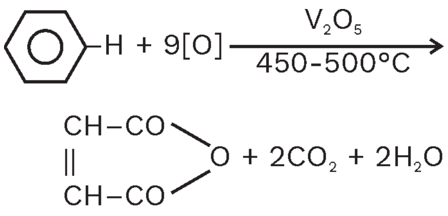
Phyenyl mercuric acetate

Reduction



Cyclohexane Methyl cyclopentane

Oxidation



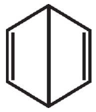
Maleic anhydride

Combustion

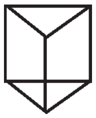
$$2C_6H_6 + 15O_2 \xrightarrow{\Delta} 12CO_2 + 6H_2O$$

Various Structural Formulae of Benzene

Dewars parallel’s formula



Landenberg prism formula



Clausing diagonal formula

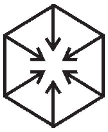
Concept Ladder

In benzene, all of the carbon-carbon bond lengths are equal. Therefore, the Kekule structure is an incorrect representation of benzene.

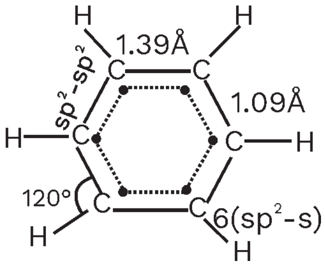
Rack your Brain

Which structure of benzene gave the first insight about it?

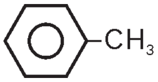
Baeyer and Armstrong centric formula



Resonance Hybrid (Kekule's structure of Benzene)



Toluene or methyl benzene

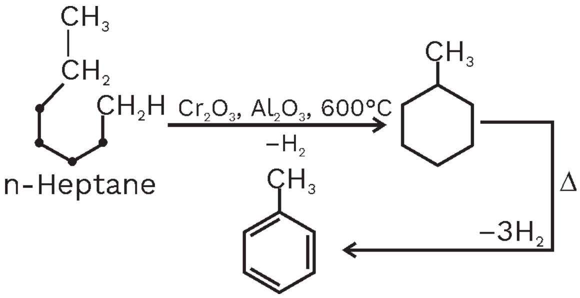


- Toluene was first profuced by tolu balsam. It is known as Toluol.

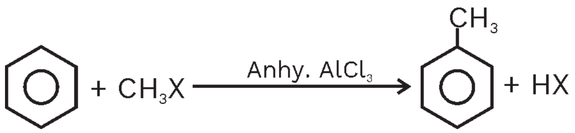
Methods of Preparation of Toluene

From light oil fraction of coal tar light fraction contains mainly C6H6, xylene and toluene. All three can be separated by fractional distillation in which toluene is collected at 110°C.

