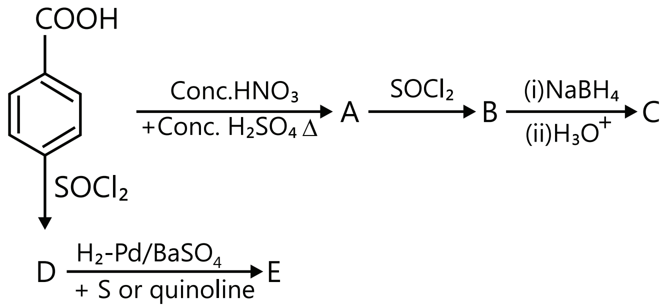
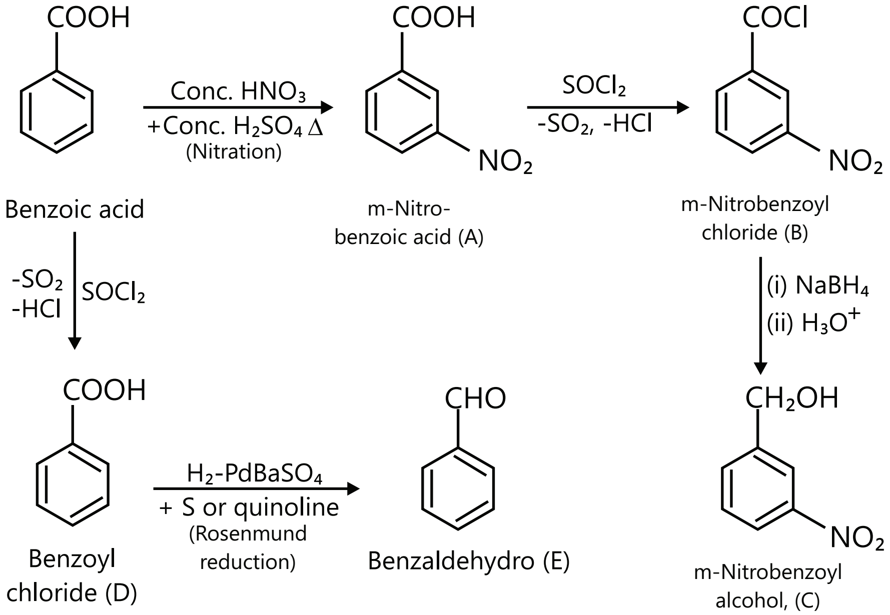
Solved Examples

JEE Main/Boards

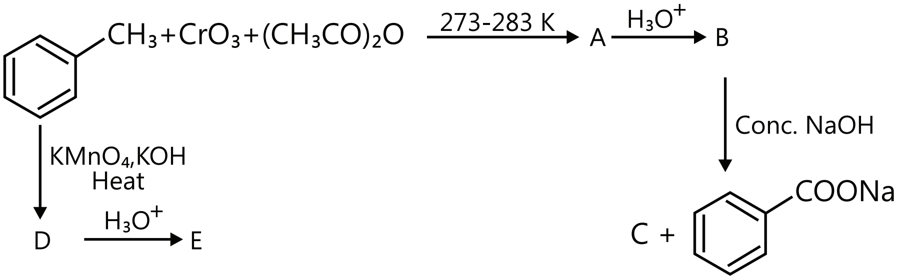
Example 1: Identify A to E in the following reactions:



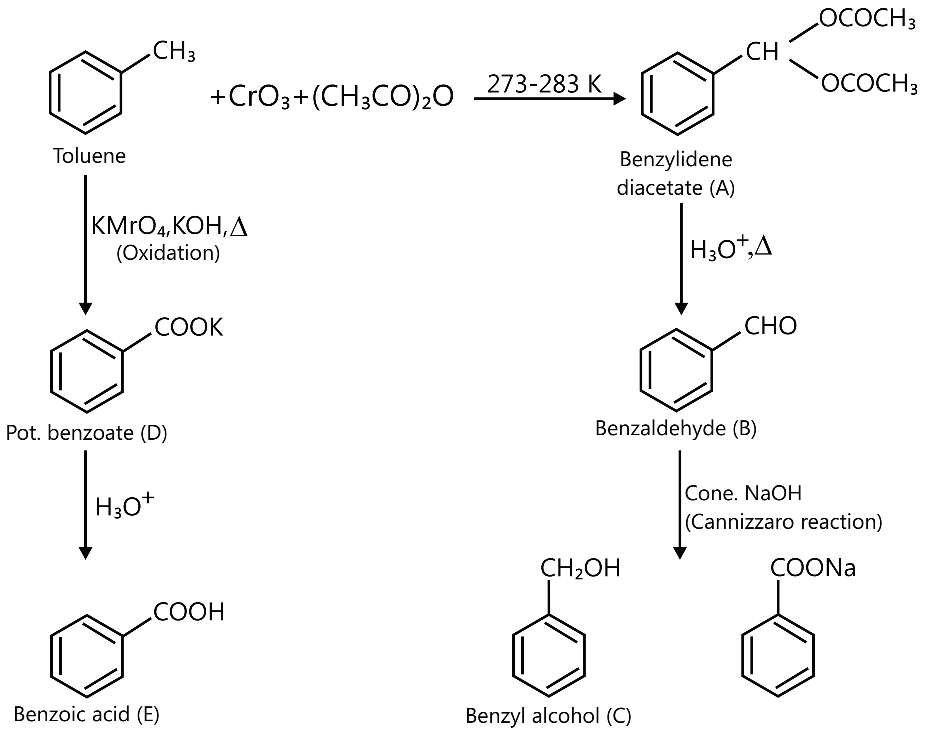
Sol: The First step is nitration, the reaction with $SOCl_2$ forms an acid chloride derivative, which on Rosenmund reduction forms a formyl group whereas the acid chloride derivative on reduction with $NaBH_4$ gives an alcohol.



Example 2: Identify A to E in the following series of reactions:



Sol: Toluene with $KMnO_4$/KOH undergoes oxidation to form Benzoic acid. On the other side, toluene with chromium oxide and acetyl acetate gives benzylidene acetate which on treatment with an acid gives aldehyde which on reaction with a strong base undergoes the Cannizzaro reaction.



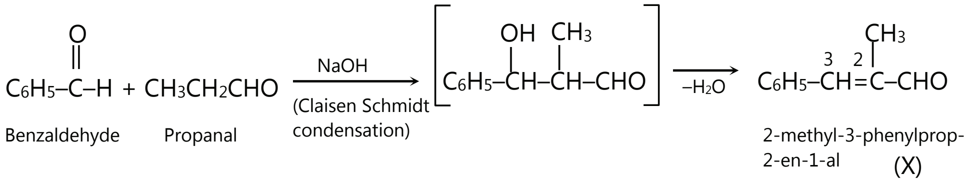
Example 3: Complete each synthesis by filling the missing starting materials, reagents or products (X, Y and Z).

(a) $C_6H_5CHO + CH_3CH_2CHO \xrightarrow{NaOH} X$

(b) $CH_3CH_2CH_2CH_2OH \xrightarrow{Y} CH_3CH_2CH_2COOH$

(c) $CH_3(CH_2)_3COOC_2H_5 \xrightarrow{Z} CH_3(CH_2)_9CHO$

Sol: (a) The reaction is Claisen-Schmidt condensation.



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H + CH_3CH_2CHO \xrightarrow[\text{(Claisen Schmidt condensation)}]{NaOH} \left[C_6H_5-\overset{\overset{\displaystyle OH}{|}}{C}H-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CHO \right] \xrightarrow[-H_2O]{} C_6H_5-\overset{3}{C}H=\overset{\overset{\displaystyle CH_3}{|}}{\overset{2}{C}}-CHO$$

(b) Oxidation of alcohol to acid thus the reagent used must be $KMnO_4$

$$\underset{\text{Butan–1–ol}}{CH_3CH_2CH_2OH} \xrightarrow[\text{(ii) } H^+, H_2O]{\text{(i) Alk.}KMnO_4} \underset{\text{Butanoic acid}}{CH_3CH_2CH_2COOH}$$

(c) $\underset{\text{Ethyl undecanoate}}{CH_3(CH_2)_9COOC_2H_5} \xrightarrow[\text{(ii) } H_2O]{\text{(i) DIBAL–H}} \underset{\text{Undecanal}}{CH_3(CH_2)_9CHO}$

Thus, Y = (i) Alk. $KMnO_{4,}$ (ii) H^+, H_2O

And Z = (i) DiBAL-H, (iii) H_2O

Example 4: (a) Identity A, B and C in the following reaction

$$HC\equiv CH \xrightarrow[HgSO_4]{dil.H_2SO_4} A \xrightarrow{dil.NaOH} B \xrightarrow{heat} C$$

(b) Give reasons: (i) p-Nitrobenozoic acid has higher K_a value than benzoic acid

(ii) Acetone is highly soluble but benzophenone is not

Sol: (a) The first step is conversion of the alkyne to an unsaturated alcohol, which then tautomerises to form an aldehyde. When this aldehyde is treated with dil NaOH and undergoes self-condensation, reaction known as aldol which form β- hydroxyl carbonyl compound On heating it gives α,β unsaturated carbonyl compound.

$$\underset{\text{Acetylene}}{HC\equiv CH} \xrightarrow[\text{(Addional of }H_2O)]{dil.H_2SO_4} \underset{\text{Vinyl alcohol}}{[H_2C=CHOH]} \xrightarrow{\text{Tautomerises}} \underset{\text{Acetaldehyde(A)}}{CH_3CHO} \xrightarrow[\text{(Aldol condensation)}]{dil.NaOH}$$

$$\underset{\substack{\beta\text{–Hydroxybutyraldehyde)(B)}\\ \text{(Analdol)}}}{CH_3-CHOH-CH_2-CHO} \xrightarrow[\text{Dehydration}(-H_2O)]{heat} \underset{\text{But–2–en–1–al(C)}}{CH_3-CH=CH-CHO}$$

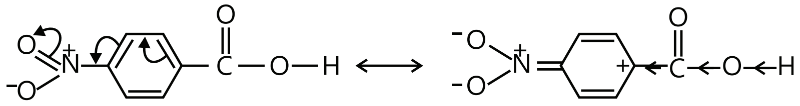
Sol: (b) (i) Higher the K_a stronger is the acid.

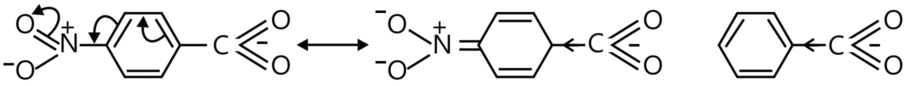
p-nitrobenzoic acid is a stronger acid than benzoic acid. This is due to the following two reasons:

I. Due to -I-and - R-effect of the $–NO_2$ group, the electron density in the O–H bond decreases. As a result, the O–H bond becomes weak and hence p-nitrobenzoic acid more easily loses a proton than benzoic acid.

II. Due to -I and R-effect of the NO_2 group, dispersal of the-ve charge occurs and hence

p-nitrobenzoate ion becomes more stable than the benzoate ion.





p-Nitrobenzoate ion (more stable)

Benzoate ion (less stable)

(ii) This is because, the carbonyl group of Acetone easily forms Hydrogen bonds with water and hence acetone is highly soluble in water.

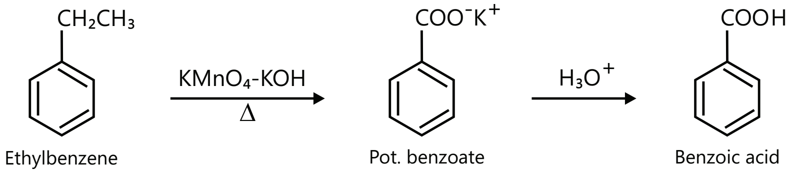
However, in Benzophenone, the phenyl groups are larger and hence C = O group cannot form hydrogen bonds with water due to steric crowding. Benzophenone is thus insoluble in water.

Example 5: Show how each of the following compounds could be converted to benzoic acid

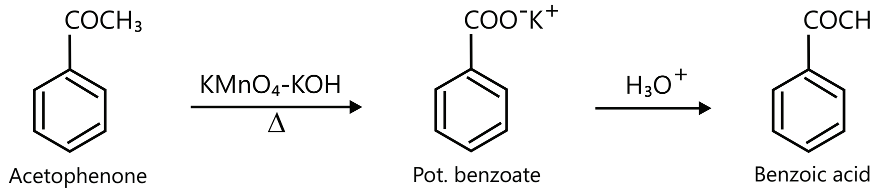
(i) Ethylbenzene (ii) Acetophenone (iii) Bromobenzene (iv) Phenylethene (Styrene)

Sol: First step is oxidation with $KMnO_4$ and KOH to for Potassium Benzoate followed by treatment. with acid.

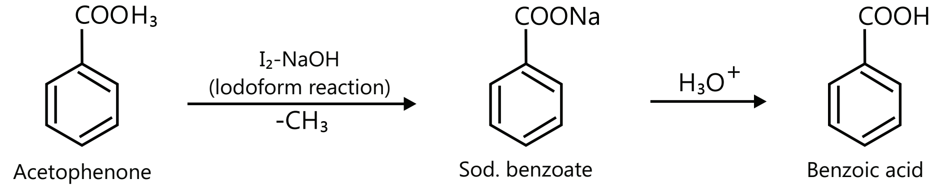
(a) This can be achieved by treating it with $KMnO_4$-KOH followed by treatment with acid.



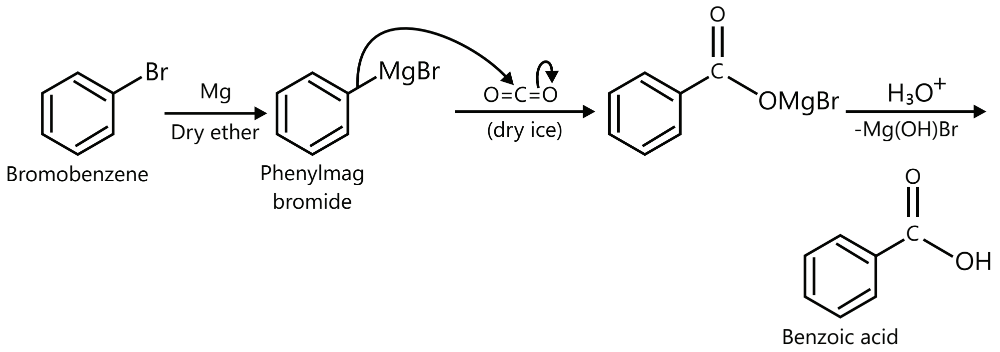
(b)



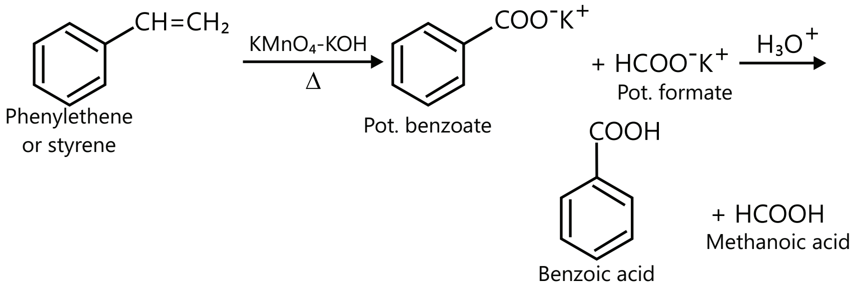
Alternatively,



(c) First of all we have to prepare the Grignard reagent. It is prepared by treating Bromobenzene with Mg in dry ether. Now this Grignard reagent is treated with dry ice followed by hydrolysis to form Benzoic acid.



(d) This can be achieved by following the same process of $KMnO_4$-KOH and acid.



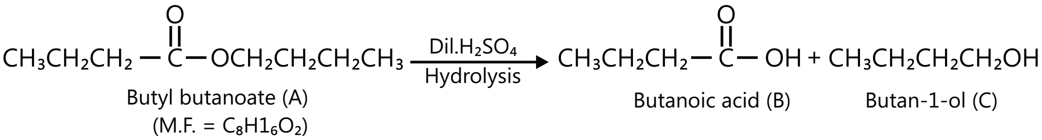
Example 6: An organic compound A (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C) Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

Sol: (i) Since the organic compound (A) on hydrolysis with dil. H_2SO_4 gives carboxylic acid (B) and the alcohol (C) therefore, (A) must be an ester. Further, since the oxidation of (C) with chromic acid produces the acid (B) therefore both the carboxylic acid (B) and the alcohol (C) must contain the same number of carbon atoms.

(ii) Since the ester (A) contains eight carbon atoms, therefore both the carboxylic acid (B) and the alcohol (C) must contain four carbon atoms each.

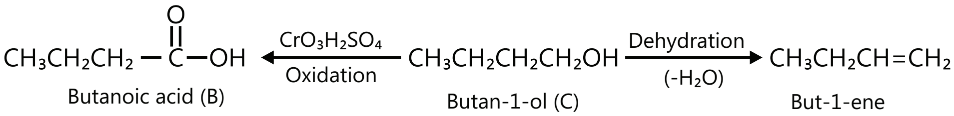
(iii) (C) on dehydration gives but-1-ene, therefore, (C) must be a straight chain alcohol. i.e. butan-1-ol.

(iv) If (C) is butan-1-ol, then acid (B) which is gives on oxidation must be butanoic acid and the ester (A) must be butyl butanoate.



$$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_2CH_2CH_3 \xrightarrow[\text{Hydrolysis}]{\text{Dil.}H_2SO_4} CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH + CH_3CH_2CH_2CH_2OH$$

Butyl butanoate (A) (M.F. = $C_8H1_6O_2$)   Butanoic acid (B)   Butan-1-ol (C)



$$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH \xleftarrow[\text{Oxidation}]{CrO_3H_2SO_4} CH_3CH_2CH_2CH_2OH \xrightarrow[(-H_2O)]{\text{Dehydration}} CH_3CH_2CH=CH_2$$

Butanoic acid (B)   Butan-1-ol (C)   But-1-ene

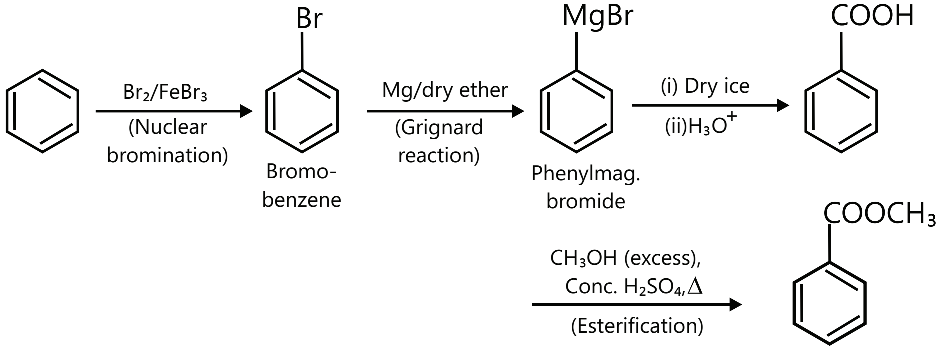
Example 7: How will you prepare the following compounds from benzene? You may use any inorganic reagent and any organic reagent having not more than one carbon atom.

(a) Methyl benzoate   (b) m-Nitrobenzoic acid   (c) p-Nitrobenzoic acid

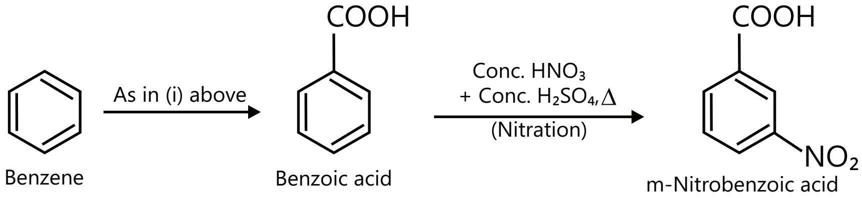
(d) phenyl acetic acid   (e) p-Nitrobenzaldehyde.

Sol:

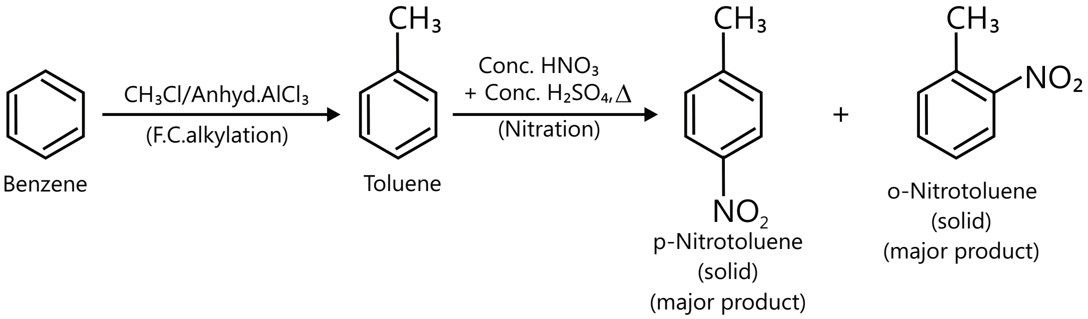
(a)

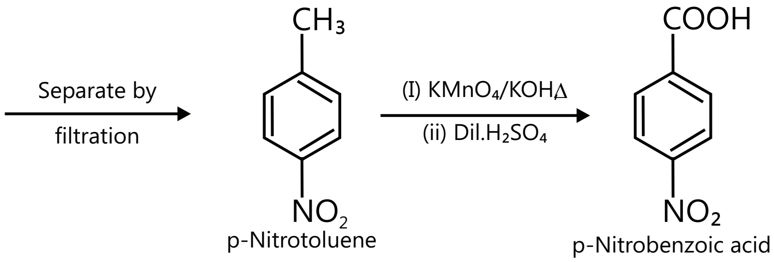


(b)

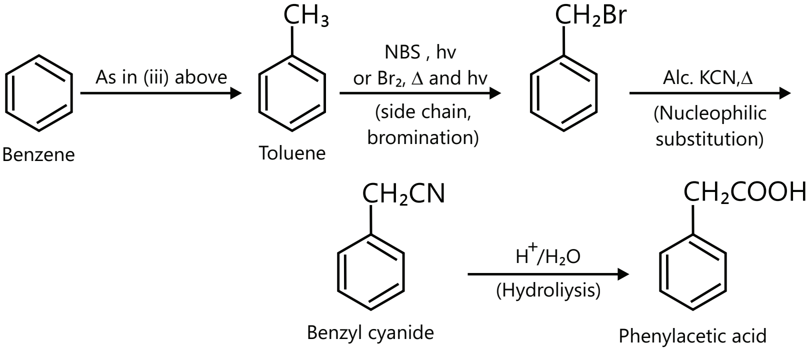


(c)

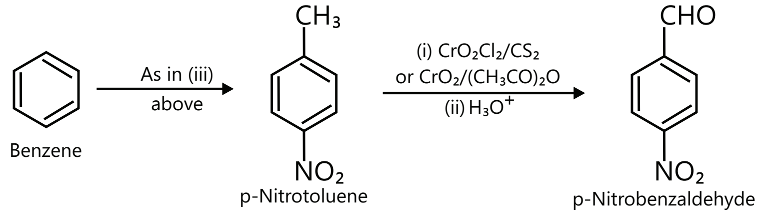




(d)

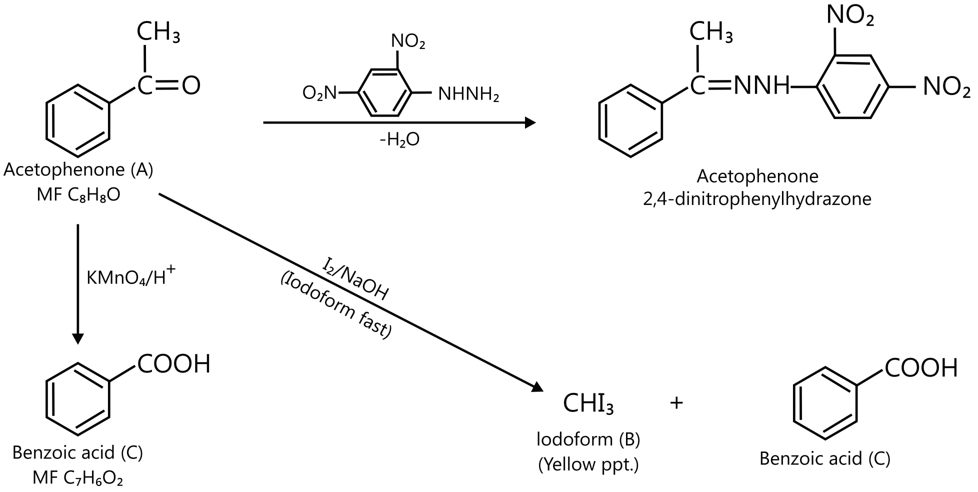


(e)



Example 8: An aromatic compound 'A' (Molecular formula C_8H_8O) gives positive 2, 4-DNP test. It gives a yellow precipitate of compound 'B' on treatment with iodine and sodium hydroxide sol. Compound 'A' does not give Tollen's or Fehling's test. On drastic oxidation with potassium permanganate is forms a carboxylic acid 'C' (Molecular formula $C_7H_6O_2$), which is also formed along with the yellow compound in the above reaction, Identify A, B and C and all the reaction involved.

Sol: (i) From the given data we can see that aromatic compound 'A' (MFC_8H_8O) gives positive 2, 4-DNP test, thus it must be an aldehyde or a ketone.



(ii) As compound 'A' does not give Tollen's test or Fehling's test, thus 'A' must be a ketone.

(iii) Compound 'A' on treatment with I_2/NaOH, gives yellow precipitate of compound 'B' therefore, compound 'B' must be iodoform and the ketone A' must be a methyl Ketone (Haloform reaction)

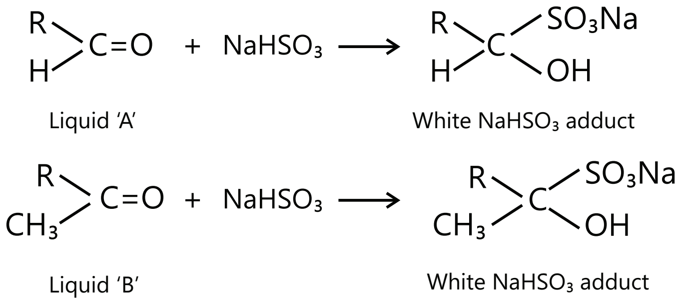
(iv) Since methyl ketone 'A' on drastic oxidation with $KMnO_4$ gives a carboxylic acid 'C' (MF$C_7H_6O_2$), therefore, 'C' must be benzoic acid and compound 'A' must be acetophonenone ($C_6H_5COCH_3$).

Example 9: When liquid 'A' is treated a freshly prepared ammonical silver nitrate sol, it gives bright silver mirror. The liquid forms a white crystalline solid on treatment with sodium hydrogensulphite. Liquid 'B' also forms a white crystalline solid with sodium hydrogensulphite but it does not give test with ammoniacal silver nitrate. Which of the two liquids is the aldehyde? Write the chemical equations of these reactions as well.

Sol: (i) As we can see, liquid 'A' forms a white crystalline solid on treatment with $NaHSO_3$, thus it may be an aldehyde or a methyl ketone. And also liquid 'A' forms a bright silver mirror on treatment with a freshly prepared ammoniacal Sol of $AgNO_3$. Therefore, liquid 'A' is an aldehyde. (Aldehyde gives positive silver mirror test)

(ii) On the other side, liquid 'B' forms a white crystalline solid on treatment with $NaHSO_3$, it may be an aldehyde or a methyl ketone. But liquid 'B' shows negative test with ammoniacal $AgNO_3$ solution therefore, liquid 'B' must be a methyl ketone.

Chemical equations for the reactions discussed are



$$\underset{\text{Liquid 'A'}}{RCHO} + \underset{\text{Tollens reagent}}{2\,[Ag(NH_3)_2]^+} + 3\,OH^- \xrightarrow{\text{warm}} \underset{\text{Carboxylate ion}}{RCOO^-} + \underset{\text{Silver mirror}}{2\,Ag\downarrow} + 4\,NH_3 + 2\,H_2O$$

$$\underset{\text{Liquid 'B'}}{RCOCH_3} \xrightarrow{\text{Tollens reagent}} \text{No silver mirror}$$

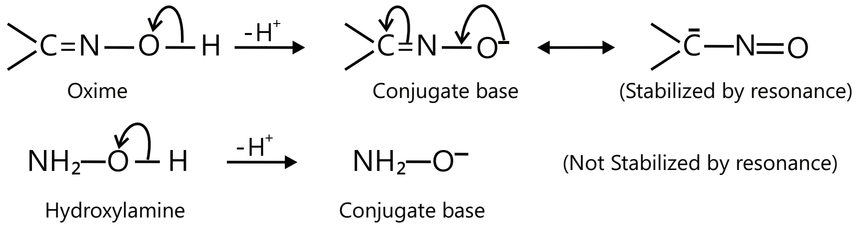
Example 10: Give reasons for the following:

(a) Oximes are more acidic than hydroxylamines

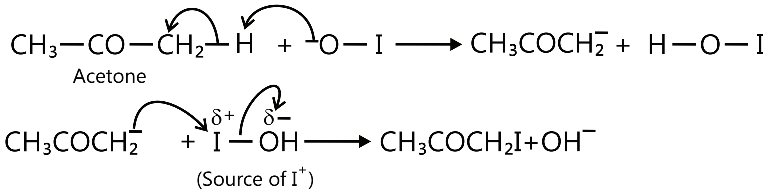
(b) Iodoform is obtained by the reaction of acetone with hypoiodite but not with the iodide ion.

(c) Oxidation of toluene to benzaldehyde with CrO_3 is carried out in presence of acetic anhydride and not in presence of H_2SO_4.

Sol: (a) In case of oxime, on proton loss it gives a conjugate base which is stabilized by resonance but the conjugate base of NH_2OH is not.



