Semester-II

18CHU203 ORGANIC CHEMISTRY II 5H 5C

(Oxygen Containing Functional Groups)

Instruction Hours/week:L:5 T:0 P:0 Marks: Internal: 40 External: 60 Total:100

Scope

The course deals with the chemistry of halogenated hydrocarbons, and oxygen containing functional groups. The chemistry involves the preparation properties and reactivity of the halogenated hydrocarbons, alcohols, phenols, carbonyl compounds, ethers, eopxides, organometallic compounds, carbonyl compounds and acids and its derivatives.

Objectives

The students will able to

1. Understand the mechanisms of nucleophilic substitution reactions.
2. Understand the preparation, properties and relative reactivity of alcohols and phenols
3. Understand the reactions of carbonyl compounds
4. Understand the preparations and reactions of epoxides, ethers and organometallic compounds
5. Understand the preparations and properties of carboxylic acid and its derivatives.

Methodology

Blackboard teaching, Power point presentation and group discussion.

UNIT I

Chemistry of Halogenated Hydrocarbons:

Alkyl halides: Methods of preparation and properties, nucleophilic substitution reactions – SN1, SN2 and SNi mechanisms with stereochemical aspects and effect of solvent; nucleophilic substitution vs. elimination.

Aryl halides: Preparation (including preparation from diazonium salts) and properties, nucleophilic aromatic substitution; SNAr, Benzyne mechanism.
Relative reactivity of alkyl, allyl, benzyl, vinyl and aryl halides towards nucleophilic substitution reactions.

UNIT II

Alcohols, Phenols:

Alcohols: preparation, properties and relative reactivity of 1°, 2°, 3° alcohols, Bouvaelt-Blanc Reduction; Oxidation of diols by periodic acid and lead tetraacetate, Pinacol-Pinacolone rearrangement;

Phenols: Preparation and properties; Acidity and factors affecting it, Ring substitution reactions, Reimer–Tiemann and Kolbe's–Schmidt Reactions, Fries and Claisen rearrangements with mechanism;

UNIT III

Carbonyl Compounds:

Structure, reactivity, preparation and properties; Nucleophilic additions, Nucleophilic addition-elimination reactions with ammonia derivatives with mechanism; Mechanisms of Aldol and Benzoin condensation, Knoevenagel condensation, Claisan-Schmidt, Perkin, Cannizzaro and Wittig reaction, Beckmann and Benzil-Benzilic acid rearrangements, haloform reaction and Baeyer Villiger oxidation, α – substitution reactions, oxidations and reductions (Clemmensen, Wolff-Kishner,$LiAlH_4$, $NaBH_4$, MPV, PDC)

UNIT IV

Organometallic compounds, Ethers and Epoxides and Addition reactions

Organometallic compounds of Mg (Grignard reagent) – Use in synthesis of organic compounds.
Ethers and Epoxides: Preparation and reactions with acids. Reactions of epoxides with alcohols, ammonia derivatives and $LiAlH_4$

Addition reactions of α, β- unsaturated carbonyl compounds: Michael addition.
Active methylene compounds: Keto-enol tautomerism. Preparation and synthetic applications of diethyl malonate and ethyl acetoacetate.

UNIT V

Acids and their Derivatives:

General methods of preparation, physical properties and reactions of monocarboxylic acids, Effect of substituents on acidic strength. Typical reactions of dicarboxylic acids, hydroxy acids and unsaturated acids.
Preparation and reactions of acid chlorides, anhydrides, esters and amides; Comparative study of nucleophilicsustitution at acyl group -Mechanism of acidic and alkaline hydrolysis of esters, Claisen condensation, Dieckmann and Reformatsky reactions, Hofmann- bromamide degradation and Curtius rearrangement.

Suggested Readings:

Text Books:

1. Madan, R.L. (2015). *Chemistry for Degree Students.* New Delhi: S. Chand and Company Pvt, Ltd.
2. Morrison, R. T. & Boyd, R. N. (2012). *Organic Chemistry*. Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).

Reference Books:

1. Finar, I. L. (2012). *Organic Chemistry.* Volume 1. Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
2. Graham Solomons, T.W. (2012). *Organic Chemistry*. John Wiley & Sons, Inc.
3. Jain M.K. & Sharma S.C. (2015). Modern organic chemistry, 4thEdition, Vishal publishing Co NewDelhi

Karpagam Academy of Higher Education

(Established Under Section 3 of UGC Act, 1956)
Coimbatore – 641021

Department of Chemistry

Lecture Plan

In charge Staff : **Dr. K. Sundaram**
Class : **I B.Sc. Chemistry**
Title : **Organic Chemistry -II**
Subject Code : **18CHU203**
Total Hours : **50**

UNIT-I

Chemistry of Halogenated Hydrocarbons **Hour's required-10**

S.No	Lecture Hour	Topics	Support Material
1	1	Alkyl halides: Methods of preparation and properties	T1:584-585 R2:422-424
2	1	Nucleophilic substitution reactions – S_N1 mechanisms	T1:590-591 R2:430
3	1	Nucleophilic substitution reactions – S_N2 mechanisms	T1:587-589
4	1	Nucleophilic substitution reactions – S_Ni mechanisms, Stereochemical aspects, Effect of solvent	R2: 430, 433-434
5	1	Nucleophilic substitution vs. Elimination	R2:427
6	1	Aryl halides: Preparation (including preparation from diazonium salts) and properties	R2:456-457
7	1	Nucleophilic aromatic substitution; SNAr, Benzyne mechanism	R2:459-461
8	1	Relative reactivity of alkyl and allyl towards nucleophilic substitution reactions	R2:443-444
9	1	Relative reactivity of benzyl towards nucleophilic substitution reactions	R2:463
10	1	Relative reactivity of vinyl halides and aryl towards nucleophilic substitution reactions. Recapitulation and discussion of important questions	R2:468-469

Supporting Materials:
Text Books

T1: R.L. Madan, 2015, Chemistry for Degree Students (B.Sc. Second Year), S. Chand and Company Pvt Ltd, Ran Nagar, Newdelhi-110055

Referance Books

R2: M.K. Jain and S.C. Sharma, 2016, Modern Organic Chemistry, 4th Edition, Vishal Publishing Co, NewDelhi-144008

UNIT-II

Alcohols, Phenols **Hours required-10**

S.No	Lecture Hour	Topics	Support Material
1	1	Preparation, properties and relative reactivity of 1° alcohols	T1:375-394
2	1	Preparation, properties and relative reactivity of 2° alcohols	T1:375-394
3	1	Preparation, properties and relative reactivity of 3° alcohols	T1:375-394
4	1	Bouvaelt-Blanc Reduction, Oxidation of diols by periodic acid and lead tetraacetate	R2:683-684 T1:403
5	1	Pinacol- Pinacolone rearrangement	T1:405-406
6	1	Preparation and properties of phenols	T1:419-425
7	1	Acidity and factors affecting phenols	T1:426-427
8	1	Ring substitution reactions: Reimer–Tiemann and Kolbe's–Schmidt reactions	T1:433-434
9	1	Fries rearrangements with mechanism Claisen rearrangements with mechanism	T1:430, T2:555 R1:1059-1060
10	1	Recapitulation and discussion of important questions	

Supporting Materials:

Text Books

T1: R.L. Madan, 2015, Chemistry for Degree Students (B.Sc. Second Year), S. Chand and Company Pvt. Ltd., Ran Nagar, Newdelhi-110055

Referance Books

R1: Arun Bahl and B.S. Bahl, 2005, Advanced Organic Chemistry, S. Chand & Company Pvt. Ltd, RamNagar, NewDelhi.

R2: M.K. Jain and S.C. Sharma, 2016, Modern Organic Chemistry, 4th Edition, Vishal Publishing Co, NewDelhi-144008

UNIT-III

Carbonyl Compounds **Hours required-11**

S.No	Lecture Hour	Topics	Support Material
1	1	Structure, reactivity, preparation and properties of carbonyl compounds	T1:467, 469-477
2	1	Nucleophilic additions, Nucleophilic addition-elimination	T1: 479-487

3	1	Reactions with ammonia derivatives	T1: 486-487
4	1	Mechanisms of aldol, benzoin and Knoevenagel condensation	T1: 489-490, 492-495
5	1	Claisan-Schmidt condensation, Perkin, Cannizzaro	T1: 491-496
6	1	Wittig reaction, Beckmann and Benzil-Benzilic acid rearrangements	T1: 498 R2: 596-597
7	1	Haloform reaction and Baeyer Villiger oxidation	R2: 591-592
8	1	α–substitution reactions, Oxidations and reductions: Clemmensen, Wolff-Kishner	T1: 498-501 R2: 589-590
9	1	$LiAlH_4$, $NaBH_4$	T1: 502-503, R2:588
10	1	MPV and PDC	T1: 503,T2:982-983
11	1	Recapitulation and discussion of important questions	

Supporting Materials:

Text Books

T1: R.L. Madan, 2015, Chemistry for Degree Students (B.Sc. Second Year), S. Chand and Company Pvt Ltd, Ram Nagar, Newdelhi-110055

Referance Books

R2: M.K. Jain and S.C. Sharma, 2016, Modern Organic Chemistry, 4^{th} Edition, Vishal Publishing Co, NewDelhi-144008

UNIT-IV

Organometallic compounds **Hour's required-9**

S.No	Lecture Hour	Topics	Support Material
1	1	Organometallic compounds of Mg	R2:857-859
2	1	Grignard reagent– Use in synthesis of organic compounds, Uses in synthesis of organic compounds	R2: 859-866
3	1	Ethers: Preparation and reactions with acids Epoxides: Preparation and reactions with acids	T1: 449-459, 461-463
4	1	Reactions of epoxides with alcohols, LiAlH4 and with ammonia derivatives	T1: 463, R2: 551, 553
5	1	Addition reactions of α, β- unsaturated carbonyl compounds: Michael addition	T2:606-607
6	1	Active methylene compounds: Keto-enol tautomerism	R2: 740
7	1	Preparation and synthetic applications of diethyl malonate	R2: 724-727
8	1	Preparation and synthetic applications of ethyl acetoacetate.	R2: 730-731, 734-737
9	1	Recapitulation and discussion of important questions	

Supporting Materials:

Text Books

T1: R.L. Madan, 2015, Chemistry for Degree Students (B.Sc. Second Year), S. Chand and Company Pvt Ltd, Ram Nagar, Newdelhi-110055
T2: R. T. Morrison, R. N. Boyd and S.K. Bhattacharjee, 2012, Organic Chemistry, 7th Edition, Dorling Kindersley (India) Pvt., Ltd. (Pearson Education)

Referance Books

R2: M.K. Jain and S.C. Sharma, 2016, Modern Organic Chemistry, 4th Edition, Vishal Publishing Co, NewDelhi-144008

UNIT-V

Acids and their Derivatives **Hours required-10**

S.No	Lecture Hour	Topics	Support Material
1	1	General methods of preparation, physical properties and reactions of monocarboxylic acids	T1: 524, 527-531,533-534
2	1	Effect of substituents on acidic strength	T1:544-547
3	1	Typical reactions of dicarboxylic acids, hydroxy acids and unsaturated acids.	T1:558-562, 569-572
4	1	Preparation and reactions of esters and amides	T1:595-599, 601-603
5	1	Preparation and reactions of acid chlorides and anhydrides, Comparative study of nucleophilic substitution at acyl group	T1: 596, 599-601, 606-607
6	1	Mechanism of acidic and alkaline hydrolysis of esters	T1: 598-599
7	1	Claisen condensation and Dieckmann reactions	R2: 730-731
8	1	Reformatsky reactions, Hofmann- bromamide degradation, Curtius rearrangement	R2:582-583, 772-773, 621
9	1	Recapitulation and discussion of important questions	
10	1	Previous year ESE question paper discussion	

Supporting Materials:

Text Books

T1: R.L. Madan, 2015, Chemistry for Degree Students (B.Sc. Second Year), S. Chand and Company Pvt Ltd, Ram Nagar, Newdelhi-110055

Referance Books

R2: M.K. Jain and S.C. Sharma, 2016, Modern Organic Chemistry, 4th Edition, Vishal Publishing Co, NewDelhi-144008

Syllabus

Chemistry of Halogenated Hydrocarbons:

Alkyl halides: Methods of preparation and properties, nucleophilic substitution reactions – SN1, SN2 and SNi mechanisms with stereochemical aspects and effect of solvent; nucleophilic substitution vs. elimination.

Aryl halides: Preparation (including preparation from diazonium salts) and properties, nucleophilic aromatic substitution; SNAr, Benzyne mechanism. Relative reactivity of alkyl, allyl, benzyl, vinyl and aryl halides towards nucleophilic substitution reactions.

CHEMISTRY OF HALOGENATED HYDROCARBONS

Classification of aliphatic halogen compounds:

Aliphatic halogen compounds can be classified as follows:

(a) **Monohalogen compounds.** Compounds such as methyl chloride, which contain one halogen in the molecule are called monohalogen compounds.

(b) **Dihalogen compounds.** Compounds such as ethylene dichloride which contain halogen atoms in the molecule are called dihalogen compounds. These can be further classified into two types:

(i)**Vicinal dihalides.** Compounds containing two halogens on neighbouring carbon atoms are called vicinal dihalides.

(ii)**Geminal dihalides.** Compounds containing two halogens on the same carbon in the molecule are called germinal dihalides. Vicinal (or vic.) and geminal (or gem.) dihalides are discussed in detail later in this chapter.

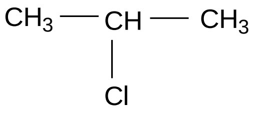
(c)**Trihalogen compounds.** Compounds such as chloroform or iodoform which contain three halogens in the molecule are called trihalogen compounds.

(d)**Tetrahalogen compounds.** Compounds such as carbon tetrachloride, which contain four halogen atoms in the molecule, are called tetrahalogen compounds.

Monohalogen compounds are further classified into primary, secondary and tertiary alkyl halides.

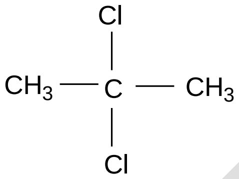
Primary alkyl halides are those compounds in which the halogen is linked to a carbon which is further linked to no carbon atom. For example, CH_3-CH_2-Cl.

Secondary alkyl halides are those compounds in which the halogen is linked to a carbon which is further linked to two carbon atoms. For example,



$$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$$

Tertiary alkyl halides are those compounds in which the halogen is linked to a carbon which is further linked to three carbon atoms. For example,



$$CH_3-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}}-CH_3$$

METHODS OF PREPARATION OF ALKYL HALIDES

Alkyl halides can be prepared by the following methods.

1. Halogenation of alkanes. Alkanes react with halogens in the presence of UV light or by heating at high temperature (400°C) to give alkyl halides along with other polyhalogen compounds

$$CH_4 \xrightarrow{Cl_2} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$$

2. Addition of halogen acids to alkenes. Halogen acids add to alkenes to produce alkyl halides. Addition takes place according to Markownikof rule. However, in the presence of peroxides.

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + HI \longrightarrow \underset{\text{Ethyl iodide}}{CH_3\text{-}CH_2\text{-}Cl}$$

$$CH_3\text{-}CH_2{=}CH_2 + HBr \longrightarrow \underset{\text{2-Bromopropane}}{CH_3CHBrCH_3}$$

$$CH_3\text{-}CH_2{=}CH_2 + HBr \xrightarrow{\text{Feroxide}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br}$$

3. Action of Halogen Acids on Alcohols. Alcohols react with HBr or HI to produce alkyl bromide or alkyl iodide. Alkyl chlorides are obtained by treating alkenes with dry HCl in presence of zinc chloride.

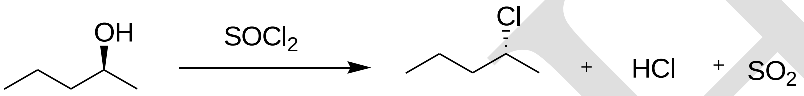
$$CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$$

Ethylchloride

$$CH_3CH_2OH + HBr \xrightarrow{ZnCl_2} CH_3CH_2Br + H_2O$$

Ethylbromide

4. Action of Thionyl Chloride on Alcohols. Alcohols react with Thionyl Chloride $SOCl_2$ in presence of pyridine to form alkyl halides. The function of pyridine is to absorb HCl as it is formed.



6. Halogen Exchange Reaction. Alkyl chloride or bromide on heating with a solution of sodium iodide in acetone gives alkyl iodide

CH_3CH_2Br + NaI $\longrightarrow$ CH_3CH_2I+ NaBr

PHYSICAL PROPERTIES OF ALKYL HALIDES

1. Alkyl halides containing one carbon atom are gases at room temperature. Other alkyl halides upto C_{18} are colourless solids.
2. Alkyl halides are soluble in organic solvents but insoluble in water. There is no possibility of hydrogen bonding in alkyl halide.
3. Alkyl bromides and iodides are heavier than water while chloride and fluorides are lighter than water.
4. For a given halogen atom, the boiling point increases with increase in the size of the alkyl group.
5. For a given alkyl group, the boiling point increases in the order.

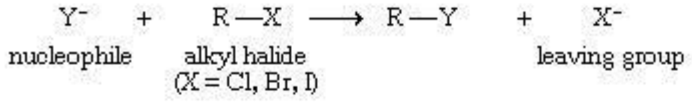
RI>RBr>RCl>RF

6. In the case of isomeric halides, the boiling point decreases with branching. This is because surface area decreases with branching and the intermolecular forces of attraction decrease with surface area.

REACTIONS OF ALKYL HALIDES

NUCLEOPHILIC SUBSTITUTION REACTIONS

The re action involving the replacement of an atom or a group of atoms by a suitable nucleophile is called nucleophilic substitution reaction. The carbon-halogen bond in alkyl halides is polar due to greater electronegativity of the halogen as compared to carbon. It is depicted as below:



The presence of partial positive charge on carbon atom makes it susceptible to nucleophilic attack. Thus, when a stronger nucleophile approaches the positively charged carbon of the alkyl halides is readily displaced as halide ion as shown below:

Nucleophilic Substitution of Alkyl halides

A few important nucleophilic substitution reactions are discussed below:

(i) **Replacement by hydroxyl group (Formation of alcohols).** Alkyl halides react with aqueous KOH or moist silver oxide, i.e.,AgOH to form alcohols.

(ii) **Replacement by cyano group (Formation of cyanides).** Alkyl halides react with alcoholic potassium cyanide to form cyanides or nitriles.

(iii) **Replacement by alkoxy group (Formation of ethers).** When treated with Sodium alkoxide, alkyl halides yield ethers.

(iv) **Replacement by alkynyl group (Formation of alkynes).** When an alkyl halide is treated with sodium salt of an alkyne, higher alkynes are formed.

(v) **Replaced by carboxylate group (Formation of a esters).** When heated with silver salts of carboxylic acids, alkyl halides give esters.

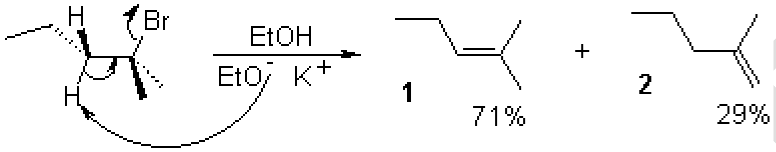
ELIMINATION REACTIONS

Reaction with alcoholic KOH. Alkyl halides react with alcoholic potassium hydroxide to form alkenes

$CH_3CH_2Br + KOH\ (alc.) \rightarrow H_2C{=}CH_2 + KBr + H_2O$

For mechanism of reaction, refer to chapter on alkenes.

If an alkyl halide can eliminate hydrogen halide in two different ways, alkenes formed will be the one which is most highly substituted (Saytzeff Rule). For example,



It may be noted that aqueous solution of KOH causes substitution in alkyl halides while alcoholic solution causes elimination. In aqueous solution, KOH ionizes to give OH⁻ ions which have a tendency to get hydrated ion being large in size is not in a position to abstract the β-hydrogen from alkyl halide and the elimination is checked. In alcoholic medium, the base gives OH⁻ ions to affect elimination to form an alkene.

ACTION WITH ACTIVE METALS

1. Action with Magnesium. Magnesium metal reacts with alkyl halide in the presence of dry ether to form organomagnesium halide known as Grignard reagents

2. Action with Sodium (Wurtz Reaction). Alkyl halides react with sodium metal in the presence of anhydrous ether to form higher alkanes.

3. Action with lead-sodium alloy. When heated with an alloy of lead and sodium, alkyl halides from tetra alkyl lead

Tetra ethyl lead (T.E.L.) is used as anti-knocking agent in gasoline

Reduction Reactions of Alkyl Halides

1.With Zn/Cu couple and alcohol

$$CH_3CH_2Br + H_2 \xrightarrow{Zn/HCl} \underset{\text{Ethane}}{CH_3CH_3} + HBr$$

2.With Zn and dil.HCl

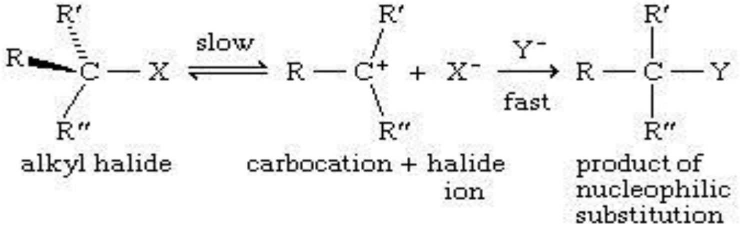
$$CH_3CH_2Br + H_2 \xrightarrow{Zn/HCl} CH_3CH_3 + HBr$$

Ethane

SN1 AND SN2 REACTIONS OF ALKYL HALIDES

SN1 Reactions means nucleophilic substitution reaction of first order.

In such reactions, there is only one species in the rate determining step. An example of SN1 reaction is:



SN2 reaction means nucleophilic substitution reaction of second order in such reactions there are two species in the rate-determining step.

An example of SN2 reaction is:

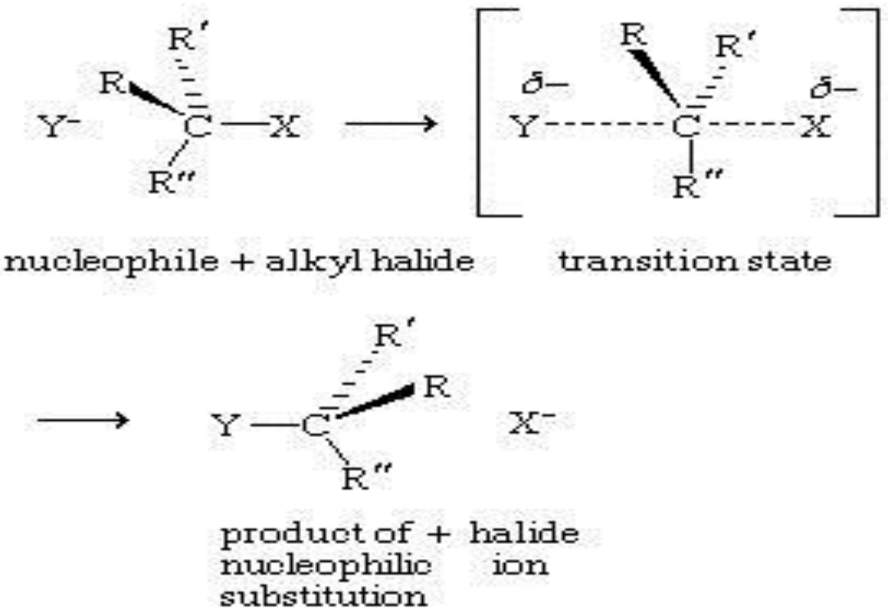
In this reaction the rate determining step of the reaction is:

As it involves two species on the reactant's side, it is a bimolecular or SN2 reaction.

SN2 REACTION MECHANISM OF SUBSTITUTION IN ALKYL HALIDES

Hydrolysis of methyl bromide proceeds by SN2,(meaning substitution nucleophilic reaction of the second order), mechanism. SN2 reaction may also be termed as bimolecular substitution reaction. The term bimolecular implies that there are two reacting species in the rate determining step of the reaction.

A simple and typical example of SN2 substitution is the hydrolysis of methyl bromide with aqueous sodium hydroxide.

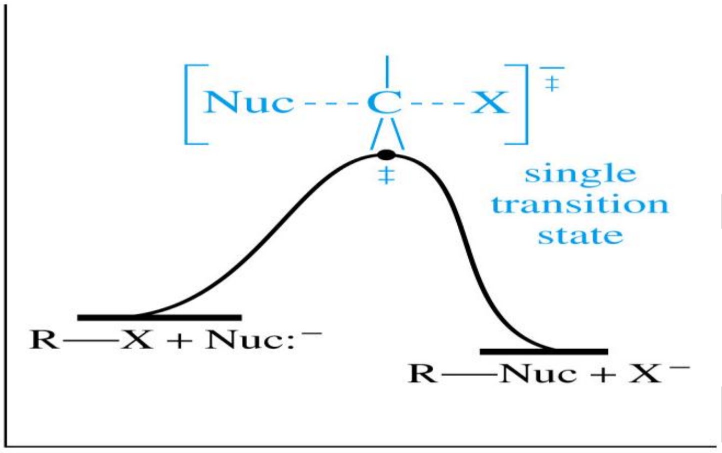


The kinetic data reveal that the rate of the reaction is dependent upon the concentration of both these reactants

The reaction is of second order and thus it proceeds by a direct diplacement mechanism in which both the reactants are present in the rate determining step. It is assumed that the nucleophile attacks the side of the carbon atom opposite to that of bromine. This is referred to as **back side attack.** As a result of this attack, a transition state is formed in which carbon atom is partially bonded to both -OH and -Br group. In the transition state, the central carbon is SP2 hybridised and the three hydrogens attached to it lie in the same place with mutual bond angles of 120 degree. The reaction may be depicted as:

It may be noted that in the transition state, the hydroxide ionhas diminished negative charge since it has started sharing its electrons with carbon. Similarly bromine develops a partial negative charge as it is tending to depart with the bonding electrons. When Carbon-Oxygen bond is completely formed, the carbon-bromine bond is altogether broken. The energy required for breaking a bond is compensated by the formation of a new bond. The over all reaction is thus a **concentrated process** occuring in one step through the intervention of a single transition state. In a single step, C-Br bond is broken and C-OH bond is formed resulting in the formation of alcohol molecule.

The potential energy diagram(energy profile diagram) for the above reaction is shown in fig.



S_N2

Stereochemistry of SN2 reaction. In SN2 reactions, it is assumed that the nucleophile (OH- in the present case) attacks the side of the carbon opposite to that of the leaving group. As a result, the configuration of the resulting product is inverted. In other words SN2 reaction proceeds with bromooctane is hydrolysed under SN2 conditions, it gives exclusively (+) -2- octanol. The reaction may thus be represented as:

we have cited the example of (-)-2-bromooctane because it contains a chiral carbon atom (a carbon linked to four different groups). The configuration of the reactant and the process are different in such SN2 reaction. We normally check the configuration by measuring the direction of rotation of plane polarised light although it is not necessary always that inversion of configuration should be accompanied by change in direction of rotation of plane-polarised light.

Relative Reactivities of Alkyl Halides in SN2 Substitution

In SN2 reactions, the nucleophilic attacks the side of the carbon opposite to that of the leaving group because both groups are to be accommodated in the transition state. Thus consider the alkaline hydrolysis of methyl bromide which follows SN2 mechanism. It involves the backside attack of the nucleophile (OH-) on the carbon bearing the bromine atom. Evidently, when the hydrogen atoms of methyl groups are successively replaced by bulkier alkyl groups such as ethyl, methyl, etc., there is an increased crowding around the central carbon both in the reactant and transition state. Due to steric hindrance of the alkyl groups, the nucleophile finds it more difficult to attack the carbon carrying the halogen. Thus, in the reaction of an alkyl bromide, simultaneous presence of -OH and -Br in the transition state becomes difficult because of overcrowding due to bulky groups. Greater the size of the alkyl group attached to halogen bearing carbon atom, greater is the difficultyin the transition state formation and thus slower will be the rate of such SN2 reaction. The overcrowding of alkyl groups also leads to strong non-bonded interactions in the transition state in which carbon is bonded to five atoms.

In general, the order of relative reactivities of alkyl halides in SN2 reactions follows the sequence:

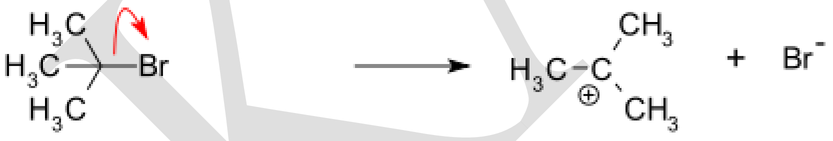
Methyl halides > Primary halides> secondary halides>Tertiary halides

MECHANISM OF SN1 REACTION OF R-X

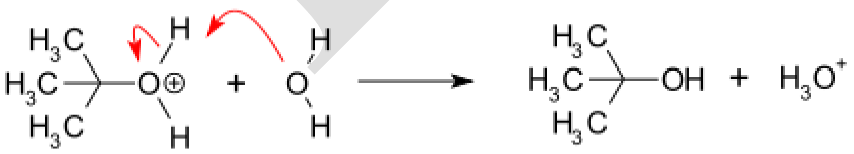
An example of unimolecular substitution reaction (SN1) is the hydrolysis of tert.butyl bromide Chemical kinetic studies reveal that the rate of this reaction depends only on the concentration of tert-butyl bromide. Thus,

The reaction is of first order and thus it is believed to occur in two steps.

Step-1

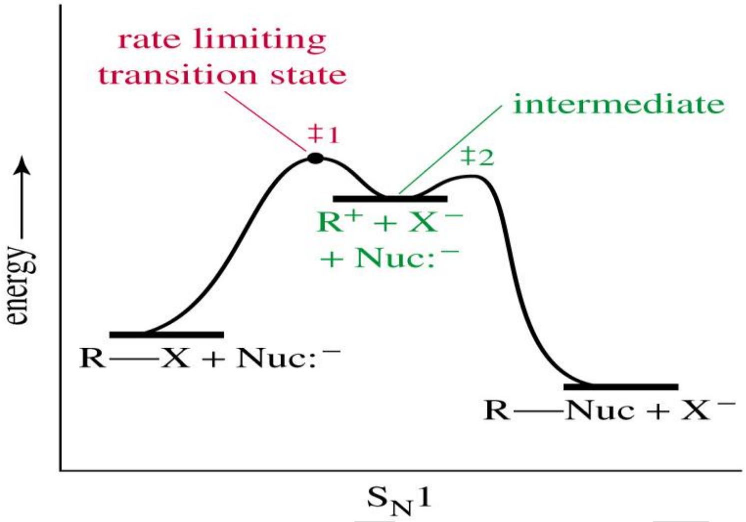


Step-2



It is thus clear that the rate determining step of the reaction is the slow ionisation is supplied by the formation of many ion-dipole bonds between the ions produced and the polar solvent molecules. The second step involving the combination of carbocation with hydroxide ion to from alcohol is fast.

The potential energy diagram for the reaction is as shown in the following diagram.(fig.7.2)



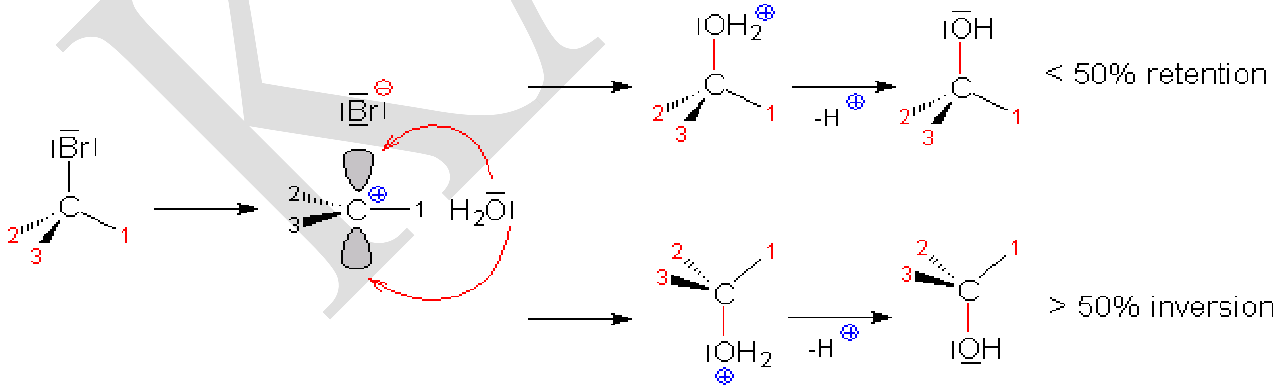
From the above diagram, it is evident that there are two transition states. The first transition state is formed when the reactants combine to form the intermediate. The second transition state is formed when the intermediate compound reacts with OH- ions to form the product. As the activation energy (E1 act) involved in the first transition state is greater than that in the formation of second transition state (E2 act), the first step in the reaction (formation of carbocation) is a slow step while the second step, in which OH- ions react with the carbocation, is a fast step.

Stereochemistry of SN1 reactions. In unimolecular nucleophilic substitution, the rate determining step involves the formation of a carbocation. The carbon atom in the carbocation is in the sp2 hybridised state. Thus the carbocation has a flat structure in which all the three substituents attached to carbon lie in a plane, making angles of 120 degree between them. The empty p- orbital lies perpendicular to the plane.

The attachment of the nucleophile to the flat carbonium ion can occur probably from the back of carbonium ion. Nucleophile will attach itself with 50% probability from the front and

50% probability from the back of carbonium ion. This may not make a difference in a simple case, but the difference in clearly made when the halogen carrying carbon is chiral i.e., linked to four different groups. Hydrolysis of an alkyl halide in which the halogen bearing carbon is chiral will produce a product which is racemic i.e., it contains 50% each of the d and l forms. Attachment of the nucleophile from front produces one configuration and that from the back products the other configuration. As a result, the final product obtained is expected to be racemic, containing equal number of molecule with retention and inversion of configuration. However, in actual practice, the product as a whole is not racemic. Usually there is a larger proportion of molecules with **inverted configuration** than those of the same configuration. This can be explained on the basis that initial ionisation of alkyl halide does not from a free carbocation. In fact ionisation of alkyl halide leads first to the formation of an **ion pair** in which the departing halide ion is still in close proximity to the carbocation.

Consequently, the attack on the front side of the carbocation which leads to a product with retention of configuration is slightly hindered on the other hand, the attack on the back side leading to a product with inversion of configuration is some what preferred. Thus, the actual product formed is **partially racemised** and the enantiomer with inverted configuration predominates. For example, when (-)-2-bromooctane is hydrolysed under SN1 conditions (low concentration of OH- ions), a partially racemised product is formed. This is further illustrated as follows:



Evidence for the formation of carbocation intermediates in SN1 reactions

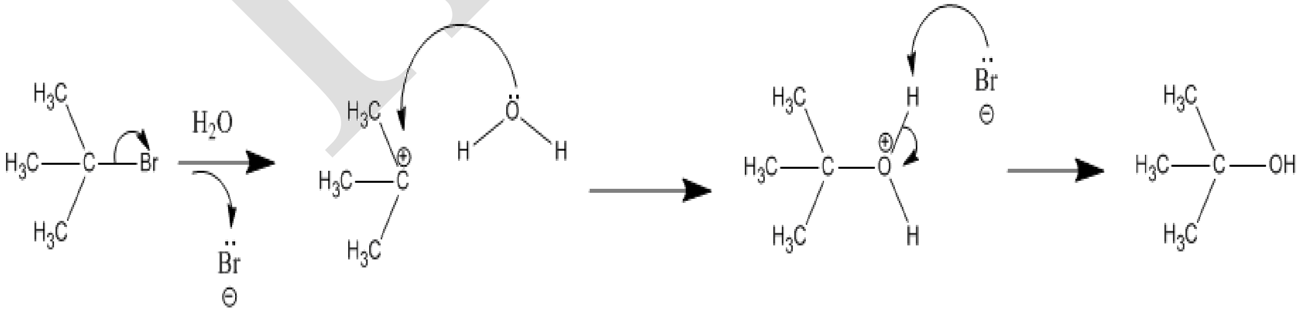
It is well known that carbocations undergo rearrangement to form more stable carbocations wherever possible. Since the carbocations are the intermediates in SN1 reactions, it is expected that these intermediates will undergo rearrangement if the structure permits. As a result, the rearranged substitution product will be obtained this is actually found to be so. For example, when 2-bromo-3-methylbutane is hydrolysed under SN1 conditions, the formation of rearranged product, 2-methyl-2-butanol and not 3-methyl butanol-2 takes place as shown below.

