ORGANIC CHEMISTRY

MISCELLANEOUS

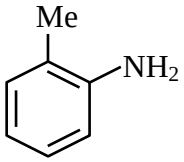
1. Match the compounds in LIST-I with the observation in LIST-II, and choose the correct option. **[JEE(Advanced) 2022]**

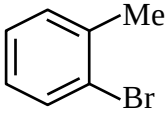
LIST-I	LIST-II
(I) Aniline	(P) Sodium fusion extract of the compound on boiling with $FeSO_4$, followed by acidification with conc. H_2SO_4, gives Prussian blue color.
(II) o-Cresol	(Q) Sodium fusion extract of the compound on treatment with sodium nitroprusside gives blood red color.
(III) Cysteine	(R) Addition of the compound to a saturated solution of $NaHCO_3$ results in effervescence.
(IV) Coprolactam	(S) The compound reacts with bromine water to give a white precipitate.
	(T) Treating the compound with neutral $FeCl_3$ solution produces violet color.

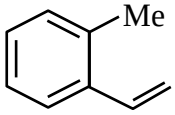
(A) I → P, Q; II → S; III → Q, R; IV → P
(B) I → P ; II → R, S; III → R; IV → Q, S
(C) I → Q, S; II → P, T; III → P; IV → S
(D) I → P, S; II → T; III → Q, R; IV → P

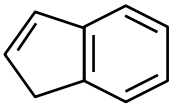
2. The maximum number of possible isomers (including stereoisomers) which may be formed on *mono*-bromination of 1-methylcyclohex-1-ene using Br_2 and UV light is _____. **[JEE(Advanced) 2021]**

3. The reaction sequence(s) that would lead to *o*-xylene as the major product is (are) **[JEE(Advanced) 2021]**

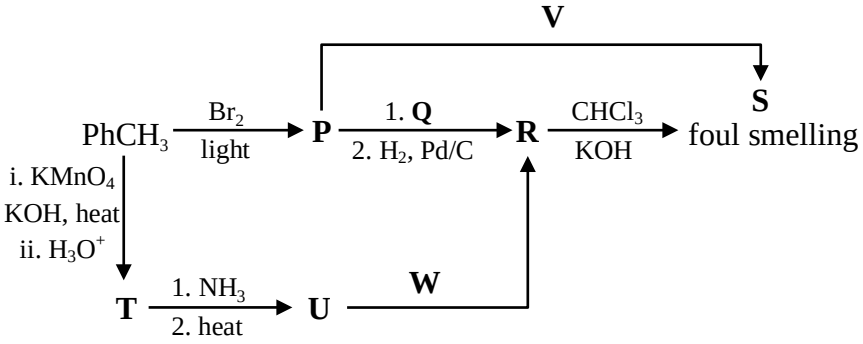
(A)  1. $NaNO_2$/HCl, 273 K, 2. CuCN, 3. DIBAL-H then H_3O^+, 4. N_2H_4, KOH, heat

(B)  1. Mg, CO_2, H_3O^+, 2. $SOCl_2$, 3. H_2, Pd-$BaSO_4$, 4. Zn-Hg, HCl

(C)  1. i. BH_3, ii. H_2O_2, NaOH, 2. PBr_3, 3. Zn, dil. HCl

(D)  1. O_3, Zn/H_2O, 2. N_2H_4, KOH, heat

4. Correct option(s) for the following sequence of reactions is(are) **[JEE(Advanced) 2021]**



(A) **Q** = KNO_2, **W** = $LiAlH_4$
(B) **R** = benzenamine, **V** = KCN
(C) **Q** = $AgNO_2$, **R** = phenylmethanamine
(D) **W** = $LiAlH_4$, **V** = AgCN

5. Fusion of MnO_2 with KOH in presence of O_2 produces a salt **W**. Alkaline solution of **W** upon eletrolytic oxidation yields another salt **X**. The manganese containing ions present in **W** and **X**, respectively, are **Y** and **Z**. Correct statement(s) is (are) **[JEE(Advanced) 2019]**

(A) **Y** is diamagnetic in nature while **Z** is paramagnetic

(B) Both **Y** and **Z** are coloured and have tetrahedral shape

(C) In both **Y** and **Z** , π-bonding occurs between p-orbitals of oxygen and d-orbitals of manganese.

(D) In aqueous acidic solution, **Y** undergoes disproportionation reaction to give **Z** and MnO_2.

6. Consider the following reactions (unbalanced)

$Zn + \text{hot conc. } H_2SO_4 \rightarrow G + R + X$

$Zn + \text{conc. } NaOH \rightarrow T + Q$

$G + H_2S + NH_4OH \rightarrow Z \text{ (a precipitate)} + X + Y$

Choose the correct option(s). **[JEE(Advanced) 2019]**

(A) The oxidation state of Zn in T is +1

(B) Bond order of Q is 1 in its ground state

(C) Z is dirty white in colour

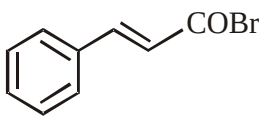
(D) R is a V-shaped molecule

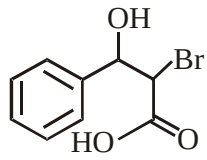
Paragraph "X"

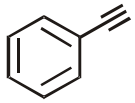
Treatment of benzene with CO/HCl in the presence of anhydrous $AlCl_3$/CuCl followed by reaction with Ac_2O/NaOAc gives compound X as the major product. Compound X upon reaction with Br_2/Na_2CO_3, followed by heating at 473 K with moist KOH furnishes Y as the major product. Reaction of X with H_2/Pd-C,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

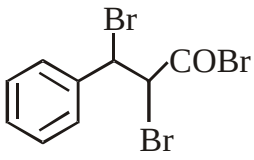
(There are two questions based on PARAGRAPH "X", the question given below is one of them)

7. The compound Y is :- **[JEE(Advanced) 2018]**

(A) 

(B) 

(C) 

(D) 

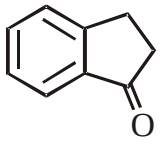
Paragraph "X"

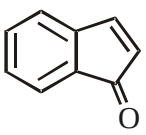
Treatment of benzene with CO/HCl in the presence of anhydrous $AlCl_3$/CuCl followed by reaction with Ac_2O/NaOAc gives compound X as the major product. Compound X upon reaction with Br_2/Na_2CO_3, followed by heating at 473 K with moist KOH furnishes Y as the major product. Reaction of X with H_2/Pd-C,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

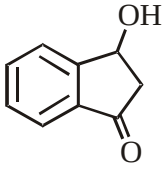
(There are two question based on PARAGARAPH "X", the question given below is one of them)

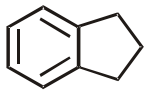
[JEE(Advanced) 2018]

8. The compound Z is :-

(A) 

(B) 

(C) 

(D) 

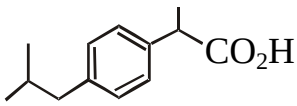
Paragraph "A"

