ADVANCED LEVEL ORGANIC CHEMISTRY

SYNTHESIS OF ORGANIC COMPOUNDS

Introduction to synthesis of organic compounds

- Synthesis of organic compounds involves applying a wide range of properties of organic compounds.
- Synthesis is only correct when the correct reagents and conditions are used.
- Thus to master different synthesis questions, learners should have a summary of the preparation and chemical properties of the different groups of organic compounds

References

- In making this compilation, the following books have been used as references.
  1. Organic Chemistry by Morrison and Boyd
  2. Principles of Organic Chemistry by Peter R. S. Murray
  3. Organic Chemistry by Solomons
  4. Organic Chemistry by Francis A. Carey
  5. Modern Organic Chemistry by Norman Waddington
  6. A-level Chemistry by Ramsden
  7. Organic Chemistry Principles and Mechanisms by Joel Karty
  8. Organic Chemistry by John McMurry
  9. Organic Chemistry by Leroy Wade
  10. Organic Chemistry by Jonathan Clayden
  11. Organic Chemistry by Paula Y. Bruice
  12. Organic Chemistry structure, mechanism and synthesis by R.J. Ouellette and J.D. Rawn

Important groups of organic compounds at advanced level

- Alkanes
- Alkenes
- Alkynes
- Benzene and methylbenzene
- Haloalkanes and halobenzene
- Alcohols and phenol
- Carbonyl compounds
- Amines
- Carboxylic acids
- Derivatives of carboxylic acids. (amides, acid halides)

1. ALKANES.

Preparation of alkanes

a. From alkyl halides (Haloalkanes) ($R-X$) where X = Cl, Br or I

(i). Reacting alkyl halides with zinc-copper couple in the presence of aqueous ethanol.

$$R-X \xrightarrow[CH_3CH_2OH(aq)]{Zn-Cu} R-R$$

(ii). By reacting alky halides with sodium metal in the presence of dry ether.

$$R-X \xrightarrow[Dry\ ether]{Na(s)} R-R$$

Note: the above reaction doubles the length of the carbon chain

b. From sodium salts of carboxylic acids (sodium alkanoates)

When heated with sodalime (a mixture of sodium hydroxide and calcium oxide), sodium alkanoates are decarboxylated to form alkanes

$$RCO\bar{O}Na^+ \xrightarrow[Heat]{Sodalime} R-H$$

Note: The $-COONa$ group is removed and replaced with hydrogen atom, H

The above reaction is used to reduce the number of carbon atoms in the chain by one.

Example:

$$CH_3CH_2CO\bar{O}Na^+ \xrightarrow[Heat]{Sodalime} CH_3CH_3$$

c. By hydrogenation of alkenes.

Alkenes react with hydrogen in the presence palladium or platinum at room temperature or (nickel at $150℃-200℃$) to form alkanes.

$$RCH=CHR \xrightarrow[Ni\ /\ 150℃]{H_2} RCH_2CH_2R$$

d. By hydrogenation of alkynes.

Alkynes react with hydrogen in the presence palladium or platinum at room temperature or (nickel at $150℃-200℃$) to form alkanes.

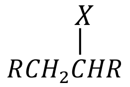
$$RC\equiv CR \xrightarrow[Ni\ /\ 200℃]{2H_2} RCH_2CH_2R$$

Reactions of alkanes

e. Halogenation

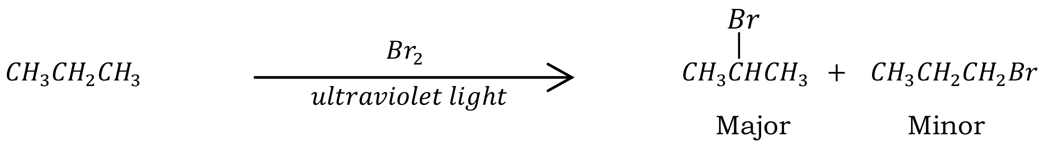
(i). Alkanes react with chlorine or bromine in the presence of ultraviolet light to form haloalkanes (alkyl halides).

$$RCH_2CH_2R \xrightarrow[ultraviolet\ light]{X_2}$$



$$RCH_2\overset{X}{\overset{|}{C}}HR$$

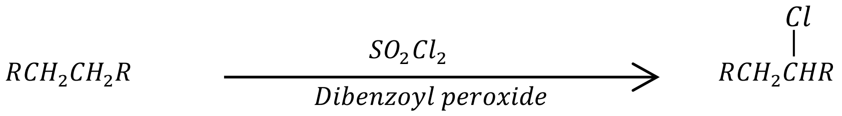
Example: propane reacts with bromine to form 2-bromopropane as a major product and 1-bromopropane is a minor product as shown below.



$$CH_3CH_2CH_3 \xrightarrow[\text{ultraviolet light}]{Br_2} CH_3\overset{\overset{Br}{|}}{C}HCH_3 + CH_3CH_2CH_2Br$$

Major Minor

(ii). Alkanes react with sulphur dioxide dichloride in the presence of dibenzoyl peroxide to form alkyl chlorides



$$RCH_2CH_2R \xrightarrow[\text{Dibenzoyl peroxide}]{SO_2Cl_2} RCH_2\overset{\overset{Cl}{|}}{C}HR$$

- **Example 1:** write equations to show how the following conversions can be made. In each case, indicate the conditions for the reactions.

(a). CH_4 (methane) to CH_3CH_3 (ethane)

***Hint**:* The conversion involves *increase* in the number of carbon atoms from one to two. We shall apply the reaction in 1(a)(ii)

$$CH_4 \xrightarrow[\text{Ultraviolet light}]{Br_2} CH_3Br \xrightarrow[\text{Dry ether}]{Na(s)} CH_3CH_3$$

OR

$$CH_4 \xrightarrow[\text{Dibenzoyl peroxide}]{SO_2Cl_2} CH_3Cl \xrightarrow[\text{Dry ether}]{Na(s)} CH_3CH_3$$

(b). CH_3COOH (ethanoic acid) to CH_3Br (bromomethane)

Solution

Hint: This conversion requires a student to decrease the number of carbon atoms. This requires us to first convert the acid to the salt. Then we can use the reaction 1 (b).

$$CH_3COOH \xrightarrow{NaHCO_3} CH_3COONa \xrightarrow[\text{Heat}]{NaOH(s)/\,CaO(s)} CH_4 \xrightarrow[\text{Ultraviolet light}]{Br_2} CH_3Br$$

2. ALKENES ($RCH = CHR$).

Preparation of alkenes

a. By dehydration of alcohols

When alcohols are heated with concentrated sulphuric acid at 170 – 180 ℃ or phosphoric acid, they are dehydrated to form alkenes

$$RCH_2CH_2OH \xrightarrow[180℃]{conc.\ H_2SO_4} RCH = CH_2$$

b. From alkyl halides (Haloalkanes) ($R - X$)

When haloalkanes are heated with potassium hydroxide (or sodium hydroxide) solution in the presence of an alcohol, an alkene is formed.

$$RCH_2CH_2X \xrightarrow[CH_3CH_2OH\ /\ heat]{KOH(aq)} RCH = CH_2$$

Note: This method is used when the alkyl halide has three or more carbon atoms.

c. **By partial reduction of alkynes**

Alkynes can be partially hydrogenated to form alkenes in the presence of a *deactivated* catalyst called the Lindlar catalys**t**. In this catalyst, palladium is supported on calcium carbonate and deactivated with lead.

$$RC \equiv CH \xrightarrow[Lindlar\ catalyst]{H_2} RCH = CH_2$$

Reactions of alkenes

In the reactions of alkenes, the double bond is broken and replaced with a single bond as the atoms of the reactants are added to the two carbon atoms across the double bond

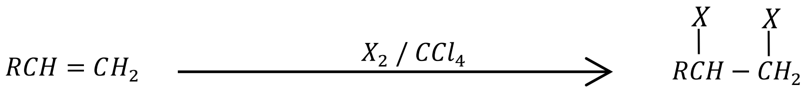
d. **Reaction with hydrogen**

Alkenes react with hydrogen in the presence of nickel at 150°C-200°C or palladium or platinum at room temperature to form alkanes.

$$RCH = CH_2 \xrightarrow{H_2\ /\ Pd} RCH_2CH_3$$

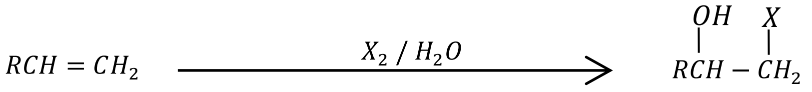
e. **Reaction with halogens, X_2 ($X = Cl, Br, I$)**

(i). Alkenes react with halogens in the presence of an inert solvent like carbon tetrachloride to form dihaloalkanes (alkyl dihalides).



$$RCH = CH_2 \xrightarrow{X_2\ /\ CCl_4} R\overset{X}{\overset{|}{C}}H - \overset{X}{\overset{|}{C}}H_2$$

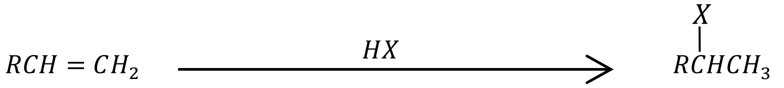
(ii). Alkenes react with chlorine and bromine in the presence of water to form halohydrins (halolacohols) [addition follows Markovnikoff's rules]



$$RCH = CH_2 \xrightarrow{X_2\ /\ H_2O} R\overset{OH}{\overset{|}{C}}H - \overset{X}{\overset{|}{C}}H_2$$

f. **Reaction with halogen acids. HX ($X = Cl, Br, I$)**

(i). Alkenes react with halogen acids to form haloalkanes



$$RCH = CH_2 \xrightarrow{HX} R\overset{X}{\overset{|}{C}}HCH_3$$

[**Note**: The halogen atom, X, attaches to the carbon atom with the fewest number of hydrogen atoms. i.e. – Markovnikoff's addition]

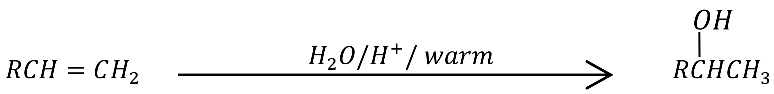
(ii). Alkenes react with hydrogen bromide in the presence of an organic peroxide ($ROOR$) to form haloalkanes. However, this follows anti-Markovnikoff's addition

$$RCH = CH_2 \xrightarrow{HBr\ /\ ROOR} RCH_2CH_2Br$$

[**Note**: The bromine atom attaches to the carbon atom with more hydrogen atoms]

g. Reaction with acidified water

Alkenes react with dilute sulphuric acid on warming to form alcohols, $(R-OH)$.

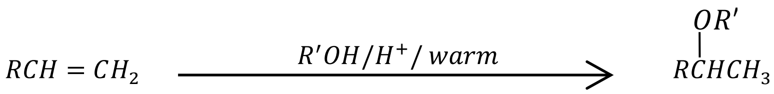


$$RCH=CH_2 \xrightarrow{H_2O/H^+/\,warm} \overset{OH}{\overset{|}{RCH}}CH_3$$

[Note: The $-OH$ group attaches to the carbon atom with the fewest number of hydrogen atoms. i.e. – Markovnikoff's addition]

h. Reaction with alcohols

Alkenes react with alcohols in the presence of dilute sulphuric acid on warming to form ethers $(R-O-R')$.

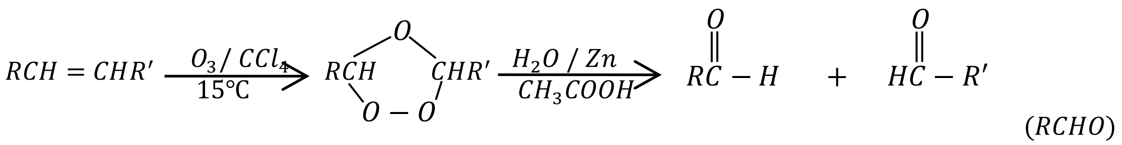


$$RCH=CH_2 \xrightarrow{R'OH/H^+/\,warm} \overset{OR'}{\overset{|}{RCH}}CH_3$$

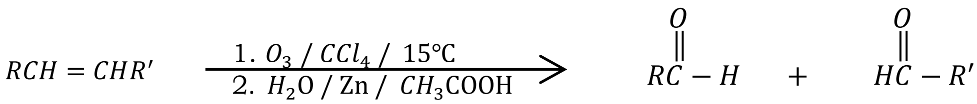
[**Note**: The $-\boldsymbol{OR'}$ group attaches to the carbon atom with the fewest number of hydrogen atoms. i.e. – Markovnikoff's addition]

i. Reaction with ozone (ozonolysis)

Alkenes react with ozone in the presence of carbon tetrachloride at 15 ℃ or lower to form an ozonide. The ozonide is hydrolysed using zinc dust in ethanoic acid to give two carbonyl compounds depending on the structure of the alkene.



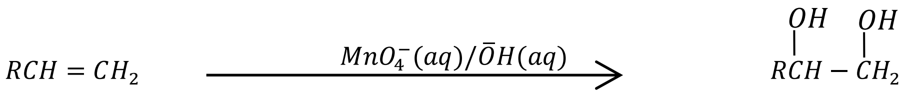
This can be simplified into



$$RCH=CHR' \xrightarrow[2.\ H_2O\,/\,Zn\,/\,CH_3COOH]{1.\ O_3\,/\,CCl_4\,/\ 15℃} \overset{O}{\overset{\|}{RC}}-H + \overset{O}{\overset{\|}{HC}}-R'$$

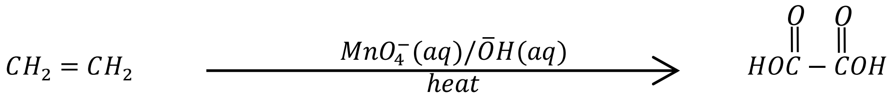
j. Reaction with potassium manganate(VII)

i. Alkenes react cold alkaline potassium manganate(VII) solution to form diols.



$$RCH=CH_2 \xrightarrow{MnO_4^-(aq)/\bar{O}H(aq)} \overset{OH}{\overset{|}{RCH}}-\overset{OH}{\overset{|}{CH_2}}$$

ii. Ethene reacts with hot alkaline potassium manganate(VII) to form **e**thanedioic acid (oxalic acid)

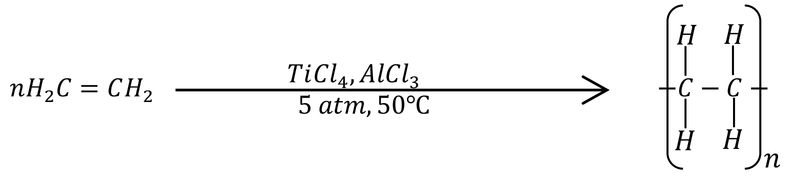


$$CH_2=CH_2 \xrightarrow[heat]{MnO_4^-(aq)/\bar{O}H(aq)} HO\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}OH$$

k. Polymerisation of alkenes

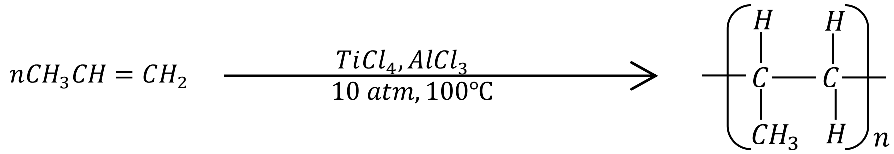
Under suitable conditions, alkenes like ethene, propene and phenylethene (styrene) polymerise to form polyethene, polypropene, and poly(phenylethene) (polystyrene)

i. Ethene polymerises in the presence of a titanium tetrachloride and triethyaluminium catalyst at 50℃ and 5 atm to form polyethene



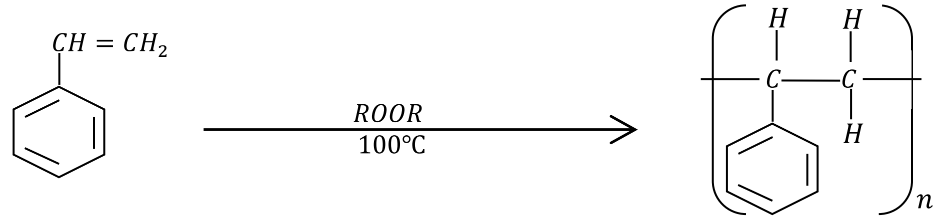
$$nH_2C=CH_2 \xrightarrow[5\,atm,\,50°C]{TiCl_4, AlCl_3} \left(-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}- \right)_n$$

ii. Propene polymerises in the presence of titanium tetrachloride and triethyaluminium catalyst at 100°C and 10 atm to form polypropene



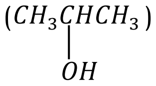
$$nCH_3CH=CH_2 \xrightarrow[10\,atm,\,100°C]{TiCl_4, AlCl_3} \left(-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}- \right)_n$$

iii. Styrene polymerises in the presence of a peroxide initiator at 100°C.

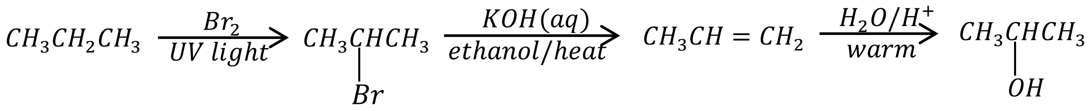


- **Example 2:**
  Write equations to show how the following conversions can be made, and in each case, indicate the conditions for the reactions

(a). Propane ($CH_3CH_2CH_3$) to propan-2-ol ($CH_3\underset{OH}{\underset{|}{C}}HCH_3$)



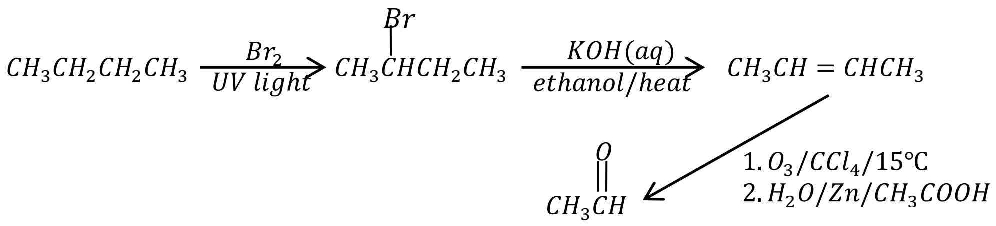
Hint: here we are to use the reaction in 1(e)(i), 2(b) and 2(g) in that order.



$$CH_3CH_2CH_3 \xrightarrow[UV\ light]{Br_2} CH_3\underset{Br}{\underset{|}{C}}HCH_3 \xrightarrow[ethanol/heat]{KOH(aq)} CH_3CH=CH_2 \xrightarrow[warm]{H_2O/H^+} CH_3\underset{OH}{\underset{|}{C}}HCH_3$$

(b). Butane ($CH_3CH_2CH_2CH_3$) to ethanal (CH_3CHO)

Hint: Ethanal is a carbonyl compound whose structure fits the general formula given in reaction in 2(i). Thus ozolysis of but-2-ene will produce ethanal.



$$CH_3CH_2CH_2CH_3 \xrightarrow[UV\ light]{Br_2} CH_3\overset{Br}{\overset{|}{C}}HCH_2CH_3 \xrightarrow[ethanol/heat]{KOH(aq)} CH_3CH=CHCH_3$$

$$CH_3CH=CHCH_3 \xrightarrow[2.\ H_2O/Zn/CH_3COOH]{1.\ O_3/CCl_4/15°C} CH_3\overset{O}{\overset{\|}{C}}H$$

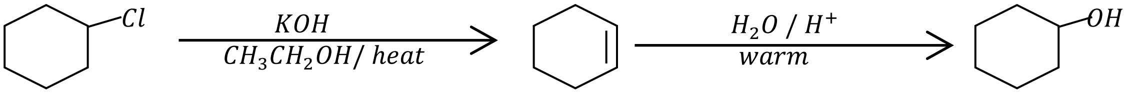
- **Question 1**

  Write equations to show how the following conversions can be made, and in each case, indicate the conditions for the reactions

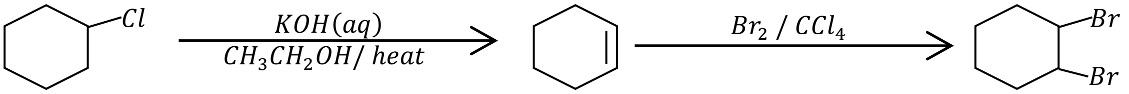
Solutions

(a). Chlorocyclohexane to

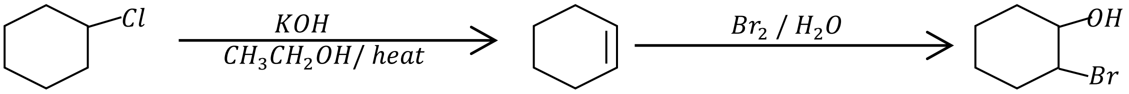
i. Cyclohexanol



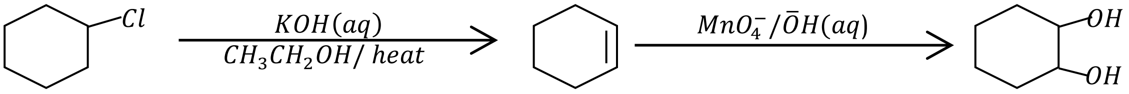
ii. 1,2-dibromocyclohexane



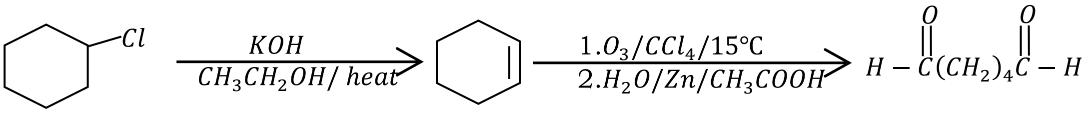
iii. 2-bromocyclohexanol



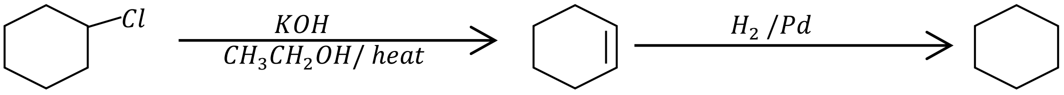
iv. Cyclohexene-1,2-diol



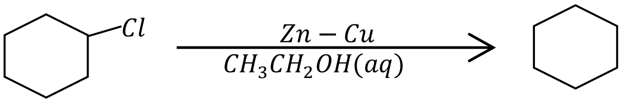
v. $OHC(CH_2)_4CHO$



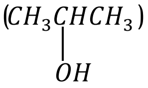
vi. Cyclohexane



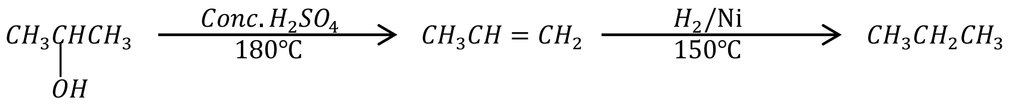
OR



- **Question 2**

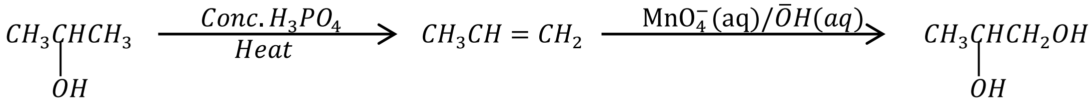
(a). Propan-2-ol ($CH_3\underset{\underset{OH}{|}}{C}HCH_3$)

i. Propane



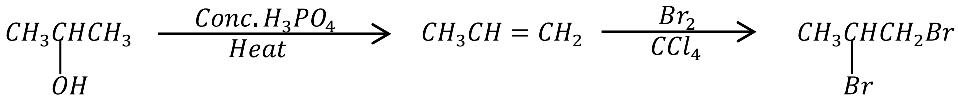
$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[180°C]{Conc.\,H_2SO_4} CH_3CH=CH_2 \xrightarrow[150°C]{H_2/\mathrm{Ni}} CH_3CH_2CH_3$$

ii. Propane-1,2-diol



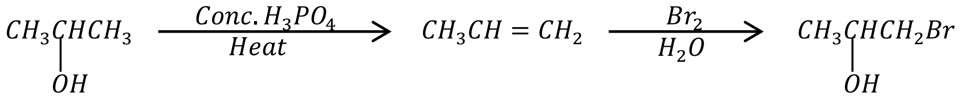
$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[Heat]{Conc.\,H_3PO_4} CH_3CH=CH_2 \xrightarrow{\mathrm{MnO_4^-(aq)}/\bar{O}H(aq)} CH_3\underset{\underset{OH}{|}}{C}HCH_2OH$$

iii. 1,2-dibromopropane



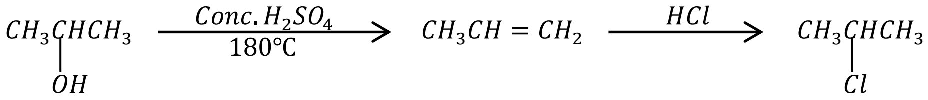
$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[Heat]{Conc.\,H_3PO_4} CH_3CH=CH_2 \xrightarrow[CCl_4]{Br_2} CH_3\underset{\underset{Br}{|}}{C}HCH_2Br$$

iv. 1-bromopropan-2-ol



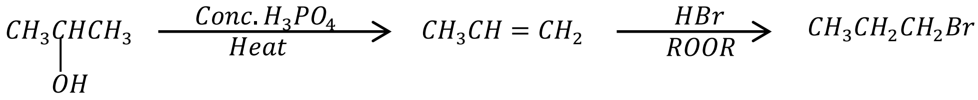
$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[Heat]{Conc.\,H_3PO_4} CH_3CH=CH_2 \xrightarrow[H_2O]{Br_2} CH_3\underset{\underset{OH}{|}}{C}HCH_2Br$$

v. 2-chloropropane



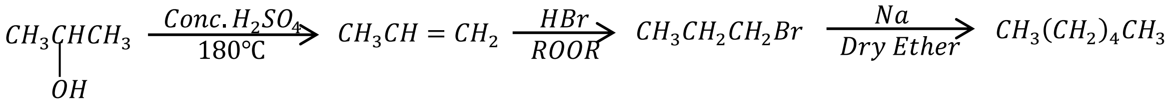
$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[180°C]{Conc.\,H_2SO_4} CH_3CH=CH_2 \xrightarrow{HCl} CH_3\underset{\underset{Cl}{|}}{C}HCH_3$$

vi. 1-bromopropane



$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[Heat]{Conc.\,H_3PO_4} CH_3CH=CH_2 \xrightarrow[ROOR]{HBr} CH_3CH_2CH_2Br$$

vii. Hexane



$$CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[180°C]{Conc.\,H_2SO_4} CH_3CH=CH_2 \xrightarrow[ROOR]{HBr} CH_3CH_2CH_2Br \xrightarrow[Dry\ Ether]{Na} CH_3(CH_2)_4CH_3$$

- **Question 3:**
  Write equations to show how ethanol can be converted to the following compounds. Include the conditions for the reactions in each case

(a). Ethane-1,2-diol

$$CH_3CH_2OH \xrightarrow[180℃]{Conc.H_2SO_4} H_2C=CH_2 \xrightarrow{MnO_4^-(aq)/\bar{O}H(aq)} HOCH_2CH_2OH$$

(b). 1,2-dichloroethane

$$CH_3CH_2OH \xrightarrow[180℃]{Conc.H_2SO_4} H_2C=CH_2 \xrightarrow[CCl_4]{Cl_2} ClCH_2CH_2Cl$$

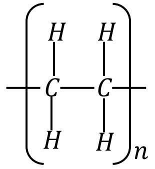
(c). Ethanedioic acid

$$CH_3CH_2OH \xrightarrow[180℃]{Conc.H_2SO_4} H_2C=CH_2 \xrightarrow[Heat]{MnO_4^-(aq)/\bar{O}H(aq)} HOOC-COOH$$

(d). Methanal

$$CH_3CH_2OH \xrightarrow[180℃]{Conc.H_2SO_4} H_2C=CH_2 \xrightarrow[2.\,H_2O/Zn/CH_3COOH]{1.\,O_3/CCl_4/15℃} HCHO$$

(e). Polyethene



$$CH_3CH_2OH \xrightarrow[180℃]{Conc.H_2SO_4} H_2C=CH_2 \xrightarrow[5\,atm/\,50\,℃]{TiCl_4Al(CH_2CH_3)_3} \left[\begin{array}{cc} H & H \\ | & | \\ -C- & C- \\ | & | \\ H & H \end{array}\right]_n$$

(f). Chloroethane

$$CH_3CH_2OH \xrightarrow[180℃]{Conc.H_2SO_4} H_2C=CH_2 \xrightarrow{HCl} CH_3CH_2Cl$$

(g). 1,2-dibromoethane

$$CH_3CH_2OH \xrightarrow[180℃]{Conc.H_2SO_4} H_2C=CH_2 \xrightarrow[CCl_4]{Br_2} BrCH_2CH_2Br$$

(h). Butane

$$CH_3CH_2OH \xrightarrow[180℃]{Conc.H_2SO_4} H_2C=CH_2 \xrightarrow{HCl} CH_3CH_2Cl \xrightarrow[\text{Dry Ether}]{Na} CH_3CH_2CH_2CH_3$$

(i). 2-bromoethanol

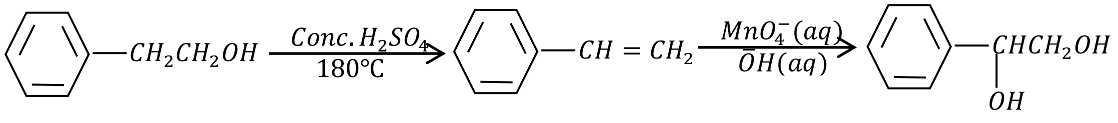
$$CH_3CH_2OH \xrightarrow[180℃]{Conc.H_2SO_4} H_2C=CH_2 \xrightarrow[H_2O]{Br_2} BrCH_2CH_2OH$$

- **Question 4**
  Write equations to show how the following conversions can be made, and in each case, state the conditions for the reactions.

(a). Ethane from ethanol

$$CH_3CH_2OH \xrightarrow[180°C]{Conc. H_2SO_4} H_2C = CH_2 \xrightarrow[Pd]{H_2} CH_3CH_3$$

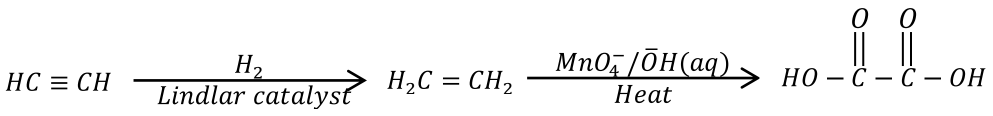
(b). 2-phenylethanol to 1-phenylethane-1,2-diol



(c). Ethanal from butan-1-ol

$$CH_3CH_2CH_2CH_2OH \xrightarrow[180°C]{Conc. H_2SO_4} CH_3CH = CHCH_3 \xrightarrow[2. H_2O/Zn/CH_3COOH]{1. O_3/CCl_4/15°C} CH_3CHO$$

(d). Ethyne to ethanedioic acid

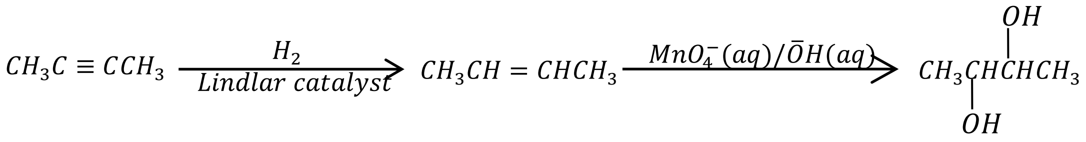


$$HC \equiv CH \xrightarrow[Lindlar\ catalyst]{H_2} H_2C = CH_2 \xrightarrow[Heat]{MnO_4^-/\bar{O}H(aq)} HO - \overset{\overset{O}{\|}}{C} - \overset{\overset{O}{\|}}{C} - OH$$

(e). (e). Propan-1-ol to propane

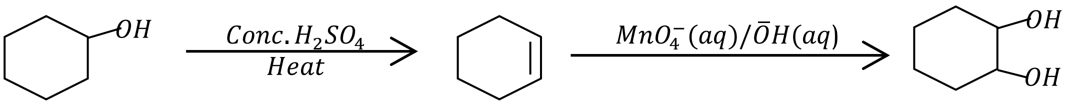
$$CH_3CH_2CH_2OH \xrightarrow[180°C]{Conc. H_2SO_4} CH_3CH = CH_2 \xrightarrow[Pd]{H_2} CH_3CH_2CH_3$$

(f). But-2-yne to butane-2,3-diol

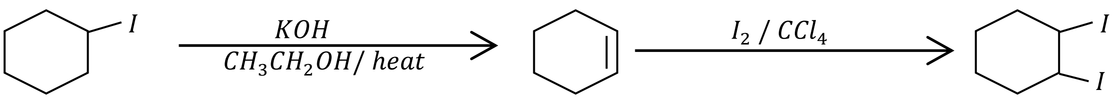


$$CH_3C \equiv CCH_3 \xrightarrow[Lindlar\ catalyst]{H_2} CH_3CH = CHCH_3 \xrightarrow{MnO_4^-(aq)/\bar{O}H(aq)} CH_3\underset{\underset{OH}{|}}{C}H\overset{\overset{OH}{|}}{C}HCH_3$$

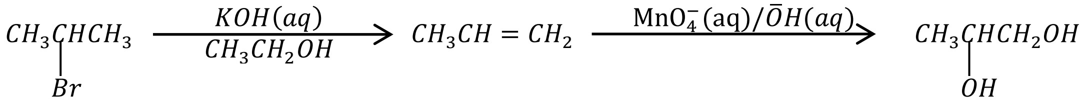
(g). Cyclohexenol to cyclohexene-1,2-diol



(h). Iodocyclohexane to 1,2-diiodocyclohexane



(i). 2-bromopropane to propane-1,2-diol



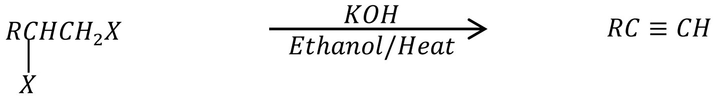
$$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow[CH_3CH_2OH]{KOH(aq)} CH_3CH=CH_2 \xrightarrow{MnO_4^-(aq)/\bar{O}H(aq)} CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2OH$$

3. **ALKYNES ($RC\equiv CR$)**

Preparation of alkynes

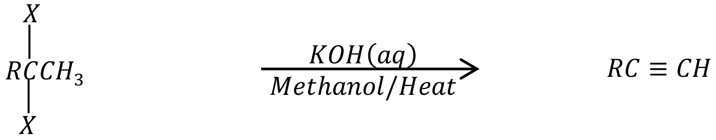
a. From alkyl dihalides (Dihaloalkanes)

Alkynes can be prepared by heating alkyl dihalides with potassium hydroxide (or sodium hydroxide solution) in the presence of an alcohol.



$$R\underset{\displaystyle X}{\underset{|}{C}}HCH_2X \xrightarrow[Ethanol/Heat]{KOH} RC\equiv CH$$

And



$$R\overset{\displaystyle X}{\overset{|}{\underset{\displaystyle X}{\underset{|}{C}}}}CH_3 \xrightarrow[Methanol/Heat]{KOH(aq)} RC\equiv CH$$

b. Preparation of ethyne from calcium dicarbide

When calcium dicarbide is reacted with water, ethyne is formed.

$$CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + HC\equiv CH(g)$$

Reactions of alkynes

c. Reaction with hydrogen

(i). Alkynes react with hydrogen in the presence of palladium or platinum catalyst at room temperature or nickel catalyst at 150°C-200°C to form alkanes

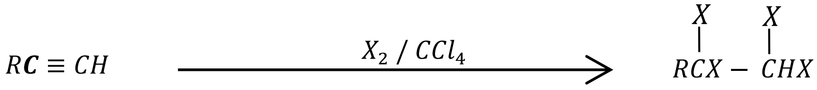
$$RC\equiv CR \xrightarrow[Ni\ /\ 150^\circ C]{2H_2} RCH_2CH_2R$$

(ii). Alkynes react with hydrogen form alkenes in the presence of the Lindlar catalyst. In this catalyst, palladium is supported on calcium carbonate and deactivated with lead.

$$RC\equiv CH \xrightarrow[Lindlar\ catalyst]{H_2} RCH=CH_2$$

d. Reaction with halogens, X_2 ($X = Cl, Br, I$)

(i). Alkynes react with halogens in the presence of an inert solvent like carbon tetrachloride to form dihaloalkanes (alkyl tetrahalides).

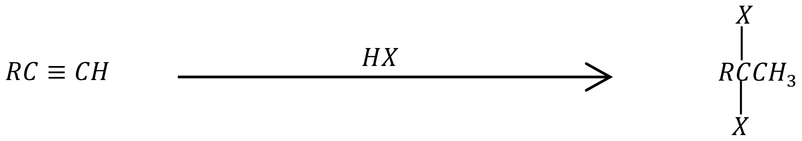


$$R\boldsymbol{C}\equiv CH \xrightarrow{X_2\ /\ CCl_4} R\overset{\displaystyle X}{\overset{|}{C}}X - \overset{\displaystyle X}{\overset{|}{C}}HX$$

(ii). Alkynes react with bromine in the presence of water more slowly. The brown solution turns colourless as it is with alkenes

e. Reaction with halogen acids

Alkynes act with halogen acids to form dihaloalkanes



$$RC \equiv CH \xrightarrow{HX} RC(X)_2CH_3$$

f. Reaction with water

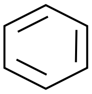
Alkynes react with water to in the presence of sulphuric acid and mercury(II) sulphate at 60°C to form carbonyl compounds. Apart from ethyne which forms ethanal (an aldehyde) the rest of the alkynes form ketones ($RCOR\ where\ R \neq H$)

$$RC \equiv CH \xrightarrow[HgSO_4\ /60°C]{H_2O/H_2SO_4} RCOCH_3$$

g. Polymerisation of ethyne

Ethyne polymerises to form benzene in the presence of heated iron catalyst or organonickel catalyst at 60°C

$$HC \equiv CH \xrightarrow[60°C]{Organonickel}$$



h. Reactions of terminal alkynes ($RC \equiv CH$)

Alkynes with a terminal triple bond ($RC \equiv CH$) have some reactions in which they differ from those that have internal triple bonds ($RC \equiv CR\ where\ R\ is\ not\ H$)

(i). Alkynes with a terminal triple bond react with sodium metal in the presence of liquid ammonia to form sodium alkynide.

$$RC \equiv CH \xrightarrow{Na(s)/\ NH_3(l)} RC \equiv C^-Na^+$$

- The alkynide reacts with primary alkyl halide to form an alkyne of longer carbon chain

$$RC \equiv C^-Na^+ \xrightarrow{CH_3X} RC \equiv CCH_3$$

NOTE:

- The alkylation reaction is limited to the use of *primary alkyl* halides because alkynide ions are sufficiently strong bases to cause elimination instead of substitution when they react with secondary and tertiary alkyl halides

(ii). Terminal alkynes react with ammoniacal silver nitrate solution to form a white precipitate of silver alkynide.

$$RC \equiv CH + Ag(NH_3)_2^+ \longrightarrow RC \equiv CAg + NH_4^+ + NH_3$$

Ethyne forms silver dicarbide

$$HC \equiv CH + 2Ag(NH_3)_2^+ \longrightarrow AgC \equiv CAg + 2NH_4^+ + 2NH_3$$

(iii). Terminal alkynes react with react with ammoniacal copper(I) chloride solution to form a red precipitate of copper(I) alkynide.

$$RC \equiv CH + Cu(NH_3)_2^+ \longrightarrow RC \equiv CCu + NH_4^+ + NH_3$$

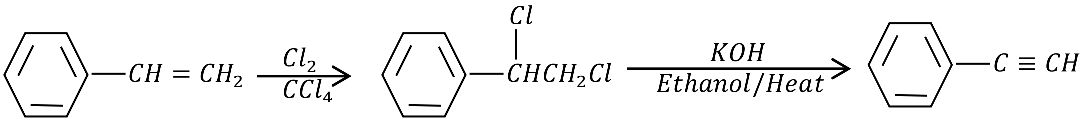
Ethyne forms copper(I) dicarbide

$$HC \equiv CH \ + \ 2Cu(NH_3)_2^+ \longrightarrow CuC \equiv CCu \ + \ 2NH_4^+ \ + \ 2NH_3$$

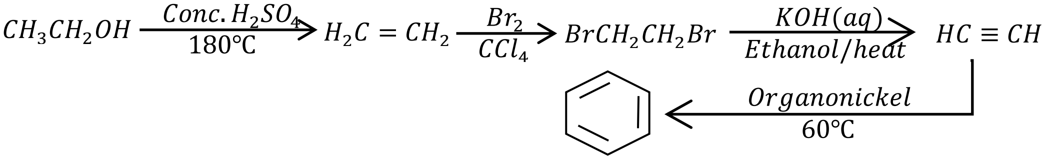
- **Examples**
  Write equations to show how the following compounds can be synthesized from each of the following substances and in each case, indicate the conditions for the reactions.
  (a). 1,2 – dibromoethane to 1-bromoethane

$$BrCH_2CH_2Br \xrightarrow[Ethanol/heat]{KOH} HC \equiv CH \xrightarrow[Lindlar\ catalyst]{H_2} H_2C = CH_2 \xrightarrow{HCl} CH_3CH_2Cl$$

(b). Phenylethene to phenylethyne



- **Question 5**
  Write equations to show how the following compounds can be synthesized from each of the following substances and in each case, indicate the conditions for the reactions.
  (a). . Ethanol to
  (i). Benzene



(ii). Propyne

$$CH_3CH_2OH \xrightarrow[180°C]{Conc. H_2SO_4} H_2C = CH_2 \xrightarrow[CCl_4]{Br_2} BrCH_2CH_2Br \xrightarrow[Ethanol/heat]{KOH(aq)} HC \equiv CH \xrightarrow{Na(s)/NH_3(l)} HC \equiv \bar{C}Na^+ \xrightarrow{CH_3Br} HC \equiv CCH_3$$

(iii). Propanone

$$CH_3CH_2OH \xrightarrow[180°C]{Conc. H_2SO_4} H_2C = CH_2 \xrightarrow[CCl_4]{Br_2} BrCH_2CH_2Br \xrightarrow[Ethanol/heat]{KOH(aq)} HC \equiv CH \xrightarrow{Na(s)/NH_3(l)} HC \equiv \bar{C}Na^+ \xrightarrow{CH_3Br} HC \equiv CCH_3 \xrightarrow[HgSO_4/60°C]{H_2O/H_2SO_4} CH_3COCH_3$$