Relative Reactivities of alkyl halides in Unimolecular Nucleophilic Substitution (SN2) Reactions

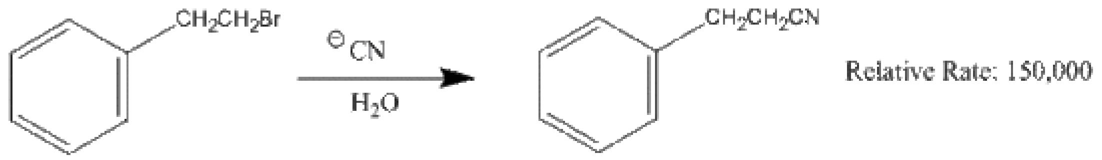
Formation of the carbocation is the rate determining step in unimolecular nucleophilic substitution (SN1). More the stability, more rapidly is the carbocation formed and hence faster is the reaction. Now the relative stability of the carbocation follows the sequences:
Benzyl,allyl > Tertiary >Secondary > Primary>Methyl carbocations. Therefore, the reactivity of alkyl halides is SN1 reaction follows the same order i.e.,
Benzyl,allyl > Tertiary >Secondary > Primary>Methyl halides

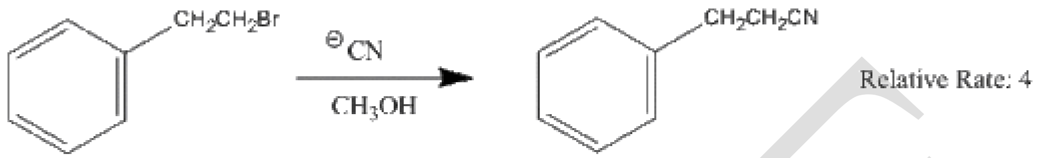
Effect of Polarity of Solvent on the Rate of SN1 and SN2 Reactions

Effect of solvent in SN1 reactions. The rate determining step in three reactions involves the ionisation of alkyl halide to form carbocation and halide ion. The energy required for the ionisation is provided by the salvation of these ions. Now polar solvent such as water, alcohols,etc, have a greater capacity as compared to non-polar solvents to solvate the ions and thus liberate considerable amount of energy. The energy released facilitates the ionisation and hence increases the rate of the reaction. It is thus obvious that SN1 reactions are favoured by polar solvents. For example,



Effect of solvent in SN2 reactions. SN2 reaction is a concerted process occurring in one step through the intervention of a transition state.





It is clear that in the transition state, the negative charge is dispersed over nucleophile and halogen while in the reactants, it is concentrated only on the nucleophile. Reactants are thus more polar than the transition state. Evidently polar solvent will solvate the reactants more strongly than the transition state and hence slow down the rate of SN2 reaction. In other words SN2 reactions are favoured by solvents of low polarity.

Comparison between SN1 and SN2 Reactions

Comparison between SN1 and SN2 Reactions is given in the form of table below:

S.No	SN1 Reactions	SN2 Reactions
1.	SN1 reactions follows first order kinetics.	SN2 reactions follows second order kinetics.
2.	Reaction rate is determined by electronic factors mainly.	Reaction rate is determined by steric factors mainly.
3.	The nucleophile attacks the carbocation from both sides although backside attack dominates.	The attack of nucleophile takes place from the backside only
4.	Partial racemisation of optically active halides takes place	Inversion of configuration takes place
5.	It is favoured by solvents of high polarity	It is favoured by solvents of low polarity
6.	Rearrangement of products takes place	There is no possibility of rearrangement
7.	It is favoured by mild nucleophiles	It is favoured by strong nucleophiles
8.	The reactivity follows the order: Tert.>	The reactivity follows the order:

	sec.>primary>methyl halide.	methyl>primary>sec.>tert. halide.

ARYL HALIDES

CLASSIFICATION AND NOMENCLATURE OF AROMATIC HALOGEN COMPOUNDS

Aromatic halogen compounds are those compounds which contain at least one benzene ring and one halogen atom in the molecule. They are classified as under :

Nuclear Halogen compounds

These are the compounds in which the halogen is directly attached to the benzene ring. For example,

Side-chain halogen compound

These are the compounds in which the halogen is attached to side chain of benzene ring. For example,

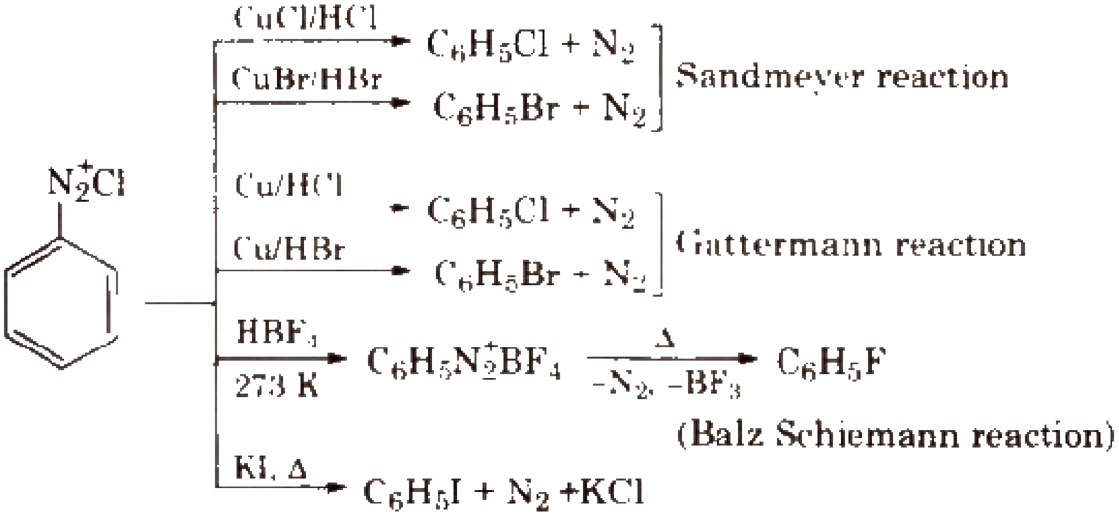
METHODS OF PREPARATION OF ARYL HALIDES

Aryl halides are prepared by the following methods:

(1) Direct halogenation. It consists in treating the aromatic compounds with halogen (chlorine or bromine only) at low temperature and in the absence of sunlight and in the presence of halogen carriers like ferrric halides or aluminium halides. Iron is mostly used which is converted into the corresponding ferric halide. For example:

The reaction stops at the mono substituted stage due to the deactivating influence of the halogen atom on the aromatic ring. However if chlorine is used in excess, further substitution tskes place and a mixture of o- and p-dichlorobenzene is obtained.

From diazonium salts (sandmeyars reaction). This is an important method for the preparation of aryl hallides, specially thosse which cannot be prepared by the direct halogenation. Aryl chlorides and bromides are obtained by treating the diazonium salt solution with cuprous chloride or bromide in the corresponding halogen acid.

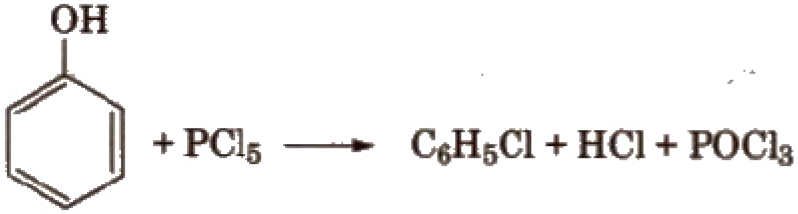


Modified form of above mentioned reaction, called **gattermann** reaction, involves the use of coper power and halogen acid instead of cuprous chloride or bromide.

Aryl iodides are obtained by warming the diazonium salt solution with potassium iodide solution.

When aromatic compounds contain highly activating groups such as -OH, NH2 etc., they undergo halogenation in the absence of halogen carries and halogen esnters the ortho and para positions.

From phenols. Phenols react with PCL5 to form aryl chlorides.

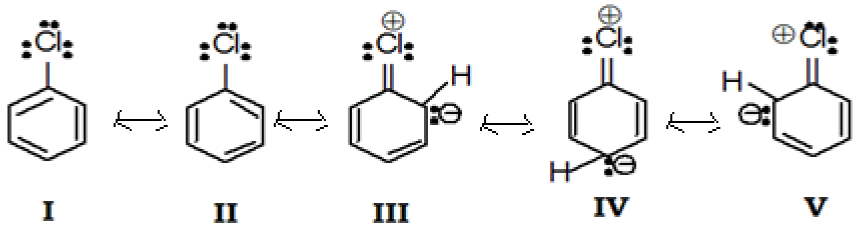


AROMATIC NUCLEOPHILIC SUNSTITUTION IN ARYL HALIDES

chlorobenzene show lower reactivity than alkyl halides towards nucleophilic substitution.

In chlorobenzene, C-Cl bond is not easily broken because chlorobenzene is a resonance hybrid of various contributing structures such as I-V show below:

Thus, the molecule of chlorobenzene is resonance stabilised. Moreover, the contribution of



structures like III to V imparts a partial double character to the carbon halogen bond in the resonance hybrid of the chlorobenzene. Carbon and chlorine are thus help together by little more than a single bond pair of electrons. On the other hand, arbon and chlorine are attached by a single bond in alkyl halides (say CH3 Cl). As a result, the carbon-chlorine bond in chlorobenzene is stronger than if it were a pure single bond and hence cannot be easily broken. The low reactivity of aryl halides is also partly due to resonance stabilisation of halides which increases the energy of activation (Eact) for displacement and thus slows down the reaction.

There is an alternative explanation for the low reactivity of aryl halides. The carbon atom attached to the halogen in aryl halides is sp2 hybridised while that in alkyl halides is sp3 hybridised. Since a sp2 hybridised orbital is smaller in size than sp3 hybridised orbital, therefore,the C-Cl bond in chlorobenzene is shorter and hence stronger than in methyl chloride.

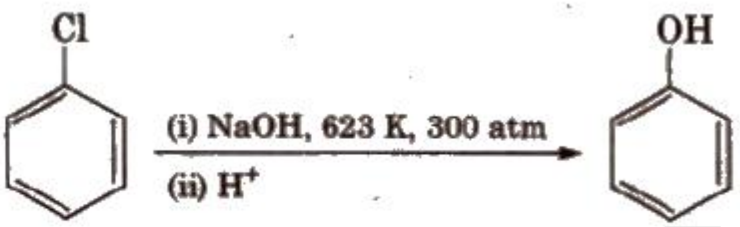
This has been confirmed by the X-Ray analysis which shows that the C-Cl bond in chlorobenzene is 1.69A while in CH3Cl it is 1.77A.

PROPERTIES OF ARYL HALIDES

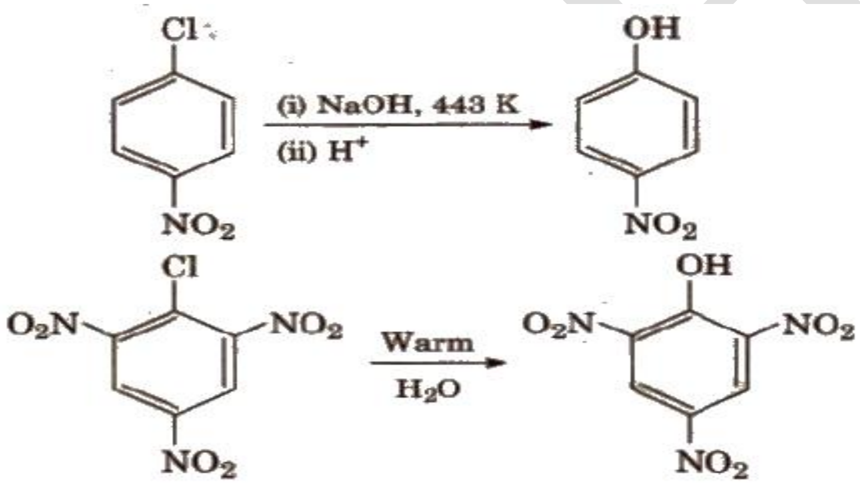
Important reactions of aryl halides are discussed below:

(1)Nucleophilic substitution reaction

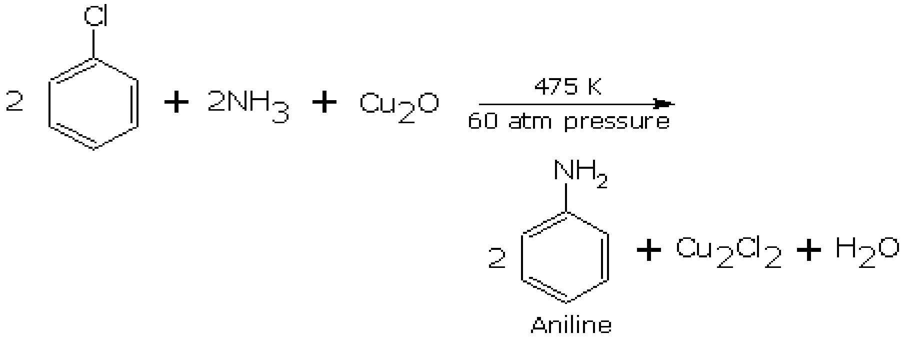
(i) Reaction with NaOH. When heated with aqueous solution of NaOH at 573K and under a pressure of 200atm,aryl halides form phenol.



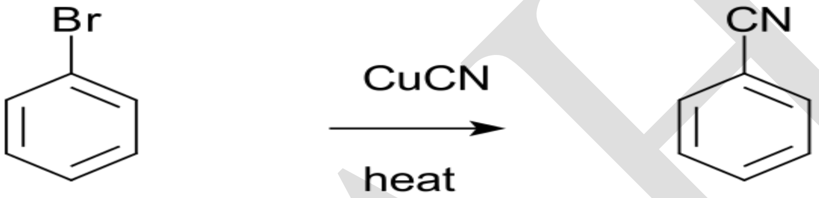
Presence of electron withdrawing group (-NO2) increases the reactivity.



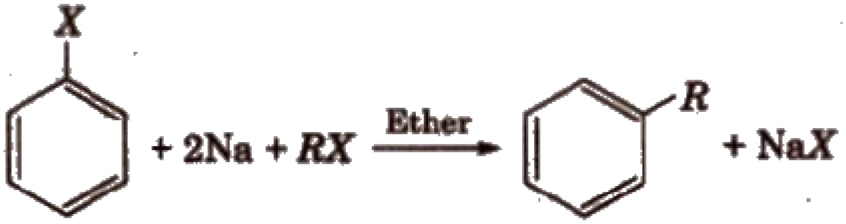
(ii) Reaction with NH3. When aryl halides are heated with aqueous NH3 at 473K in the presence of Cu2O as catalyst under a presssure of 60atm,amino compounds are obtained.



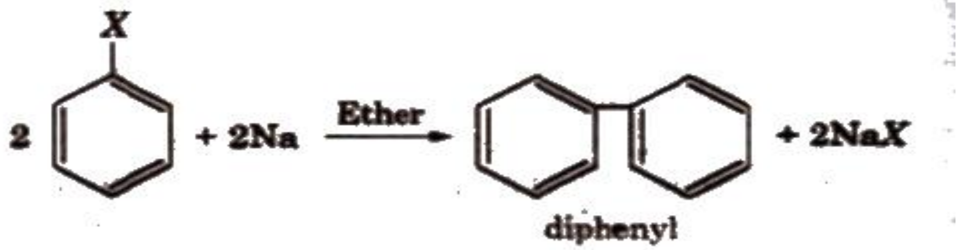
(iii) Reaction with cuprous cyanide. When aryl halides are heated with cuprous cyanide at 473K in the presence of pyridine, the halogen atom is replaced by -CN groups.



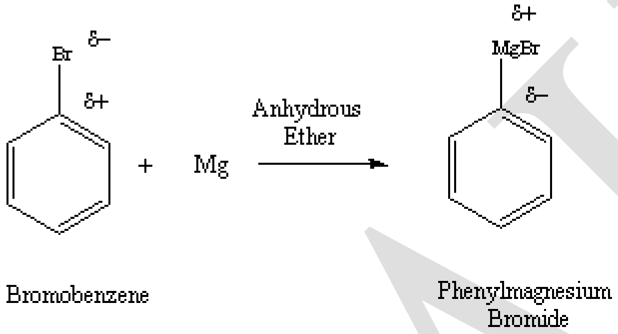
(2) Wurtz-Fittig Reaction. When aryl halide is treated with ethereal solution of alkyl halide in the presence of sodium, an alkyl benzene is formed.



But, diaryls are produced when only aryl halide treated with sodium. This reaction is called Fittig's Reaction.



(3) Formation of Grignard Reagent. Aryl bromides and iodides form Grignard reagent when they are treated with magnesium turnings in dry ether. Aryl chlorides form Grignard reagents only when the reaction is carried out in dry tetrahydrofuran(THF) as solvent.



THF stands for tetrahydrofuran

NUCLEOPHILIC SUBSTITUTION IN ARYL HALIDES IN THE PRESENCE OF ACTIVATING AND DEACTIVATING GROUPS

As already discussed, aryl halides undergo nucleophilic substitution under drastic conditions on the other hand, when powerful electron-withdrawing groups such as -NO_2, >C=O, -CHO,-COOH and -SO3H etc. are present in o- and/or p- position with respect to the halogen atom, replkacement of the latter by nucleophilic reagents take place under moderate or even ordinary conditions. For example,

on the other hand electron releasing groups such as -NH2,-OH,-OR,-R etc. deactivate the aryl halides towards nucleophilic substitution. Thus we see that these groups show just the opposite influence on the electrophilic aromatic substitution,i.e., electron withdrawing groups show deactivating influence and electron releasing groups produce activating influence.

BIMOLECULAR DISPLACEMENT MECHANISM FOR NUCLEOPHILIC AROMATIC SUBSTITUTION

According to this mechanism the reaction is believed to proceed in two steps. The first step involves the attack of the nucleophile on the carbon carrying the halogen. This results in the formation of carbanion which is stabilised by resonance.

During the formation of intermediate carbanion there is a change of hybridisation of the carbon involved from sp2 to sp3. As a result the aromatic charecter of the benzene ring is destroyed. Consequently, this step is slow and hence is the rate determining step of the reaction.

In the second step, the carbon loses the halide ion to form the product in which aromaticity is regenerated. General bimolecular displacement mechanism is represented as :

As two molecular species participate in the slow and rate detertmining step, it is a bimolecular reaction.

It may be mentioned that the above bimolecular mechanism is applicable mainly to activated aryl halides containing electron withdrawing groups such as -NO2,-C=-N,-COOH,etc.at the ortho and para positions.

Evidence in support of this mechanism. The rate determining step in bimolecular displacement reactions involves the formation of carbanion in which there is no cleavage of carbon-halogen bond. In other words, the rate of the reaction is independent of the strength of carbon-halogen bond.This has actually been verified by the absence of element effect. For example,there is only a little difference in the reactivity of aryl halides, bromides,chlorides and fluorides in nucleophilic aromatic substitution reactions. This lends supports to the proposed mechanism.

LOW REACTIVITY OF ARYL AND VINYL HALIDES

(i) Aryl halides are less reactive than alkyl halides towards nucleophilic substitution reactions because of the resonance stabilization of aryl halide.

Since C-X double bond is not easily broken, SN reaction does not take place easily.

(ii) vinyl halides are also less reactive than alkyl halides because of a similar reason.

Double bond between C and X and presence of a positive charge on X prevent the SN reaction from taking place.

Vinyl chloride is an aliphatic halide but it resembles chlorobenzene in its properties. Explain.

Solution. Because of low reactivity or both towards nucleophilic substitution reactions, they resemble each other.

In both compounds, because of resonance phenomenone, a double bond is created between carbon and halogen and a positive charge is created on the halogen and a negative charge is created on the rest of the molecule. These two factors go against the nucleophilic substitution reaction. For the resonating structures of aryl and vinyl halide, sec. 7.35.

describe with the help of molecular orbital structure that an aryl radical is more stable as compared to primary radical.

Or

How do you account for unusual high stability of aryl free radical?

Solution. The orbital structure of allyl radical is illustrated as under.

The delocalisation of pi electron could lends stability to the aryl radical. It is belived that p orbitals of the

doubly bonded carbon atoms and the single electron of the third carbon are in the same plane and overlap. This type of delocalisation is not possible in alkyl radicals.

Bromobenzene does not give precipitate even on prolonged heating with alcoholic silvernitrate. Explain.

Solution.

Aromatic halides, does not give nucleophilic substitution reactions easily.

As a result,bromine is not displaced as bromide ion in the solution, consequently a precipitate is not obtained.

An alcoholic solution of butyl bromide when heated with silver nitrate gives a white precipitate but pentyl bromide does not give precipitate of silver bromide even on prolonged heating with AgNO3. Explain why.

Solution. Butyl bromide and Pentyl bromide are expected to give butyl and pentyl alcohol respectively on treatement with alcoholic silver nitrate by SN2 mechanism. The bromide ions produced in the reaction react with AgNO3 to give a precipitate of silver bromide.

The success of an SN2 reaction depends upon the ease with which a nucleophile, can attach itself to the halogen carrying carbon.

In the case of *n*-butyl chloride, the groups attached to this carbon are H, H and C3H7.

In case of pentyl chloride, the groups attached are H, H and C4H9. Thus there is greater crowding and smaller change of SN2 reaction to take place in the case of pentyl chloride. Therefore, no precipitate is obtained.

Example 11. **whereas Chlorobenzene reacts with sodamide in the presence of liquid ammonia, 2-bromo-3-methyl anisole fails to react. Explain.**

Solution.Chlorobenzene reacts with sodamide dissolved in liquid ammonia by benzyne mechanism to form aniline. In 2-bromo-3-methyl anisole both the ortho positions adjacent to the bromine atom are occupied in the ring. As a result, the ortho hydrogen atoms are not available to be eliminated.

COMPARISION OF REACTIVITY OF ALLYL, VINYL, ALKYL, ARYL AND BENZYL HALIDES

Reactivity's of allyl, vinyl and alkyl halides have already been compared under alkyl halides which follow the order.

Allyl halide > Alkyl halide > Vinyl halide

Benzyl halide is most reactive because the benzyl carbocation that is obtained has intermediate can stabilize itself to the maximum because of a number of resonating structures (I-V).

Aryl halide is the least reactive because the molecule as a whole stabilizes by means of a number of resonating structures as opposed to only two structures in vinyl chloride.

The double bond between chlorine and carbon in aryl chloride is thus, most diffecult to break in aryl halide. The order of reactivity of halides is therefore as:

Benzyl > Allyl > Alkyl > Vinyl > Aryl.

POSSIBLE QUESTIONS

Part-B (Two Marks Questions)

1. Aryl halides are less reactive than alkyl halides. Explain

2. Boiling points of alkyl halides are higher as compared to those of corresponding alkanes, why?

3. Define Nucleophilic substitution reaction. Give an example.

4. Give reasons and arrange the following in decreasing order of activity.
   T-Butyl alcohol, Ethyl alcohol, Methyl alcohol and Isopropyl alcohol

5. Draw the structure of isobutyl chloride and secondary butyl chloride and write their IUPAC name.

Part-C (8 Marks Questions)

1. Discuss the mechanism, stereochemistry and kinetics of S_N1 reactions.

2. Starting from ethyl bromide how will you prepare the following?
   (i) Ethyl alcohol ii) Diethyl ether iii) Ethyl acetate

3. Discuss the mechanism, stereochemistry and kinetics of S_N2 reactions.

4. Discuss the preparation of aryl halides from diazonium salts. Write the reaction name also.

5. Describe the benzyne mechanism for Nucleophilic aromatic substitution.

6. Write notes on i) Fifttig reaction ii) Ullmann reaction iii) Wurtz reaction

7. Why Chlorobenzene shows lower reactivity than alkyl halides towards Nucleophilic substitutions.

8. Explain the electrophilic aromatic substitution reactions of chlorobenzene.

9. Describe SNAr mechanism.

10. What are alkyl halides? How will you classified? Write any two preparation and properties of alkyl halides.

11. What are nucleophilic substitution reactions? Compare the important features of S_N1 and S_N2 reactions.

OBJECTIVE QUESTIONS

S. no	Questions	Option A	Option B	Option C	Option D	Answer
1.	The Hydrogen atom of an alkane are replaced by the halogen are termed as	Alkyl halides	Alkenyl halides	Alkynyl halides	Halo alkynes	Alkyl halides
2.	The Hydrogen atom of an alkene are replaced by the halogen are termed as	Alkyl halides	Alkenyl halides	Alkynyl halides	Halo alkynes	Alkenyl halides
3.	The Hydrogen atom of an alkyne are replaced by the halogen are termed as	Alkyl halides	Halo alkanes	Alkynyl halides	Alkenyl halides	Alkynyl halides
4.	Write the structural formula for dichloromethane	CH_3Cl	$CHCl_3$	CH_2Cl_2	CH_3CH_2Cl	CH_2Cl_2
5.	Choose the write structural formula for 2-Chloropentane	CH_3-CH_2- CH_2-CH (Cl)-CH_3	CH_3-CH(Cl)- CH_2- CH_2-CH_3	CH_3-CH_2- CH (Cl)-CH_3	CH_3-CH(Cl)- CH_2- CH_3	CH_3-CH_2- CH_2-CH (Cl)-CH_3
6.	Alkyl halides are those compounds in which the halogen is linked to a carbon which is further linked to one carbon is known as	Primary alkyl halide	Secondary alkyl halide	Mono halogen compounds	Tertiary alkyl halide	Primary alkyl halide
7.	Alkyl halides are those compounds in which the halogen is linked to a carbon which is further linked to two carbon atoms are known as	Primary alkyl halide	Secondary alkyl halide	Dihalogen compounds	Tertiary alkyl halide	Secondary alkyl halide
8.	Alkyl halides are those compounds in which the halogen is linked to a carbon which is further linked to three carbon atoms are known as	Primary alkyl halide	Secondary alkyl halide	Tertiary alkyl halide	Trihalogen compounds	Tertiary alkyl halide
9.	Which of the following is an example of	Dichloromethane	1,2-Dichloro ethane	Ethylidene chloride	Allyl chloride	1,2-Dichloro ethane

	vicinal - dihalide?					
10.	Ehthylidene chloride is a / an	Vic- Dihalide	Gem- Dihalide	Allylic halide	Vinylic halide	Gem- Dihalide
11.	Chlorobenzene is formed by the reaction of chlorine with benzene in the Presence of $AlCl_3$ which of the following species attacks the benzene ring in this reaction?	Cl^-	Cl^+	$AlCl_3$	$[AlCl_4]^-$	Cl^+
12.	A primary alkyl halide would prefer to undergo	SN^1 Reaction	SN^2 Reaction	Elimination reaction	Racemisation	SN^2 Reaction
13.	Which of the following alkyl halides will undergo SN^1 reaction most readily	$(CH_3)_3$ C- F	$(CH_3)_3$ C- Cl	$(CH_3)_3$ C- Br	$(CH_3)_3$ C- I	$(CH_3)_3$ C- I
14.	Which is the correct IUPAC name for $CH_{3-}CH(C_2H_5)_-\ CH_{2-}$ Br	1- Bromo -2-ethyl propane	1- Bromo -2-ethyl -2-methyl ethane	1- Bromo -2- methyl Butane	2- Methyl -1-Bromo butane	1- Bromo -2- methyl Butane
15.	What should be the correct IUPAC name for Diethyl bromo ethane?	1-Bromo1,1-Diethoxyethane	3-Bromo pentane	1-Bromo-1-ethyl Propane	1- Bromo pentane	3-Bromo pentane
16.	Which of the following compounds are gem-Dihalides?	Ethylidene Chloride	Ethylenedichloride	Methylene Chloride	Benzyl chloride	Methylene Chloride
17.	Alkyl halides are prepared from alcohols by treating with	HCl + $ZnCl_2$	Red P	KI	H_2SO_4	HCl + $ZnCl_2$
18.	For a given alkyl group, the boiling point increases in the order of	RI > RBr > RCl > RF	RI > RCl > RF > RBr	RF > RCl > RBr > RI	RF > RI > RBr > RCl	RI > RBr > RCl > RF
19.	The reaction involving the replacement of an atom (or) a group of atoms by a suitable Nucleophile is called	Nucleophilic addition	Elimination	Nucleophilic substitution	Addition	Nucleophilic substitution
20.	The carbon-halogen bond in alkyl halides	Electropositivity	Electronegativity	Electron affinity	Electron with-	Electronegativity

	is polar due to gfreater				drawing nature	
21.	Among the following which is known as Grignard reagent?	Organo magnesium halide	Organo sodium halide	Organo lead halide	Organo potassium halide	Organo magnesium halide
22.	Alkyl halides undergo	Electrophilic substitution reactions	Electrophilic addition reactions	Nucleophilic substitution reactions	Nucleophilic addition reactions	Nucleophilic substitution reactions
23.	1-Bromo butane reacts with alcoholic KOH to mainly give	1-Butene	2- Butene	1- Butanol	2- Butanol	2- Butene
24.	2-Bromo butane reacts with alcoholic KOH to mainly give	1-Butene	2- Butene	1- Butanol	2- Butanol	2- Butene
25.	n-Propyl iodide reacts with sodium ethoxide to give	CH_3CH_2 O CH_2 CH_3	CH_3CH_2 O CH_2 CH_2CH_3	CH_3CH_2 O CH_3	CH_3 O CH_2 CH_2CH_3	CH_3CH_2 O CH_2 CH_2CH_3
26.	Isopropyl bromide reacts with alc.KOH to give	Propene	Isopropyl alcohol	Propane	n-Propyl alcohol	Propene
27.	SN^1 Reaction Mechanism is a ---- step mechanism	Two	Zero	One	Three	One
28.	SN^2 Reaction Mechanism is a ------------- step mechanism	One	Three	Two	Four	Two
29.	Which reagent is a goood Nucleophile	NH_3	HBr	Br_2	BH_3	NH_3
30.	Write the mechanism involved in the reaction of CH_3Br and NaOH is	SN^1	SN^2	E_1	E_2	SN^2
31.	Toluene reacts with a halogen in the presence of Iron (III) Chloride giving O and P-halo compounds. The reaction is	Electrophilic Elimination reaction	Electrophilic substitution reaction	Free radical addition reaction	Nucleophilic substitution reaction	Electrophilic substitution reaction

32.	Which of the following compound can be classified as aryl halide	P- Cl C_6H_4 CH_2CH $(CH_3)_2$	P- CH_3 CH Cl (C_6H_4) CH_2CH_3	O- Br C- C_6H_4CH (CH_3) CH_2CH_3	C_6H_6	P- Cl C_6H_4 CH_2CH $(CH_3)_2$
33.	The order of relative creativities of alkyl halides in SN^2 reactions are	methyl halides > Primary halides > Sec. halides > Tertiary halides	Primary halides > Sec. halides > Tertiary halides > methyl halides	Tertiary halides > Sec. halides > Primary halides > methyl halides	methyl halides < Primary halides < Sec. halides < Tertiary halides	methyl halides > Primary halides > Sec. halides > Tertiary halides
34.	Hydrolysis of Tertiary butyl bromide undergo	SN^1 Reaction mechanism	SN^2 Reaction mechanism	SN^i reaction mechanism	E^2 reaction mechanism	SN^1 Reaction mechanism
35.	Nucleophilic aromatic substitution is understood by	SN^2	SN^1	Benzyne	E_2	Benzyne
36.	Benzene diazonium chloride on reaction with Cu_2Cl_2 / HCl gives	Benzoyl chloride	Benzene	Phenol	Chloro benzene	Chloro benzene
37.	Benzyne mechanism is also called	SN^2 Mechanism	Addition-Elimination mechanism	Aromatic Nucleophilic substitution	SNAr Mechanism	Addition-Elimination mechanism
38.	The relative order of stability of carbocations in SN1 reactions are	Benzyl, Allyl > Tertiary > secondary >Primary > methyl carbo cations	Methyl carbo cations > primary > secondary > Tertiary >Benzyl, Allyl	Benzyl, Allyl < Tertiary < secondary < Primary < methyl carbo cations	Methyl carbo cations < primary < secondary < Tertiary <Benzyl, Allyl	Benzyl, Allyl > Tertiary > secondary >Primary > methyl carbo cations
39.	The order of nucleophilic strength of halide ions are	$I^- > Br^- > Cl^- > F^-$	$I^- < Br^- < Cl^- < F^-$	$F^- > Cl^- > Br^- > I^-$	$F^- < Cl^- < Br^- < I^-$	$I^- > Br^- > Cl^- > F^-$
40.	Write the correct order of rate of elimination reaction for a given alkyl group	RI > RBr > RCl > RF	RI< RBr < RCl< RF	RF > RCl > RBr > RI	RF < RCl < RBr < RI	RI > RBr > RCl > RF
41.	Aryl halides are less reactive towards nucleophilic substitution as compared to	Inductive effect	Resonance	Tautomerism	Steroisomerism	Resonance

	alkyl halides due to		stabilization			stabilization
42.	Benzene diazonium chloride on reaction with Cu powder / HCl gives chloro benzene is known as	Sandmeyer's reaction	Wurtz-Fittig reaction	Gattermann reaction	Ullmann reaction	Gattermann reaction
43.	Chlorobenzene is treated with etheral solution of methyl chloride in the presence of sodium, gives	Phenol	Toluene	Aniline	ethyl benzene	Toluene
44.	Diaryls are formed when only aryl halide treated with sodium . This reaction is called	Wurtz reaction	Wurtz-Fittig reaction	Fittig reaction	Gattermann reaction	Fittig reaction
45.	Which of the following is used to reduce chlorobenzene to benzene	Ni-Al alloy in alkali	Zn-Al alloy in alkali	Na-Mg alloly in alkali	Na-Al alloy in alkali	Ni-Al alloy in alkali
46.	Among the following which is the electron with drawing group	NH2	OR	COOH	OH	COOH
47.	THF stands for	Tri hydro furan	Tetra hydroxy furan	Tetra hydro furan	Tri hydro flurine	Tetra hydro furan
48.	Chlorobenzene reacts with $NaNH_2$ / liq. NH_3 to give	Anisole	Aniline	O-Chloro anoline	P-Chloro aniline	Aniline
49.	The order of reactivities of allyl, vinyl and alkyl halides are	Allyl halide < Alkyl halide < Vinyl halide	Vinyl halide < Alkyl halide < Allyl halide	Vinyl halide > Alkyl halide > Allyl halide	Allyl halide > Alkyl halide > Vinyl halide	Allyl halide > Alkyl halide > Vinyl halide
50.	The order of reactivities of halides are	Benzyl < allyl< Alkyl< Vinyl< Aryl	Benzyl > allyl > Alkyl > Vinyl > Aryl	Aryl < Vinyl < Alkyl < Allyl < Benzyl	Aryl > Vinyl > Alkyl > Allyl > Benzyl	Benzyl > allyl > Alkyl > Vinyl > Aryl
51.	Nitrating mixture is	Con. HNO_3 + Con. HCl	Con. HCl + Con.H_2SO_4	Con. HNO_3 + Con.H_2SO_4	Con. HNO_3 + CH_3COOH	Con. HNO_3 + Con.H_2SO_4

52.	Which aryl halide gives O and P-Chloro benzene when heated with	Con. HNO_3 + Con. HCl	Con. HCl + Con.H_2SO_4	Con. HNO_3 + Con.H_2SO_4	Con. HNO_3 + CH_3COOH	Con. HNO_3 + Con. HCl
53.	The reaction of chlorobenzene with CH_3Cl / Anhy. $AlCl_3$ gives O and P-Chloro toluene. This reaction is known as	Direct halogenation	reduction	Fridel-Crafts reaction	Nucleophilioc substitution	Fridel-Crafts reaction
54.	Formation of Diphenyl from the reaction of iodobenzene with Cu powder is	Gattermann reaction	Ullmann reaction	Sandmeyer reaction	Fittig reaction	Ullmann reaction
55.	Among the following which is known as Fridel-Crafts reagent	Ni-Al / NaOH	$FeCl_3$	Na-Hg / Alcohol	Anhy.$AlCl_3$	Anhy.$AlCl_3$
56.	When 2,4-Dinitro chloro benzene heated with ammonia at 443 K , gives	2,4-Dinitro Phenol	2,4,6-Trinitro Phenol	2,4-Dinitro aniline	2,4,6-Tri nitro aniline	2,4-Dinitro aniline
57.	When bromo benzene treated with Mg in dry ether form	Diphenyl	Benzene	Phenyl Magnesium bromide	Benzoyl chloride	Phenyl Magnesium bromide
58.	Phenyl magnesium chloride is formed by the reaction of chlorobenzene with Mg in presence of	Dry ether	Dry THF	Ni-Al / NaOH	$FeCl_3$	Dry THF
59.	When chlorobenzene heated with aq.NaOH at 573 k and 200 atm. Pressure forms	Aniline	Phenol	Toluene	Diphenyl	Phenol
60.	Which is used to prepare chlorobenzene from phenol	PCl_5	PCl_3	$AlCl_3$	CH_3Cl	PCl_5

Syllabus

Alcohols: preparation, properties and relative reactivity of 1°, 2°, 3° alcohols, Bouvaelt- Blanc Reduction; Oxidation of diols by periodic acid and lead tetraacetate, Pinacol-Pinacolone rearrangement.

