JEE Advanced 2014 Solution Paper-2 Chemistry (Code-7)

21. The product formed in the reaction of $SOCl_2$ with white phosphorous is
(A) PCl_3 (B) SO_2Cl_2 (C) SCl_2 (D) $POCl_3$

Solution: (A)

The reaction goes as follows:

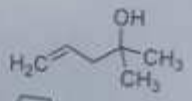
$$P_4(s) + 8SOCl_2(l) \longrightarrow 4PCl_3(l) + 4SO_2(g) + 2S_2Cl_2(g)$$

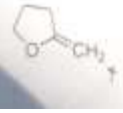
22. The major product in the following reaction is

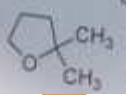
[Figure]

1. CH_3MgBr, dry ether, 0 °C
2. aq. acid

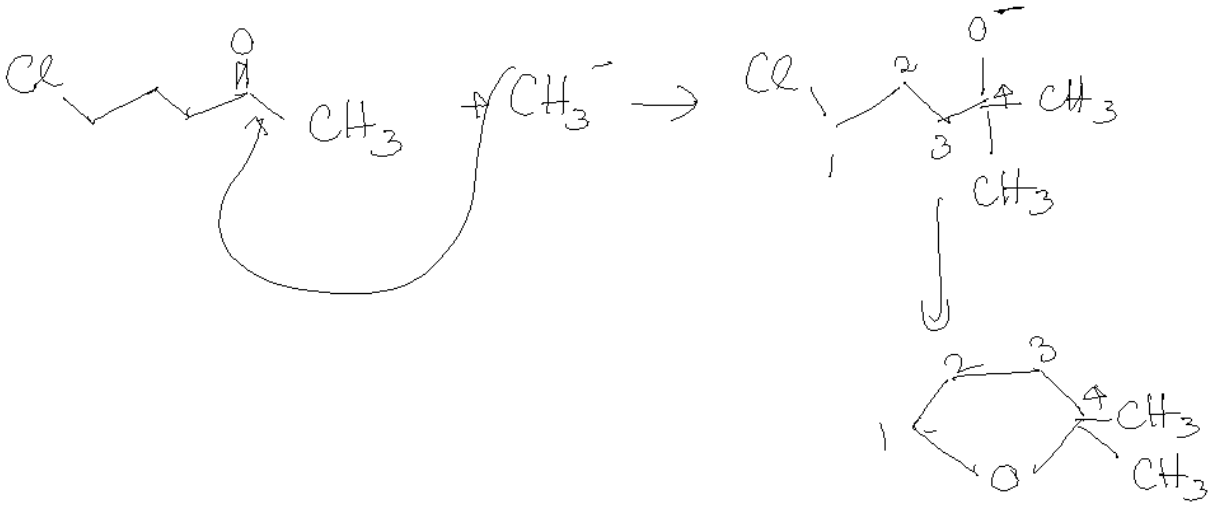
(A) 

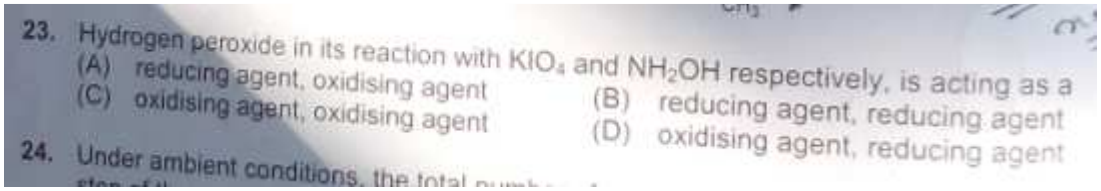
(B) 

(C) 

(D) 

Solution: (D)




23. Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively, is acting as a
(A) reducing agent, oxidising agent
(B) reducing agent, reducing agent
(C) oxidising agent, oxidising agent
(D) oxidising agent, reducing agent
24. Under ambient conditions, the total

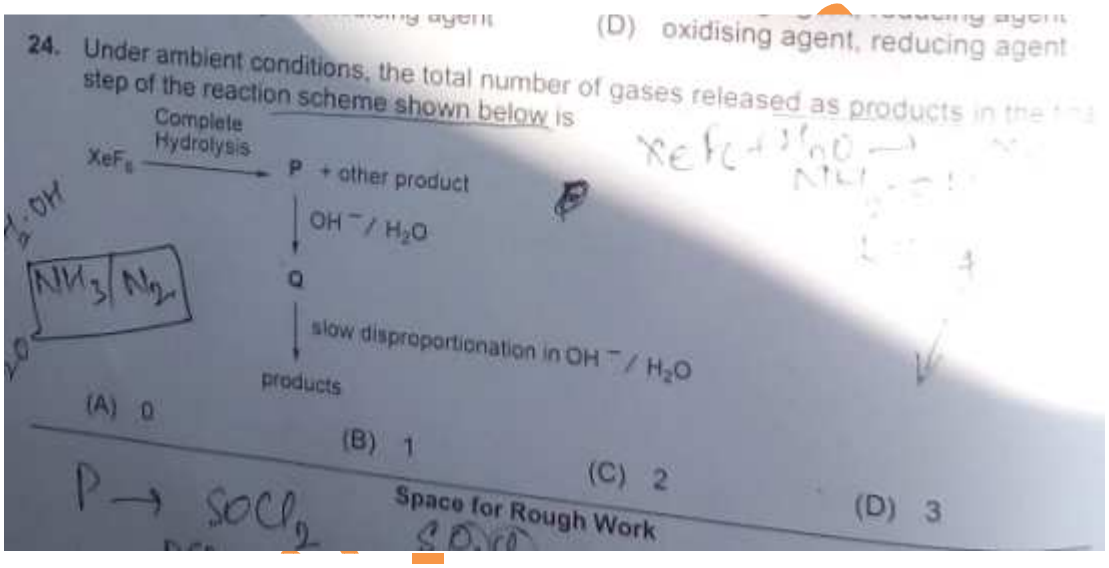
Solution: (A)