(b) During the course of reaction, I^+ is required which is supplied by IO^- ion but not by I^- ion thus iodide ion is not used. The reaction is as shown below:



$$CH_3COCH_2I \xrightarrow[-OH^-]{+IO^-} CH_3COCHI_2 \xrightarrow[-OH^-]{+IO^-} \underset{\text{1, 1, 1, -Tri-iodoacetone}}{CH_3COCI_3} \xrightarrow{OH^-} \underset{\text{Iodoform}}{CH_3I} + \underset{\text{Acetate ion}}{CH_3COO^-}$$

(c) This is because CrO_3/H_2SO_4 is a powerful oxidizing agent. During the oxidation of toluene with CrO_3/H_2SO_4 the intermediate benzaldehyde formed readily undergoes oxidation to form benzoic acid due to the presence of H_2O in H_2SO_4.

$$\underset{\text{Toluene}}{C_6H_5-CH_3} \xrightarrow[\Delta]{CrO_3/H_2SO_4} \underset{\text{Benzaldehyde}}{C_6H_5-CHO} \xrightarrow{H_2O} \underset{\text{Benzaldehyde hydrate}}{C_6H_5CH(OH)_2} \xrightarrow{CrO_3/H_2SO_4} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

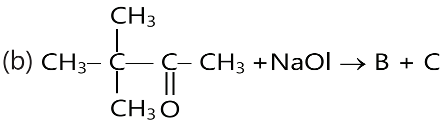
However, with CrO_3 in $(CH_3CO)_2$ O, due to the absence of H_2O as soon as benzaldehyde is formed, it reacts with acetic anhydride to form benzylidene diacetate which does not undergo further oxidation. In this way, oxidation of benzaldehyde to benzoic acid is prevented. The gem-diacetate this formed upon subsequent hydrolysis with alkali or acid gives benzaldehyde.

$$\underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[273\text{-}283\text{ K}]{CrO_3\text{-}(CH_3CO)_2O} \underset{\substack{\text{Benzylidene diacetate}\\ \text{(gem-diacetate)}}}{C_6H_5CH(OCOCH_3)_2} \xrightarrow[\text{(Hydrolysis)}]{H_3O^+,\Delta} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$

JEE Advanced/Boards

Example 1: Complete the following reaction by identifying (A), (B) and (C)

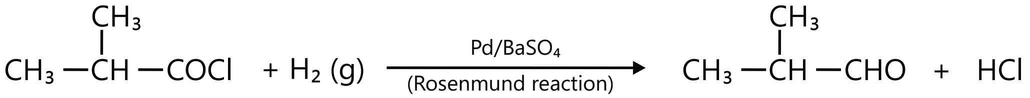
(a) $A + H_2(g) \xrightarrow{Pd/BaSO_4} (CH_3)_2CH-CHO$



(b) $CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-\underset{\underset{\large O}{||}}{C}-CH_3 + NaOI \rightarrow B + C$

Sol: (a) This is a well-known Rosenmund reduction reaction. The catalyst used is palladium poisoned with $BaSO_4$ supported on carbon.

The reagent is specific and acts only upon acid chloride group. Since acid chlorides on Rosenmund reduction give aldehydes, therefore, compound (A) must be an acid chloride, $(CH_3)_2CH–COCl$

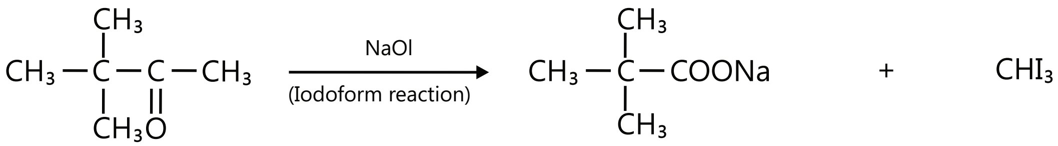


$$CH_3-\overset{\overset{\large CH_3}{|}}{CH}-COCl + H_2(g) \xrightarrow[\text{(Rosenmund reaction)}]{Pd/BaSO_4} CH_3-\overset{\overset{\large CH_3}{|}}{CH}-CHO + HCl$$

2-Methylpropanoyl chloride (A)

2-Methylpropanal

(b) This is an example of an Iodoform reaction. A Ketone containing methyl group undergoes this reaction. This method is used to identify methyl ketone specifically. Yellow precipitate of Iodoform confirms the presence of a methyl group. Methyl ketone on oxidation with NaOI (I_2 + NaOH) gives iodoform and the sodium salt of the acid. Thus,



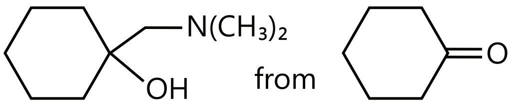
$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-\underset{\underset{\large O}{||}}{C}-CH_3 \xrightarrow[\text{(Iodoform reaction)}]{NaOI} CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-COONa + CHI_3$$

3,3-Dimethylbutan-2-one

Sod. 2, 2-dimethylpropanoate (B)

Iodoform (C)

Example 2: Suggest a sequence of reactions to carry out the following transformation, but one intermediate must be an alkene.



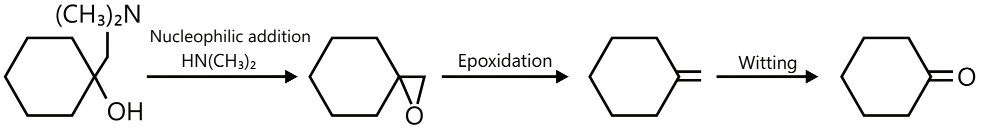
Sol: Here we can apply new approach for the following transformation. i.e Retrosynthesis. This is achieved by transforming a target molecule into simpler precursor structures without assumptions regarding starting materials.

There are many alkene reactions, so this is really not a significant restriction. The starting compound ketone suggests that a Wittig route might be possible

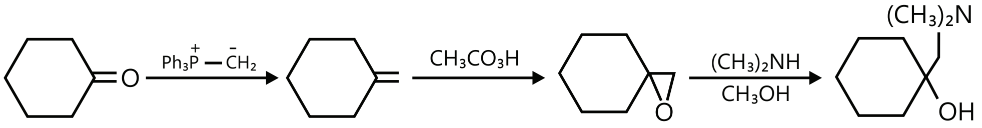
Retro synthesis:

1. First locate the Bond which has been broken to form the end product.
2. Presence of two alkyl group and OH outside the Cyclohexane shows that it must be an Epoxy group.
3. Nucleophilic addition of $(CH_3)_2NH$ open ups the ring.
4. Now we all know Epoxide is formed from a double bond so there must be a double bond outside the cyclohexane ring. (We have satisfied the demand of the question that transformation should contains one alkene intermediate.)
5. As our starting material is a carbonyl group we can easily convert it into an alkene by a well-known wittig reaction.
6. The Retrosynthetic approach for the above transformation can be written in form of reaction as follows:

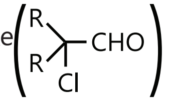
Retrosynthesis:



Forward direction:



Example 3: Explain:

(a) α-Halocarbonyl compounds, even the 3° types like  , do not undergo S_N1 reaction.

(b) Which is more reactive: (i) PrCl or (ii) $MeCOCH_2Cl$ with NaI/acetone?

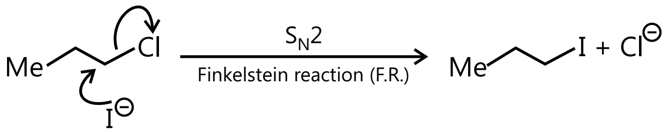
(c) Acetals and ketal are regenerated back to carbonyl, compounds with $H_3O^{\oplus}$ but not with $\bar{O}H$.

(d) Cyclohexanone is more reactive than cyclopentanonone with HCN.

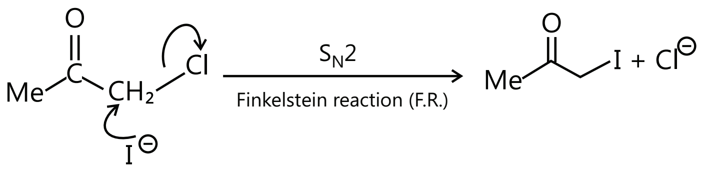
Sol: (a) S_N1 reaction involves formation of Carbocation, although it contains adjacent two alkyl group the carbocation formed is unstable this is because of the presence of positive charges on adjacent C atoms.(Electron withdrawing effect of chlorine makes two alkyl group slightly electron deficient)

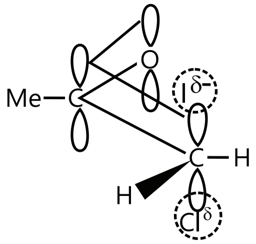
(b) Both are Primary alkyl halide and undergo S_N2 (Substitution nucleophilic bimolecular) reaction. Orde of reactivity is (ii) >> (i).

The high reactivity of (ii) in S_N2 reaction is due to the stabilizing effect produced in the transition state of ketone by the overlap of adjacent π-bond with the p-orbital of the sp^2-hybridised C atom. This type of overlap is also responsible for the high reactivity of halides in S_N2 reaction.

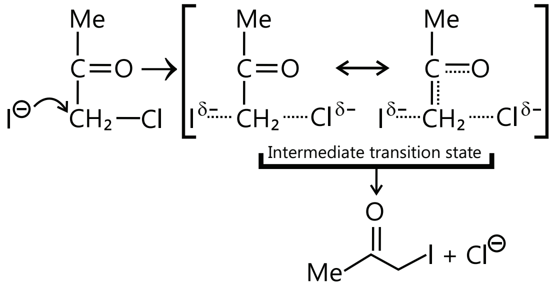
i. 

ii.





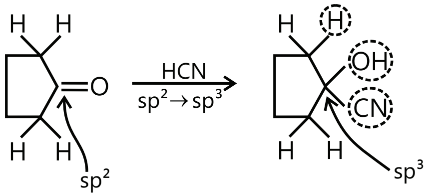
(Orbital diagram of the intermediate transition state of the ketone)



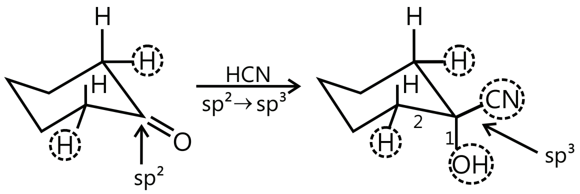
(c) The formation of hemiacetal or half hydrate takes place in acid only. OH^- is a weaker base than OR^- It's not possible in base because a weaker base (OH^-) cannot displace stronger base (RO^-). But the formation of acetal from hemiacetal can take place by both acid and base. So the reverse process of hemiacetal to (C=O) compound can occur only with acid but not with base.

(d) (i) Cyclopentanone suffers from ring strain. In Cyclopentanone, the hybridization of C atom of (C=O) group changes from $sp^2 \rightarrow sp^3$, and the adjacent hydrogen atoms are in eclipsed position which increases the strain due to eclipsing interaction.

(ii) In cyclohexanone, the hybridization of C atom of (C=O) group changes from $sp^2 \rightarrow sp^3$, the ring is free from strain and after nucleophilic addition, all the adjacent H and OH atoms are in staggered position hence destabilization effect is lost as there no eclipsing interaction.



All adjacent H atoms are in eclipsed position : more strained and high energy.



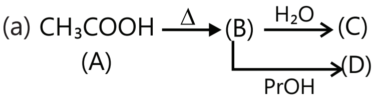
(Initially (C=O) is in eclipsed position with the adjacent equatorial H atoms)

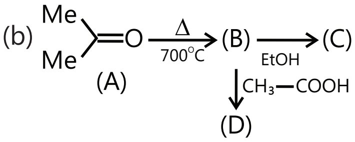
(All adjacent H atoms and (OH) are in staggered position)

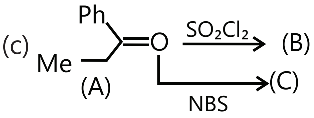
(No eclipsing interaction)
(More stable)

(High energy eclipsing interaction
(Less stable))

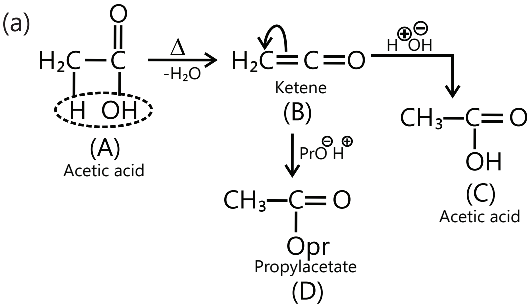
Example 4: Complete the following reaction

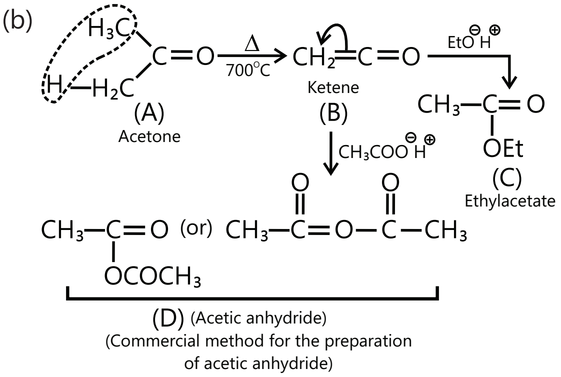




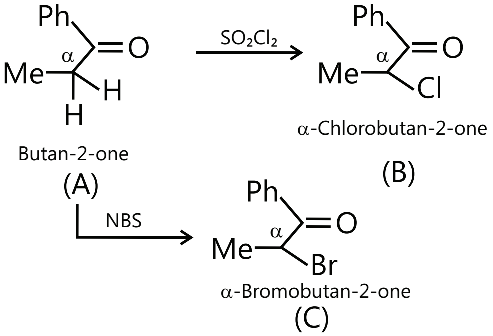


Sol: The formation of (B) in both (a) and (b) is industrial method for the preparation of ketone .

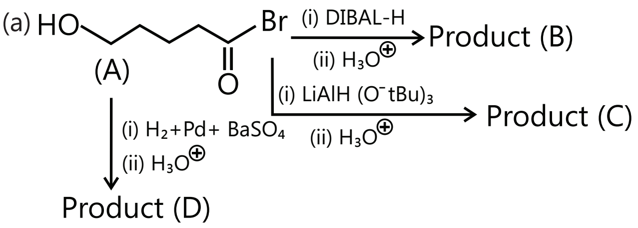




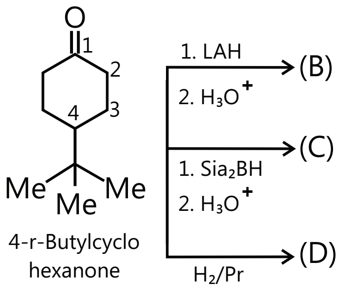
(c) Halogenation occurs at the α-position of the (C=O) group, via free radical mechanism. NBS (N-Bromosuccinimide) is commonly used brominating agent.



Example 5: Complete the following reactions:



(b) Give the major products of the following

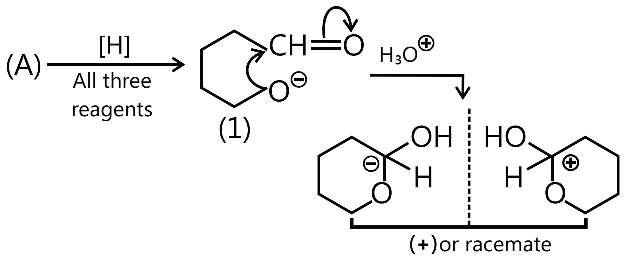


4-r-Butylcyclo hexanone

Sol: (a) After looking at the question you will notice that all the three reagents, namely, DIBAL-H, LiAlH (O-t-But)$_3$, and (H_2+Pd +$BaSO_4$) (Rosenmund reduction) are reducing agents.

Thus they will reduce the acid halides to aldehydes.

The products (B), (C), and (D) are same Hydroxyl aldehydes than undergo intramolecular reaction to give cyclic hemiacetal. On reduction with all three reagents give (I) Hydroxyaldehyde anion, which undergoes ring closure. A chiral center is formed during the ring closure reaction and as a result, two enantiomer forms are obtained and the product is a racemic mixture. (Optically inactive)

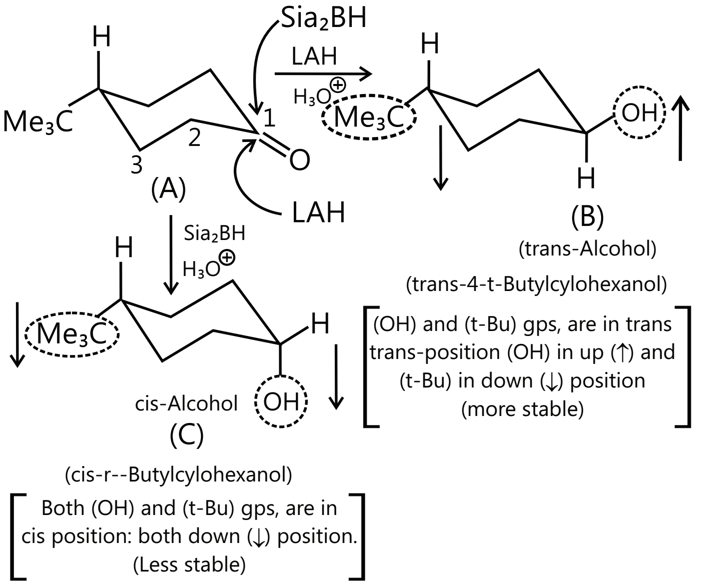


(b) Bulky-1-butyl group always occupies less hindered equatorial in cyclohexane.

(i) Sia$_2$BH is a bulky group. Thus it approaches (C=O) from the less hindered equatorial side, pushing (OH) to axial position which result in the formation of less stable cis-isomer.

(ii) Less bulky LAH approaches (C=O) from the more hindered axial side, pushing (OH) to equatorial position. Resulting in the more stable trans-isomer.

(iii) With H_2+Pt : Cis-alcohol is formed in major amount, because H_2 is adsorbed on the surface of a finely divided catalyst, and H approaches from the less hindered equatorial side and gives cis-alcohol as in (i)



(trans-Alcohol)

(trans-4-t-Butylcylohexanol)

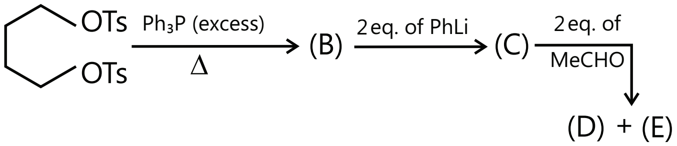
[(OH) and (t-Bu) gps, are in trans trans-position (OH) in up (↑) and (t-Bu) in down (↓) position (more stable)]

(cis-r--Butylcylohexanol)

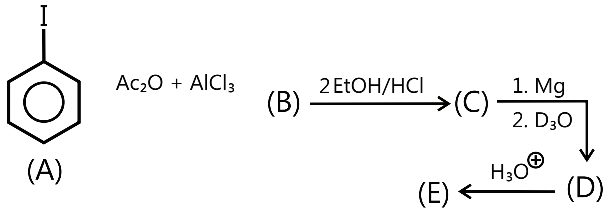
[Both (OH) and (t-Bu) gps, are in cis position: both down (↓) position. (Less stable)]

Example 6: Complete the following reactions:

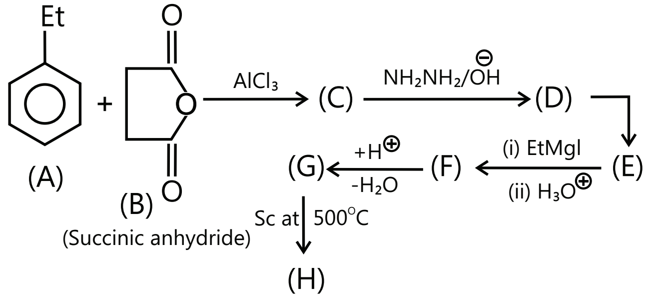
(a)



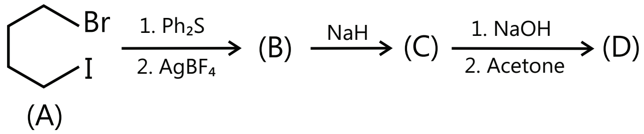
(b)



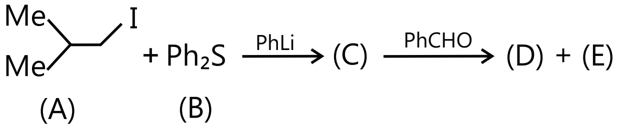
(c)



(d)

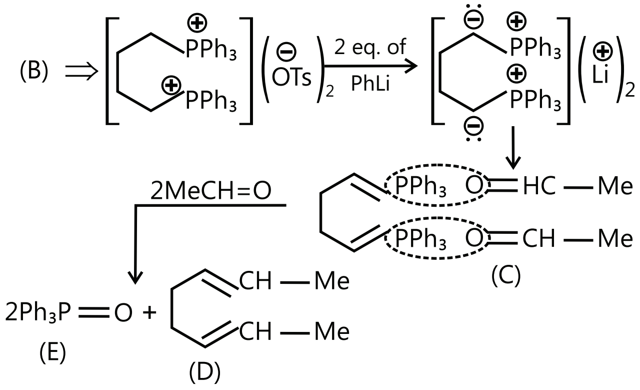


(e)

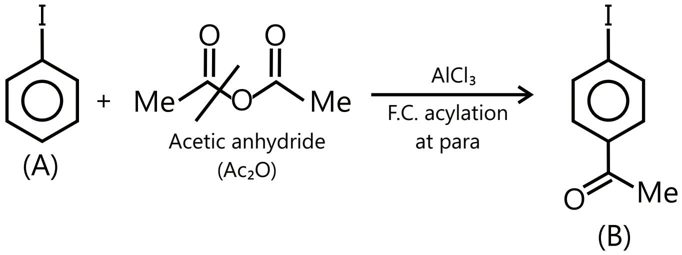


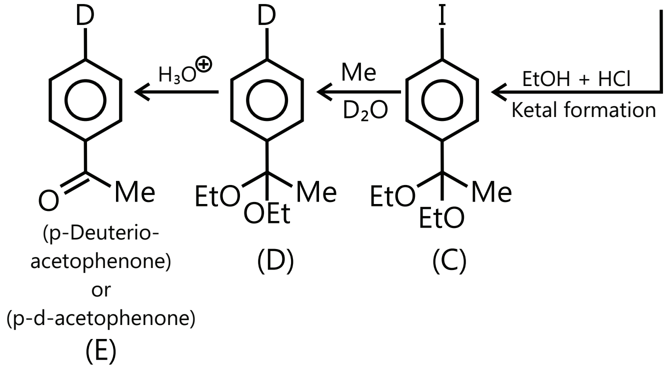
Sol:

(a)

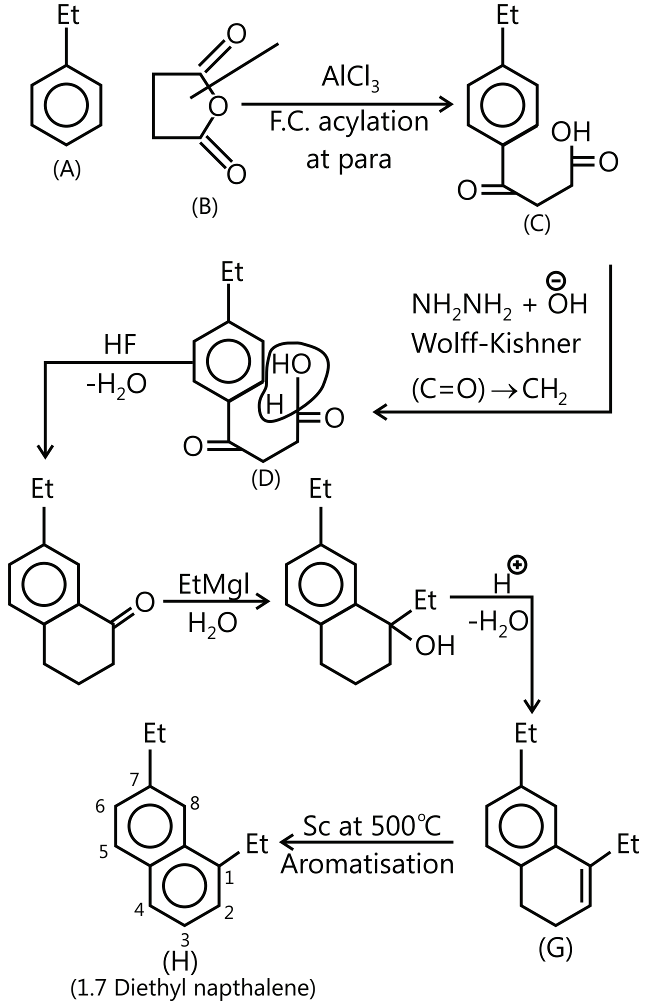


(b)

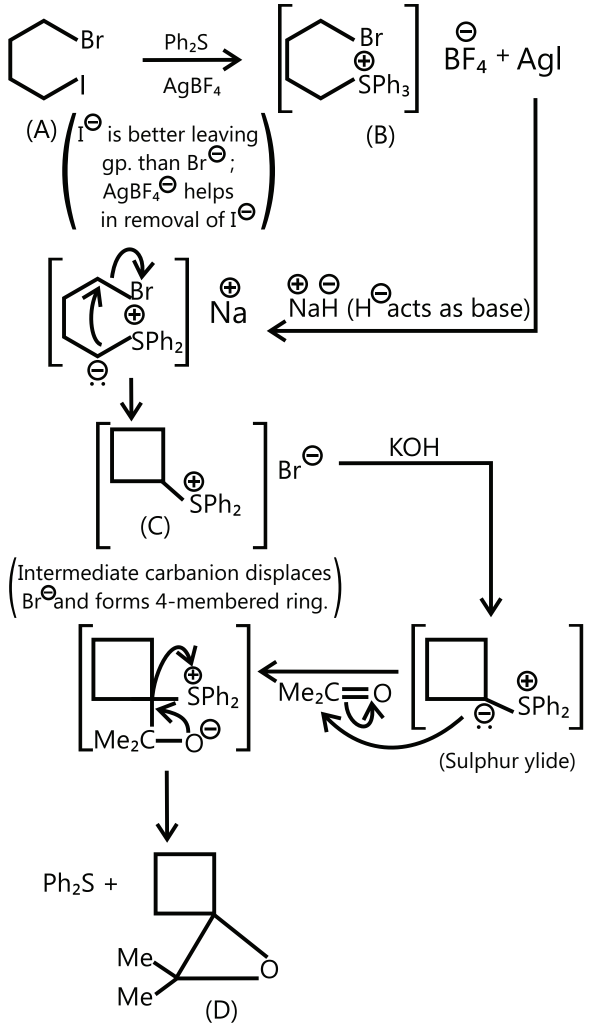




(c) First step is Friedal craft acylation that takes place at para position followed by Wolf kishner reduction. Further steps involved are Grignard reaction and aromatization.

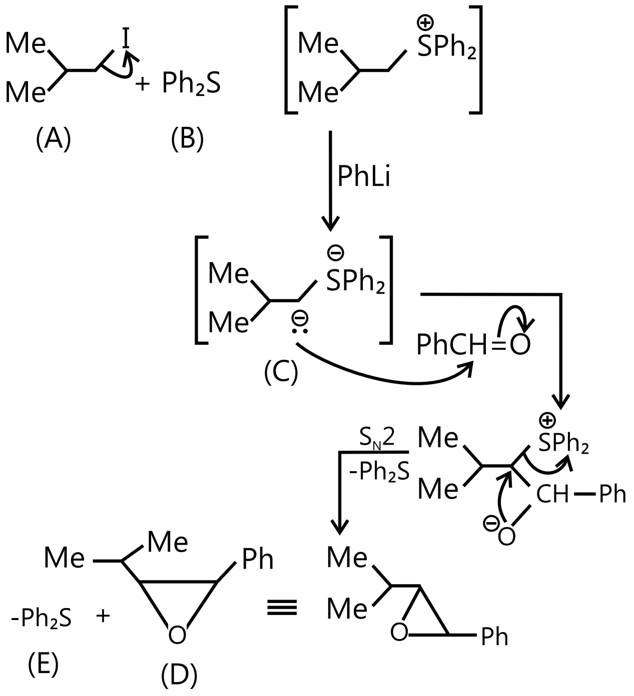


(d) It is a Wittig type reaction and proceeds via-sulphur ylide. Dihalide compound is treated with Ph_2S in $AgBF_4$ Followed by the treatment with a strong base to form Witting reagent. Now this Wittig reagent when treated with KOH forms sulphurylide which reacts with carbonyl compound to form a Spiro compound.



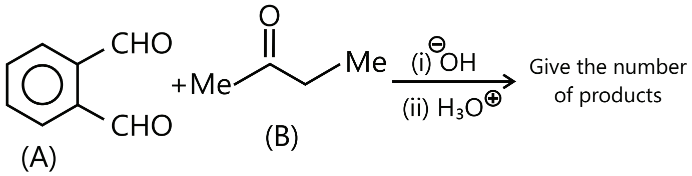
(Spiro compound) (Spiranyl epoxide)

(e) It is a Wittig type reaction and proceeds via sulphur ylide, the product formed is a substituted epoxide ring.

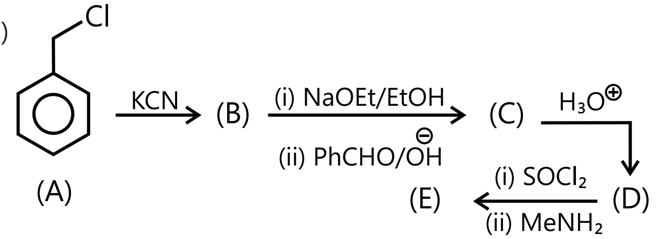


Example 7: Complete the following reactions:

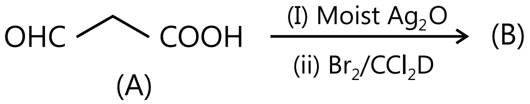
(a)



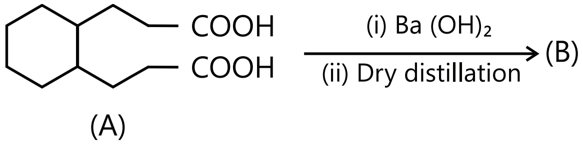
(b)



(c)



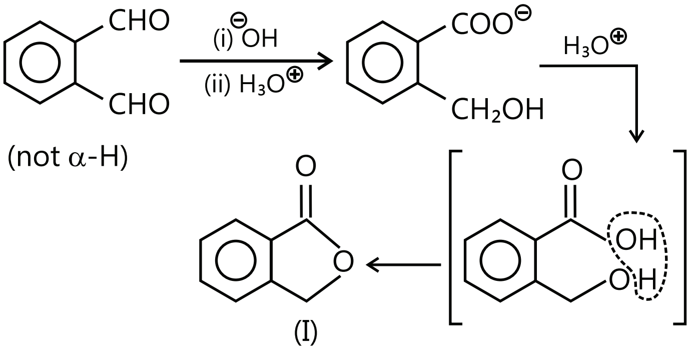
(d)



Sol: (a) In this reaction, 4 products are possible.

