

SHORT QUESTIONS

1. Write at least any two differences between meso-compounds and racemic modifications.

Ans:- Racemic Mixture : 1) A racemic mixture is a mixture of organic compounds known as enantiomers. 2) Contains non-identical isomers. 3) Contains chiral compounds. **Meso compound :** 1) A meso compound is a molecule having more than one identical stereocenter and an identical or superimposable mirror image. 2) Contains identical mirror images. 3) Considered as achiral compounds.

2. Define intramolecular forces with examples.

Ans:- Intermolecular forces are responsible for most of the physical and chemical properties of matter. **Example:** Dipole-dipole interactions occur in HCl molecules. Chlorine is comparatively more electronegative than hydrogen and it, therefore, acquires a partial negative charge. The dipole-dipole interaction then takes place between the HCl molecules.

3. Molecules that are superimposable on their mirror images are ____.

Ans:- Achiral compounds.

4. A carbon atom to which four different groups are attached is known as chiral centre.

5. Define the following terms with examples : Nitrene and Nitrenium ions.

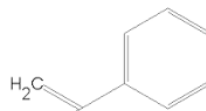
Ans:- Nitrene : In chemistry, a nitrene or imene is the nitrogen analogue of a carbene. The nitrogen atom is uncharged and univalent, so it has only 6 electrons in its valence level—two covalent bonded and four non-bonded electrons. It is therefore considered an electrophile due to the unsatisfied octet.

Nitrenium ions : A nitrenium ion in organic chemistry is a reactive intermediate based on nitrogen with both an electron lone pair and a positive charge and with two substituents.

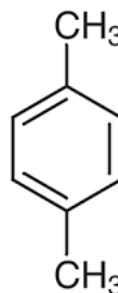
Nitrenium ions are isoelectronic with carbenes, and can exist in either a singlet or a triplet state.

6. Draw the structures of vinylbenzene and p-xylene.

Ans : Vinyl benzene : $C_6H_5CH = CH_2$



P-xylene : C_8H_{10} or $C_6H_4(CH_3)_2$



7. The acidic reagents are seeking a pair of electrons are called ____ (nucleophilic reagents / electrophilic reagents).

Ans:- electrophilic reagents.

8. Stereoisomers that are not mirror images of each other are called ____ (enantiomers/diastereomers).

Ans:- enantiomers

9. Arrange the following compounds of each set in order of reactivity towards S_N2 displacement :

- 1-Bromo-3-methylbutane
- 2-Bromo-2-methylbutane
- 3-Bromo-2-methylbutane

Ans:- b,c,a

10. Write the chemical structural formulae for :

- n-Butyl methyl ether
Ans:- $C_5H_{12}O$
- n-Octyl alcohol = $C_8H_{18}O$
- 2-Methoxypentane = $C_6H_{14}O$
- 1-Methoxy-2-propanol = $C_4H_{10}O_2$

11. Give wave equation.

Ans:- A wave equation is a differential equation involving partial derivatives, representing some medium competent in transferring waves. The one-dimensional wave equation of a vibrating elastic

string is given by:

$$\partial^2 u / \partial t^2 = c^2 (\partial^2 u / \partial x^2) \text{ Where } c^2 = T/\rho$$

12. Give the name of atomic orbitals.

Ans:- There are four basic types of orbitals: s, p, d, and f. An s orbital has a spherical shape and can hold two electrons. There are three p orbitals, each of which has the same basic dumbbell shape but differ in its orientation in space. The p orbitals can hold up to six electrons.

13. What is bond dissociation energy?

Ans:- The bond dissociation energy is the energy required—an endothermic process—to break a bond and form two atomic or molecular fragments, each with one electron of the original shared pair.

14. What is conjugated acids?

Ans:- A conjugate acid contains one more H atom and one more + charge than the base that formed it. Conjugate acid is formed when an acid donates a proton to a base. A conjugate base contains one less H atom and one more - charge than the acid that formed it. It is left over substance after acid loses its hydrogen ion.

15. Define geometrical isomers.

Ans:- Geometrical Isomer:

- Isomers refer to the compounds that contain the same empirical formula but differ in the structural arrangement of atoms.
- A geometric isomer describes the orientation of a functional group in a compound.
- Generally in a geometric isomer, the atoms are bonded by a double bond that does not rotate but it can also happen because of the ring structure.

16. What is Markovnikov rule?

Ans:- When a protic acid (HX) is added to an asymmetric alkene, the acidic hydrogen attaches itself to the carbon having a greater number of hydrogen substituents whereas the halide group attaches itself to the carbon atom which has a greater number of alkyl substituents.

17. Why is chloroacetic acid more acidic than acetic acid?

Ans:- Due to the inductive effect of the chlorine atom the electron density is reduced over the already weakened O-H bond in the carboxylic moiety (due to the presence of alpha carbonyl group) which in turn make it a stronger acid than acetic acid as the ease of releasing the hydrogen to the base is increased.

18. Why benzene does not give addition reactions?

Ans:- Benzene ring does not undergo addition reaction readily because after addition reaction benzene ring loses its aromaticity.

19. Why methoxide ion is more stable than ethoxide ion?

Ans:- Weaker bases have negative charges on more electronegative atoms; stronger bases have negative charges on less electronegative atoms. Thus, the methoxide anion is the most stable (lowest energy, least basic) of the three conjugate bases, and the ethyl carbanion anion is the least stable (highest energy, most basic).

