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) $POCl_3$

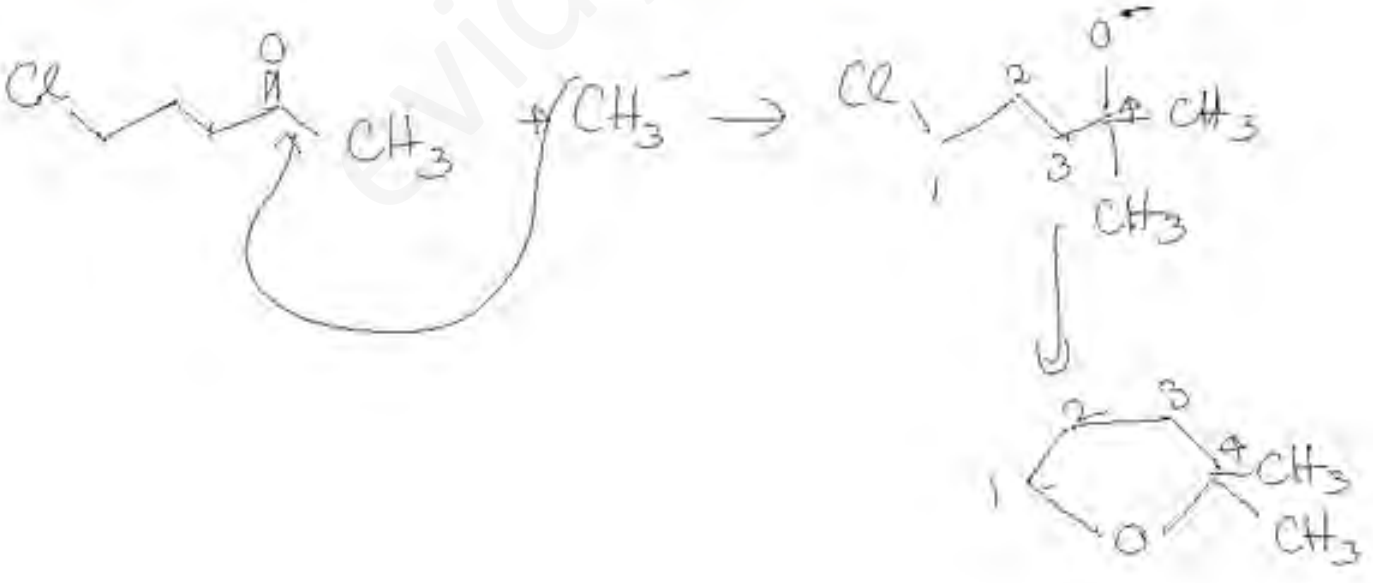
Solution: (A)

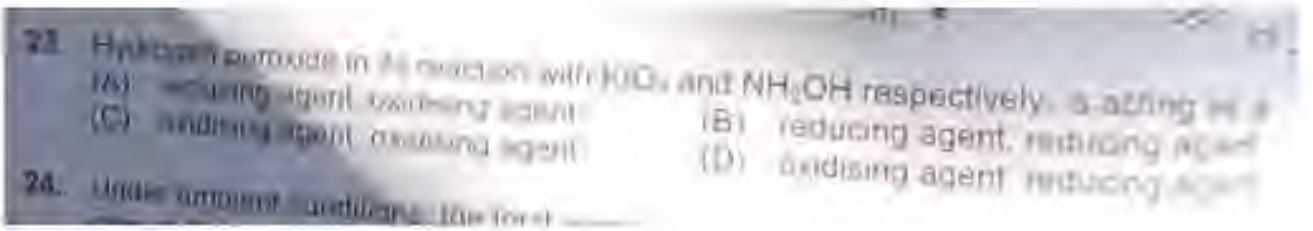
The reaction goes as follows:

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

22. The major product in the following reaction is
[Figure]
(A)
(B)
(C)
(D)

Solution: (D)