First of all it can undergo intermolecular Cannizzaro reactions. Other is it can undergo aldol condensation here 2 products are formed. And third is Claisen Schmidt reaction (Reaction between A and B)

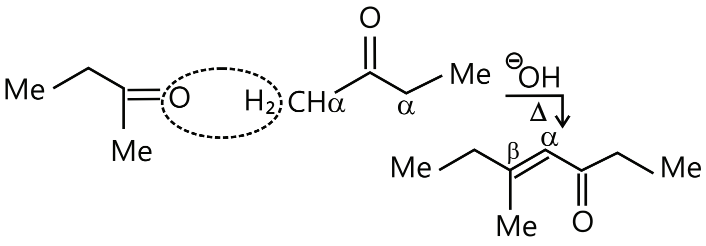
(i) Intramolecular Cannizzaro reaction of (A):



(I)

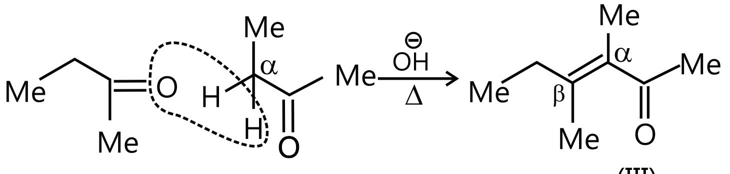
(ii) Aldol condensation of (B)

(1)



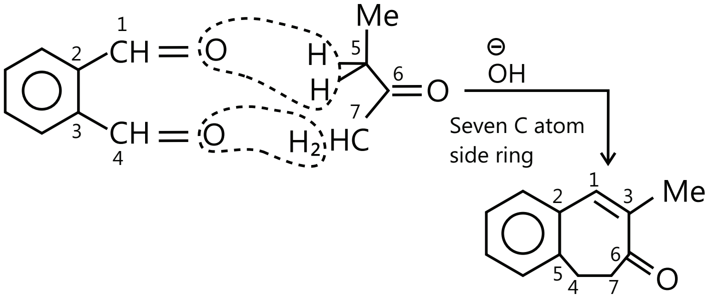
(II)

(2)



(III)

(iii)



(IV)

(Numbering in accordance with problem understanding)

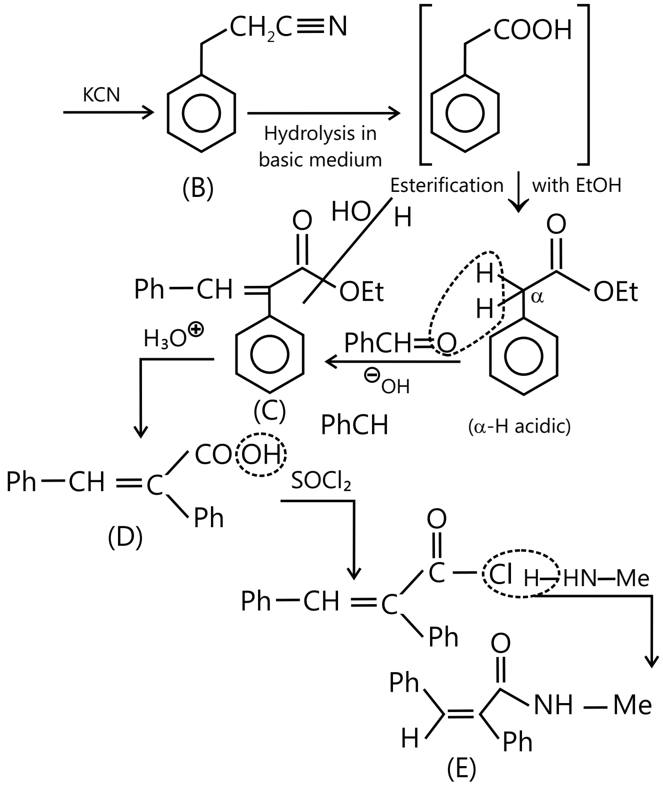
(b) (i) First step is nucleophilic substitution.

(ii) Second step is hydrolysis, thus acid is formed(CN→COOH)

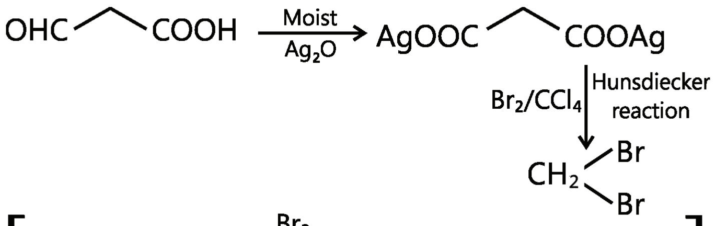
(iii) Third step is esterification using ethanol (COOH→$COOC_2H_5$)(protection of acid group)

(iv) Fourth step is Knoevenagel Condensation, product obtained is hydrolysized to obtain acid group.(Deprotection)

(v) Reaction with $SOCl_2$ produces acid chloride group which on treatment with methyl amine gives the product.

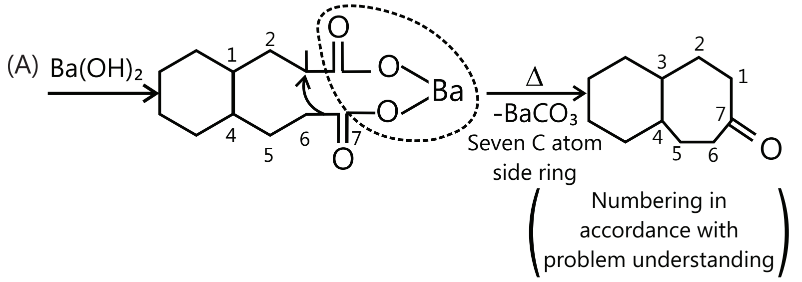


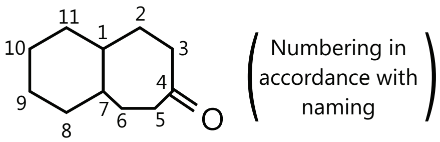
(c) Moist Ag_2O gives AgOH which acts as an oxidising agent and oxidises (–CHO) group to (–COOAg); the (COOH) group also change to (–COOAg), which then undergoes Hunsdiecker reaction.



$$\left[CH_3CH_2COOAg \xrightarrow[OCl_4]{Br_2} CH_3CH_2Br + CO_2 + AgBr\right]$$

(d) First step is a simple acid base neutralization reaction forming a salt of Ba which on heating gives off $BaCO_3$ and bicyclic ketone as a final product.

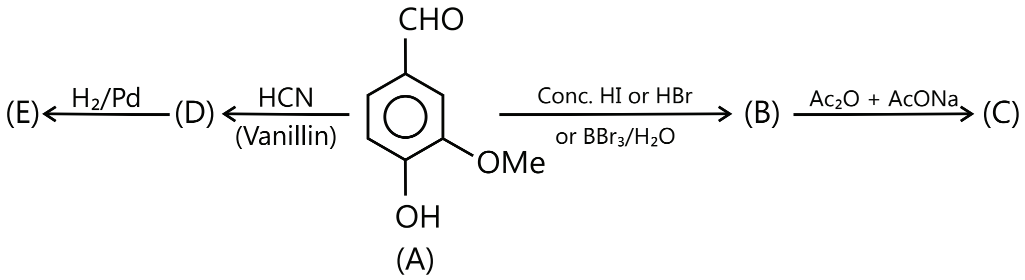




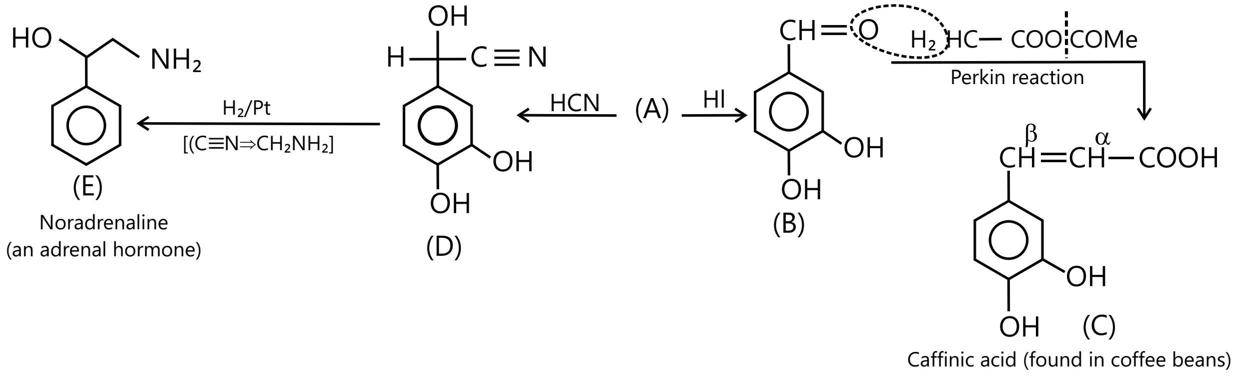
(Bicyelo-[5.4.0] undecan-4-one)

(B)

Example 8: Complete the following reaction:



Sol:



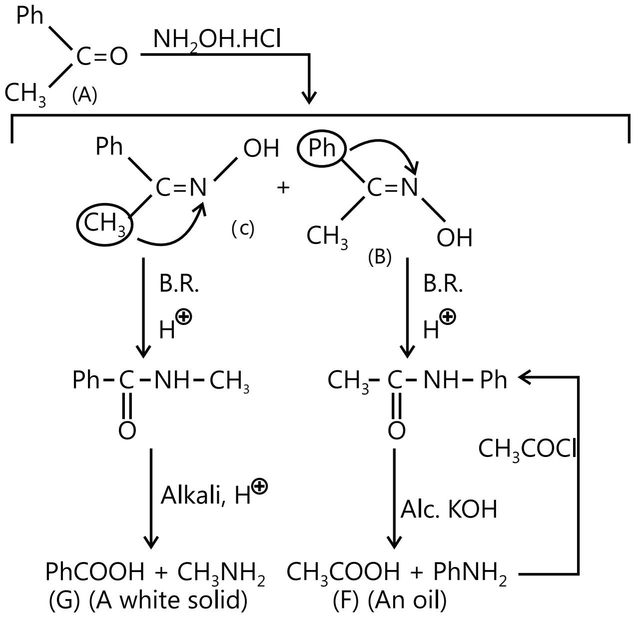
Example 9: (A) $(C_8H_8O) \xrightarrow{NH_2OH,HCl} (B) + (C) \xrightarrow[\text{Rearrangement}]{H^{\oplus}}$ (D) + (E)

(B,C,D, E all are isomers of C_8H_9NO)

(D) $\xrightarrow[\text{Alc.KOH}]{\text{Boiled with}}$ An oil (F) $(C_6H_7N) \xrightarrow{CH_3COCl}$ (D)

(E) $\xrightarrow[\text{(ii) } H^{\oplus}]{\text{(i) Alkali}}$ (G) $(C_7H_6O_2)$ A white solid

Sol: Degree of unsaturation = 5° (aromatic and ketone), i.e. Beckmann rearrangement



Example 10: Complete the following:

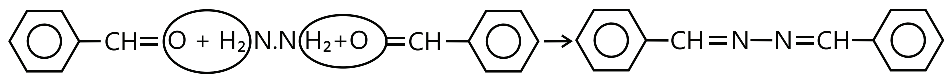
(a) $2PhCHO + NH_2NH_2 \rightarrow$

(b) Reduction of PhCHO with the following

(i) Tollens reagent (ii) Zn/HCl (iii) LAH (iv) Clemmensen's reduction (Zn (Hg)/conc. HCl)

(v) Wolff-Kishner reduction (NH_2NH_2 + Glycol + $\overset{-}{O}H$) vi. Two moles of PhCHO with Zn+HCl

Sol: (a)



Benzylidenazine (A)

(b) (i) with Tollen's regent, it will form PhCOOH

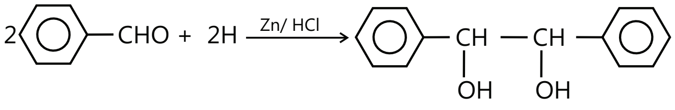
(ii) Zn/HCl is a reducing agent so it will reduce the aldehyde in to primary alcohol, i.e. $PhCH_2OH$

(iii) LAH is also a reducing agent thus it will form the same product, i.e. $PhCH_2OH$

(iv) and (v) Wolf kishner reduction and Clemensen's reduction-It will reduce the carbonyl group ($CHO \rightarrow CH_2$)

Thus hydrocarbon will be formed. i.e $PhCH_3$

(vi) A pinacol will be formed.



(Pinacol) (Hydrobenzoin)

JEE Main/Boards

Exercise 1

Q.1 Explain Knovengeal Reaction with mechanism?

Q.2 Which of the following compounds would undergo aldol condensation, which the Cannizzaro reaction and which neither? Write the structures of the expected products of aldol condensation and Cannizzaro reaction.

(i) Methanal (ii) 2-Methylpentanal

(iii) Benzaldehyde (iv) Benzophenone

(v) Cyclohexanone (vi) 1-Phenylpropanone

(vii) Phenylacetaldehyde

(viii) Butan-1-ol

(ix) 2,2-Dimethylbutanal

Q.3 How will you convert ethanal into the following compounds?

(i) Butane-1, 3-diol (ii) But-2-enal

(iii) But-2-enoic acid

Q.4 Write structural formulas and names of four possible aldol condensation products from propanal and butanal. In each case, indicate whichaldehyde acts as nucleophile and which as electrophile.

Q.5 An organic compound with the molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identity the compound.

Q.6 Describe the following reactions

(i) Cannizzaro's reaction

(ii) Cross aldol reaction

Q.7 Give chemical tests to distinguish between

(i) Acetaldehyde and Benzaldehyde

(ii) Propanone and propanol.

Q.8 Write the names of the reagents and equations in the conversion of

(i) Phenol to salicylaldehyde.

(ii) Anisole to p -methoxyacetophenone.

Q.9 Write one chemical reaction each to exemplify the following

(i) Rosenmund reduction (ii) Tollens' reagent

Q.10 Explain Pinacole-Pinacolone Rearrangement?

Q.11 Write reactions for obtaining

(i) Acetone from acetic acid.

(ii) Benzene from toluene.

Q.12 a) How will you obtain an aldehyde by using following process

(i) Dehydrogenation (ii) Catalytic hydrogenation?

b) (i) Why do aldehydes behave like polar compounds?

(ii) Why do aldehydes have lower boiling point than corresponding alcohols?

Q.13 Explain witting reaction with mechanism?

Q.14 Convert:

(i) Acetaldehyde to Acetone

(ii) Acetone to Acetylene

Q.15 An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-I-ene. Write equations for the reactions involved.

Q.16 Give simple chemical tests to distinguish between the following pairs of compounds.

(i) Propanol and Propanone

(ii) Acetophenone and Benzophenone

(iii) Phenol and Benzoic acid

Q.17 How will you bring about the following conversions in not more than two steps?

(i) Propanone to Propene

(ii) Ethanol to 3-Hydroxybutanal

(iii) Benzaldehyde to Benzophenone

Q.18 Give possible explaination for each of the following:

(i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6-trimethylcyclohexanone does not.

(ii) There are two -NH; groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

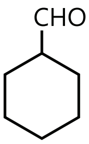
Q.19 An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acid. Write the possible structure of the compound.

Q.20 Write the difference between aldol condensation and cannizzaro reaction.

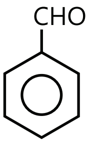
Q.21 A compound with molecular formula $C_8H_{18}O_4$ does not give litmus test and does not give color with 2, 4-DNP. It reacts with excess MeCOCl to give a compound whose vapour density is 131. Compound A contains how many hydroxy groups?

Q.22 Which of the following compounds will give Fehling's test positive?

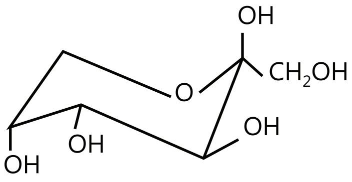
(i)



(ii)

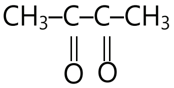


(iii)



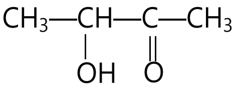
(iv) HCOOH

(v)



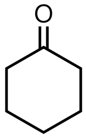
$CH_3-\underset{\|}{\underset{O}{C}}-\underset{\|}{\underset{O}{C}}-CH_3$

(vi)

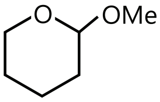


$CH_3-\underset{|}{\underset{OH}{CH}}-\underset{\|}{\underset{O}{C}}-CH_3$

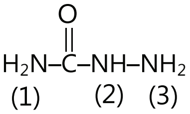
(vii)



(viii)



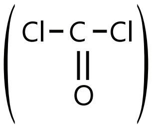
Q.23 Which of the amino group in semi carbazide will react with Ph-CH = O carbonyl group?



$\underset{(1)}{H_2N}-\overset{\overset{O}{\|}}{C}-\underset{(2)}{NH}-\underset{(3)}{NH_2}$

Q.24 How many organic products are formed in good amount in above reaction?

Q.25 How many molecules of MeMgCl will be consumed for per molecule of phosgene

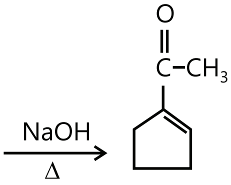


$\left(Cl-\underset{\underset{O}{\|}}{C}-Cl\right)$

Exercise 2

Single Correct Choice Type

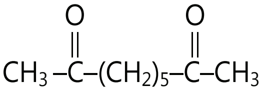
Q.1 (A)



III

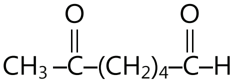
reactant (A) is

(A)



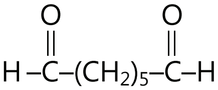
$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_5-\overset{\overset{O}{\|}}{C}-CH_3$

(B)



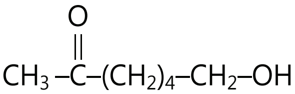
$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-H$

(C)



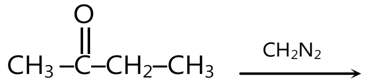
$H-\overset{\overset{O}{\|}}{C}-(CH_2)_5-\overset{\overset{O}{\|}}{C}-H$

(D)



$CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_4-CH_2-OH$

Q.2

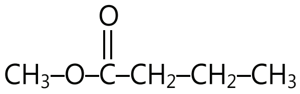


$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3 \xrightarrow{CH_2N_2}$

A(Major) $\xrightarrow{CH_3CO_3H}$ B(Major)

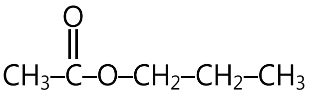
Product B is

(A)



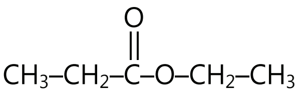
$CH_3-O-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_3$

(B)



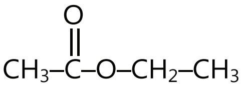
$CH_3-\overset{\overset{O}{||}}{C}-O-CH_2-CH_2-CH_3$

(C)



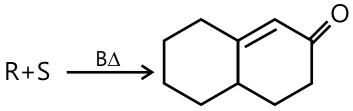
$CH_3-CH_2-\overset{\overset{O}{||}}{C}-O-CH_2-CH_3$

(D)



$CH_3-\overset{\overset{O}{||}}{C}-O-CH_2-CH_3$

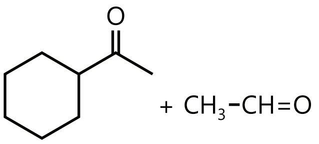
Q.3 The product Octalone is obtained by Michael addition followed by aldol condensation of reactants R and S in presence of a base. S gives positive iodoform test.



Octalone

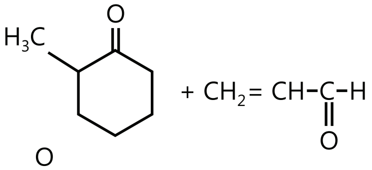
R and S respectively.

(A)



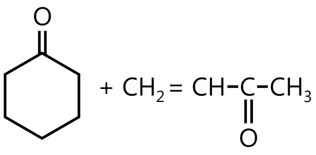
+ $CH_3-CH=O$

(B)



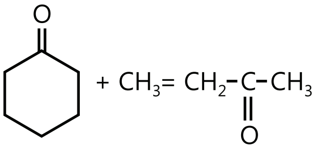
H_3C + $CH_2= CH-\underset{\underset{O}{||}}{C}-H$

(C)



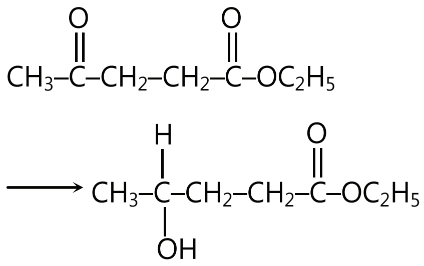
+ $CH_2= CH-\underset{\underset{O}{||}}{C}-CH_3$

(D)



+ $CH_3= CH_2-\underset{\underset{O}{||}}{C}-CH_3$

Q.4



$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-\overset{\overset{O}{||}}{C}-OC_2H_5 \longrightarrow CH_3-\underset{OH}{\overset{H}{C}}-CH_2-CH_2-\overset{\overset{O}{||}}{C}-OC_2H_5$

The conversion is carried out by using which of the following

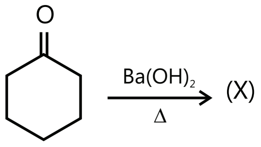
(A) $NaBH_4$ (B) $LiAlH_4$ (C) Pd/H_2 (D) Na-EtOH

Q.5 Which of the following compounds can undergo aldol condensation.

(A) Me_3C-CHO (B) PhCHO

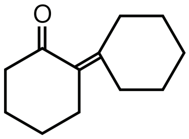
(C) MeCHO (D) HCHO

Q.6

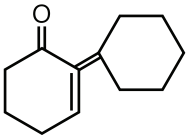


Major product (X) is

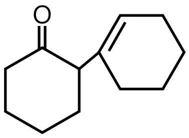
(A)



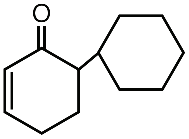
(B)



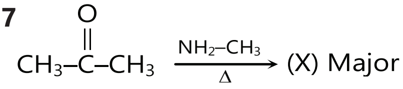
(C)



(D)



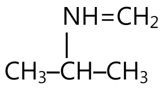
Q.7



$CH_3-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow[\Delta]{NH_2-CH_3}$ (X) Major

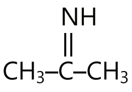
Major product (X) is

(A)



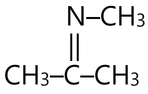
$CH_3-\overset{\overset{NH=CH_2}{|}}{CH}-CH_3$

(B)



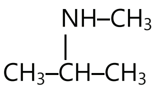
$CH_3-\overset{\overset{NH}{||}}{C}-CH_3$

(C)



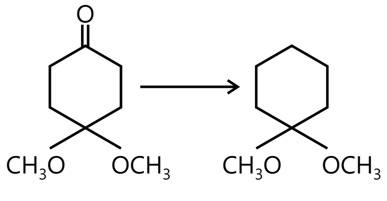
$CH_3-\overset{\overset{N-CH_3}{||}}{C}-CH_3$

(D)



$CH_3-\overset{\overset{NH-CH_3}{|}}{CH}-CH_3$

Q.8



Conversion can be achieved by

(A) Clemmenson reduction

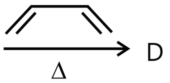
(B) Wolf-Kishner reduction

(C) $Pd/BaSO_4$

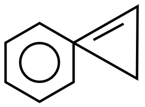
(D) Sn/HCl

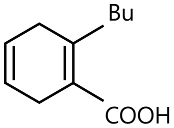
Q.9 $BuC \equiv CH \xrightarrow{LiNH_2} \xrightarrow[(ii)\ H_2O]{(i)\ PhCHO} \xrightarrow{MnO_2}$

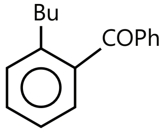
A B C

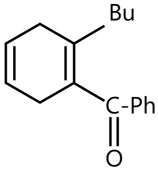


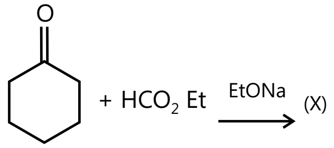
Compound D of the above reaction is -

(A)


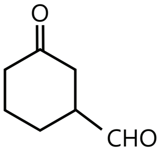
(B)


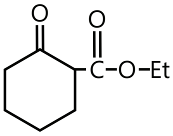
(B)


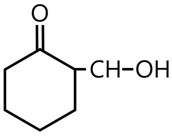
(D)


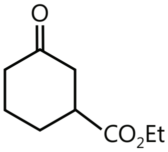
Q.10


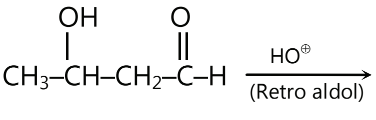
Identify unknown (X) in

(A)


(B)


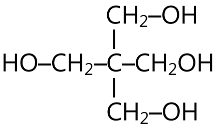
(C)


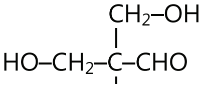
(D)


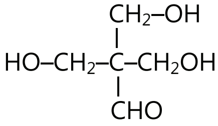
Q.11

$CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{||}{C}}-H \xrightarrow[\text{(Retro aldol)}]{HO^{\oplus}}$

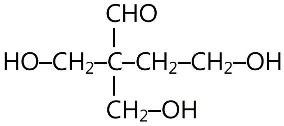
(A), $3HCHO + A \xrightarrow[40°C]{Na_2CO_3}$ (B) 82%

Product (B) of above reaction is -

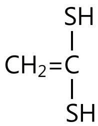
(A)

$HO-CH_2-\underset{\underset{CH_2-OH}{|}}{\overset{\overset{CH_2-OH}{|}}{C}}-CH_2OH$

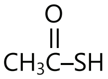
(B)

$HO-CH_2-\overset{\overset{CH_2-OH}{|}}{C}-CHO$

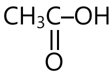
(C)

$HO-CH_2-\underset{\underset{CHO}{|}}{\overset{\overset{CH_2-OH}{|}}{C}}-CH_2OH$

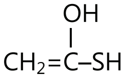
(D)

$HO-CH_2-\underset{\underset{CH_2-OH}{|}}{\overset{\overset{CHO}{|}}{C}}-CH_2-CH_2-OH$

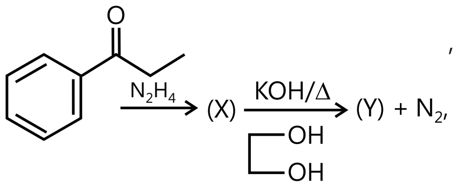
Q.12 Principal product of following reaction is isolated in form of $CH_2=C=O+H_2S \rightarrow$?

(A)

$CH_2=\underset{\underset{SH}{|}}{\overset{\overset{SH}{|}}{C}}$

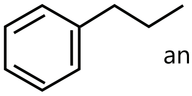
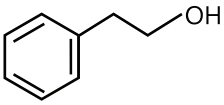
(B)

$CH_3\overset{\overset{O}{||}}{C}-SH$

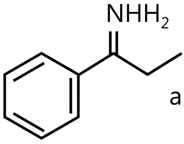
(C)

$CH_3\underset{\underset{O}{||}}{C}-OH$

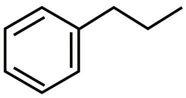
(D)

$CH_2=\overset{\overset{OH}{|}}{C}-SH$

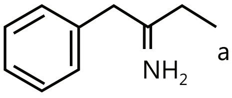
Q.13


the structures of (X) and (Y) are-

(A)

and


(B)


and


(C)


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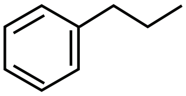
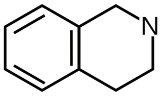
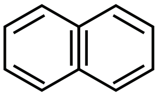
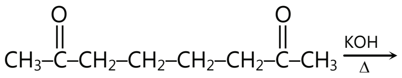
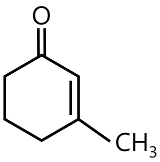


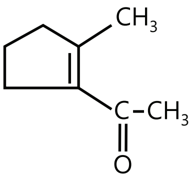
(D)


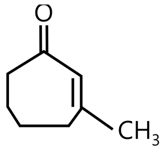
and


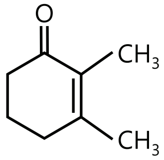
Q.14

$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow[\Delta]{KOH}$

Possible products are-

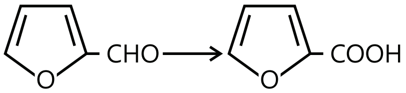
(A)


(B)


(C)


(D)


Q.15 The given reaction can not be performed by the use of which of the following reagents?