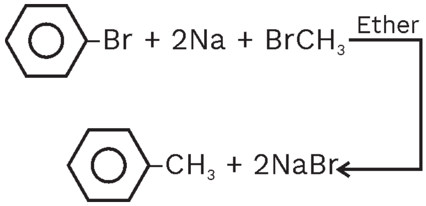
From petroleum



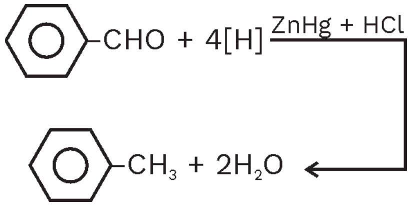
Friedel–Crafts reaction



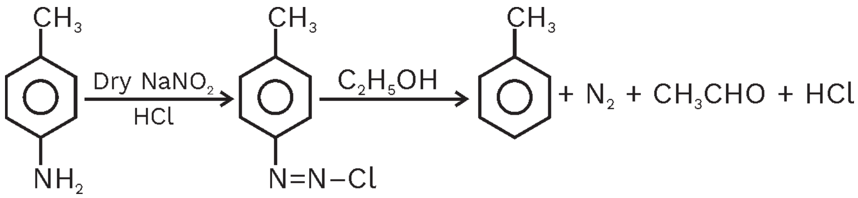
By Wurtz –Fittig reaction



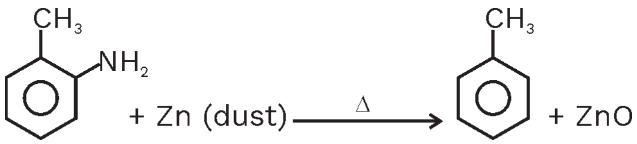
By the reduction of benzaldehyde



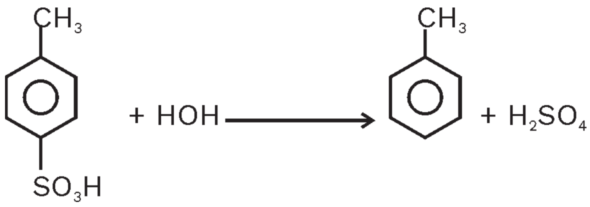
From toluidine



From cresol



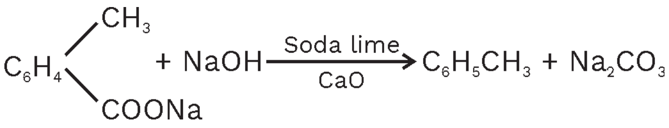
From toluene sulphonic acid



From Grignard reagent

$$C_6H_5MgX + CH_3X \longrightarrow C_6H_5CH_3 + MgX_2$$

From decarboxylation of sodium toluate



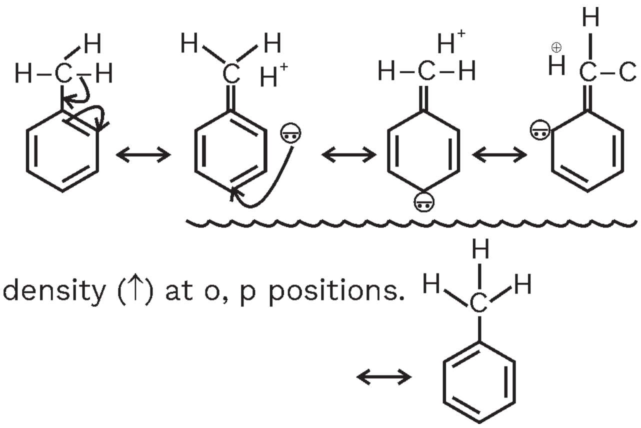
$$C_6H_4\begin{matrix}CH_3\\COONa\end{matrix} + NaOH \xrightarrow[CaO]{\text{Soda lime}} C_6H_5CH_3 + Na_2CO_3$$

Physical Properties

- Toluene is a colourless liquid.
- It is used as a solvent and in synthesis of other compounds.
- Its boiling point is 111°C.
- It is not miscible in water.

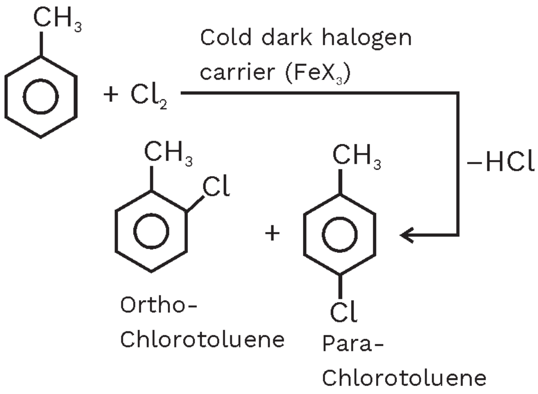
Chemical Properties

Reactions due to benzene ring: In this, methyl group activates benzene ring, Further substitution reaction takes place at ortho and para positions and rate of substitution reaction is more fast than in benzene.

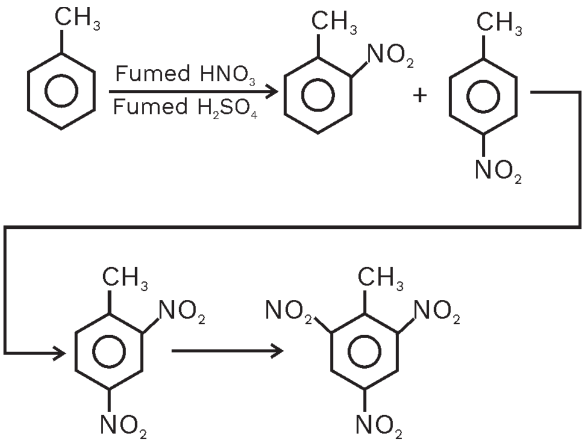


e- density (↑) at o, p positions.

