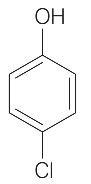
31

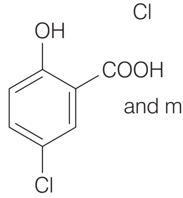
Aromatic Aldehydes, Ketones and Acids

Objective Questions I (Only one correct option)

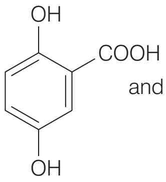
1. The major products of the following reaction are **(2019 Main, 12 April I)**



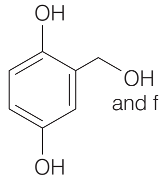
$\xrightarrow[\substack{\text{(2) HCHO, NaOH (conc.)}\\ \text{(3) } H_3O^+}]{\text{(1) } CHCl_3/aq.\text{ NaOH}}$

(a)


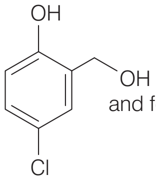
and methanol

(b)


and methanol

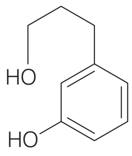
(c)


and formic acid

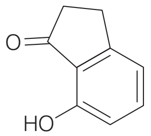
(d)


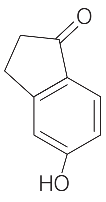
and formic acid

2. The major product of the following reaction is **(2019 Main, 12 April I)**



$\xrightarrow{\substack{\text{(i) } CrO_3\\ \text{(ii) } SOCl_2/\Delta\\ \text{(iii) } \Delta}}$

(a)


(b)


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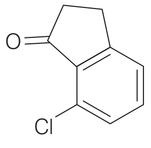

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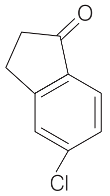
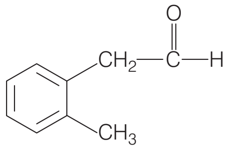


3. Compound $A(C_9H_{10}O)$ shows positive iodoform test. Oxidation of A with $KMnO_4/KOH$ gives acid $B(C_8H_6O_4)$. Anhydride of B is used for the preparation of phenolphthalein. Compound A is **(2019 Main, 10 April II)**

(a)


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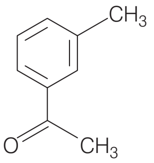
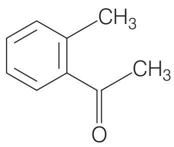


(c)


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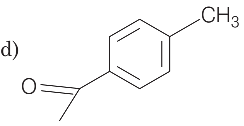
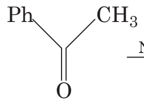
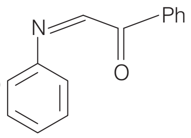
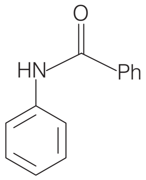


4. The major product Y in the following reaction is **(2019 Main, 10 April II)**



$\xrightarrow{NaOCl} X \xrightarrow[\text{(ii) Aniline}]{\text{(i) } SOCl_2} Y$

(a)


(b)


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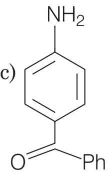

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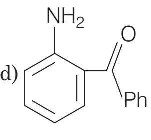
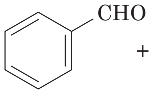


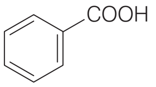
5. Major products of the following reaction are **(2019 Main, 10 April I)**



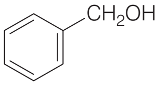
$+ \text{HCHO} \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) 50\% NaOH}}$

(a) CH_3OH and HCO_2H

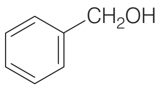
(b) CH_3OH and



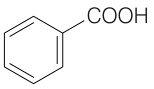
(c) HCOOH and



(d)

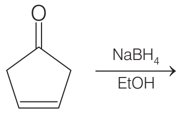


and

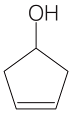


6. The major product of the following reaction is

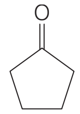
(2019 Main, 12 Jan II)



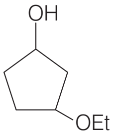
(a)



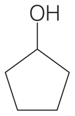
(b)



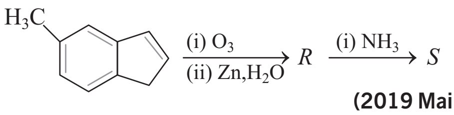
(c)



(d)

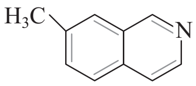


7. In the following reactions, the product *S* is



(2019 Main, 12 Jan I)

(a)



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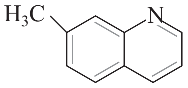

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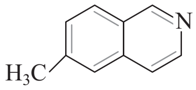
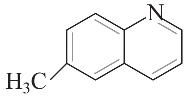
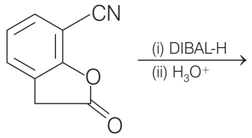


(d)

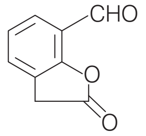


8. The major product of the following reaction is

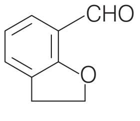


(2019 Main, 12 Jan I)

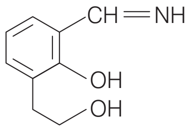
(a)



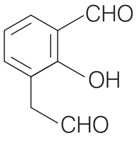
(b)



(c)

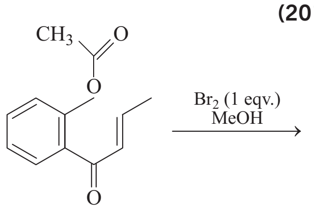


(d)

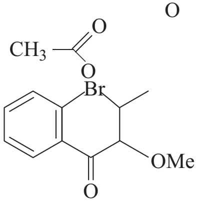


9. The major product obtained in the following conversion is

(2019 Main, 11 Jan II)



(a)



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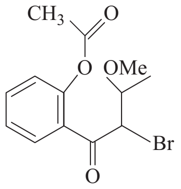
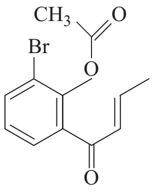
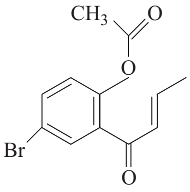


(c)

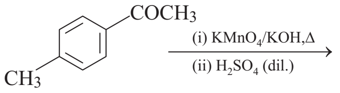


(d)

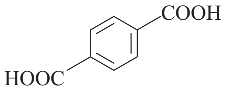


10. The major product of the following reaction is

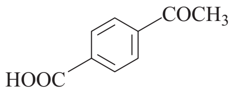
(2019 Main, 11 Jan I)



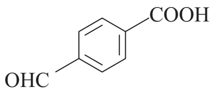
(a)



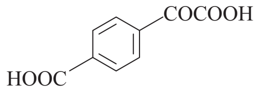
(b)



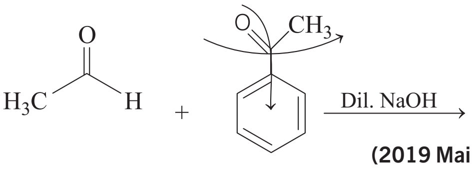
(c)



(d)

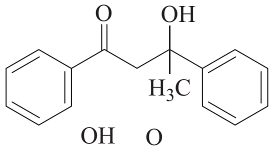


11. The major product formed in the following reaction is

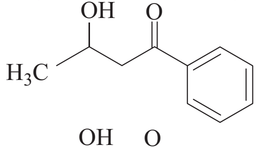


(2019 Main, 9 Jan II)

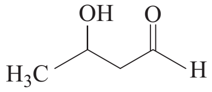
(a)



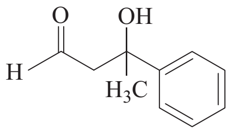
(b)



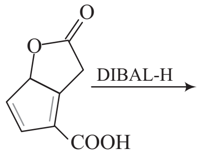
(c)



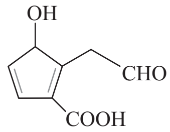
(d)



12. The major product obtained in the following reaction is



(2017 Main)

(a)


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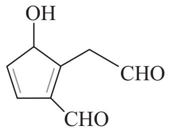
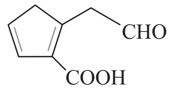
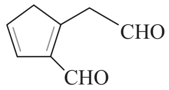


(c)


(d)


13. In the following sequence of reaction,

$$\text{Toluene} \xrightarrow{KMnO_4} A \xrightarrow{SOCl_2} B \xrightarrow[BaSO_4]{H_2/Pd} C$$

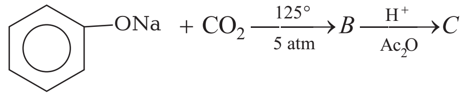
(2015 Main)