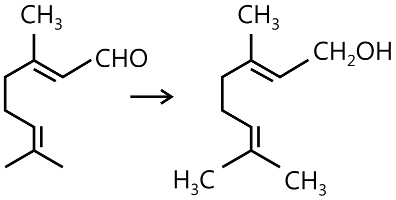
(A) $KMnO_4/H_2SO_4$

(B) $K_2Cr_2O_7/H_2SO_4$

(C) $Ag_2O/NaOH$

(D) $LiAlH_4$

Q.16 Citral can be converted into geraniol by the use of



Which reagent

(A) $H_2/Pd–C$

(B) $LiAlH_4$

(C) $H_2/Pd\text{-}BaSO_4–CaCO_3$

(D) $NaBH_4$

Previous Years' Questions

Q.1 Which of the following on heating with aqueous KOH produces acetaldehyde ***(2009)***

(A) CH_3COCl

(B) CH_3CH_2Cl

(C) CH_2ClCH_2Cl

(D) CH_3CHCl_2

Q.2 Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of ***(2011)***

(A) Two ethylenic double bonds

(B) A vinyl group

(C) An isopropyl group

(D) An acetylenic triple bond

Q.3 Trichloroacetaldehyde was subjected Cannizzaro's reaction by using NaOH. The mixture of the products contains sodium trichloroacetate ion and another compound. The other compound is ***(2001)***

(A) 2.2, 2-Trichloroethanol

(B) Trichloromethanol

(C) 2.2, 2-Trichloropropanol

(D) Chloroform

Q.4 In Cannizzaro reaction given below

$2PhCHO \xrightarrow{\bar{O}H} PhCH_2OH + PhCO_2^-$ the slowest step is ***(2009)***

(A) The attack of at the carboxyl group

(B) The transfer of hydride to the carboxylic group

(C) The abstraction of proton from the carboxylic group

(D) The deprotonation of $PhCH_2OH$

Q.5 A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives ***(2001)***

(A) Benzyl alcohol and sodium formate

(B) Sodium benzoate and methyl alcohol

(C) Sodium benzoate and sodium formate

(D) Benzyl alcohol and methyl alcohol

Q.6 Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid ***(2007)***

(A) Butanal

(B) Benzaldehyde

(C) Phenol

(D) Benzoic acid

Q.7 The increasing order of the rate of HCN addition to compounds A-D is ***(2006)***

(a) HCHO (b) CH_3COCH_3 (c) $PhCOCH_3$ (d) PhCOPh

(A) a < b < c < d

(B) d < b < c < a

(C) d < c < b < a

(D) c < d < b < a

Q.8 The pair of compounds in which both the compounds give positive test with Tollen's reagent is ***(2004)***

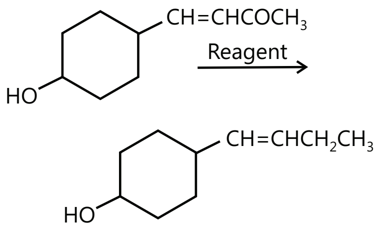
(A) Glucose and Sucrose

(B) Fructose and Sucrose

(C) Acetophenone and Hexanal

(D) Glucose and fructose

Q.9 In the given transformation which the following is the most appropriate reagent ***(2012)***



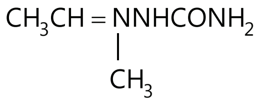
(A) $NH_2NH_2\,\bar{O}H$ (B) Zn–Hg/HCl

(C) Na, Liq, NH_3 (D) $NaBH_4$

Q.10 Compound 'A' (molecular formula C_3H_5O) is treated with acidified potassium dichromate to form a product 'B' (molecular formula C_3H_6O.) 'B' forms a shining silver mirror on warming with ammonical silver nitrate. 'B' when treated with an aqueous Sol: of $H_2NCONHNH_2$. HCl and sodium acetate gives a product 'C'. Identify the structure of 'C **(2002)**

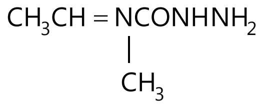
(A) $CH_3CH_2CH = NNHCONH_2$

(B)



$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H = NNHCONH_2$

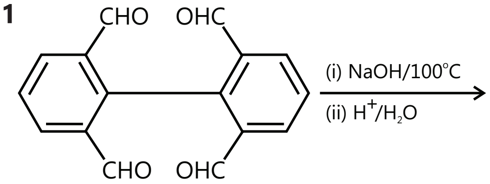
(C)



$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H = NCONHNH_2$

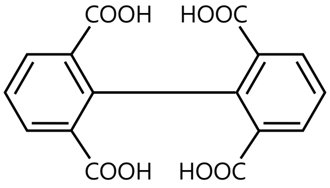
(D) $CH_3CH_2CH–NCONHNH_2$

Q.11

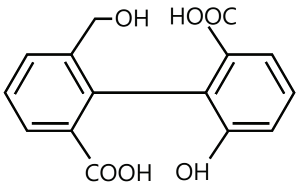


Major product is. **(2003)**

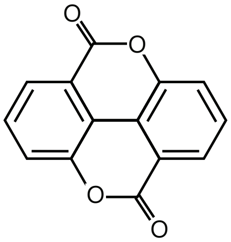
(A)



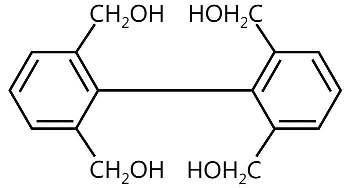
(B)



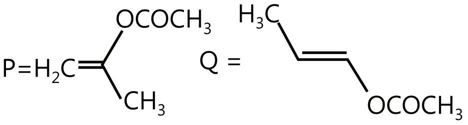
(C)



(D)



Q.12 The product of acid hydrolysis of P and Q can be distinguished by **(2003)**



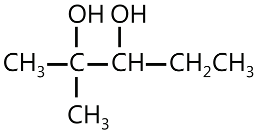
(A) Lucas Reagent (B) 2, 4-DNP

(C) Fehling's solution (D) $NaHSO_3$

Q.13 On vigorous oxidation by permanganate solution

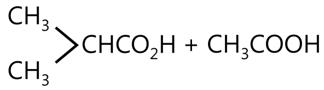
$(CH_3)_2C= CH –CH_2CH_2CH_3$ gives **(2002)**

(A)



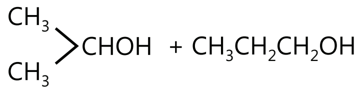
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-\overset{\displaystyle OH}{\overset{|}{C}H}-CH_2CH_3$

(B)



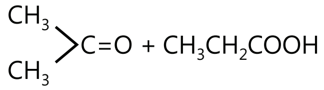
$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHCO_2H + CH_3COOH$

(C)



$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH + CH_3CH_2CH_2OH$

(D)



$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O + CH_3CH_2COOH$

Q.14 Silver Mirror test is given by which one of the following compounds **(2011)**

(A) Acetaldehyde (B) Acetone

(C) Formaldehyde (D) Benzophenone

Q.15 In the following sequence of reactions, the alkene affords the compound 'B'

$$CH_3CH = CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B.$$

The compound B is **(2008)**

(A) CH_3CH_2CHO (B) CH_3COCH_3

(C) $CH_3CH_2COCH_3$ (D) CH_3CHO

Q.16 Which of the following on heating with aqueous KOH, produces acetaldehyde? ***(2009)***

(A) CH_3COCl (B) CH_3CH_2Cl

(C) CH_2ClCH_2Cl (D) CH_3CHCl_2

Q.17 In Cannizzaro reaction given below,

$$CH_3CHCl_2 \xrightarrow{\text{aqu.KOH}} CH_3CH(OH)_2 \xrightarrow[-H_2O]{} CH_3CHO$$

the slowest step is:

$$2PhCHO \xrightarrow{\overset{(-)}{:OH}} PhCH_2OH + PhCO_2^{(-)}$$ ***(2009)***

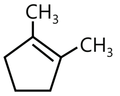
(A) The attack of OH at the carboxyl group

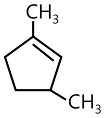
(B) The transfer of hydride to the carbonyl group

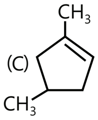
(C) The abstraction of proton from the carboxylic group

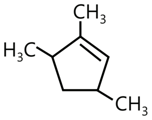
(D) The decomposition of CH_2OH

Q.18 Which compound would give 5-keto -2-methylhexanal upon ozonolysis. ***(2015)***

(A) 

(B) 

(C) 

(D) 

Q.19 Ozonolysis of an organic compound gives formaldehyde as one of the product. This confirms the presence of: ***(2011)***

(A) A vinyl group

(B) An isopropyl group

(C) An acetylenic triple bond

(D) Two ethylenic double bonds

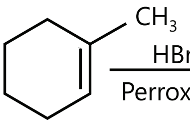
JEE Advanced/Boards

Exercise 1

Complete the following equations and identify the products A, B, C, D, E, F, G, H etc in the following reactions

Q.1 $o-HOOC-C_6H_4-CH_2-C_6H_5 \xrightarrow{SOCl}$

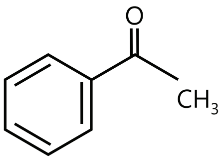
$$G \xrightarrow[AlCl_3]{\text{anhydrous}} H \xrightarrow[HCl]{Zn-Hg} I$$

Q.2 

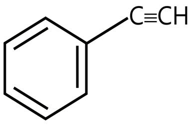
$\xrightarrow[\text{Perroxide}]{HBr}$ [E]

Q.3 $[J] \xleftarrow[H_2O]{H_2CrO_4} [I] \xrightarrow[\text{(Pyridine)}]{CrO_3} CH_3CHO$

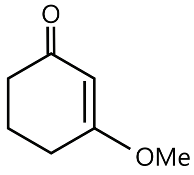
Q.4 Acetone (2mol.) $\xrightarrow{OH} [K] \xrightarrow{NaHSO_4} [L]$

Q.5 

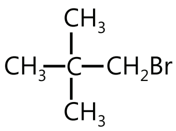
$\xrightarrow[\text{(ii) } NaBH_4]{\text{(i) } Br_2 \text{ (I equivalent)}}$

Q.6 

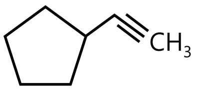
$\xrightarrow[\text{(ii) } NH_2OH]{\text{(i) } HgSO_4,\ H_3O^+}$?

Q.7 

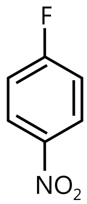
$\xrightarrow[\text{(ii) aq HCl}]{\text{(i) MeMgBr}}$?

Q.8 

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2Br \xrightarrow[\Delta]{C_2H_5OH}$

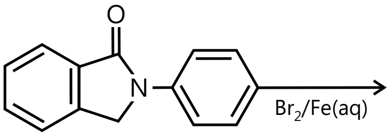
Q.9 

$\xrightarrow[\text{Lindlar Catalyst}]{H_2}$?

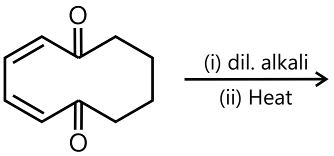
Q.10 

$\xrightarrow[\Delta]{NaOCH_3}$

Q.11

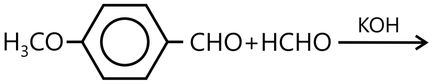


Q.12

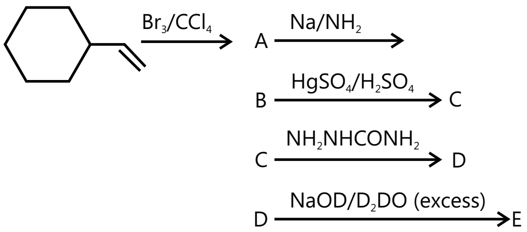


Q.13 $H_3C-CH_2-CHCl_2 \xrightarrow{\text{Boil.alkali}} ?$

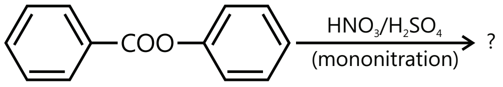
Q.14



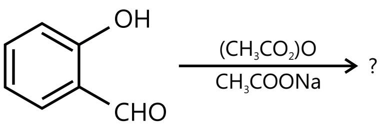
Q.15



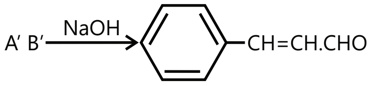
Q.16



Q.17



Q.18



Q.19 $CH_3COOH + NH_3 \longrightarrow$

$$A \xrightarrow{\text{heat}} B \xrightarrow{C} CH_3NH_2$$

Q.20 $CH_3CH_2OH \xrightarrow{(O)} A \xrightarrow{Cl_2}$

$$B \xrightarrow{\text{dil.NaOH}} CHCl_3$$

Q.21 $CH_3CH_2COOH \xrightarrow{\text{P and } Br_2} A$

$$\xrightarrow{\text{(i) alc.KOH(excess)}} B$$

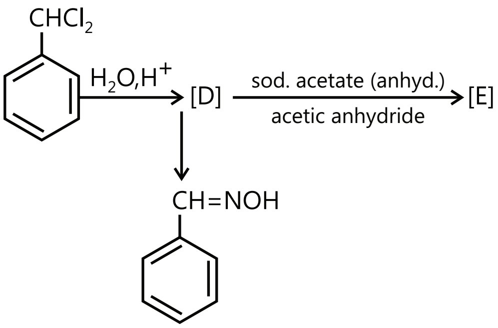
Q.22 $C_2H_5I \xrightarrow[Ag_2O]{\text{moist}} A \xrightarrow{H_2SO_4} B \xrightarrow[140°C]{C_2H_5OH} C$

Q.23 $CH_3COOH \xrightarrow{X} ClCH_2COOH \xrightarrow[NH_3]{\text{excess}} Y$

Q.24 [A] or [B] + $H_2O \xrightarrow[H_2SO_4]{HgSO_4}$

$CH_3CH_2\,COCH_3 \xrightarrow{NaOI} [C]+[D]$

Q.25 $CH_4 \xrightarrow{[A]} CH_2Br \xrightarrow[AlCl_3\text{(anhy.)}]{C_6H_5} [B] \xrightarrow{[C]}$



Q.26 Explain giving reasons

(i) Solubility of carbonyl compounds decreases with the increase in their molecular masses.

(ii) Sodium bisulphite is used for the purification of aldehydes and ketones.

(iii) Oxidation of toluene with chromium trioxide to benzaldehyde is carried out in presence of acetic anhydride.

(iv) Although aldehydes are easily oxidisable yet propanal can conveniently be prepared by the oxidation of propanol by acidic dichromate.

(v) $\overset{\overset{\displaystyle O}{\|}}{-C-}$ part of the $\overset{\overset{\displaystyle O}{\|}}{-C-OH}$ group does not react with hydroxylamine hydrochloride.

Q.27 Give Reason

(i) Me_3CCH_2COOH is more acidic than Me_3SiCH_2COOH.

(ii) The K_2 for fumaric acid is greater than for maleic acid.

(iii) Carbon oxygen bond lengths in formic acid are 1.23 Å and 1.36 Å and both the carbon oxygen bonds in sodium formate have the same value ie. 1.27 Å.

(iv) The reaction $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$ is slow in the beginning but fast subsequently)

(v) Although both > C = O and > C = C < groupings have double bond, they exhibit different types of addition reaction.

Q.28 An organic compound (A) $C_9H_{12}O$ was subjected to a series of tests in the laboratory. It was found that this compound.

(i) Rotates the plane of polarised light.

(ii) Evolves hydrogen with sodium.

(iii) Reacts with I_2 and NaOH to produce a pale yellow solid compound.

(iv) Does not react with Br_2/CCl_4.

(v) Reacts with hot $KMnO_4$ to form compound (B) $C_7H_6O_2$ which also be synthesised by the reaction of benzene and carbonyl chloride followed by hydrolysis.

(vi) Loss optical activity as a result of formation of compound (C) on being heated with HI and P.

(vii) Reacts Lucas reagent in about 5 min. Give structure of A and C with proper reasoning and draw Fischer projections for (A). Give reactions for the steps wherever possible.

Q.29 When 0.0088 g of a compound (A) was dissolved in 0.5 g of camphor, the melting point of camphor was lowered by 8°C. Analysis of (A) gave 68.18% C and 13.63% H. Compound (A) showed the following reactions:

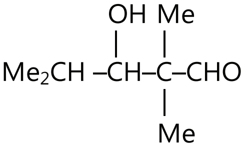
(a) It reacted with acetyl chloride and evolved hydrogen with sodium.

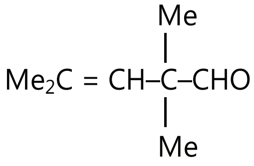
(b) When reacted with HCl + $ZnCl_2$, a dense oily layer separated out immediately. Compound (A) was passed over Al_2O_3 at 350°C to give compound (B) which on ozonolysis gives (C) and (D) which gave positive test with carbonyl reagents but only (C) gave a positive test with Fehling Sol: and resinous substance with NaOH. Identify (A), (B), (C) and (D) with proper reasoning. K_f for camphor = 40 K kg mol^{-1}.

Exercise 2

Single Correct Choice Type

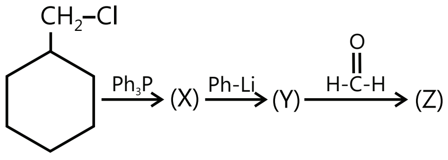
Q.1 $Me_2CH-CHO \xrightarrow[\Delta]{NaOH}$ Major products of this reaction is -

(A) 
$Me_2CH-\overset{OH}{CH}-\underset{Me}{\overset{Me}{C}}-CHO$

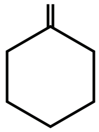
(B) 
$Me_2C=CH-\underset{Me}{\overset{Me}{C}}-CHO$

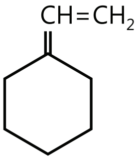
(C) Me_2CH-CH_2-OH

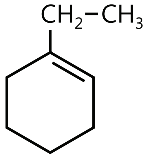
(D) $Me_2CH-COOH$

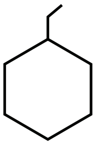
Q.2 

End product (Z) in above reaction

(A) 

(B) 

(C) 

(D) 

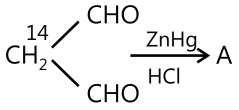
Q.3 If 3-hexanone is reacted with $NaBH_4$ followed by hydrolysis with D_2O the product will be

(A) $CH_3CH_2CH(OD)CH_2CH_2CH_3$

(B) $CH_3CH_2D(OH)CH_2CH_2CH_3$

(C) $CH_3CH_2CH(OH)CH_2CH_2CH_3$

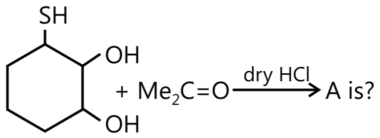
(D) $CH_3CH_2CD(OD)CH_2CH_2CH_3$

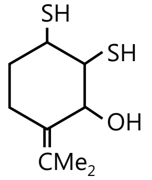
Q.4 

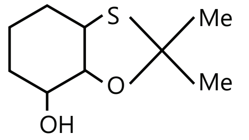
Final major product of this reaction is

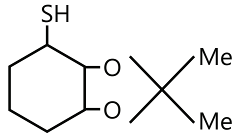
(A) $CH_3\overset{14}{CH_2}CH_3$ (B) $\overset{14}{CH_3}CH_2CH_3$

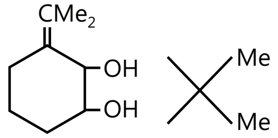
(C) $\overset{14}{CH_3}CH_2-CHO$ (D) $\overset{14}{CH_3}-CH_2-CHO$

Q.5 

(A)


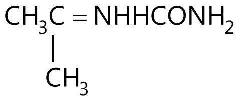
(B)


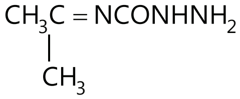
(C)


(D)


Q.6 Compound A (molecular formula C_2H_8O) is treated with acidified potassium dichromate to form a product B (molecular formula C_3H_6O). B forms a shining silver mirror on warming with ammoniacal silver nitrate, B when treated with an aqueous sol of $NH_2NHCONH_2$ and sodium acetate gives a product C.Identify the structure of C.

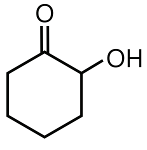
(A) $CH_3CH_2CH{=}NNHCONH_2$

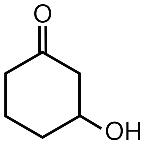
(B)

$\underset{\displaystyle CH_3}{CH_3\overset{|}{C}}=NHHCONH_2$

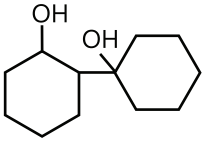
(C)

$\underset{\displaystyle CH_3}{CH_3\overset{|}{C}}=NCONHNH_2$

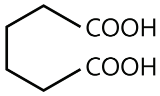
(D) $CH_2CH_2CH{=}NCONHNH_2$

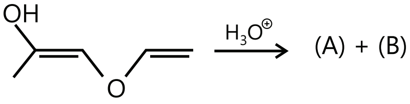
Q.7 When cyclohexanone is treated with Na_2CO_3 sol, we get

(A)


(B)


(C)


(D)


Q.8


(A) + (B) formed can be distinguished by -

(A) Iodoform (B) Fehling

(C) $NaHSO_3$ (D) 2, 4-DNP

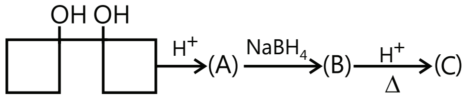
Q.9 $(X)+(Y)\xrightarrow[\text{methanol}]{NaBH_2CN}C_6H_5CH_2NHCH_2CH_3$

(A) $C_6H_5CH_2OH + C_2H_5NH_2$

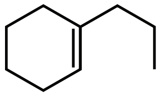
(B) $C_6H_6 + CH_3 + NH\ CH_2\ CH_3$

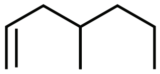
(C) $C_6H_5\ CHO{+}CH_3 + NH\ CH_2\ CH_3$

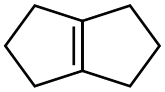
(D) $C_6H_5CHO{+}C_2H_5NH_2$

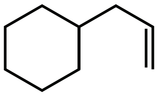
Q.10


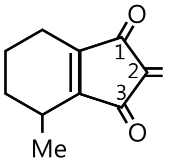
(Major). Product C is

(A)


(B)


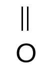
(C)


(D)


Q.11


above compound is hydrated maximum at which position?

(A) 1 (B) 2 (C) 3 (D) Equal

Q.12

$Et-\underset{\underset{\displaystyle O}{\|}}{C}-Me$ is prepared as one of the products by dry distillation of calcium salt of which o the following acids:

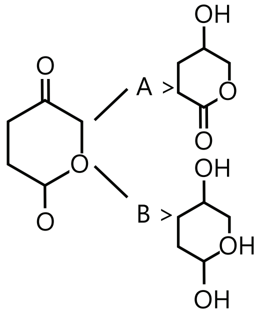
(A) Ethanoic acid and methonoic acid

(B) Propanoic acid and methonoic acid

(C) Propanoic acid and ethanoic acid

(D) None of these

Q.13 Reagents A & B are

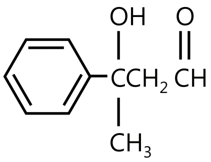


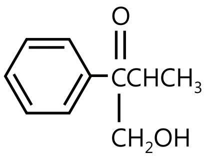
(A) H_2/Pd & $LiAlH_4$
(B) $LiAlH_4$ & $NaBH_4$
(C) $NaBH_4$ & $LiAlH_4$
(D) $LiAlH_4$ & H_2/Pd

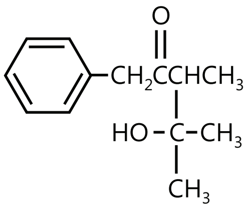
Q.14 The reagent used to distinguish ethanol & acetone is

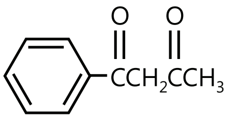
(A) Schiff's reagent
(B) Fehling's sol.
(C) Ceric ammonium nitrate
(D) Iodine with NaOH

Q.15 Which one of the following compounds is the best candidate for being prepared by an efficient mixed aldol addition reaction?

(A)


(B)


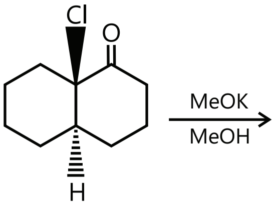
(C)


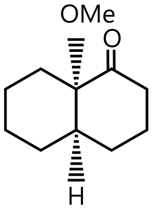
(D)


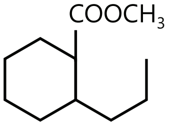
Q.16 PhCHO and HCHO will behave differently with which of the following reagents

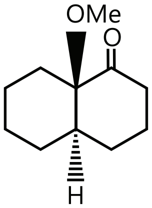
(A) Tollen's Reagent
(B) Fehling's sol.
(C) Schiffs reagent
(D) $NaBH_4$

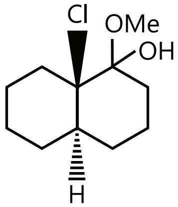
Q.17 Major product of this reaction is



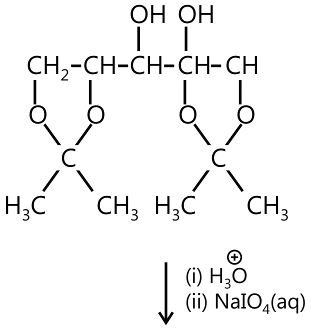
(A)


(B)


(C)


(D)


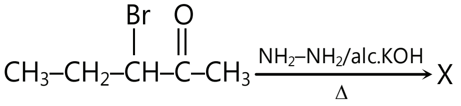
Q.18 In the given reaction



Product will be -

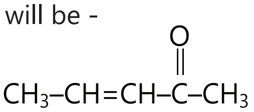
(A) 1 mole HCOOH and 1 mole HCHO
(B) 2 mole HCOOH and 1 mole HCHO
(C) 2 mole HCHO and 1 mole HCOOH
(D) 2 mole HCHO and 4 mole HCOOH

Q.19 In the given reaction

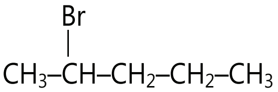


$$CH_3–CH_2–\overset{\overset{Br}{|}}{CH}–\overset{\overset{O}{||}}{C}–CH_3 \xrightarrow[\Delta]{NH_2–NH_2/alc.KOH} X$$

[X] will be -

(A)


$CH_3–CH=CH–\overset{\overset{O}{||}}{C}–CH_3$

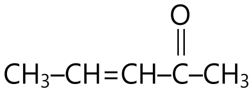
(B)


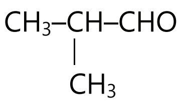
$CH_3–\overset{\overset{Br}{|}}{CH}–CH_2–CH_2–CH_3$

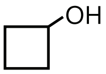
(C) $CH_3–CH=CH–CH_2–CH_3$
(D) $CH_3–CH_2–CH_2–CHO$

Multiple Correct Choice Type

Q.20 Compound (X) C_4H_8O, which gives 2, 4-Dinitrophenyl hydrazine derivative (orange or red or yellow colour) and negative haloform test.

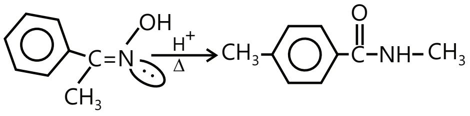
(A) 
$CH_3–CH=CH–\overset{O}{\overset{||}{C}}–CH_3$

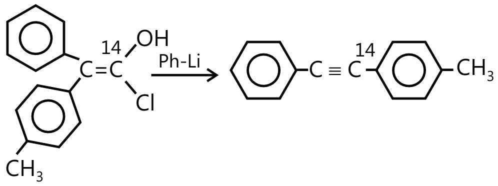
(B) 
$CH_3–\underset{CH_3}{\underset{|}{CH}}–CHO$

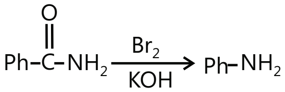
(C) 

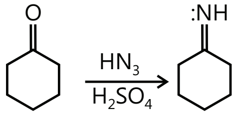
(D) $CH_3–CH_2–CH_2–CHO$

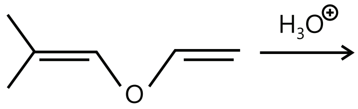
Q.21 Which of the following reaction is not representing major product -

(A) 

(B) 

(C) 
Hoffman Brommamide

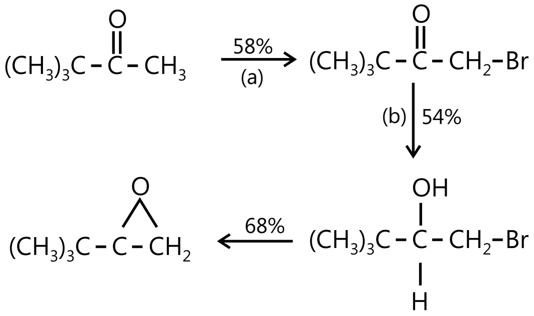
(D) 

Q.22  (A) + (B) formed

cannot be differentiated by

(A) Iodoform	(B) Fehling
(C) $NaHSO_3$	(D) 2, 4-DNP

Comprehension Type



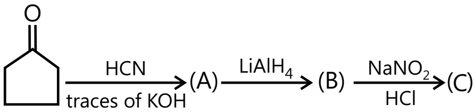
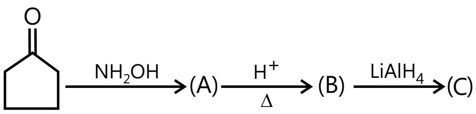
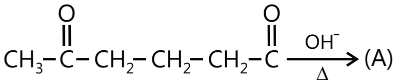
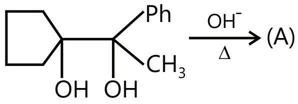
Q.23 Suggest a reagent appropriate step (a) the synthesis -

(A) HO^- / Br_2 (1 mole)	(B) H^+ / Br_2 (1 mole)
(C) Both (A) and (B)	(D) None of these

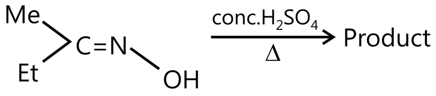
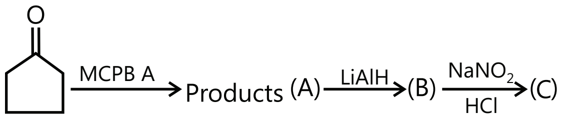
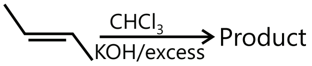
Q.24 Yield of each step as actually carried out in laboratory is given each arrow. What is over all yield of the reaction ?

(A) 60% (B) 21% (C) 40% (D) 68%

Q.25 Match the column

	Column I	Column II
(A)		(p) Formation of six member ring takes place
(B)		(q) Final product is Ketone
(C)	 $CH_3–\overset{O}{\overset{\|\|}{C}}–CH_2–CH_2–CH_2–\overset{O}{\overset{\|\|}{C}} \xrightarrow[\Delta]{OH^-} (A)$	(r) Final product will give positive Tollen's test
(D)		(s) Final product formed will react with 2, 4-DNP, (2, 4-Di-nitrophenyl hydrazine)

Q.26 Match the column

	Column I		Column II
(A)		(p)	Carbene formation is involved
(B)		(q)	Nitrene formation is involved
(C)	$CH_2 = CH_2 + NH_3 \xrightarrow{\Delta}$ Product	(r)	Carbocation formation is involved
(D)		(s)	Final product is a cyclic compound
		(t)	Azonium ion formation is involved

Previous Years' Questions

Q.1 A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH Solution gives ***(2001)***

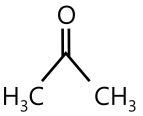
(A) Benzyl alcohol and sodium formate

(D) Sodium benzoate and methyl alcohol

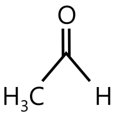
(C) Sodium benzoate and sodium formate

(D) Benzyl alcohol and methyl alcohol

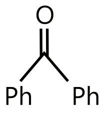
Q.2 The order of reactivity of phenyl magnesium bromide with following compounds is ***(2004)***



(I)



(II)



(III)

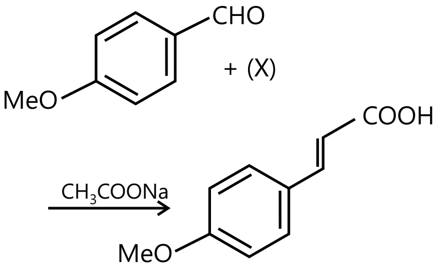
(A) II > III > I

(B) I > III > II

(C) II > I > III

(D) All the above react with the same rate

Q.3 What is X? ***(2005)***



(A) CH_3COOH

(B) $BrCH_2COOH$

(C) $(CH_3CO)_2O$

(D) HOC–COOH

Q.4 Butan-2-one can be converted to propanoic acid by which of the following? ***(2006)***

(A) NaOH, NaI/H^+

(B) Fehling Sol:

(C) NaOH, I_2/H^+

(D) Tollen's reagent

Q.5 The smallest ketone and its homologue are reacted with NH_2OH to form oxime ***(2006)***

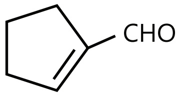
(A) Two different oximes are formed

(B) Three different oximes are formed

(C) Two oximes are optically active

(D) All oximes.are optically active

Q.6 Cyclohexene on ozonolysis following reaction with zinc dust and water gives compound. Compound E on further treatment with aqueous KOH yields compound F. Compound F is - ***(2007)***

(A)


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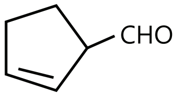

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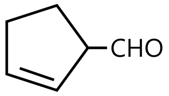

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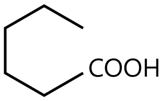


Q.7 Among the following compounds, which will react with acetone to give a product containing $\rangle C{=}N-$? ***(2014)***

(A) $C_6H_5NH_2$ (B) $(CH_3)_3N$

(C) $C_6H_5NHC_6H_5$ (D) $C_6H_5NHNH_2$

Q.8 A new carbon bond formation is possible is ***(1998)***

(A) Cannizzaro's reaction

(B) Friedel-Craft's reaction

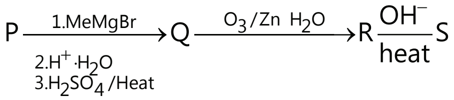
(C) Clemmensen's reduction

(D) Reimer-Tiemann reaction

Paragraph 1

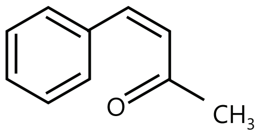
A corbonyl compound P, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olelfin Q. Ozonolysis of Q leads to a dicarbonyl compound R, which undergoes intramolecular aldol reaction to give predominantly S.