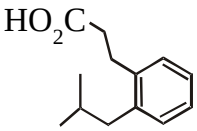
An organic acid P ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethyleneglycol to produce a polymer dacron. Upon ozonolysis, **P** gives an aliphatic ketone as one of the products. **P** undergoes the following reaction sequences to furnish **R** via **Q.** The compound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

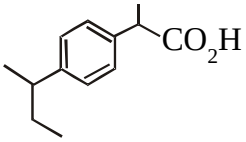
$$S \xleftarrow[(4)\ CHCl_3,KOH,\ \Delta]{\substack{(1)\ H_2/Pd\text{-}C\\(2)\ NH_3/\Delta\\(3)\ Br_2/NaOH\\(5)\ H_2/Pd\text{-}C}} S \xrightarrow[(3)\ MeMgBr,\ CdCl_2]{\substack{(1)\ H_2/Pd\text{-}C\\(2)\ SOCl_2\\(4)\ NaBH_4}} Q \xrightarrow[(3)\ CO_2(dry\ ice)]{\substack{(1)\ HCl\\(2)\ Mg/Et_2O\\(4)\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

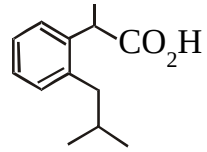
(There are two questions based on PARAGRAPH "A", the question given below is one of them)

9. The compound **R** is

(A) 

(B) 

(C) 

(D) 

Paragraph "A"

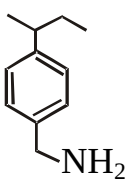
An organic acid P ($C_{11}H_{12}O_2$) can easily be oxidized to a dibasic acid which reacts with ethyleneglycol to produce a polymer dacron. Upon ozonolysis, P gives an aliphatic ketone as one of the products. P undergoes the following reaction sequences to furnish R via Q. The compound P also undergoes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

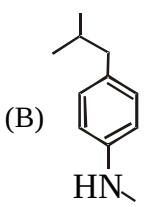
$$S \xleftarrow[(4)\ CHCl_3,KOH,\ \Delta]{\substack{(1)\ H_2/Pd\text{-}C\\(2)\ NH_3/\Delta\\(3)\ Br_2/NaOH\\(5)\ H_2/Pd\text{-}C}} S \xrightarrow[(3)\ MeMgBr,\ CdCl_2]{\substack{(1)\ H_2/Pd\text{-}C\\(2)\ SOCl_2\\(4)\ NaBH_4}} Q \xrightarrow[(3)\ CO_2(dry\ ice)]{\substack{(1)\ HCl\\(2)\ Mg/Et_2O\\(4)\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

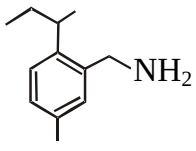
(There are two questions based on PARAGRAPH "A", the question given below is one of them)

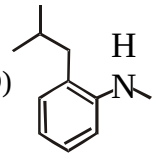
[JEE(Advanced) 2018]

10. The compound **S** is

(A) 

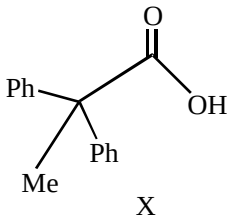
(B) 

(C) 

(D) 

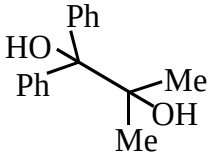
11. The desired product X can be prepared by reacting the major product of the reactions in LIST-I with one or more appropriate reagents in LIST-II. **[JEE(Advanced) 2018]**

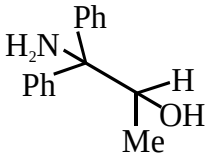
(given, order of migratory aptitude: aryl > alkyl > hydrogen)

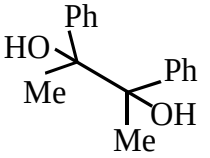


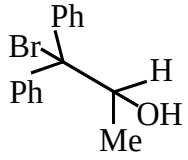
X

LIST-I **LIST-II**

P.  + H_2SO_4 1. I_2, NaOH

Q.  + HNO_2 2. $[Ag(NH_3)_2]OH$

R.  + H_2SO_4 3. Fehling solution

S.  + $AgNO_3$ 4. HCHO, NaOH

5. NaOBr

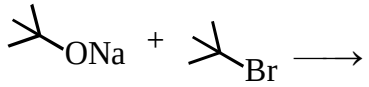
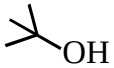
The correct option is

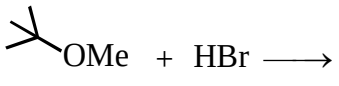
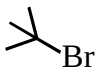
(A) P → 1; Q → 2,3; R → 1,4; S → 2,4 (B) P → 1,5; Q → 3,4; R → 4,5; S → 3

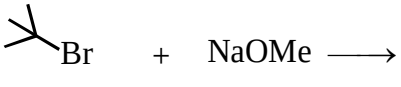
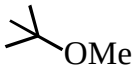
(C) P → 1,5; Q → 3,4; R → 5; S → 2,4 (D) P → 1,5; Q → 2,3; R → 1,5; S → 2,3

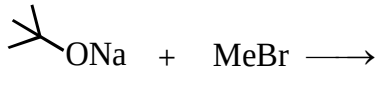
12. LIST-I contains reactions and LIST-II contains major products. **[JEE(Advanced) 2018]**

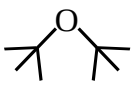
LIST-I **LIST-II**

P.  1. 

Q.  2. 

R.  3. 

S.  4. 

5. 

Match each reaction in LIST-I with one or more product in LIST-II and choose the correct option.

(A) P → 1,5; Q → 2; R → 3; S → 4 (B) P → 1,4; Q → 2; R → 4; S → 3

(C) P → 1,4; Q → 1,2; R → 3,4; S → 4 (D) P → 4,5; Q → 4; R → 4; S → 3,4

Answer Q.13, Q.14 and Q.15 by appropriately matching the information given in the three columns of the following table. **[JEE(Advanced) 2017]**

Columns 1, 2 and 3 contains starting materials, reaction conditions, and type of reactions, respectively.		
Column-1	**Column-2**	**Column-3**
(I) Toluene	(i) $NaOH/Br_2$	(P) Condensation
(II) Acetophenone	(ii) Br_2 / hν	(Q) Carboxylation
(III) Banzaldehyde	(iii) $(CH_3CO)_2O/CH_3COOK$	(R) Substitution
(IV) Phenol	(iv) $NaOH/CO_2$	(S) Haloform

13. For the synthesis of benzoic acid, the only CORRECT combination is

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

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

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

15. The only CORRECT combination that gives two different carboxylic acids is

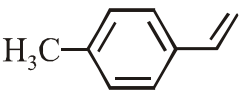
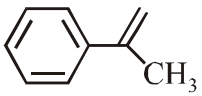
(A) (IV) (iii) (Q) (B) (III) (iii) (P) (C) (II) (iv) (R) (D) (I) (i) (S)

