

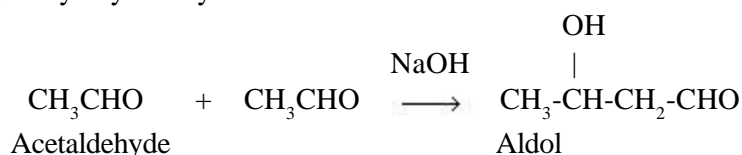


*Notes for XII (ISC): prepared by S.Narayana Iyer, M.Sc, M.Phil*

*A few important organic name reactions, conversions and problems are listed below for ready reference*

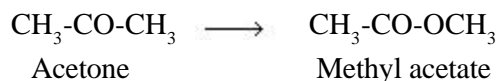
### 1. Aldol condensation

Two molecules of aldehyde or ketone containing  $\alpha$ -hydrogen atom (hydrogen atom attached to the carbon atom adjacent to the carbonyl group) in presence of dilute alkali condense to form  $\beta$ -hydroxyaldehyde or  $\beta$ -hydroxyketone. The condensation products are called aldols. For example, acetaldehyde can condense in presence of dilute NaOH to give  $\beta$ -hydroxybutyraldehyde.



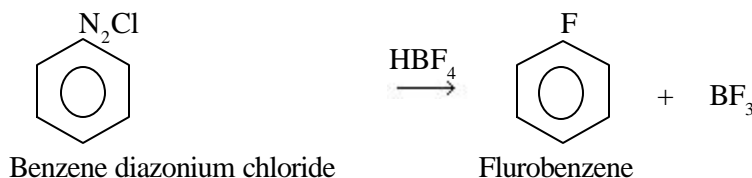
### 2. Baeyer-Villiger oxidation

It involves the oxidation of ketones with organic peroxy acid like perbenzoic acid ( $\text{C}_6\text{H}_5\text{COOOH}$ ) to form esters.



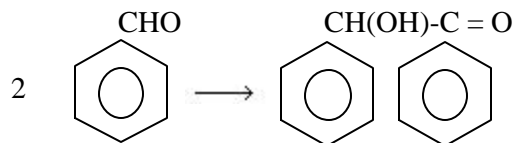
### 3. Balz-Schiemann reaction

This reaction involves the conversion of aryl diazonium halide to aryl fluoride by treatment with fluoroboric acid ( $\text{HBF}_4$ )



### 4. Benzoin condensation

Two molecules of aromatic aldehyde like benzaldehyde on heating in presence of alcoholic KCN condense to give benzoin.



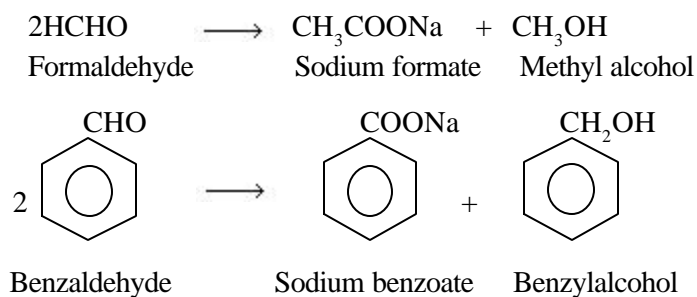
### 5. Bouveault-Blanc reduction

Esters may be converted into alcohol by treating the ester with sodium and alcohol. Eg. Preparation of ethanol from ethyl acetate.



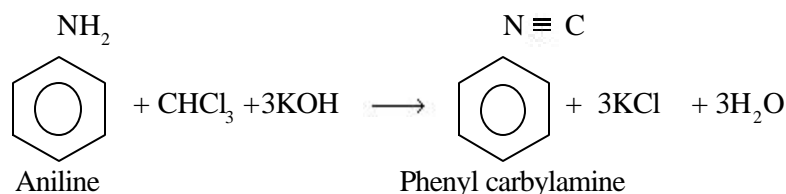
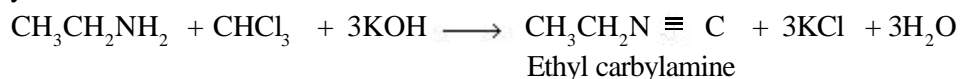
## 6. Cannizzaro reaction

Aldehydes which do not contain  $\alpha$ -hydrogen atom undergo auto redox reaction in presence of concentrated alkali. One molecule of the aldehyde is oxidised to the corresponding carboxylic acid and the other molecule is reduced to the corresponding alcohol. For example, formaldehyde on treatment with conc. NaOH solution gives sodium formate and methyl alcohol. Similarly benzaldehyde on treatment with conc. NaOH solution gives sodium benzoate and benzyl alcohol.



## 7. Carbylamine reaction

When a primary amine (aliphatic or aromatic) is warmed with chloroform and alcoholic KOH, it forms carbylamine or isocyanide having offensive smell. This reaction is called carbylamine reaction.



Secondary and tertiary amines do not give this reaction. So it is used as a test for primary amines and also for the distinction of primary amines from secondary and tertiary amines.

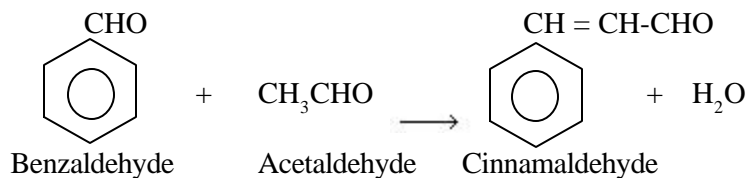
## 8. Claisen condensation

The self-condensation of two molecules of an ester containing  $\alpha$ -hydrogen in presence of a strong base such as sodium ethoxide to form  $\beta$ -ketoester is called Claisen condensation. For example, when anhydrous ethyl acetate is refluxed in presence of a little alcohol and sodium, two molecules of ethyl acetate condense to form aceto-acetic ester.



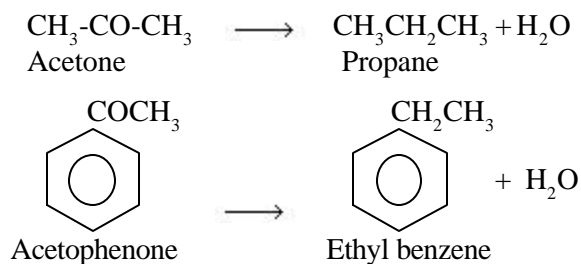
### 9. Claisen-Schmidt reaction

Aromatic aldehydes like benzaldehyde react with aliphatic aldehydes or ketones, having  $\alpha$ -hydrogen atom in presence of dilute alkali to give  $\alpha, \beta$ -unsaturated aldehydes or ketones.



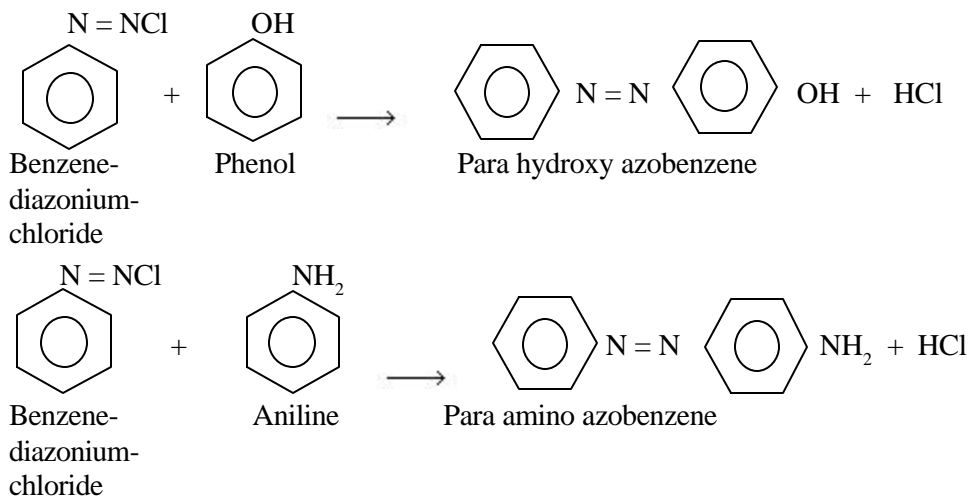
### 10. Clemmensen reduction

The reduction of aldehydes and ketones to the corresponding hydrocarbons with amalgamated zinc and concentrated hydrochloric acid is called Clemmensen reduction. For example,



### 11. Coupling reaction

The reaction of diazonium salts with phenols and aromatic amines to form azo compounds of the formula  $\text{Ar-N=N-Ar}$  is called coupling reaction. The coupling usually takes place at the para position with respect to the hydroxyl or the amino group. The coupling with phenols takes place in mild alkaline medium while that with amines in mild acidic medium.



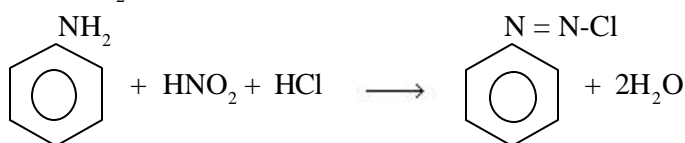
## 12. Darzen reaction

It involves the reaction of a straight chain primary alcohol with thionyl chloride to form chloro derivative without rearrangement.



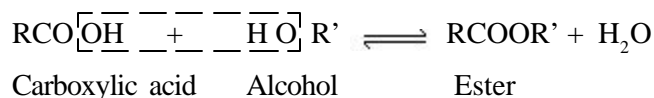
## 13. Diazotisation reaction

It is the formation of diazonium salt when a cold solution of a primary aromatic amine in dilute HCl is treated with a cold solution of nitrous acid (generated *in situ* by the action of dilute HCl on  $\text{NaNO}_2$ ) at 273-278K.



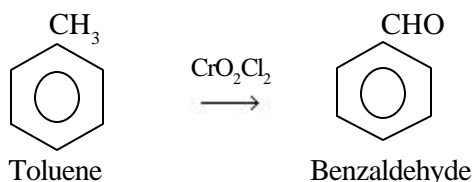
## 14. Esterification reaction

Alcohols react with carboxylic acids in presence of dry HCl gas to form esters. This reaction is slow and reversible.