The reactions are as follows:

$H_2O_2 + KIO_4 \rightarrow KIO_3 + O_2 + H_2O$

$40\ NH_2OH + 10\ H_2O_2 \rightarrow 7\ H_20 + 20\ N_2O_3$

Thus it acts as: Reducing Agent in the first reaction and Oxidising Agent in the second reaction.


(D) oxidising agent, reducing agent

24. Under ambient conditions, the total number of gases released as products in the step of the reaction scheme shown below is

Complete Hydrolysis
XeF_6 → P + other product
OH^- / H_2O
Q
slow disproportionation in OH^- / H_2O
products

(A) 0
(B) 1
(C) 2
(D) 3

Space for Rough Work

Solution: (D)

The first reaction goes as follows:

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

This is followed by the following reaction:

$$XeO_3 + OH^- \longrightarrow HXeO_4^-$$
hydrogenxenate ion

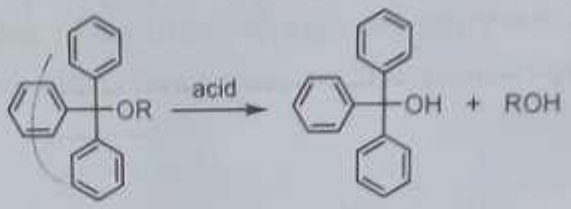
This ion when followed by further reaction gives:

$$2HXeO_4^- + 2OH^- \longrightarrow XeO_4^{6-} + Xe + O_2 + 2H_2O$$

Thus three gases including water, xenon and oxygen are produced.

25. The acidic hydrolysis of ether (X) shown below is fastest when

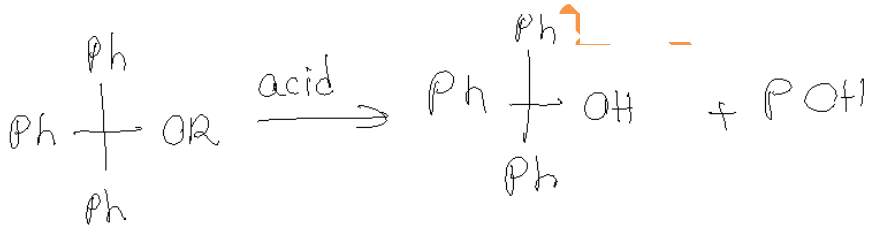
[Figure]



[X]

(A) one phenyl group is replaced by a methyl group.
(B) one phenyl group is replaced by a *para*-methoxyphenyl group.
(C) two phenyl groups are replaced by two *para*-methoxyphenyl groups.
(D) no structural change is made to **X**.

Solution: (C)

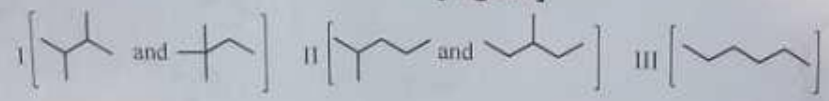


groups attached to O_2 should be electron donating.

So if 2 phenyl groups are replaced by 2 para methoxy phenyl group, then reaction would be fastest

26. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.

[Figure]



The correct order of their boiling point is

(A) I > II > III (B) III > II > I (C) II > III > I (D) III > I > II

27. For the identification of β-naphthol using dye test, it is necessary to use

(A) dichloromethane solution of β-naphthol. (B) acidic solution of β-naphthol.

(C) neutral solution of β-naphthol. (D) alkaline solution of β-naphthol.

28. Assuming 2s-2p mixing is NOT operative, the paramagnetic species among the following is

(A) Be_2 (B) B_2 (C) C_2 (D) N_2

29. For the elementary reaction M → N, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is

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

30. For the process

Solution: (B)

This is due to the fact that branching of the chain makes the molecule more compact and thereby decreases the surface area. Therefore, the intermolecular attractive forces which depend upon the surface area, also become small in magnitude on account of branching. Consequently, *the boiling points of the branched chain alkanes are less than the straight chain isomers.*

Solution: (B)

β −Naphthol or 2- Naphthol is identified by using a due test using an acidic solution.