Halogenation



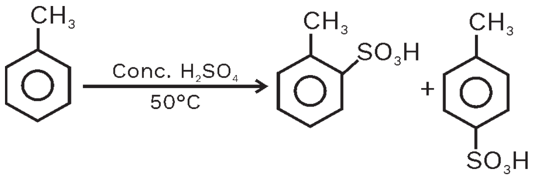
Nitration



2, 4, 6-Trinitrotoluene
(T.N.T.)

NOTE : Amatol is an explosive. It is basically a mixture of TNT and ammonium nitrate.

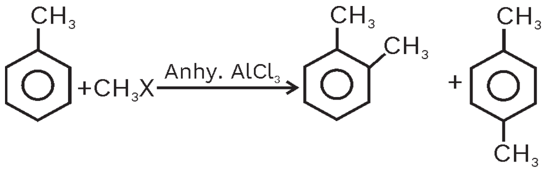
Sulphonation



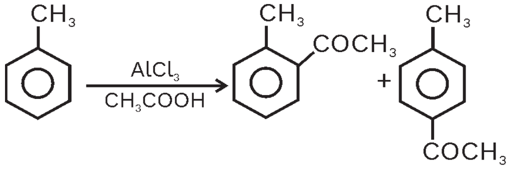
Ortho-toluene Sulphonic acid

Para-toluene Sulphonic acid

Friedel–Crafts reaction



'o' and 'p' xylene

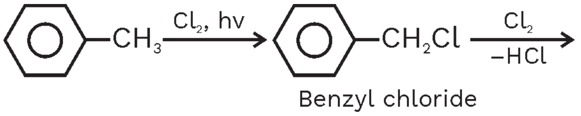


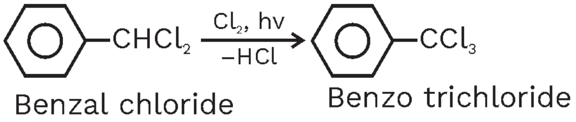
Ortho-
methyl
acetophenone

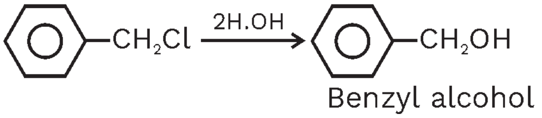
Para-
methyl
acetophenone

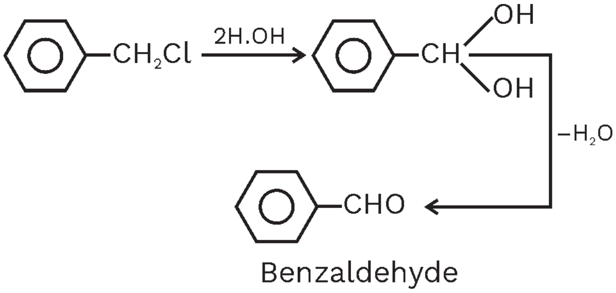
Reactions due to methyl group or side chainreactions