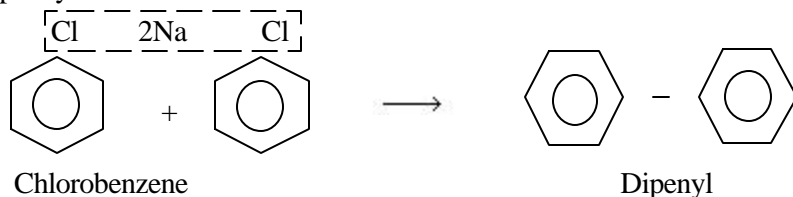
## 15. Etard reaction

The oxidation of toluene with chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ) to give benzaldehyde is called Etard reaction.



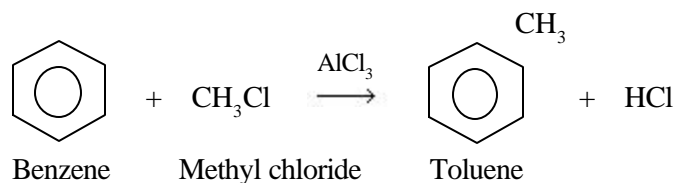
## 16. Fittig reaction

Two molecules of a haloarene react with sodium in presence of dry ether to form diphenyl.



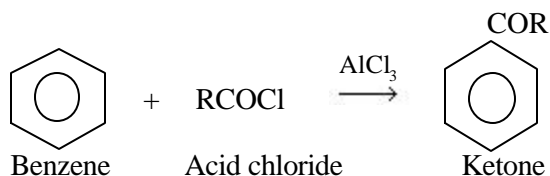
## 17. Friedel-Craft alkylation

Benzene reacts with alkyl halides in the presence of anhydrous aluminium chloride to form alkyl benzenes. This reaction is very vigorous at room temperature.



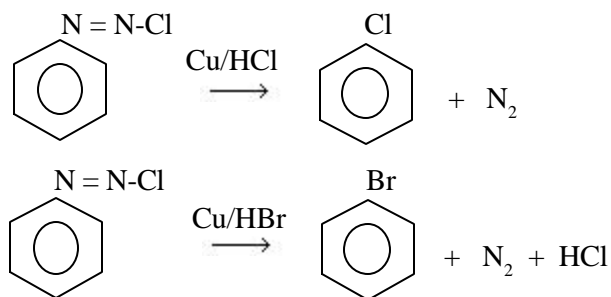
### 18. Friedel Craft acylation

Benzene reacts with acid chlorides in presence of anhydrous aluminium chloride to form ketones.



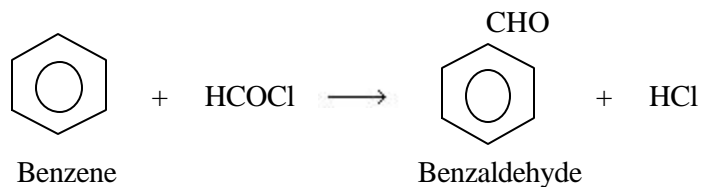
### 19. Gattermann reaction

The reaction involves the preparation of chloro or bromo benzene from benzene diazonium chloride by treatment with Cu/HCl or Cu/HBr respectively.



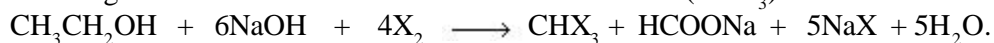
### 20. Gattermann Koch reaction

When a mixture of carbon monoxide and hydrogen chloride gas is passed over benzene in the presence of anhydrous  $\text{AlCl}_3$  and traces of cuprous chloride, benzaldehyde is obtained.



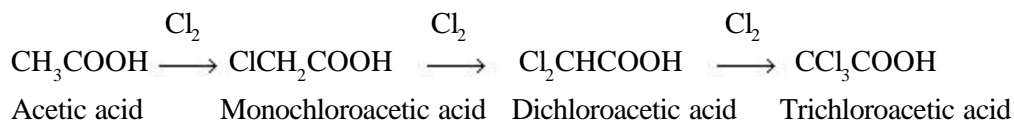
### 21. Haloform reaction

Compounds containing  $\text{CH}_3\text{CHOH}$ - grouping or  $\text{CH}_3\text{CO}$ - grouping on treatment with a halogen and excess of alkali or NaOX form haloform ( $\text{CHX}_3$ ).



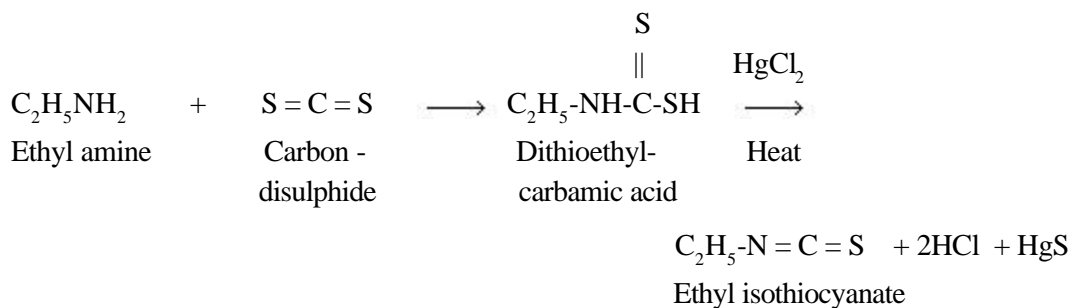
## 22. Hell-Volhard- Zelinsky (HVZ) reaction

The reaction of an aliphatic carboxylic acid containing  $\alpha$ -hydrogens with chlorine or bromine in presence of a small amount of red phosphorus to give  $\alpha$ -halo acids is called HVZ reaction. With excess of halogen, all the  $\alpha$ -hydrogen atoms of the aliphatic carboxylic acid are replaced by halogen atoms.



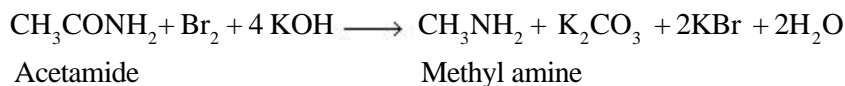
## 23. Hofmann mustard oil reaction

When a mixture of aliphatic primary amine, carbon disulphide and mercuric chloride is heated, alkyl isothiocyanate having the characteristic smell of mustard oil is formed.



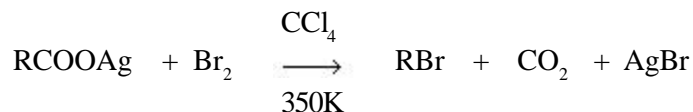
## 24. Hofmann degradation reaction

When an amide is heated with  $\text{Br}_2$  and  $\text{KOH}$ , a primary amine with one carbon atom less than the parent amide is formed. This reaction is also called Hofmann bromamide reaction.



## 25. Hunsdiecker reaction

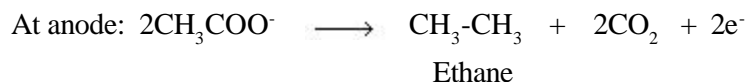
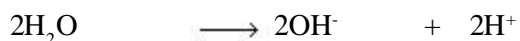
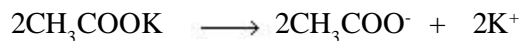
When silver salt of a carboxylic acid dissolved in  $\text{CCl}_4$  is heated with  $\text{Br}_2$ , an alkyl bromide with one carbon atom less than the original acid is formed.



## 26. Kolbe electrolytic reaction

This reaction is used to prepare alkanes, alkenes and alkynes by the electrolysis of aqueous solution of sodium or potassium salt of a carboxylic acid.

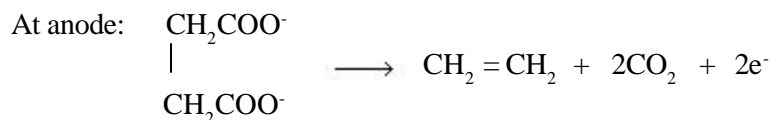
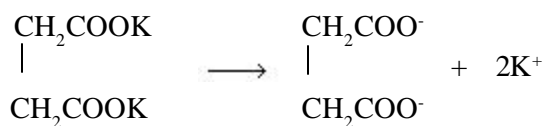
Ethane is produced when an aqueous solution of potassium acetate is electrolysed.



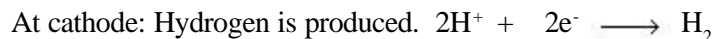
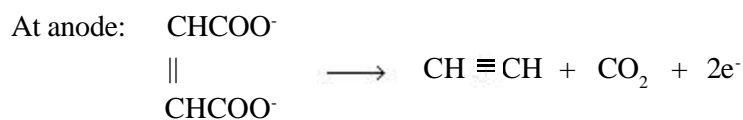
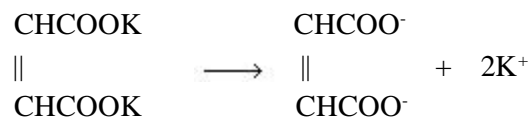
At cathode: both  $\text{K}^+$  and  $\text{H}^+$  are present but  $\text{H}^+$  ions are preferentially discharged due to their lower discharge potential.



Ethylene is produced when potassium salt of succinic acid is electrolysed.

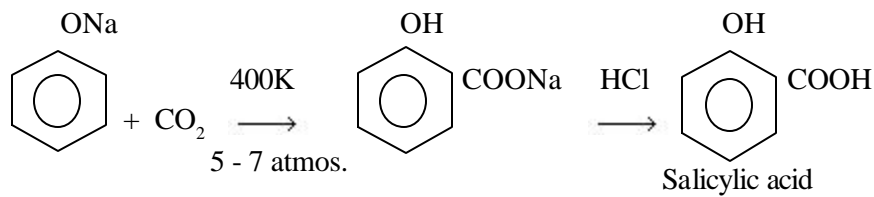


Acetylene is produced by the electrolysis of aqueous solution of potassium maleate.



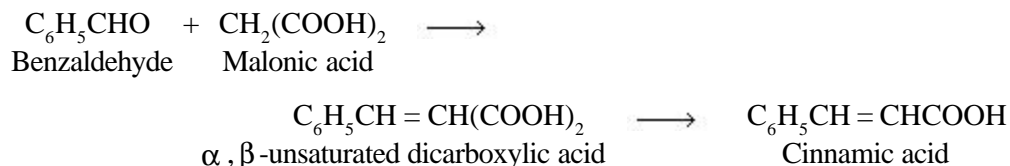
### 27. Kolbe reaction (Kolbe-Schmidt reaction)

When sodium phenoxide is treated with carbon dioxide under pressure at 400K, sodium salt of salicylic acid is formed. This on acidification with HCl gives salicylic acid.