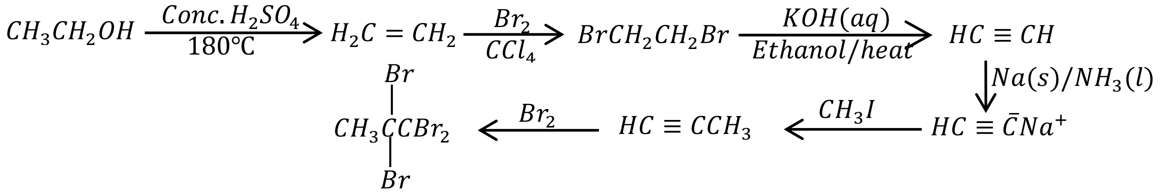
(iv). But-2-yne

$$\begin{tikzcd}
CH_3CH_2OH \arrow[r, "Conc.\,H_2SO_4", "180°C"'] & H_2C=CH_2 \arrow[r, "Br_2", "CCl_4"'] & BrCH_2CH_2Br \arrow[rr, "KOH(aq)", "Ethanol/heat"'] & & HC\equiv CH \arrow[d, "Na(s)/NH_3(l)"] \\
CH_3C\equiv CCH_3 & CH_3C\equiv\bar{C}Na^+ \arrow[l, "CH_3Br"'] & HC\equiv CCH_3 \arrow[l, "Na(s)"', "NH_3(l)"] & & HC\equiv\bar{C}Na^+ \arrow[ll, "CH_3Br"']
\end{tikzcd}$$

(v). Butanone

$$\begin{tikzcd}
CH_3CH_2OH \arrow[r, "Conc.\,H_2SO_4", "180°C"'] & H_2C=CH_2 \arrow[r, "Br_2", "CCl_4"'] & BrCH_2CH_2Br \arrow[rr, "KOH(aq)", "Ethanol/heat"'] & & HC\equiv CH \arrow[d, "Na(s)/NH_3(l)"] \\
CH_3C\equiv CCH_3 \arrow[dr, "H_2O/H_2SO_4", "HgSO_4/60°C"'] & CH_3C\equiv\bar{C}Na^+ \arrow[l, "CH_3Br"'] & HC\equiv CCH_3 \arrow[l, "Na(s)"', "NH_3(l)"] & & HC\equiv\bar{C}Na^+ \arrow[ll, "CH_3Br"'] \\
 & CH_3CH_2COCH_3 & & &
\end{tikzcd}$$

(vi). 1,1,2,2-tetrabromopropane



$$\begin{tikzcd}
CH_3CH_2OH \arrow[r, "Conc.\,H_2SO_4", "180°C"'] & H_2C=CH_2 \arrow[r, "Br_2", "CCl_4"'] & BrCH_2CH_2Br \arrow[r, "KOH(aq)", "Ethanol/heat"'] & HC\equiv CH \arrow[d, "Na(s)/NH_3(l)"] \\
CH_3\overset{Br}{\underset{Br}{C}}CBr_2 & HC\equiv CCH_3 \arrow[l, "Br_2"'] & & HC\equiv\bar{C}Na^+ \arrow[ll, "CH_3I"']
\end{tikzcd}$$

(b). 1,2-dichloroethane to

(i). Ethanol

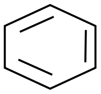
$$ClCH_2CH_2Cl \xrightarrow[Ethanol/heat]{KOH(aq)} HC\equiv CH \xrightarrow[Lindlar\ catalys]{H_2} H_2C=CH_2 \xrightarrow[warm]{H_2O/H^+} CH_3CH_2OH$$

(ii). Bromoethanol

$$ClCH_2CH_2Cl \xrightarrow[Ethanol/heat]{KOH(aq)} HC\equiv CH \xrightarrow[Lindlar\ catalys]{H_2} H_2C=CH_2 \xrightarrow[H_2O]{Br_2} BrCH_2CH_2OH$$

(iii). Benzene

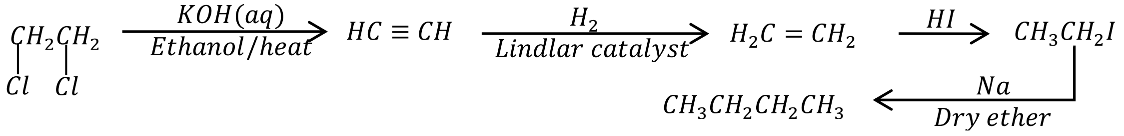
$$ClCH_2CH_2Cl \xrightarrow[Ethanol/heat]{KOH(aq)} HC\equiv CH \xrightarrow[60°C]{Organonickel}$$



(iv). Ethanal

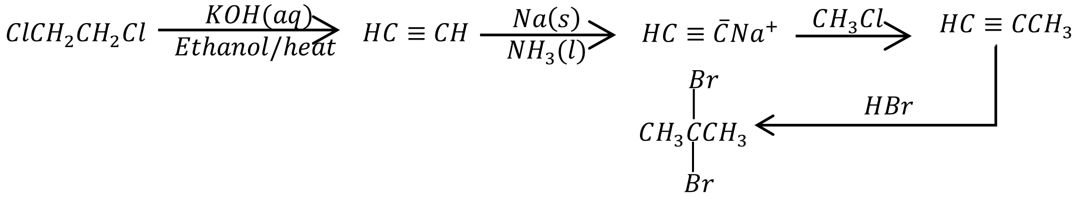
$$ClCH_2CH_2Cl \xrightarrow[Ethanol/heat]{KOH(aq)} HC\equiv CH \xrightarrow[HgSO_4/60°C]{H_2O/H_2SO_4} CH_3CHO$$

(v). Butane



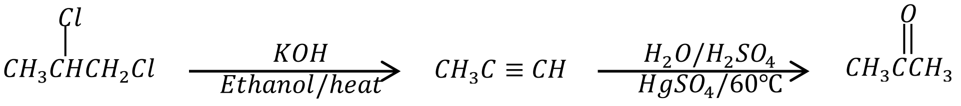
$$\underset{Cl}{CH_2}\underset{Cl}{CH_2} \xrightarrow[Ethanol/heat]{KOH(aq)} HC\equiv CH \xrightarrow[Lindlar\ catalyst]{H_2} H_2C=CH_2 \xrightarrow{HI} CH_3CH_2I \xrightarrow[Dry\ ether]{Na} CH_3CH_2CH_2CH_3$$

(vi). 2,2-dibromopropane



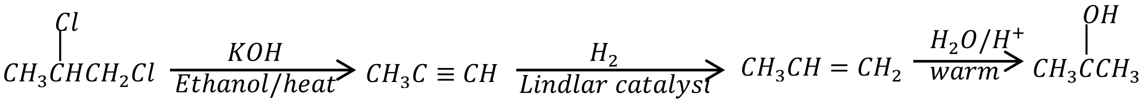
$$ClCH_2CH_2Cl \xrightarrow[Ethanol/heat]{KOH(aq)} HC\equiv CH \xrightarrow[NH_3(l)]{Na(s)} HC\equiv \bar{C}Na^+ \xrightarrow{CH_3Cl} HC\equiv CCH_3 \xrightarrow{HBr} CH_3\overset{Br}{\underset{Br}{C}}CH_3$$

- **Question 6**
  Write equations to show how the following compounds can be synthesized from each of the following substances and in each case, indicate the conditions for the reactions.
  (a). 1,2-dichloropropane to
  (i). Propanone



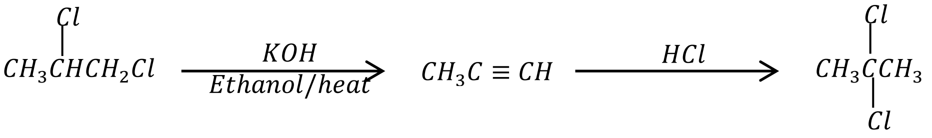
$$CH_3\overset{Cl}{C}HCH_2Cl \xrightarrow[Ethanol/heat]{KOH} CH_3C\equiv CH \xrightarrow[HgSO_4/60℃]{H_2O/H_2SO_4} CH_3\overset{O}{\overset{\|}{C}}CH_3$$

(i). Propan-2-ol



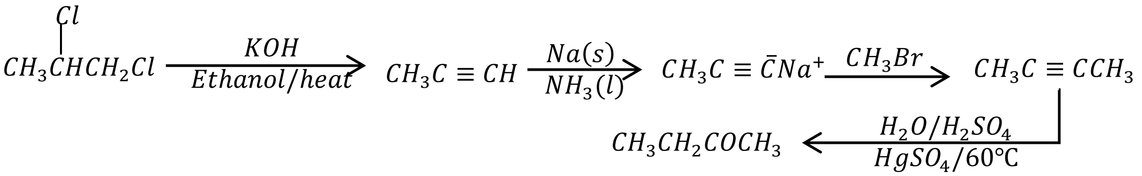
$$CH_3\overset{Cl}{C}HCH_2Cl \xrightarrow[Ethanol/heat]{KOH} CH_3C\equiv CH \xrightarrow[Lindlar\ catalyst]{H_2} CH_3CH=CH_2 \xrightarrow[warm]{H_2O/H^+} CH_3\overset{OH}{C}CH_3$$

(ii). 2,2-dichloropropane



$$CH_3\overset{Cl}{C}HCH_2Cl \xrightarrow[Ethanol/heat]{KOH} CH_3C\equiv CH \xrightarrow{HCl} CH_3\overset{Cl}{\underset{Cl}{C}}CH_3$$

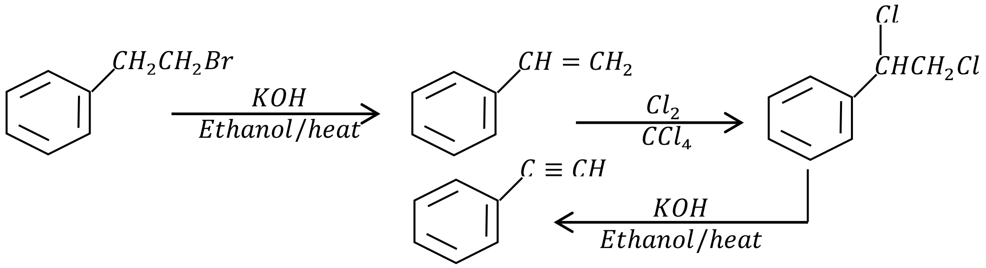
(iii). Butanone



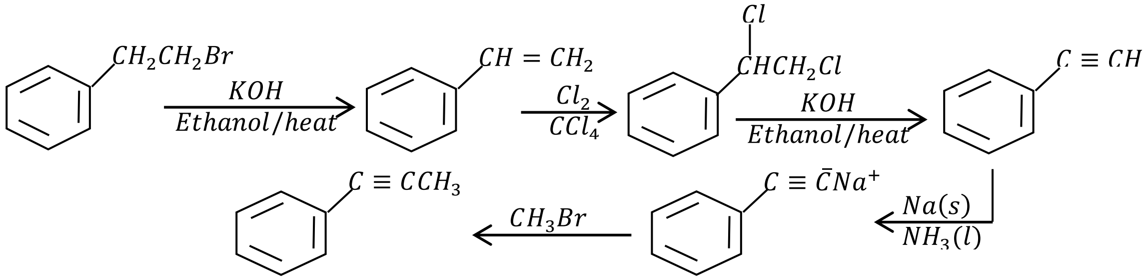
$$CH_3\overset{Cl}{C}HCH_2Cl \xrightarrow[Ethanol/heat]{KOH} CH_3C\equiv CH \xrightarrow[NH_3(l)]{Na(s)} CH_3C\equiv \bar{C}Na^+ \xrightarrow{CH_3Br} CH_3C\equiv CCH_3 \xrightarrow[HgSO_4/60℃]{H_2O/H_2SO_4} CH_3CH_2COCH_3$$

(b). 1-bromo-1-phenylethane to

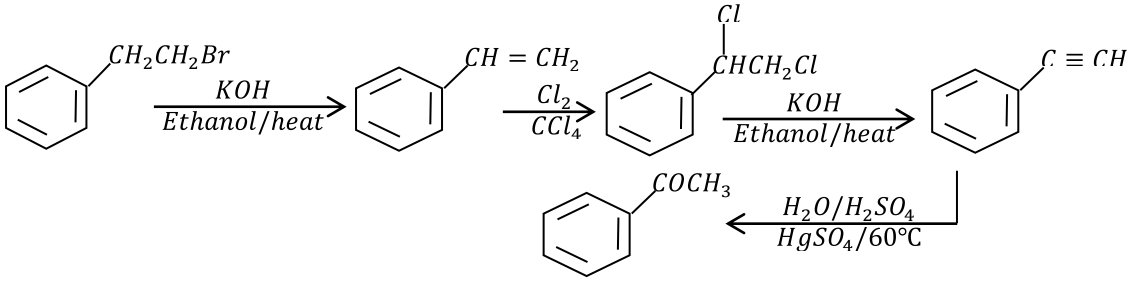
(i). Phenylethyne



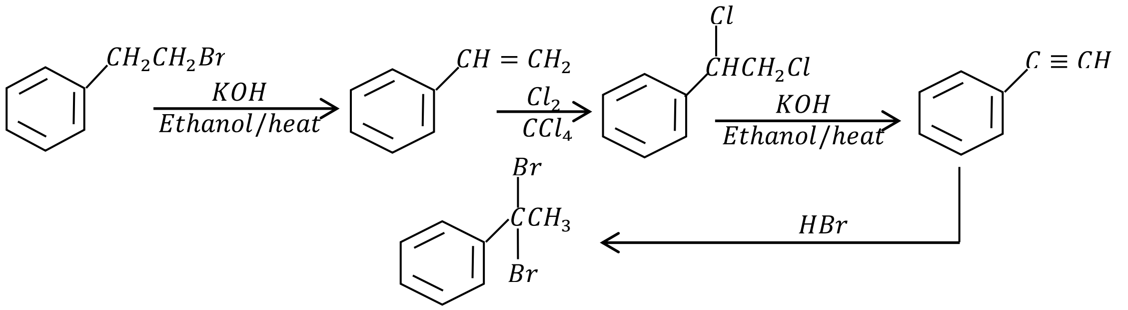
(ii). Pheylpropyne



(iii). Phenylethanone



(iv). 1,1-dibromo-1-phenylethane

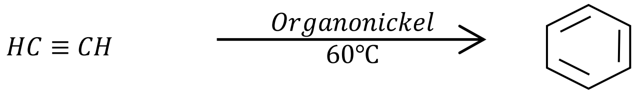


4. BENZENE

Preparation of benzene

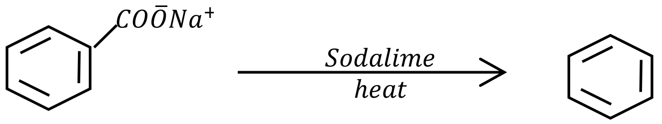
a. From ethyne

Ethyne polymerises to form benzene in the presence of heated iron catalyst or organonickel catalyst at 60°C



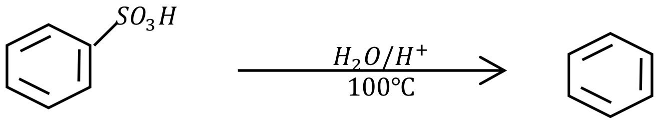
b. From sodium benzoate

When heated with sodalime (a mixture of sodium hydroxide and calcium oxide), sodium benzoate is decarboxylated to form benzene



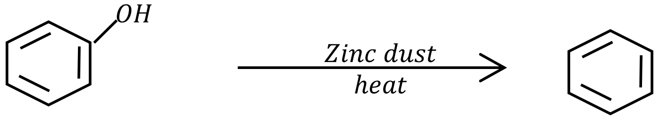
c. From benzenesulphonic acid

Benzenesulphonic acid is desulphonated by heating it to 100 - 150°C with dilute acid ($Organic\ Chemistry\ by\ Paula\ Bruice$)



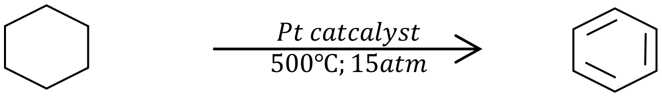
d. From phenol

When phenol is heated with zinc dust, benzene is formed



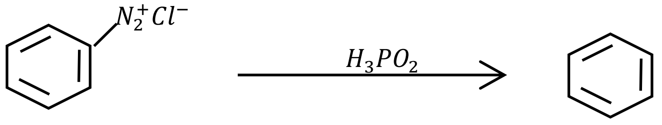
e. By catalytic reforming

When cyclohexane (or hexane) is vaporised at 500°C and passed over aluminium oxide at 40atm (or platinum at 15atm), it is dehydrogenated to form benzene



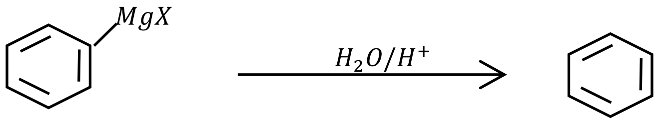
f. From benzene diazonium chloride

When benzene diazonium chloride is treated with hypophosphorous (phosphinic) acid, benzene is formed



g. From Phenylmagnesium halide(A Grignard reagent)

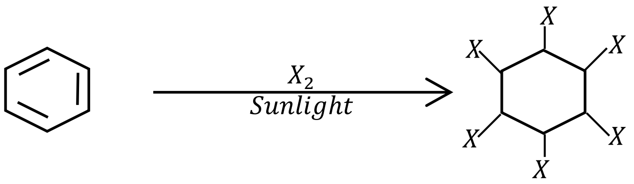
When phenylmagnesium halides are hydrolysed in dilute acids, they form benzene. (water alone can be used in the hydrolysis). ($Organic\ Chemistry\ by\ R.T.Morrison$)



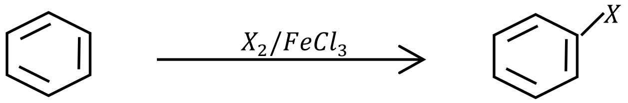
Reactions of benzene

a. Halogenation ($X = Cl$ or Br)

(i). Benzene reacts with chlorine and bromine in the presence of sunlight to form 1,2,3,4,5,6-hexahalobenzene

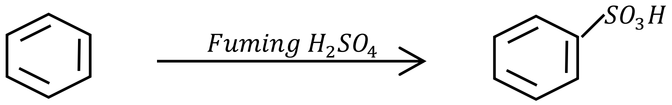


(ii). Benzene reacts with chlorine and bromine in the presence of a catalysts like aluminium halides or iron(III) halides (Lewis acids) to form chlorobenzene or bromobenzene.



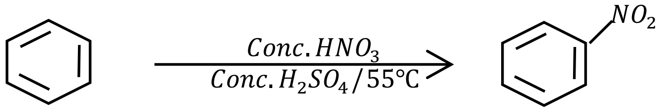
b. Sulphonation

Benzene reacts with fuming sulphuric acid (or hot concentrated sulphuric acid) to form benzenesulphonic acid



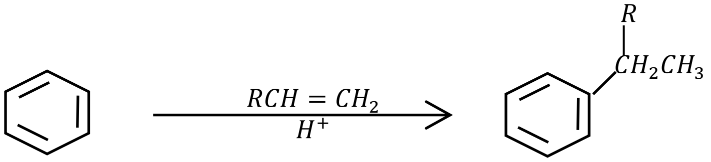
c. Nitration

Benzene reacts with a concentrated nitric acid in the presence of concentrated sulphuric acid at 55 to 60°C to form nitrobenzene

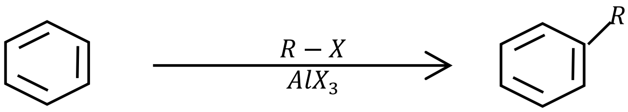


d. Alkyation

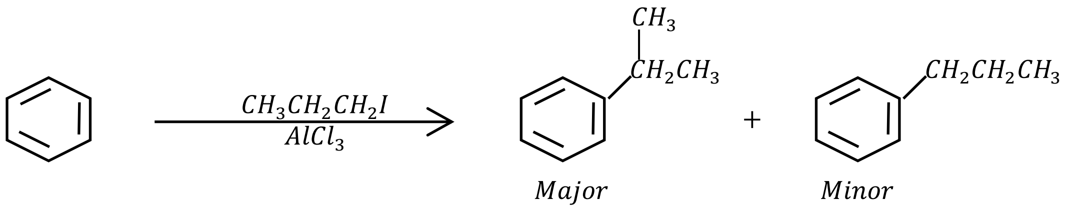
(i). Benzene reacts with alkenes in the presence of an acid to for alkyl benzene



(ii). Benzene reacts with alkyl halides in the presence of aluminium halides or iron(III) halides to form alkyl benzene.



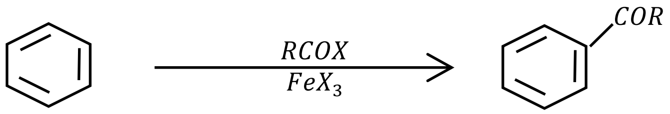
Note: When a primary alkyl halide has 3 or more carbon atoms, two products are formed. This is due to rearrangement that the primary carbocation undergoes to form a stable one. For example



Hence for synthesis of a compound like 1-phenylpropane, another indirect route is chosen that involves acylation.

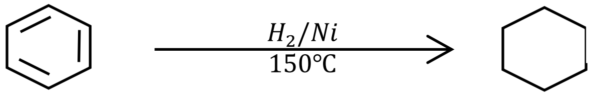
e. **Acylation**

Benzene reacts with acid halides in the presence of aluminium halides or iron(III) halides to form phenyl ketones



f. **Acylation**

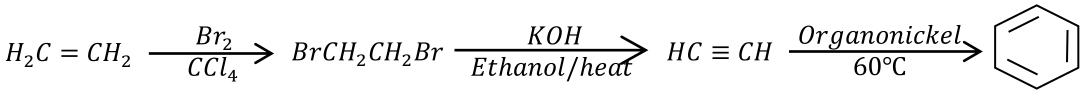
Benzene reacts with hydrogen in the presence of nickel catalyst at 150°C-200°C to form cyclohexane



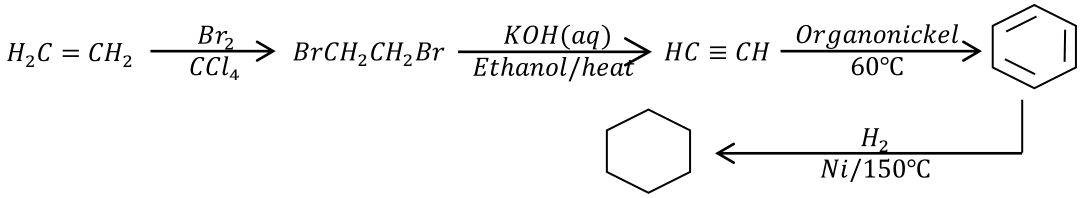
- **Question 7**

  Write equations to show how the following conversions can be made, and in each case, state the conditions for the reactions.

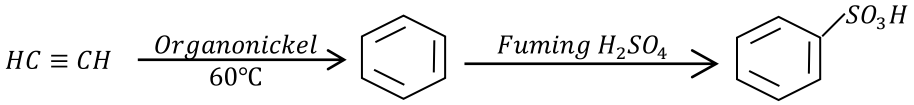
(a). Ethene to benzene



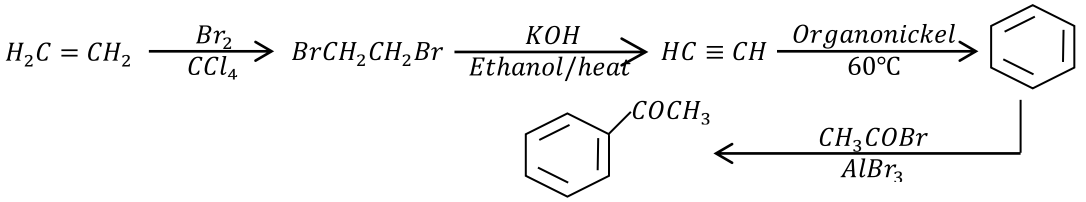
(b). Ethene to cyclohexane



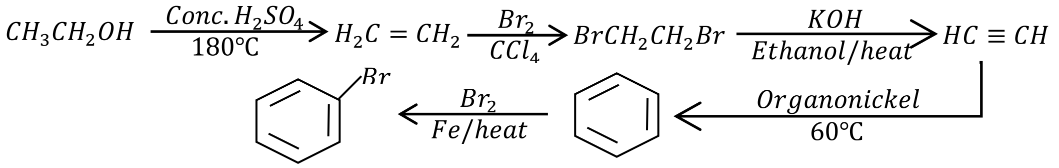
(c). Ethyne to benzenesulphonic acid



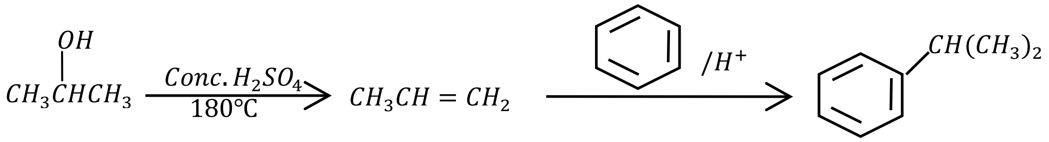
(d). Phenylethanone from ethene



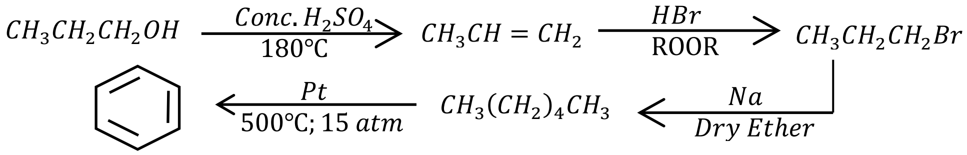
(e). Bromobenzene from ethanol



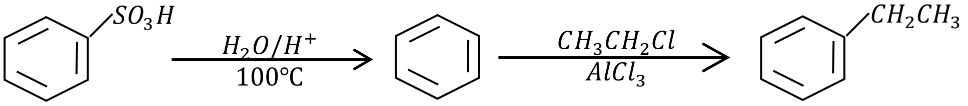
(f). Propan-2-ol to 2-phenylpropane



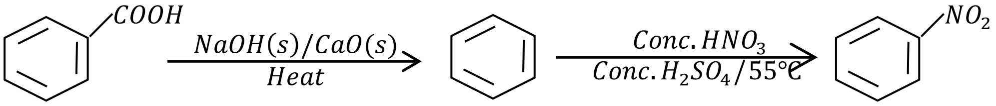
(g). Propan-1-ol to benzene



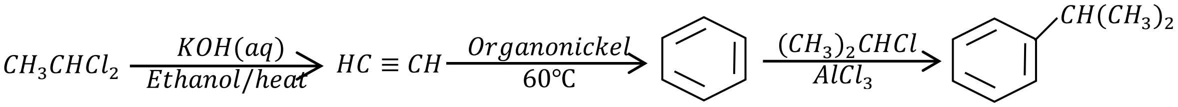
(h). Benzenesulphonic acid to Ethylbenzene



(i). Benzoic acid to Nitrobenzene



(j). 1,1-dichloroethane to 2-phenylpropane

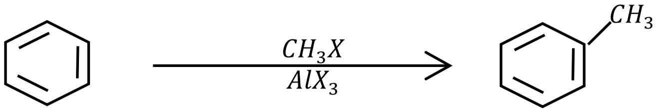


5. METHYLBENZENE (TOLUENE)

Preparation of methylbenzene

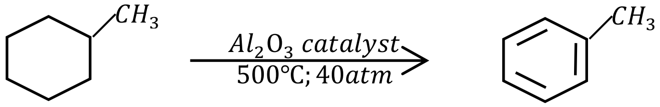
a. From benzene

Benzene reacts with methyl halides in the presence of aluminium halides or iron(III) halides to form methylbenzene.



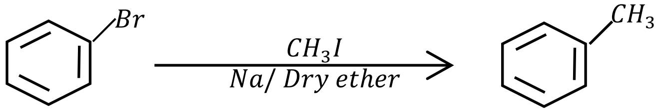
b. From methylcyclohexane

c. When methylcyclohexane is vaporised at 500°C and passed over aluminium oxide at 40atm (or platinum at 15atm), it is dehydrogenated to form methylbenzene



d. From bromobenzene

Bromobenzene reacts with iodomethane in the presence of sodium metal in dry ether to form methylbenzene.

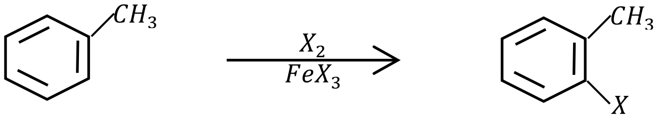


Reactions of methylbenzene

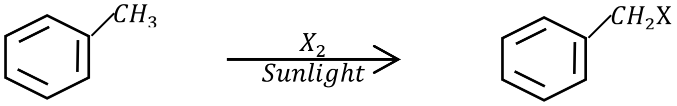
e. Reaction with chlorine and bromine

Methylbenzene reacts with chlorine or bromine in the presence of

(i). Aluminium halide or iron(III) halide to form 2-halomethylbenzene

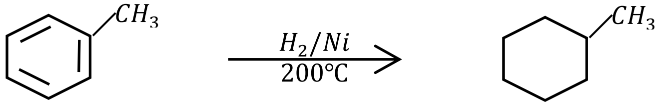


(ii). Sunlight or ultraviolet light to form (halomethyl)benzene



f. Reaction with hydrogen

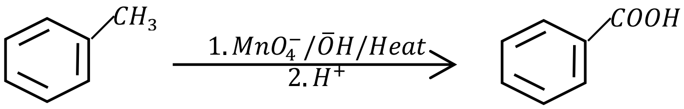
Methylbenzene reacts with hydrogen in the presence of nickel catalyst at 150°C-200°C to form methylcyclohexane



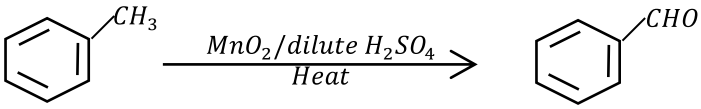
g. Oxidation reactions

(i). Methylbenzene is oxidised by strong oxidizing agents like potassium manganate(VII) in acid or alkaline conditions on heating to form benzoic acid

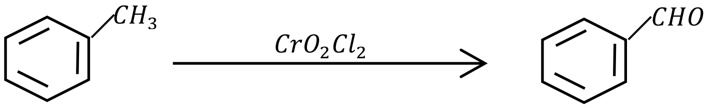
Using alkaline potassium manganate(VII), potassium benzoate is obtained as the product to which an acid is added to liberate benzoic acid



(i). Methylbenzene is oxidised by mild oxidizing agents like manganese(IV) oxide (or chromyl chloride) to form benzaldehyde



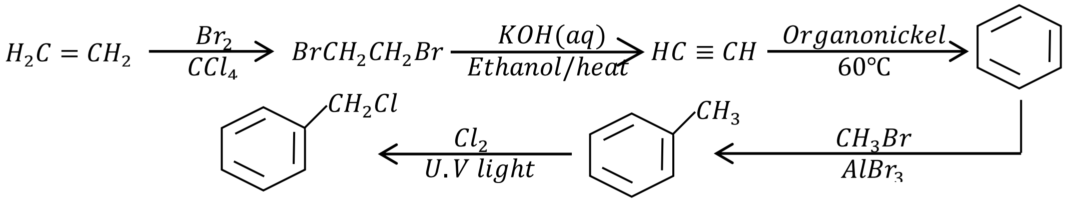
Or



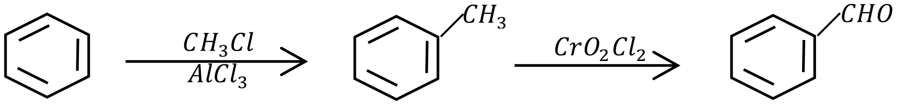
- **Question 8**

Write equations to show the conversion of the following

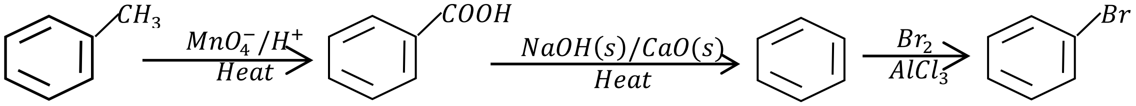
(a). Ethene to benzylchloride



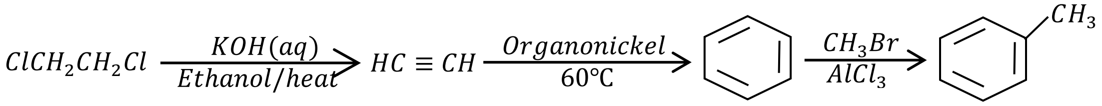
(a). Benzene to benzaldehyde



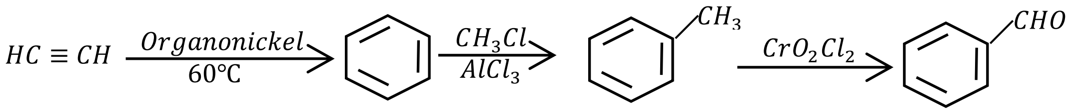
(b). Bromobenzene from methylbenzene



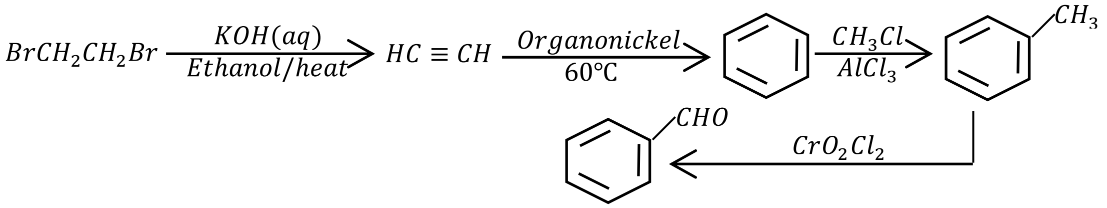
(c). 1,2-dichloroethane to methylbenzene



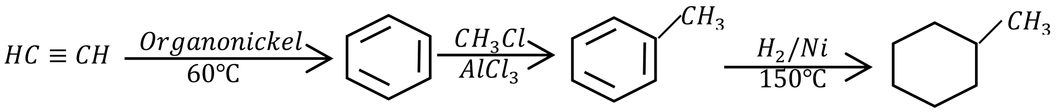
(d). Ethyne to benzaldehyde



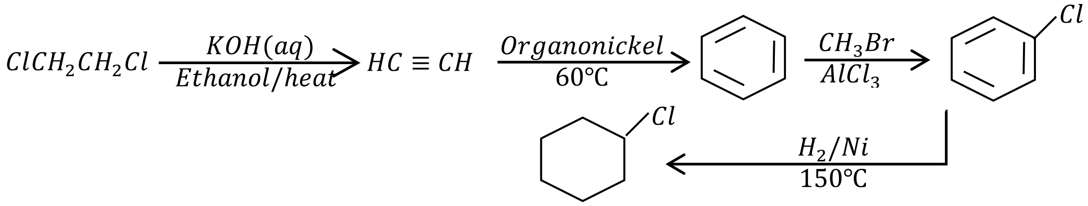
(e). 1,2-dibromoethane to benzaldehyde



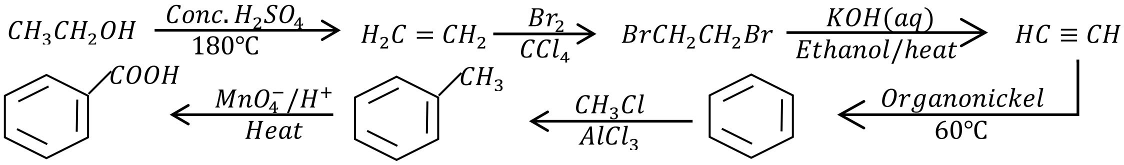
(f). Ethyne to methylcyclohexane



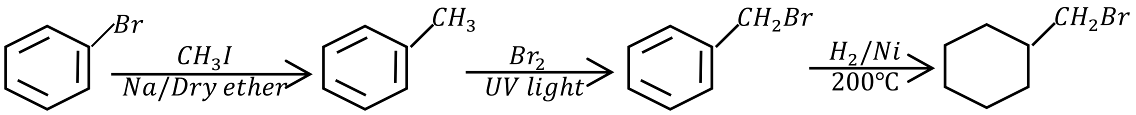
(g). Chlorocyclohexane from 1,2-dichloroethane



(h). Benzoic acid from ethanol.



(i). Bromobenzene from (bromomethyl)cyclohexane.

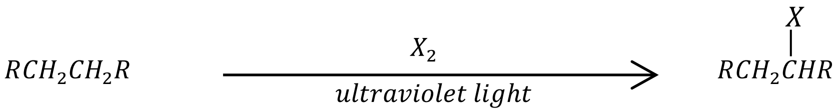


6. ALKYL HALIDES AND ALKYL DIHALIDES

Preparation of alkyl halides

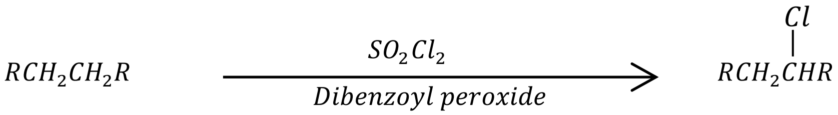
a. From alkanes: Alkanes react with

(i). Chlorine or bromine in the presence of ultraviolet light to form haloalkanes



$$RCH_2CH_2R \xrightarrow[ultraviolet\ light]{X_2} RCH_2\overset{\overset{X}{|}}{C}HR$$

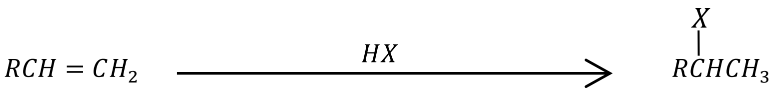
(ii). Sulphur dioxide dichloride in the presence of dibenzoyl peroxide to form alkyl chlorides



$$RCH_2CH_2R \xrightarrow[Dibenzoyl\ peroxide]{SO_2Cl_2} RCH_2\overset{\overset{Cl}{|}}{C}HR$$

b. From alkenes

(i). Alkenes react with halogen acids to form haloalkanes



$$RCH = CH_2 \xrightarrow{HX} R\overset{\overset{X}{|}}{C}HCH_3$$

(ii). Alkenes react with hydrogen bromide in the presence of an organic peroxide ($ROOR$) to form haloalkanes. However, this follows anti-Markovnikoff's addition

$$RCH = CH_2 \xrightarrow{HBr\ /\ ROOR} RCH_2CH_2Br$$

c. From alcohols

(iii). Alcohols react with phosphorus(V) chloride (or when refluxed phosphorus trihalides) to form the corresponding alkyl halides.

$$ROH \xrightarrow{PCl_5} RCl$$

$$ROH \xrightarrow[reflux]{PX_3} RX$$

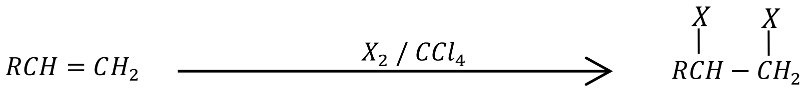
(iv). Alcohols react when refluxed with thionyl chloride in the presence of pyridine to form haloalkanes

$$ROH \xrightarrow[Pyridine/reflux]{SOCl_2} RCl$$

Preparation of of dihaloalkanes

d. From alkenes

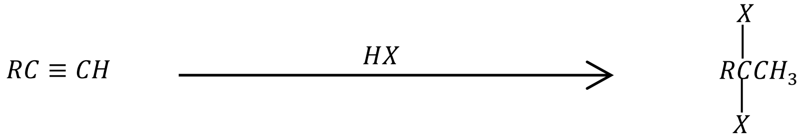
Alkenes react with halogens in the presence of an inert solvent like carbon tetrachloride to form vicinal dihaloalkanes (alkyl dihalides).



$$RCH = CH_2 \xrightarrow{X_2\ /\ CCl_4} R\overset{\overset{X}{|}}{C}H - \overset{\overset{X}{|}}{C}H_2$$

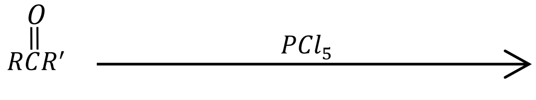
e. **From alkynes**

Alkynes act with halogen acids to form gem dihaloalkanes



$$RC \equiv CH \xrightarrow{HX} R\overset{X}{\underset{X}{C}}CH_3$$

f. **From carbonyl compounds (aldehydes and ketones)**



$$R\overset{O}{\overset{\|}{C}}R' \xrightarrow{PCl_5} R\overset{Cl}{\underset{Cl}{C}}R'$$

$(Aldehyde\ if\ R' = H;\ Ketone\ if\ R' \neq H)$

Reactions of alkyl halides

g. **Reaction with aqueous sodium hydroxide solution**

Alkyl halides react with aqueous sodium hydroxide on refluxing (or heating) on to form alcohols

$$RCH_2X \xrightarrow[reflux]{NaOH(\text{aq})} RCH_2OH$$

If alcohols are required then primary and secondary alkyl halides are used because the tertiary alkyl halides undergo elimination to form much of the alkene instead.

h. **Reaction of tertiary alkyl halides with water**

Tertiary alkyl halides react with water on boiling to form tertiary alcohols

$$R_3C - X \xrightarrow[Boil]{H_2O} R_3C - OH$$

i. **Reaction with hot alcoholic potassium hydroxide (or sodium hydroxide) solution**

Alkyl halides react to form alkenes.

$$RCH_2CH_2X \xrightarrow[CH_3CH_2OH\ /\ heat]{KOH(aq)} RCH = CH_2$$

j. **Reaction with alkoxides to form ethers (Williamson's synthesis)**

Primary alkyl halides sodium alkoxides on boiling (reflux) to form ethers. (ROR).

$$R'X \xrightarrow[boil]{RO^-Na^+} R'OR$$

Secondary and tertiary alkyl halides would give mainly alkenes because they easily undergo elimination reactions.

k. **Reaction with potassium cyanide**

Primary and secondary alkyl halides react with alcoholic potassium cyanide on heating to form nitriles

$$R'CH_2X \xrightarrow[Ethanol/Heat]{KCN} R'CH_2CN$$

Note: This reaction increases the length of the carbon chain in the compound.

Secondary alkyl halides form mixed products but tertiary alkyl halides give only the elimination product because the cyanide ion is a strong base.

l. Reaction with silver alkanoates

Silver(I) alkanoates ($RCO\bar{O}Ag^+$) react with alkyl halides to form esters

$$RX \xrightarrow{R'CO\bar{O}Ag^+} R'COOR$$

m. Reaction with ammonia

Alkyl halides react with ammonia in the presence of an alcohol when heated in a sealed tube to form mixture of amines. The products can be separated by fractional distillation

$$RX \xrightarrow[\text{Heat in sealed tube}]{NH_3/ethanol} RNH_2 + R_2NH + NR_3$$

n. Reaction with magnesium (Formation of Grignard reagents)

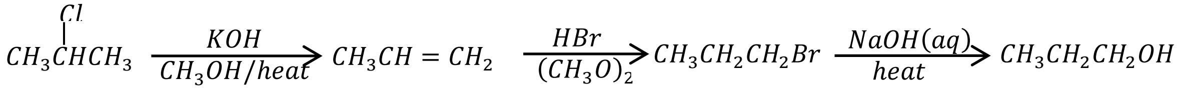
Alkyl halides react with magnesium in the presence of dry ether to form alkylmagnesium halides. All types of alkyl halides undergo this reaction

$$R'X \xrightarrow[\text{Dry ether}]{Mg} R'MgX$$

Question 9

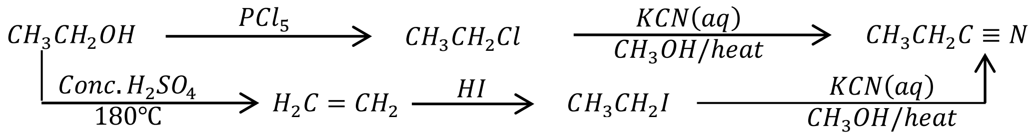
Write equations to show how the following compounds can be synthesised from each of the following substances and in each case, indicate the conditions for the reactions.