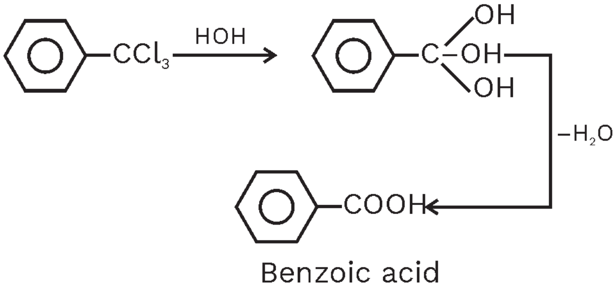
Halogenation



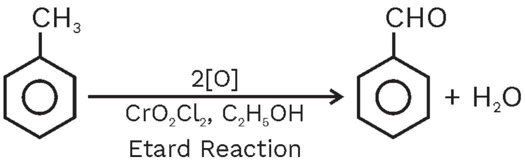




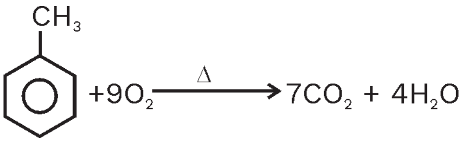




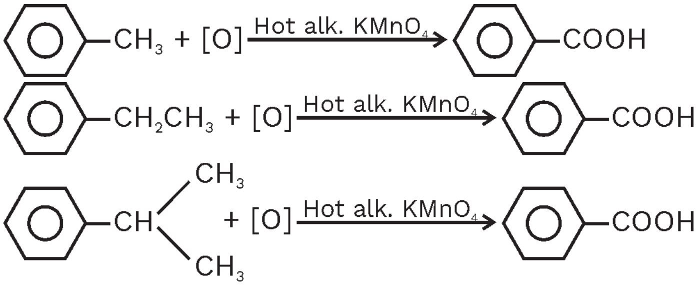
Oxidation



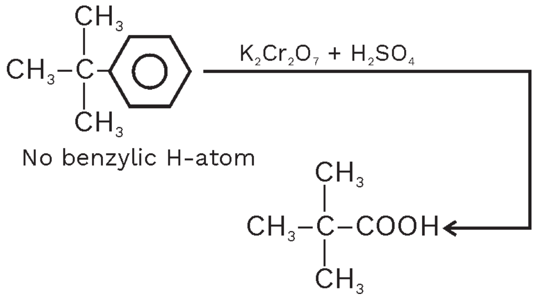
Combustion

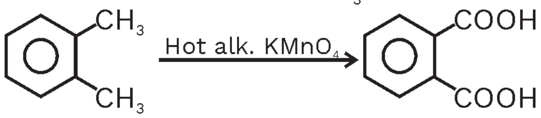


Reaction with hot alkaline $KMnO_4$ or $Na_2Cr_2O_7$. In this, alkyl group having α-hydrogen atom is oxidized into COOH group.



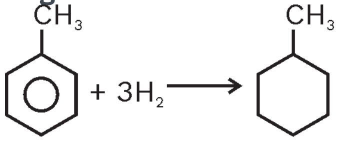
If alkyl group has no α-H atom or benzylic H- atom benzene ring gets oxidized into –COOH group otherwise no reaction takes place in normal way.





O-Xylene O-Xylene

Hydrogenation



Methyl cyclohexane

Fractional Distillation of Petroleum

S.No.	Fraction	Boiling range in K	Composition or number of C-atoms	Uses
1	Gaseous hydrocarbons	110–303	C1 – C4	Preparation of gasoline, carbon black
2	Crude naphthalene	303–424	C5 – C10	
	(a) Light petrol	303–362	C5 – C7	As a useful solvent for fats, oils
	(b) Petrol or gasoline	362–394	C7 – C9	Fuel for motors, production of petrol gas
3	Kerosene	424–514	C10 – C13	As fuel for stoves, in production of oil gas
4	Fuel oils like diesel, gas oil	514–624	C13 – C18	As a fuel
5	Lubricants for example motor oil, grease, medicinal oil	> 540	C15 – C18	As transformer oil, paint oil
6.	Parafn wax like petroleum wax, petroleum jelly	> 672	C18 – C30	In the manufacture of candles, ointments
7	Heavy oil and bitumen	Forming residue	> C30	Used mainly for road surfacing

Petroleum

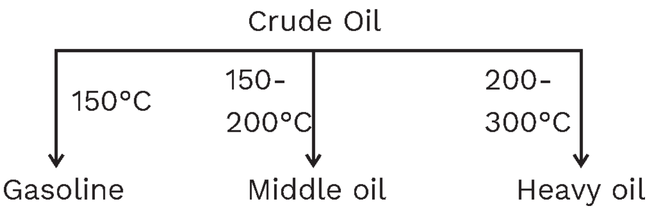
It is a dark coloured, viscous, fluorescent liquid which is a mixture of aliphatic hydrocarbons cycloalkanes or aromatic hydrocarbons. Various theories given on the origin of petroleum are:

1. Mendeleev’s carbide theory
2. Engler theory
3. Modern theory

Synthetic petrol is manufactured by the following method:

Bergius method

$$\text{Coal} + H_2 \xrightarrow{Fe_2O_3,\ 250\ \text{atm},\ 400°C\text{-}500°C} \text{Crude Oil}$$



Fischer Tropsch method

$$C + H_2O \xrightarrow{1200°C} \underset{\substack{\text{water gas} \\ \text{In half volume of} \\ \text{water gas under volume}}}{CO + H_2} \xrightarrow{\Delta,\ H_2} \text{Mixture of hydrocarbons}$$

Refning of petroleum

Refining of petroleum is separation of useful components of petroleum and removal of various undesirable impurities. It is done by fractional distillation of crude oil.

LPG (Liquefied petroleum gas): It is a mixture of propane and butane, main component being butane. LPG has a smell like ethanthiol (C_2H_5SH), which is known as ethyl mercapton. The smell helps in detection of leakage of LPG.

Natural gas: It has 80% methane, 10% C_2H_6 and 10% long chain hydrocarbons.

$$\text{Natural gas} \xrightarrow[\text{Limited air}]{\Delta} \underset{\substack{\text{Carbonblack} \\ \text{orlampblack}}}{C} + 2H_2O$$

Concept Ladder

Refining of petroleum is the separation of useful fractions of petroleum and the removal of various undesirable impurities. It is mainly carried out by fractional distillation of crude oil.

Previous Year’s Question

Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by

[NEET]

(1) Oxidation
(2) Cracking
(3) Distillation under reduced pressure
(4) Hydrolysis

Rack your Brain

A petroleum product being used for making Ointments, candles is_____.

CNG(Compressed Natural Gas): It has 95% CH_4, 5% C_2H_6, C_3H_8, N_2, He and CO_2. CNG is liquefied natural gas.

Knocking

Knocking is metallic sound produced due to pre-ignition of fuel in cylinder of an internal combustion engine.

Following hydrocarbons are arranged in decreasing order of knocking produced in them:

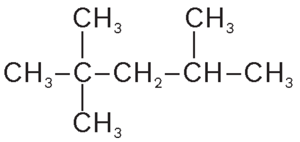
Straight chain alkanes > branched chain alkane > olefns > cycloalkenes > atomatic hydrocarbons

Tetraethyl lead (TEL) is used as an anti-knocking agent. It has $(C_2H_5)_4Pb$ (63%), $C_2H_4Br_2$ (26%), $C_2H_4Cl_2$ (9%) anddyes (2%).

Octane number

- Quality of automobile fuel is measured with respect to octane number. Hydrocarbon iso-octane (2,2,4-trimethyl pentane) which has good resistance to knocking even in the highest compression motors is arbitrarily given an octane number of 100; whereas n-heptane which knocks maximum is arbitrarily given the value of zero. Thus, higher octane number, better will be fuel.

$$\underset{\substack{\text{n-heptane}\\ \text{octane number=0}}}{CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3}$$



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

2, 2, 4-tri methyl pentane — 91
[octane number = 100]

- The octane number of gasoline is defined as the percentage of iso-octane present in a mixture of iso-octane and n-heptane, when the mixture has the same knocking in the engine, as the gasoline under examination.
- Thus, a motor fuel is said to have an octane number of 80 when it is as good as a mixture of 20 % n-heptane and 80% of iso-octane.

Concept Ladder

Two standards have been chosen-n–Heptane has octane number 0 whereas 2, 2, 4–Trimethylpentane (isooctane) has been given an octane number 100.

Previous Year's Question

Which of the following is used as an anitknocking material?

[NEET]

(1) Glyoxal
(2) Freon
(3) T.E.I.
(4) Ethyl alcohol

Rack your Brain

How does octane number changes with Branching?

- Octane number can be increased by:

1. increasing the percentage of branched or cycloalkanes,
2. by addition of BTX,
3. by addition of TEL,
4. by addition of power alcohol (C_2H_5OH).

Cetane number: It is the percentage of cetane (hexadecane) in a given diesel sample. For example, if a diesel sample contains 75% cetane and 25% α-methyl naphthalene, its cetane number is 75.

Flash point: Flash point or the ignition temperature may be defned as the minimum temperature at which an oil gives off enough vapours to form a momentary flash of light when a naked flame is brought near its surface.