The product C is

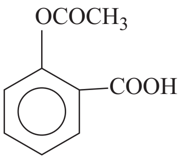
(a) C_6H_5COOH (b) $C_6H_5CH_3$

(c) $C_6H_5CH_2OH$ (d) C_6H_5CHO

14. Sodium phenoxide when heated with CO_2 under pressure at 125°C yields a product which on acetylation produces C.



The major product C would be **(2014 Main)**

(a)


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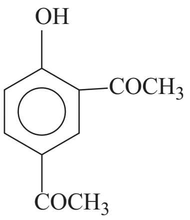
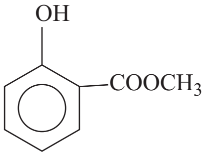
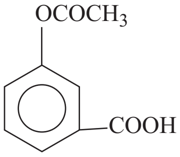
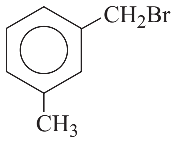
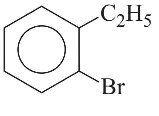


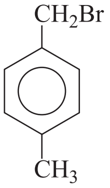
(c)


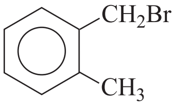
(d)


15. Compound (A), C_8H_9Br gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A). **(2013 Main)**

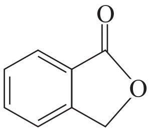
(a)


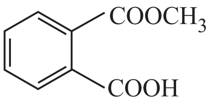
(b)


(c)


(d)


16. Which of the following reactants on reaction with conc. NaOH followed by acidification gives following lactone as the main product? **(2006, 5M)**



(a)


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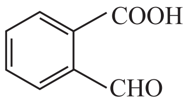

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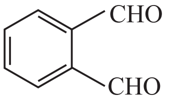

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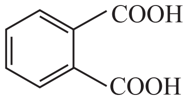
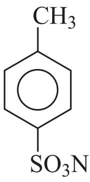
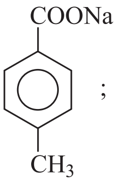


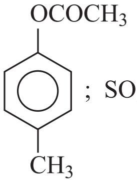
17. 4-methyl benzene sulphonic acid reacts with sodium acetate to give **(2005, 1M)**

(a)


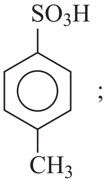
; CH_3CO_2H

(b)


; SO_3

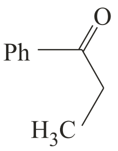
(c)


; SO_3

(d)


; NaOH

18. $Ph—C \equiv C—CH_3 \xrightarrow{Hg^{2+}/H^+} A$, A is **(2003, 1M)**

(a)


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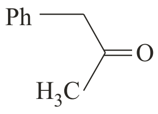

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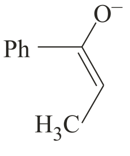

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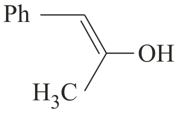
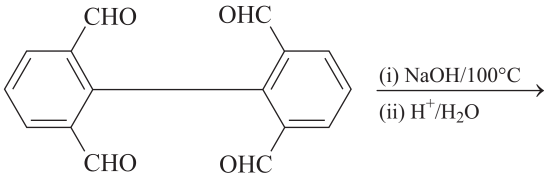
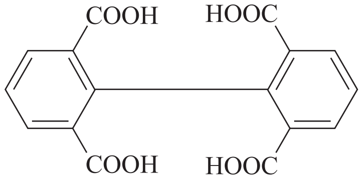


19.


Major product **(2003, 1M)**

(a)


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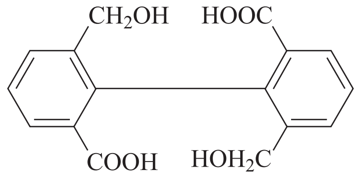

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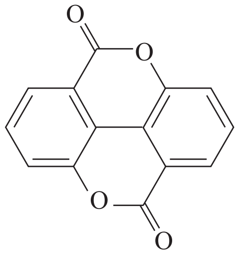

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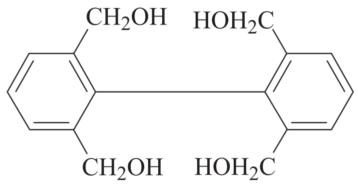
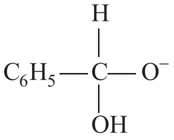
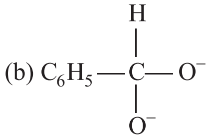


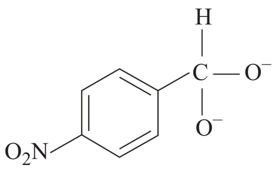
20. In Cannizzaro's reaction, the intermediate which is the best hydride donor is **(1997)**

(a) 

$C_6H_5-\overset{H}{\underset{OH}{C}}-O^-$

(b) 

$C_6H_5-\overset{H}{\underset{O^-}{C}}-O^-$

(c)


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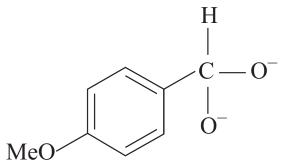


21. In the Cannizzaro's reaction given below :

$$2Ph-CHO \xrightarrow{KOH} Ph-CH_2OH + PhCO_2^-$$

The slowest step is **(1996, 1M)**

(a) the attack of —OH at the carbonyl group
(b) the transfer of hydride to the carbonyl group
(c) the abstraction of proton from the carboxylic acid
(d) the deprotonation of Ph—CH_2OH

22. *m*-chlorobenzaldehyde on reaction with conc. KOH at room temperature gives **(1991, 1M)**

(a) potassium *m*-chlorobenzoate and *m*-chlorobenzyl alcohol
(b) *m*-hydroxy benzaldehyde and *m*-chlorobenzyl alcohol
(c) *m*-chlorobenzyl alcohol and *m*-hydroxy benzyl alcohol
(d) potassium *m*-chlorobenzoate and *m*-hydroxy benzaldehyde

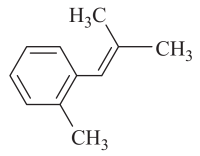
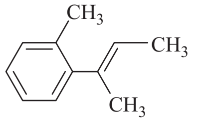
Objective Questions II

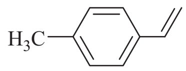
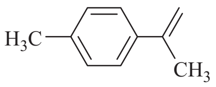
(One or more than one correct option)

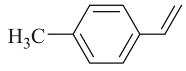
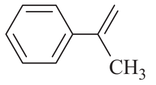
23. Compound *P* and *R* upon ozonolysis produce *Q* and *S*, respectively. The molecular formula of *Q* and *S* is C_8H_8O. *Q* undergoes Cannizzaro reaction but not haloform reaction, whereas *S* undergoes haloform reaction but not Cannizzaro reaction. **(2017 Adv.)**

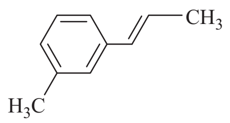
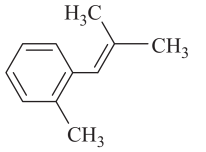
(i) $P \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3/\text{CH}_2\text{Cl}_2} \underset{(C_8H_8O)}{Q}$ (ii) $R \xrightarrow[\text{(ii) Zn/H}_2\text{O}]{\text{(i) O}_3/\text{CH}_2\text{Cl}_2} \underset{(C_8H_8O)}{S}$

The option(s) with suitable combination of *P* and *R*, respectively, is(are)

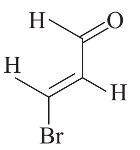
(a)  and 

(b)  and 

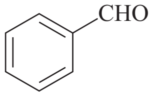
(c)  and 

(d)  and 

24. Positive Tollen's test is observed for



(a)



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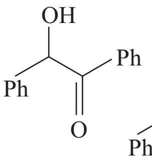

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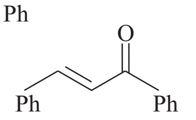
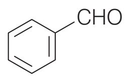
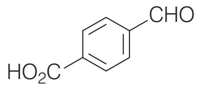
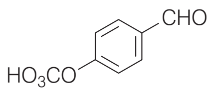


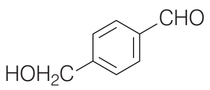
(d)

25. The aldehydes which will not form Grignard product with one equivalent Grignard reagents are **(2019 Main 12 Jan II)**

(a) 

(b) 

(c) 

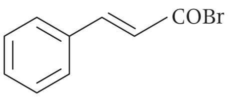
(d) 

Passage Based Questions

Paragraph X

Treatment of benzene with CO / HCl in the presence of anhydrous $AlCl_3$ / CuCl followed by reaction with Ac_2O / NaOAc gives compound X as the major product. Compound X upon reaction with Br_2 / Na_2CO_3 followed by heating at 473 K with moist KOH furnishes Y as the major product. Reaction of X with H_2 / Pd - C, followed by H_3PO_4 treatment gives Z as the major product.