LONG QUESTIONS

1. Write short notes on any two of the following :

a. Molecular orbital theory

Ans:- The Molecular Orbital Theory (often abbreviated to MOT) is a theory on chemical bonding developed at the beginning of the twentieth century by F. Hund and R. S. Mulliken to describe the structure and properties of different molecules. The valence-bond theory failed to adequately explain how certain molecules contain two or more equivalent bonds whose bond orders lie between that of a single bond and that of a double bond, such as the bonds in resonance-stabilised molecules. This is where the molecular orbital theory proved to be more powerful than the valence-bond theory (since the orbitals

described by the MOT reflect the geometries of the molecules to which it is applied).

b. Bond dissociation energy

Ans:- The bond-dissociation energy (BDE, D_0 , or DH°) is one measure of the strength of a chemical bond A–B. It can be defined as the standard enthalpy change when A–B is cleaved by homolysis to give fragments A and B, which are usually radical species. The enthalpy change is temperature-dependent, and the bond-dissociation energy is often defined to be the enthalpy change of the homolysis at 0 K (absolute zero), although the enthalpy change at 298 K (standard conditions) is also a frequently encountered parameter.

c. Acids and bases

Ans:- An acid is any hydrogen-containing substance that is capable of donating a proton (hydrogen ion) to another substance. A base is a molecule or ion able to accept a hydrogen ion from an acid. Acidic substances are usually identified by their sour taste. An acid is basically a molecule which can donate an H^+ ion and can remain energetically favourable after a loss of H^+ . **Acids are known to turn blue litmus red.**

Bases, on the other hand, are characterized by a bitter taste and a slippery texture. A base that can be dissolved in water is referred to as an alkali. When these substances chemically react with acids, they yield salts.

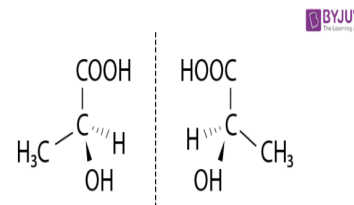
Bases are known to turn red litmus blue.

2.

a. Discuss in detail about the enantiomers with examples.

Ans :- Enantiomers are a pair of molecules that exist in two forms that are mirror images of one

another but cannot be superimposed one upon the other. A common example of a pair of enantiomers is dextro [lactic acid](#) and laevo lactic acid, whose chemical structures are illustrated below.



b. Write about the methods for the preparation of racemic modification.

Ans :- Methods of Racemic Modifications :

1) Mixing : A racemic modification can be achieved when two equal amounts of Dextro (+) and Levo (-) isomers are closely mixed together.

2) Chemical synthesis : Without chiral catalyst, a chiral starting material will always produce a chiral racemate as a product of the reaction. A reaction between hydrogen cyanide and acetaldehyde (chiral) leads to $CH_3CHOHCN$, which contains both forms of acetonitrile in equal amounts.

3) Thermal racemization : Heat can cause racemization in optically active materials. This leads to a temporary break in one of the four stereocenter bonds. A separating atom or group joins back to the stereocenter to yield another enantiomer, e.g., when the optically active enantiomer of α -phenethyl chloride is distilled, it is converted into its racemic enantiomer.

4) Walden inversion - This process is called Walden inversion, in which 2-isooctane is racemized by potassium iodide in refluxing acetone.

5) Epimerization - Specifically, it describes the change in carbon atom configuration at a stereocenter in a compound having multiple stereocenters. Diastereomers are therefore converted to one another.

3.

a. Define carbanions. Explain structure, relative stabilities and stabilisation of carbanions.

Ans :- A carbanion can be defined as a negatively charged ion in which a carbon atom exhibits trivalence (implying it forms a total of three bonds) and holds a formal negative charge whose magnitude is at least -1. When pi delocalization does not occur in the organic molecule (as it does in the case of aromatic compounds), carbanions typically assume a bent, linear, or a trigonal pyramidal molecular geometry. It is important to note that all carbanions are conjugate bases of some carbon acids.

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An illustration detailing the possible resonance structures of a carbanion in which the carbon holding the negative charge is bound to three different R groups is provided above. It can be noted that each of the R-groups in this illustration can either denote an alkyl group, an aryl group, or a hydrogen atom.

The stability of a carbanion is determined by a variety of factors. The order of stability is as follows: tertiary > secondary > primary. The stability of a carbanion can be increased by the inductive effect and by

resonance. Carbanions are most stable in aromatic systems such as benzene. This article deals with the stability of carbanion order, carbanion stability inductive effect, and stability of carbanion in benzene. Thanks for reading! I hope this gives you a better understanding of carbanion stability.

b. Discuss aromaticity of benzene in detail

Ans :- Benzene is one of the most important organic compounds with the chemical formula C_6H_6 . Benzene is the parent compound of the various aromatic compound.

Aromaticity of benzene

Benzene is an [aromatic compound](#), as the C-C bonds formed in the ring are not exactly single or double, rather they are of intermediate length. Aromatic compounds are divided into two categories: benzenoids (one containing benzene ring) and non-benzenoids (those not containing benzene ring), provided they follow Huckel rule. According to Huckel rule, for a ring to be aromatic it should have the following property:

- Planarity
- Complete delocalization of the π electrons in the ring
- Presence of $(4n + 2)$ π electrons in the ring where n is an integer ($n = 0, 1, 2, \dots$)

4.

a. What is S_N1 reaction? Explain its mechanism with suitable examples.

Ans :- The S_N1 reaction is a nucleophilic substitution reaction where the rate-determining step is unimolecular. It is a type of organic substitution reaction. S_N1 stands for substitution

nucleophilic unimolecular. Thus, the [rate equation](#) (which states that the S_N1 reaction is dependent on the electrophile but not on the nucleophile) holds in situations where the amount of the nucleophile is far greater than the amount of the carbocation intermediate.

This reaction involves the formation of a carbocation intermediate. It is generally seen in the reactions of tertiary or secondary alkyl halides with secondary or tertiary alcohols under strongly acidic or strongly basic conditions. The S_N1 reaction is often referred to as the dissociative mechanism in inorganic chemistry. Given below are some examples of an S_N1 type of nucleophilic substitution reaction.