(2009)



$$P \xrightarrow[\substack{2.H^+\cdot H_2O\\3.H_2SO_4/\text{Heat}}]{1.\text{MeMgBr}} Q \xrightarrow{O_3/Zn\ H_2O} R \xrightarrow[\text{heat}]{OH^-} S$$

Q.9 The structure of the carbonyl compound P, is

(A)


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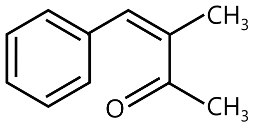

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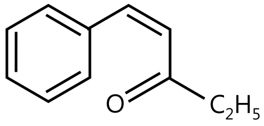

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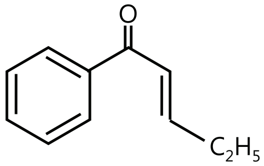
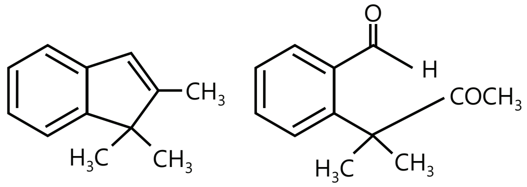
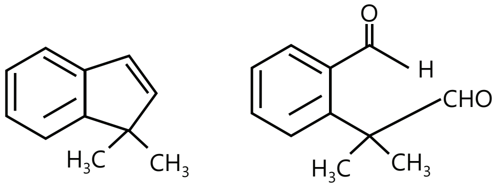


Q.10 The structure of the product Q and R, respectively, are

(A)


(B)


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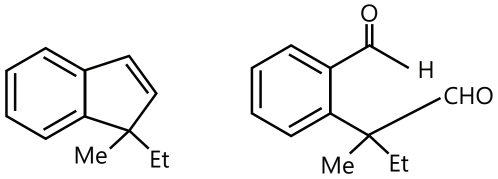

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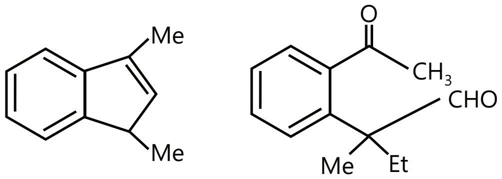
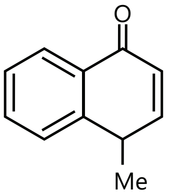
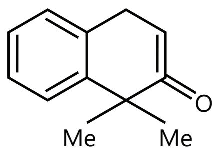
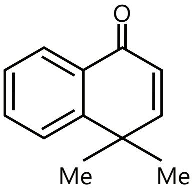
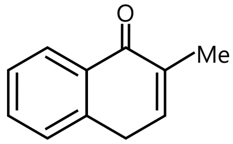


Q.11 The structure of the product S, is-

(A)


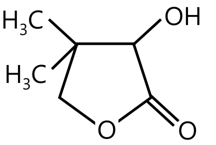
(B)


(C)


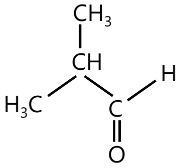
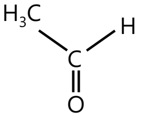
(D)


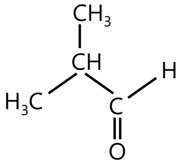
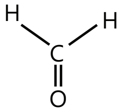
Paragraph 2

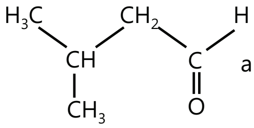
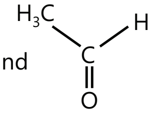
Two alipbatic aldehydes P and Q react in the presence of aqueous K_2CO_3 to give compound R, which upon treatment with HCN provides compound S. On acidification and heating. S gives the product shown below: ***(2010)***

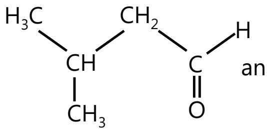
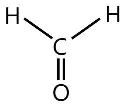


Q.12 The compounds P and Q respectively are

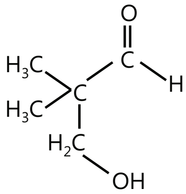
(A)  and 

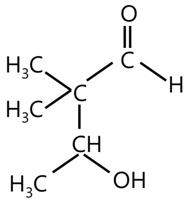
(B)  and 

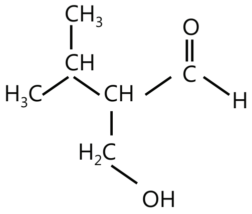
(C)  and 

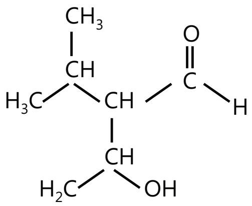
(D)  and 

Q.13 The compound R is -

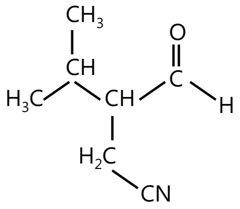
(A) 

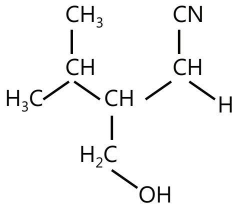
(B) 

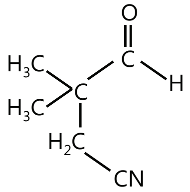
(C) 

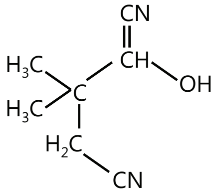
(D) 

Q.14 The compound S is -

(A) 

(C) 

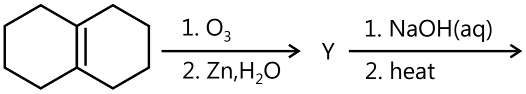
(B) 

(D) 

Q.15 Match compounds/ions in column I with their properties / reactions in column II. ***(2007)***

	Column I		**Column II**
(A)	C_6H_5CHO	(p)	gives precipitate with 2,4-dinitrophenylhydrazine
(B)	$CH_3C \equiv CH$	(q)	gives precipitate with $AgNO_3$
(C)	CN^-	(r)	is a nucleophile
(D)	I^-	(s)	is involved in cyanohydrin formation

Q.16 In the scheme given below, the total number of intramolecular aldol condensation products formed from 'Y' is: ***(2010)***



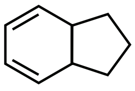
Paragraph for Questions 17 and 18

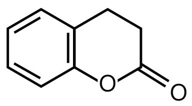
In the following reactions sequence, the compound J is an intermediate ***(2012)***

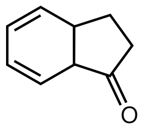
$$I \xrightarrow[CH_3COONa]{(CH_3CO)_2O} J \xrightarrow[(ii)\,SOCl_2/Anhy.AlCl_3]{(i)\,H_2,Pd/C} K$$

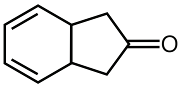
$J(C_9H_8O_2)$gives effervescences on treatment with $NaHCO_3$ and positive Baeyer's test.

Q.17 The compound K is

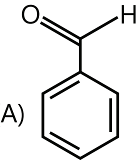
(A) 

(B) 

(C) 

(D) 

Q.18 The compound I is

(A)


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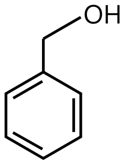

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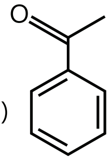

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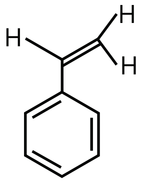
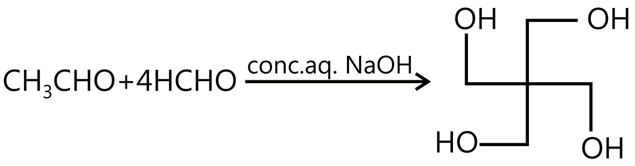


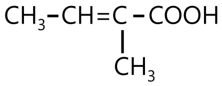
Q.19 The number of aldol reaction(s) that occurs in the given transformation is ***(2012)***

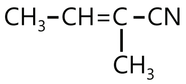


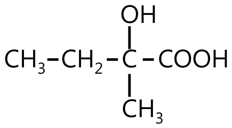
(A) 1 (B) 2 (C) 3 (D) 4

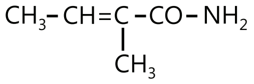
Q.20 The major product H in the given reaction sequence is ***(2012)***

$$CH_3-CH_2-CO-CH_3 \xrightarrow{^{\ominus}CN} G \xrightarrow[\text{Heat}]{95\%\ H_2SO_4} H$$

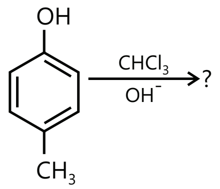
(A)

$CH_3-CH=\underset{\substack{|\\ CH_3}}{C}-COOH$

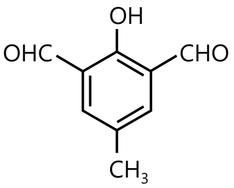
(B)

$CH_3-CH=\underset{\substack{|\\ CH_3}}{C}-CN$

(C)

$CH_3-CH_2-\overset{\substack{OH\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-COOH$

(D)

$CH_3-CH=\underset{\substack{|\\ CH_3}}{C}-CO-NH_2$

Q.21 In the following reaction, the product(s) formed is (are) ***(2013)***





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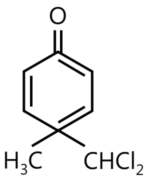
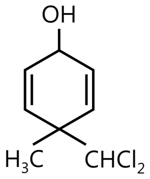
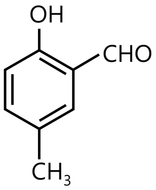


Q



R

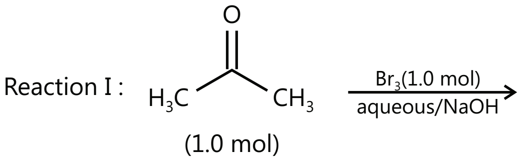


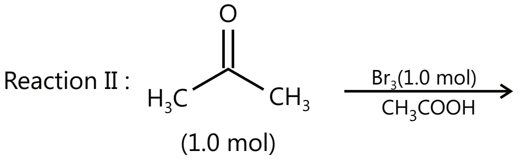
S

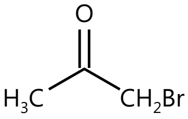
(A) P(major) (B) Q(minor)

(C) R(minor) (D) S(major)

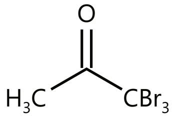
Q.22 After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are) ***(2013)***



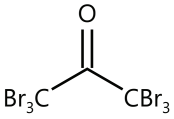




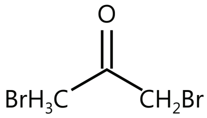
P



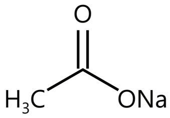
O



R



S



T

$CHBr_3$

U

(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

Q.23 The most suitable reagent for the conversion of $R-CH_2-OH \rightarrow R-CHO$ is: ***(2014)***

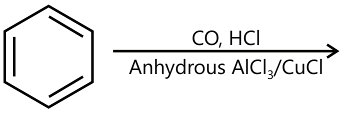
(A) $KMnO_4$

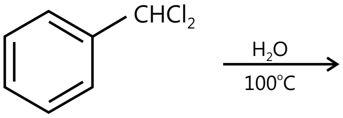
(B) $K_2Cr_2O_7$

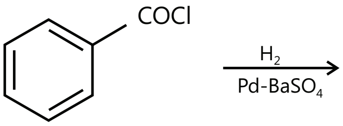
(C) CrO_3

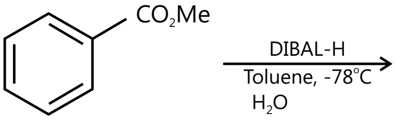
(D) PCC (Pyridinium chlorochromate)

Q.24 Among the following, the number of reaction(s) that produce(s) benzaldehyde is ***(2015)***

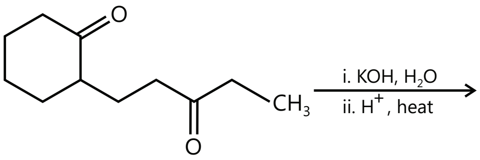
(A) 

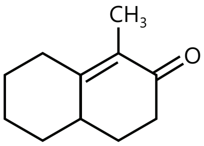
(B) 

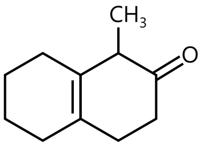
(C) 

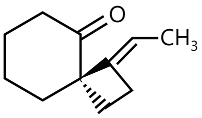
(D) 

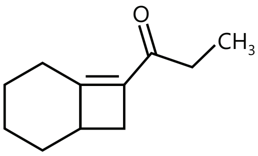
Q.25 The major product of the following reaction is ***(2015)***



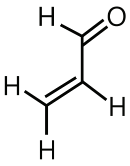
(A) 

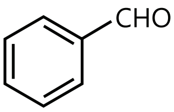
(B) 

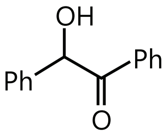
(C) 

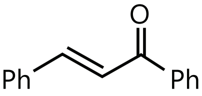
(D) 

Q.26 Positive test is observed for ***(2016)***

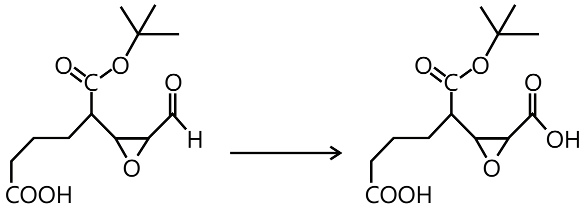
(A) 

(B) 

(C) 

(D) 

Q.27 Reagents which can be used to bring about the following transformation is ***(2016)***



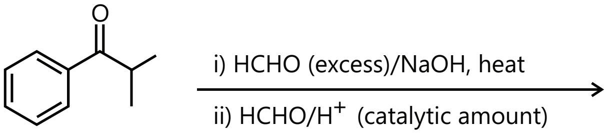
(A) $LiAlH_4$ in $(C_2H_5)_2O$

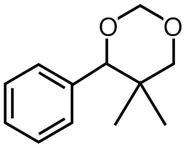
(B) BH_3 in THF

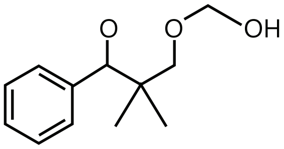
(C) $NaBH_4$ in C_2H_5OH

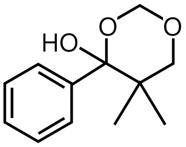
(D) Raney Ni/H_2 in THF

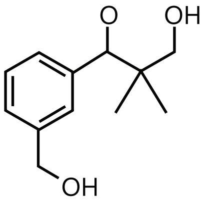
Q.28 ***(2016)***



(A) 

(B) 

(C) 

(D) 

MASTERJEE Essential Questions

JEE Main/Boards

Exercise 1

Q.1 Q.3 Q.9
Q.10 Q.16 Q.22

Exercise 2

Q.3 Q.8 Q.12
Q.15

Previous Years' Questions

Q.2 Q.7 Q.8
Q.12

JEE Advanced/Boards

Exercise 1

Q.11 Q.12 Q.15
Q.25 Q.26 (4) Q.27 (3)
Q.28 (5-i)

Exercise 2

Q.2 Q.6 Q.8
Q.9 Q.17 Q.18
Q.25

Previous Years' Questions

Q.9 Q.14

Answer Key

JEE Main/Boards

Exercise 2

Single Correct Choice Type

Q.1 B **Q.2** B **Q.3** C **Q.4** A **Q.5** C **Q.6** A
Q.7 C **Q.8** B **Q.9** D **Q.10** C **Q.11** C **Q.12** C
Q.13 B **Q.14** B **Q.15** D **Q.16** D

Previous Years' Questions

Q.1 D **Q.2** B **Q.3** A **Q.4** B **Q.5** A **Q.6** B
Q.7 C **Q.8** D **Q.9** A **Q.10** A **Q.11** B **Q.12** C
Q.13 D **Q.14** A, C **Q.15** D **Q.16** D **Q.17** A **Q.18** B
Q.19 A

JEE Advanced/Boards

Exercise 2

Single Correct Choice Type

Q.1 C **Q.2** C **Q.3** A **Q.4** B **Q.5** B **Q.6** A **Q.7** C
Q.8 A **Q.9** D **Q.10** C **Q.11** B **Q.12** C **Q.13** C **Q.14** C
Q.15 B **Q.16** B **Q.17** B **Q.18** D **Q.19** C

Multiple Correct Choice Type

Q.20 B, D **Q.21** A, B, D **Q.22** B, C, D

Comprehension Type

Q.23 C **Q.24** B

Match the Columns

Q.25 A → p, q, s; B → p; C→ p, q, s; D → p, q, s; **Q.26** A → r; B → r, s; C → q, s; D → p

Previous Years' Questions

Q.1 A **Q.2** C **Q.3** C **Q.4** C **Q.5** B **Q.6** A **Q.7** A, D
Q.8 B, D **Q.9** B **Q.10** A **Q.11** B **Q.12** B **Q.13** A **Q.14** D
Q.15 A → p, q, s; B → q, r; C → q, r, s; D → q, r **Q.16** 1 **Q.17** C **Q.18** A **Q.19** C
Q.20 B **Q.21** B, D **Q.22** C **Q.23** D **Q.24** A, B, C, D **Q.25** A **Q.26** A, B, C
Q.27 C **Q.28** A

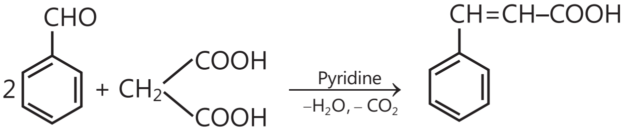
Solutions

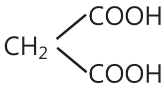
JEE Main/Boards

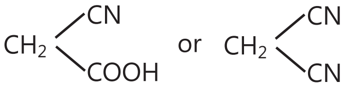
Exercise 1

Sol 1: Knovengeal reaction

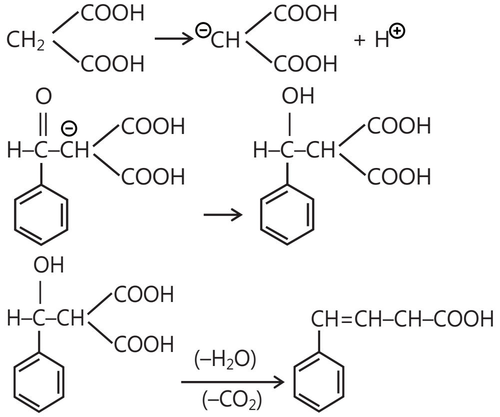
It is the condensation of any carbonyl compounds with compounds containing in active methylene compound in the presence of pyridine

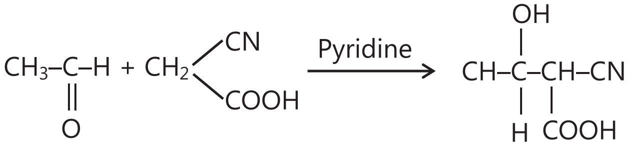


Instead of  $CH_2(COOH)_2$ we can also use

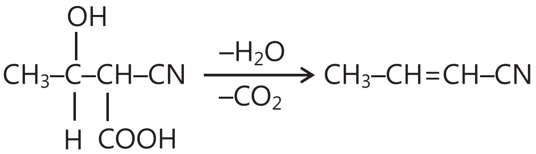


Mechanism





$$CH_3-\underset{\underset{O}{\|}}{C}-H + CH_2\begin{cases}CN\\COOH\end{cases} \xrightarrow{\text{Pyridine}} CH-\overset{OH}{\overset{|}{\underset{\underset{H}{|}}{C}}}-\underset{\underset{COOH}{|}}{CH}-CN$$

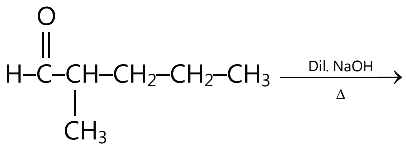


$$CH_3-\overset{OH}{\overset{|}{\underset{\underset{H}{|}}{C}}}-\underset{\underset{COOH}{|}}{CH}-CN \xrightarrow[-CO_2]{-H_2O} CH_3-CH=CH-CN$$

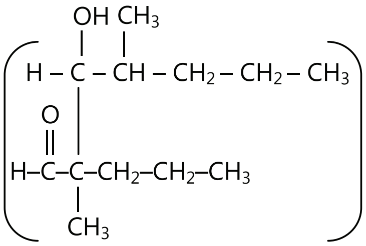
Sol 2: (i) $CH_2 = O$ it will undergo cannizzaro reaction :

$$2CH_2 = O \xrightarrow[\Delta]{\text{Conc. NaOH}} HCOONa + CH_3OH$$

(ii) Aldol condensation



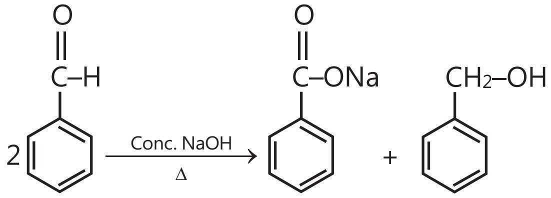
$$H-\overset{O}{\overset{\|}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3 \xrightarrow[\Delta]{\text{Dil. NaOH}}$$



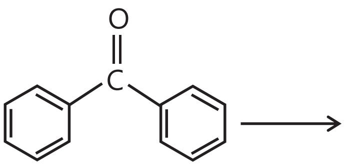
$$\left(\begin{array}{l} H-\overset{OH}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-CH_3 \\ \quad\;| \\ H-\overset{O}{\overset{\|}{C}}-\underset{\underset{CH_3}{|}}{C}-CH_2-CH_2-CH_3 \end{array}\right)$$

Cannizzaro reaction

(iii) Benzaldehyde

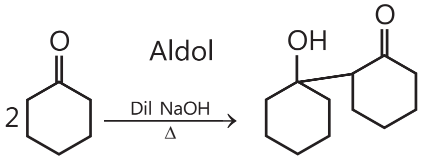


(iv) Benzophenone

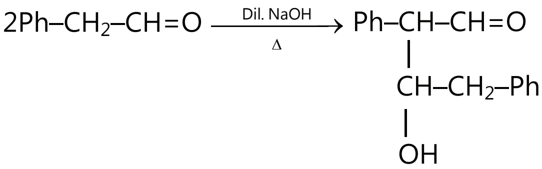


It will not undergo aldol or cannizzaro reaction

(v)



(vii)

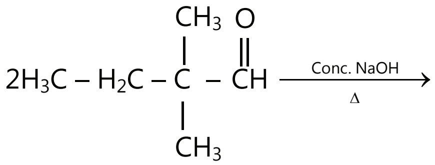


$$2Ph-CH_2-CH=O \xrightarrow[\Delta]{\text{Dil. NaOH}} Ph-\underset{\underset{\underset{\underset{OH}{|}}{CH}-CH_2-Ph}{|}}{CH}-CH=O$$

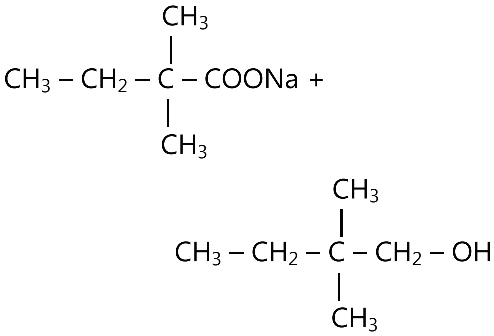
(viii) $2CH_3-CH_2-CH_2-CH_2-OH \longrightarrow$

It will not undergo any reaction

(ix)



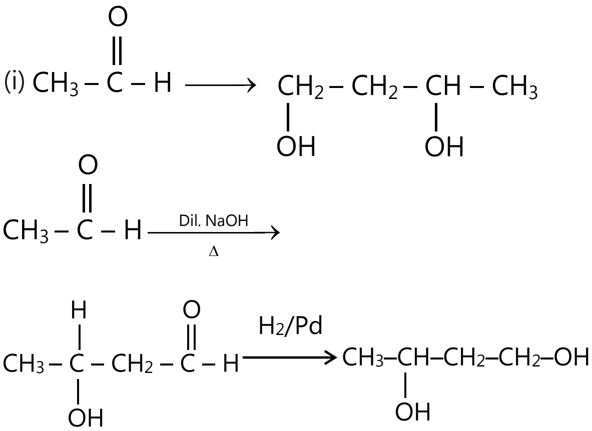
$$2H_3C-H_2C-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-\overset{O}{\overset{\|}{CH}} \xrightarrow[\Delta]{\text{Conc. NaOH}}$$



$$CH_3-CH_2-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-COONa + CH_3-CH_2-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_2-OH$$

Sol 3:

(i)

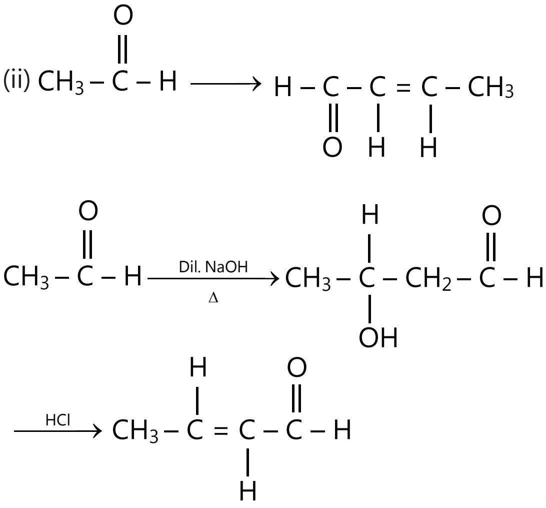


$$CH_3-\overset{O}{\overset{\|}{C}}-H \longrightarrow \underset{\underset{OH}{|}}{CH_2}-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$$

$$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{\text{Dil. NaOH}}$$

$$CH_3-\overset{H}{\overset{|}{\underset{\underset{OH}{|}}{C}}}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{H_2/Pd} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-OH$$

(ii)

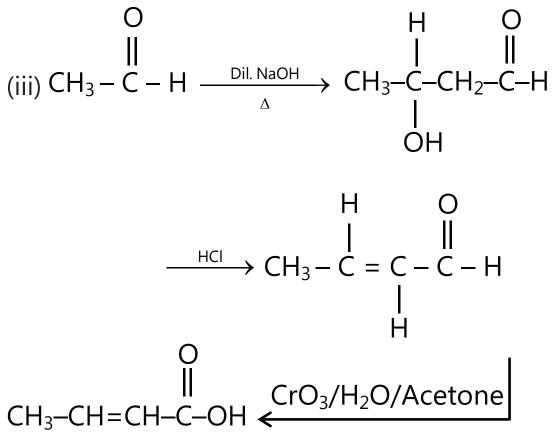


$$CH_3-\overset{O}{\overset{\|}{C}}-H \longrightarrow H-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-CH_3$$

$$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{\text{Dil. NaOH}} CH_3-\overset{H}{\overset{|}{\underset{\underset{OH}{|}}{C}}}-CH_2-\overset{O}{\overset{\|}{C}}-H$$

$$\xrightarrow{\text{HCl}} CH_3-\overset{H}{\overset{|}{C}}=\underset{\underset{H}{|}}{C}-\overset{O}{\overset{\|}{C}}-H$$

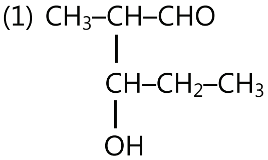
(iii)



$$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{\text{Dil. NaOH}} CH_3-\underset{OH}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{HCl} CH_3-\overset{H}{\overset{|}{C}}=\underset{H}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{CrO_3/H_2O/Acetone} CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-OH$$

Sol 4: CH_3-CH_2-CHO + $CH_3-CH_2-CH_2-CHO \xrightarrow{\text{Aldol}}$

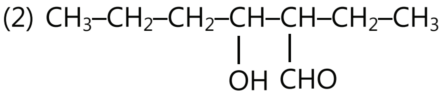
(1)



$$CH_3-\underset{\underset{OH}{\underset{|}{CH-CH_2-CH_3}}}{\underset{|}{CH}}-CHO$$

$\left(\begin{array}{l} CH_3-CH_2-CHO \text{ is nucleophile} \\ CH_3-CH_2-CHO \text{ is electrophile} \end{array}\right)$

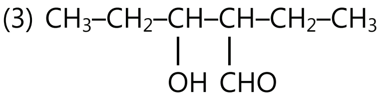
(2)



$$CH_3-CH_2-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{CHO}{\underset{|}{CH}}-CH_2-CH_3$$

$\left(\begin{array}{l} CH_3-CH_2-CH_2-CHO \text{ is nucleophile} \\ CH_3-CH_2-CH_2-CHO \text{ is electrophile} \end{array}\right)$

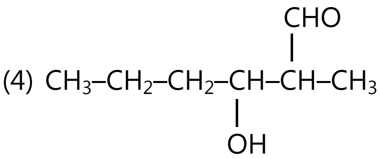
(3)



$$CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-\underset{CHO}{\underset{|}{CH}}-CH_2-CH_3$$

$\left(\begin{array}{l} CH_3-CH_2-CHO \text{ is electrophile} \\ CH_3-CH_2-CH_2-CHO \text{ is nucleophile} \end{array}\right)$

(4)



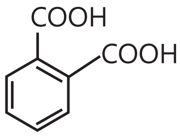
$$CH_3-CH_2-CH_2-\underset{OH}{\underset{|}{CH}}-\overset{CHO}{\overset{|}{CH}}-CH_3$$

$\left(\begin{array}{l} CH_3-CH_2-CH_2-CHO \text{ is electrophile} \\ CH_3-CH_2-CHO \text{ is nucleophile} \end{array}\right)$

Sol 5: $C_9H_{10}O \rightarrow$ gives +ve tollen's test

$\Rightarrow$ It is a aldehyde $\rightarrow$ undergoes cannizzaro

$\Rightarrow$ α hydrogens not present $\rightarrow$ vigorous oxidation $\rightarrow$

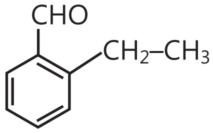


$\Rightarrow$ $C_9H_{10}O$ has two groups attached at neighbouring positions

$\Rightarrow$ 1 group is aldehyde with no α-hydrogen

$\Rightarrow$ 2nd group is ethyl group

So $C_9H_{10}O$ is



Sol 6: (i) Refer page-23.15 Section-6 in the sheet

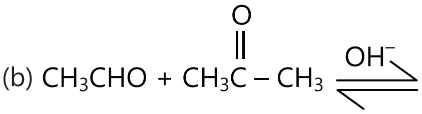
(ii) When the condensation is between two different carbonyl compounds, it is called crossed aldol condensation.

For example.