Phenols: Preparation and properties; Acidity and factors affecting it, Ring substitution reactions, Reimer–Tiemann and Kolbe's–Schmidt Reactions, Fries and Claisen rearrangements with mechanism.

After reading this lesson, you should be able to

- Classify alcohols as primary, secondary or tertiary;
- Name simple alcohols according to IUPAC system of nomenclature;
- List general methods of preparation of alcohols;
- Discuss the properties of alcohols in the light of their structure;
- Explain various reactions exhibited by alcohols to give other categories of organic compounds;
- Give the names of common phenolic compounds;
- Describe the laboratory and industrial methods of preparation of phenols;
- Explain the greater acidity of phenols as compared to alcohols;
- Discuss the reactions of phenols;

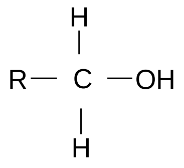
Alcohols

Alcohols are organic compounds that have one or more hydroxy (-OH) groups bonded tothe *carbon atoms in aliphatic compounds*. They occur widely in nature and have manyindustrial and pharmaceutical applications. For example, methanol and ethanol are twoindustrially important alcohols.

CH_3-OH	CH_3CH_2-OH
Methanol	**Ethanol**
(Methyl alcohol)	**(Ethyl alcohol)**

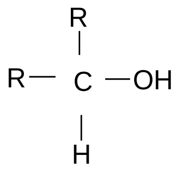
Classification of Alcohols

In alcohols, -OR group is attached to Sp3 hybridised carbon. These alcohols are usually classified as primary, secondary and tertiary alcohols.



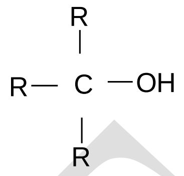
$R-\overset{H}{\underset{H}{C}}-OH$

Primary(1^0)



$R-\overset{R}{\underset{H}{C}}-OH$

Secondary(2^0)



$R-\overset{R}{\underset{R}{C}}-OH$

ttertiary(3^0)

Alcohols may be

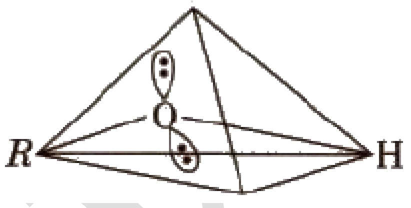
(i) monohydric-containing one – OR group,

(ii) dihydric-containing two – OR groups and

(iii) polyhydric-containing three or more -OR groups.

Structure of Alcohols

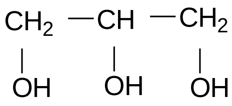
The oxygen atom of alcohols is Sphybridised and they have tetrahedral position of hybrid atomic orbitals .



The value of LROH bond angle depends upon the R group. For methyl alcohol, it is (O – H) 108.9° due to repulsion of lone pairs.

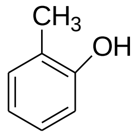
Nomenclature of Alcohols

In IUPAC, system, alcohol or alkanols are named by replacing the last word 'e' of the corresponding alkane by 'ol'. e.g.,

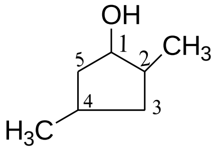


$CH_2(OH)-CH(OH)-CH_2(OH)$

propan-1,2,3-triol



2-Methyi phenol

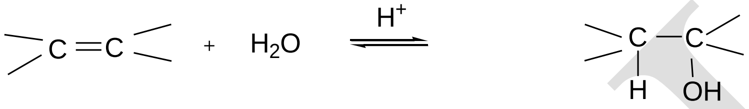


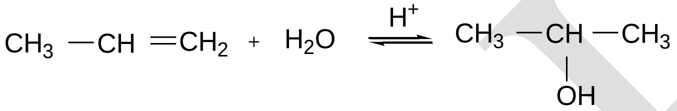
2,4-dimethylcyclopentanol

Preparation of Alcohols

(i) From alkenes

(a) By acid catalysed hydration in accordance with Markownikoff's rule.



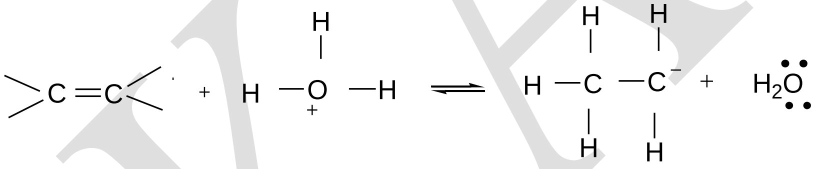


$CH_3-CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-CH(OH)-CH_3$

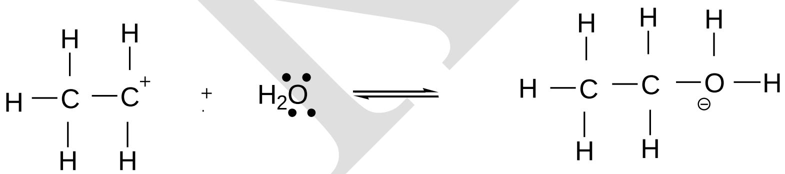
Mechanism

Step I Protonation of alkene by attack of H_3O^+

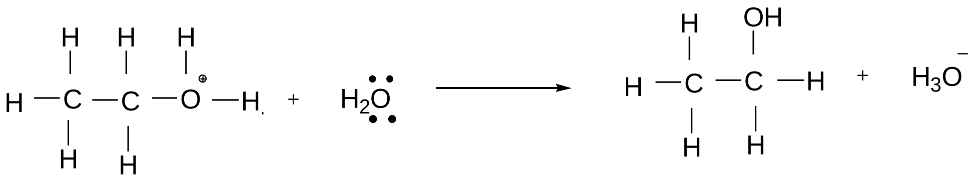
$$H_2O + H^+ \longrightarrow H_3O^+$$



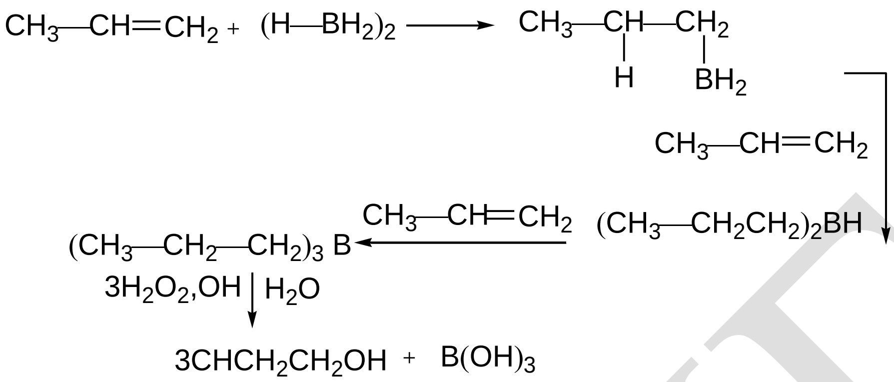
Step II Nucleophilic attack



Step III Deprotonation to form an alcohol



(b) By hydroboration-oxidation



$$CH_3-CH=CH_2 + (H-BH_2)_2 \longrightarrow CH_3-\underset{H}{CH}-\underset{BH_2}{CH_2}$$

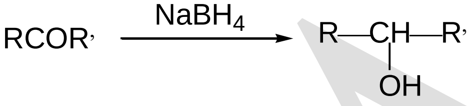
$$\xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2CH_2)_2BH \xrightarrow{CH_3-CH=CH_2} (CH_3-CH_2-CH_2)_3\,B$$

$$(CH_3-CH_2-CH_2)_3\,B \xrightarrow{3H_2O_2, OH \mid H_2O} 3CHCH_2CH_2OH + B(OH)_3$$

(ii) From carbonyl compounds

(a) By reduction of aldehydes and ketones

$$R-CHO + H_2 \xrightarrow{Pd} RCH_2-OH$$



$$RCOR' \xrightarrow{NaBH_4} R-\underset{OH}{CH}-R'$$

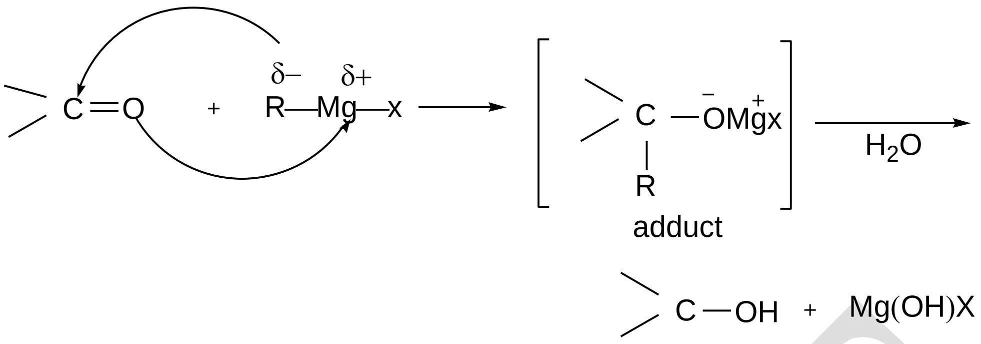
Aldehydes yield primary alcohols whereas ketones give secondary alcohols, when subjected to reduction.

(b) By reduction of carboxylic acids and ester

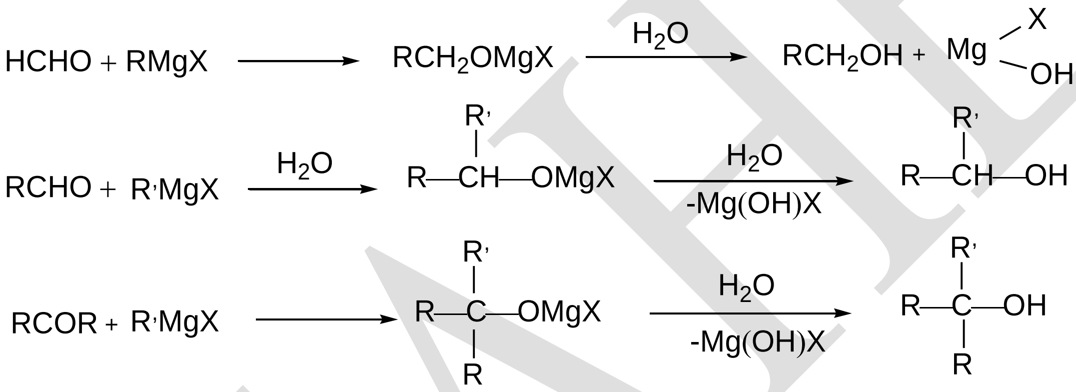
$$RCOOH \xrightarrow[(ii)\ H_2O]{(I)\ LiAlH_4} RCH_2OH$$

$$RCOOR' \xrightarrow[Catalyst]{H_2O} RCH_2OH + R'OH$$

Reduction of aldehyde, ketones and esters with No Alcohol is called Bouveault-blancreduction.



The reaction produces a primary alcohol with methanol, a secondary alcohol with aldehydes (except methanal) and tertiary alcohol with ketones



$$HCHO + RMgX \longrightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg\genfrac{}{}{0pt}{}{X}{OH}$$

$$RCHO + R'MgX \xrightarrow{H_2O} R{-}\overset{R'}{\overset{|}{C}H}{-}OMgX \xrightarrow[-Mg(OH)X]{H_2O} R{-}\overset{R'}{\overset{|}{C}H}{-}OH$$

$$RCOR + R'MgX \longrightarrow R{-}\underset{\underset{R}{|}}{\overset{R'}{\overset{|}{C}}}{-}OMgX \xrightarrow[-Mg(OH)X]{H_2O} R{-}\underset{\underset{R}{|}}{\overset{R'}{\overset{|}{C}}}{-}OH$$

(iv) Hydrolysis of alkyl halides

R – X + KOH(aq) → ROH + KX

To avoid dehydrohalogenation of RX, mild alkalies like moist

Ease of hydrolysis of alkyl halides RI > R – Br > RCI > and t > s > p alkyl halides.

(v) Hydrolysis of ethers

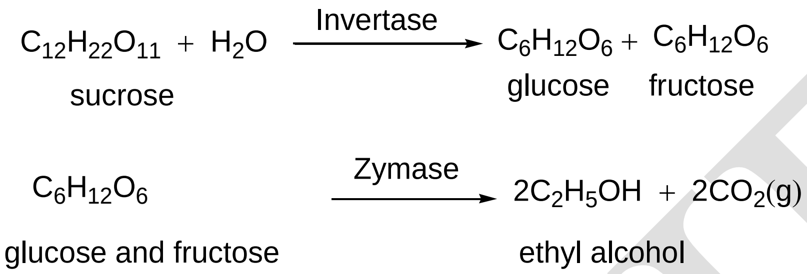
$$R{-}\ddot{O}{-}R + H_2O \xrightarrow{H_2SO_4} 2ROH$$

(vi) From primary amines by treatment with nitrous acid.

$$RNH_2 + HONO \xrightarrow{(NaNO_2 + HCl)} ROH + N_2 + H_2O$$

Methylamine does not give methyl alcohol when treated with HNO2 . It gives CH3OCH3and CH3ONO.

(vii) By alcoholic fermentation



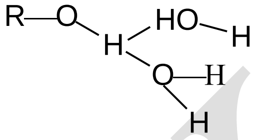
$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{glucose and fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2CO_2(g)$$

Physical Properties of Alcohols

1. Lower alcohols are colorless liquids, members from C – C are oily liquids and higher members are waxy solids.

2. The hydroxyl groups in alcohols can form H-bonds with water, so alcohols are miscible with water. The solubility decreases with increase in molecular mass



3. Boiling points of alkanes are higher than expected because of the presence of intermolecular hydrogen bonding in the polar molecules.

[The boiling point decreases in the order 1° > 2° > 3° as the van der Waals' forces of attraction decreases]

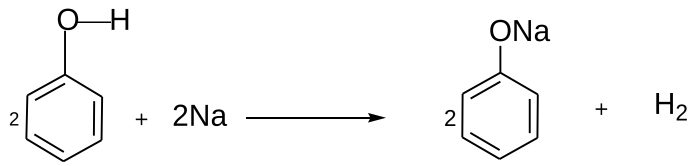
Chemical Reactions of Alcohols

(i) Reactions involving cleavage of O – H Bond

(a) Acidity of alcohols and phenols

$$2R—O—H + 2Na \longrightarrow 2R—O—Na + H_2$$

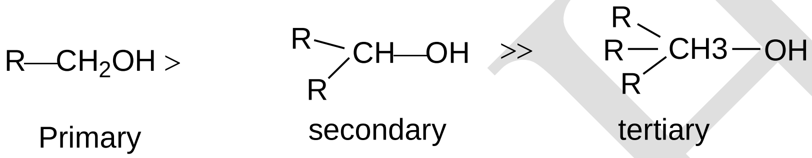
Sodium alkoxide



Sodium phenoxide

Alcohols are weaker acids than water due to +1 group present in alcohols, which decreases the polarity of -O-H bond.

Acid strength of alcohols



Electron releasing group increases electron density on oxygen to decrease the polarity of – OH bond.

Order of acidity is

RCOOH >H2CO3 > C6H5OH > H2O > R – OH.

(b) Esterification

$$Ar/R—O—H + R'COOH \xrightleftharpoons{H^+} Ar/R—OCOR' + H_2O$$

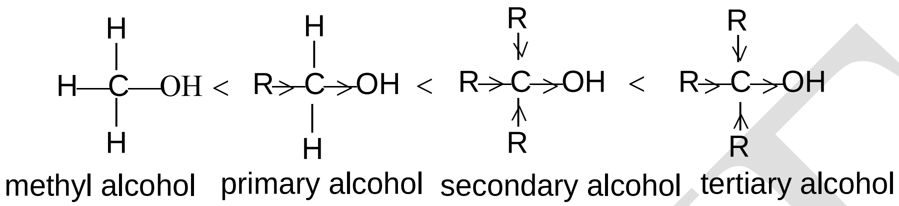
$$Ar/R—OH + (R'CO)_2O \xrightleftharpoons{H^+} A/R—OCOR' + R'COOH$$

$$R/Ar—OH + R'COCl \xrightarrow[\text{Pyridine}]{} R/Ar—OCOR' + HCl$$

The reaction with R’COOH and (R’ CO) O is reversible, so cone, H SO is used to removewater.

The reaction with R’ COCI is carried out in the presence of pyridine so as to neutralize HCI which is formed during the reaction.

(ii) Reaction involving cleavage of C-O bond in alcohols In these reactions, the reactivity order of different alcohols:



Alkyl group due to +1 effect increases the electron density on the carbon and oxygen atom of C-OH bond. As a result, the bond cleavage becomes easy. Greater the number of alkyl groups present, more will be the reactivity of alcohol. Thus, the relative order of reactivity of the alcohols is justified.

(a) Reaction with halogen acids Alcohols can be converted into haloalkanes by the action of halogen acids.

R – OH + HX (HCI, HBr, HI) → R-X +H2O

For a given alcohol order of reactivity of HX is
H-I > H-Br > H-Cl

For a given halogen acid order of reactivity of alcohols
Tertiary > Secondary > Primary

Lucas test

Primary alcohols	**Secondary alcohols**	**Tertiary alcohols**
$RCH_2OH \xrightarrow[\text{Anhy ZnO2}]{\text{Conc HCl}}$ No reaction and hence, no white cloudiness or trubidity at room temperature	$R_2CH—OH \xrightarrow[\text{Anhy ZnCl2}]{\text{Conc HCl}} R_2CHCl$ White cloudiness or turbidity appears with in about 5 minutes.	$R_3—OH \xrightarrow[\text{Anhy ZnCl2}]{\text{Conc HCl}} R_3CCl$ White cloudiness or trubidity appears immediately

(b) Reaction with phosphorus halides

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

$$3ROH + PBr_3 \xrightarrow{P/Br_2} 3RBr + H_3PO_3$$

$$3ROH + PI_3 \xrightarrow{P/I_2} 3RI + H_3PO_3$$

(c) Reaction with thionyl chloride

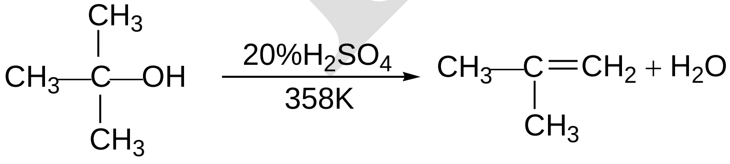
$$ROH + SOCl_2 \longrightarrow RCl + SO_2\uparrow + HCl\uparrow$$

d) Dehydration of alcohols It requires acid catalyst and the reaction proceeds via intermediate carbonium ion. Acidic catalyst converts hydroxyl group into a good leaving group.

Since, the rate determining step is the formation of carbocation, the ease of dehydration is

$$3^0 > 2^0 > 1^0$$

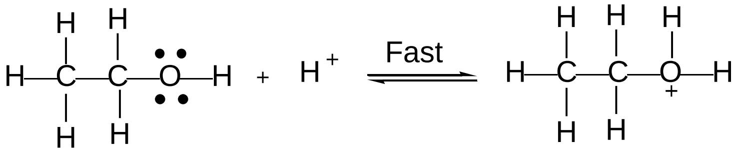
$$C_2H_5OH \xrightarrow[443K]{H_2SO_4} CH_2{=}CH_2 + H_2O$$



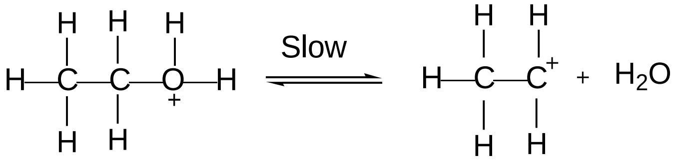
$$(CH_3)_3C—OH \xrightarrow[358K]{20\%H_2SO_4} CH_3—\underset{CH_3}{C}{=}CH_2 + H_2O$$

Mechanism

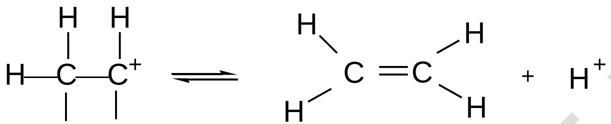
Step I Formation of protonated alcohol



Step II Formation of carbocation



Step III Formation of ethene by elimination of a proton



In dehydration reaction, highly substituted alkene is the major product and if the major product is capable of showing cis-trans isomerism, trans-product is the major product.(Saytzeff's rule).

(iii) Oxidation reactions Oxidising reagents used for the oxidation of alcohols are neutral, acidic or alkaline $KMnO_4$ and acidified $K_2C_2rO_7$.

Primary alcohols	**Secondary alcohols**	tertiary alcohols
CH_3CH_2OH $\downarrow$ [O] CH_3CHO $\downarrow$ [O] CH_3COOH	$CH_3CHOH{-}CH_3$ $\downarrow$ [O] CH_3COCH_3 $\downarrow$ [O] $CH_3COOH + CO_2 + H_2O$	$(CH_3)_3C{-}OH$ $\downarrow$ [O] $CH_3COOH_3 + CO_2 + H_2O$ $\downarrow$ [O] $CH_3COOH + CO_2 + H_2O$

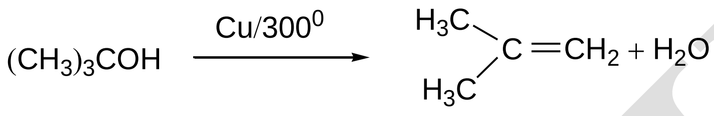
A common reagent that selectively oxidises a primary alcohol to an aldehyde (and no further) is pyridiniumchlorochromate (pCC).

$$CH_3CH{=}CH{-}CH_2OH \xrightarrow{PCC} CH_3CH{=}CH{-}CHO$$

(iv) Dehydrogenation

$$\underset{1^0\ \text{alcohol}}{RCH_2OH} \xrightarrow{Cu/300^0C} \underset{\text{aldehyde}}{RCHO} + H_2\uparrow$$

$$\underset{2^0\ \text{alcohol}}{RCHOH{-}R} \xrightarrow{Cu/300^0\ C} \underset{\text{Ketone}}{R.CO.R} + H_2\uparrow$$



3^0 alcohol

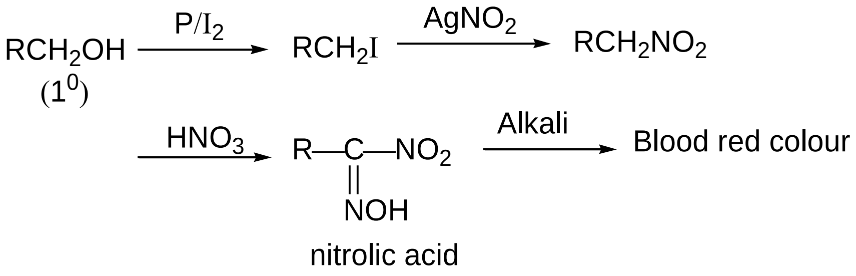
alkene (iso- butylene)

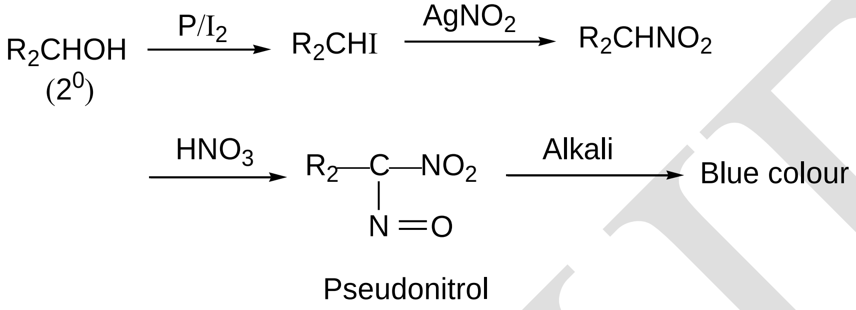
Distinction among 1°,2° and 3° Alcohols

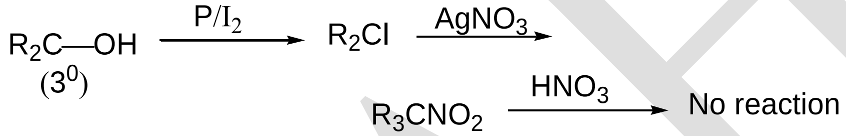
1°, 2° and 3° alcohols are distinguished by Lucas test, oxidation and reduced copper.

Victor Meyer's test is also used to distinguish them.

In this test, primary (1°) alcohols give red colour, secondary (2°) alcohols give blue colour and tertiary (3°) alcohols give no colouration.







Terms Related to Alcohols

(a) **Rectified spirit**It contains 95% ethyl alcohol and 45% water. It is an azeotrope (constant boiling mixture) and boils at 74° C.

(b) **Absolute alcohol**Alcohol containing no water, i.e; 100% C H OH is known asabsolute alcohol. It is prepared as follows.

(i) Quick lime process

(ii) Azeotropic method

(c) **Methylated spirit**The rectified spirit rendered poisonous by addition of 4-5% methyl alcohol, traces of pyridine and some copper sulphate and is known as methylated spirit or denatured alcohol.

(d) **Power alcohol** Alcohol mixed with petrol or fuel and used In internal combustion engines Is known as power alcohol.

(e) **Wood spirit** Methyl alcohol (CH3OH) is also called wood spirit. It is obtained by destructive distillation of wood. Pyroligneous add, the product of destructive distillation of wood, contains acetic acid (10%), methyl alcohol (25%) and acetone (05%). Drinking of methanol causes blindness.

(f) Grain alcohol Ethyl alcohol C2H5OH is also called grain alcohol. It is used in the preparation of various beverages containing different percentages.

Dihydric Alcohols

These are generally called glycols because of their sweet taste. Ethylene glycol (CH2OH–CH2OH) is the first and most important member of dihydric alcohol series.

Methods of Preparation

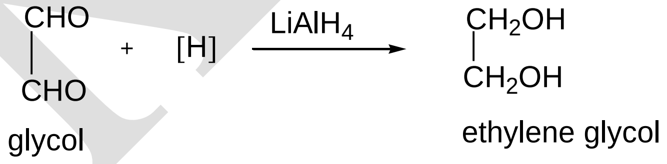
(i) From ethylene

$$CH_2{=}CH_2 + [O] + H_2O \xrightarrow{\text{Baeyer' reagent}} CH_2OH{-}CH_2OH$$

(1% alkaline $KMnO_4$ is called Baeyer' reagent)

$$CH_2{=}CH_2 \xrightarrow[\text{Na}_2\text{SO}_3\text{ / H}_2\text{O}]{\text{OsO}_4\text{ / pyridine}} CH_2OH{-}CH_2OH$$

(ii) By reduction of glyoxal



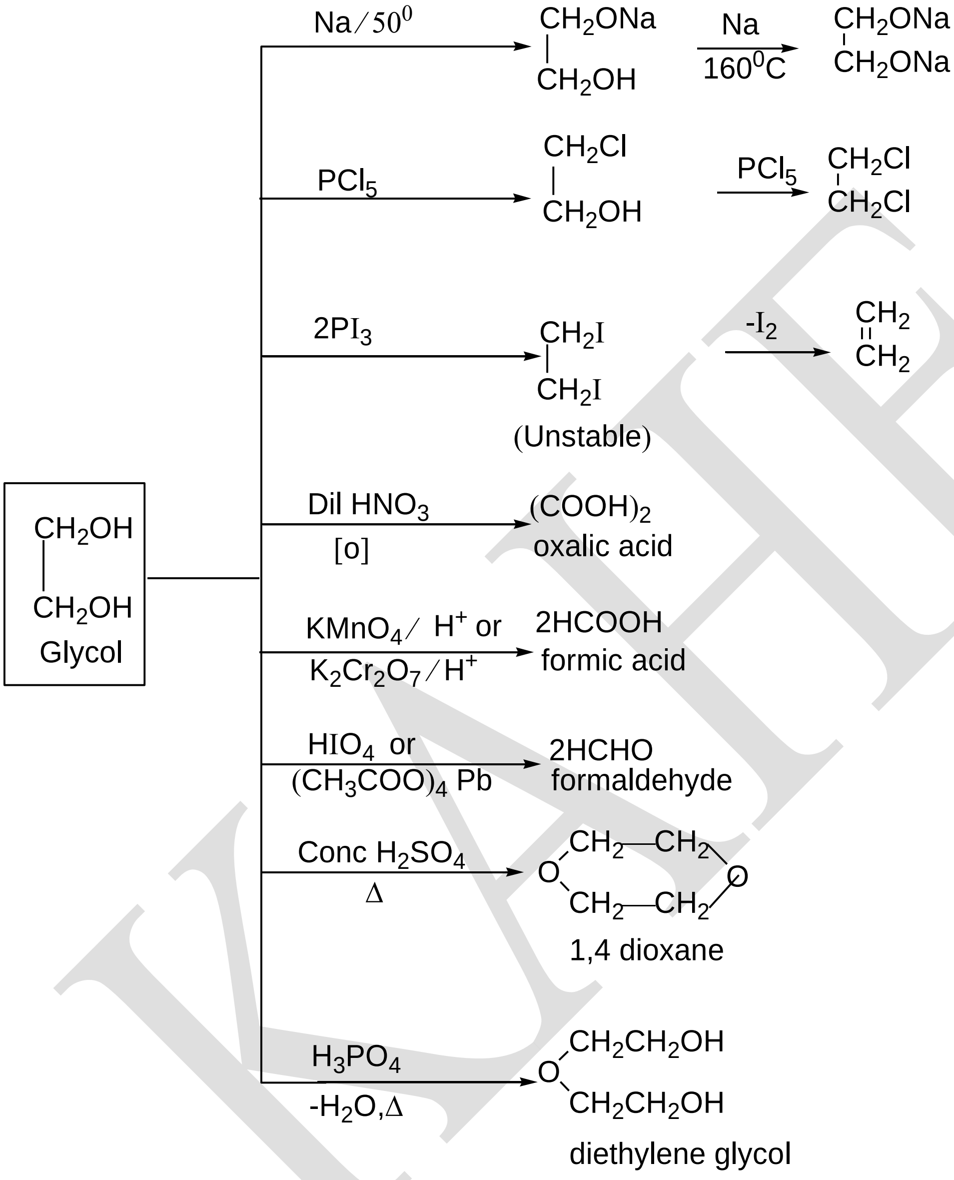
$$\begin{array}{c}CHO\\ |\\ CHO\end{array} + [H] \xrightarrow{LiAlH_4} \begin{array}{c}CH_2OH\\ |\\ CH_2OH\end{array}$$

Physical Properties

1. It is a colourless, syrupy liquid with sweet taste.
2. Because of its tendency of formation of H-bonds, it is miscible with H2O and ethanol but not with ether.

Chemical Properties

It gives all the general reactions of -OH group.



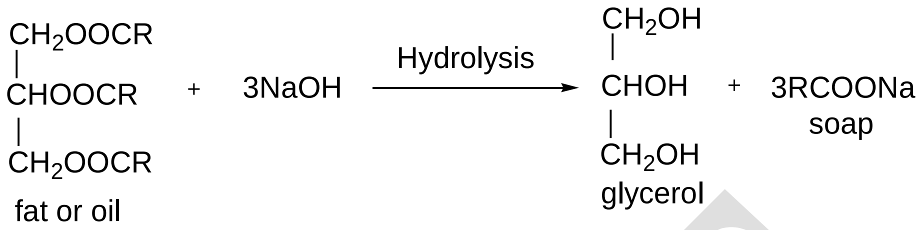
The per-iodic acid cleavage of 1,2-g1ycols is sometimes called Malaprade reaction.

Trihydric Alcohols

Glycerol or glycerine, CH2OH –CH(OH)-CH2OH is the first member of this group. Its IUPAC name is propane-l,2,3-triol.

Method of Preparation

It is obtained as a by product in saponification reaction.



$$\begin{array}{l} CH_2OOCR \\ | \\ CHOOCR \\ | \\ CH_2OOCR \end{array} + 3NaOH \xrightarrow{\text{Hydrolysis}} \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3RCOONa$$

(where, $R = C_{17}H_{35}$ or $C_{15}H_{31}$ or $C_{17}H_{33}$)

Physical Properties

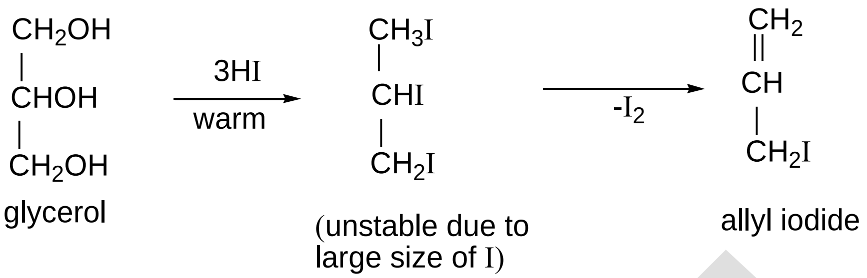
1. It is a colourless, odourless, viscous and hygroscopic liquid.
2. It is sweet in taste and steam volatile.
3. It is soluble in water but insoluble in ether.
4. Due to excessive H-bonding, it is highly viscous and has high boiling point.

Chemical Properties

It gives all the general reactions given by -OR group but 2° OR is less reactive as compared to 1°.

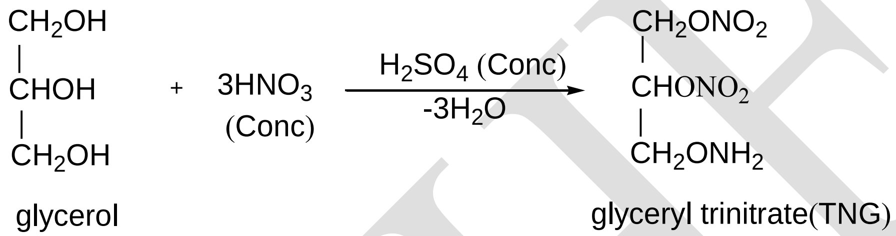
Some of its specific reactions are :

(i) Reaction with HI



$$\begin{array}{c}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} \xrightarrow[\text{warm}]{3HI} \begin{array}{c}CH_3I\\|\\CHI\\|\\CH_2I\end{array} \xrightarrow[-I_2]{} \begin{array}{c}CH_2\\||\\CH\\|\\CH_2I\end{array}$$

(ii) Reaction with HNO_3

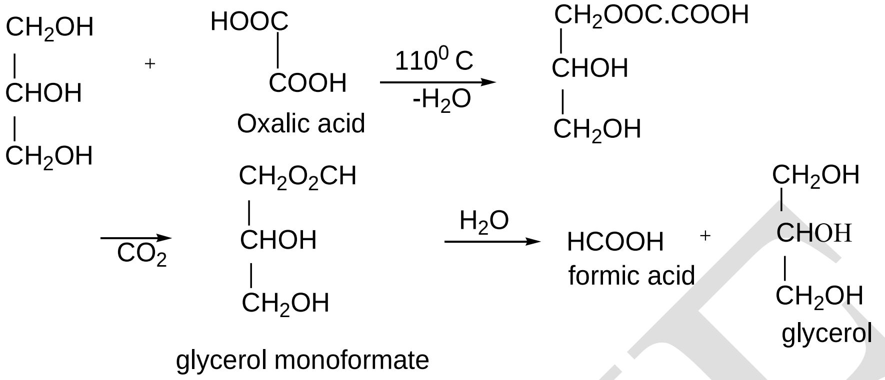


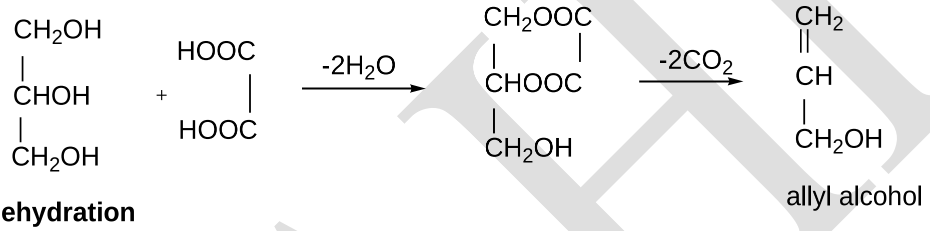
$$\begin{array}{c}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array} + \underset{(Conc)}{3HNO_3} \xrightarrow[-3H_2O]{H_2SO_4\ (Conc)} \begin{array}{c}CH_2ONO_2\\|\\CHONO_2\\|\\CH_2ONH_2\end{array}$$

Glyceryltrinitrate or tri nitroglycerine, when adsorbed on Kieselguhr is known as dynamite. Mixture of TNG and cellulose trinitrate is called blasting gelatin.