- A fuel used in cold climates must have a low boiling point whereas the fuel used in tropical climate must have a high boiling point. Therefore, the flash point fixed for fuels in cold countries is low whereas in hot countries it is high. It is measured using Abel's apparatus.
- Gasoline, which has a pungent odour due to the pressence of sulphur compounds is called sour gasoline.The odour is removed by doctor sweetening process.

Cracking: In this process, the less valuable higher fraction of petroleum nun is converted into more valuable lower fractions by heating. The process involved for this is as follows:

Liquid phase cracking

$$\text{Heavy oil}\,(C_{18}-C_{43})\xrightarrow[\text{catalyst }1000\text{–}1200\,\text{Psi}]{475\text{–}530°\text{C}}(C_4-C_{10})$$

Catalyst: Zinc oxide, ferric oxide, silica, titanium dioxide, , or alumina is used as. High pressure keeps oil in liquid state. Octane number of product: 65–70.

Vapour phase cracking

$$\text{Kerosene oil or gas oil} \xrightarrow[\text{50–150 Psi}]{\text{600–800°C}} \text{Lower fractions}$$

Cracking in presence of hydrogen

$$R-R+H_2 \xrightarrow{\text{catalyst}} 2RH$$

$$ROH+H_2 \longrightarrow RH+H_2O$$

$$R_2S+2H_2 \longrightarrow 2RH+H_2S$$

$$R_2NH+2H_2 \longrightarrow 2RH+NH_3$$

Following are the reactions that take place during cracking:

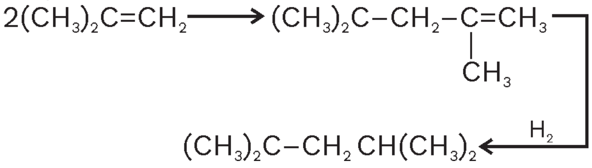
1. Carbonization

$$CH_4 \xrightarrow{1000°C} C+2H_2$$

2. Dehydrogenation

$$CH_3-CH_3 \xrightarrow{450°C} CH_2=CH_2+H_2$$

3. Polymerization



$$2(CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_2C-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_3 \xrightarrow{H_2} (CH_3)_2C-CH_2\,CH(CH_3)_2$$

4. Alkylation

$$(CH_3)_2CH-CH_3+CH_2=CH_2 \longrightarrow (CH_3)_3C-CH_2-CH_3$$

5. Aromatization

$$CH_3-(CH_2)_4-CH_3 \longrightarrow C_6H_6+4H_2$$

6. Chain fission

$$C_{16}H_{34} \longrightarrow C_8H_{18}+C_8H_{16} \text{ or } C_6H_{14}+C_{10}H_{20}$$

Q1 Why do alkenes prefer to undergo electrophilic addition reaction while arenes prefer electrophilic substitution reactions? Explain.

Sol. Alkenes undergo addition reacttion to give a more stable saturated product. In this reaction hybridization changes from sp^2 to sp^3.
The resonace stability of arene is maintained by a substitution reaction.

Q2 Alkynes on reduction with sodium in liquid ammonia from trans alkenes. Will the butene thus formed on the reduction of the 2-butyne show the geometrical isomerism?

Sol. Negative charge developed on one carbon, attacks proton from NH3 and another sodium atom loses electron which develops a second negative charge on atom. The negative charge is finally neutralised by attack of second proton to produce a trans but-2-ene.
The 2-butene produced gives geometrical isomers as cis and trans.

Q3 Rotation around carbon-carbon single bond of ethane is not completely free. Justify the statement.

Sol. The single bond in ethane is a s-bond, which is a coaxial overlap of orbitals, so the C—C bond can be rotated on its axis. But, the rotation is not completely free due to torsional strain that bond undergoes due to rotation.

Q4 The intermediate carbocation formed in the reactions of HI, HBr and HCl with propane is the same and the bond energy of HCl, HBr and HI is 430.5 kJ mol^{-1}, 363.7 kJ mol^{-1} and 296.8 kJ mol^{-1} respectively. What will be the order of reactivity of these halogen acids?