26. The compound Y is **(2018 Adv.)**

(a)


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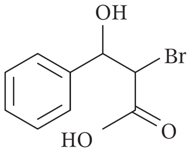

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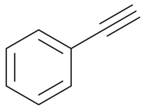

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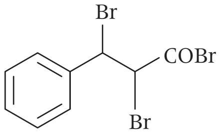
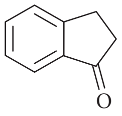


27. The compound Z is

(a)


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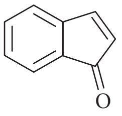

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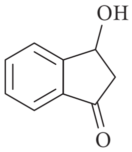

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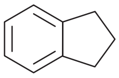
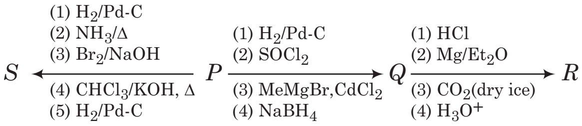


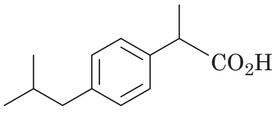
Paragraph A

An organic acid P ($C_{11}H_{12}O_2$) can easily be oxidised to a dibasic acid which reacts with ethylene glycol to produce a polymer dacron. Upon ozonolysis, P gives an aliphatic ketone as one of the products. P undergoes the following reaction sequences to furnish R via Q. The compound P also undergoes another set of reactions to produce S. **(2018 Adv.)**



$$S \xleftarrow[\substack{(4)\ CHCl_3/KOH,\ \Delta\\ (5)\ H_2/Pd\text{-}C}]{\substack{(1)\ H_2/Pd\text{-}C\\ (2)\ NH_3/\Delta\\ (3)\ Br_2/NaOH}} P \xrightarrow[\substack{(3)\ MeMgBr, CdCl_2\\ (4)\ NaBH_4}]{\substack{(1)\ H_2/Pd\text{-}C\\ (2)\ SOCl_2}} Q \xrightarrow[\substack{(3)\ CO_2(\text{dry ice})\\ (4)\ H_3O^+}]{\substack{(1)\ HCl\\ (2)\ Mg/Et_2O}} R$$

28. The Compound R is

(a)


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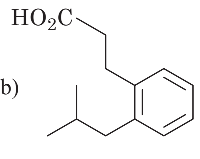

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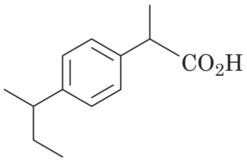

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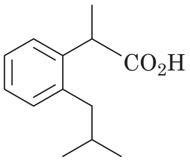
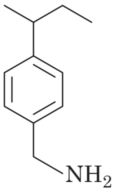


29. The compound S is

(a)


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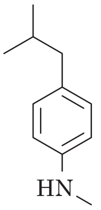

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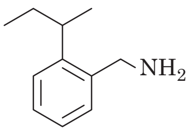

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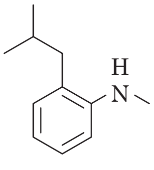
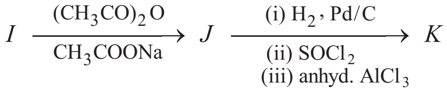


Passage

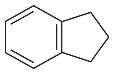
In the following reactions sequence, the compound J is an intermediate.



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

J ($C_9H_8O_2$) gives effervescence on treatment with $NaHCO_3$ and positive Baeyer's test. **(2012)**

30. The compound K, is

(a)


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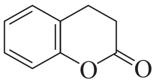

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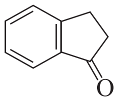

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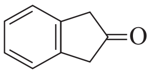
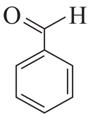
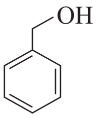
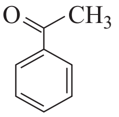
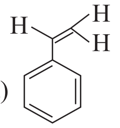


31. The compound I, is

(a)


(b)


(c)


(d)


Fill in the Blanks

32. The structure of the intermediate product formed by the oxidation of toluene with CrO_3 and acetic anhydride, whose hydrolysis gives benzaldehyde is …………… **(1992, 2M)**

True/False

33. Benzaldehyde undergoes aldol condensation in an alkaline medium. **(1982 , 1M)**

Subjective Questions

34. Five isomeric *para*-disubstituted aromatic compounds *A* to *E* with molecular formula $C_8H_8O_2$ were given for identification.
Based on the following observations, give structures of the compounds : **(2002, Main, 5M)**

(i) Both *A* and *B* form a silver mirror with Tollen's reagent; also, *B* gives a positive test with $FeCl_3$ solution.
(ii) *C* gives positive iodoform test .
(iii) *D* is readily extracted in aqueous $NaHCO_3$ solution.
(iv) *E* on acid hydrolysis gives 1, 4-dihydroxy benzene.

35. An organic compound *A*, $C_8H_4O_3$, in dry benzene in the presence of anhydrous $AlCl_3$ gives compound *B*. The compound *B* on treatment with PCl_5, followed by reaction with $H_2/Pd/(BaSO_4)$ gives compound *C*, which on reaction with hydrazine gives a cyclised compound *D* ($C_{14}H_{10}N_2$). Identify *A*, *B*, *C* and *D*. Explain the formation of *D* from *C*. **(2000, 5M)**

36. Explain, why *o*-hydroxy benzaldehyde is a liquid at room temperature while *p*-hydroxy benzaldehyde is a high melting solid? **(1999, 2M)**

Matching Type Questions

Answer Q. 22, Q. 23 and Q. 24 by appropriately matching the information given in the three columns of the following table.
Column 1, 2 and 3 contain starting materials, reaction conditions, and type of reactions, respectively. **(2017 Adv.)**

	Column 1		Column 2		Column 3
(I)	Toluene	(i)	NaOH/ Br_2	(P)	Condensation
(II)	Acetophenone	(ii)	$Br_2/h\nu$	(Q)	Carboxylation
(III)	Benzaldehyde	(iii)	$(CH_3CO)_2O/$ CH_3COOK	(R)	Substitution
(IV)	Phenol	(iv)	$NaOH/CO_2$	(S)	Haloform

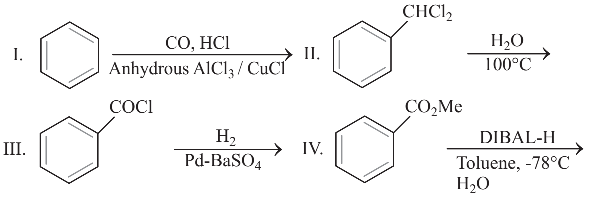
37. The only **CORRECT** combination in which the reaction proceeds through radical mechanism is
(a) (IV) (i) (Q) (b) (III) (ii) (P)
(c) (II) (iii) (R) (d) (I) (ii) (R)

38. For the synthesis of benzoic acid, the only CORRECT combination is
(a) (II) (i) (S) (b) (I) (iv) (Q)
(c) (IV) (ii) (P) (d) (III) (iv) (R)

30. The only **CORRECT** combination that gives two different carboxylic acids is
(a) (IV) (iii) (Q) (b) (II) (iv) (R)
(c) (I) (i) (S) (d) (III) (iii) (P)

Integer Type Questions

40. Among the following the number of reaction(s) that produce(s) benzaldehyde is **(2015 Adv.)**



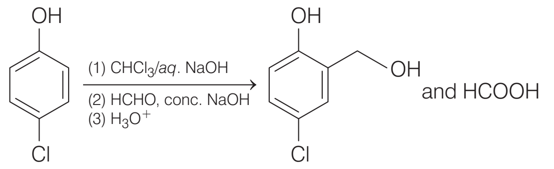
Answers

1. (d) **2.** (b) **3.** (c) **4.** (b)
5. (c) **6.** (a) **7.** (a) **8.** (d)
9. (b) **10.** (a) **11.** (c) **12.** (a)
13. (d) **14.** (a) **15.** (d) **16.** (c)
17. (a) **18.** (a) **19.** (b) **20.** (d)

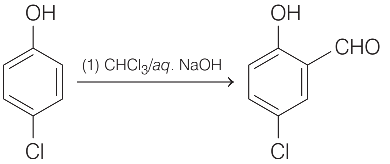
21. (b) **22.** (a) **23.** (b,c) **24.** (a,b,c)
25. (b,d) **26.** (c) **27.** (a) **28.** (a)
29. (b) **30.** (c) **31.** (a)
32. $C_6H_5—CH(OAc)_2$ **33.** False **37.** (a)
38. (d) **39.** (b) **40.** (4)