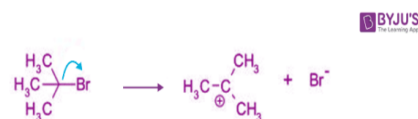
S_N1 Reaction Mechanism

Taking the hydrolysis of tertiary butyl bromide as an example, the mechanism of the S_N1 reaction can be understood via the following steps.

Step 1

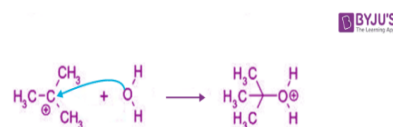
- The carbon-bromine bond is a polar covalent bond. The cleavage of this bond allows the removal of the leaving group (bromide ion).
- When the bromide ion leaves the tertiary butyl bromide, a carbocation intermediate is formed.
- As mentioned earlier, this is the rate-determining step of the S_N1 mechanism.
- It is important to note that the breaking of the carbon-bromine bond is

endothermic.



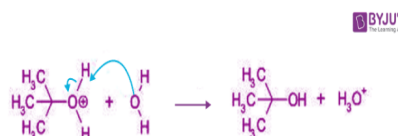
Step 2

- In the second step of the S_N1 reaction mechanism, the carbocation is attacked by the nucleophile.
- Since water is used as a solvent, an oxonium ion intermediate is formed.
- Since the solvent is of a neutral nature, a third step where deprotonation occurs is necessary.



Step 3

- The positive charge on the carbocation was shifted to the oxygen in the previous step.
- The water solvent now acts as a base and deprotonates the oxonium ion to yield the required alcohol along with a hydronium ion as the product.
- Step 2 and Step 3 of this reaction are fast.



b. Explain nucleophilic aliphatic substitution reaction and its mechanism with examples.

Ans :- Aliphatic nucleophilic substitution is a mouthful, but each piece tells you something important about this kind of reaction.

In *substitution* reactions, one piece of a molecule is replaced by another. For example, ligands

can be replaced in transition metal complexes. Oxygen atoms in organic carbonyl compounds can be replaced by nitrogen atoms or sulfur atoms, in a particular variation of carbonyl addition reactions.

These reactions all involve the addition of a *nucleophile* to an electrophilic atom or ion. They are all nucleophilic substitution reactions.

Aliphatic systems involve chains of saturated hydrocarbons, in which carbons are attached to each other only through single bonds. Aliphatic nucleophilic substitution is the substitution of a nucleophile at a tetrahedral or sp^3 carbon.

Aliphatic nucleophilic substitutions do not play a glamorous, central role in the world of chemistry. They don't happen in every important process, the way carbonyl additions and carboxylic substitutions appear to in biochemistry. Instead, they are ubiquitous little reactions that play important, small roles in all kinds of places.

In considering possible **mechanisms for this reaction**, we ought to think about overall bond-making and bond-breaking steps. In the addition of sodium cyanide to alkyl chloride to make an alkyl nitrile, there is one bond-making step (the C-C bond) and one bond-breaking step (the C-Cl bond). The simplest reaction mechanism would involve some combination of these steps.

Two possibilities immediately present themselves:

Mechanism A

The C-C bond forms and then the C-Cl bond breaks.

Mechanism B

The C-Cl bond breaks and then

the C-C bond forms.

However, some familiarity with bonding in the second row of the periodic table may suggest to you that mechanism A is not very likely. That mechanism would require forming five bonds to carbon before the C-Cl bond eventually breaks. We can safely ignore this possibility.

Instead, there may be a third possibility to consider.

Mechanism C

The C-Cl bond breaks and the C-C bond forms at the same time.

Mechanism C is a concerted mechanism; two bond-making and -breaking events happen at once. However, no octet rules are violated.

5.

a. **Write any five chemical properties of alkyne.**

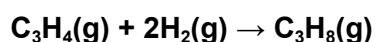
Ans :- Chemical Properties of Alkynes

1) **Acidic nature :** Coming to the chemical properties of alkynes, we begin with their slightly acidic nature. Now Alkynes are slightly electronegative in nature. The triply bonded carbon atoms in alkynes are sp hybridized, Whereas like in alkanes the single bond atoms are sp^3 hybridized, causing the difference in the electronegativity. This makes it easier for them to attract the shared electron pair of the C-H bond.

2) **Addition Reactions :** Under suitable conditions (temperature and pressure) alkynes will undergo hydration reactions quite easily. Alkynes will react with

halogens, hydrogen and other such elements to give a saturated compound as a product. Since they have a triple bond, two atoms of H₂ or halides or halogens can be added to its structure.

- a) **Addition of Dihydrogen: A catalyst, such as Nickel, Platinum, or Palladium, is used to speed up the process. When hydrogen is added to an alkyne, we get an alkene.**



- b) **Addition of Halogens:** When alkynes and halogens like chlorine react, the halogen bonds to the alkynes' structure, resulting in halogen-substituted alkenes.

Tetrachloroethane will be the end product.

- c) **Addition of Halogens:** When alkynes and halogens like chlorine react, the halogen bonds to the alkynes' structure, resulting in halogen-substituted alkenes. Tetrachloroethane will be the end product.

- d) **Addition of Water:** Alkynes do not react with water molecules like other hydrocarbons (alkanes and alkenes). This is referred to as immiscibility. A

reaction occurs when alkynes are bubbled through dilute sulphuric acid (approximately 40%) in the presence of the catalyst mercuric Sulphate. Carbonyl molecules will be the end products of this process, which is known as a hydration reaction.

- b. **Give physical and chemical properties of aliphatic aldehydes.**

Ans :- Physical Properties of Aldehydes

Because both ketones and aldehydes include the carbonyl functional group, they are often used interchangeably in chemical processes. However, they have significant differences in the most critical processes, such as oxidation. Ketones are resistant to oxidation, but aldehydes are easily converted to carboxylic acids by the action of oxygen. Aldehydes are a class of chemical compounds that are easily oxidised by the environment. The ease with which they oxidise aids in their identification.