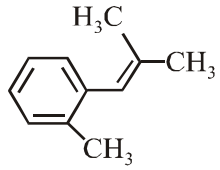
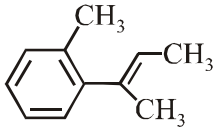
16. Compound **P** and **R** upon ozonolysis produce **Q** and **S**, respectively. The molecular formula of **Q** and **S** is C_8H_8O. **Q** undergoes Cannizzaro reaction but not haloform reaction, whereas **S** undergoes haloform reaction but not Cannizzaro reaction. **[JEE(Advanced) 2017]**

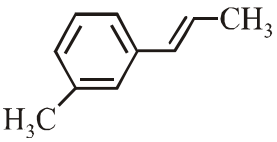
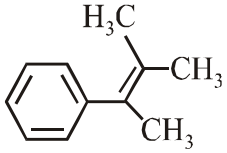
(i) P $\xrightarrow[\text{ii) } Zn/H_2O]{\text{i) } O_3/CH_2Cl_2}$ Q (C_8H_8O)

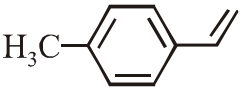
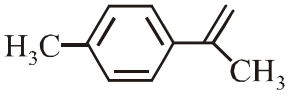
(ii) R $\xrightarrow[\text{ii) } Zn/H_2O]{\text{i) } O_3/CH_2Cl_2}$ S (C_8H_8O)

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

(A)  and 

(B)  and 

(C)  and 

(D)  and 

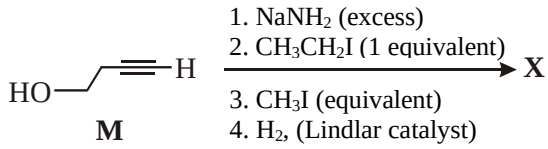
17. Among $[Ni(CO)_4]$, $[NiCl_4]^{2-}$, $[Co(NH_3)_4Cl_2]Cl$, $Na_3[CoF_6]$, Na_2O_2 and CsO_2, the total number of paramagnetic compounds is - **[JEE(Advanced) 2016]**

(A) 2 (B) 3 (C) 4 (D) 5

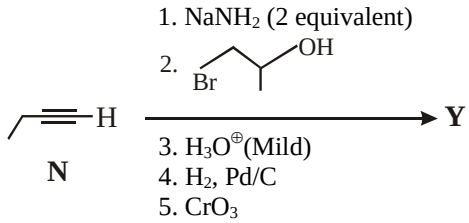
18. In dilute aqueous H_2SO_4 , the complex diaquodioxalatoferrate(II) is oxidized by MnO_4^-. For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is - **[JEE(Advanced) 2015]**

Paragraph for Question No. 19 and 20

Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both the schemes. **[JEE(Advanced) 2014]**

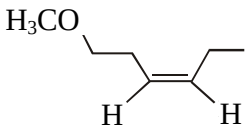


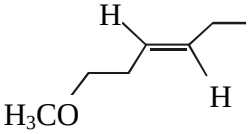
Scheme-1

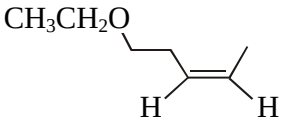


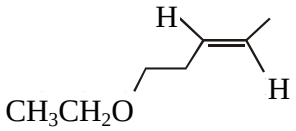
Scheme-2

19. The product X is -

(A) 

(B) 

(C) 

(D) 

20. The correct statement with respect to prodcut Y is -

(A) It gives a positive Tollens test and is a functional isomer of X

(B) It gives a positive Tollens test and is a geometrical isomer of X

(C) It gives a positive Iodoform test and is a functional isomer of X

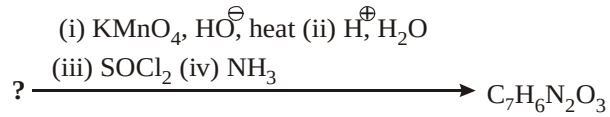
(D) It gives a positive Iodoform test and is a geometrical isomer of X

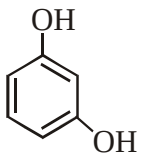
21. Match the four starting materials (P , Q, R, S) given in List I with the corresponding reaction scheme (I, II, III, IV) provided in List - II and select the correct answer using the code given below in lists.

List - I **List – II** **[JEE(Advanced) 2014]**

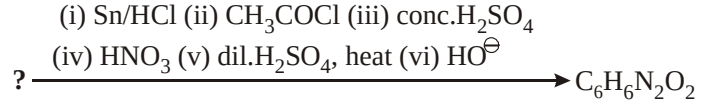
(P) 

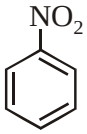
(1) Scheme I



(Q) 

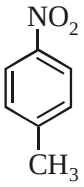
(2) Scheme II



(R) 

(3) Scheme III

$$? \xrightarrow[\text{(iii) } H_2S.NH_3 \text{ (iv) } NaNO_2,\ H_2SO_4 \text{ (v) hydrolysis}]{\text{(i) red hot iron, 873 K (ii) fuming } HNO_3,\ H_2SO_4,\ \text{heat}} C_6H_5NO_3$$

(S) 

(4) Scheme IV

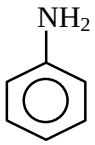
$$? \xrightarrow[\text{(ii) conc. } HNO_3,\ \text{conc. } H_2SO_4 \text{ (iii) dil. } H_2SO_4,\ \text{heat}]{\text{(i) conc. } H_2SO_4,\ 60^{\circ}C} C_6H_5NO_4$$

Code :

	P	Q	R	S
(A)	1	4	2	3
(B)	3	1	4	2
(C)	3	4	2	1
(D)	4	1	3	2

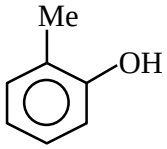
SOLUTIONS

1. Ans. (D)

Sol. 

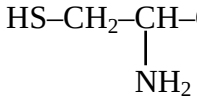
: Blue colour in Lassign test due to presence of N

Aniline



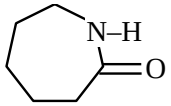
:Violet colour with $FeCl_3$ due to presence of phenolic OH

o-Cresol



: It gives blod red colour with NaSCN

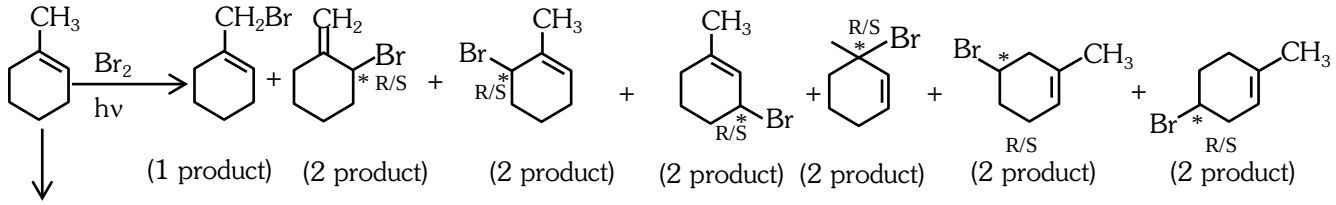
Cystein



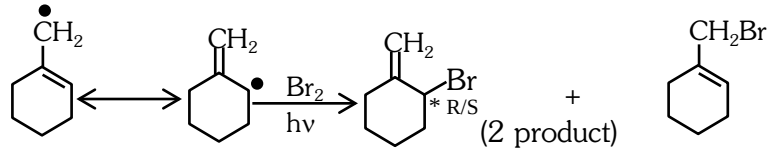
: Blue colour in Lassign test due to presence of N

