

CARBONYL COMPOUNDS (ALDEHYDES & KETONES) & CARBOXYLIC ACIDS

CONTENTS

Particular	Page No.
Theory	001 – 035
Exercise - 1	036 – 044
Part - I : Subjective Questions	
Part - II : Only One Option Correct Type	
Part - III : Match the Columns	
Exercise - 2	044 – 054
Part - I : Only One Option Correct Type	
Part - II : Single or Double Digit Integer Type Questions	
Part - III : One or More Than One Options Correct Type	
Part - IV : Comprehensions	
Exercise - 3	054 – 068
Part - I : JEE(ADVANCED) / IIT-JEE Problems (Previous Years)	
Part - II : JEE(MAIN) / AIEEE Problems (Previous Years)	
Answers	069 – 073
Additional Problems for Self Practice (APSP)	074 – 095
Part - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))	
Part - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I	
Part - III : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))	
APSP Answers	096 – 097
APSP Solutions	097 – 107

JEE (Advanced) Syllabus

Carbonyl Compounds (Aldehydes & Ketones) & Carboxylic Acids : Aldehydes and Ketones:
oxidation, reduction, oxime and hydrazone formation; aldol condensation, Perkin reaction; Cannizzaro reaction; haloform reaction and nucleophilic addition reactions (Grignard addition).

Carboxylic acids: Formation of esters, acid chlorides and amides, ester hydrolysis.

JEE(Main) Syllabus

Carbonyl Compounds (Aldehydes & Ketones) & Carboxylic Acids : Aldehyde and Ketones: Nature of Carbonyl group ; Nucleophilic addition to $>\text{C}=\text{O}$ group, relative reactivities of aldehydes and ketones; Important reactions such as - Nucleophilic addition reactions (addition of HCN, NH_3 and its derivatives), Grignard reagent; oxidation ; reduction (Wolff Kishner and Clemmensen) ; acidity of α -hydrogen, aldol condensation, Cannizzaro reaction, Haloform reaction ; Chemical tests to distinguish between aldehydes and Ketones.

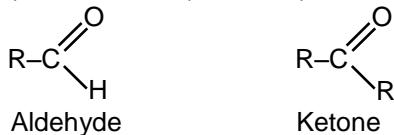
Carboxylic Acids : Acidic strength and factors affecting it.



Carbonyl Compounds (Aldehydes & Ketones)

1. Introduction

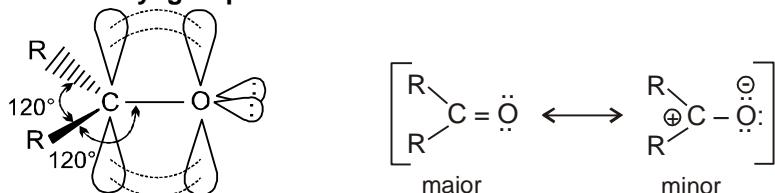
Aldehydes & ketones have general formula $C_nH_{2n}O$ and contains $>C=O$ group. Thus aldehydes ($R-CHO$) and ketones ($R-CO-R$) are collectively called as carbonyl compounds.



2. Structure and bonding in aldehydes and ketones

The carbonyl carbon atom is sp^2 hybridized. The unhybridized p-orbital overlaps with a p-orbital of oxygen to form a pi bond. The double bond between carbon and oxygen is shorter, stronger, and polarized.

Orbital diagram of carbonyl group :

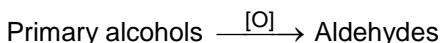


The double bond of the carbonyl group has a large dipole moment because oxygen is more electronegative than carbon.

Section (A) : Preparation of carbonyl compounds

3. Preparation methods of Aldehydes and Ketones

3.1 By oxidation of alcohols :



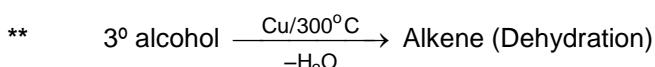
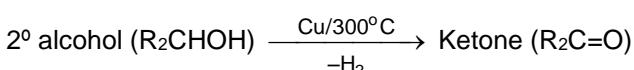
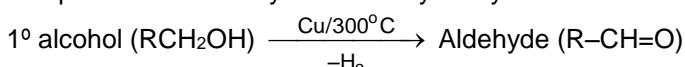
For oxidising primary alcohols to aldehydes PCC (Pyridiniumchloro chromate ($C_6H_5NH^+CrO_3Cl^-$)) may be used.



For oxidising 2° alcohols to ketones $CrO_3/K_2Cr_2O_7$ may be used.

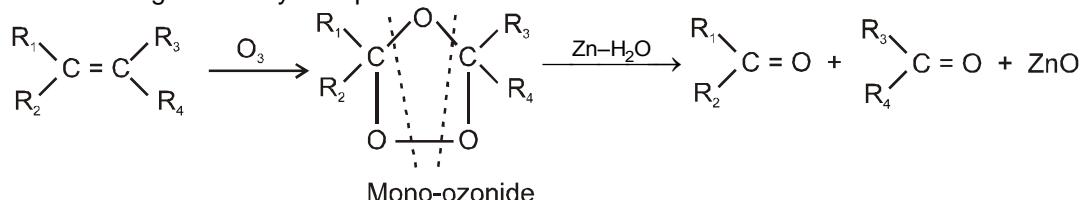
3.2 By dehydrogenation of (1° & 2°) alcohols :

Dehydrogenation means removal of hydrogen and reagent used is heated copper or silver. The alcohol vapours are passed over heavy metal catalyst to yield the following products.



3.3 Ozonolysis of alkene :

It is used to get carbonyl compounds from alkene. The reaction is

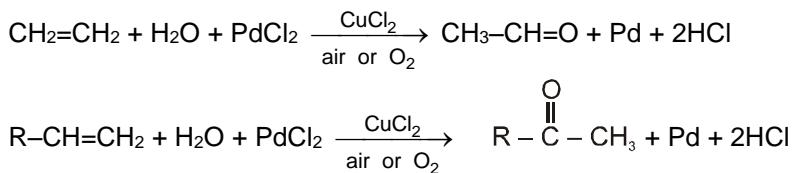




- Note :**
- (i) During the cleavage of ozonide Zn is used to check further oxidation of aldehyde into acid.
 - (ii) By this method we can locate double bond in olefin or exact structure of hydrocarbon can be determined by knowing ozonolysis product i.e. by placing double bond at the place of two carbonyl oxygen atoms of two carbonyl compounds.
 - (iii) Among the three molecules of carbonyl compounds.
 - (a) If one molecule contains two carbonyl groups, then hydrocarbon will be alkadiene.
 - (b) If all the three molecules contain two carbonyl group then hydrocarbon will be cycloalkatriene.
 - (iv) This method is used for aliphatic carbonyl compounds.

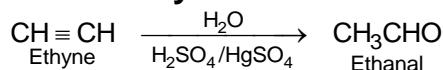
3.4 Wacker process :

Alkenes can directly be oxidised to corresponding aldehydes or ketones by treating them with a solution of $PdCl_2$ containing a catalytic amount of $CuCl_2$ in presence of air or O_2 . Except ethene any higher alkene will give ketone.

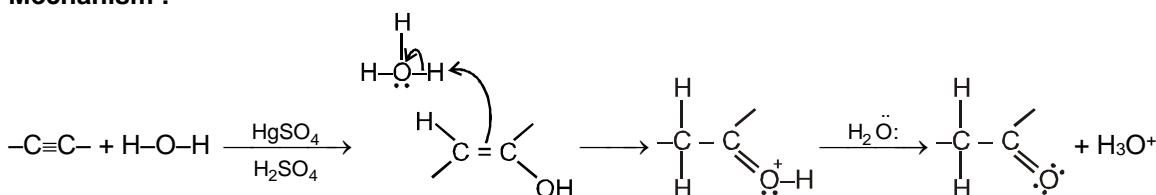


Note : During the reaction $PdCl_2$ is reduced to Pd and $CuCl_2$ is reduced to $Cu(I)$

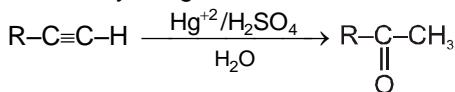
3.5 Hydration of alkynes :



Mechanism :

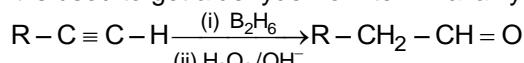


Other alkynes give ketones in this reaction.



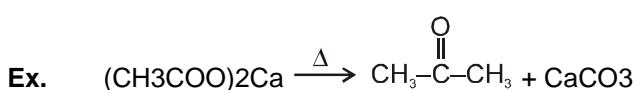
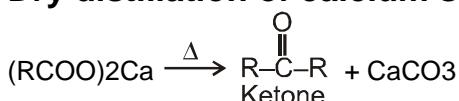
3.6 Hydroboration of alkyne :

It is used to get aldehyde from terminal alkyne. Here reagent is (i) diborane (B_2H_6) (ii) H_2O_2 , OH^-



In this reaction Borane (BH_3) is act as electrophile.

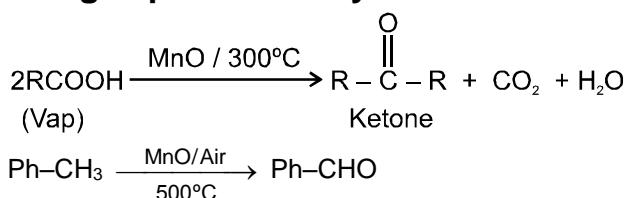
3.7 Dry distillation of calcium salt of acid :



On dry distillation of calcium salt of acetic acid with calcium salt of formic acid we get a mixture of aldehyde, ketone and formaldehyde. Calcium salt of dibasic acid (1, 4 & higher) on distillation gives cyclic ketones.



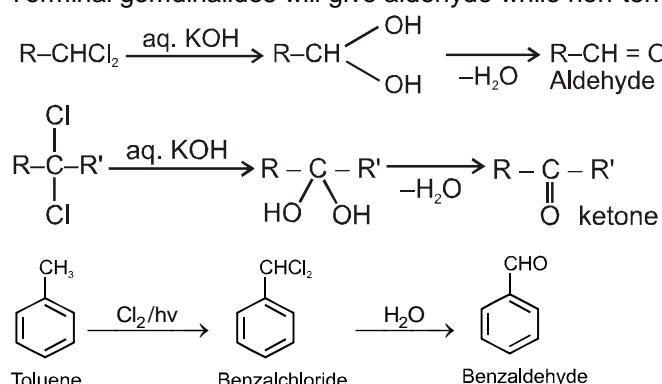
3.8 On passing vapours of fatty acids over Mangnous oxide at 300°C :



On passing mixture of vapours of fatty acid with formic acid we get a mixture of aldehyde, ketone and formaldehyde.

3.9 On alkaline hydrolysis of gem-dihalides :

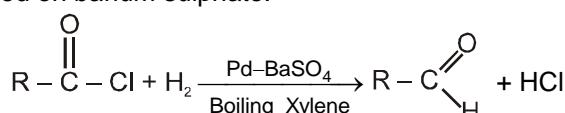
Terminal gemdihalides will give aldehyde while non-terminal will give ketone as follows



4. Methods used for the preparation of Aldehydes only.

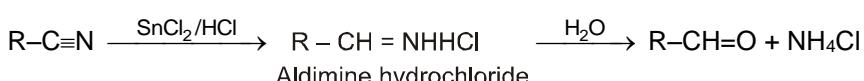
4.1 Rosenmund's reduction :

Here acid chlorides are reduced to aldehyde with H₂ in boiling xylene using palladium as a catalyst supported on barium sulphate.



Note : (a) Pd Catalyst is poisoned by BaSO₄ (Lindlars catalyst) to check further reduction of aldehyde to alcohol.
 (b) Formaldehyde cannot be obtained by this method because HCOCl is unstable at common temperature.
 (c) Reaction with acid chloride and dialkyl cadmium or Lithium dialkyl cuprate we can obtain ketone.

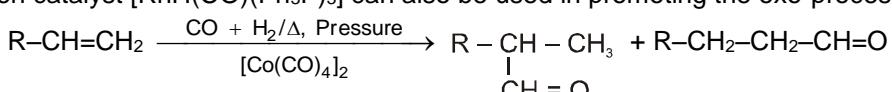
4.2 Stephen's reduction :



4.3 Oxo-process :

It is also called as carbonylation. Here terminal alkene reacts with water gas at high temperature and pressure in the presence of cobalt carbonyl catalyst to give aldehyde.

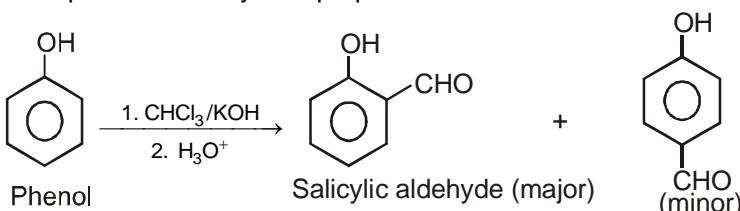
Wilkinson catalyst [RhH(CO)(Ph₃P)₃] can also be used in promoting the oxo-process.



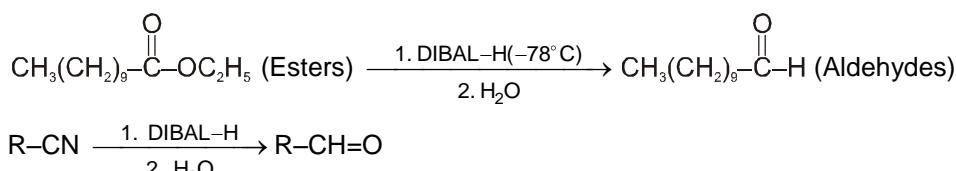


4.4 Reimer-Tiemann reaction :

By this method phenolic aldehyde is prepared



4.5 From esters or nitrile :

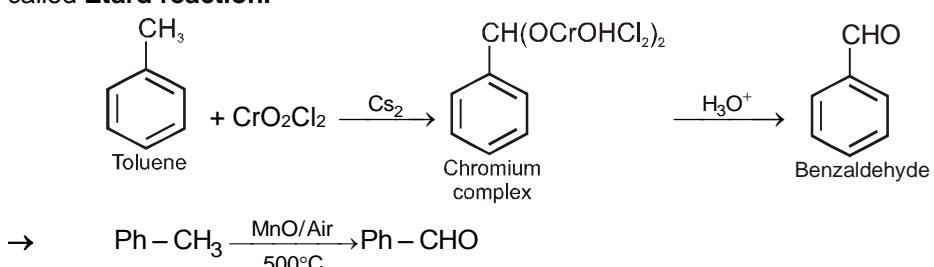


DIBAL-H : Diisobutyl aluminium hydride $[\text{AlH}(\text{i-Bu})_2]$ is a reducing agent.

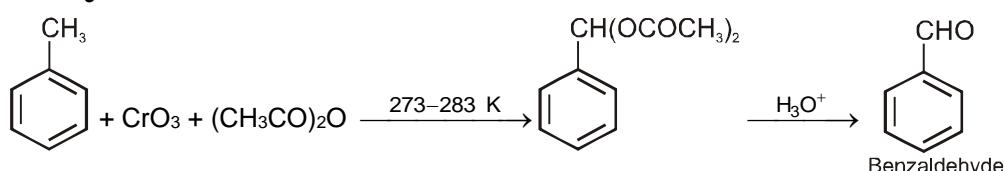
This is less reactive than LiAlH_4 and is more sterically hindered and has difficulty in transferring hydride ions.

4.6 From hydrocarbons :

By oxidation of methyl benzene and its derivative using chromyl chloride (CrO_2Cl_2). This reaction is called **Etard reaction**.

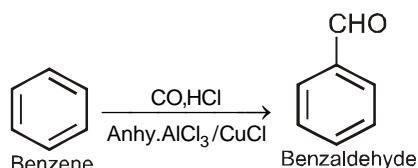
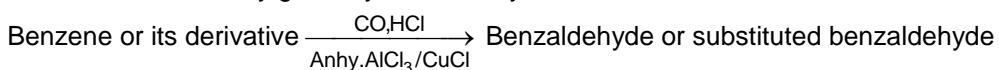


4.7 By oxidation of methyl benzene and its derivative using chromic oxide (CrO_3) in acetic anhydride:



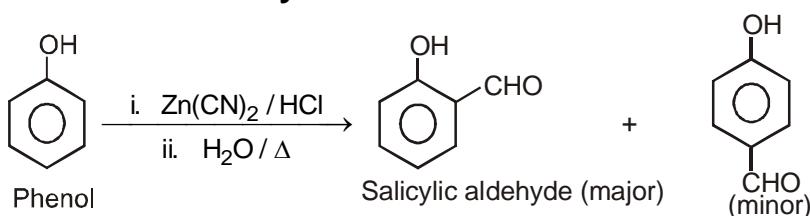
4.8. By Gatterman-Koch reaction:

This reaction is mainly given by aromatic hydrocarbons & Halobenzene



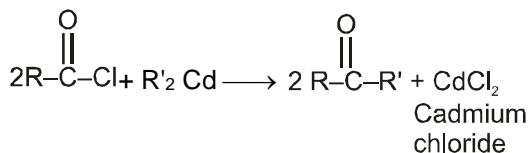
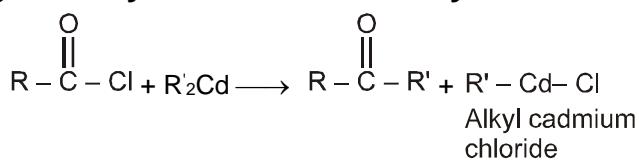


4.9 Gattermann formylation:

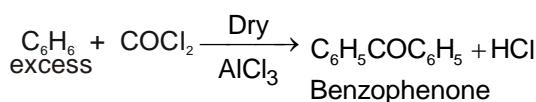
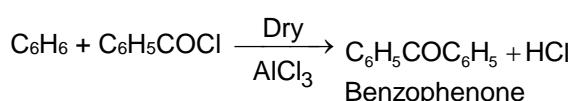
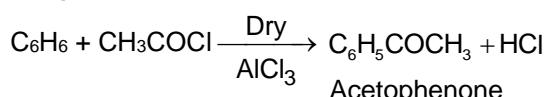


5. Methods used for the preparation of Ketones only

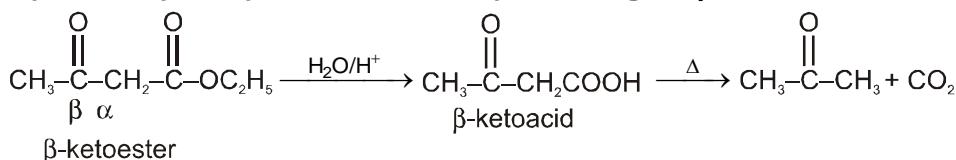
5.1 Using alkanoylchloride and dialkyl cadmium:



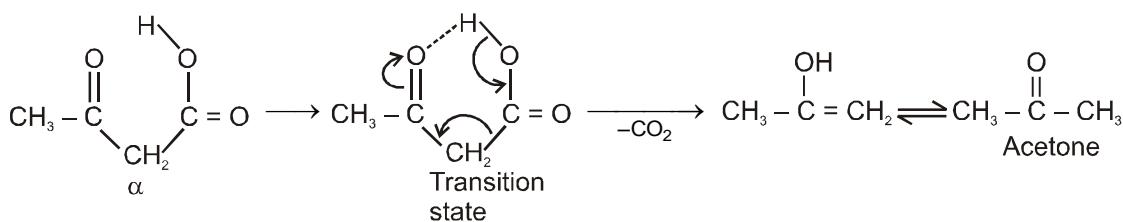
5.2 By acylation or benzylation of aromatic hydrocarbon (Friedel-Craft Reaction)



5.3 By acid hydrolysis followed by heating of β -Ketoester:



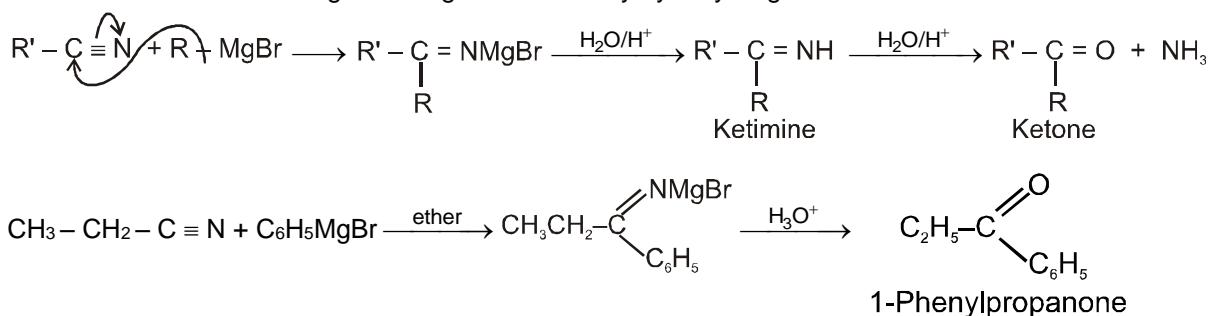
Note : It is β -ketoacid which decarboxylate more readily as it proceeds via six membered cyclic transition-state.





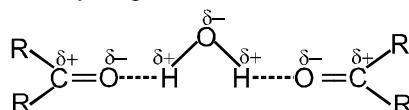
5.4 From nitriles :

Treatment of nitrile with Grignard reagent followed by hydrolysis gives a ketone.



6. Physical properties of Aldehydes and Ketones :

- ☛ Methanal - Gas at room temperature
- ☛ Ethanal - Volatile liquid
- ☛ Other aldehydes and ketones - Liquid or solid at room temperature
- ☛ Boiling points of aldehydes and ketones are higher than those of hydrocarbons and ethers of comparable molecular masses.
Reason: Weak molecular association in aldehydes and ketones, arising out of the dipole-dipole interactions.
- ☛ Boiling points of aldehydes and ketones are lower than those of alcohols of similar molecular masses.
Reason : Absence of intermolecular hydrogen bonding
- ☛ Lower members of aldehydes and ketones are miscible with water in all proportions.
Reason : They form hydrogen bonds with water.



- ☛ Solubility of aldehydes and ketones decreases rapidly on increasing the length of the alkyl chain.
- ☛ All aldehydes and ketones are fairly soluble in organic solvents such as ether, methanol, etc.
- ☛ Lower aldehydes have sharp pungent odours.
- ☛ As the size of aldehydes increases, the odour becomes less pungent and more fragrant.

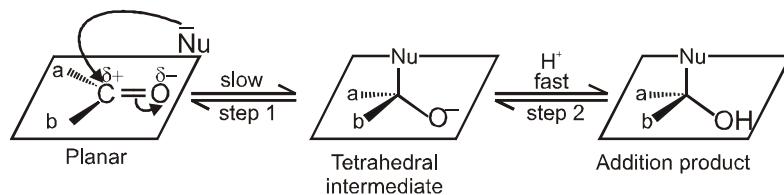
Section (B) : Nucleophilic addition reactions

7. Chemical reactions

7.1 Nucleophilic addition reactions :

Addition of a nucleophile and a proton across the (C=O) double bond: The reactivity of the carbonyl group arises from the electronegativity of the oxygen atom and the resulting polarization of the carbon-oxygen double bond. The electrophilic carbonyl carbon atom is sp^2 hybridized and flat, leaving it relatively unhindered and open to attack from either face of the double bond.

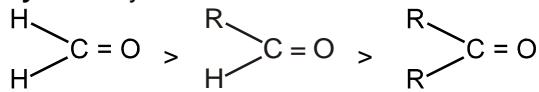
Mechanism :





Nucleophile (Nu^-) attacks the carbonyl group perpendicular to the plane of sp^2 hybridised orbitals of carbonyl carbon. In the process, hybridisation of carbon changes from sp^2 to sp^3 . A tetrahedral alkoxide is formed as intermediate.

Reactivity : Aldehydes are more reactive than ketones in nucleophilic addition reactions.



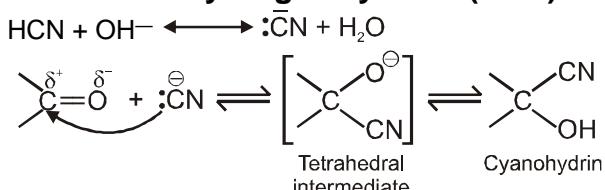
There are two factors which influence the reactivity of ketone and aldehyde.

- (i) Inductive effect (ii) steric factor
- (i) +I effect of alkyl group decrease the amount of charge on $\text{C}=\text{O}$ group.
- (ii) Steric effect also decreases the reactivity of carbonyl group.
- (iii) The Aryl group stabilizes the reactant by resonance and causes a net deactivation effect of the reactant.

Que. Compare reactivity between Benzaldehyde & Propanal.

Ans. Benzaldehyde < Propanal.

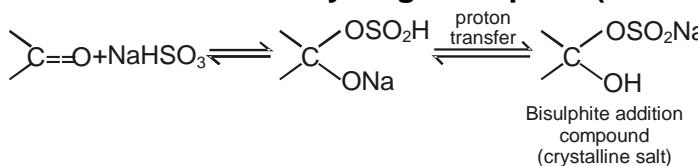
(I) Addition of hydrogen cyanide (HCN)



Note : (i) Addition of HCN over aldehyde and ketones gives cyanohydrin.

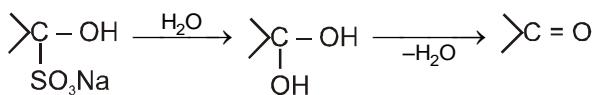
- (ii) Cyanohydrin on acid hydrolysis gives α -hydroxy acid.
- (iii) Cyanohydrin on treating with $\text{NH}_3(l)$ followed by acid hydrolysis gives α -amino acid.
- (iv) In case of ketone, cyanohydrin formation is reversible due to bulky group of ketone which hinder the formation.
- (v) Reaction occurs slowly with pure HCN hence catalysed by a base. CN^- is a stronger nucleophile than OH^- ions and adds readily.

(II) Addition of sodium hydrogen sulphite (NaHSO_3)

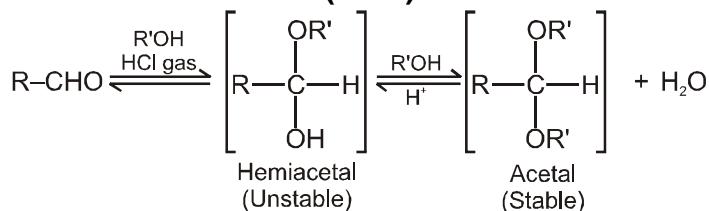


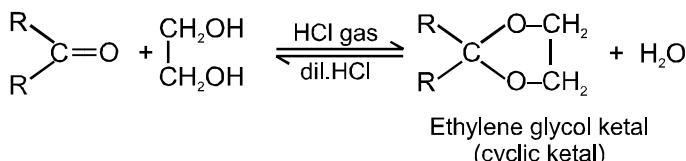
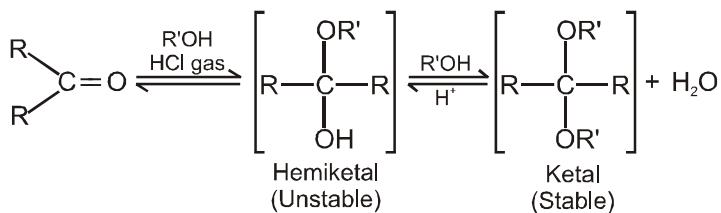
Salt on hydrolysis gives carbonyl compounds again, this reaction is used to separate the aldehydes from mixture.

Position of equilibrium lies largely to the right side for most aldehydes and to the left side for most ketones due to steric factors.



(III) Addition of alcohols (ROH) :



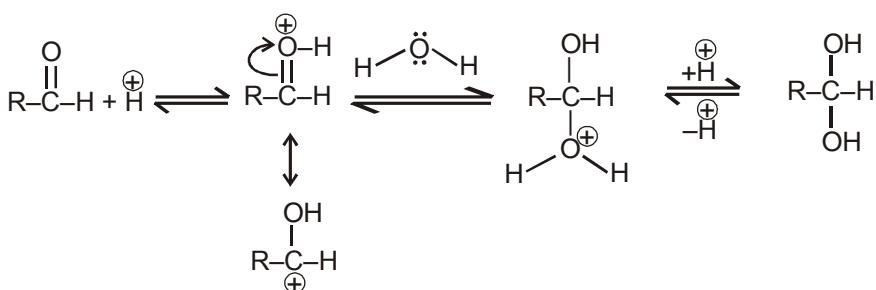


- Note :**
- (i) Acetal is formed to protect aldehyde for a long time.
 - (ii) Acetal has functional groups ether.
 - (iii) Acetal formed can be decomposed to original aldehyde by dilute acid.
 - (iv) On treating with ethyleneglycol we get cyclic acetal or ketal.
 - (v) Acetal formation is found to be more favourable than ketal formation if both the carbonyl groups are present within the molecule.

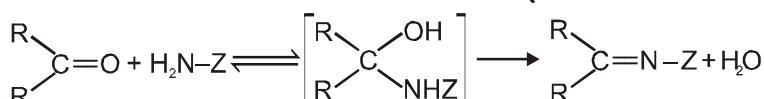
(IV) Addition of water :

Aldehyde or ketone reacts with water to form gem-diols. Water is a poor nucleophile and therefore adds relatively slowly to the carbonyl group, but the rate of reaction can be increased by an acid catalyst.

Mechanism:

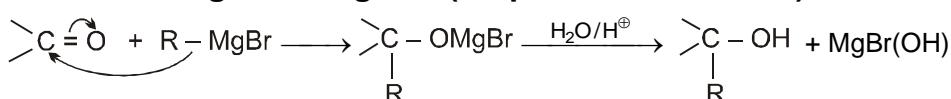


(V) Addition of ammonia and its derivatives (addition elimination reactions) :



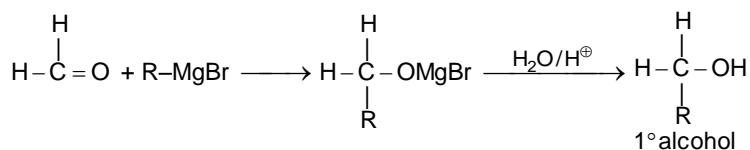
If Z are	Reagents Name	Products
-OH	Hydroxylamine	Oxime
-NH ₂	Hydrazine	Hydrazone
-NH-C ₆ H ₅	Phenylhydrazine	Phenylhydrazone
-NH--NO ₂	2,4-dinitrophenylhydrazine (Brady's reagent) or 2,4-DNP	2,4-dinitrophenylhydrazone (Solid orange precipitate)
-NH-C(=O)-NH ₂	Semicarbazide	Semicarbazone

(VI) Addition of Grignard reagents (Preparation of alcohol) :

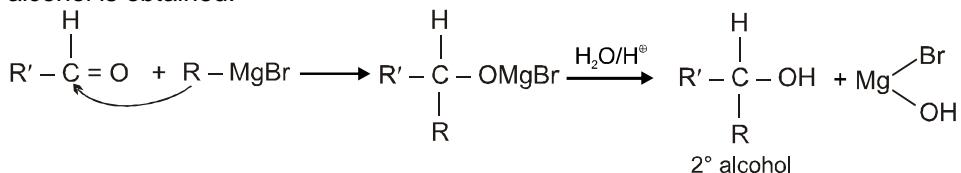




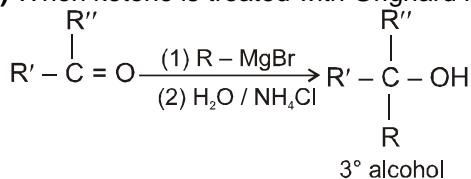
(a) When formaldehyde is treated with Grignard reagent followed by acid hydrolysis primary alcohol is obtained.



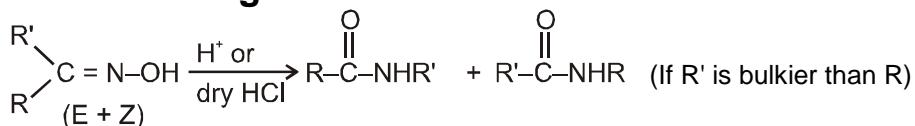
(b) When aldehyde except formaldehyde is treated with Grignard reagent followed by hydrolysis 2° alcohol is obtained.



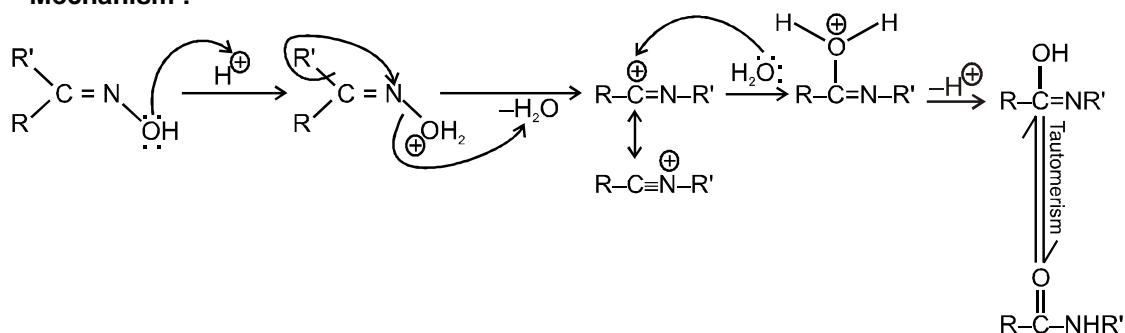
(c) When ketone is treated with Grignard reagent followed by acid hydrolysis 3° alcohol is obtained.



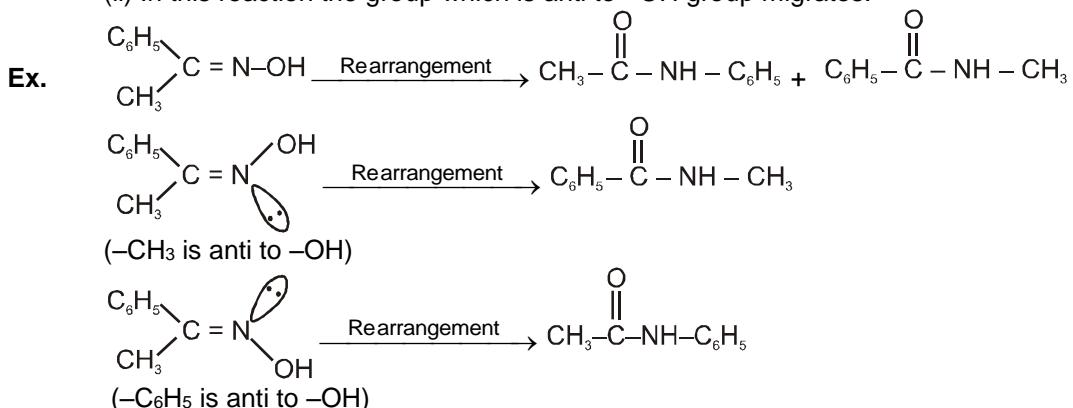
7.2 Beckmann rearrangement in oximes:



Mechanism :



Note : (i) Oxime undergoes Beckmann rearrangement to give its isomer amide.
 (ii) In this reaction the group which is anti to $-\text{OH}$ group migrates.



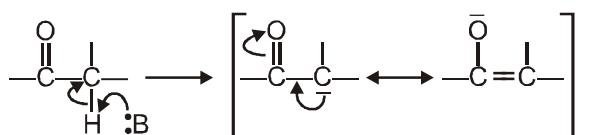


Section (C) : Condensation reactions

7.3 Reactions due to α -hydrogen

α -Hydrogen of aldehydes and ketones are acidic: They undergo a number of reactions due to the acidic nature of α -hydrogen.

Reason for the acidity of α -hydrogen: Strong electron-withdrawing effect of the carbonyl group, and resonance stabilisation of the conjugate base



Resonating structure of conjugate base

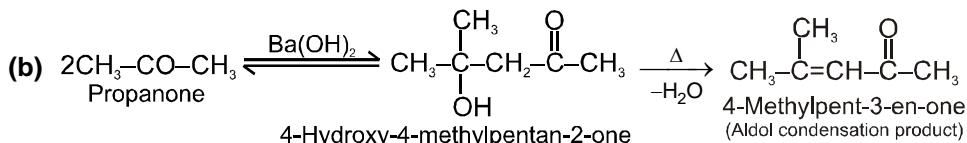
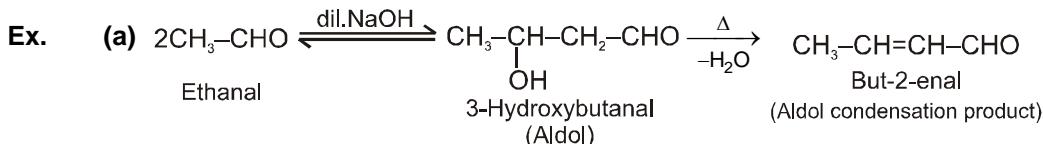
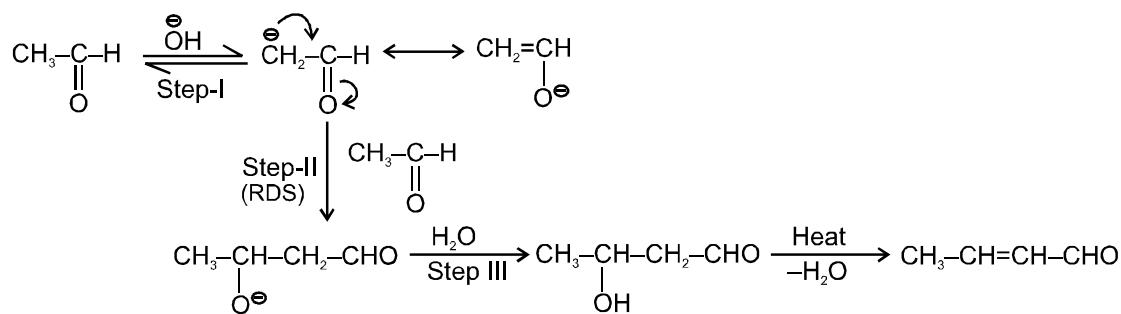
(I) Aldol condensation (or aldol reaction)

Aldehydes and ketones with at least one α -hydrogen undergo a reaction in the presence of dilute alkali as catalyst.

Aldol is derived from two functional groups aldehyde(s) and alcohol.

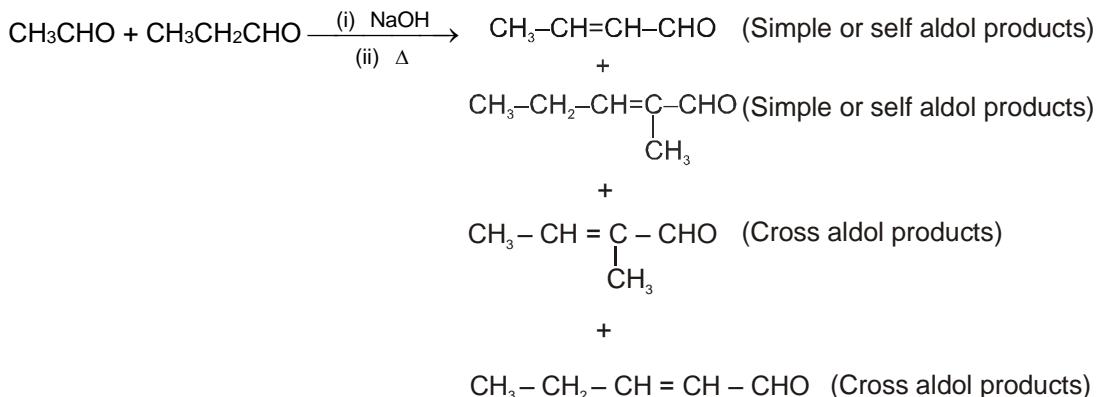
Ketones gives ketols (keto + alcohols) groups. The name aldol condensation still applies to their reactions.

Mechanism

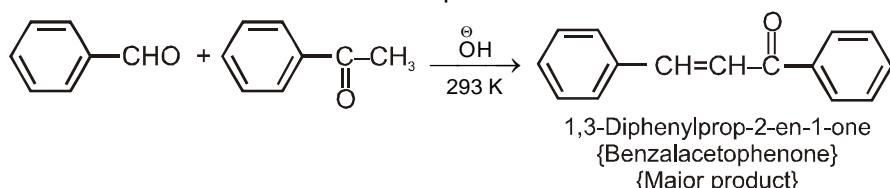


(II) Cross-Aldol condensation :

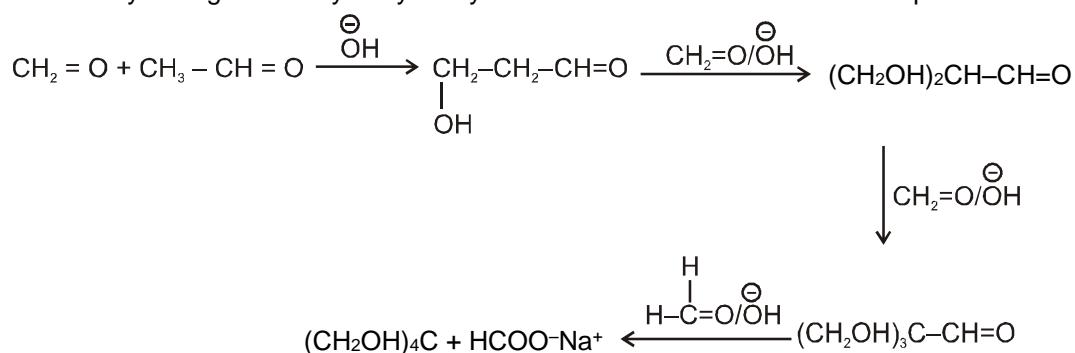
On using two types of carbonyl compounds both having α -hydrogen atoms we get a mixture of four condensed product because two types of carbonyl compounds will give two type of carbanions which will be nucleophile for itself and other molecule.



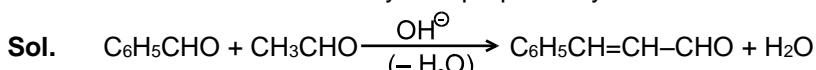
Ketones can also be used as one component in cross-aldol reactions.



Note : On using formaldehyde and acetaldehyde during crossed aldol all the α -hydrogen atom of acetaldehyde are replaced one by one by hydroxymethyl group because of smaller size of formaldehyde to give trihydroxymethylacetaldehyde which undergoes crossed cannizaro's reaction with formaldehyde to give tetrahydroxymethyl methane and formate ion as a final product.

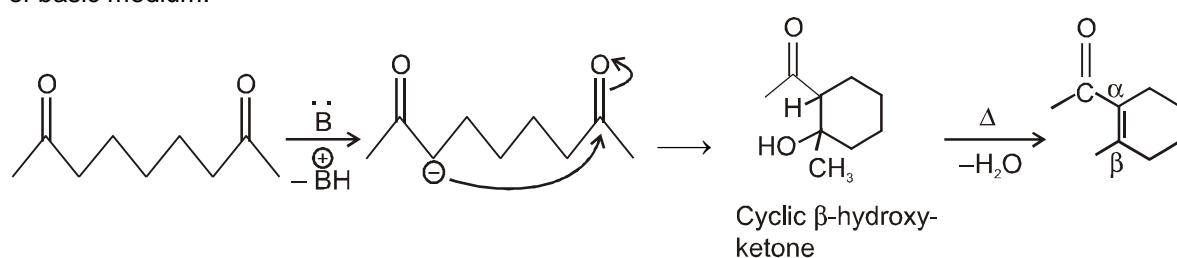


Ex. Show how cinnamaldehyde is prepared by crossed aldol condensation ?



(III) Intramolecular aldol condensation :

If two carbonyl groups with α -hydrogen atoms are present within the same molecule, then we get cyclic α , β -unsaturated aldehyde / ketones via the formation of cyclic- β -hydroxy aldehyde / ketone in presence of basic medium.

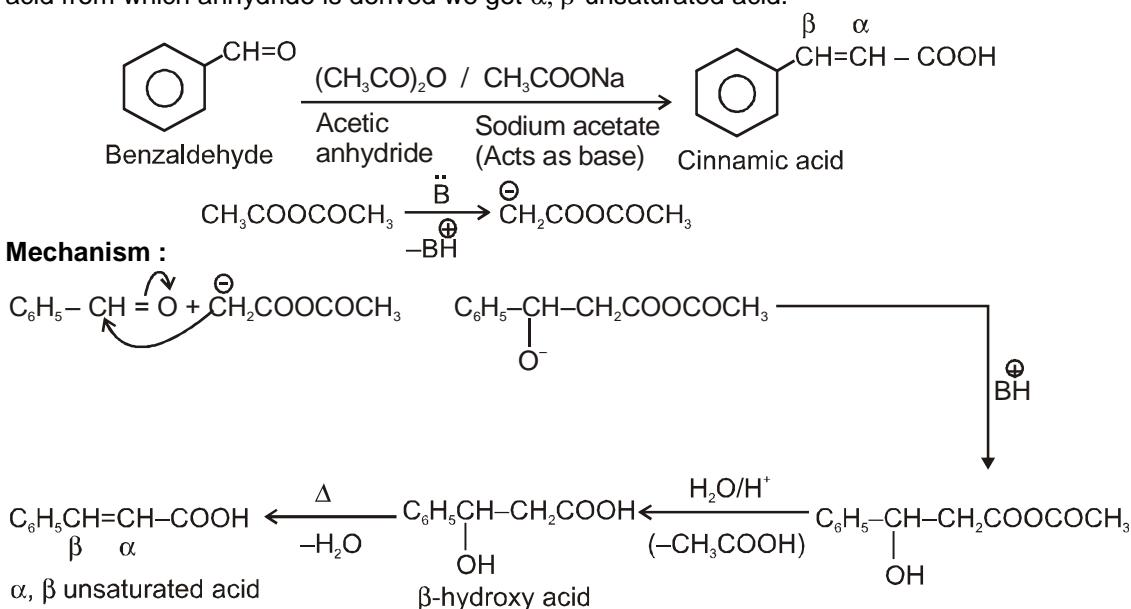


By knowing product we can get reactant as in case of intermolecular aldol condensation :



7.4 Perkin reaction :

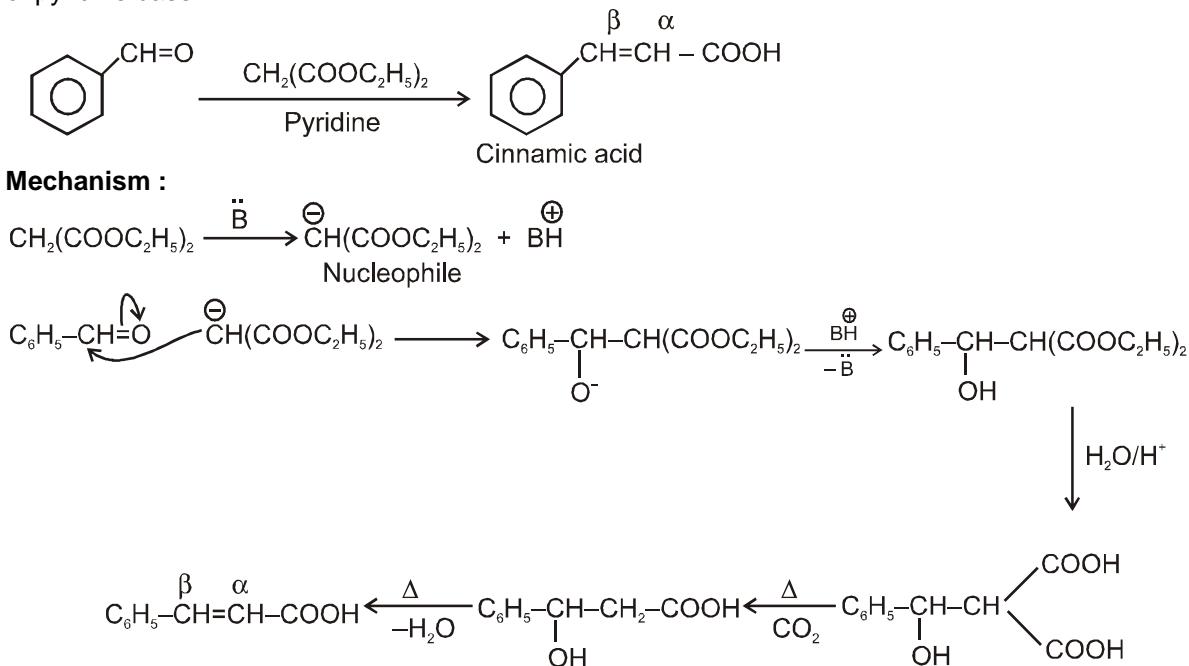
When aromatic aldehyde like benzaldehyde is treated with anhydride in the presence of sodium salt of acid from which anhydride is derived we get α, β -unsaturated acid.



Note : By knowing α, β -unsaturated acid we can get idea about the anhydride used in perkin reaction. This can be done by keeping 'H' at α and $-\text{OH}$ at β -carbon atom followed by breaking α, β carbon. By this we can know about acid and it will be anhydride of this acid only.

7.5 Knoevenagel reaction :

It is preparation of α, β -unsaturated acid with carbonyl compound using malonic ester in the presence of pyridine base.



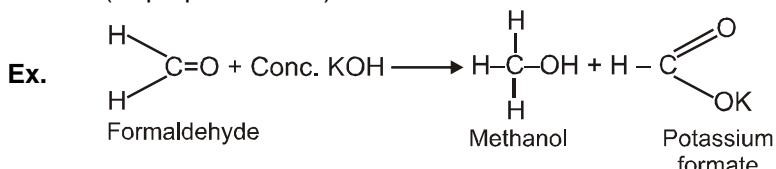
that is we reflux the ester with dilute aqueous HCl or dilute aqueous H_2SO_4 .



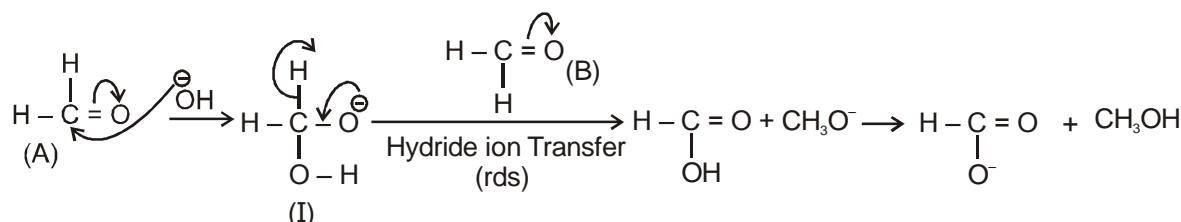
Section (D) : Cannizzaro's reactions

7.6 Cannizzaro reaction :

Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with a concentrated alkali.