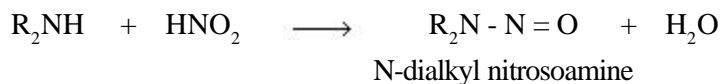
### 28. Knoevenagel reaction

Aldehydes and ketones react with active methylene compounds in presence of a base to form  $\alpha, \beta$ -unsaturated compounds.



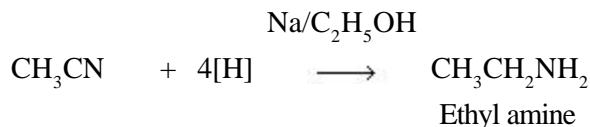
### 29. Liebermann nitroso reaction

Secondary aliphatic as well as aromatic amines react with nitrous acid ( $\text{NaNO}_2 + \text{dil.HCl}$ ) to give N-nitrosoamines, which are generally yellow oily compounds and insoluble in dilute mineral acids.



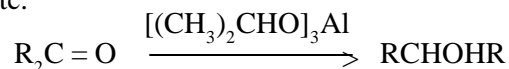
### 30. Mendius reaction

The reduction of alkyl or aryl cyanide with nascent hydrogen formed by the action of sodium amalgam on alcohol to produce a primary amine is called Mendius reaction.



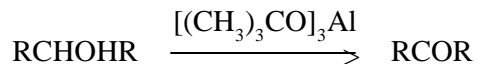
### 31. Meerwein-Pondorf-Verley reduction.(M.P.V reduction)

This involves the reduction of an aldehyde or a ketone to alcohol with aluminium isopropoxide in 2-propanol solution. The reducing agent is specific for  $>\text{C} = \text{O}$  group and converts it into  $-\text{CHOH}$  group but it does not reduce other groups such as  $>\text{C} = \text{C}<$  or  $-\text{NO}_2$  etc.



### 32. Oppenaur oxidation

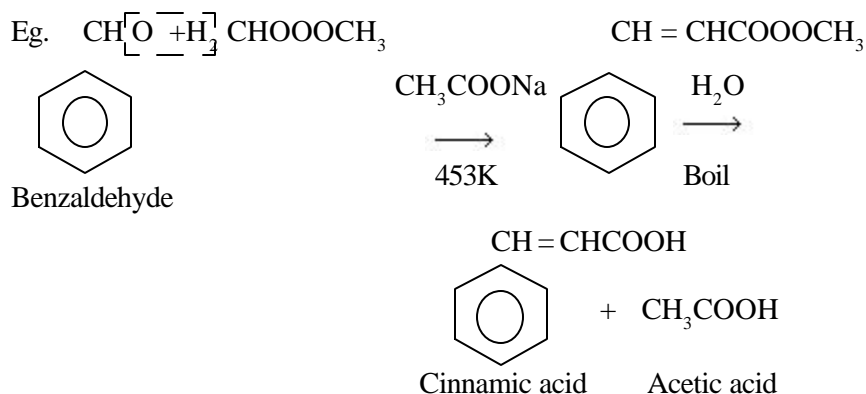
This is the reverse of M.P.V reduction. It involves the oxidation of secondary alcohol to ketone with aluminium tertiary butoxide in acetone solution.



### 33. Perkin reaction

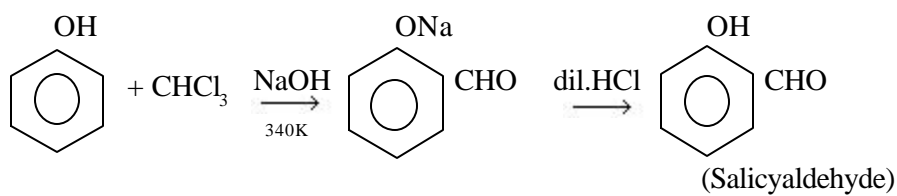
Aromatic aldehyde on heating with an aliphatic acid anhydride in presence of sodium salt of the same acid forms a product, which on acid hydrolysis gives  $\alpha, \beta$ -unsaturated acid.



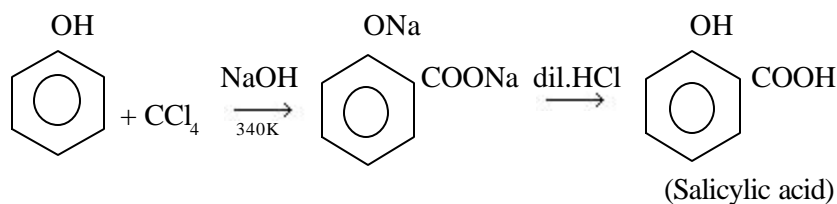


### 34. Reimer-Tiemann reaction

Phenol on treatment with chloroform in presence of aqueous sodium hydroxide at 340K, followed by hydrolysis of the resulting product gives salicylaldehyde.

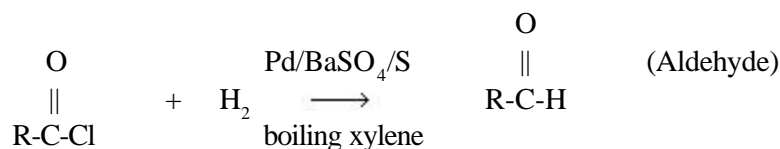


If instead of chloroform, carbon tetrachloride is used, salicylic acid is formed.



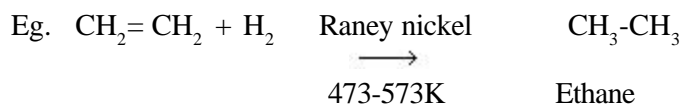
### 35. Rosenmund reduction

Catalytic reduction of acid chlorides to the corresponding aldehydes is called Rosenmund reduction. This reaction is carried out by passing  $\text{H}_2$  gas through boiling xylene solution of the acid chloride in presence of palladium catalyst supported over barium sulphate partially poisoned by the addition of sulphur or quinoline.



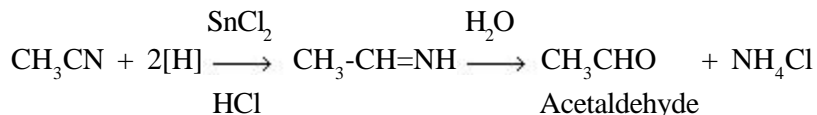
### 36. Sabatier and Senderen reduction

When an unsaturated hydrocarbon is treated with  $\text{H}_2$  in presence of Raney nickel as catalyst at 473-573K reduction takes place to get a saturated hydrocarbon.



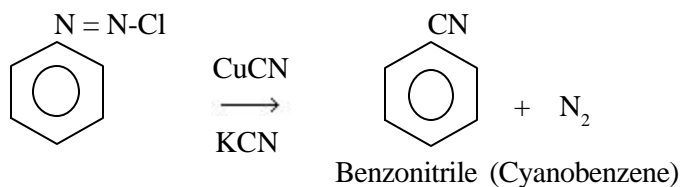
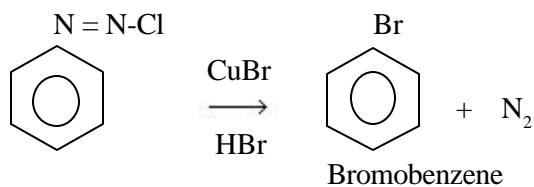
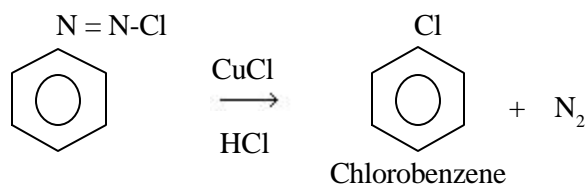
### 37. Stephen reduction

Cyanides on reduction with stannous chloride and HCl in absolute ether followed by hydrolysis give aldehydes.



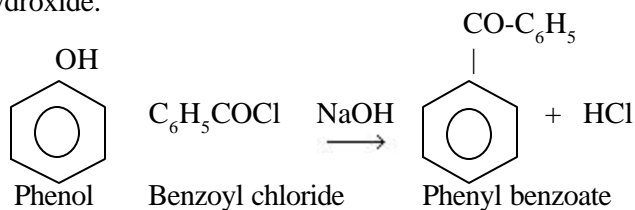
### 38. Sandmeyer reaction

When benzene diazonium chloride is treated with CuCl/HCl, CuBr/HBr or CuCN/KCN in presence of pyridine the product is chlorobenzene, bromobenzene or benzonitrile respectively.



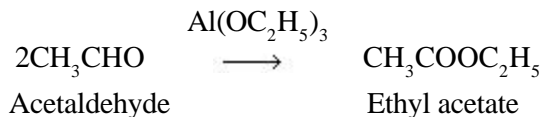
### 39. Schotten-Baumann reaction

This reaction involves benzylation of the compounds containing active hydrogen such as phenol, aniline, alcohol etc. with benzoyl chloride in presence of aqueous sodium hydroxide.



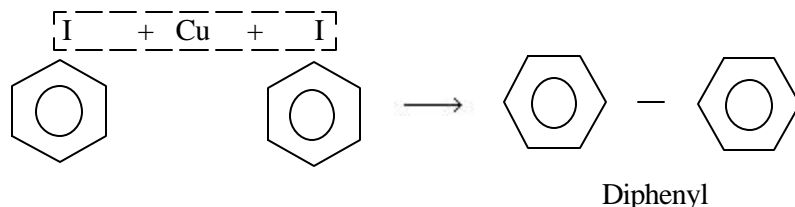
#### 40. Tischenko reaction

Aldehydes in presence of aluminium ethoxide undergo condensation accompanied by auto-oxidation and reduction to form an ester.



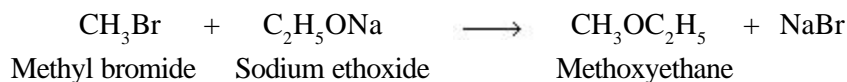
#### 41. Ullmann reaction

When iodobenzene is heated with copper powder in a sealed tube, diphenyl is produced.