Caprolactam

2. Ans. (9 or 13 or 12)

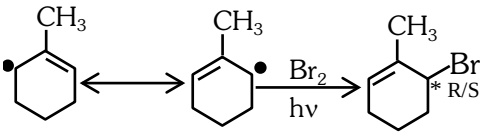


(1 product) (2 product) (2 product) (2 product) (2 product) (2 product) (2 product)

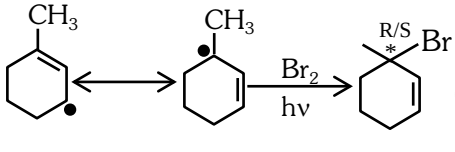


(2 product)

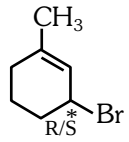
(1 product)



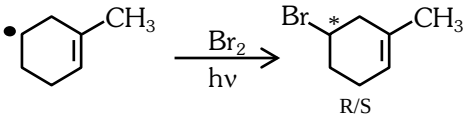
(same as already mentioned above as one the product)



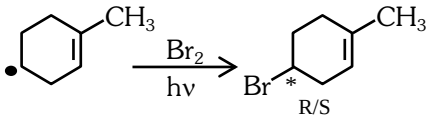
(2 product)



(2 product)



(2 product)

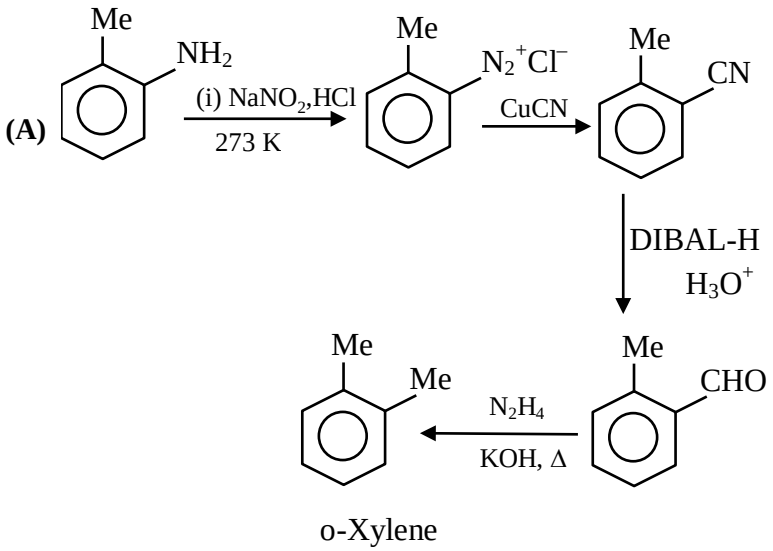


(2 product)

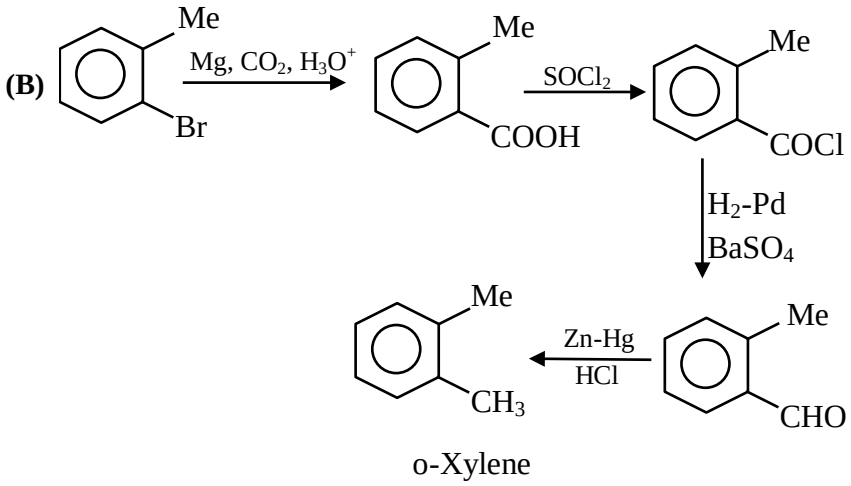
Total 13 product

3. Ans. (A, B)

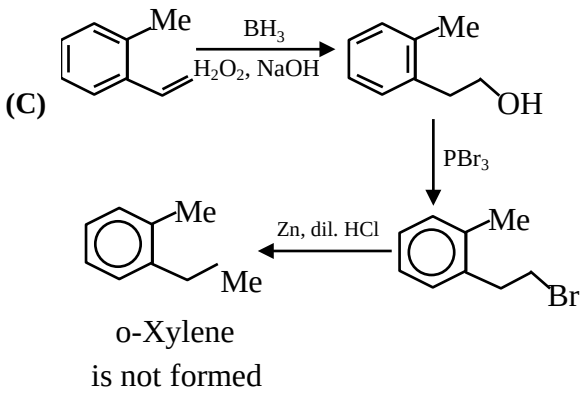
Sol.



o-Xylene

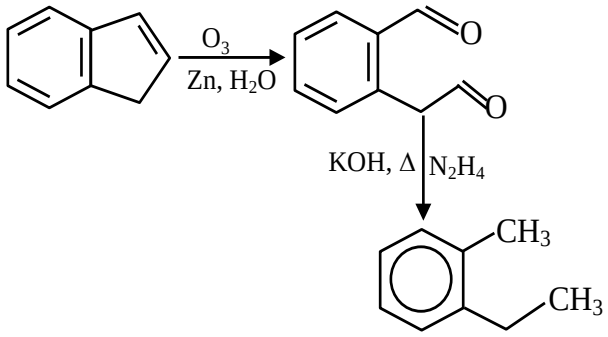


o-Xylene



o-Xylene
is not formed

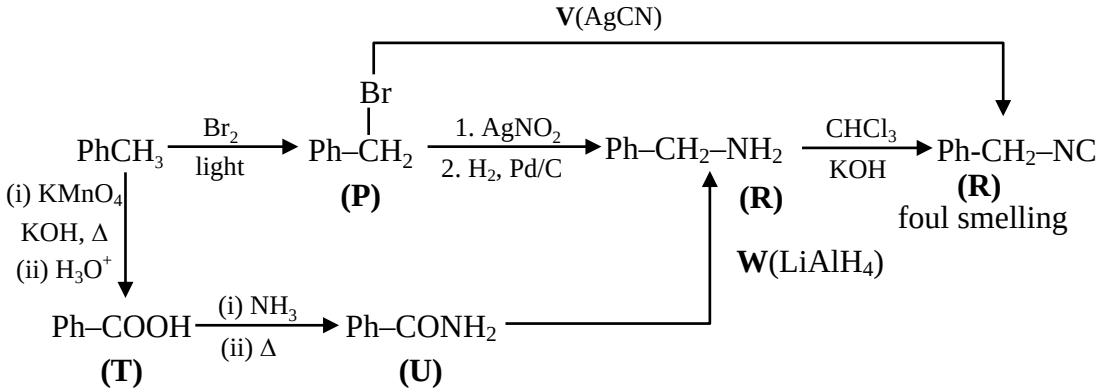
(D)



o-Xylene is not formed

4. Ans. (C, D)

Sol.