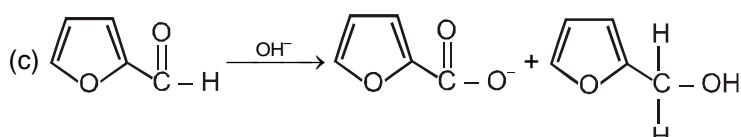
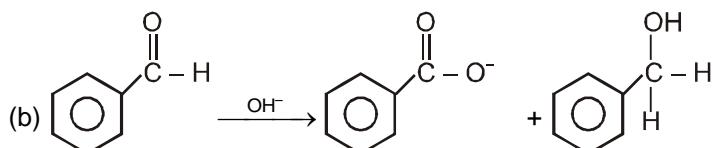
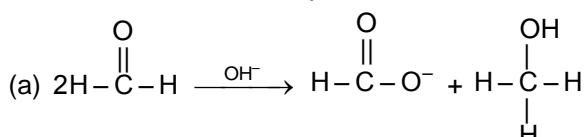
Mechanism :



By this mechanism it is clear that acid corresponds to that carbonyl compound over which OH^- can attack easily as nucleophile.

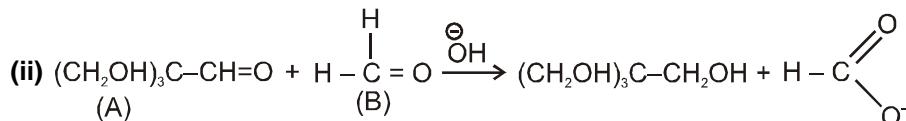
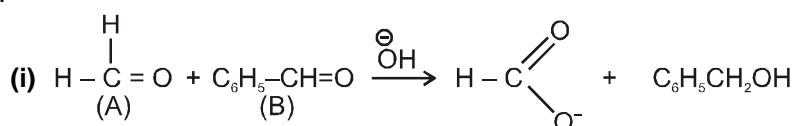
Note : It is observed that hydride ion transfer from (I) to Carbonyl compound (B) is rate determining step.

Ex. Predict the condensation products of these reactions :



Crossed Cannizzaro reaction :

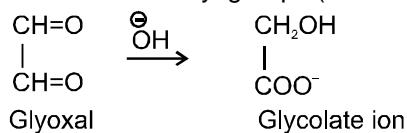
When ever two different aldehyde or ketons without α -hydrogen atom is treated with strong base, the reaction is known as cross cannizzaro reaction. In this reaction one of the reactant (with lesser electron density) get oxidized to carboxylate ion, where as the one with greater electron density is reduced to alcohol.



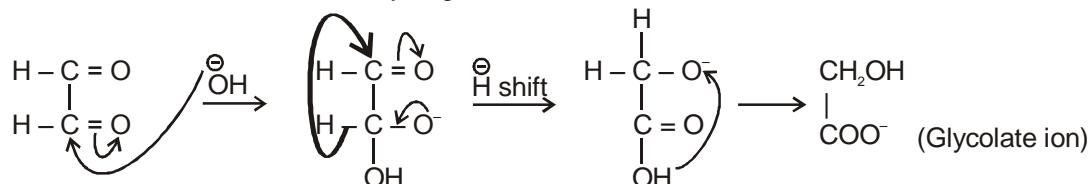


Intramolecular Cannizzaro reaction :

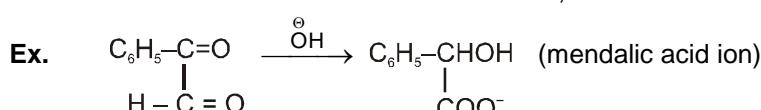
Here two carbonyl groups (without α -hydrogen atom) are present within the same molecule.



Mechanism : \Rightarrow α -keto aldehyde gives internal cannizzaro reaction.



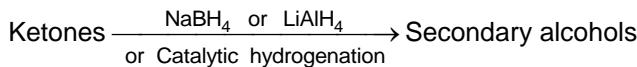
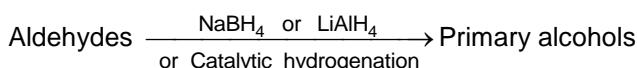
When the reaction is carried out in D_2O , the obtained alcohol contains no α -deuterium.



Note : 1. CH_3CHO does not give cannizzaro reaction.
2. $(\text{CH}_3)_2\text{CH}-\text{CH=O}$ gives cannizzaro reaction.

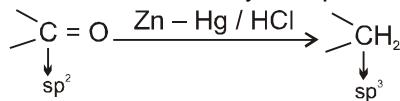
7.7 Reduction reactions

(I) Reduction to alcohols :



(II) Clemmensen reduction :

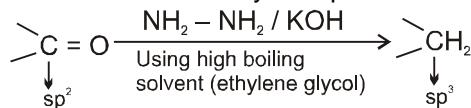
Used to get alkane from carbonyl compounds.



Note : Generally this reaction is avoided if **acid sensitive** groups are present in the carbonyl compounds.

(III) Wolf-Kishner reduction :

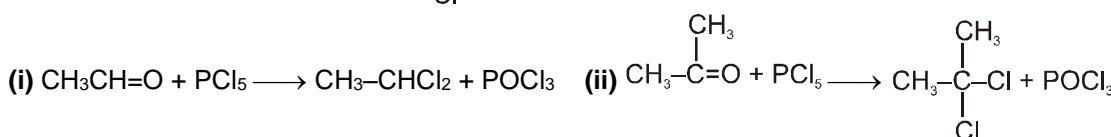
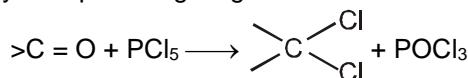
Used to get alkane from carbonyl compounds.



Note : Generally this reaction is avoided if **base sensitive** groups are present in the carbonyl compounds

(IV) Reaction with PCl_5 :

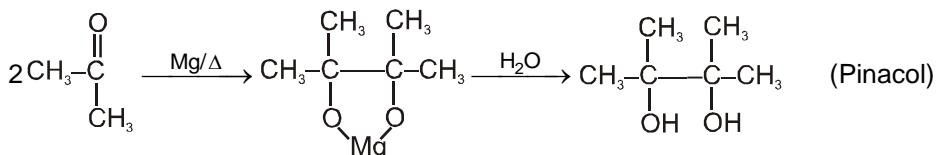
Carbonyl compounds give gemdihalides



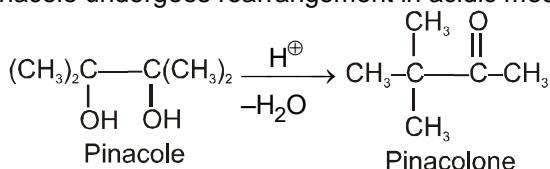


(V) Preparation of Pinacol:

Pinacole is obtained when 2 moles of acetone are heated with magnesium metal followed by treating with water.



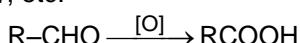
Pinacole undergoes rearrangement in acidic medium to give pinacolone



Section (E) : Redox reactions

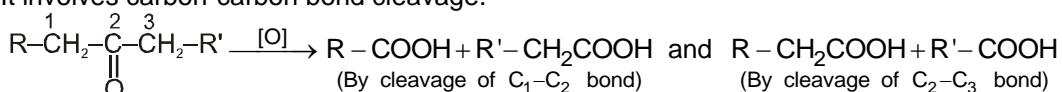
7.8 Oxidation of Aldehydes :

- Aldehydes are oxidised to carboxylic acids by common oxidising agents such as KMnO_4 , HNO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, etc.



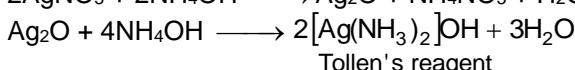
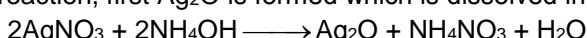
- Aldehydes are also oxidised by mild oxidising agents such as Tollen's reagent and Fehling's reagent. On the other hand, ketones are not oxidised by mild oxidising agents.
- Ketones are oxidised under vigorous conditions, i.e., by strong oxidising agents and at elevated temperatures.

It involves carbon-carbon bond cleavage.

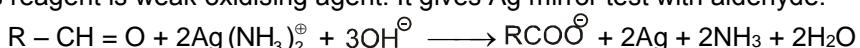


(a) Tollen's reagent :

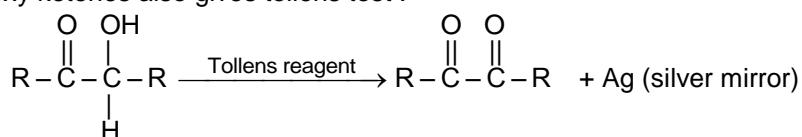
It is ammonical silver nitrate solution, prepared by adding ammonium hydroxide to AgNO_3 solution. During reaction, first Ag_2O is formed which is dissolved in ammoniumhydroxide to give Tollen's reagent.



Tollen's reagent is weak oxidising agent. It gives Ag mirror test with aldehyde.



Note : α -hydroxy ketones also gives tollens test :



(b) Fehling's solution :

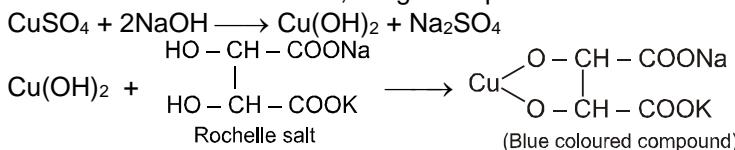
It is an alkaline solution of cupric ion complexed with sodium potassium tartarate.

There are two solutions in Fehling solution

Solution (A) : CuSO_4 solution and

Solution (B) : Alkaline solution of sodium potassiumtartarate.

When these two solutions are mixed, we get deep blue coloured solution.

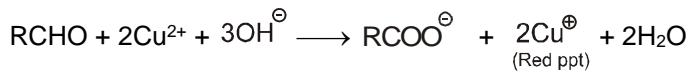




Equal volume of both the solutions are heated with aldehyde to give red brown precipitate of cuprous oxide (Cu_2O) which confirms the presence of aldehyde.



Blue

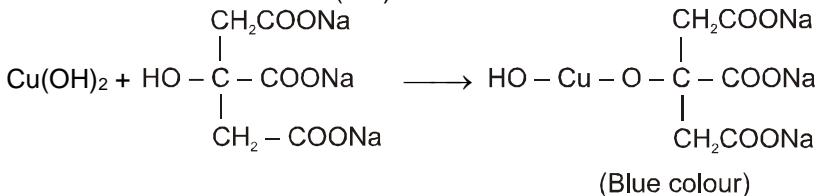
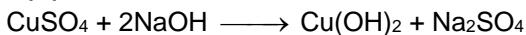


(c) Benedict solution :

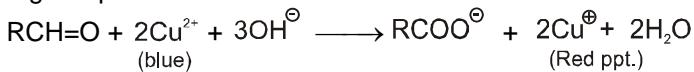
It also consists of two solutions.

Solution (A) : CuSO_4 solution and

Solution (B) : Alkaline solution of sodium Citrate.



Aldehyde gives positive test with Benedict solution.



(d) Schiff's reagent :

It is dilute solution of rosaniline hydrochloride whose pink colour has been discharged by passing SO_2 . Aldehyde restores pink colour when treated with schiff's reagent (Magenta solution in H_2SO_3).

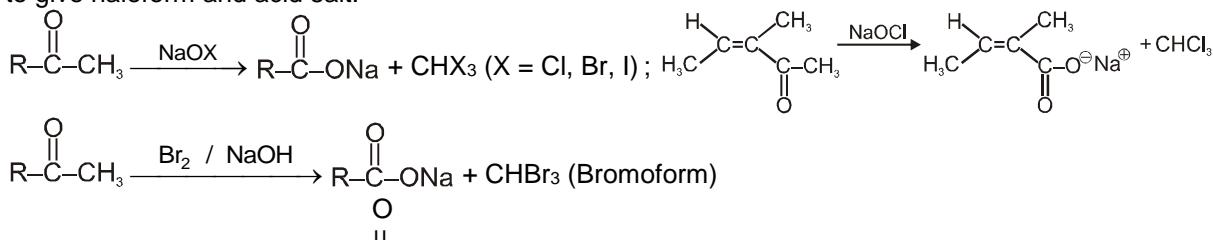
Benzaldehyde does not gives Fehling, Benedict & Schiff's test

Section (F) : α -Halogenation, haloform, α -deuteration reactions

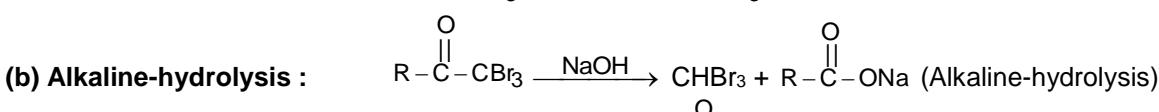
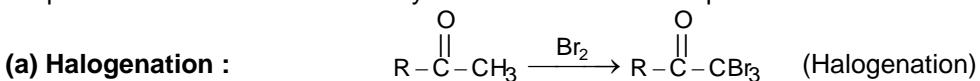
7.9 Oxidation reactions

(I) Haloform reaction :

Acetaldehyde and methylalkyl ketones react rapidly with halogen (Cl_2 , Br_2 or I_2) in the presence of alkali to give haloform and acid salt.



In this reaction $-\text{CH}_3$ of $\text{CH}_3-\text{C}-$ group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone give acid salt having carbon atom corresponding to alkyl ketone. Preparation of haloform from methylketone involves two steps.

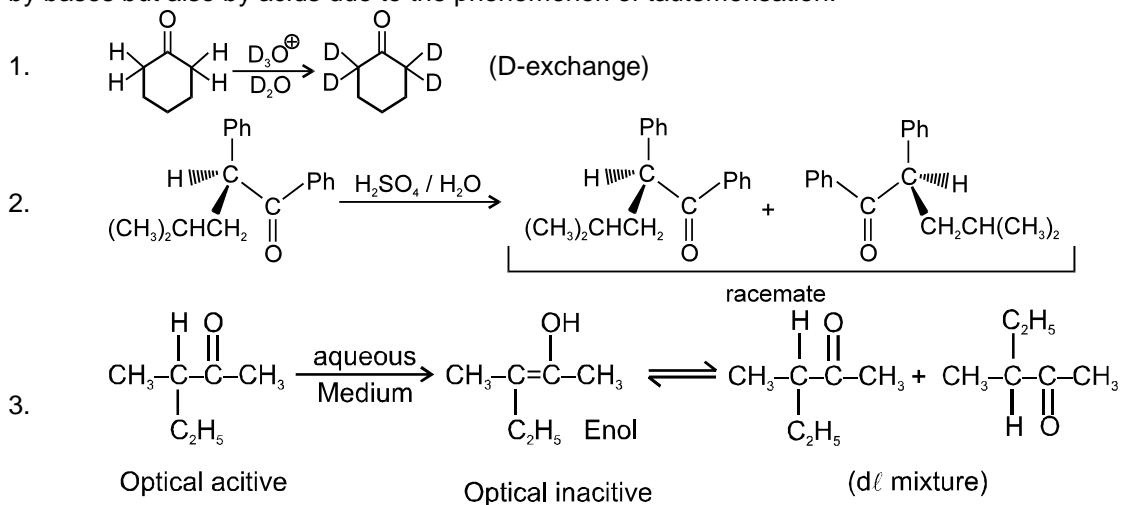


Note : This reaction is used to distinguish the presence of $\text{CH}_3-\text{C}-$ group.

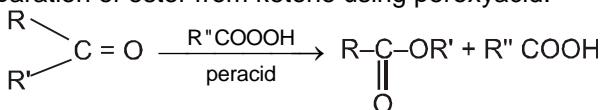
Acetoacetic ester does not give this reaction because it contains active methylene group.


(II) Racemisation and D-exchange :

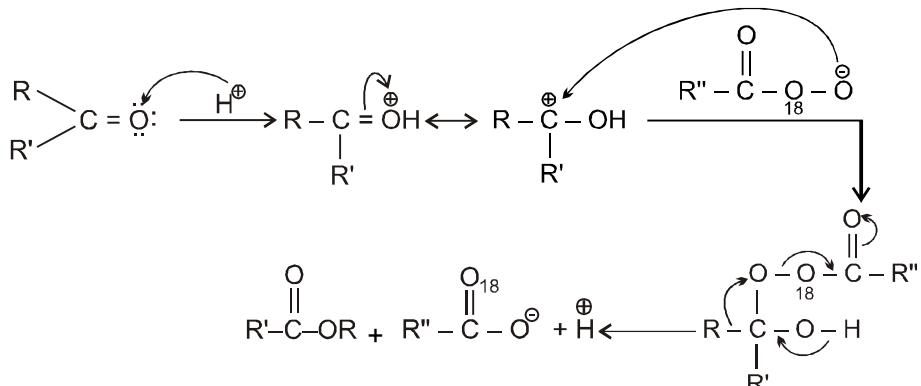
Exchange of α -hydrogen from deuterium as well as racemization at the α -carbon are catalyzed not only by bases but also by acids due to the phenomenon of tautomerisation.


(III) Baeyer-Villiger oxidation :

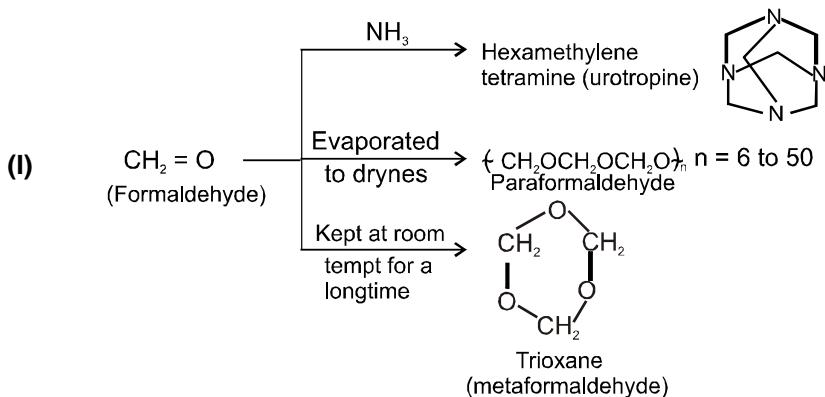
It is preparation of ester from ketone using peroxyacid.

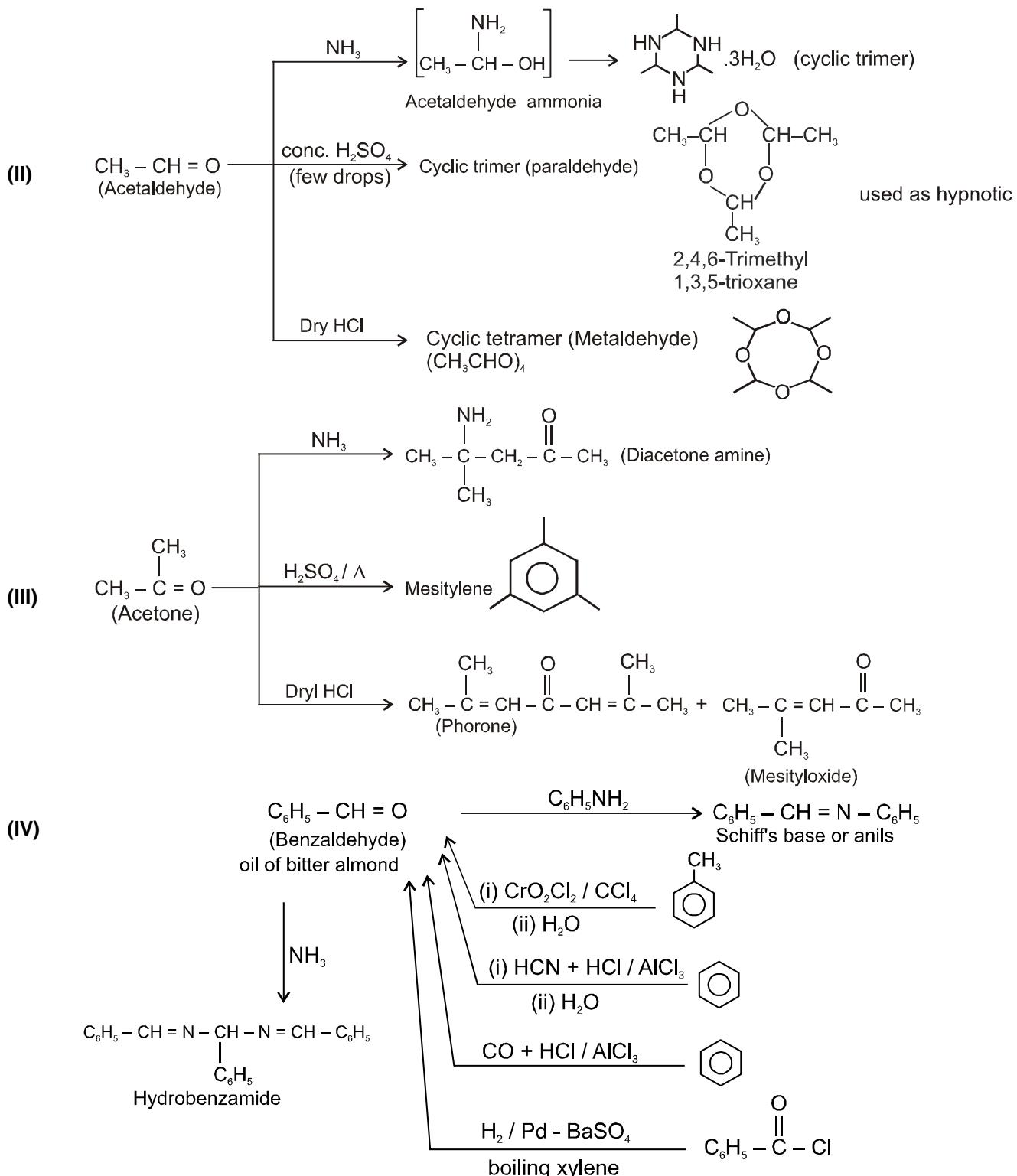


Mechanism :



Note : In unsymmetrical ketones, preference of insertion of oxygen atom in decreasing order is : $\text{H} > 3^\circ\text{R} > 2^\circ\text{R} > \text{Ph} > 1^\circ\text{R} > \text{CH}_3$

7.10 Other miscellaneous reactions :




8. Uses of Aldehydes and Ketones

- ☛ Act as solvents.
- ☛ Act as starting materials and reagents for the synthesis of other products.
- ☛ Formalin (40% solution of formaldehyde)- Used for preserving biological specimens, bakelite, urea , formaldehyde glues and other polymers products.
- ☛ Acetaldehyde used in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.



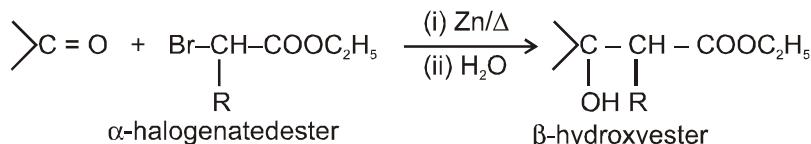
- ☞ Benzaldehyde used in perfumery and in dye industries.
- ☞ Butyraldehyde, vanillin, camphor, etc., are well known for their odours and flavours.
- ☞ Acetone and ethyl methyl ketone are common industrial solvents.

9. Other miscellaneous named reactions :

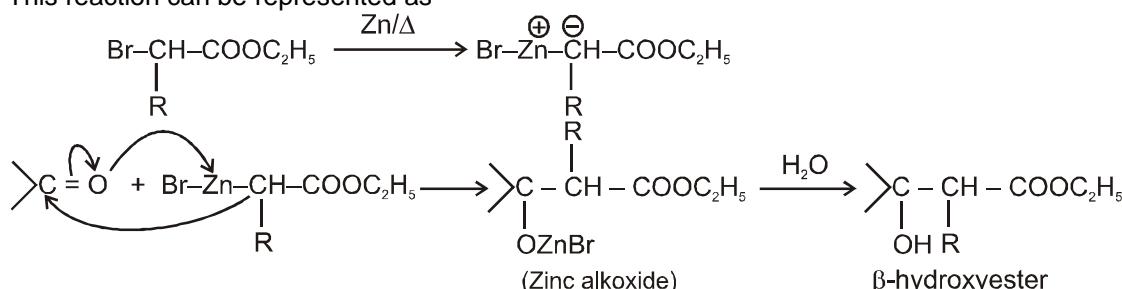
9.1 Reformatsky reaction :

When carbonyl compound and α -halogenated ester are heated with zinc followed by treating with water we get β -hydroxyester.

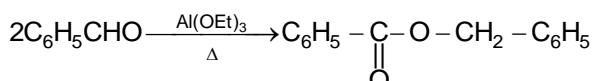
The organozinc reagent generated is less reactive than a Grignard reagent, it does not add to the ester group.



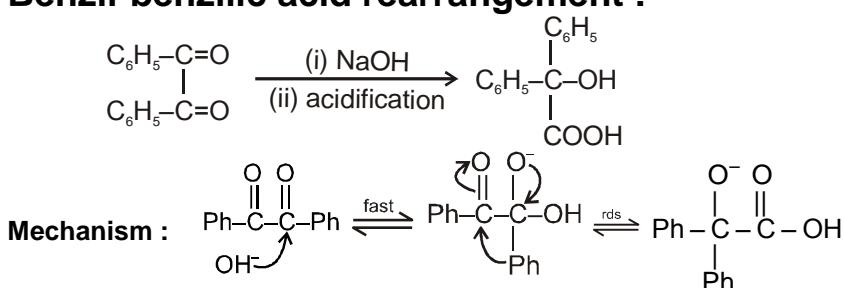
This reaction can be represented as –



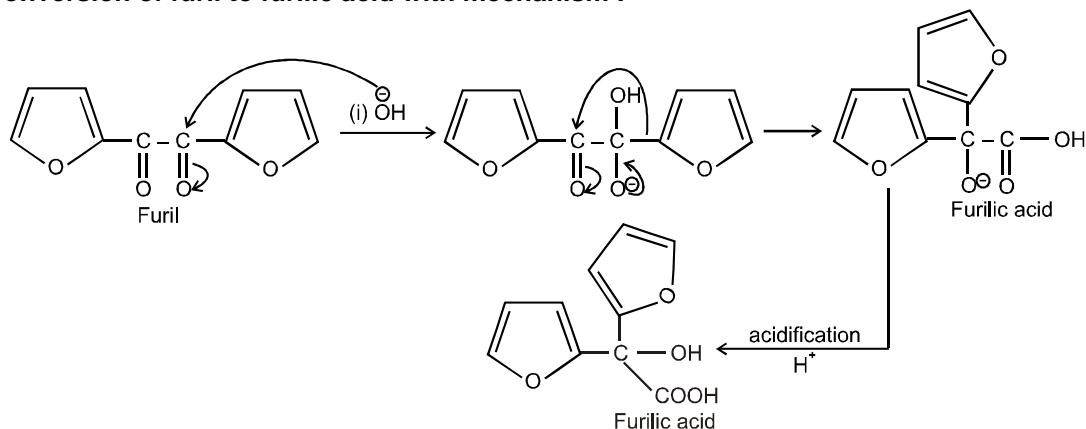
9.2 Tischenko reaction:



9.3 Benzil-benzilic acid rearrangement :

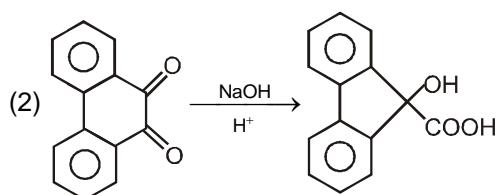
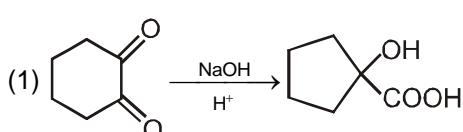


Conversion of furil to furilic acid with mechanism :



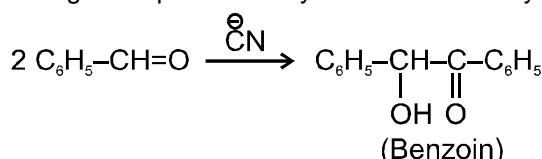


Predict the products of the following reactions :

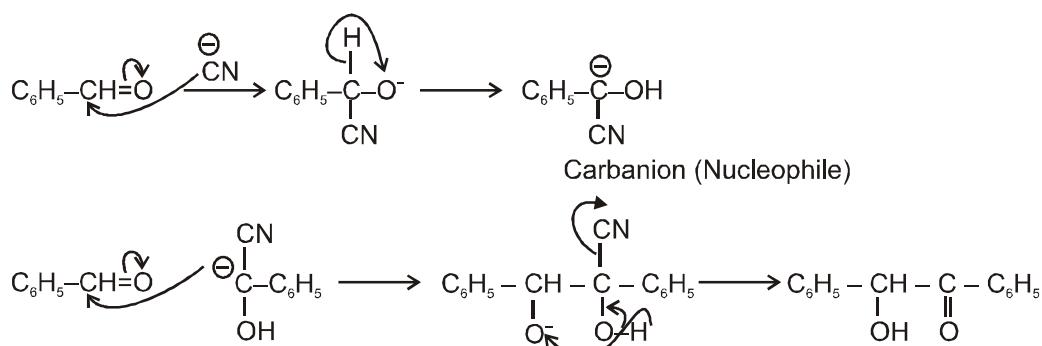


9.4 Benzoin Condensation :

During this reaction benzoin is obtained when an ethanolic solution of benzaldehyde is heated with strong alkali potassium cyanide or sodium cyanide.

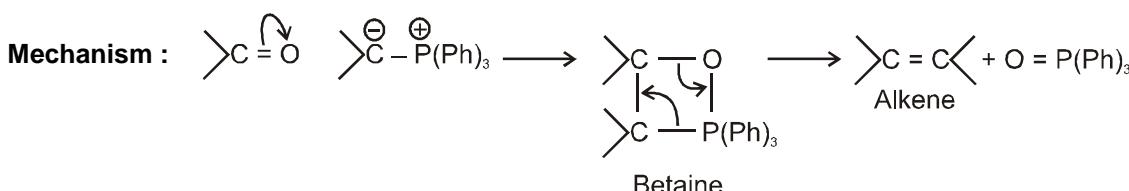


Mechanism :

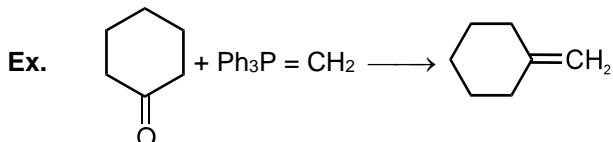
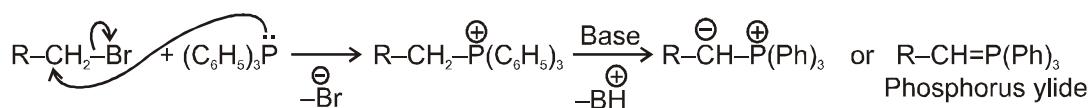


9.5 Wittig reaction :

It is used to get alkene from carbonyl compound using phosphorus ylide via the formation of cyclic structure betaine.



Note : Phosphorus ylides are prepared from alkylhalide and triphenylphosphine in the presence of base like sodium ethoxide as –

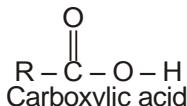




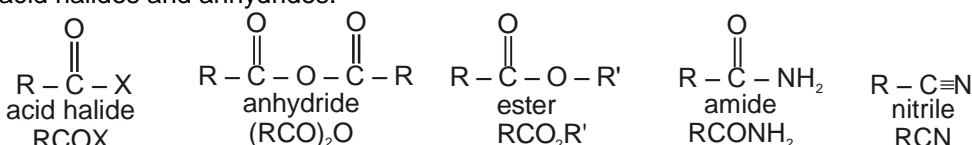
Carboxylic Acids & Acid Derivatives

Introduction :

Compounds containing the carboxyl group are distinctly acidic and are called **carboxylic acids**. Their general formula is $C_nH_{2n}O_2$.



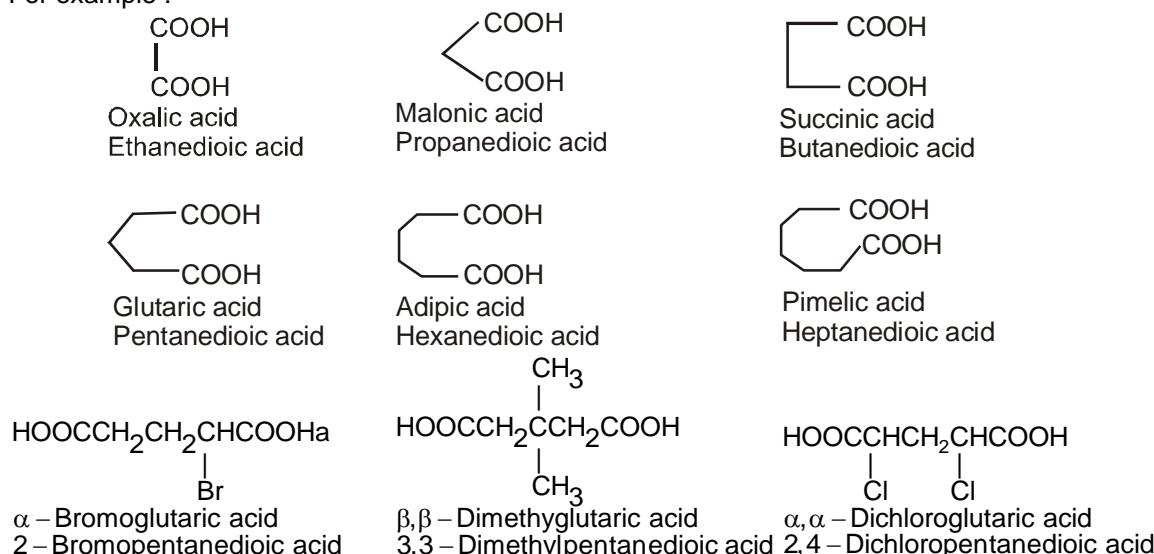
Carboxylic acid derivatives are compounds with functional groups that can be converted to carboxylic acids by a simple acidic or basic hydrolysis. The most important acid derivatives are esters, amides, nitriles, acid halides and anhydrides.



Dicarboxylic acids :

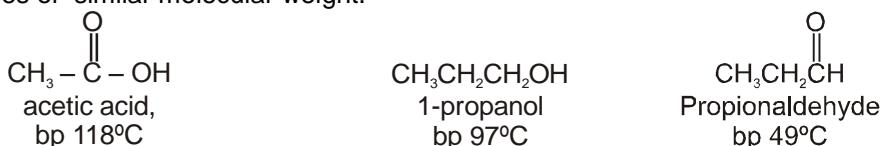
If the compound containing two carboxyl groups, these are known as dicarboxylic acid.

For example :

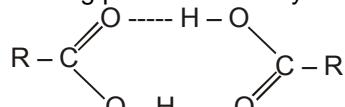


Physical properties of acids and acid derivatives :

(1) **Boiling point** : The boiling point of carboxylic acids are higher than that of alcohols, ketones or aldehydes of similar molecular weight.



The high boiling points of carboxylic acids is the result of formation of a stable hydrogen-bonded dimer.



hydrogen bonded acid dimer

**(2) Melting points :**

Melting point of carboxylic acids : There is no regular pattern in melting point of carboxylic acid (up to 10 carbon atoms) having even number of C atoms are higher than neighbouring members having odd number of C atoms because carboxylic acid and methyl group in even members lie in opposite side of zig-zag carbon chain hence they fit better into crystal lattice resulting in higher melting points. Vice-versa is observed in case of carboxylic acid having odd no. of carbon atoms.



Higher melting point



Lower melting point

Amides have surprisingly high boiling points and melting points compared with other compounds of similar molecular weight. Primary and secondary amides participate in strong hydrogen bonding.

(3) Solubility:

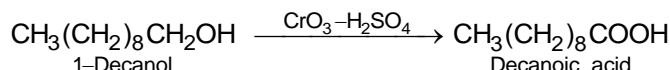
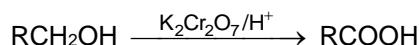
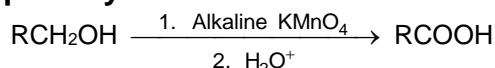
Carboxylic acids form hydrogen bonds with water and the lower molecular - weight carboxylic acids (upto 4 carbon atoms) are miscible with water.

Acid derivatives (esters, acid chlorides, anhydrides, nitriles and amides) are soluble in common organic solvents such as alcohols, ethers, chlorinated alkanes and aromatic hydrocarbons. Acid chlorides and anhydrides cannot be used in nucleophilic solvents such as H_2O and alcohols, because they react with these solvents.

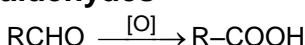
(4) Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature, higher acids are wax like solids due to their low volatility.

Section (G) : Carboxylic acid (Preparation Methods)

1. From primary alcohols



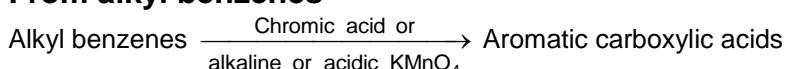
2. From aldehydes



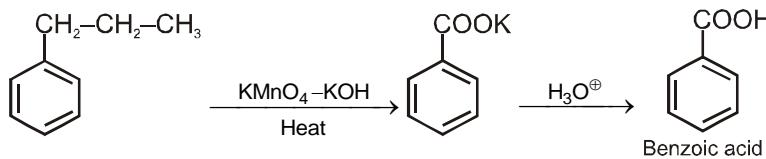
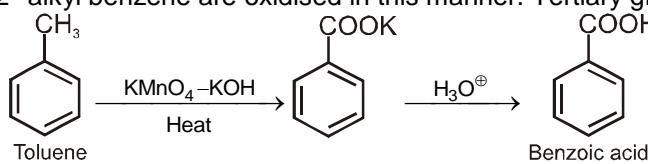
Oxidising agents - HNO_3 , KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$

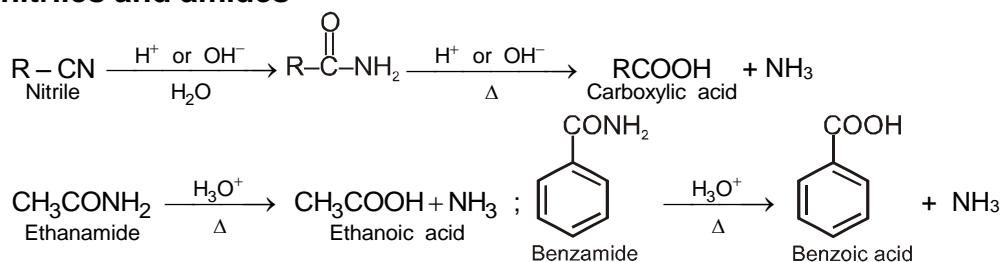
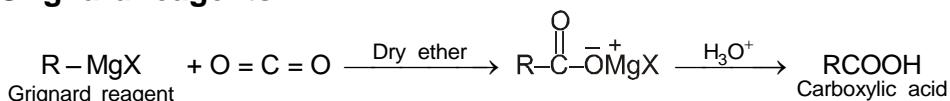
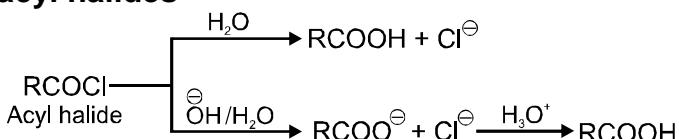
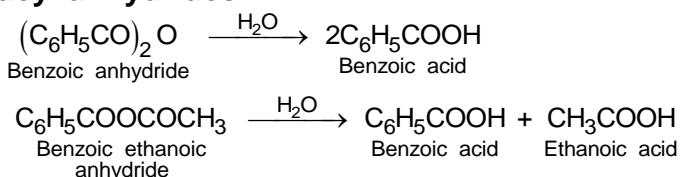
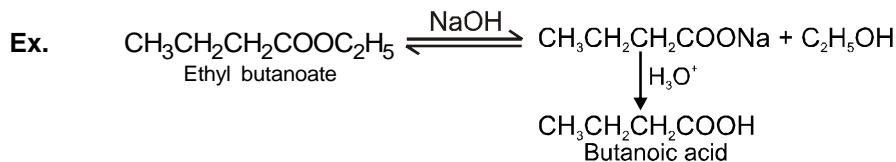
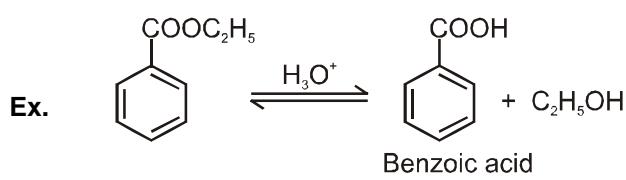
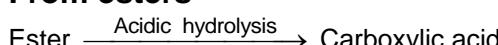
Mild oxidising agents - Tollen's reagent and Fehling's reagent

3. From alkyl benzenes



1° and 2° alkyl benzene are oxidised in this manner. Tertiary group is not affected.

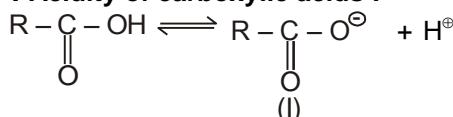



4. From nitriles and amides

5. From Grignard reagents

6. From acyl halides

7. From acyl anhydrides

8. From esters


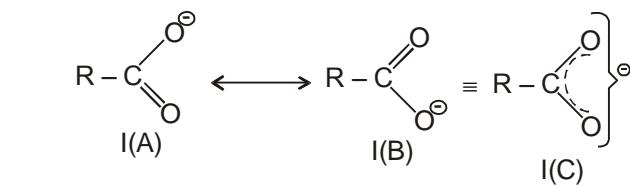
Section (H) : Carboxylic acid (Chemical Properties)

Chemical Reactions of carboxylic acid :

(1) Acidic Nature : Acidity of carboxylic acids :

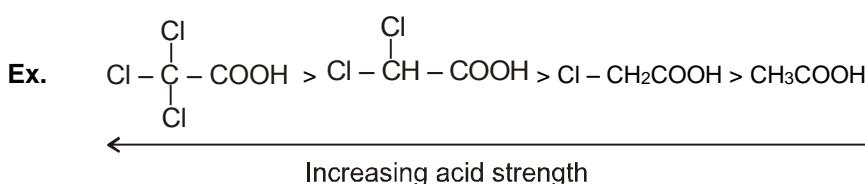
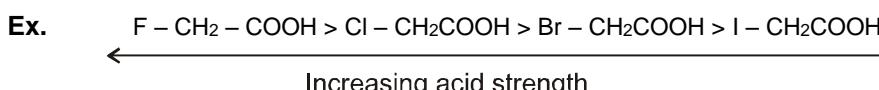


(i) $\text{R}-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{O}^\ominus$ (I) exists as two equivalent canonical structures I(A) and I(B). This ion is resonance stabilised and resonance hybrid structure is I(C).

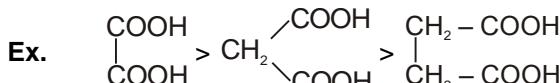


(ii) $\text{R}-\text{C}(=\text{O})-\text{O}^-$ ion is more stable due to resonance, hence carboxylic acids are acidic in nature.

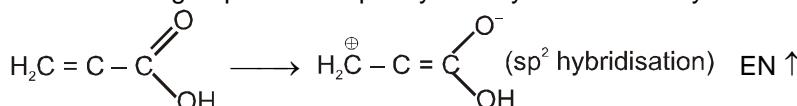
(iii) Electron withdrawing group ($-I$ effect) stabilises the anion and hence, increases acidic nature.



(iv) Electron releasing group ($+I$ effect) destabilises the anion and hence decreases acidic nature.



Direct attachment of groups such as phenyl or vinyl to the carboxylic acid increases its acidity.



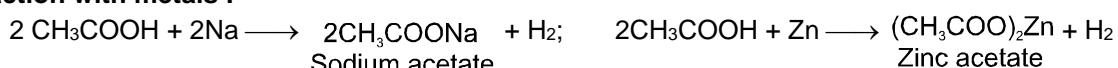
Ex. Relative acid strength is: $\text{RCOOH} > \text{HOH} > \text{ROH} > \text{HC} \equiv \text{CH} > \text{NH}_3 > \text{RH}$

Note : Acidity of acids is compared by comparing stability of conjugate base.

(2) Reaction involving removal of proton from $-\text{OH}$ group :

(i) **Action with blue litmus :** All carboxylic acids turn blue litmus into red.

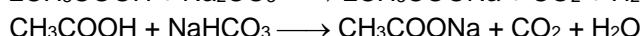
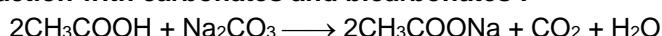
(ii) **Reaction with metals :**



(iii) **Reaction with alkalies :**

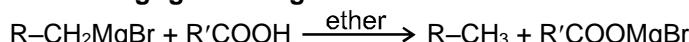


(iv) **Reaction with carbonates and bicarbonates :**

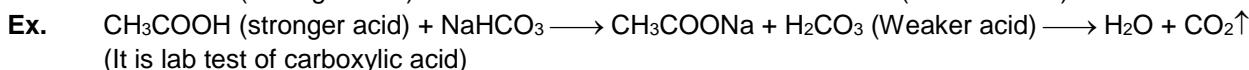


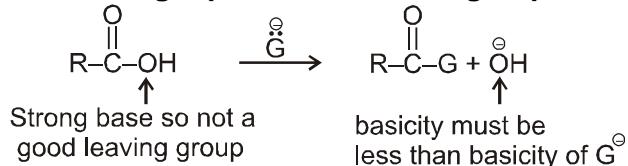
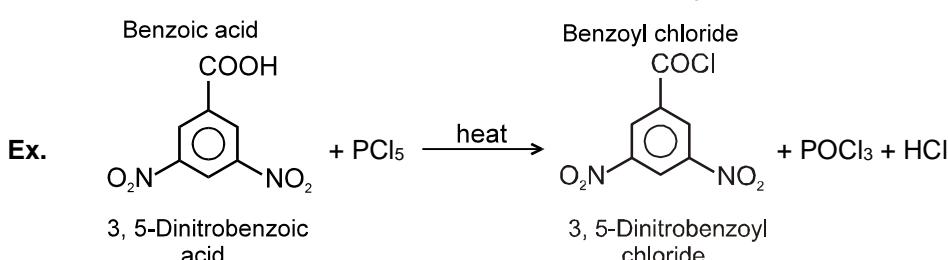
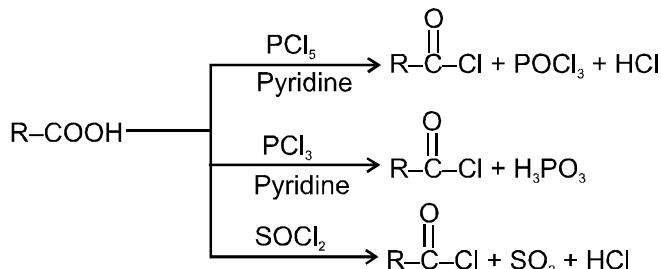
Reaction of carboxylic acid with aqueous sodium bicarbonate solution produces brisk effervescence. However most phenols do not produce effervescence. Therefore, the reaction may be used to distinguish between carboxylic acids and phenols.

(v) **Reaction with grignard reagent :**

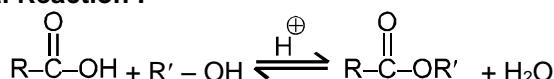
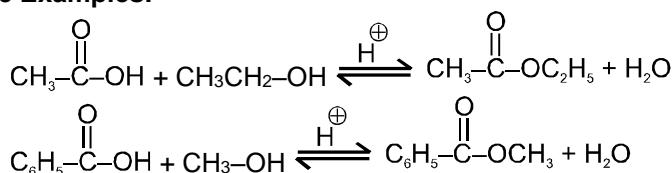
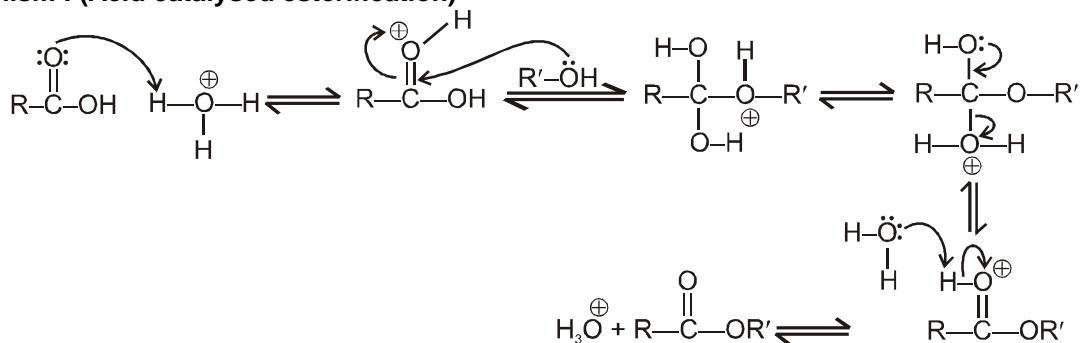


Feasible reaction : A stronger acid displaces a weaker acid from the salt of the weaker acid.



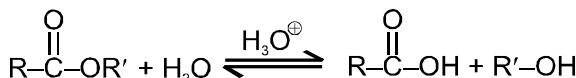

(3) Reaction involving replacement of -OH group :

(i) Formation of acid chlorides :

(ii) Fisher Esterification :

Carboxylic acid react with alcohol to form esters through a condensation reaction known as esterification.

General Reaction :

Specific Examples:

Mechanism : (Acid catalysed esterification)


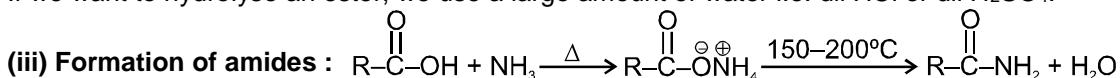
If we follow the forward reactions in this mechanism, we have the mechanism for the acid catalysed esterification of an acid. If however, we follow the reverse reactions, we have the mechanism for the acid catalysed hydrolysis of an ester.

Acid catalysed ester hydrolysis.