Hints & Solutions

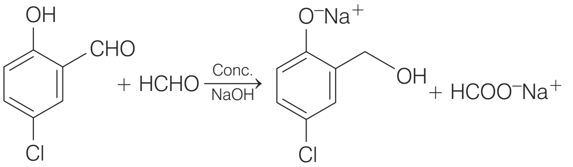
1. The major products of the given reaction are as follows:



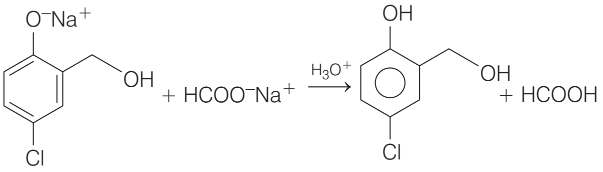
In step-I, substituted phenol undergoes Reimer-Tiemann reaction in presence of $CHCl_3$ / *aq.* NaOH



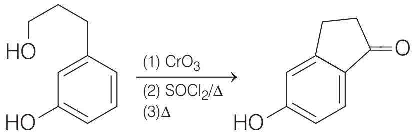
The aldehyde obtained in above equation does not possess α-hydrogen. In presence of formaldehyde and conc. NaOH it undergoes Cannizaro reaction. In this reaction, one molecule of aldehyde is reduced to alcohol while another molecule is oxidised to salt of carboxylic acid.



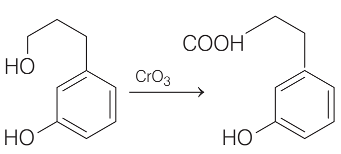
Upon hydrolysis, following reaction takes place



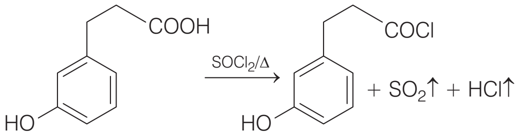
2. The major product formed in the reaction is as follows :



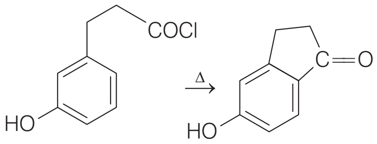
Primary alcohol readily oxidised to corresponding carboxylic acid with oxidising agent, chromium trioxide (CrO_3) in acidic medium.



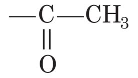
—OH group of carboxylic acid get substituted by —Cl in presence of $SOCl_2$ (Thionyl chloride).



Further, heating of product leads to intramolecular cyclisation.



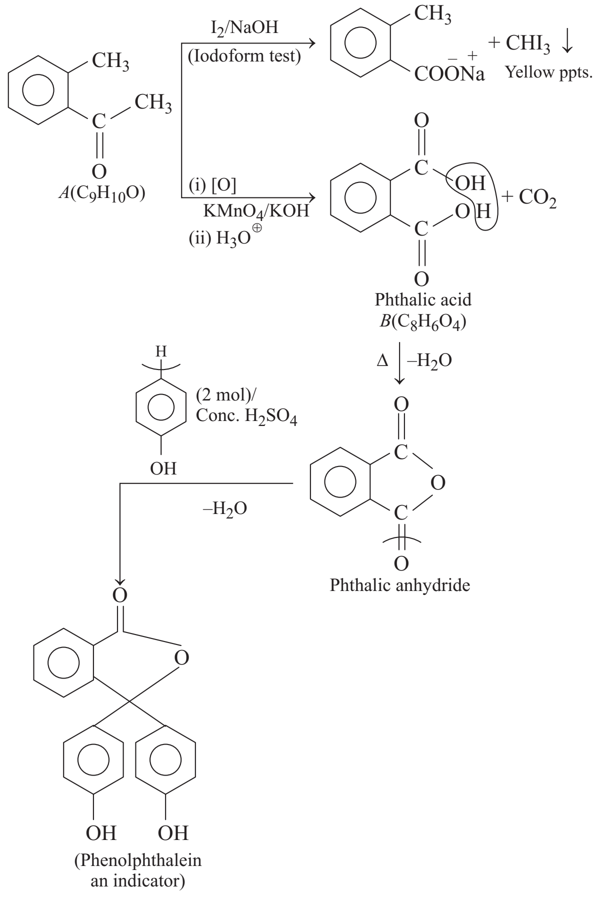
3. (i) $C_9H_{10}O$ shows positive iodoform test thus, —C—CH_3 group is present.


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

(ii) $C_9H_{10}O$ on strong oxidation ($KMnO_4$ / KOH), gives acid ($C_8H_6O_4$), indicating it can be a dicarboxylic acid. So, '*A*' contains —$COCH_3$ and one —CH_3 group which get oxidised into —COOH and —COOH respectively.

(iii) In the preparation of phenolphthalein from phenol, phthalic anhydride is used. So, '*B*' can be phthalic acid (benzene-1,2-dicarboxylic acid) which readily forms anhydride.

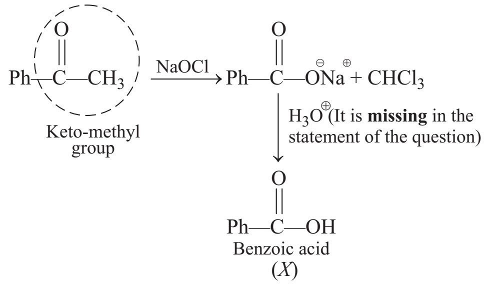
Thus, the reaction sequence is as follows :

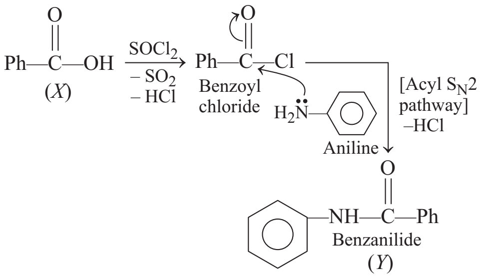


4. NaOCl (sodium hypochlorite) is the reagent of haloform (chloroform formation) reaction.

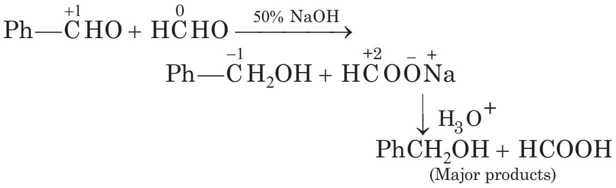
$$2NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$$

The given reaction takes place as follows :



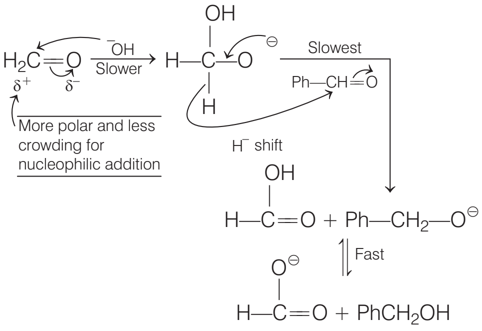


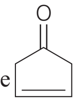
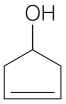
5. The given reaction is a crossed Cannizzaro reaction which is a redox reaction too. Oxidation number of carbon atom of the —CHO groups of Ph—CHO and H—CHO are +1 and zero respectively. So, HCHO is the stronger reducing agent than PhCHO. As a result, HCHO is oxidised to HCOONa (by donation of hydride, H^-) and PhCHO (H^- acceptor) is reduced to $PhCH_2OH$.



$$\text{Ph—}\overset{+1}{\text{C}}\text{HO} + \text{H}\overset{0}{\text{C}}\text{HO} \xrightarrow{50\%\ \text{NaOH}} \text{Ph—}\overset{-1}{\text{C}}\text{H}_2\text{OH} + \text{H}\overset{+2}{\text{C}}\text{OO}\overset{-}{\text{O}}\overset{+}{\text{Na}} \xrightarrow{H_3O^+} \underset{\text{(Major products)}}{PhCH_2OH + HCOOH}$$

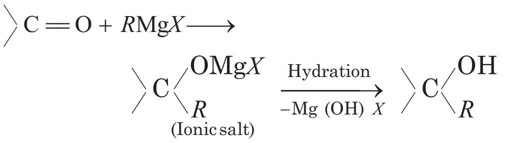
The reaction proceed *via* following mechanism.



6. Reducing agents like $LiAlH_4$, $NaBH_4$, i.e. complex hydrides usually does not affect olifenic or π-bonds. Thus, if $NaBH_4$ is applied to a compound like  then its $\rangle C=O$ bond will be reduced only and we get  as the final product.

Thus, option (a) is correct answer.