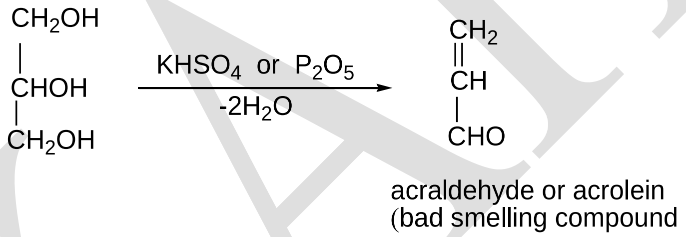
(i) Reaction with oxalic acid

(a) At 110^0C

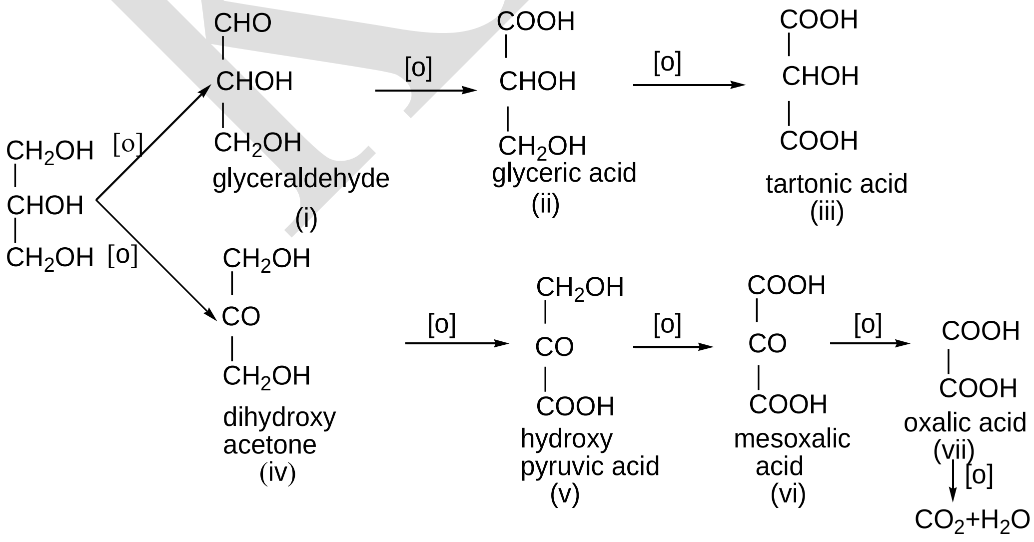




(iv) Dehydration



(v) Oxidation: Different products are obtained by different oxidising agent



Cone HNO_3 gives II; dil HNO_3 gives II and III; $Bi(NO_3)_3$ or $NaNO_3$ gives VI; Fenton's reagent or NaOBr or Br_2 water in Na_2CO_3 gives a mixture of I and IV.

Solid $KMnO_4$ oxidises glycerol to VII and CO_2 and H_2O.

With HIO_4 (periodic acid). glycerol gives HCOOH and HCHO.

Oxidation of diols by periodic acid and lead tetraacetate

1,2-Glycols are easily cleaved under mild conditions and in good yield with periodic acid or lead tetraacetate. The products are 2 equivalents of aldehyde, or 2 equivalents of ketone, or 1 equivalent of each, depending on the groups attached to the two carbons. The yields are so good that alkenes are often converted to glycols, and then cleaved with HIO_4 or $Pb(OAc)_4$ rather than being cleaved directly with ozone or dichromate or permanganate. The diol can be generated and cleaved in situ from an alkene to give the carbonyl compounds.

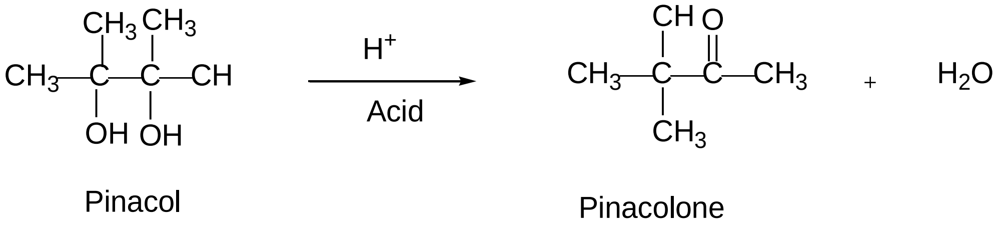
A number of other oxidizing agents also give the same products, among them activated MnO_2, and a ruthenium catalyst, PPh_3–DEAD, and pyridiniumchlorochromate. Permanganate, dichromate, and several other oxidizing agents also cleave glycols, giving carboxylic acids rather than aldehydes, but these reagents are seldom used synthetically. Electrochemical oxidation is an efficient method, and is useful not only for diols, but also for their mono- and dimethoxy derivatives. The two reagents (periodic acid and lead tetraacetate) are complementary, since periodic acid is best used in water and lead tetraacetate in organic solvents. Chiral lead carboxylates have been prepared for the oxidative cleavage of 1,2-diols. When three or more OH groups are located on adjacent carbons, the middle one (or ones) is converted to formic acid.

Pinacol Rearrangement

Pinacol Rearrangement is also called as **Pinacol-Pinacolone rearrangement**. It is an acid catalyzed organic chemical reaction in which 1, 2-diols are converted to carbonyl compounds. The name comes from the reactant and the product that is pinacol to pinacolone. This reaction is named after a German chemist *Wilhelm Rudolph Fittig* in 1860.

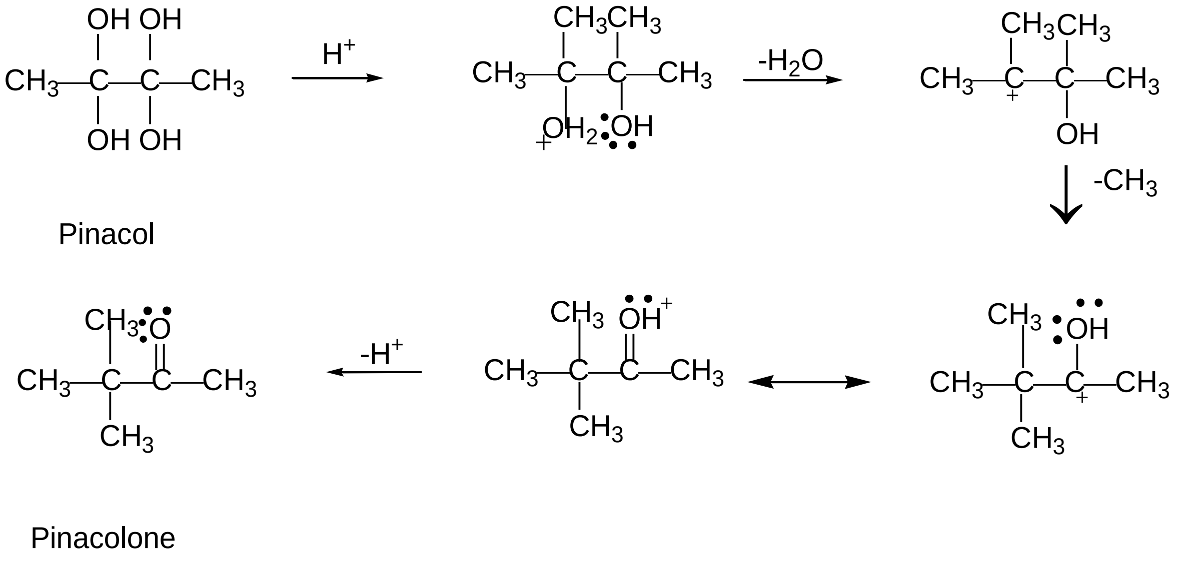
This reaction proceeds through the positively charged intermediate in which the methyl group migrates from one carbon atom to other.

For example, consider the following reaction:



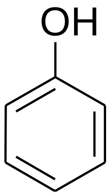
Mechanism

- In the first step, the hydroxide ion gets protonated in the presence of acid.
- Carbocation is formed after the removal of water molecule and it is stable because it is tertiary carbocation.
- Rearrangement takes place and the methyl group gets shifted to the positive carbon.
- Hydrogen ion is removed so that the pinacolone is generated.

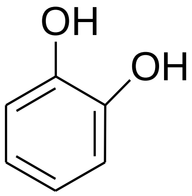


Phenols

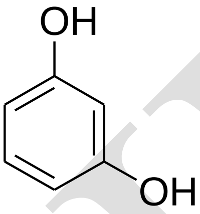
In phenols, -OR group is attached to Sphybridised carbon. These may also be monohydric, dihydric, etc. The dihydric phenol further rosy be ortho, meta' or para derivative.



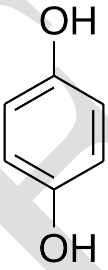
Phenol



catehol



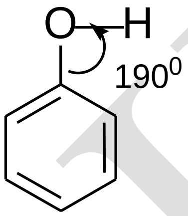
resorcinol



quinol or
hydroquinone

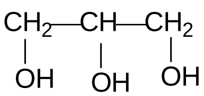
Structure of Phenols

In phenols, the – OH group is attached to Sp2 hybridised carbon and thus, the C – Obond acquires a partial double bond character.



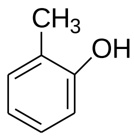
Nomenclature of Phenol

In IUPAC, system, alcohol or alkanols are named by replacing the last word 'e' of the corresponding alkane by 'ol'. e.g.,

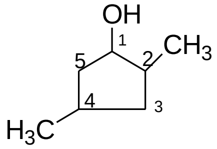


$CH_2-CH-CH_2$ with OH on each carbon

Propane-1,2,3-triol



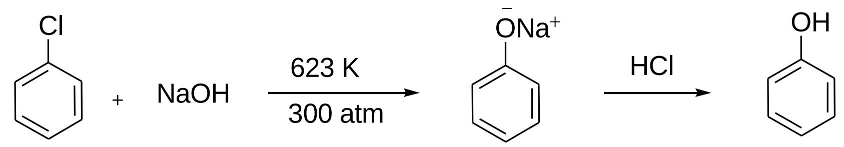
2-methyl phenol



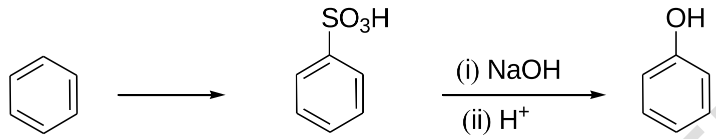
2,4-dimethylcyclopentanol

Preparation of Phenols

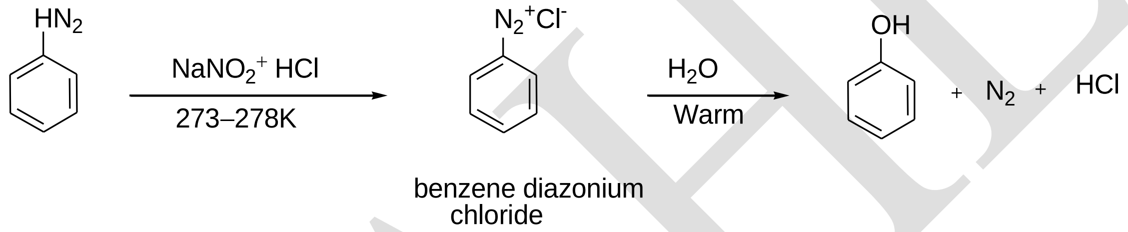
(i) From haloarenes



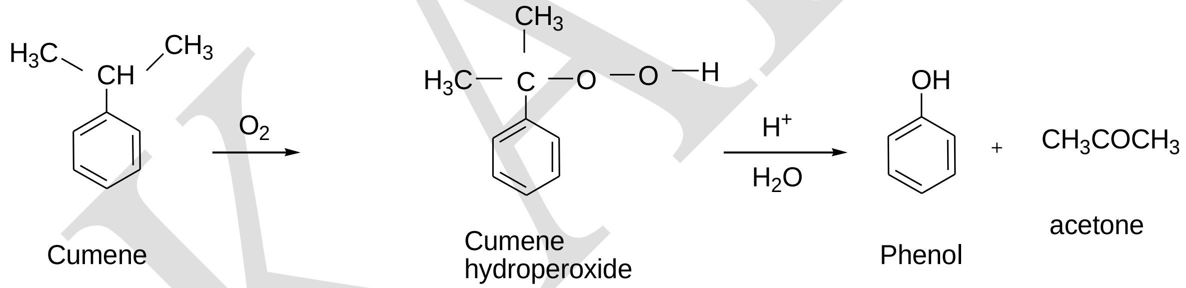
(ii) From benzene sulphonic acid



(iii) From diazonium salts



(iv) Fromcumene



Physical Properties of Phenols

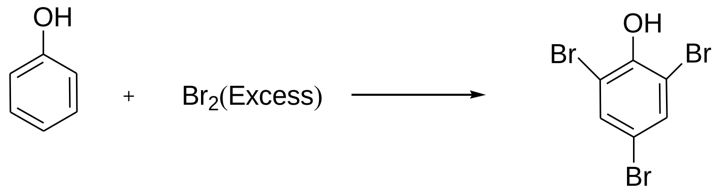
1. These are colourless liquids or crystalline solids but become coloured due to slow oxidation with air.

2. Phenol is also called carbolic acid.

3. Because of the presence of polar -OH bond, phenols form intermolecular H-bonding with other phenol molecules and with water.

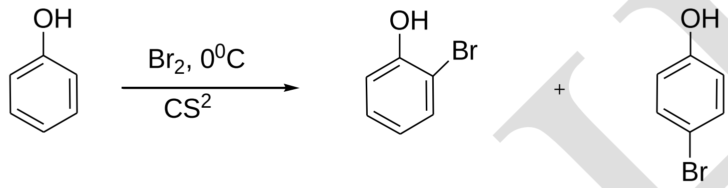
Reactions of Phenols

(a) Halogenation



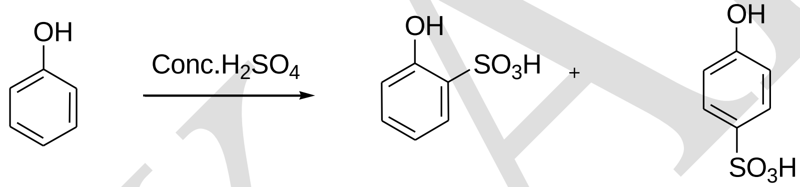
2,4,6-tribromophenol

With calculated amount of Br2 in CS2 or CHCl3 it gives ortho and para product.



O-bromophenol m-bromophenol

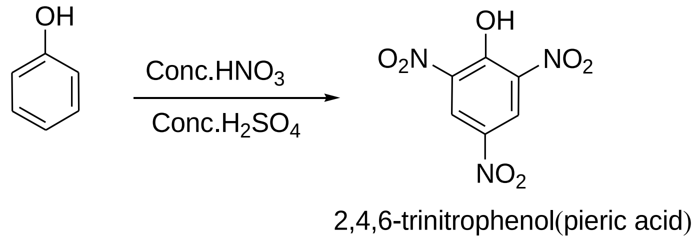
(b) Sulphonation

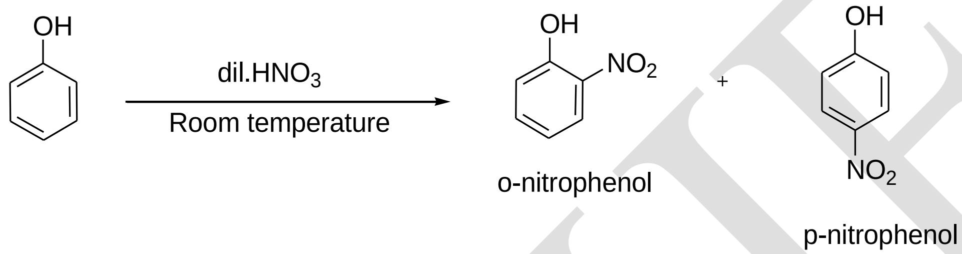


o-hydroxybenzene
sulphonic acid

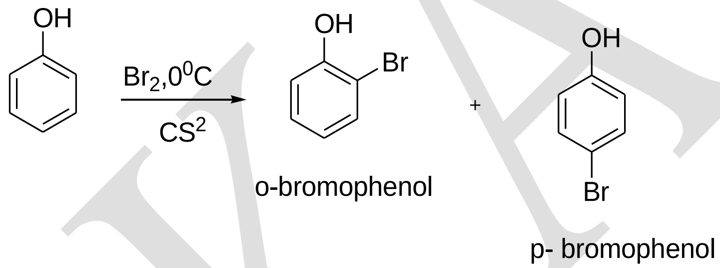
p-hydroxybenzene
sulphonic acid

(c) Nitration

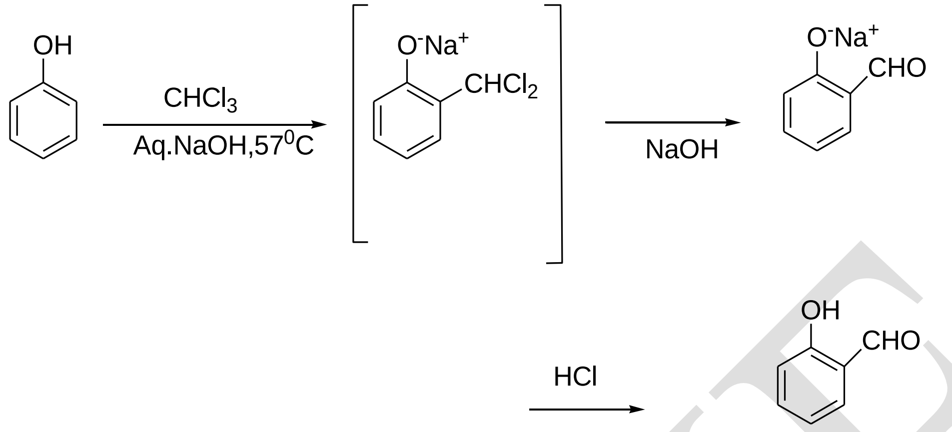




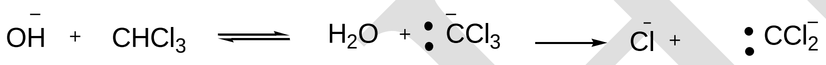
The ortho and para isomers can be separated by steam distillation. This is because o-nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.



(d) Reimer-Tiemann reaction



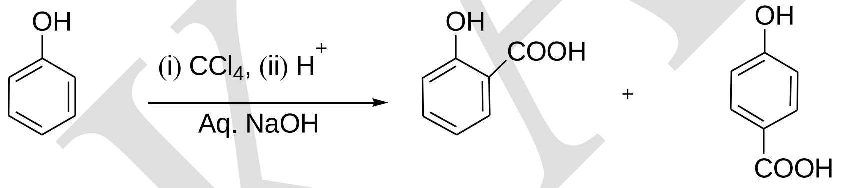
Salicylaldehyde
(chief product)



dichloro carbene
(intermediate)

This reaction is an electrophilic substitution reaction and electrophile is dichlorocarbene.

Similarly with carbon tetrachloride and alkali, c- and p-hydroxybenzoic acid are obtained

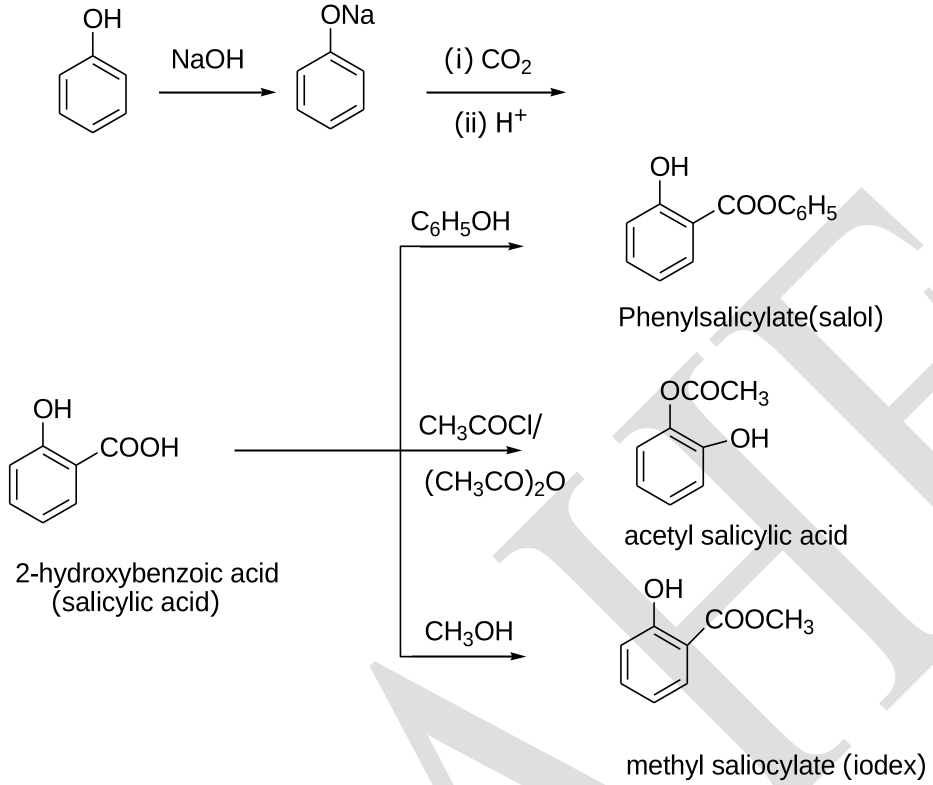


Phenol

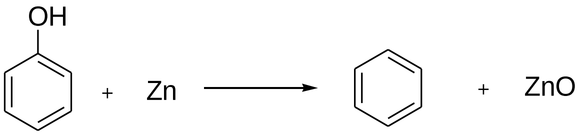
Salicylic acid
(major)

p-hydroxybenzoic acid
(minor)

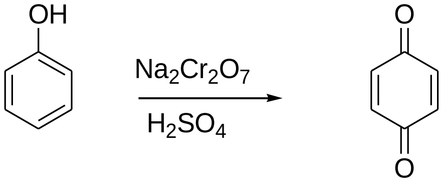
(ii) Kolbe's reaction



(iii) Reaction with zinc dust

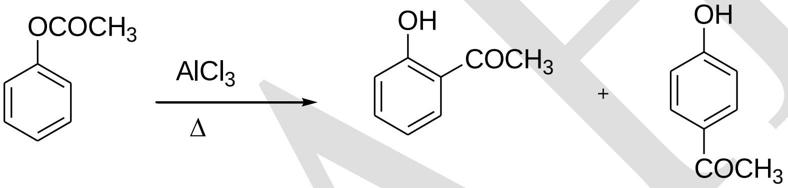


(iv) **Oxidation**



benzoquinone

(v) **Fries rearrangment**



POSSIBLE QUESTIONS

PART B (2 Marks Questions)

1. Explain why ethanol has higher boiling than dimethyl ether.

2. What happens when acetone is treated with Grignard reagent?

3. How are alcohols classified? Give one example of each type.

4. Why are phenols more acidic than alcohols?

5. How will you prepare phenolphthalein from phenol? Why does it acquire a pink colour in the basic medium?

PART C (8 Marks Questions)

1. How will you achieve the following convertions
    (i) Formaldehyde - Ethyl alcohol
    (ii) Acetaldehyde -- Isopropyl alcohol
    (iii) Acetone - T-Butyl alcohol

2. What are primary, secondary and tertiary alcohols? How will you distinguish them with the help of oxidation and Victor's Mayer method?

3. What are alcohols? How will you classified. Write any two preparation and properties of alcohols.

4. Give the mechanism of Pinacol-Pinacolone rearrangement.

5. Explain
    i) Why alcohols have higher boiling points than ethers of comparable molecular weights.
    ii) Why lower members of alcohols soluble in water while higher members are not.
    iii) Acidic character of alcohols

6. Write note on i) Reimer –Tiemann reaction ii) Kolbe's Schmidt reaction

7. How do the following react with ethyl alcohol
    (i) Hot reduced copper (ii) PCl_5 (iii) Acetyl chloride (iv) Na (v) CH_3MgBr

8. Give the mechanism of (i) Fries rearrangement (ii) Claisen rearrangement

9. i) Discuss the relative rate of reactivity of halogen acid w.r.t primary, secondary and tertiary alcohols, giving reasons.

(ii) Starting from Grignard reagent, how will you prepare primary and secondary alcohols?

10. How will you prepare the following from Phenol?
(i) Salicylic acid (ii) Benzene (iii) Picric acid (iv) p-Hydroxy benzoic acid

OBJECTIVE QUESTIONS

S. no	Questions	Option A	Option B	Option C	Option D	Answer
1.	Alcohols having two alcoholic groups in the molecule are called	Tri hydric alcohol	Dihydric alcohol	Secondary alcohol	Primary alcohol	Dihydric alcohol
2.	Alcohols having One alcoholic groups in the molecule are called	Tri hydric alcohol	Dihydric alcohol	Monohydric alcohol	Primary alcohol	Monohydric alcohol
3.	Alcohols having three alcoholic groups in the molecule are called	Monohydric alcohol	Dihydric alcohol	Tri hydric alcohol	Tertiary alcohol	Tri hydric alcohol
4.	The alcohols having just one (or) none alkyl group linked to the carbon attached to hydroxyl group are known as	Tertiary alcohol	Secondary alcohol	Primary alcohol	Mono hydric alcohol	Primary alcohol
5.	The alcohols which have two alkyl groups linked to the carbon attached to hydroxyl group are known as	Tertiary alcohol	Secondary alcohol	Primary alcohol	Mono hydric alcohol	Secondary alcohol
6.	The alcohols which have three alkyl groups linked to the carbon attached to hydroxyl group are known as	Primary alcohol	Secondary alcohol	Tertiary alcohol	Trihydric alcohol	Tertiary alcohol
7.	Which of the following gives positive Iodoform test?	1-Propanol	2- Propanol	3-Propanol	n- Propyl alcohol	2- Propanol
8.	The compound which reacts mostly with Lucas reagent	CH_3CH_2Cl	CH_3CH_{2}.OH	$(CH_3)_2CH$-OH	$(CH_3)_3C$-OH	$(CH_3)_3C$-OH
9.	Which of the following reagent will replace hydroxyl group by a halogen atom?	HOCl	Br_2	$SOCl_2$	I_2	$SOCl_2$

10.	Which of the following compound is least soluble in water?	$HOCH_2\ CH_2OH$	$CH_3CH_2\ CH_2OH$	CH_3CH_2OH	$CH_3\ CH_2\ CH_2CH_2OH$	$CH_3\ CH_2\ CH_2CH_2OH$
11.	Ethyl alcohol can react with Con.H_2SO_4 to give	Ethylene	Acetic acid	Acetaldehyde	Acetone	Ethylene
12.	Hydroboration-oxidation of propene gives	Iso propyl alcohol	n-Propyl alcohol	Isobutyl alcohol	Tertiary butyl alcohol	n-Propyl alcohol
13.	Oxidation of a primary alcohol with $KMnO_4$ / OH^- produces	a carboxylic acid	An ether	a ketone	an ester	a carboxylic acid
14.	Oxidation of a secondary alcohol with $KMnO_4$ / OH^- produces	an ether	an aldehyde	an acid	an ester	an acid
15.	Oxidation of a Tertiary alcohol with $KMnO_4$ / OH^- produces	Secondary alcohol	an acid	an aldehyde	an ester	an acid
16.	The major product of acid-catalysed dehydration of 2-butanol is	2-butene	2-butyne	1-Butene	1-Butyne	2-butene
17.	Oxidation of secondary alcohol with $K_2Cr_2O_7$ / H^{+-} produces	a carboxylic acid	a ketone	an aldehyde	an ester	a ketone
18.	Isopropyl alcohol can be converted to acetone by treatment with	HCl /$ZnCl_2$	$Na_2Cr_2O_7$ / H_2SO_4	$NaOH$	$LiAlH_4$	$Na_2Cr_2O_7$ / H_2SO_4
19.	Dehydrogenation of a primary alcohol with Cu at 473-573K produces	an Acid	a ketone	an ester	an Aldehyde	an aldehyde
20.	Dehydrogenation of a Secondary alcohol with Cu at 473-573K produces	an Acid	a ketone	an ester	an Aldehyde	a ketone
21.	Dehydrogenation of a tertiary alcohol with Cu at 473-573K produces	an alkene	a ketone	an acid	an ester	an alkene

22.	Among the following which is known as Baeyer's reagent	Cold alk.$KMnO_4$	Cold alk. $K_2Cr_2O_7$	Cold alk.$Na_2Cr_2O_7$	HCl /$ZnCl_2$	Cold alk.$KMnO_4$
23.	In cold countries ethylene glycol is added to water in car radiators. This helps to	reduce the viscosity	make water a better lubricant	lower the freezing point	lower the boiling point	lower the freezing point
24.	Ethylene glycol reacts with excess of PCl_5 to give	Chloroethane	1,2-Dichloro ethane	Hexa chloro ethane	1,3-Dichloro ethane	1,2-Dichloro ethane
25.	Ethylene glycol undergoes oxidation with hot acidic $KMnO_4$ to form	Formic acid	Formaldehyde	Acetic acid	Acetaldehyde	Formic acid
26.	When ethylene glycol is heated with concentrated nitric acid , it forms	oxalic acid	Ethylene oxide	Dioxane	Diethylene glycol	oxalic acid
27.	When glycerol is heated with potassium hydrogen sulphate KHSO4, it forms	Acrolein	Acetic acid	Allyl alcohol	Propionic acid	Acrolein
28.	When glycerol is treated with a mixture of Conc. $HNO_3 + H_2SO_4$, it forms	Nitro ethane	1-Nitropropane	NitroGlycerine	2-Nitro propane	NitroGlycerine
29.	The isomers of ortho and para nitro phenol can be seperated by	steam distillation	fractional distillation	sublimation	evaporation	steam distillation
30.	Phenol reacts with chloroform and sodium hydroxide to give salicylaldehyde in the usual way by	electrophilic substitution	nucleophilic substitution	nucleophilic addition	electrophilic addition	electrophilic substitution
31.	Which of the following one is known as Tollen's reagent?	CuO	Ag_2O	Fe_2O_3	AuO	Ag_2O
32.	The following one is imparts violet colour with ferric chloride	resorcinol	phenol	quinol	picric acid	resorcinol
33.	Phenol is stronger acid than:	carbonic acid	o-cresol	o-nitrophenol	p-nitrophenol	o-cresol

34.	Which of the following one is used as an anti-septic for skin disease	4n-hexyl resorcinol	4n-hexyl quinol	3n-hexyl resorcinol	4n-hexyl phenol	4n-hexyl resorcinol
35.	Which of the following one is used as a developer in photography?	alizarin	resorcinol	quinol	pholoroglucinol	quinol
36.	Phenols on distillation with zinc dust yield	benzaldehyde	benzene	benzoic acid	cyclo hexane	benzene
37.	In phenol, which group is directly attached to an aromatic ring	CHO	COOH	OH	CH_3	OH
38.	The common name of phenol is	Hydroxybenzene	Hydroxybenzoic acid	Hydroxy acetophenone	Catechol	Hydroxybenzene
39.	The compounds which contain an OH group in a side chain attached to an aromatic ring are not phenols, they are called	Aromatic acid	Aromatic alcohol	Aromatic ketone	Aromatic aldehyde	Aromatic alcohol
40.	Most pure phenols are	colourless liquids or solids	colourless solid or gas	colourless gas	violet	colourless liquids or solids
41.	Phenols have a characteristic	Carbolic odour	pleasant odour	fruty odour	fishy odour	Carbolic odour
42.	Phenol reacts with excess bromine water to give	o- plus *p*-Bromophenol	Bromobenzene	2,4,6-Tribromophenol	*m*-Bromophenol	2,4,6-Tribromophenol
43.	Phenol reacts with phthalic anhydride in the presence of sulfuric acid to form	Salicylaldehyde	Phenolsulphonic acid	Phenolphthalein	Hydroxybenzene	Phenolphthalein
44.	In phenols, all ring carbon atoms are	sp^3	sp^2	sp	dsp^3	sp^2
45.	In Phenol, the oxygen atom of the OH group is	sp^3	sp^2	sp	dsp^3	sp^3

46.	Anisole is formed when phenol is treated with	CH_3I/NaOH	CH_3CH_2I/NaOH	$CHCl_3$/NaOH	Acetic anhydride	CH_3I/NaOH
47.	Which reaction involves the treatment of phenol with chloroform in aqueous sodium hydroxide solution followed by acid-hydrolysis the salicylaldehyde is formed is known as	Kolbe's reaction	Perkin reaction	Wurtz reaction	Riemer-Tiemann reaction	Riemer-Tiemann reaction
48.	Phenols forms a condensation product with formaldehyde known as	fluorescein	*p*-hydroxy azobenzene	bakelite	phenolphthalein	bakelite
49.	Which of the following is not a characteristic of phenols?	they are weakly acidic in nature	they have corrossive action on skin	they are highly soluble in water	they are having antiseptic property	they are highly soluble in water
50.	Which of the following is a trihydric phenol?	catechol	pyrogallol	resorcinol	quinol	pyrogallol
51.	Which of the following is not a trihydric phenol?	pyrogallol	catechol	quinol	resorcinol	catechol
52.	When phenol is treated with neutral $FeCl_3$ solution, it develops	Violet colour	Yellow colour	Green colour	No reaction	Violet colour
53.	Which of the following compound is aspirin?	Methyl Salicylate	Salicylic acid	Phenyl salicylate	Acetyl salicylic acid	Acetyl salicylic acid
54.	Phenol is used	in alcoholic beverages	as anesthetic	in antiseptics	as moth repellent	in antiseptics
55.	Phenol is acidic because of	Resonance	Electromeric effect	Inductive effect	Peroxide effect	Resonance
56.	Anisole on heating with Concentrated HI gives	Iodobenzene	Phenol + CH_3I	Iodobenzene + CH_3OH	Phenol + CH_3OH	Phenol + CH_3I
57.	Which group forms the strongest H-Bonds	Alcohols	Ethers	Phenols	All equally strong	Phenols

	to water molecules?					
58.	Which of the following compound is most acidic?	O-Cresol	P-Cresol	P-Nitro Phenol	P-Chloro Phenol	P-Nitro Phenol
59.	Which of the following compound is least acidic?	HCl	Phenol	Acetylene	Picric acid	Acetylene
60.	Which of the follwing compound is most acidic?	Water	Cyclohexanol	Ethanol	Phenol	Phenol

Syllabus

Structure, reactivity, preparation and properties; Nucleophilic additions, Nucleophilic addition-elimination reactions with ammonia derivatives with mechanism; Mechanisms of Aldol and Benzoin condensation, Knoevenagel condensation, Claisan-Schmidt, Perkin, Cannizzaro and Wittig reaction, Beckmann and Benzil-Benzilic acid rearrangements, haloform reaction and Baeyer Villiger oxidation, α – substitution reactions, oxidations and reductions (Clemmensen, Wolff-Kishner,LiAlH4, NaBH4, MPV, PDC)

NUCLEOPHILIC ADDITION REACTION:

A nucleophilic addition reaction is a reaction in which the addition of a molecule to the carbonyl compound takes place with the initiation of the negative part of the adding molecule. The negative part of the adding molecule (eg.CN in HCN) adds first to the positive carbon of the carbonyl group,followed by the attachment of the positive part of the adding molecule to the negative oxygen of the carbonyl group. The addition of a nucleophile(:Z) to a carbonyl compound may be represented as shown below:

Carbonyl compound has a trigonal configuration. In the transition state,it starts acquiring sp^3 configuration which is accomplished in the final product. Ability of oxygen to acquire negative charge is the reason for nucleophilic reactions in carbonyl compounds.

Acetaldehyde is more reactive than acetone towards nucleophilic addition reactions:

Aldehydes are observed to be more reactive than ketones particularly in giving nucleophilic reactions for the following reasons:

STERIC FACTORS.

As has been explained earlier,the nucleophile attaches itself to the positive carbon of the carbonyl group. With the ketone,the transition state will experience steric hindrance because of bulky alkyl groups.consequently the transition state will not be stable. Hence the reaction will not take place easily. With an aldehyde,steric hindrance will be less as there is only one alkyl group in the transition state.this accounts for greater reactivity of aldehyde group compared to the ketonic group.