(a). 2-bromopropane to propan-1-ol



$$CH_3\overset{Cl}{\overset{|}{C}}HCH_3 \xrightarrow[CH_3OH/heat]{KOH} CH_3CH=CH_2 \xrightarrow[(CH_3O)_2]{HBr} CH_3CH_2CH_2Br \xrightarrow[heat]{NaOH(aq)} CH_3CH_2CH_2OH$$

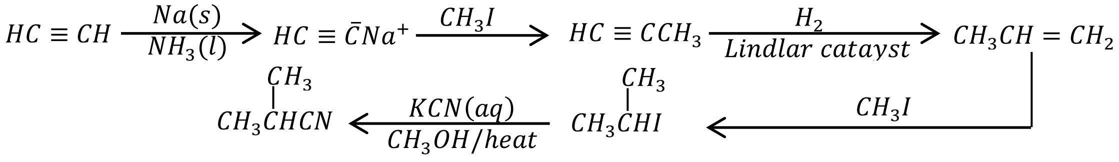
(b). Ethanol to propanenitrile



$$CH_3CH_2OH \xrightarrow{PCl_5} CH_3CH_2Cl \xrightarrow[CH_3OH/heat]{KCN(aq)} CH_3CH_2C\equiv N$$

$$CH_3CH_2OH \xrightarrow[180°C]{Conc.\,H_2SO_4} H_2C=CH_2 \xrightarrow{HI} CH_3CH_2I \xrightarrow[CH_3OH/heat]{KCN(aq)} CH_3CH_2C\equiv N$$

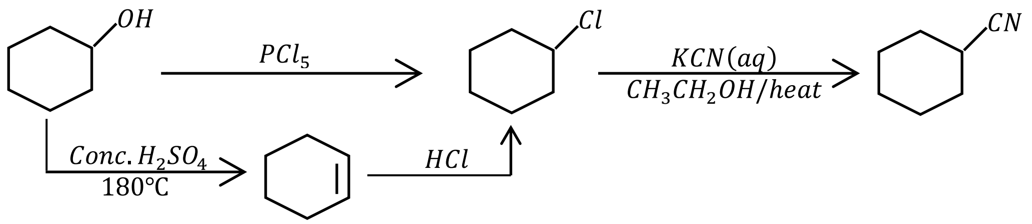
(c). Ethyne to 2-methylpropanenitrile



$$HC\equiv CH \xrightarrow[NH_3(l)]{Na(s)} HC\equiv\bar{C}Na^+ \xrightarrow{CH_3I} HC\equiv CCH_3 \xrightarrow[\text{Lindlar catayst}]{H_2} CH_3CH=CH_2$$

$$CH_3CH=CH_2 \xrightarrow{CH_3I} CH_3\overset{CH_3}{\overset{|}{C}}HI \xrightarrow[CH_3OH/heat]{KCN(aq)} CH_3\overset{CH_3}{\overset{|}{C}}HCN$$

(d). Cyclohexanol to cyclohexanecarbonitrile

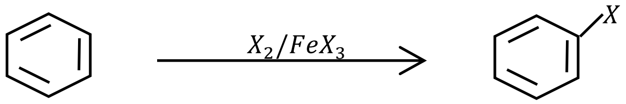


7. HALOBENZENE

Preparation of halobenzene

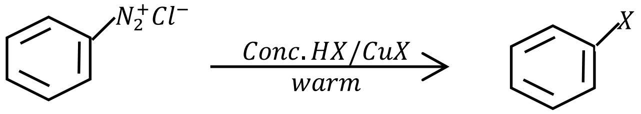
a. From benzene.

Benzene reacts with chlorine and bromine in the presence of aluminium halides or iron(III) halides to form chlorobenzene or bromobenzene ($X = Cl\ or\ Br$)

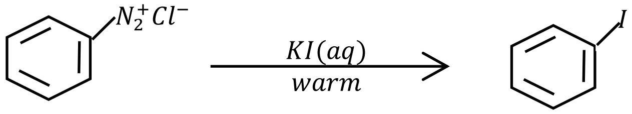


b. From Benzene diazonium chloride

When Benzene diazonium is warmed to 100℃ with concentrated HCl and HBr in the presence of copper(I) chloride and copper(I) bromide respectively, the corresponding halobenzene halobenzene if formed.



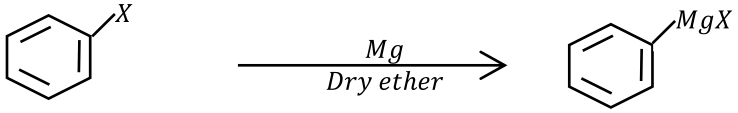
Iodobenzene is obtained by warming a mixture of the benzenediazonium chloride with potassium iodide solution.



Reaction of halobenzene

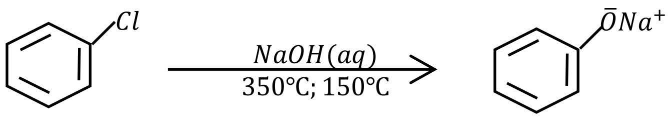
c. Formation of Grignard reagents

Halobezenes react with magnesium in dry ether to form phenylmagnesium halides

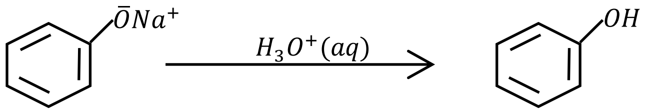


d. Reaction with concentrated sodium hydroxide solutoin

Chlorobenzene is allowed to react with aqueous sodium hydroxide at a temperature of about 350°C and a pressure of 150 atm to form sodium phenoxide.

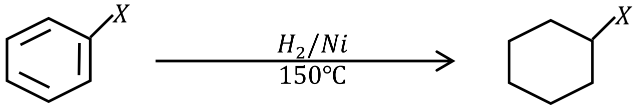


Reacting sodium phenoxide with a dilute acid produces a phenol



e. **Reaction with hydrogen**

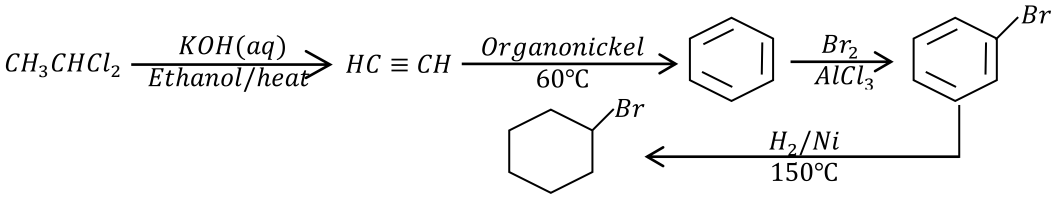
Halobenzenes react with hydrogen in the presence of nickel at a temperature range of 150℃ – 200℃ to form to halocyclohexane



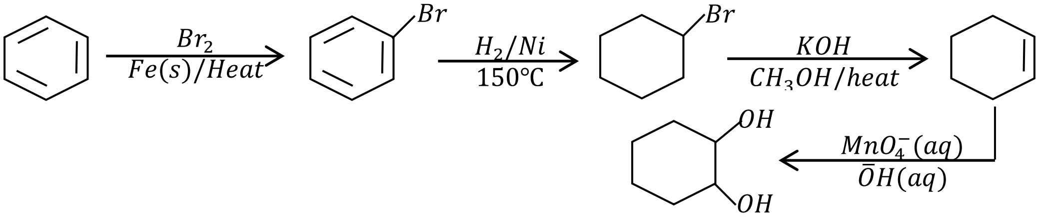
- **Question 10**

Write equations to show how the following conversions can be made

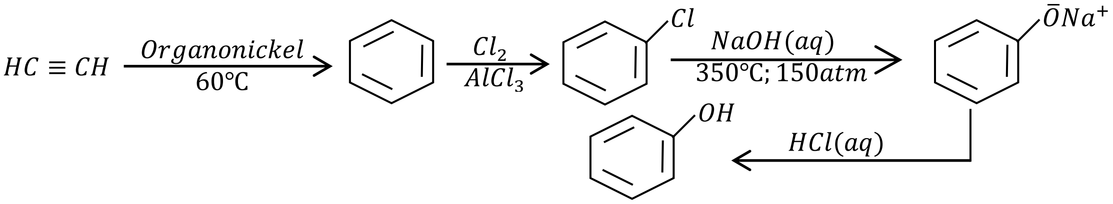
a. 1,1-dibromoethane to bromocyclohexane.



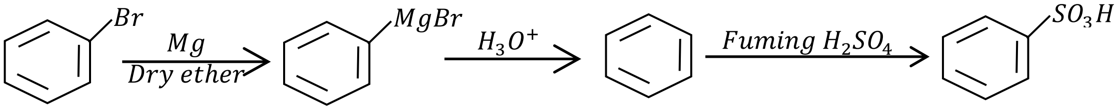
b. Benzene to cyclohexane-1,2-diol



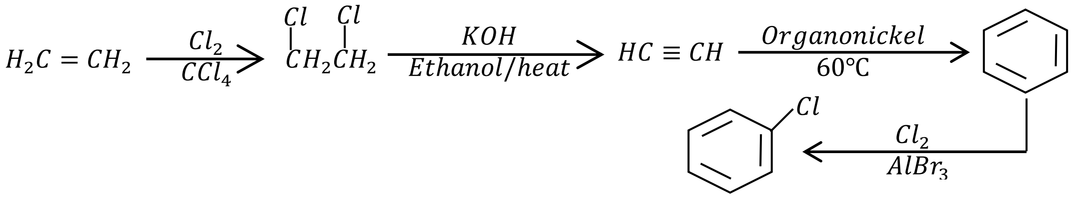
c. Ethyne to phenol



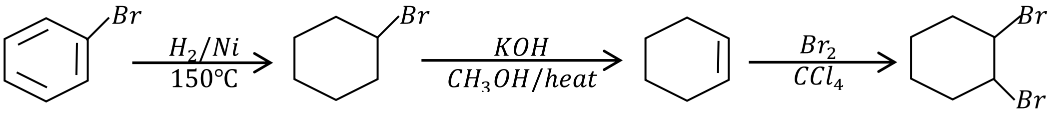
d. Bromobenzene to benzenesulphonic acid



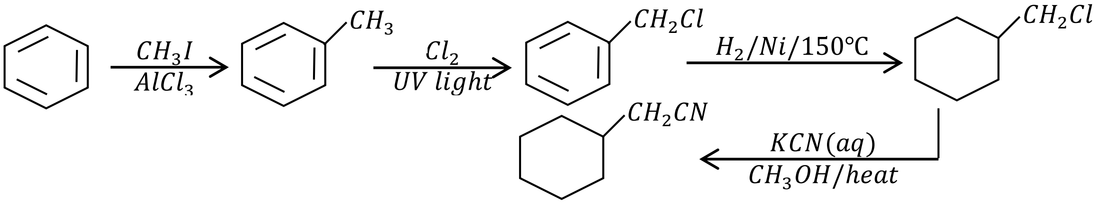
e. Ethene to chlorobenzene



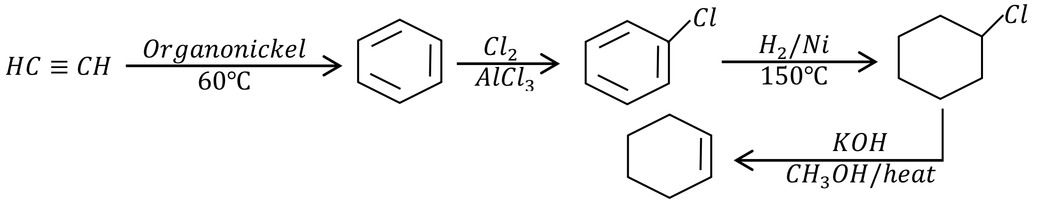
f. Bromobenzene to 1,2-dibromocyclohexane



g. Benzene to cyclohexylethanenitrile



h. Ethyne to cyclohexene

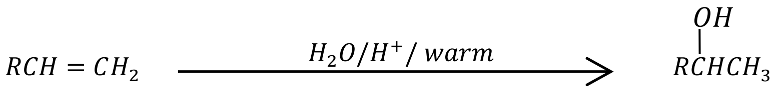


8. ALCOHOLS

Preparation of alcohols

a. From alkenes

Alkenes react with dilute sulphuric acid on warming to form alcohols, $(R - OH)$.



$$RCH = CH_2 \xrightarrow{H_2O/H^+/\ warm} RCH(OH)CH_3$$

b. From alkyl halides

(i). Alkyl halides react with aqueous sodium hydroxide on refluxing (or heating) on to form alcohols

$$RCH_2X \xrightarrow[reflux]{NaOH(\text{aq})} RCH_2OH$$

NOTE: Primary and secondary alkyl halides are used to form primary and secondary alcohols because the tertiary alkyl halides undergo elimination to form much of the alkene instead.

(ii). Tertiary alkyl halides react with water on boiling to form tertiary alcohols

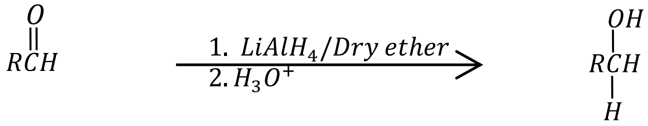
$$R_3C - X \xrightarrow[Boil]{H_2O} R_3C - OH$$

c. **From carbonyl compounds**

Carbonyl compounds when reduced (addition of hydrogen) form alcohols. Common reducing agents are

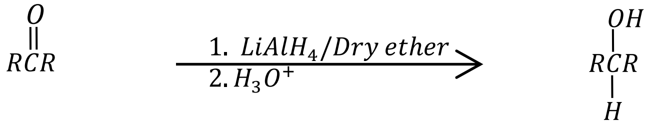
- Lithium aluminium hydride ($LiAlH_4$) which is always dissolved in dry ether.
- Sodium boron hydride (AlH_4) which can be dissolved in alcohol or water.
  Sodium boron hydride is weaker reducing agent than lithium aluminium hydride
  The reduction in each case is completed by hydrolysis in acidified water to yield the desired product

(i). Aldehydes are reduced to primary alcohols



$$R\overset{\overset{O}{\|}}{C}H \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4/Dry\ ether} R\overset{OH}{\underset{H}{C}}H$$

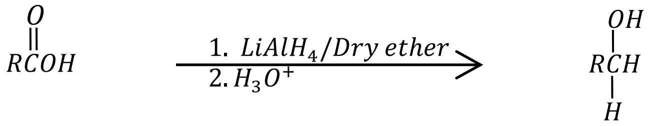
(ii). Ketones are reduced to secondary alcohols. ($R\ R \neq H\ alkyl\ group$)



$$R\overset{\overset{O}{\|}}{C}R \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4/Dry\ ether} R\overset{OH}{\underset{H}{C}}R$$

d. **From carboxylic acids**

Carboxylic acids are reduced by lithium aluminium hydride to primary alcohols

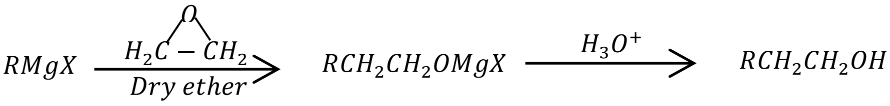


$$R\overset{\overset{O}{\|}}{C}OH \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4/Dry\ ether} R\overset{OH}{\underset{H}{C}}H$$

e. **From Grignard reagents**

Grignard reagents react with

(i). Epoxyethane in the presence of dry ether to form primary alcohols



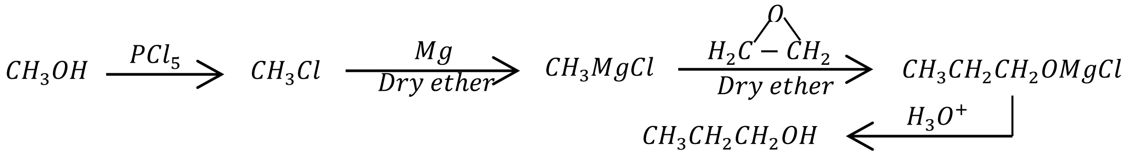
$$RMgX \xrightarrow[Dry\ ether]{H_2C - CH_2\ (O)} RCH_2CH_2OMgX \xrightarrow{H_3O^+} RCH_2CH_2OH$$

NOTE: this reaction increases the length of the carbon chain by two carbon atoms

Example

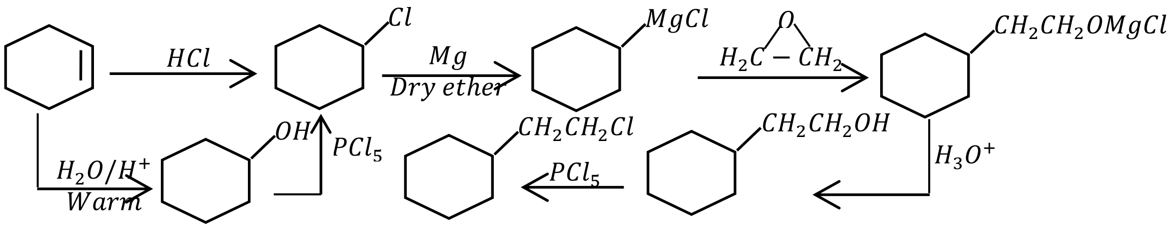
Show how the following conversions can be made

- Methanol to propanal

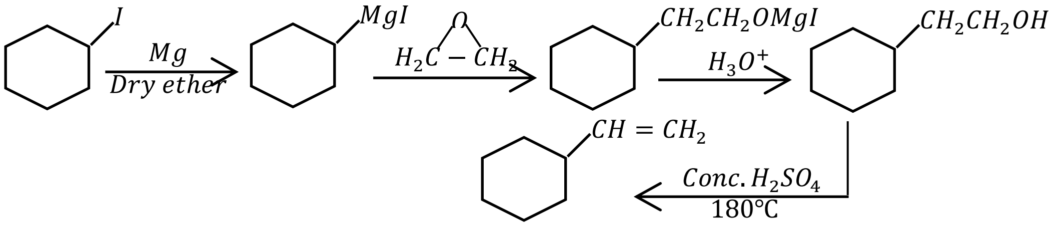


$$CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow[Dry\ ether]{Mg} CH_3MgCl \xrightarrow[Dry\ ether]{\overset{O}{H_2C - CH_2}} CH_3CH_2CH_2OMgCl \xrightarrow{H_3O^+} CH_3CH_2CH_2OH$$

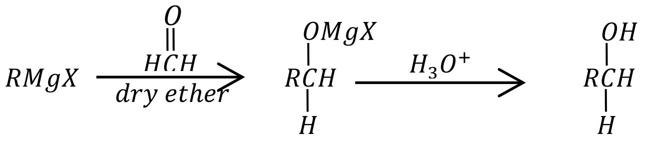
- Cyclohexene to 1-chloro-2-cyclohexylethane



- Iodocyclohexane to cyclohexylethene



(ii). Methanal in the presence of dry ether to form primary alcohols



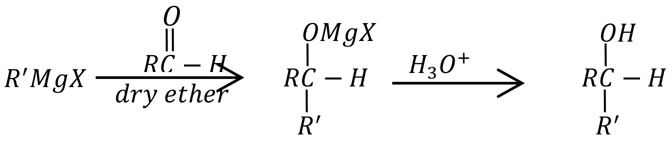
$$RMgX \xrightarrow[dry\ ether]{\overset{\overset{O}{\|}}{HCH}} \overset{OMgX}{\underset{H}{RCH}} \xrightarrow{H_3O^+} \overset{OH}{\underset{H}{RCH}}$$

NOTE: The number of carbon atoms is increased by one

Example: Write equations to show how iodomethane can be converted to ethanol

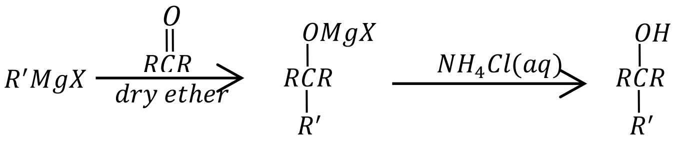
$$CH_3I \xrightarrow[Dry\ ether]{Mg} CH_3MgI \xrightarrow[Dry\ ether]{HCHO} CH_3CH_2OMgI \xrightarrow{H_3O^+} H_3CH_2OH$$

(iii). Aldehydes with two or more carbon atoms to form secondary alcohols



$$R'MgX \xrightarrow[dry\ ether]{\overset{\overset{O}{\|}}{RC - H}} \overset{OMgX}{\underset{R'}{RC - H}} \xrightarrow{H_3O^+} \overset{OH}{\underset{R'}{RC - H}}$$

(iv). Ketones to form tertiary alcohols. Hydrolysis is done using aqueous ammonium chloride not an acid. This is to prevent elimination reactions from taking place



$$R'MgX \xrightarrow[dry\ ether]{R\overset{O}{\overset{\|}{C}}R} R\overset{OMgX}{\underset{R'}{C}}R \xrightarrow{NH_4Cl(aq)} R\overset{OH}{\underset{R'}{C}}R$$

Reactions of alcohols

f. Reaction with sodium

Alcohols react with sodium to form sodium alkoxides and hydrogen gas

$$2ROH \ + \ 2Na \longrightarrow 2RO^-Na^+ + \ + H_2$$

g. Formation of alkyl halides

(i). Alcohols react with phosphorus(V) chloride (or when refluxed phosphorus trihalides) to form the corresponding alkyl halides.

$$ROH \xrightarrow{PCl_5} RCl$$

$$ROH \xrightarrow[reflux]{PX_3} RX$$

(ii). Alcohols react when refluxed with thionyl chloride in the presence of pyridine to form haloalkanes

$$ROH \xrightarrow[Pyridine/reflux]{SOCl_2} RCl$$

h. Oxidation of alcohols

Common oxidizing agents are

- Acidified potassium manganate(VII) [Strong]
- Acidified potassium dichromate(VI) [Weaker than permanganate]
- Oxygen / copper at 300°C. [Mild]
- Hypochlorous acid $(NaOCl\ /CH_3COOH).[Mild]$ $(Organic\ chemistry\ by\ Paula\ Bruice)$

(i). Primary alcohols are oxidised to

- Aldehydes by mild oxidising agents

$$RCH_2OH \xrightarrow[Heat]{Cr_2O_7^{2-}/H^+} RCHO$$

$$RCH_2OH \xrightarrow[300°C]{O_2/Cu} RCHO$$

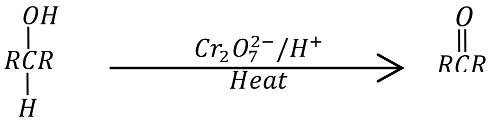
$$RCH_2OH \xrightarrow[0°C]{NaOCl\ /CH_3COOH} RCHO$$

- Carboxylic acids by strong oxidising agents.

$$RCH_2OH \xrightarrow[Heat]{Cr_2O_7^{2-}/H^+} RCOOH$$

$$RCH_2OH \xrightarrow[Heat]{MnO_4^-/H^+} RCOOH$$

(ii). Secondary alcohols are oxidised to ketones by all the above oxidising agents

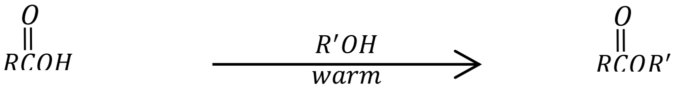


$$R\overset{OH}{\underset{H}{C}}R \xrightarrow[Heat]{Cr_2O_7^{2-}/H^+} R\overset{O}{\overset{\|}{C}}R$$

(iii). Tertiary alcohols are not oxidised

i. Reaction with carboxylic acids

Alcohols react with carboxylic acid when warmed in the presence of concentrated sulphuric acid or dry hydrogen chloride gas to form esters.



$$R\overset{O}{\overset{\|}{C}}OH \xrightarrow[warm]{R'OH} R\overset{O}{\overset{\|}{C}}OR'$$

j. Reaction with concentrated sulphuric acid

(i). Alcohols react with cold concentrated sulphuric acid to for alkyl hydrogensulphate

$$ROH \xrightarrow[0℃]{Conc. H_2SO_4} ROSO_3H$$

(ii). Primary alcohols react with concentrated sulphuric acid at 140℃ to form ethers. The alcohol should be in excess.

$$2ROH \xrightarrow[140℃]{Conc. H_2SO_4} ROR$$

(iii). Alcohols are dehydrated by hot concentrated sulphuric acid to form alkenes. The temperature at which dehydration occurs depends on the type of alcohol

- Primary alcohols – 170 – 180℃
- Secondary alcohols – 100 – 120℃
- Tertiary alcohols – 80 – 90℃

For this reason, some reactions will have heat instead of specific temperature especially for secondary and tertiary alcohols.

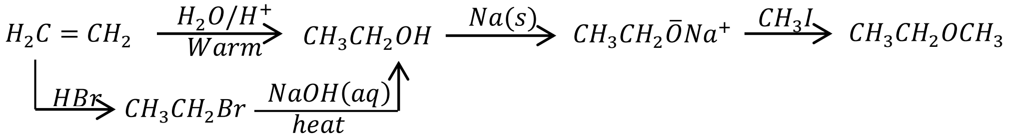
Always, the most stable alkene is formed as the major product

$$RCH_2CH_2OH \xrightarrow[180℃]{Conc. H_2SO_4} RCH = CH_2$$

- **Question 11**

  Write equations to show how the following conversions can be made, and in each case, state the conditions for the reactions.

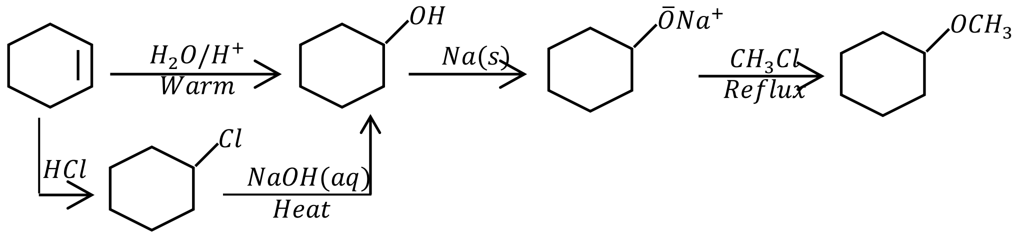
(a). Ethene to methoxyethane



$$H_2C = CH_2 \xrightarrow[Warm]{H_2O/H^+} CH_3CH_2OH \xrightarrow{Na(s)} CH_3CH_2\bar{O}Na^+ \xrightarrow{CH_3I} CH_3CH_2OCH_3$$

$$H_2C = CH_2 \xrightarrow{HBr} CH_3CH_2Br \xrightarrow[heat]{NaOH(aq)} CH_3CH_2OH$$

(b). Cyclohexene to methoxycyclohexane



(c). 2-methylpropene to 3-methylbutanal

$$(CH_3)_2C=CH_2 \xrightarrow[ROOR]{HBr} (CH_3)_2CHCH_2Br \xrightarrow[Dry\ ether]{Mg} (CH_3)_2CHCH_2MgBr \xrightarrow[Dry\ ether]{HCHO}$$

$$(CH_3)_2CHCHO \xleftarrow[300^\circ C]{O_2/Cu} (CH_3)_2CHCH_2OH \xleftarrow{H^+(aq)} (CH_3)_2CHCH_2OMgBr$$

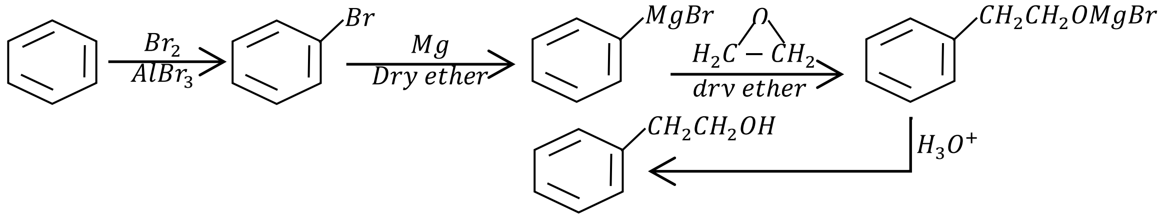
(d). 2-methylpropene to 2-methoxy-2-methylpropane

$$(CH_3)_2C=CH_2 \xrightarrow[warm]{H_2O/H^+} (CH_3)_3C-OH \xrightarrow{Na(s)} (CH_3)_3C-\bar{O}Na^+ \xrightarrow[reflux]{CH_3OH} (CH_3)_3C-OCH_3$$

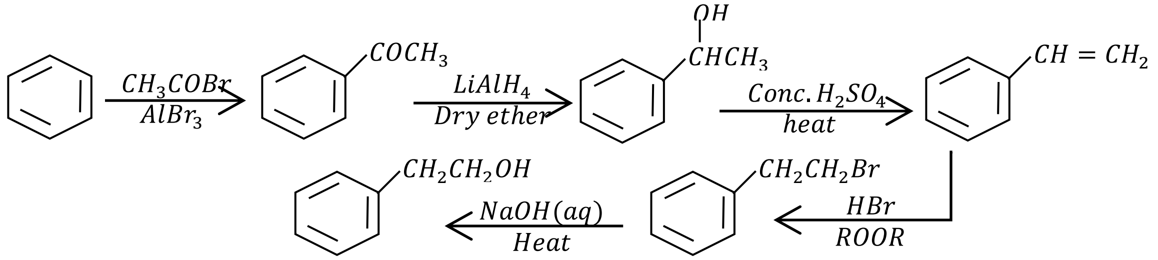
(e). 2-iodopropane to propanoic acid

$$CH_3CH=CH_2 \xrightarrow[ROOR]{HBr} CH_3CH_2CH_2Br \xrightarrow[Heat]{NaOH(aq)} CH_3CH_2CH_2OH \xrightarrow[Heat]{Cr_2O_7^{2-}/H^+} CH_3CH_2COOH$$

(f). Benzene to 1-phenylethanol



Or



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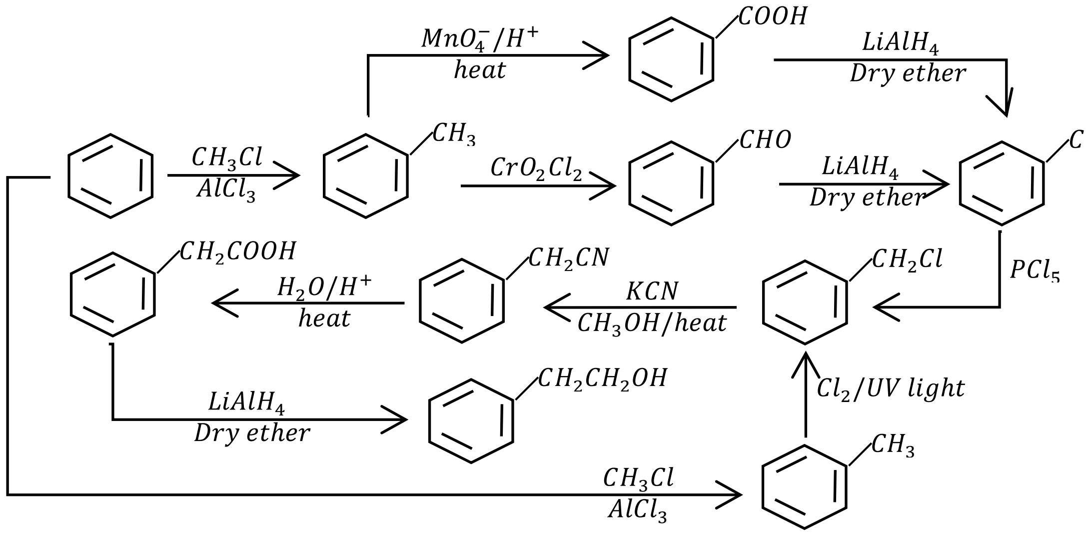
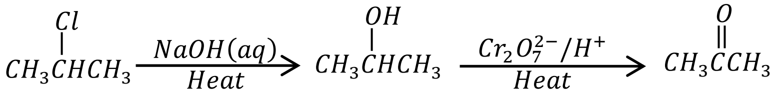


- **Question 12**

Write equations to show how the following compounds can be synthesised

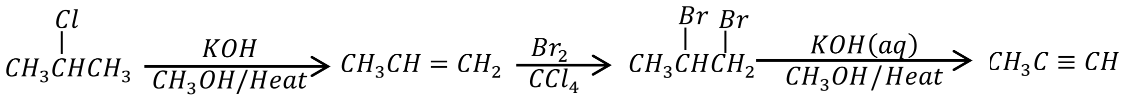
(a). 2-chloropropane to

(i). Propanone



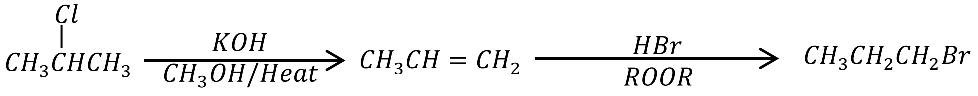
$$CH_3\overset{\overset{Cl}{|}}{C}HCH_3 \xrightarrow[Heat]{NaOH(aq)} CH_3\overset{\overset{OH}{|}}{C}HCH_3 \xrightarrow[Heat]{Cr_2O_7^{2-}/H^+} CH_3\overset{\overset{O}{\|}}{C}CH_3$$

(ii). Propyne



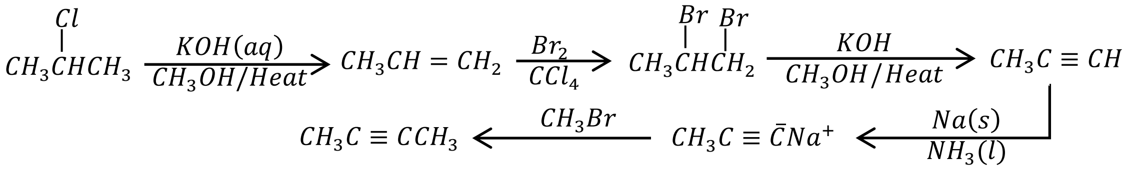
$$CH_3\overset{\overset{Cl}{|}}{C}HCH_3 \xrightarrow[CH_3OH/Heat]{KOH} CH_3CH=CH_2 \xrightarrow[CCl_4]{Br_2} CH_3\overset{\overset{Br}{|}}{C}H\overset{\overset{Br}{|}}{C}H_2 \xrightarrow[CH_3OH/Heat]{KOH(aq)} CH_3C\equiv CH$$

(iii). 1-bromopropane



$$CH_3\overset{\overset{Cl}{|}}{C}HCH_3 \xrightarrow[CH_3OH/Heat]{KOH} CH_3CH=CH_2 \xrightarrow[ROOR]{HBr} CH_3CH_2CH_2Br$$

(iv). But-2-yne

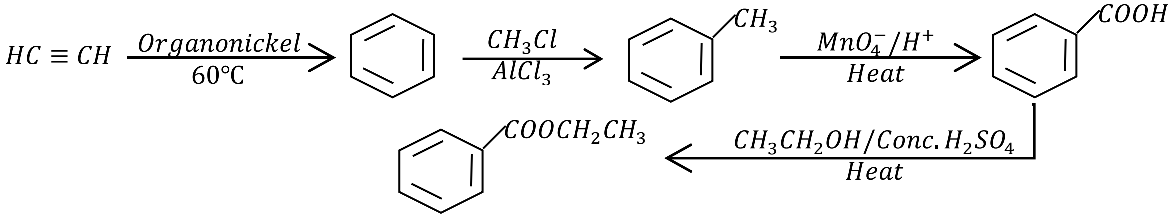


$$CH_3\overset{\overset{Cl}{|}}{C}HCH_3 \xrightarrow[CH_3OH/Heat]{KOH(aq)} CH_3CH=CH_2 \xrightarrow[CCl_4]{Br_2} CH_3\overset{\overset{Br}{|}}{C}H\overset{\overset{Br}{|}}{C}H_2 \xrightarrow[CH_3OH/Heat]{KOH} CH_3C\equiv CH$$

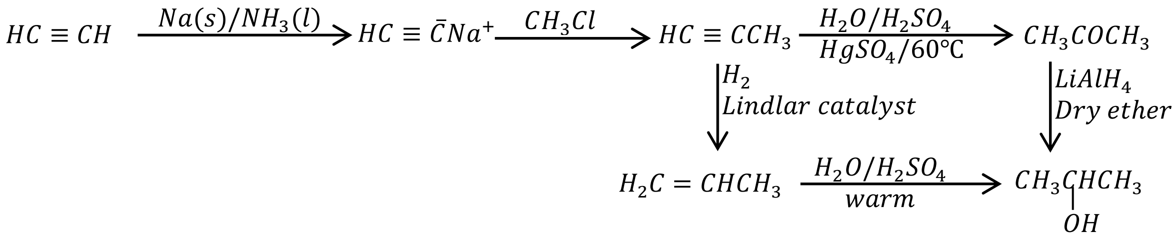
$$CH_3C\equiv CH \xrightarrow[NH_3(l)]{Na(s)} CH_3C\equiv\bar{C}Na^+ \xrightarrow{CH_3Br} CH_3C\equiv CCH_3$$

(b). Ethyne

(i). Ethyl benzoate



(ii). Propan-2-ol



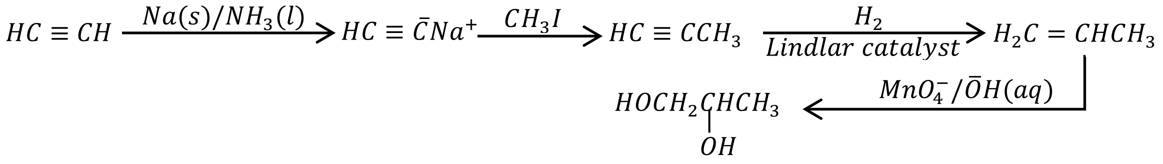
$$HC\equiv CH \xrightarrow{Na(s)/NH_3(l)} HC\equiv \bar{C}Na^+ \xrightarrow{CH_3Cl} HC\equiv CCH_3 \xrightarrow[HgSO_4/60^\circ C]{H_2O/H_2SO_4} CH_3COCH_3 \xrightarrow[Dry\ ether]{LiAlH_4} CH_3CH(OH)CH_3$$

$$HC\equiv CCH_3 \xrightarrow[Lindlar\ catalyst]{H_2} H_2C=CHCH_3 \xrightarrow[warm]{H_2O/H_2SO_4} CH_3CH(OH)CH_3$$

(iii). Propan-1-ol

$$HC\equiv CH \xrightarrow{Na(s)/NH_3(l)} HC\equiv \bar{C}Na^+ \xrightarrow{CH_3Br} HC\equiv CCH_3 \xrightarrow[Lindlar\ catalyst]{H_2} H_2C=CHCH_3 \xrightarrow[ROOR]{HBr} BrCH_2CH_2CH_3 \xrightarrow[Heat]{NaOH(aq)} HOCH_2CH_2CH_3$$

(iv). Propane1,2-diol



$$HC\equiv CH \xrightarrow{Na(s)/NH_3(l)} HC\equiv \bar{C}Na^+ \xrightarrow{CH_3I} HC\equiv CCH_3 \xrightarrow[Lindlar\ catalyst]{H_2} H_2C=CHCH_3 \xrightarrow{MnO_4^-/\bar{O}H(aq)} HOCH_2CH(OH)CH_3$$

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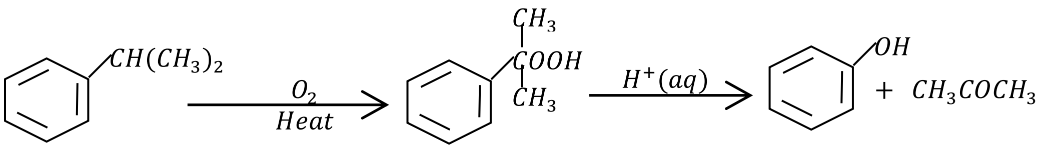
9. PHENOL

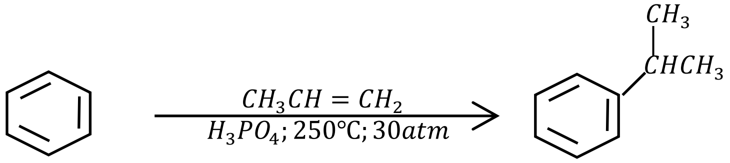
Preparation of phenol

a. From cumene (2-phehylpropane)

Cumene is reacted with hot air to form cumene hydroperoxide. This is reacted with an acid to produce phenol and propanone

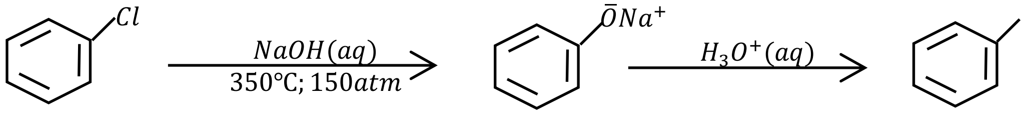


The cumene is produced by reacting benzene with propene in the presence of phosphoric acid catalyst at 250°C and 30 atm.