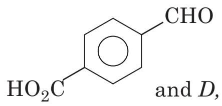
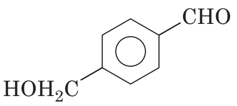
7. **Key Idea** Grignard reagent usually attacks on $> C=O$ group as :

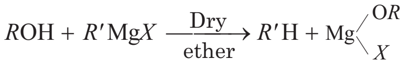


$$\rangle C=O + RMgX \longrightarrow \rangle C\langle^{OMgX}_{R} \xrightarrow[-Mg(OH)X]{\text{Hydration}} \rangle C\langle^{OH}_{R}$$

(Ionic salt)

The question is related to above reaction only with the condition that the consumption of $RMgX$ will be more than 1 equivalent in some of the given cases.

Among the given compounds B, i.e.  and D, i.e.  contain additional groups which can give active hydrogens. Grignard reagents produce alkanes whenever come in contact with any group or compound which can give active hydrogen as:



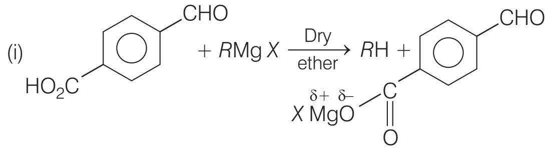
$$ROH + R'MgX \xrightarrow[\text{ether}]{\text{Dry}} R'H + Mg\langle^{OR}_{X}$$

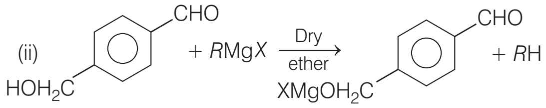
These reactions are equivalent to acid-base reactions. So, in both of these compounds more than one equivalent will be required to form Grignard products. Remember these compounds will give 2 type of products as:

(i) from the $>C=O$ group

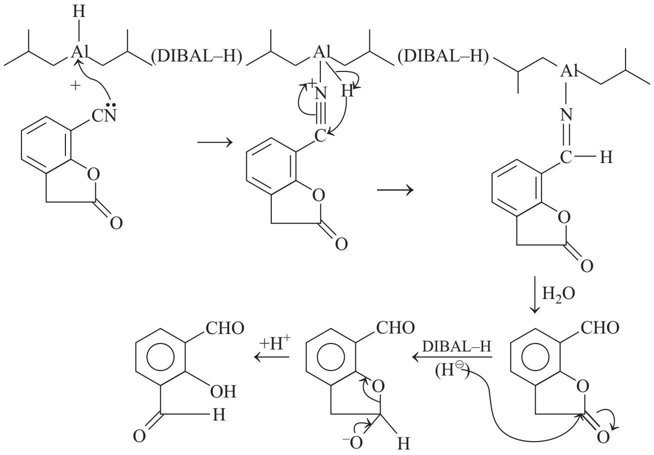
(ii) from the group which release active hydrogen

The additional reactions involved are:

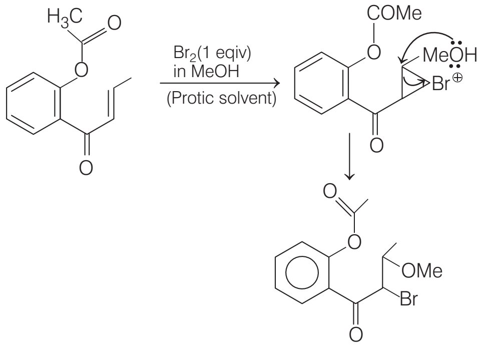




8. DIBAL-H (Diisobutylaluminium hydride) is a reducing agent with formula $[\lambda\text{-}Bu_2AlH]$. At ordinary temperatures, nitriles give imines which are readily converted in aldehydes by hydrolysis whereas lactones are reduced directly to aldehydes.

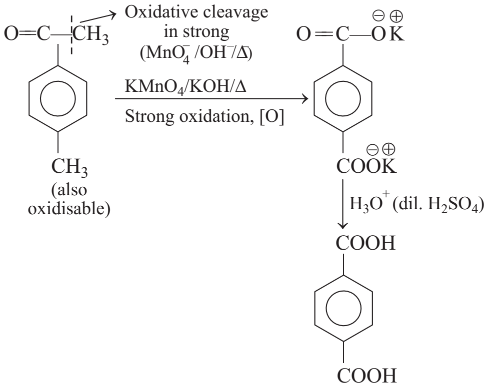


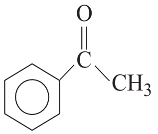
9. In presence of $Br_2/EtOH$, the reactant containing double bond undergoes electrophilic addition reaction *via* the formation of bromonium ion. On further attack of $-\ddot{\underset{\cdot\cdot}{O}}Me$ on bromonium ion gives the addition product.



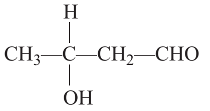
(Major)

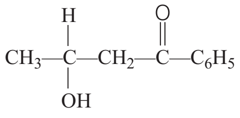
10. In presence of alkaline $KMnO_4$, vigorous oxidation of alkyl or acyl benzene takes place. During oxidation, aromatic nucleus remains intact but the entire chain is oxidised to —COOH group irrespective of the length of carbon chain.

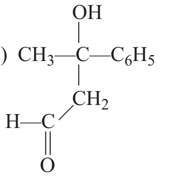


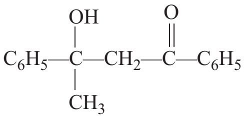
11. In aldol condensation, generally aldehydes react at a faster rate than ketones towards base. In the given case CH_3CHO will lose α-hydrogen faster than  due to one more reason, i.e. conjugation between benzene ring and $>C=O$ group. Along with sterically less hindered nucleophile of CH_3CHO will also add to the major product formation.

Following four products are possible in the reaction:

(i) 
$CH_3-\underset{OH}{\overset{H}{C}}-CH_2-CHO$ (Self Aldol condensation of CH_3CHO)

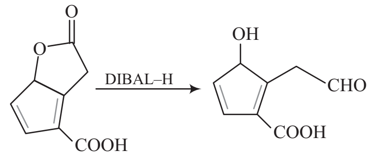
(ii) 
$CH_3-\underset{OH}{\overset{H}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-C_6H_5$ (Cross Aldol condensation of CH_3CHO and $CH_3COC_6H_5$ in which >C=O group of CH_3CHO is carbanion acceptor).

(iii) 
$CH_3-\overset{OH}{\underset{CH_2-CHO}{C}}-C_6H_5$ (Cross Aldol condensation of CH_3CHO and $CH_3COC_6H_5$ in which >C=O group of $C_6H_5COCH_3$ is carbanion acceptor).

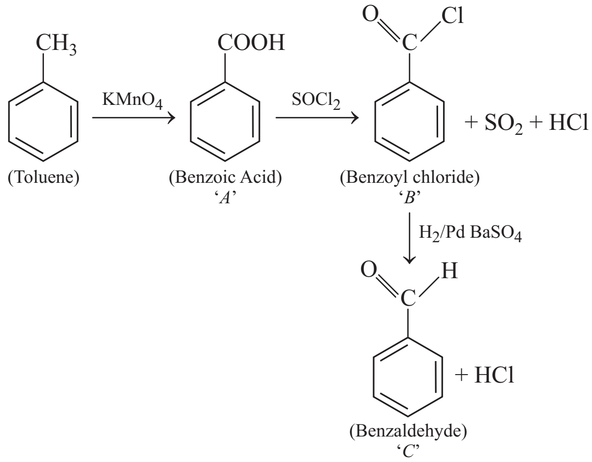
(iv) 
$C_6H_5-\underset{CH_3}{\overset{OH}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-C_6H_5$ (Self Aldol condensation product of $C_6H_5COCH_3$)

$\bar{O}H$ of base will prefer to attack on $-CH_3$ group of CH_3CHO for the formation of carbanion and as among the $>C=O$ groups available, the $>C=O$ group of CH_3CHO is the best carbanion acceptor. Hence, self condensation product of CH_3CHO will be the major product.

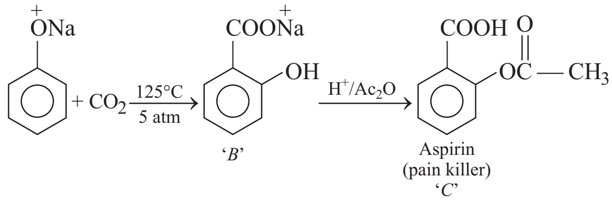
12. DIBAL-H (Di-isobutyl aluminium hydride) is a reducing agent with formula. This is generally used for the preparation of aldehydes. Using DIBAL $-$H, Lactones are reduced directly to aldehydes.