5. Ans. (2, 3, 4)

Sol. $MnO_2 + 2KOH + \frac{1}{2}O_2 \xrightarrow{\Delta} \underset{(W)}{K_2MnO_4} + H_2O$

$$\left[(W) = K_2MnO_{4(aq)} \rightleftharpoons 2K^{\oplus}_{(aq)} + \underset{(Y)}{MnO^{2-}_{4(aq)}}\right]$$

$$K_2MnO_4 + H_2O \xrightarrow[\text{Redox}]{\text{Electolytic}} H_2 + KOH + \underset{(X)}{KMnO_4}$$

[anion of X = $\underset{(Z)}{MnO_4^-}$]

$$\left[\because \underset{(Y)}{MnO_4^{2-}} \xrightarrow[\text{Oxidation}]{\text{Electrolytic}} \underset{(Z)}{MnO_4^-} + e^-\right]$$

$\because$ In acidic solution; Y undergoes disproportionation reaction

$$\left[3\underset{(Z)}{MnO^{2-}_{4(aq)}} + 4H^{\oplus} \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O\right]$$

6. Ans. (2, 3, 4)

Sol. $Zn + 2H_2SO_4$ (Hot and conc.) $\rightarrow ZnSO_4 + SO_2 + 2H_2O$

(G) (R) (X)

$Zn + 2NaOH$ (conc.) $\rightarrow Na_2ZnO_2 + H_2$

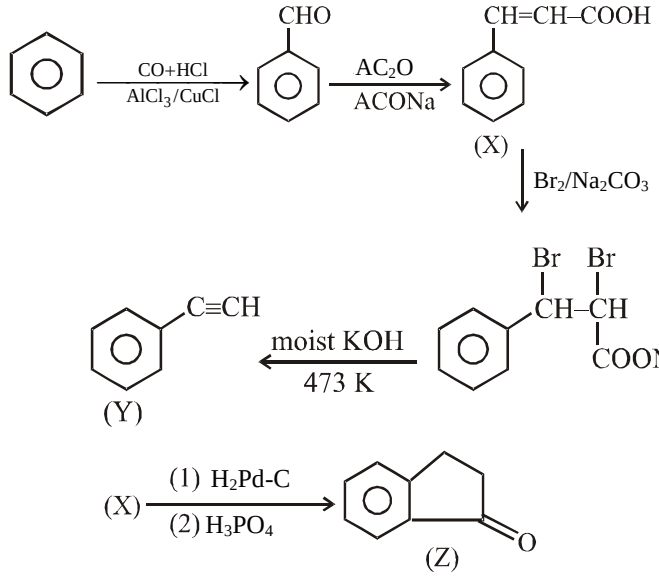
(T) (Q)

$ZnSO_4 + H_2S + 2NH_4OH \rightarrow ZnS\downarrow + 2H_2O + (NH_4)_2SO_4$

(Z) (X) (Y)

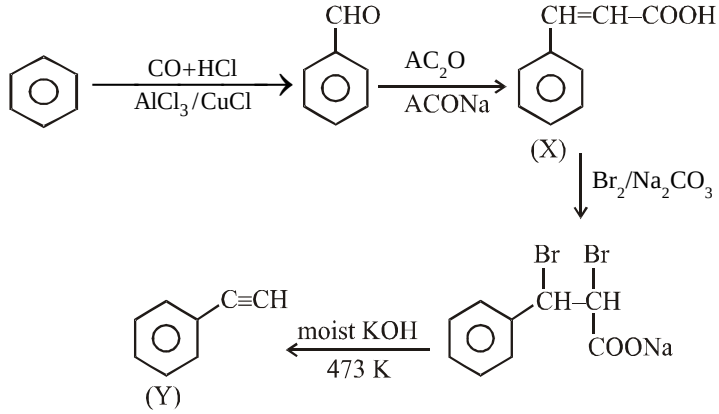
7. Ans. (C)

Sol.



8. Ans. (A)

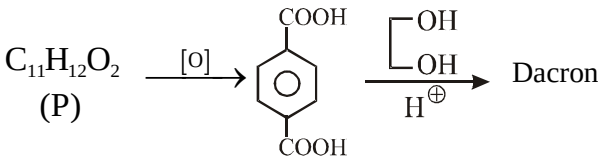
Sol.