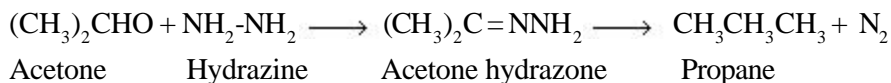
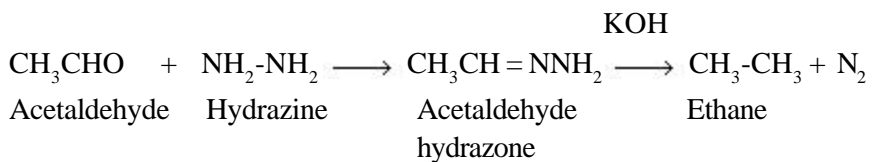
#### 42. Williamson synthesis

This is the reaction of alkyl halide with sodium alkoxide to form ether.



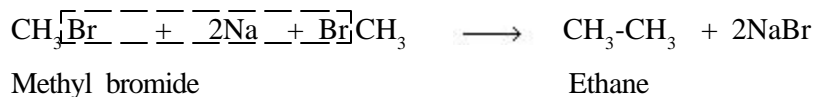
#### 43. Wolf-Kishner reduction

It is the reduction of aldehyde or ketone to hydrocarbon by heating with hydrazine and KOH in presence of ethylene glycol.



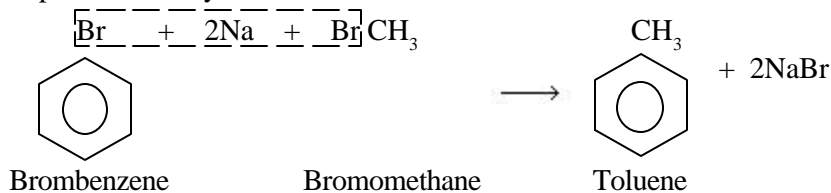
#### 44. Wurtz reaction

This involves the interaction of two molecules of an alkyl halide (preferably bromide or iodide) with metallic sodium in presence of dry ether to form symmetrical higher alkane containing twice the number of carbon atoms present in the alkyl halide.



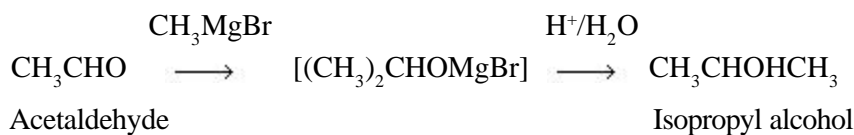
#### 45. Wurtz-Fittig reaction

This reaction is a modification of Wurtz reaction and is used for preparing homologues of benzene by warming a mixture of an aryl halide and an alkyl halide with metallic sodium in presence of dry ether.

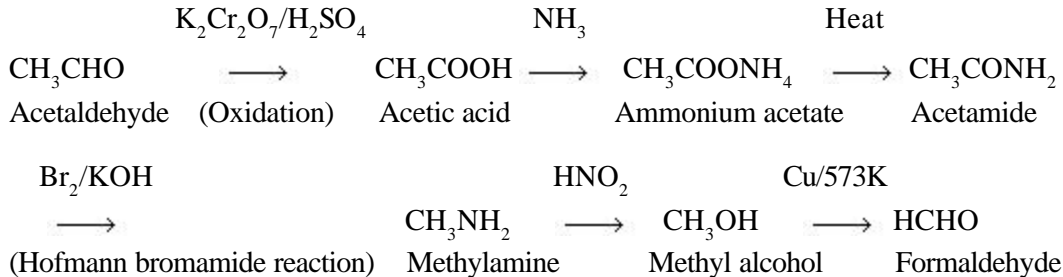


#### SOME IMPORTANT ORGANIC CONVERSIONS

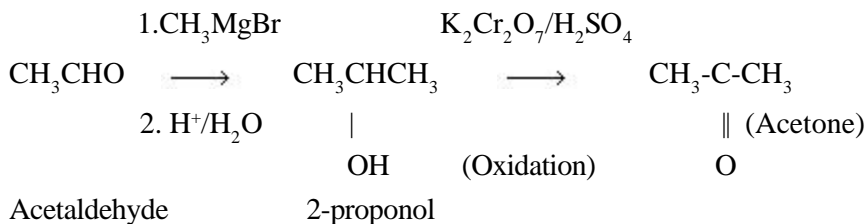
##### 1. Acetaldehyde to isopropyl alcohol



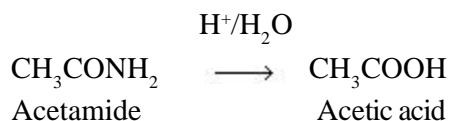
##### 2. Acetaldehyde to formaldehyde



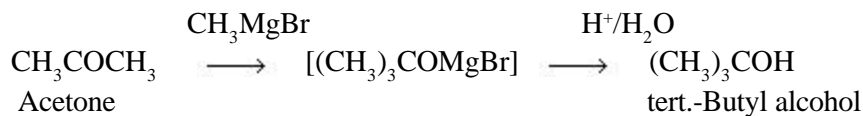
##### 3. Acetaldehyde to acetone



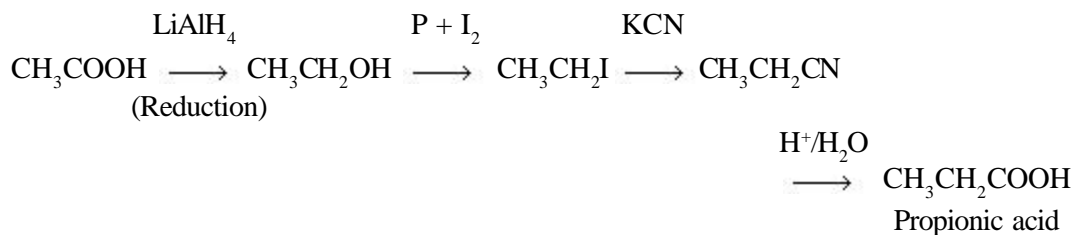
##### 4. Acetamide to acetic acid



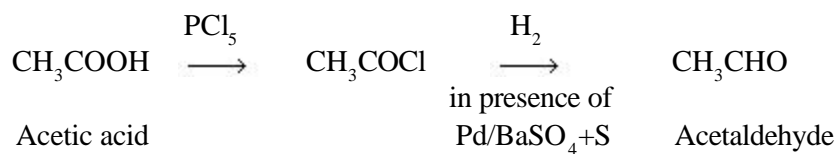
### 5. Acetone to tert.-butyl alcohol



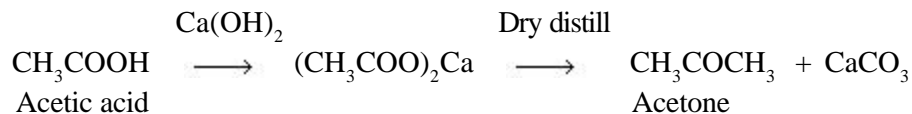
### 6. Acetic acid to propionic acid



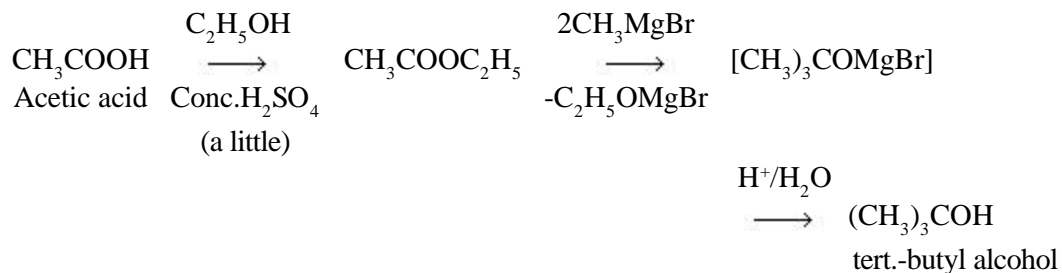
### 7. Acetic acid to acetaldehyde



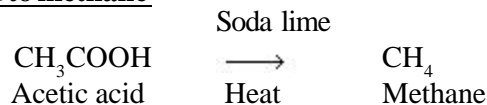
### 8. Acetic acid to acetone



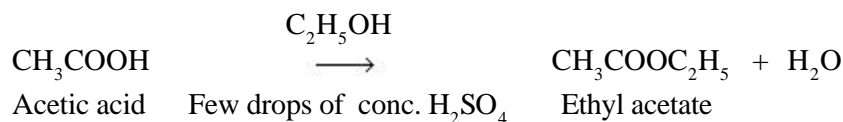
### 9. Acetic acid to tert.-butyl alcohol