(a) $R_3C-CHO + CH_3CHO \xrightarrow{\overset{\Theta}{OH}}$

$R_3C-CH(OH)-CH_2-CHO$ crossed product

(b)



$$CH_3CHO + CH_3\overset{O}{\overset{\|}{C}}-CH_3 \xrightleftharpoons{OH^-}$$

$CH_3-CH(OH)-CH_2-COCH_3$

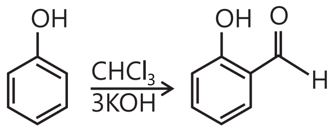
4-Hydroxypentan-2- one (crossed product)

(c) $C_6H_5CHO + CH_3COCH_3 \xrightleftharpoons{OH^-}$

$C_6H_5-CH=CH-CO-CH_3$

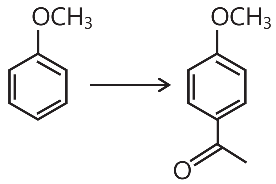
Sol 7: (i) Fehling's Test, (ii) 2, 4 DNP Test

Sol 8: (i)



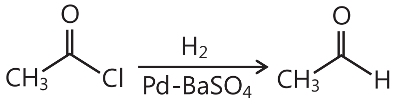
Reimer – Tiemann reaction

(ii)



Friedel Craft Acylation

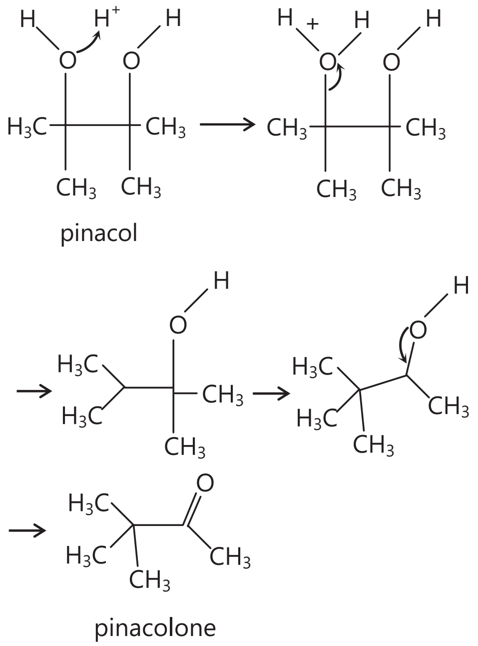
Sol 9: (i) Rosenmund Reduction



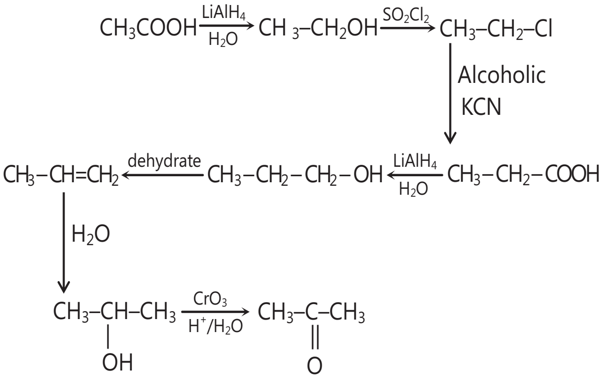
(ii) Tollen's Reagent

$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \rightarrow RCOO^- + 2Ag + 2H_2O + 4NH_3$

Sol 10: The pinacol-pinacolone rearrangement is a method for converting a 1, 2- dial to a carbonyl compound in organic chemistry. This 1, 2-rearrangement takes place under acidic conditions. The name of the reaction comes from the rearrangement of pinacole to pinacolone.



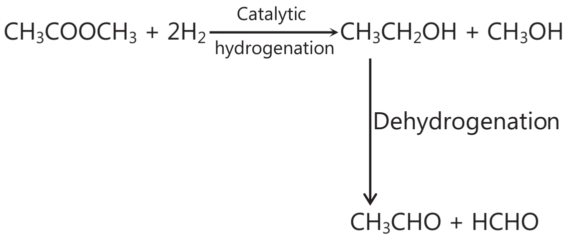
Sol 11: (i)



(ii) Friedel – Craft reaction

Benzene $\xrightarrow{CH_3Cl+FeCl_3}$ Toluene + HCl + $FeCl_3$

Sol 12: (a)



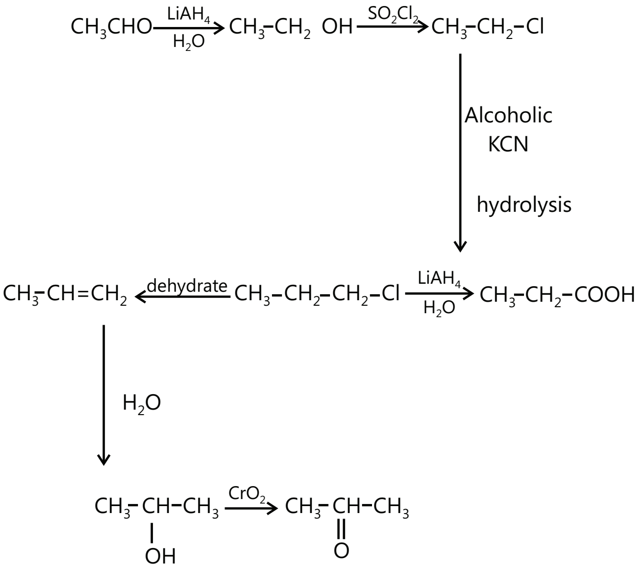
(b) (i) Due to the presence of $>C=O$ group with is polar

(ii) Aldehydes have lower boiling points as they are not associated with intermolecular

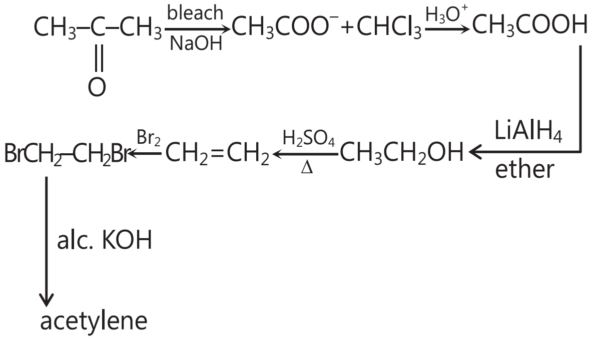
H-bonding whereas alcohols are associated with intermolecular H-bonding. Aldehydes have lower B. P.

Sol 13: Refer theory.

Sol 14: (i)



(ii)



Sol 15: A $C_8H_{16}O_2 \xrightarrow[\text{hydrolysis}]{H_2SO_4} B + C$

$C \xrightarrow[\text{Chromic acid}]{} B$

$C \xrightarrow{\text{dehydration}}$ but-1-ene

$\Rightarrow C = CH_3CH_2CH_2CH_2OH$

$\Rightarrow B \rightarrow CH_3CH_2CH_2CH_2COOH$

$\Rightarrow A \rightarrow CH_3–CH_2CH_2\,COOCH_2CH_2CH_2CH_3$

Sol 16: (i) 2-4 DNP test

Only carbonyl compounds give positive test

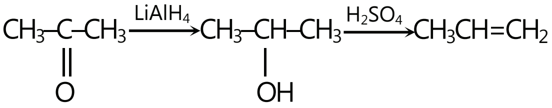
(ii) Acetophenone - It give iodoform test

Benzophenone-It doesn't give Iodoform test

(iii) Phenol - It give violet colour with $FeCl_3$ test.

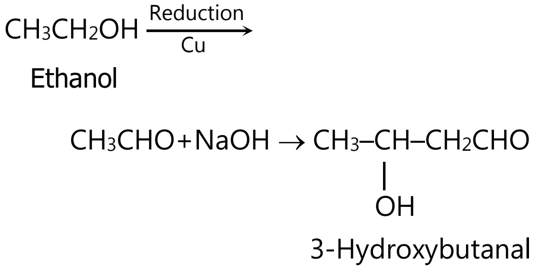
Benzoic acid-It doesn't give violet colour with $FeCl_3$

Sol 17: (i)



$CH_3–\underset{\underset{O}{\|}}{C}–CH_3 \xrightarrow{LiAlH_4} CH_3–\underset{\underset{OH}{|}}{CH}–CH_3 \xrightarrow{H_2SO_4} CH_3CH=CH_2$

(ii)

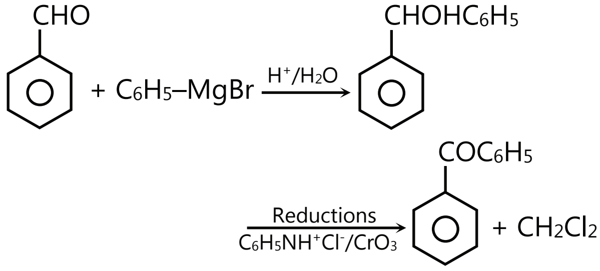


$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[Cu]{\text{Reduction}}$

$CH_3CHO + NaOH \rightarrow CH_3–\underset{\underset{OH}{|}}{CH}–CH_2CHO$

3-Hydroxybutanal

(iii)



Sol 18: (i) 2, 2, 6-trimethyl cyclohexanone has three methyl group at the alpha position. There is a lot of steric hindrance in this molecule. Due to steric hindrance the CN ion do not attack the molecule. These is not steric hindrance in cyclohexanone. Therefore its forms cyanohydrin in good percentage.

(ii) Semicarbazide has two $–NH_2$ groups. The attachment of the two $–NH_2$ groups on the

C = O is different one $–NH_2$ is directly attached to C = O while the other $–NH_2$ is not directly attached out attached through –NH. Therefore due to resonance the electron density on this $–NH_2$ group decrease and therefore cannot act as a nucleophile. The lone pair of electrons in $–NH_2$ which is attached through –NH is not involved in resonance and therefore is available for nucleophilic attack on the C = O.

(iii) The reaction between carboxylic acid and alcohol is a reversible reaction. The ester and the water which is formed as a product of can again react to form carboxylic acid and alcohol so for a reaction to proced in the forward direction in a reversible reaction, one of the product should be removed. That is the reason during the preparation of esters form a carboxylic acid and an alcohol in the presence of an acid catalyst, the water on the ester should be removed as soon as it is formed.

Sol 19: Calculation of molecular formula :-

% of C = 69. 77

% of H = 11.63

% of O = 100 – (69. 77 + 11.63) = 18. 6%

Ratio of C = 69. 77 / 12 = 5. 88

Ratio of H = 11.63 / 1 = 11 63

Ratio of O = 18.6 / 16 = 1. 16

smallest ratio

C = 5. 88/1. 16 = 5

H = 11.63/1. 16 = 10

O = 1. 16/1. 16 = 1

Empirical formula = $C_5H_{10}O_1$

Mol mass = 86

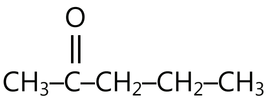
n = molecular mass/Empirical formula mass = 86/86 = 1

MF = $C_5H_{10}O$

Since the compound forms on addition compounds with sodium hydrogensulphite, the said compound should be ketone as aldehyde.

Since the compound does not reduce Tollen's reagent, therefore it is a ketone. Since the compound gives positive iodoforms test, the compound should be methyl ketone. On vigorous oxidation it gives ethanoic and propanoic acid therefore the given compound should be pentan-2-one.

The structure is



$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_3$$

Sol 20: Aldol takes place in the presence of α-hydrogen and cannizzaro takes place in the absence of α-hydrogen.

Sol 21: A does not give litmus test $\Rightarrow$ A does not contain –COOH group.

A does not give 2, 4-DNP test $\Rightarrow$ A does not contain $>C=O$ group

$A + MeCOCl \rightarrow \underset{262}{B}$

Initial mass = 178

Final mass = 262 difference is 84

Now A has lost hydrogen and gained $(Me-\overset{\overset{O}{||}}{C}-)$ group so change in mass corespnding to

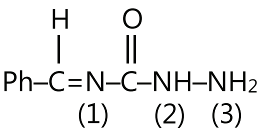
1(–OH) group 43 – 1 = 42

So no of hydroxy groups $= \frac{84}{42} = 2$

Sol 22: (i) (3) (4) will give positive fehling test as they are aldehydes (6) will give positive Fehling test as it has α-hydroxy ketone.

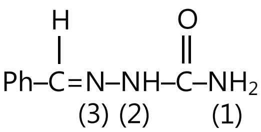
Sol 23: 3 nitrogen will give reaction with $>C=O$ because it has maximum electron density. The other two nitrogens are in conjugation with $(-\overset{\overset{O}{||}}{C}-)$ group so they are loss electron density.

Sol 24: 2 products are formed in good amount 1 with 1st nitrogen



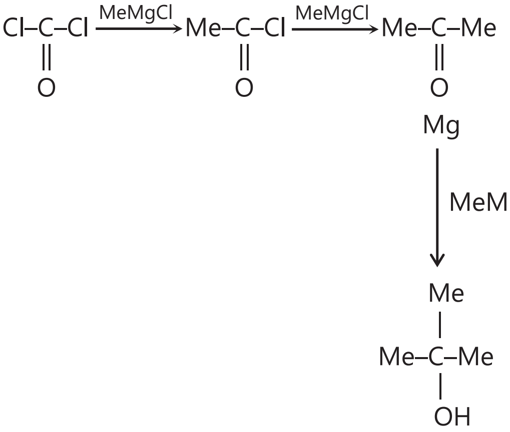
$$Ph-\overset{\overset{H}{|}}{C}=\underset{(1)}{N}-\underset{(2)}{\overset{\overset{O}{||}}{C}}-\underset{(3)}{NH}-NH_2$$

1 with 3rd nitrogen



$$Ph-\overset{\overset{H}{|}}{C}=\underset{(3)}{N}-\underset{(2)}{NH}-\overset{\overset{O}{||}}{C}-\underset{(1)}{NH_2}$$

Sol 25:



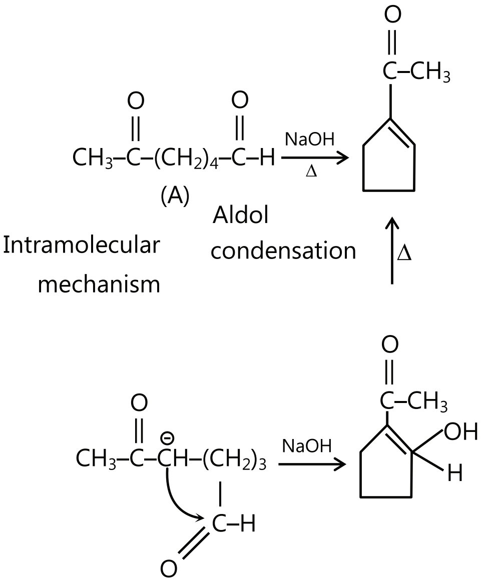
$$\begin{array}{c} Cl-\underset{\underset{O}{||}}{C}-Cl \xrightarrow{MeMgCl} Me-\underset{\underset{O}{||}}{C}-Cl \xrightarrow{MeMgCl} Me-\underset{\underset{O}{||}}{C}-Me \\ Mg \\ \downarrow MeMgCl \\ Me-\overset{\overset{Me}{|}}{\underset{\underset{OH}{|}}{C}}-Me \end{array}$$

So 3 moles of MeMgCl required for 1 mole $Cl-\underset{\underset{O}{||}}{C}-Cl$

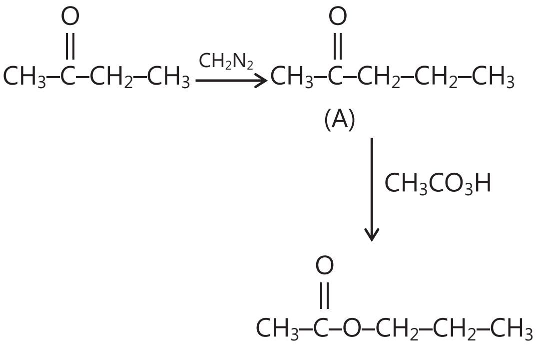
Exercise 2

Single Correct Choice Type

Sol 1: (B)



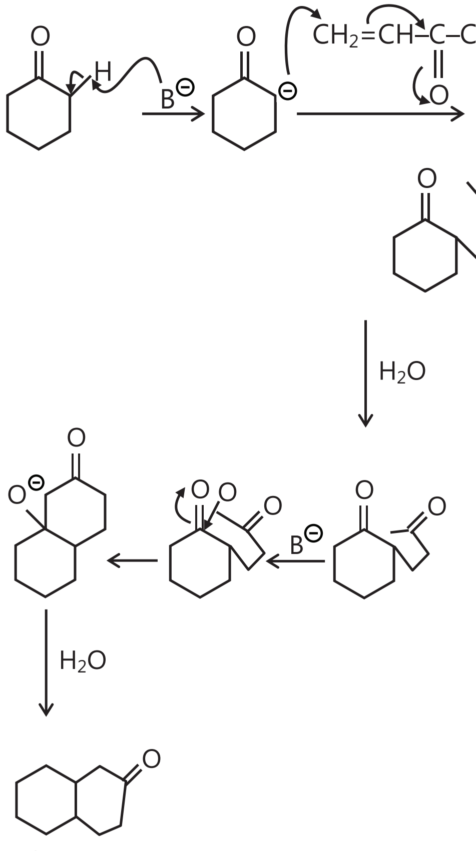
Sol 2: (B)



$$CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_3 \xrightarrow{CH_2N_2} \underset{(A)}{CH_3-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_3} \xrightarrow{CH_3CO_3H} CH_3-\overset{\overset{O}{||}}{C}-O-CH_2-CH_2-CH_3$$

(Bayer villiger)

Sol 3: (C)

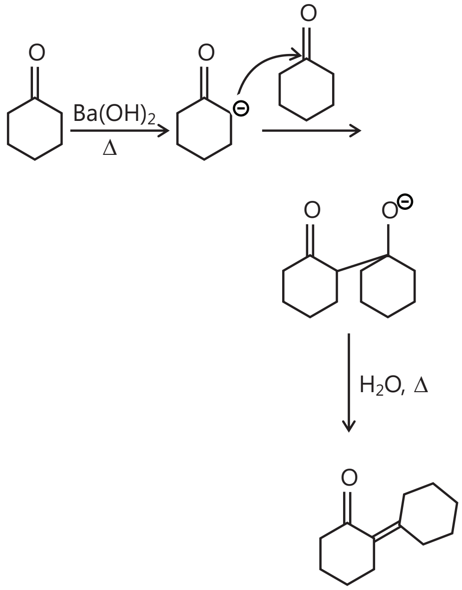


Octane

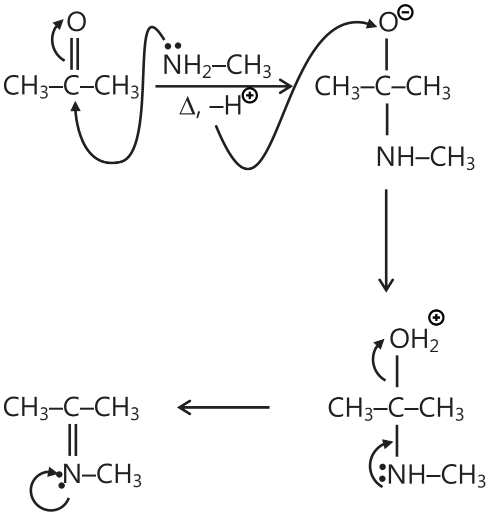
Sol 4: (A) It is carried out using $NaBH_4$ as $NaBH_4$ will not reduce ester and reduces only carbonyl part.

Sol 5: (C) MeCHO can undergo aldel condensation as its has more than 1 α hydrogen present.

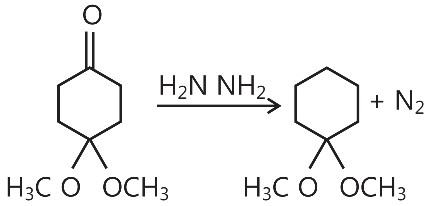
Sol 6: (A)



Sol 7: (C)



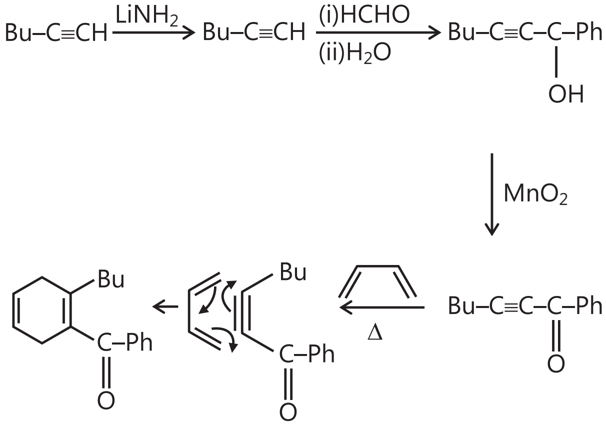
Sol 8: (B)



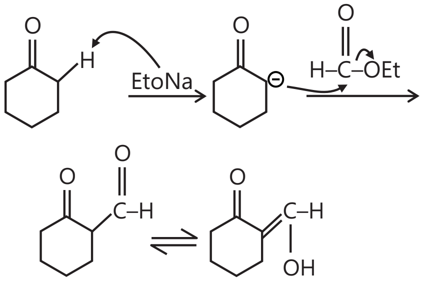
Wolf-kishner - reduction

In clemmension reduction HCl will break ether bonds.

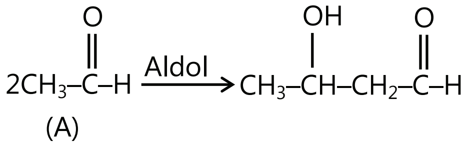
Sol 9: (D)



Sol 10: (C)

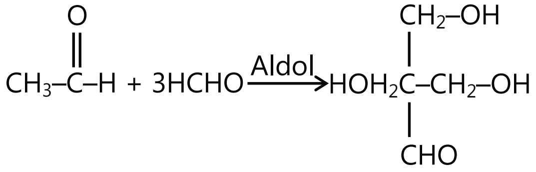


Sol 11: (C)



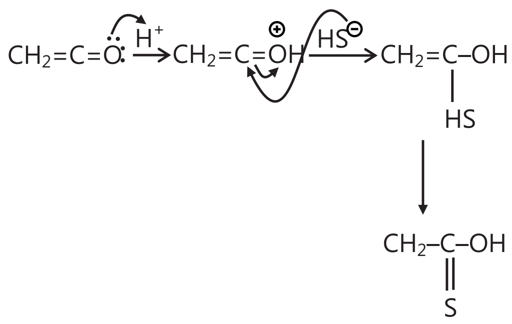
$$2CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{Aldol} CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-\overset{\overset{O}{\|}}{C}-H$$

(A)

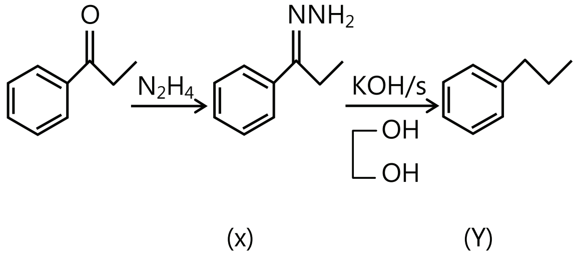


$$CH_3-\overset{\overset{O}{\|}}{C}-H + 3HCHO \xrightarrow{Aldol} HOH_2\overset{\overset{CH_2-OH}{|}}{\underset{\underset{CHO}{|}}{C}}-CH_2-OH$$

Sol 12: (C) $CH_2 = C = O + H_2S \longrightarrow$

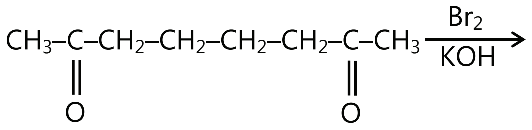


Sol 13: (B)



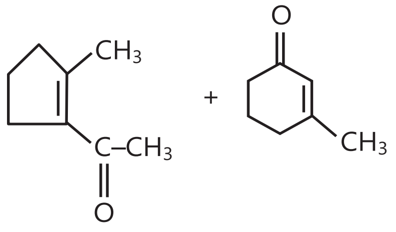
Wolf kishner reaction

Sol 14: (B)



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[KOH]{Br_2}$$

Intramolecular aldol condensation will take place.

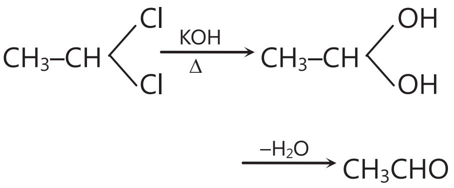


Sol 15: (D) $KMnO_4$ / H_2SO_4 ; $K_2Cr_2O_7$ / H_2SO_4 ; Ag_2O / NaOH will oxidise $-CHO \rightarrow -COOH$ but $LiAlH_4$ is a strong reducing reagent so it will reduce –CHO.

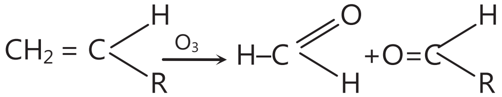
Sol 16: (D) H_2 / Pd–C will reduce –C= C and –CHO. H_2/ Pd – $BaSO_4$ – $CaCO_3$ will reduce only $-C \equiv C-$ $LiAlH_4$ and $NaBH_4$ will reduce –CHO to $-CH_2OH$.

Previous Years' Questions

Sol 1: (D)

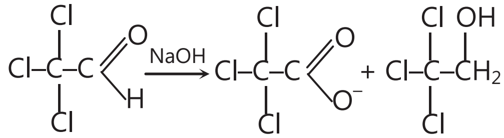


Sol 2: (B)

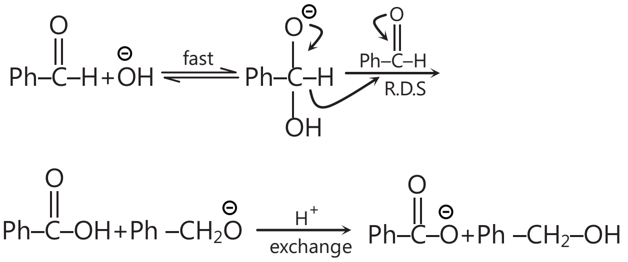


Presence of one vinyl group gives formaldehyde as one of the product in ozonolysis

Sol 3: (A) The cannizzaro product of given reaction yields 2, 2, 2-trichloroethanol.



Sol 4: (B)

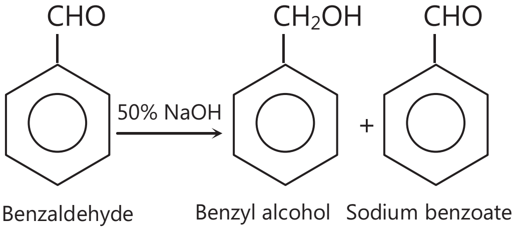


Sol 5: (A) Crossed aldol reaction gives benzyl alcohol and sodium formate.

$$\underset{\text{Bezaldehyde}}{C_6H_5CHO} + \underset{\text{Formaldehyde}}{HCHO} \xrightarrow{NaOH(aq)}$$

$$\underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sod. formate}}{HCOONa}$$

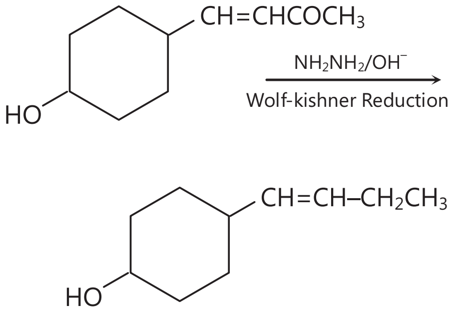
Sol 6: (B) Benzaldehyde will undergo Cannizzaro's reaction on treatment with 50% NaOH to produce benzyl alcohol and benzoic acid as it does not contain α-hydrogen



Sol 7: (C) It is a nucleophilic addition whose reactivity depends upon the electrophilic character of carbonyl carbon and steric hindrance only, So. the ease of the reaction would be HCHO > CH_3COCH_3 > $PhCOCH_3$ > PhCOPh

Sol 8: (D) Tollen's reagent oxidizes the compound having aldehyde group like glucose and also oxidizes α–hydroxy ketone having $–COCH_2OH$ group as in fructose -

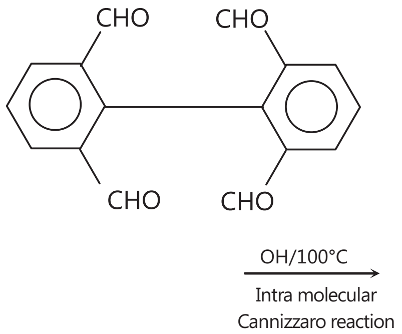
Sol 9: (A)

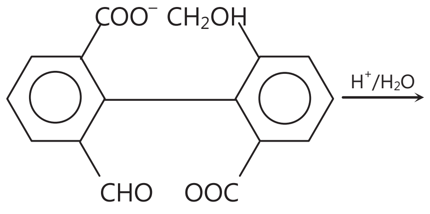


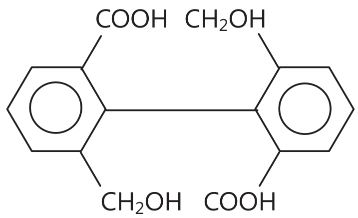
–OH group and alkene are acid sensitive groups so clemensen reduction can not be used.

Sol 10: (A) $\underset{(A)}{CH_3CH_2CH_2OH} \xrightarrow{(O)} \underset{(B)}{CH_3CH_2-CHO}$

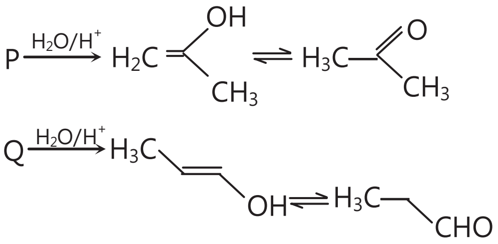
Sol 11: (B)



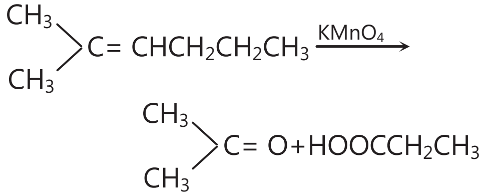




Sol 12: (C)

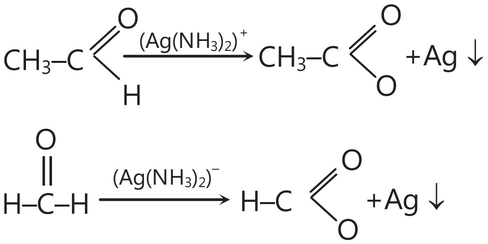


Sol 13: (D)

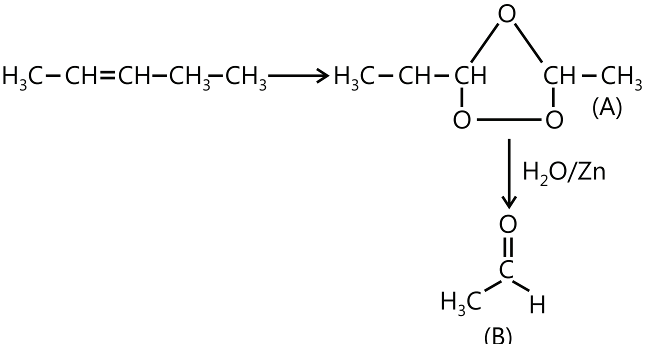


$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=CHCH_2CH_2CH_3 \xrightarrow{KMnO_4} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O+HOOCCH_2CH_3$$

Sol 14: (A, C)



Sol 15: (D)

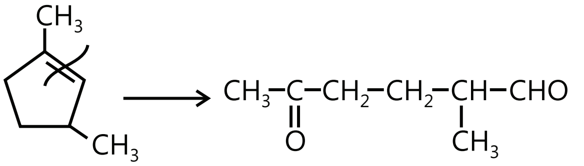


Sol 16: (D)

$$CH_3CHCl_2 \xrightarrow{\text{aqu.KOH}} CH_3CH(OH)_2 \xrightarrow[-H_2O]{} CH_3CHO$$

Sol 17: (A) In Cannizzaro reaction given below, the slowest step is the attack of OH at the carboxyl group

Sol 18 : (B)



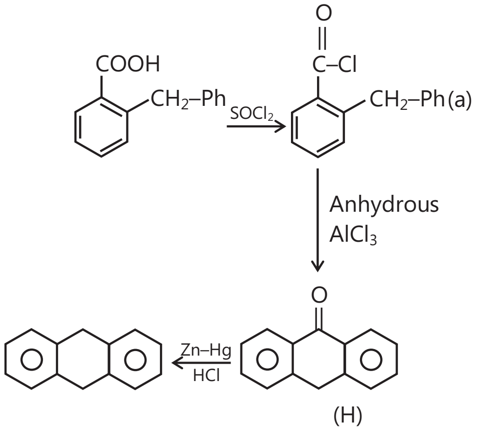
(5-keto-2-methyl hexanal)

Sol 19: (A) Vinyl group $\left(CH_2=CH-\right)$ on ozonolysis give formaldehyde

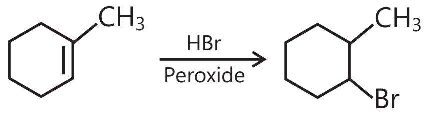
JEE Advanced/Boards

Exercise 1

Sol 1: Chlorination



Sol 2:



HBr/Peroxide → Anti-Markownikoff's Addition.