● **Physical State**

In its gaseous state at ambient temperature, formaldehyde, while acetaldehyde is a volatile liquid, are two different chemicals. Therefore, C₁₁ and below are colourless liquids, while C₁₂ and higher are solids. All other aldehydes and ketones are colourless liquids.

● **Tautomerism**

An aldehyde's oxygen atom can migrate to the carbonyl group's hydrogen atom if it has at least

one hydrogen atom on the carbon atom next to it, termed the alpha (α) carbon. Afterwards, the double bond moves toward the carbon.

Tautomers are two isomeric forms of carbonyl compounds having a α -hydrogen. There are two distinct forms of ketosis, with the hydrogen connected to the α -carbon and the carbonyl oxygen linked by the migration of the double bond.

- **Boiling Point**

Because they are non-polar chemicals, ketone and aldehyde boiling points are greater than those of the other non-polar compounds. Although the boiling temperatures of ketones and aldehydes are lower than those of the equivalent carboxylic acids and alcohols, this is due to the fact that they do not form hydrogen bonds with one another.

- **Dipole Moment**

A double bond exists between carbon and oxygen in the carbonyl group of aldehydes and ketones. In addition, because oxygen has a higher electronegative charge than carbon, it draws the shared pair of electrons, making the carbonyl group more reactive and polar. As a result, aldehydes and ketones have strong dipole moments.

- **Solubility**

Hydrogen bonding makes it possible for the lower members of the ketones and aldehydes to be soluble in water, and this is especially true for those with up to four carbons in their structure. However, their higher members do not dissolve in water due to the high concentration of hydrocarbons in the solution, which prevents the formation of H-bonds with the water molecules in the solution. In addition, there are dipole-dipole interactions and dispersive forces between the water molecules and the aldehydes and ketones.

Chemical Properties of Aldehydes

- **Nucleophilic addition**

Nucleophilic addition reactions are a type of chemical reaction in which two nucleophiles combine to form a nucleophile.

The following mechanisms characterise the nucleophilic addition reactions:

In the polar carbonyl group, a nucleophile contacts the electrophilic carbon atom from a direction that is essentially perpendicular to the plane of the sp^2 hybridised orbitals of the polar carbonyl group.

A tetrahedral alkoxide intermediate is formed due to the hybridisation of carbon, which shifts from sp^2 to sp^3 in this reaction. A proton is captured by this intermediate and transferred to the reaction medium, yielding the electrically neutral product. You get a net outcome when you put Nu^- and H^+ together across the carbon-oxygen double bond.

- **Reactivity**

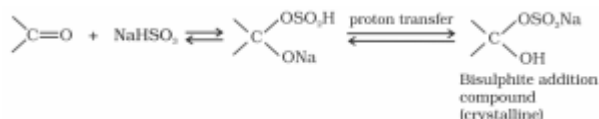
Reactivity includes steric and electronic differences, making aldehydes more reactive than ketones in nucleophilic addition processes. In addition, because ketones have two relatively large substituents, the approach of a nucleophile to carbonyl carbon is more difficult in ketones than in aldehydes, which contain only one of these substituents.

- **Reaction with Hydrogen Cyanide**

Aldehydes and ketones react with hydrogen cyanide (HCN) to produce cyanohydrins, a type of cyanide compound. In the presence of pure HCN, this reaction takes place very slowly. Therefore, a base catalyses it, and the cyanide ion (CN^-), a stronger nucleophile than carbonyl compounds, quickly reacts with them to produce the appropriate cyanohydrin. A class of synthetic intermediates known as cyanohydrins exists.

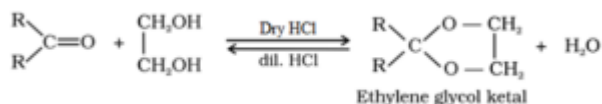
- **Addition of sodium hydrogen sulphite**

Sodium hydrogen sulfite reacts with aldehydes and ketones to create the compounds known as additional products.



• Addition of Alcohol

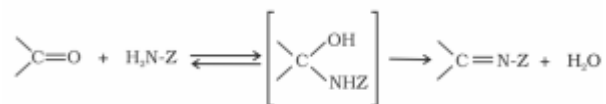
When combined with monohydric alcohol in the presence of dry HCl, Aldehydes generate hemiacetal, which, when combined with one additional molecule of alcohol, transforms into acetal.



• Addition of ammonia and its derivatives

Adding ammonia and its derivatives to aldehydes and ketones: Nucleophiles such as ammonia and its derivatives $\text{H}_2\text{N}-\text{Z}$ react with the carbonyl group of aldehydes and ketones to form a bond.

Z can be any of the following: alkyl, aryl, OH, NH_2 , $\text{C}_6\text{H}_5\text{NH}$, NHCONH_2 , or any other combination.



• Reduction

When aldehydes and ketones react with sodium borohydride (NaBH_4) or lithium aluminium hydroxide, they form primary and secondary alcohols, respectively (LiAlH_4).

6. Write short notes on any two of the following :

a. Carboxylic acids

Ans :- The carboxylic acids are the *most important functional group that present C=O* . This type of organic compounds can be obtained by different routes, some carboxylic acids, such as citric acid, lactic acid or fumaric acid are produced by

fermentation, most of these types of carboxylic acids are applied in the food industry.

Carboxylic acids are hydrocarbon compounds in which a carboxyl group has substituted one or more of the hydrogen atoms in the hydrocarbon. Methanoic acid (HCOOH), ethanoic acid (CH_3COOH), propanoic acid ($\text{C}_2\text{H}_5\text{COOH}$), and butanoic acid ($\text{C}_3\text{H}_7\text{COOH}$) are the first four carboxyl acids derived from alkanes.

b. Cycloalkanes

Ans :- Cycloalkanes are the class of hydrocarbons having a ring-like structure. This ring is formed due to their saturated nature, and they have three compounds of alkane present in the structure which helps them in forming a ring. They have the general formula C_nH_{2n} , Where n is said to be the number of carbon atoms present in the organic compound.