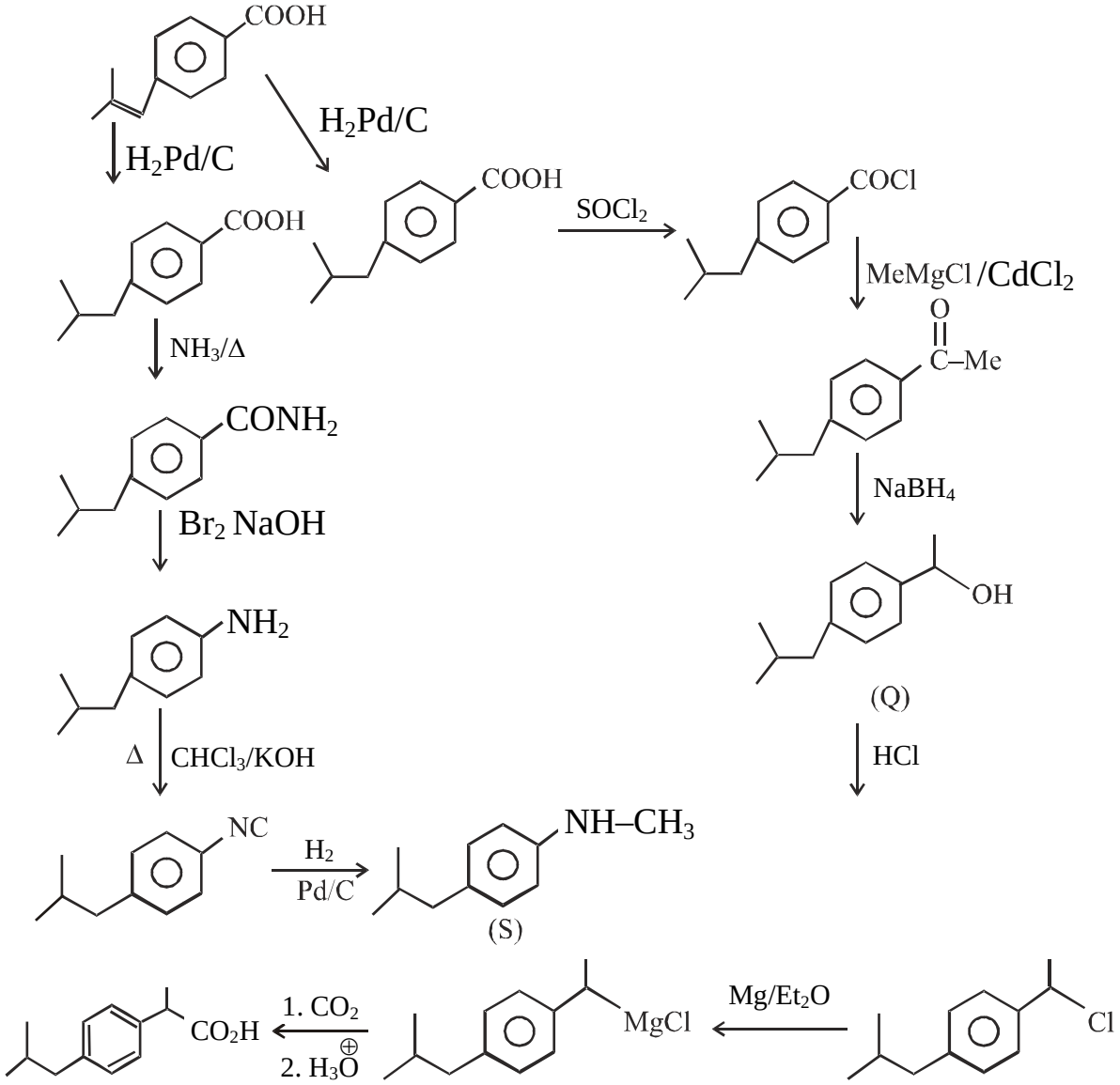


9. Ans. (A)

10. Ans. (B)

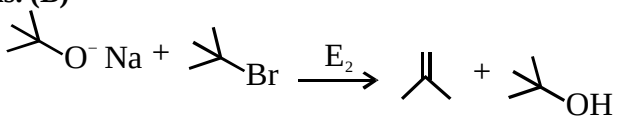
Solution for Q. No. 9 & 10



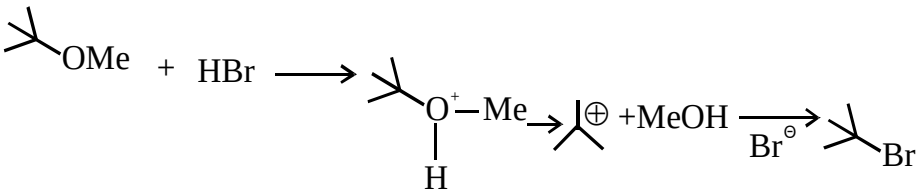


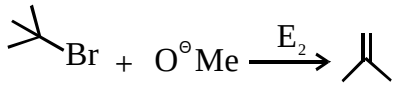
11. Ans. (D)

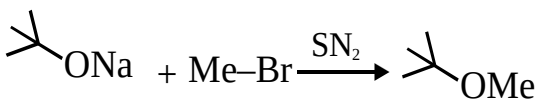
12. Ans. (B)

Sol. P. 

(Elimination product)

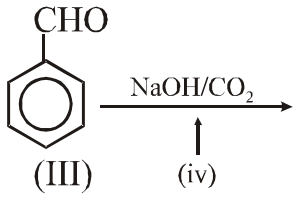
Q. 

R. 

S. 

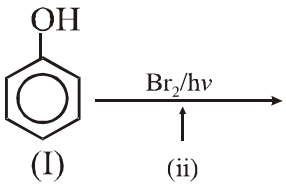
13. Ans. (D)

Sol. (II)(i)(S)

(A) 

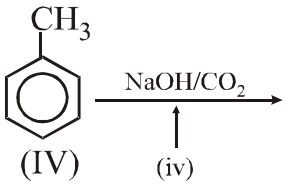
Benzoic acid is not formed

(R)

(B) 

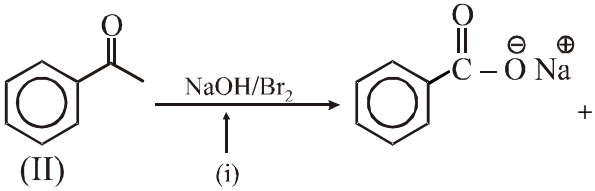
Benzoic acid is not formed

(P)

(C) 

Benzoic acid is not formed

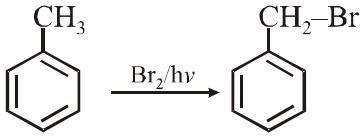
(Q)

(D) 

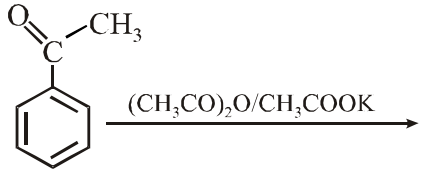
+ $CHBr_3$ (haloform reaction)

(S)

14. Ans. [A](I)(ii)(R)

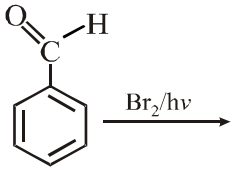
Sol. 

mechanism involved is free radical substitution

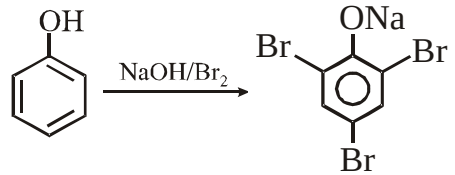
(B) 

Condensation reaction (No radical mechanism involved)

Acetophenone

(C) 

Condensation is not involved.