Sol. HI > HBr > HCl is the increasing order of reactivity. The increasing order of reactivity of halogen is same as their increase in bond energies.

Q5 Despite their –I effect, halogens are o- and p-directing in halo-arenes. Explain.

Sol. Halogens have an outer configuration of ns^2np^5 which shows it can accept one electron and are close to completing its octate, halogens show a strong affinity to attract one electron and thus having a higher electronegativity and show negative inductive effect.

Q6 Why does the presence of a nitro group make the benzene ring less reaction in comparison to the unsubstituted benzene ring? Explain.

Sol. Nitro group ahs a nitrogen atom bonded to two highly electronegative oxygen atoms. This results ina net decrease of electron density around nitrogen atom and imparts a positive $\delta+$ charge on nitrogen.

Q7 The relative reactivity of 1°, 2°, 3° hydrogen's towards chlorination is 1: 3.8 :5. Calcualte the precentages of all mono-chlorinated products obtained from 2-methyl butane.

Sol. Amount of mono-chlorinated products = No. of hydrogen reactivity
Mono-chlorinated products from 1°H = 9 1 = 9
Mono-chlorinated products from 2°H = 2 3.8 = 7.6
Mono-chlornated products from 3°H = 1 5 = 5
Total mono-chlorinated products = 9 + 7.6 + 5 = 21.6
Yield % for 1°H chlorination = 9 × 100/21.6 = 41.67%
Yield % for 2°H chlorination = 7.6 × 100/21.6 = 35.18%
Yield % for 3°H chlorination = 5 × 100/21.6 = 23.15%

Q8 Suggest a route for the preparation of nitrobenzene starting from acetylene?

Sol. (i) By intermolecular condensatino method, we can cycle acetylene and then treated at high temperature in a red hot iron tube.
(ii) The aliphatic compound thus converted int o benzene is treated with conc. HNO_3 and conc. H_2SO_4 which undergoes nitration to give nitrobenzene.

Q9 Alcoholic solution of caustic potash is a specific reagent for

(1) Dehydration
(2) Dehydrohalogenation
(3) Dehydrogenation
(4) Hydration

Sol. (2)
Alcoholic solution of KOH brings about dehydrohalogenation in alkyl halides forming alkenes.

Q10 Aromatization of n-heptane yields

(1) Toluene
(2) Xylene
(3) Benzene
(4) Methylcyclohexane

Sol. (1)

$$CH_3-(CH_2)_5-CH_3 \xrightarrow{-4H_2} C_6H_5-CH_3$$

Q11 Markownikov's rule is applicable to

(1) $CH_2 = CH_2$
(2) $CH_3 — CH_2 — CH_3$
(3) $CH_3 — CH = CH—CH_3$
(4) $(CH_3)_2 — C = CH_2$

Sol. (4)

Markownikoff's rule is applicable to unsymmetical alkenes.

Q12 Acetylene when treated with dilute HCl at 60°C (333 K) in presence of $HgCl_2$ produces

(1) Methyl chloride
(2) Vinyl chloride
(3) Acetaldehyde
(4) Formaldehyde

Sol. (2)

$$H-C\equiv C-H+HCl \xrightarrow[60^\circ]{HgCl_2} \underset{\text{Vinyl chloride}}{CH_2=CH-Cl}$$

Q13 Explain why 1-hexene does not react with H_2 gas when no other reagent is present?

Sol. Diatomic hydrogen gas (H—H) is not polarized and is not very polarizable. When the alkene comes into close proximity to H_2, there is no "H^+" or "H" for alkene to react with. The only way H_2 can react with an alkene is when another reagent is present that can react with H_2 to break the H—H bond.

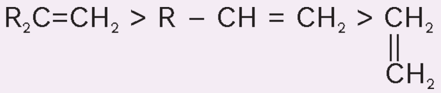
Q14 Compare and explain the relative rates of addition to alkenes (reactivities) of HCl, HBr and HI.

Sol. The relative reactivity depends on the ability of HX to donate and H^+ (acidity) to form an R^+ in the rate-controlling first step. The acidity and reactivity order is HI > HBr > HCl.

Summary

- Alkanes are inert at room temperature as (C–C), (C–H) bonds are non-polar.
- Liquid paraffins when burnt cannot be extinguished by water as it is lighter than water, so it will float over water.