Some uses are given below-

- In the medical applications, cycloalkanes are used as an organic solvent in the production of drugs
- These are utilised in the manufacture of hair products as well as in the food industries
- The cycloalkane called cyclopropane is used as an anaesthetic agent in the medical field
- Carboplatin which is derived from the cyclobutane is used to treat cancers
- They are also employed in the petroleum industries.

c. Epoxides

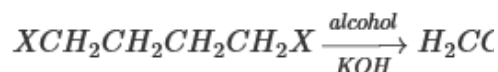
Ans :- Epoxides are an important class of compounds in organic synthesis, because nucleophilic ring opening takes place easily in an $\text{S}_\text{N}2$ pathway with inversion of configuration at the reacting carbon center. The driving force of the high reactivity is the

inherent strain of the three-membered heterocycle. A variety of 1,2-difunctionalized compounds with two contiguous stereogenic centers are, thus, provided in a single step reaction of epoxides. Therefore, a number of methods have been developed for the synthesis of optically active epoxides, including catalytic asymmetric methods. Some of the most interesting and useful chiral ring-opened adducts, such as *trans*-1,2-functionalized cycloalkanes and stilbene skeletons, are, however, derived from symmetric *meso*-epoxides to which enantioselective epoxidation approaches are not applicable. Thus, enantioselective ring opening reaction of *meso* epoxides, via 'meso-trick,' is required as a conceptually different method for the synthesis of chiral building blocks.

7. Write the preparation methods of (any two) :

a. Dienes

Synthesis of Dienes
Dehydrohalogenation of Dihalides
Dienes can be prepared by Dehydrohalogenation of dihalides by successive elimination reactions.



Dehydration of Diols
Dienes can be prepared by dehydration of diols by two successive elimination reactions.

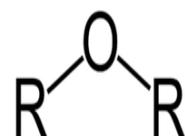


Other Methods of Preparation of Dienes
Butadiene is prepared in industries by thermal cracking of Butane.

Dicyclopentadiene is prepared in industries from Coal tar.

b. Ethers

1) Preparation of Ethers by Dehydration of Alcohols
In the presence of protic acids (sulphuric acid), alcohols undergo dehydration to produce alkenes and ethers under different conditions. For example: in the presence of sulphuric acid, dehydration of ethanol at 443 K yields ethene. On the other hand, it yields ethoxyethane at 413 K. This is an ideal method of preparation for primary alcohols.



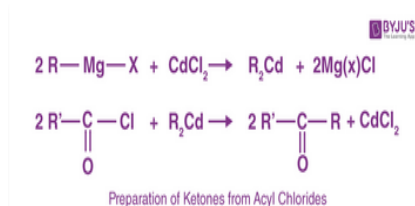
The preparation of ethers by dehydration of an alcohol is a nucleophilic substitution reaction. There are two major roles of the alcohol that we find in this reaction. One is that the alcohol molecule can act as the substrate while the other is that it acts as a nucleophile. It can follow either SN¹ or SN² mechanism. The choice of mechanism is dependent on whether the protonated alcohol loses water before or simultaneously upon the attack of a second alcohol molecule. Generally, we will find that the secondary and tertiary alcohols follow S_N1 mechanism. While on the other hand, the primary alcohols follow SN² mechanism.

c. Ketones

Preparation of Ketones from Acyl Chlorides

Acyl chlorides upon treatment with Grignard reagent and a metal halide, yield ketones. For example: when cadmium chloride

is reacted with the Grignard reagent, dialkyl cadmium is formed. Dialkylcadmium thus formed is further reacted with acyl chlorides to form ketones.



8. Write the chemical properties of any two of the following :

a. Phenol

Chemical Properties of Phenol

The chemical reactions of phenols can be classified under two headings – one is involving the cleavage of the O–H bond and the other one involves the cleavage of the C–O bond in it.

1. Reactions involving O–H bond cleavage:

1. With metals:

Phenols react with metals such as Na, K, Al, etc., to form phenoxide with the release of the hydrogen gas. Apart from active metals, phenol gives sodium phenoxide on reaction with aqueous NaOH(sodium hydroxide) too, by releasing a water molecule.

1. Formation of Esters (Esterification)

Esterification reaction with acid chloride takes place in the presence of pyridine in order to neutralize the HCl formed during the esterification reaction.

1. Acetylation

The reaction of phenols with an acid anhydride and the introduction of acetyl ($\text{CH}_3\text{CO}-$) are called acetylation, and the product obtained is called acetylsalicylic acid or aspirin.

1. Electrophilic Aromatic Substitution

The –OH group in the phenol activates the benzene ring and pushes it towards the electrophilic substitution. Also, the substituents or the incoming groups are directed by the OH group towards the ortho and para positions of the benzene ring. The reason behind this is that the resonance effect of the ring structure makes these positions electron-rich in the whole benzene.

1. Nitration Reaction

The Addition of an –NO₂ group to the benzene ring is called nitration. Phenol reacts with dilute nitric acid at 298K to yield ortho and para nitrophenols.

1. Halogenation Reaction

The phenol reacts with bromine in low polarity solvents, such as chloroform or CS₂, at low temperatures to form mono bromophenols. The reason is that the non-polar or low-polar solvents can only activate the benzene ring in the 1 and 4 positions. Hence, only mono-substituted products are formed.

The presence of a highly activating group, –OH in phenol, makes polarization of the bromine molecule much easier.

1. Kolbe's Reaction

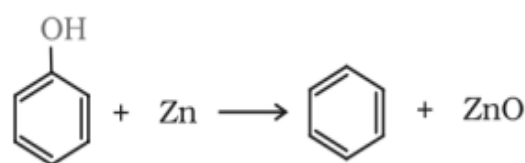
The Phenol reacts with sodium hydroxide and carbon dioxide to form sodium salicylate. It is acidified to yield 2-hydroxy benzoic acid or known as salicylic acid. The phenoxide ion formed with NaOH has higher reactivity than the phenol towards aromatic, electrophilic substitution, and thus, acidifies to produce salicylic acid.