13. Toluene undergoes oxidation with $KMnO_4$, forms benzoic acid. In this conversion, alkyl part of toluene converts into carboxylic group. Further, benzoic acid reacts with thionyl chloride ($SOCl_2$) to give benzoyl chloride which upon reduction with H_2/Pd or $BaSO_4$ forms benzaldehyde (Rosenmund reduction) The conversion look like,

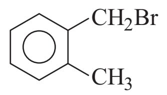


14. It is a Kolbe Schmidt reaction.

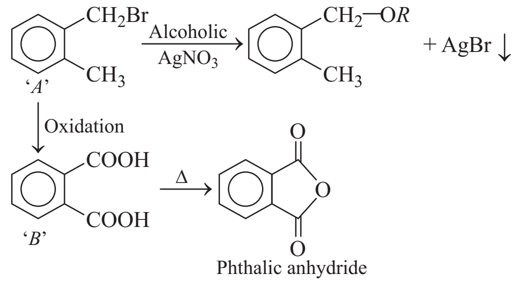


The second step of the reaction is an example of acetylation reaction.

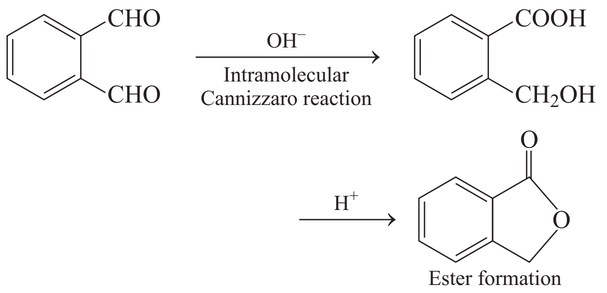
15. Compound *A* gives a precipitate with alcoholic $AgNO_3$, so it must contains Br in side chain. On oxidation, it gives $C_8H_6O_4$, which shows the presence of two alkyl chains attached directly with the benzene nucleus. Since, compound *B* gives anhydride on heating, the two alkyl substituent must occupy adjacent (1, 2) position. Thus, A must be



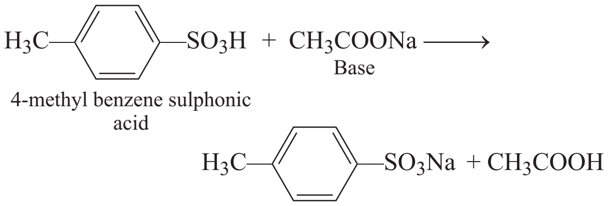
and the reactions are as follows :



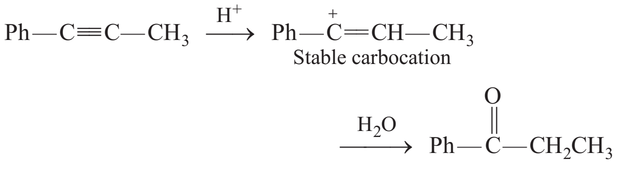
16.



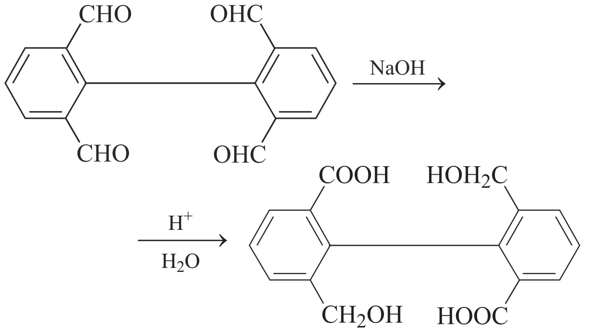
17.



18.

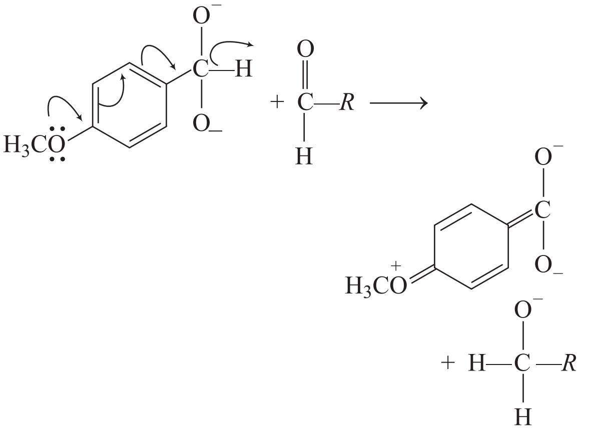

$$Ph—C{\equiv}C—CH_3 \xrightarrow{H^+} \underset{\text{Stable carbocation}}{Ph—\overset{+}{C}{=}CH—CH_3} \xrightarrow{H_2O} Ph—\overset{\overset{O}{\|}}{C}—CH_2CH_3$$

19.

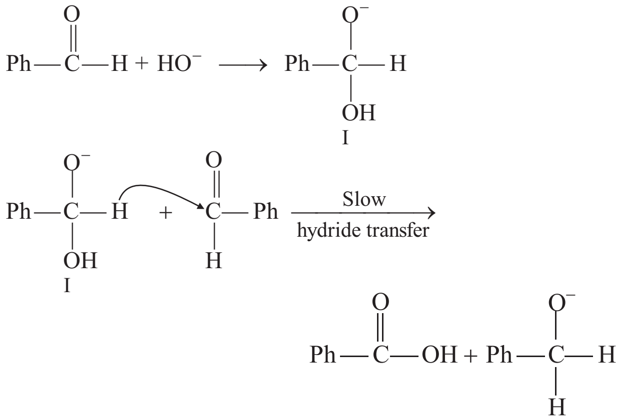


The above reaction is an example of intramolecular Cannizzaro reaction.

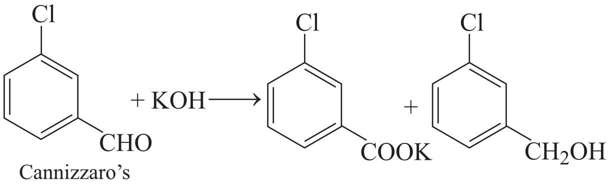
20. Dioxoanion is better hydride donor. Electron donating group at *ortho/para* position further promote H^- transfer.



21.

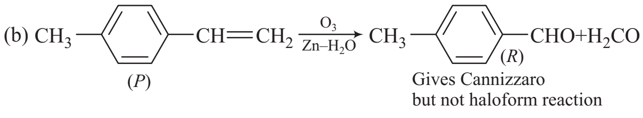


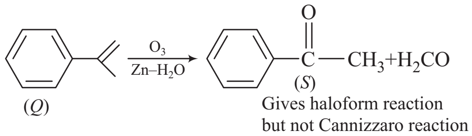
22.

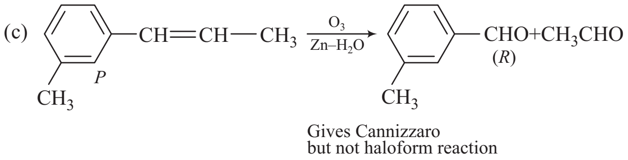


Cannizzaro's reaction

23.

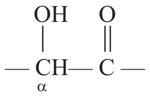




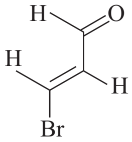


24. $$R\text{CHO} + \underset{\text{(Tollen's reagent)}}{\text{Ag}_2\text{O}} \xrightarrow{\text{OH}^-} R\text{COOH} + \underset{\text{Silver mirror}}{2\text{Ag}}$$

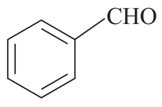
Tollen's test is given by all aldehydes and all reducing sugars as glucose, fructose and α-hydroxy ketones.



$$-\underset{\alpha}{\overset{\text{OH}}{\overset{|}{\text{CH}}}}-\overset{\text{O}}{\overset{\|}{\text{C}}}-$$

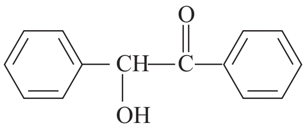


having an aldehyde group gives Tollen's test.



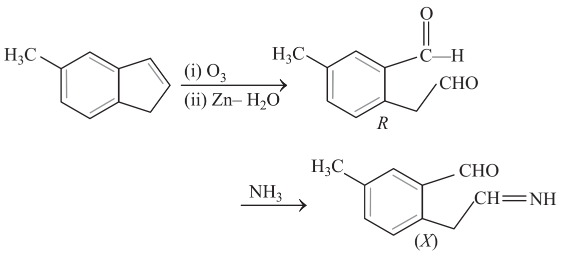
Aldehyde

(c)

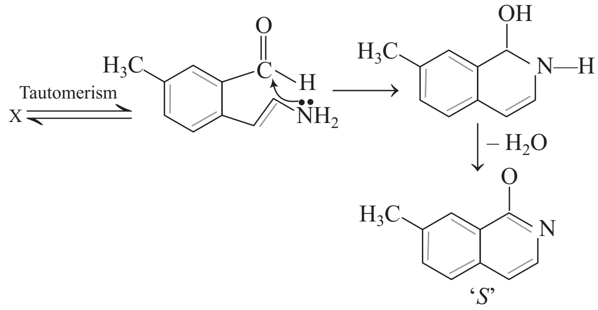


α-hydroxy ketone give positive Tollen's test.