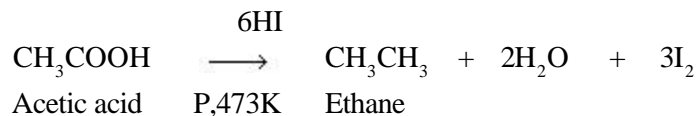
### 10. Acetic acid to methane



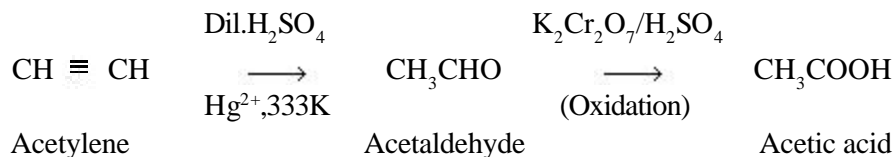
### 11. Acetic acid to ethyl acetate



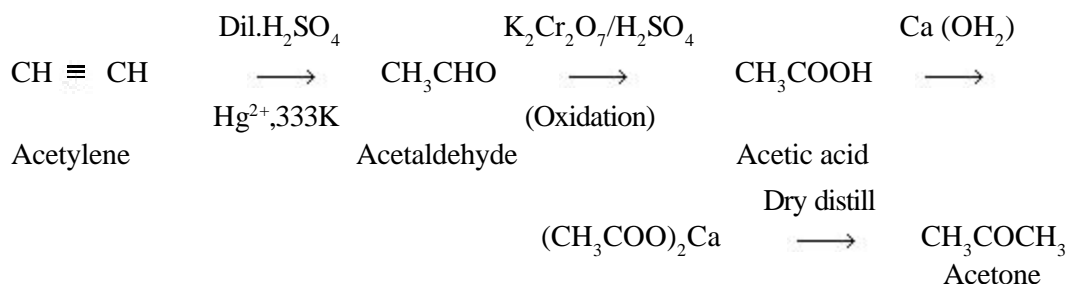
### 12. Acetic acid to ethane



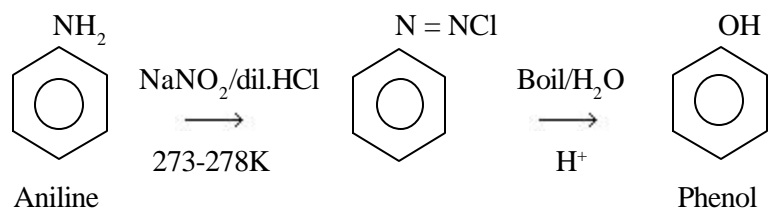
### 13. Acetylene to acetic acid



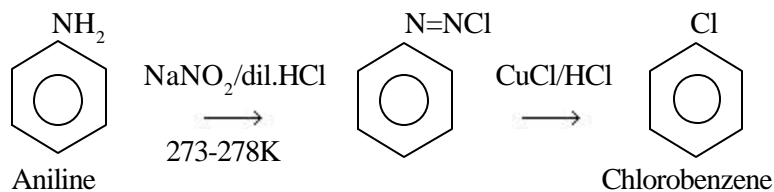
### 14. Acetylene to acetone



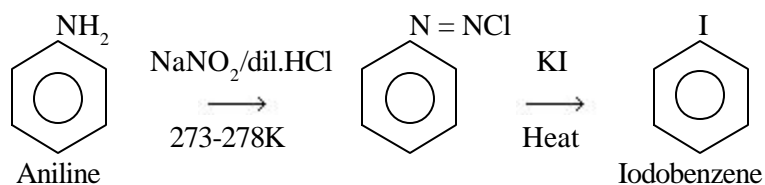
### 15. Aniline to phenol



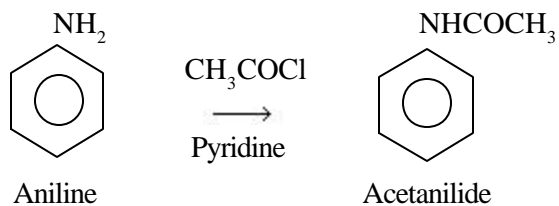
### 16. Aniline to chlorobenzene



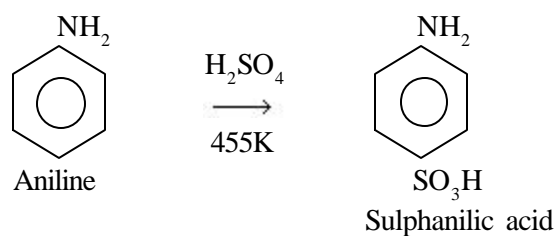
### 17. Aniline to iodobenzene



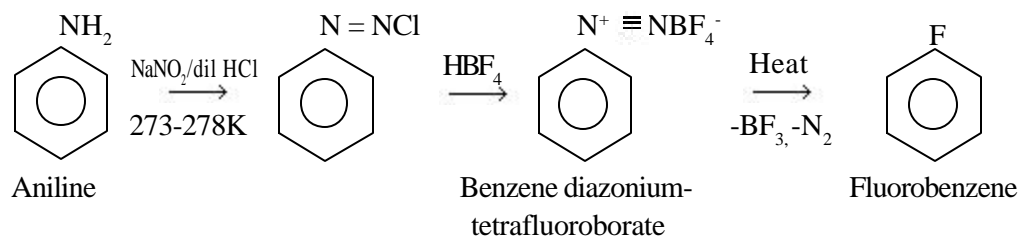
### 18. Aniline to acetanilide



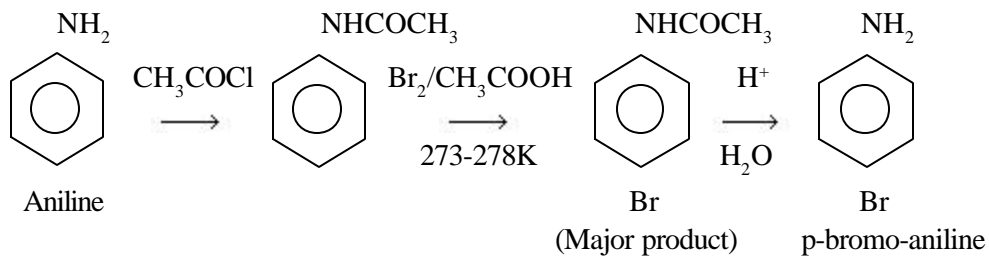
### 19. Aniline to sulphanilic acid



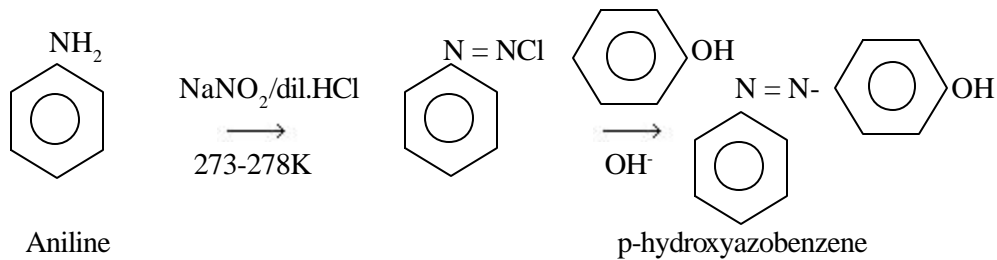
### 20. Aniline to fluorobenzene



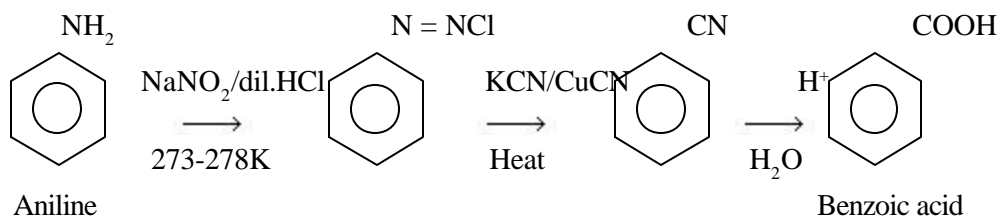
### 21. Aniline to p-bromoaniline



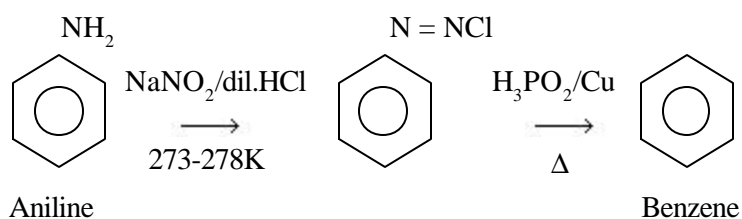
### 22. Aniline to p-hydroxyazobenzene



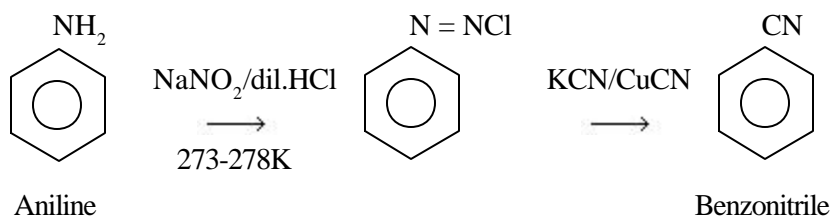