1. Reimer-Tiemann Reaction

The Phenol, in reaction with chloroform (CHCl_3), in the presence of NaOH, forms an aryl aldehyde compound. A –CHO group is introduced into the benzene ring, this reaction is known as the Reimer-Tiemann reaction. The electrophile formed in this reaction ($:\text{CCl}_2$) is called the dichlorocarbene. An intermediate, substituted benzyl chloride is formed, which is then hydrolyzed into salicylaldehyde, the product, in the presence of an alkali.

1. Reaction with Zinc Dust

The Phenol, on heating with zinc dust, gets converted into benzene. The reaction is shown below:



1. Oxidation of Phenol

The Phenol, on oxidation with chromic acid, forms a conjugated diketone called benzoquinone. In the presence of air, the oxidation reaction of phenols produces a dark-coloured mixture containing quinones.

b. Acetyl chloride

Chemical properties of acyl halides

They are the most reactive of all the derivatives of carboxylic acids.

They are readily hydrolysed water to form the corresponding carboxylic acids.

Alcohols and phenols combines with acyl chlorides to form esters.

They are reduced by hydrogen in the presence of palladium with BaSO₄.

Molecular Weight: 78.4981

Calculated Log P: 0.821

Rotatable Bonds: 1

H Acceptors: 1

H Donators: 0

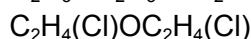
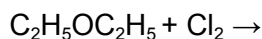
Reactions having this substance as a reactant: 12219

Reactions having this substance as a product: 48

c. Diethyl ether

Chemical Properties of Diethyl Ether – (C₂H₅)₂O

1. Combustion – Ether is highly flammable liquid and undergoes combustion reaction resulting in the formation of carbon dioxide and water. $C_2H_5OC_2H_5 + 6O_2 \rightarrow 4CO_2 + 5H_2O$
2. Halogenation – Ether reacts with halogens like chlorine or bromine forming halo substituted ether undergoes substitution reaction in the absence of sunlight.



Uses of Diethyl Ether – (C₂H₅)₂O

Used as a common laboratory solvent.

Used as an excellent solvent for alkaloids, dyes, fats, oils, resins and waxes.

Used in the recovery of acetic acid from aqueous solutions in cellulose acetate and plastic industry.

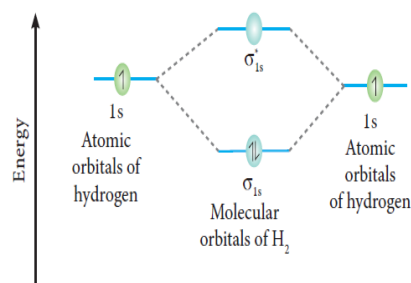
- 9. Discuss molecular orbital theory. Explain it with suitable examples.**

Ans :- The Molecular Orbital Theory (often abbreviated to MOT) is a theory on chemical bonding developed at the beginning of the twentieth century by F. Hund and R. S. Mulliken to describe the structure and properties of different molecules. The valence-bond theory failed to adequately explain how certain molecules contain two or more equivalent bonds whose bond orders lie between that of a single bond and that of a double bond, such as the bonds in resonance-stabilized molecules. This is where the molecular orbital theory proved to be more powerful than the valence-bond theory (since the orbitals described by the MOT reflect the geometries of the molecules to which it is applied).

An example of molecular orbitals is hydrogen molecules.

The number of bonds in a hydrogen molecule is one and the number of an electron is two.

The molecular orbital diagram of the hydrogen molecule is given below,



The bond order of the hydrogen molecule is one.

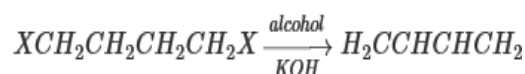
10. Give the synthesis and chemical reactions of dienes.

Ans :- Synthesis of Dienes

Dehydrohalogenation of Dihalides

Dienes can be prepared by

Dehydrohalogenation of dihalides by successive elimination reactions.



Dehydration of Diols

Dienes can be prepared by dehydration

of diols by two successive elimination reactions.



Other Methods of Preparation of Dienes
Butadiene is prepared in industries by thermal cracking of Butane.

Dicyclopentadiene is prepared in industries from Coal tar.

11. Classify stereoisomerism. Explain enantiomer, diastereomer and mesomer.

Ans :- *Stereoisomerism* refers to molecules with identical chemical and molecular structures but a different spatial organisation of groups around a chiral atom (usually carbon). Chiral atoms are present in all stereoisomers and have bonds entirely occupied by dissimilar functional groups.

Stereoisomers are subclassified by the direction in which they rotate plane polarised light (optical isomerism) and/or by the spatial arrangement of atomic groups around the chiral centre. When polarised light is travelling towards the viewer, it can be rotated clockwise (termed dextrorotatory (*d*) or +) or anticlockwise (laevorotatory (*l*) or -).

Enantiomers are a pair of molecules that exist in two forms that are mirror images of one another but cannot be superimposed one upon the other.

Diastereomers are defined as non-mirror image, non-identical stereoisomers. Hence, they occur when two or more stereoisomers of a compound have different configurations at one or more (but not all) of the equivalent (related) stereocenters and are not mirror images of each other.

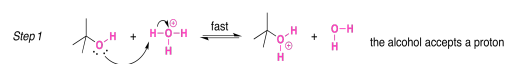
Mesomers are the type of organic compounds in which two chiral carbons are present and those two are similar. A meso compound is a kind of stereoisomer that has two or more chiral centres but is optically inactive because it has an internal plane of symmetry.