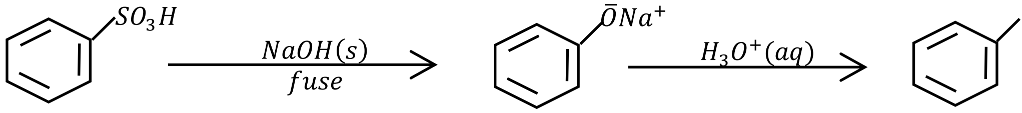
b. From chlorobenzene

Chlorobenzene is allowed to react with aqueous sodium hydroxide at a temperature of about 350°C and a pressure of 150 atm to form sodium phenoxide. Reacting sodium phenoxide with a dilute acid produces a phenol



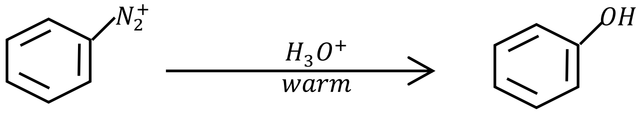
c. From benzenesulphonic acid

Benzenesulphonic acid is fused sodium hydroxide at a temperature of about 300°C to form sodium phenoxide. Reacting sodium phenoxide with a dilute acid produces a phenol.



d. From benzene diazonium salts

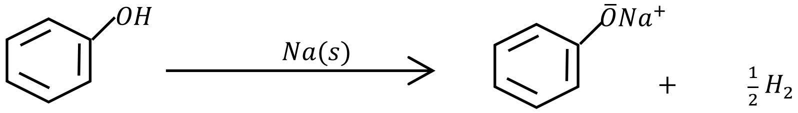
When benzene diazonium chloride is heated with a dilute, phenol is formed



Reaction of phenol

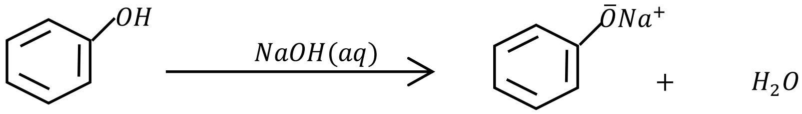
e. Reaction with sodium

Phenol reacts with sodium metal to form sodium phenoxide and hydrogen gas



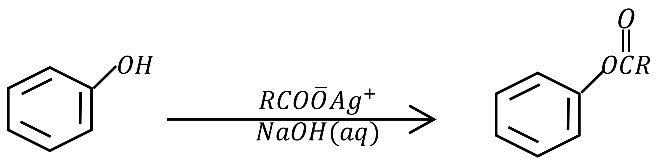
f. Reaction with sodium hydroxide

Phenol reacts with sodium metal to form sodium phenoxide



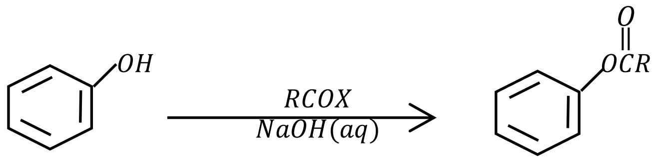
g. Reaction with silver alkanoates

Phenols react with silver salts of carboxylic acids to form ester in the presence of sodium hydroxide



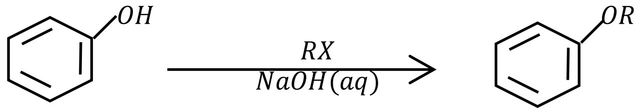
h. Reaction with acid halides

Acid halides react with alkaline solutions of phenols to form esters



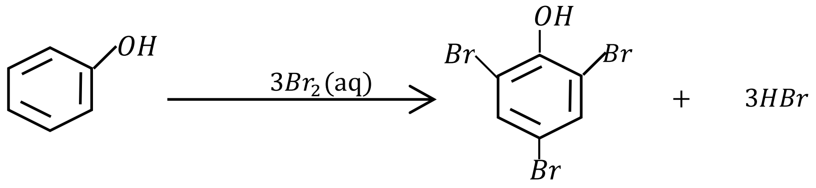
i. Reaction with alkyl halides

Alkyl halides react with alkaline solutions of phenols to form ethers



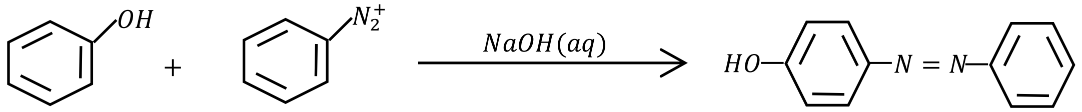
j. Reaction with bromine water

Phenol reacts with bromine water to form a white precipitate of 2,4,6-tribromophenol



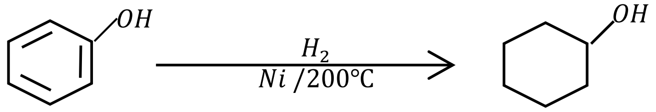
k. Reaction with diazonium salts

Benzene diazonium salts react with alkaline solutions of phenols to for azo dyes



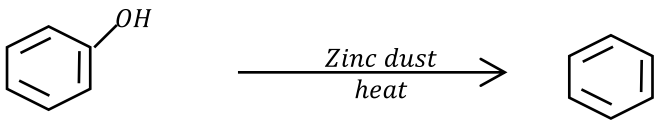
l. Reaction with hydrogen

Phenol reacts with hydrogen in the presence of nickel catalyst at $150 - 200℃$ to form cyclohexanol



m. Reaction with zinc dust

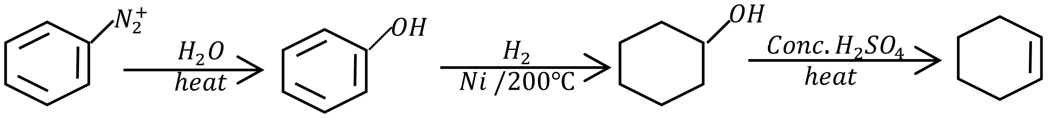
When phenol is heated with zinc dust, benzene is formed



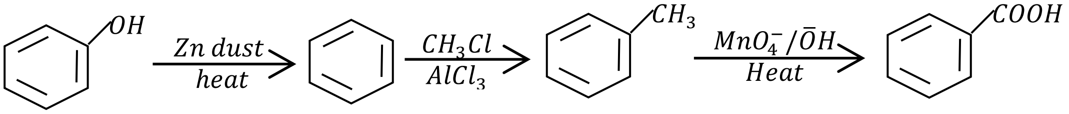
- **Question 13**

Write equations to show how the following compounds can be synthesised

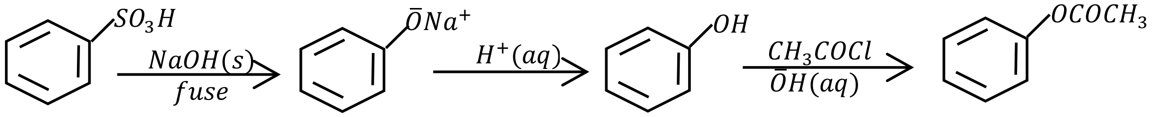
(a). Benzene diazonium chloride to cyclohexene



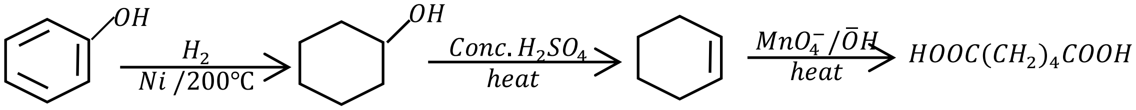
(b). Phenol to benzoic acid



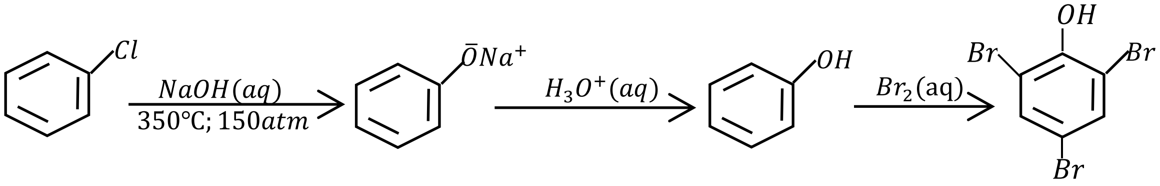
(c). Benzenesulphonic acid to phenyl ethanoate



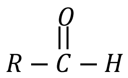
(d). Phenol to hexane-1,6-dioic acid



(e). Chlorobenzene to 2,4,6-tribromophenol



10. CARBONYL COMPOUNDS ($RCOR$) (ALDEHYDES AND KETONES)

Preparation aldehydes,  $R-\overset{\overset{O}{||}}{C}-H$ ***($RCHO$ not $RCOH$)***

a. By oxidation of primary alcohols

Primary alcohols are oxidised to aldehydes by mild oxidising agents

$$RCH_2OH \xrightarrow[Heat]{Cr_2O_7^{2-}/H^+} RCHO$$

$$RCH_2OH \xrightarrow[300℃]{O_2/Cu} RCHO$$

$$RCH_2OH \xrightarrow[0°C]{NaOCl\,/CH_3COOH} RCHO$$

b. By heating calcium salts of carboxylic acids

When calcium methanoate is heated, methanal is formed

$$(HCOO)_2Ca \xrightarrow{Heat} HCHO$$

When other Calcium salts of carboxylic acids are heated with calcium methanoate, a corresponding aldehydes is formed as shown

$$(RCOO)_2Ca \xrightarrow[Heat]{(HCOO)_2Ca} RCHO$$

c. From ethene

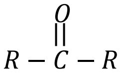
Ethene mixed with oxygen react with acidified water in the presence of palladium(II) chloride and copper(II) chloride catalysts at a temperature of 20 to 60°C to form ethanal

$$H_2C = CH_2 \xrightarrow[PdCl_2/CuCl_2/20°C]{O_2/H_2O/HCl} CH_3CHO$$

d. By hydration of ethyne to form ethanal

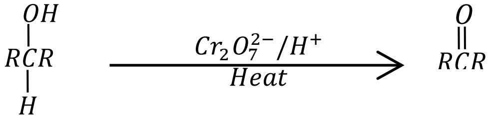
Ethyne react with water to in the presence of sulphuric acid and mercury(II) sulphate at 60°C to form ethanal (an aldehyde)

$$HC \equiv CH \xrightarrow[HgSO_4\,/60°C]{H_2O/H_2SO_4} CH_3CHO$$

Preparation of ketones  $R-\overset{\overset{O}{\|}}{C}-R$ (both R are alkyl groups)

e. By oxidation of secondary alcohols

Secondary alcohols are oxidised to ketones by all the above oxidising agents



$$R\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}R \xrightarrow[Heat]{Cr_2O_7^{2-}/H^+} R\overset{\overset{O}{\|}}{C}R$$

f. From alkenes

Terminal alkenes with three or more carbon carbons mixed with oxygen react with acidified water in the presence of palladium(II) chloride and copper(II) chloride catalysts at a temperature of 20 to 60°C to form ketones

$$RCH = CH_2 \xrightarrow[PdCl_2/CuCl_2/20°C]{O_2/H_2O/HCl} RCOCH_3$$

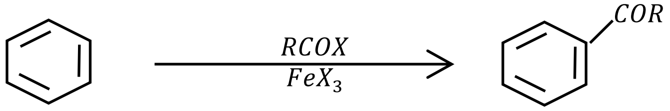
g. From alkynes

Alkynes react with water to in the presence of sulphuric acid and mercury(II) sulphate at 60°C to form carbonyl compounds.

$$RC \equiv CH \xrightarrow[HgSO_4\,/60°C]{H_2O/H_2SO_4} RCOCH_3$$

h. From acylation of benzene

Benzene reacts with acid halides in the presence of aluminium halides or iron(III) halides to form phenyl ketones



i. From Grignard reagents

Grignard reagents when refluxed with nitriles react to form imines which are hydrolysed to ketones

$$RMgX \xrightarrow[2.\ H_2O/H^+]{1.\ R'C\equiv N/dry\ ether} RCOR'$$

j. By heating calcium salts of carboxylic acids

When calcium salts of carboxylic acids are heated, the form ketones (except calcium methanoate)

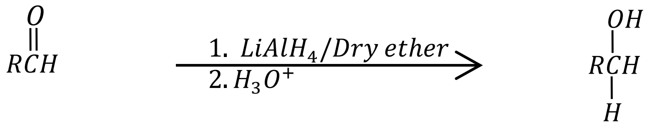
$$(RCOO)_2Ca \xrightarrow[Heat]{(HCOO)_2Ca} RCOR$$

–

Reactions of carbonyl compounds

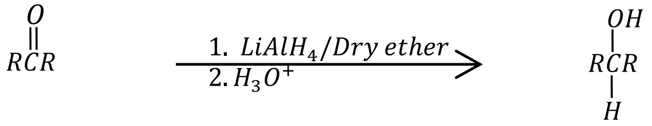
k. Reduction of carbonyl compounds

(i). Aldehydes are reduced to primary alcohols



$$R\overset{O}{\overset{\|}{C}}H \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4/Dry\ ether} R\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}H$$

(ii). Ketones are reduced to secondary alcohols.



$$R\overset{O}{\overset{\|}{C}}R \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4/Dry\ ether} R\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}R$$

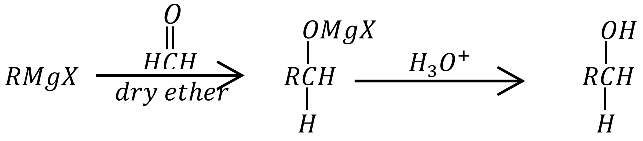
l. Reaction with amalgamated zinc.

Carbonyl compounds react with amalgamated zinc in the presence of concentrated hydrochloric acid to form alkanes

$$RCOR' \xrightarrow[Conc.HCl]{Zn/Hg} RCH_2R'$$

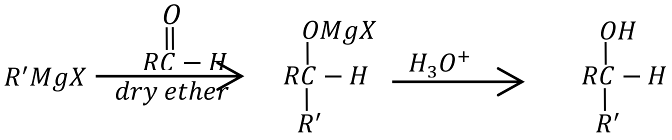
m. Reaction with Grignard reagent

(i). Methanal in the presence of <u>dry ether</u> to form primary alcohols



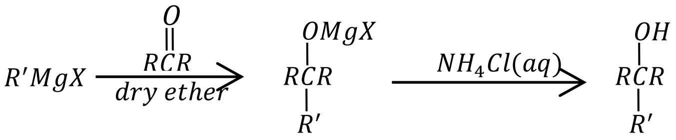
$$RMgX \xrightarrow[dry\ ether]{H\overset{O}{\overset{\|}{C}}H} R\underset{\underset{H}{|}}{\overset{\overset{OMgX}{|}}{C}}H \xrightarrow{H_3O^+} R\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}H$$

(v). Aldehydes with two or more carbon atoms react to form secondary alcohols



$$R'MgX \xrightarrow[dry\ ether]{R\overset{O}{\overset{\|}{C}}-H} R\overset{OMgX}{\underset{R'}{C}}-H \xrightarrow{H_3O^+} R\overset{OH}{\underset{R'}{C}}-H$$

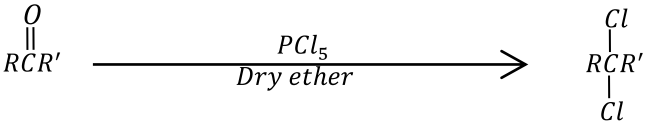
(vi). Ketones to form tertiary alcohols. Hydrolysis is done using aqueous ammonium chloride not an acid. This is to prevent elimination reactions from taking place



$$R'MgX \xrightarrow[dry\ ether]{R\overset{O}{\overset{\|}{C}}R} R\overset{OMgX}{\underset{R'}{C}}R \xrightarrow{NH_4Cl(aq)} R\overset{OH}{\underset{R'}{C}}R$$

n. Reaction with phosphorus(V) chloride

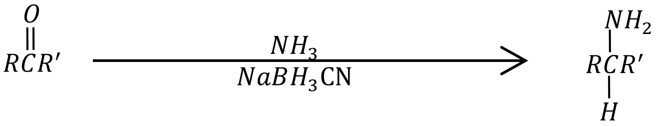
Gem dichlorides are formed



$$R\overset{O}{\overset{\|}{C}}R' \xrightarrow[Dry\ ether]{PCl_5} R\overset{Cl}{\underset{Cl}{C}}R'$$

o. Reaction with ammonia

Carbonyl compounds react with ammonia to form primary amines. This occurs in a weakly acidic medium with a reducing agent such as sodium cyanoborohydride or hydrogen and palladium to form amines

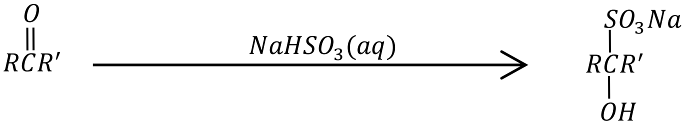


$$R\overset{O}{\overset{\|}{C}}R' \xrightarrow[NaBH_3\text{CN}]{NH_3} R\overset{NH_2}{\underset{H}{C}}R'$$

When a primary or secondary amine is used instead of ammonia, then a secondary or tertiary amine is formed respectively.

p. Reaction with sodium hydrogensulphite

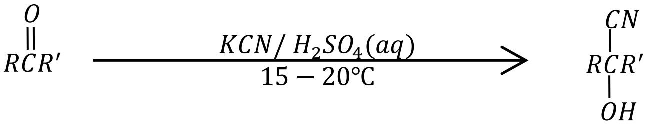
a white precipitate of aldehydes or ketone sodium hydrogensulphite is formed



$$R\overset{O}{\overset{\|}{C}}R' \xrightarrow{NaHSO_3(aq)} R\overset{SO_3Na}{\underset{OH}{C}}R'$$

q. Reaction with hydrogen cyanide

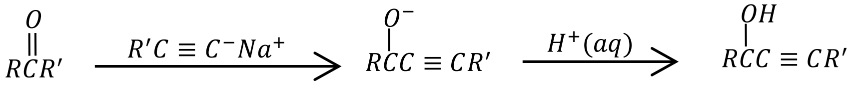
Hydrogen cyanide is generated in situ by reacting sodium cyanide with dilute sulphuric acid 2-hydroxynitriles.



$$R\overset{O}{\overset{\|}{C}}R' \xrightarrow[15-20℃]{KCN/\ H_2SO_4(aq)} R\overset{CN}{\underset{OH}{C}}R'$$

r. Reaction with alkynides (Acetylides)

Carbonyl compounds react with alkynides (Acetylides) to form alpha hydroxyl alkyne (alkynol). The reaction is completed by hydrolysis in a weakly acidic solution.

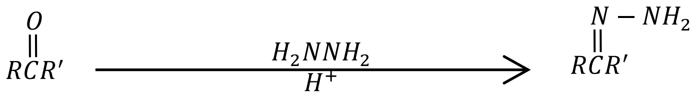


$$R\overset{O}{\overset{\|}{C}}R' \xrightarrow{R'C\equiv C^-Na^+} R\overset{O^-}{\overset{|}{C}}C\equiv CR' \xrightarrow{H^+(aq)} R\overset{OH}{\overset{|}{C}}C\equiv CR'$$

s. Reaction with hydrazine (H_2NNH_2) and its derivatives

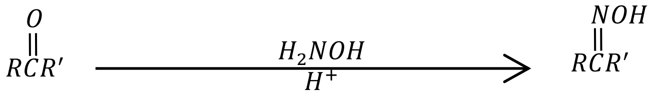
Carbonyl compounds react with hydrazine and its derivatives to form hydrazones. The reactions are usually acid catalysed

(i). Reaction with hydrazine



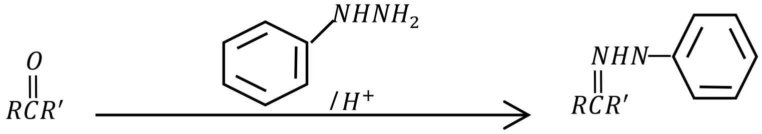
$$R\overset{O}{\overset{\|}{C}}R' \xrightarrow[H^+]{H_2NNH_2} R\overset{N-NH_2}{\overset{\|}{C}}R'$$

(ii). Reaction with hydroxylamine

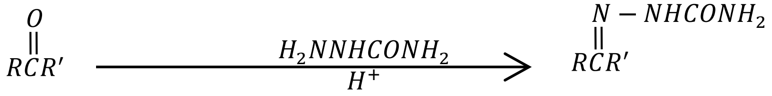


$$R\overset{O}{\overset{\|}{C}}R' \xrightarrow[H^+]{H_2NOH} R\overset{NOH}{\overset{\|}{C}}R'$$

(iii). Reaction with phenylhydrazine

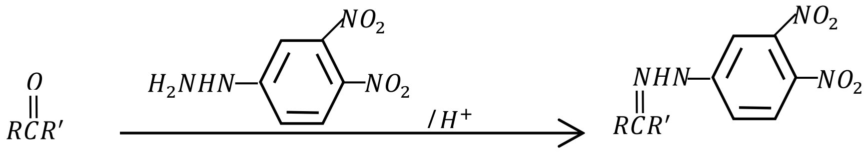


(i). Reaction with semicarbazine



$$R\overset{O}{\overset{\|}{C}}R' \xrightarrow[H^+]{H_2NNHCONH_2} R\overset{N-NHCONH_2}{\overset{\|}{C}}R'$$

(ii). Reaction with 2,4-dinitrophenylhydrazine: This results in the formation of a yellow precipitate (identification of carbonyl campounds)

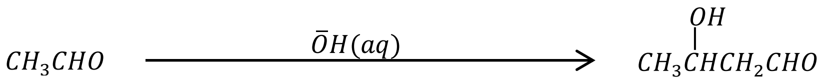


t. Reaction with sodium hydroxide

(i). Carbonyl compounds without an alpha hydrogen atom react with dilute sodium hydroxide to form two products, a carboxylate (salt) and alcohol.

$$2HCHO \xrightarrow{\bar{O}H} HCOO^- \quad + \quad CH_3OH$$

(i). Carbonyl compounds with a hydrogen atom on the carbon atom adjacent to the carbonyl group (alpha hydrogen atoms) react with dilute sodium hydroxide to form hydroxycarbonyl compounds Example:

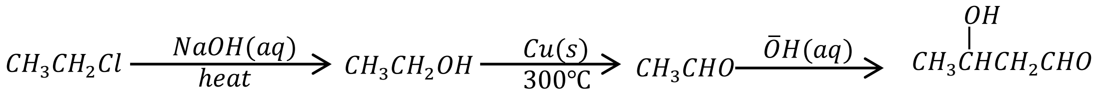


$$CH_3CHO \xrightarrow{\bar{O}H(aq)} CH_3\overset{\overset{OH}{|}}{C}HCH_2CHO$$

Note: This reaction is useful in preparing compounds of longer carbon chains

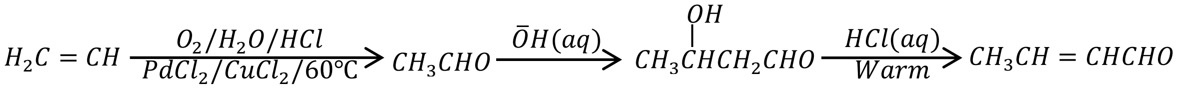
- **Example:** Write equations to show how the following compounds can be synthesised

(a). Chloroethane to 2-hydroxybutanal



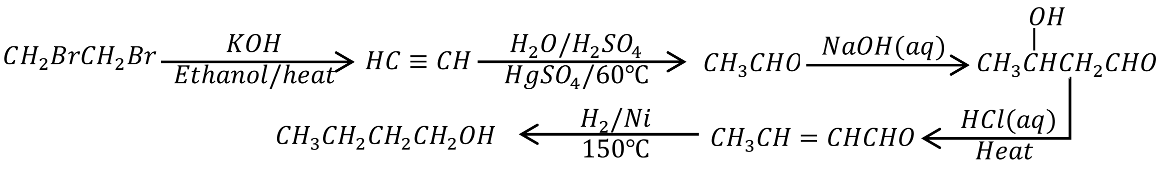
$$CH_3CH_2Cl \xrightarrow[heat]{NaOH(aq)} CH_3CH_2OH \xrightarrow[300℃]{Cu(s)} CH_3CHO \xrightarrow{\bar{O}H(aq)} CH_3\overset{\overset{OH}{|}}{C}HCH_2CHO$$

(b). Ethene to but-2-enal.



$$H_2C = CH \xrightarrow[PdCl_2/CuCl_2/60℃]{O_2/H_2O/HCl} CH_3CHO \xrightarrow{\bar{O}H(aq)} CH_3\overset{\overset{OH}{|}}{C}HCH_2CHO \xrightarrow[Warm]{HCl(aq)} CH_3CH = CHCHO$$

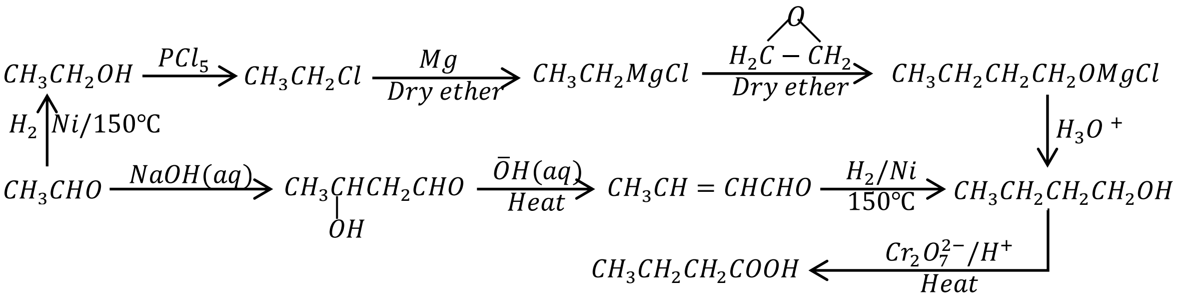
(c). 1,2-bromoethane to butan-1-ol



$$CH_2BrCH_2Br \xrightarrow[Ethanol/heat]{KOH} HC \equiv CH \xrightarrow[HgSO_4/60℃]{H_2O/H_2SO_4} CH_3CHO \xrightarrow{NaOH(aq)} CH_3\overset{\overset{OH}{|}}{C}HCH_2CHO$$

$$CH_3CH_2CH_2CH_2OH \xleftarrow[150℃]{H_2/Ni} CH_3CH = CHCHO \xleftarrow[Heat]{HCl(aq)}$$

(d). Ethanal to butanoic acid

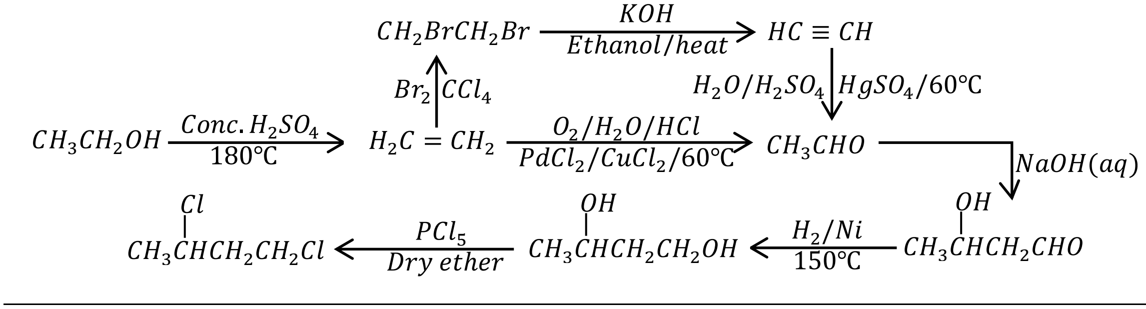


$$CH_3CHO \xrightarrow{H_2\ Ni/150℃} CH_3CH_2OH \xrightarrow{PCl_5} CH_3CH_2Cl \xrightarrow[Dry\ ether]{Mg} CH_3CH_2MgCl \xrightarrow[Dry\ ether]{H_2C - CH_2\ (O)} CH_3CH_2CH_2CH_2OMgCl \xrightarrow{H_3O^+} CH_3CH_2CH_2CH_2OH$$

$$CH_3CHO \xrightarrow{NaOH(aq)} CH_3\underset{\underset{OH}{|}}{C}HCH_2CHO \xrightarrow[Heat]{\bar{O}H(aq)} CH_3CH = CHCHO \xrightarrow[150℃]{H_2/Ni} CH_3CH_2CH_2CH_2OH$$

$$CH_3CH_2CH_2COOH \xleftarrow[Heat]{Cr_2O_7^{2-}/H^+}$$

(e). Ethanol to 1,3-dichlorobutane

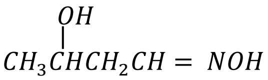


$$H_2C = CH_2 \xrightarrow{Br_2\ CCl_4} CH_2BrCH_2Br \xrightarrow[Ethanol/heat]{KOH} HC \equiv CH \xrightarrow{H_2O/H_2SO_4\ HgSO_4/60℃} CH_3CHO$$

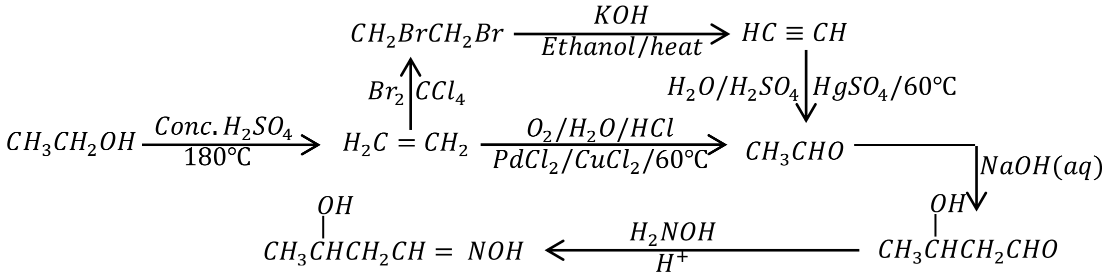
$$CH_3CH_2OH \xrightarrow[180℃]{Conc. H_2SO_4} H_2C = CH_2 \xrightarrow[PdCl_2/CuCl_2/60℃]{O_2/H_2O/HCl} CH_3CHO \xrightarrow{NaOH(aq)}$$

$$CH_3\overset{\overset{Cl}{|}}{C}HCH_2CH_2Cl \xleftarrow[Dry\ ether]{PCl_5} CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_2OH \xleftarrow[150℃]{H_2/Ni} CH_3\overset{\overset{OH}{|}}{C}HCH_2CHO$$

(f). Ethanol to



$CH_3\overset{OH}{\overset{|}{C}}HCH_2CH=NOH$



$$\begin{tikzcd}
 & CH_2BrCH_2Br \arrow[r, "KOH", "Ethanol/heat"'] & HC\equiv CH \arrow[d, "H_2O/H_2SO_4"', "HgSO_4/60^\circ C"] \\
CH_3CH_2OH \arrow[r, "Conc.H_2SO_4", "180^\circ C"'] & H_2C=CH_2 \arrow[u, "Br_2"', "CCl_4"] \arrow[r, "O_2/H_2O/HCl", "PdCl_2/CuCl_2/60^\circ C"'] & CH_3CHO \arrow[d, "NaOH(aq)"] \\
 & CH_3\overset{OH}{\overset{|}{C}}HCH_2CH=NOH & CH_3\overset{OH}{\overset{|}{C}}HCH_2CHO \arrow[l, "H_2NOH"', "H^+"]
\end{tikzcd}$$

<u>Reactions of aldehydes which differ from ketones</u>

(i). **<u>Oxidation of aldehydes</u>**

Aldehydes are oxidised to carboxylic acids while ketones are not oxidised

$$RCHO \xrightarrow[Heat]{Cr_2O_7^{2-}/H^+} RCOOH$$

$$RCHO \xrightarrow[Heat]{MnO_4^-/H^+} RCOOH$$

(ii). **<u>Reaction with ammoniacal silver nitrate</u>**

Aldehydes react with ammoniacal silver nitrate solution to form silver which is deposited on the walls of the test tube forming a silver mirror

$$RCHO + 2Ag(NH_3)_2^+ + 3\bar{O}H \longrightarrow RCOO^- + 2Ag + 2NH_3 + 2H_2O$$

(iii). **<u>Reaction with Fehling's solution</u>**

<u>Aliphatic aldehydes</u> react with Fehling solution on heating to form a brown precipitate of copper(I) oxide. Benzaldehyde and ketones do not react.

$$RCHO + 2Cu^{2+} + 5\bar{O}H \longrightarrow RCOO^- + Cu_2O + 3H_2O$$

- **<u>Question 14</u>**

Write equations to show how the following compounds can be synthesised.

(a). Ethanoic to

(i). Ethane-1,2-diol

$$CH_3COOH \xrightarrow[dry\ ether]{LiAlH_4} CH_3CH_2OH \xrightarrow[180^\circ C]{Conc.H_2SO_4} H_2C=CH_2 \xrightarrow[\bar{O}H(aq)]{MnO_4^-} HOCH_2CH_2OH$$

(ii). Bromoethane

$$\begin{tikzcd}
CH_3COOH \arrow[r, "LiAlH_4", "dry\ ether"'] & CH_3CH_2OH \arrow[r, "Conc.H_2SO_4", "180^\circ C"'] \arrow[rr, bend right, "PBr_3/reflux"'] & H_2C=CH_2 \arrow[r, "HBr"] & CH_3CH_2Br
\end{tikzcd}$$

(iii). Ethyne

$$\begin{tikzcd} CH_3COOH \arrow[r, "LiAlH_4", "Dry\ ether"'] & CH_3CH_2OH \arrow[r, "Conc.H_2SO_4", "180^\circ C"'] & H_2C=CH_2 \arrow[r, "Br_2", "CCl_4"'] & BrCH_2CH_2Br \arrow[dl, "KOH", "Ethanol/heat"'] \\ & & HC\equiv CH & \end{tikzcd}$$

(iv). Methanal

$$CH_3COOH \xrightarrow[Dry\ ether]{LiAlH_4} CH_3CH_2OH \xrightarrow[180^\circ C]{Conc.H_2SO_4} H_2C=CH_2 \xrightarrow[2.\ H_2O/Zn/CH_3COOH]{1.O_3/CCl_4/15^\circ C} 2HCHO$$

(v). Methanol

$$\begin{tikzcd} CH_3COOH \arrow[r, "LiAlH_4", "Dry\ ether"'] & CH_3CH_2OH \arrow[r, "Conc.H_2SO_4", "180^\circ C"'] & H_2C=CH_2 \arrow[r, "1.O_3/CCl_4/15^\circ C", "2.\ H_2O/Zn/CH_3COOH"'] & HCHO \arrow[dl, "LiAlH_4", "Dry\ ether"'] \\ & & CH_3OH & \end{tikzcd}$$

(vi). Chloromethane

$$\begin{tikzcd} CH_3COOH \arrow[r, "LiAlH_4", "Dry\ ether"'] & CH_3CH_2OH \arrow[r, "Conc.H_2SO_4", "180^\circ C"'] & H_2C=CH_2 \arrow[r, "1.O_3/CCl_4/15^\circ C", "2.\ H_2O/Zn/CH_3COOH"'] & HCHO \arrow[dl, "LiAlH_4", "Dry\ ether"'] \\ & CH_3Cl & CH_3OH \arrow[l, "PCl_5"'] & \end{tikzcd}$$

(vii). Propyne

$$\begin{tikzcd} CH_3COOH \arrow[r, "LiAlH_4", "Dry\ ether"'] & CH_3CH_2OH \arrow[r, "Conc.H_2SO_4", "180^\circ C"'] & H_2C=CH_2 \arrow[r, "Br_2", "CCl_4"'] & BrCH_2CH_2Br \arrow[dl, "KOH", "Ethanol/heat"'] \\ HC\equiv CCH_3 & HC\equiv \bar{C}Na^+ \arrow[l, "CH_3I"'] & HC\equiv CH \arrow[l, "Na"', "NH_3(l)"] & \end{tikzcd}$$

(b). Bromoethane to

(i). Ethanoic acid

$$CH_3CH_2Br \xrightarrow[heat]{NaOH(aq)} CH_3CH_2OH \xrightarrow[heat]{Cr_2O_7^{2-}/H^+} CH_3COOH$$

(ii). Ethyne

$$\begin{tikzcd} CH_3CH_2Br \arrow[r, "NaOH(aq)", "heat"'] & CH_3CH_2OH \arrow[r, "Conc.H_2SO_4", "180^\circ C"'] & H_2C=CH_2 \arrow[r, "Cl_2", "CCl_4"'] & ClCH_2CH_2Cl \arrow[dl, "KOH", "Ethanol/heat"'] \\ & & HC\equiv CH & \end{tikzcd}$$

(iii). Ethanedioic acid

$$CH_3CH_2Br \xrightarrow[heat]{NaOH(aq} CH_3CH_2OH \xrightarrow[180°C]{Conc. H_2SO_4} H_2C = CH_2 \xrightarrow[heat]{MnO_4^-/\bar{O}H(aq)} HOOCCOOH$$

(iv). Ethyl ethanoate

$$CH_3CH_2Br \xrightarrow[heat]{NaOH(aq)} CH_3CH_2OH \xrightarrow[Conc. H_2SO_4/warm]{CH_3COOH} CH_3COOCH_2CH_3$$

(v). Ethanal

$$CH_3CH_2Br \xrightarrow[heat]{NaOH(aq)} CH_3CH_2OH \xrightarrow[heat]{Cr_2O_7^{2-}/H^+(aq)} CH_3CHO$$

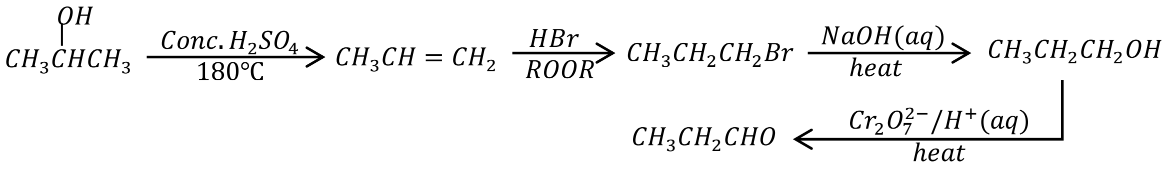
(vi). Ethane-1,2-diol

$$CH_3CH_2Br \xrightarrow[heat]{NaOH(aq)} CH_3CH_2OH \xrightarrow[180°C]{Conc. H_2SO_4} H_2C = CH_2 \xrightarrow[\bar{O}H(aq)]{MnO_4^-} HOCH_2CH_2OH$$

- **Question 15**

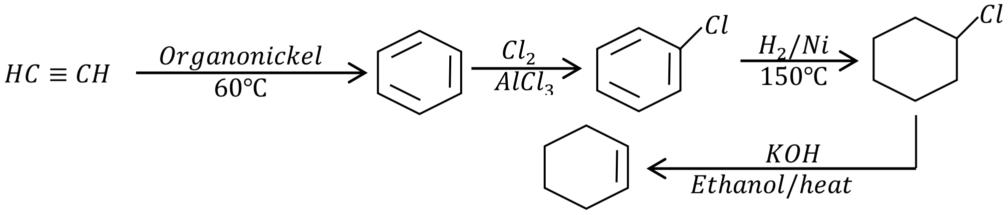
Write equations to show how the following conversions can be made,.

(a). Propan-2-ol to propanal

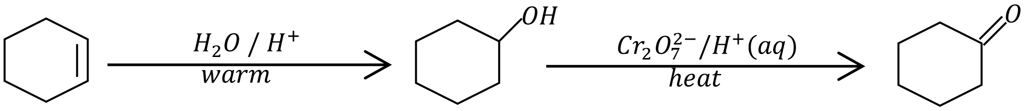


$$CH_3\overset{OH}{C}HCH_3 \xrightarrow[180°C]{Conc. H_2SO_4} CH_3CH = CH_2 \xrightarrow[ROOR]{HBr} CH_3CH_2CH_2Br \xrightarrow[heat]{NaOH(aq)} CH_3CH_2CH_2OH \xrightarrow[heat]{Cr_2O_7^{2-}/H^+(aq)} CH_3CH_2CHO$$

(a). Ethyne to cyclohexene



(b). Cyclohexene to cylohaxanone



(c). 1-bromopropane to propanone

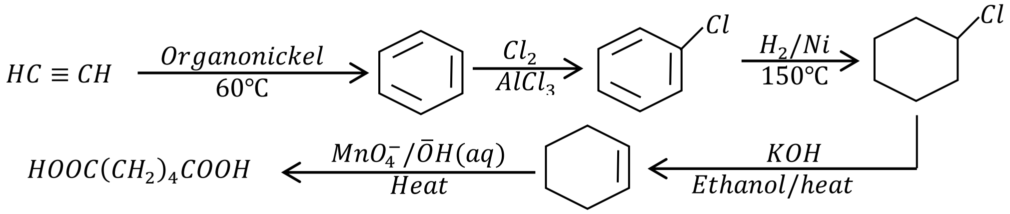
$$CH_3CH_2CH_2Br \xrightarrow[ethanol/heat]{KOH(aq)} CH_3CH=CH_2 \xrightarrow[heat]{H_2O/H^+} CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[heat]{Cr_2O_7^{2-}/H^+(aq)} CH_3COCH_3$$

(d). 2-chloropropane to propanal

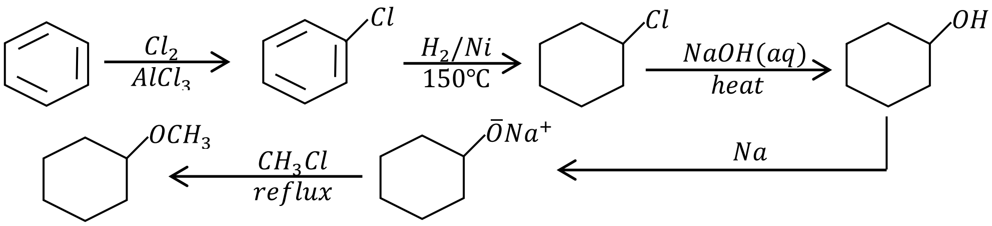
$$CH_3\overset{Cl}{\overset{|}{C}}HCH_3 \xrightarrow[heat]{NaOH(aq)} CH_3CH=CH_2 \xrightarrow[ROOR]{HBr} CH_3CH_2CH_2Br \xrightarrow[heat]{NaOH(aq)} CH_3CH_2CH_2OH$$

$$CH_3CH_2CH_2OH \xrightarrow[heat]{Cr_2O_7^{2-}/H^+(aq)} CH_3CH_2CHO$$

(e). Ethyne to hexane-1,6-dioic acid



(f). Benzene to methoxycyclohexane (cyclohexyl methyl ether)



(g). Ethanal to propanone

$$CH_3CHO \xrightarrow{PCl_5} CH_3CHCl_2 \xrightarrow[Ethanol/heat]{KOH} HC\equiv CH \xrightarrow[NH_3(l)]{Na(s)} HC\equiv \bar{C}Na^+$$

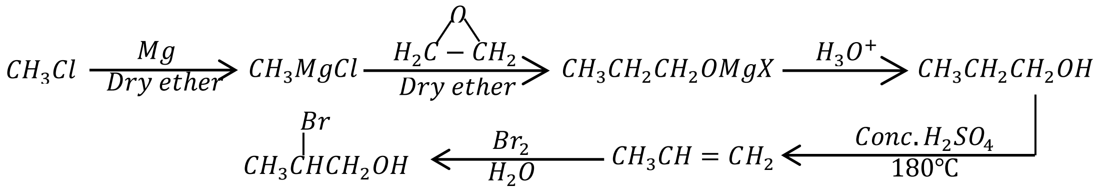
$$HC\equiv \bar{C}Na^+ \xrightarrow{CH_3Br} HC\equiv CCH_3 \xrightarrow[HgSO_4/60℃]{H_2O/H_2SO_4} CH_3COCH_3$$

(h). Chloromethane to propanal

$$CH_3Cl \xrightarrow[Dry\ ether]{Mg} CH_3MgCl \xrightarrow[Dry\ ether]{\overset{O}{H_2C-CH_2}} CH_3CH_2CH_2OMgX \xrightarrow{H_3O^+} CH_3CH_2CH_2OH$$

$$CH_3CH_2CH_2OH \xrightarrow[heat]{Cr_2O_7^{2-}/H^+(aq)} CH_3CH_2CHO$$

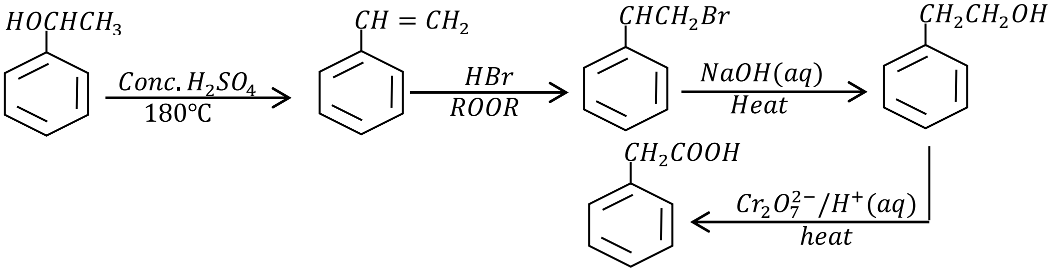
(i). Bromomethane to 1-bromopropan-2-ol



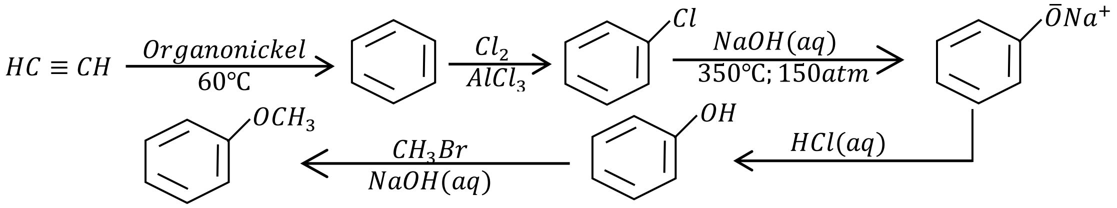
- **Question 16**

  Write equations to show how the following compounds can be synthesised from benzene and in each case, indicate the conditions for the reactions.