ELECTRONIC FACTORS.

Alkyl groups exert electron releasing inductive effect which increases the negative charge density on the carbon making it difficult for the nucleophile to attach to carbon. This would destabilize the transition state

With ketones,this destabilizing effect will be doubled because of two alky groups. This is the reason why ketones are less reactive than aldehydes.

Aromatic aldehydes and ketones are less reactive than aliphatic aldehydes and ketones:

Phenyl group has electron withdrawing inductive effect. Thus we would expext the transition state to get stabilizrd in the nucleophilic addition reaction of an aromatic aldehyde or ketone. But this is not actually so. As a matter fact,aromatic aldehydes and ketonnes are less reactive than their aliphatic counterparts. This is so because aromatic aldehydes and ketones get stabilized due to resonance as shown below:

This creates a positive charge on the rigid instead of carbonyl carbon thus decreasing chances of nucleophilic attack. Moreover, there are steric factors due to bulky size of phenyl group.

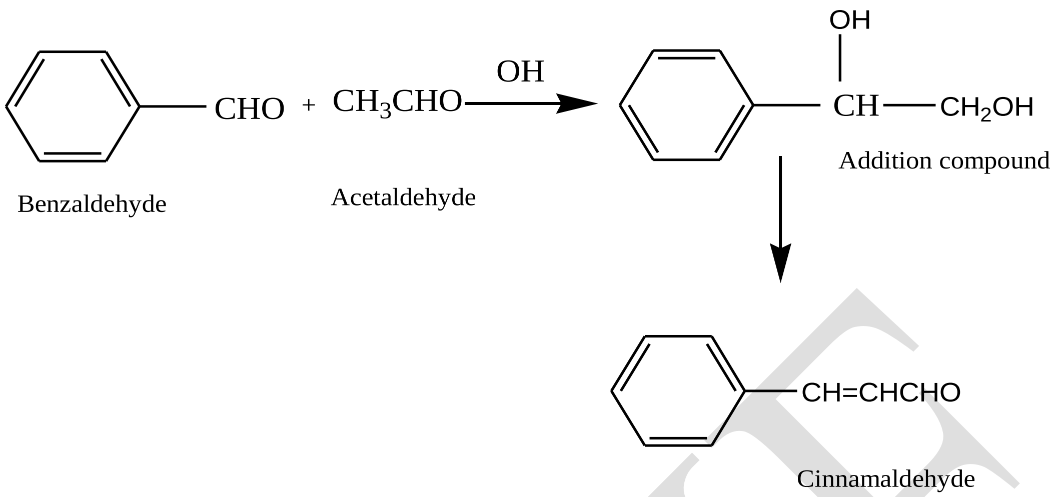
We conclude that the presence of alkyl group decreases the reactivity of the aldehydes and ketones towards nucleophilic adition while the presence of phrnyl group further decreases the reactivity. Thus, greater the number of such groups present or bigger the size of the groups,smaller will be the reactivity. Thus the decreasing order of reactivity of carbonyl compounds towards nucleophilic addition is:

CARBONYL COMPOUNDS :

CLAISEN-SCHMIDT REACTION:

This reaction may be considered as a special case of crossed aldol condensation. It involves condensation of aromatic carbonyl compound with an aliphatic carbonyl compound in the presence of a base. Hydroxy derivative first obtained loses a water molecule to yield α,β-unsaturated aldehyde or ketone.

For example



MECHANISM:

Step 1. Formation of carbanion.

α- hydrogen of the aliphatic carbonyl compound is removed by the hydroxide ions, thus creating carbanions.

Step 2. Attack by carbanion on the aromatic carbonyl compound.

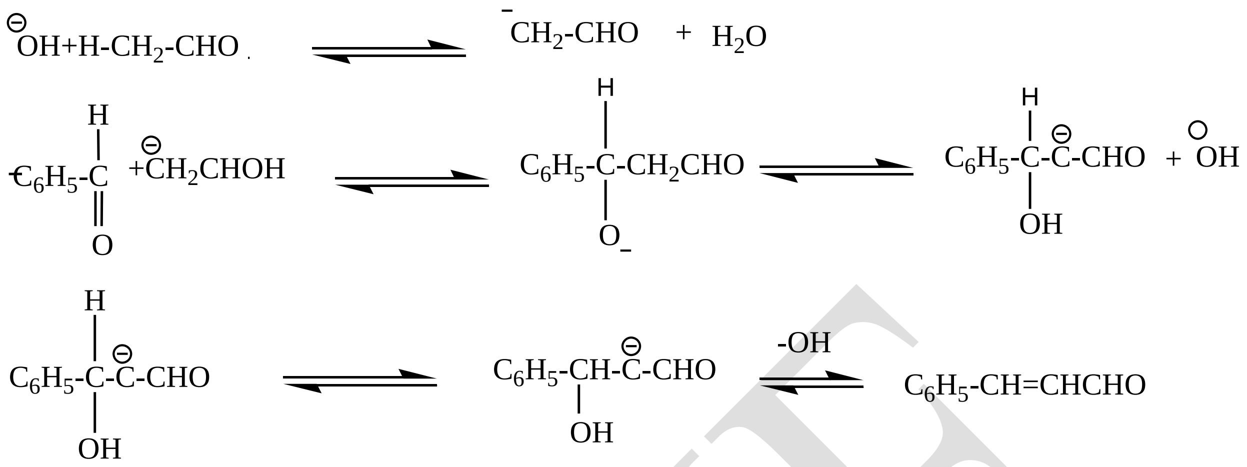
The carbanion obtained in step 1 attacks the aromatic carbonyl group by nucleophilic addition mechanism to form the alkoxide ion.

Step 3. Attachment of a proton.

The alkoxide ion removes a proton from water and attaches to itself to give β-hydroxy compound.

Step 4.

α-hydrogen atom in the hydroxyl compound is removed by the base followed by the removal of-OH group, thus removing a water molecule finally. The sequence of the above steps is shown below:



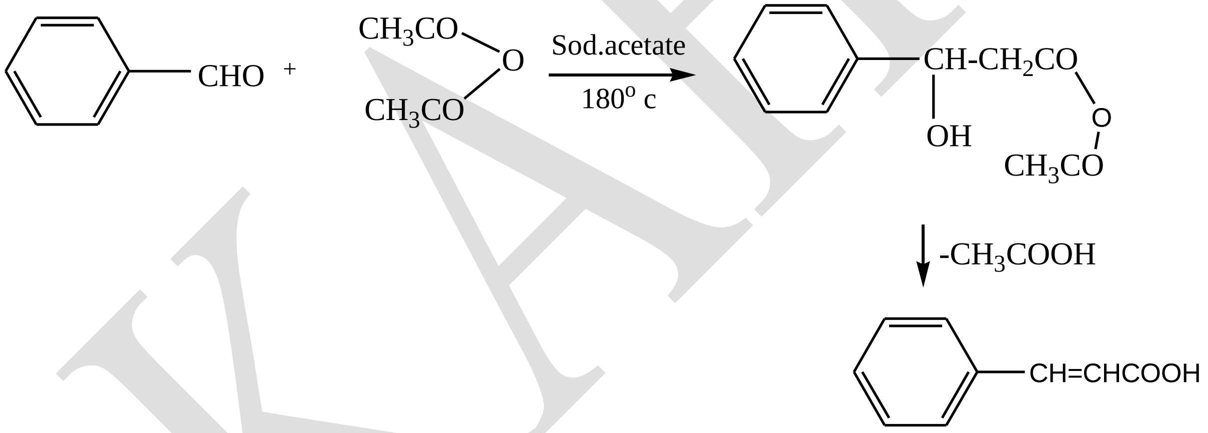
$$^{\ominus}OH + H\text{-}CH_2\text{-}CHO \rightleftharpoons {}^{-}CH_2\text{-}CHO + H_2O$$

$$C_6H_5\text{-}\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{C}} + {}^{\ominus}CH_2CHOH \rightleftharpoons C_6H_5\text{-}\underset{\underset{O^-}{|}}{\overset{\overset{H}{|}}{C}}\text{-}CH_2CHO \rightleftharpoons C_6H_5\text{-}\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}\text{-}\overset{\ominus}{C}\text{-}CHO + {}^{\ominus}OH$$

$$C_6H_5\text{-}\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}\text{-}\overset{\ominus}{C}\text{-}CHO \rightleftharpoons C_6H_5\text{-}\underset{\underset{OH}{|}}{CH}\text{-}\overset{\ominus}{C}\text{-}CHO \xrightleftharpoons{-OH} C_6H_5\text{-}CH{=}CHCHO$$

PERKIN'S REACTION:

It is a kind of aldol condensation in which an aromatic aldehyde condenses with acetic anhydride in the presence of sodium acetate to yield unsaturated carboxylic acid. Thus benzaldehyde on treatment with acetic anhydride and sod.acetate yields cinnamic acid.



Cinnamic acid

MECHANISM:

Step 1.Formation of a carbanion.

Acetic anhydride in the presence of acetate ion loses a hydrogen forming a carbanion.

Step 2.Attack of the carbanion on the carboxyl group.

Carbanion obtained in the above steps attacks the carbonyl carbon atom(nucleophilic attack) forming alkoxide.

Step 3. Protanation of the alkoxide ion.

Alkoxide gets protanated to form an aldol type compound.

Step 4.Dehydration.

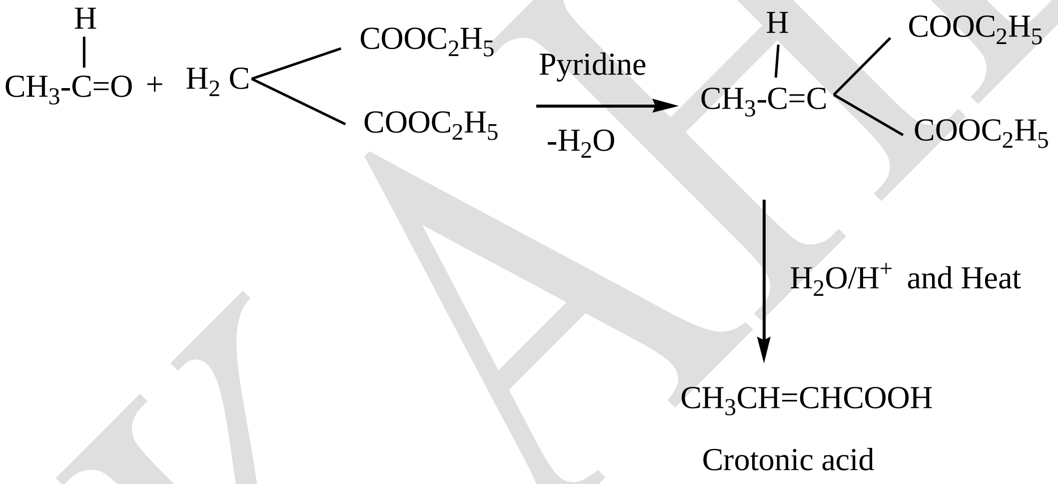
The hydroxyl group and neighbouring hydrogen are removed as water forming an unsaturated product.

Step 5. Hydration.

The alkenic compound obtained above gets hydrolysed giving the final product.

Knoevenagal condensation.

An aldehyde or a ketone on condensation with a compound having an active methylene group (such as malonic ester or acetoacetic ester) in the presence of a base such as pyridine gives an unsaturated compound.



Mechanism.

Mechanism of the reaction is explained by the example of reaction between an aldehyde and acetoacetic ester.

Step 1. Formation of a carbanion.

The base B. attracts a hydrogen from the acetoacetic ester forming a carbanion.

Step2. Attack by the carbanion.

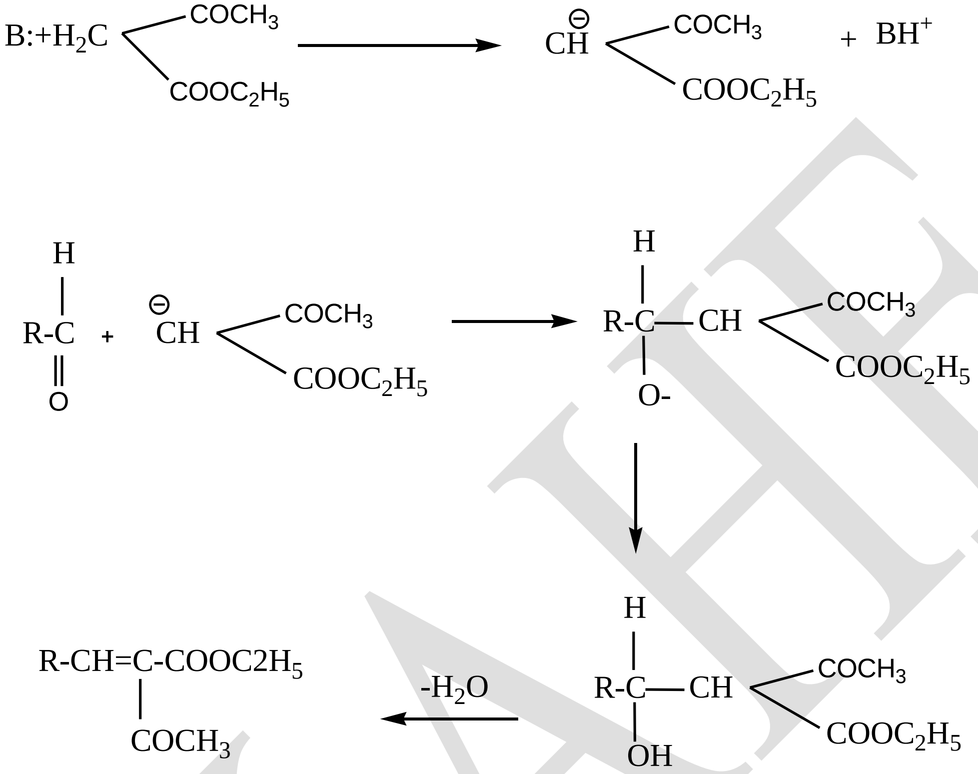
The carbanion as obtained above attacks the carbonyl carbon by nucleothilic chains forming an alkoxide ion.

Step3. Protonation.

The alkoxide draws a proton tp convert itself into a hydroxyl compound.

Step 4. Dehydration.

Hydroxy and hydrogen and hydrogen from the neighbouring carbon atoms are removed as water, and an unsaturated compound is obtained. The above steps are illustared as follows**.**



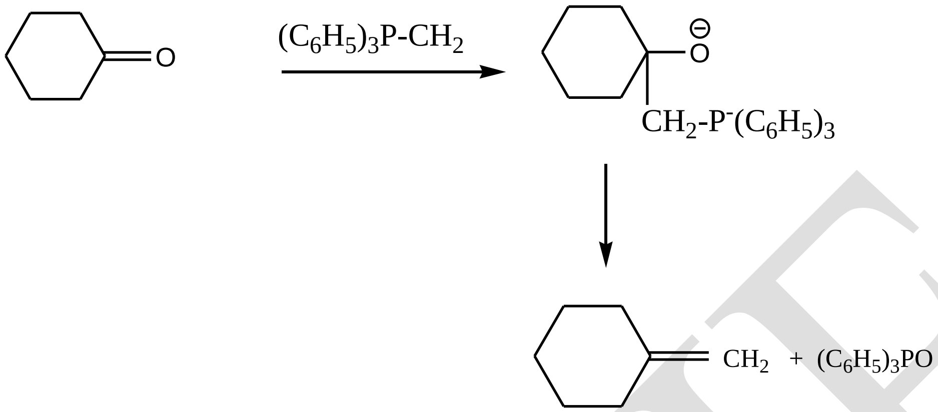
WITTIG'S REACTION:

This reaction takes place between an aldehyde or ketone and phosphorusylides to from substituted alkenenes. The phosphorous ylides required in the reaction are obtained by the action of a base on suitable alkyl triphenyl phosphonium halides (prepared from alkyl halide and triphenyl phophine).For example,

$$\underset{\text{Triphenyl phosphorous}}{(C_6H_5)_3P + CH_3I} \longrightarrow [(C_6H_5)_3\ PCH_3]I \xrightarrow{C_6H_5Li} \underset{\text{methylene triphenyl phospharane(ylide)}}{(C_6H_5)_3\ P = CH_2 + C_6H_6 + Li}$$

The ylides obtained as shown as above are not separated but are made to react as such with the aldehydes or ketones in solution.

$$(C_6H_5)_3P = CH_2 \longrightarrow (C_6H_5)_3\ P\text{-}CH_2$$



Methylene cyclohexane

MECHANISM.

The following steps are involved in the reaction:

Step 1. Attack by ylides.

The phosphorous ylides exists as a resonance hybrid of two structures.

Structure [B] has a negative charge on carbon thus it acts as a carbanion and initiates the nucleophilic attack on the carbonyl carbon.The resulting addition product is known as betaine.

Step 2.Elimination of triphenyl phosphine oxide.

Betaine obtained above undergoes elimination of triphenyl phosphine oxide to yield the alkene.The above steps are illustrated hereunder.

CANNIZARO REACTION.

Aldehydes having no α-hydrogen like formaldehyde and benzaldehyde undergo self oxidation and reduction.This reaction is given when an aldehyde is treated with a conc.solution of sodium or potassium hydroxide.An alcohol and a salt of carboxylic acid are produced.For example:

$$2HCHO + NaOH \longrightarrow CH_3OH + HCOONa$$

Formaldehyde Methanol sod.formate

MECHANISM.

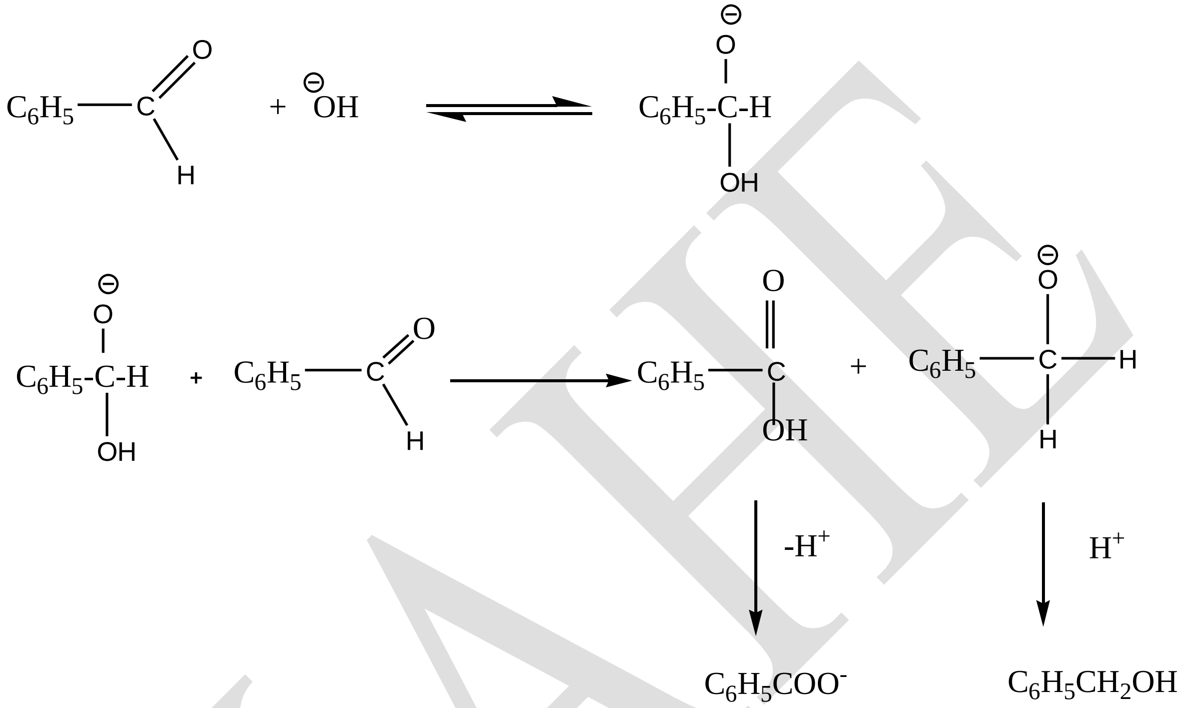
The following steps are involved:

Step 1.Attack by OH.

Hydroxide ion attacks the aldehyde molecule to form an anion.

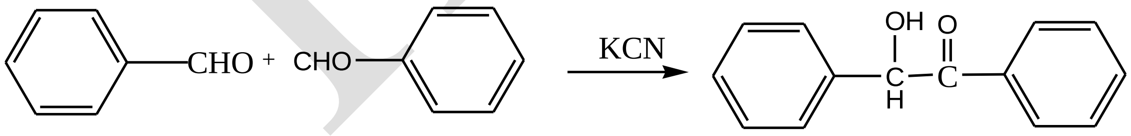
Step 2.Hydride ion transfer.

Oxidation –reduction takes place between the anion formed in step 1 and the second molecule of aldehyde through transfer of a hydride ion.These two steps are illustrated hereunder.



BENZOIN CONDENSATION.

Aldol condensation is a property of carbonyl compounds containing α-hydrogen atoms. Thus benzaldehyde which does not containing α-hydrogen atom is not capable of givimg this reaction. Such aromatic aldehydes condense in the presence of KCN(which act asa a base)to yield benzoins. This reaction is known as BENZOIN CONDENSATION.



MECHANISM

STEP 1.Formation of a carbanion.

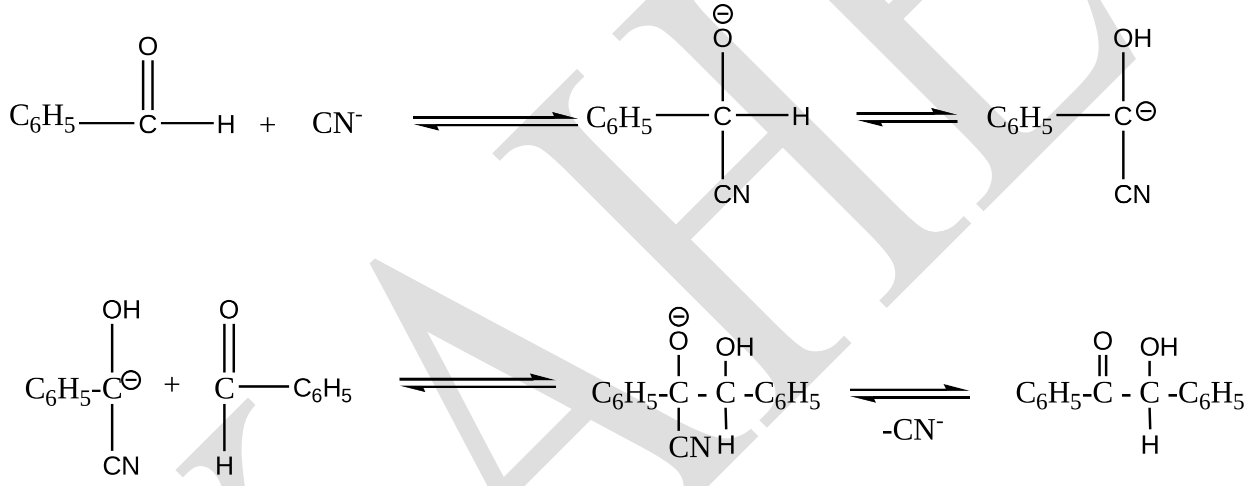
Direct formation of a carbanion is not possible as there areα-hydrogen atoms. Hence this carbonion formation takes place after some rearrangement. It involves attachment of CN to the carbonyl carbon with simultaneous shifting of electrons to oxygen. This results in the formation of carbanion.

Step 2. Attack of the carbanion(nucleophile)on the second molecule.

Carbanion obtained in step 1 above attacks the carbonyl group of the second molecule forming an addition product,an alkoxide.

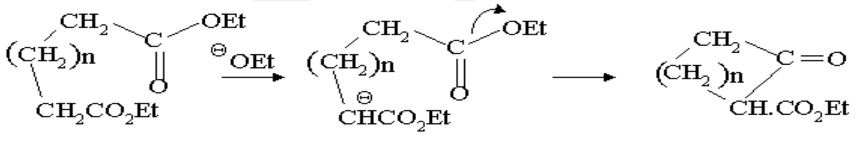
Step 3.Loss of cyanide ion.

The alkoxide ion loses cyanide ion with simultaneous loss of hydrogen from the same carbon atom. Hydrogen combines with the oxygen on the neighbouring carbon atom giving the final products. The sequence of steps is illustrated below:

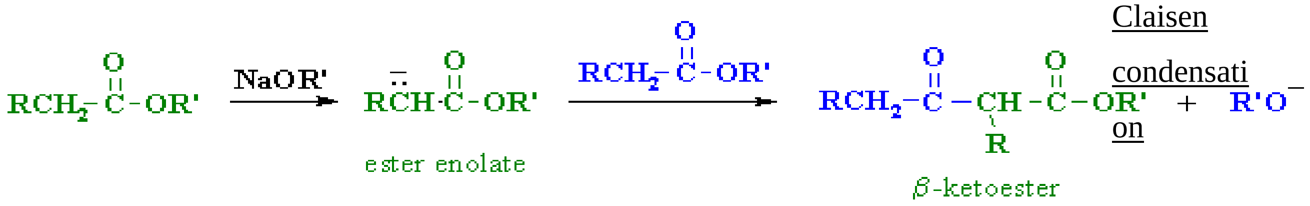


Dieckman Reaction

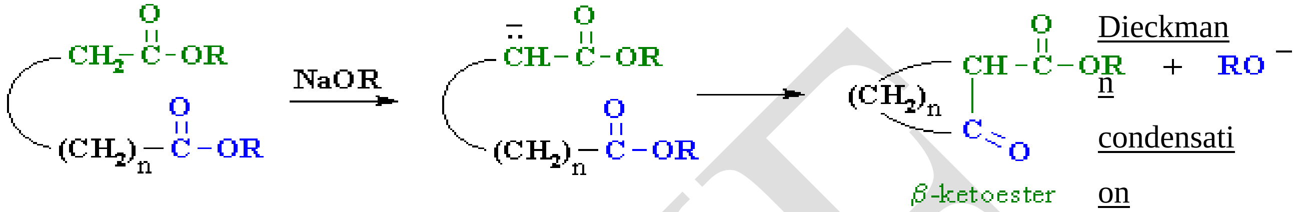
When two ester groups are part of the same molecule, cyclisation can result. This type of condensation is known as Dieckman reaction.



The most important reactions of ester enolates are the Claisen and Dieckmann condensations. However, ester groups are common as part of active methylene enolates. Remember that enolates are sources of nucleophilic **C** that react with electrophiles.



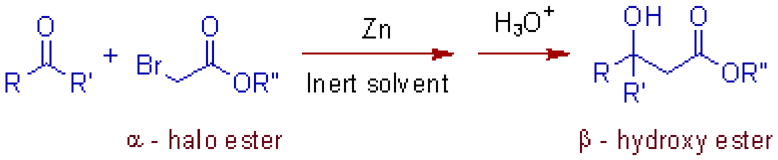
Claisen condensation



Dieckmann condensation

Reformatsky reaction

* The involves the treatment of a α-halo ester with zinc metal and subsequent reaction with aldehyde/ketone to get β- hydroxy ester.

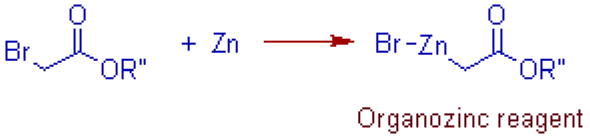


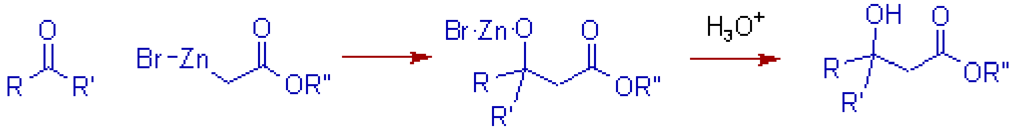
* Usually inert solvents like diethyl ether or THF are used in Reformatsky reaction.

* Better yields are obtained by using Zn-Cu couple or in situ preparation of zinc by reduction of zinc halides by potassium (also known as Rieke zinc).

Mechanism of Reformatsky Reaction

* Initially zinc reacts with α-halo ester to give an organozinc reagent called reformatsky enolate. It is just like the Grignard reagent. It is added to the carbonyl group of aldehyde or ketone to furnish β- hydroxy ester.

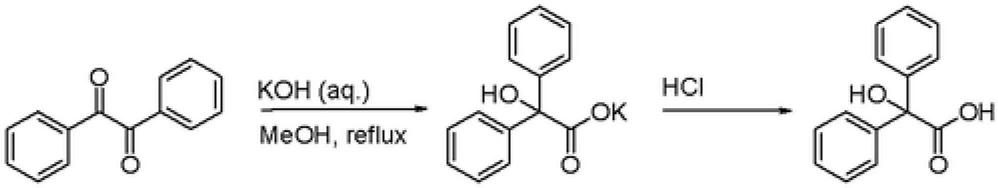




The organozinc reagents are less reactive and hence the nucleophilic addition to the ester group seldom occurs. Some of them are quite enough stable to be isolated and can be elucidated for the structure by techniques like X-ray analysis.

Benzil- Benziolic acid Rearrangement

The **benzilic acid rearrangement** is the rearrangement reaction of benzil with potassium hydroxide to benzilic acid. First performed by Justus Liebig in 1838 this reaction type is displayed by 1,2-diketones in general. The reaction product is an α-hydroxy–carboxylic acid.



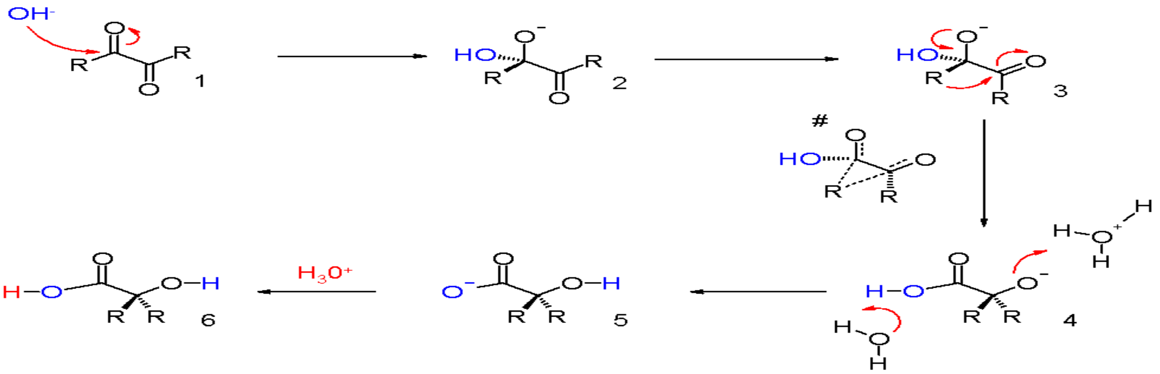
Certain acyloins also rearrange in this fashion.

This diketone reaction is related to other rearrangements: the corresponding keto-aldehyde (one alkyl group replaced by hydrogen) rearranges in a Cannizzaro reaction, the corresponding 1,2-diol reacts in a pinacol rearrangement.

Mechanism

The reaction is a representative of 1,2-rearrangements. These rearrangements usually have migrating carbocations but this reaction is unusual because it involves a migrating carbanion. The long established reaction mechanism updated with in silico data [3] is outlined in *scheme 2*.

A hydroxide anion attacks one of the ketone groups in **1** in a nucleophilic addition to the hydroxyl anion **2**. The next step requires a bond rotation to conformer **3** which places the migrating group R in position for attack on the second carbonyl group in a concerted step with reversion of the hydroxyl group back to the carbonyl group. This sequence resembles a nucleophilic acyl substitution. Calculations show that when R is methyl the charge build-up on this group in the transition state can be as high as 0.22 and that the methyl group is positioned between the central carbon carbon at a separation of 209 pm.



POSSIBLE QUESTIONS

PART B (2 Marks Questions)

1. Arrange the following in the increasing order of reactivity. CH_3CHO, HCHO, CH_3CH_2CHO

2. Write a note on Wolf-Kishner reduction.

3. Why does aromatic aldehydes and ketones are less reactive than the corresponding aliphatic aldehydes and ketones?

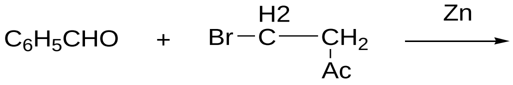
4. Formaldehyde gives Cannizarro reaction while acetaldehytde does not. Assign the reason.

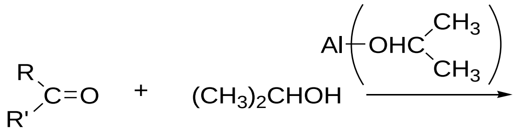
5. What happens when acetone is treated with CH_3MgBr followed by hydrolysis?

PART C (8 Marks Questions)

1. Give the mechanism of
(i) Aldol condensation (ii) Cannizaro reaction (iii) Claisen reaction

2. Complete the following reaction and Give mechanism.

i)


ii)


3. Explain the following reaction and mechanism:
(i) Knovenegal reaction (ii) M.P.V. reduction

4. What happens when
(i) Butanone is treated with $LiAlH_4$
(ii) Butanone is reduced with amalgamated Zn and HCl
(iii) Acetophenone is trteated with hydrazine and KOH
(iv) $CH_3CH = CHCHO$ is reduced with $NaBH_4$

5. Complete the following reactions and identify the products
i) Acetic anhydride + CH_3COO^- → A + ?
ii) A + C_6H_5CHO → B
iii) B is hydrolysed and heated → C + ?