(D) 

(No free radical mechanism)

15. Ans. (B)

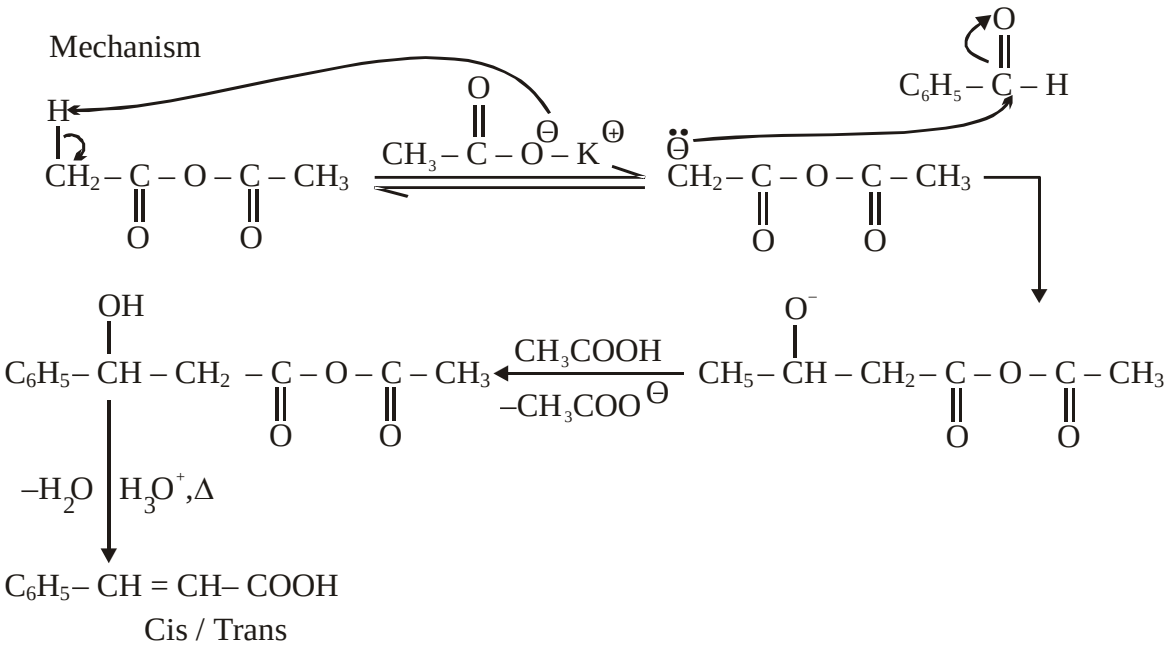
Sol. $C_6H_5CHO + CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{CH_3COOK} C_6H_5CH=CH-COOH$

Cinnamic acid

Cis and Trans

It is perkin condensation reaction

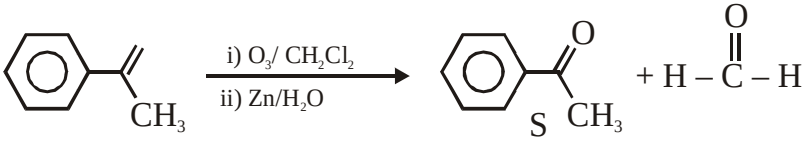
Mechanism



16. Ans. (A, C)

Sol. (A) CH_3–(C6H4)–$CH=CH_2$ (P) $\xrightarrow[\text{ii) } Zn/H_2O]{\text{i) } O_3/\ CH_2Cl_2}$ CH_3–(C6H4)–$CHO + H-\underset{\underset{O}{\|}}{C}-H$ (Q)

Q give cannizzaro reaction but no haloform



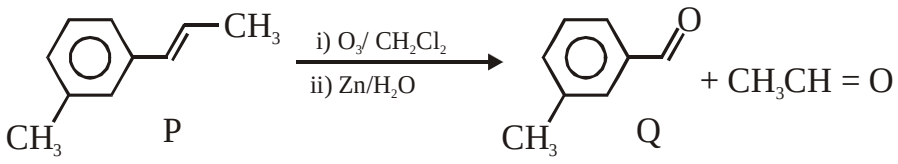
R

S

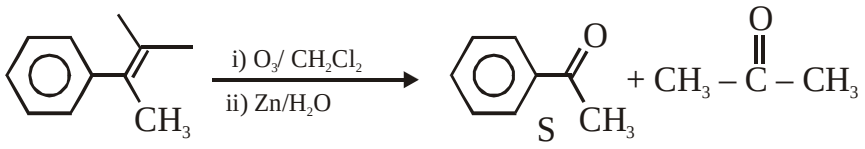
R no cannizzaro but give haloform

(B) Product of ozonolysis of R is having 9 carbon.

(C)



give cannizzaro reaction
but no haloform



no cannizzaro
but give haloform

(D) Product of ozonolysis of R is having 9 carbon.

17. Ans. (B)

Sol.	**Compound/Ion**	**Magnetic nature of compound**
1.	$[Ni(CO)_4]$	Diamagnetic
2.	$[NiCl_4]^{2-}$	Paramagnetic
3.	$[Co(NH_3)_4Cl_2]Cl$	Diamagnetic
4.	$Na_3[CoF_6]$	Paramagnetic
5.	Na_2O_2	Diamagnetic
6.	CsO_2	Paramagnetic

So total number of paramagnetic compounds is 3.

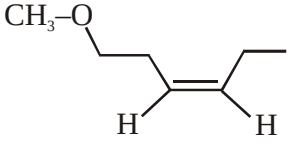
18. Ans. (8)

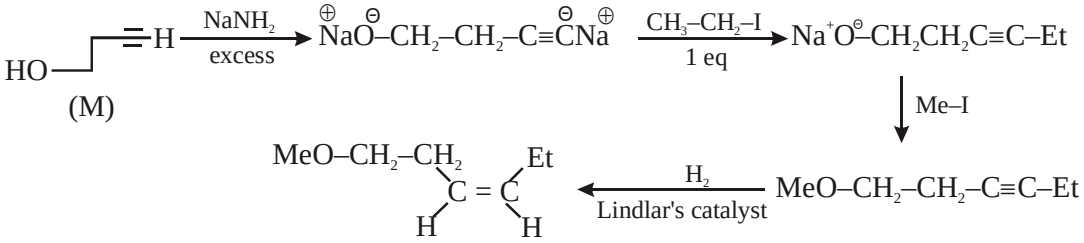
Sol. $MnO_4^- + [Fe(H_2O)_2(C_2O_4)_2]^{2-} + 8H^+ \longrightarrow Mn^{2+} + Fe^{3+} + 4CO_2 + 6H_2O$