(a). 1-phenylethanol to 2-phenylethanoic acid



(a). Ethyne to methoxybenzene (methyl phenyl ether)

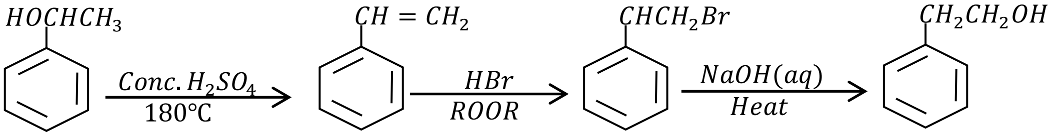


(a). Methanol to 2-methylpropan-2-ol

$$CH_3OH \xrightarrow[Dry\ ether]{PCl_5} CH_3Cl \xrightarrow[Dry\ ether]{Mg} CH_3MgCl \xrightarrow[Dry\ ether]{CH_3COCH_3} (CH_3)_3COMgX$$

$$(CH_3)_3COMgX \xrightarrow{NH_4Cl(aq)} (CH_3)_3COH$$

(b). 1-phenylethanol to 2-phenylethanol

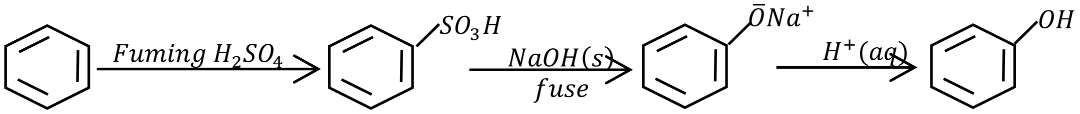


(c). Methanol to 2-methylpropene

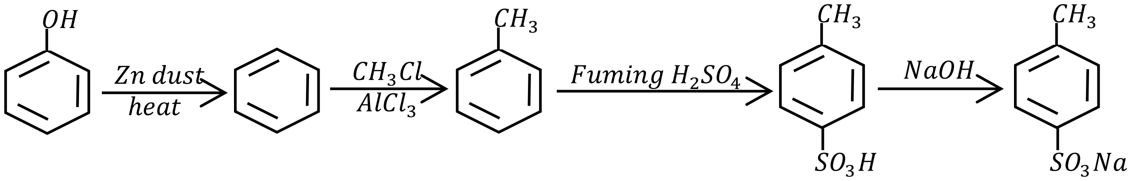
$$CH_3OH \xrightarrow[Dry\ ether]{PCl_5} CH_3Cl \xrightarrow[Dry\ ether]{Mg} CH_3MgCl \xrightarrow[Dry\ ether]{CH_3COCH_3} (CH_3)_3COMgX$$

$$(CH_3)_2C = CH_2 \xleftarrow[heat]{Conc.\, H_2SO_4} (CH_3)_3COH \xleftarrow{NH_4Cl(aq)}$$

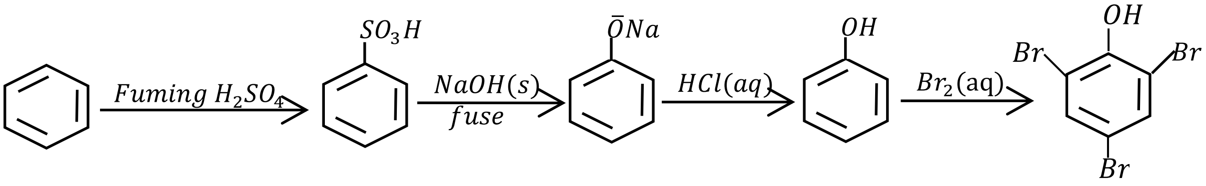
(d). Benzene to phenol



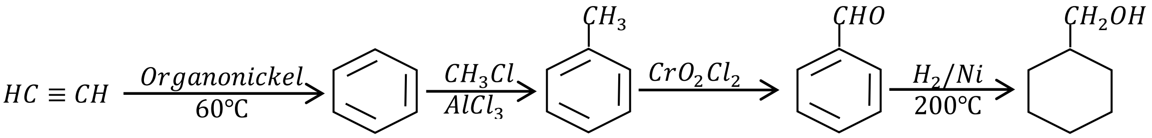
(e). Phenol to sodium methylbenzenesulphonate



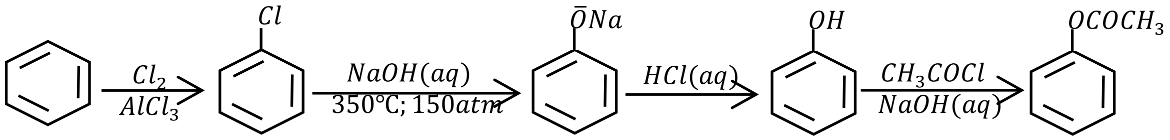
(f). Benzene to 2,4,6-tribromophenol



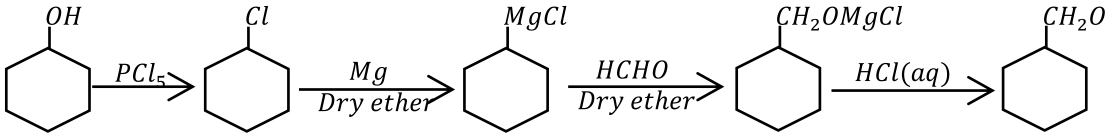
(g). Ethyne to cyclohexylmethanol



(h). Benzene to phenyl ethanoate



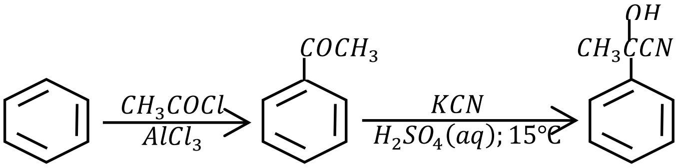
(i). Cyclohexanol to cyclohexylmethanol



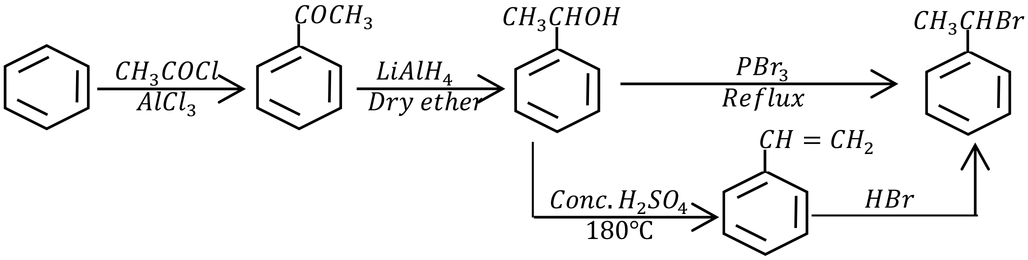
- **Question 17**

  Write equations to show how the following compounds can be synthesised from benzene

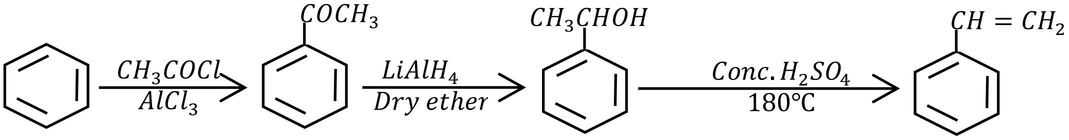
(a). 2-hydroxy-2-phenylpropanenitrile



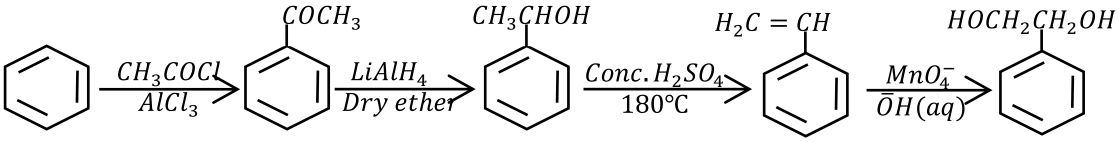
(b). 1-bromo-1-phenylethane



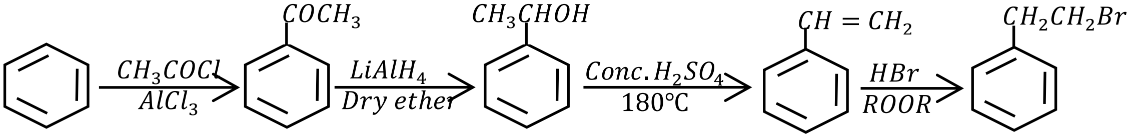
(c). Phenylethene



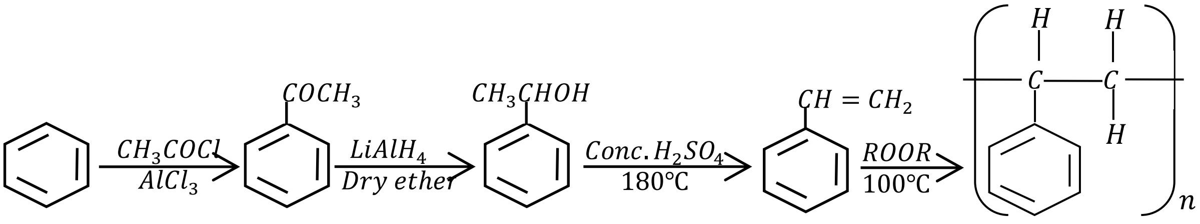
(d). 1-phenylethane-1,2-diol



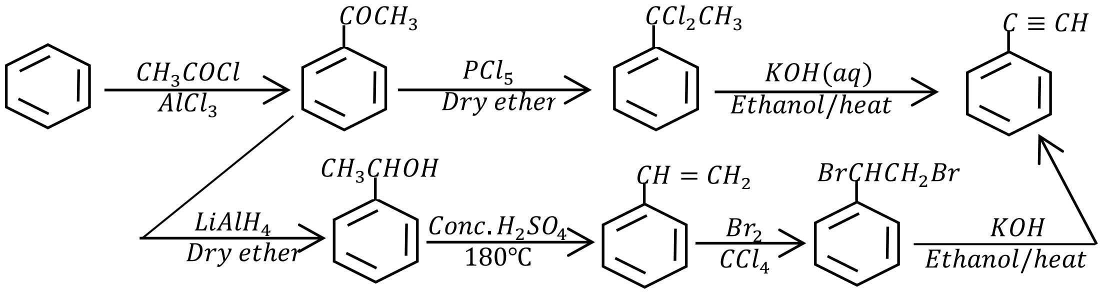
(e). 1-bromo-2-phenylethane



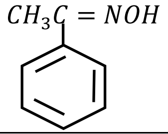
(a). Poly(phenylethene)

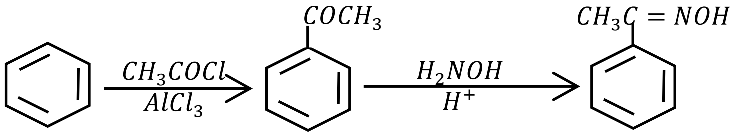


(b). Phenylethyne

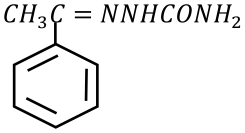


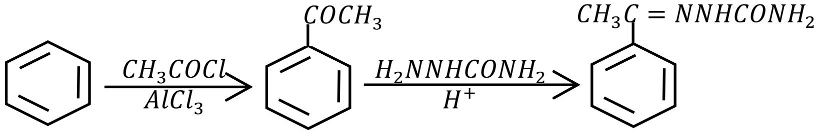
(h).



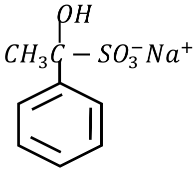


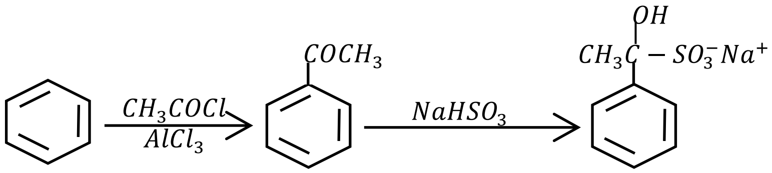
(i).





(j).





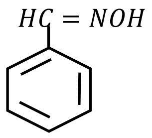
- **Question 18**

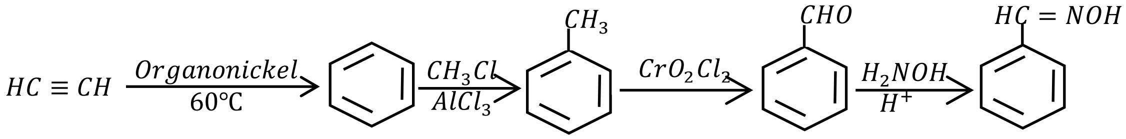
Write equations to show how the following conversions can be made,

(a). But-2-ene to ethene

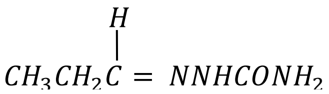
$$CH_3CH = CHCH_3 \xrightarrow[2.\ H_2O/Zn/CH_3COOH]{1.\ O_3/CCl_4/15°C} CH_3CHO \xrightarrow[Dry\ ether]{LiAlH_4} CH_3CH_2OH \xrightarrow[180°C]{Conc.\ H_2SO_4} H_2C = CH_2$$

(b). Ethyne to

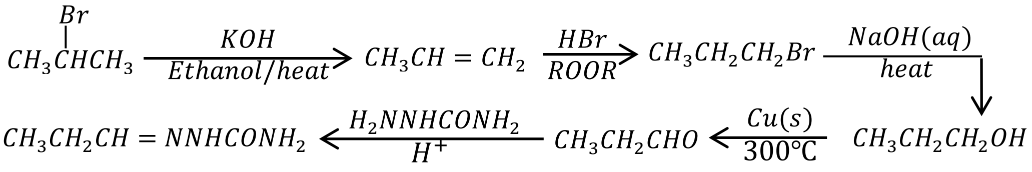




(c). 2-bromopropane to



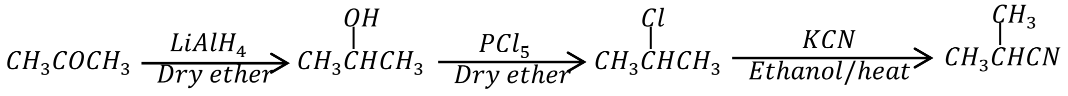
$$CH_3CH_2\overset{H}{\overset{|}{C}} = NNHCONH_2$$



$$CH_3\overset{Br}{\overset{|}{C}}HCH_3 \xrightarrow[Ethanol/heat]{KOH} CH_3CH = CH_2 \xrightarrow[ROOR]{HBr} CH_3CH_2CH_2Br \xrightarrow[heat]{NaOH(aq)} CH_3CH_2CH_2OH$$

$$CH_3CH_2CH = NNHCONH_2 \xleftarrow[H^+]{H_2NNHCONH_2} CH_3CH_2CHO \xleftarrow[300°C]{Cu(s)} CH_3CH_2CH_2OH$$

(d). Propanone to 2-methylpropanenitrile



$$CH_3COCH_3 \xrightarrow[Dry\ ether]{LiAlH_4} CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[Dry\ ether]{PCl_5} CH_3\overset{Cl}{\overset{|}{C}}HCH_3 \xrightarrow[Ethanol/heat]{KCN} CH_3\overset{CH_3}{\overset{|}{C}}HCN$$

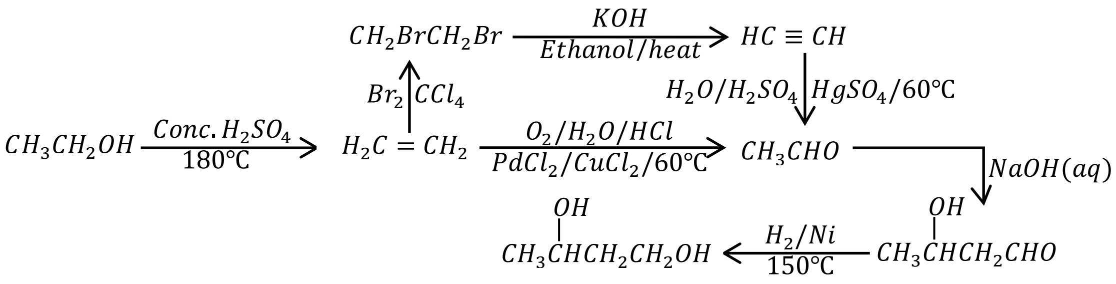
(e). Ethanal to methanal

$$CH_3CHO \xrightarrow[Dry\ ether]{LiAlH_4} CH_3CH_2OH \xrightarrow[Dry\ ether]{Conc.\ H_2SO_4} H_2C = CH_2 \xrightarrow[2.\ H_2O/Zn/CH_3COOH]{1.\ O_3/CCl_4/15°C} HCHO$$

(f). 2-chloropropane to 2,2-dichloropropane

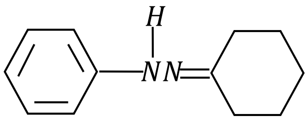
$$(CH_3)_2CHCl \xrightarrow[heat]{NaOH(aq)} (CH_3)_2CHOH \xrightarrow[heat]{Cr_2O_7^{2-}/H^+} (CH_3)_2C = O \xrightarrow{PCl_5} (CH_3)_2CCl_2$$

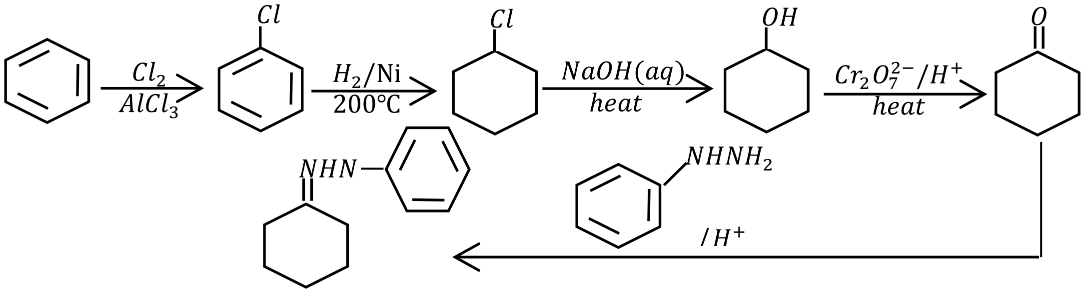
(g). Ethanol to butane-1,3-diol



$$\begin{tikzcd}
 & CH_2BrCH_2Br \arrow[r, "KOH", "Ethanol/heat"'] & HC\equiv CH \arrow[d, "H_2O/H_2SO_4"', "HgSO_4/60°C"] & \\
CH_3CH_2OH \arrow[r, "Conc. H_2SO_4", "180°C"'] & H_2C=CH_2 \arrow[u, "Br_2", "CCl_4"'] \arrow[r, "O_2/H_2O/HCl", "PdCl_2/CuCl_2/60°C"'] & CH_3CHO \arrow[r, dash] & {} \arrow[d, "NaOH(aq)"] \\
 & & CH_3CH(OH)CH_2CH_2OH & CH_3CH(OH)CH_2CHO \arrow[l, "H_2/Ni", "150°C"']
\end{tikzcd}$$

(h). Benzene to

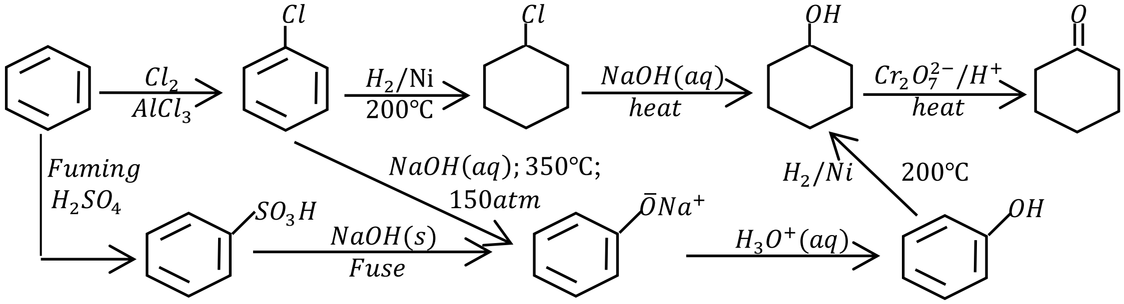




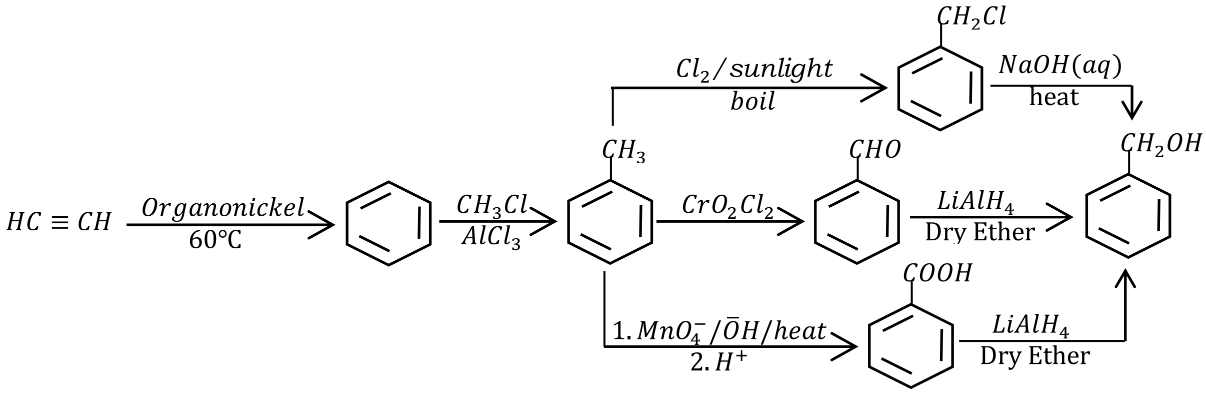
(i). 2,2-dibromopropane to $(CH_3)_2C = NNHCONH_2$

$$(CH_3)_2CBr_2 \xrightarrow[Ethanol/heat]{KOH} CH_3C\equiv CH \xrightarrow[HgSO_4/60°C]{H_2O/H_2SO_4} (CH_3)_2CO \xrightarrow[H^+]{H_2NNHCONH_2} (CH_3)_2C = NNHCONH_2$$

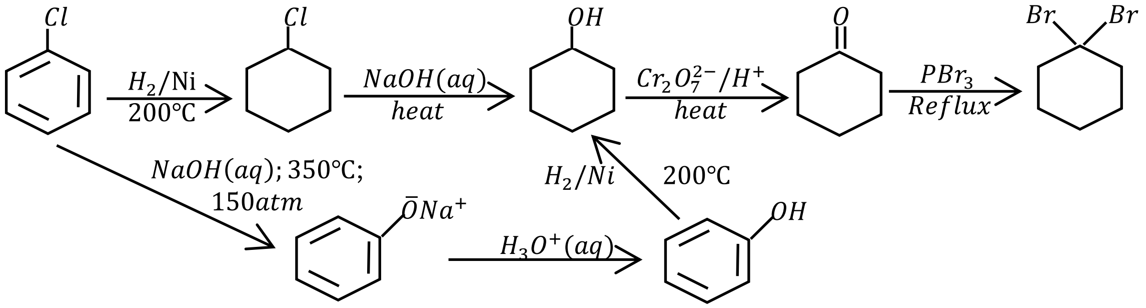
(j). Benzene to cyclohexanone



(k). Ethyne to phenylmethanol



(l). chlorobenzene to 1,1-dibromocyclohexane



11. CARBOXYLIC ACIDS

Preparation of carboxylic acids

a. From primary alcohols

Primary alcohols are oxidised to carboxylic acids by strong oxidising agents.

$$RCH_2OH \xrightarrow[Heat]{Cr_2O_7^{2-}/H^+} RCOOH$$

$$RCH_2OH \xrightarrow[Heat]{MnO_4^-/H^+} RCOOH$$

b. From aldehydes

Aldehydes are oxidised to carboxylic acids

$$RCHO \xrightarrow[Heat]{Cr_2O_7^{2-}/H^+} RCOOH$$

$$RCHO \xrightarrow[Heat]{MnO_4^-/H^+} RCOOH$$

c. From alkanenitriles

Alkanenitriles are hydrolysed on heating with dilute acid to form amides which are hydrolysed further to form carboxylic acids

$$RCN \xrightarrow[Heat]{H_2O/H^+} RCOOH$$

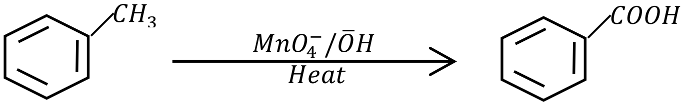
d. From Grignard reagents

Grignard reagents react carbon dioxide (dry ice) in the presence of dry ether which upon hydrolysis, liberated a carboxylic acid.

$$RMgX \xrightarrow[dry\ ether]{CO_2} RCOOMgX \xrightarrow{H_2O/H^+} RCOOH$$

e. From methylbenzene

Methylbenzene is oxidised by strong oxidizing agents like potassium manganate(VII) in acid or alkaline conditions on heating to form benzoic acid



Reactions of carboxylic acids

f. Salt formation

Carboxylic acids react with metals, bases, and carbonates or hydrogencarbonates to form salts

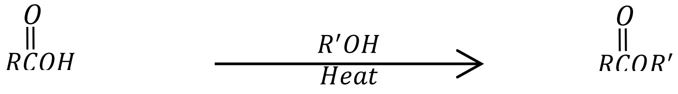
$$2RCOOH + 2Na \longrightarrow 2RCOONa + H_2$$

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + CO_2 + H_2O$$

g. Esterification

Carboxylic acids react with alcohols when warmed in the presence of concentrated sulphuric acid or dry hydrogen chloride gas to form esters.



$$\overset{\overset{O}{\|}}{RCOH} \xrightarrow[Heat]{R'OH} \overset{\overset{O}{\|}}{RCOR'}$$

Esterification can also be effected by use of acid chlorides (as shown below)

h. Formation of acid chlorides

Carboxylic acids react with phosphorus and thionyl chlorides on refluxing to form acid chlorides.

$$RCOOH \xrightarrow[reflux]{PCl_3\ or\ PCl_5\ or\ SOCl_2} RCOCl$$

Acid chlorides react with alcohols and phenols to form esters

$$RCOCl \xrightarrow{R'OH} RCOR'$$

Acid chlorides react with concentrated ammonia and other amines to form amides

$$RCOCl \xrightarrow{Conc. NH_3} RCONH_2$$

$$RCOCl \xrightarrow{CH_3NH_2} RCONHCH_3$$

Amides are particularly useful in the synthesis of amines

i. Formation of amides

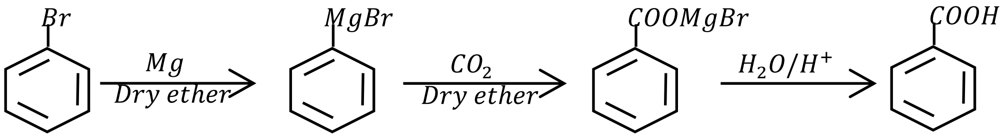
Carboxylic acids react with ammonium carbonate an ammonium salt which when heated in the presence of excess acid forms an amide

$$RCOOH \xrightarrow[Excess\ RCOOH/Heat]{(NH_4)_2CO_3} RCONH_2$$

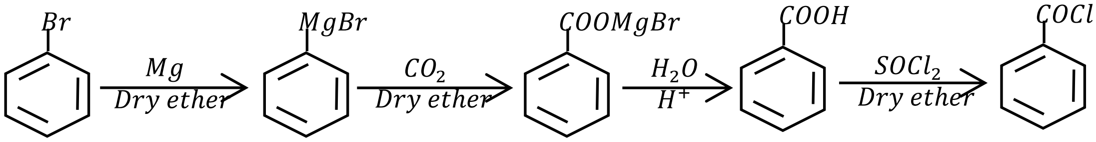
- **Question 19**

Write equations to show how the following conversions can be made

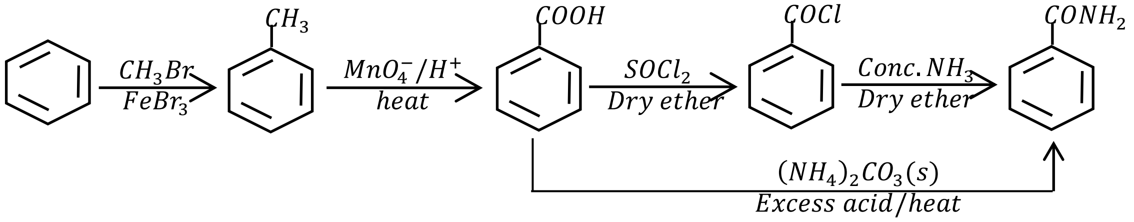
(a). Bromobenzene to benzoic acid



(b). Chlorobenzene to benzoyl chloride



(c). Benzene to benzamide



(d). Methanol to ethanoic acid

$$CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow[Ethanol/heat]{KCN} CH_3CN \xrightarrow[Heat]{H_2O/H^+} CH_3COOH$$

(e). Methanol to ethanol

$$CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow[Ethanol/heat]{KCN} CH_3CN \xrightarrow[Heat]{H_2O/H^+} CH_3COOH \xrightarrow[Dry\ ether]{LiAH_4} CH_3CH_2OH$$

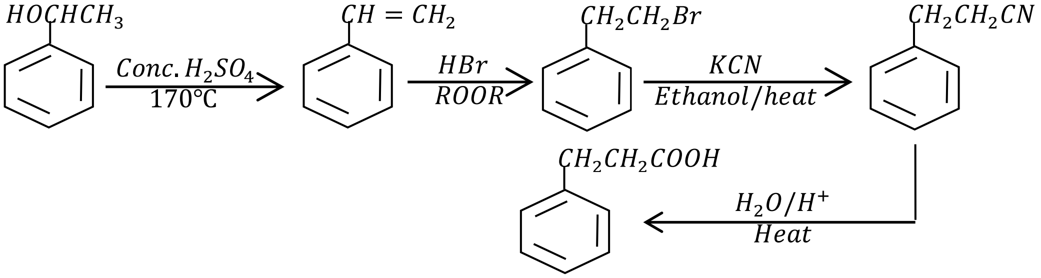
(f). Methanoic acid to ethanoic acid

$$HCOOH \xrightarrow[Dry\ ether]{LiAlH_4} CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow[Ethanol/heat]{KCN} CH_3CN \xrightarrow[Heat]{H_2O/H^+} CH_3COOH$$

(g). Propan-2-ol to butanoic acid

$$\begin{tikzcd}
(CH_3)_2CHOH \arrow[r, "Conc. H_2SO_4", "170°C"'] & CH_3CH = CH_2 \arrow[r, "HBr", "ROOR"'] & CH_3CH_2CH_2Br \arrow[d, "KCN", "Ethanol/heat"'] \\
& CH_3CH_2CH_2COOH & CH_3CH_2CH_2CN \arrow[l, "H_2O/H^+"', "Heat"]
\end{tikzcd}$$

(h). 1-phenylethanol to 3-phenylpropanoic acid



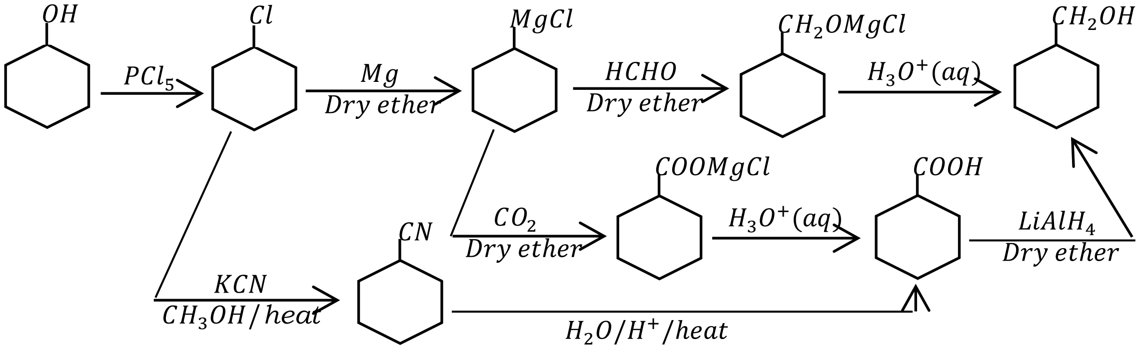
(j). Bromoethane to 1-chloropropane

$$\begin{tikzcd}
& CH_3CH_2CN \arrow[r, "H_2O/H^+", "heat"'] & CH_3CH_2COOH \arrow[dr, "LiAlH_4", "Dry\ ether"'] & \\
CH_3CH_2Br \arrow[ur, "KCN", "Ethanol/heat"'] \arrow[r, "Mg", "Dry\ ether"'] & CH_3CH_2MgBr \arrow[r, "HCHO", "Dry\ ether"'] & CH_3CH_2CH_2OMgBr \arrow[r, "H_2O", "H^+"'] & CH_3CH_2CH_2OH \arrow[dl, "PCl_5"', "Dry\ ether"] \\
& & CH_3CH_2CH_2Cl &
\end{tikzcd}$$

(k). Ethene to butanedioic acid

$$H_2C = CH_2 \xrightarrow[CCl_4]{Br_2} BrCH_2CH_2Br \xrightarrow[CH_3OH/heat]{KCN} CNCH_2CH_2CN \xrightarrow[Heat]{H_2O/H^+} HOOCCH_2CH_2COOH$$

(l). Cyclohexanol to cyclohexylmethanol



12. ALIPHATIC AMINES

Preparation of aliphatic amines

a. From alkyl halides

Alkyl halides react with ammonia in the presence of an alcohol when heated in a sealed tube to form mixture of amines. The products can be separated by fractional distillation

$$RX \xrightarrow[\text{Heat in sealed tube}]{NH_3/ethanol} RNH_2 + R_2NH + NR_3$$

Alkyl halides react with primary amines to form secondary amines and secondary amines to form tertiary

$$RX \xrightarrow[\text{Heat in sealed tube}]{R'NH_2/ethanol} RNHR'$$

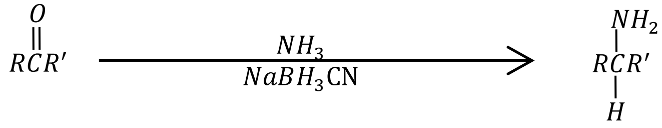
b. From alkanenitriles

Alkanenitriles are reduced by lithium aluminium hydride to form amines
Primary and secondary alkyl halides react with alcoholic potassium cyanide on heating to form nitriles

$$RCN \xrightarrow[\text{dry ether}]{LiAlH_4} RCH_2NH_2$$

c. From carbonyl compounds

Carbonyl compounds react with ammonia to form primary amines. This occurs in a weakly acidic medium with a reducing agent such as sodium cyanoborohydride or hydrogen and palladium, platinum or nickel to form amines



$$R\overset{\overset{O}{\|}}{C}R' \xrightarrow[NaBH_3\text{CN}]{NH_3} R\underset{\underset{H}{|}}{\overset{\overset{NH_2}{|}}{C}}R'$$

When a primary or secondary amine is used instead of ammonia, then secondary or tertiary amine is formed respectively.

d. By reaction of amides

Amides are reduced by lithium aluminium hydride to form amines. The number of carbon atoms remains the same

$$RCONH_2 \xrightarrow[\text{dry ether}]{LiAlH_4} RCH_2NH_2$$

e. By degradation of amides

When an amide is warmed with a mixture of bromine and concentrated sodium hydroxide solution, an amine is formed. The amine has one carbon atom less than the amide.

$$RCONH_2 \xrightarrow[\text{warm}]{Br_2/NaOH(aq)} RNH_2$$

f. By reduction of oximes

When oximes are reduced by lithium aluminium hydride, they form amines

$$RC=NOH \xrightarrow[\text{dry ether}]{LiAlH_4} RCH_2NH_2$$

Reactions of aliphatic amines

a. Reaction with nitrous acid

Because it is unstable, nitrous acid is generated during the reaction by mixing sodium nitrite and a dilute acid, commonly hydrochloric acid

(i). Primary amines react with nitrous acid to form alcohols and nitrogen gas

$$RNH_2 \xrightarrow{NaNO_2/HCl(aq)} ROH \quad + \quad N_2$$

(ii). Secondary amines react with nitrous acid to form yellow liquids of alkyl nitrosoamines

$$R_2NH \xrightarrow{NaNO_2/HCl(aq)} R_2N-N=O$$

(iii). Tertiary amines react with nitrous acid to form alkyl ammonium nitrites

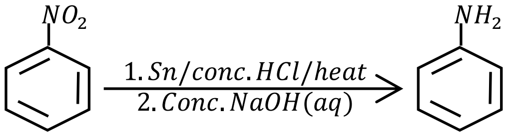
$$R_3N \xrightarrow{NaNO_2/HCl(aq)} R_3NHNO_2$$

13. ANILINE (PHENYL AMINE/ AMINOBENZENE)

Preparation of aniline

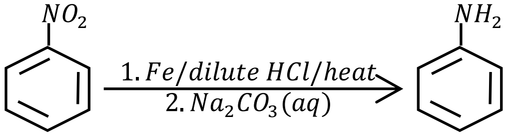
a. From reduction of nitrobenzene.

A mixture of nitrobenzene, tin and concentrated hydrochloric acid is heated. This forms a phenyl ammonium salt which when treated with a concentrated solution of sodium hydroxide liberated phenyl amine



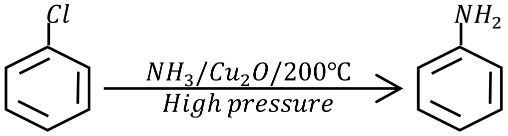
b. From reduction of nitrobenzene.