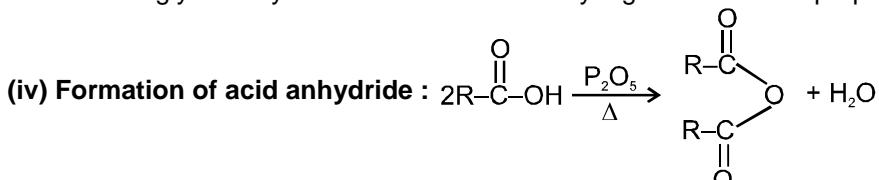


which depends upon condition we choose. If we want to esterify an acid, use an excess amount of the alcohol and, if possible remove the water as it is formed.

If we want to hydrolyse an ester, we use a large amount of water i.e. dil HCl or dil H₂SO₄.

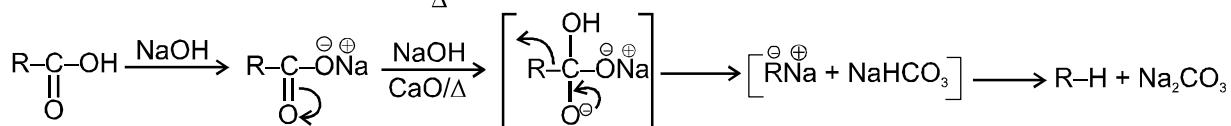
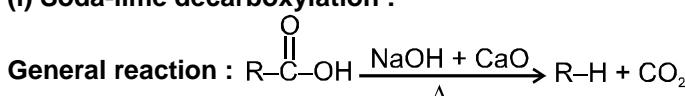


In fact amides can not be prepared from carboxylic acids and amines unless the ammonium salt is heated strongly to dehydrate it. This is not usually a good method of preparing amides.



(4) Decarboxylation reactions :

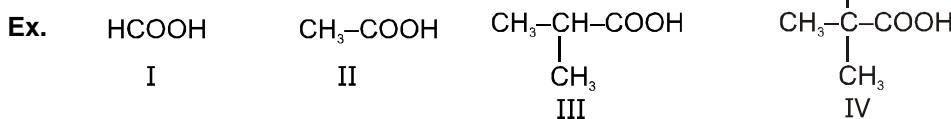
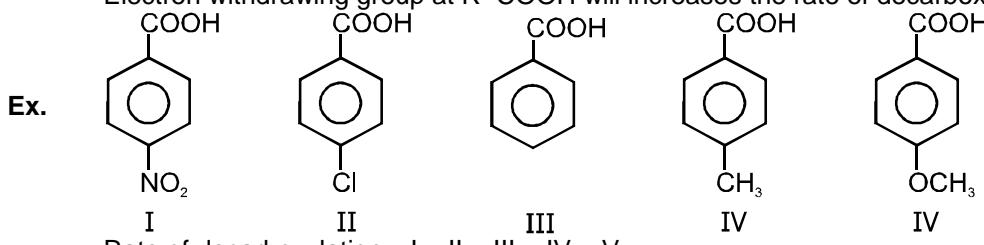
(i) Soda-lime decarboxylation :



In this reaction carbanion intermediate is formed.

Rate of reaction depends upon the stability of carbanion intermediate.

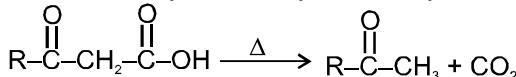
Electron withdrawing group at R-COOH will increases the rate of decarboxylation.



Rate of decarboxylation. I > II > III > IV

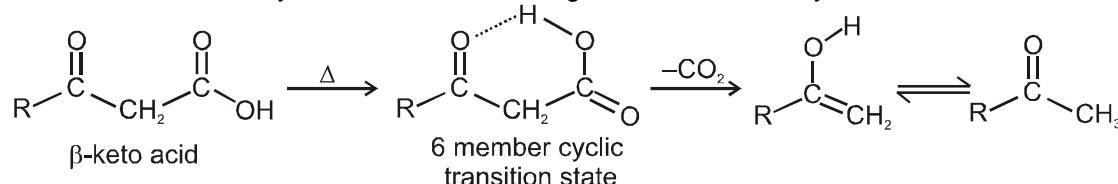
(ii) Decarboxylation of β -keto carboxylic acids:

β -keto acids decarboxylate readily when they are heated to 100–150°C.



There are two reasons for ease of decarboxylation.

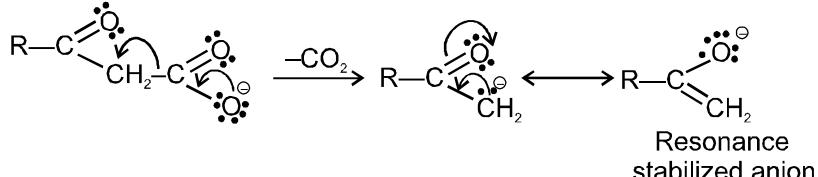
When the acid itself decarboxylates, it can do so through a six membered cyclic transition state :



This reaction produces an enol directly and avoids an anionic intermediate. The enol then tautomerises to a methyl ketone.



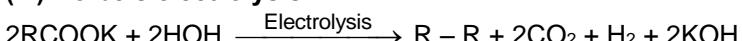
When the carboxylate anion decarboxylates, it forms a resonance stabilized enolate anion.



Aliphatic acids that do undergo successful decarboxylation have certain functional groups or double or triple bonds in the α or β positions.

		Acid type	Decarboxylation product
(1)	Malonic	$\text{HOOC}-\underset{ }{\text{C}}-\text{COOH}$	$\text{HOOC}-\underset{ }{\text{C}}-\text{H}$
(2)	α -Cyano	$\text{NC}-\underset{ }{\text{C}}-\text{COOH}$	$\text{NC}-\underset{ }{\text{C}}-\text{H}$
(3)	α -Nitro	$\text{O}_2\text{N}-\underset{ }{\text{C}}-\text{COOH}$	$\text{O}_2\text{N}-\underset{ }{\text{C}}-\text{H}$
(4)	α -Aryl	$\text{Ar}-\underset{ }{\text{C}}-\text{COOH}$	$\text{Ar}-\underset{ }{\text{C}}-\text{H}$
(5)	β -Keto	$\begin{matrix} -\text{C} & \text{C}-\text{COOH} \\ \parallel & \\ \text{O} & \end{matrix}$	$\begin{matrix} -\text{C} & \text{C}-\text{H} \\ \parallel & \\ \text{O} & \end{matrix}$
(6)	β,γ -Unsaturated	$\begin{matrix} -\text{C} & =\text{C}-\text{C}-\text{COOH} \\ & & \\ & & \end{matrix}$	$\begin{matrix} -\text{C} & =\text{C}-\text{C}-\text{H} \\ & & \\ & & \end{matrix}$

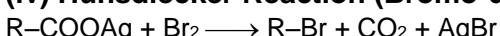
(iii) Kolbe's electrolysis



If n is the number of carbon atoms in the salt of carboxylic acid, the alkane formed has $2(n-1)$ carbon atoms.



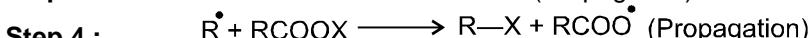
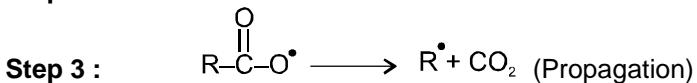
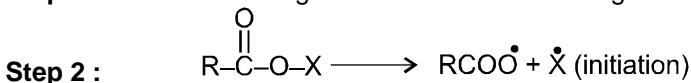
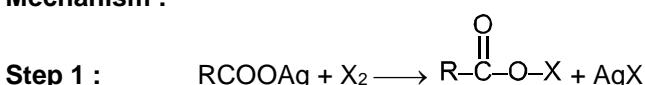
(iv) Hunsdiecker Reaction (Bromo-decarboxylation) :



Heavy metal salt of acid is heated with Br_2 it results in decarboxylations.

Metal can be silver ion, mercuric ion, or lead (IV) ion.

Mechanism :



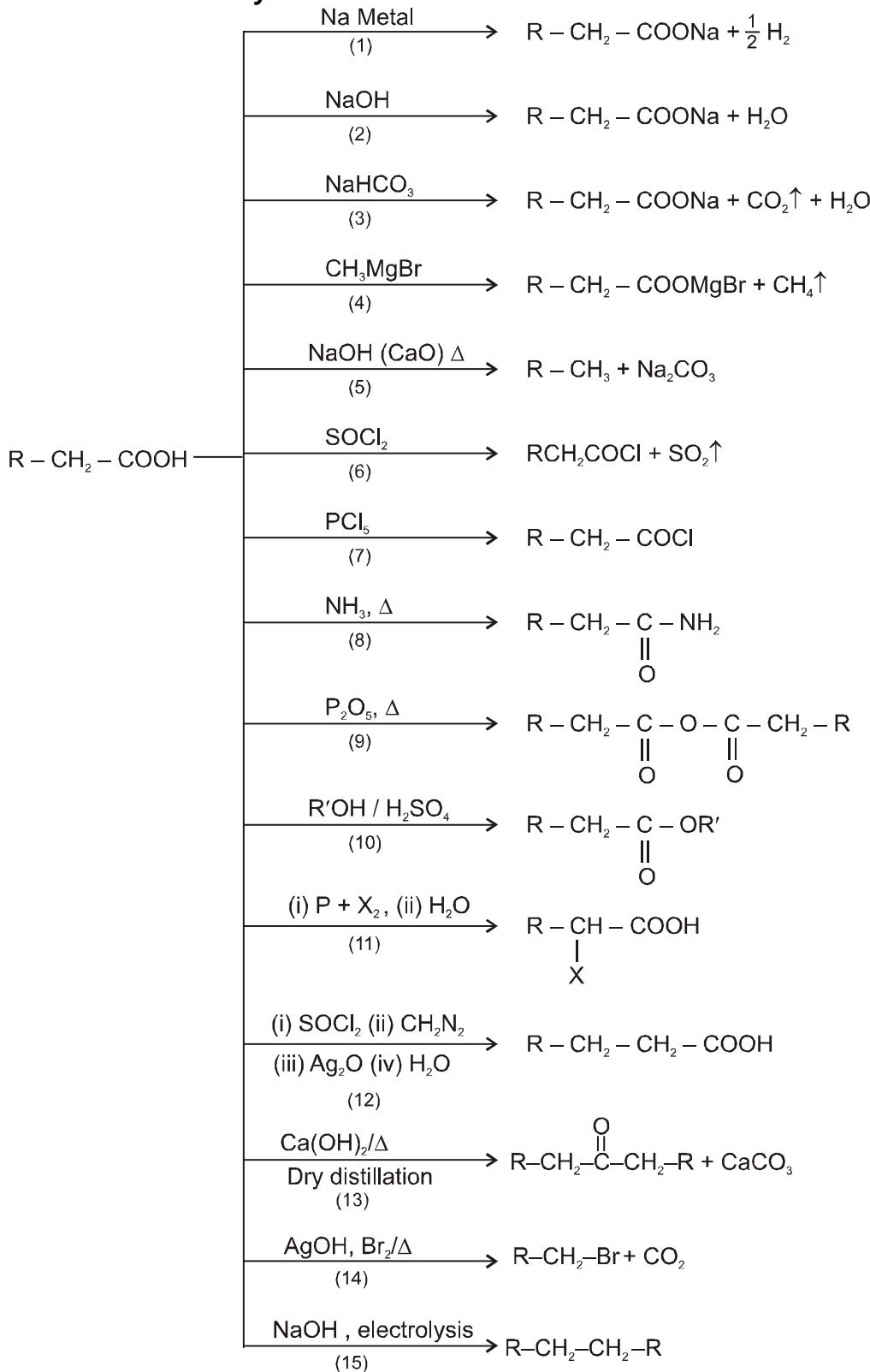
Although bromine is the most often used halogen, chlorine and iodine have also been used.

When iodine is the reagent, the ratio between the reactant is very important and determines the product.

A 1 : 1 ratio of salt to iodine gives alkyl halide, as above. A 2 : 1 ratio, however gives the ester RCOOR . This is called Simonini reaction and sometimes used to prepare carboxylic ester. The yield of alkyl halide follows the order Primary > Secondary > Tertiary


(5) HVZ Reaction (Halogenation of aliphatic acids and Substituted acids) :

In the presence of a small amount of phosphorus, aliphatic carboxylic acids react smoothly with chlorine or bromine to yield a compound in which α -hydrogen has been replaced by halogen.


Summary of reactions of carboxylic acids :




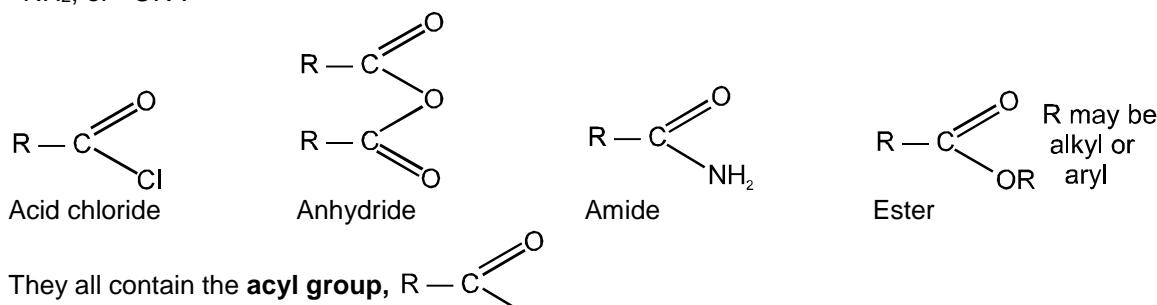
Uses of Carboxylic Acids

- * Methanoic acid - In rubber, textile, dyeing, leather and electroplating industries.
- * Ethanolic acid - As a solvent and as a vinegar in food industry.
- * Hexanoic acid - In the manufacture of nylon-6, 6.
- * Higher fatty acids - For the manufacture of soaps and detergents.
- Esters of benzoic acid - In perfumery.
- Sodium benzoate - As a food preservative.

Section (I) : Acid Derivatives (Acid Halide, Ester, Anhydride & Amide)

Carboxylic Acid Derivatives :

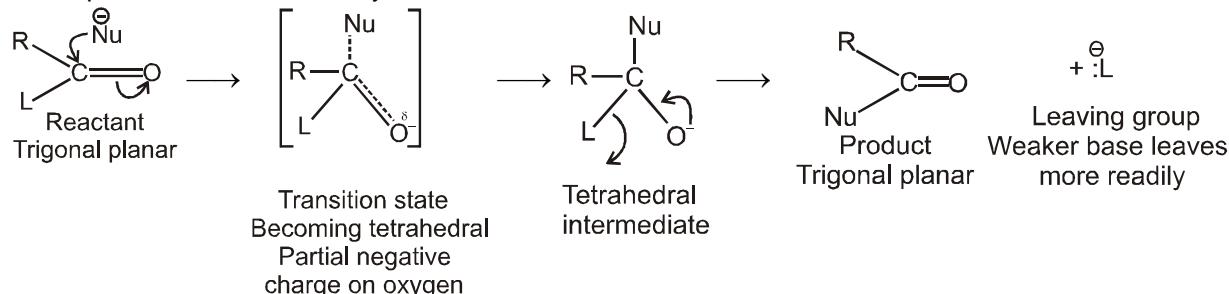
Closely related to the carboxylic acids and to each other are a number of chemical families known as **functional derivatives of carboxylic acids**: acid chlorides, anhydrides, amides, and esters, These derivatives are compounds in which the –OH of a carboxyl group has been replaced by –Cl, –OOCR, –NH₂, or –OR`.



Like the acid to which it is related, an acid derivative may be aliphatic or aromatic, substituted or unsubstituted; whatever the structure of the rest of the molecule, the properties of the functional group remain essentially the same.

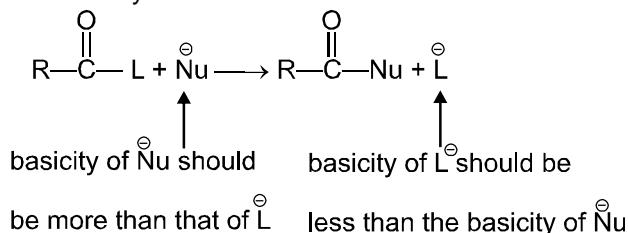
Characteristic reaction of acid derivatives (Nucleophilic acyl substitution) :

Nucleophilic acyl substitution usually takes place by an **addition-elimination** mechanism. The incoming nucleophile adds to the carbonyl to form a tetrasubstituted intermediate with a tetrahedral carbon.



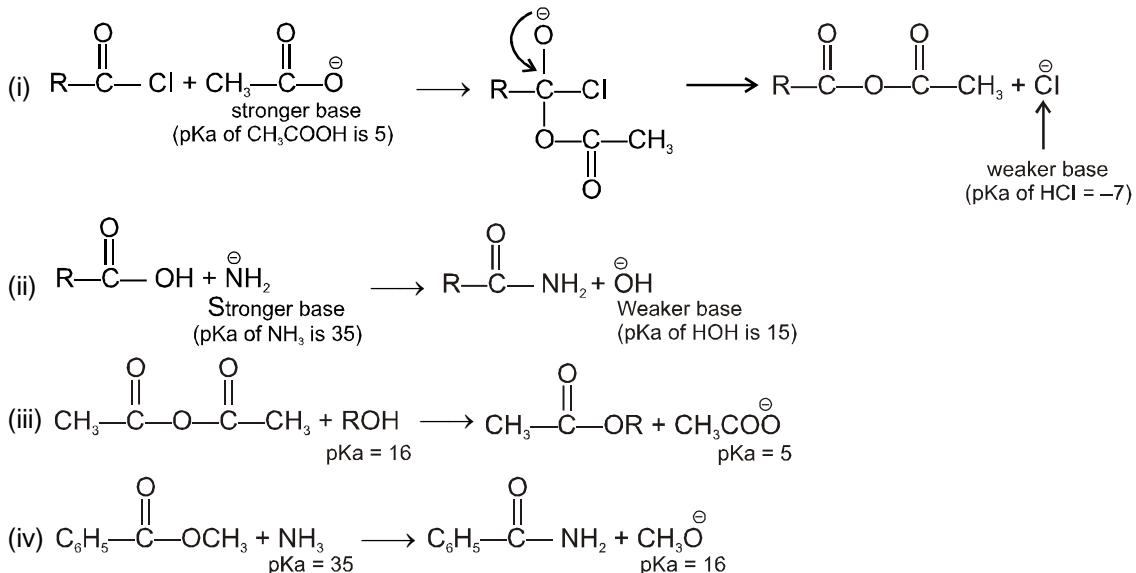
The tetrahedral intermediate formed when a nucleophile attacks the carbonyl carbon of a carboxylic acid derivative is not stable and cannot be isolated.

A pair of nonbonding electrons on the oxygen reforms the π bond, and either L⁻ or Nu⁻ is eliminated with its bonding electrons. Whether L⁻ or Nu⁻ is eliminated depends on their relative basicities. The weaker base is preferentially eliminated because the weaker the base, the better it is a leaving group.

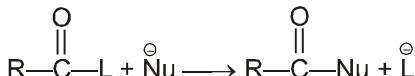




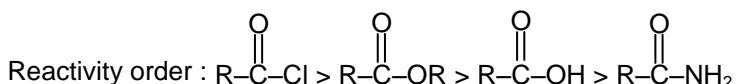
Thus carboxylic acid derivative will undergo a nucleophilic acyl substitution reaction provided that the incoming nucleophile is a stronger base than the group that is to be replaced. If the incoming nucleophile and the group attached to acyl group in the starting material have similar basicities, the tetrahedral intermediate can expect either group with similar ease. A mixture of starting material and substitution product will result.



Condition for acyl nucleophilic substitution reaction :



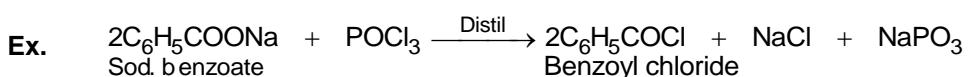
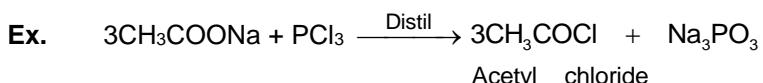
- (i) L must be better leaving group than Nu^- , i.e., basicity of Nu should be more than that of L
- (ii) Nu^- must be a strong enough nucleophilic to attack RCOL.
- (iii) Carbonyl carbon must be enough electrophilic to react with Nu^- .

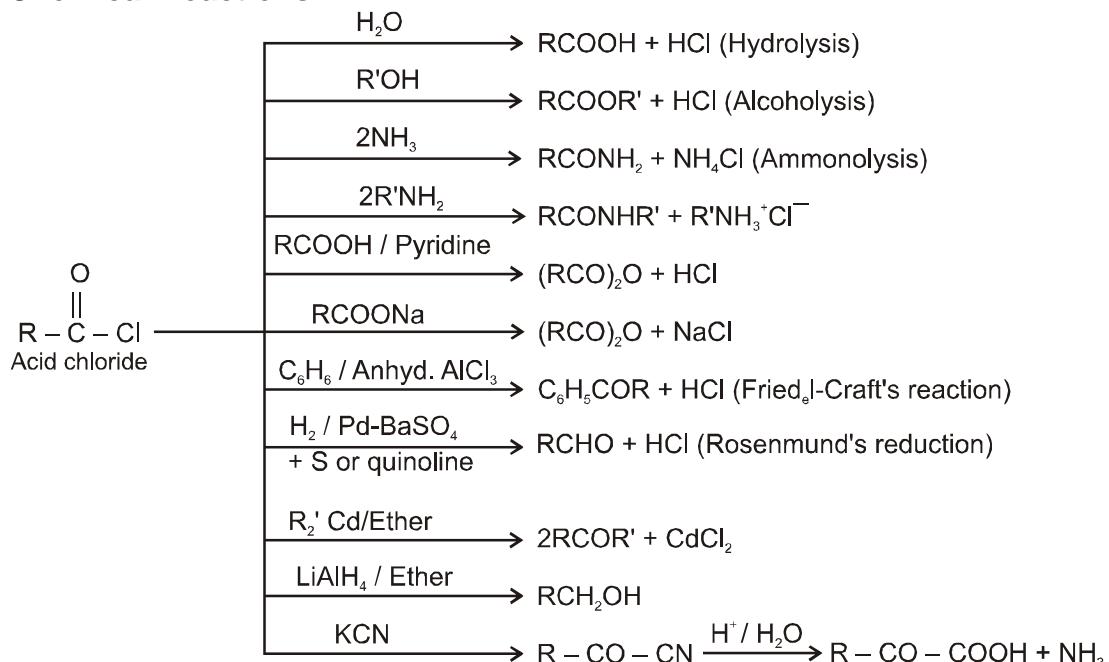
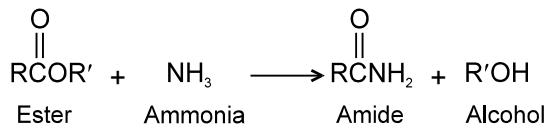


(A) Acid halides :

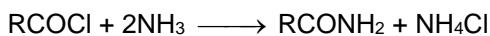
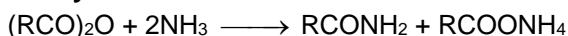
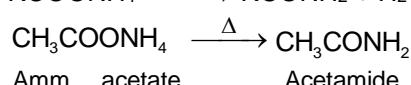
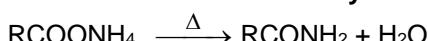
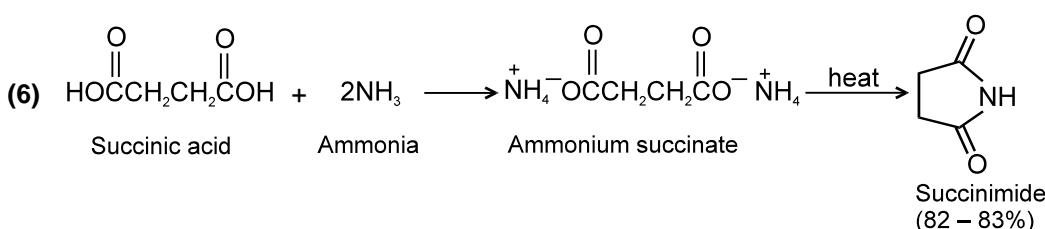
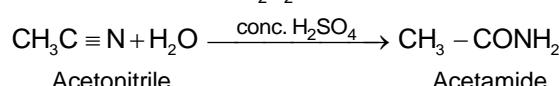
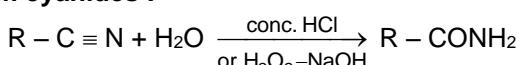
Methods of preparation of Acyl halides :

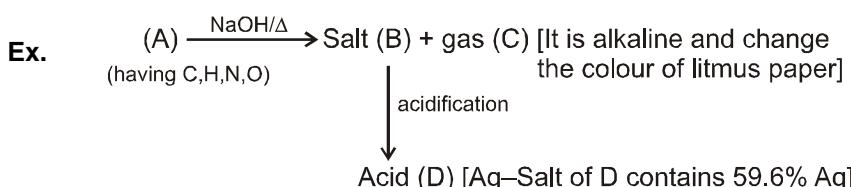
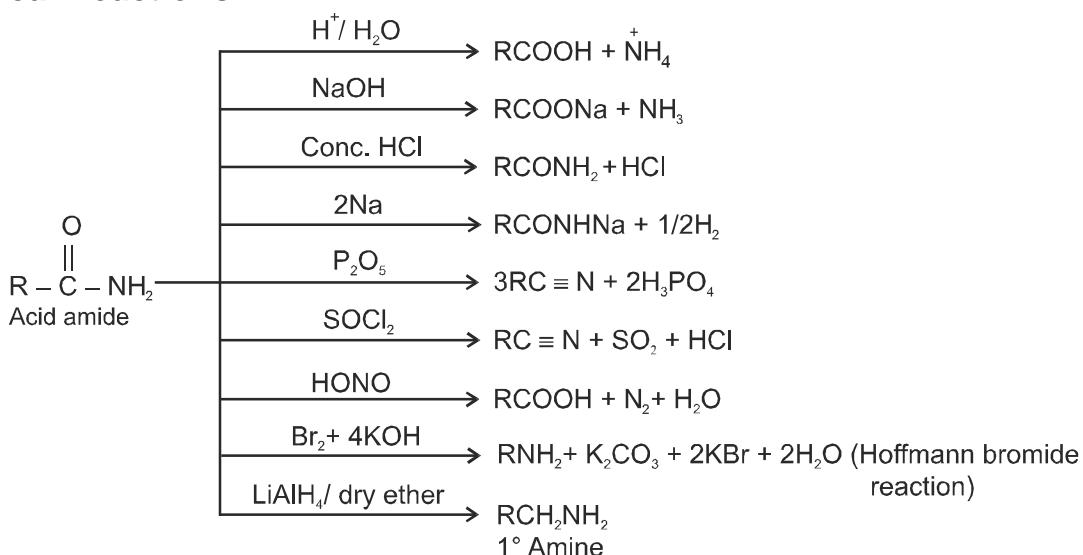
- (i) $\text{RCOOH} + \text{PCl}_5 \longrightarrow \text{RCOCl} + \text{POCl}_3 + \text{HCl}$
- (ii) $3\text{RCOOH} + \text{PCl}_3 \longrightarrow 3\text{RCOCl} + \text{H}_3\text{PO}_3$
- (iii) $\text{RCOOH} + \text{SOCl}_2 \xrightarrow{\text{Pyridine}} \text{RCOCl} + \text{SO}_2 + \text{HCl}$



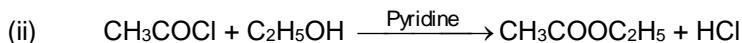
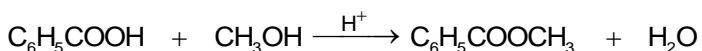
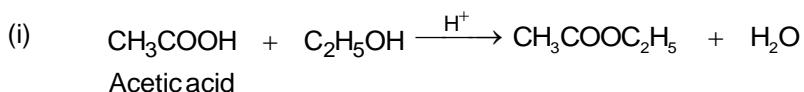

Chemical Reactions :

(B) Acid amides :
Methods of preparation of acids amides :
(1) By reaction of esters with ammonia and amines :


Ammonia is more nucleophilic than water, making it possible to carry out this reaction using aqueous ammonia.

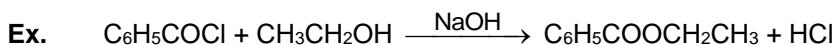
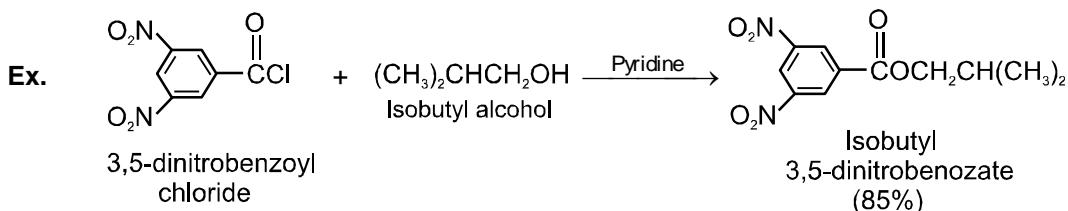
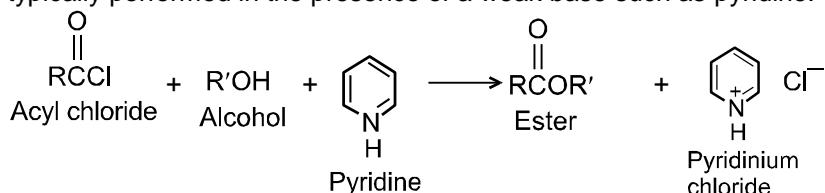
(2) From acid halides :

(3) From anhydride :

(4) From ammonium salt of carboxylic acid :

(5) From cyanides :


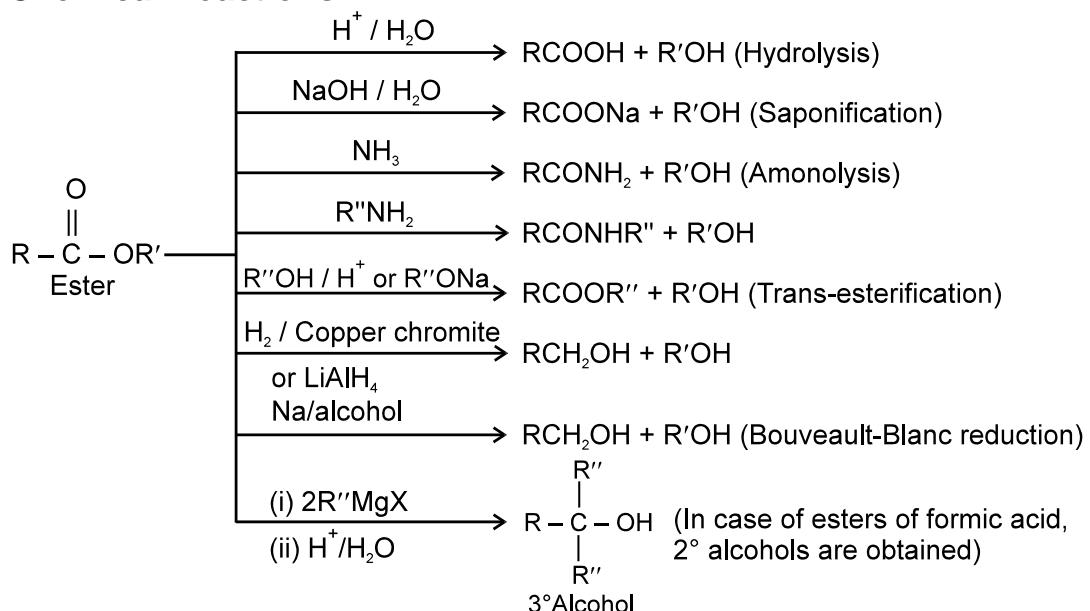
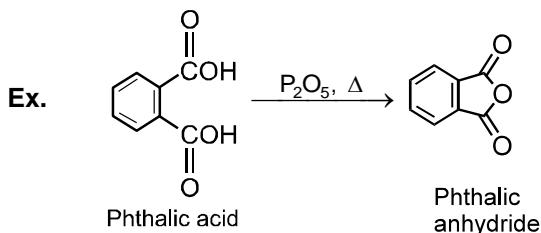
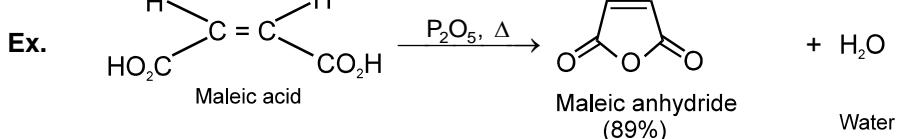
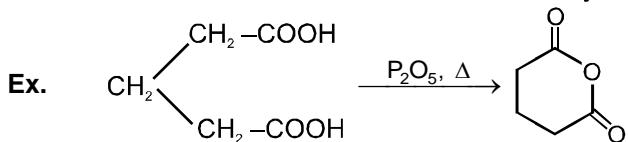
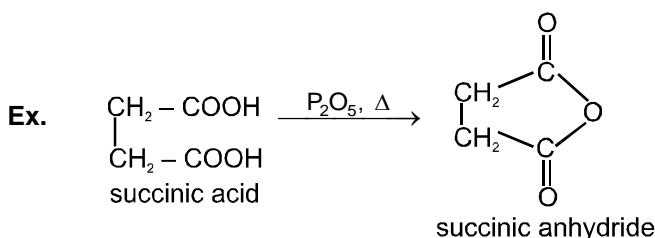
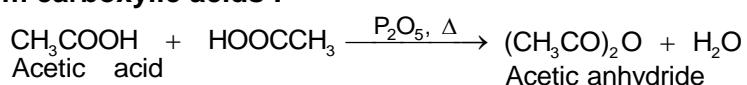
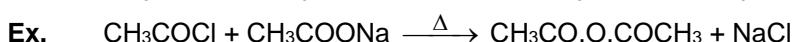
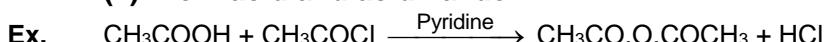

Chemical Reactions :


Ans. $\text{CH}_3\text{CH}_2\text{CONH}_2$

(C) Esters :
Methods of Preparation :


Alcohols react with acyl chlorides by nucleophilic acyl substitution to yield esters. These reactions are typically performed in the presence of a weak base such as pyridine.

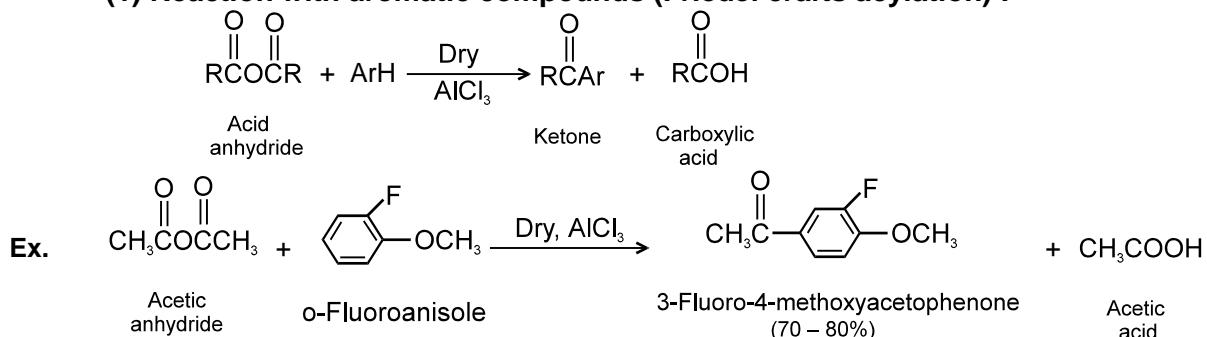


**Chemical Reactions :****(D) Acid anhydrides :****Methods of Preparation of acid anhydrides :****(1) From carboxylic acids :****Five or six membered cyclic anhydride are stable****(2) From acid and acid halide :**



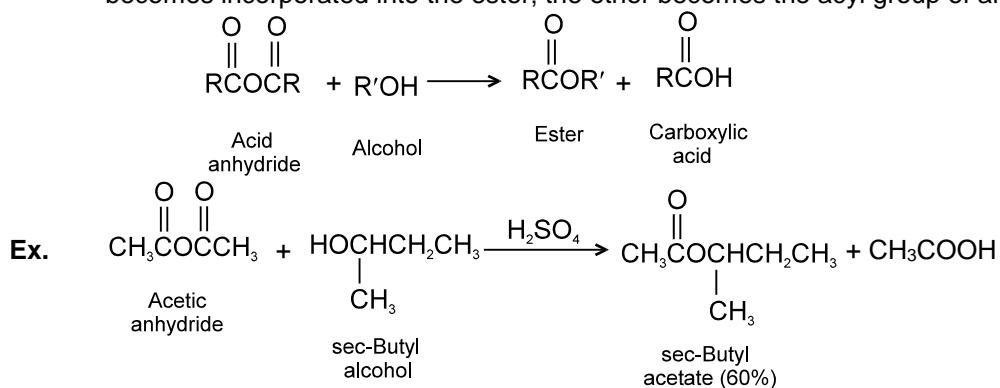
Chemical Reactions

(1) Reaction with aromatic compounds (Friedel crafts acylation) :



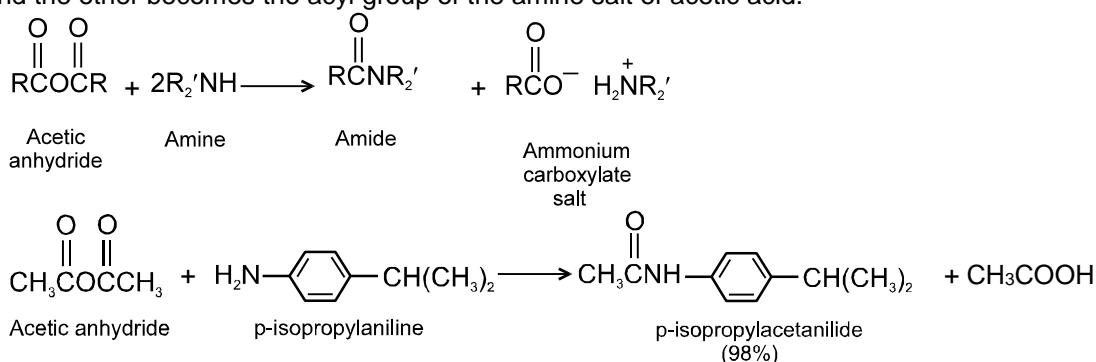
(2) Reaction with alcohols :

Acid anhydrides react with alcohols to form esters. The reaction may be carried out in the presence of pyridine or it may be catalysed by acids. In the example shown, only one acyl group of acetic anhydride becomes incorporated into the ester; the other becomes the acyl group of an acetic acid molecule.



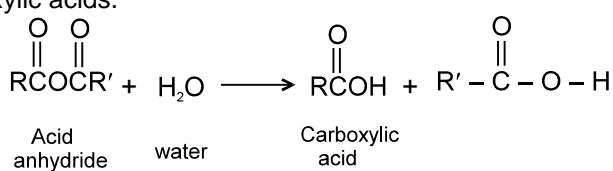
(3) Reaction with ammonia and amines :

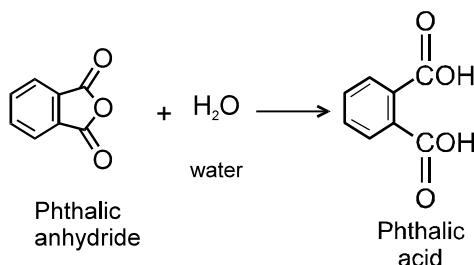
Acid anhydrides react with ammonia and amines to form amides. Two molar equivalents of amine are required. In the example shown, only one acyl group of acetic anhydride becomes incorporated into the amide and the other becomes the acyl group of the amine salt of acetic acid.



(4) Hydrolysis :

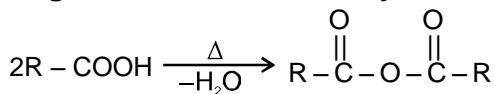
Acid anhydrides react with water to yield two carboxylic acid functions. Cyclic anhydrides yield dicarboxylic acids.



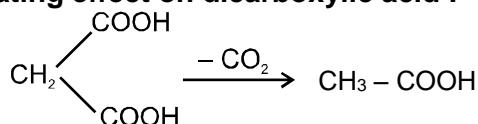


Heating Effects :

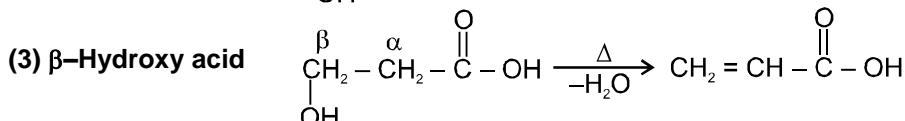
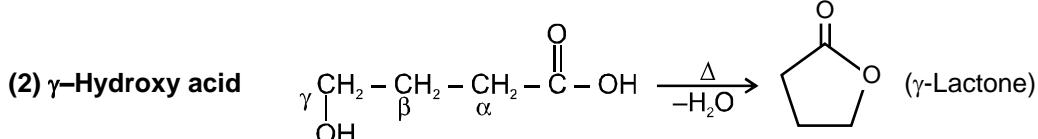
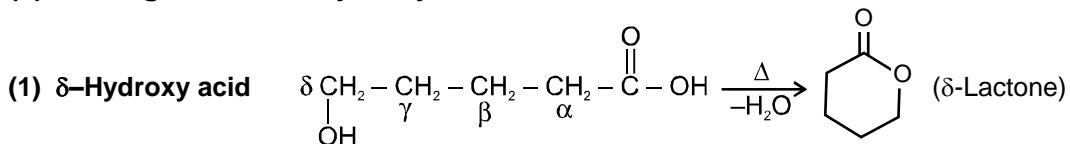
(a) Heating effect on monocarboxylic acid :



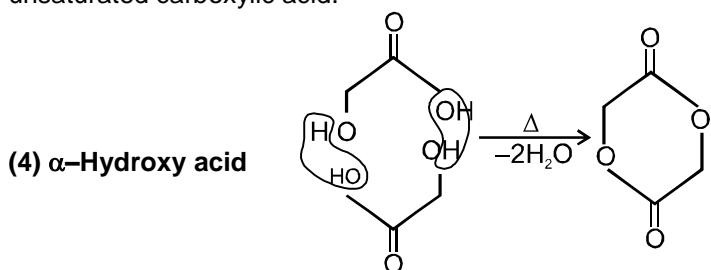
(b) Heating effect on dicarboxylic acid :



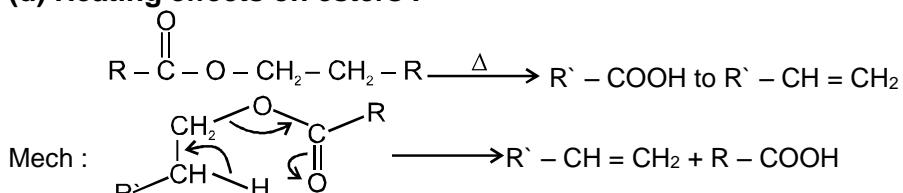
(c) Heating effects on Hydroxy acids :



Since 4 or 8 membered rings are less stable therefore β -Hydroxy acids on heating produce α, β unsaturated carboxylic acid.



(d) Heating effects on esters :



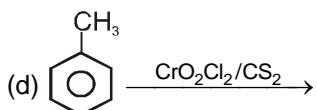
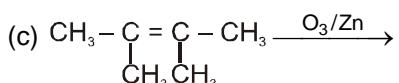
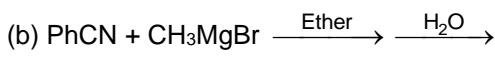
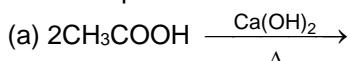
This reaction follows syn elimination & hoffman product is formed.

**Exercise-1**

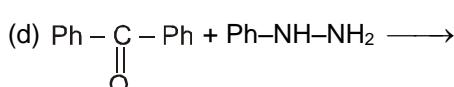
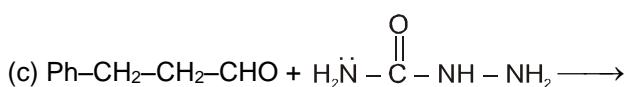
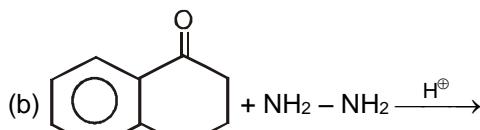
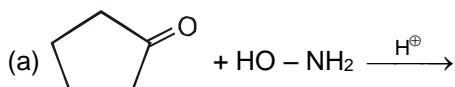
Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS**Section (A) : Preparation of carbonyl compounds**

A-1. Write the products of following reactions

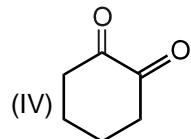
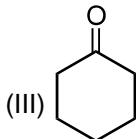
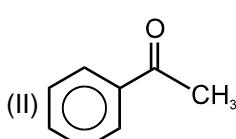
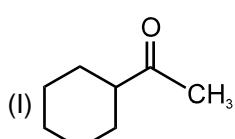
**Section (B) : Nucleophilic addition reactions**

B-1. Write the product of the following reaction



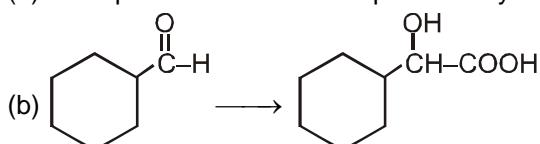
- B-2. (a) Cis-1,2-Cyclopentanediol reacts with acetone in the presence of dry HCl to yield compound K, $\text{C}_8\text{H}_{14}\text{O}_2$, which is resistant to boiling alkali, but which is readily converted into the starting material by aqueous acids. What is structure of K ?
 (b) Trans-1,2-Cyclopentanediol does not form an analogous compound. Explain why ?

B-3. Arrange the following compounds in decreasing orders of nucleophilic addition with semicarbazide $\text{NH}_2\text{NHCONH}_2$ i.e., NH_2-Z :

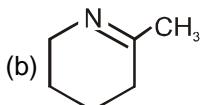
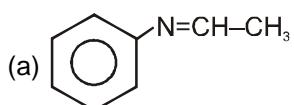


B-4. How the following conversions takes place?

(a) Acetophenone \longrightarrow Acetophenone cyanohydrin

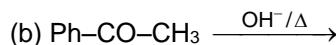
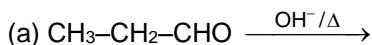


B-5. Give the structure of the carbonyl compound and amine used to form the following imines.

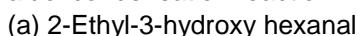



Section (C) : Condensation reactions

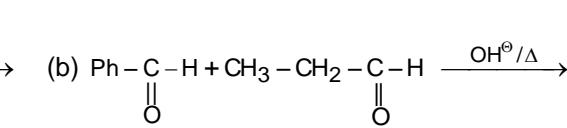
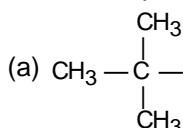
C-1. Predict the product of following aldol condensation reaction :



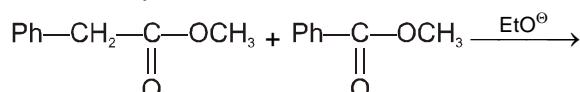
C-2. Indicate the starting aldehyde or ketone from which each of the following compounds are formed by an aldol condensation reaction.



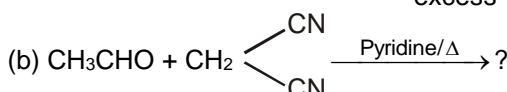
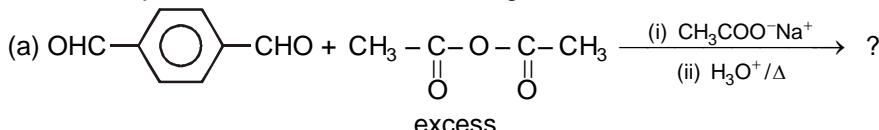
C-3. Predict the products of following cross condensation reactions.



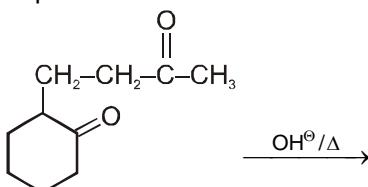
C-4. Predict the product from claisen condensation of the following pair of esters.



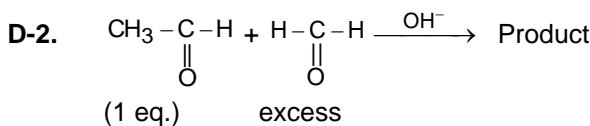
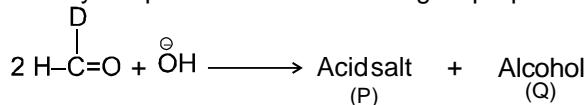
C-5. Predict the product for each of the following reactions.



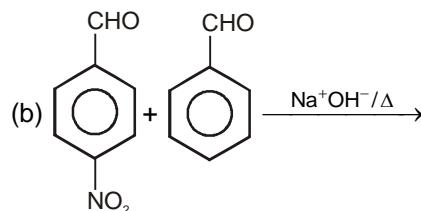
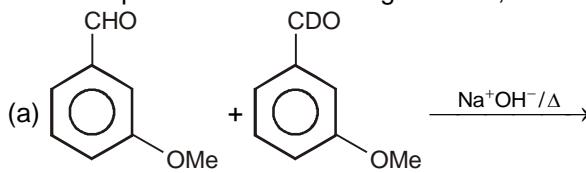
C-6. Predict the product for each of the following reactions.

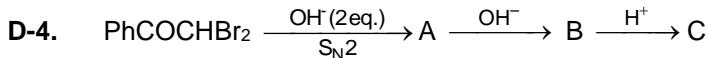

Section (D) : Cannizzaro's reactions

D-1. Identify the products in the following disproportionation reaction and also mention rate determining step.



D-3. Write the product of the following reaction,



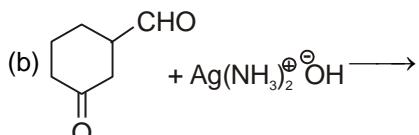
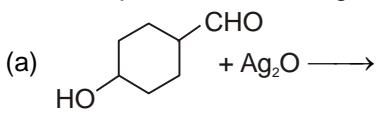


The compound 'C' is :

D-5. Glyoxal (CHOCHO) on being heated with concentrated NaOH forms.