Solution: (B)

B_2 exists in the gas phase as a paramagnetic radical.

Solution: (B)

Let the rate of reaction be given by:

$$r \propto [M]^n$$

Let the initial concentration and rate be given by: x, r_1.

Then the final concentration and rate would be given by: $2x, r_2$

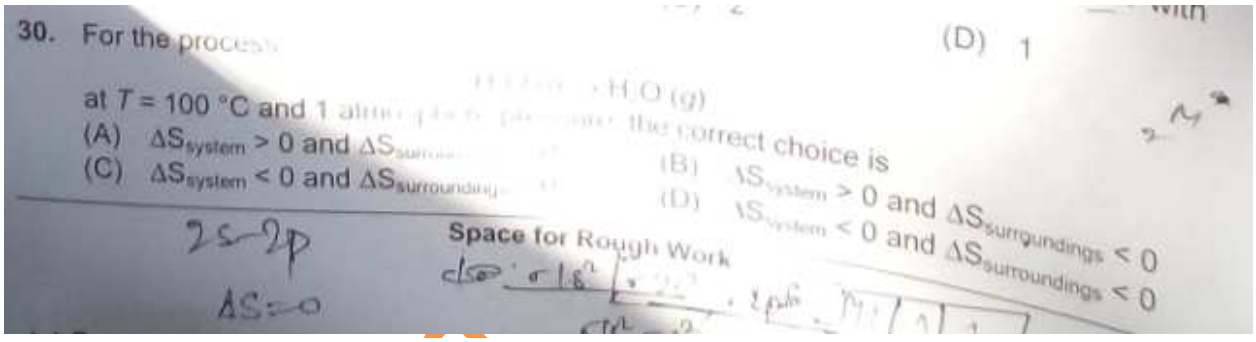
So, we get:

$$\frac{r_2}{r_1} = \frac{(2x)^n}{(x)^n} = (2)^n$$

But, we know that:

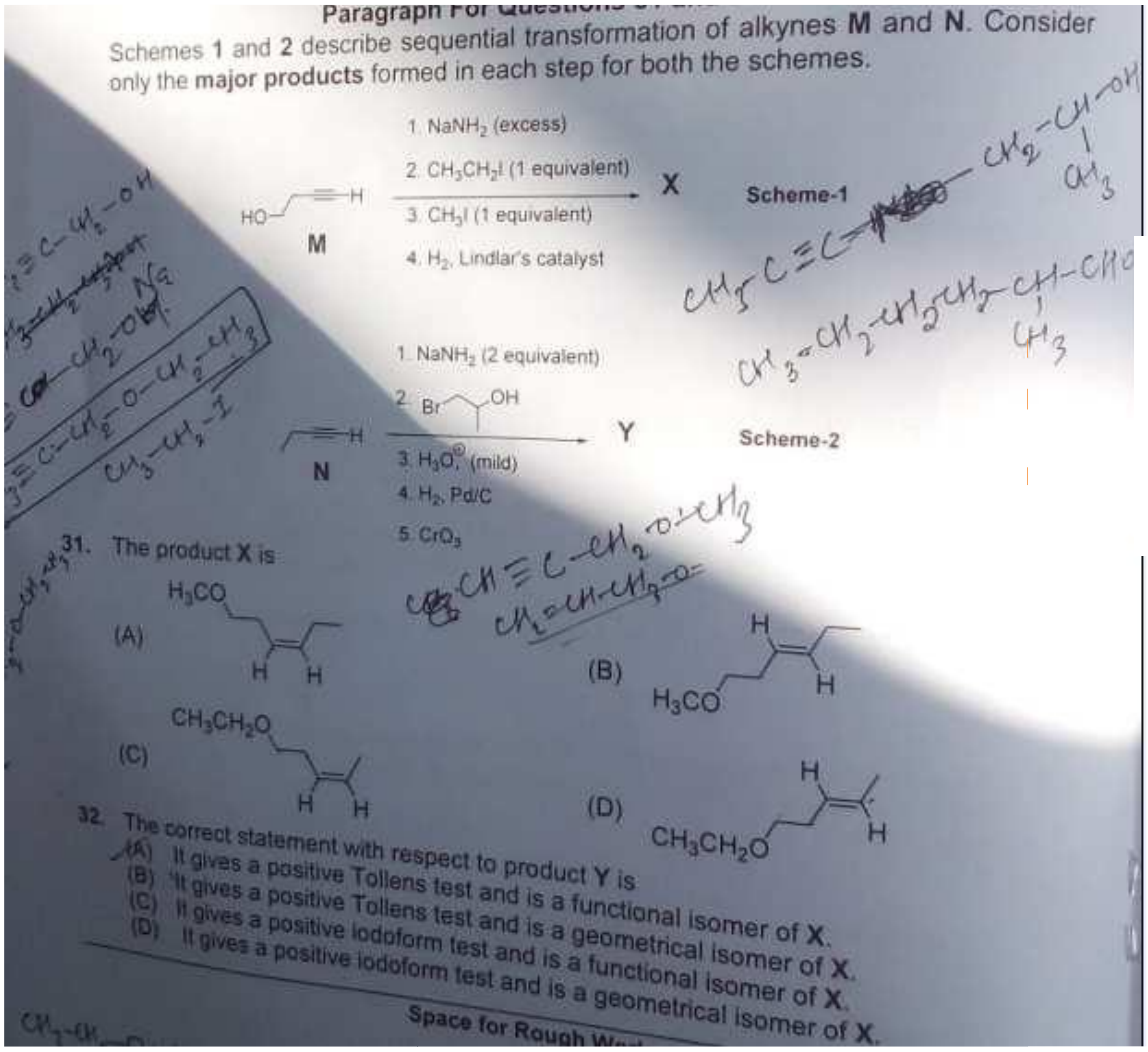
$$\frac{r_2}{r_1} = 8$$

So, we get: $n = 3$.



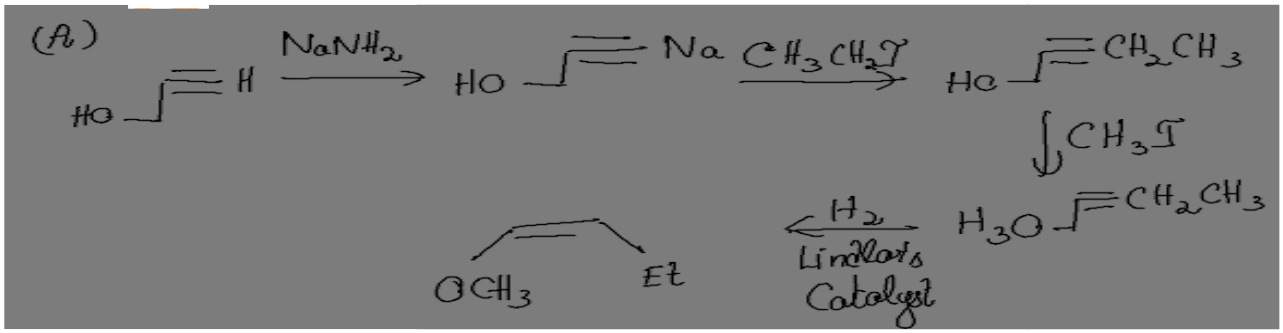
Solution: (B)

As the reaction is an endothermic reaction, this results into a decrease in entropy of the surroundings and since a orderely arrangement of liquid changes to gas, the entropy of the system increases.

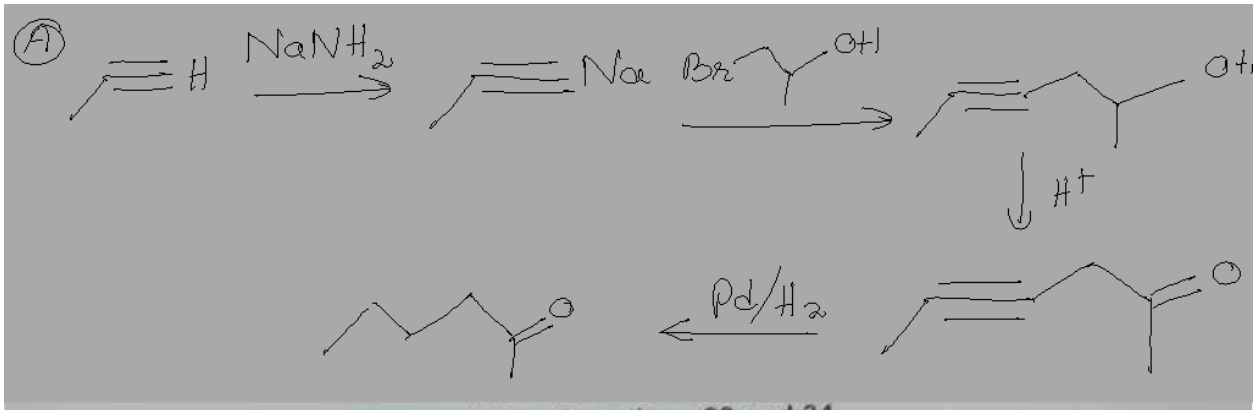


31. Solution: (A)

The reaction goes as follows:



32. Solution: (A)



Paragraph For Questions 33 and 34

An aqueous solution of metal ion **M1** reacts separately with reagents **Q** and **R** in excess to give tetrahedral and square planar complexes, respectively. An aqueous solution of another metal ion **M2** always forms tetrahedral complexes with these reagents. Aqueous solution of **M2** on reaction with reagent **S** gives white precipitate which dissolves in excess of **S**. The reactions are summarized in the scheme given below:

SCHEME:

Tetrahedral $\xleftarrow[\text{excess}]{Q}$ **M1** $\xrightarrow[\text{excess}]{R}$ Square planar