6. Write notes on i) Perkin reaction ii) Beckmann reaction

7. Complete and name the following reactions
i) $(CH_3)_3CCHO + (CH_3)_3CCHO \xrightarrow{50\ \%\ NaOH}$

ii) $C_6H_5CHO + (C_6H_5)_3P = CH_2 \longrightarrow$

iii) $C_6H_5CHO + BrCH_2\text{-}COOC_2H_5 \xrightarrow{Zn\ /Ether}$

iv) $C_6H_5CHO + CH_2.COO(C_2H_5)_2 \xrightarrow{Base}$

Or

9. Give the mechanism of the following (i) Knovenagel condensation (ii) Benzoin condensation

10. Write notes on
i) Clemmensen reduction ii) Wolf-Kishner reduction iii) MPV reduction

11. Discuss the various methods employed for the reduction of carbonyl compounds.

OBJECTIVE QUESTIONS

S. no	Questions	Option A	Option B	Option C	Option D	Answer
1.	Ethylene oxide reacts with Grignard reagents to furnish	tert-alcohol	sec-alcohol	hydrocarbon	primary alcohol	primary alcohol
2.	The decreasing order of Grignard reagents formation among following alkyl halides is	$CH_3X > C_2H_5X > C_3H_7X$	$C_3H_7X > C_2H_5X > CH_3X$	$CH_3X > C_3H_7X > C_2H_5X$	$C_2H_5X > C_2H_5X > C_3H_7X$	$CH_3X > C_2H_5X > C_3H_7X$
3.	Which one among the following compounds is not an organometallic compound?	$(C_2H_5)_2Pb$	$(CH_3)_2$	CH_3MgBr	CH_3COONa	CH_3COONa
4.	Grignard reagents react with ketone followed by acid hydrolysis to give	primary alcohol	secondary alcohol	tert-alcohol	isopropyl alcohol	tert-alcohol
5.	Which one of the following alkyl halides cannot be used for the preparation of Grignard reagent	CH_3Br	$C_6H_5CH_2Cl$	$HOCH_2CH_2Cl$	$CH_2=CH-CH_2Cl$	$HOCH_2CH_2Cl$
6.	The compound that does not undergo Cannizzaro reaction is	formaldehyde	acetaldehyde	benzaldehyde	trimethyl acetaldehyde	acetaldehyde
7.	Grignard reagents prepared by the reaction of organic halide and dry magnesium metal in the presence of suitable solvent	dry alcohol	dry benzene	dry ether	dry chloroform	dry ether
8.	Among the halides, the ease of formation of Grignard reagent is	iodide > bromide > chloride	bromide > chloride > iodide	iodide > chloride > bromide	bromide > iodide > chloride	iodide > bromide > chloride
9.	Which one is not true of Grignard Reagents?	the solvent must be absolutely dry	solvent must be completely free form of alcohol	the apparatus must be thoroughly dried	nitrogen atmosphere should not be maintained	nitrogen atmosphere should not be maintained
10.	Grignard reagents react with esters of formic	primary alcohol	secondary alcohol	tertiary alcohol	isopropyl alcohol	secondary alcohol

	acid to give					
11.	Reaction of Grignard reagents and carbonyl compounds undergoes by	electrophilic addition	nucleophilic addition	elcetrophilic substitution	nucleophilic substitution	nucleophilic addition
12.	The reaction of tert-butylmagnesium chloride and formaldehyde to gives	neopentyl alcohol	tert-alcohol	iso butyl alcohol	iso propyl alcohol	neopentyl alcohol
13.	Neopentyl alcohol prepared by the reaction of	tert-butylmagnesium chloride + acetaldehyde	tert-butylmagnesium chloride + formaldehyde	tert-butylmagnesium chloride + benzaldehyde	tert-butylmagnesium chloride + acetone	tert-butylmagnesium chloride + formaldehyde
14.	What two components, when treated with NaOEt in ethanol, would NOT give a successful crossed aldol reaction?	acetaldehyde and acetone	formaldehyde and acetone	benzaldehyde and acetone	2,4-pentanedione and acetone	acetaldehyde and acetone
15.	Ammonia reacts with formaldehyde to give a	formaldehyde ammonia	hexamethylene tetramine	formalin	imine	hexamethylene tetramine
16.	Hexamethylene tetramine is used as	ear drops	bactericidal	antiseptics in burns wounds	urinary antiseptics	urinary antiseptics
17.	Acetone reacts with HCN to from a cyanohydrins. It is a example	electrophilic addition	electrophilic substitution	nucleophilic addition	nucleophilic substitution	nucleophilic addition
18.	Ketones are prepared by the oxidation of	primary alcohol	secondary alcohol	tertiary alcohol	isopropyl alcohol	secondary alcohol
19.	Which of the following reagents will react readily with both aldehydes and ketones?	Grignard reagents	Fehlings reagents	Tollens reagents	Schiffs reagents	Grignard reagents
20.	Acetone undergoes reduction with hydrazine in the presence of NaOH to form propane. The reaction is known as	Clemmensen reduction	Wolf-kishner reduction	Rosenmund reduction	Reformatsky reaction	Wolf-kishner reduction
21.	Cannizaro reaction is not given by	formaldehyde	trimethylacetaldehyd	acetaldehyde	benzaldehyde	acetaldehyde

			e			
22.	A hydrazone will result from the reaction of hydrazine with	a phenol	an aldehyde	an alcohol	an acid	an aldehyde
23.	In the reactions of aldehydes and ketones, the carbonyl carbon is mostly attacked by	electrophiles	free radicals	nucleophiles	carbenes	nucleophiles
24.	The nucleophilic addition reactions of carbonyl compounds are catalysed by	acids	bases	ampholytes	water	acids
25.	Grignard reagents add to the carbonyl group of ketones to form	primary alcohol	secondary alcohol	tertiary alcohol	isobutyl alcohol	tertiary alcohol
26.	Perkin reaction is a reaction related to	aldol condensation	cannizzaroreaction	witting reaction	mannich reaction	aldol condensation
27.	Perkin reaction involves the addition of acid anhydrides to which type of aldehydes in the presence of the sodium salts of the acids from which the anhydride is derived.	aliphatic	aromatic	alicyclic	cyclic	aromatic
28.	Knoevenagal reaction involves the interaction of an aromatic aldehyde and an active methylene compound in the presence of an amine like	piperidine	methylamine	aniline	triethylamine	piperidine
29.	Reformatsky reaction consists in reacting aldehydes and ketones with α-bromo esters in the presence of	magnesium	zinc	cadmium	zinc amalgam	zinc
30.	Aldol condensation provides a useful route for the preparation of	α,β-unsaturated carbonyl compounds	β,γ- unsaturated carbonyl compounds	β-hydroxy carbonyl compounds	γ-hydroxy carbonyl compounds	α,β-unsaturated carbonyl compounds
31.	Reformatsky reaction provides a suitable route for the preparation of	α-hydroxy esters	β- hydroxy esters	γ- hydroxy esters	α,β- hydroxy esters	β- hydroxy esters

32.	Wolff-kishner reduction of carbonyl compounds to hydrocarbons involves the treatment of the carbonyl compound in the presence of strong base, with	semicarbazide	hydroxylamine	hydrazine	2,4-dinitrophenylhydrazine	hydrazine
33.	Which one of the following compound will give cannizzaro’s reaction?	CH_3CHO	$C_6H_5CH_2CHO$	$(CH_3)_2C-CHO$	CH_3CH_2CHO	$(CH_3)_2C-CHO$
34.	Acetophenone undergoes self condensation in the presence of aluminium tert-butoxide to give	syn-triphenyl benzene	benzalacetophenone	dipnone	acetophenone	dipnone
35.	Acrolein is formed by the reaction of	formaldehyde and acetaldehyde	acetaldehyde and benzaldehyde	benzaldehyde and formaldehyde	acetaldehyde and acetone	formaldehyde and acetaldehyde
36.	Effect of dehydration of diacetone alcohol to give mesityl oxide in presence of	NaoH	pyridine	iodine	primary amine	iodine
37.	Aldol obtained by the condensation of benzaldehyde and acetaldehyde is unstable and looses a molecule of water to give	benzyledeneacetone	chinnamic acid	diacetone alcohol	cinnamaldehyde	cinnamaldehyde
38.	Claisen condensation is carried out by using ester having α-hydrogen atom to give	β-keto ester	γ- keto ester	α- keto ester	σ- keto ester	β-keto ester
39.	Dickmann condensation also known as intramolecular	knoevenagal condensation	cannizaro reaction	claisen condensation	aldol condensation	claisen condensation
40.	Cyclic ketones are prepared by the	cannizaro reaction	dickmann condensation	claisen condensation	aldol condensation	dickmann condensation
41.	Ethyl esters of adipic acid undergoes a Dickmann condensation to give	cyclo butanone	cyclo hexanone	cycloheptanone	cyclopentanone	cyclopentanone
42.	In cannizzaro reaction, alkoxide is used as	ketones	esters	alcohol	salts of acids	esters

	base the product is					
43.	In knoevenagal condensation, acetaldehyde treated with malonic acid in presence of very weak base to give	acrolein	mesityl oxide	crotonic acid	cinnamic acid	crotonic acid
44.	Cinnamic acid is obtained from the reaction of	acetaldehyde + malonic ester	benzaldehyde + malonic ester	formaldehyde + malonic acid	acetaldehyde + cyanoacetic ester	benzaldehyde + malonic ester
45.	Aldehydes are more reactive than ketones because of the presence of	Free hydrogen atom	Carbonyl group	Electron with drawing oxygen	Alkyl group	Free hydrogen atom
46.	What is the IUPAC name of Acetone	Dimethyl ketone	Propanone	Butanone	Diethyl ketone	Propanone
47.	Which of the following will react with Fehling's Solution giving a red precipitate?	CH_3CH_2CHO	CH_3CH_2 O CH_2CH_3	CH_3CH_2 CH_2OH	CH_3COCH_3	CH_3CH_2CHO
48.	An Organic compound (A), C_3H_8O, On Oxidation gives (B), C_3H_6O. The compound (A) could be	an Aldehyde	a Ketone	an Alcohol	an ester	an aldehyde
49.	An Organic compound (A), C_4H_8O, does not react with sodium or PCl_5. However, it reduces an alkaline solution of a copper (II) salt on heating. Compound (A) could be	an Aldehyde	a primary alcohol	a ketone	a secondary alcohol	an aldehyde
50.	Boiling acetaldehyde reacts with chlorine gas to give	CH_3COCl	CCl_3COH	$CH_3CH_2Cl_2$	$CHCl_3$	CCl_3COH
51.	Which of the following compounds reacts with sodium bisulphite and ammoniacal silver nitrate solution?	CH_3CH_2COOH	CH_3CH_2CHO	$CH_3CH_2CH=CH_2$	$CH_3C \equiv CCH_3$	CH_3CH_2CHO
52.	The reaction of σ-bromo esters with carbonyl compounds in presence of zinc to produce β-	perkin reaction	aldol condensation	reformatsky reaction	claisen reaction	reformatsky reaction

	hydroxy esters, this reaction is known as					
53.	Lithium aluminium hydride converts acetophenone to	primary alcohol	secondary alcohol	tertiary alcohol	hydrocarbons	secondary alcohol
54.	In wolff-kishner reduction, treatment of carbonyl compounds with hydrazine followed by a strong base in solvents like	benzene	piperidine	diethylene glycol	polyethylene glycol	diethylene glycol
55.	In meerwein pondorf verley reduction, carbonyl compounds treated with aluminium isopropoxide in isopropyl alcohol to give	alcohol + amine	alcohol + acetone	ester + acetone	acid + acetone	alcohol + acetone
56.	Which of the following compounds will give a positive test with Fehling's solution?	Formaldehyde	Acetone	Ethyl acetate	Acetic acid	Formaldehyde
57.	Reduction of acetaldehyde with H_2 / Ni gives	Ethyl alcohol	Acetic acid	Ethylene	Ethane	Ethyl alcohol
58.	The appearance of a silver mirror in Tollen's test indicates the presence of	an aldehyde	a ketone	an alcohol	an alkene	an aldehyde
59.	Aldehydes undergo oxidation with $KMnO_4$ / H^+ to give	Alcohols	Acetals	Ketones	Acids	Acids
60.	Which action best accounts for the solubility of aldehydes and ketones in water?	polar interactions in solute molecules	H-Bonding between solute molecules	Vander Waals forces	H -Bonding between solute and solvent molecules	H -Bonding between solute and solvent molecules

Syllabus

Organometallic compounds, Ethers and Epoxides and Addition reactions

Organometallic compounds of Mg (Grignard reagent) – Use in synthesis of organic compounds. *Ethers and Epoxides:* Preparation and reactions with acids. Reactions of epoxides with alcohols, ammonia derivatives and $LiAlH_4$.

Addition reactions of α, β- unsaturated carbonyl compounds: Michael addition. Active methylene compounds: Keto-enol tautomerism. Preparation and synthetic applications of diethyl malonate and ethyl acetoacetate.

Ethers

Ethers are the organic compounds in which two alkyl or aryl groups are attached to divalent oxygen known as ethereal oxygen. These are represented by the general formula R–O-R" where R may be alkyl or aryl groups. e.g.,

$CH_3—O—CH_3$, $C_2H_5—O—C_2H_5$
dimethyl ether, diethyl ether

Mixed ethers $CH_3—O—C_2H_5$, $CH_3—O—C_3H_7$
ethyl methyl ether, methyl *n*-propyl ether

These are the functional isomers of alcohols. These also exhibit chain isomerism and metamerism.

Nomenclature of Ethers

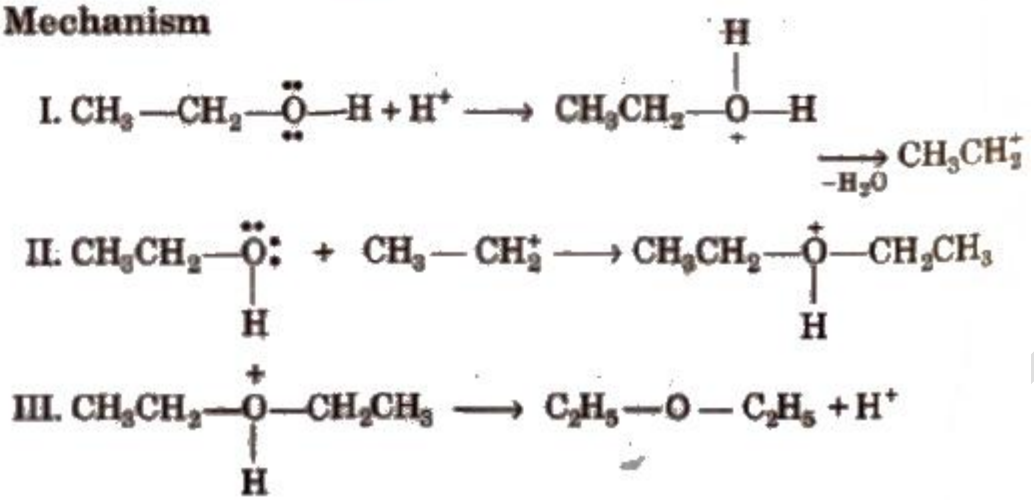
In the IUPAC system, ethers are regarded as 'alkoxy alkanes' in which the ethereal oxygen is taken along with smaller alkyl group while the bigger alkyl group is regarded as a part of the alkane.

Preparation of Ethers

(i) By dehydration of alcohols

$$\underset{\text{excess}}{2CH_3CH_2-OH} \xrightarrow[413\,K]{H_2SO_4\ (\text{conc.})} CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-CH_2-CH_3 + H_2O$$

Mechanism



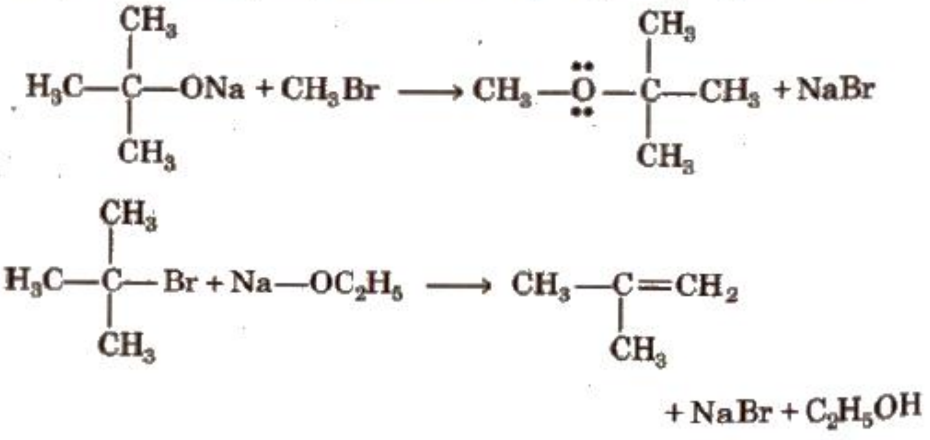
$$\text{I. } CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H + H^+ \longrightarrow CH_3CH_2-\overset{H}{\underset{+}{O}}-H \xrightarrow[-H_2O]{} CH_3CH_2^+$$

$$\text{II. } CH_3CH_2-\underset{H}{\ddot{O}}: + CH_3-CH_2^+ \longrightarrow CH_3CH_2-\underset{H}{\overset{+}{O}}-CH_2CH_3$$

$$\text{III. } CH_3CH_2-\underset{H}{\overset{+}{O}}-CH_2CH_3 \longrightarrow C_2H_5-O-C_2H_5 + H^+$$

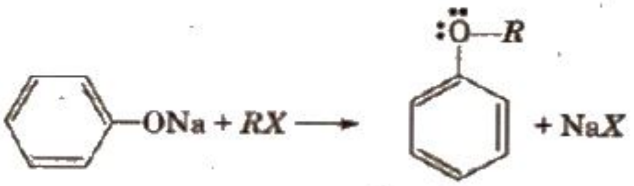
(ii) Williamson's synthesis Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halides give alkene due to steric hindrance.

$$CH_3CH_2Br + CH_3CH_2ONa \longrightarrow CH_3CH_2OCH_2CH_3 + NaBr$$



$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-ONa + CH_3Br \longrightarrow CH_3-\ddot{\underset{\cdot\cdot}{O}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + NaBr$$

$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-Br + Na-OC_2H_5 \longrightarrow CH_3-\underset{CH_3}{C}=CH_2 + NaBr + C_2H_5OH$$



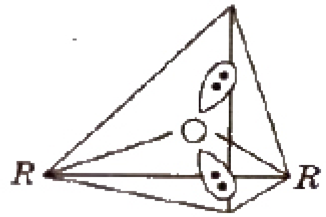
alkoxy benzene

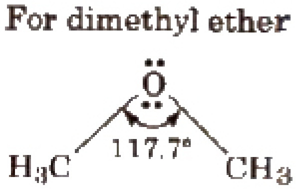
Physical Properties of Ethers

Ethers are polar but insoluble inH20 and have low boiling point than alcohols of comparable molecular masses because ethers do not form hydrogen bonds with water.

Structure of Ether

The hybridisation of 0 atom in ethers is sp3 (tetrahedral) and its shape is V-shape.

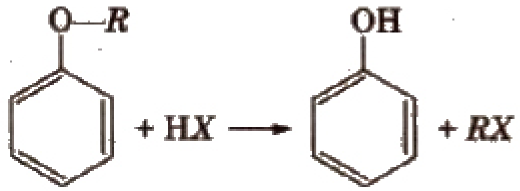




Chemical Reactions of Ether

(i) Reaction with HX

$$R{-}O{-}R + HX \longrightarrow RX + R{-}OH$$



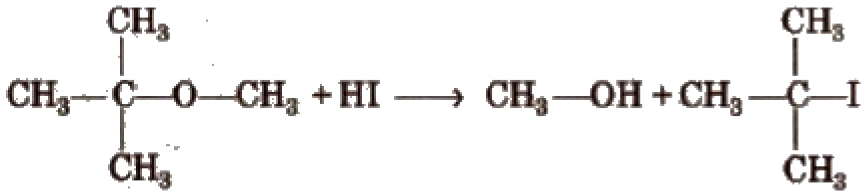
Ethers with two different alkyl groups are also cleaved in the same manner and resultsin the formation of a primary halide (or smaller and less complex alkyl halide) by SN2mechanism.

R-O-R’ + HX → RX + R’OR

The order of reactivity of hydrogen halides is as follows

HI > HBr > HCl

In ethers if one of the alkyl groups is a tertiary group, the halide formed is a tertiaryhalide by SN1 mechanism.



$$(CH_3)_3C-O-CH_3 + HI \longrightarrow CH_3-OH + (CH_3)_3C-I$$

(ii) Halogenation

$$CH_3CH_2OCH_2CH_3 \xrightarrow[\text{Dark}]{Cl_2} \underset{(\alpha\text{-monochloro diethyl ether})}{CH_3CHClOCH_2CH_3}$$

$$C_2H_5OC_2H_5 + \underset{(\text{excess})}{10Cl_2} \xrightarrow[(\text{light})]{h\nu} \underset{(\text{perchlorodiethyl ether})}{C_2Cl_5OC_2Cl_5} + 10HCl$$

(iii) Reaction with PCl_5

$$R-O-R + PCl_5 \xrightarrow{\Delta} 2RCl + POCl_3$$

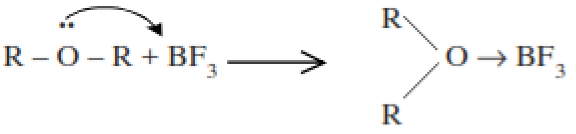
(iv) Reaction with CO

$$ROR + CO \xrightarrow[500\text{ atm}]{BF_3/150°C} RCOOR$$

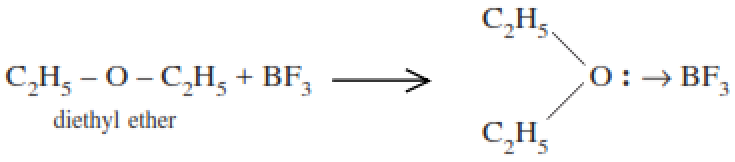
(v) Electrophilic substitution reactions in ethers,-OR is ortho, para directing group and activate the aromatic ring towards electrophilic substitution reaction.

Reaction with Lewis acids.

Similarly with Lewis acids like BF3 and , AlCl3

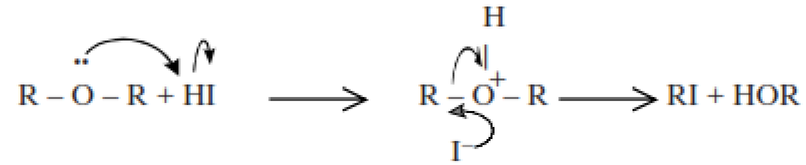


(Boron trifluoride etherate)



(ii) Reaction with HX

On treating with HBr or HI ether gets cleaved to form alcohol and alkyl halide.



Halogen prefers to attack the carbon atom of **the smaller alkyl group.**

$$C_2H_5 - O - CH_3 \xrightarrow{HI} C_2H_5OH + CH_3I$$

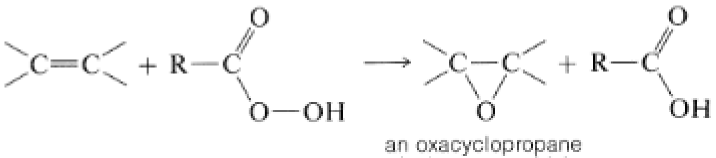
(iii) With excess hot concentrated hydroidic acid, alkyl iodides are formed.

$$CH_3 - O - C_2H_5 \xrightarrow{2HI} CH_3I \quad + \quad C_2H_5I \quad + \quad H_2O$$

This reaction also follows the mechanism mentioned in the previous reaction. This reaction is used in the **Zeisel's method of detection and estimation of alkoxy (especially methoxy) group** in natural products like alkaloids.

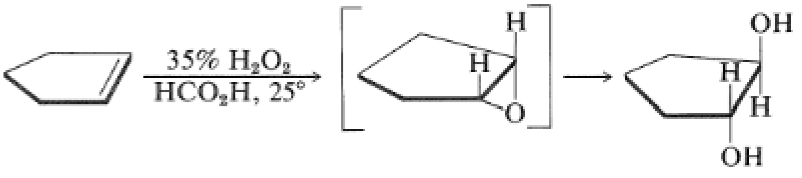
Epoxides

Alkenes can be oxidized with peroxycarboxylic acids, RCO,H, to give oxacy- clopropanes (oxiranes, epoxides), which are three-membered cyclic ethers:



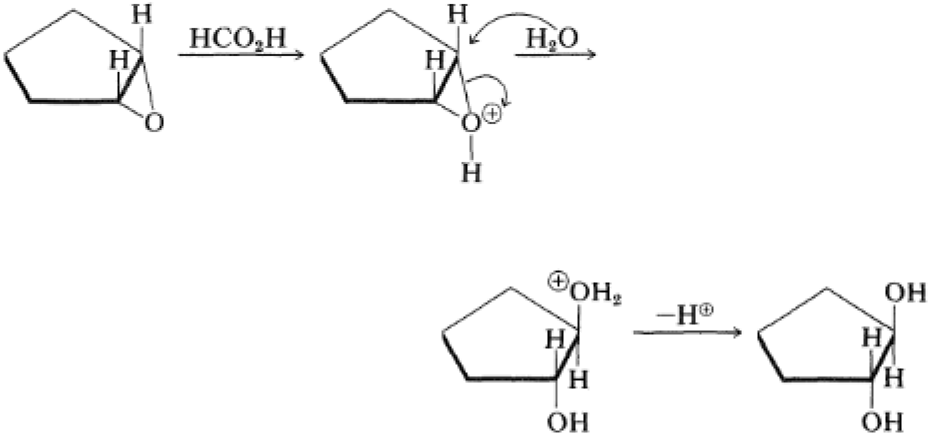
an oxacyclopropane
(oxirane, epoxide)

This is an alternative scheme for the hydroxylation of alkenes. However, the overall stereochemistry is opposite to that in permanganate hydroxylation. For instance, cyclopentene gives trans- 1,2-cyclopen-tanediol. First the oxirane forms by suprafacial addition and then undergoes ring opening to give the trans product:

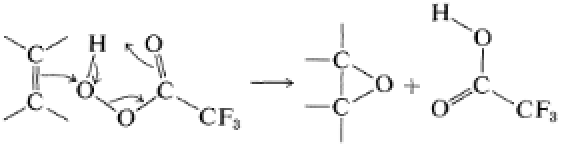


trans-1,2-cyclopentanediol

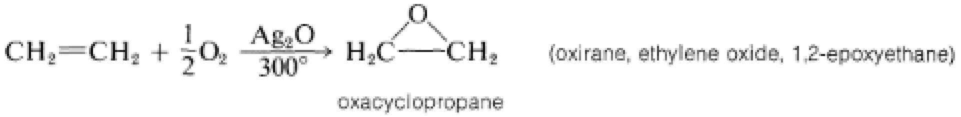
The ring opening is a type of **S,2** reaction. Methanoic acid is sufficiently acidic to protonate the ring oxygen, which makes it a better leaving group, thus facilitating nucleophilic attack by water. The nucleophile always attacks from the side remote from the leaving group:



The peroxyacids that are used in the formation of oxacyclopropanes include Peroxyethanoic (CH3COOH), peroxybenzoic (C6H5COOH) , and trifluoroper- oxyethanoic (CF3COOH) acids. A particularly useful peroxyacid is 3-chloro- peroxybenzoic acid, because it is relatively stable and is handled easily as the crystalline solid. The most reactive reagent is trifluoroperoxyethanoic acid, which suggests that the peroxyacid behaves as an electrophile (the electro- negativity of fluorine makes the CF3 group strongly electron-attracting). The overall reaction can be viewed as a **cycloaddition,** in which the proton on oxygen is transferred to the neighboring carbonyl oxygen more or less simultaneously with formation of the three-membered ring:



A reaction of immense industrial importance is the formation of oxacy- clopropane itself (most often called ethylene oxide) by oxidation of ethene with oxygen over a silver oxide catalyst at 300":



Oxacyclopropane is used for many purposes, but probably the most important reaction is ring opening with water to give 1,2-ethanediol (ethylene glycol, bp 197 °C. This diol, mixed with water, is employed widely in automotive cooling systems to provide both a higher boiling and lower freezing coolant than water alone:

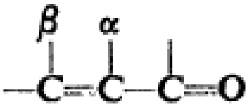
Propene and higher alkenes are not efficiently epoxidized by oxygen and Ag_2O in the same way as ethene is because of competing attack at other than the double-bond carbons.

Addition reactions of α, β- unsaturated carbonyl compounds

In general, a compound that contains both a **carbon-carbon double bond and a carbon-oxygen double bond** has properties that are characteristic of both functional groups.

At the **carbon-carbon double bond** an unsaturated ester or unsaturated ketone undergoes electrophilic addition of acids and halogens, hydrogenation, hydroxylation, and cleavage;

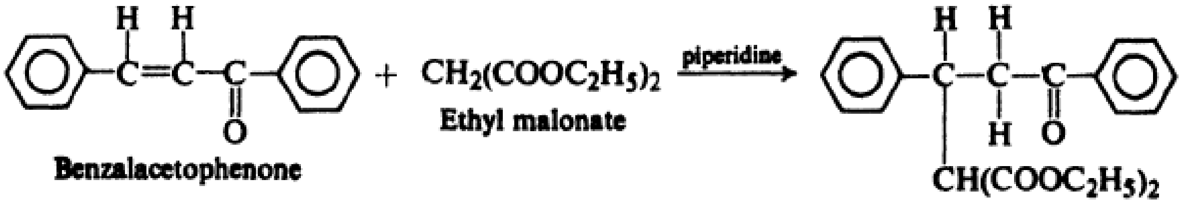
at the **carbonyl group** it undergoes the nucleophilic substitution typical of an ester or the nucleophilic addition typical of a ketone.

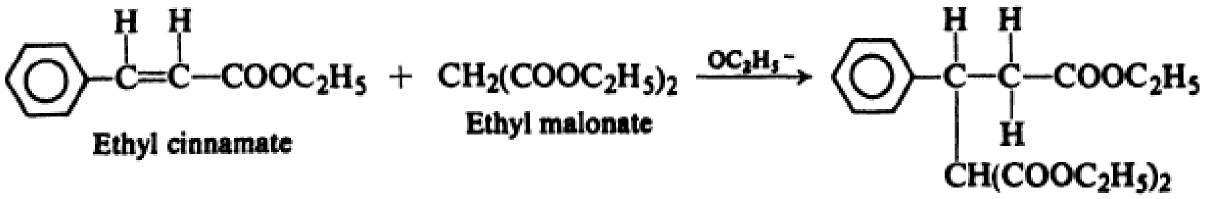


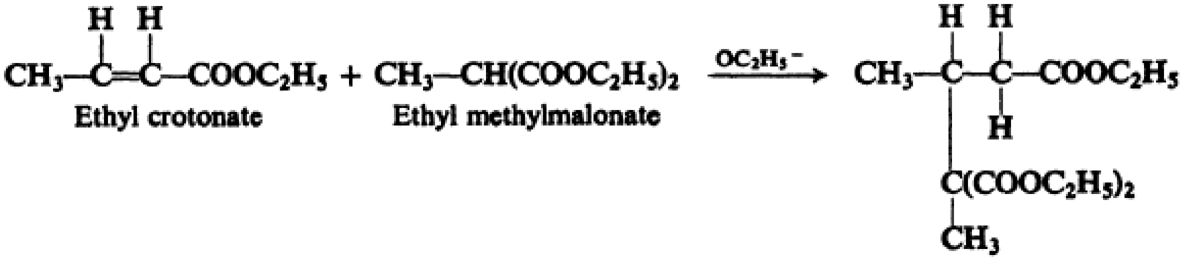
α,β-Unsaturated carbonyl compound
Conjugated system

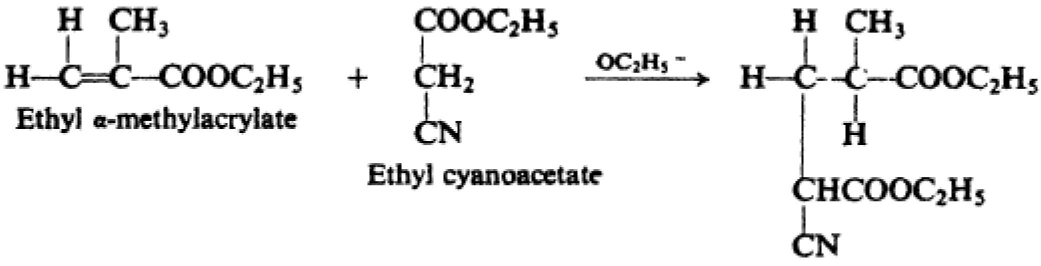
As a result of conjugation, such compounds possess not only the properties of the individual functional groups, but certain other properties besides. In this chapter we shall concentrate on the a,ß-unsaturated compounds, and on the special reactions characteristic of the conjugated system.

The Michael addition:

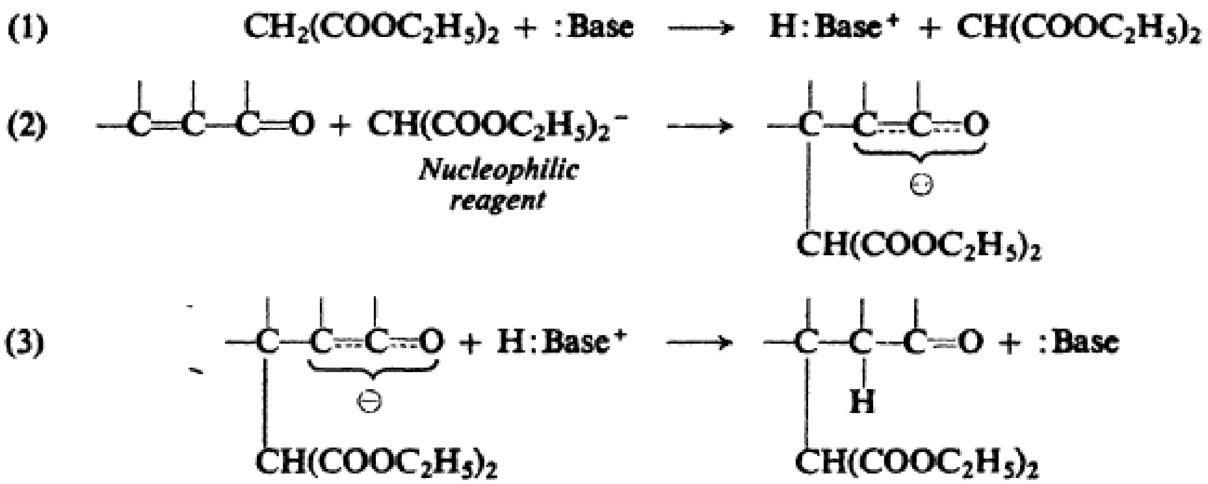






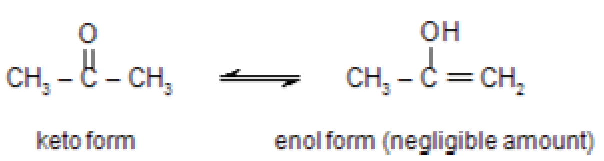


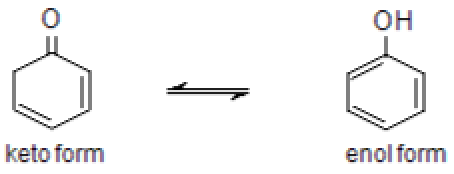
The mechanism:



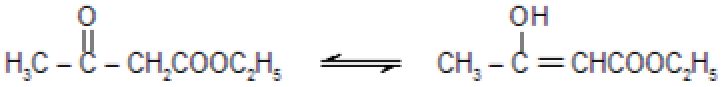
Keto–Enol Tautomerism

Tautomerism Tautomerism may be defined as the phenomenon in which a single compound exists in two readily interconvertible structures that differ markedly in the relative position of at least one atomic nucleus, generally hydrogen. The two different structures are known as tautomers of each other. Sometimes the term tautomerism is also called as desmotropism (Greek desmos-bond; tropos-turn), since the interconversion of the two forms involves a change of bonds or dynamic isomerism as the two forms are in dynamic equilibrium with each other. Other names for tautomerism are kryptomerism, allelotropism or merotropy; however, tautomerism is the most widely accepted term. There are several types of tautomerism of which keto-enol tautomerism is the most important. In this type, one form (tautomer) exists as a ketone while the other exists as an enol. The two simplest examples are of acetone and phenol.





However, the most widely studied example of keto-enol tautomerism is that of acetoacetic ester (ethyl acetoacetate).



$$H_3C-\overset{\overset{O}{\parallel}}{C}-CH_2COOC_2H_5 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CHCOOC_2H_5$$

keto form (92.3 %) enol form (7.7 %)

The two forms are readily interconvertible by acid or base catalysts, and under ordinary conditions surface of the glass is sufficient to catalyse the interconversion. The exact composition of the equilibrium depends upon the nature of the compound, solvent, temperature, etc. The conversion of a keto form into enol from is known as **enolisation.** The two forms of acetoacetic ester have been isolated under suitable conditions. Keto-enol tautomerism in acetoacetic ester is proved by the fact that under ordinary conditions the compound gives the properties of the ketonic group as well as that of the enolic group.

$$H_3C-\overset{\overset{O}{\parallel}}{C}-CH_2COOC_2H_5 \rightleftharpoons H_3C-\overset{\overset{OH}{|}}{C}=CHCOOC_2H_5$$

ketonic form enolic form

(note the presence of a ketonic group) (note the presence of a double bond and acidic –OH group)

Note that in all the examples of keto-enol tautomerism the two isomeric forms are interconvertible by the migration of a proton from one atom (carbon) to the other with the simultaneous shifting of bonds.

Grignard reagents

Organic Compounds in which alkyl or aryl groups are directly attached to a metal are called organometallic compounds. Many metals form organometallic compounds. For example,

CH_3Li C_2H_5MgI
$(C_2H_5)_2Zn$ $Pb(C_2H_5)_4$

Organomagnesium halides are called Grignard reagents. They are named after the French Chemist, Victor Grignard, who discovered them and developed them as synthetic reagents.

Preparation of methylmagnesium iodide

Methylmagnesium iodide is prepared by the action of methyl iodide on magnesium suspended in dry ether. All the reagents used should be pure and dry. Dry magnesium ribbon is washed with ether to remove grease and then with dilute acid to remove any oxide and then dried. The ether is kept absolutely dry by distilling over metallic sodium to make it free from ethanol. Methyl iodide is dried over anyhydrous calcium chloride and then distilled over phosphorus pentoxide.

Clean dry magnesium is placed in dry ether in a flask fitted with reflex condenser. Pure dry methyl iodide is added gradually. When the reaction starts, the ether becomes cloudy and also begins to boil. It is necessary to cool the mixture. If the reaction does not start, one or two crystals of iodine are dropped into the flask. When the reaction is complete, a clear solution of methyl magnesium iodide is obtained. this is used as such in all the reactions.

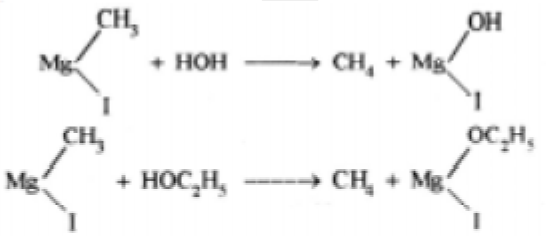
$$CH_3I + Mg \xrightarrow[\text{ether}]{\text{dry}} CH_3MgI$$

Synthetic uses of methylmagnesium iodide

Grignard regents are generally one of the most reactive compounds. These are used for the synthesis of a variety of organic compounds. The following reactions illustrate the synthetic uses of methylmagnesium iodide.