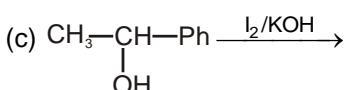
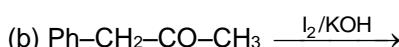
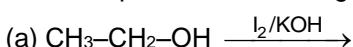
Section (E) : Redox reactions

E-1. Write the product of following reaction :



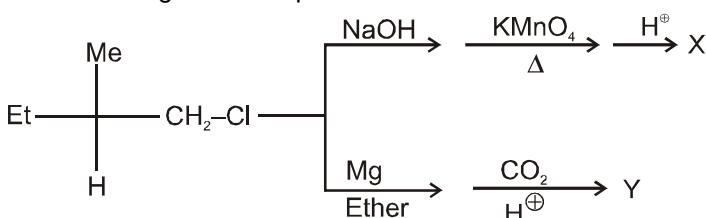
Section (F) : α -Halogenation, haloform, α -deuteration reactions

F-1. Write the product of following reaction,



Section (G) : Carboxylic acid (Preparation Methods)

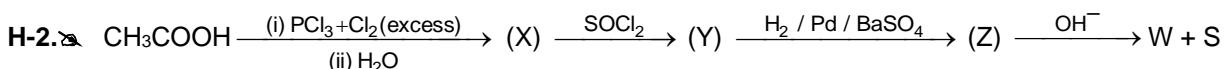
G-1. In the following reactions products X & Y are



G-2. A benzenoid compound D($\text{C}_8\text{H}_{10}\text{O}$) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid E ($\text{C}_7\text{H}_6\text{O}_2$). Write the structures of D.E and explain the formation of E.

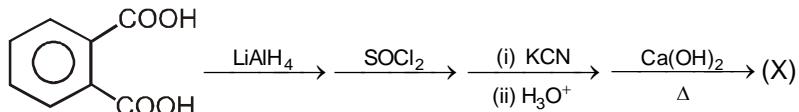
Section (H) : Carboxylic acid (Chemical Properties)

H-1. The product P of the following reaction is



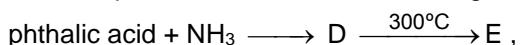
Write the structure of X, Y, Z, W and S.

H-3. The product (X) for the following conversion reaction is :

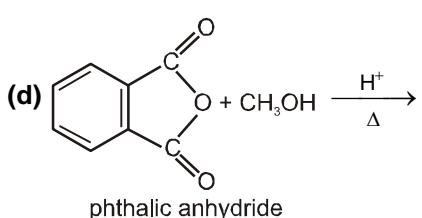
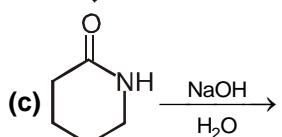
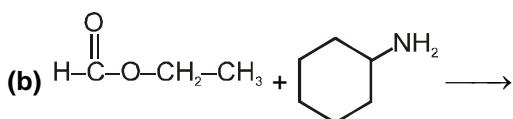



Section (I) : Acid Derivatives (Acid Halide, Ester, Anhydride & Amide)

- I-1.** Give the product of each of the following reactions :



- I-2.** Predict the products of the following reactions.



phthalic anhydride

PART - II : ONLY ONE OPTION CORRECT TYPE
Section (A) : Preparation of carbonyl compounds

- A-1.** On heating calcium propionate, the product formed is

- (A) 3-Pentanone (B) 2-Pentanone
 (C) 3-Methyl-2-butanone (D) Propanone

- A-2.** A mixed salt of calcium acetate formate on dry distillation gives

- (A) ethanal (B) methanal
 (C) propanone (D) All the three above.

- A-3.** Acetic acid when heated (300°C) with MnO gives

- (A) formaldehyde (B) acetaldehyde (C) acetone (D) butaone

- A-4.** Ethyldene chloride on treatment with aq. KOH gives

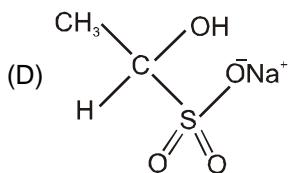
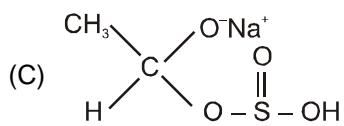
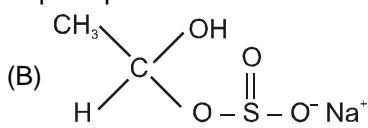
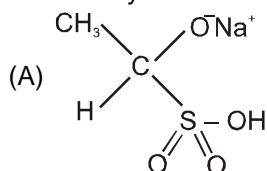
- (A) CH_3CHO (B) $(\text{CH}_2\text{OH})_2$ (C) HCHO (D) $(\text{CHO})_2$

Section (B) : Nucleophilic addition reactions

- B-1.** Arrange the following compounds in decreasing orders of rate of hydration.

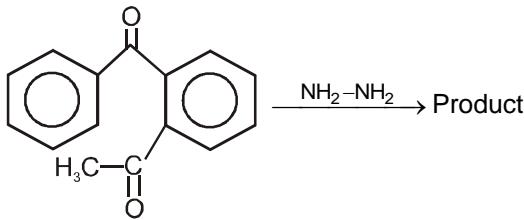
- (X) CCl_3CHO (Y) CH_3CHO (Z) CH_3COCH_3 (W) CF_3CHO
 (A) W > Z > X > Y (B) W > X > Y > Z (C) W > Y > Z > X (D) W > Z > Y > X

- B-2.** Acetaldehyde on reaction with sodium hydrogen sulphite produces

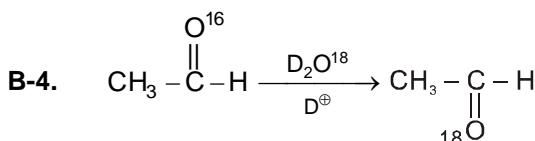




B-3. Write the product of following reaction :



- (A) (B) (C) (D)



Given the following reaction intermediate is :

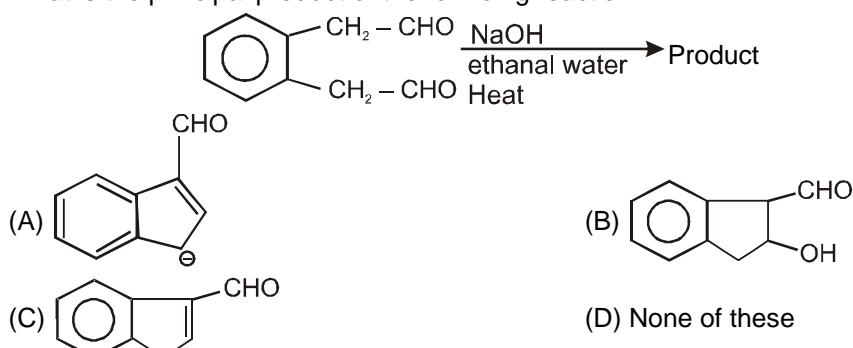
- (A) (B) (C) (D)

Section (C) : Condensation reactions

C-1. (X) is the product of cross aldol condensation between benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) and acetone. What is its structure ?

- (A) $\text{C}_6\text{H}_5\text{-CH=CH}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$ (B) $\text{C}_6\text{H}_5\text{-CH=C-(CH}_3)_2$
 (C) $\text{C}_6\text{H}_5\text{-CO-CH}_2\text{-C=(CH}_3)_2$ (D) None of these

C-2. What is the principal product of the following reaction ?

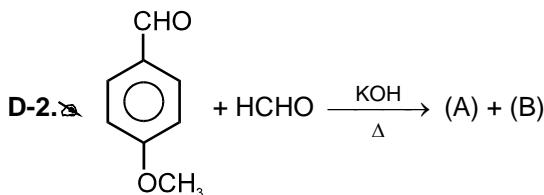


Section (D) : Cannizzaro's reactions

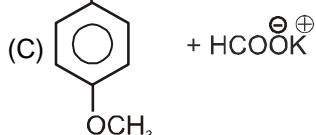
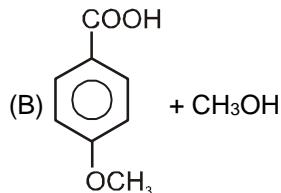
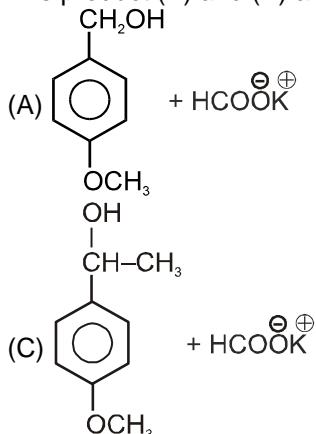
D-1. In the reaction, $(\text{CH}_3)_3\text{CCHO} + \text{HCHO} \xrightarrow[\text{heat}]{\text{NaOH}} \text{A} + \text{B}$.

the products (A) and (B) are respectively :

- (A) $(\text{CH}_3)_3\text{CCH}_2\text{OH}$ and $\text{HCOO}^- \text{Na}^+$. (B) $(\text{CH}_3)_3\text{CCOONa}$ and CH_3OH .
 (C) $(\text{CH}_3)_3\text{CCH}_2\text{OH}$ and CH_3OH . (D) $(\text{CH}_3)_3\text{COONa}$ and $\text{HCOO}^- \text{Na}^+$.

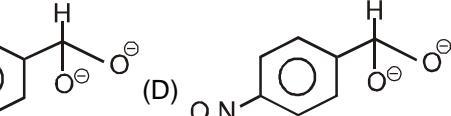
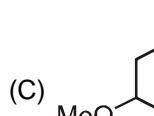
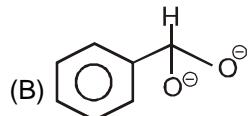
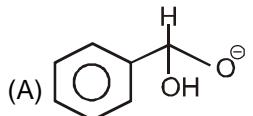


The product (A) and (B) are respectively :

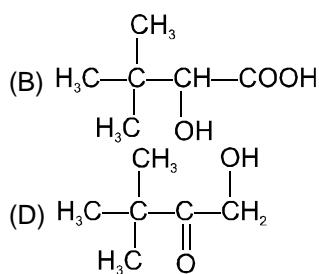
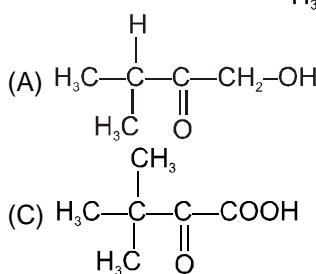


(D) Both (A) and (B)

D-3. In the cannizzaro's reaction the intermediate that will be the best hydride donor ?

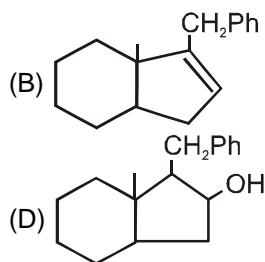
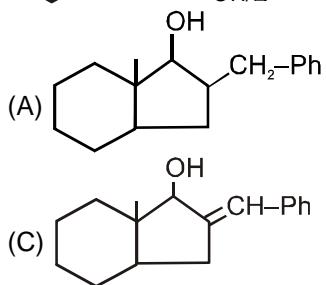
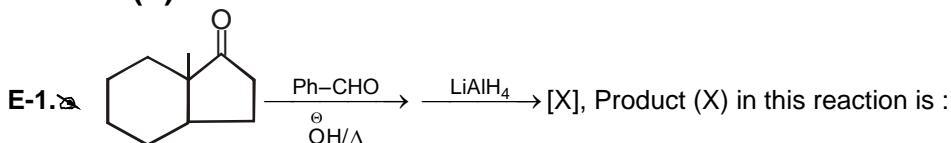


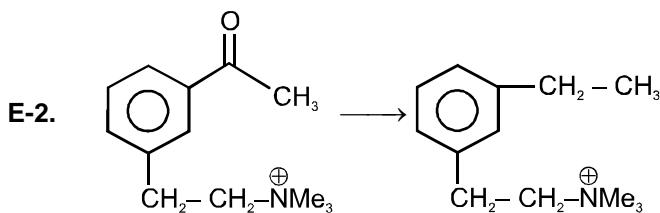
D-4. In the given reaction $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{H}_3\text{C}}{\text{C}}}(\text{C}\text{H}_3)-\overset{\text{CHO}}{\underset{\text{O}}{\text{C}}}-\text{CH}_2-\text{OH} \xrightarrow[\text{(ii) H}^+]{\text{(i) Conc. NaOH}}$ Product is



(C)

Section (E) : Redox reactions

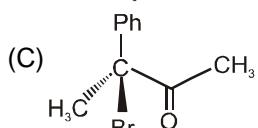
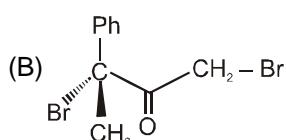
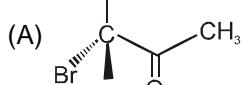
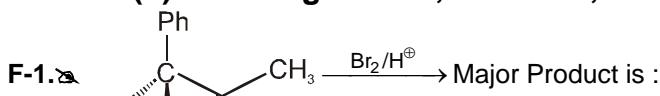




Above conversion can be achieved by

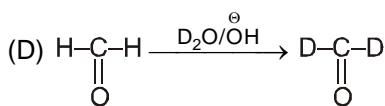
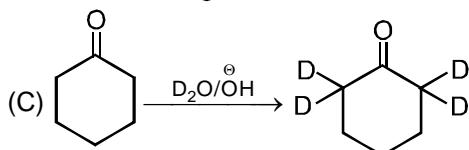
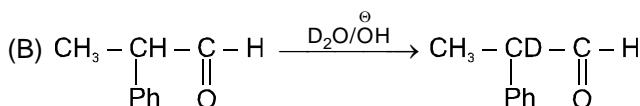
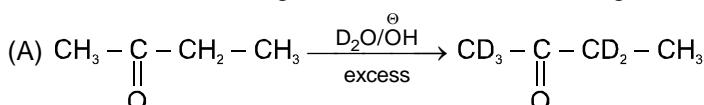
- (A) $\text{NH}_2\text{-NH}_2/\text{NaOH}$ (B) Zn-Hg/HCl (C) LiAlH_4 (D) NaBH_4 .

Section (F) : α -Halogenation, haloform, α -deuteration reactions



- (D) Both A and C

F-2. In which of the following reaction deuterium exchange is not observed ?



Section (G) : Carboxylic acid (Preparation Methods)

G-1. In the following reaction final product is :

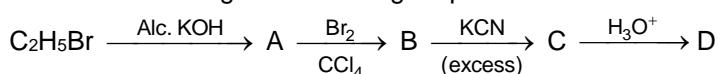


- (A) Benzoic acid (B) Benzaldehyde (C) Benzamide (D) Benzene

G-2. Which of the following does not give benzoic acid salt on oxidation with hot alkaline KMnO_4 .

- (A) $\text{Ph}-\text{CH}_3$ (B) $\text{Ph}-\text{CH}=\text{CH}-\text{CH}_3$ (C) $\text{Ph}-\text{C}\equiv\text{C}-\text{CH}_3$ (D) $\text{Ph}-\text{C}(\text{CH}_3)_3$

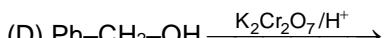
G-3. The acid D obtained through the following sequence of reactions is



- (A) Succinic acid (B) Malonic acid (C) Maleic acid (D) Oxalic acid



G-4. In which of the following reaction the final product is neither an acid nor an acid salt.



Section (H) : Carboxylic acid (Chemical Properties)

H-1. Formic acid can be distinguished from acetic acid because formic acid :

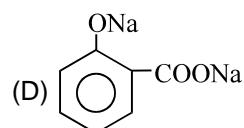
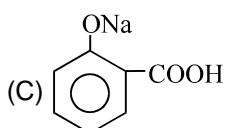
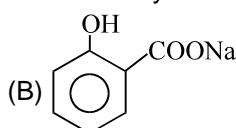
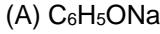
(A) releases H_2 with sodium

(B) gives ester with alcohol

(C) reduces ammonical AgNO_3

(D) turns red litmus to blue

H-2. Sodium bicarbonate reacts with salicylic acid to form:



H-3. Which of the following will not undergo Hell-Volhard-Zelinsky (HVZ) reaction?

(A) HCOOH

(B) CH_3COOH

(C) $\text{CH}_3\text{CH}_2\text{COOH}$

(D) $\text{CH}_3\text{CHBrCOOH}$



This reaction is called

(A) Cannizzaro reaction

(B) Aldol condensation reaction

(C) Hell Volhard Zelinsky reaction

(D) Reimer tiemann reaction

H-5. What product is formed when acetic acid heated with P_2O_5 ?

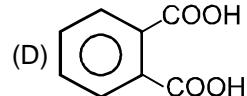
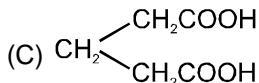
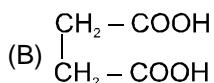
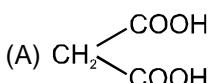
(A) Acetyl chloride

(B) Acetate ester

(C) Acetic anhydride

(D) Acetaldehyde

H-6. Which of the following will not yield a cyclic compound on heating:



H-7. The reaction : $\text{RCOOAg} + \text{Br}_2 \xrightarrow{\text{CCl}_4, \text{Reflux}} \text{R-Br} + \text{AgBr} + \text{CO}_2$

is called

(A) Wurtz reaction

(B) Hunsdiecker bromo decarboxylation reaction

(C) Friedel-Crafts reaction

(D) Kolbe's reaction

H-8. $\text{RCOOH} \longrightarrow \text{RCH}_2\text{COOH}$. This conversion is known as reaction:

(A) Arndt-Eistert reaction

(B) Hunsdicker reaction

(C) HVZ reaction

(D) Cannizaro reaction

Section (I) : Acid Derivatives (Acid Halide, Ester, Anhydride & Amide)

I-1. Acetic anhydride is prepared in the laboratory by heating sodium acetate with

(A) ethyl chloride

(B) acetyl chloride

(C) conc. H_2SO_4

(D) zinc dust

I-2. A compound with molecular formula $\text{C}_4\text{H}_{10}\text{O}_4$ on acylation with acetic anhydride gives a compound with molecular formula $\text{C}_{12}\text{H}_{18}\text{O}_8$. How many hydroxyl groups are present in the compound?

(A) one

(B) Two

(C) Three

(D) Four

**PART - III : MATCH THE COLUMN**

1. Match the column :

	Column-I		Column-II
	Aldol product		Reactant required
(A)		(p)	
(B)		(q)	HCHO
(C)		(r)	Ph-CHO
(D)	Ph-CH=CH-CHO	(s)	CH ₃ -CHO

2. Match the column :

	Column-I		Column-II
	(Reaction)		(Reactions involved)
(A)		(p)	Hydrolysis
(B)		(q)	Esterification
(C)		(r)	Saponification
(D)		(s)	Acid base reaction

Exercise-2

Marked questions are recommended for Revision.

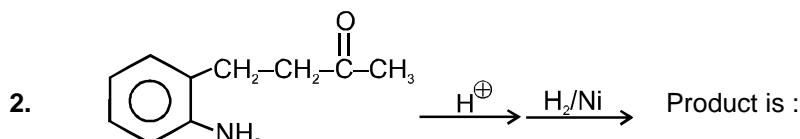
PART - I : ONLY ONE OPTION CORRECT TYPE**ALDEHYDES & KETONES**

1. In the given reaction,

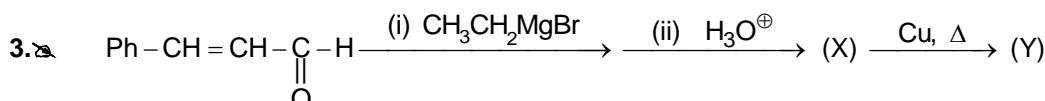
(Y) is

- (A)
- (B)
- (C)

- (B)
- (D)

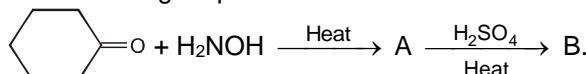


- (A) (B) (C) (D)



- (A) X is 1, 4-addition product ; Y is
- (B) X is 1, 2-addition product ; Y is
- (C) X is 1, 4-addition product ; Y is
- (D) X is 1, 2-addition product ; Y is

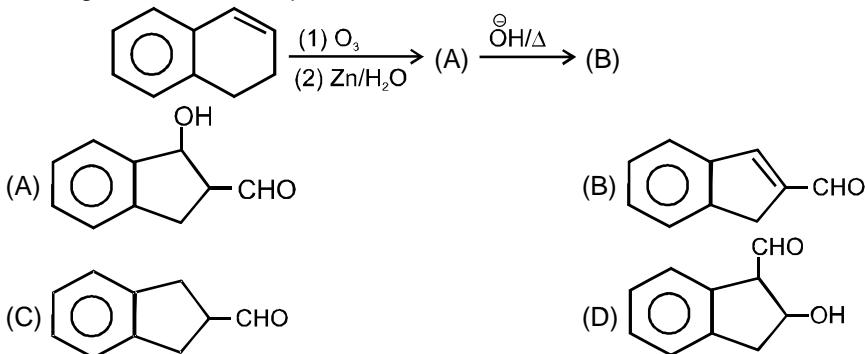
4. Consider the following sequence of reactions :

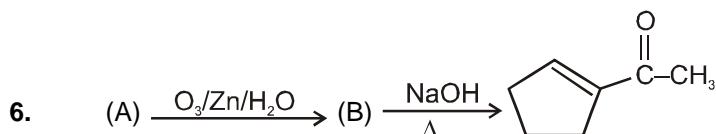


The products (A) and (B) are, respectively :

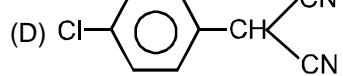
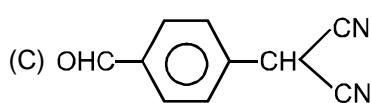
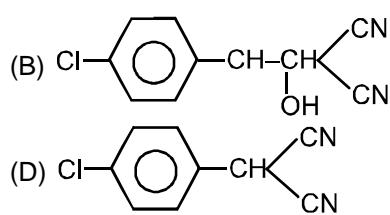
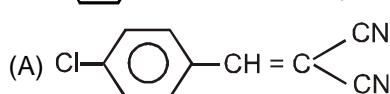
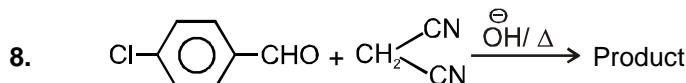
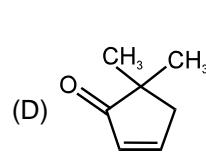
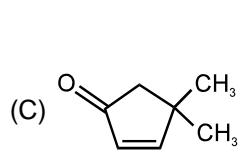
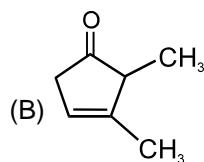
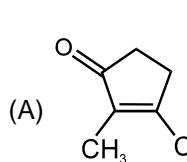
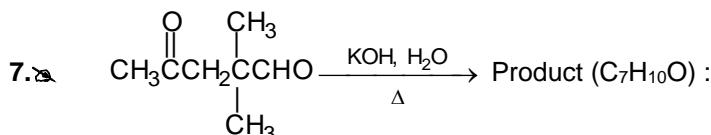
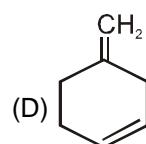
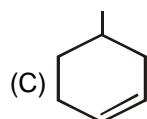
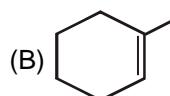
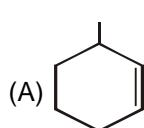
- (A) and
- (C)
- (D)

5. In the given reaction sequence B is

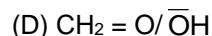
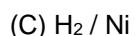
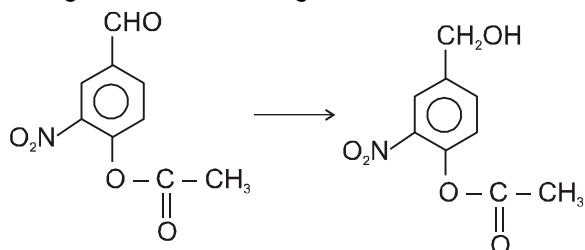




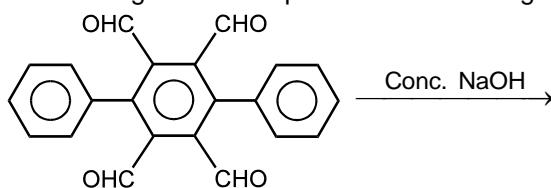
The reactant (A) will be :

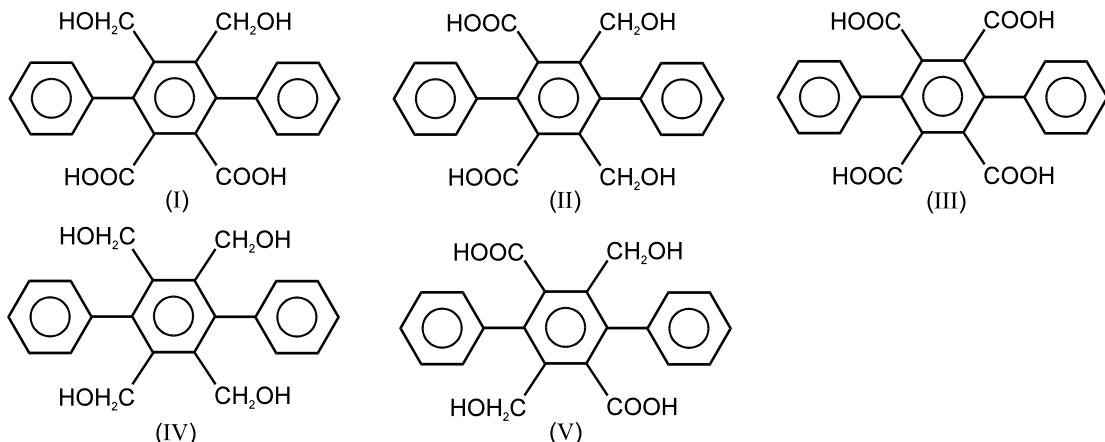


9. The suitable reagent for the following reaction is :



10. Which of the following can be the product/s of following reaction.



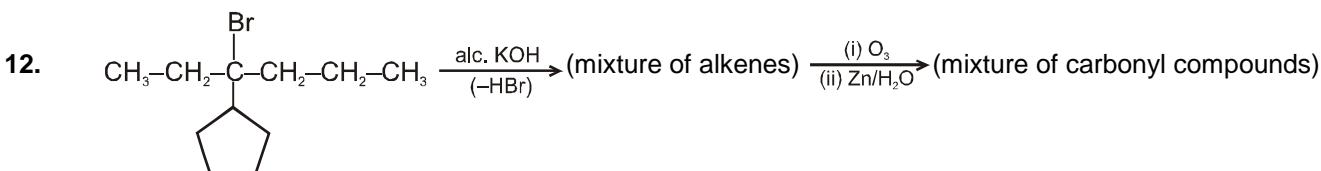
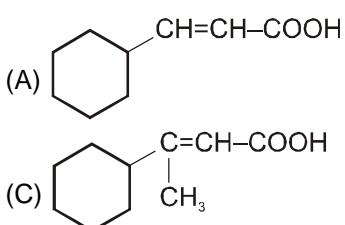
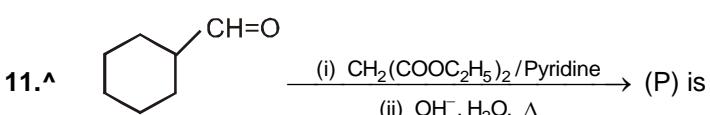


(A) I, II, IV

(B) III, IV

(C) II, V

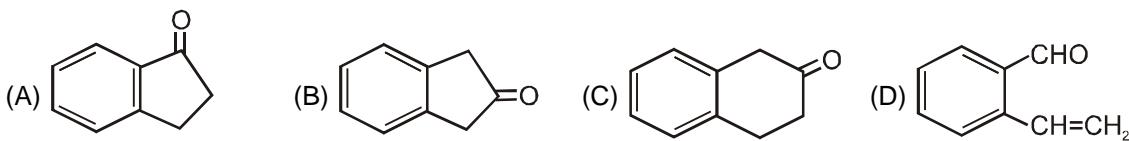
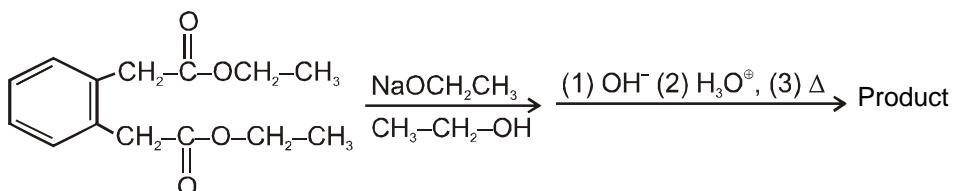
(D) I, V

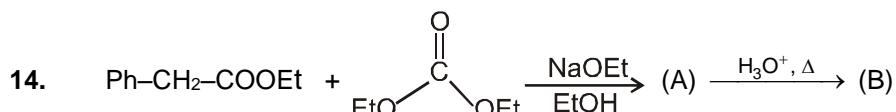


The incorrect statement is

- (A) Total five alkynes are obtained.
 (B) Total six different carbonyl compounds are obtained on ozonolysis.
 (C) All carbonyl compounds can give aldol reaction when treated with dil KOH.
 (D) Only two carbonyl compounds give positive iodoform test.

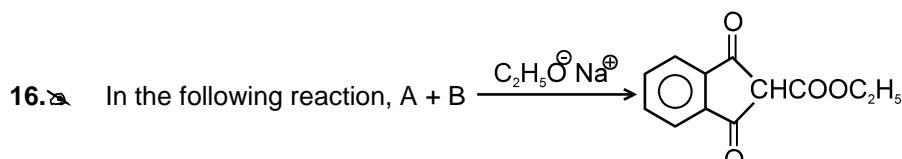
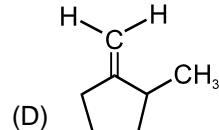
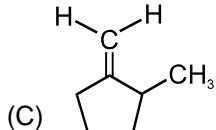
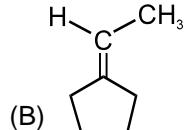
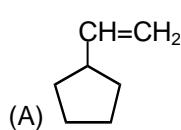
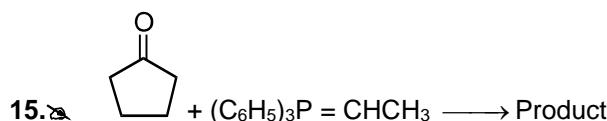
13.^ What is the final product of this sequence of reactions ?



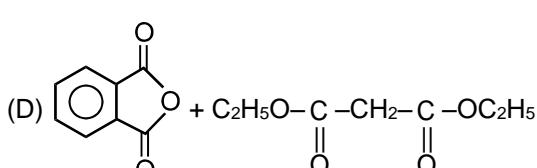
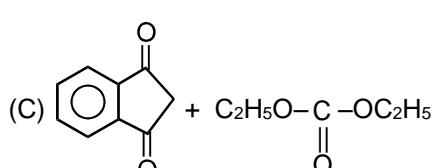
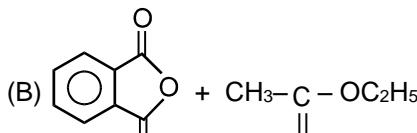
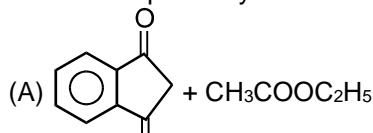


Product B is :

- (A) $\text{Ph}-\text{CH}_2-\text{COOH}$ (B) $\text{Ph}-\text{CH}_2-\text{COOEt}$ (C) $\text{Ph}-\text{CH}(\text{COOH})(\text{COOH})$ (D) None of these

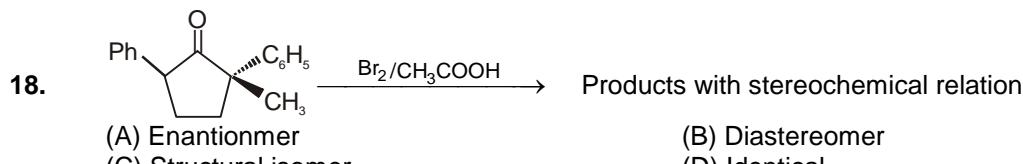


A and B respectively are :



17. Aromatic carbonyl compounds having molecular formula $\text{C}_8\text{H}_8\text{O}$ react with NH_2OH how many oximes can be formed :

- (A) 8 (B) 10 (C) 12 (D) 6



- (A) Enantiomer
(C) Structural isomer

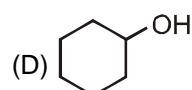
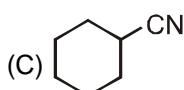
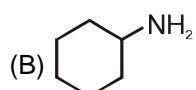
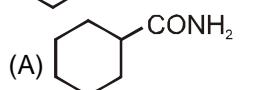
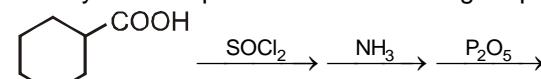
- (B) Diastereomer
(D) Identical

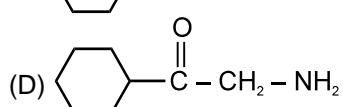
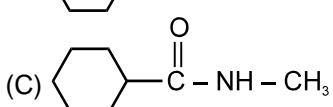
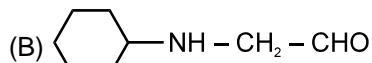
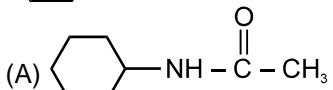
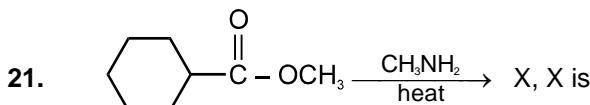
CARBOXYLIC ACID & DERIVATIVES

19. Which of the following does not give benzoic acid on hydrolysis ?

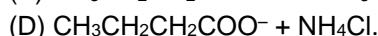
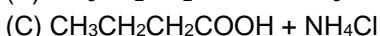
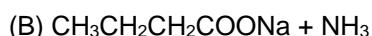
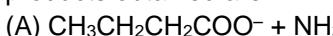
- (A) Phenyl cyanide (B) Benzoyl chloride (C) Benzyl chloride (D) Methyl benzoate

20. Identify the final product in the following sequence of reaction.

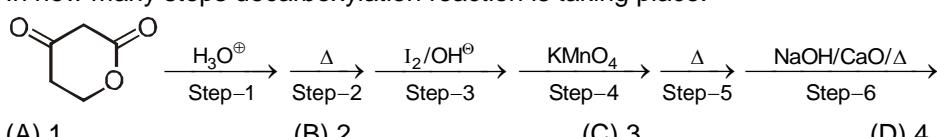




22. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$ is boiled with aqueous NaOH , then the reaction mixture is acidified with HCl . The products obtained are



23. In how many steps decarboxylation reaction is taking place.



(A) 1

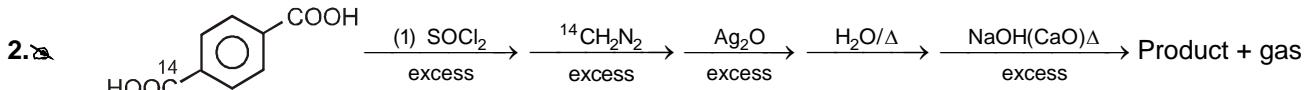
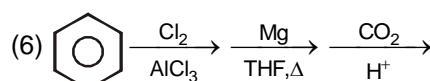
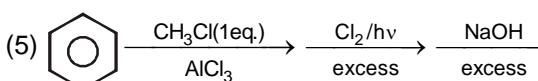
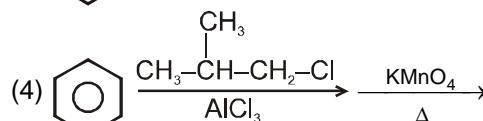
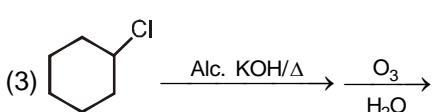
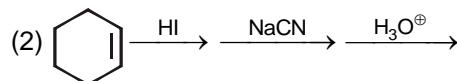
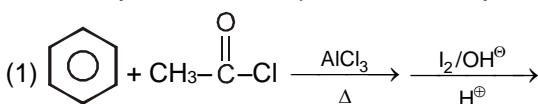
(B) 2

(C) 3

(D) 4

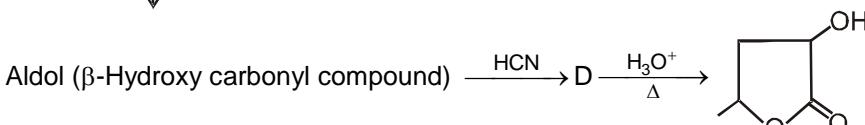
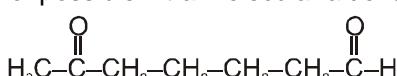
PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. How many reactions will produce carboxylic acid, as their end product.



How many C^{14} atoms are present in the product.

3. Number of possible intra molecular aldol condensation products on heating with NaOH .

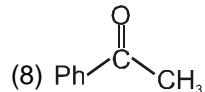
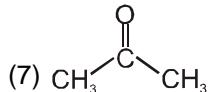
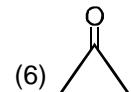
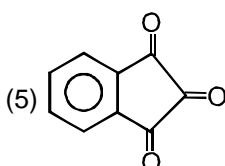
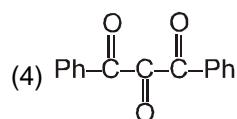
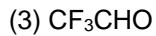
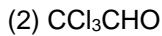
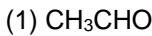


No. of carbon atoms in structure of A is ?



5. Total aldol condensation products (including stereoisomers) formed by the reaction between acetaldehyde and acetophenone is :

6. How many of the following will form stable hydrate :



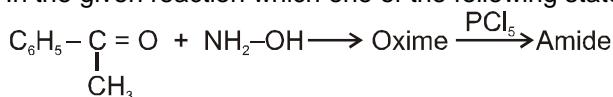
PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Observe the following reaction $\text{CH}_3-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3 \xrightarrow{\text{HCN (excess)}} \xrightarrow{\text{H}_3\text{O}^+ / \Delta} \text{Products.}$

The correct statement is

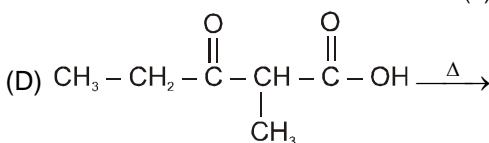
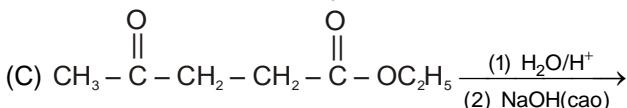
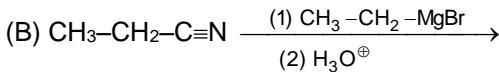
- (A) The product is a mixture of two compounds
- (B) The product is optically inactive
- (C) The product is a mixture of two chiral and one achiral stereoisomer
- (D) The product is a mixture of three stereoisomers.

2. In the given reaction which one of the following statement is correct –

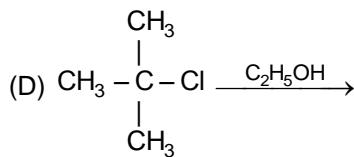
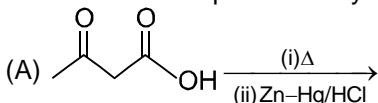


- (A) Oxime may be E/Z.
- (B) Amide on hydrolysis gives a mixture acetic acid, benzoic acid, Aniline and methylamine.
- (C) Preparation of oxime is nucleophilic addition followed by elimination reaction.
- (D) Oxime and amides are isomers.

3. Which of the following will give 3-pentanone.

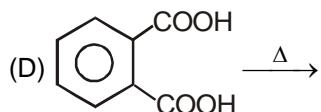
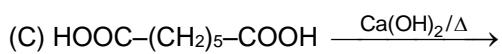
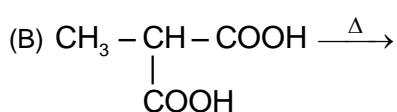
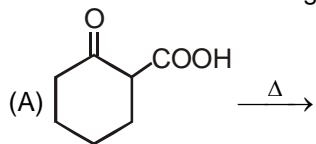


4. In which reaction product is hydrocarbon?

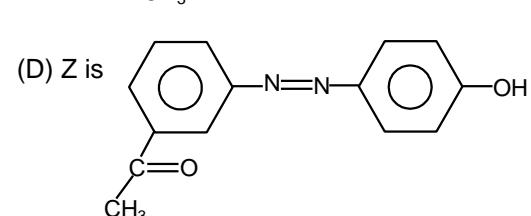
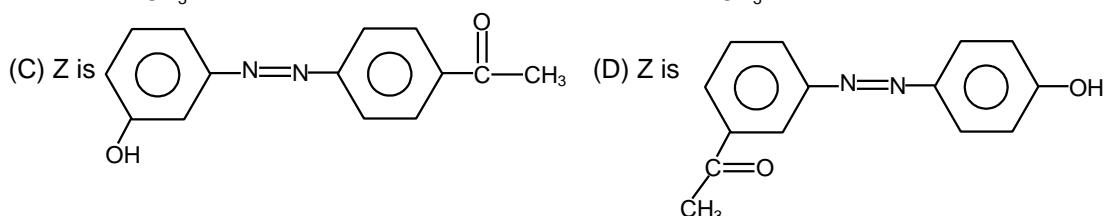
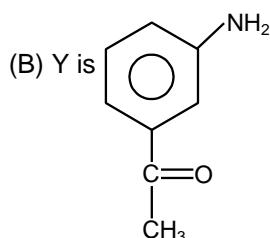
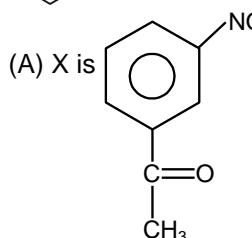
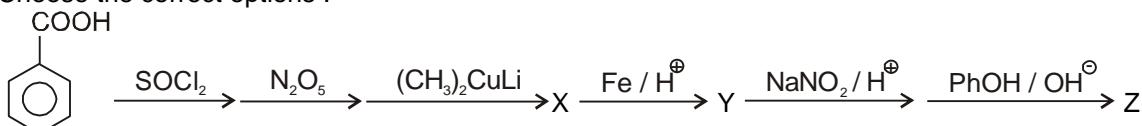




5. Which of them liberate a gas which turns lime water milky.



6. Choose the correct options :

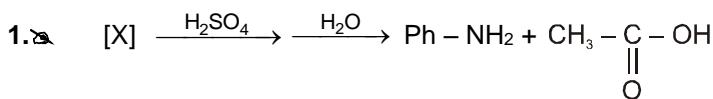
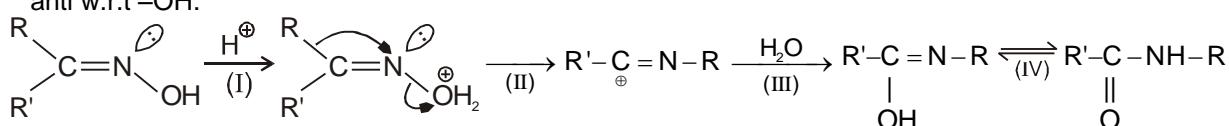


PART - IV : COMPREHENSION

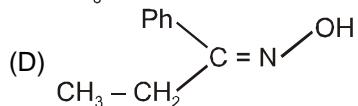
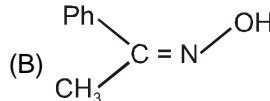
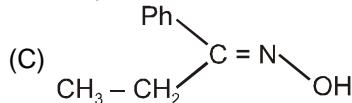
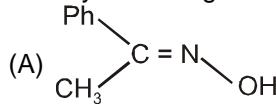
Read the following passage carefully and answer the questions.

Comprehension # 1

Aldehydes and Ketones reacts with NH_2OH to form Aldoximes and Ketoximes respectively. Configuration of these can be determined by Beckmann rearrangement as that group migrates which is anti w.r.t $-\text{OH}$.



Identify the configuration of [X] compound :





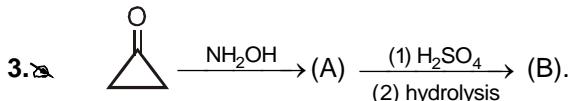
2. Which step is Rate determining step?

(A) I

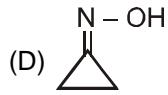
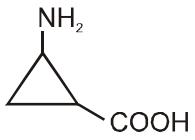
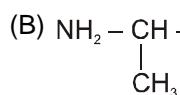
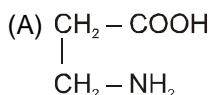
(B) II

(C) III

(D) IV

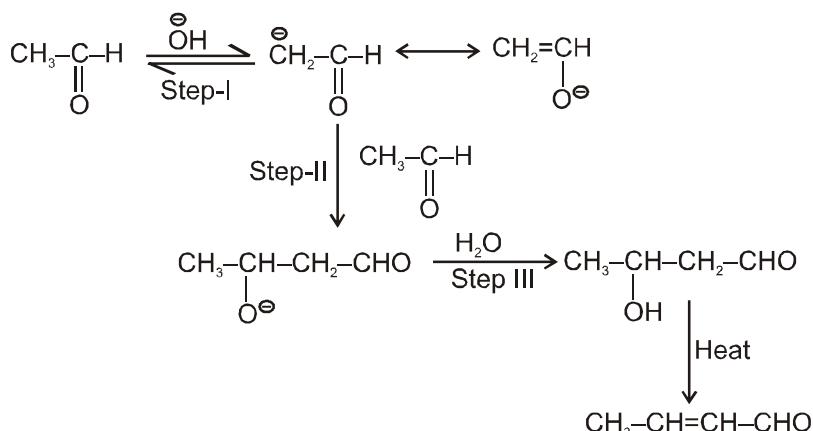


The product (B) is :

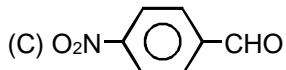
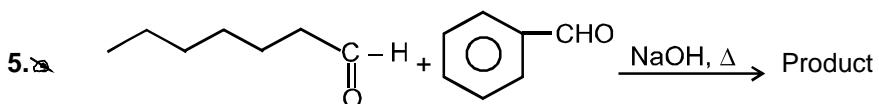


Comprehension # 2

Carbonyl compound which contains α -H gives aldol condensation reaction in presence of alkaline medium. The reaction between two molecules of acetaldehyde take place as follows in presence of base.



4. Aldol condensation reaction is given by

(A) C_6H_5-CHO (B) CX_3-CHO (D) $C_6H_5-CH_2-CHO$ (A) $Ph-CH=CH-(CH_2)_5-CHO$ (B) $Ph-(CH_2)_5-CH=CH-CHO$

(C) $Ph-CH=CH-(CH_2)_4-CHO$
CHO

(D) $Ph-CH=CH-(CH_2)_4-CH_3$
CHO

6. Intramolecular aldol condensation reaction is given by

(A) 2,5-diketone

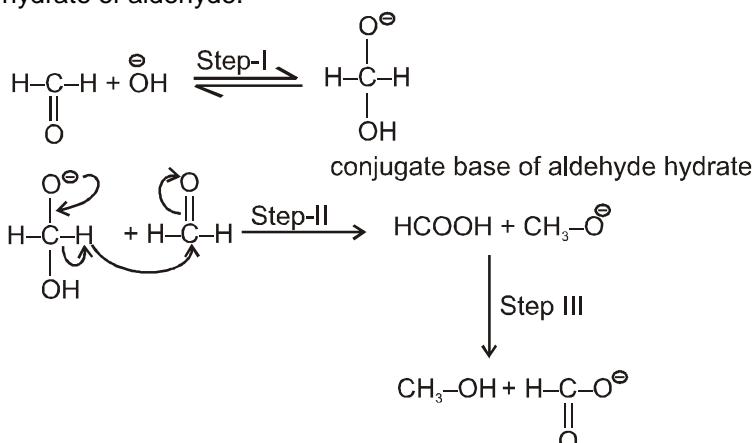
(B) 2,7-diketone

(C) 2,6 and 2,8-diketone

(D) All of these

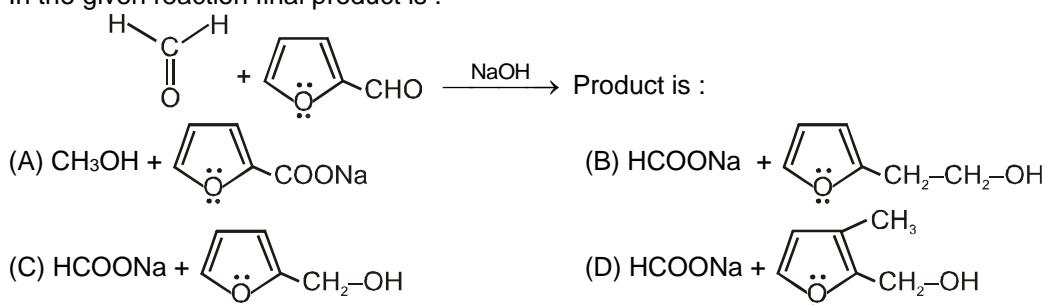

Comprehension # 3

The conversion of aldehyde having no alpha hydrogen to a mixture of carboxylic acid and primary alcohol is known as cannizzaro reaction. The most important feature of this reaction is the conjugate base of hydrate of aldehyde.

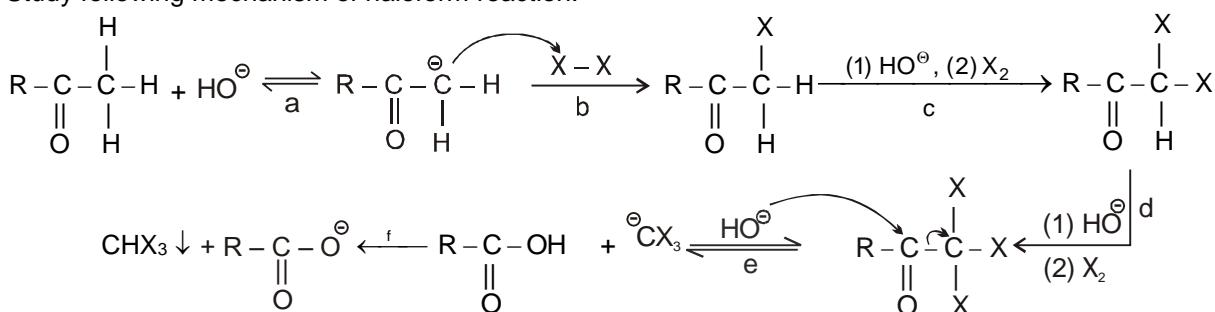


7. Which step is rate determining step
 (A) step I (B) step II (C) step III (D) step I and II both

8. In the given reaction final product is :

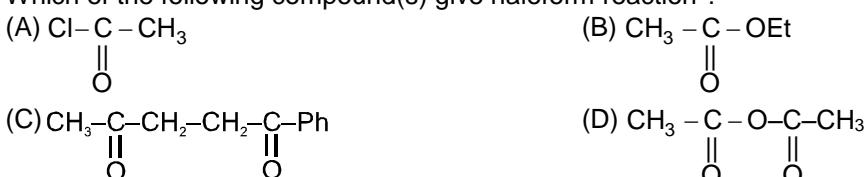

Comprehension # 4

Study following mechanism of haloform reaction.