12. Give the mechanism of substitution and elimination reactions in alcohol.

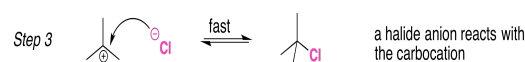
Discuss chemical reactions of alcohols.

Ans :-

The S_N1 mechanism is illustrated by the reaction tert-butyl alcohol and aqueous hydrochloric acid (H_3O^+ , Cl^-). The first two steps in this S_N1 substitution mechanism are protonation of the alcohol to form an oxonium ion. Although the oxonium ion is formed by protonation of the alcohol, it can also be viewed as a Lewis acid-base complex between the cation (R^+) and H_2O . Protonation of the alcohol converts a poor leaving group (OH^-) to a good leaving group ($(\text{H}_2\text{O})^+$), which makes the dissociation step of the S_N1 mechanism more favourable.



In step 3, the carbocation reacts with a nucleophile (a halide ion) to complete the substitution.



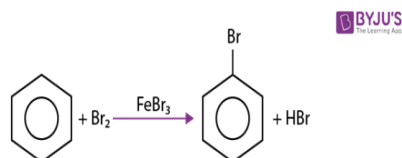
When we convert an alcohol to an alkyl halide, we perform the reaction in the presence of acid and in the presence of halide ions and not at elevated temperatures. Halide ions are good nucleophiles (they are much stronger nucleophiles than water), and because halide ions are present in a high concentration, most of the carbocations react with an electron pair of a halide ion to form a more stable species, the alkyl halide product. The overall result is an S_N1 reaction.

13. Discuss electrophilic substitution reactions in aromatic compounds. Explain nitration and alkylation in benzene.

Ans :- Electrophilic aromatic substitution reactions are organic reactions wherein an electrophile replaces an atom which is attached to an aromatic ring. Commonly, these reactions involve the replacement of a hydrogen atom

belonging to a benzene ring with an electrophile.

The aromaticity of the aromatic system is preserved in an electrophilic aromatic substitution reaction. For example, when bromobenzene is formed from the reaction between benzene and bromine, the stability of the aromatic ring is not lost. This reaction can be illustrated as follows.



Aryl halides or haloarenes can be prepared via electrophilic aromatic halogenation reactions of aromatic rings with iodine, chlorine, or bromine. These reactions generally involve the use of aluminium trihalides as catalysts.

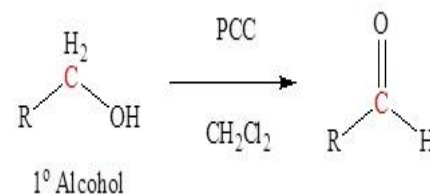
14.

a. Discuss factors affecting acidity of carboxylic acids.

Ans :- The presence of groups near the -COOH group of a carboxylic acid has an effect on acidity. Generally, electron-withdrawing groups increase acidity by increasing the stability of the carboxylate ion. The presence of, electron-donating groups decrease acidity by destabilizing the carboxylate ion.

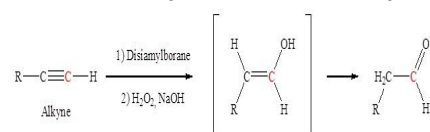
b. Give synthesis of aldehydes and ketone.

Aldehydes and ketones can be prepared using a wide variety of reactions. Although these reactions are discussed in greater detail in other sections, they are listed here as a summary and to help with planning multistep synthetic pathways. Please use the appropriate links to see more details about the reactions. Oxidation of 1° alcohols with PCC to form aldehydes

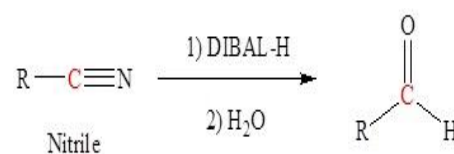
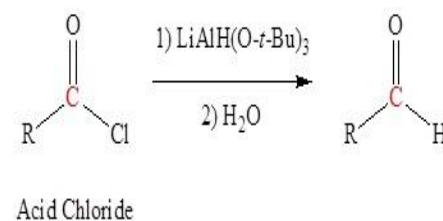
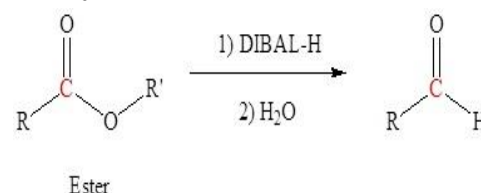


Hydration of an alkyne to form aldehydes

Anti-Markovnikov addition of a hydroxyl group to an alkyne forms an aldehyde. The addition of a hydroxyl group to an alkyne causes tautomerization which subsequently forms a carbonyl.

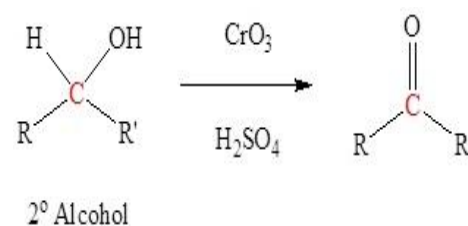


Reduction of an ester, acid chloride or nitrile to form aldehydes



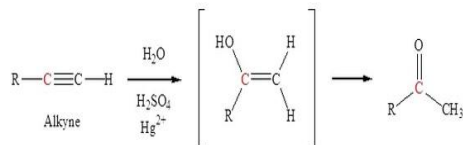
Oxidation of 2° alcohols to form ketones

Typically uses Jones reagent (CrO₃ in H₂SO₄) but many other reagents can be used

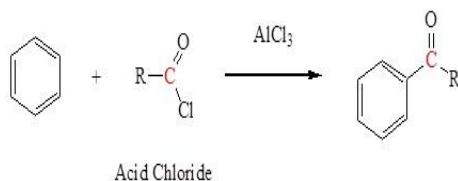


Hydration of an alkyne to form ketones

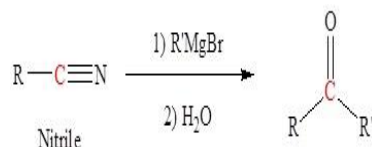
The addition of a hydroxyl group to an alkyne causes tautomerization which subsequently forms a carbonyl. Markovnikov addition of a hydroxyl group to an alkyne forms a ketone.