Tetrahedral $\xleftarrow[\text{excess}]{Q}$ **M2** $\xrightarrow[\text{excess}]{R}$ Tetrahedral

S, stoichiometric amount

White precipitate $\xrightarrow[\text{excess}]{S}$ precipitate dissolves

CHEMISTRY

33. **M1**, **Q** and **R**, respectively are
(A) Zn^{2+}, KCN and HCl (B) Ni^{2+}, HCl and KCN
(C) Cd^{2+}, KCN and HCl (D) Co^{2+}, HCl and KCN

34. Reagent **S** is
(A) $K_4[Fe(CN)_6]$ (B) Na_2HPO_4 (C) K_2CrO_4 (D) KOH

33. Solution: (B)

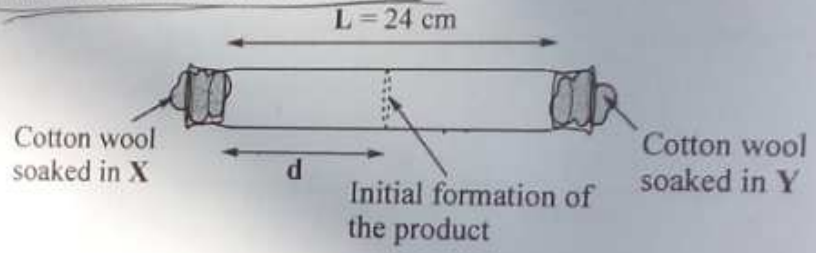
We know that $NiCl_4^{2-}$ is tetrahedral and $NiCN_4^{2-}$ is square planar.

Thus it satisfies the given relation and thus the choice is B.

34. Solution (B)

Na_2HPO_4 forms white salts the precipitate of which dissolves in excess.

X and Y are two volatile liquids with molar weights of 10 g mol^{-1} and 40 g mol^{-1} respectively. Two cotton plugs, one soaked in X and the other soaked in Y, are simultaneously placed at the ends of a tube of length L = 24 cm, as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300 K. Vapours of X and Y react to form a product which is first observed at a distance d cm from the plug soaked in X. Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours.



35. The value of d in cm (shown in the figure), as estimated from Graham's law, is
(A) 8 (B) 12 (C) 16 (D) 20

36. The experimental value of d is found to be smaller than the estimate obtained using Graham's law. This is due to
(A) larger mean free path for X as compared to that of Y.
(B) larger mean free path for Y as compared to that of X.
(C) increased collision frequency of Y with the inert gas as compared to that of X with the inert gas.
(D) increased collision frequency of X with the inert gas as compared to that of Y with the inert gas.

35. Solution: (C)

$$\frac{r_x}{r_y} = \sqrt{\frac{M_x}{M_y}} = \sqrt{\frac{40}{10}} = \frac{2}{1}$$

Now since the rate of diffusion is proportional to distance covered, so we have:

$$\frac{d}{24-d} = \frac{2}{1}$$

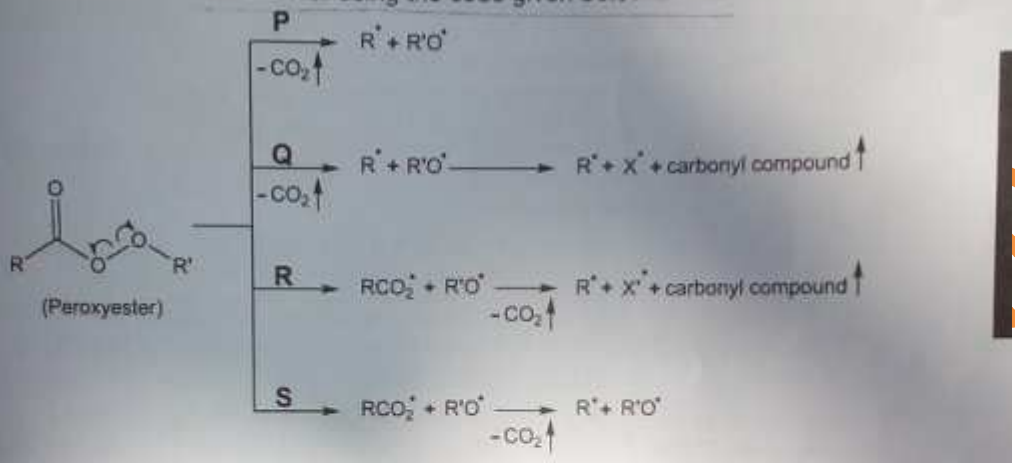
Hence, we have:

$$3d = 24 \times 2 \Rightarrow d = 16$$

36. Solution (B)

The reason being the molecular mass would influence the mean free path of the gas.

37. Different possible **thermal** decomposition pathways for peroxyesters are shown below. Match each pathway from **List I** with an appropriate structure from **List II** and select the correct answer using the code given below the lists.