9. Which step is RDS
 (A) a (B) b (C) c (D) f

10. Which of the following compound(s) give haloform reaction ?





11. Which step produces most acidic compound

(A) a

(B) c

(C) d

(D) b

Comprehension # 5

Answer Q.12, Q.13 and Q.14 by appropriately matching the information given in the three columns of the following table.

Column-1		Column-2		Column-3	
(I)	$\text{H}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H} + \text{OH}^- \xrightarrow{\Delta}$	(i)	Hydride shift	(P)	Product with same no. of carbon as it is an reactant.
(II)	$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H} + \text{OH}^- \longrightarrow$	(ii)	Carbanion	(Q)	Product with lesser no. of carbon than reactant.
(III)	$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{H} + \text{I}_2 / \text{OH}^- \longrightarrow$	(iii)	Enolate anion	(R)	Product with greater no. of carbon than reactant.
(IV)	$\text{CH}_3-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{CH}_3 + \text{OH}^- \longrightarrow$	(iv)	sp^3 hybrid intermediate	(S)	Product shows stereoisomerism.

12. Which of the given combination is correct ?

(A) (I) (i) (Q)

(B) (II) (ii) (P)

(C) (III) (iii) (S)

(D) (IV) (iv) (Q)

13. In which of the following combination, β -hydroxy carbonyl is obtained ?

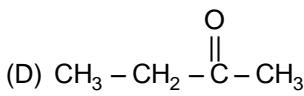
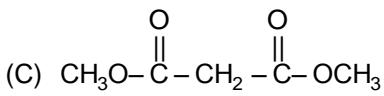
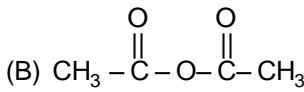
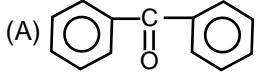
(A) (I) (i) (P)

(B) (II) (ii) (S)

(C) (III) (ii) (P)

(D) (IV) (ii) (Q)

14. Which of the following reactant will give the same product as (III), (ii), (Q) with NaOI ?



Exercise-3

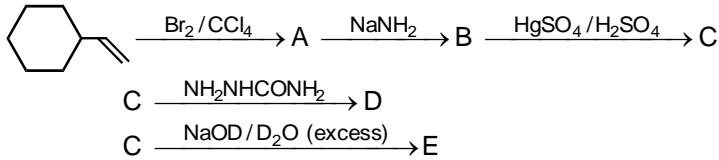
* Marked Questions are having more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

ALDEHYDES & KETONES

1. Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures :

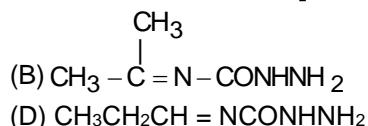
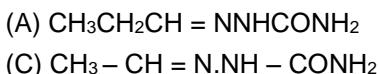
[IIT-JEE 2001(M), 5/100]

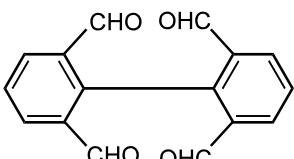


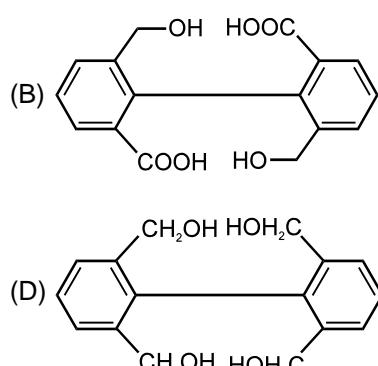
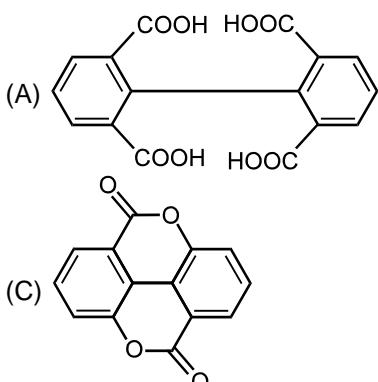


2. An alkene (A) $C_{16}H_{16}$ on ozonolysis gives only one product (B) C_8H_8O . Compound (B) on reaction with $NaOH / I_2$ yields sodium benzoate. Compound (B) reacts with KOH / NH_2NH_2 yielding a hydrocarbon (C) C_8H_{10} . Write the structures of compound (B) & (C). Based on this information to isomeric structures can be proposed for alkene (A). Write their structure and identify the isomer which on catalytic hydrogenation ($H_2/Pd-C$) gives a racemic mixture. [IIT-JEE 2001(M), 5/60]
3. Compound 'A' (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product 'B' (mol. Formula C_3H_6O). 'B' forms a shining silver mirror on warming with ammonical $AgNO_3$. 'B' when treated with an aqueous solution of $H_2NCONHNH_2$, HCl & sodium acetate gives a product 'C'. Identify the structure of 'C'.

[IIT-JEE 2002(S), 3/90]

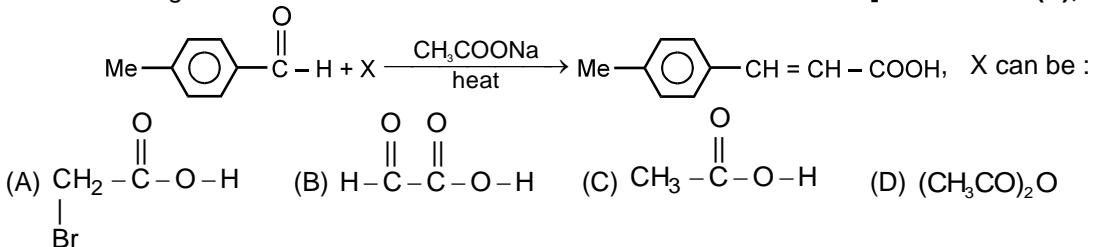


4.  $\xrightarrow{\substack{(i) NaOH / 100^\circ C \\ (ii) H^+ / H_2O}}$ Major Product is [IIT-JEE 2003(S), 3/84]

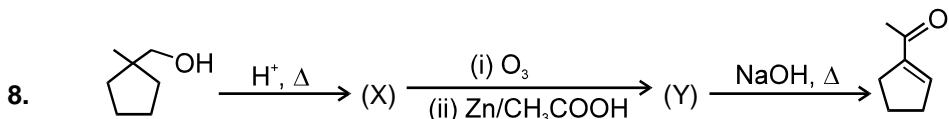


5. A (C_6H_{12}) \xrightarrow{HCl} B + C ($C_6H_{13}Cl$)
 B $\xrightarrow{alc\ KOH}$ D (isomer of A)
 D $\xrightarrow{ozonolysis}$ E (it gives negative test with Fehling solution but responds to iodoform test).
 A $\xrightarrow{ozonolysis}$ F + G (both give positive Tollen's test but do not give iodoform test).
 F + G $\xrightarrow{conc.\ NaOH}$ $HCOONa$ + a primary alcohol
 Identify to A to G. [IIT-JEE 2003(M), 4/60]

6. In the following reaction [IIT-JEE 2005(S), 3/84]



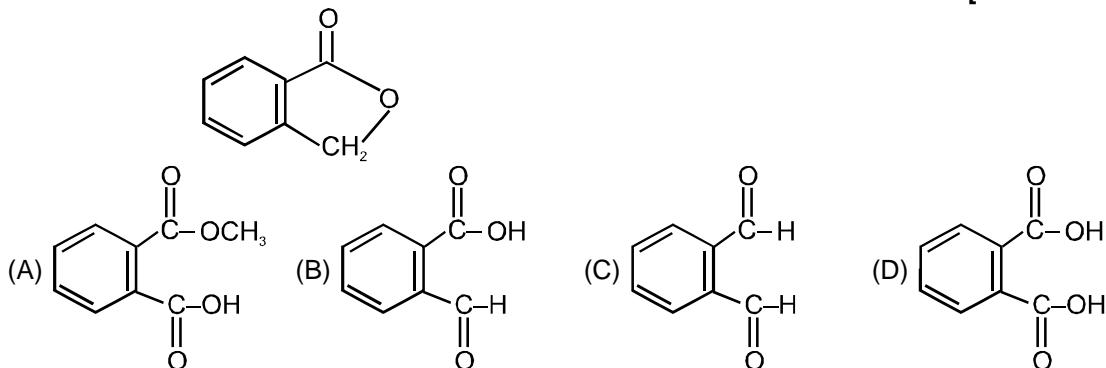
7. In conversion of 2-butanone to propanoic acid which reagent is used. [IIT-JEE 2005(S), 3/84]
 (A) $NaOH, NaI / H^\ominus$ (B) Fehling solution (C) $NaOH, I_2 / H^\ominus$ (D) Tollen's reagent



Identify X and Y.

[IIT-JEE-2005(M), 2/60]

9. Which of the following reagent on reaction with conc. NaOH followed by acidification gives following lactone as the :



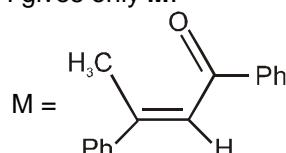
10. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous KOH yields compound F. Compound F is :

[JEE 2007, 3/162]



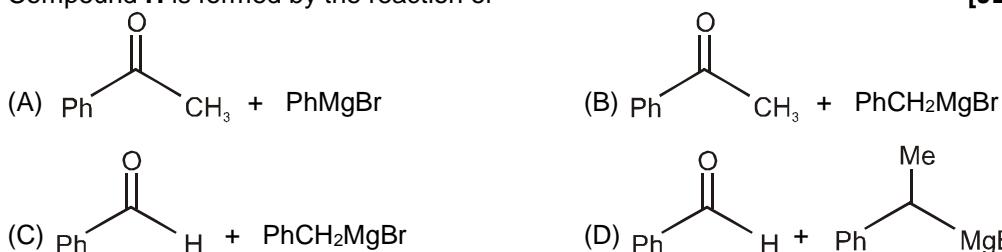
Comprehension # 1

A tertiary alcohol **H** upon acid catalysed dehydration gives a product **I**. Ozonolysis of **I** leads to compounds **J** and **K**. Compound **J** upon reaction with KOH gives benzyl alcohol and compound **L**, whereas **K** on reaction with KOH gives only **M**.



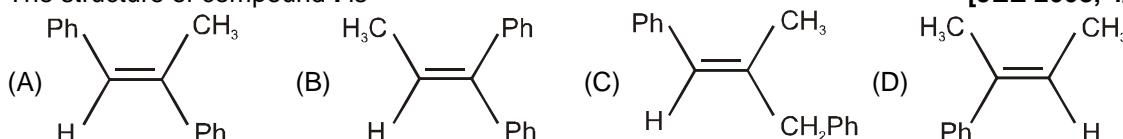
11. Compound **H** is formed by the reaction of

[JEE 2008, 4/163]



12. The structure of compound **I** is

[JEE 2008, 4/163]



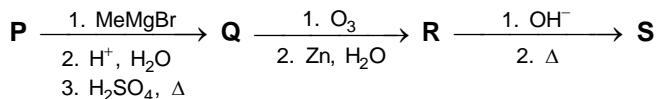
13. The structure of compounds **J**, **K** and **L** respectively, are :

[JEE 2008, 4/163]

- (A) PhCOCH_3 , $\text{PhCH}_2\text{COCH}_3$ and $\text{PhCH}_2\text{COO}^- \text{K}^+$
 (B) PhCHO , PhCH_2CHO and $\text{PhCOO}^- \text{K}^+$
 (C) PhCOCH_3 , PhCH_2CHO and $\text{CH}_3\text{COO}^- \text{K}^+$
 (D) PhCHO , PhCOCH_3 and $\text{PhCOO}^- \text{K}^+$

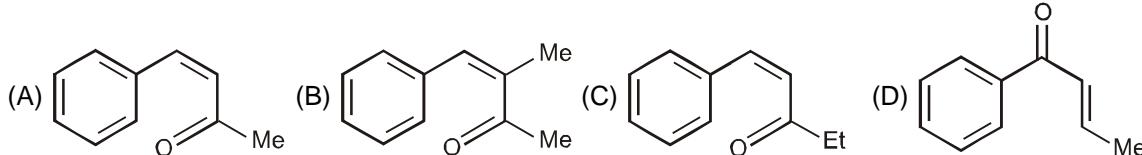

Comprehension # 2

A carbonyl compound **P**, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin **Q**. Ozonolysis of **Q** leads to a dicarbonyl compound **R**, which undergoes intramolecular aldol reaction to give predominantly **S**.



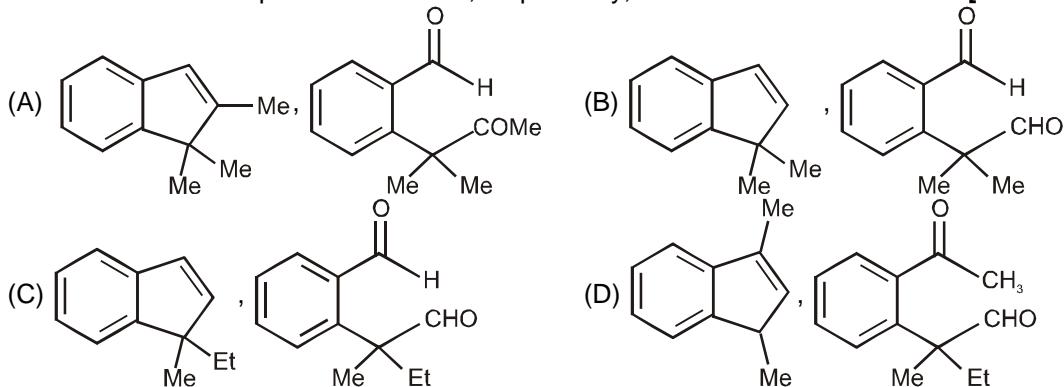
14. The structure of the carbonyl compound **P** is :

[JEE 2009, 4/160]



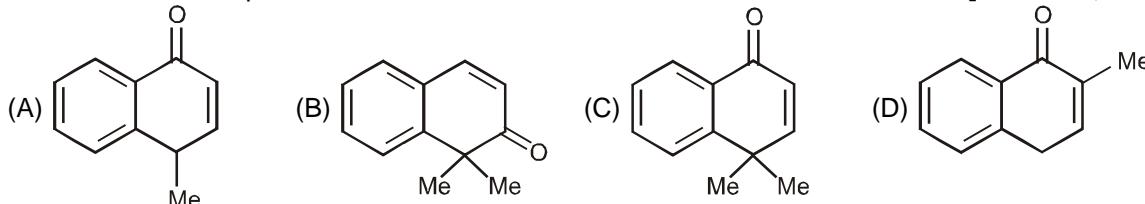
15. The structures of the products **Q** and **R**, respectively, are :

[JEE 2009, 4/160]



16. The structure of the product **S** is :

[JEE 2009, 4/160]



17. Match each of the compounds given in **Column I** with the reaction(s), that they can undergo, given in **Column II**.

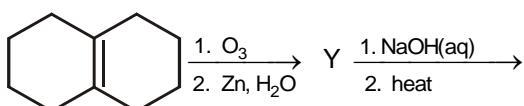
[JEE-2009, 8/160]

Column I
Column II

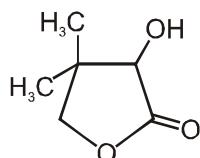
(A)	(p) Nucleophilic substitution
(B)	(q) Elimination
(C)	(r) Nucleophilic addition
(D)	(s) Esterification with acetic anhydride (t) Dehydrogenation



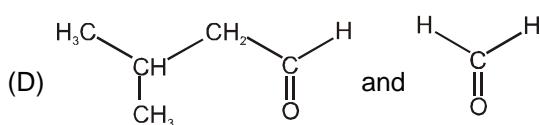
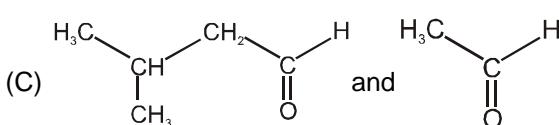
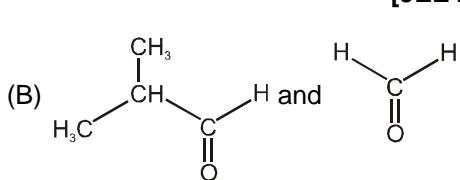
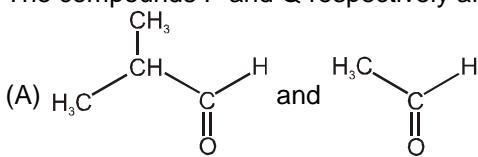
18. In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is:
[JEE 2010, 3/163]


Comprehension # 3

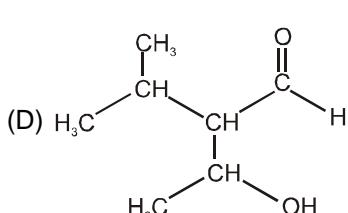
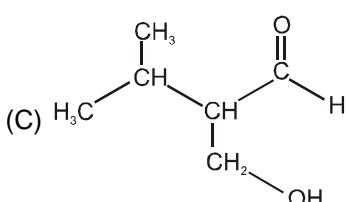
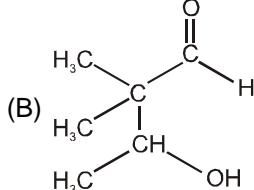
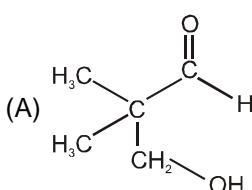
Two aliphatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below :



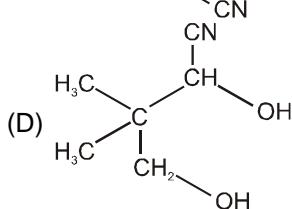
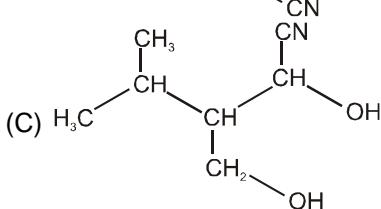
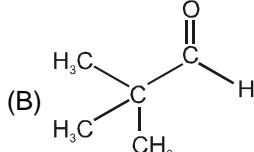
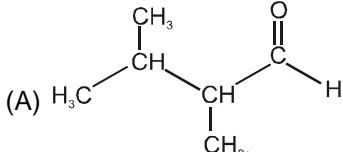
19. The compounds P and Q respectively are :

[JEE 2010, 3/163]


20. The compound R is :

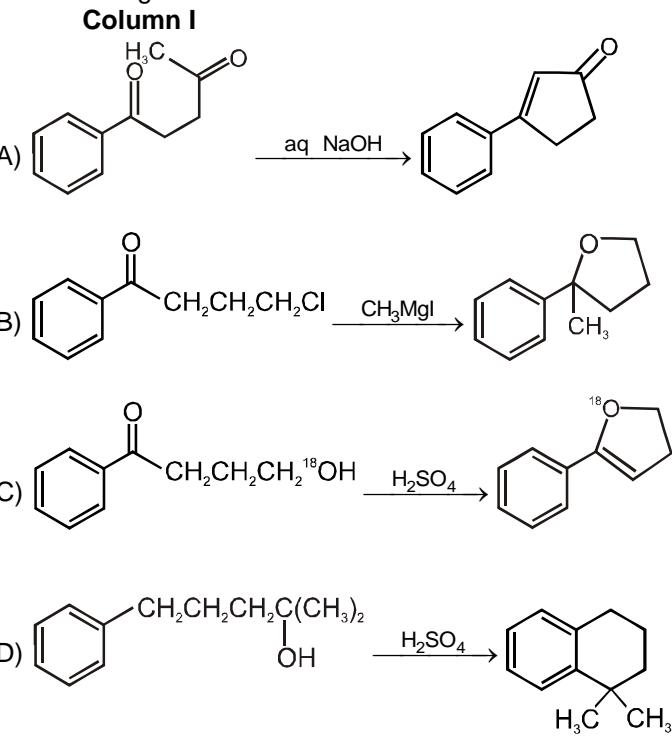
[JEE 2010, 3/163]


21. The compound S is :

[JEE 2010, 3/163]




22. Match the reactions in **column I** with appropriate type of steps/reactive intermediate involved in these reactions as given in **column II**


Column II

(p) Nucleophilic substitution

(q) Electrophilic substitution

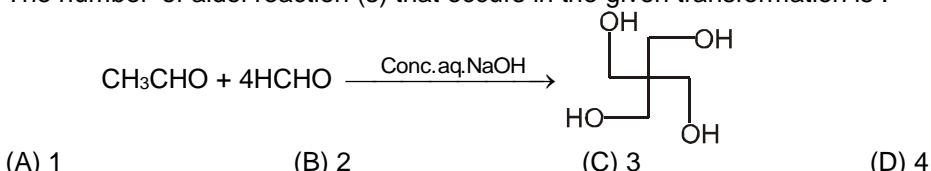
(r) Dehydration

(s) Nucleophilic addition

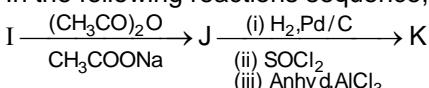
(t) Carbanion

23. The number of aldol reaction (s) that occurs in the given transformation is :

[IIT-JEE 2012, 3/136]


Comprehension # 4

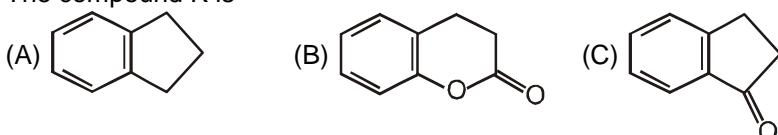
In the following reactions sequence, the compound J is an intermediate.



J ($\text{C}_9\text{H}_8\text{O}_2$) gives effervescence on treatment with NaHCO_3 and positive Baeyer's test

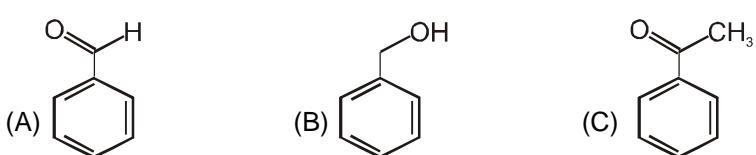
24. The compound K is

[IIT-JEE 2012, 3/136]



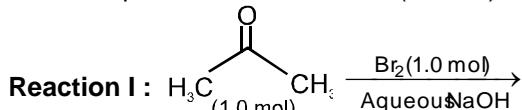
25. The compound I is

[IIT-JEE 2012, 3/136]

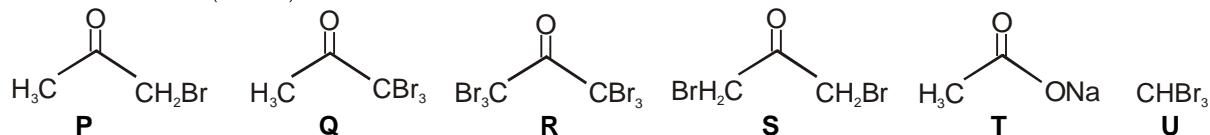
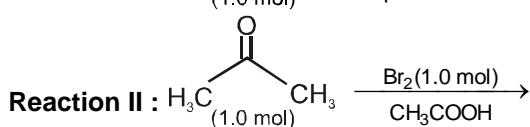




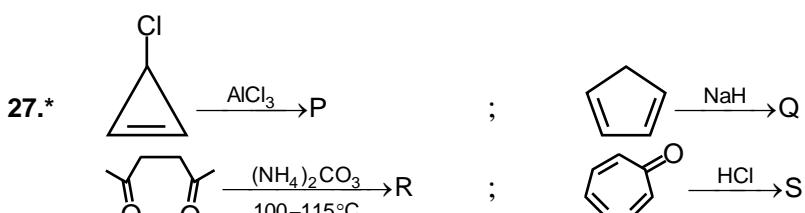
26. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is (are)



[IIT-JEE 2013, 3/120]



- (A) Reaction I : P and Reaction II : P
 (B) Reaction I : U, acetone and Reaction II : Q, acetone
 (C) Reaction I : T, U, acetone and Reaction II : P
 (D) Reaction I : R, acetone and Reaction II : S, acetone

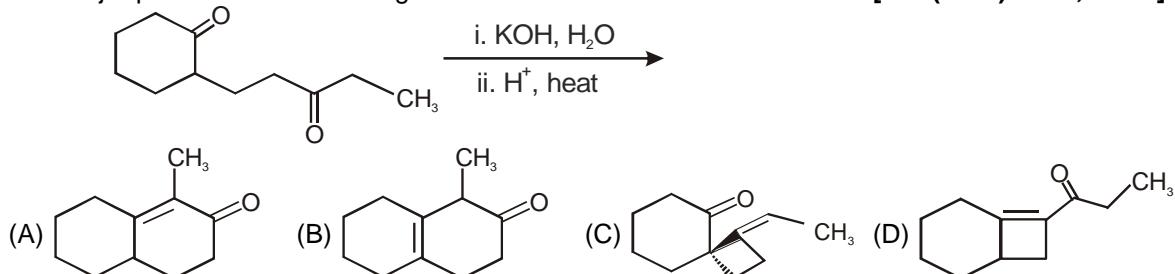


- Among P, Q, R and S, the aromatic compound(s) is/are :
 (A) P (B) Q (C) R (D) S

[IIT-JEE 2013, 4/120]

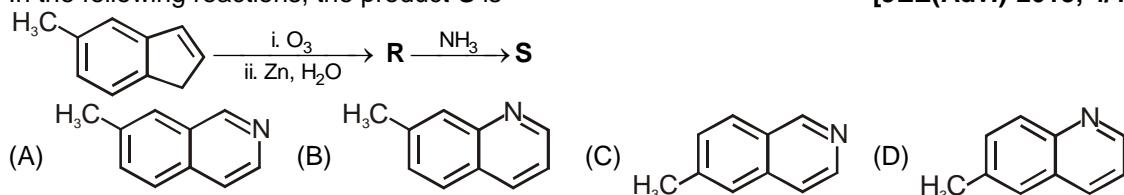
28. The major product of the following reaction is :

[JEE(Adv.)-2015, 4/168]



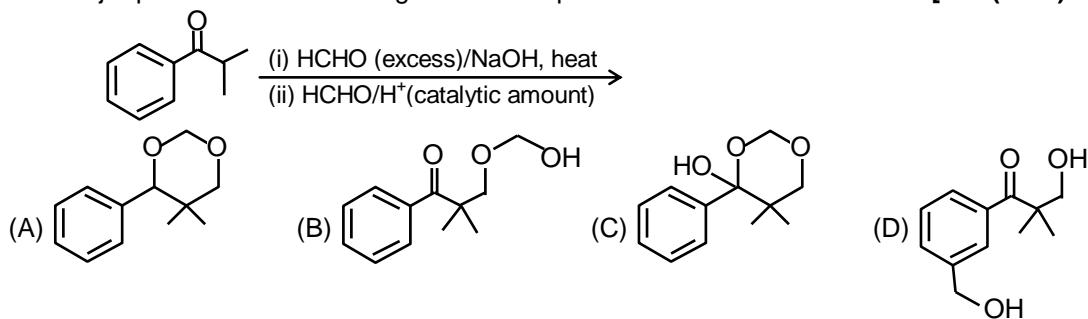
29. In the following reactions, the product S is

[JEE(Adv.)-2015, 4/168]



30. The major product of the following reaction sequence is

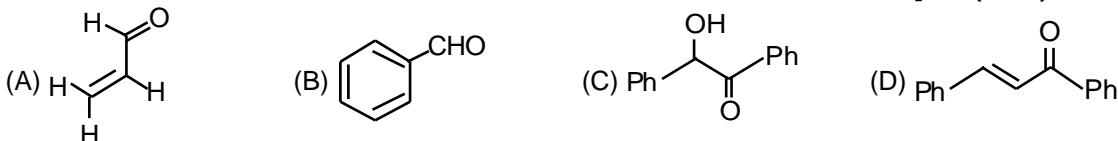
[JEE(Adv.)-2016, 3/124]



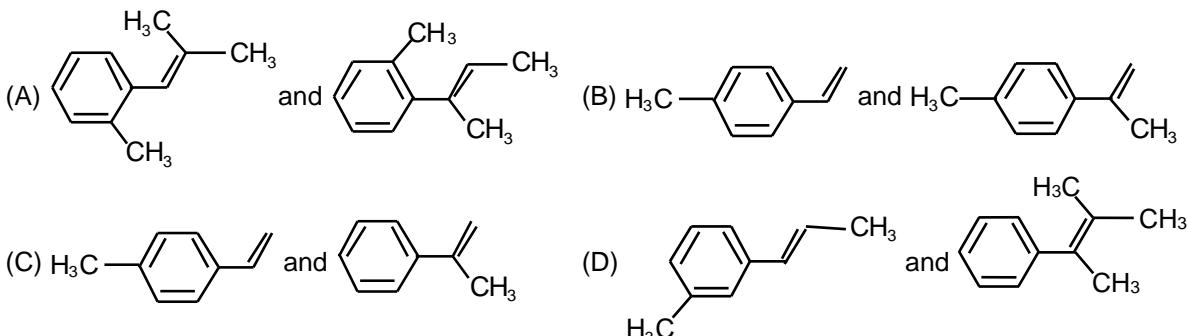


31.* Positive Tollen's test is observed for :

[JEE(Adv.)-2016, 4/124]


 32.* Compound P and R upon ozonolysis produce Q and S, respectively. The molecular formula of Q and S is C_8H_8O . Q undergoes Cannizzaro reaction but not haloform reaction, whereas S undergoes haloform reaction but not Cannizzaro reaction.


The options(s) with suitable combination of P and R, respectively, is(are) : [JEE(Adv.)-2017, 4/122]



CARBOXYLIC ACID & DERIVATIVES

33. There is a solution of p-hydroxy benzoic acid and p-amino benzoic acid. Discuss one method by which we can separate them and also write down the confirmatory test of the functional groups present.

[JEE-2003, 4/60]

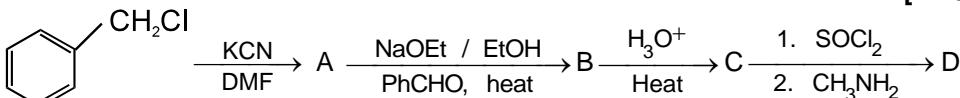
 34. $\text{Ph}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{NH}_2 \xrightarrow{\text{POCl}_3}$ Product,

product is :

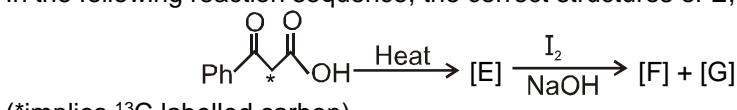
- (A) Benzonitrile (B) Benzamine
 (C) Chloro benzene (D) Aniline

[IIT-JEE 2004, 3/84]

35. Identify the structure of the major products A, B, C and D formed in the following sequence of reactions [IIT-JEE 2004(M), 2/60]



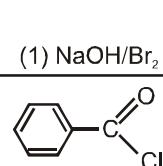
36. In the following reaction sequence, the correct structures of E, F and G are : [JEE 2008, 3/163]



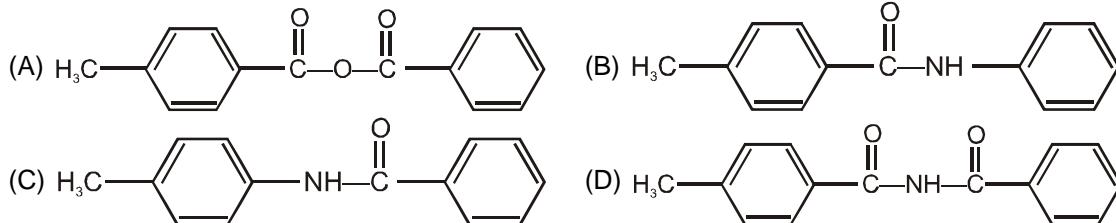
- (A) $\text{E} = \text{Ph}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_2-\overset{*}{\text{C}}(\text{OH})-\text{CO}_2\text{Ph}$ $\text{F} = \text{Ph}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_2-\overset{*}{\text{C}}(\text{O}^- \text{Na}^+)-\text{CO}_2\text{Ph}$ $\text{G} = \text{CHI}_3$
 (B) $\text{E} = \text{Ph}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_2-\overset{*}{\text{C}}(\text{OH})-\text{CO}_2\text{Ph}$ $\text{F} = \text{Ph}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_2-\overset{*}{\text{C}}(\text{O}^- \text{Na}^+)-\text{CO}_2\text{Ph}$ $\text{G} = \text{CHI}_3$
 (C) $\text{E} = \text{Ph}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_2-\overset{*}{\text{C}}(\text{OH})-\text{CO}_2\text{Ph}$ $\text{F} = \text{Ph}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_2-\overset{*}{\text{C}}(\text{O}^- \text{Na}^+)-\text{CO}_2\text{Ph}$ $\text{G} = \overset{*}{\text{C}}\text{HI}_3$
 (D) $\text{E} = \text{Ph}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_2-\overset{*}{\text{C}}(\text{OH})-\text{CO}_2\text{Ph}$ $\text{F} = \text{Ph}-\overset{\text{O}}{\underset{||}{\text{C}}}-\text{CH}_2-\overset{*}{\text{C}}(\text{O}^- \text{Na}^+)-\text{CO}_2\text{Ph}$ $\text{G} = \text{CH}_3\text{I}$



37. In the reaction $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{NH}_2 + (\text{1}) \text{NaOH}/\text{Br}_2 \rightarrow \text{T}$, the structure of the Product T is :



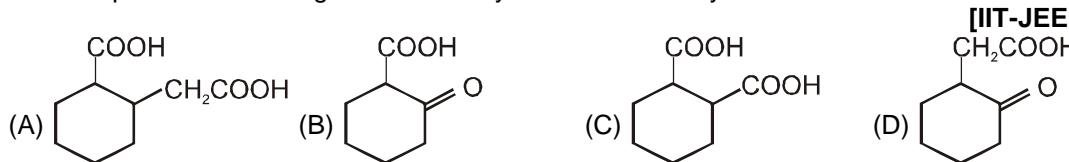
[JEE-2010, 3/163]



38. The carboxyl functional group ($-\text{COOH}$) is present in : [JEE-2012]

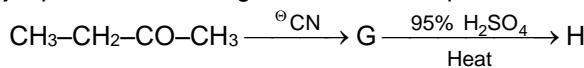
(A) picric acid (B) barbituric acid (C) ascorbic acid (D) aspirin

39. The compound that undergoes decarboxylation most readily under mild condition is



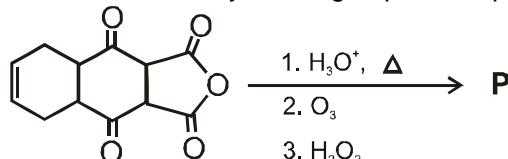
[IIT-JEE 2012, 3/136]

40. The major product H in the given reaction sequence is



[IIT-JEE 2012, 3/136]

41. The total number of carboxylic acid groups in the product P is : [JEE(Advanced)-2013, 4/120]



Answer Q.42, Q.43 and Q.44 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2 and 3 contain starting materials, reaction conditions, and type of reactions, respectively.

Column 1

- (I) Toluene
 (II) Acetophenone
 (III) Benzaldehyde
 (IV) Phenol

Column 2

- (i) NaOH/Br_2
 (ii) Br_2/hv
 (iii) $(\text{CH}_3\text{CO})_2\text{O}/\text{CH}_3\text{COOK}$
 (iv) NaOH/CO_2

Column 3

- (P) Condensation
 (Q) Carboxylation
 (R) Substitution
 (S) Haloform

42. The only CORRECT combination in which the reaction proceeds through radical mechanism is :

[JEE(Adv.)-2017, 3/122]

- (A) (IV) (i) (Q) (B) (III) (ii) (P) (C) (II) (iii) (R) (D) (I) (ii) (R)

43. For the synthesis of benzoic acid, the only CORRECT combination is : [JEE(Adv.)-2017, 3/122]

- (A) (II) (i) (S) (B) (I) (iv) (Q) (C) (IV) (ii) (P) (D) (III) (iv) (R)



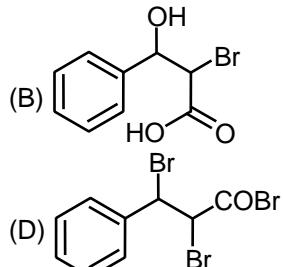
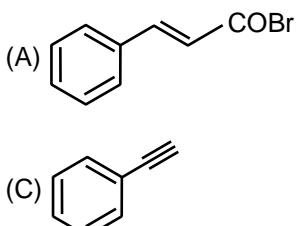
44. The only CORRECT combination that gives two different carboxylic acids is : [JEE(Adv.)-2017, 3/122]
 (A) (IV) (iii) (Q) (B) (II) (iv) (R) (C) (I) (i) (S) (D) (III) (iii) (P)

Comprehension # 5

Treatment of benzene with CO/HCl in the presence of anhydrous AlCl₃/CuCl followed by reaction with Ac₂O/NaOAc gives compound **X** as the major product. Compound **X** upon reaction with Br₂/Na₂CO₃, followed by heating at 473 K with moist KOH furnishes **Y** as the major product. Reaction of **X** with H₂/Pd-C, followed by H₃PO₄ treatment gives **Z** as the major product.

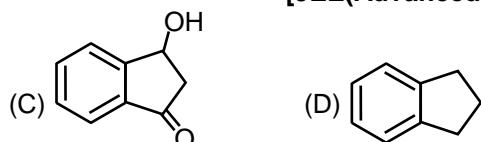
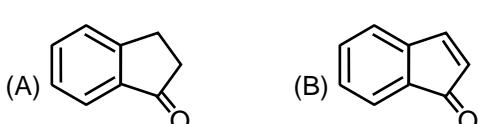
45. The compound **Y** is

[JEE(Advanced)-2018, 3/120]

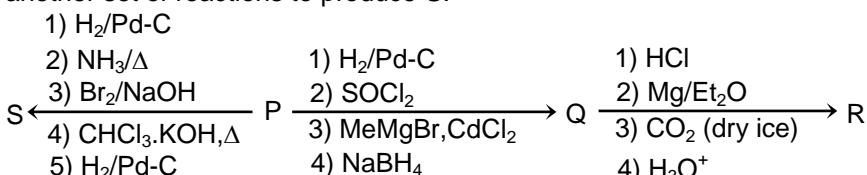


46. The compound **Z** is

[JEE(Advanced)-2018, 3/120]

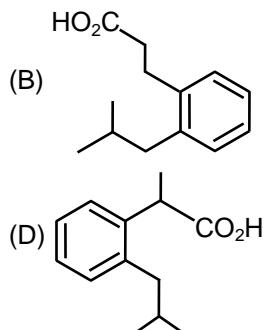
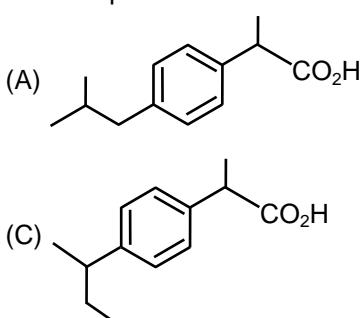

Comprehension # 6

An organic acid **P** (C₁₁H₁₂O₂) can easily be oxidized to a dibasic acid which reacts with ethyleneglycol to produce a polymer Dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** via **Q**. The compound **P** also undergoes another set of reactions to produce **S**.



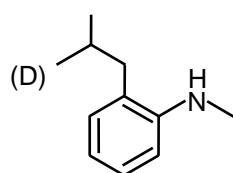
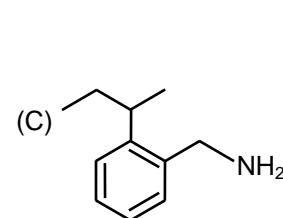
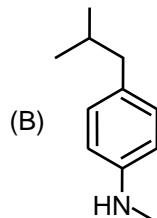
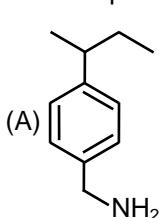
47. The compound **R** is

[JEE(Advanced)-2018, 3/120]



48. The compound **S** is

[JEE(Advanced)-2018, 3/120]



**PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)****OFFLINE JEE-MAIN****ALDEHYDES & KETONES**

1. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid ? [AIEEE-2004, 3/225]
 - (1) Phenol
 - (2) Benzoic acid
 - (3) Butanal
 - (4) Benzaldehyde

 2. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid is [AIEEE-2004, 3/225]
 - (1) gammexene
 - (2) DDT
 - (3) freon
 - (4) hexachloroethane.

 3. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as [AIEEE-2005, 4½/225]
 - (1) Amine
 - (2) Imine
 - (3) Enamine
 - (4) Schiff's base

 4. In the following sequence of reactions, [AIEEE-2007, 3/120]

$$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{P+I}_2} \text{A} \xrightarrow[\text{Ether}]{\text{Mg}} \text{B} \xrightarrow{\text{HCHO}} \text{C} \xrightarrow{\text{H}_2\text{O}} \text{D}$$

The compound 'D' is

 - (1) n-propyl alcohol
 - (2) propanal
 - (3) butanal
 - (4) n-butyl alcohol

 5. In Cannizzaro reaction given below [AIEEE-2009, 4/144]
- $$2\text{Ph CHO} \xrightarrow{\text{:}\overset{\circ}{\text{O}}\text{H}} \text{PhCH}_2\text{OH} + \text{PhCO}_2^{\circ}$$
- the slowest step is :
- (1) the transfer of hydride to the carbonyl group
 - (2) the abstraction of proton from the carboxylic group
 - (3) the deprotonation of PhCH_2OH
 - (4) the attack of $\text{:}\overset{\circ}{\text{O}}\text{H}$ at the carboxyl group
6. Trichloroacetaldehyde was subjected to Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is : [AIEEE 2011, 4/120]
 - (1) 2, 2, 2-Trichloroethanol
 - (2) Trichloromethanol
 - (3) 2, 2, 2-Trichloropropanol
 - (4) Chloroform

 7. Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds : [AIEEE 2011, 4/120]
 - (1) 1-Pentene
 - (2) 2-Pentene
 - (3) 2-Methyl-2-pentene
 - (4) 2-Methyl-1-pentene

 8. Iodoform can be prepared from all except : [AIEEE 2012, 4/120]
 - (1) Ethyl methyl ketone
 - (2) Isopropyl alcohol
 - (3) 3-Methyl-2-butanone
 - (4) Isobutyl alcohol

CARBOXYLIC ACID & DERIVATIVES

9. On vigorous oxidation by permanganate solution $(\text{CH}_3)_2\text{C} = \text{CHCH}_2\text{CHO}$ gives [AIEEE-2002, 3/225]
 - (1) $(\text{CH}_3)_2\text{CO}$ and OHCCH_2CHO
 - (2) $(\text{CH}_3)_2\text{C}-\text{CH}(\text{OH})\text{CH}_2\text{CHO}$
 - (3) $(\text{CH}_3)_2\text{CO}$ and $\text{OHCCH}_2\text{COOH}$
 - (4) $(\text{CH}_3)_2\text{CO}$ and $\text{CH}_2(\text{COOH})_2$

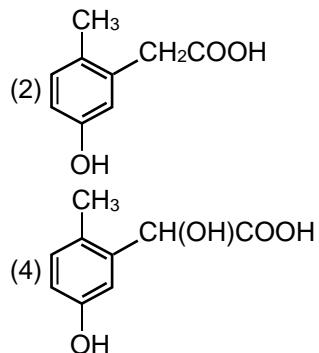
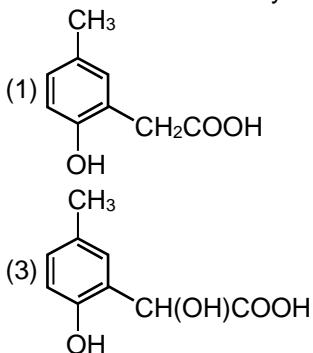
10. End product of the following reaction is : [AIEEE-2002, 3/225]

$$\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[\text{red P}]{\text{Cl}_2} \xrightarrow{\text{alcoholic KOH}} \text{(1) CH}_3\text{CHCOOH} \quad \text{(2) CH}_2\text{CH}_2\text{COOH} \quad \text{(3) CH}_2 = \text{CHCOOH} \quad \text{(4) CH}_2\text{CHCOOH}$$

$\begin{array}{c} | \\ \text{OH} \end{array}$ $\begin{array}{c} | \\ \text{OH} \end{array}$ $\begin{array}{c} | \\ \text{CH}_2 \end{array}$ $\begin{array}{c} | \\ \text{Cl} \end{array}$ $\begin{array}{c} | \\ \text{OH} \end{array}$



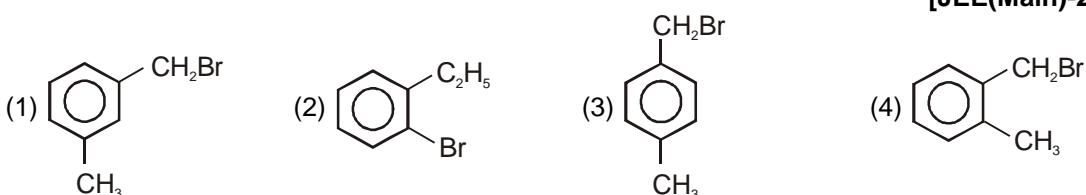
11. p-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is : [AIEEE-2005, 4½/225]



12. An organic compound having molecular mass 60 is found to be contain C = 20%, H = 6.67% and N = 46.67% while rest is oxygen. On heating it gives NH₃ along with a solid residue. The solid residue give violet colour with alkaline copper sulphate solution. The compound is : [AIEEE-2005, 4½/225]
- (1) CH₃CH₂CONH₂ (2) (NH₂)₂CO (3) CH₃CONH₂ (4) CH₃NCO
13. A liquid was mixed with ethanol and a drop of concentrated H₂SO₄ was added. A compound with a fruity smell was formed. The liquid was : [AIEEE-2009, 4/144]
- (1) HCHO (2) CH₃COCH₃ (3) CH₃COOH (4) CH₃OH
14. A compound with molecular mass 180 is acylated with CH₃COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is : [JEE(Main)-2013, 4/120]

- (1) 2 (2) 5 (3) 4 (4) 6

15. Compound (A), C₈H₉Br, gives a white precipitate when warmed with alcoholic AgNO₃. Oxidation of (A) gives an acid (B), C₈H₆O₄. (B) easily forms anhydride on heating. Identify the compound (A). [JEE(Main)-2013, 4/120]



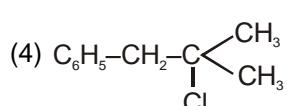
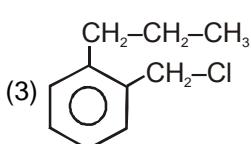
JEE(MAIN) ONLINE PROBLEMS

ALDEHYDES & KETONES

1. Which one of the following reactions will not result in the formation of carbonation bond ? [JEE(Main) 2014 Online (09-04-14), 4/120]
- (1) Reimer-Tieman reaction (2) Friedel Craft's acylation
 (3) Wurtz reaction (4) Cannizzaro reaction
2. Tischenko reaction is a modification of [JEE(Main) 2014 Online (11-04-14), 4/120]
- (1) Aldol condensation (2) Claisen condensation
 (3) Cannizzaro reaction (4) Pinacol-pinacolone reaction
3. A compound A with molecular formula C₁₀H₁₃Cl give a white precipitate on adding silver nitrate solution. A on reacting with alcoholic KOH gives compound B as the main product. B on ozonolysis gives C and D. C gives Cannizaro reaction but not aldol condensation. D gives aldol condensation but not Cannizaro reaction. A is : [JEE(Main) 2015 Online (10-04-15), 4/120]

- (1) C₆H₅-CH₂-CH₂-CH₂-CH₂-Cl

- (2) C₆H₅-CH₂-CH₂-CH₂-CH(Cl)-CH₃





4. In the reaction sequence



- (1) $\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---OH}$
 (2) $\text{CH}_3\text{---CH=CH---CHO}$
 (3) $\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---CH}_3$
 (4) $\text{CH}_3\text{---C}(=\text{O})\text{---CH}_2$

[JEE(Main) 2015 Online (11-04-15), 4/120]

5. The correct statement about the synthesis of erythritol ($\text{C}(\text{CH}_2\text{OH})_4$) used in the preparation of PETN is:

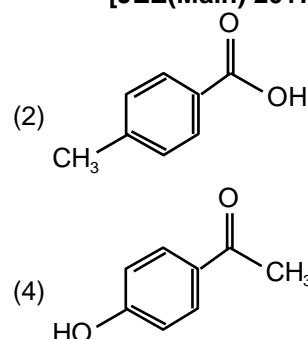
[JEE(Main) 2016 Online (10-04-16), 4/120]

- (1) The synthesis requires two aldol condensations and two Cannizzaro reactions.
 (2) Alpha hydrogens of ethanol and methanol are involved in this reaction.
 (3) The synthesis requires four aldol condensations between methanol and ethanol.
 (4) The synthesis requires three aldol condensations and one Cannizzaro reaction.