$$\frac{r_{H^+}}{r_{MnO_4^-}} = 8$$

19. Ans. (A)

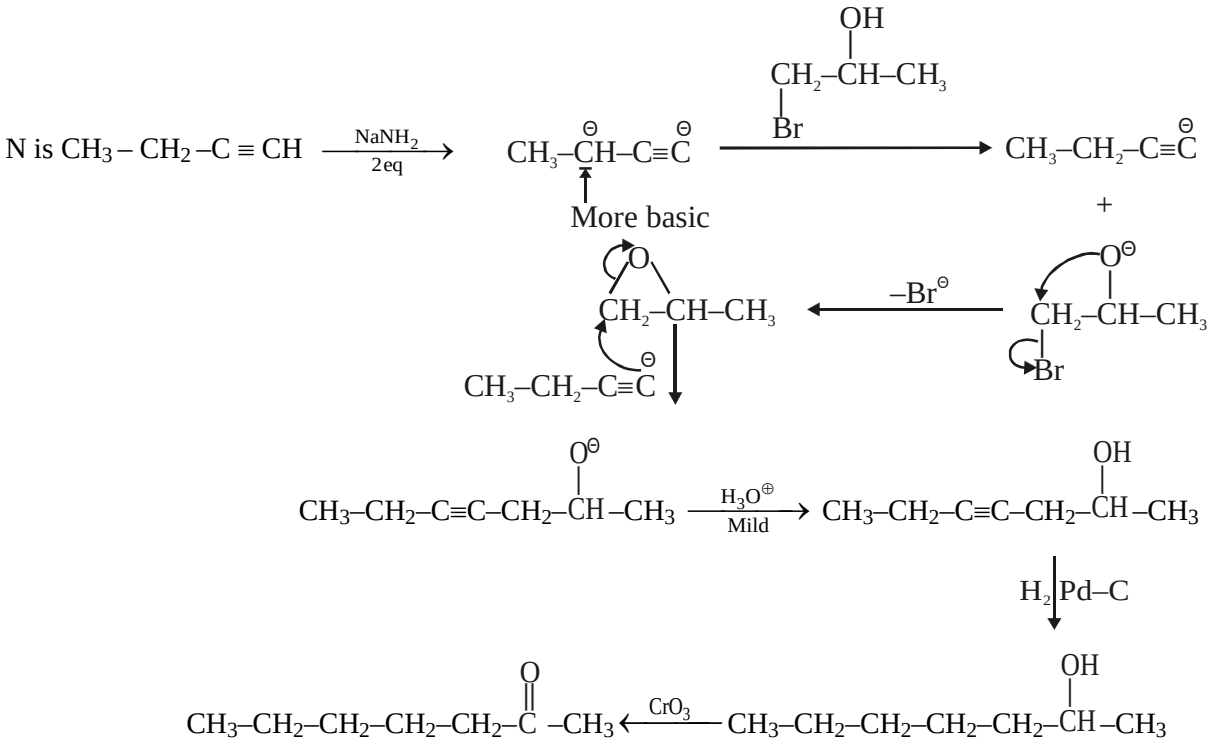
Sol. The product X is



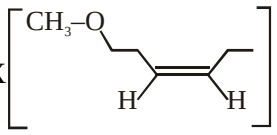


20. Ans. (C)

Sol.

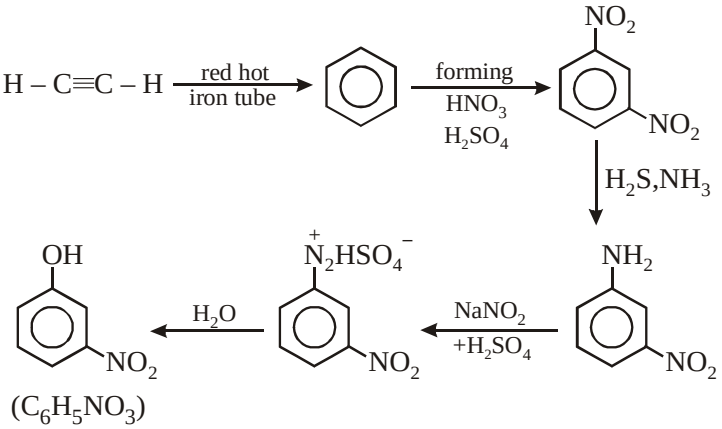


[Y]

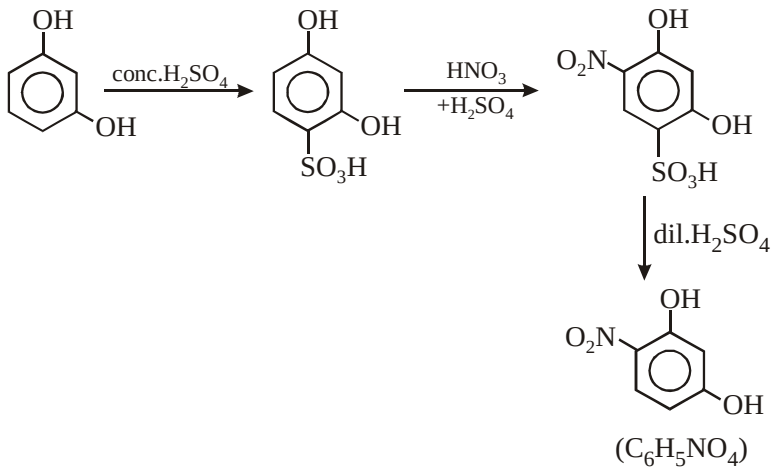
Y is functional isomer of X  and Y will give Iodoform test positive but Tollen's test negative.

21. Ans. (C)

Sol.

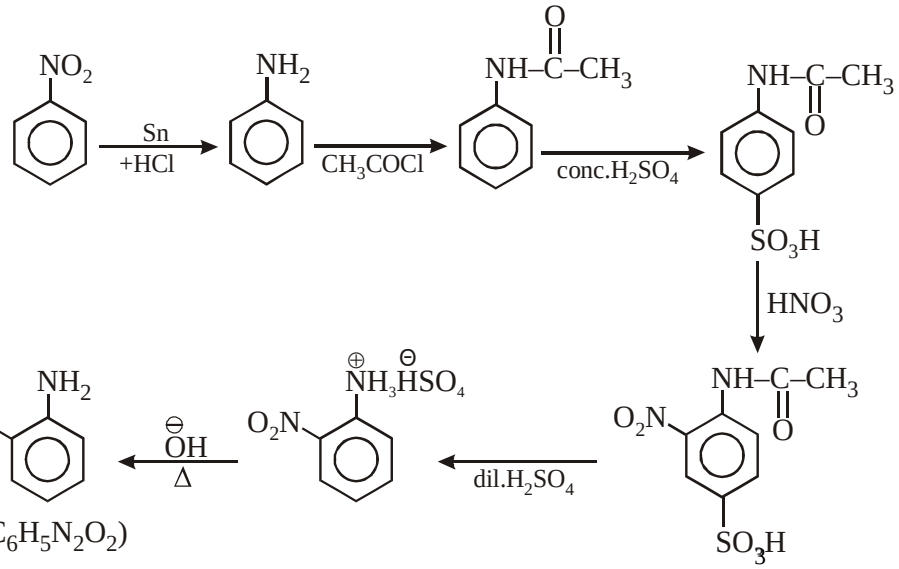


(Q)



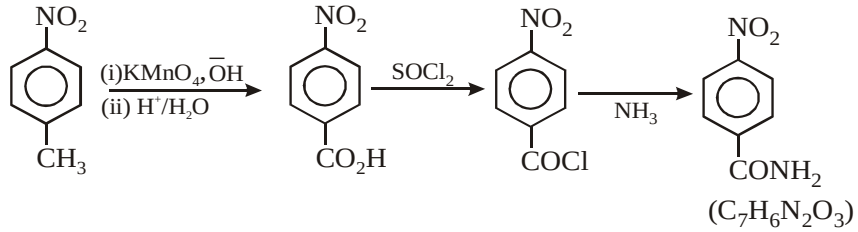
$(C_6H_5NO_4)$

(R)



$(C_6H_5N_2O_2)$

(S)



$(C_7H_6N_2O_3)$