A mixture of nitrobenzene, iron and dilute hydrochloric acid is heated to form phenyl ammonium chloride which when treated with sodium carbonate solution, yields aniline



c. From chlorobenzene

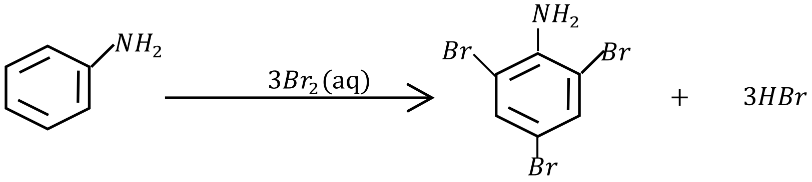
Chlorobenzene is reacted with ammonia in the presence of copper(I) oxide catalyst at 200°C and high pressure to form aniline



Reaction of aniline

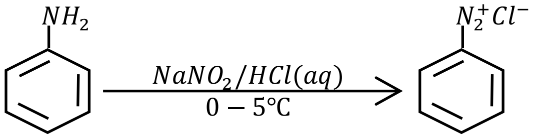
d. Reaction with bromine water

Phenol reacts with bromine water to form a white precipitate of 2,4,6-tribromoaniline



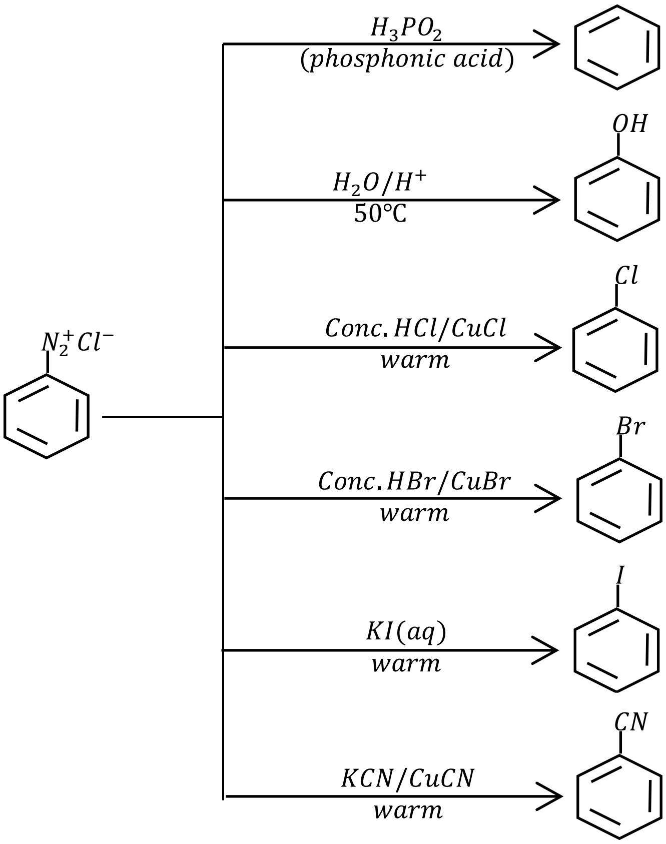
e. Reaction with nitrous acid

Aniline reacts with nitrous acid at a temperature of 0°C to 5°C to form benzene diazonium chloride salt



f. Reactions of diazonium salt

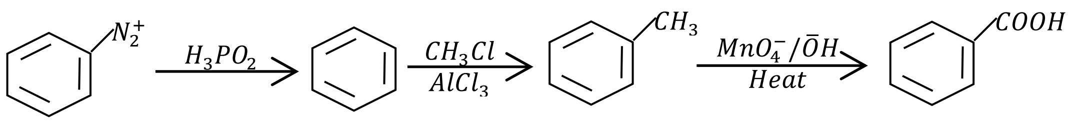
(i). Replacement of the diazo group



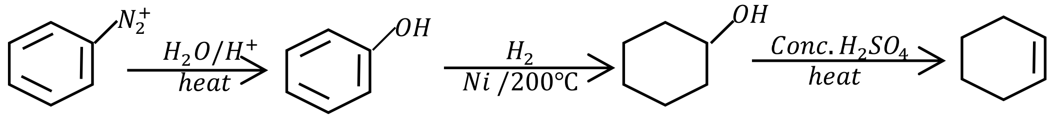
- **Question 20**

  Write equations to show how the following conversions can be made from benzene diazonium chloride

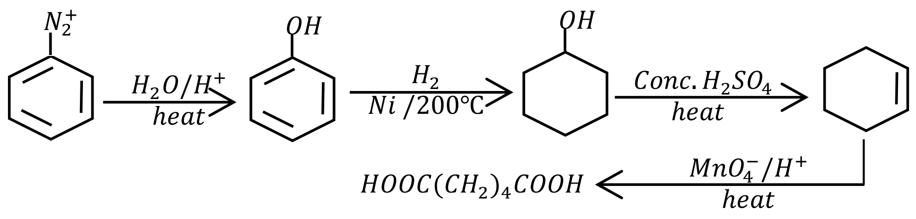
(a). Benzoic acid



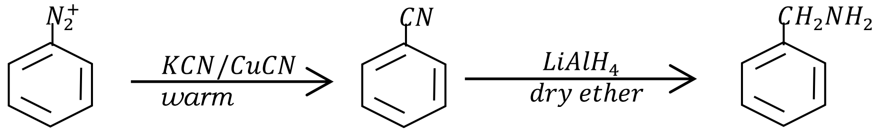
(b). Cyclohexene



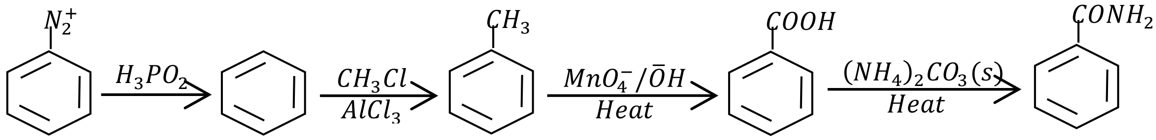
(c). Hexane-1,6-dioic acid



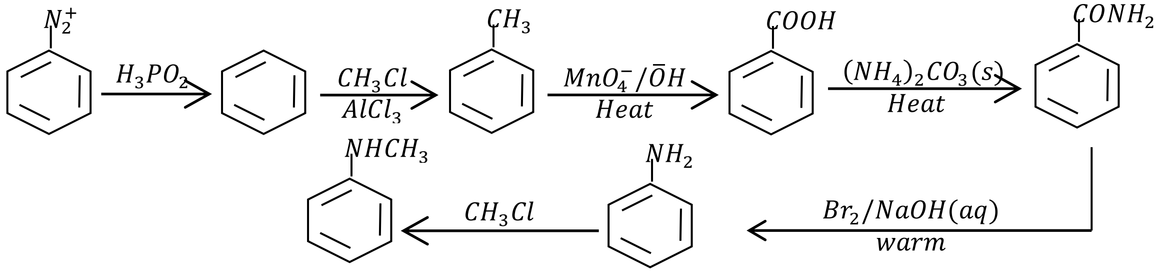
(d). 1-phenylmethanamine (Benzyl amine)



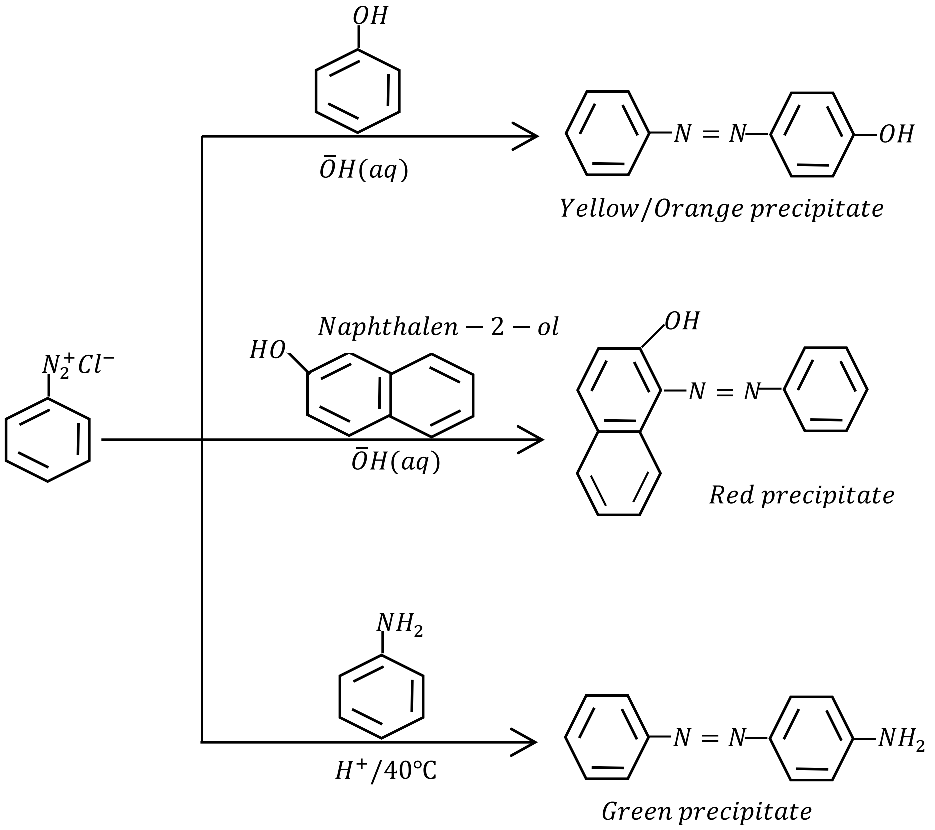
(e). Benzamide



(f). N-methylaniline



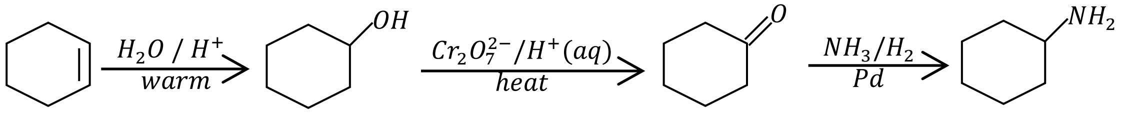
(ii). Diazonium coupling reactions



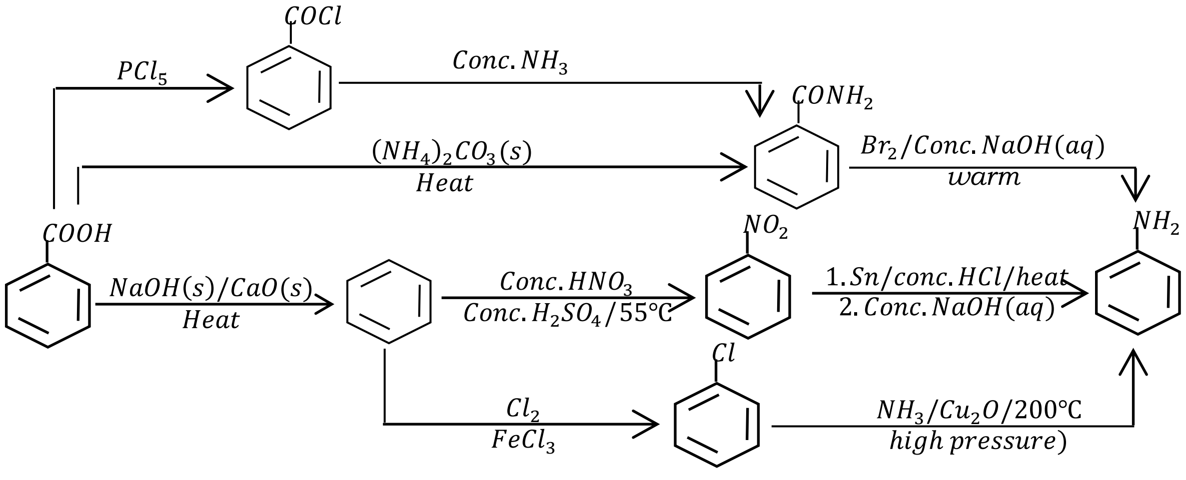
- **Question 21**

Write equations to show how the following conversions can be made.

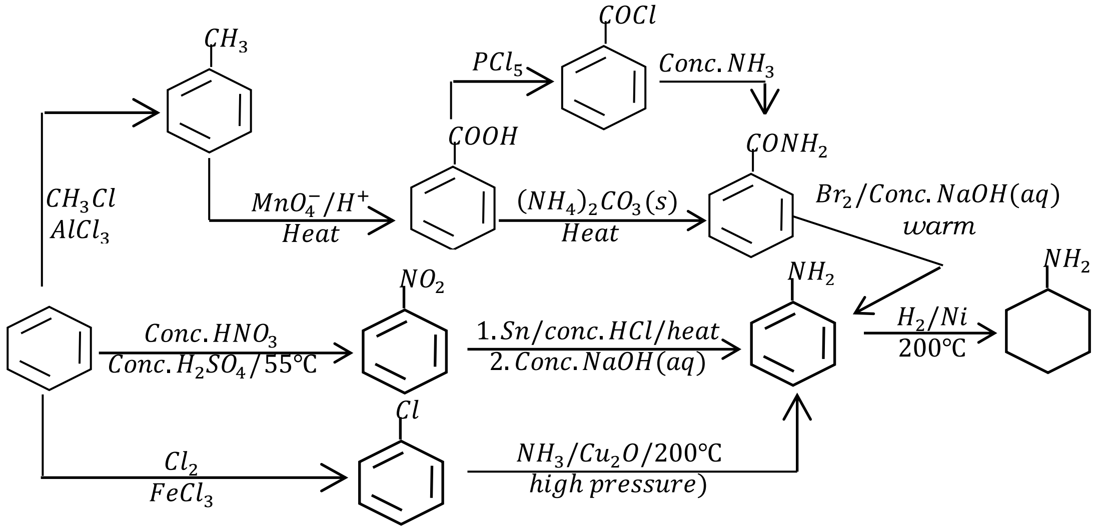
(a). Cyclohexene to Cyclohexanamine



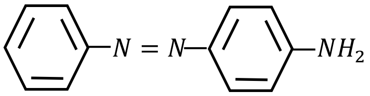
(b). Benzoic acid to aniline

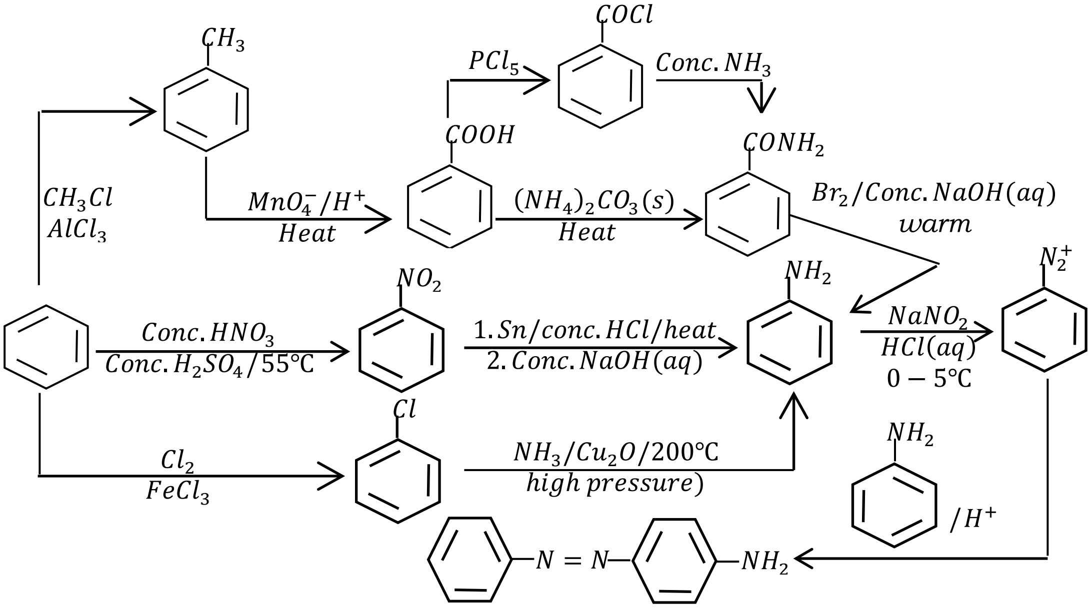


(c). Benzene to Cyclohexanamine



(d). Benzene to





(e). 2-methylpropene to 3-methylbutanamine

$$(CH_3)_2C = CH_2 \xrightarrow[ROOR]{HBr} (CH_3)_2CHCH_2Br \xrightarrow[Ethanol/heat]{KCN} (CH_3)_2CHCH_2CN$$

$$\xrightarrow[Dry\ ether]{LiAlH_4} (CH_3)_3CHCH_2NH_2$$

- **Question 22**

Write equations to show how the following substances can be synthesised from ethene.

(a). Ethanoyl chloride

$$H_2C = CH_2 \xrightarrow[warm]{H_2O/H_2SO_4} CH_3CH_2OH \xrightarrow[heat]{Cr_2O_7^{2-}/H^+} CH_3COOH \xrightarrow{PCl_5} CH_3COCl$$

(b). Ethanoic acid

$$H_2C = CH_2 \xrightarrow[warm]{H_2O/H_2SO_4} CH_3CH_2OH \xrightarrow[heat]{Cr_2O_7^{2-}/H^+} CH_3COOH$$

(c). Ethyl ethanoate

$$H_2C = CH_2 \xrightarrow[warm]{H_2O/H_2SO_4} CH_3CH_2OH \xrightarrow[Conc.H_2SO_4/warm]{CH_3COOH} CH_3COOCH_2CH_3$$

(d). Propanoic acid

$$H_2C = CH_2 \xrightarrow{HBr} CH_3CH_2Br \xrightarrow[Ethanol/heat]{KCN} CH_3CH_2CN \xrightarrow[Heat]{H_2O/H^+} CH_3CH_2COOH$$

(e). Ethanamide

$$\begin{tikzcd}
 & & & CH_3COCl \arrow[dr, "Conc.NH_3"] & \\
H_2C = CH_2 \arrow[r, "H_2O/H_2SO_4", "warm"'] & CH_3CH_2OH \arrow[r, "Cr_2O_7^{2-}/H^+", "heat"'] & CH_3COOH \arrow[ur, "PCl_5"] \arrow[rr, "(NH_4)_2CO_3(s)", "heat"'] & & CH_3CONH_2
\end{tikzcd}$$

(f). Ethanamine

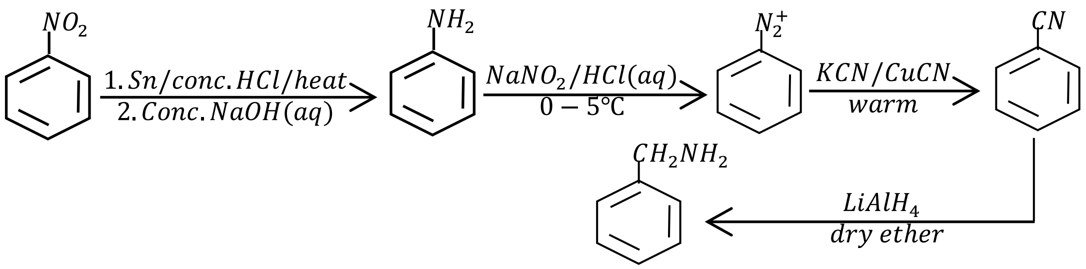
$$\begin{tikzcd}
 & & & CH_3COCl \arrow[dr, "Conc.NH_3"] & \\
H_2C = CH_2 \arrow[r, "H_2O/H^+", "warm"'] \arrow[dr, "HCl"'] & CH_3CH_2OH \arrow[r, "Cr_2O_7^{2-}/H^+", "heat"'] \arrow[d, "PCl_5"] & CH_3COOH \arrow[ur, "PCl_5"] \arrow[rr, "(NH_4)_2CO_3(s)", "heat"'] & & CH_3CONH_2 \arrow[dll, "LiAlH_4", "Dry\ ether"'] \\
 & CH_3CH_2Cl \arrow[r, "NH_3/Ethanol", "heat\ in\ sealed\ tube"'] & CH_3CH_2NH_2 & &
\end{tikzcd}$$

OR

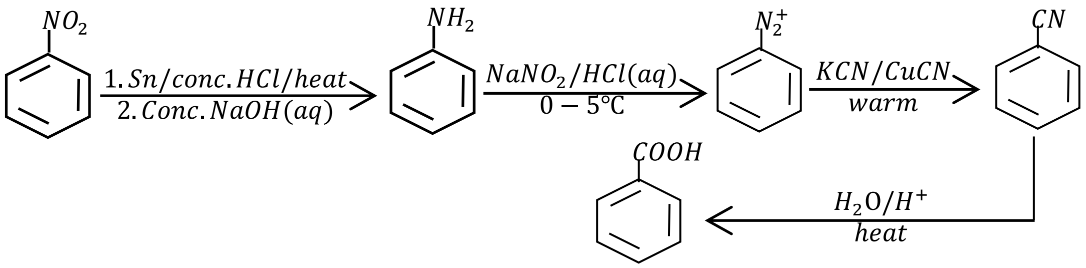
$$\begin{tikzcd}
H_2C = CH_2 \arrow[r, "H_2O/H^+", "warm"'] \arrow[rr, bend right, "O_2/H_2O/HCl", "PdCl_2/CuCl_2/60^\circ C"'] & CH_3CH_2OH \arrow[r, "Cr_2O_7^{2-}/H^+", "heat"'] & CH_3CHO \arrow[r, "NH_3/H_2", "NaBH_3CN"'] & CH_3CH_2NH_2
\end{tikzcd}$$

- **Question 23**
  Write equations to show how the following substances can be synthesised from nitrobenzene

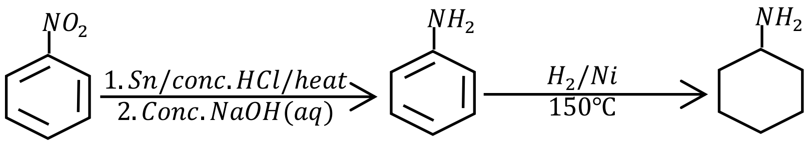
  (a). Phenylmethanamine



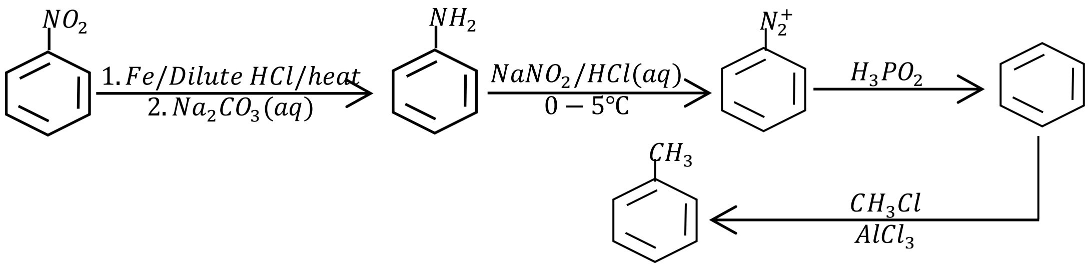
  (b). Benzoic acid



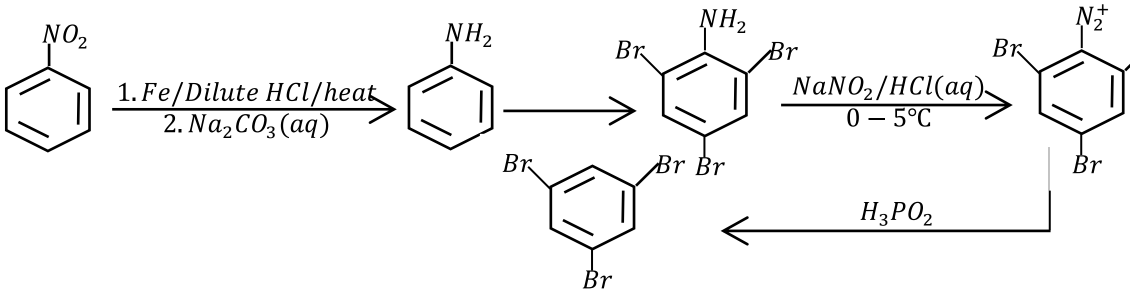
  (c). Cyclohexanamine



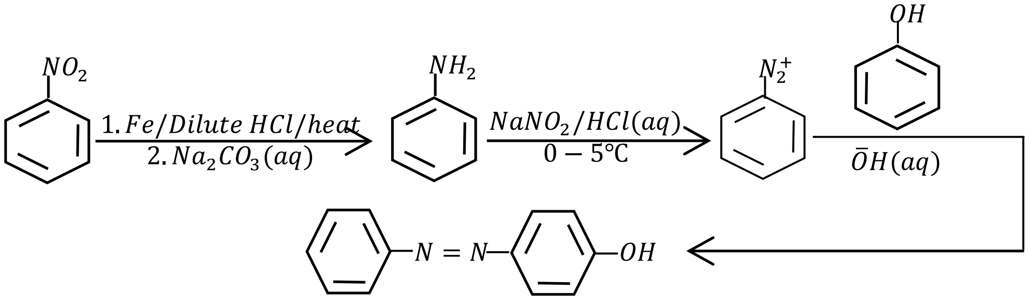
  (d). Methylbenzene

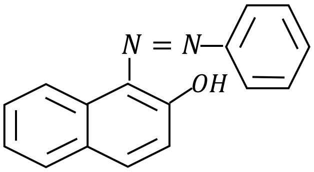


(e). 1,3,5-tribromobenzene

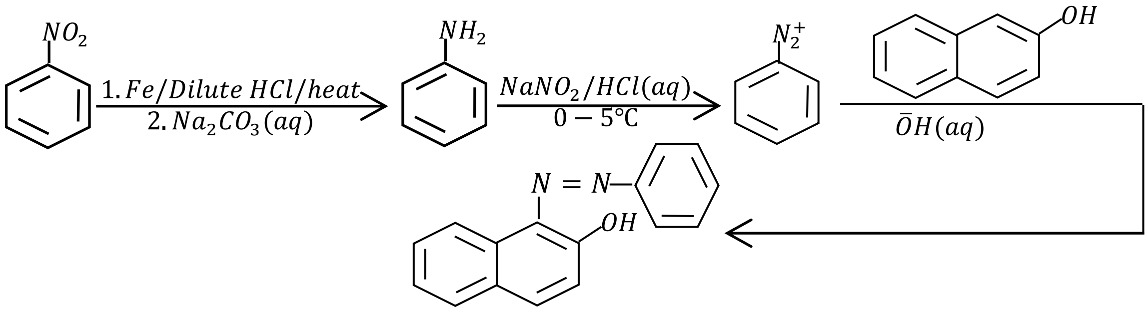


(f). 4-hydroxyazobenzene





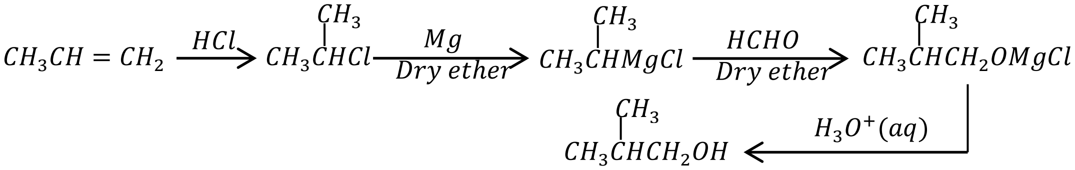
(g).



- **Question 24**

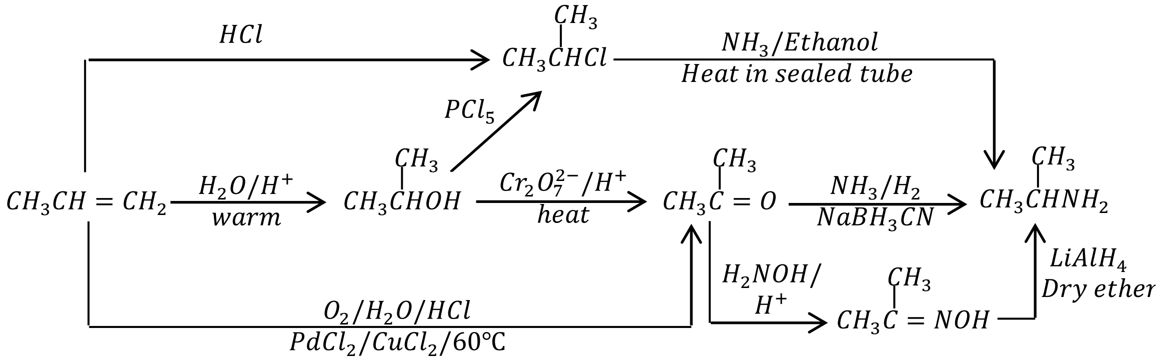
  Write equations to show how the following substances can be synthesised from propene

(a). 2-methylpropan-1-ol

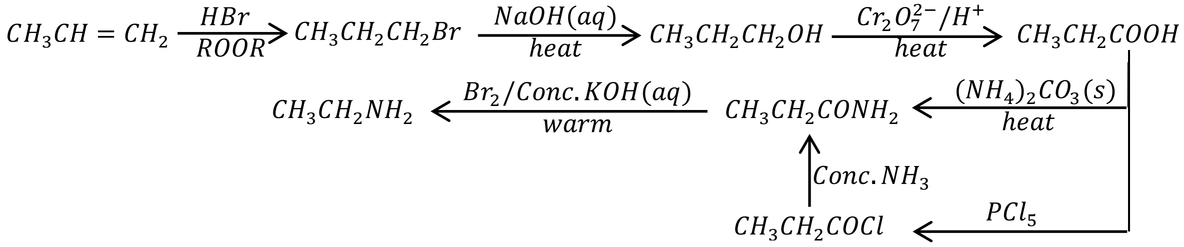


$$CH_3CH=CH_2 \xrightarrow{HCl} CH_3\overset{CH_3}{\overset{|}{C}}HCl \xrightarrow[\text{Dry ether}]{Mg} CH_3\overset{CH_3}{\overset{|}{C}}HMgCl \xrightarrow[\text{Dry ether}]{HCHO} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2OMgCl \xrightarrow{H_3O^+(aq)} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2OH$$

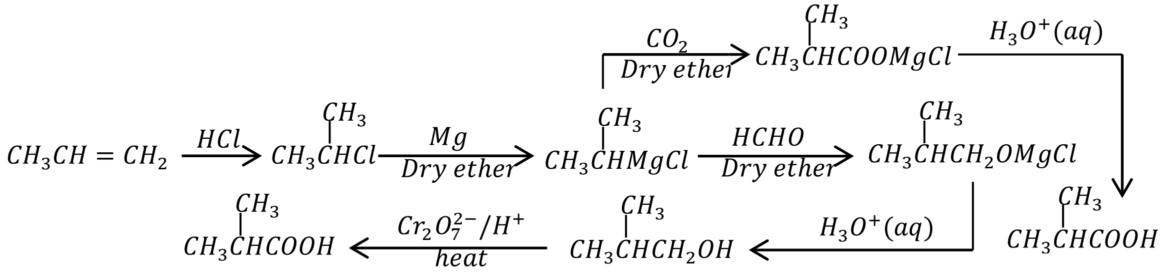
(b). Propan-2-amine



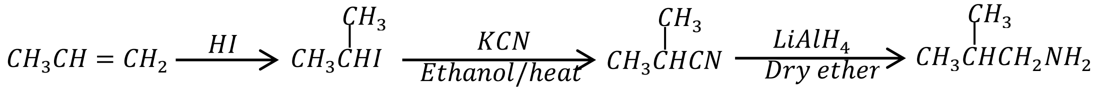
(c). Ethanamine



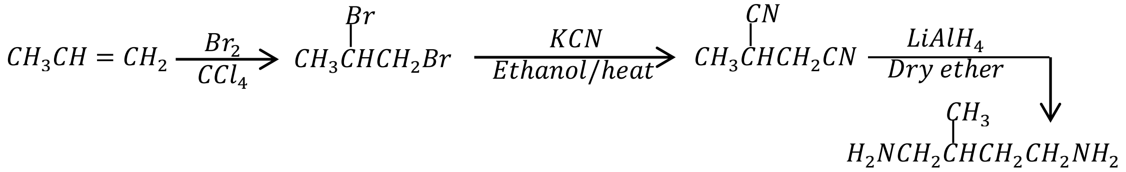
(d). 2-methylpropanoic acid



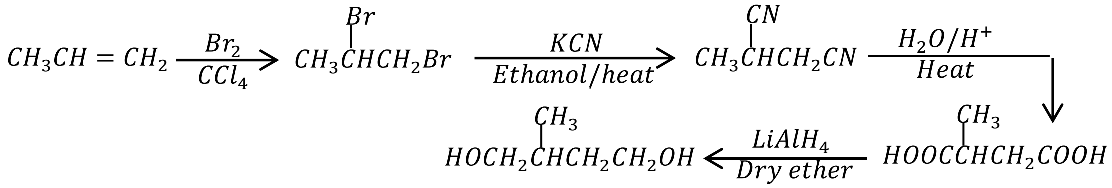
(e). 2-methylpropan-1-amine



(f). 2-methylbutane-1,4-diamine

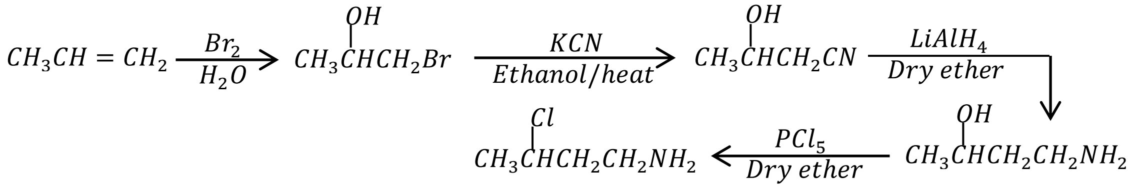


(g). 2-methylbutane-1,4-diol



$$CH_3CH=CH_2 \xrightarrow[CCl_4]{Br_2} CH_3\overset{Br}{C}HCH_2Br \xrightarrow[Ethanol/heat]{KCN} CH_3\overset{CN}{C}HCH_2CN \xrightarrow[Heat]{H_2O/H^+} HOOC\overset{CH_3}{C}HCH_2COOH \xrightarrow[Dry\ ether]{LiAlH_4} HOCH_2\overset{CH_3}{C}HCH_2CH_2OH$$

(h). 2-chlorobutanamine

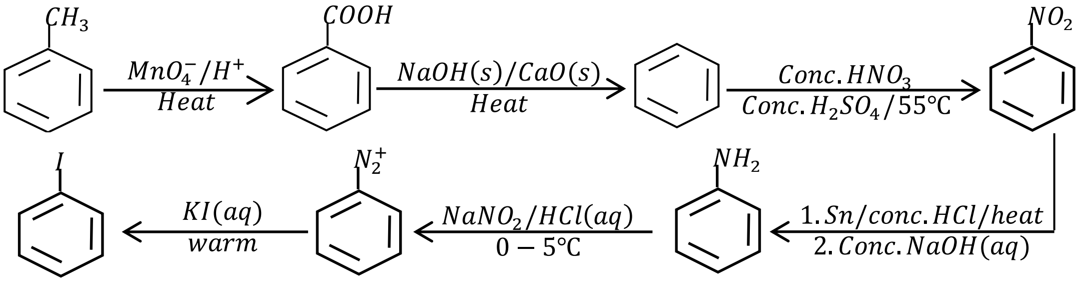


$$CH_3CH=CH_2 \xrightarrow[H_2O]{Br_2} CH_3\overset{OH}{C}HCH_2Br \xrightarrow[Ethanol/heat]{KCN} CH_3\overset{OH}{C}HCH_2CN \xrightarrow[Dry\ ether]{LiAlH_4} CH_3\overset{OH}{C}HCH_2CH_2NH_2 \xrightarrow[Dry\ ether]{PCl_5} CH_3\overset{Cl}{C}HCH_2CH_2NH_2$$

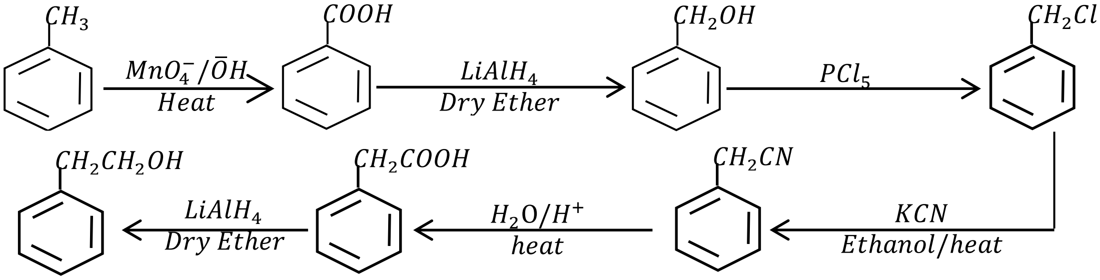
- **Question 25**

  Write equations to show how the following compounds can be synthesised from Methylbenzene

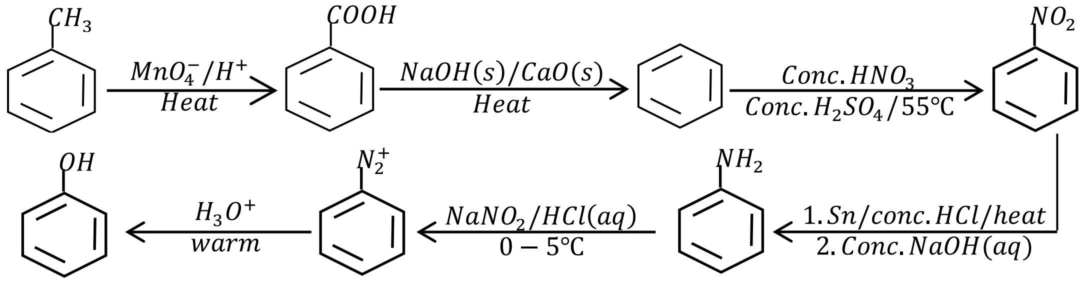
(a). Iodobenzene



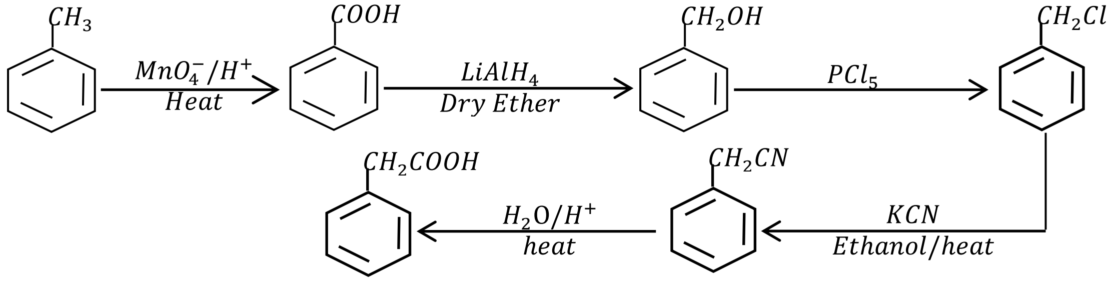
(b). 2-phenylethanol



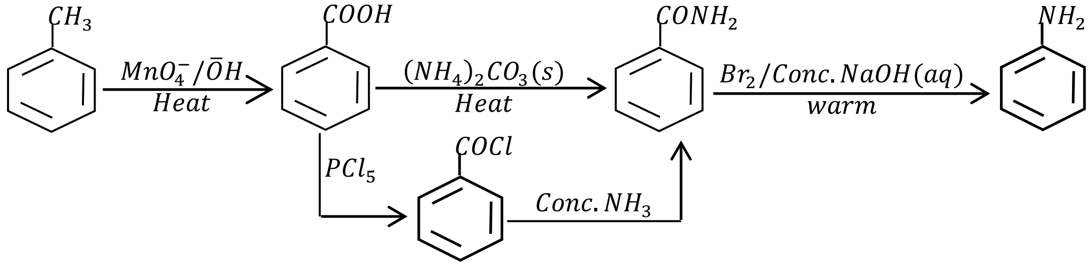
(c). Phenol



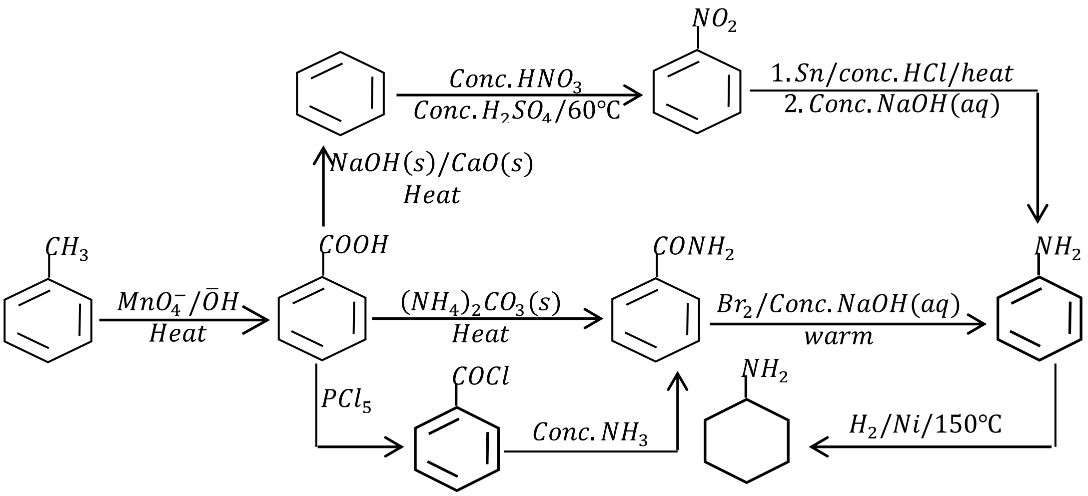
(d). Phenylethanoic acid



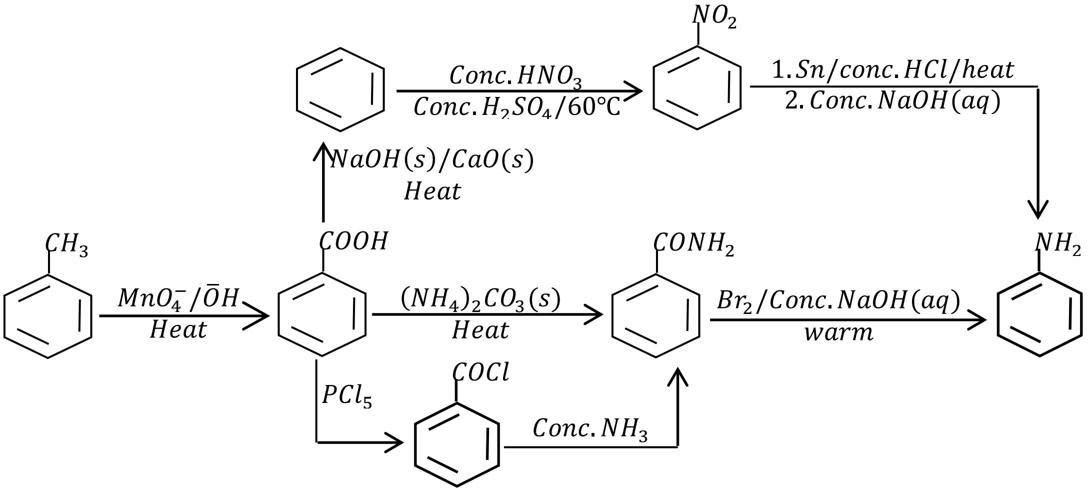
(e). Phenylmethanamine



(f). Cyclohexanamine



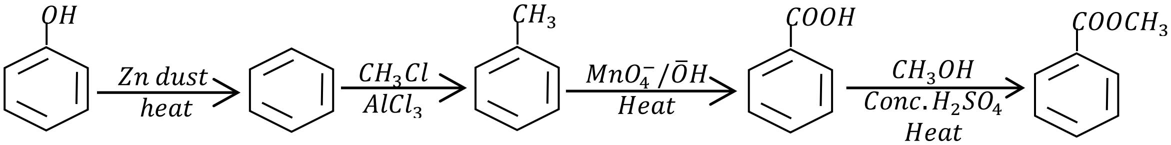
(g). Phenylamine



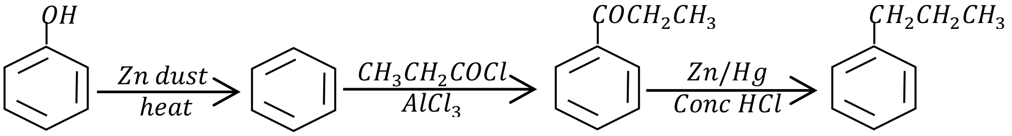
- **Question 26**

  Write equations to show how the following conversions can be made,

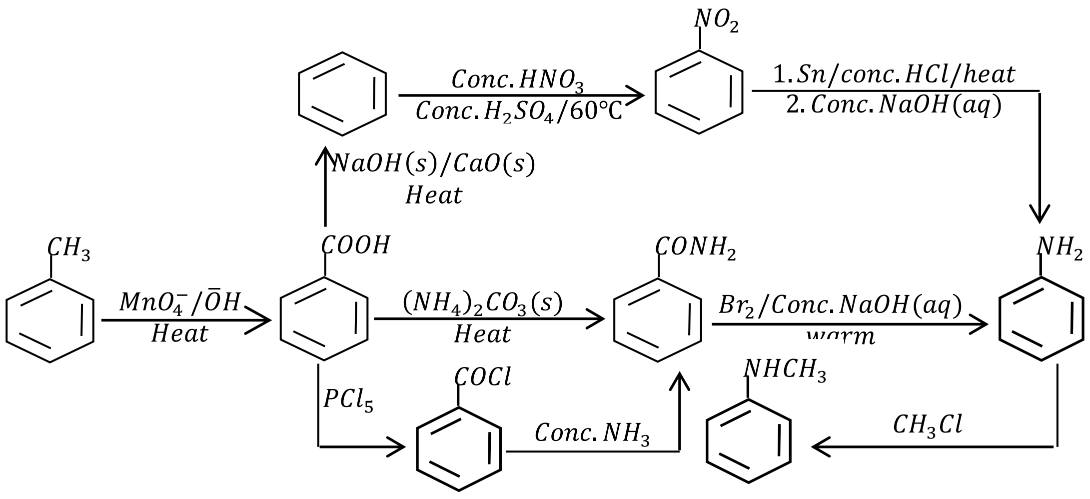
  (a). Methyl benzoate from phenol



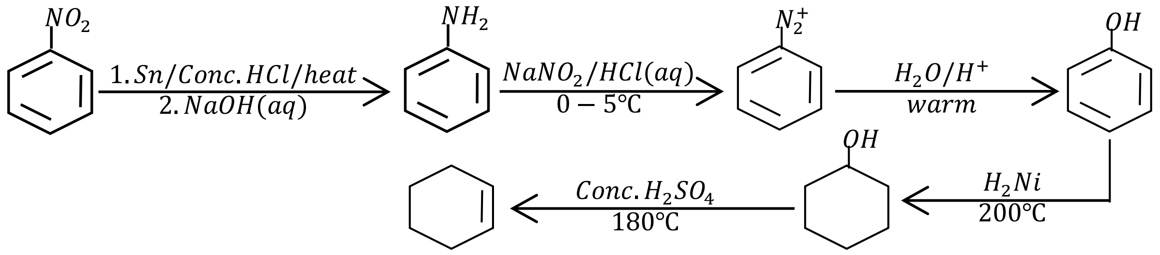
(b). Benzene to 1-phenylpropane



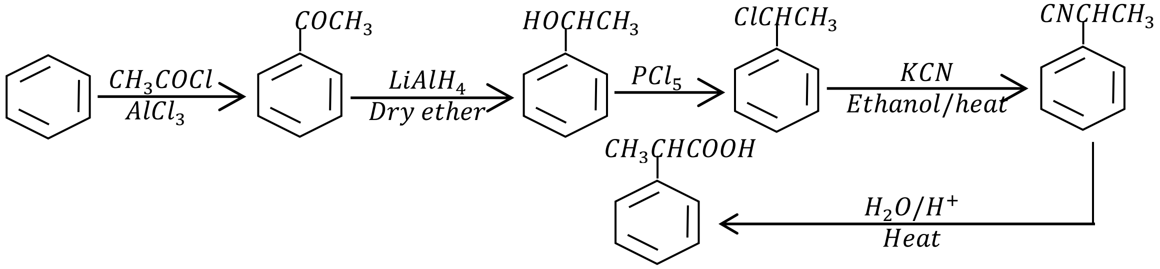
(c). methylbenzene to N-methyl-N-phenylamime