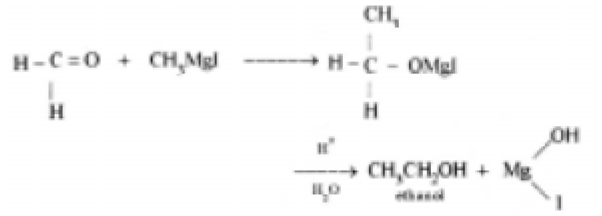
1. Preparation of alkanes

Methylmagnesium iodide undergoes double decomposition with water and alcohol to produce alkanes.



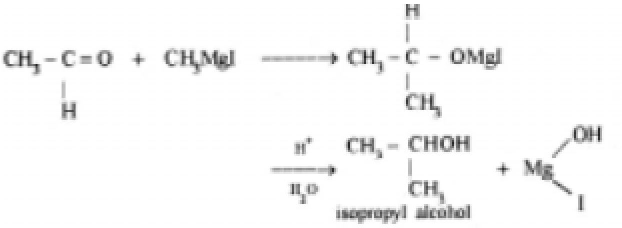
2. Preparation of primary alcohols

Formaldehyde reacts with methylmagnesium iodide to give addition product which on hydrolysis yield primary alcohol.



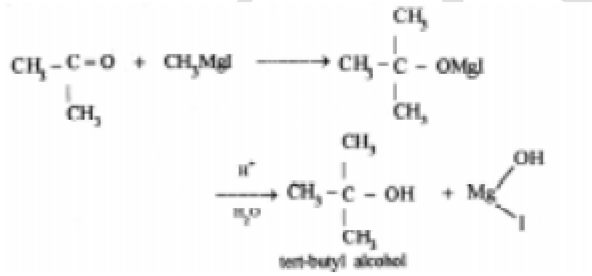
3. Preparation of secondary alcohols

When methylmagnesium iodide is treated with any aldehyde other than formaldehyde, a secondary alcohol is obtained.



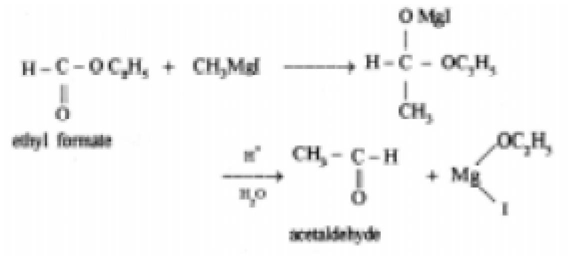
4. Preparation of tertiary alcohols

Methylmagnesium iodide reacts with ketones to give an addition compound which on hydrolysis yield tertiary alcohols.

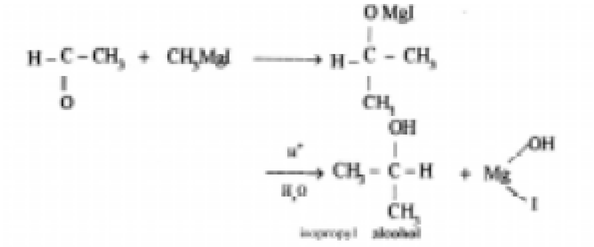


5. Preparation of aldehydes

An aldehyde is prepared by treating one molecule of methylmagnesium iodide with one molecule of ethyl formate.

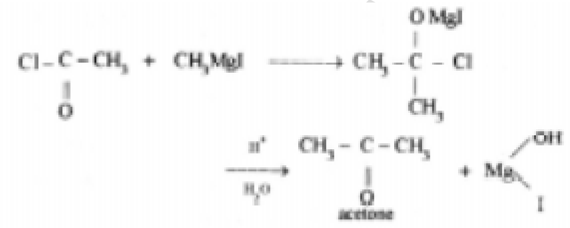


A secondary alcohol is obtained if methylmagnesium iodide is in excess. Aldehyde produced reacts further to give secondary alcohol.



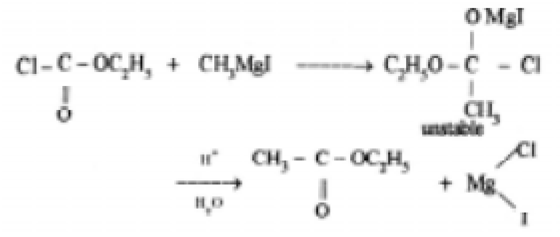
6. Preparation of ketones

Methylmagnesium iodide reacts with acid chlorides to form ketones.



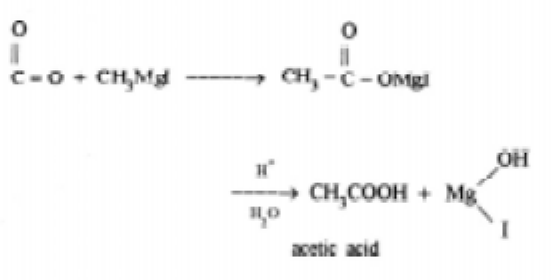
7. Preparation of esters

Methylmagnesium iodide reacts with ethyl chloroformate to form higher esters



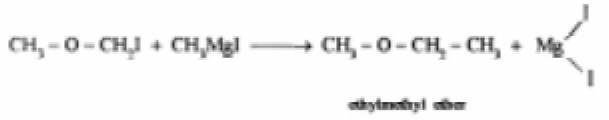
8. Preparation of acids

Methylmagnesium iodide reacts with solid carbon dioxide to give addition product which on hydrolysis in the presence of acid yields carboxylic acid.



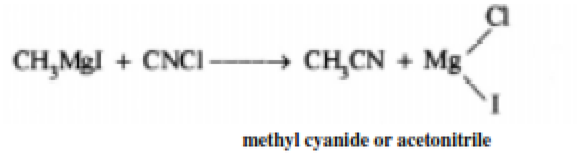
9. Preparation of ethers

When a monohalogen derivative of an ether is treated with methylmagnesium iodide, ether homologue is obtained.



10. Preparation of alkyl cyanide

Methylmagnesium iodide reacts with cyanogen chloride to form an alkyl cyanide or alkyl nitrile.



POSSIBLE QUESTIONS

PART B (2 Marks Questions)

1. What are organometallic compounds? Give two examples.
2. Give the preparation of Anisole.
3. What are epoxides? Why are epoxides more reactive than ethers?
4. Give the preparations of secondary alcohol using Grignard reagents
5. How will you convert malonic ester into acetoacetic ester?

PART C (8 Marks Questions)

1. Give the following preparations using Grignard reagents
(i) primary alcohol (ii) secondary alcohol (iii) tertiary alcohol (iv) aldehyde

2. Outline the synthesis of ethers by Williamson’s method. Explain its mechanism.

3. Discuss the laboratory preparation of Grignard reagents. How does it react with
(i) acetaldehyde (ii) carbon dioxide?

4. Identify X, Y and Zin the following sequence of reactions:

(i) $C_2H_5OH \xrightarrow{Na} X \xrightarrow{C_2H_5I} Y \xrightarrow{Cl_2\,(h\nu)} Z$

(ii) $C2H5ONa \xrightarrow{C_2H_5I} X \xrightarrow[(373\text{ K})]{\text{Excess of HBr}} Y \xrightarrow{\text{Alc. KOH}} Z$

(iii) $C_2H_5OC_2H_5 \xrightarrow[\text{Pressure}]{\text{Dil } H_2SO_4} X \xrightarrow{\text{Conc. } H_2SO_4} Y \xrightarrow{HBr} Z$

5. Write the reactions of epoxide with
(i) HCl and HCN (ii) C_2H_5OH and NH_3 (iii) CH_3MgI and $LiAlH_4$

6. Define Michael addition. Give its mechanism.

7. What are epoxides? How are they formed? Discuss the mechanism of epoxide formation.

8. Starting from acetoacetic ester, How can you synthesise the following:
(i) n-Butyric acid (ii) Acetylacetone (iii) Crotonic acid

9. What is meant by tautomerism? How can you estimate the proportion of keto-enol forms in a given sample of acetoacetic ester?

10. Outline the preparation and applications of diethyl malonate.

OBJECTIVE QUESTIONS

S. no	Questions	Option A	Option B	Option C	Option D	Answer
1.	Which one of the following Grignard reaction give chiral product	CH3CH2MgBr + CH3CH=O	CH3CH2CH=O + CH3CH2MgBr	C6H5CH2MgBr + HCH=O	CH=CH-CH=O + CH3CH2MgBr	CH3CH2MgBr + CH3CH=O
2.	Ethylene oxide reacts with a G.R. to furnish-	tert-Alcohol	(sec-Alcohol	hydrocarbon	primary alcohol	primary alcohol
3.	Primary alcohol is obtained when Grignard reagent is treated with	ethylene oxide	dimethyl ether	acetone	ethyl acetate	ethylene oxide
4.	The decreasing order of G.R. formation among following alkyl halides is	CH3X > C2H5X > C3H7X	C3H7X > C2H5X > CH3X	CH3X > C3H7X > C2H5X	C3H7X > C2H6X > CH3X	CH3X > C2H5X > C3H7X
5.	Which one among the following compounds is not an organometallic compound	(C2H5)2Pb	(CH3)3B	CH3MgBr	CH3COONa	CH3COONa
6.	Grignard reagent reacts with ketone followed by acid hydrolysis to give	primary alcohol	secondary alcohol	Tert-alcohol	None of these	Tert-alcohol
7.	Tertiary alcohol is obtained when Grignard reagent is treated with	aldehyde	acid	ester	ketone	ketone
8.	Which one of the following alkyl halides cannot be used for the preparation of Grignard reagent	CH3Br	C6H5CH2Cl	HOCH2CH2Cl	CH2=CH-CH2Cl	HOCH2CH2Cl
9.	Dibenzyl ether reacts with phenyl lithium followed by acid hydrolysis to form benzyl phenyl carbinol. This reaction is known as	reformatsky reaction	witting rearrangement	wolff rearrangement	Williamson synthesis	witting rearrangement
10.	Which one of the following combination will be suitable for the preparation of	(CH3)2CHLi +	(CH3)2CHMgX +	(CH3)CHMgX +	(CH3)CHMgX +	(CH3)2CHLi +

	[(CH3)2CH]3C-OH	[(CH3)2CH]2C=O	[(CH3)2CH]2C=O	[(CH3)2CH]2C=O	[(CH3)CH]2C=O	[(CH3)2CH]2C=O
11.	Ethyl bromoacetate reacts with acetonitrile in presence of zinc to form addition product which on hydrolysis gives acetoacetic ester. This reaction is known as	reformatsky reaction	witting rearrangement	wurtz reaction	gilman synthesis	reformatsky reaction
12.	Alky lithium in excess reacts with CO2 followed by acid hydrolysis to give	carboxylic acid	ketone	β-ketoacid	none of these	ketone
13.	Alkyl lithium in excess reacts with------------ followed by acid to give ketone.	CO	CO_2	SO_2	NO_2	CO_2
14.	CO_2 is reacting with an excess of alkyl lithium to form	carboxylic acid	β-ketoacid	ester	ketone	ketone
15.	Trimethyl chlorosilane can be used for the protection of	ether group	carbonyl group	primary alcoholic group	ester group	primary alcoholic group
16.	Which metal-carbon bond will be most ionic	C-Mg	C-Zn	C-Li	C-Cd	C-Li
17.	What is the hybridization state of Zn in dialkyl zinc compounds	sp1	sp2	sp3	Unhybridized	sp1
18.	Which one of the following organometallic compound react with ethylene to give a polymer	RMgX	R2Zn	R2CuLi	R-Li	R-Li
19.	Which one of the following organometallic compound react with di isopropyl ketone to give tert-alcohol containing bulky tri-isopropyl group?	(CH3)2CH-MgX	(CH3)2CHLi	[(CH3)2CH]2Zn	R2CuLi	(CH3)2CHLi
20.	Which one of the following organometallic	CH3MgBr	(CH3CH2)2Zn	BrCH2COOC2H5	C2H5Li	BrCH2COOC2H5

	compound can be used to synthesis citric acid from oxalacetic ester?					
21.	The reaction of a sodium alkoxide with an alkyl halide is called	wurtz-fitting reaction	Perkin reaction	Williamsons synthesis	aldol condensation	Williamsons synthesis
22.	Ethers are stored in brown bottles. This is because on exposure to air and light ethers are converted to	peroxide	oxonium ions	ozonides	electrophiles	peroxide
23.	Which of the following reagents readily react with ethyl methyl ether?	NaOH	Conc HI	KMnO4	H2O	Conc HI
24.	Diethyl ether on heating with excess concentrated HI gives	methyl iodide	isopropyl iodide	ethyl iodide	n-propyl iodide	ethyl iodide
25.	Ethanol is isomeric with	dimethyl ether	ethanol	diethyl ether	propanone	dimethyl ether
26.	Diethyl ether reacts with sodium metal to give	ethanol	sodium ethoxide	ethanol	nothing happens	nothing happens
27.	Diethyl ether and methyl propyl ether are	conformational isomer	metamers	geometrical isomers	enantiomers	metamers
28.	Ethyl alcohol reacts with concentrated H2SO4 at 140 °C to form	acetone	ethylene	diethyl ether	acetic acid	diethyl ether
29.	Diethyl ether reacts with excess of hot concentrated HI to form	CH3CH2I + CH3CH2OH	only CH3CH2OH	CH3CH2OH + CH2=CH2	only CH3CH2I	only CH3CH2I
30.	Ethylene oxide reacts with ammonia to give	1-aminoethanol	ethylamine	2-aminoethanol	acetamide	2-aminoethanol
31.	Ethylene oxide reacts with HBr to give	1-bromoethanol	ethyl bromide	2-bromoethanol	ethylene glycol	2-bromoethanol

32.	The following compounds have identical molecular weights. Which would have the lowest boiling point?	1-methoxypropane	1-butanol	1,1-dimethylethanol	2-butanol	1-methoxypropane
33.	The compound with the lowest boiling point is	H2O	CH2CH3OH	CH3OCH3	CH3CH2CH3	CH3CH2CH3
34.	The product of the reaction of ethylene oxide with acidic methanol is	CH3OCH2CH2OH	CH3CH2CH2OH	HOCH2CH2OH	CH3CH2OCH2CH3	CH3OCH2CH2OH
35.	Cyclic ethers with three-membered ring are called	lactonea	oxiranes	alkoxides	epoxy resins	oxiranes
36.	Williamson ether synthesis is an example of substitution known as	electrophilic	nucleophilic	free redical	none of these	nucleophilic
37.	Ethers are basic, as they form salts with strong acid which are known as	oxonium satls	hydronium salts	hydrogen sulphates	hydrogen peroxide	oxonium satls
38.	When ethyl methy ether is treated with HI, the resulting iodide will be	ethyl iodide	methyl iodide	both ethyl and methyl iodide	hydrogen iodide	methyl iodide
39.	Halohydrins when treated with a base form epoxides. This is an example of nucleophilic substitution involving	SN1 reaction	neighbouring group participation	SNi	SN2	neighbouring group participation
40.	Ethylene oxide undergoes molecular rearrangement when heated to give	acetaldehyde	vinyl alcohol	benzaldehyde	acetophenone	acetaldehyde
41.	In the reactions of aldehydes and ketones, the carbonyl carbon is mostly attacked by	electrophiles	free radicals	nucleophiles	carbenes	nucleophiles
42.	Base catalysed condensation of two ester molecules to form an alcohol and β- keto ester is called	claisen condensation	corey-house reaction	aldol condensation	transesterification	claisen condensation

43.	Ethyl acetoacetate undergoes acid-hydrolysis with dilute HCl to form	acetoacetic acid	succinic acid	acetic acid	adipic acid	acetoacetic acid
44.	The ethyl derivative of acetoacetic ester on basic-hydrolysis gives	acetic acid	acetic acid and propionic acid	propionic acid	acetic acid and n-butyric acid	acetic acid
45.	Ethyl acetate on heating with sodium ethoxide gives	ethyl acetoacetate	sodium acetate	ethyl alcohol	diethyl ether	ethyl acetoacetate
46.	When ethyl acetoacetate is subjected to ketonic hydrolysis, the ketone obtained is	dimethyl ketone	methyl ethyl ketone	diethyl ketone	methyl n-propyl ketone	diethyl ketone
47.	Ethyl acetoacetate reacts with phenylhydrazine to give	antipyrine	aspirin	4-methyl uracil	DDT	antipyrine
48.	Keto-enol tautomerism is shown by	benzaldehyde	acetone	benzophenone	acetic acid	acetone
49.	Diethyl malonate reacts with urea to give	butyric acid	barbituric acid	glutaric acid	mandelic acid	barbituric acid
50.	The reactive methylene group is a methylene group present between	carbonyl group	electron donating group	hydroxyl group	amino group	carbonyl group
51.	Keto-enol tautomerism arises due to	migration of proton	migration of keto group	migration of enolic group	migration of hydroxyl grouo	migration of proton
52.	Tautomers must have the following	same functional group	dynamic equilibrium between functional isomers	same position of double bond	static equilibrium between functional isomers	dynamic equilibrium between functional isomers
53.	Ethyl acetoacetate may be used to prepare	Carboxylic acid	amino acids	aldehyde	acetaldehyde	Carboxylic acid
54.	Which of the following is not a reaction of enolic form of acetoacetic ester?	colouration with $FeCl_3$	addition of bromine	reaction with HCN	acetylation	reaction with HCN
55.	The enolic form of acetoacetic ester as	one extra double bond	one extra lone pair	one less double	both have same number of σ, π	both have same number of σ, π

	compared to ketonic form contains			bond	bonds and lone pairs	bonds and lone pairs
56.	Ethyl acetoacetate is also called as	acetoacetic ester	acetic acid	adipic acid	acetone	acetoacetic ester
57.	Diethyl malonate is also called	malonic acid	malonic ester	crotonic acid	adipic acid	malonic ester
58.	The reaction used for the preparation of ethyl acetoacetate starting from ethyl acetate is known as	cannizzaro reaction	claisen-schmidt reaction	michael condensation	claisen ccondensation	claisen ccondensation
59.	Reaction of ethyl acetoacetate with pheyl hydrazine forms	methyl isoxazolone	3-methyl-1-phenylpyrazolone	methyl isoxapyrazolone	dimethyl phenyl oxazolone	3-methyl-1-phenylpyrazolone
60.	Reaction of sodium ethoxide with malonic ester forms a	resonance stabilised anion	resonance stabilised cation	resonance stabilised free radical	resonance stabilised electrophile	resonance stabilised anion

Syllabus

Acids and their Derivatives:

General methods of preparation, physical properties and reactions of monocarboxylic acids, Effect of substituents on acidic strength. Typical reactions of dicarboxylic acids, hydroxy acids and unsaturated acids.

Preparation and reactions of acid chlorides, anhydrides, esters and amides; Comparative study of nucleophilicsustitution at acyl group -Mechanism of acidic and alkaline hydrolysis of esters, Claisen condensation, Dieckmann and Reformatsky reactions, Hofmann- bromamide degradation and Curtius rearrangement.

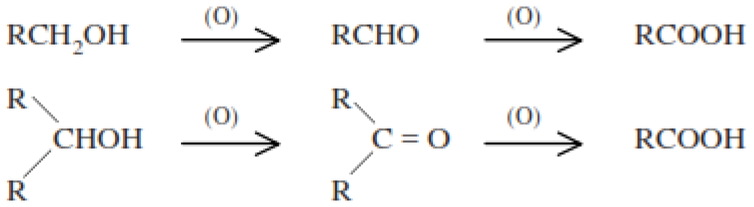
Carboxylic acids

Organic compounds containing the carboxyl group, arecalled carboxylic acids. The acid may be monocarboxylic acid, if it containsone –COOH group ; a dicarboxylic acid if it contains two –COOH groups ;a tricarboxylic acid if it contains three –COOH groups etc.

The aliphatic mono carboxylic acids are called fatty acids and the higher members like Stearic acid ($C_{17}H_{35}COOH$), palmitic acid (CCOOH),oleic acid ($C_{16}H_{33}COOH$) etc., occur as glycerides in oils and fats.O— $C_{15}H_{31}OH$

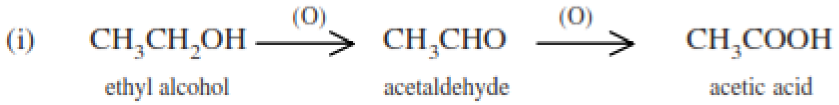
Preparation of monocarboxylic acids:

1. Oxidation: Carboxylic acids are prepared by the oxidation of alcohols,aldehydes or ketones with $K_2Cr_2O_7$ and H_2SO_4. Primary alcohol is firstoxidised to aldehyde and then to carboxylic acid. On the otherhand secondary alcohols are first oxidised to ketone and then to acid with lesser number of carbon atoms.

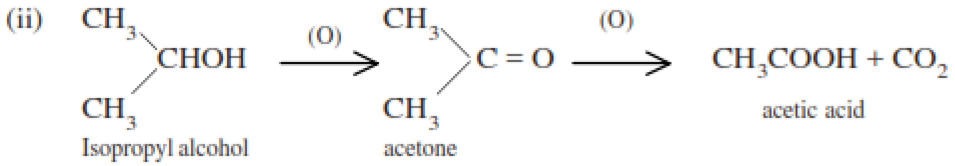


$$RCH_2OH \xrightarrow{(O)} RCHO \xrightarrow{(O)} RCOOH$$

$$R_2CHOH \xrightarrow{(O)} R_2C=O \xrightarrow{(O)} RCOOH$$



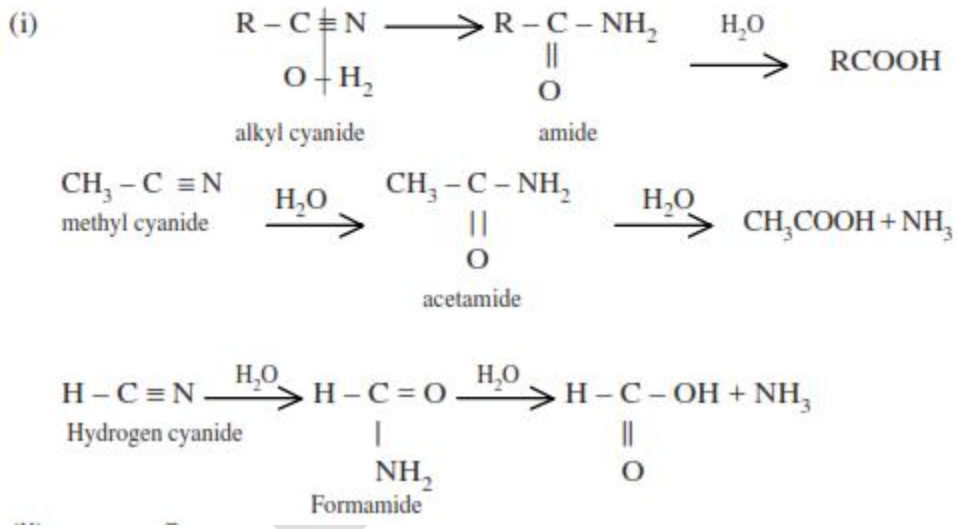
$$\text{(i)}\quad CH_3CH_2OH \xrightarrow{(O)} CH_3CHO \xrightarrow{(O)} CH_3COOH$$



$$\text{(ii)}\quad (CH_3)_2CHOH \xrightarrow{(O)} (CH_3)_2C=O \xrightarrow{(O)} CH_3COOH + CO_2$$

2. Hydrolysis methods :

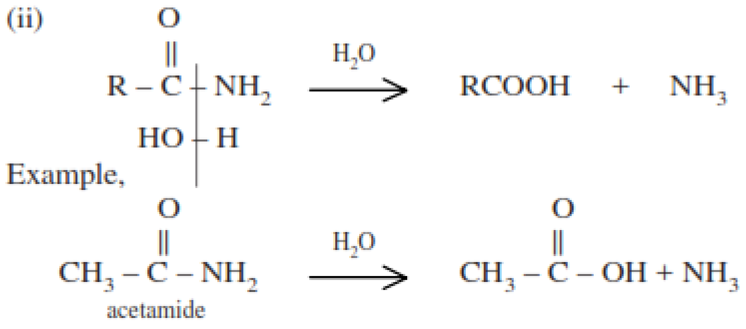
(a) Hydrolysis of cyanides, amides and esters : Alkyl cyanides, amides, esters are hydrolysed with aqueous acid or alkali to give carboxylic acid.



$$\text{(i)}\quad R-C\equiv N \longrightarrow R-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O} RCOOH$$

$$CH_3-C\equiv N \xrightarrow{H_2O} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O} CH_3COOH+NH_3$$

$$H-C\equiv N \xrightarrow{H_2O} H-\underset{NH_2}{\underset{|}{C}}=O \xrightarrow{H_2O} H-\overset{\displaystyle O}{\overset{\|}{C}}-OH+NH_3$$

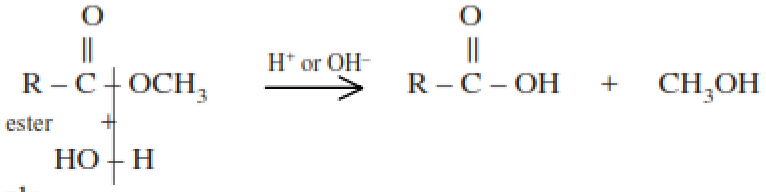


$$\text{(ii)}\quad R-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O} RCOOH + NH_3$$

Example,

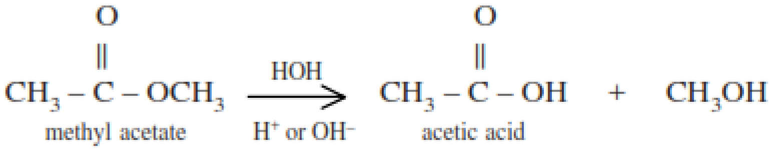
$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_2O} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH+NH_3$$

(iii)



$$\underset{\text{ester}}{R-\overset{\overset{O}{\|}}{C}-OCH_3} + HO-H \xrightarrow{H^+ \text{ or } OH^-} R-\overset{\overset{O}{\|}}{C}-OH + CH_3OH$$

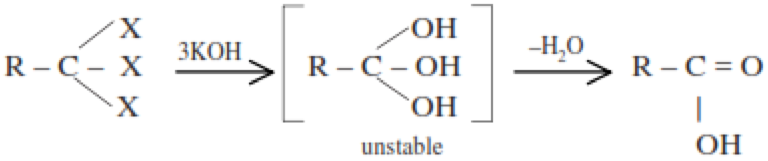
Example,



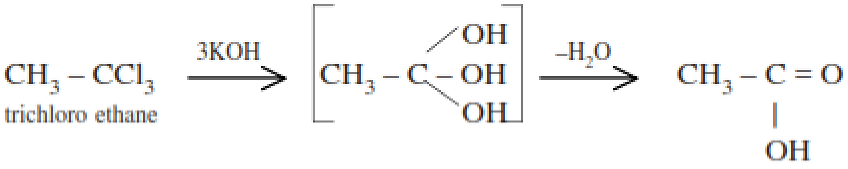
$$\underset{\text{methyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-OCH_3} \xrightarrow[H^+ \text{ or } OH^-]{HOH} \underset{\text{acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + CH_3OH$$

(acid or alkaline hydrolysis)

(b) Hydrolysis of trihalides : By the hydrolysis of trihalides containing three halogen atoms attached to the same carbon atom, carboxylic acids are formed.

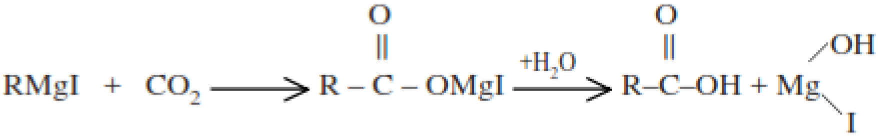


$$R-CX_3 \xrightarrow{3KOH} \underset{\text{unstable}}{\left[R-C(OH)_3\right]} \xrightarrow{-H_2O} R-\underset{\underset{OH}{|}}{C}=O$$



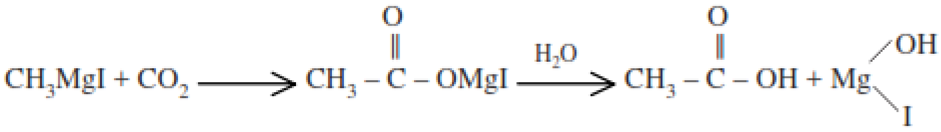
$$\underset{\text{trichloro ethane}}{CH_3-CCl_3} \xrightarrow{3KOH} \left[CH_3-C(OH)_3\right] \xrightarrow{-H_2O} CH_3-\underset{\underset{OH}{|}}{C}=O$$

3. From Grignard reagent :



$$RMgI + CO_2 \longrightarrow R-\overset{\overset{O}{\|}}{C}-OMgI \xrightarrow{+H_2O} R-\overset{\overset{O}{\|}}{C}-OH + Mg\begin{matrix}OH\\I\end{matrix}$$

Methyl magnesium iodide with carbondioxide gives acetic acid.



$$CH_3MgI + CO_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OMgI \xrightarrow{H_2O} CH_3-\overset{\overset{O}{\|}}{C}-OH + Mg\begin{matrix}OH\\I\end{matrix}$$

Formic acid cannot be prepared by Grignard reagent since the acid contains only one carbon atom.

Preparation of formic acid

4. From CH3OH or HCHO

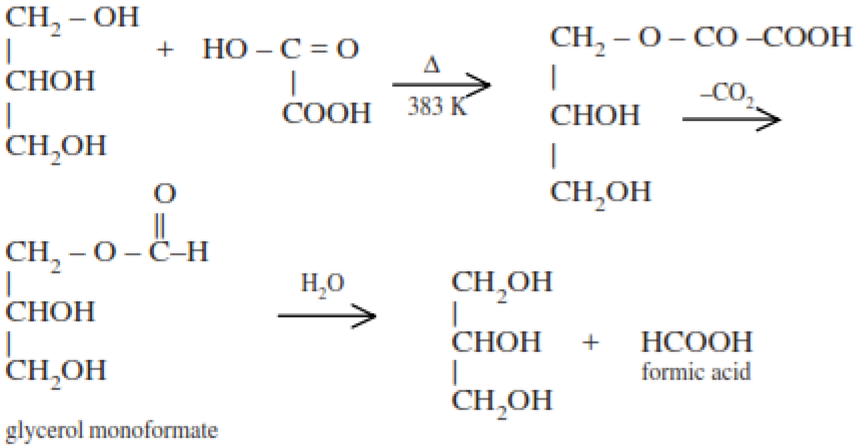
By the oxidation of methyl alcohol or formaldehyde with K2Cr2O7/H2SO4

$$CH_3OH \xrightarrow{3(O)} HCOOH$$

$$HCHO \xrightarrow{(O)} HCOOH$$

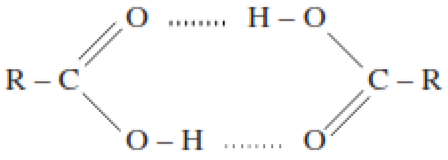
5. From glycerol

By heating glycerol with oxalic acid at 373 K – 383 K



Properties

1. Lower members are pleasant smelling liquids with higher boiling points. The higher members are waxy solids. The higher boiling points are explained on the basis of **association by hydrogen bonding.**



2. The first few members are highly soluble in water and higher members are insoluble. This can also be explained on the basis of hydrogen bonding between acids and water. With higher members the size of the alkyl group is increased which repels the hydrophilic groups.

Chemical Properties:

1. Fatty acids react with alkalies to form salt and water and liberates CO2 with carbonates (stronger than carbonic acid).

$$CH_3COOH + NaOH \longrightarrow \underset{\text{(sodium acetate salt)}}{CH_3COONa} + H_2O$$

$$2\,HCOOH + 2Na_2CO_3 \longrightarrow \underset{\text{(sodium formate)}}{2\,HCOONa} + H_2O + CO_2$$

2. They liberate hydrogen, when react with electropositive metals like zinc or magnesium.

$$2CH_3COOH + Zn \longrightarrow \underset{\text{(zinc acetate)}}{(CH_3COO)_2\,Zn} + H_2$$

$$2HCOOH + Mg \longrightarrow \underset{\text{(magnesium formate)}}{(HCOO)_2\,Mg} + H_2$$

3. **Reaction involving - hydroxyl group :** carboxylic acid reacts with alcohols in presence of mineral acid as catalyst and forms esters. This reaction is called **esterification.**

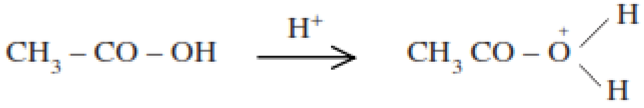
$$CH_3COOH + C_2H_5OH \xrightarrow{H^+} \underset{\text{(ethyl acetate)}}{CH_3COOC_2H_5} + H_2O$$

$$HCOOH + CH_3OH \xrightarrow{H^+} \underset{\text{(methyl formate)}}{HCOOCH_3} + H_2O$$

Mechanism of esterification

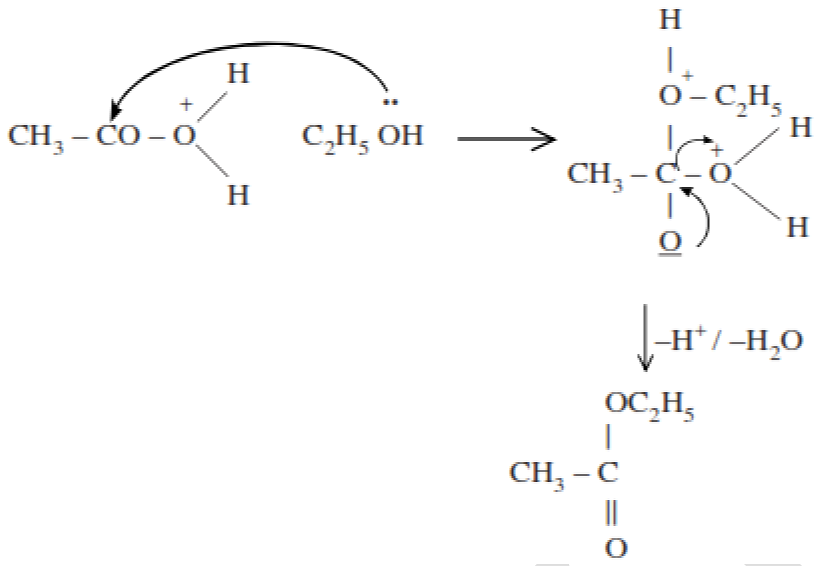
Protonation of the –OH group of the acid, enhances the nucleophilic attack by alcohol to give the ester.

Step 1. Protonation of carboxylic acid



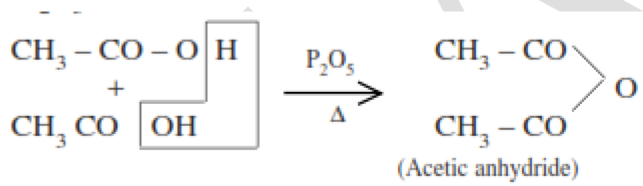
$$CH_3-CO-OH \xrightarrow{H^+} CH_3\,CO-\overset{+}{O}\begin{matrix}\diagup H\\ \diagdown H\end{matrix}$$

Step 2. Attack by nucleophile.

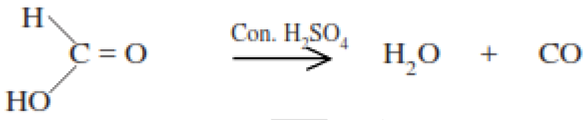


4. Dehydration

Except formic acid others undergo intermolecular dehydration on heating with P2O5 forming anhydride.

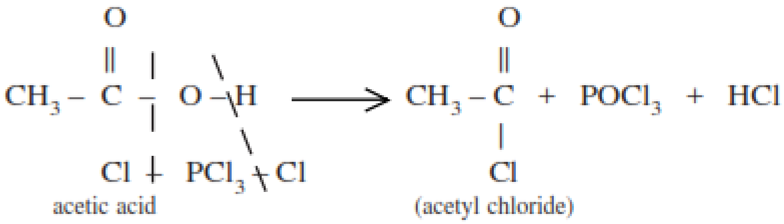


HCOOH on dehydration forms carbon monoxide.