Sol 3:

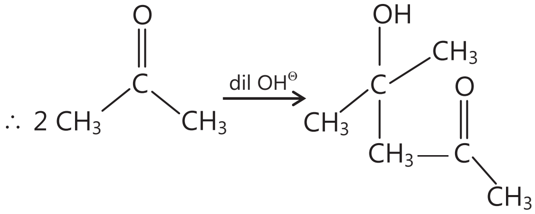
$$[J] \xleftarrow[H_2O]{H_2CrO_4} [I] \xleftarrow[\text{(Pyridine)}]{CrO_3} CH_3–CHO$$

↓ Strong oxidizing agent ↓ Weak oxidising agent

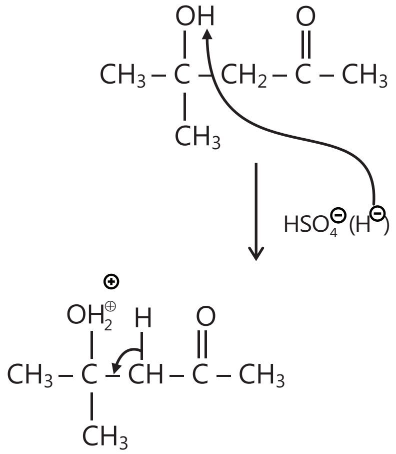
$J \rightarrow CH_3COOH$ $I \rightarrow CH_3\,CH_2–OH$

Sol 4: Acetone (2 mol) $\xrightarrow{OH^{\ominus}} [K] \xrightarrow{HSO_4^{\ominus}} [L]$

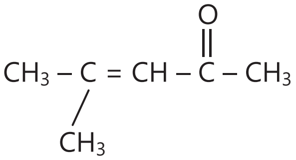
The first reaction. Aldol condensation.



Thus, K is

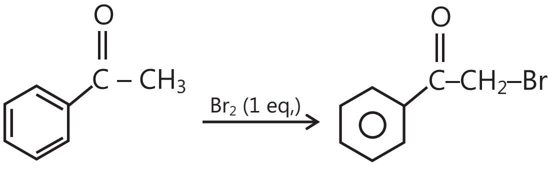


∴ L is



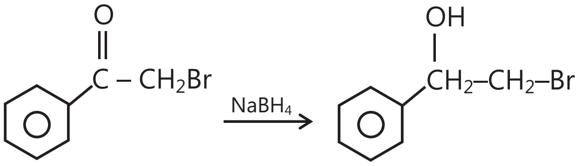
$$CH_3-\underset{CH_3}{C}=CH-\overset{O}{\overset{\|}{C}}-CH_3$$

Sol 5:

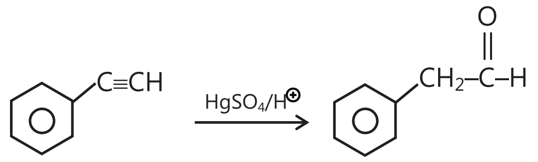


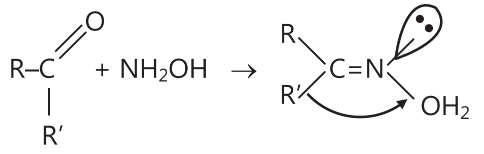
As only 1 equivalent is used, Br will be added to the alkyl group otherwise the phenyl ring also would have be substituted.

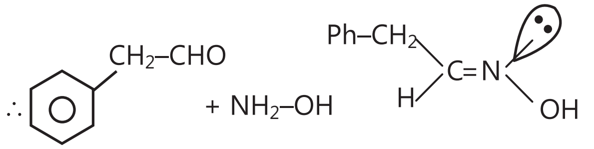
[$NaBH_4 \rightarrow$ weak reducing agent.]



Sol 6: $R{-}C{\equiv}CH \xrightarrow{HgSO_4/H^{\oplus}} R{-}C{-}CHO$

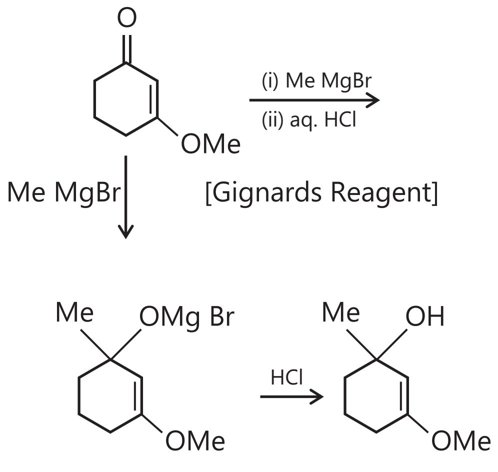




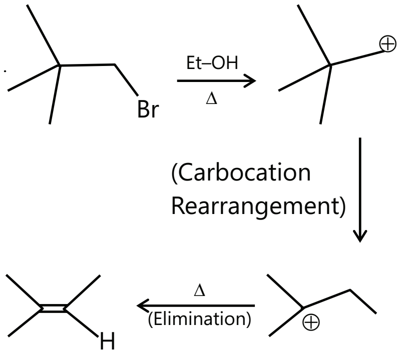


(geometrical isomer)

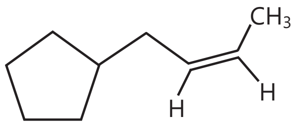
Sol 7:



Sol 8:

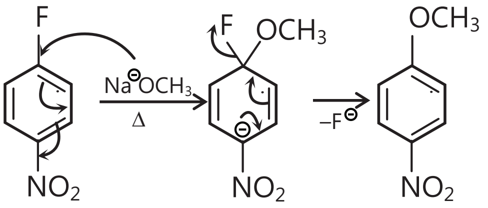


Sol 9:



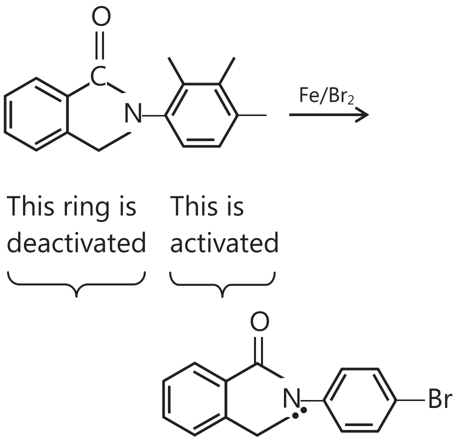
[H_2/indlar's catalyst is addition of H_2]

Sol 10:

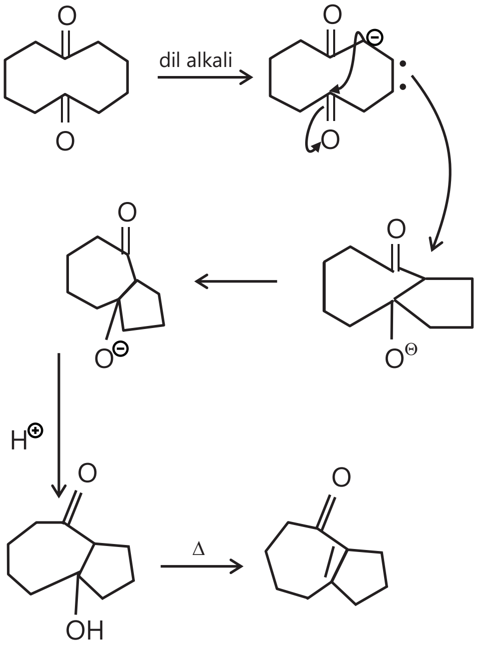


(This is ArS_N
Aromatic Substitution)

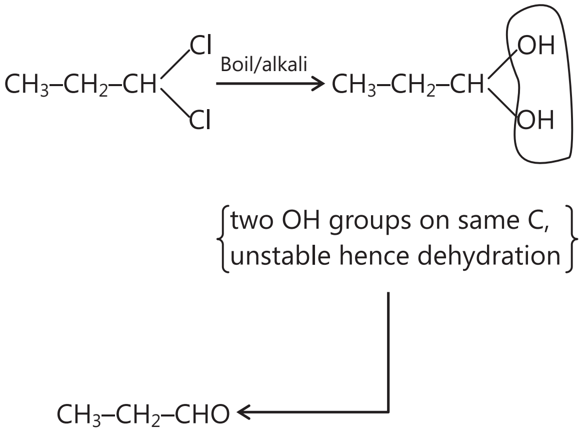
Sol 11:



Sol 12:

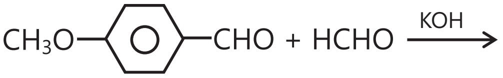


Sol 13:

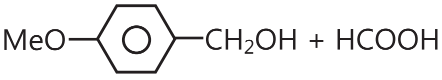


{two OH groups on same C, unstable hence dehydration}

Sol 14:



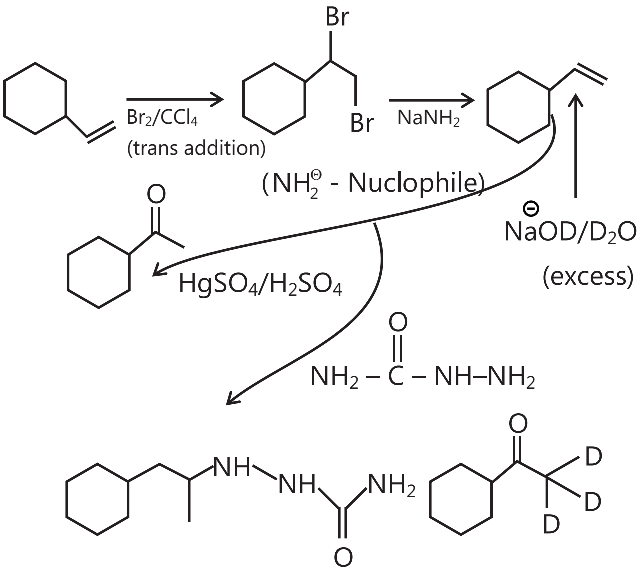
(Cannizaro Reaction)



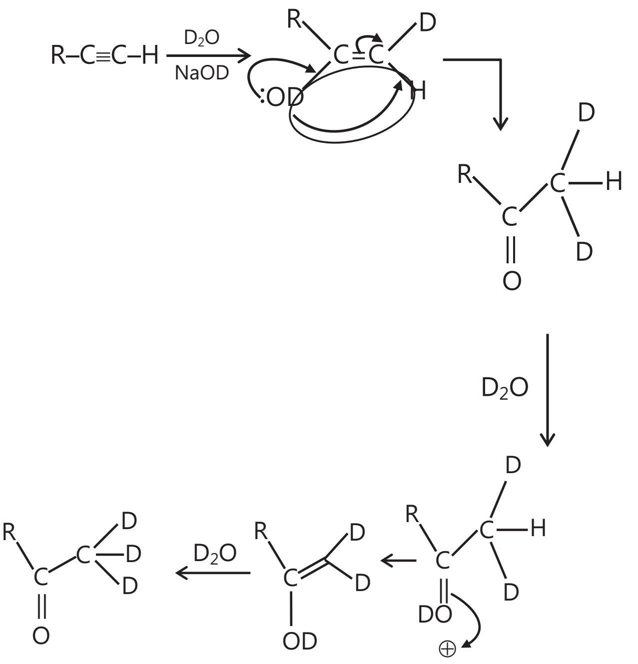
Here, alcohol is formed on the phenyl ring

Note :- as the (MeO –) group. Favours +ve charge (stabilizes)

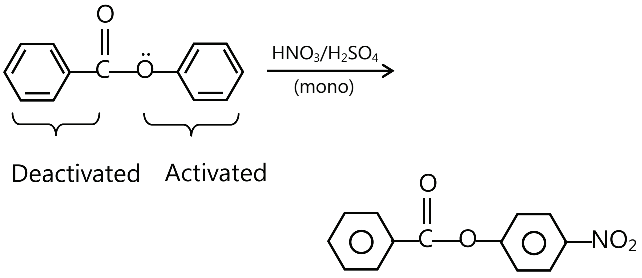
Sol 15:



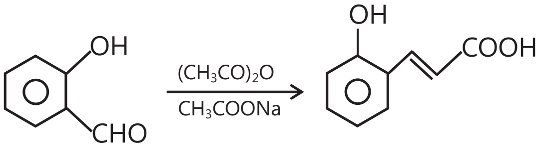
Mechanism with NaOD/D_2O (excess)



Sol 16:

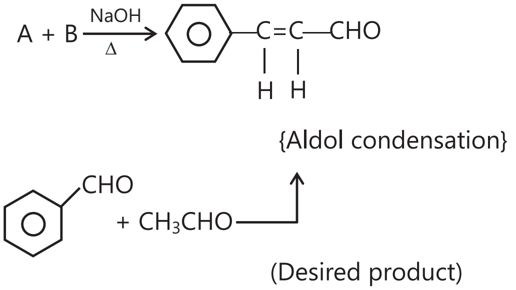


Sol 17:

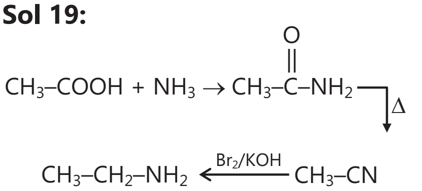


This is a very standard example of Perkin's condensation {If possible remember it}

Sol 18:



Sol 19:



$$CH_3\text{–}COOH + NH_3 \rightarrow CH_3\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}NH_2 \xrightarrow{\Delta} CH_3\text{–}CN$$

$$CH_3\text{–}CH_2\text{–}NH_2 \xleftarrow{Br_2/KOH} CH_3\text{–}CN$$

Step 1 is : Nucleophilic substitution of –OH by $–NH_2$

Step 2 is : Clearly dehydration

Step 3: Hoffman Bromanide Reaction (through the intermediate R–N=C=O)

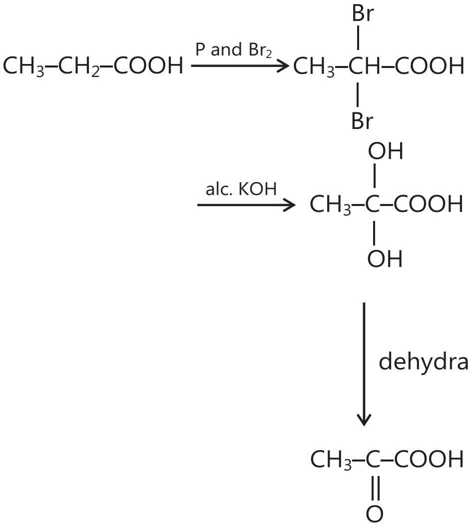
Sol 20: $CH_3\text{–}CH_2\text{–}OH \xrightarrow{(O)} CH_3\text{–}CH=O$

$$\xrightarrow[\text{(ii) dil NaOH}]{\text{(i) } Cl_2} HCOOH + CHCl_3$$

[Chloroform reaction]

Iodoform → presence of α-hydrogen

Sol 21:

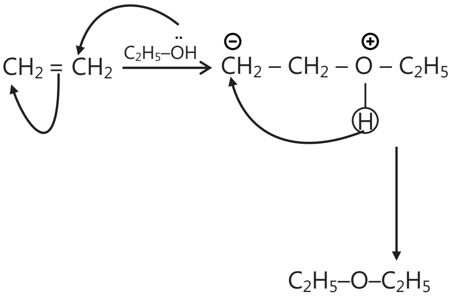


$$CH_3\text{–}CH_2\text{–}COOH \xrightarrow{\text{P and } Br_2} CH_3\text{–}\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle Br}{|}}{CH}}\text{–}COOH$$

$$\xrightarrow{\text{alc. KOH}} CH_3\text{–}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}\text{–}COOH \xrightarrow{\text{dehydration}} CH_3\text{–}\underset{\underset{\displaystyle O}{\|}}{C}\text{–}COOH$$

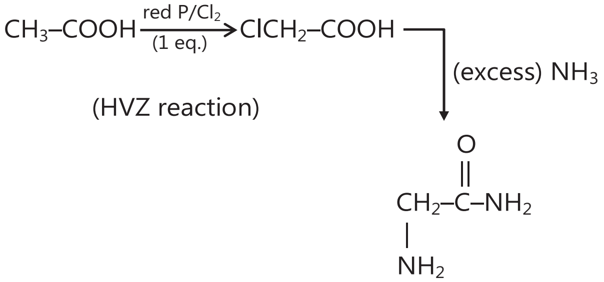
red P/Br_2 → Hell – Volhard Zelinski Reaction (HVZ) [α - bromination]

Sol 22: $C_2H_5I \xrightarrow[Ag_2O]{\text{Moist}} \underset{(A)}{C_2H_5OH} \xrightarrow{H_2SO_4} \underset{(B)}{CH_2=CH_2} \xrightarrow[140°C]{C_2H_5OH}$



∴ (C) → Et – O – Et

Sol 23:

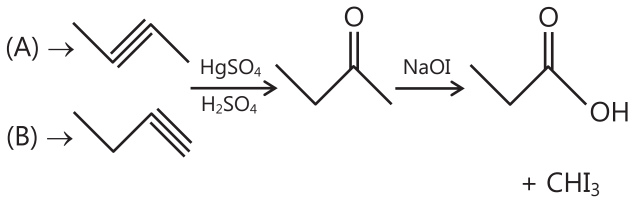


$$CH_3\text{–}COOH \xrightarrow[(1\text{ eq.})]{\text{red } P/Cl_2} ClCH_2\text{–}COOH \xrightarrow{\text{(excess) } NH_3} \underset{\underset{\displaystyle NH_2}{|}}{CH_2}\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}NH_2$$

(HVZ reaction)

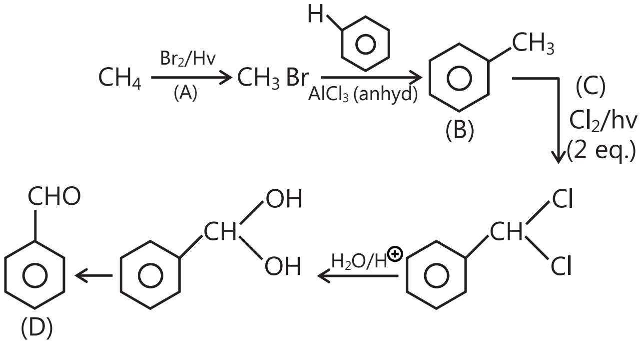
($NH_2^{\ominus}$ is a nucleophile)

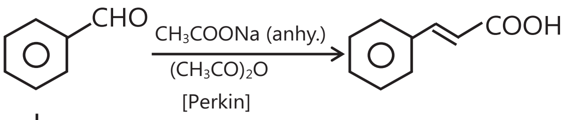
Sol 24:

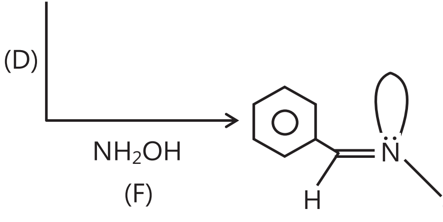


(Iodoform Reaction)

Sol 25:

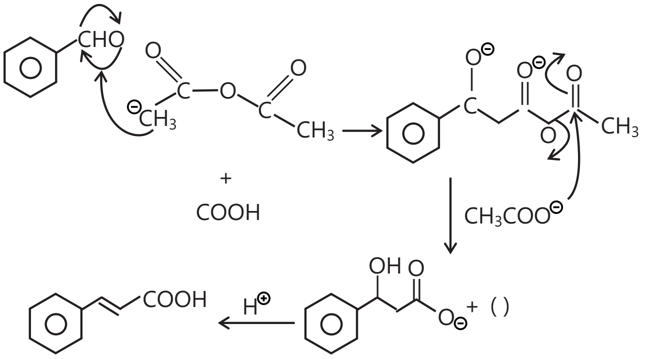




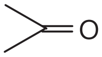


(Mechanism)

Perkins



Sol 26: (i) Higher carbonyl compounds aare insoluble in water due to more covalent character.

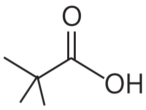
(ii) Bisulphites of  are soluble in water

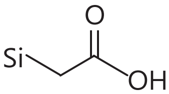
∴ Carbonyl compounds form solid additive products with $NaHSO_3$ which are separated out. The solid bisulphites of carbonyl compounds on hydrolysis by dil. acid regenerate original carbonyl compound.

(iii) Oxidation of toluene with chromium trioxide to benzaldehyde is carried out in presence of acetic anhydride because it converts benzaldehyde into its diacetate so preventing its further oxidation to acid form.

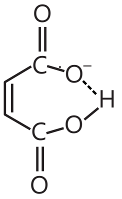
(iv) This is because aldehyde is more volatile than corresponding acid or alcohol.

(v) In a carboxylic acid, there is a pair of electrons on the oxygen in conjugation with carbonyl oxygen. This prevents the creation of a positive centre at carboxyl carbon. Therefore nucleophilic addition of phenyl hydrazine to give phenyl hydrazine is not possible.

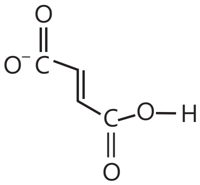
Sol 27: (i)  is more acidic than

 because Si has empty orbital so can do backbonding and by this decreases the acidity.

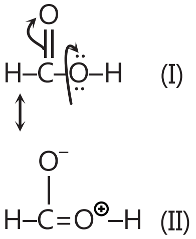
(ii) After first ionisation maleic acid ion is stabilised by hydrogen bonding but there is no such stabilisation in fumeric acid.



Mallic
acid



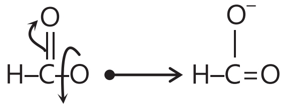
fumaric

(iii) In formic acid 

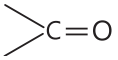
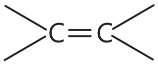
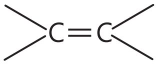
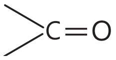
Structure (I) is more stable than structure (II)

So C=O bond length will be less than C–O in (I)

But in sodium formate resonance is equivalent



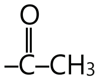
(iv) Because in the first step cleavage of ester is done which is diffcult to do.

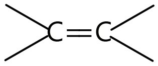
(v) Because in addition reaction, electron donating tendency of  and  are different  is better than 

Sol 28: (A) $C_9H_{12}O$

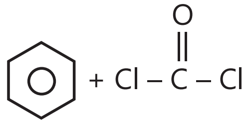
(i) Optically active

(ii) acidic hydrogen –OH

(iii)  $-\overset{O}{\overset{\|}{C}}-CH_3$ group

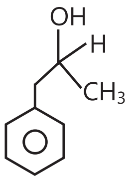
(iv)  do not present

(v) $(A) \xrightarrow[KMnO_4]{hot} \underset{C_7H_6O_2}{(B)} \xleftarrow{H^+}$



(vi) $(A) \xrightarrow[HI]{P} (e)$
Optically
inactive compound

(vii) 2 alcohol

(A) → 

Sol 29: $\frac{H}{5\times10^{-4}}\times40\ =8$

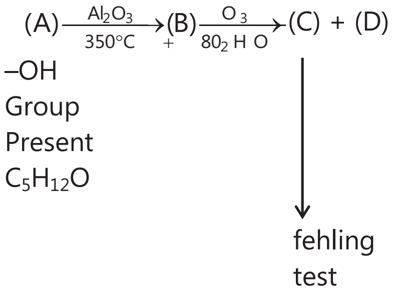
$\Delta T = \text{kg m}\frac{\text{moles}}{\text{mass in kg}}$

$\frac{0.088}{M}=10^{-6}$

mass = 88

carbon atom = $\frac{68.18}{12}\approx 12$

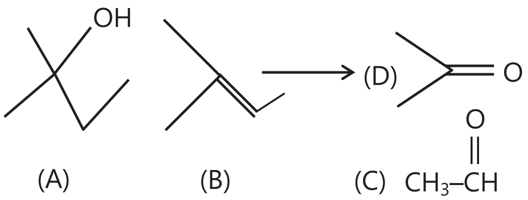
oxygen = 1



$(A)\xrightarrow[350°C]{Al_2O_3}(B)\xrightarrow[80_2\ H\ O]{O_3}(C) + (D)$

–OH
Group
Present
$C_5H_{12}O$

fehling
test



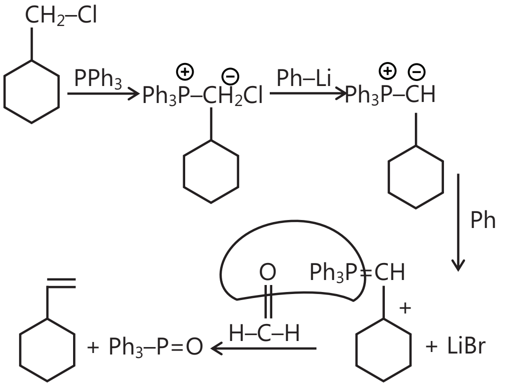
Exercise 2

Single Correct Choice Type

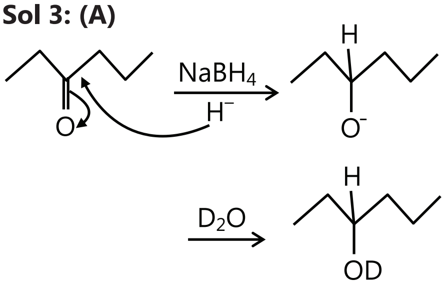
Sol 1: (C) 2 MeCH–CHO $\xrightarrow[\Delta]{NaOH}$ MeCH–CH$_2$–OH + MeCH–COONa

Cannizzaro reaction

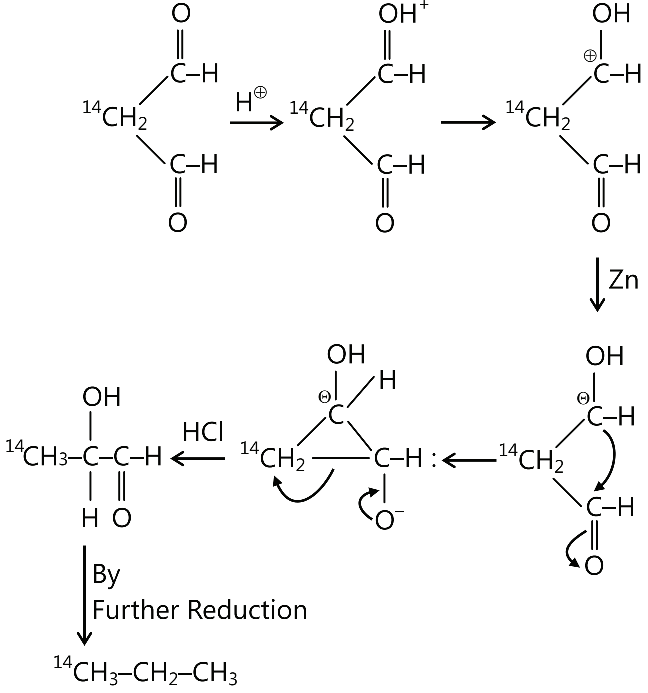
Sol 2: (C)



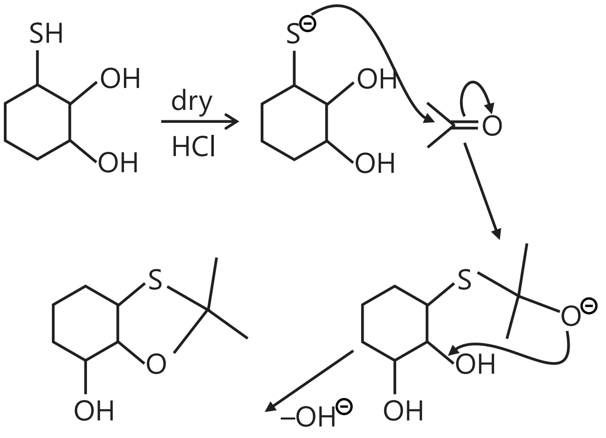
Sol 3: (A)



Sol 4: (B)



Sol 5: (B)



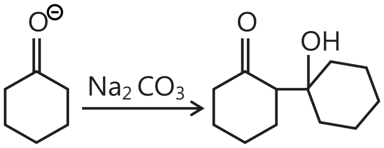
Sol 6: (A) $CH_3–CH_2–CH_2OH \xrightarrow[K_2Cr_2O_7]{H^+} CH_3–CH_2–CHO$
(A) (B)

B forms a shining silver mirron on wesming

$$\underset{(B)}{CH_3–CH_2–CHO} \xrightarrow{NH_2\,NH\ CONH_2}$$

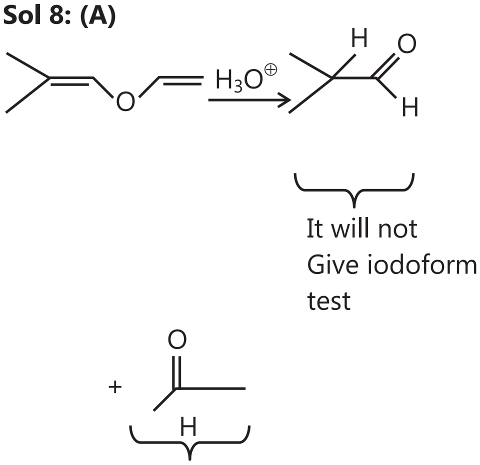
$$CH_3CH_2CH{=}N\ NH\ CO\ NH_2$$

Sol 7: (C)



aldol condensation will occur as Na_2CO_3 is a base.

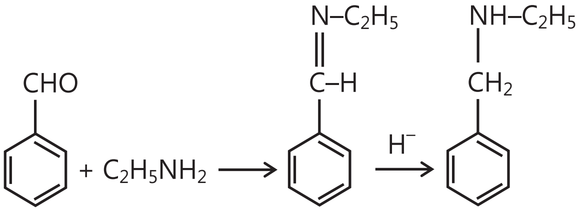
Sol 8: (A)



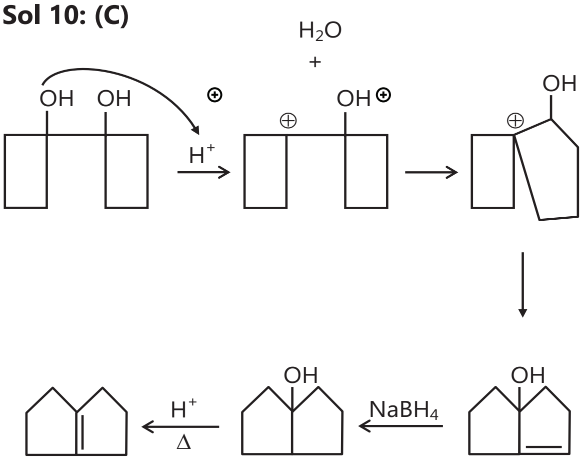
It will not Give iodoform test

It will give positive iodoform test

Sol 9: (D)

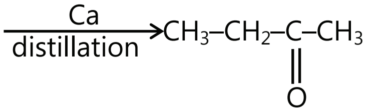


Sol 10: (C)



Sol 11: (B) Hydration will occur at position 2 as carbon at positive 2 has maximum δ+ charge due to –I effect of other carbonyl groups.