25.

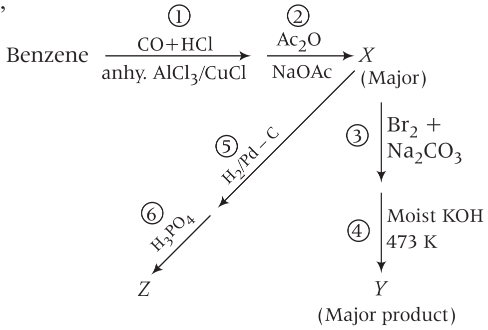


In the above reaction, NH_3 prefer to attack at aliphatic aldehyde group than an less reactive aromatic aldehyde group.



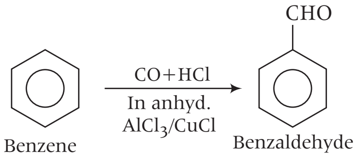
'S'

26. Given,



For this question we require only reaction 1 to 4 written above. Let us explore them one by one.

Reaction 1 It is called formylation or Gatterman Koch reaction. *A* — CHO group is introduced to benzene ring through this reaction as

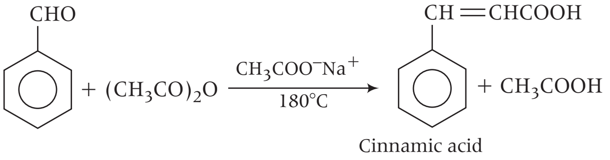


The attacking electrophile is $\text{H}-\overset{+}{\text{C}}=\text{O}$ which is generated as

(i) $\text{CO} + \text{HCl} \rightleftharpoons \text{H}-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{Cl}$

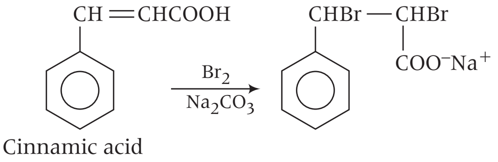
(ii) $\text{H}-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{Cl} + \text{AlCl}_3 \rightleftharpoons \text{H}-\underset{\underset{\text{O}}{\|}}{\overset{+}{\text{C}}} + \text{AlCl}_4^-$

Reaction 2 It is Perkin condensation which results in α, β unsaturated acid as

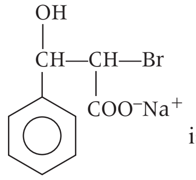


Note Besides $CH_3COO^-Na^+$, quinoline, pyridine, Na_2CO_3, triethylamine can also be used as bases in this reaction.

Reaction 3 It is simple addition of bromine to unsaturated acid formed through reaction 2.

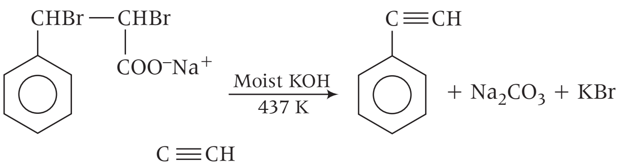


Na_2CO_3 works as a base in the reaction to trap H^+ to be released by — COOH of the reactant.

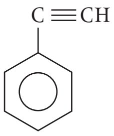


is also formed in the reaction as the minor product.

Reaction 4 It is decarboxylation and dehydrohalogenation of product produced by reaction 3 as

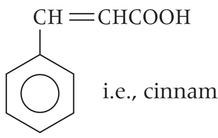


Hence, *Y* is



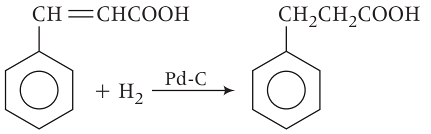
i.e., (c) is the correct answer.

27. **Reaction 5** The Perkin condensation product *X* is



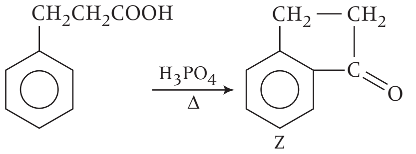
i.e., cinnamic acid (Ref. Q. 15)

This compound on hydrogenation with H_2 in the presence of Pd activated with charcoal (Pd – C) gives



3-Phenyl propanoic acid

Reaction 6 The product of reaction 5 on heating with H_3PO_4 dehydrates to give



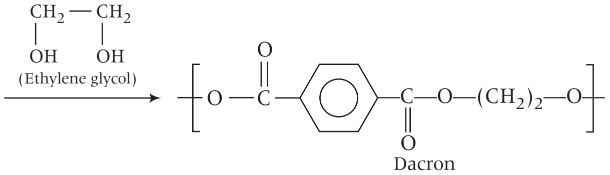
28. (a) Given,

(i) $C_{11}H_{12}O_2 \xrightarrow{\text{Oxidation}} \text{Dibasic acid}$

(An organic acid '*P*')

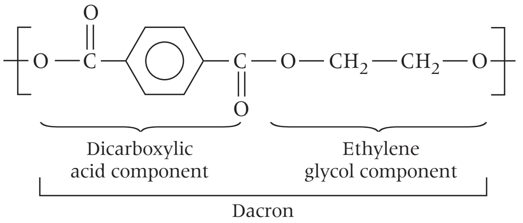
This indicates the presence of alkyl or alkenyl branch in *P* along with –COOH group.

(ii) Dibassic acid produced by oxidation of *P*



Dacron

This indicates presence of benzene ring in *P*; as concluded from the structure of dacron given below.

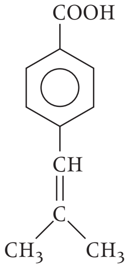


Attachment of —COO group in dacron also confirm the *para* position of branch with respect to —COOH group in *P*.

(iii) $P \xrightarrow{\text{Ozonolysis}}$ Aliphatic ketone + other oxidised products.

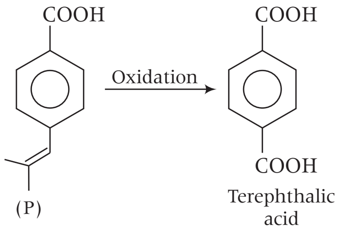
This reaction confirms the presence of multiple bonded branch i.e., alkenyl group in *P*.

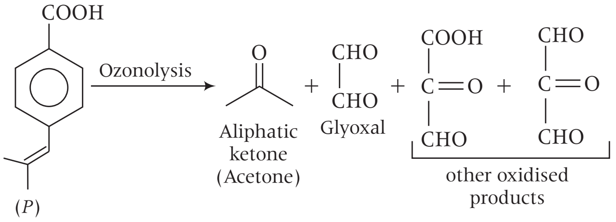
Thus *P* can be



IUPAC name : 4-(2-methyl) prop-l-enyl benzoic acid

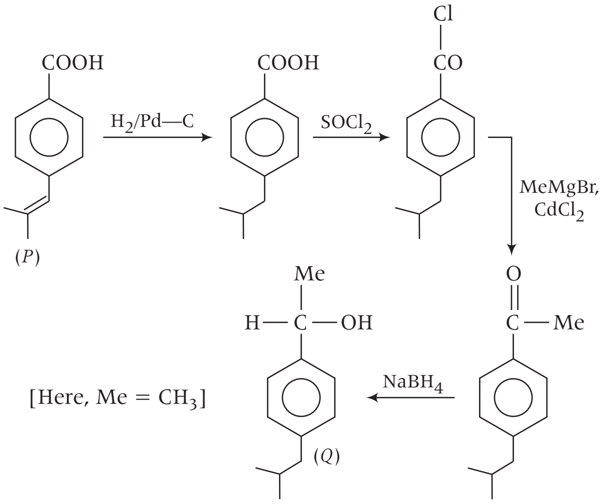
Now look for the reactions





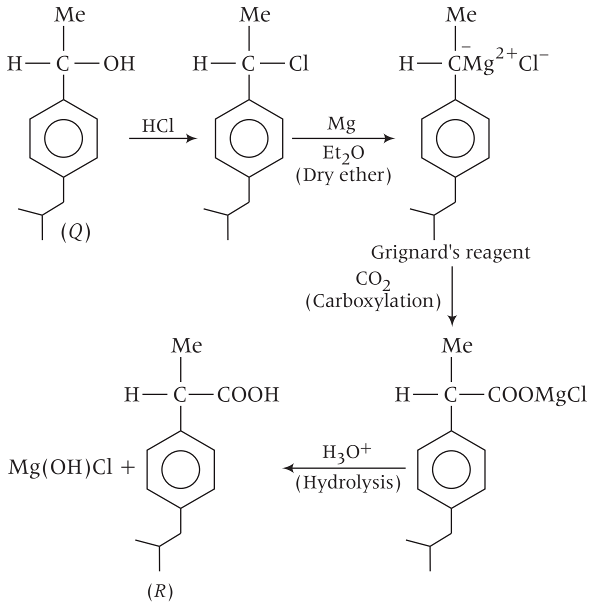
Given, $P \xrightarrow[\text{3. MeMgBr, CdCl}_2 \ \text{4. NaBH}_4]{\text{1. H}_2\text{/Pd–C} \ \text{2. SOCl}_2} Q$