### 23. Aniline to benzoic acid



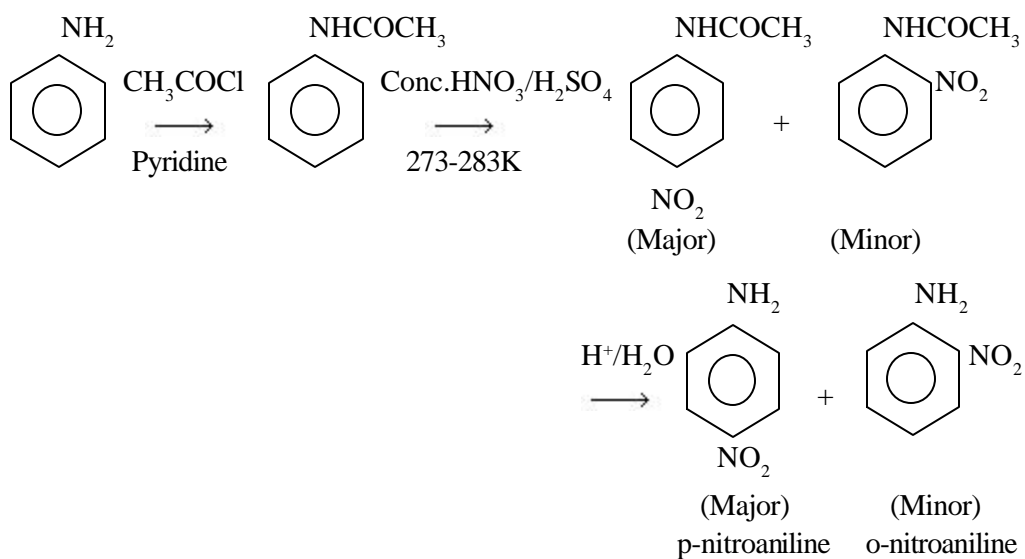
### 24. Aniline to benzene



### 25. Aniline to benzonitrile

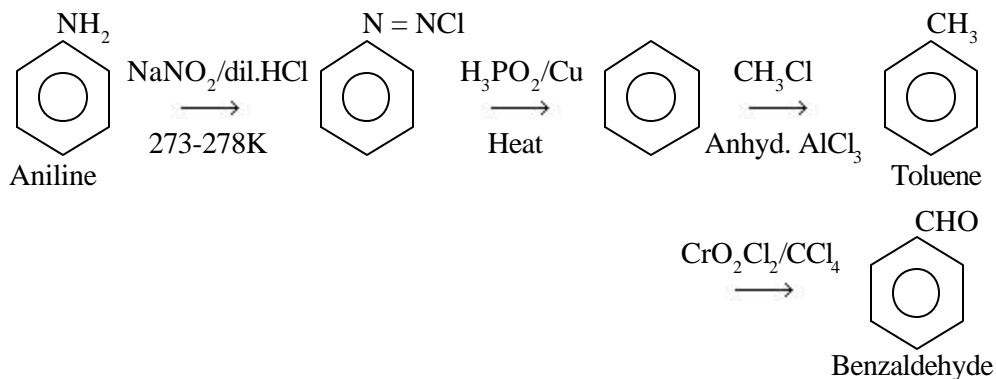


### 26. Aniline to o and p-nitroaniline

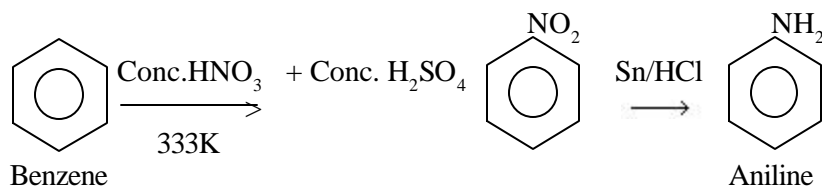




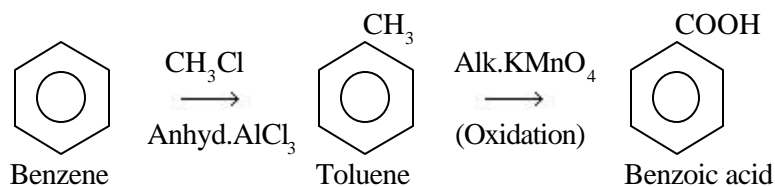
### 27. Aniline to benzaldehyde



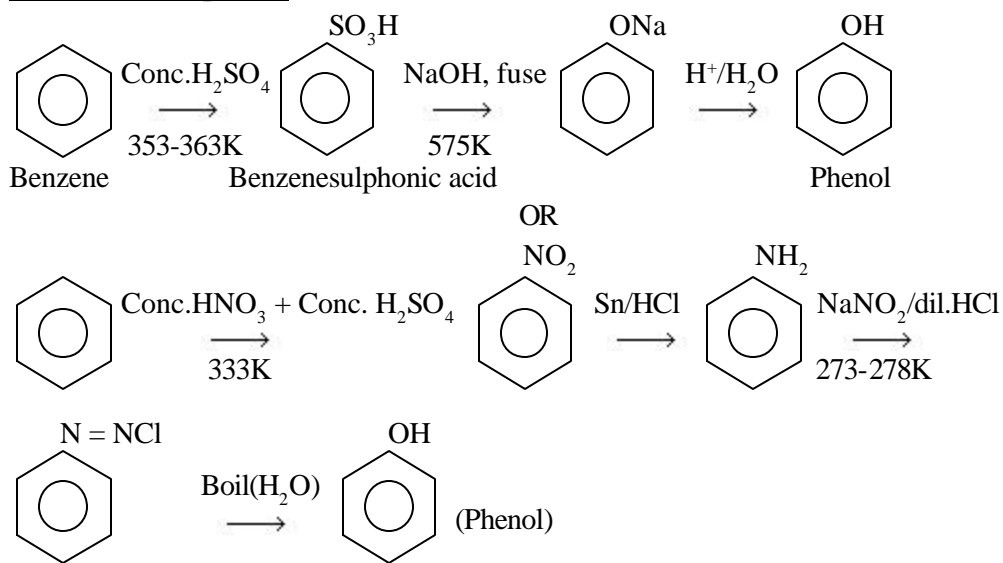
### 28. Benzene to aniline



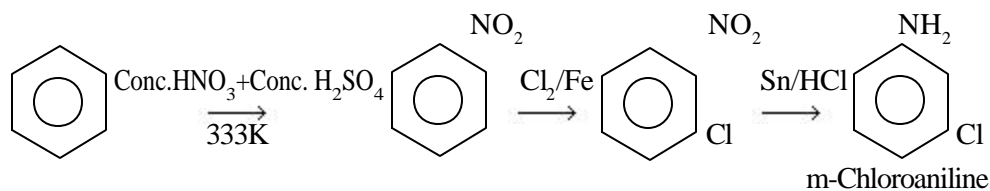
### 29. Benzene to benzoic acid



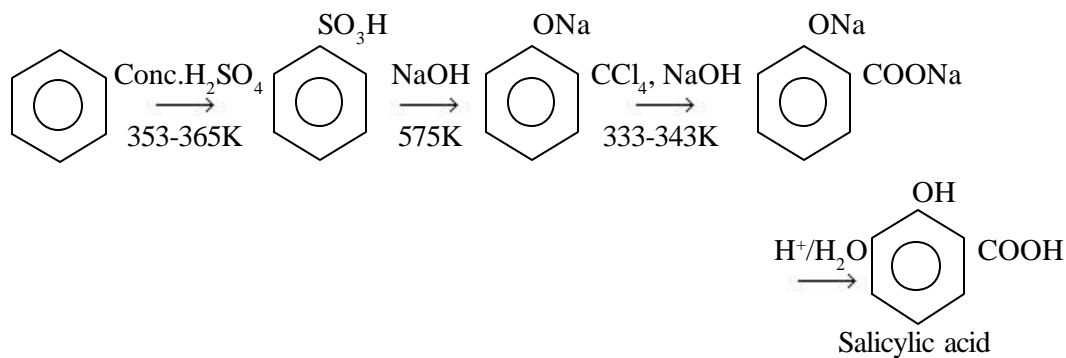
### 30. Benzene to phenol



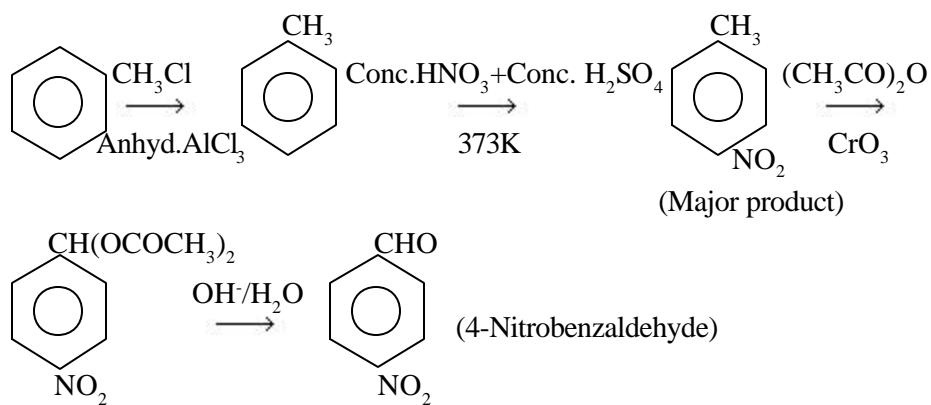
### 31. Benzene to m-chloroaniline



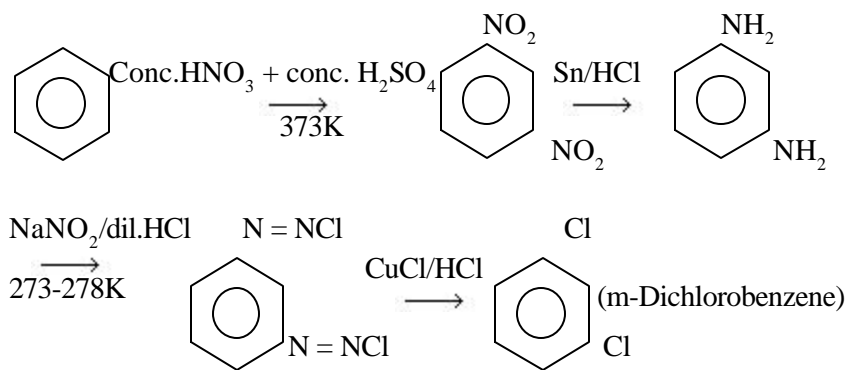
### 32. Benzene to salicylic acid



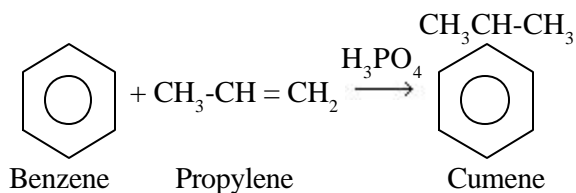
### 33. Benzene to 4-nitrobenzaldehyde



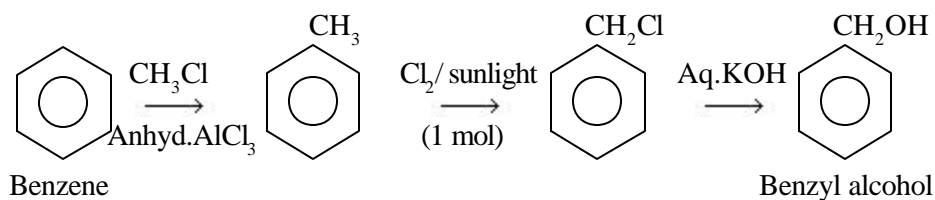
### 34. Benzene to m-dichlorobenzene



**35. Benzene to cumene**



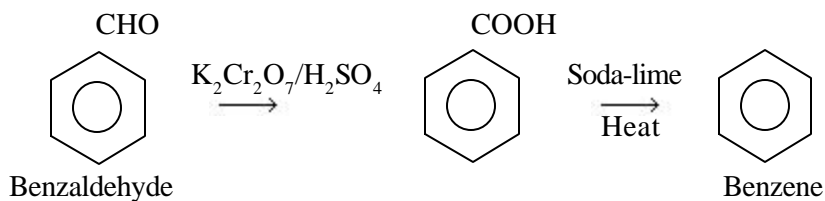
**36. Benzene to benzyl alcohol**



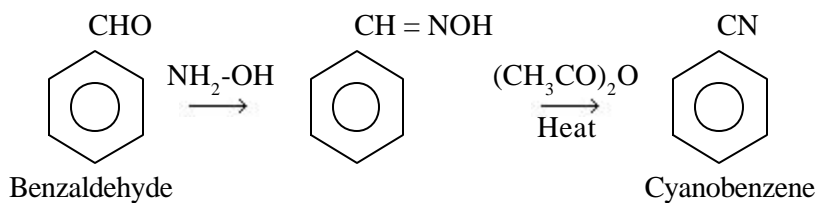