List-I

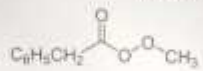
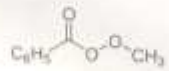
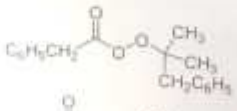
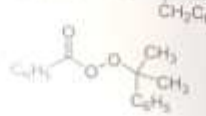
P. Pathway P

Q. Pathway Q

R. Pathway R

S. Pathway S

List-II

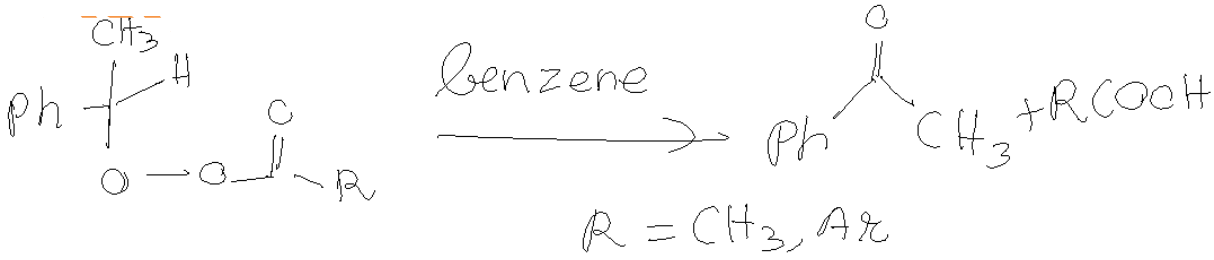
1. 
2. 
3. 
4. 

Codes :

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

Solution: (B)

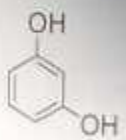
The reaction is as follows:

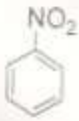


38. Match the four starting materials (**P**, **Q**, **R**, **S**) given in **List I** with the corresponding reaction schemes (**I**, **II**, **III**, **IV**) provided in **List II** and select the correct answer using the code given below the lists.

List-I

P. 

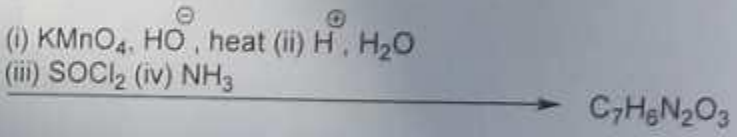
Q. 

R. 

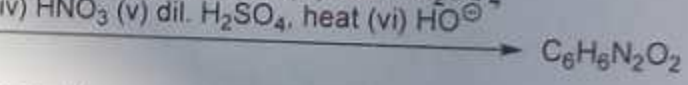
S. 