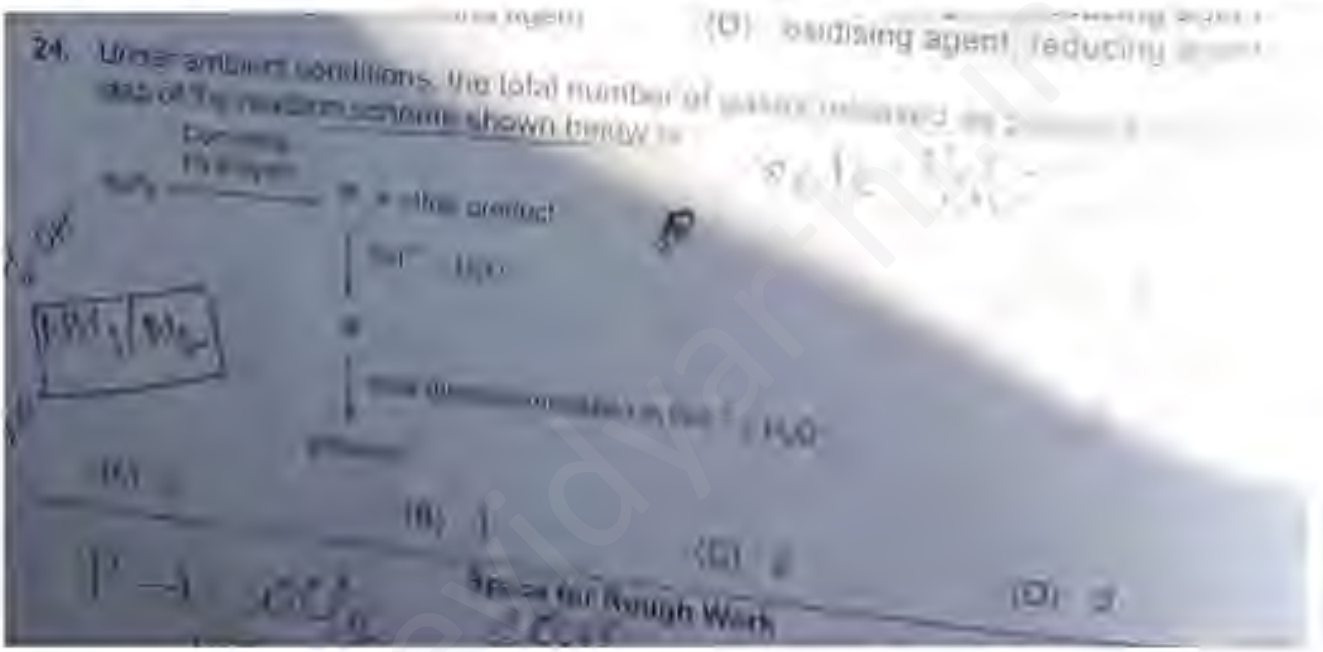
Solution: (A)

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.



Solution: (D)

The first reaction goes as follows:

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

This is followed by the following reaction:

$$XeO_3 + OH^- \longrightarrow \underset{\text{hydrogenxenate ion}}{HXeO_4^-}$$

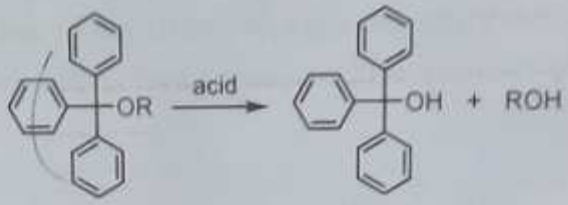
This ion when followed by further reaction gives:

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

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

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

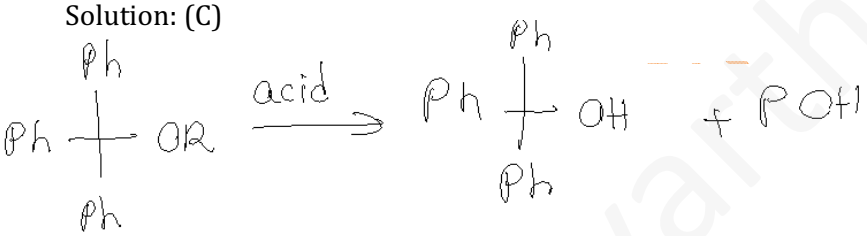
[Figure]



[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)

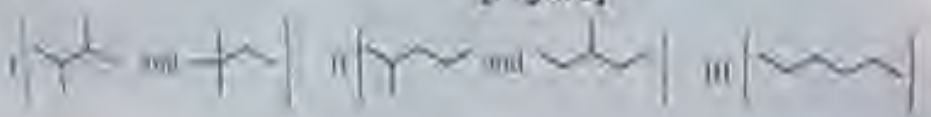


groups attached to C_2 should be electron donating.

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

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.*

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

Solution: (B)

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

28. Assuming ... NOT operative, the paramagnetic species among the following is

(A) ... (C) C_2 (D) N_2

Solution: (B)

B_2 exists in the gas phase as a paramagnetic radical.