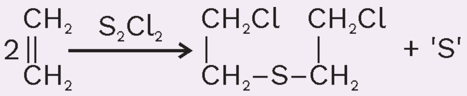
  The acid catalysed hydration of alkene is Regioselective and for various alkenes order of hydration is



$$R_2C=CH_2 > R-CH=CH_2 > \begin{array}{c}CH_2\\ \|\\ CH_2\end{array}$$

- Viscosity of Alkanes α Mol.wt. α Branching

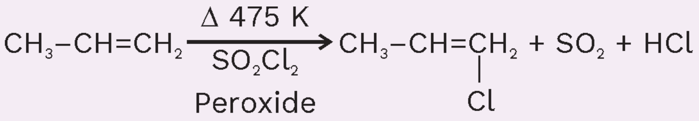
  E.g.,: n-Heptane > 2, 3 dimethyl butane > Isohexane > n-Hexane > n-pentane
- Presence of O_2 inhibits Halogenation as it forms a less Reactive Peroxy Radicle (R–O–O)
- Thermal Chlorination in case of an alkane is known as McBee Reaction
- C_2H_4 on reaction with S2Cl2 (Sulphur meno chlorides gives Mustard gas. (wargas)



$$2\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} \xrightarrow{S_2Cl_2} \begin{array}{ccc}CH_2Cl & & CH_2Cl\\ | & & |\\ CH_2 & -S- & CH_2\end{array} + \text{'S'}$$

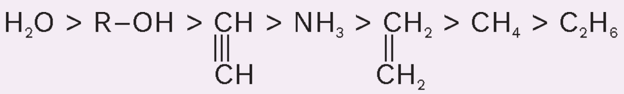
Mustard gas

- Anti-MarkonikoffadditionofHBronpropenecan be prevented by using inhibitors like catehol or diphenylamine.

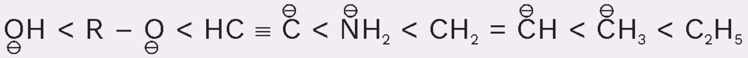


$$CH_3-CH=CH_2 \xrightarrow[\substack{SO_2Cl_2\\ \text{Peroxide}}]{\Delta\ 475\ K} CH_3-CH=\underset{\underset{Cl}{|}}{CH_2} + SO_2 + HCl$$

- Decreasing order of acidic nautre and increasing order of conjugate base strength:



$$H_2O > R-OH > \begin{array}{c}CH\\ |||\\ CH\end{array} > NH_3 > \begin{array}{c}CH_2\\ \|\\ CH_2\end{array} > CH_4 > C_2H_6$$



$$\underset{\ominus}{O}H < R-\underset{\ominus}{O} < HC\equiv\overset{\ominus}{C} < \overset{\ominus}{N}H_2 < CH_2=\overset{\ominus}{C}H < \overset{\ominus}{C}H_3 < C_2H_5$$

- Buna-N [General purpose rubber acrylonitrile] is a synthetic rubber which is a polymer of butadiene and acrylo nitrile.
- Buna-S [General purpose rubber styrene] is a synthetic rubber which is a polymer of butadiene and styrene.

- Natural rubber is a polymer of isoprene, that is, cis-2-methyl buta-1, 3,-diene.
- Guta pircha It is a polymer of trans-2-methyl buta-1, 3,-diene.
- Neoprene is a polymer of 2-chloroprene.
- On heating ethyne in the presence of spongy copper or Cu_2O, a cork like substance cuprene is formed which is used in the manufacture of linoleum.
- The light oil fraction of coal tar is composed of the hydrocarbons benzene (72%), toluene (13%) and xylene (4%), and is therefore known as BTX.
- When toluene is treated with Cl_2 in presence of a Lewis acid catalyst (FeCl3), substitution takes place at ortho and para positions. These products thus formed do not give white precipitate with alcoholic $AgNO_3$.
- Benzene hexachloride (BHC) can exist in nine stereoisomeric forms.
- Chloramine-T is the sodium salt of n-chloro-p-toluene sulphonamide.
- Actylene is used as an anaesthetic under the name Naraceylene.