List-II

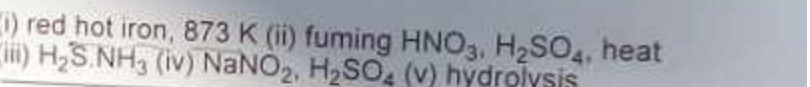
1. Scheme I



2. Scheme II



3. Scheme III

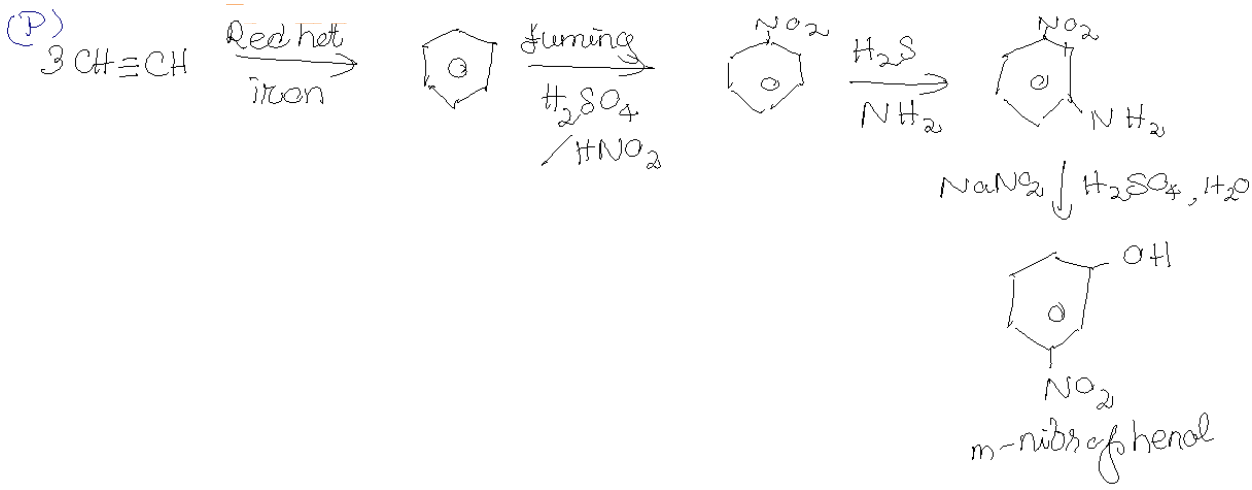


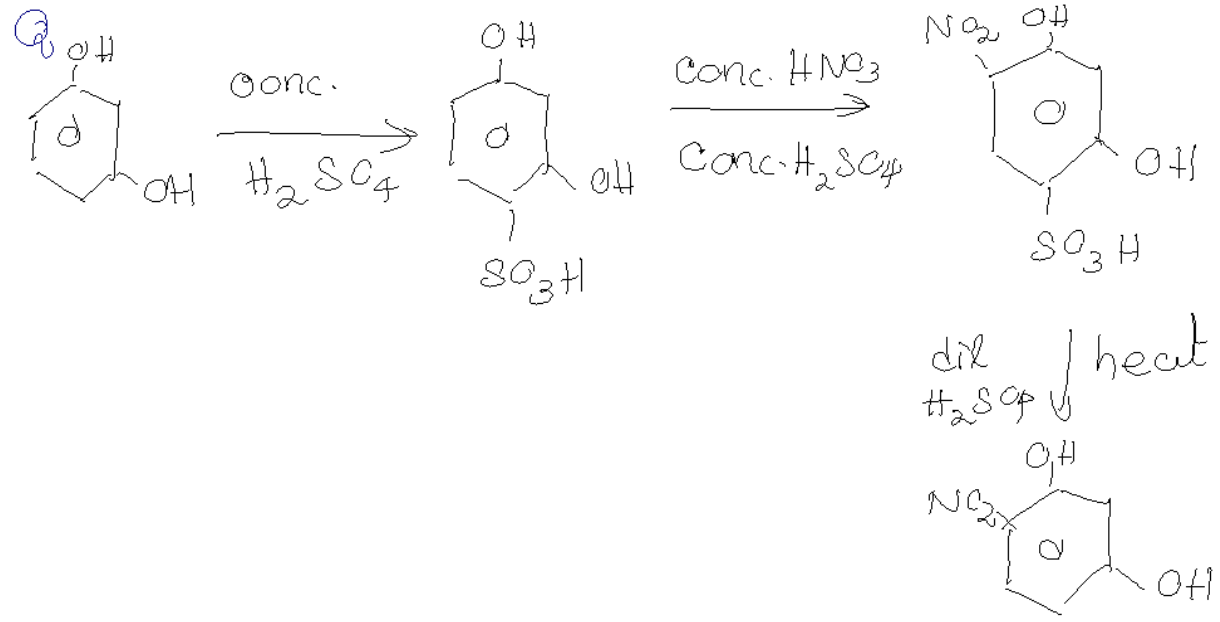
4. Scheme IV

Code :

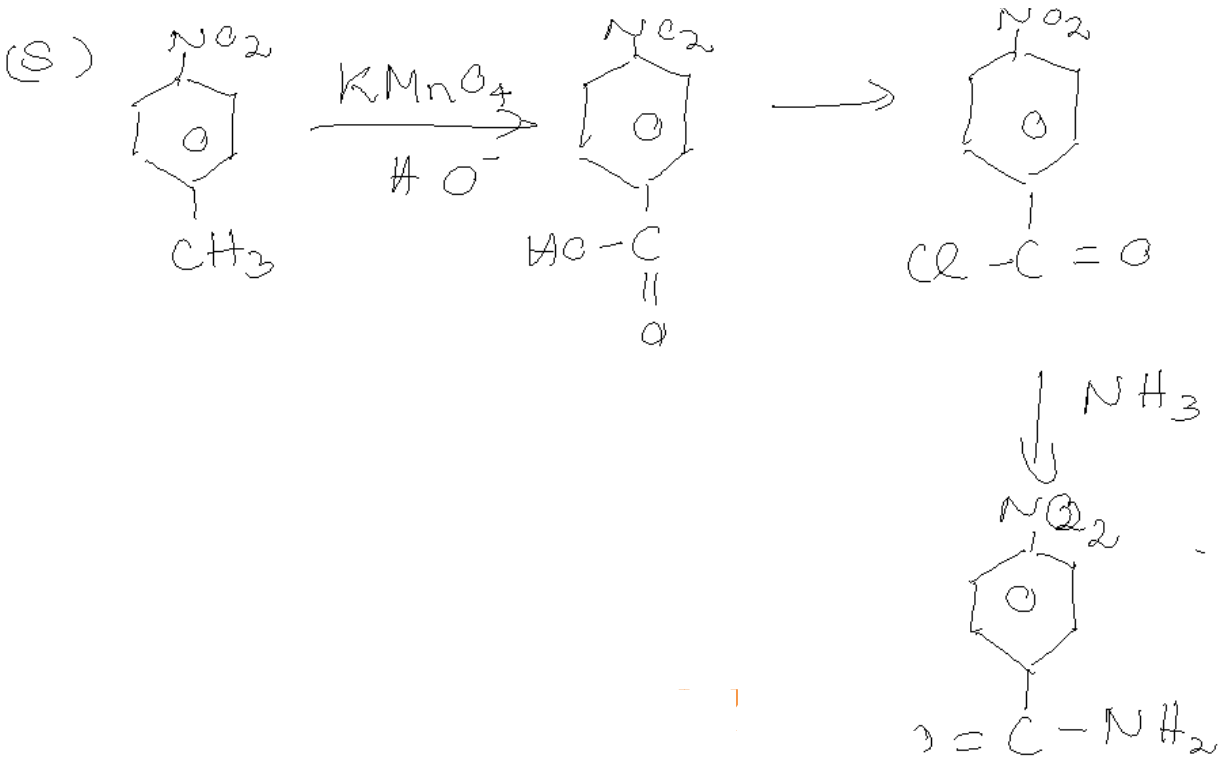
	P	Q	R	S
(A)	1	4	2	3
(B)	3	1	4	2
(C)	3	4	2	1
(D)	4	1	3	2