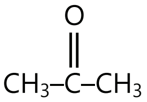
Sol 12: (C) $CH_3–CH_2–COOH + CH_3–COOH$



$$\xrightarrow[\text{distillation}]{Ca} CH_3–CH_2–\underset{\underset{O}{\|}}{C}–CH_3$$

Sol 13: (C) $NaBH_4$ is weak reducing agent. So it will reduce only the ketone but $LiAlH_4$ is strong reducing so it will reduce both ester and ketone.

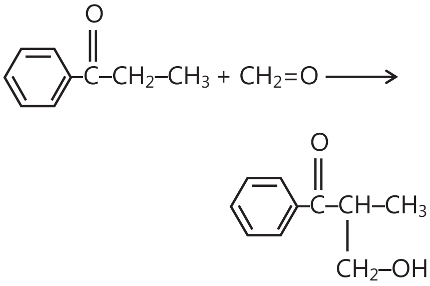
Sol 14: (C) $CH_3–CH_2–OH$ &



$$CH_3–\overset{\overset{O}{\|}}{C}–CH_3$$

LAN oxidises alcohol to aldehyde or ketone so only $CH_3–CH_2–OH$ will give positive test.

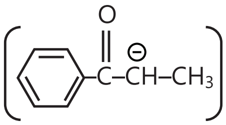
Sol 15: (B)



best

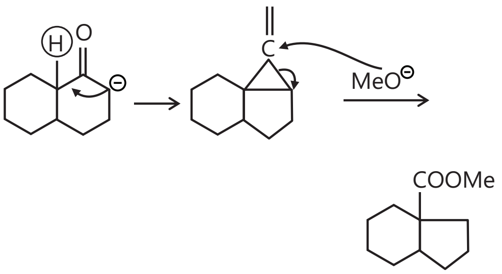
most reactive carbonion $\left[\,>C{=}O\,\right]$

group

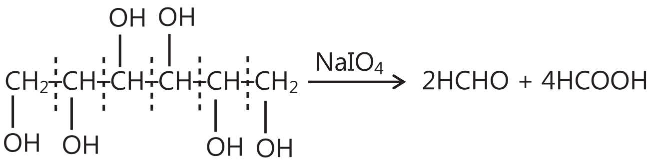


Sol 16: (B) Aromatic aldehydes do not give positive test with Fehling's solution.

Sol 17: (B)

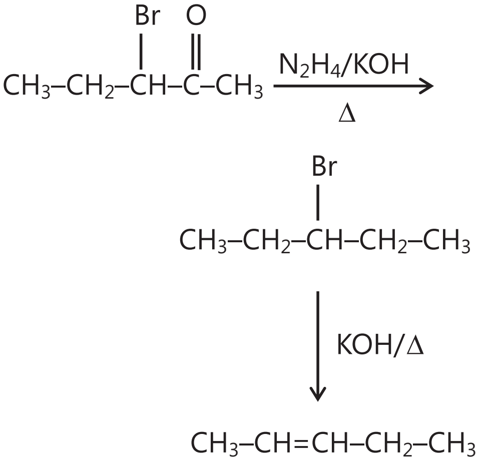


Sol 18: (D)



$$CH_2(OH)-CH(OH)-CH(OH)-CH(OH)-CH(OH)-CH_2(OH) \xrightarrow{NaIO_4} 2HCHO + 4HCOOH$$

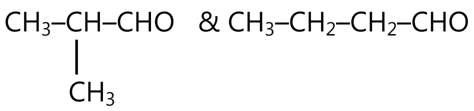
Sol 19: (D)



$$CH_3-CH_2-CH(Br)-C(=O)-CH_3 \xrightarrow[\Delta]{N_2H_4/KOH} CH_3-CH_2-CH(Br)-CH_2-CH_3 \xrightarrow{KOH/\Delta} CH_3-CH=CH-CH_2-CH_3$$

Multiple Correct Choice Type

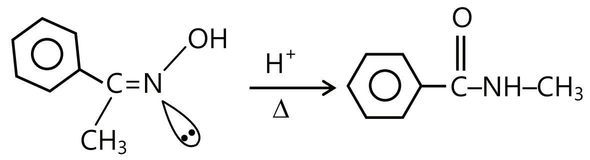
Sol 20: (B, D) Aldehydes gives 2, 4-DNP test so (x) should have aldehyde x gives negative Iodoform ⇒ $\left(-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3\right)$ group is absent so possible structure of (x) are



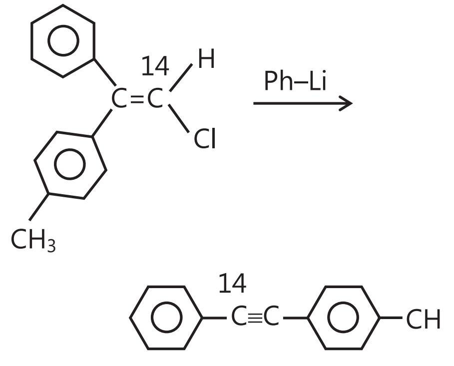
$$CH_3-CH(CH_3)-CHO \quad \& \quad CH_3-CH_2-CH_2-CHO$$

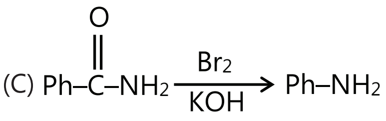
Sol 21: (A, B, D)

(A)



(B)

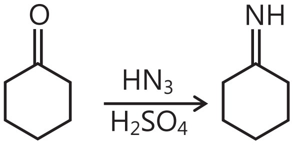




$$(C)\ Ph-C(=O)-NH_2 \xrightarrow[KOH]{Br_2} Ph-NH_2$$

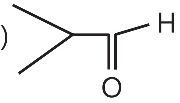
Hoffmann
Brommamide

(D)

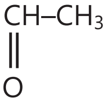


Sol 22: (B, C, D)

(A)



(B)

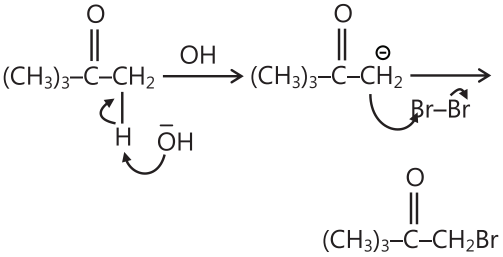


$$CH-CH_3 \ (=O)$$

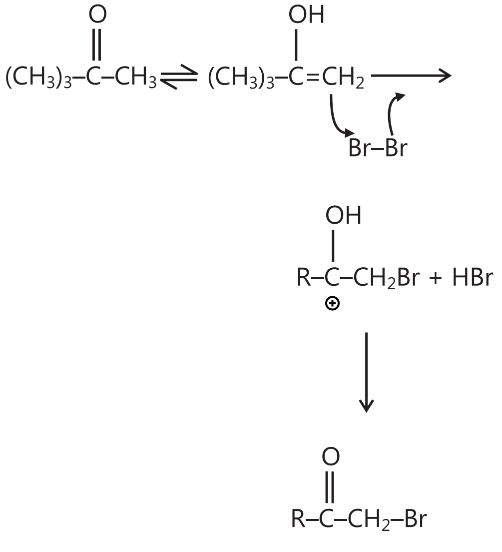
So only Iodoform can distinguish between them.

Comprehension Type

Sol 23: (C)



$$(CH_3)_3-C(=O)-CH_2-H \xrightarrow{\bar{O}H} (CH_3)_3-C(=O)-\overset{\ominus}{C}H_2 \xrightarrow{Br-Br} (CH_3)_3-C(=O)-CH_2Br$$



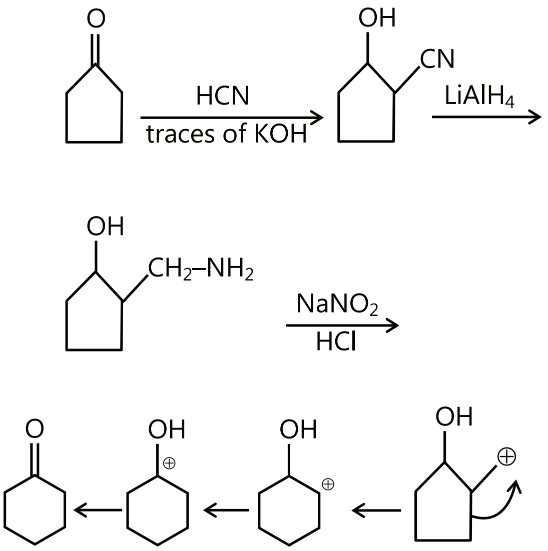
$$(CH_3)_3-C(=O)-CH_3 \rightleftharpoons (CH_3)_3-C(OH)=CH_2 \xrightarrow{Br-Br} R-\overset{\oplus}{C}(OH)-CH_2Br + HBr \longrightarrow R-C(=O)-CH_2-Br$$

Sol 24: (B) Overall yield = 0. 58 × 0. 54 × 0. 68

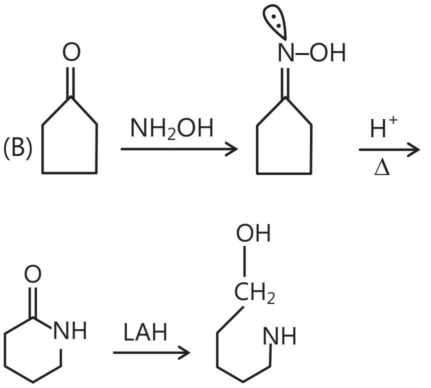
Overall yield = 0. 21 = 21%

Sol 25: A → p, q, s; B → p; C → p, q, s; D → p, q, s

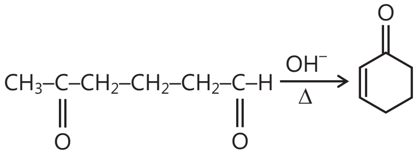
(A)



(B)

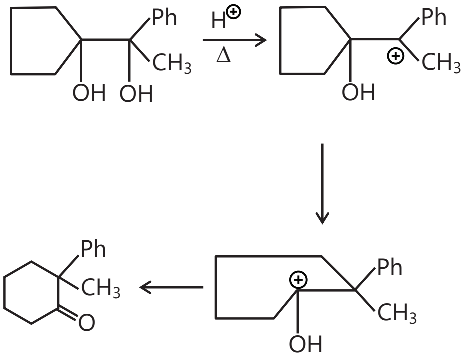


(C)



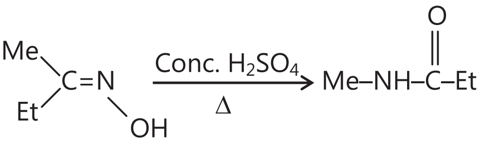
$CH_3\text{–}\underset{\overset{\|}{O}}{C}\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}\underset{\overset{\|}{O}}{C}\text{–}H \xrightarrow[\Delta]{OH^-}$

(D)

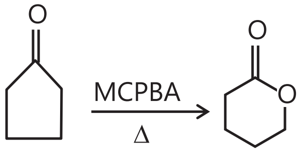


Sol 26: A → r; B → r, s; C → q, s; D → p

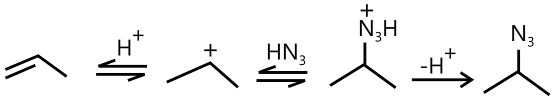
(A)



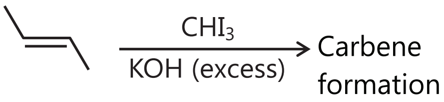
(B)



(C)

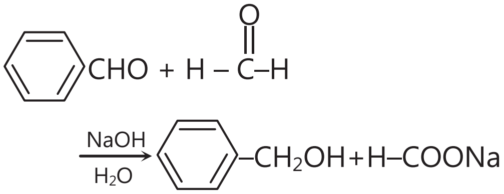


(D)



Previous Years' Questions

Sol 1: (A)



This is an example of cross Cannizzaro reaction in which formaldehyde is always oxidized.

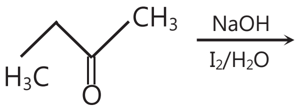
Sol 2: (C) The reactivity of carbonyl compound towards nucleophilic addition of Grignard's reagent depends on extent of steric hindrance at α-carbon. Greater the steric hindrance smaller the reactivity. Hence. reactivity order is

$CH_3CHO > CHI_3\text{–}CO\text{–}CH_3 > Ph\text{–}CO\text{–}Ph$

II I III

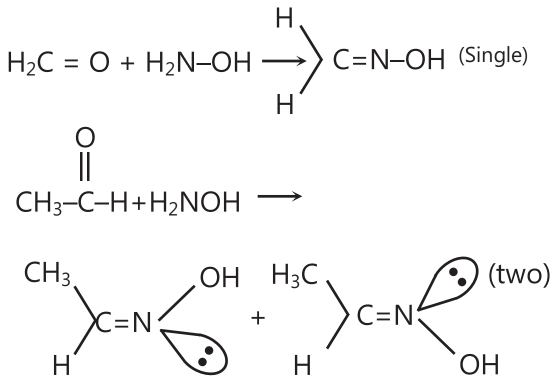
Sol 3: (C) X is $(CH_3CO)_2O$ and it is an example of Perkins reaction.

Sol 4: (C)

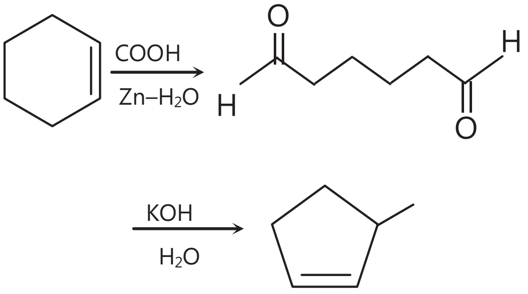


$CHI_3 + CH_3CH_2COONa \xrightarrow{H^+} CH_3CH_2COOH$

Sol 5:

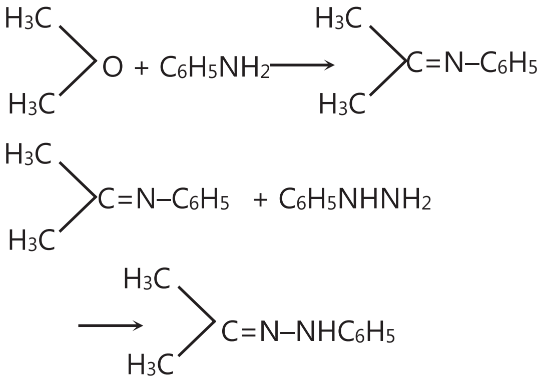


Sol 6:

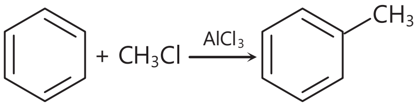


intramolecular aldol condension reaction

Sol 7:



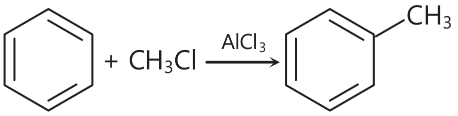
Sol 8: In both Friedel-Crafts reaction and Reimer-Tiemann's reaction new carbon-carbon bond is formed.



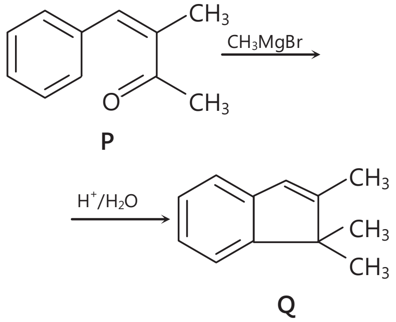
Friedel -Crafts alkylation

Comprehension 1 (Questions 9 to 11)

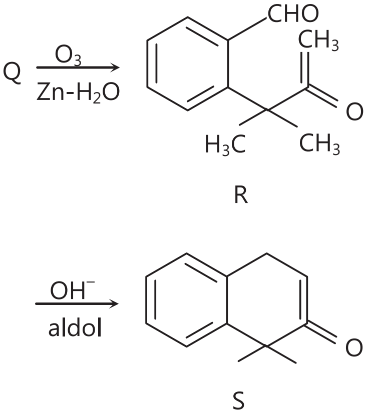
Sol: Q.9 B, Q.10 A and Q.11 B

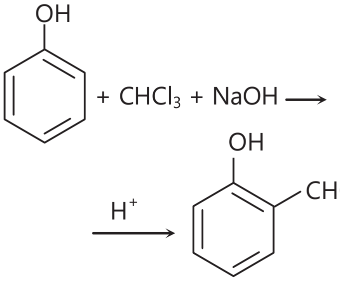


Friedel -Crafts alkylation



(gives possible iodoform test)





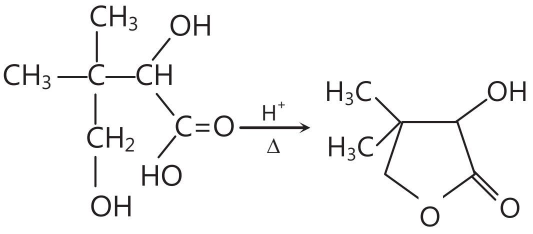
Reimer-Tiemann's reaction

All those carbonyl compounds containing α-H to sp^2 carbon show keto-enol tautomerism.

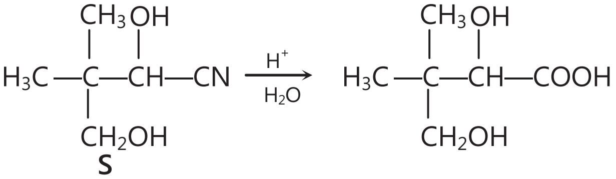
Comprehension 2 (Questions 12 to 14)

Sol: Q.12 B Q.13 A and Q.14 D

The given product an ester, obtained by condensation of a hydroxy acid obtained through hydrolysis of a cyanohydrin –

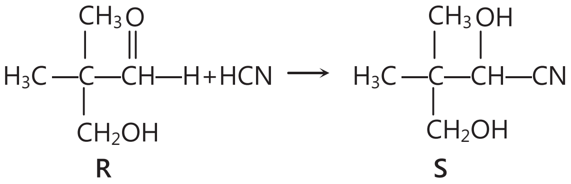


Acid above is obtained by acid hydrolysis of cyanohydrin S as



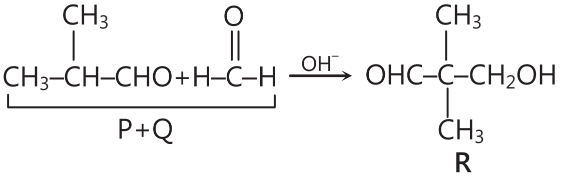
$$\underset{\textbf{S}}{H_3C-\overset{CH_3}{\underset{CH_2OH}{C}}-\overset{OH}{CH}-CN} \xrightarrow[H_2O]{H^+} H_3C-\overset{CH_3}{\underset{CH_2OH}{C}}-\overset{OH}{CH}-COOH$$

S is obtained by nucleophile addition of HCN on R, hence R is



$$\underset{\textbf{R}}{H_3C-\overset{CH_3}{\underset{CH_2OH}{C}}-\overset{O}{\overset{\|}{CH}}-H}+HCN \longrightarrow \underset{\textbf{S}}{H_3C-\overset{CH_3}{\underset{CH_2OH}{C}}-\overset{OH}{CH}-CN}$$

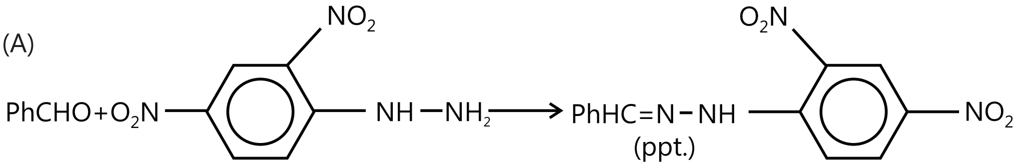
R is obtained by treatment of P and Q aqueous K_2CO_3 Through aldol condensation reaction as



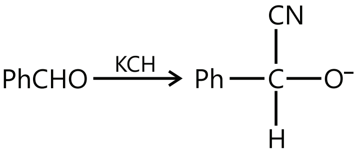
$$\underbrace{CH_3-\overset{CH_3}{CH}-CHO+H-\overset{O}{\overset{\|}{C}}-H}_{P+Q} \xrightarrow{OH^-} \underset{\textbf{R}}{OHC-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH}$$

Sol 15: A → p, q; B → q, r; C → q, r, s; D → q, r

(A)



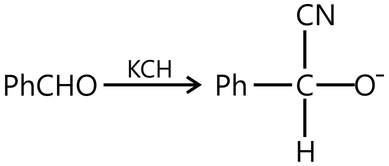
$PhCHO+Ag_2O \xrightarrow{NH_3} PhCOO^- + Ag\downarrow$
(white ppt.)



$$PhCHO \xrightarrow{KCH} Ph-\overset{CN}{\underset{H}{C}}-O^-$$

(B) $CH_3C\equiv CH \xrightarrow{\text{Ammonical AgNO}_3} \underset{\text{White ppt}}{CH_3C\equiv C^-Ag^+}$

(C)

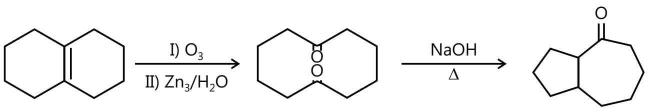


$$PhCHO \xrightarrow{KCH} Ph-\overset{CN}{\underset{H}{C}}-O^-$$

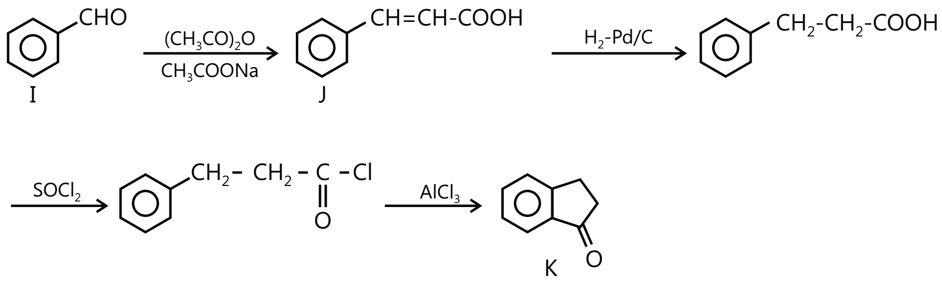
(D) $AgNO_3+CN^- \rightarrow AgCN\downarrow$

$AgNO_3+I^- \rightarrow AgI\downarrow$

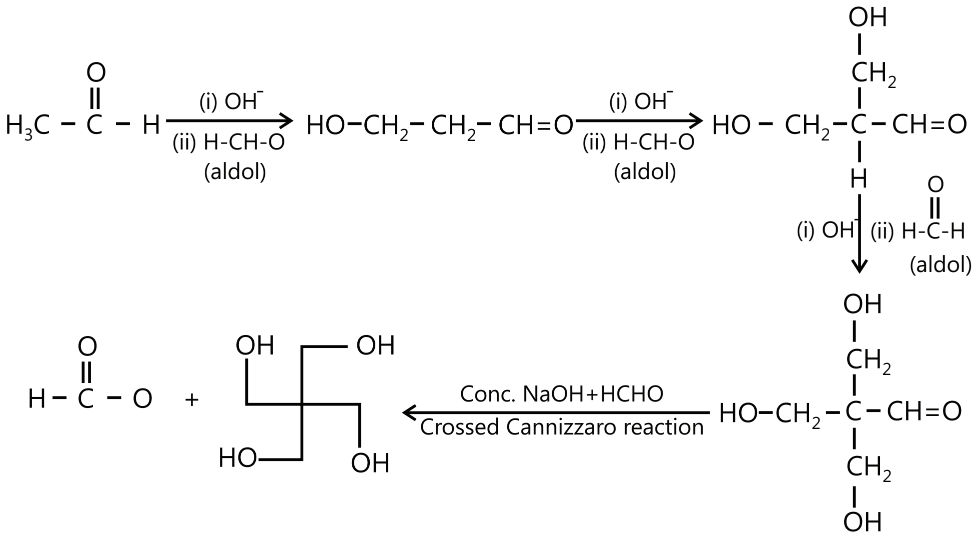
Sol 16: (1)



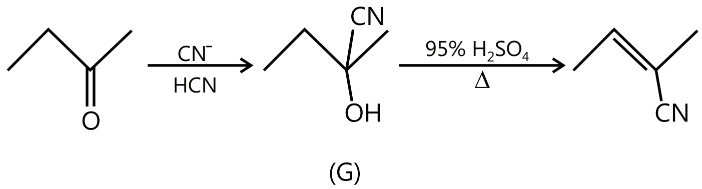
Sol 17 and 18: (C) and (A)



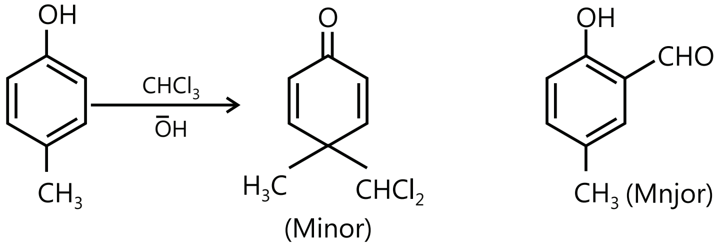
Sol 19: (C)



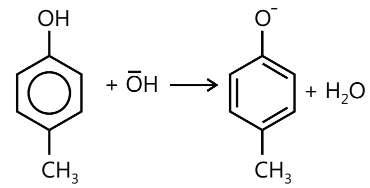
Sol 20: (B)

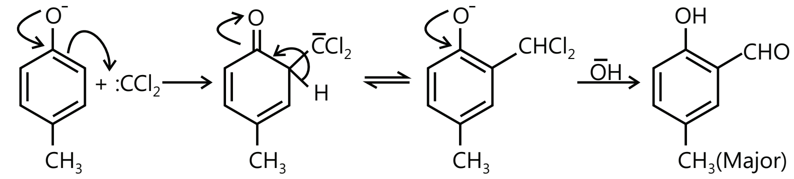


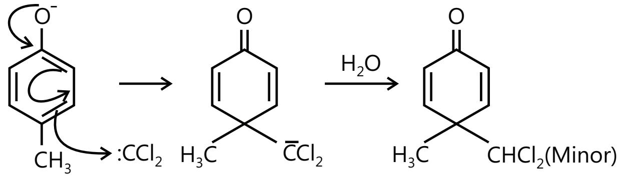
Sol 21: (B, D)



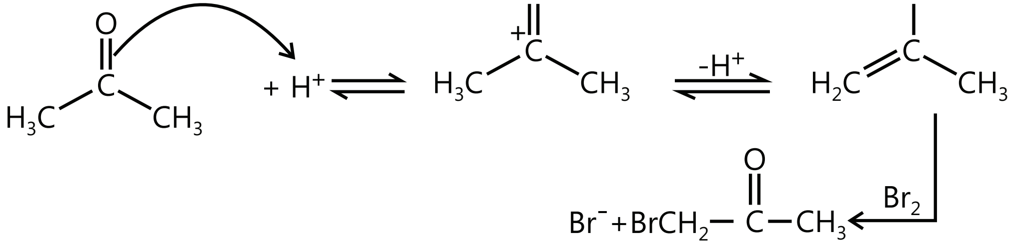
$CHCl_3 + \bar{O}H \longrightarrow :CCl_2 + H_2O + Cl^-$





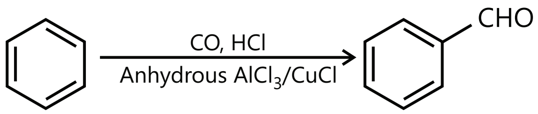


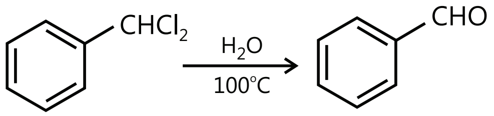
Sol 22: (C) Solve as per law of limiting reagent.

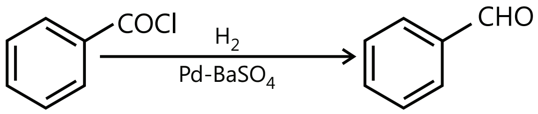


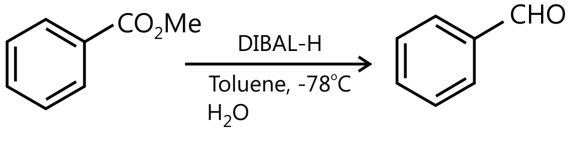
Sol 23: (D) PCC (Pyridinium chlorochromate) is a mild oxidising agent. It oxidises alcohol to aldehyde.

Sol 24: (A, B, C, D)

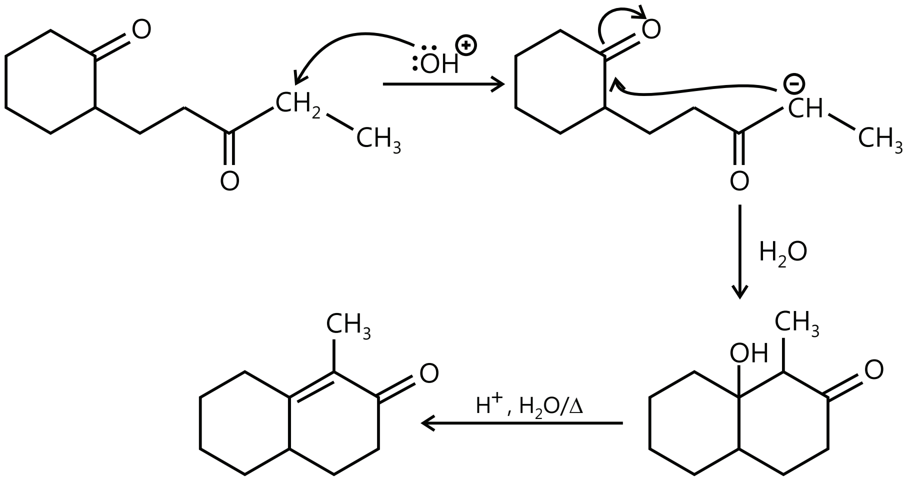
(I) 

(II) 

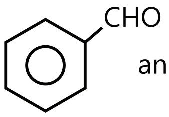
(III) 

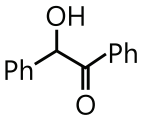
(IV) 

Sol 25: (A)



Sol 26: (A, B, C)

$CH_2 = CH - CHO$, 

and 

Gives positive test with Tollen's reagent.

Sol 27: (C) $NaBH_4$ in C_2H_5OH selectively reduces aldehydic group.

Sol 28 : (A)