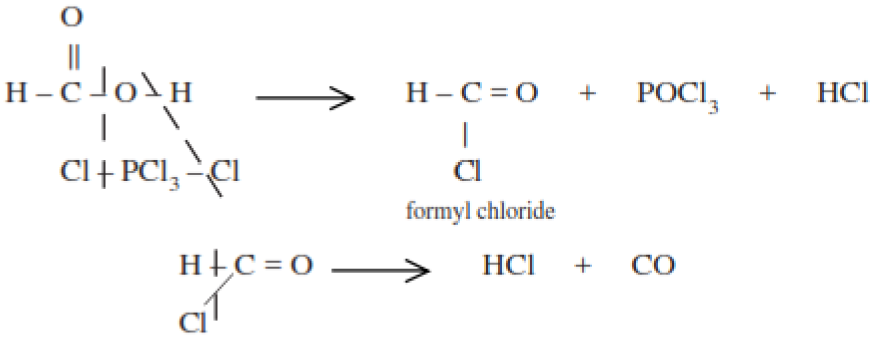
5. With phosphorous pentachloride or thionyl chloride.

(i) Acid chloride is formed.

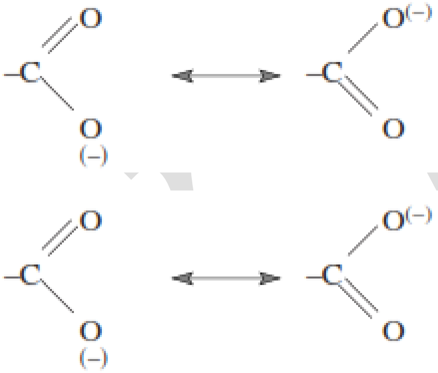


(ii) Formic acid forms formyl chloride.

Formyl chloride being unstable decomposes to carbon monoxide and hydrogen chloride.



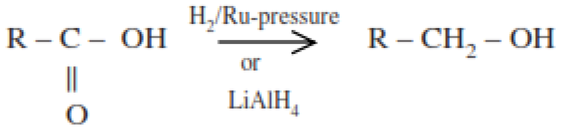
The carboxyl group is involved in resonance.



Hence reactions characteristic of >**C=O is almost absent with acids.** They do not form addition product with HCN, N2H4 etc.

6. Reduction

(i) Carboxylic acid group is not reduced easily. But it is reduced to primary alcoholic group by LiAlH4 or H2/Ru under pressure. This reaction works under higher pressure.

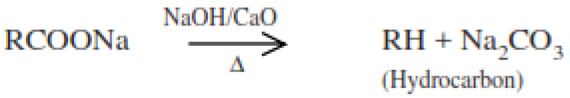


$$R-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[\text{or}\ \text{LiAlH}_4]{H_2/\text{Ru-pressure}} R-CH_2-OH$$

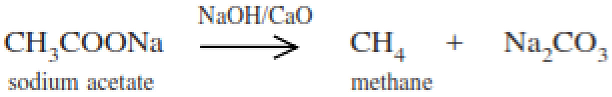
(ii) Heating with HI/P converts the carboxylic acid to alkane.

$$CH_3COOH \xrightarrow[\Delta]{HI/P} CH_3-CH_3$$

7. **Decarboxylation :** When anhydrous sodium salt of carboxylic acids are heated with sodalime, carboxyl group is removed with the formation of hydrocarbon containing one carbon atom less.

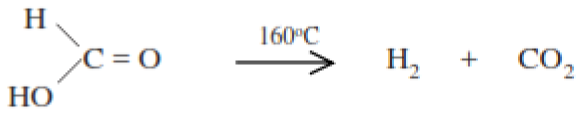


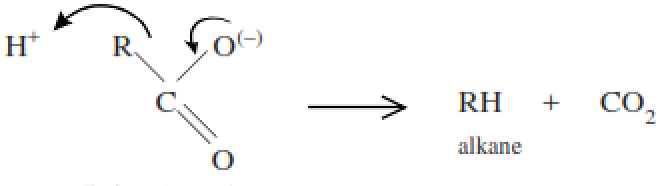
$$RCOONa \xrightarrow[\Delta]{NaOH/CaO} \underset{\text{(Hydrocarbon)}}{RH} + Na_2CO_3$$



$$\underset{\text{sodium acetate}}{CH_3COONa} \xrightarrow{NaOH/CaO} \underset{\text{methane}}{CH_4} + Na_2CO_3$$

Formic acid gets decarboxylated on heating.

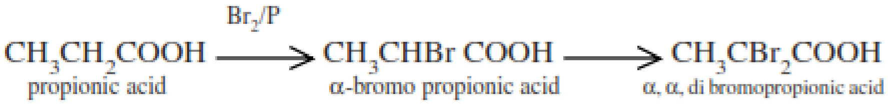




Carboxylate anion

8. Halogenation:

(i) Fatty acids having a-hydrogen atoms, can be **converted** to a-**halo acids** by halogen in presence of **halogen carrier** like red phosphorous.

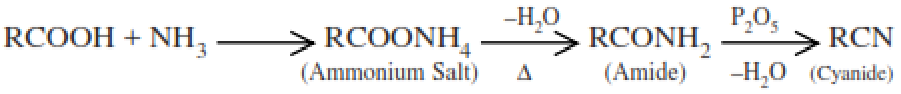


$$\underset{\text{propionic acid}}{CH_3CH_2COOH} \xrightarrow{Br_2/P} \underset{\alpha\text{-bromo propionic acid}}{CH_3CHBr\,COOH} \longrightarrow \underset{\alpha,\,\alpha,\text{ di bromopropionic acid}}{CH_3CBr_2COOH}$$

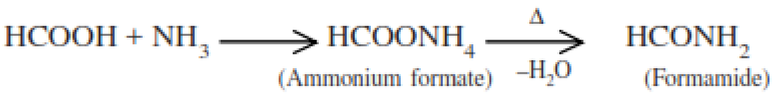
(ii) **HVZ - reaction :** When the halogenation is carried out with halogen and phosphorous trihalide, this reaction is known as **Hell-Volhard Zelinsky** reaction. (HVZ reaction).

$$RCH_2COOH \xrightarrow{Br_2/PBr_3} RCH_2COBr \longrightarrow RCHBrCOBr \xrightarrow{H_2O} RCHBrCOOH$$

9. Reactions with ammonia : Carboxylic acid reacts with NH3 to form ammonium salt which on heating undergoes dehydration to amides, ultimately alkyl cyanide results.

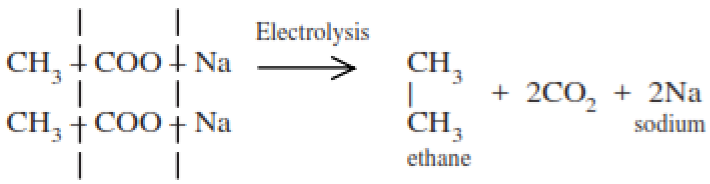


$$\underset{}{RCOOH + NH_3} \longrightarrow \underset{\text{(Ammonium Salt)}}{RCOONH_4} \xrightarrow[\Delta]{-H_2O} \underset{\text{(Amide)}}{RCONH_2} \xrightarrow[-H_2O]{P_2O_5} \underset{\text{(Cyanide)}}{RCN}$$



$$HCOOH + NH_3 \longrightarrow \underset{\text{(Ammonium formate)}}{HCOONH_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{(Formamide)}}{HCONH_2}$$

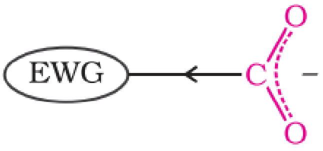
10. **Kolbe's electrolytic reaction :** Electrolysis of concentrated aqueous solution of sodium salt of acids gives hydrocarbon.



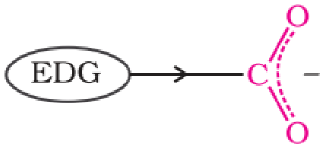
$$\begin{matrix} CH_3 - COO - Na \\ CH_3 - COO - Na \end{matrix} \xrightarrow{\text{Electrolysis}} \underset{\text{ethane}}{\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix}} + 2CO_2 + \underset{\text{sodium}}{2Na}$$

Under this condition Formic acid gives hydrogen.

Effect of substituents on the acidity of Carboxylic Acids



Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid

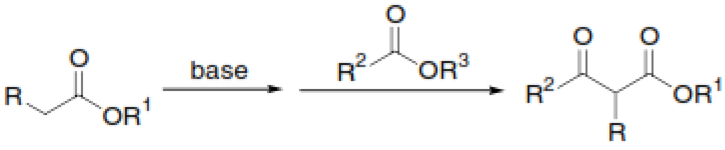


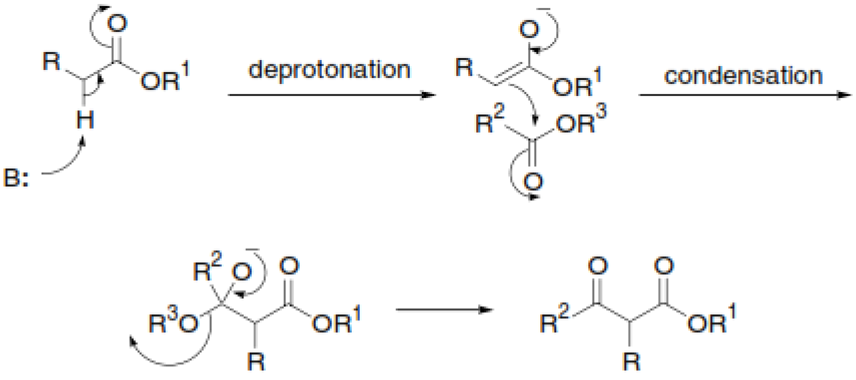
Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

Any factor that stabilizes the anion more than it stabilizes the acid would increase the acidity of carboxylic acids. While any factor that decreases the stability of anion would decrease the acidity of carboxylic acids. Electron withdrawing groups disperse the negative charge and thus stabilize the anion which results in increase in acidity of the carboxylic acids. Electron donating groups intensify the negative charge and the destabilize the anion which results in decrease in acidity of carboxylic acid.

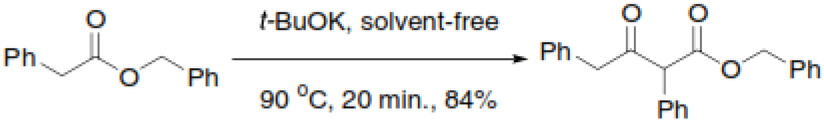
Claisen condensation

Base-catalyzed condensation of esters to afford -keto esters.

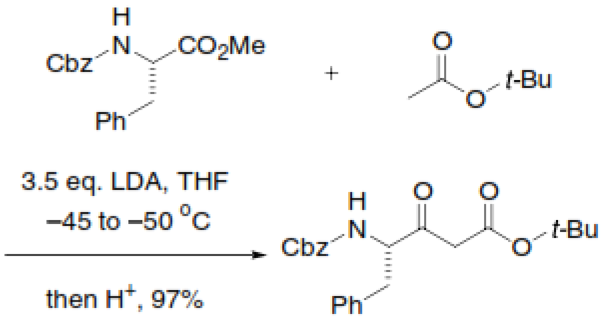




Example 1[9]

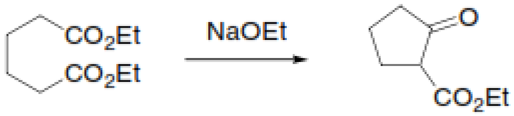


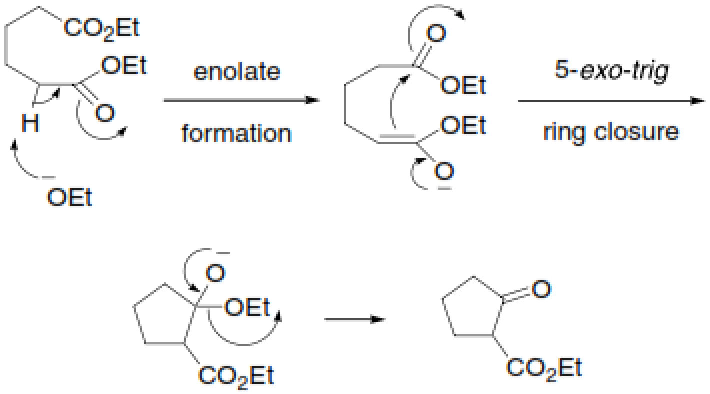
Example 2[12]



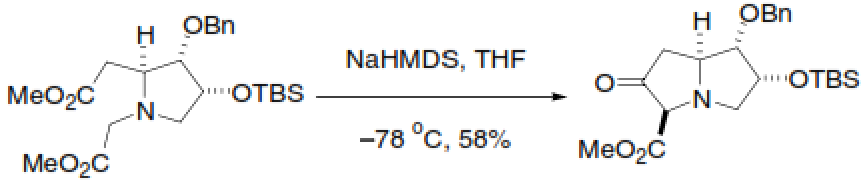
Dieckmann condensation

The Dieckmann condensation is the intramolecular version of the Claisen condensation.

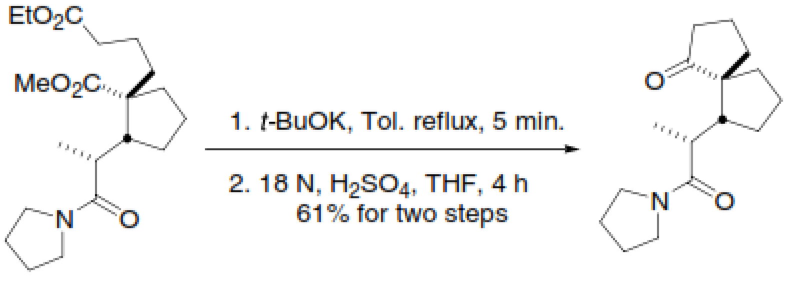




Example 1

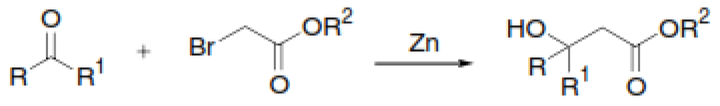


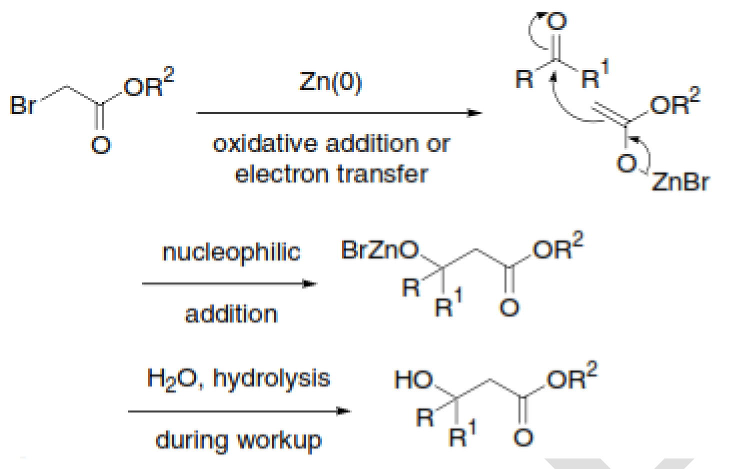
Example 2



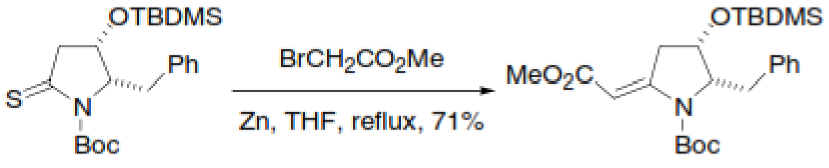
Reformatsky reaction

Nucleophilic addition of organozinc reagents generated from -haloesters to carbonyls.

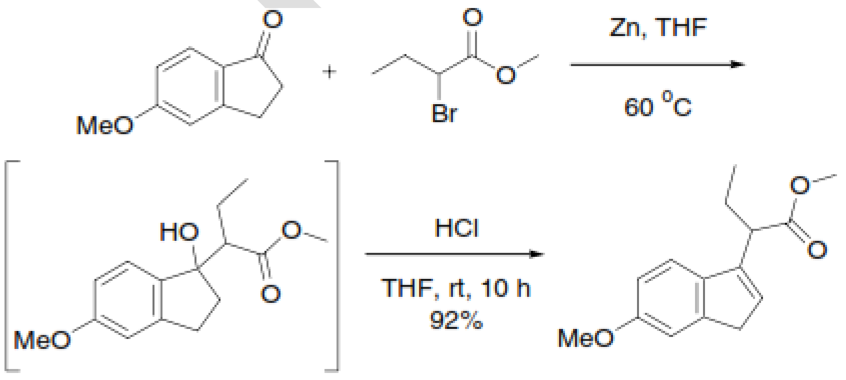




Example 1



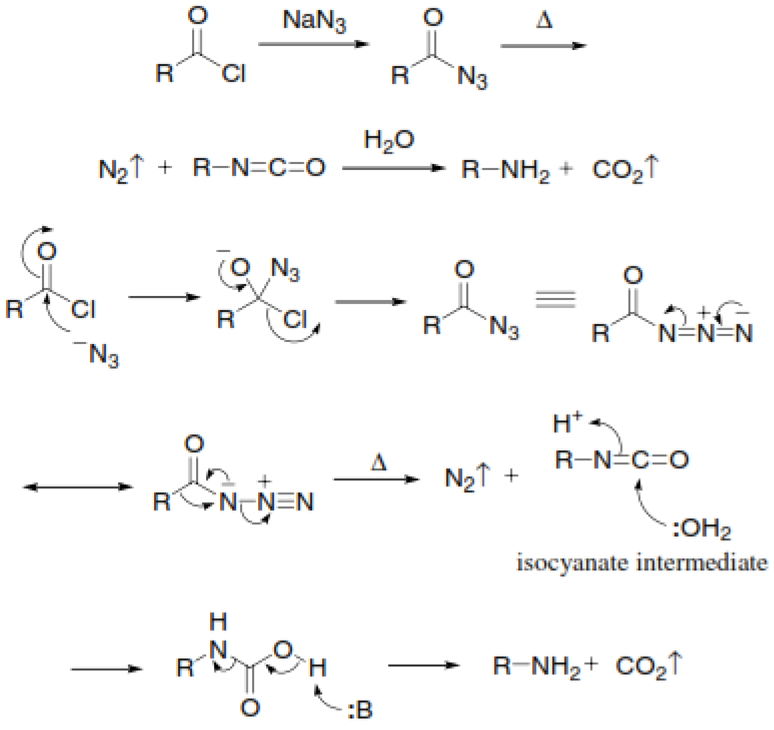
Example 2



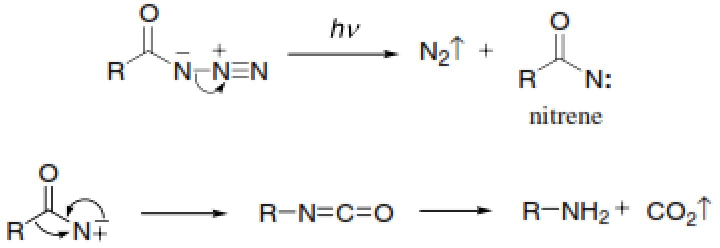
Curtius rearrangement

Thermal or photochemical rearrangement of acyl azides into amines *via* isocyanate intermediates. While the thermal rearrangement is a concerted process, the photochemical rearrangement goes through a nitrene intermediate.

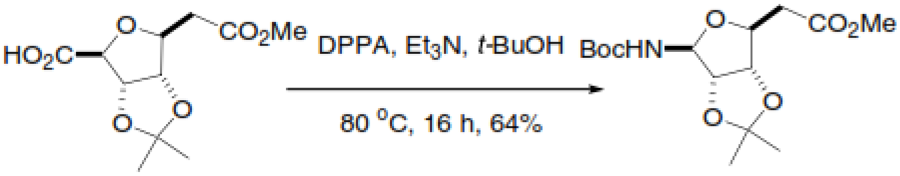
The thermal rearrangement:



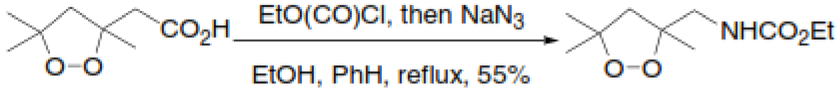
The photochemical rearrangement:



Example 1

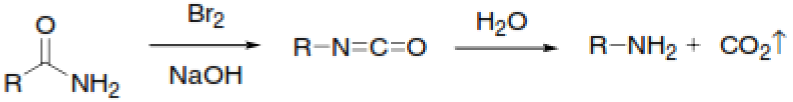


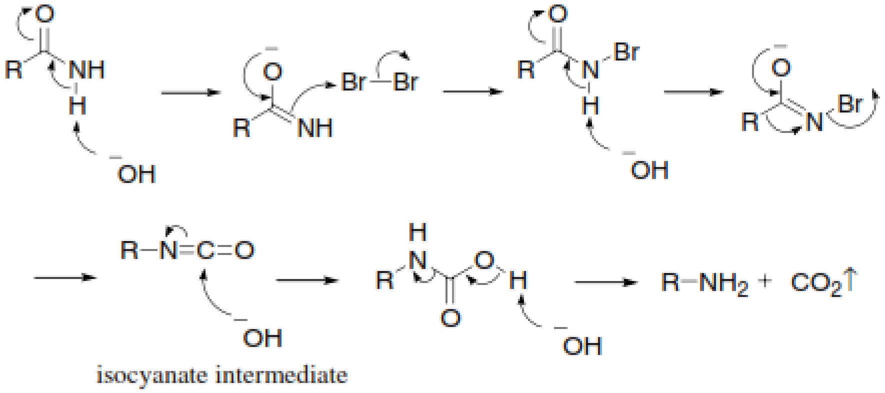
Example 2



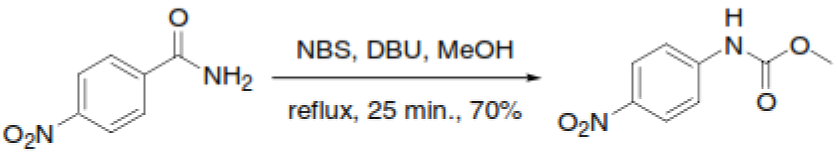
Hofmann rearrangement

Upon treatment of primary amides with hypohalites, primary amines with one less carbon are obtained *via* the intermediacy of isocyanate. Also know as the Hofmann degradation reaction.

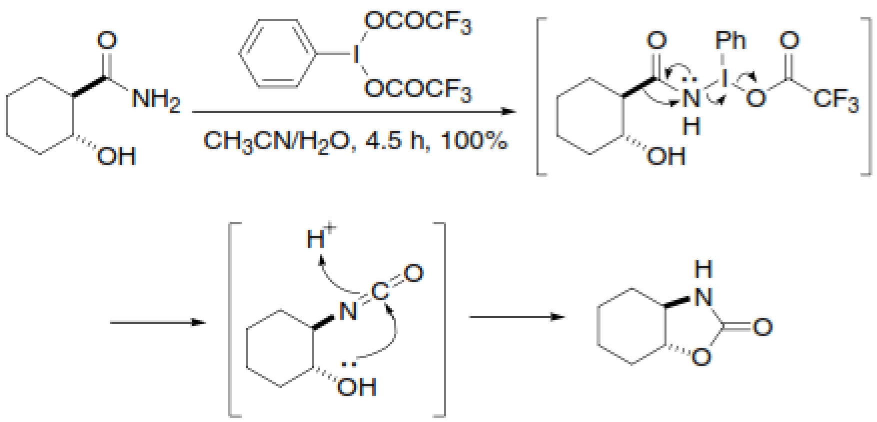




Example 1



Example 2



POSSIBLE QUESTIONS

PART B (2 Marks Questions)

1. Explain why carboxylic acids shows higher boiling point?

2. What is meant by acids?

3. Arrange the following in order of their acidic strength:
   (i) p-nitrobenzoic acid (ii)o-nitrobenzoic acid (iii) m-nitrobenzoic acid

4. Complete the following reactions

   (i) $CH_3COCl + H_2 \xrightarrow{Pd/\ BaSO_4}$

   (ii) $CH3COCl + CH_3COONa \longrightarrow$

5. How will you convert acetamide into methylamine?

PART C (8 Marks Questions)

1. Write short notes on
(i) Kolbe's electrolytic reduction (ii) Hundsdiecker reaction (iii) Hell-Volhard-Zelinsky reaction

2. Describe the effect of substituents on the acidity of an acid.

3.Write the following preparations
(i) Glycolic acid from chloroacetic acid (ii) Lactic acid from a-aminopropionic acid
(iii) Acrylic acid from vinyl magnesium halide (iv) Cinnamic acid from benzaldehyde
(v) Oxalic acid from sodium oxalate (vi) Formic acid from oxalic acid

4. Discus the following properties of amides
(i) Hydrogen bonding (ii) Reactivity (iii) Amphoteric nature

5. What are acid chlorides? How can acetyl chloride can be converted into :
(i) Acetamide (ii) Acetic anhydride (iii) Ethyl acetate (iv) Ethyl methyl ketone

6. Describe the mechanism of acid-catalysed and base-catalysed hydrolysis of esters.

7. (i) What is nucleophilic acyl substitution? Give its mechanism.
(ii) Compare and contrast acyl nucleophilic substitution reactions with alkyl nucleophilic substitution reactions.

8. Discus the mechanism of the following
(i) Curtius rearrangement (ii) Claisen condensation

9. Give the mechanism of the following reaction
(i) Hofmann-bromide degradation (ii) Curtius rearrangement

10. Describe the mechanism of acid-catalysed and base-catalysed hydrolysis of esters.

OBJECTIVE QUESTIONS

S. no	Questions	Option A	Option B	Option C	Option D	Answer
1.	Arrange the following compounds in order of increasing acidity $ClCH_2COOH$, $Cl_2CHCOOH$, Cl_3CCOOH	$ClCH_2COOH$> $Cl_2CHCOOH$> Cl_3CCOOH	Cl_3CCOOH> $Cl_2CHCOOH$> $ClCH_2COOH$	$Cl_2CHCOOH$> Cl_3CCOOH> $ClCH_2COOH$	Cl_3CCOOH > $ClCH_2COOH$> $Cl_2CHCOOH$	Cl_3CCOOH> $Cl_2CHCOOH$> $ClCH_2COOH$
2.	Organic compound which contain the carboxyl functional group are called the	ester	carboxylic acids	ketone	aldehyde	carboxylic acids
3.	The long-chain monocarboxylic acids are commonly called	fatty acids	formic acids	acetic acids	valeric acids	fatty acids
4.	Carboxylic acids are isomeric with	ethers	esters	acid anhydrides	diols	esters
5.	The acidic nature of carboxylic group is due to	resonance stabilization of carboxylic group	(+ inductive effect of alkyl group)	tautomeric displacement of hydrogen	greater resonance stabilization of carboxylate anion	greater resonance stabilization of carboxylate anion
6.	Which of the following is not a fatty acids?	formic acid	stearic acid	palmitic acid	gallic acid	gallic acid
7.	Which of the following carboxylic acids has the highest boiling point?	heptanoic acid	octanoic acid	nonanoic acid	decanoic acid	decanoic acid
8.	Which of the following is not true for dicarboxylic acids?	they are stronger acids compared to corresponding monocarboxylic acids	their first dissociation constant is higher than second one	acids with even carbon atom are more soluble in water compared to proceding or following acid with odd carbon atoms	acids with even carbon atoms have higher m.p as compared to acids proceding or following with odd number of carbon atoms.	acids with even carbon atom are more soluble in water compared to proceding or following acid with odd carbon atoms
9.	Carbonation of Grignard’s reagent followed	aldehyde	ketone	acids	ester	acids

	by hydrolysis gives					
10.	Which of the following is the strongest acid?	methanoic acid	ethanoic acid	propanoic acid	butanoic acid	methanoic acid
11.	What is the typical mode of reaction of acid derivatives?	nucleophilic acyl substitution	alpha elimination-addition	electrophilic addition	beta elimination	nucleophilic acyl substitution
12.	What is the product of the reaction of acetyl chloride with ammonia?	methylamine	acetonitrile	ethylamine	acetamide	acetamide
13.	What carboxylic acid derivatives are most reactive toward nucleophilic acyl substitution?	anhydrides	esters	amides	acid chlorides	acid chlorides
14.	Rank the acid derivatives with respect to their reactivity with water. (most reactive >> least reactive)	acid halide> ester> acid anhydride> amide	acid anhydride> amide> acid halide> ester	amide> ester> acid anhydride> acid halide	acid halide> acid anhydride> ester> amide	acid halide> acid anhydride> ester> amide
15.	Which of the following compounds will react most rapidly with water?	acetone	acetyl chloride	acetic anhydride	ethyl acetate	acetyl chloride
16.	What acid derivative react with Li(*tert*-$C_4H_9O)_3$AIH to produce an aldehyde?	nitrile	amide	acid chloride	ester	acid chloride
17.	Acetic anhydride is obtained by the reaction of	acetic acid and sodium	acetic acid and water	acetic acid and diethylether	acetic acid and P_2O_5	acetic acid and P_2O_5
18.	What is the first step in acid-catalyzed transesterification?	protonation of the alcohols oxygen	protonation of the esters carbonyl oxygen	nucleophilic attack by alcohol on the carbonyl carbon	protonation of the esters carbonyl carbon	protonation of the esters carbonyl carbon
19.	What is an important use of diazomethane in organic chemistry?	preparation of carboxylic acids from alkenes	conversion of carboxylic acid to their methyl esters	preparation of carboxylic acids from alcohols	preparation of carboxylic acids from alkanes	conversion of carboxylic acid to their methyl esters

20.	Which of the following compounds would react with C_2H_5MgBr to make	ethanol	ethyl formate	acetic acid	acetone	ethyl formate
21.	What is the product of the reaction of ethyl acetate with C_2H_5MgBr, followed by H_3O^+?	2-methyl-2-butanol	acetone	methyl acetate	2-methyl-2-propanol	2-methyl-2-propanol
22.	Methyl butyrate is reacted with excess ammonia, and the product is then treated with bromine in aqueous NaOH. What is the expected product?	butylamine	pentylamine	propylamine	N-bromobutyramide	propylamine
23.	Basic- hydrolysis of ester is called	Saponification	acidification	esterification	acetylation	saponification
24.	Which of the following statement is false about acetamide?	react with Br_2/NaOH to form teritary amine	undergoes acid-hydrolysis to form acetic acid	undergoes dehydration with P_2O_5 to form a nitrile	is a white crystalline solid, soluble in water	react with Br_2/NaOH to form teritary amine
25.	For a given carbon content, which of the following have the highest boiling point?	acid chlorides	methyl esters	carboxylic acids	primary amides	primary amides
26.	Which one of the following can provide a hydrogen for a hydrogen-bond?	ethyl acetate	acetonitrile	dimethylpropinamide	N-methylacetamide	N-methylacetamide
27.	Which of the following will have the highest boiling point?	diethyl ether	n-butane	acetamide	n-propylamine	acetamide
28.	Which of the following acid-derivatives are most stable?	acid chlorides	esters	amides	anhydrides	amides
29.	By which of the following methods can CH_3CONH_2 be converted to CH_3CN?	oxidize with $Na_2Cr_2O_7/H^+$	heat with concentrated sulfuric acid	heat to 200°C	warm with P_2O_5	warm with P_2O_5
30.	Which of the following reagents will react	$LiAlH_4$	Br_2/NaOH	PCl_5	H_2/Ni	Br_2/NaOH

	with acetamide to form methylamine?					
31.	What is the product of the hofmann rearrangement of an amide?	an amine	an isomeric amide	an N,N-dialkylamide	a nitrile	an amine
32.	Which is the best set of reagents to use for producing N-methylacetamide?	ethyl acetate and methylamine	acetaldehyde and methylamine	acetyl chloride and methylamine	acetic acid and methylamine	acetyl chloride and methylamine
33.	Which reaction involves the treatment of an aldehyde or ketone with α-bromo ester in the presence of zinc?	Reformatsky reaction	cannizzaro reaction	claisen condensation	dieckmann reaction	Reformatsky reaction
34.	In which reaction involves the base-catalyzed condensation of two ester molecules to form an alcohol and a β-keto ester.	Reformatsky reaction	cannizzaro reaction	claisen condensation	dieckmann reaction	claisen condensation
35.	In which reaction the amide is converted into pure amine	Reformatsky reaction	cannizzaro reaction	dieckmann reaction	hofmann's degradation	hofmann's degradation
36.	In which reaction the acyl azide is converted into 1 amine?	Reformatsky reaction	curtius rearrangement	dieckmann reaction	dieckmann reaction	curtius rearrangement
37.	What is the product of curtius rearrangement	an amine	an isomeric amide	an N,N-dialkylamide	a nitrile	an amine
38.	What is the product of reformatsky reaction	nitrile	β-hydroxy ester	α-bromo ester	an isomeric amide	β-hydroxy ester
39.	Intramolecular condensation of esters of dicarboxylic acids in the presence of sodium alkoxide forms a cyclic ketone. This reaction is known as	freund's reaction	perkins reaction	curtius rearrangement	dieckmann's reaction	dieckmann's reaction
40.	Which of the following reaction may not be used for the preparation of only primary amines?	Hofmann's	mentius method	curtius reaction	hofmann's bromamide method	Hofmann's

41.	During alkaline hydrolysis of optically active sec-butylacetate, the resulting sec. butyl alcohol has	inversion of configuration	retention of configuration	racemisation	resolution	retention of configuration
42.	Claisen condensation is a base-catalysed condensation of esters to form	α,β- unsaturated esters	β- keto esters	β-hydroxy esters	α-hydroxy esters	β- keto esters
43.	Esters react with hydroxylamine to form	urethanes	hydroxamine acids	uracil	substituted ureas	hydroxamine acids
44.	Ethyl benzoate, on reduction with lithium aluminium hydride, yields	benzaldehyde	benzyl alcohol	benzoin	none of these	benzyl alcohol
45.	Ethyl formate reacts with Grignard reagent gives	primary alcohol	secondary alcohol	tertiary alcohol	primary amines	secondary alcohol
46.	Tripalmitin, on being refluxed with a large excess of methyl alcohol in the presence of sodium methoxide, yields a mixture of glycerol and	palmitic acid	methyl palmitate	dipalmityl glycerol	monopalmityl glycerol	methyl palmitate
47.	Reaction of acid chlorides with ammonia to form amides is called	ammonolysis	amidation	aminolysis	amination	ammonolysis
48.	Esters, when reduced with sodium in benzene, give rise to	primary alcohol	acyloins	aldehydes	sec. alcohol	acyloins
49.	Acid chlorides, on Rosenmund reduction, yields	alcohols	aldehyde	alkyl chlorides	ketone	aldehyde
50.	Amides, on reduction with lithium aluminium hydride, yield	primary amines	secondary amines	nitriles	isonitriles	primary amines
51.	Which one of the following is the best acetylating agent?	CH_3COCl	$(CH_3CO)_2O$	CH_3COOR	CH_3CONH_2	CH_3COCl

52.	Which one of the following cannot be used as acetylating agent in Friedel-Crafts reaction?	CH_3COCl	$(CH_3CO)_2O$	CH_3COOR	none of these	CH_3COOR
53.	Which one of the following has the greatest tendency to undergo nucleophilic substitution?	$(CH_3CO)_2O$	CH_3COOR	CH_3CONH_2	CH_3COCl	CH_3COCl
54.	Arndt-Einstert synthesis is used to convert carboxylic acids into its	lower homolog	higher homologs	aldehydes	ketones	higher homologs
55.	Which reagent is used to reduce ester into alcohol by Bouveault Blanc method	Na + C_2H_5OH	$LiAlH_4$	Na + C_6H_6	$NaBH_4$	Na + C_2H_5OH
56.	Amides when treated with bromine and pot.hydroxide gives primary amine containing one carbon less than parent amide. This reaction is known as	Hofmann's degradation	bromolysis	amide reduction	Bouveault Blanc reduction	Hofmann's degradation
57.	Arndt- Eistert reaction takes place through the formation of intermediate	carbanion	carbocation	nitrene	ketene	ketene
58.	A neutral monovalent, electron deficient species formed as intermediate in Hofmann reaction	nitrene	carbene	carbanion	carbocation	nitrene
59.	Cyclization of aliphatic dicarboxylic ester to 2- carbalkoxy cycloalkanone in the presence of C_2H_5ONa is known as	Thrope-ziegler condensation	Dieckmann condensation	Simmon Smith reaction	freund's reaction	Dieckmann condensation
60.	Reformatsky reaction provides a suitable route for the preparation of	α-hydroxy ester	β-hydroxy esters	ϒ-hydroxy esters	none of these	β-hydroxy esters