Solution: (C)




Q
OH
OH
conc.
H_2SO_4
OH
OH
SO_3H
Conc. HNO_3
Conc. H_2SO_4
NO_2
OH
OH
SO_3H
dil H_2SO_4
heat
OH
NO_2
OH
(R)
NO_2
Sn/HCl
NH_2
$CH_3-\overset{O}{\overset{\|}{C}}-Cl$
Acylation
$C_6H_5-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-CH_3$
conc. H_2SO_4
$O=C-CH_3$
$H-N$
SO_3H
HNO_3
$O=C-CH_3$
$H-N$
dil H_2SO_4
NH_2
NO_2

(5)



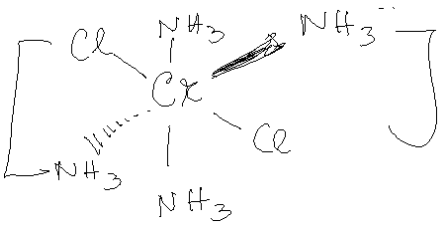
39. Solution: (B)

We have P as: $(NH_3)_4Cl_2]Cl$.

Now the central atom shows an oxidation number of +3.

Therefore it shows paramagnetic behaviors and therefore exhibits cis-trans isomerism.

The structure is given by:



For Q, we have:

Q

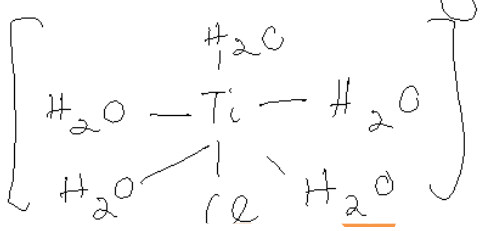
$[Ti(H_2O)_5Cl](NO_3)_2$

$\Rightarrow x - 1 = 2$ Ti (II)

$\Rightarrow x = 3$

But H_2O and Cl_2 are weak ligands

$\therefore$ Paramagnetic.



Q → 1

For R we have:

R → 4

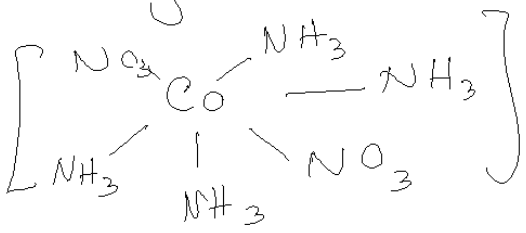
$[Pt(en)(NH_3)Cl]NO_3$

⇒ As (en) and NH_3 are strong, so it is going to show diamagnetism and exhibits ionisation isomerism

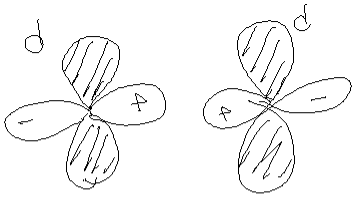
for S ; S → 2

$[Co(NH_3)_4(NO_3)_2]NO_3$

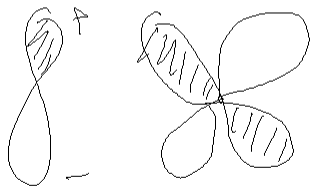
Diamagnetic & exhibits cis-trans isomerism



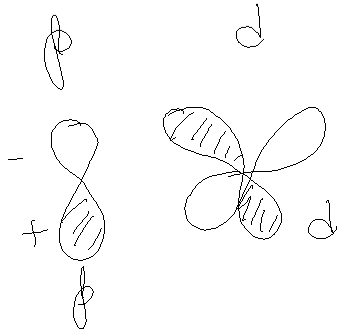
40. Solution: (C)



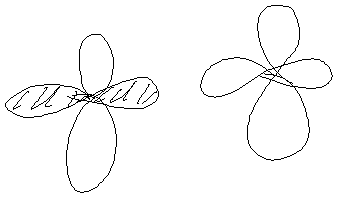
d-d ⇒ positive overlap
(d-d σ bond)



p-d positive overlap
(p-d π bond)



p-d negative overlap
(p-d π bond)



d-d negative overlap
(d-d σ anti bonding)