**37. Benzaldehyde to acetophenone**



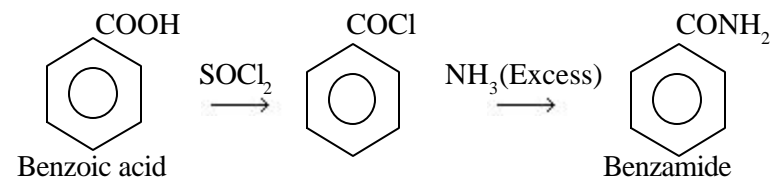
**38. Benzaldehyde to benzene**



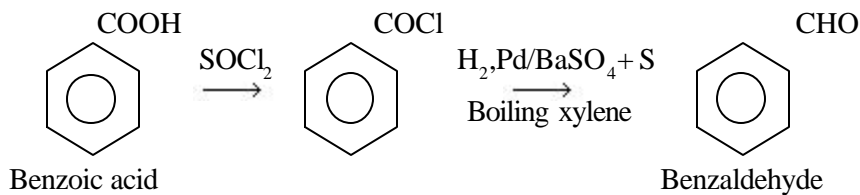
**39. Benzaldehyde to cyanobenzene**



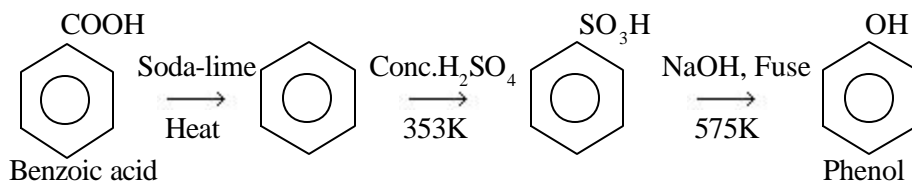
**40. Benzoic acid to benzamide**



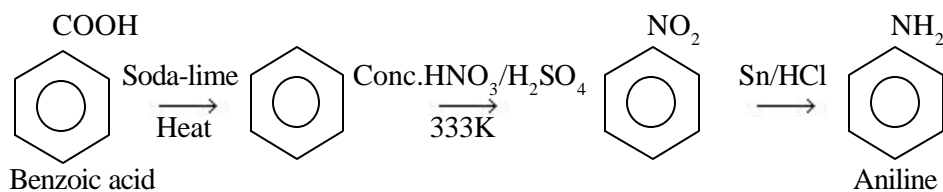
#### 41. Benzoic acid to benzaldehyde



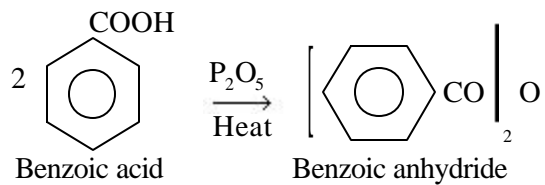
#### 42. Benzoic acid to phenol



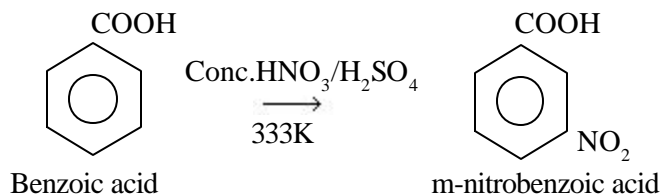
#### 43. Benzoic acid to aniline



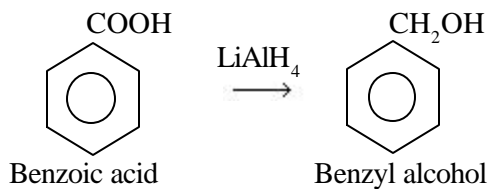
#### 44. Benzoic acid to benzoic anhydride



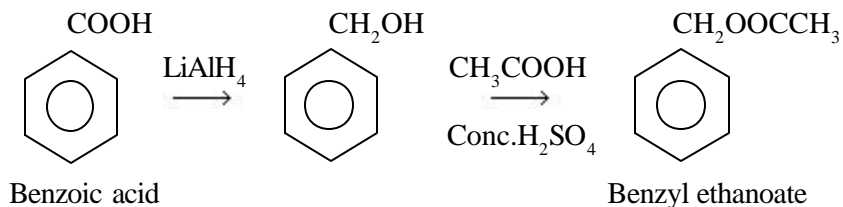
#### 45. Benzoic acid to m-nitrobenzoic acid



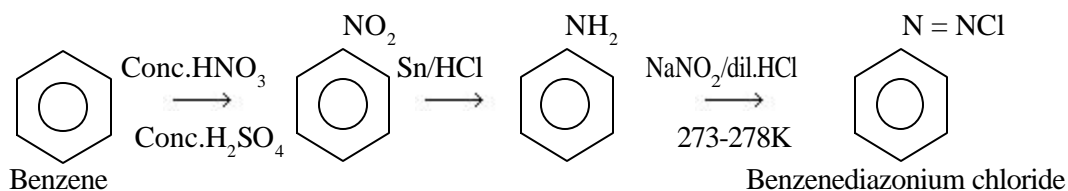
#### 46. Benzoic acid to benzyl alcohol



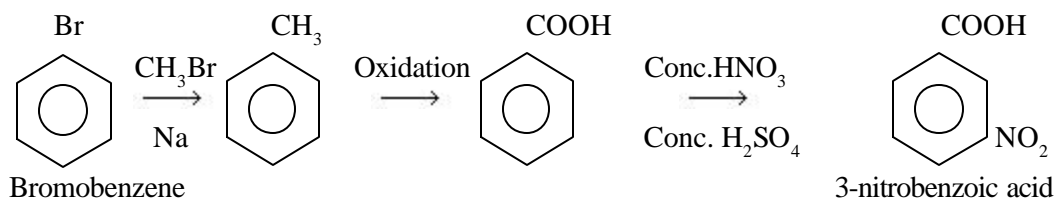
#### 47. Benzoic acid to benzyl ethanoate



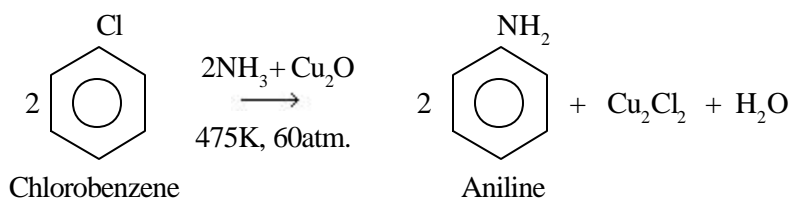
#### 48. Benzene to benzenediazonium chloride



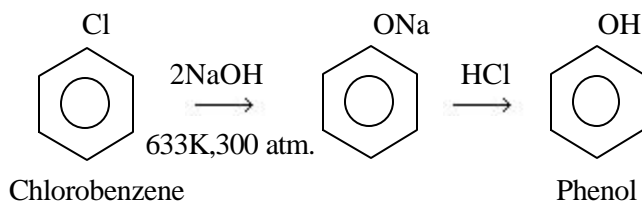
#### 49. Bromobenzene to 3-nitrobenzoic acid