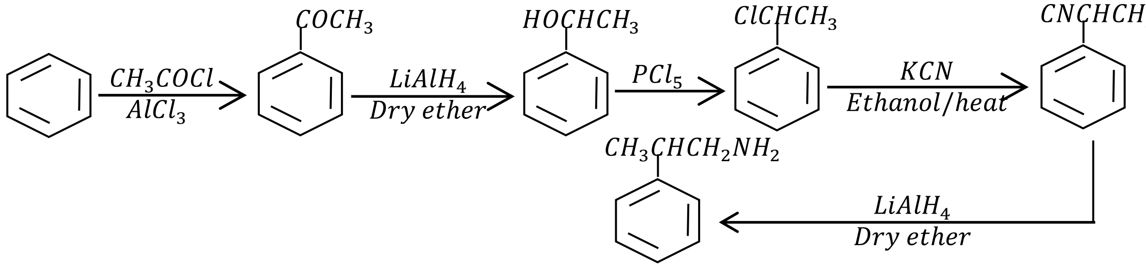
(d). Cyclohexene from nitrobenzene



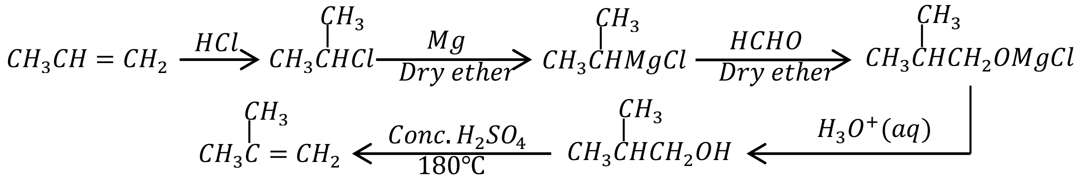
(e). Benzene to 2-phenylpropanoic acid



(f). Benzene to 2-phenylpropan-1-amine

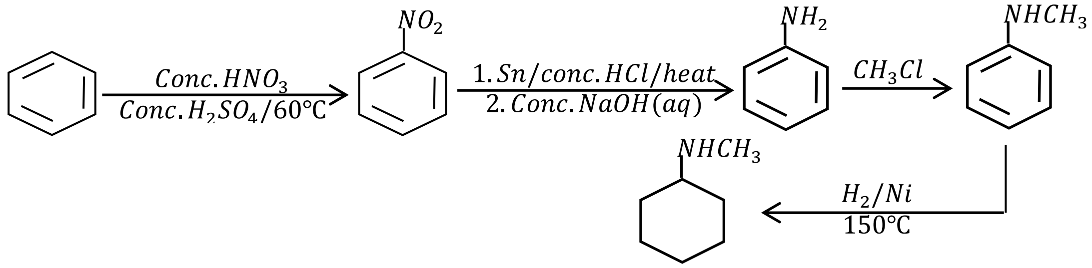


(g). Propene to 2-methylpropene

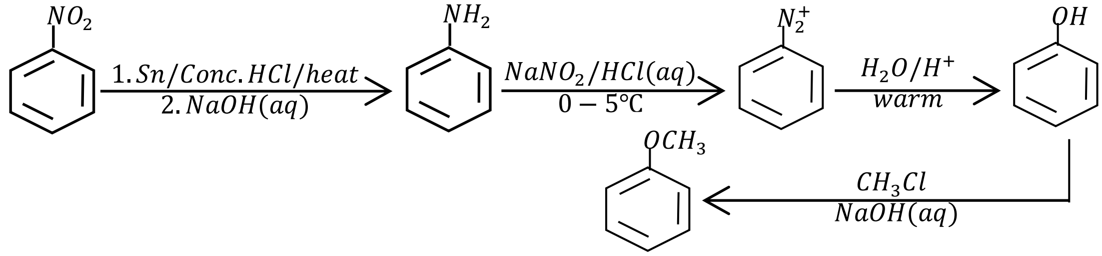


$$CH_3CH=CH_2 \xrightarrow{HCl} CH_3\overset{CH_3}{\overset{|}{C}}HCl \xrightarrow[\text{Dry ether}]{Mg} CH_3\overset{CH_3}{\overset{|}{C}}HMgCl \xrightarrow[\text{Dry ether}]{HCHO} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2OMgCl \xrightarrow{H_3O^+(aq)} CH_3\overset{CH_3}{\overset{|}{C}}HCH_2OH \xrightarrow[180℃]{Conc.\,H_2SO_4} CH_3\overset{CH_3}{\overset{|}{C}}=CH_2$$

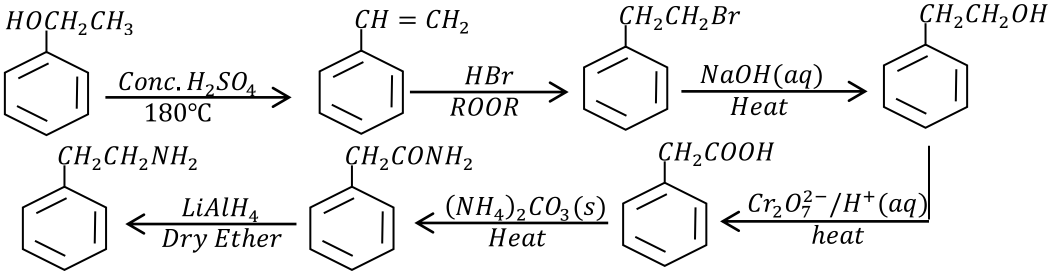
(h). Benzene to cyclohexylmethanamine



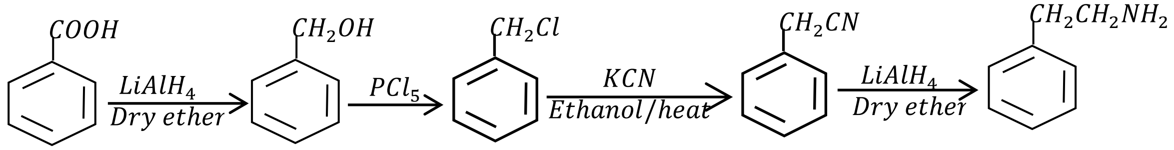
(i). Nitrobenzene to methoxybenzene



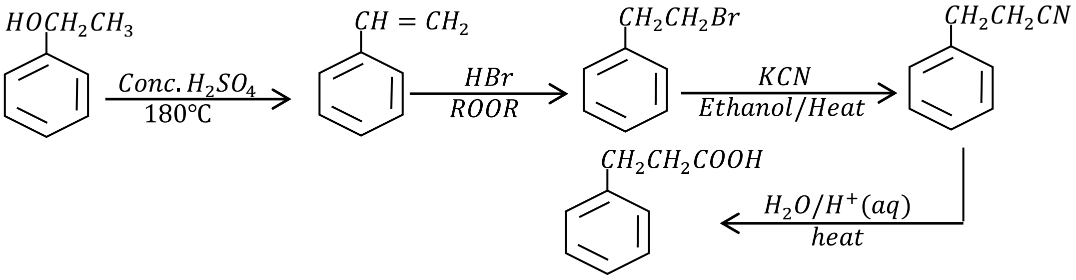
(j). 1-phenylethanol to 2-phenylethanamine



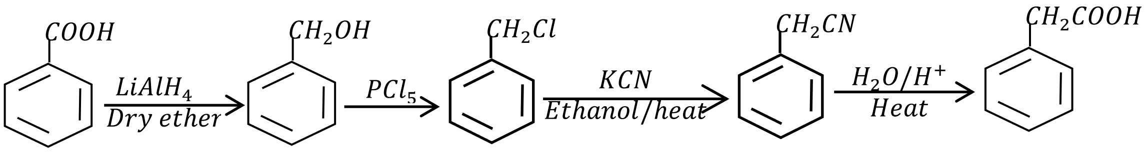
(k). Benzoic acid to 2-phenylethanamine



(l). 1-phenylethanol to 3-phenylpropanoic acid



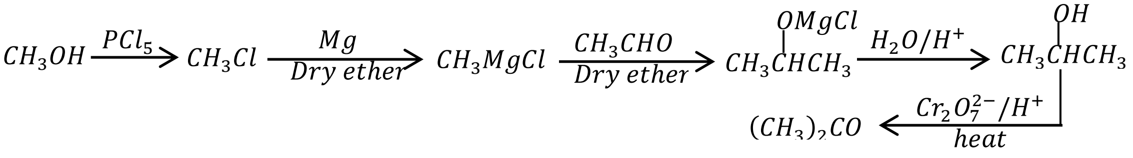
(m). Benzoic acid to Phenylethanoic acid



- **Question 27**

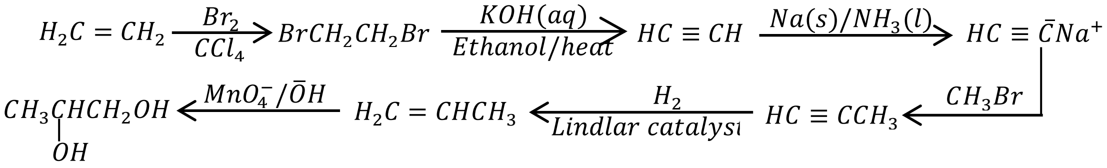
Write equations to show how the following conversions can be made

(a). Propanone from methanol



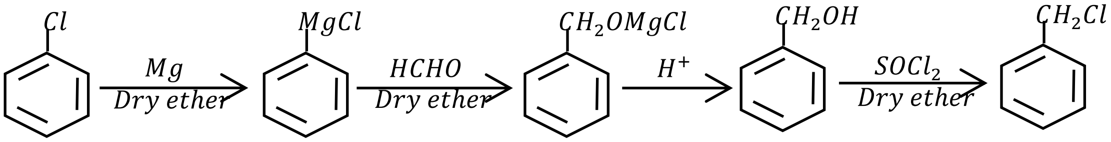
$$CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow[\text{Dry ether}]{Mg} CH_3MgCl \xrightarrow[\text{Dry ether}]{CH_3CHO} CH_3\overset{OMgCl}{C}HCH_3 \xrightarrow{H_2O/H^+} CH_3\overset{OH}{C}HCH_3 \xrightarrow[heat]{Cr_2O_7^{2-}/H^+} (CH_3)_2CO$$

(b). Ethene to propane-1,2-diol

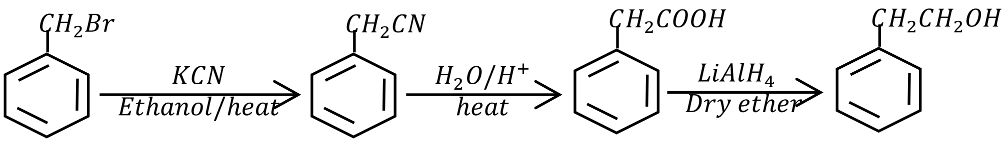


$$H_2C = CH_2 \xrightarrow[CCl_4]{Br_2} BrCH_2CH_2Br \xrightarrow[\text{Ethanol/heat}]{KOH(aq)} HC \equiv CH \xrightarrow{Na(s)/NH_3(l)} HC \equiv \bar{C}Na^+ \xrightarrow{CH_3Br} HC \equiv CCH_3 \xrightarrow[\text{Lindlar catalys}]{H_2} H_2C = CHCH_3 \xrightarrow{MnO_4^-/\bar{O}H} CH_3\underset{OH}{C}HCH_2OH$$

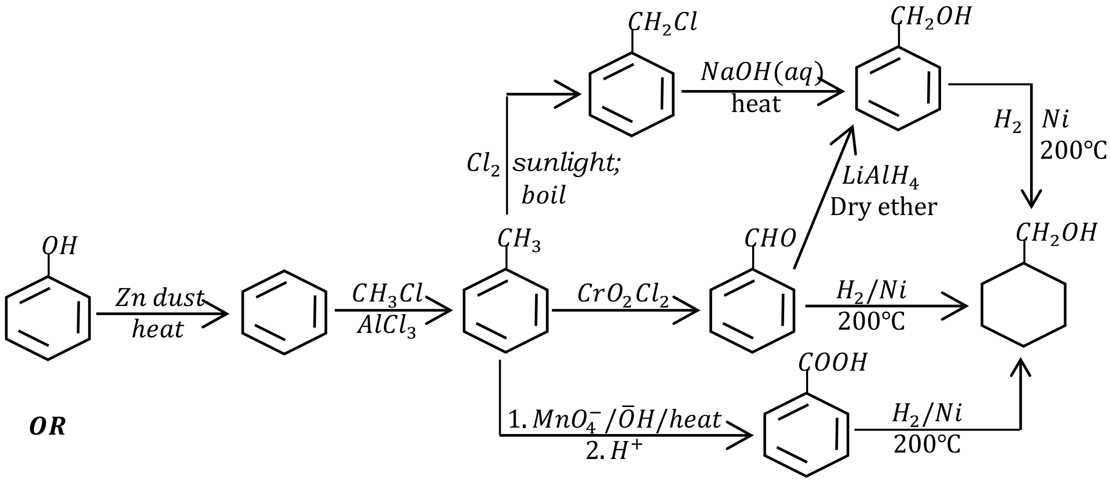
(c). Chlorobenzene to (chloromethyl)benzene [Benzyl chloride]



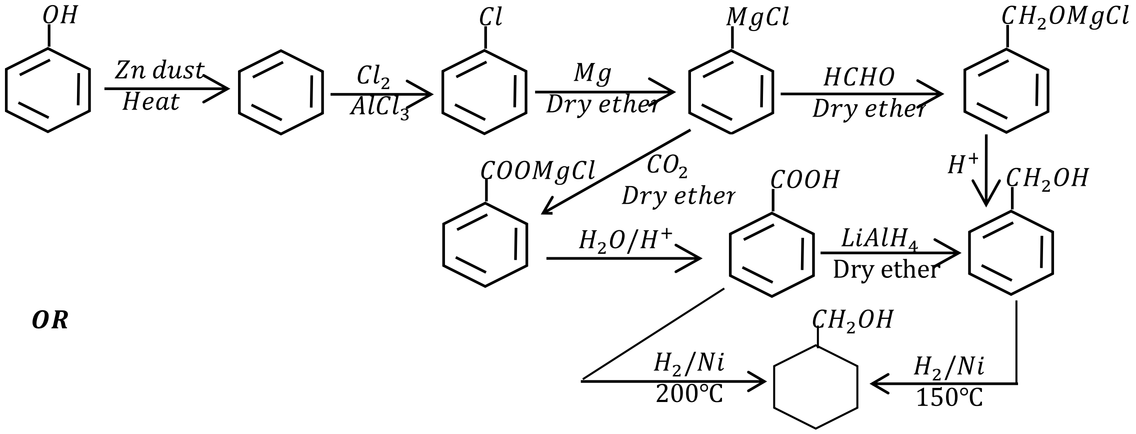
(d). (Bromomethyl)benzene to 2-phenylethanol



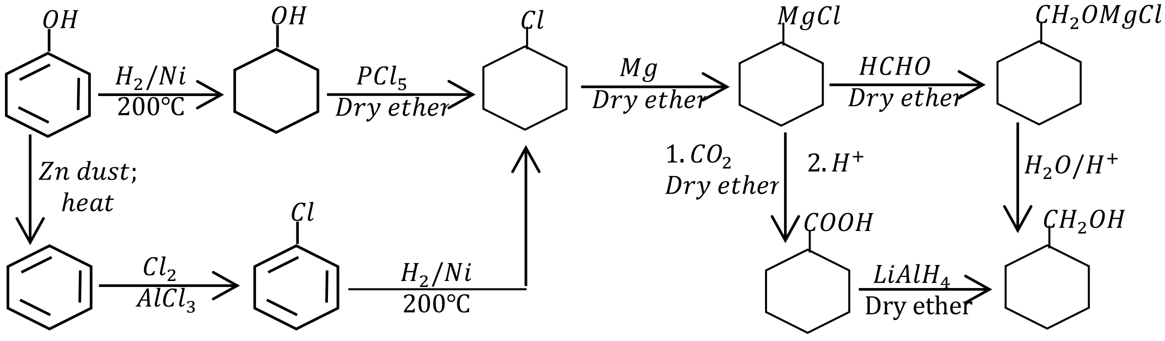
(e). Phenol to cyclohexylmethanol



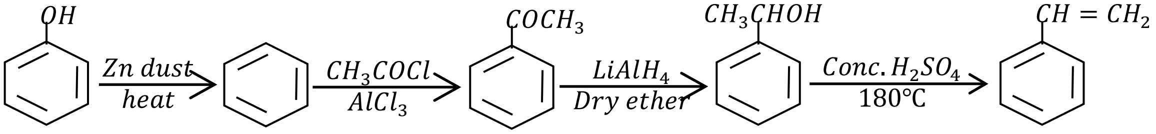
OR



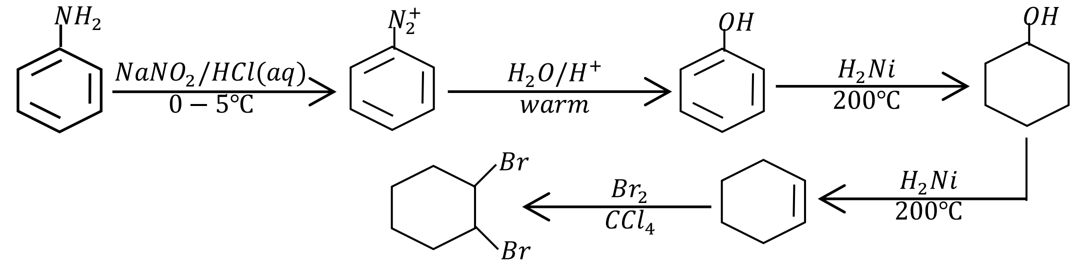
OR



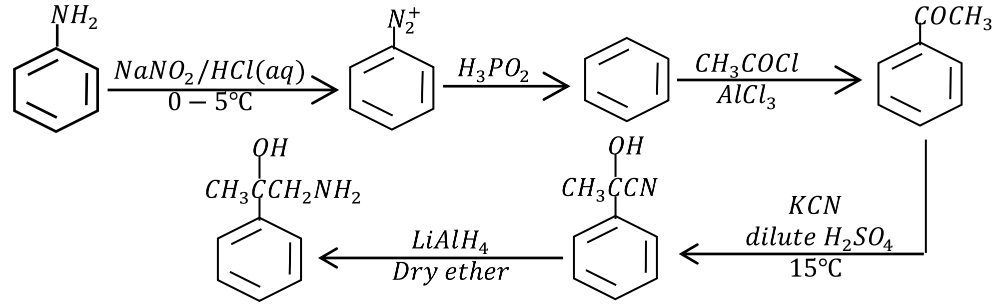
(f). Phenol to phenylethene



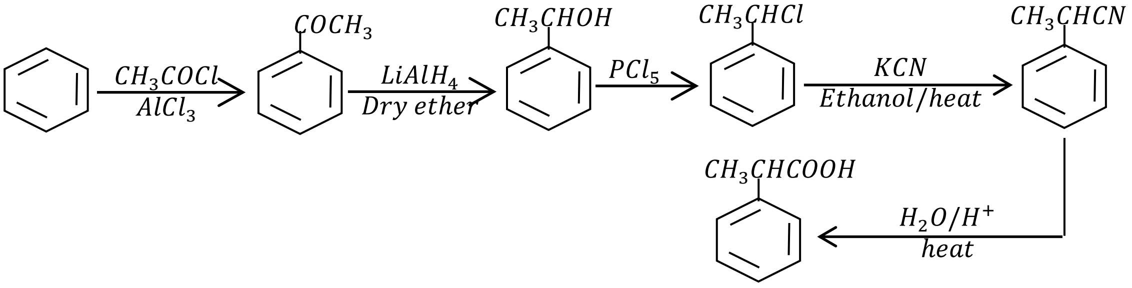
(g). 1,2-dibromocyclohexane from aniline



(h). Phenylamine to 2-hydroxy-2-phenylpropan-1-amine



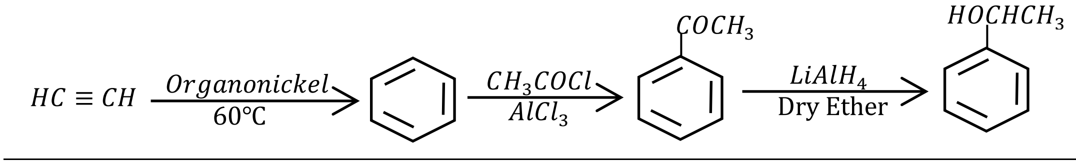
(i). Benzene to 2-phenylpropanoic acid



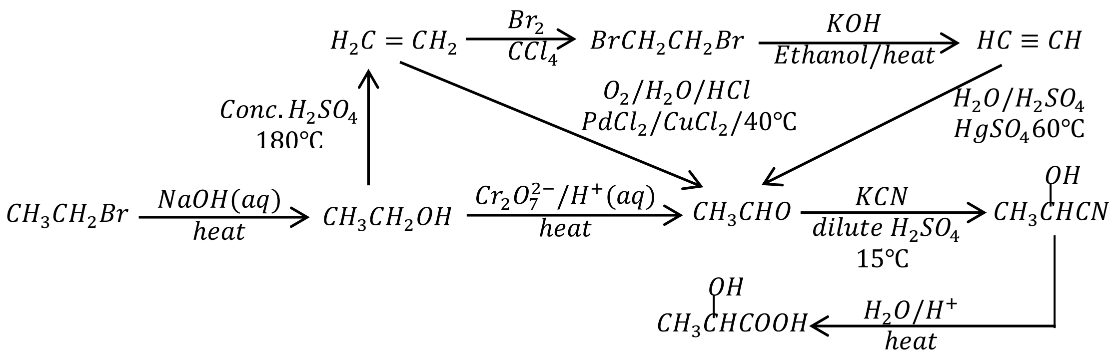
(j). Chloroethane to 1,1-dicloroethane

$$\begin{tikzcd}
CH_3CH_2Br \arrow[r, "NaOH(aq)", "heat"'] & CH_3CH_2OH \arrow[r, "Cr_2O_7^{2-}/H^+(aq)", "heat"'] \arrow[d, "Conc. H_2SO_4"', "180°C"'] & CH_3CHO \arrow[r, "PCl_5"] & CH_3CHCl_2 \\
 & H_2C=CH_2 \arrow[ur, "O_2/H_2O/HCl", "PdCl_2/CuCl_2/40°C"'] \arrow[r, "Br_2", "CCl_4"'] & BrCH_2CH_2Br \arrow[r, "KOH", "Ethanol/heat"'] & HC\equiv CH \arrow[ul, "H_2O/H_2SO_4", "HgSO_4/60°C"']
\end{tikzcd}$$

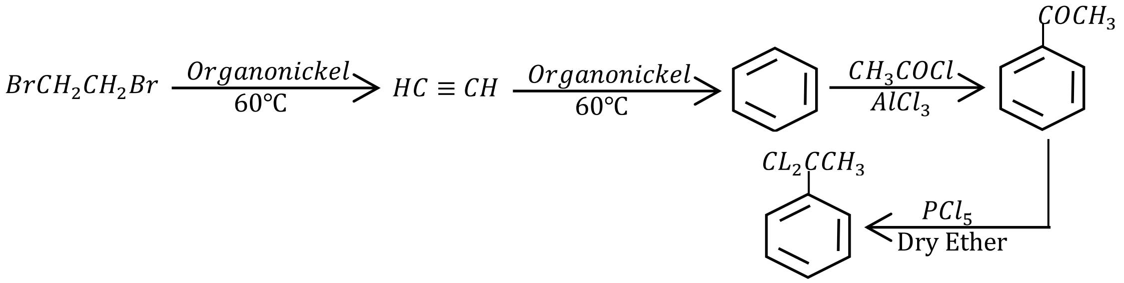
(k). Ethyne to 1-phenylethanol



(l). Ethene to 2-hydroxypropanoic acid



(m). 1,2-dibromoethane to 1,1-dichloro-1-phenylethane



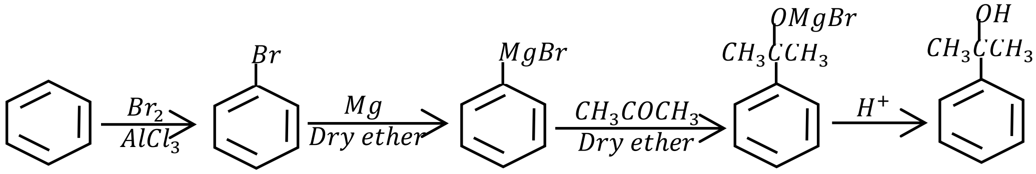
- **Question 28**

Write equations to show how the following conversions can be made, and in each case, state the conditions for the reactions.

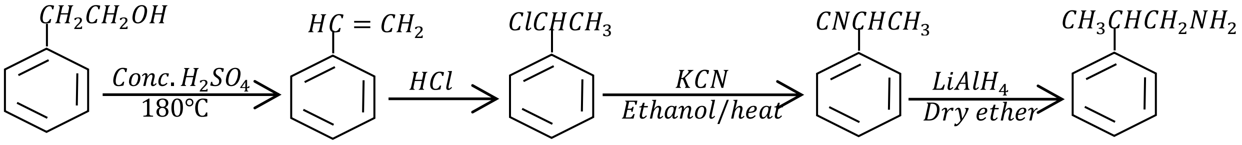
(a). N-methylethanamine from ethanol

$$CH_3CH_2OH \xrightarrow{PCl_5} CH_3CH_2Cl \xrightarrow[\text{Heat in sealed tube}]{CH_3NH_2/ethanol} CH_3CH_2NHCH_3$$

(b). Benzene to 2-phenylpropan-2-ol



(c). 2-phenylethanol to 2-phenylpropan-1-amine



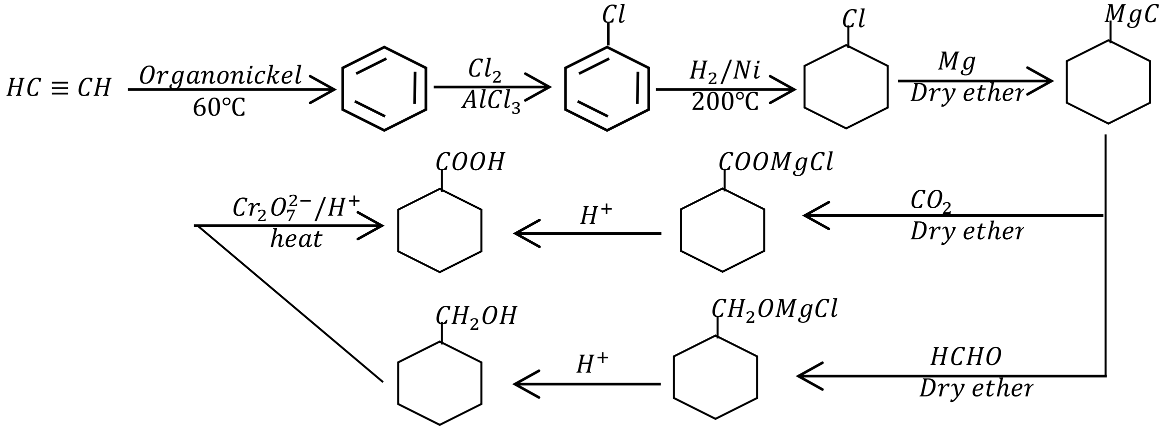
(d). 1-chloropropane to ethanamine

$$\begin{tikzcd}
CH_3CH_2CH_2Cl \arrow[r, "NaOH(aq)", "heat"'] & CH_3CH_2CH_2OH \arrow[r, "Cr_2O_7^{2-}/H^+", "heat"'] & CH_3CH_2COOH \arrow[dl, "(NH_4)_2CO_3(s)", "heat"'] \arrow[ddl, "PCl_5"] \\
CH_3CH_2NH_2 & CH_3CH_2CONH_2 \arrow[l, "Br_2/Conc.KOH(aq)"', "warm"] & \\
 & CH_3CH_2COCl \arrow[u, "Conc.NH_3"'] &
\end{tikzcd}$$

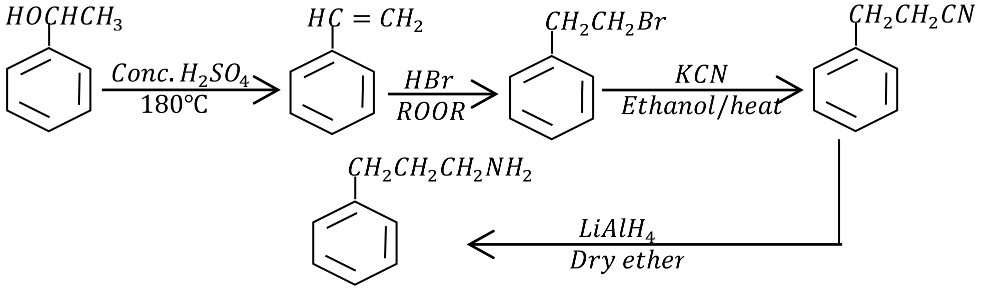
(e). 1,2-dibromoethane to ethanamide

$$\begin{tikzcd}
ClCH_2CH_2Cl \arrow[r, "KOH(aq)", "Ethanol/heat"'] & HC \equiv CH \arrow[r, "H_2O/H_2SO_4", "HgSO_4/60°C"'] & CH_3CHO \arrow[r, "Cr_2O_7^{2-}/H^+", "heat"'] & CH_3COOH \arrow[dl, "(NH_4)_2CO_3(s)", "heat"'] \arrow[ddl, "PCl_5"] \\
 & & CH_3CONH_2 & \\
 & & CH_3COCl \arrow[u, "Conc.NH_3"] &
\end{tikzcd}$$

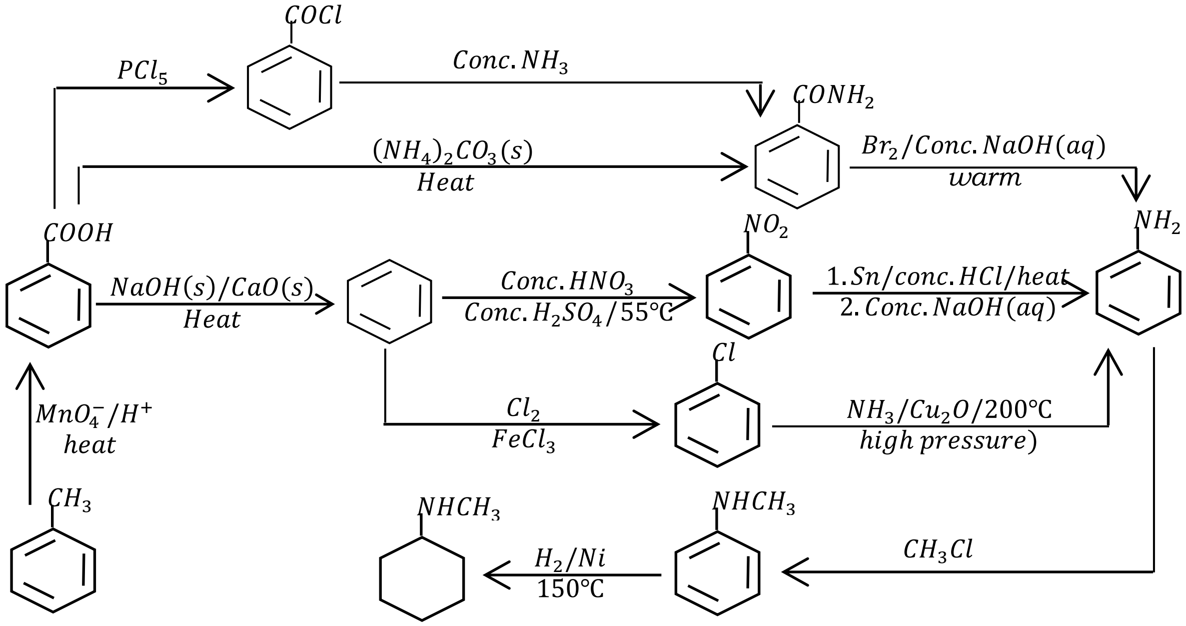
(f). Ethyne to cyclohexanecarboxylic acid



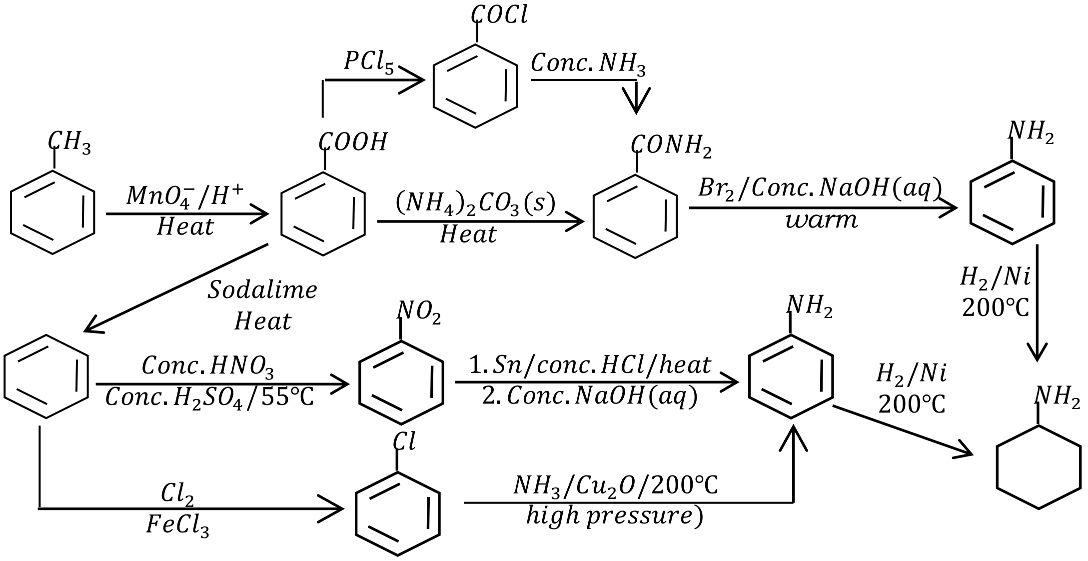
(a). 1-phenylethanol to 3-phenylpropan-1-amine



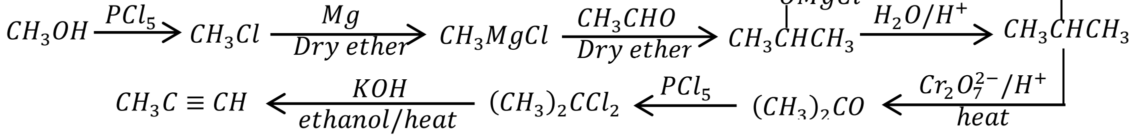
(b). Methylbenzene to cyclohexylmethanamine



(c). Methylbenzene to cylohexanamine



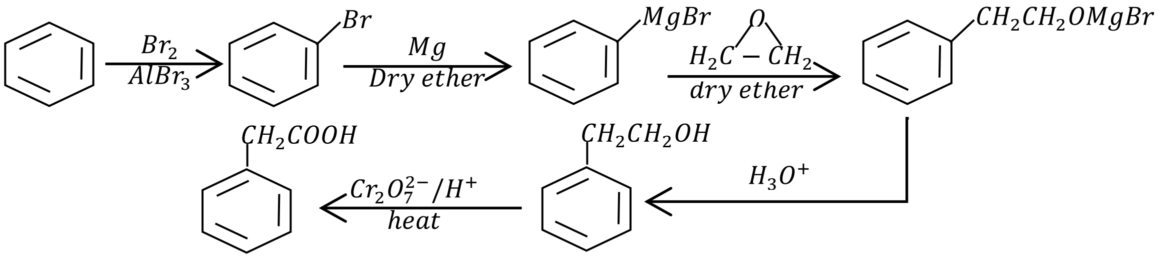
(d). Methanol to propyne



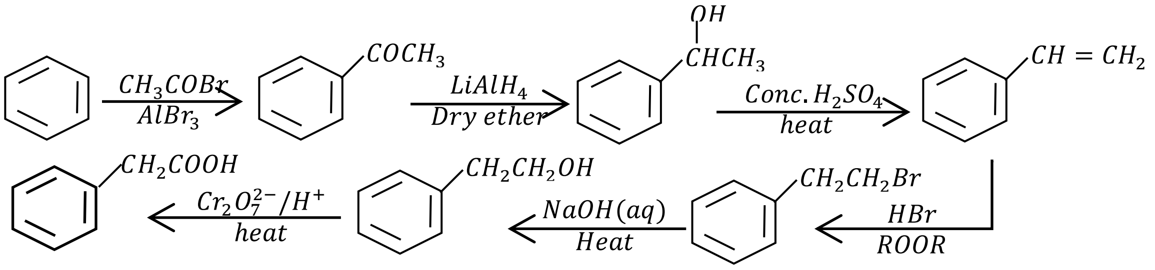
$$CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow[\text{Dry ether}]{Mg} CH_3MgCl \xrightarrow[\text{Dry ether}]{CH_3CHO} CH_3\overset{OMgCl}{\overset{|}{C}}HCH_3 \xrightarrow{H_2O/H^+} CH_3\overset{OH}{\overset{|}{C}}HCH_3$$

$$CH_3C \equiv CH \xleftarrow[\text{ethanol/heat}]{KOH} (CH_3)_2CCl_2 \xleftarrow{PCl_5} (CH_3)_2CO \xleftarrow[\text{heat}]{Cr_2O_7^{2-}/H^+}$$

(e). Benzene to Phenylethanoic acid



OR



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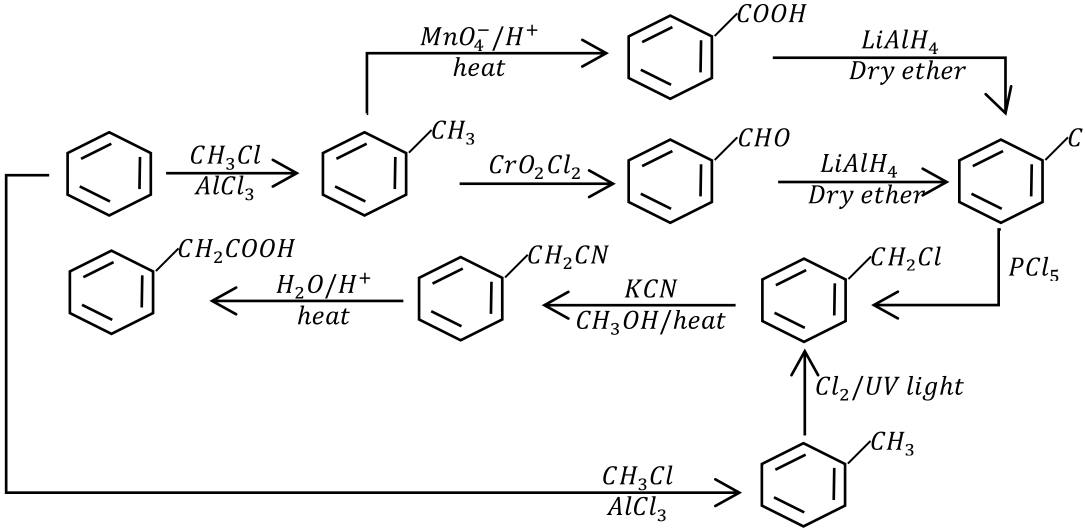
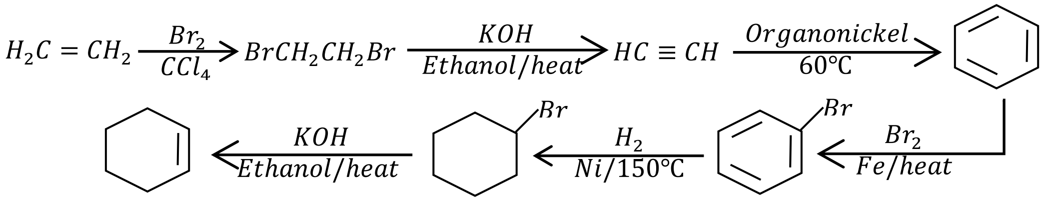
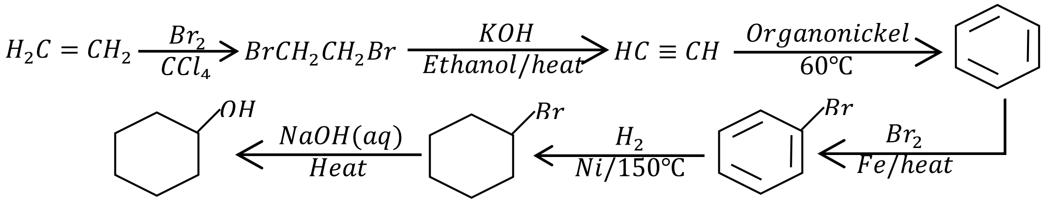


(f). Ethene to cyclohexene



(g). Ethene to Cyclohexanol



- **Question 29**

  Write equations to show how the following compounds can be synthesised from each of the following substances and in each case, indicate the conditions for the reactions.