30. For the ... of M increases by a factor of ... of M. The order of the reaction with ...

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: $2x, r_2$

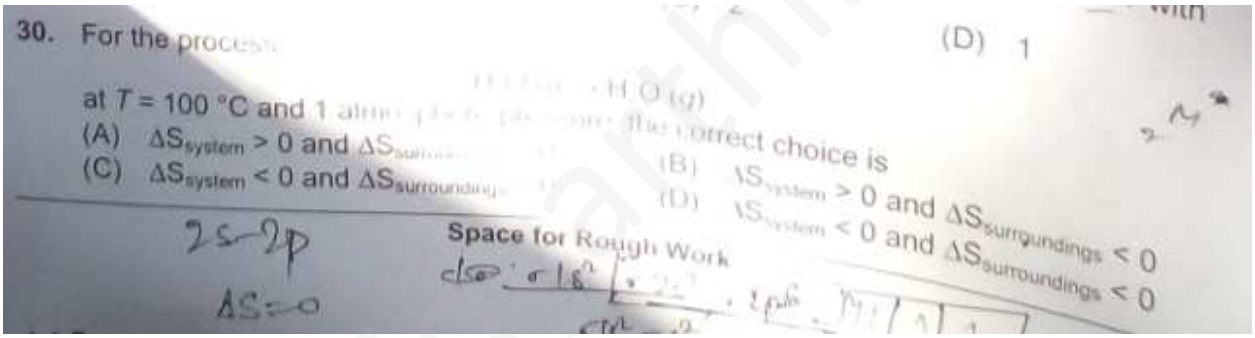
So, we get:

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

But, we know that:

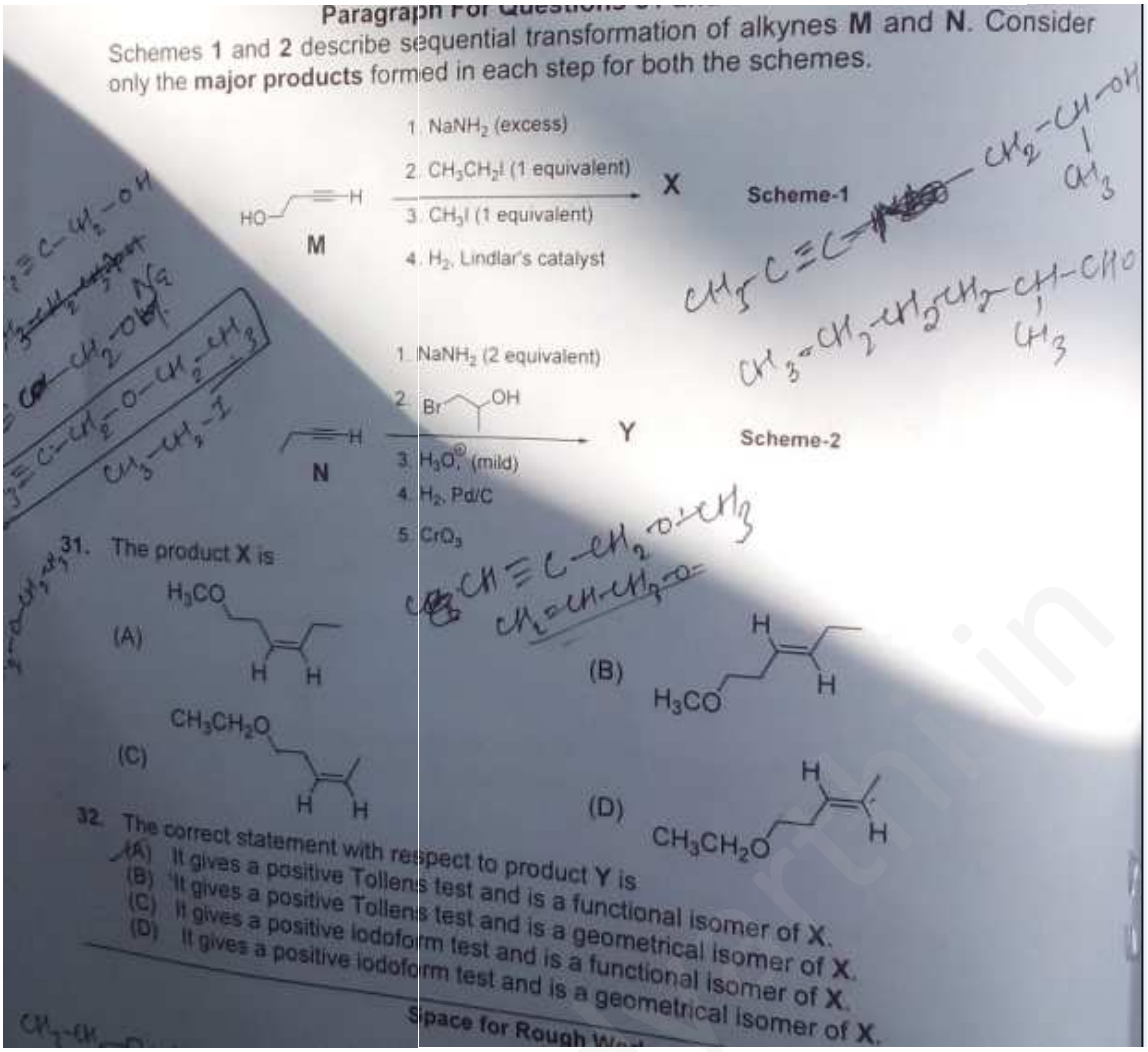
$$\frac{r_2}{r_1} = 8$$

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.