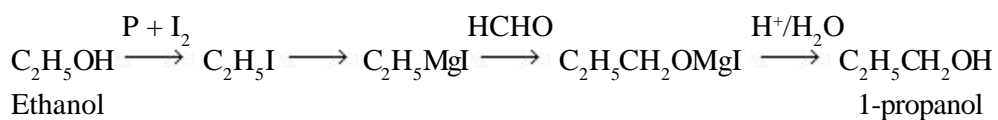
#### 50. Chlorobenzene to aniline



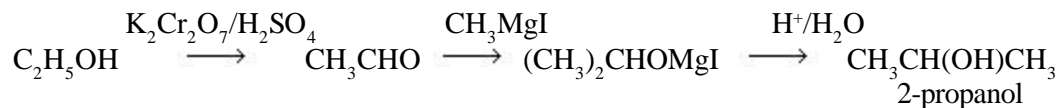
#### 51. Chlorobenzene to phenol



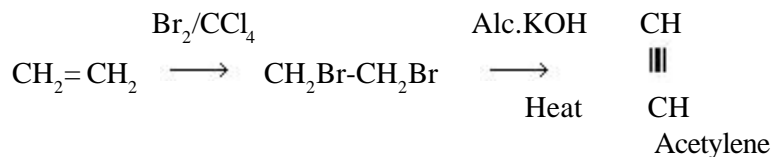
#### 52. Ethanol to 1-propanol



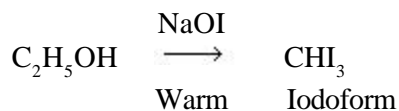
**53. Ethanol to 2-propanol**



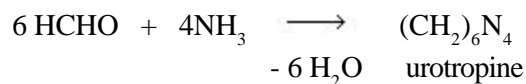
**54. Ethylene to acetylene**



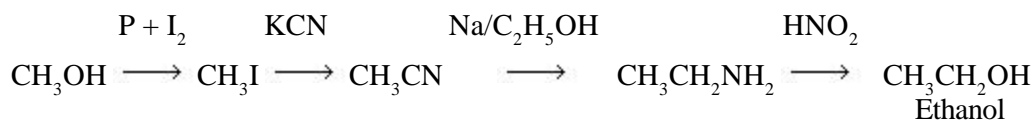
**55. Ethanol to Iodoform**



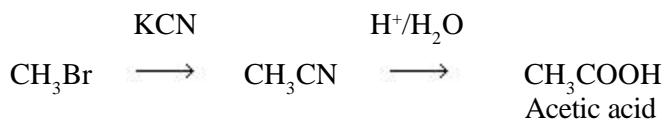
**56. Formaldehyde to urotropine**



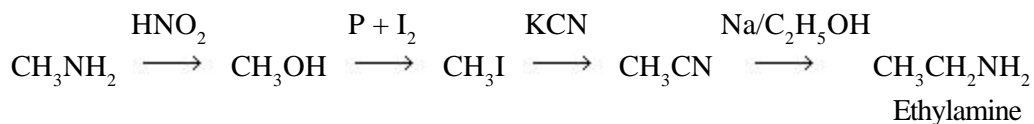
**57. Methanol to ethanol**



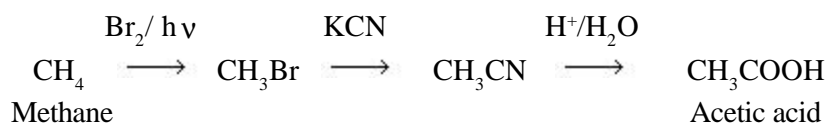
**58. Methyl bromide to acetic acid**



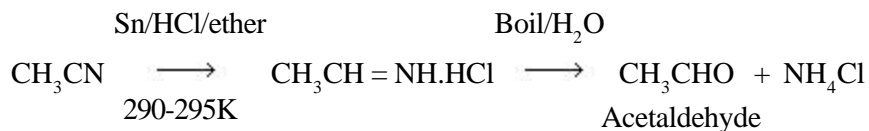
**59. Methylamine to ethylamine**



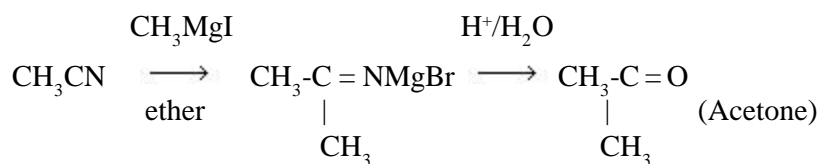
**60. Methane to acetic acid**



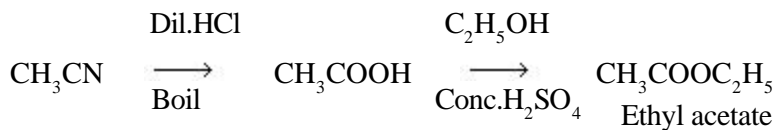
### 61. Methyl cyanide to acetaldehyde



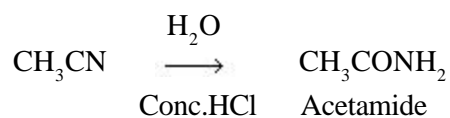
### 62. Methyl cyanide to acetone



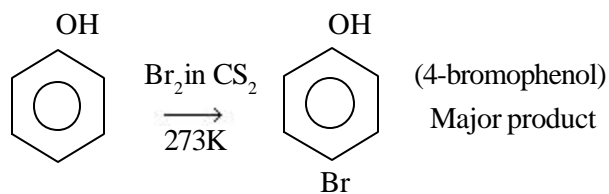
### 63. Methyl cyanide to ethyl acetate



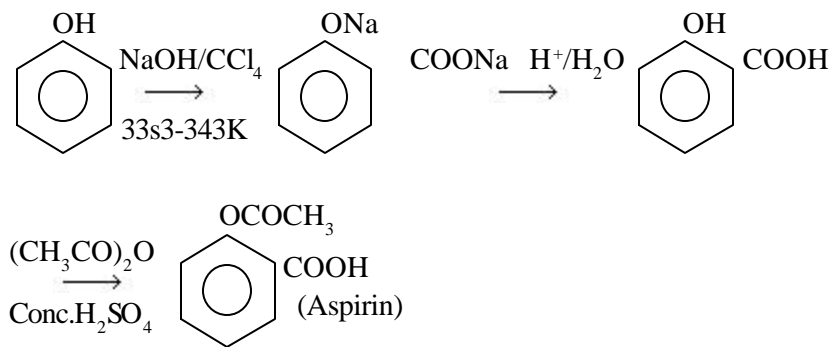
### 64. Methyl cyanide to acetamide



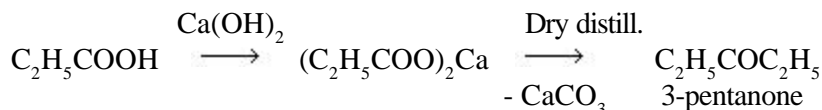
### 65. Phenol to 4-bromophenol



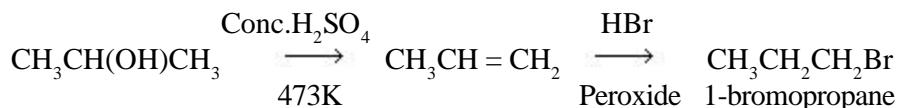
### 66. Phenol to aspirin



### 67. Propanoic acid to 3-pentanone



### 68. 2-Propanol to 1-bromopropane



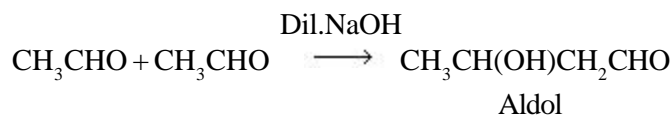
### PROBLEMS BASED ON ORGANIC REACTIONS

1. An organic compound  $\text{C}_2\text{H}_4\text{O}$  gives a red precipitate when warmed with Fehling's solution. It also undergoes aldol condensation in the presence of alkali.

- Write IUPAC name of the compound.
- What is the state of hybridization of carbon atoms in the compound?
- Write balanced equation for the reaction.

**Solution:** a)  $\text{CH}_3\text{CHO}$  Ethanal

b)  $\text{sp}^3$  and  $\text{sp}^2$ -hybridizations



2. Compound A ( $\text{C}_5\text{H}_{10}\text{O}$ ) forms phenylhydrazone, gives negative Tollen's and iodoform tests and is reduced to pentane. What is the structure of the compound?

**Solution:** A forms phenylhydrazone. So it should be either an aldehyde or ketone. But it gives negative Tollen's test. So it is a ketone. Since it gives pentane on reduction, it should contain 5 carbon atoms in a straight chain with a keto group. A does not give iodoform test, so it does not contain  $-\text{COCH}_3$  group. Hence the structure of A is  $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$

3. A ketone A gives iodoform on reacting with iodine and sodium hydroxide. A on reduction gives B, which on heating with sulphuric acid gives C. C, on ozonolysis gives acetaldehyde and acetone. Identify A, B and C.

**Solution:** Since the compound C on ozonolysis gives acetaldehyde and acetone, its structure should be  $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2$ . C is obtained by heating B with conc.  $\text{H}_2\text{SO}_4$  which induces dehydration. Hence B is an alcohol.

Ketone A undergoes haloform reaction. So it must contain  $-\text{COCH}_3$  group. So its structure may be  $\text{CH}_3\text{COR}$ . The products of ozonolysis of C indicate that R must be  $-\text{CH}(\text{CH}_3)_2$

Hence A  $\text{CH}_3\text{COCH}(\text{CH}_3)_2$  B  $\text{CH}_3\text{CH(OH)CH}(\text{CH}_3)_2$  C  $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2$

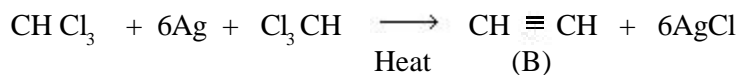
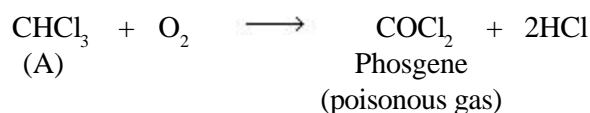


4. A sweet smelling organic compound A is slowly oxidised by air in the presence of light to a highly poisonous gas. On warming with silver powder, it forms a gaseous substance B, which is also produced by the action of calcium carbide on water. Identify A and B and write the chemical equations of the reactions involved.

**Solution:**

Calcium carbide reacts with water forming acetylene. Hence B is acetylene. Acetylene is formed by treating chloroform with silver powder. Chloroform is a sweet smelling liquid. Hence A is chloroform.

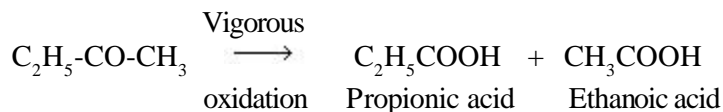
Equations:



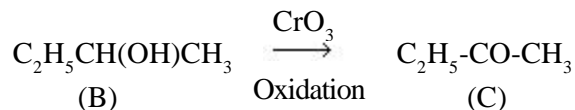
5. Compound A of molecular formula  $\text{C}_4\text{H}_9\text{Br}$ , yields a compound B of molecular formula  $\text{C}_4\text{H}_{10}\text{O}$  when treated with aqueous NaOH. On oxidation, the compound B yields a ketone C. Vigorous oxidation of the ketone yields a mixture of ethanoic and propanoic acids. Deduce the structures of A, B and C.

**Solution:**

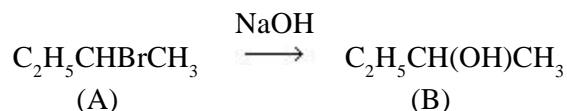
The compound B on oxidation yields a ketone C. The structure of C is  $\text{C}_2\text{H}_5\text{-CO-CH}_3$  since on vigorous oxidation C gives a mixture of ethanoic and propanoic acids.



The structure of B should be  $\text{C}_2\text{H}_5\text{CH(OH)CH}_3$  since on oxidation B gives the ketone C.



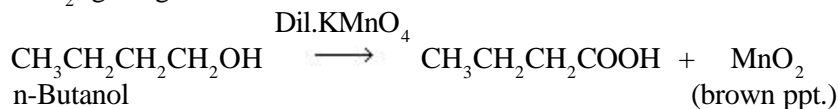
The structure of A should be  $\text{C}_2\text{H}_5\text{CHBrCH}_3$  since on treatment with aqueous NaOH A gives B.



6. When t-butanol and n-butanol are separately treated with a few drops of dilute  $\text{KMnO}_4$ , in one case only, the purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate?

**Solution:**

n-Butanol can be readily oxidised by dilute  $\text{KMnO}_4$  solution. The purple colour of  $\text{KMnO}_4$  disappears and the brown precipitate of  $\text{MnO}_2$  is formed. n-Butanol reduces  $\text{KMnO}_4$  to  $\text{MnO}_2$ , getting itself oxidised to butanoic acid.



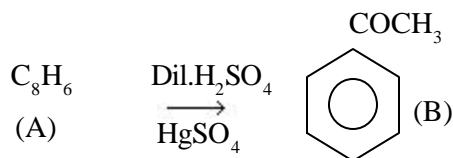
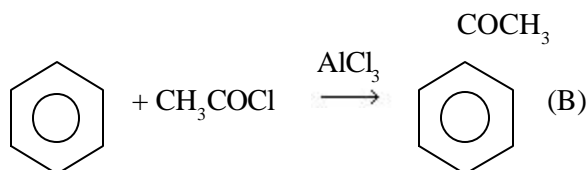
But t-butanol resists oxidation.

7. An organic compound A ( $\text{C}_8\text{H}_6$ ) on treatment with dilute sulphuric acid containing mercuric sulphate, gives a compound B which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous KOH, yields C and a yellow compound D. Identify A, B, C and D with justification. Show how B is formed from A?

**Solution:**

B gives iodoform test and so it must be a methyl ketone. The compound B is also obtained from the Friedel Craft's reaction of benzene and acid chloride. So it must be a phenyl methyl ketone. The compound B must contain  $\text{CH}_3\text{CO}$ - grouping.

Reactions:



The reaction involves addition of water to a triple bond. Hence A will be phenyl acetylene.