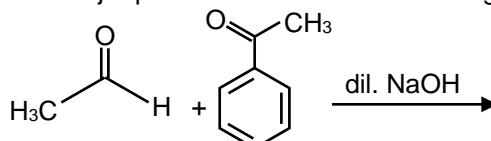
6. A compound of molecular formula $\text{C}_8\text{H}_8\text{O}_2$ reacts with acetophenone to form a single cross-aldol product in the presence of base. The same compound on reaction with conc. NaOH forms benzyl alcohol as one of the products. The structure of the compound is :

[JEE(Main) 2017 Online (09-04-17), 4/120]

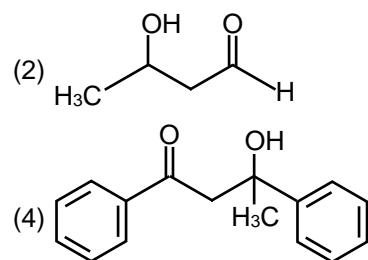
- (1)
- (2)
- (3)



7. The major product formed in the following reaction is : [JEE(Main) 2019 Online (09-01-19), 4/120]

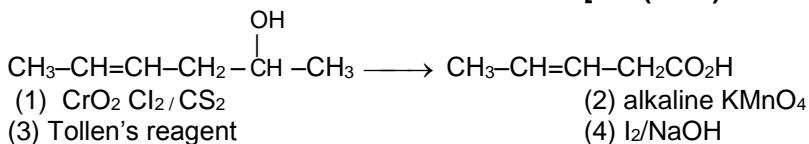


- (1)
- (2)
- (3)



8. Which is the most suitable reagent for the following transformation?

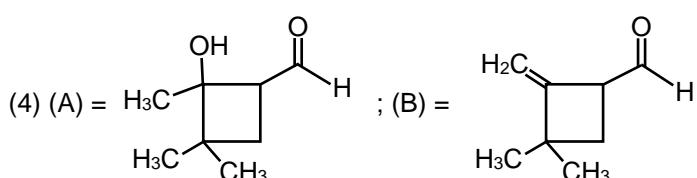
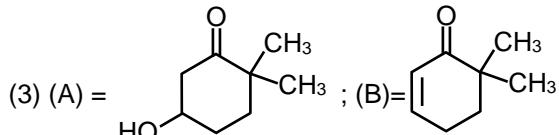
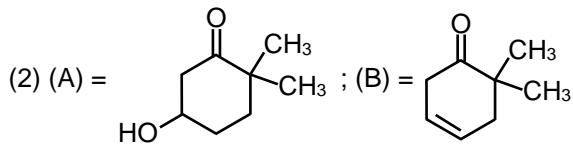
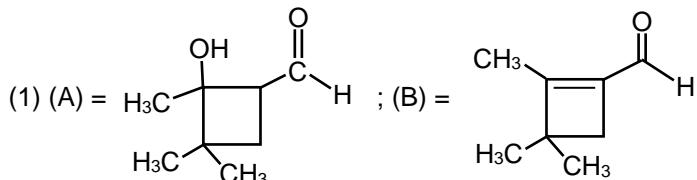
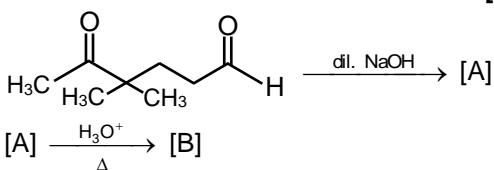
[JEE(Main) 2019 Online (10-01-19), 4/120]





9. In the following reactions, products A and B are :

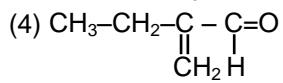
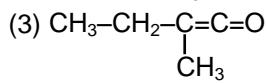
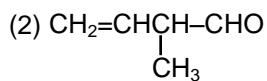
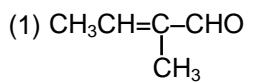
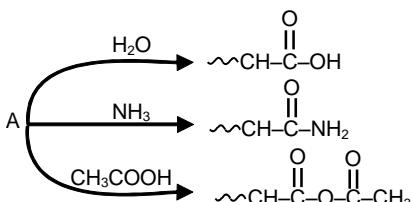
[JEE(Main) 2019 Online (12-01-19), 4/120]



CARBOXYLIC ACID & DERIVATIVES

10. An organic compound A, $\text{C}_5\text{H}_8\text{O}$; reacts with H_2O , NH_3 and CH_3COOH as described below, A is :

[JEE(Main) 2014 Online (11-04-14), 4/120]



11. Among the following organic acids, the acid present in rancid butter is :

[JEE(Main) 2014 Online (19-04-14), 4/120]

- (1) Pyruvic acid (2) Lactic acid (3) Butyric acid (4) Acetic acid

12. In the presence of small amount of phosphorous, aliphatic carboxylic acids react with chlorine or bromine to yield a compound in which α -hydrogen has been replaced by halogen. This reaction is known as :

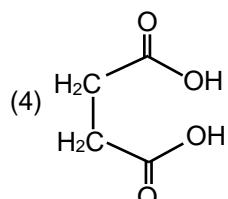
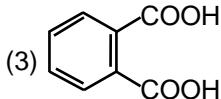
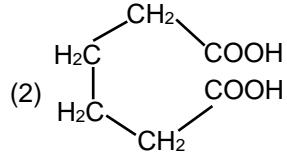
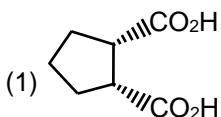
[JEE(Main) 2015 Online (10-04-15), 4/120]

- (1) Wolff-Kishner reaction
 (3) Rosenmund reaction
 (2) Etard reaction
 (4) Hell-Volhard-Zelinsky reaction



13. Which dicarboxylic acid in presence of a dehydrating agent is least reactive to give an anhydride?

[JEE(Main) 2019 Online (10-01-19), 4/120]



14. In the following reaction



Aldehyde Alcohol

HCHO ^tBuOH

CH₃CHO MeOH

The best combination is :

(1) HCHO and ^tBuOH

(3) HCHO and MeOH

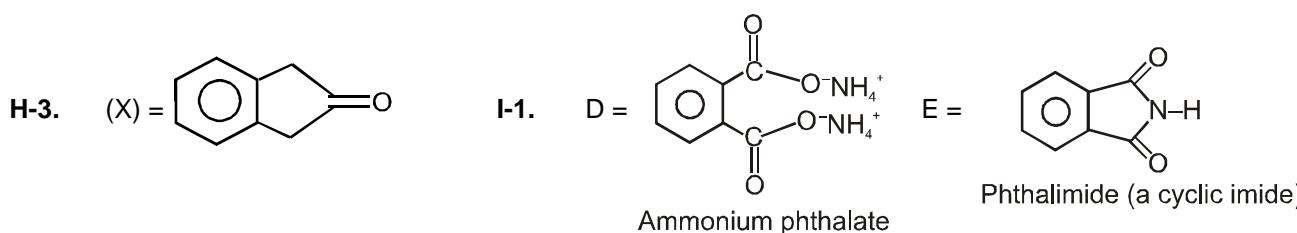
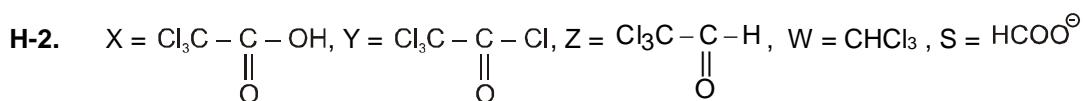
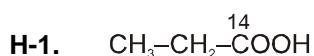
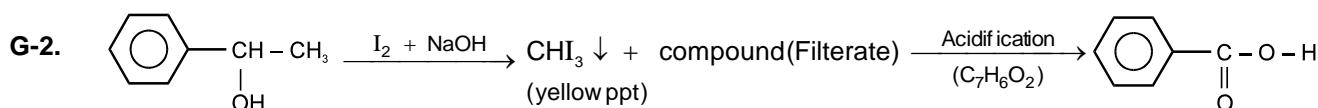
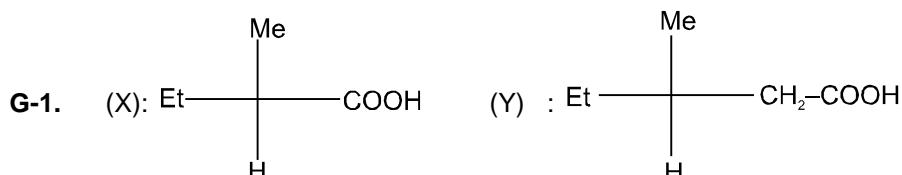
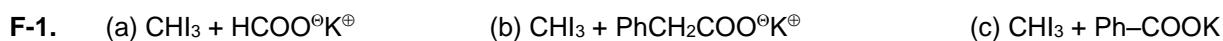
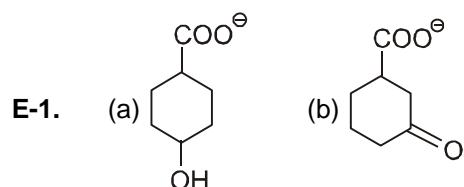
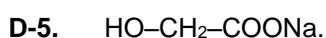
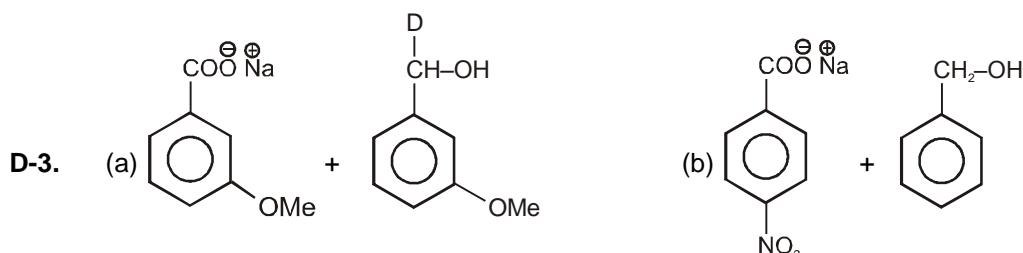
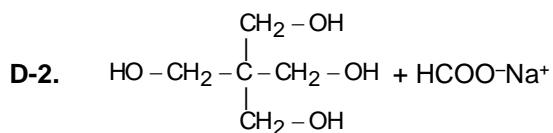
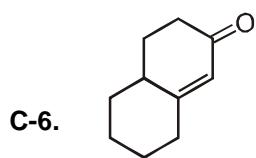
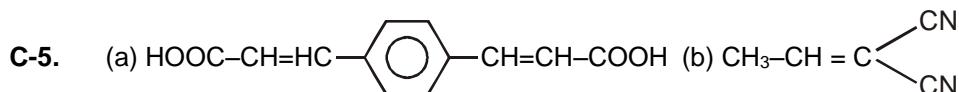
[JEE(Main) 2019 Online (12-01-19), 4/120]

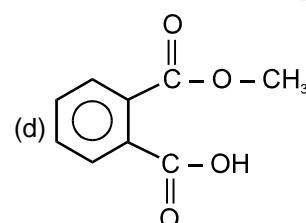
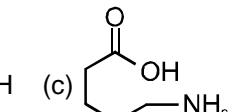
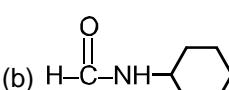
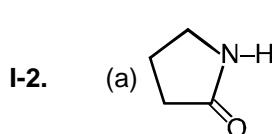
(2) CH₃CHO and ^tBuOH

(4) CH₃CHO and MeOH

**Answers****EXERCISE - 1****PART - I**

- A-1.** (a) (b) + NH3 + Mg(OH)Br (c) (d)
- B-1.** (a) (b)
- (c) (d)
- B-2.** (a) + CH₃-C(=O)-CH₃ $\xrightarrow{\text{dry HCl}}$
- (K)
A cyclic ketal
- (b) The – OH groups in the trans isomer are too far apart to form cyclic structure.
- B-3.** IV > III > I > II
- B-4.** (a) $\xrightarrow[\text{or KCN/dil. H2SO4}]{\text{HCN/ dil. NaOH}}$ CN
- (b)
- $\xrightarrow[(2) \text{ H}_2\text{O}/\text{H}^{\oplus}]{(1) \text{ HCN/ dil. NaOH}}$
- B-5.** (a) + CH₃-CHO (b) H₂N – CH₂ – CH₂ – CH₂ – CO – CH₃
- C-1.** (a) (b)
- C-2.** (a) CH₃CH₂CH₂CHO (b) CH₃COCH₃
- C-3.** (a) (b)
- C-4.**





PART - II

- | | | | | |
|----------|----------|----------|----------|----------|
| A-1. (A) | A-2. (A) | A-3. (C) | A-4. (A) | B-1. (B) |
| B-2. (D) | B-3. (A) | B-4. (B) | C-1. (A) | C-2. (A) |
| D-1. (A) | D-2. (A) | D-3. (C) | D-4. (B) | E-1. (A) |
| E-2. (B) | F-1. (D) | F-2. (D) | G-1. (A) | G-2. (D) |
| G-3. (A) | G-4. (C) | H-1. (C) | H-2. (B) | H-3. (A) |
| H-4. (C) | H-5. (C) | H-6. (A) | H-7. (B) | H-8. (A) |
| I-1. (B) | I-2. (D) | | | |

PART - III

1. (A - p,q) ; (B - p,r) ; (C - q,s) ; (D - r,s) 2. (A - s) ; (B - q) ; (C - p) ; (D - p, r)

EXERCISE - 2

PART - I

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (B) | 2. (B) | 3. (B) | 4. (D) | 5. (B) |
| 6. (B) | 7. (C) | 8. (A) | 9. (D) | 10. (C) |
| 11. (A) | 12. (D) | 13. (B) | 14. (A) | 15. (B) |
| 16. (C) | 17. (B) | 18. (B) | 19. (C) | 20. (C) |
| 21. (C) | 22. (C) | 23. (C) | | |

PART - II

- | | | | | |
|------------------|------|------|------|------|
| 1. 5(1,2,3,5,6) | 2. 2 | 3. 3 | 4. 9 | 5. 8 |
| 6. 5 (2,3,4,5,6) | | | | |

PART - III

- | | | | | |
|----------|-----------|----------|---------|----------|
| 1. (BCD) | 2. (ABCD) | 3. (ABD) | 4. (AC) | 5. (ABC) |
| 6. (ABD) | | | | |

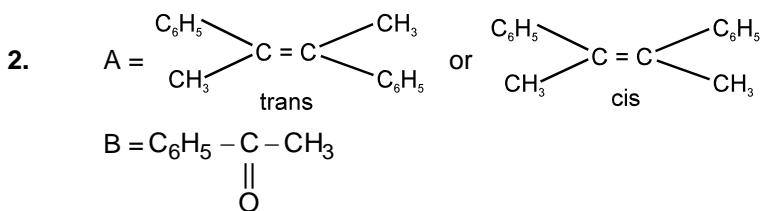
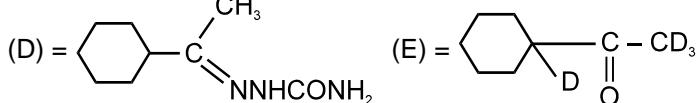
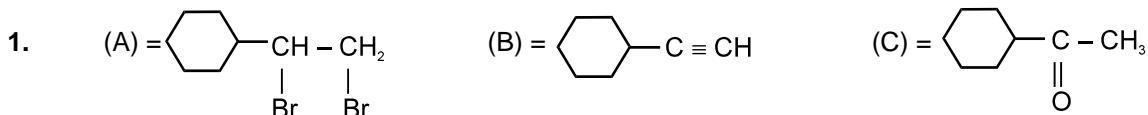
PART - IV

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (A) | 2. (B) | 3. (A) | 4. (D) | 5. (D) |
| 6. (D) | 7. (B) | 8. (C) | 9. (A) | 10. (C) |
| 11. (B) | 12. (D) | 13. (B) | 14. (D) | |



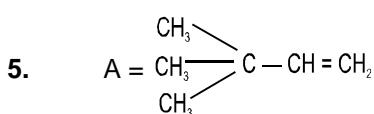
EXERCISE - 3

PART - I

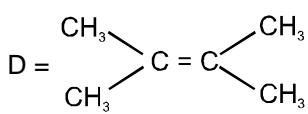
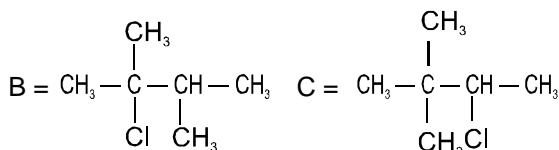


Trans isomer give racemic mixture.

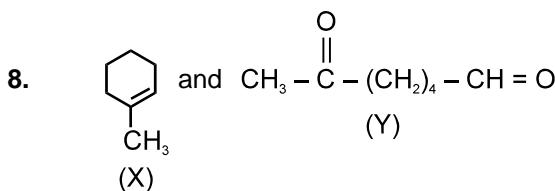
3. (A)



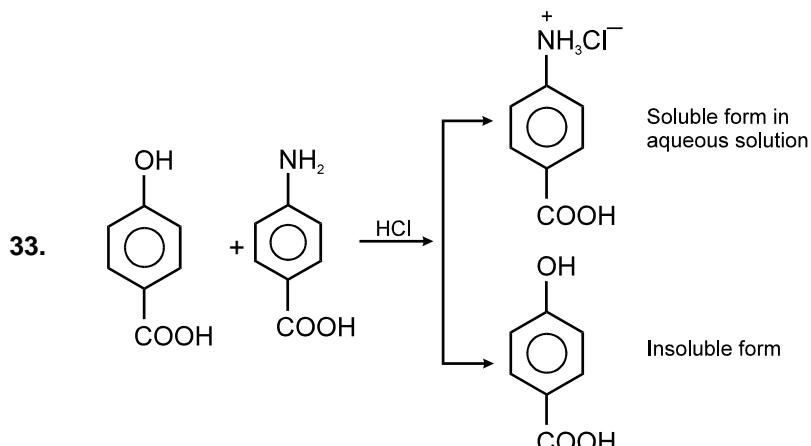
4. (B)



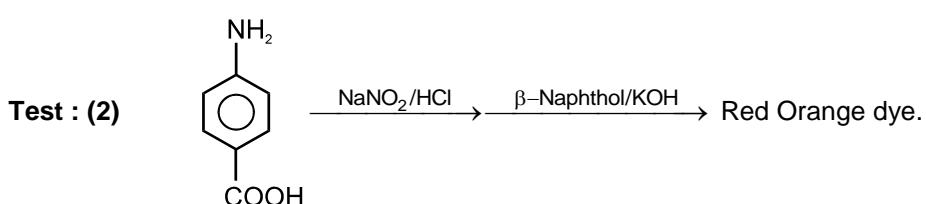
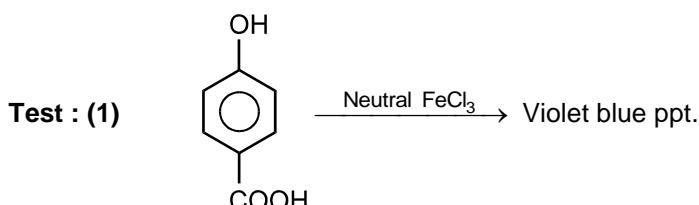
6. (D)



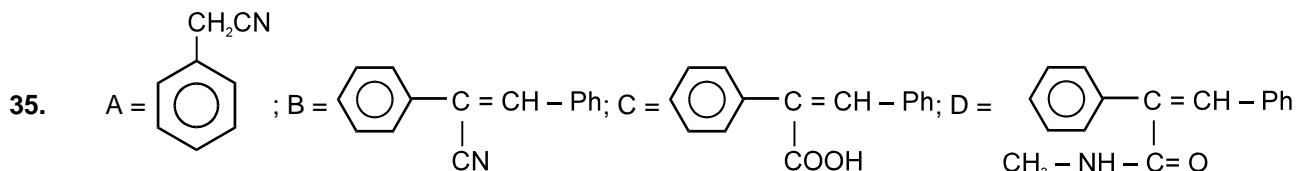
- | | | | | |
|--|---------|--|------------|----------|
| 9. (C) | 10. (A) | 11. (B) | 12. (A) | 13. (D) |
| 14. (B) | 15. (A) | 16. (B) | | |
| 17. (A) - p, q, t ; (B) - p, s, t ; (C) - r, s ; (D) - p | | | 18. 1 | 19. (B*) |
| 20. (A) | 21. (D) | 22. (A-r, s, t) ; (B-p, s) ; (C-r, s) ; (D-q, r) | | 23. (C) |
| 24. (C) | 25. (A) | 26. (C) | 27. (ABCD) | 28. (A) |
| 29. (A) | 30. (A) | 31. (ABC) | 32. (CD) | |



These can be separated by aq. HCl.



34. (A)



36. (C)

37. (C)

38. (D)

39. (B)

40. (A)

41. 2

42. (D)

43. (A)

44. (D)

45. (C)

46. (A)

47. (A)

48. (B)

PART - II JEE(MAIN) OFFLINE PROBLEMS

1. (4)

2. (2)

3. (3)

4. (1)

5. (1)

6. (1)

7. (3)

8. (4)

9. (4)

10. (3)

11. (3)

12. (2)

13. (3)

14. (2)

15. (4)

JEE(MAIN) ONLINE PROBLEMS

1. (4)

2. (3)

3. (4)

4. (2)

5. (4)

6. (1)

7. (3)

8. (4)

9. (3)

10. (3)

11. (3)

12. (4)

13. (2)

14. (3)



Additional Problems for Self Practice (APSP)

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time : 1 Hr.

Max. Marks : 120

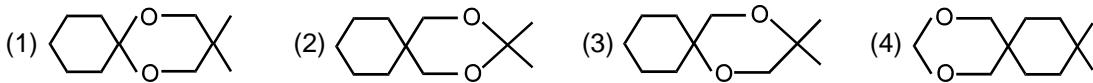
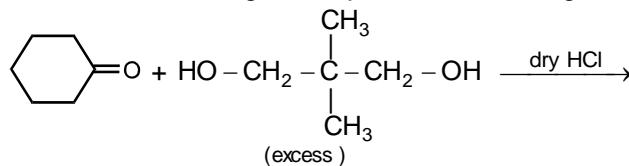
Important Instructions

- The test is of **1 hour** duration.
- The Test Booklet consists of **30** questions. The maximum marks are **120**.
- Each question is allotted **4 (four)** marks for correct response.
- Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question. **1/4 (one fourth)** marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

- Among the given compounds, the most susceptible to nucleophilic attack at the carbonyl carbon is :

(1) MeCOCl (2) MeCHO (3) MeCOOMe (4) MeCOOCOMe

- Which of the following will be product of following reaction ?

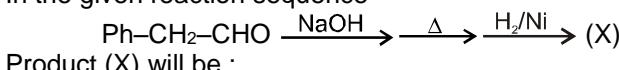


- Under Wolf Kishner reduction conditions, the conversion which may be brought about is ?

(1) Benzaldehyde into Benzyl alcohol (2) Cyclohexanol into Cyclohexane
 (3) Cyclohexanone into Cyclohexanol (4) Benzophenone into Diphenylmethane
- An organic compound C3H6O does not give a precipitate with 2,4-dinitrophenyl hydrazine reagent and also does not react with metallic sodium it could be :

(1) CH3-CH2-CHO (2) CH3-COCH3
 (3) CH2=CH-CH2-OH (4) CH2=CH-OCH3

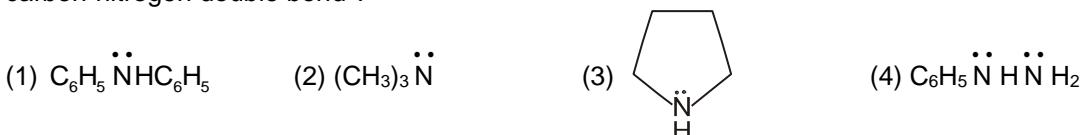
- In the given reaction sequence



Product (X) will be :

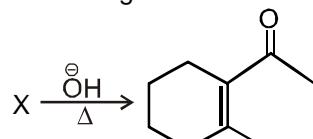


- Among the following compounds which one will react with acetone to give a product that contains carbon-nitrogen double bond ?

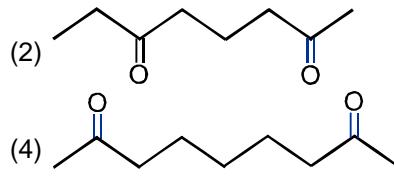
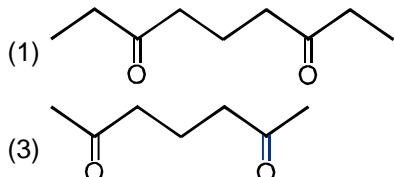




7. Consider following intramolecular aldol condensation reaction.



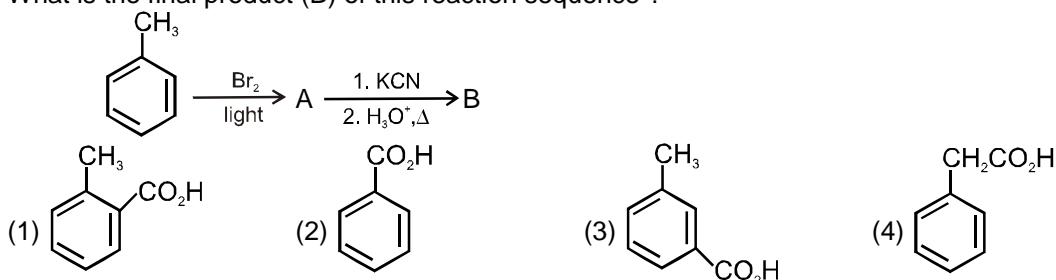
X can be :



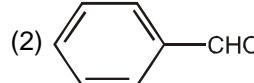
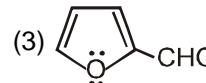
8. An organic compound X (C_3H_8O) on treatment with acidified $K_2Cr_2O_7$ gives compound Y which reacts with I_2 and sodium carbonate to form Triiodomethane. The compound X can be :

- (1) $CH_3-CH_2-CH_2-OH$ (2) $CH_3-CH_2-O-CH_3$
 (3) $CH_3-CH_2-CH=O$ (4) $CH_3CH(OH)CH_3$.

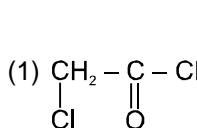
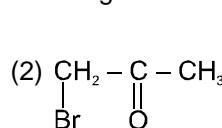
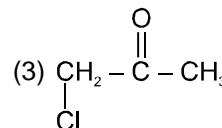
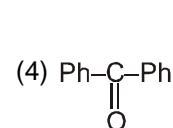
9. What is the final product (B) of this reaction sequence ?



10. Cannizzaro reaction does not take place with

- (1) $(CH_3)_3CCHO$ (2)  (3)  (4) CH_3CHO .

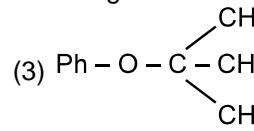
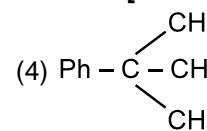
11. Which of the following does not give haloform reaction :

- (1)  (2)  (3)  (4) 

12. Synthesis of an ester involves the reaction of alcohols with

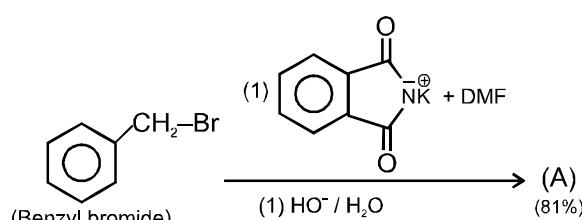
- (1) a ketone (2) an amide (3) CH_3MgBr (4) $RCOCl$

13. Phenyl magnesium bromide reacting with t-Butyl alcohol gives

- (1) $Ph-OH$ (2) $Ph-H$ (3)  (4) 

[JEE-2005, 3/60]

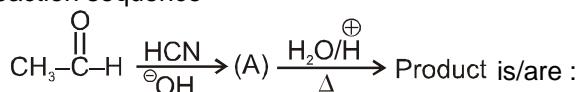
14.



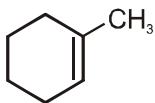
- Product (A) of the above reaction is :
 (1) $Ph-NH_2$ (2) $Ph-CH_2-NH_2$ (3) $Ph-CH_2-NH-CO_2H$ (4) $Ph-CH_2-NH-CHO$



15. In the reaction sequence



- (1) Diasteromers (2) Racemic mixture of hydroxy acid
 (3) Product is racemic mixture of cyanohydrin (4) Product is optically inactive



16. On reductive ozonolysis yields

- (1) 6-oxoheptanal (2) 6-oxoheptanoic acid
 (3) 6-hydroxyheptanal (4) 3-hydroxypentanal

17. The cyanohydrin of a carbonyl compound on hydrolysis gives lactic acid. The carbonyl compound is

- (1) HCHO (2) CH₃CHO (3) CH₃COCH₃ (4) CH₃COCH₂CH₃

18. Which of the following will not undergo aldol condensation ?

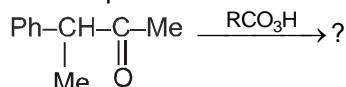
- (1) CH₃CHO (2) CH₃CH₂CHO (3) CD₃CHO (4) PhCHO

19. PhCHO + (CH₃CO)₂O $\xrightarrow[(2) \text{ hydrolysis, } \Delta]{(1) \text{ CH}_3\text{COONa}} \text{A} \xrightarrow{\text{HBr}} \text{B B}$

The product B is :

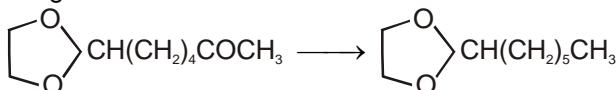
- (1) PhCH = CHCH₂Br (2) PhCH – CH₂ – COOH
 (3) PhCH₂ CH(Br) COOH (4) PhCH = CH – COBr

20. What will be the product of the following reaction



- (1) Ph–CH–O–C–Me (2) Ph—CH
 (3) PhCH(Me)OCOOMe (4) None of these

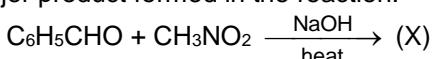
21. In the following conversion



Which of the following regents is suitable ?

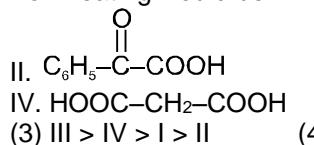
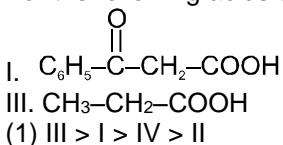
- (1) NH₂NH₂, KOH, DMSO (2) NaBH₄
 (3) Zn-Hg, concentrated H₂SO₄ (4) LiAlH₄

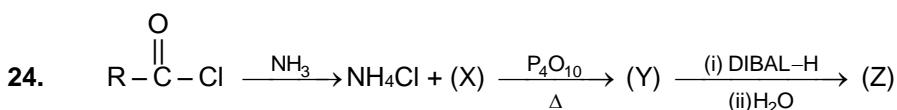
22. The major product formed in the reaction.



- (1) C₆H₅ – CH – CH – NO₂ (2) C₆H₅CHCH₂NO₂
 (3) C₆H₅CH = CH – NO₂ (4) C₆H₅CH – CH₂NO₂
 |
 CH₂NO₂

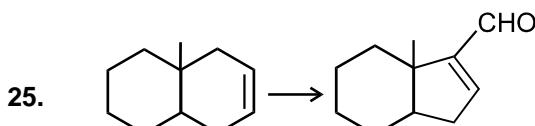
23. For the following acids the rate of decarboxylation on heating would be :



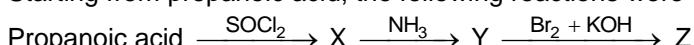


The compound (Z) is :

- (1) R-COOH (2) R-CH₂-OH (3) R-C≡N (4) RCHO



26. Starting from propanoic acid, the following reactions were carried out



What is the compound Z

- (1) CH₃-CH₂-Br (2) CH₃-CH₂-NH₂
 (3) CH₃-CH₂-C(=O)Br (4) CH₃-CH₂-CH₂-NH₂

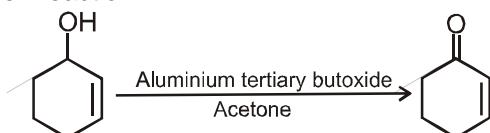
27. Which of the following acids remains unaffected on heating

- (1) Malonic acid (2) Malic acid (3) Fumaric acid (4) Succinic acid

28. m-chlorobenzaldehyde on reaction with conc. KOH at room temperature gives : [JEE 91]

- (1) Potassium m-chlorobenzoate and m-hydroxybenzaldehyde
 (2) m-hydroxybenzaldehyde and m-chlorobenzyl alcohol
 (3) m-chlorobenzyl and m-hydroxybenzyl alcohol
 (4) Potassium m-chlorobenzoate and m-chlorobenzyl alcohol.

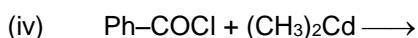
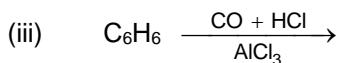
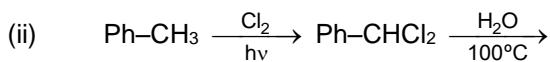
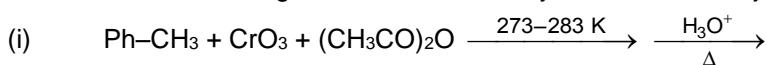
29. The given reaction



is known as :

- (1) Kolbe reaction (2) Tischenko reaction
 (3) MPV reaction (4) Oppeneur oxidation

30. In which of the following reactions Benzaldehyde is the final major product ?



- (1) i & ii only (2) ii & iii only
 (3) iii & iv only (4) i, ii & iii only

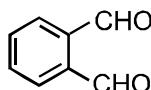
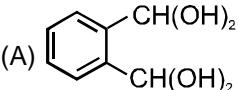
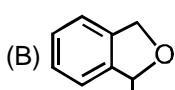
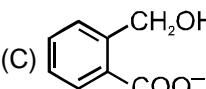
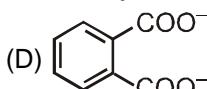
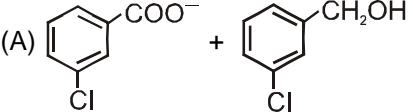
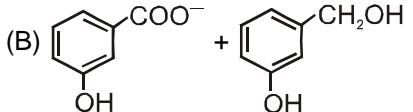
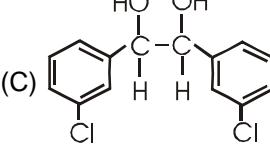
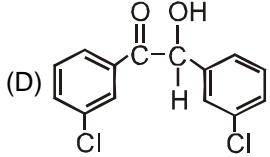


Practice Test-1 (IIT-JEE (Main Pattern))
OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

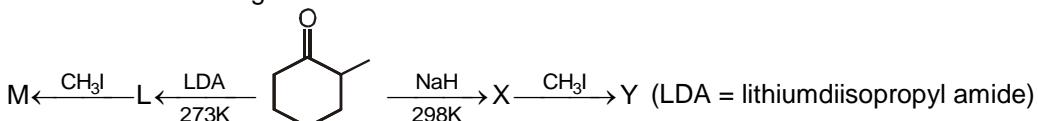
PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

ALDEHYDES & KETONES

1. The treatment of  with concentrated NaOH gives [NSEC-2003]
- (A)  (B) 
- (C)  (D) 
2. Compound  (B) 
- (C)  (D) 

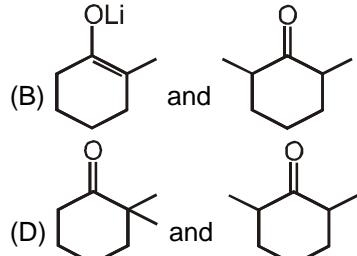
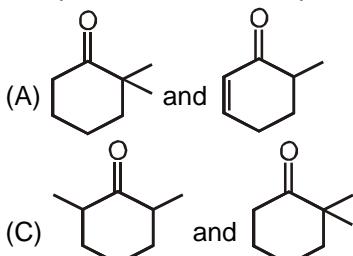


6. Consider the following reactions :



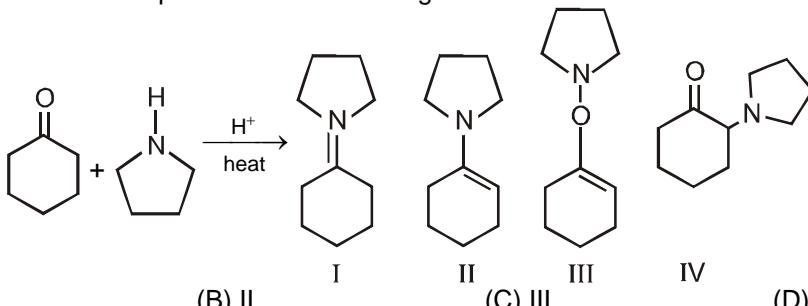
The product M and Y respectively are :

[NSEC-2007]



7. The most favourable product of the following reaction is :

[NSEC-2009]



(A) I

(B) II

(C) III

(D) IV

8. The compound that would undergo hydration very easily is :

[NSEC-2010]

(A) $\text{CH}_3\text{COCH}_2\text{Cl}$ (B) $\text{CH}_3\text{CH}_2\text{CHO}$ (C) $\text{Cl}_3\text{C}-\text{CHO}$ (D) $\text{Cl}_3\text{CCH}_2\text{COCH}_3$

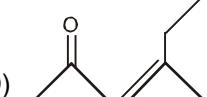
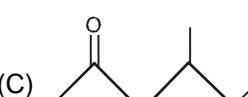
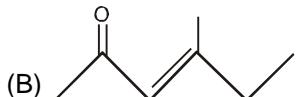
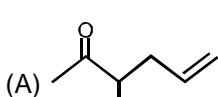
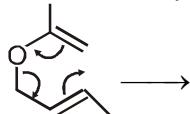
9. Cyclohexanone oxime is converted into ϵ -caprolactam by treatment with

[NSEC-2010]

(A) dil HCl (B) NaOC_2H_5 (C) ammonia (D) conc. H_2SO_4

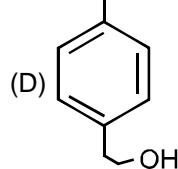
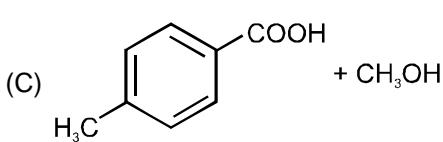
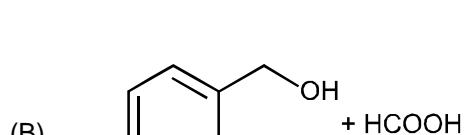
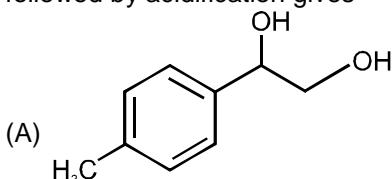
10. Curved arrows are used in Organic Chemistry to show the movements of electrons in the mechanism of a reaction. The correct product of the following reaction is

[NSEC-2011]



11. The reaction of 50% aq KOH on an equimolar mixture of 4-methylbenzaldehyde and formaldehyde followed by acidification gives -

[NSEC-2011]





12. Which of the following reaction mechanism does not involve carbocation as an intermediate?

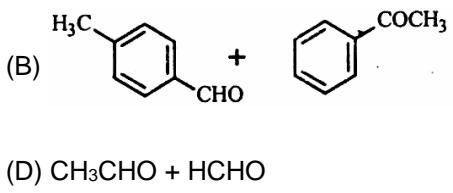
[NSEC-2012]

- (A) Baeyer-Villiger Oxidation
(B) Beckman rearrangement
(C) Fries Rearrangement
(D) Diels-Alder Reaction

13. The pair of equimolar compounds that would give a single condensation product when treated with an alkali is

[NSEC-2014]

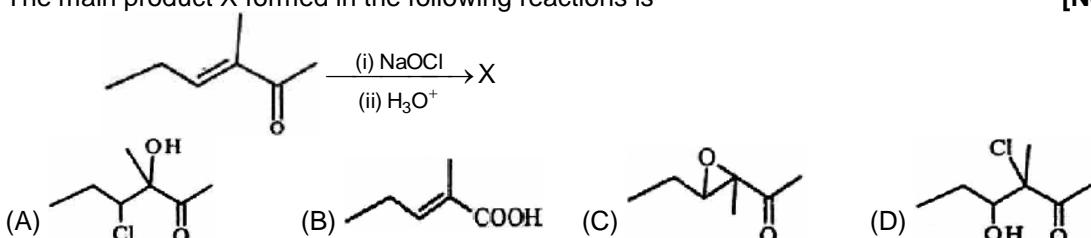
- (A) $\text{CH}_3\text{-CHO} + \text{CH}_3\text{CH}_2\text{CHO}$
(C) + $\text{CH}_3\text{CH}_2\text{CHO}$



- (D) $\text{CH}_3\text{CHO} + \text{HCHO}$

14. The main product X formed in the following reactions is

[NSEC-2014]



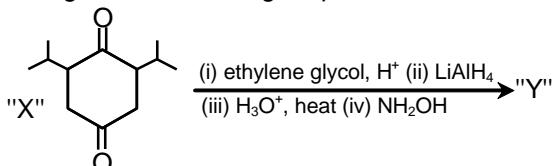
15. An organic compound ("X") is a disubstituted benzene containing 77.8% carbon and 7.4% hydrogen. Heating an alkaline solution of "X" with chloroform gives a steam volatile compound "Y". Heating "Y" with acetic anhydride and sodium acetate gives a sweet smelling crystalline solid "Z". "Z" is

[NSEC-2015]

- (A)
- (B)
- (C)
- (D)

16. Compound "X" undergoes the following sequence of reactions to form "Y".

[NSEC-2015]

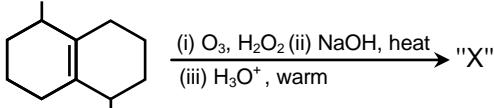


Compound "Y" is-

- (A)
- (B)
- (C)
- (D)

17. The product ("X") of the following sequence of reactions is

[NSEC-2015]

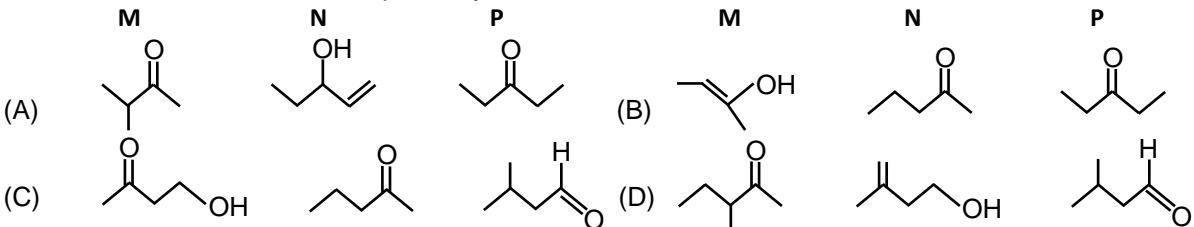


- (A)
- (B)
- (C)
- (D)

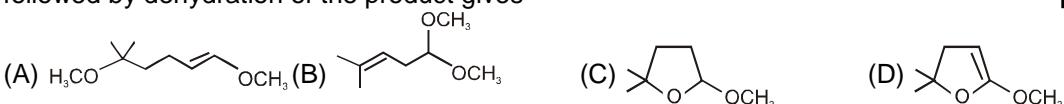


18. Three isomeric compounds M, N, and P ($C_5H_{10}O$) give the following tests: [NSEC-2015]
- M and P react with sodium bisulfite to form an adduct J
 - N consumes 1 mol of bromine and also gives turbidity with conc. HCl/anhydrous $ZnCl_2$ after prolong heating'
 - M reacts with excess of iodine in alkaline solution to give yellow crystalline compound with a characteristic smell.
 - p-Rosaniline treated with sulphur dioxide develops pink colour on shaking with P

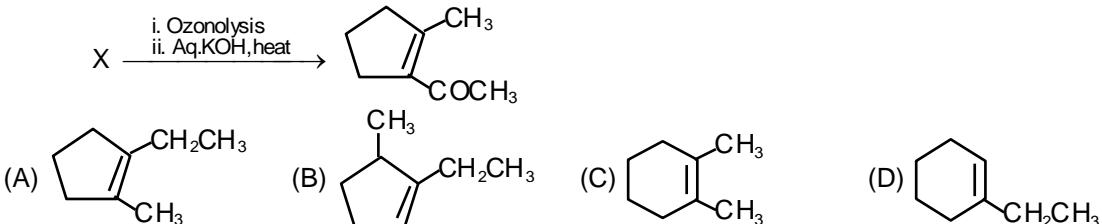
The structure of M, N, and P, respectively are



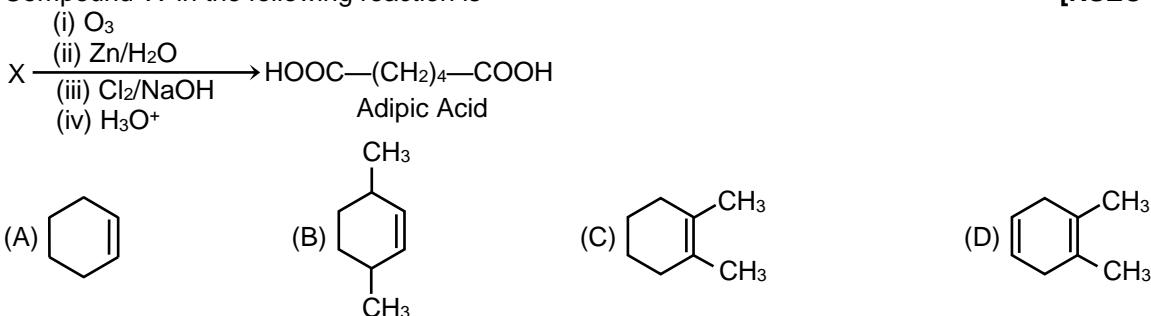
19. 4-Hydroxy-4-methylpentanal on heating with excess of methanol in the presence of an acid catalyst followed by dehydration of the product gives [NSEC-2015]



20. Compound 'X' in the following reaction is [NSEC-2016]

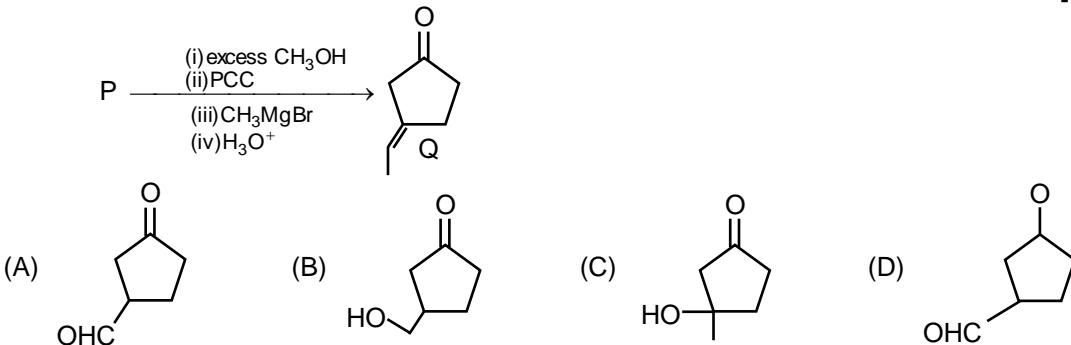


21. Compound 'X' in the following reaction is [NSEC-2018]



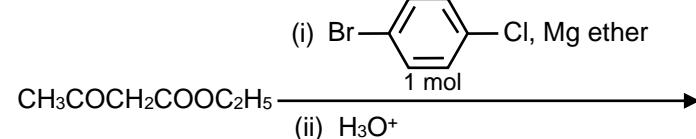
22. Compound 'P' that undergoes the sequence of reactions given below to give the product Q is

[NSEC-2018]





23. The major product of the following reaction is



- (A) (B)
- (C) (D)

CARBOXYLIC ACID & DERIVATIVES

21. The reaction $\text{RCH}_2\text{CH}_2\text{COOH} \xrightarrow[\text{Br}_2]{\text{Red P}} \text{RCH}_2-\underset{\text{Br}}{\text{CHCOOH}}$ is called as :

[NSEC-2001]

- (A) Cannizzaro reaction (B) Hell Volhared Zelinsky reaction
 (C) Reimer Teimann reaction (D) Sandmeyer reaction

22. Formic acid and acetic acid differ in

[NSEC-2002]

- (A) turning blue litmus red (B) forming an ester with methanol
 (C) replacement of hydrogen atom by sodium (D) reduction of Fehling's solution.

23. The electrolysis of the disodium salt of pentanedioic acid gives

[NSEC-2002]

- (A) pentane (B) butane (C) Cyclopropane (D) ethane.

24. The compound that gives a lactone on heating is

[NSEC-2003]

- (A) pentanedioic acid (B) 4-hydroxypentanoic acid
 (C) 4-aminopentanoic acid (D) 2-hydroxypentanoic acid.

25. The compound that readily undergoes decarboxylation is

[NSEC-2003]

- (A) $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$ (B) $\text{C}_6\text{H}_5-\text{COOH}$
 (C) $\text{HOOC}-\text{CH}_2-\text{COOH}$ (D) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$.

26. The most unstable compound is

[NSEC-2003]

- (A) 2-oxobutanoic acid (B) 3-oxobutanoic acid
 (C) 3-amino-2-butanone (D) 2-hydroxybutanal.

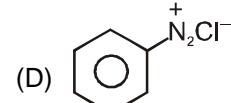
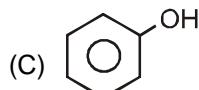
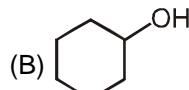
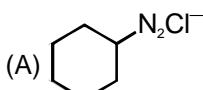
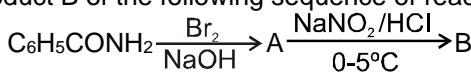
27. The product obtained when propanamide is distilled with phosphorus pentoxide is

[NSEC-2004]

- (A) $(\text{CH}_3\text{CH}_2\text{CO})_2\text{O}$ (B) $\text{CH}_3\text{CH}_2\text{CN}$
 (C) $\text{CH}_3\text{CH}_2\text{COOCH}_2\text{CH}_3$ (D) $(\text{CH}_3\text{CH}_2\text{COO})_3\text{PO}$.

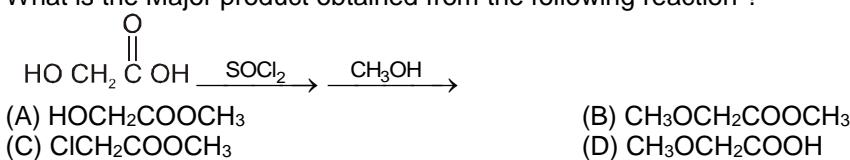
28. The product B of the following sequence of reactions is

[NSEC-2004]



29. What is the Major product obtained from the following reaction ?

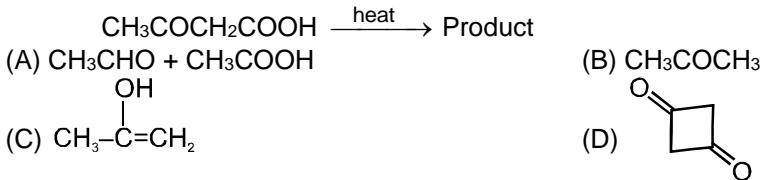
[NSEC-2007]



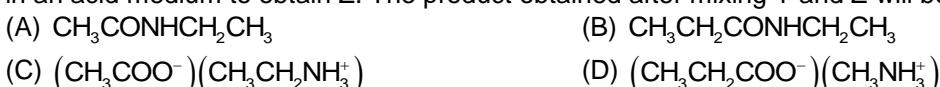


[NSEC-2007]

30. What is the major product obtained from the following reaction ?



31. A nitrile X is treated with LiAlH_4 to obtain compound Y($\text{C}_2\text{H}_7\text{N}$). In a separate reaction X is hydrolyzed in an acid medium to obtain Z. The product obtained after mixing Y and Z will be : [NSEC-2014]



32. $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{CH}_3)_2 + \text{CH}_3\text{COCl} \xrightarrow{\text{base}} \text{CH}_3\text{CH}_2\text{CH}(\text{OCOCH}_3)\text{CH}(\text{CH}_3)_2 + \text{HCl}$
In the above reaction, if the reactant alcohol is pure R-isomers, the product would.