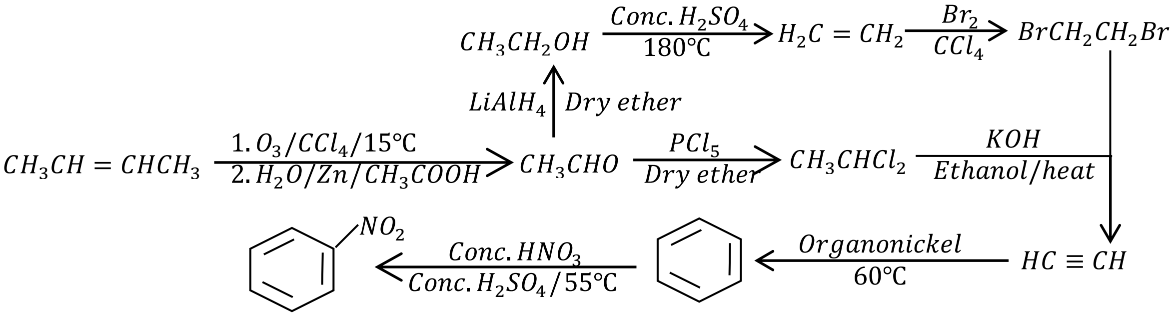
(a). Propan-2-ol to propanoic acid

$$\begin{tikzcd}
CH_3\overset{\overset{OH}{|}}{C}HCH_3 \arrow[r, "Conc.H_2SO_4", "180℃"'] & CH_3CH = CH_2 \arrow[r, "HBr", "ROOR"'] & CH_3CH_2CH_2Br \arrow[r, "NaOH(aq)", "heat"'] & CH_3CH_2CH_2OH \arrow[dl, "Cr_2O_7^{2-}/H^+", "heat"'] \\
 & & CH_3CH_2COOH &
\end{tikzcd}$$

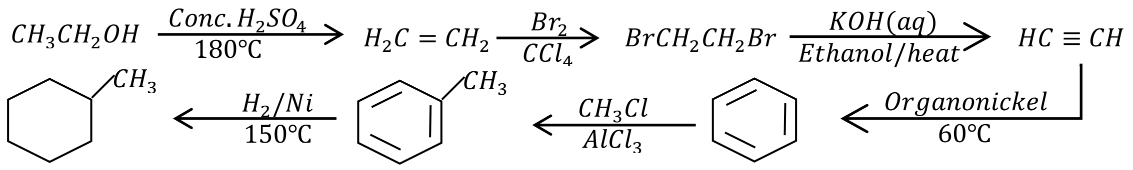
(b). 1-bromopropane to ethanol

$$\begin{tikzcd}
 & & & CH_3CH_2COCl \arrow[ddr, "Conc.NH_3"] & \\
CH_3CH_2CH_2Br \arrow[r, "NaOH(aq)", "heat"'] & CH_3CH_2CH_2OH \arrow[r, "Cr_2O_7^{2-}/H^+", "heat"'] & CH_3CH_2COOH \arrow[ur, "PCl_5"] \arrow[ddr, "(NH_4)_2CO_3(s)", "heat"'] & & \\
 & CH_3CH_2OH & CH_3CH_2NH_2 \arrow[l, "NaNO_2", "HCl(aq)"'] & & CH_3CH_2CONH_2 \arrow[ll, "Br_2/Conc.KOH(aq)", "warm"']
\end{tikzcd}$$

(c). But-2-ene to nitrobenzene



(d). Ethanol to methylcyclohexane

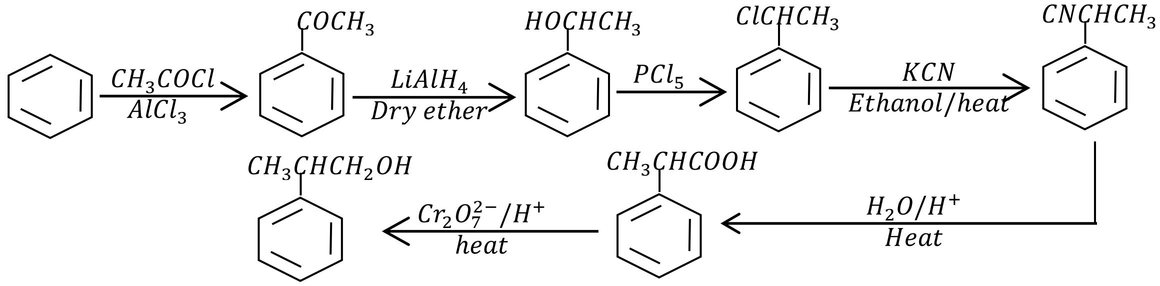


(e). Ethanol to 1,4-dichlorobutane

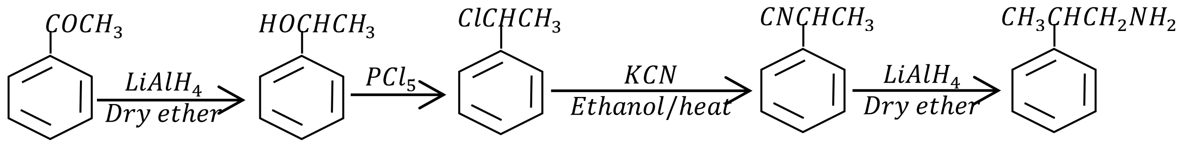
$$H_2C=CH_2 \xrightarrow[CCl_4]{Br_2} BrCH_2CH_2Br \xrightarrow[CH_3OH/heat]{KCN} CNCH_2CH_2CN \xrightarrow[Heat]{H_2O/H^+} HOOCCH_2CH_2COOH$$

$$ClCH_2CH_2CH_2CH_2Cl \xleftarrow{PCl_5} HOCH_2CH_2CH_2CH_2OH \xleftarrow[Dry\ ether]{LiAlH_4}$$

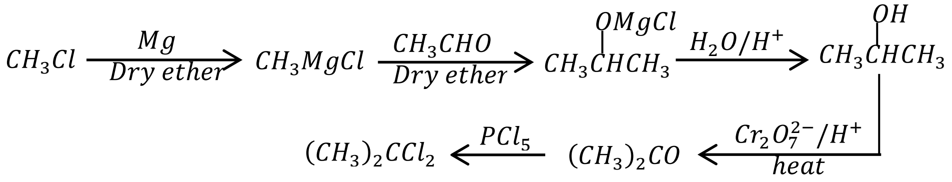
(f). Benzene to 2-phenylpropan-1-ol



(g). Phenylethanone to 2-phenylpropan-1-amine



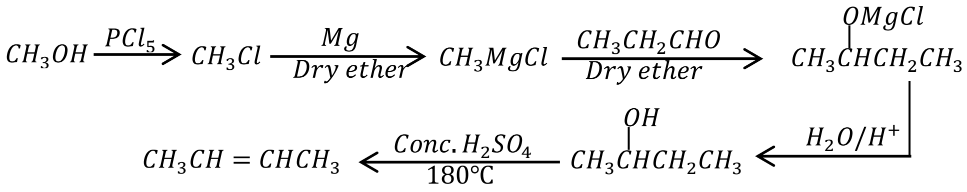
(h). Chloromethane to 2,2-dichloropropane



$$CH_3Cl \xrightarrow[Dry\ ether]{Mg} CH_3MgCl \xrightarrow[Dry\ ether]{CH_3CHO} CH_3\overset{OMgCl}{C}HCH_3 \xrightarrow{H_2O/H^+} CH_3\overset{OH}{C}HCH_3$$

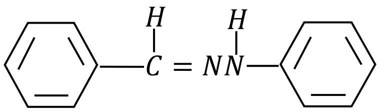
$$(CH_3)_2CCl_2 \xleftarrow{PCl_5} (CH_3)_2CO \xleftarrow[heat]{Cr_2O_7^{2-}/H^+}$$

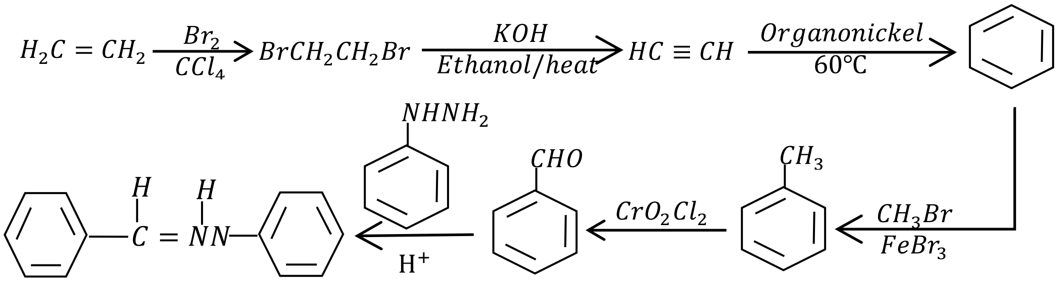
(i). Methanol to but-2-ene



$$CH_3OH \xrightarrow{PCl_5} CH_3Cl \xrightarrow[Dry\ ether]{Mg} CH_3MgCl \xrightarrow[Dry\ ether]{CH_3CH_2CHO} CH_3\overset{OMgCl}{C}HCH_2CH_3$$

$$CH_3CH=CHCH_3 \xleftarrow[180°C]{Conc.\ H_2SO_4} CH_3\overset{OH}{C}HCH_2CH_3 \xleftarrow{H_2O/H^+}$$

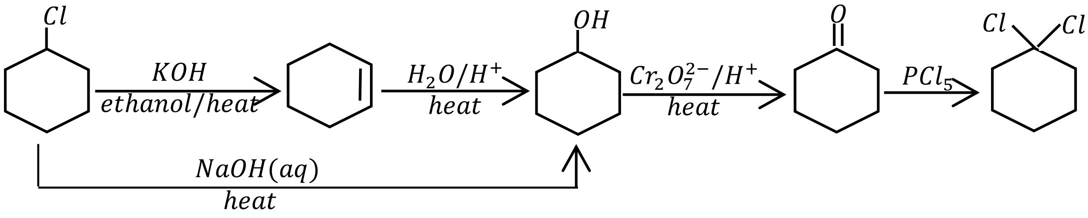
(j). Ethene to 



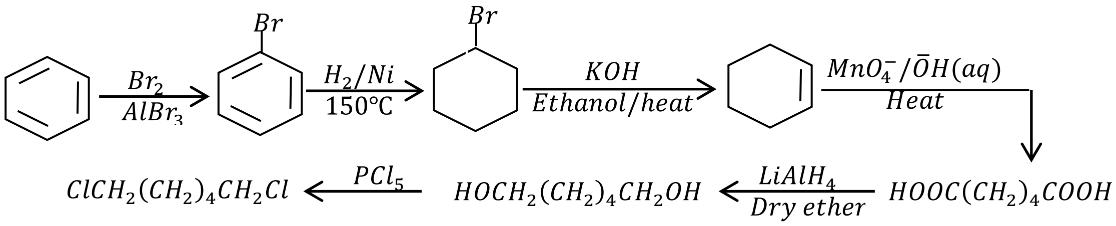
- **Question 30**

  Write equations to show how the following conversions can be made, and in each case, state the conditions for the reactions.

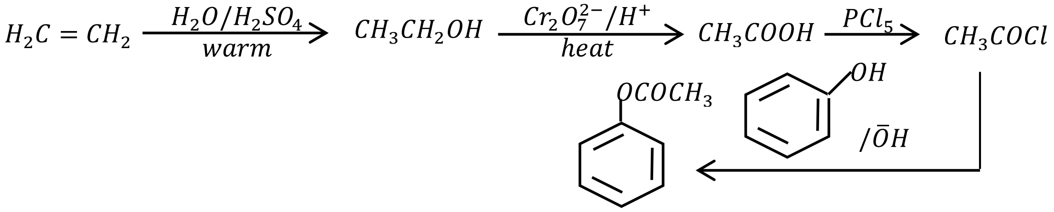
(a). Chlorocyclohexane to 1,1-chlorocyclohexane



(b). Benzene to 1,6-dibromohexane



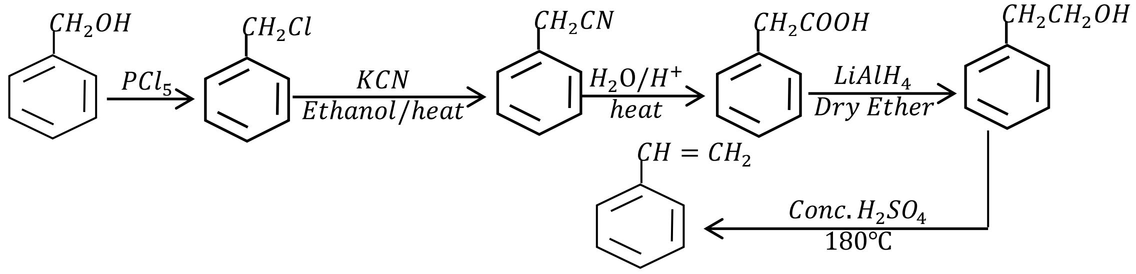
(c). Ethene to phenyl ethanoate



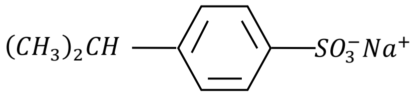
(d). Chloromethane to 1,1-dibromoethane

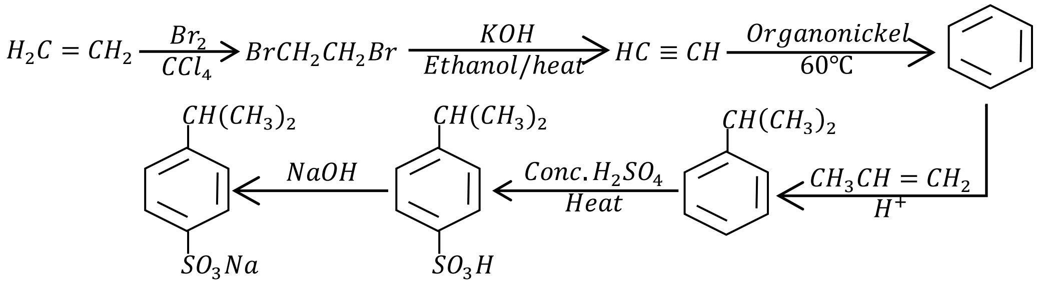
$$CH_3Cl \xrightarrow[Ethanol/heat]{KCN} CH_3CN \xrightarrow[Heat]{H_2O/H^+} CH_3COOH \xrightarrow[Dry\ ether]{LiAH_4} CH_3CH_2OH \xrightarrow[300°C]{Cu} CH_3CHO$$

(e). Phenylmethanol to phenylethene



(f). Ethene to





(g). $CH_3(CH_2)_4CH_3$ from 2-chloropropane

$$\underset{Cl}{CH_3\underset{|}{C}HCH_3} \xrightarrow[ROH/heat]{KOH} CH_3CH = CH_2 \xrightarrow[ROOR]{HBr} CH_3CH_2CH_2Br \xrightarrow[Dry\ Ether]{Na} CH_3(CH_2)_4CH_3$$

- **Question 31**

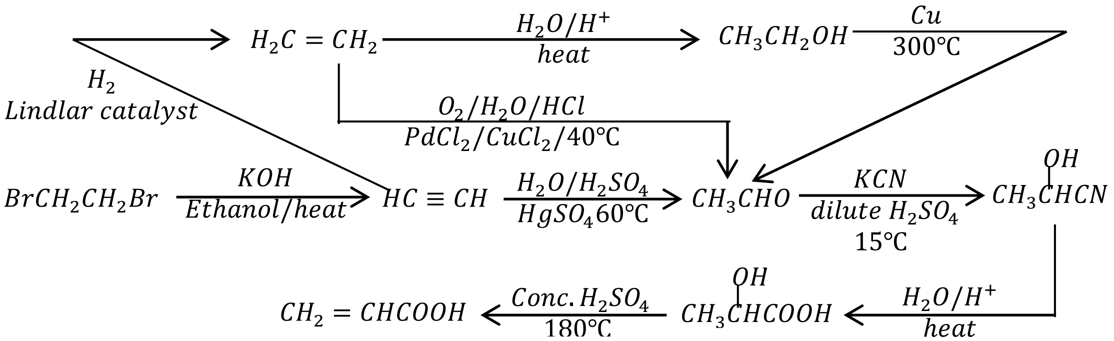
  Write equations to show how the following compounds can be synthesised from each of the following substances and in each case, indicate the conditions for the reactions.

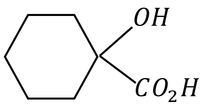
(a). Ethanoic acid to butanedioic acid

$$CH_3COOH \xrightarrow[dry\ ether]{LiAlH_4} CH_3CH_2OH \xrightarrow[180°C]{Conc.H_2SO_4} H_2C = CH_2 \xrightarrow[CCl_4]{Br_2} BrCH_2CH_2Br$$

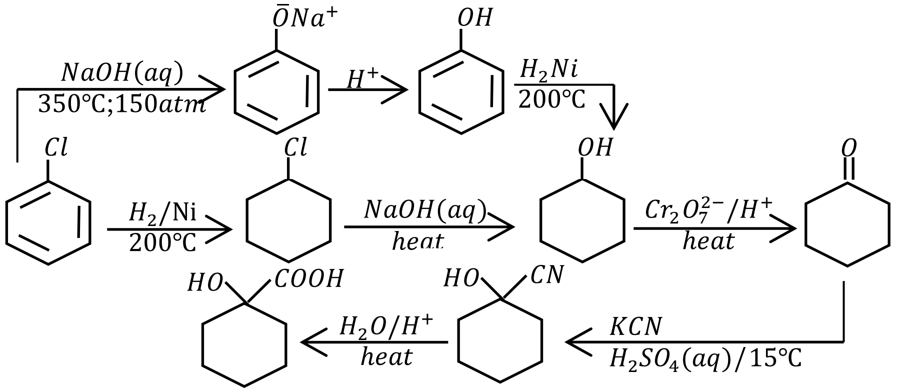
$$HOOCCH_2CH_2COOH \xleftarrow[Heat]{H_2O/H^+} CNCH_2CH_2CN \xleftarrow[CH_3OH/heat]{KCN}$$

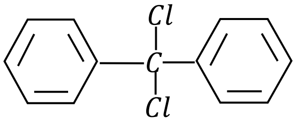
(b). Propenoic acid from 1,2-dibromoethane



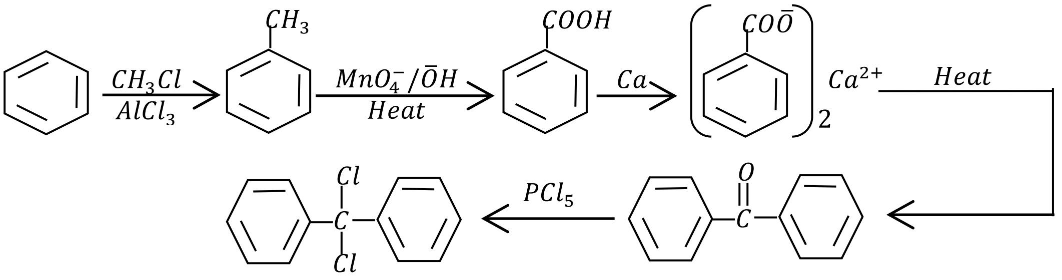


(c). from Chlorobenzene

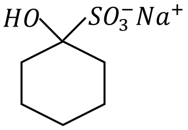


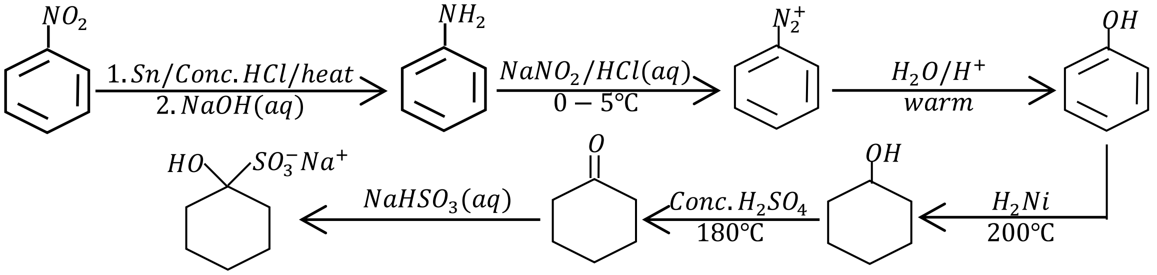


(d). Benzene to

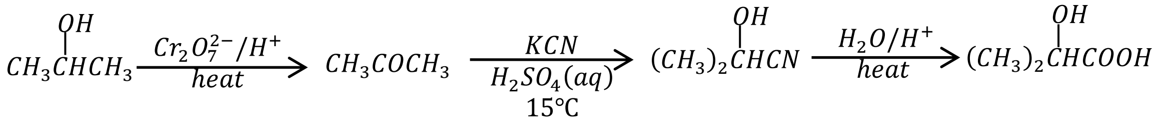


(e). Nitrobenzene to



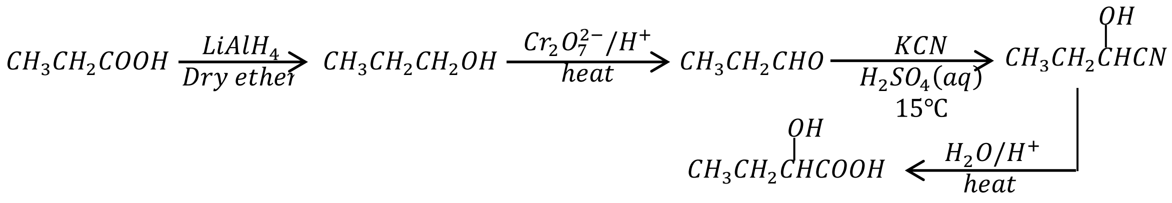


(f). Propan-2-ol to 2-hydroxy-2-methylpropanoic acid



$$CH_3\overset{OH}{C}HCH_3 \xrightarrow[heat]{Cr_2O_7^{2-}/H^+} CH_3COCH_3 \xrightarrow[H_2SO_4(aq),\ 15°C]{KCN} (CH_3)_2\overset{OH}{C}HCN \xrightarrow[heat]{H_2O/H^+} (CH_3)_2\overset{OH}{C}HCOOH$$

(g). Propanoic acid to 2-hydroxybutanoic acid

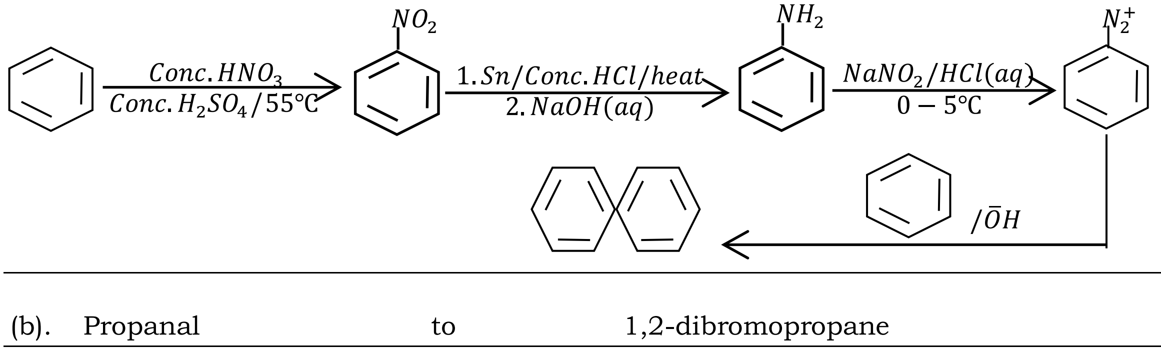


$$CH_3CH_2COOH \xrightarrow[Dry\ ether]{LiAlH_4} CH_3CH_2CH_2OH \xrightarrow[heat]{Cr_2O_7^{2-}/H^+} CH_3CH_2CHO \xrightarrow[H_2SO_4(aq),\ 15°C]{KCN} CH_3CH_2\overset{OH}{C}HCN \xrightarrow[heat]{H_2O/H^+} CH_3CH_2\overset{OH}{C}HCOOH$$

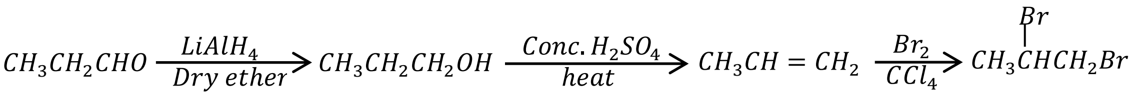
- **Question 32**

  Write equations to show how the following compounds can be synthesised from each of the following substances and in each case, indicate the conditions for the reactions.

  (a). Benzene to biphenyl



(b). Propanal to 1,2-dibromopropane



$$CH_3CH_2CHO \xrightarrow[Dry\ ether]{LiAlH_4} CH_3CH_2CH_2OH \xrightarrow[heat]{Conc. H_2SO_4} CH_3CH = CH_2 \xrightarrow[CCl_4]{Br_2} CH_3\overset{Br}{C}HCH_2Br$$

(c). Propene from ethylmagnesium chloride

$$\begin{tikzcd}
CH_3CH_2MgCl \arrow[r, "HCHO", "Dry\ ether"'] \arrow[d, "CO_2", "Dry\ ether"'] & CH_3CH_2CH_2OMgCl \arrow[r, "H^+"] & CH_3CH_2CH_2OH \arrow[r, "Conc.H_2SO_4", "180^\circ C"'] & CH_3CH = CH_2 \\
CH_3CH_2CH_2OMgCl \arrow[rr, "H^+"] & & CH_3CH_2COOH \arrow[u, "LiAlH_4", "Dry\ ether"'] &
\end{tikzcd}$$

(d). Ethanoic acid to N-methylethanamide

$$\begin{tikzcd}
 & CH_3COCl \arrow[dr, "Conc.NH_3"] & & & \\
CH_3COOH \arrow[ur, "PCl_5"] \arrow[rr, "(NH_4)_2CO_3", "Heat"'] & & CH_3CONH_2 \arrow[r, "CH_3Cl"] & CH_3CONHCH_3 \arrow[r, "LiAlH_4", "Dry\ ether"'] & CH_3CH_2NHCH_3
\end{tikzcd}$$

(e). Bromoethane to 1,2-dibromopropane

$$\begin{tikzcd}
 & CH_3CH_2CH_2OMgBr \arrow[rr, "H^+"] & & CH_3CH_2COOH \arrow[d, "LiAlH_4", "Dry\ ether"'] \\
CH_3CH_2Br \arrow[r, "Mg", "Dry\ ether"'] & CH_3CH_2MgBr \arrow[u, "CO_2", "Dry\ ether"'] \arrow[r, "HCHO", "Dry\ ether"'] & CH_3CH_2CH_2OMg \arrow[r, "H^+"] & CH_3CH_2CH_2OH \arrow[dl, "Conc.H_2SO_4", "heat"'] \\
 & CH_3\overset{\overset{Br}{|}}{C}HCH_2Br & CH_3CH = CH_2 \arrow[l, "Br_2", "CCl_4"'] &
\end{tikzcd}$$

(f). Propanal to propanone

$$\begin{tikzcd}
CH_3CH_2CHO \arrow[r, "LiAlH_4", "Dry\ ether"'] & CH_3CH_2CH_2OH \arrow[r, "Conc.H_2SO_4", "heat"'] & CH_3CH = CH_2 \arrow[r, "H_2O/H^+", "warm"'] & CH_3\overset{\overset{OH}{|}}{C}HCH_3 \arrow[dl, "Cr_2O_7^{2-}/H^+", "heat"'] \\
 & & CH_3COCH_3 &
\end{tikzcd}$$

OR

$$\begin{tikzcd}
CH_3CH_2CHO \arrow[r, "LiAlH_4", "Dry\ ether"'] & CH_3CH_2CH_2OH \arrow[r, "Conc.H_2SO_4", "heat"'] & CH_3CH = CH_2 \arrow[r, "Br_2", "CCl_4"'] & CH_3\overset{\overset{Br}{|}}{C}HCH_2Br \arrow[dl, "KOH/ethanol", "heat"'] \\
 & CH_3COCH_3 & CH_3C \equiv CH \arrow[l, "H_2O/H_2SO_4", "HgSO_4/60^\circ C"'] &
\end{tikzcd}$$

OR

$$CH_3CH_2CHO \xrightarrow[\text{Dry ether}]{LiAlH_4} CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{\text{Conc.} H_2SO_4} CH_3CH=CH_2$$

$$CH_3COCH_3 \xleftarrow[PdCl_2/CuCl_2/60°\text{C}]{O_2/H_2O/HCl}$$

(g). Propanal to 2,2-dichloropropane

$$CH_3CH_2CHO \xrightarrow[\text{Dry ether}]{LiAlH_4} CH_3CH_2CH_2OH \xrightarrow[\text{heat}]{\text{Conc.} H_2SO_4} CH_3CH=CH_2 \xrightarrow[\text{warm}]{H_2O/H^+} CH_3\overset{OH}{\overset{|}{C}}HCH_3$$

$$CH_3CCl_2CH_3 \xleftarrow[\text{Dry ether}]{PCl_5} CH_3COCH_3 \xleftarrow[\text{heat}]{Cr_2O_7^{2-}/H^+}$$

(h). Propanone ` to propanal

$$CH_3COCH_3 \xrightarrow[\text{Dry ether}]{LiAlH_4} CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[\text{heat}]{\text{Conc.} H_2SO_4} CH_3CH=CH_2 \xrightarrow[ROOH]{HBr} CH_3CH_2CH_2Br$$

$$CH_3CH_2CHO \xleftarrow[\text{heat}]{Cr_2O_7^{2-}/H^+} CH_3CH_2CH_2OH \xleftarrow[\text{heat}]{NaOH(aq)}$$

(i). Propan-2-ol to 1,1-dichloropropane

$$CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[\text{heat}]{\text{Conc.} H_2SO_4} CH_3CH=CH_2 \xrightarrow[ROOH]{HBr} CH_3CH_2CH_2Br \xrightarrow[\text{heat}]{NaOH(aq)} CH_3CH_2CH_2OH$$

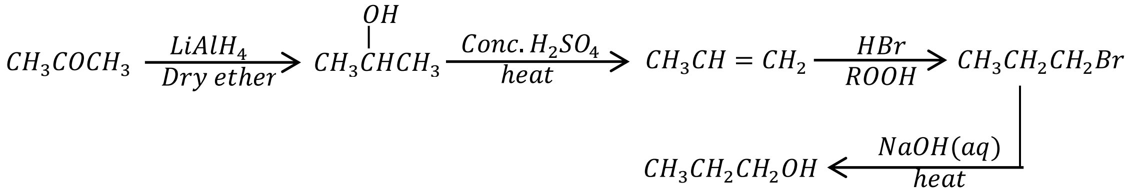
$$CH_3CH_2CHCl_2 \xleftarrow[\text{Dry ether}]{PCl_5} CH_3CH_2CHO \xleftarrow[\text{heat}]{Cr_2O_7^{2-}/H^+}$$

(j). Propan-2-ol to $CH_3CH_2CH=NOH$

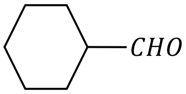
$$CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[\text{heat}]{\text{Conc.} H_2SO_4} CH_3CH=CH_2 \xrightarrow[ROOH]{HBr} CH_3CH_2CH_2Br \xrightarrow[\text{heat}]{NaOH(aq)} CH_3CH_2CH_2OH$$

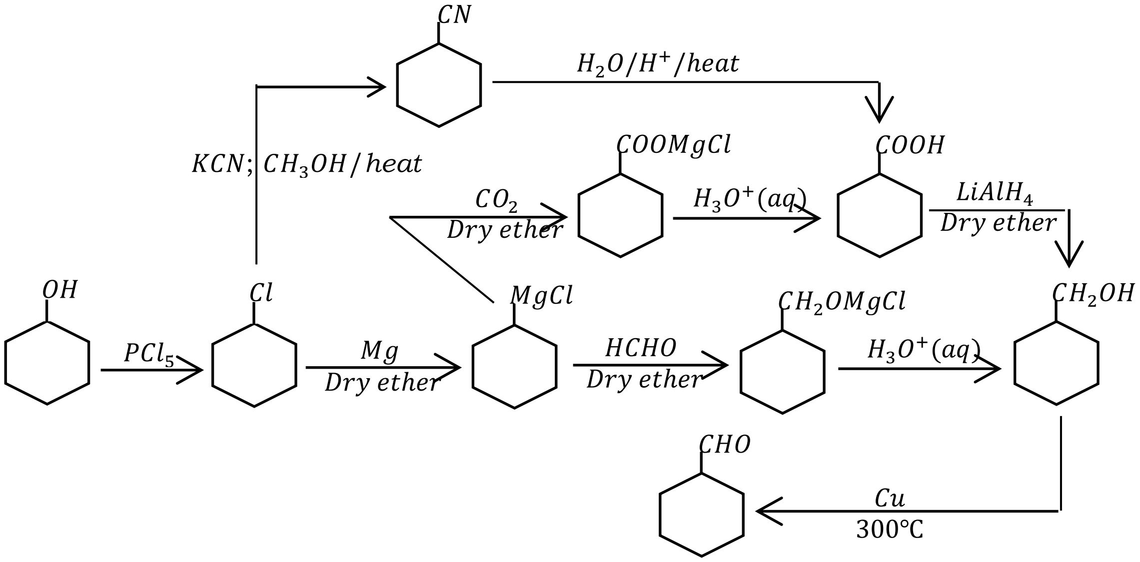
$$CH_3CH_2CH=NOH \xleftarrow[H^+]{H_2NOH} CH_3CH_2CHO \xleftarrow[300°\text{C}]{Cu}$$

(k). Propanone to propan-1-ol



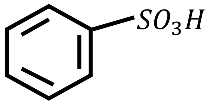
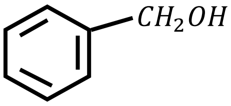
$$CH_3COCH_3 \xrightarrow[Dry\ ether]{LiAlH_4} CH_3\overset{\overset{OH}{|}}{C}HCH_3 \xrightarrow[heat]{Conc.H_2SO_4} CH_3CH=CH_2 \xrightarrow[ROOH]{HBr} CH_3CH_2CH_2Br \xrightarrow[heat]{NaOH(aq)} CH_3CH_2CH_2OH$$

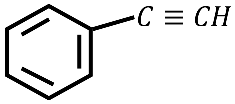
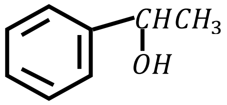
(l). Cyclohexanol to 

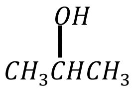


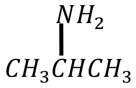
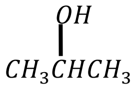
TRIAL QUESTIONS

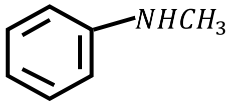
1. Write equations to show how the following compounds can be synthesised. [**UNEB 2019**]

(a).  from  (4½ marks)

(b).  from  (3½ marks)

(c).  $CH_3\overset{OH}{\overset{|}{C}}HCH_3$ from CH_3CH_2COOH (3½ marks)

(d).  $CH_3\overset{NH_2}{\overset{|}{C}}HCH_3$ from  $CH_3\overset{OH}{\overset{|}{C}}HCH_3$ (03 marks)

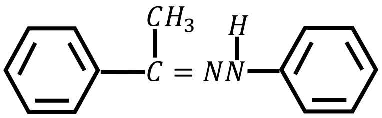
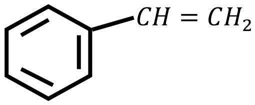
(e).  from $HC \equiv CH$ (5½ marks)

2. Write equations to show how the following compounds can be synthesised. [**UNEB 2018**]

(a). Benzene from chlorobenzene (04 marks)

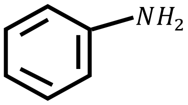
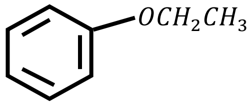
(b). But-2-yne from but-2-ol. (4½ marks)

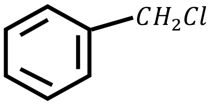
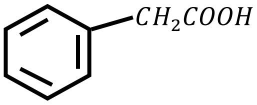
(c). CH_3COCH_3 from $CH_3CH_2CH_2OH$. (05 marks)

(d).  from  (4½ marks)

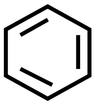
(e). $CH_3CH_2CH_2CH_3$ from CH_3CH_2OH. (02 marks)

3. Write equations to show how the following compounds can be synthesised. [**UNEB 2016**]

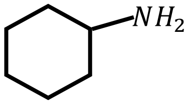
(a).  to  (05 marks)

(b).  to  (03 marks) (c). $CH_3CH = CHCH_3$ to $CH_3COCHCH_3$. (03 marks)

(d).



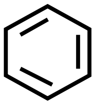
to



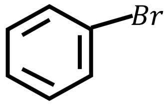
(04 marks)

(e). $CH_3CH = CH_2$ to $CH_3C \equiv CH$ (revised) (03 marks)

(f).



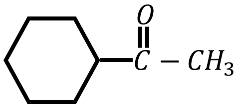
to



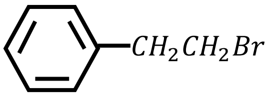
(02 marks)

4. Write equations to show how the following compounds can be synthesised. [**UNEB 2014**]

(a).

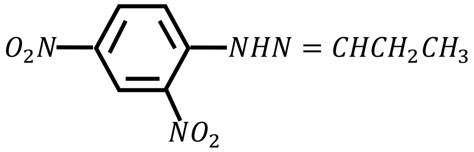


from



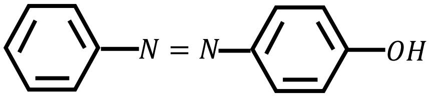
(05 marks)

(b).

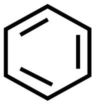


from $CH_3CH_2CH_2Br$ (04 marks)

(c).



from

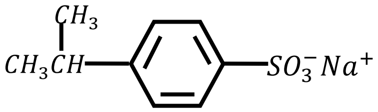


(06 marks)

(d). $CH_3CH_2C \equiv CCH_3$ from CaC_2 (05 marks)

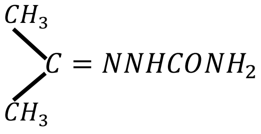
5. Write equations to show how the following compounds can be synthesised. [**UNEB 2012**]

(a). Benzene to



(04 marks)

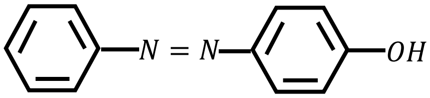
(b). Propan-2-ol to



$(CH_3)_2C = NNHCONH_2$

(03 marks)

(c). Nitrobenzene to

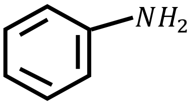


(5½ marks)

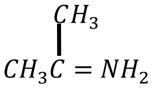
(d). 2-chloropropane to $CH_3CH_2CH_2NH_2$ (4½ marks)

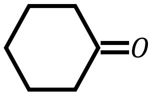
(e). Ethene to $CH_3COOCH_2CH_3$ (03 marks)

6. Write equations to show how the following compounds can be synthesised. [**UNEB 2008**]

(a).  from benzoic acid (5½ marks)

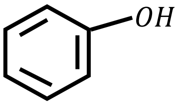
(b). $CH_3C \equiv CH$ from ethene (5½ marks)

(c).  $CH_3\overset{CH_3}{\overset{|}{C}} = NH_2$ from ethanol (05 marks)

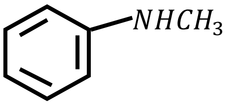
(d).  from cyclohexene (04 marks)

7. Write equations to show how the following compounds can be synthesised. [**UNEB 2007**]

(a). $CH_3C \equiv CH$ from propan-2-ol (5½ marks)

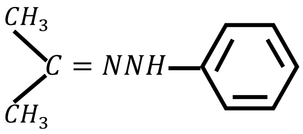
(b).  from benzene (3½ marks)

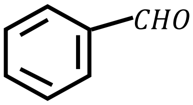
(c). CH_3COCl from ethene (04 marks)

(d).  from benzene (04 marks)

(e). $CH_3CO_2CH_3$ from bromoethane (04 marks)

8. Write equations to show how the following compounds can be synthesised. [**UNEB 2006**]

(a).  from propene (05 marks)

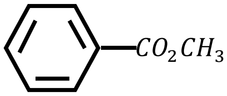
(b).  from benzene (02 marks) (c). $CH_3CH_2C \equiv CH$ from ethanol (7½ marks)

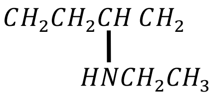
(d). $CH_3CH_2NH_2$ from ethanal (03 marks)

(f). $CH_3CO_2CH_3$ from ethene (2½ marks)

9. Write equations to show how the following compounds can be synthesised. [**UNEB 2004**]

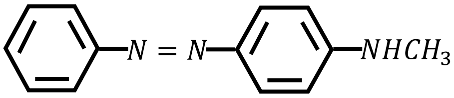
(a). $CH_3CH_2OCH_2CH_3$ from ethene (04 marks)

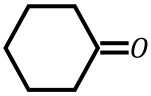
(b).  from benzene (05 marks)

(c). 

$$\underset{\displaystyle HNCH_2CH_3}{CH_2CH_2\underset{|}{C}H\;CH_2}$$

from but-2-ene (02 marks)

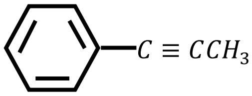
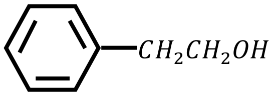
(d).  from benzene (06 marks)

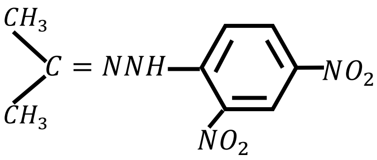
(e).  from bromocyclohexane (03 marks)

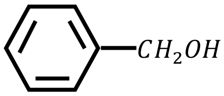
10. Write equations to show how the following compounds can be synthesised. [**UNEB 2002**]

(a). $CH_3CH_2CH_2CO_2H$ from propan-2-ol. (04 marks)

(b). $CH_3CH_2CH_3$ from 1-bromobutane (04 marks)

(c).  from  (06 marks)

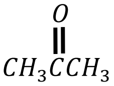
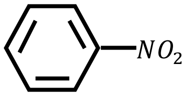
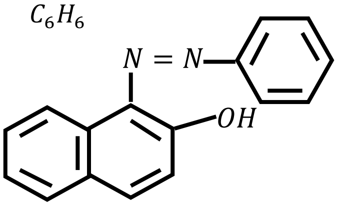
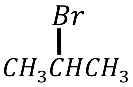
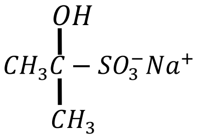
(d).  from propene. (3½ marks)

(e).		From	benzene.	(2½ marks)

11. Write equations to show how the following compounds can be synthesised. [**UNEB 2001**]

(a).	Benzoic acid	from	benzene	(2½ marks)
(b).	Hexane	from	1-bromopropane	(01 mark)
(c).	Ethyne	from	ethanol	(4½ marks)
(d).	Propanoic acid	from	bromoethane	(02 marks)
(e).	Aminomethane	from	ethene	(5½ marks)
(f).	Methylethanoate	from	bromoethane	(4½ marks)

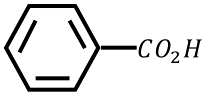
12. Write equations to show how the following compounds can be synthesised. [**UNEB 2000**]

(a).	CH_3CH_2I	to	$CH_3CH_2COOH.$	(03 marks)
(b).	$CH_3CH_2CH_2OH$	to	 $CH_3\overset{\overset{O}{\parallel}}{C}CH_3$	(05 marks)
(c).	$C_6H_5CH_2OH$	to	C_6H_6	(03 marks)
(d).		to		(5½ marks)
(e).	 $CH_3\overset{\overset{Br}{\vert}}{C}HCH_3$	to	 $CH_3\underset{\underset{CH_3}{\vert}}{\overset{\overset{OH}{\vert}}{C}} - SO_3^-Na^+$	(3½ marks)

13. Write equations to show how the following compounds can be synthesised. [**UNEB 1998**]

(a).	$CH_3CH_2CH_2Cl$	to	$CH_3CH_2CH_2CH_2NH_2$	(04 marks)
(b).	$CH_3CH_2CH_2OH$	to	$CH_3CH_2CH_2COOH$	(06 marks)
(c).	CH_3CH_2COOH	to	$CH_3CH_2NH_2$	(04 marks)
(d).	$CH_3CH = CH_2$	to	$CH_3CH_2CH_3CH_2Br$	(06 marks)

14. Write equations to show how the following compounds can be synthesised. [**UNEB 1998**]

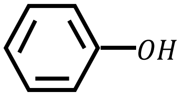
(a). 

from benzene (05 marks)

(b). $CH_3CH_2NH_2$ from $CH_3CH_2CONH_2$ (01 mark)

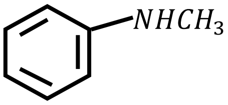
(c). $CH_3C \equiv CH$ from propene (05 marks)

(d). $CH_3CH_2COCH_3$ from $CH_3CH = CHCH_3$ (04 marks)

(e). 

from benzene (05 marks)

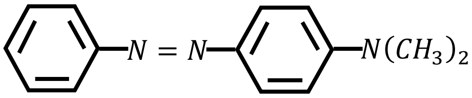
15. Write equations to show how the following compounds can be synthesised. [**UNEB 1997**]

(a). 

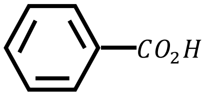
from benzene (04 marks)

(b). $CH_3C \equiv CCH_3$ from $CH_3CHBrCH_2CH_3$ (05 marks)

(c). CH_3CONH_2 from ethene (04 marks)

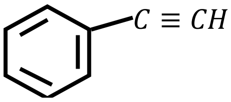
(d). 

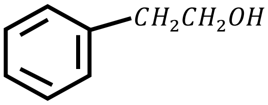
from nitrobenzene (4½ marks)

(e). 

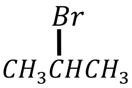
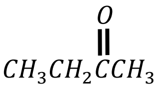
from bromobenzene (2½ marks)

16. Write equations to show how the following compounds can be synthesised. [**UNEB 1987**]

(a). 

to 

(05 marks)

(b). 
$CH_3CH(Br)CH_3$
to 
$CH_3CH_2C(=O)CH_3$
(05 marks)

(c). $CH_3CH_2CH_2CH_2I$ to $CH_3CH_2CH_3$ (05 marks)

(d). CH_3CHO to $CH_3CH_2NH_2$ (05 marks)

END