So,



[Here, Me = CH_3]

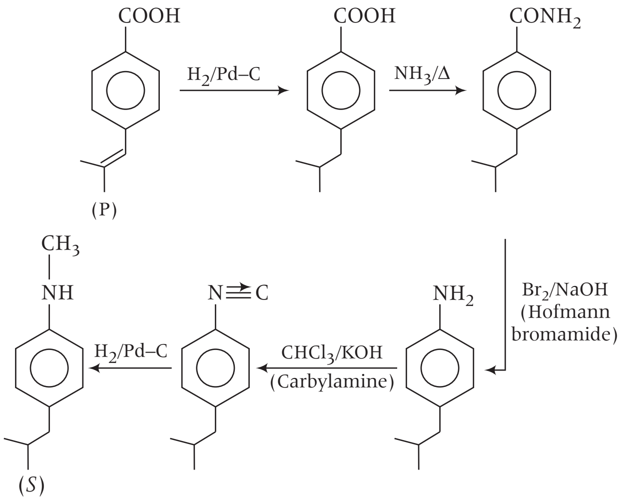
Further, $Q \xrightarrow[\text{3. CO}_2 \text{ (Dry ice)} \ \text{4. H}_3\text{O}^+]{\text{1. HCl} \ \text{2. Mg/Et}_2\text{O}} R$



29. Given (In connection with Q. 17)

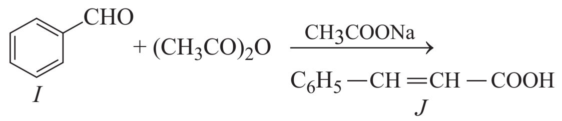
$$P \xrightarrow[\substack{\text{4. CHCl}_3/\text{KOH},\Delta \\ \text{5. H}_2/\text{ Pd–C}}]{\substack{\text{1. H}_2/\text{Pd–C} \\ \text{2. NH}_3/\Delta \\ \text{3. Br}_2/\text{NaOH}}} S$$

So,



Passage

Sol for (Q. Nos. 30 to 31) The first step of reaction is Perkin's condensation.



J being a carboxylic acid gives effervescence with $NaHCO_3$. Also, J has olefinic bond, it will decolourise Baeyer's reagent.

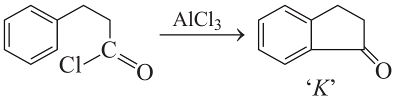
In the second step, J on treatment with H_2 / Pd / C undergo hydrogenation at olefinic bond only as :

$$J + H_2 / Pd \longrightarrow C_6H_5—CH_2—CH_2—COOH$$

The hydrogenated acid, on treatment with $SOCl_2$ gives acid chloride.

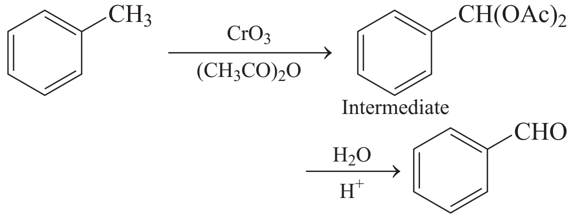
$$C_6H_5—CH_2—CH_2—COOH + SOCl_2 \longrightarrow C_6H_5—CH_2—CH_2—COCl + HCl + SO_2$$

In the final step, acid chloride formed above undergo intramolecular Friedel-Craft acylation as:



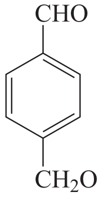
'K'

32.



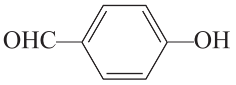
33. For aldol condensation, presence of at least one α-H is essential, which is not available to benzaldehyde.

34.



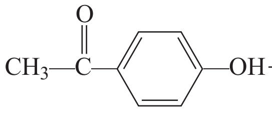
A

⟶ Gives positive Tollen's test but does not give $FeCl_3$ test.



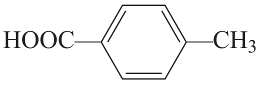
B

⟶ Gives positive Tollen's test and $FeCl_3$ test.

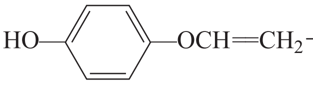


C

⟶ Gives positive iodoform test.

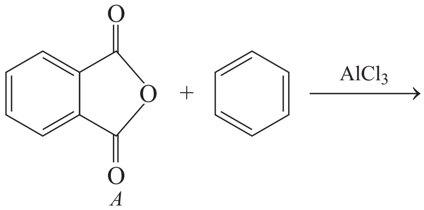


⟶ Can be extracted with $NaHCO_3$.

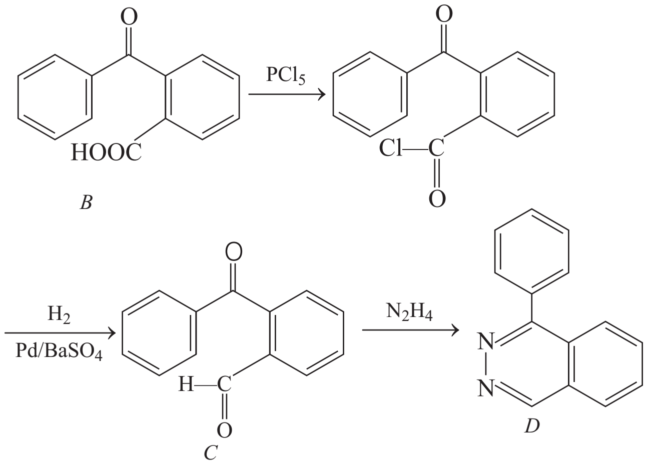


⟶ On hydrolysis give 1,4-dihydroxy benzene.

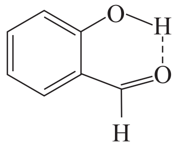
35.



A



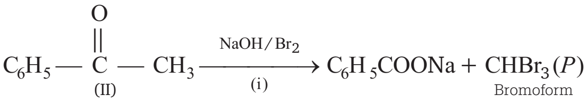
36. Intramolecular H-bonding in *ortho* hydroxy benzaldehyde is responsible for decrease in melting and boiling points.



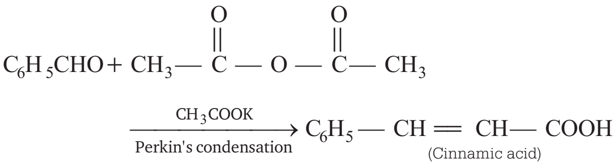
Intramolecular H-bonding

p-hydroxy benzaldehyde molecules are associated by intermolecular H-bonding, has higher melting and boiling points.

37. $C_6H_5—CH_3 \xrightarrow[hv]{Br_2} C_6H_5—CH_2Br + HBr$ (Free radical bromination)

38. 

$C_6H_5—\overset{\overset{O}{||}}{\underset{(II)}{C}}—CH_3 \xrightarrow[(i)]{NaOH/Br_2} C_6H_5COONa + \underset{\text{Bromoform}}{CHBr_3(P)}$

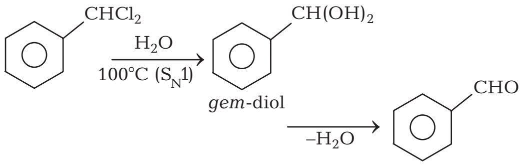
39. 

$C_6H_5CHO + CH_3—\overset{\overset{O}{||}}{C}—O—\overset{\overset{O}{||}}{C}—CH_3 \xrightarrow[\text{Perkin's condensation}]{CH_3COOK} \underset{\text{(Cinnamic acid)}}{C_6H_5—CH=CH—COOH}$

Cinnamic acid shows *cis-trans* isomerism.

40. I. Gattermann-Koch reaction.

II.



III. Rosenmund's reduction.

IV. Acid chloride, anhydride and ester undergo controlled reduction with di-iso-butylaluminium hydride (DIBAL-H) at – 78℃ to give aldehydes.