[NSEC-2014]

- (A) have configuration inverted at the chiral atom
(B) be a racemic mixture
(C) have the same configuration at the chiral atom
(D) be optically inactive

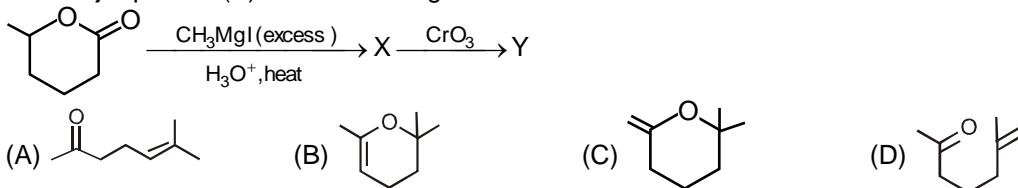
33. Compound P on treatment with CH_2N_2 (diazomethane) produces compound Q. Compound Q on reaction with HI produces two alkyl iodides R and S. Alkyl iodide S with higher number of carbon atoms on reaction with KCN followed by hydrolysis gives 3-methylbutanoic acid. The compound P is :

[NSEC-2015]

- (A) 2-butanol
- (B) 1-butanol
- (C) 2-methyl-2-propanol
- (D) 2-methyl-1-propanol

34. The major product(Y) of the following reaction is –

[NSEC-2015]



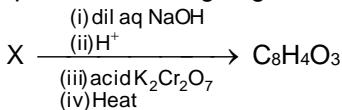
35. 4-amino-3-methylbutanoic acid is treated with thionyl chloride followed by ammonia to obtain compound "X". "X" on reaction with bromine in an alkaline medium gave compound "Y". For estimation, "Y" was titrated with perchloric acid. The volume of 0.1 M perchloric acid needed to react with 0.22 g of "Y" is

[NSEC-2015]

- (A) 50 mL (B) 80 mL (C) 120 mL (D) 200 mL

39. The compound 'X' undergoing the following reaction is

[NSEC-2018]



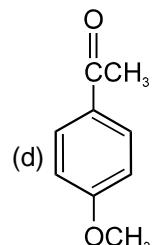
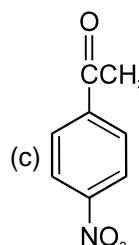
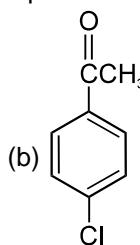
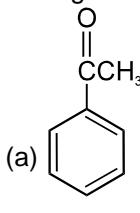


PART - III : HIGH LEVEL PROBLEMS (HLP)

SUBJECTIVE QUESTIONS

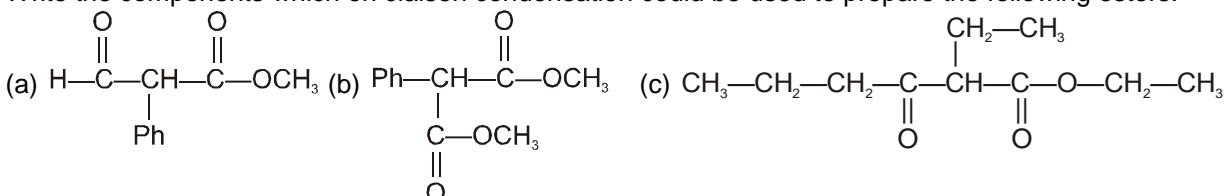
1. When semicarbazide reacts with a ketone (or aldehyde) to form semicarbazone. Only one nitrogen atom of semicarbazide acts as a nucleophile and attack the carbonyl carbon of the ketone. The product of the reaction consequently is $R_2C=N-NH-CONH_2$ rather than $R_2C=NCONH-NH_2$. What factor account for the fact that two nitrogen atoms of semicarbazide are relatively non nucleophilic ?

2. Arrange the following compounds in decreasing orders of K_{eq} for hydrate formation.

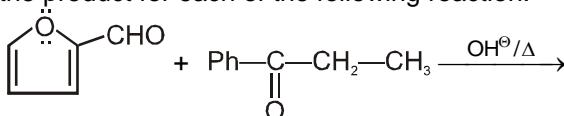


3. When acetone is treated with excess of benzaldehyde in the presence of base, the crossed condensation add two equivalents of benzaldehyde and expels two equivalent of water and forms [X]. Identify the structure of [X] when [X] reacts with NH_2OH how many stereoisomers are formed.

4. Write the components which on claisen condensation could be used to prepare the following esters.

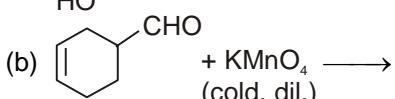
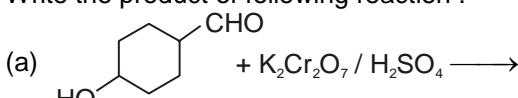


5. Predict the product for each of the following reaction.



- 6.
- +
- $\xrightarrow{(i) \text{ conc. NaOH, } \Delta}$ (ii) H_3O^+
- Product is :

7. Write the product of following reaction :



8. An organic compound A, $C_4H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$ gives compound B. The compound B on treatment with PCl_5 , followed by reaction with $H_2/Pd(BaSO_4)$ gives compound C, which on reaction with hydrazine gives a cyclised compound D ($C_{10}H_{10}N_2$). Identify A, B, C and D. Explain the formation of D from C.

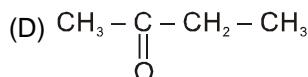
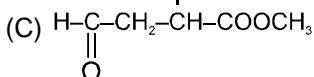
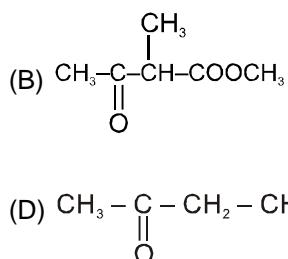
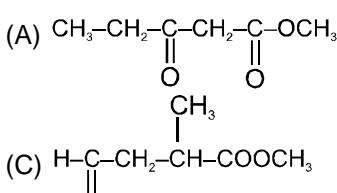
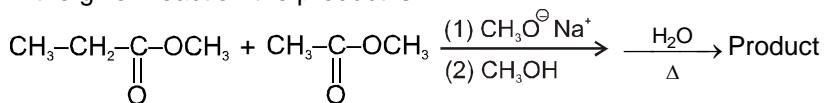
- 9.
- $\xrightarrow[\Delta]{dil. H_2SO_4} A + B, \text{ find A and B.}$

10. $C_6H_{12}O_2 (X) \xrightarrow{H_3O^+} C_2H_5CO_2H + C_3H_7OH, X \text{ is :}$

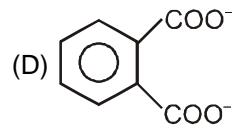
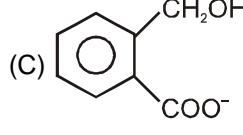
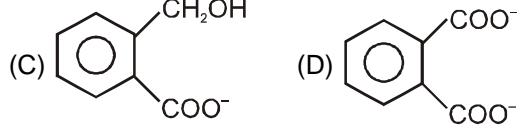
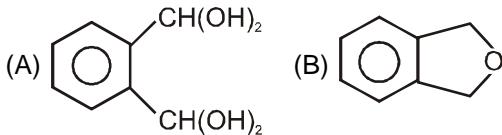
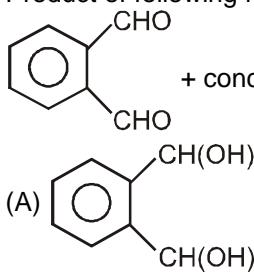


ONLY ONE OPTION CORRECT TYPE

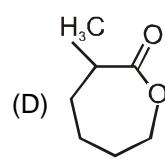
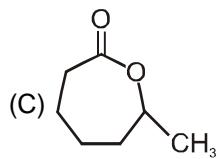
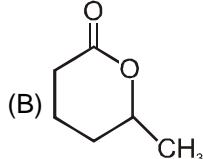
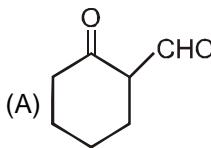
11. In the given reaction the product is :



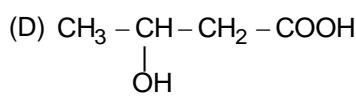
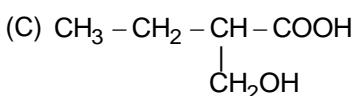
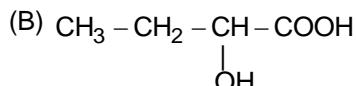
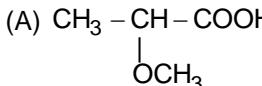
12. Product of following reaction is



13. 2-Methylcyclohexanone is allowed to react with metachloroperbenzoic acid. The major product in the reaction is

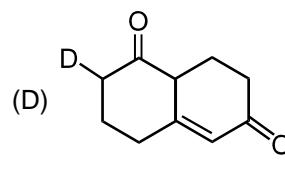
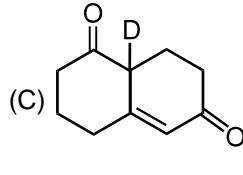
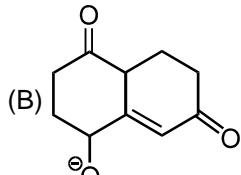
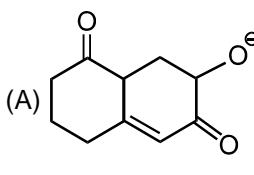
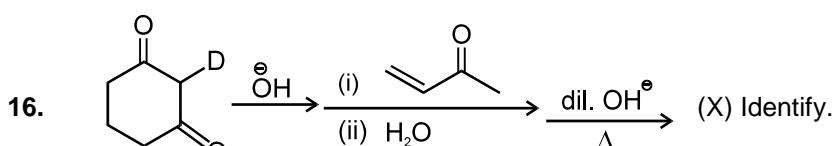


14. Which optically active compound on reduction with LiAlH_4 will give optically inactive compound?



15. The reaction, $\text{RCOOR}' + \text{R''OH}$ (excess) $\xrightarrow{\text{H}^+ \text{ or } \text{OH}^-} \text{RCOOR}'' + \text{R' OH}$ is called.

- (A) Esterification
 (B) Trans-esterification
 (C) Saponification
 (D) Hydrolysis



**MATCH THE COLUMN**

17. Match the product of **Column- II** with the reaction given in **Column- I**.

Column- I

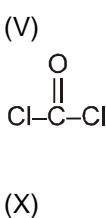
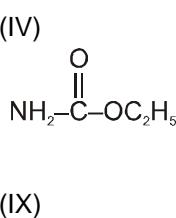
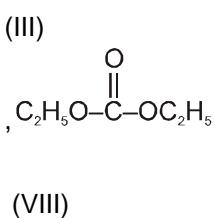
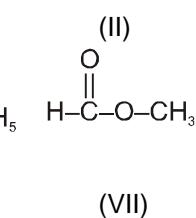
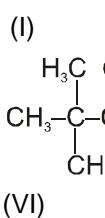
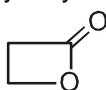
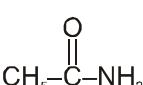
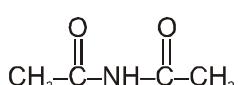
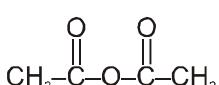
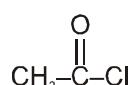
- (A) RMgI + Acetonitrile ($\text{CH}_3\text{C}\equiv\text{N}$)
 (B) RMgI + Carbon disulphide
 (C) RMgI.(1eq) + Ethyl chloroformate
 (D) RMgI + Oxirane

Column- II

- (p) Alkanone
 (q) Ester
 (r) 1° Alcohol
 (s) Dithionic acid

SINGLE AND DOUBLE VALUE INTEGER TYPE

18. How many compounds out of the following are more reactive than ethyl acetate towards hydrolysis.



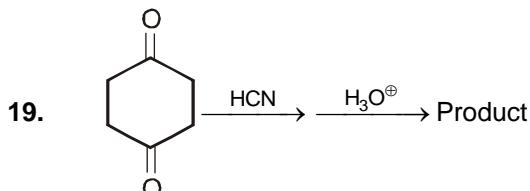
(VI)

(VII)

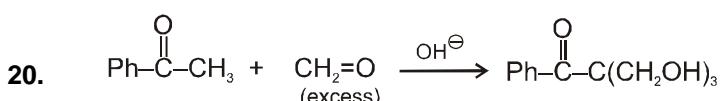
(VIII)

(IX)

(X)



The product of the following reactions is optically inactive and exist in Y diasteromeric forms, report your answer as $10 \times Y$



In the above reaction how many times of aldol reaction takes place ?

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

21. Which are correct against property mentioned ?

- (A) $\text{CH}_3\text{COCl} > (\text{CH}_3\text{CO})_2\text{O} > \text{CH}_3\text{COOEt} > \text{CH}_3\text{CONH}_2$ (Rate of hydrolysis)

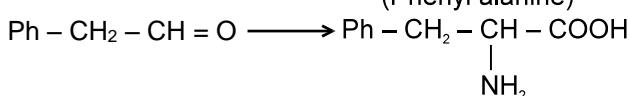
- (B) $\text{CH}_3-\text{CH}_2-\text{COOH} > \text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{COOH} > \text{CH}_3-\underset{\text{CH}_3}{\text{C}}(\text{CH}_3)-\text{COOH}$ (Rate of esterification)

- (C)

- (D) $\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{COOH} > \text{CH}_3-\text{C}-\text{CH}_2-\text{COOH} > \text{Ph}-\text{CH}_2-\text{COOH}$ (Rate of decarboxylation)



22. The following conversion is/are possible by
(Phenyl alanine)



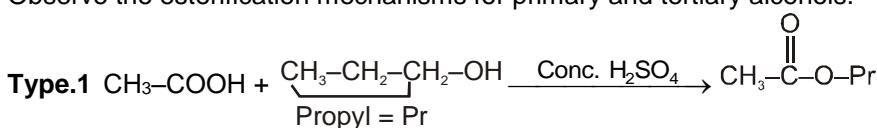
- (A) $\text{KCN} / \text{H}_2\text{O} \xrightarrow{\text{NH}_3, \Delta} \text{H}_3\text{O}^\oplus, \Delta \longrightarrow$
- (B) $\text{KCN} / \text{NH}_4\text{Cl} \xrightarrow{\text{H}_3\text{O}^\oplus, \Delta}$
- (C) $\text{HCN} / \text{NaOH} \xrightarrow{\text{SOCl}_2} \text{NH}_3 \xrightarrow{\text{H}_3\text{O}^\oplus, \Delta}$
- (D) $\text{Br}_2 / \text{CH}_3\text{COOH} \xrightarrow{\text{NH}_3} \text{CrO}_3 / \text{H}^\oplus$

COMPREHENSION

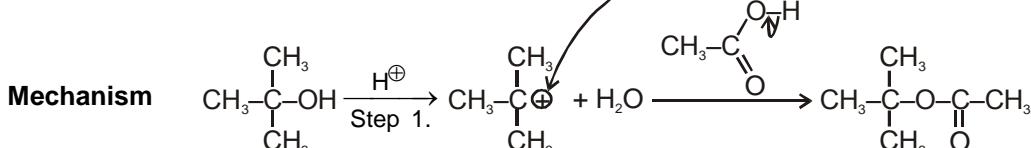
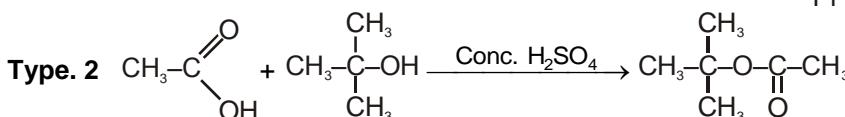
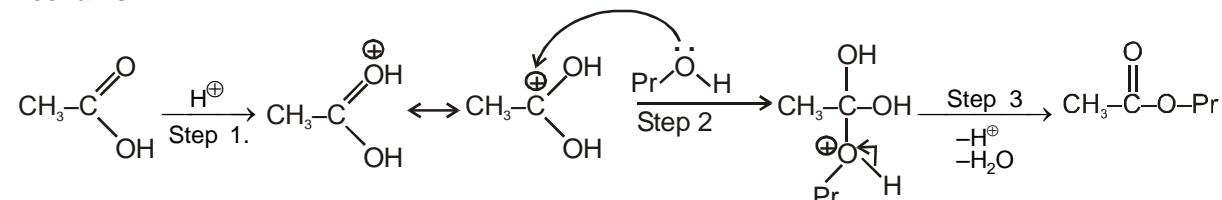
Read the following passage carefully and answer the questions.

Comprehension # 1

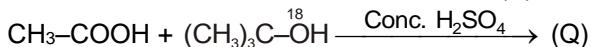
Observe the esterification mechanisms for primary and tertiary alcohols.



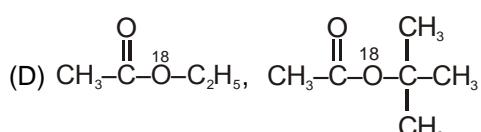
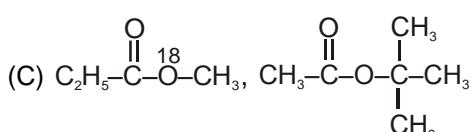
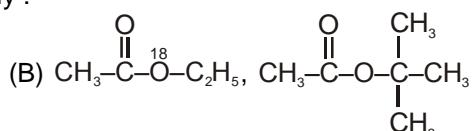
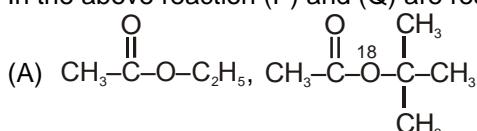
Mechanism

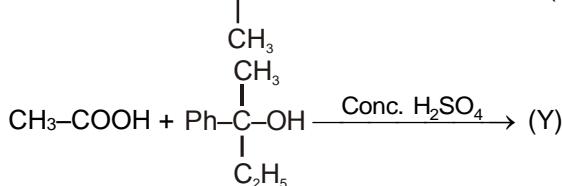
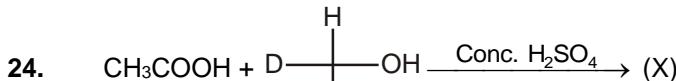


23. $\text{CH}_3\text{-COOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} (\text{P})$



In the above reaction (P) and (Q) are respectively :



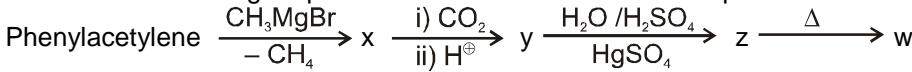


- (A) (X) is optically active while (Y) is optically inactive.
 (B) Both (X) and (Y) are optically active.
 (C) Both (X) and (Y) are optically inactive.
 (D) (X) is optically inactive while (Y) is optically active.

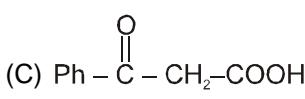
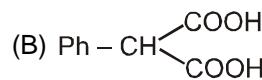
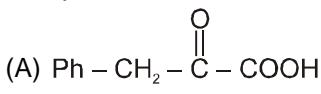
25. (+) Octan-2-ol esterifies with Acetic acid to give optically inactive racemised product. It must have gone by
 (A) Type I mechanism (B) Type II mechanism
 (C) Mix type I and type II mechanism (D) More by type I and less by type II mechanism

Comprehension # 2

Observe the following sequence of reaction and answer the questions based on it



26. Compound z is :



27. Which of the following statement is not correct

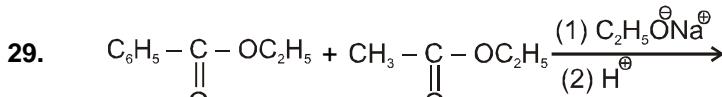
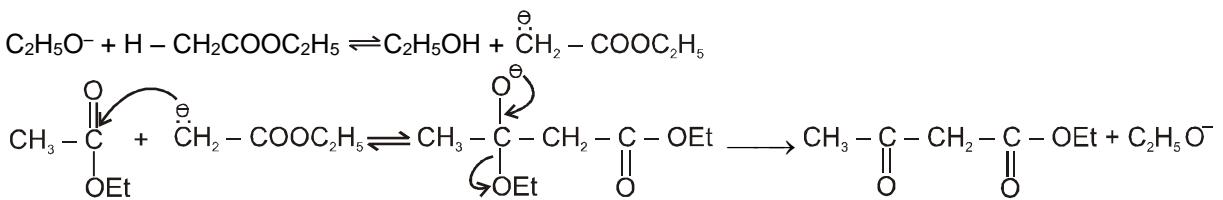
- (A) y decolourises $\text{Br}_2/\text{H}_2\text{O}$ solution
 (B) z on heating liberates CO_2 gas
 (C) w on reaction with NaOCl gives yellow ppt
 (D) x liberates H_2 gas with Na metal

28. Which of the following compound give benzoic acid on KMnO_4 oxidation

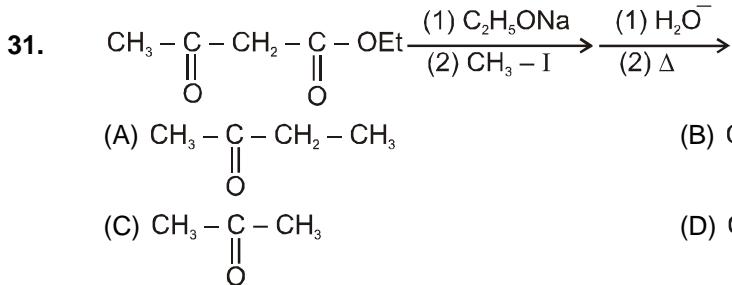
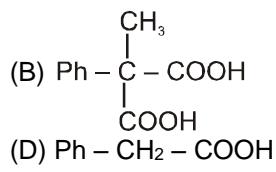
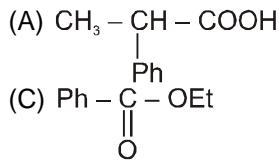
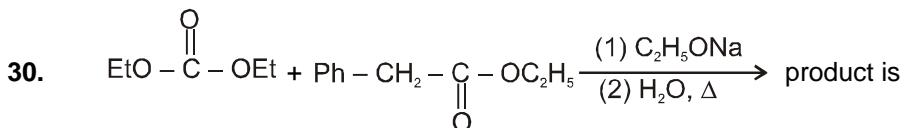
- (A) w (B) y (C) z (D) all.

Comprehension # 3

Ester having α -hydrogen on treatment with a strong base eg. $\text{C}_2\text{H}_5\text{ONa}$ undergoes self condensation to produce β -keto esters. This is called claisen condensation.



- (A) $\text{C}_6\text{H}_5-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$
 (B) $\text{C}_6\text{H}_5-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{CH}_2-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$
 (C) $\text{C}_6\text{H}_5-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{OC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH}$
 (D) None of these



PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 69

Important Instructions

A. General :

- The test is of 1 hour duration.
- The Test Booklet consists of 23 questions. The maximum marks are 69.
- Each part consists of five sections.
- Section 1 contains 11 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
- Section 2 contains 4 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
- Section 3 contains 1 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
- Section 4 contains 2 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
- Section 5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

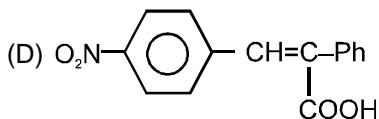
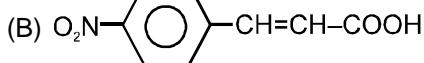
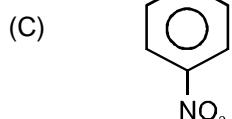
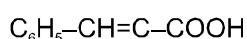
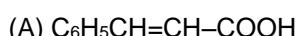
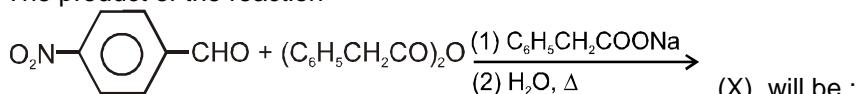
C. Marking Scheme

- For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (- 1) mark will be awarded.
- For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be awarded for incorrect answer in this section.
- For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.


SECTION-1 : (Only One option correct Type)

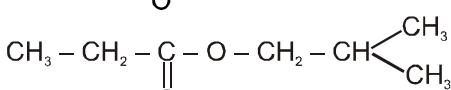
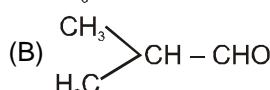
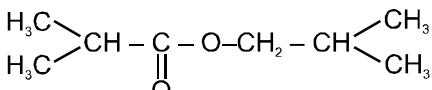
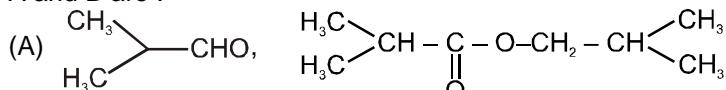
This section contains 10 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

1. The product of the reaction

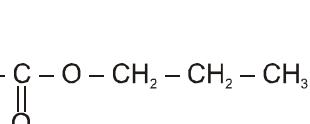
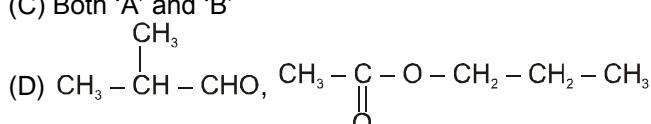


2. $\text{C}_4\text{H}_8\text{O} \xrightarrow[\text{(Aldehyde)}]{\text{Al(OEt)}_3} \text{(B)} \xrightarrow{\text{HOH}/\text{H}^+} \text{H}_3\text{C}-\text{CH}-\text{COOH} + \text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{OH}$

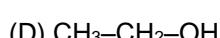
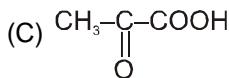
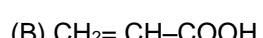
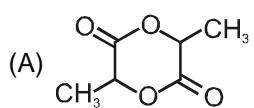
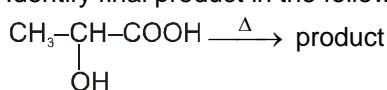
A and B are :



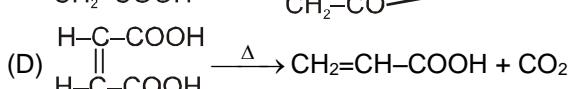
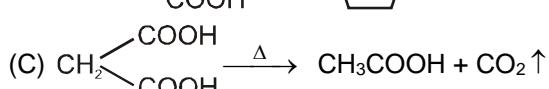
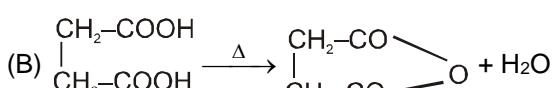
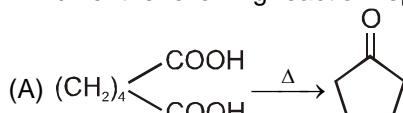
(C) Both 'A' and 'B'



3. Identify final product in the following reaction



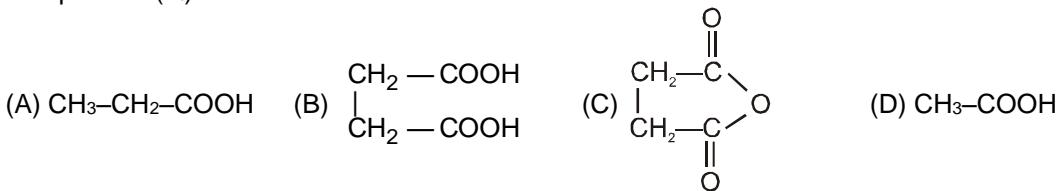
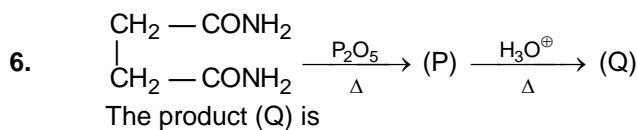
4. Which of the following reaction represents **incorrect** product.



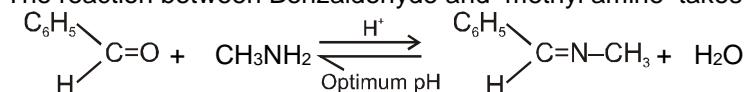
- 5.
- $$\xrightarrow{\Delta} \text{(A)} \xrightarrow{\text{NH}_3} \text{(B)} \xrightarrow[\text{H}_2\text{O}]{\text{NaOH}} \text{(C)} \xrightarrow{\text{Br}_2 + \text{KOH}} \text{(D)} \xrightarrow{\text{HCl}} \text{(E)}$$

In this reaction the product (E) is :

- (A) o-nitrobenzoic acid (B) Salicylic acid (C) anthranilic acid (D) Crotonic acid



7. The reaction between Benzaldehyde and methyl amine takes place in a very narrow pH range.



For the above reaction optimum pH is :

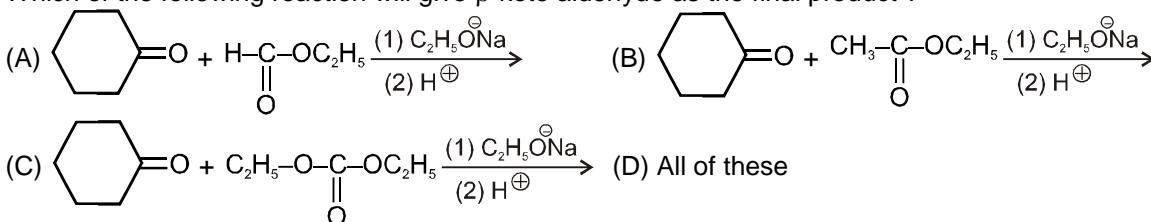
- (A) 2 to 3 (B) 4 to 5 (C) 5 to 9 (D) 12 to 13

8. In the given reaction $\xrightarrow[(2) \text{H}_2\text{O}/\text{OH}^{\ominus}]{(1) (\text{CH}_3)_2\text{CuLi}^{\oplus}} (\text{P})$

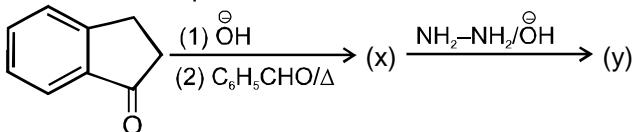
Product (P) will be :



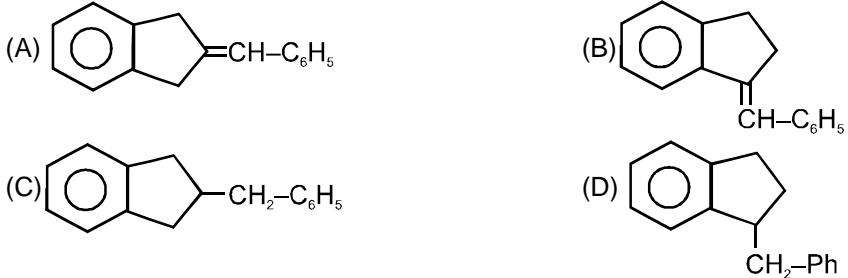
9. Which of the following reaction will give β -keto aldehyde as the final product ?



10. In the given reaction sequence

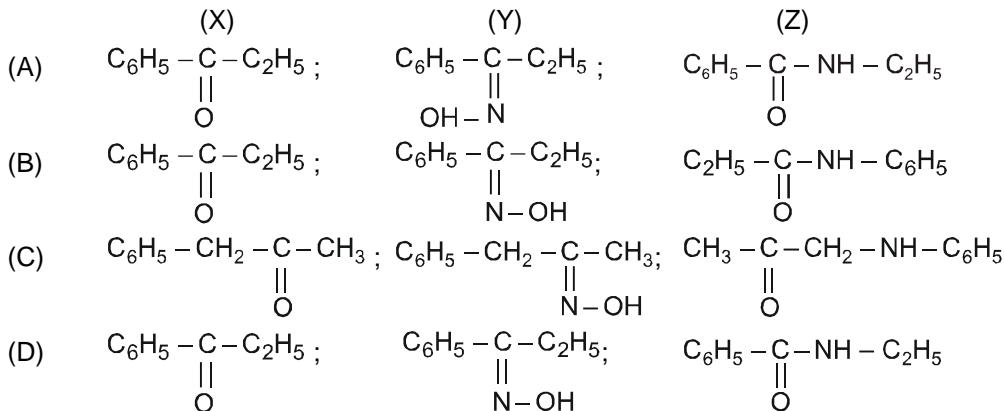


Product (y) will be :



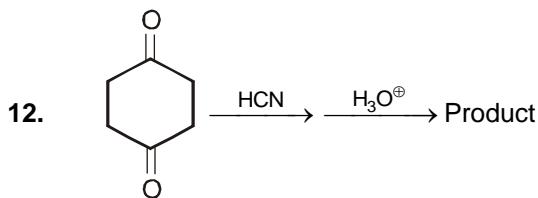


11. Compound (X) $C_9H_{10}O$ gives yellow coloured ppt with 2,4 DNP but does not give red coloured ppt with Fehling's solution. (X) on treatment with NH_2OH/H^+ gives compound (Y) $C_9H_{11}NO$. (Y) when treated with PCl_5 gives isomeric compound (Z). (Z) on hydrolysis gives propanoic acid and aniline. What will be the correct structure of (X), (Y) and (Z) ?



Section-2 : (One or More than one options correct Type)

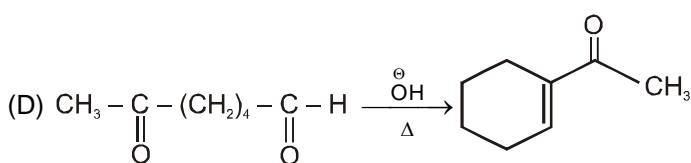
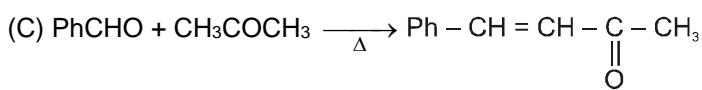
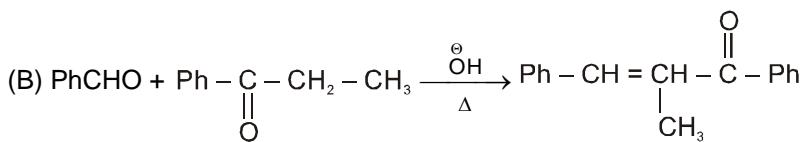
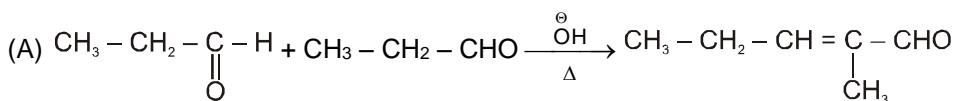
This section contains 4 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.



The correct statements about products is/are

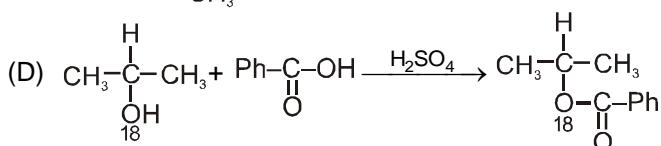
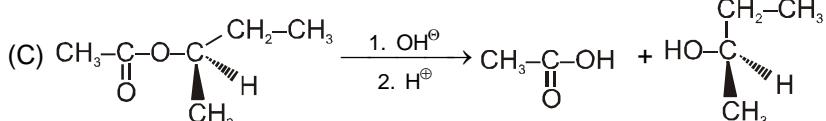
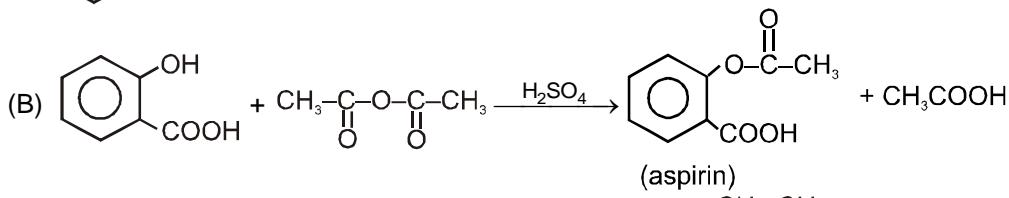
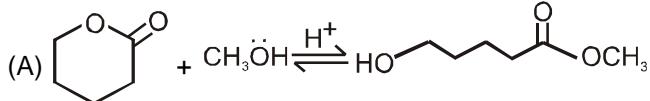
- (A) The product are optical inactive
- (B) The product is meso compound
- (C) The product is mixture of two enantiomers
- (D) Product exist in two diastereomeric forms

13. Which of the following aldol reaction product is correctly mention :





14. In which of the following reactions correct major product is mentioned?



15. Which of the following methods would serve to prepare 1-phenylpropan-2-ol.

- (A) Addition of benzyl grignard reagent to ethanol.
 (B) Addition of phenyllithium to methyloxirane
 (C) Addition of methyl grignard reagent to phenyl acetaldehyde.
 (D) Addition of phenyl Magnesium bromide with ethanal.

Section-3 : (One Integer Value Correct Type.)

This section contains 4 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

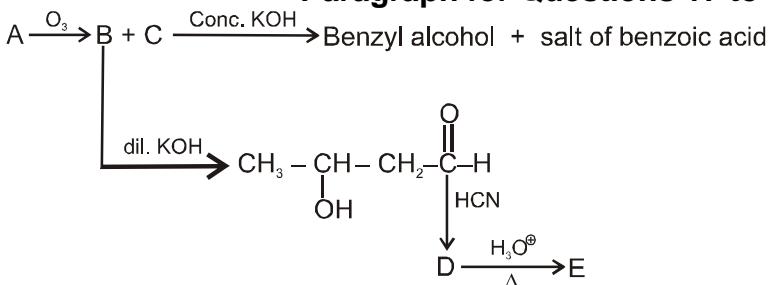
16. How many of the following will give 2,4-DNP test.



SECTION-4 : Comprehension Type (Only One options correct)

This section contains 2 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph for Questions 17 to 19



17. Structure of A is :

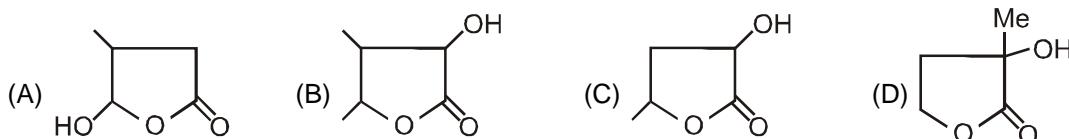
- (A) $\text{H}_2\text{C}=\text{CH}-\text{CHO}$ (B) $\text{Ph}-\text{CH}=\text{CH}-\text{CH}_3$ (C) $\text{Ph}-\underset{\text{CH}_3}{\text{C}}-\text{CH}$ (D) $\text{Ph}-\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CH}_3$

18. Structure of (B) and (C) differentiated by :

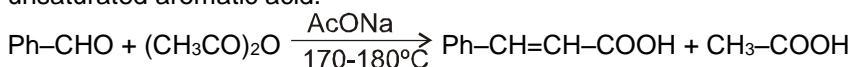
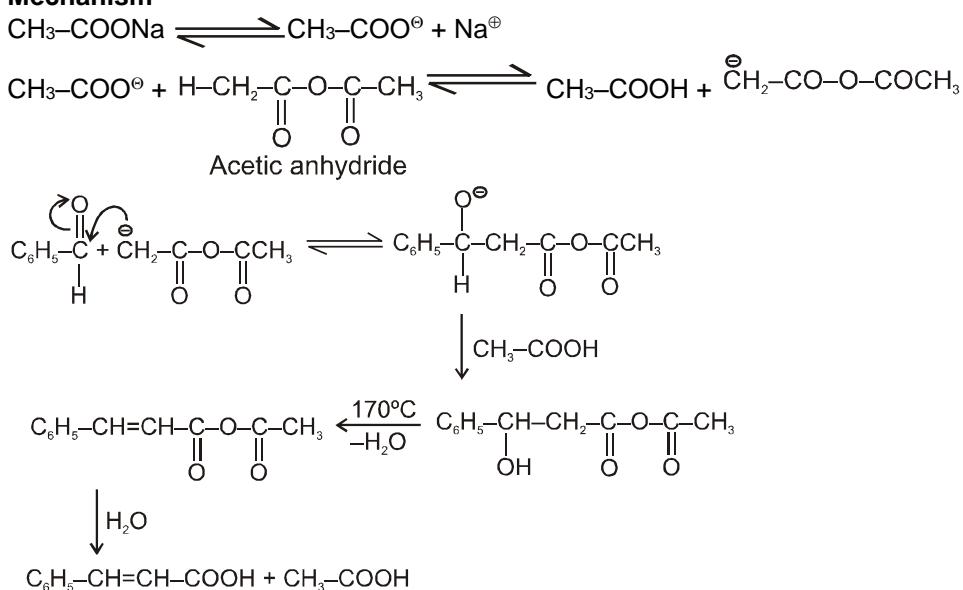
- (A) Tollen's reagent (B) Fehling solution (C) 2,4-DNP (D) NaHSO_3



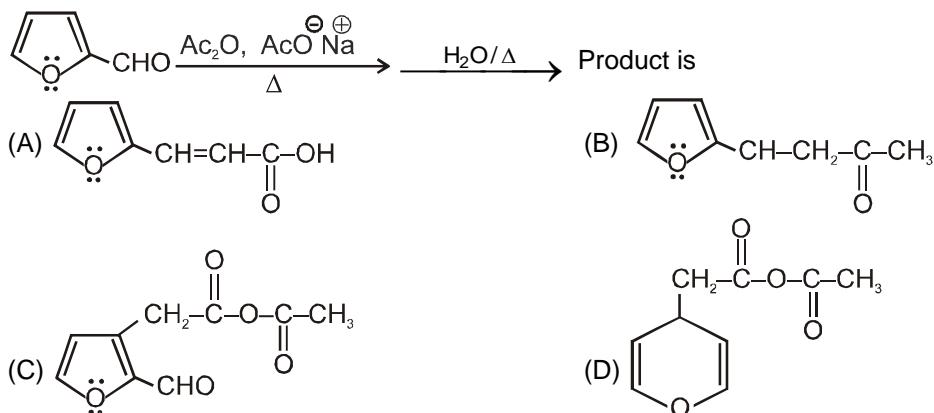
19. Structure of E is :


Paragraph for Questions 20 to 22

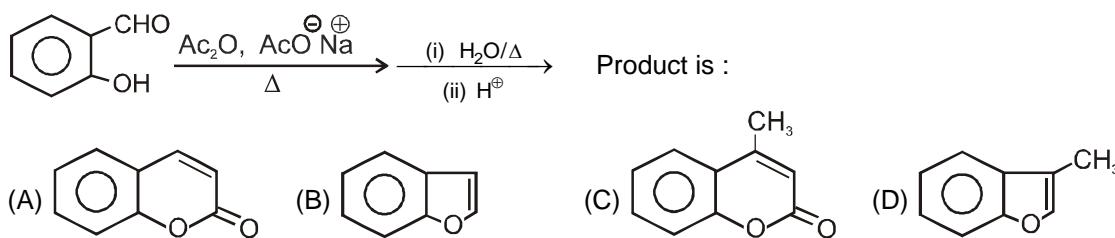
Perkin reaction is the condensation reaction between aromatic aldehyde and aliphatic acid anhydride in the presence of sodium or potassium salt of the acid of the corresponding anhydride to yield α , β unsaturated aromatic acid.

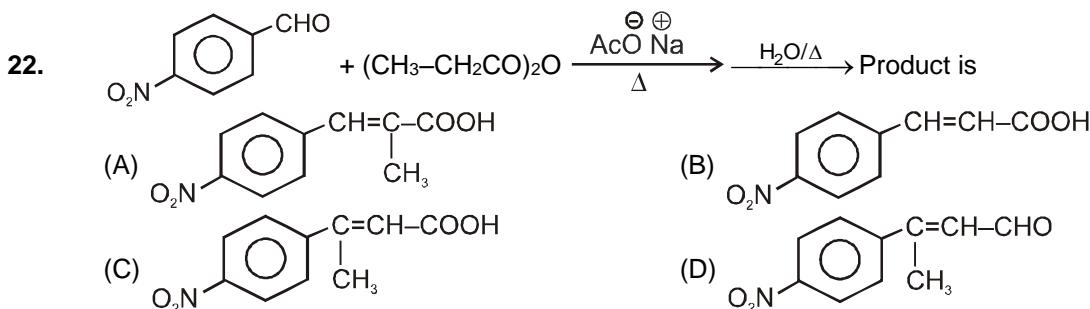

Mechanism


20.



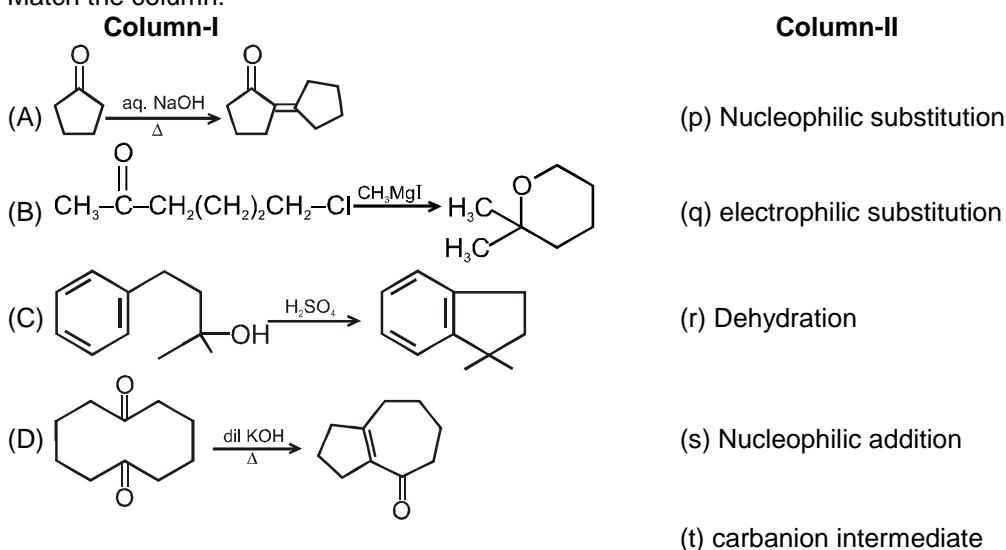
21.




SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

23. Match the column:


**Practice Test-2 ((IIT-JEE (ADVANCED Pattern))
OBJECTIVE RESPONSE SHEET (ORS))**

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23							
Ans.			(A)		(B)		(C)		(D)	

**APSP Answers****PART - I**

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (1) | 2. (1) | 3. (4) | 4. (4) | 5. (2) |
| 6. (4) | 7. (4) | 8. (4) | 9. (4) | 10. (4) |
| 11. (4) | 12. (4) | 13. (2) | 14. (2) | 15. (2) |
| 16. (1) | 17. (2) | 18. (4) | 19. (2) | 20. (1) |
| 21. (1) | 22. (3) | 23. (4) | 24. (4) | 25. (1) |
| 26. (2) | 27. (3) | 28. (4) | 29. (4) | 30. (4) |

PART - II

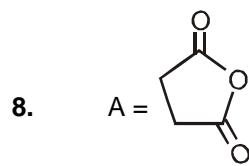
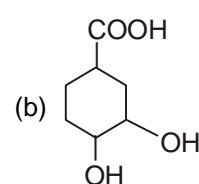
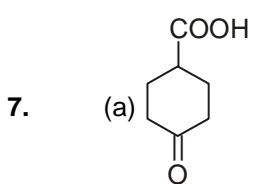
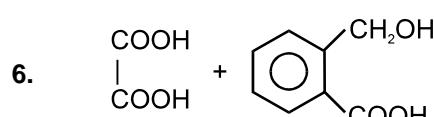
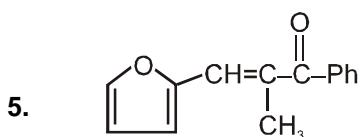
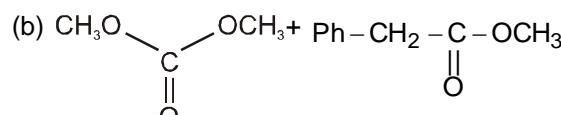
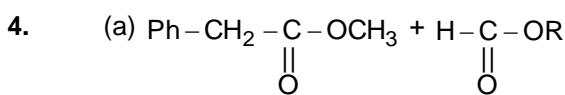
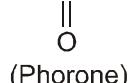
- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (C) | 2. (C) | 3. (C) | 4. (A) | 5. (A) |
| 6. (C) | 7. (B) | 8. (C) | 9. (D) | 10. (C) |
| 11. (B) | 12. (D) | 13. (D) | 14. (B) | 15. (C) |
| 16. (B) | 17. (D) | 18. (D) | 19. (B) | 20. (C) |
| 21. (C) | 22. (B) | 23. (A) | 24. (B) | 25. (D) |
| 26. (C) | 27. (B) | 28. (C) | 29. (B) | 30. (B) |
| 31. (D) | 32. (C) | 33. (B) | 34. (C) | 35. (C) |
| 36. (D) | 37. (A) | 38. (A) | 39. (C) | |

PART - III

1. Two nitrogen atoms of semicarbazide that are adjacent to the (C=O) group have their lone pair present in conjugation so nucleophilicity decreases.

2. c > b > a > d

3. $[X] = \text{Ph} — \text{CH} = \text{CH} — \underset{\underset{\text{(Phorone)}}{\text{O}}}{\text{C}} — \text{CH} = \text{CH} — \text{Ph}$, Four stereoisomers are formed.