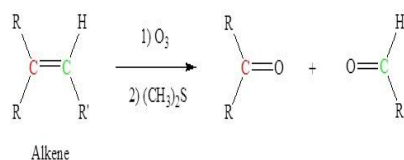
Friedel-Crafts acylation to form a ketone



Reaction of Grignard reagents with nitriles to form ketones



Alkenes can be cleaved using ozone (O₃) to form aldehydes and/or ketones



This is an example of a Ozonolysis reaction.

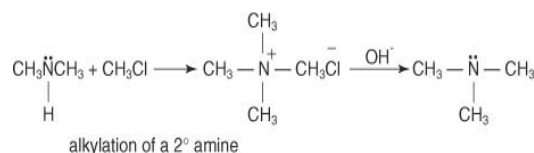
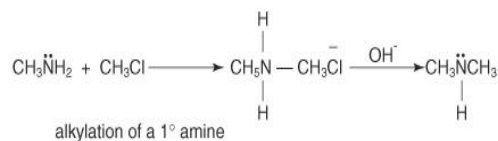
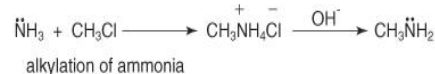
15. Give synthesis and chemical reactions of aliphatic amines.

Ans :- The alkylation of ammonia, Gabriel synthesis, reduction of nitriles, reduction of amides, reduction of nitrocompounds, and reductive amination of aldehydes and ketones are methods commonly used for preparing amines.

Alkylation of ammonia

- 16.** The reaction of ammonia with an alkyl halide leads to the formation of a primary amine. The primary amine that is formed can also react with the alkyl halide,

which leads to a disubstituted amine that can further react to form a trisubstituted amine. Therefore, the alkylation of ammonia leads to a mixture of products.



Aliphatic and aromatic, primary and secondary amines **react with acid chlorides, anhydrides and esters by the process of nucleophilic substitution reaction**. This is known as acylation. Amides are the end products of acylation. The reactions are carried out in the presence of a stronger base as compared to amines.

17. Write notes on any two of the following :

a. Hybridization

Hybridization:

- Hybridization is defined as the intermixing of atomic orbitals with the same energy levels to give the same number of a new type of hybrid orbitals.
- This intermixing usually results in the formation of hybrid orbitals having entirely different energies, shapes, etc.
- The atomic orbitals of the same energy level mainly take part in hybridization.

Types of Hybridization:

sp³ hybridization:

- When one s orbital and three p orbitals from the same shell of an atom mix together to form a new equivalent orbital then this is called sp³ hybridization.

sp² hybridization:

- When one s orbital and two p orbitals from the same shell of an atom mix together to form a new equivalent orbital then this is called sp² hybridization.

sp hybridization:

- When one s and one p orbital from the same shell of an atom mix together to form a new equivalent orbital then this is called sp hybridization.
- The molecules which show sp hybridization, have a linear shape and an angle of 180° .

sp³d Hybridization:

- sp³d hybridization involves the mixing of one- s orbital, three- p orbitals and one- d orbital to form 5 sp³d hybridized orbitals of equal energy. They have trigonal bipyramidal geometry.
- The mixture of s, p and d orbital forms trigonal bipyramidal symmetry.
- Three hybrid orbitals lie in the horizontal plane inclined at an angle of 120° to each other known as the equatorial orbitals.
- The remaining two orbitals lie in the vertical plane at 90 degrees plane of the equatorial orbitals known as axial orbitals.

sp³d² hybridization:

- sp³d² hybridization has one- s, three- p, and two -d orbitals, that undergo intermixing to form 6 identical sp³d² hybrid orbitals.
- These 6 orbitals are directed toward the corners of an octahedron.
- They are inclined at an angle of to one another.

sp³d³ hybridization:

- The process of mixing one s- orbital, three p- orbitals, and three d-orbitals in an atom to form seven sp³d³ hybrid orbitals of equivalent energy is called sp³d³ hybridization.

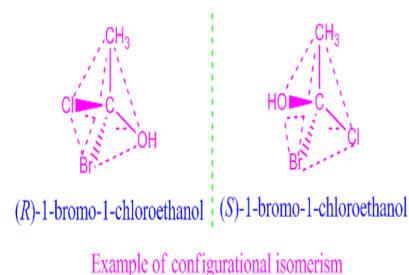
b. Configurational isomerism

Configurational isomerism is a part of stereo isomerism that arises due to the spatial arrangement of atoms and groups about a rigid part of the molecule, that is, about a double bond or ring and about a dissymmetric part of the molecule.

Actually, geometrical and optical isomerism are together called configurational isomerism.

An example of configurational isomerism is

1-bromo-1-chloro-ethanol.



c. Stability of reaction intermediates

They are short-lived (10–6 seconds to a few seconds). The most effective chemical species in which most organisms occur are called reaction intermediates. This is produced by breaking the solid bond of the substrate. The reaction intermediate rapidly transforms into a stable molecule when produced by chemical reactions. Only in rare cases, such as low temperatures or matrix fragmentation, intermediate reaction compounds can be isolated and retained. For example, Tert-butyl carbocation, ethyl carbocation, acetaldehyde carbanion, chlorine-free radical, benzyl free radical, phenyl free radical, dichlorocarbene, etc. stability of carbocation intermediates

A carbocation is an ion with a well-charged carbon atom. A carbocation is very poor with electrons, so anything that gives electron density to the centre of electron poverty will help to stabilize it. Conversely, carbocation will be rendered ineffective by the electron withdrawal group.