- 18
- | | | | | |
|--------------------------------|--|---------|----------|---------|
| 9. (A) = PhCOOH, (B) = PhOH | 10. X = C ₂ H ₅ COOC ₃ H ₇ | | | |
| 11. (D) | 12. (C) | 13. (C) | 14. (C) | 15. (B) |
| 16. (C) | 17. (A) - (p) ; (B) - (s) ; (C) - (q) ; (D) - (r) | | | |
| 18. 6 (I, II, III, V, VII & X) | 19. 20 | 20. 3 | 21. (AB) | |
| 22. (ABC) | 23. (B) | 24. (A) | 25. (B) | 26. (C) |
| 27. (D) | 28. (D) | 29. (A) | 30. (D) | 31. (A) |

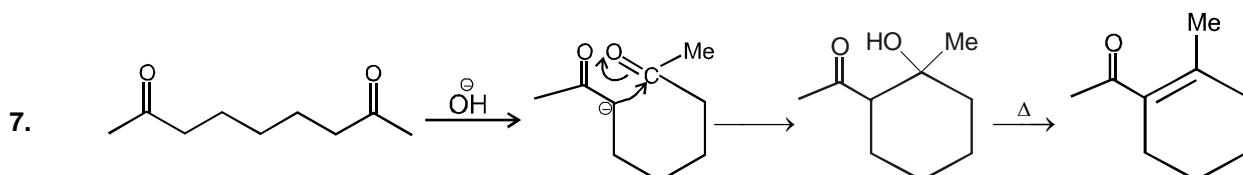
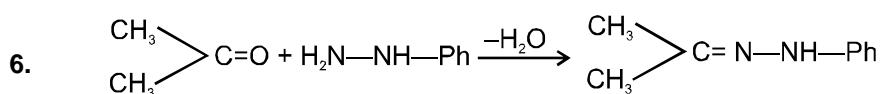
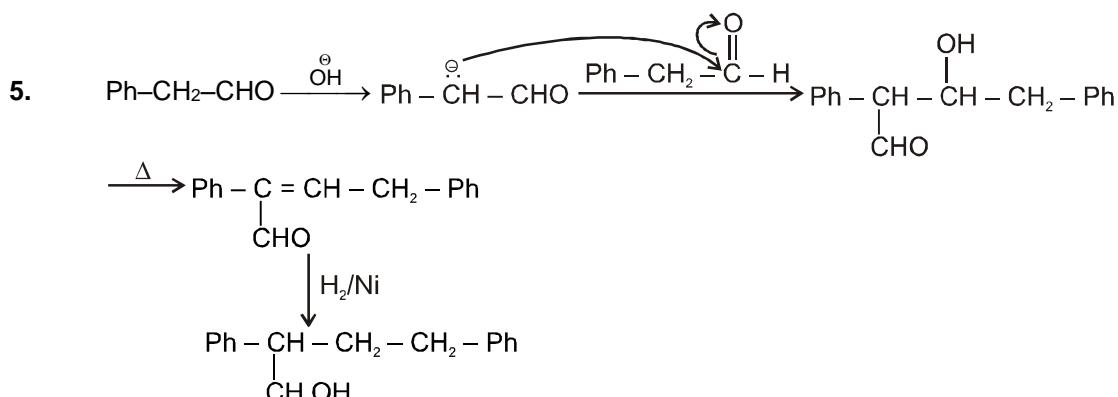
PART - IV

- | | | | | |
|----------------|----------|---|------------|-----------|
| 1. (D) | 2. (A) | 3. (A) | 4. (D) | 5. (C) |
| 6. (C) | 7. (B) | 8. (A) | 9. (A) | 10. (A) |
| 11. (B) | 12. (AD) | 13. (ABC) | 14. (ABCD) | 15. (ABC) |
| 16. 4(1,2,3,4) | 17. (B) | 18. (B) | 19. (C) | 20. (A) |
| 21. (A) | 22. (A) | 23. (A - r,s,t) ; (B - p,s) ; (C - q, r) ; (D - r,s,t). | | |

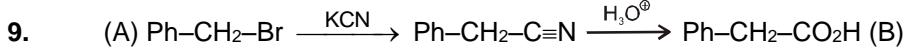
APSP Solutions

PART - I

- Rate of nucleophilic attack \propto amount of +ve charge at carbonyl carbon.
- It is a protection of carbonyl group.
- In Wolf-Kishner reduction carbonyl compound is converted to hydrocarbon.
- Vinyl ether does not react with 2,4-DNP and metallic sodium.

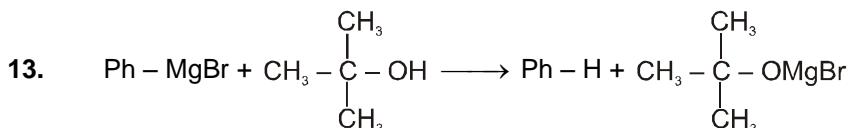


8. K₂Cr₂O₇ oxidised secondary alcohol which gives iodoform test.

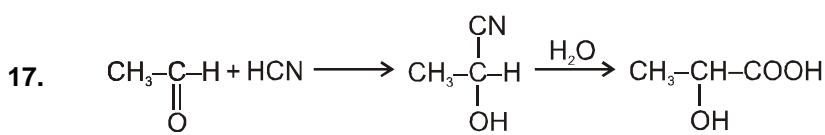
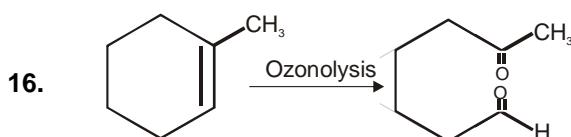
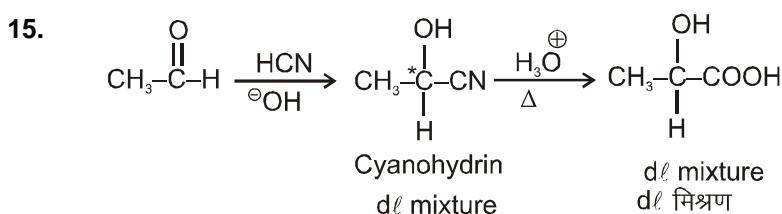


10. CH_3-CHO (α -Hydrogen is present)

11. Haloform reaction

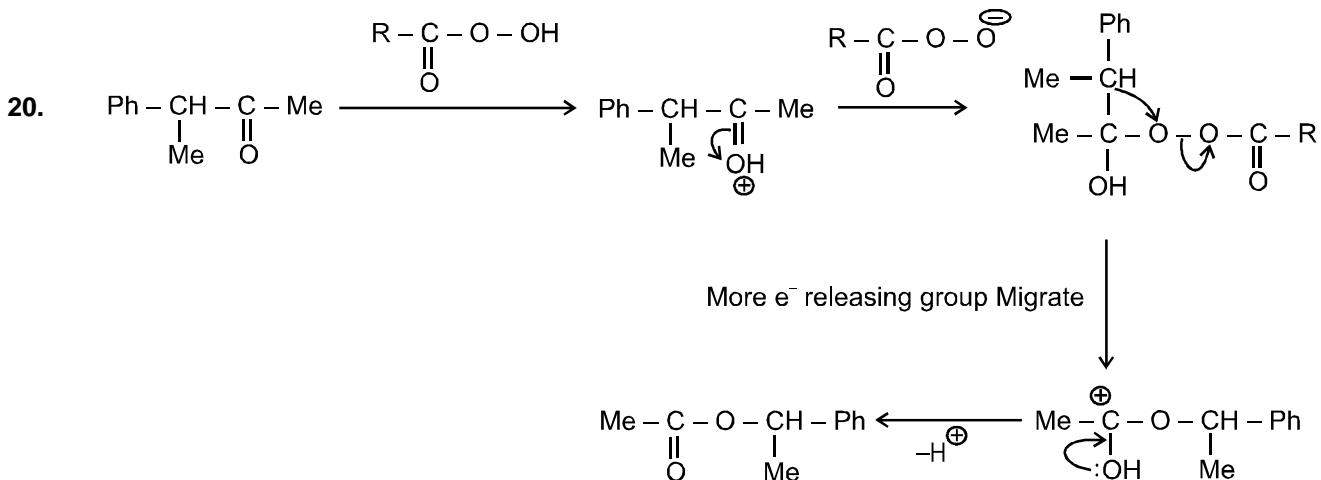
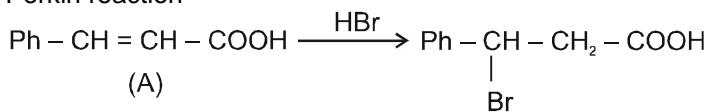


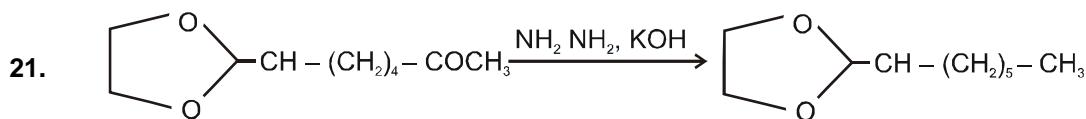
14. Its Gabriel phthalimide reaction.



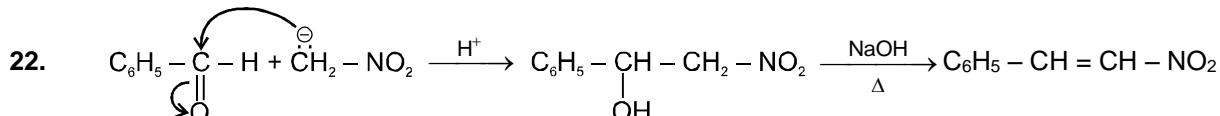
18. α -hydrogen absent.

19. Perkin reaction



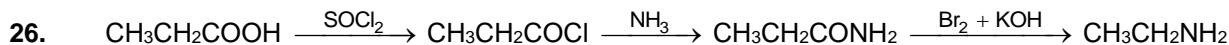
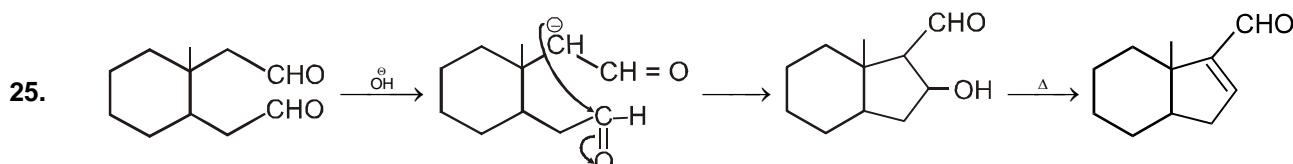


Acetal is hydrolysed in acidic Medium so clemmensen reduction is not used.



23. Rate of decarboxylation – m effect of substituent at α position.

24. (X) : RCONH₂ (Y) : R-C≡N (Z) : R-CHO



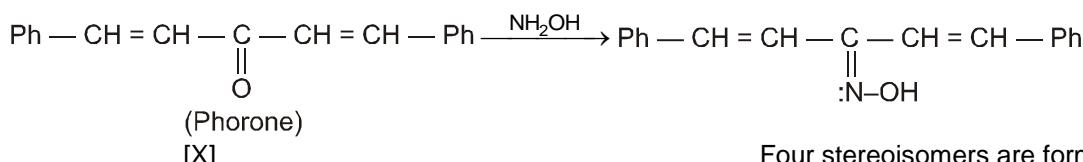
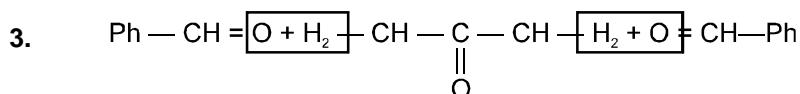
27. In fumaric acid both COOH groups are present on opposite side so it is unaffected on heating.

28. It is cannizaro reaction.

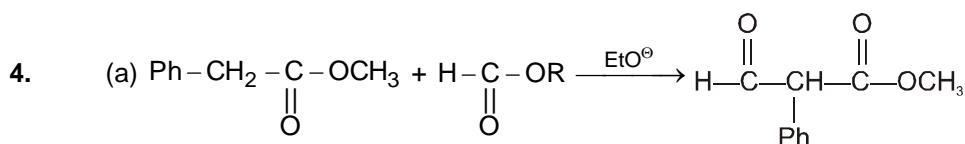
30. (i) $\text{Ph}-\text{CH}_3 + \text{CrO}_3 + (\text{CH}_3\text{CO})_2\text{O} \xrightarrow{273-283 \text{ K}} \text{Ph}-\text{CH}(\text{OCOCH}_3)_2 \xrightarrow[\Delta]{\text{H}_3\text{O}^+} \text{Ph}-\text{CHO}$
 (ii) $\text{Ph}-\text{CH}_3 \xrightarrow[\text{hv}]{\text{Cl}_2} \text{Ph}-\text{CHCl}_2 \xrightarrow[100^\circ\text{C}]{\text{H}_2\text{O}} \text{Ph}-\text{CHO}$
 (iii) $\text{C}_6\text{H}_6 \xrightarrow[\text{AlCl}_3]{\text{CO} + \text{HCl}} \text{Ph}-\text{CHO}$
 (iv) $\text{Ph}-\text{COCl} + (\text{CH}_3)_2\text{Cd} \longrightarrow \text{Ph}-\text{CO}-\text{CH}_3$

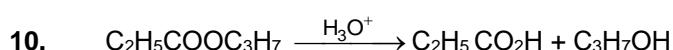
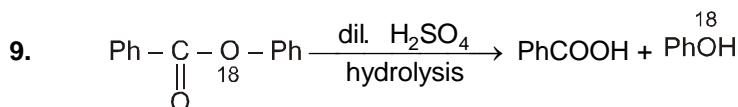
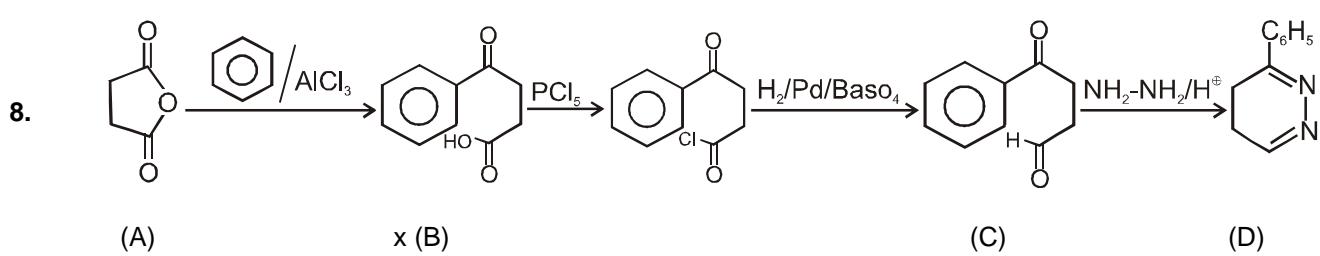
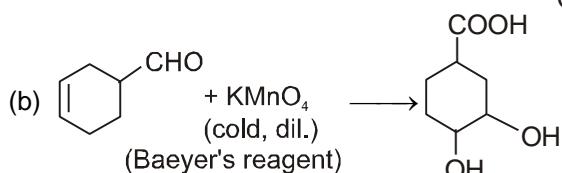
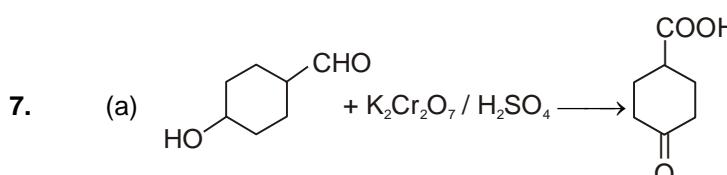
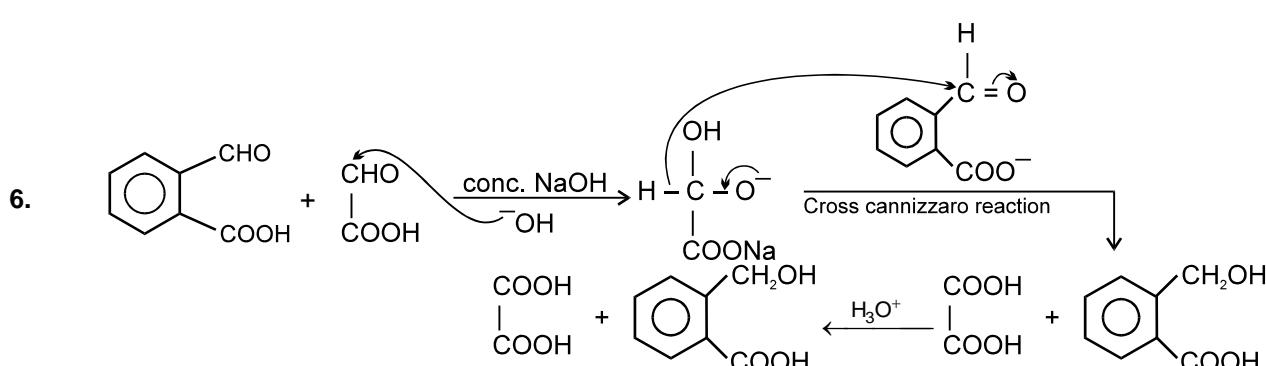
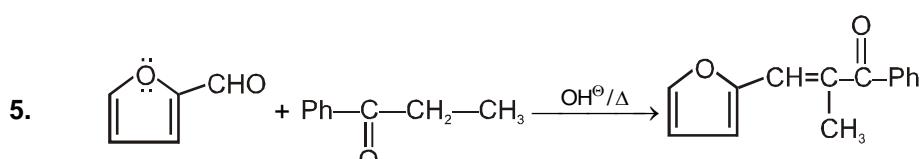
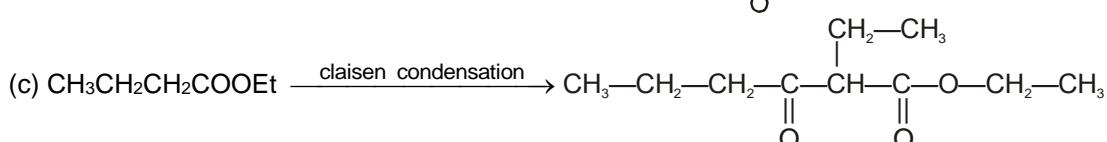
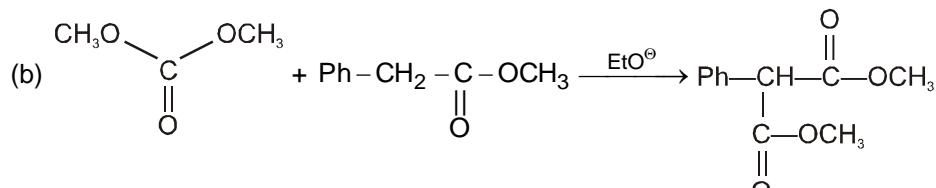
PART - III

2. Rate of nucleophilic addition reactions depends on the amount of +ve charge present at carbonyl carbon.



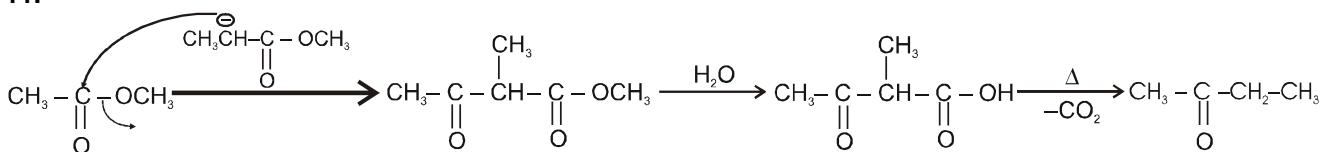
Four stereoisomers are formed.



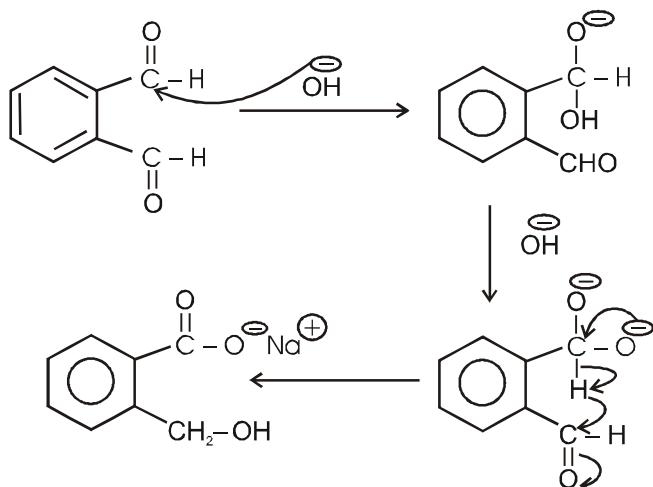




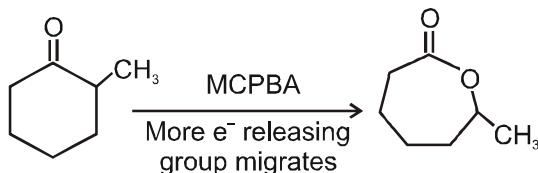
11.



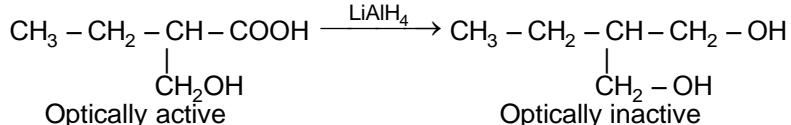
12.



13.



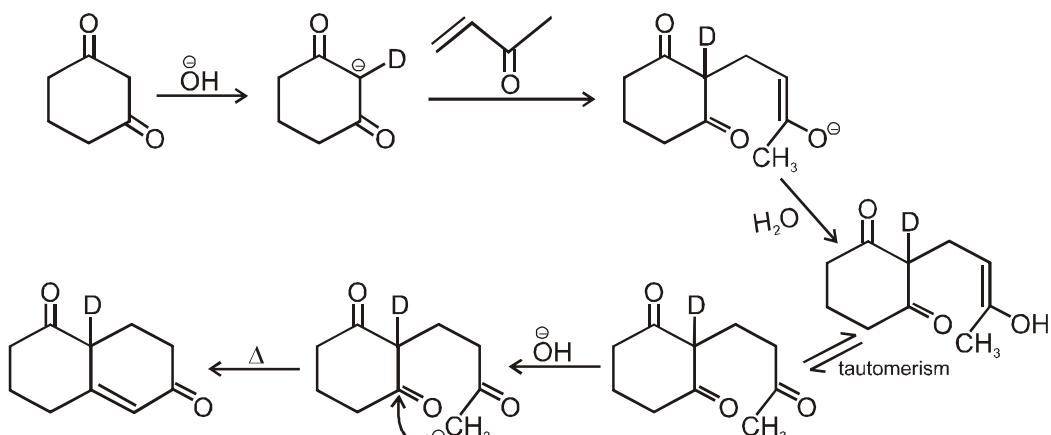
14.

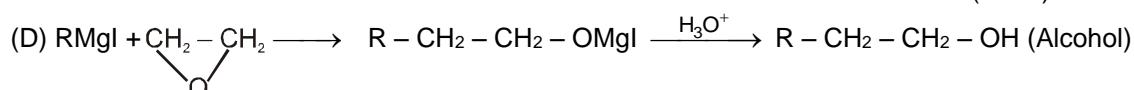
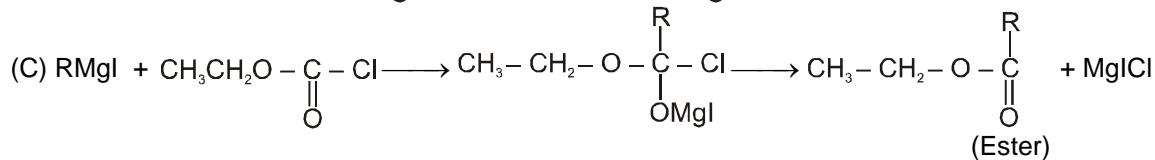
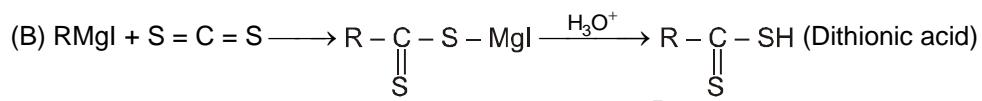
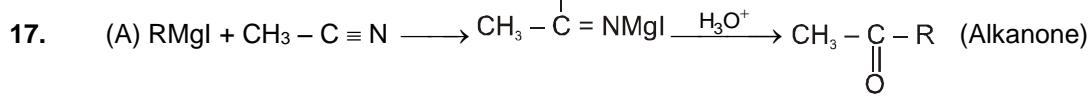


15.

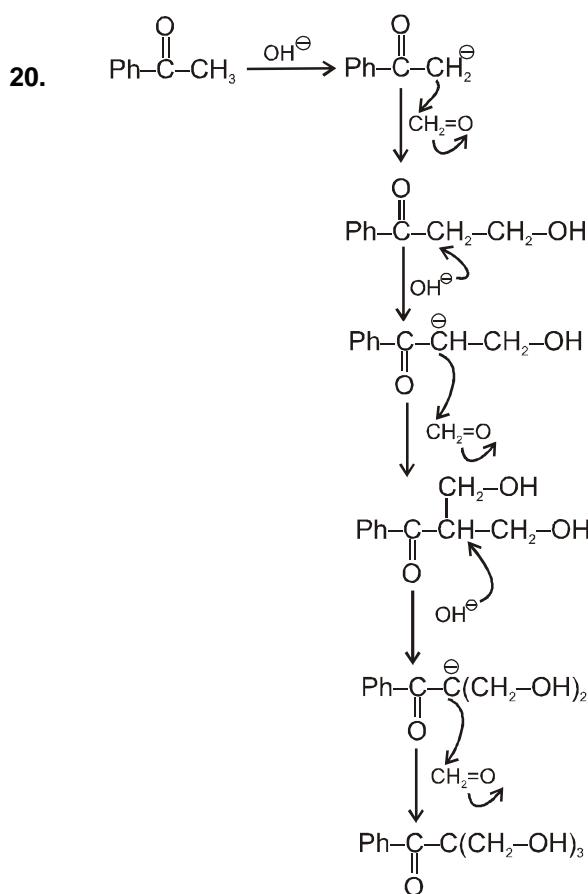
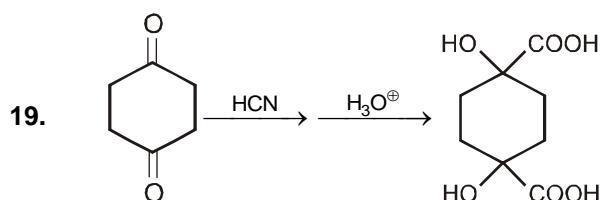
When an ester converts into another ester, it is called trans esterification.

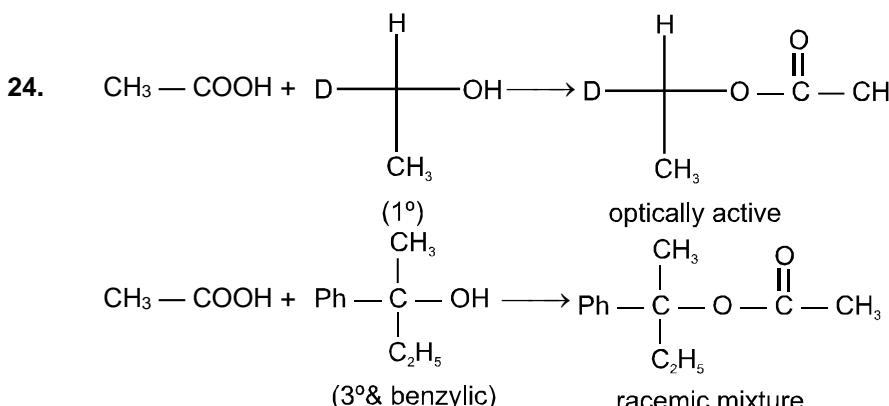
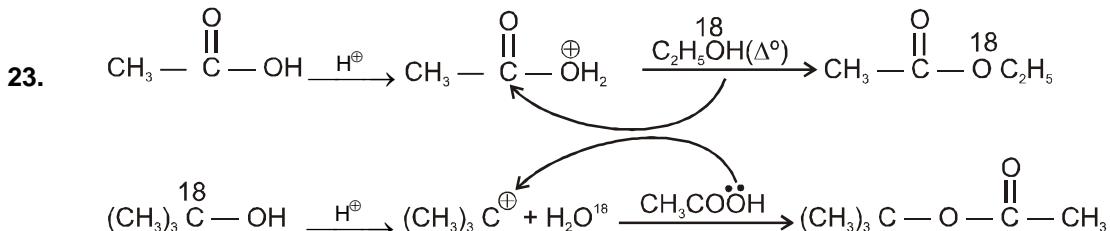
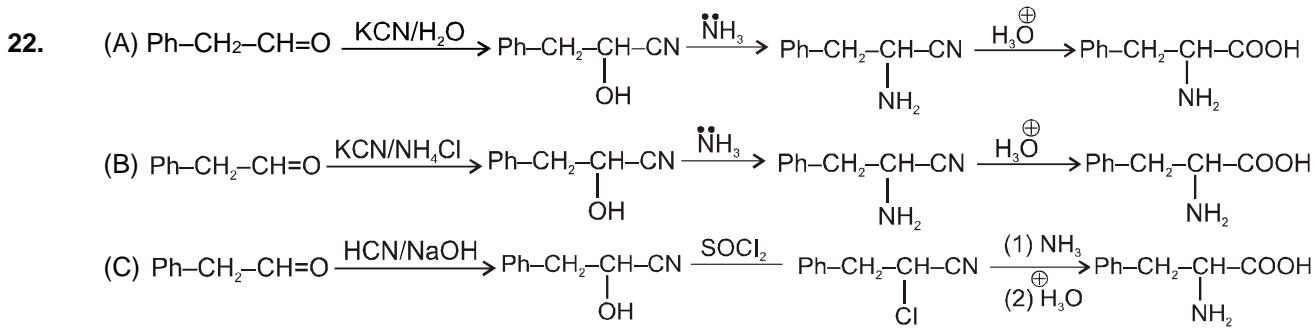
16.



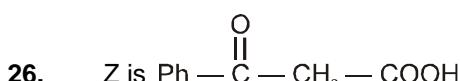


18. All molecules which have greater positive charge centre at acyl carbon (more than ethyl acetate) are more reactive than it towards hydrolysis.



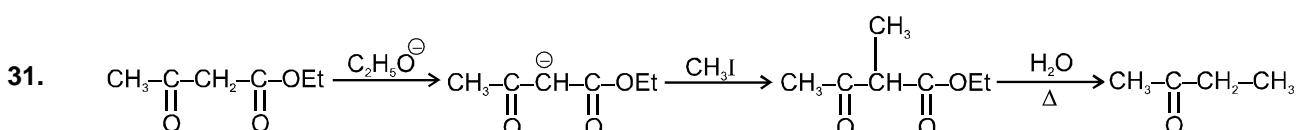
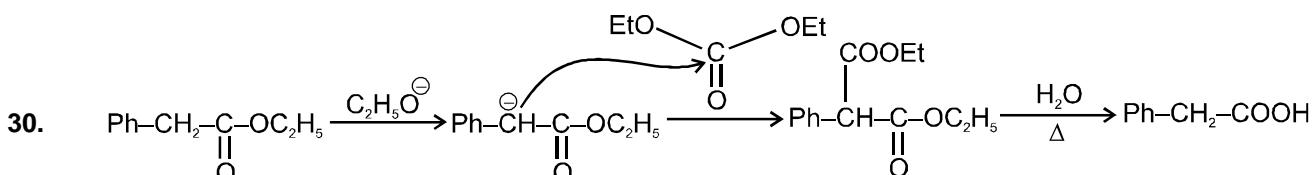
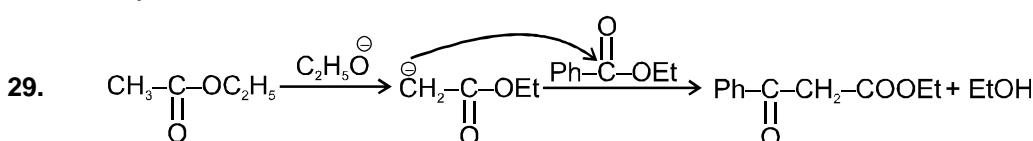


25. Since (+) Octan-2-ol racemises on reaction with acetic acid, therefore it must have gone through an $\text{S}_{\text{N}}1$ reaction i.e., type II reaction.



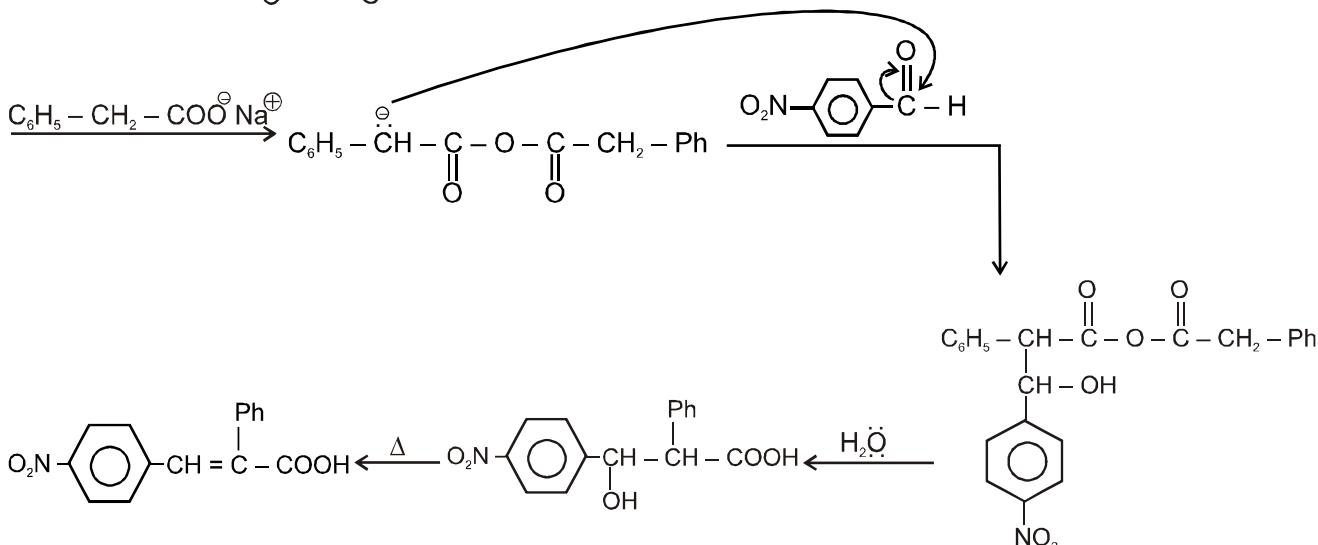
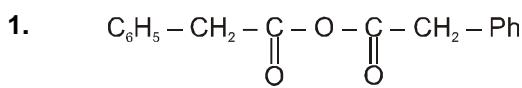
27. X is an anion and it has no acidic hydrogen.

28. Any mono substituted benzene oxidises to benzoic acid.

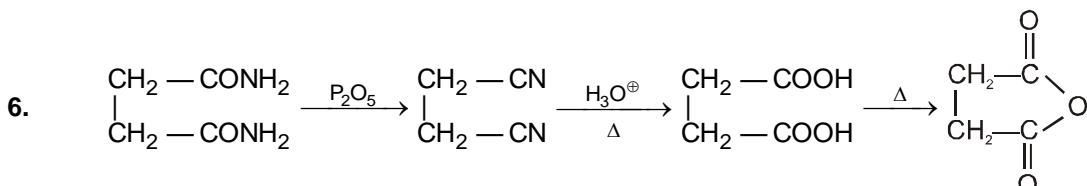
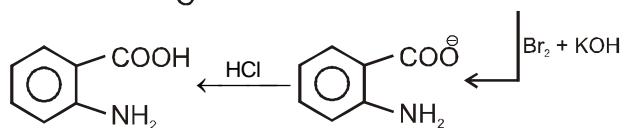
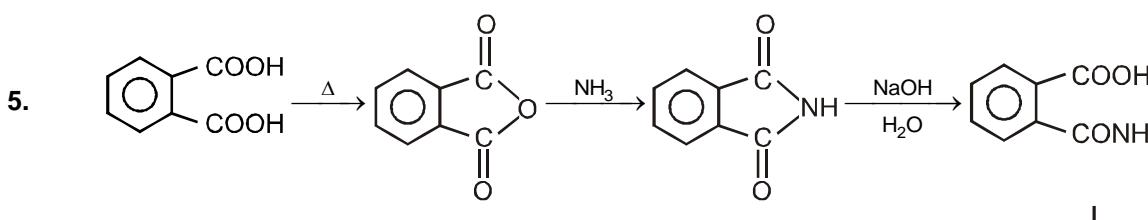
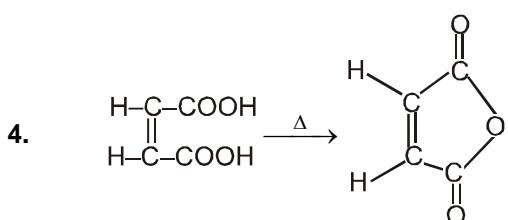
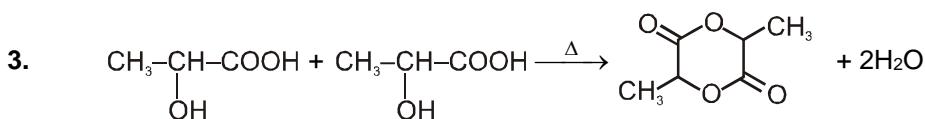
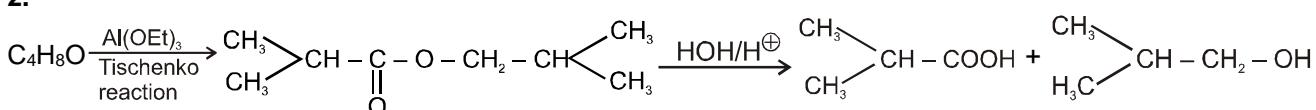




PART - IV

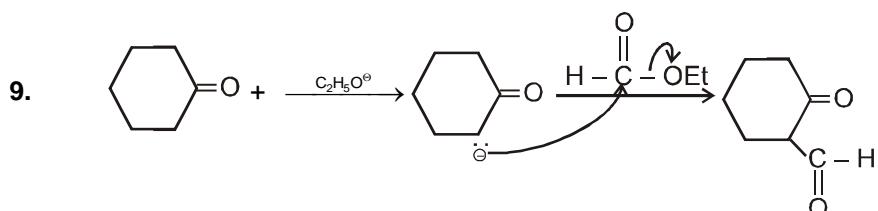
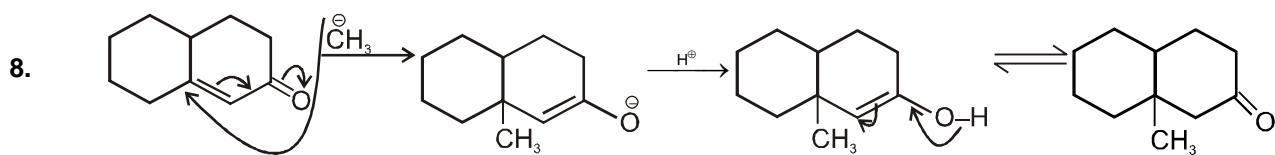


2.

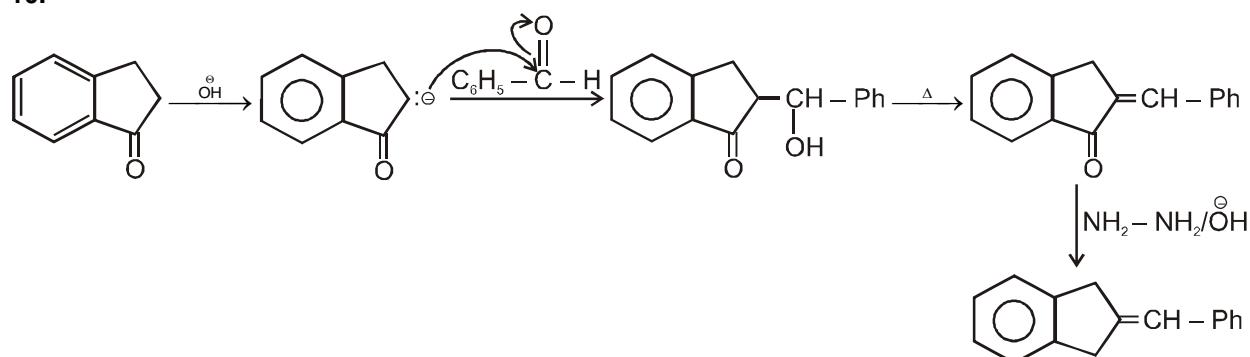




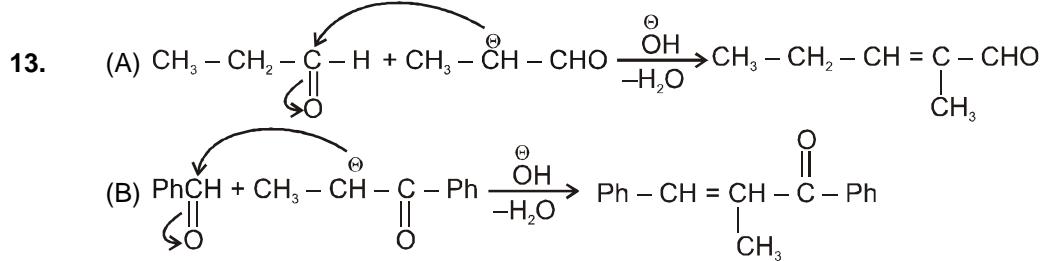
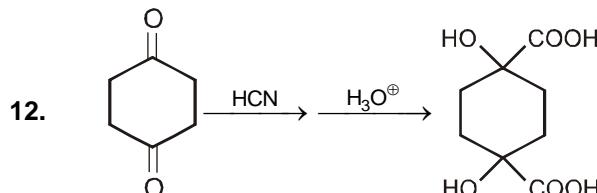
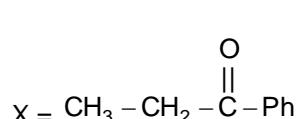
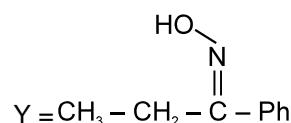
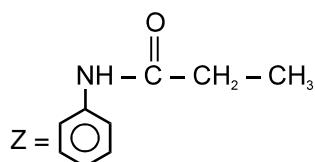
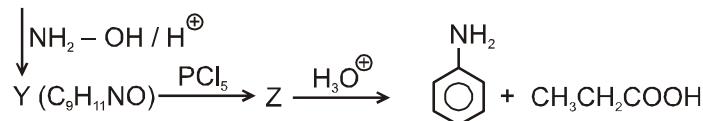
7. Optimun pH for the above reaction = 4–5

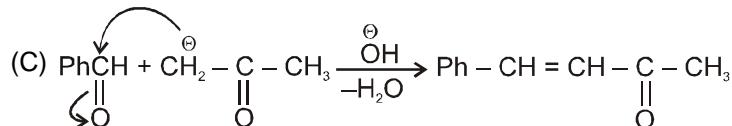


10.

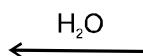
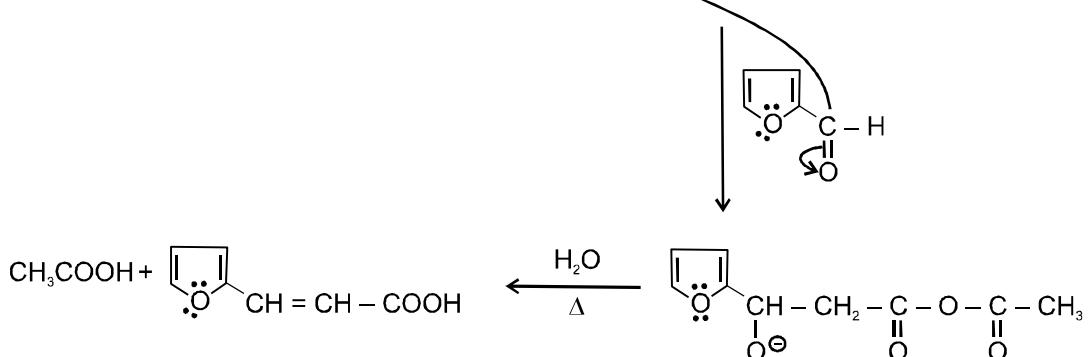
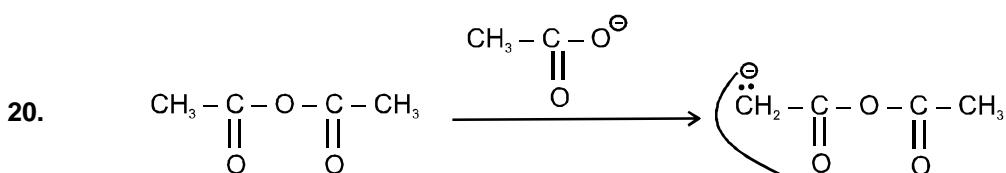
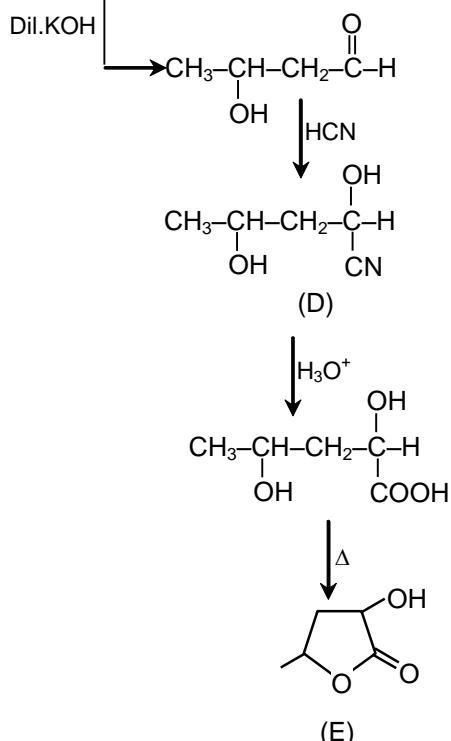
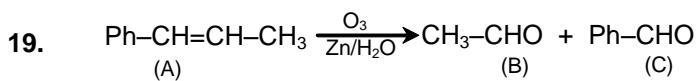


11. No Cloured ppt $\xleftarrow{\text{Fehling Solution}}$ X ($C_9H_{10}O$) $\xrightarrow{2,4 \text{ DNP}}$ yellow coloured ppt.



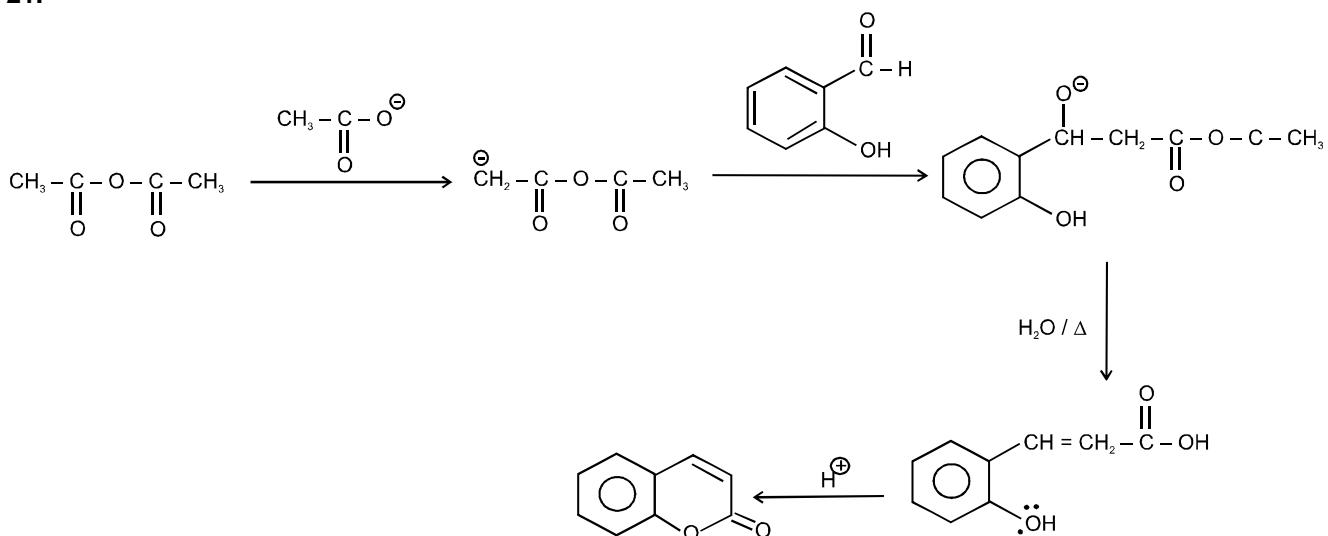


15. Option (A), (B) & (C) are true

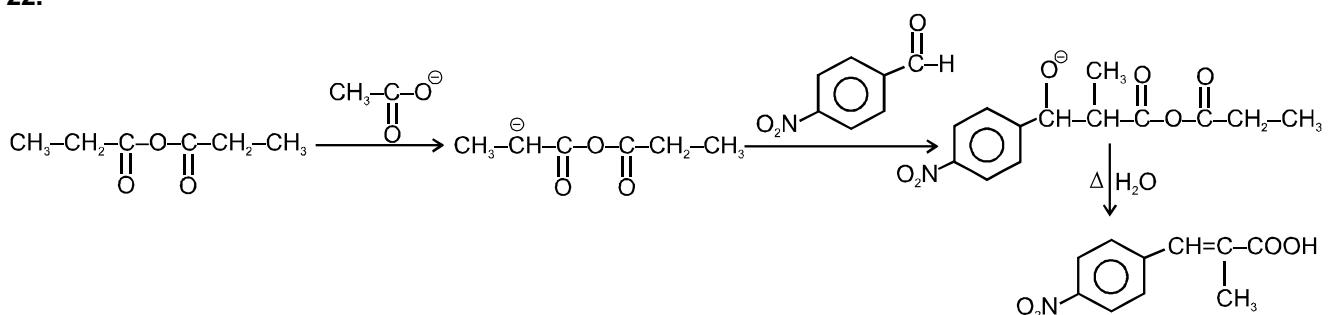




21.



22.



- 23.
- (A) Aldol condensation: (In which carbanion (nucleophile) gives nucleophilic addition and last step is dehydration).
 - (B) G.R. attacks on carbonyl group, followed by internal nucleophilic substitution.
 - (C) H_2SO_4 protonates OH group and changes it into good leaving group to give electrophilic carbon which undergoes ArSE_2 intermolecular reaction for ring closure.
 - (D) Intra molecular aldol condensation involves carbanion, nucleophilic addition and dehydration.