Paragraph For Questions

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.

Scheme-1

1. $NaNH_2$ (excess)
2. CH_3CH_2I (1 equivalent)
3. CH_3I (1 equivalent)
4. H_2, Lindlar's catalyst

Scheme-2

1. $NaNH_2$ (2 equivalent)
2. Br, OH
3. $H_3O^{\oplus}$ (mild)
4. H_2, Pd/C
5. CrO_3

31. The product **X** is

(A) H_3CO

(B) H_3CO

(C) CH_3CH_2O

(D) CH_3CH_2O

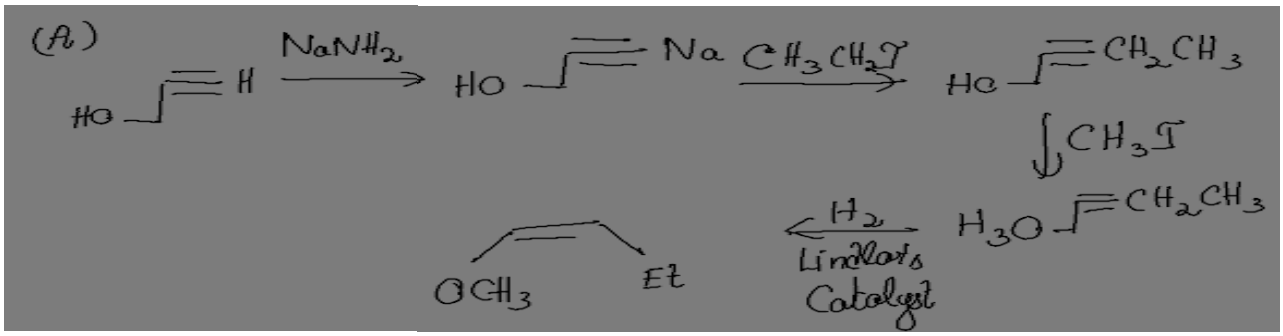
32. The correct statement with respect to product **Y** is

(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**.

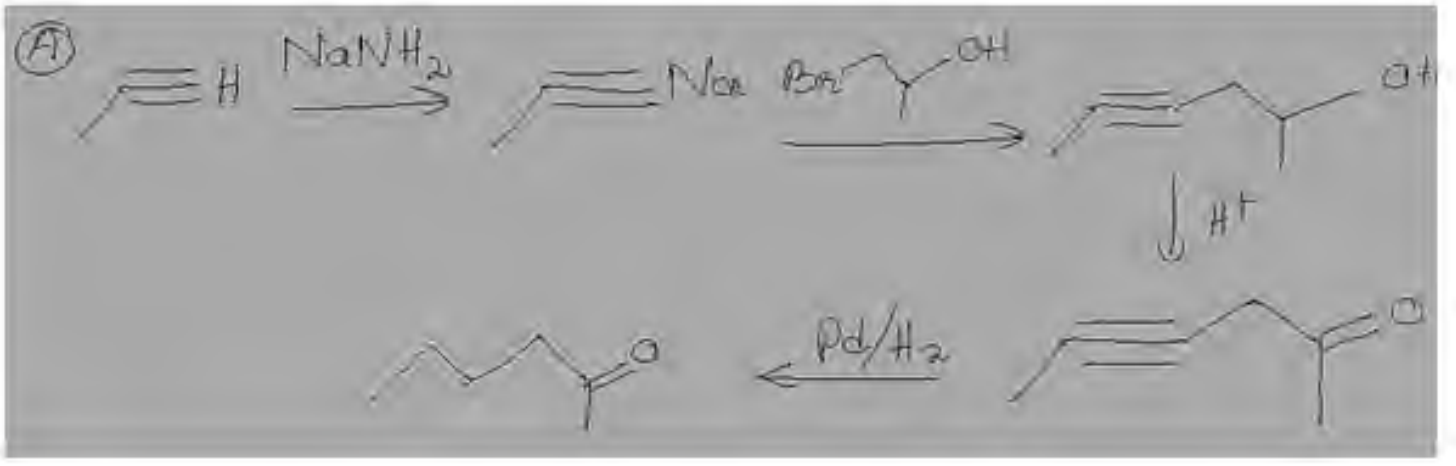
Space for Rough Work

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

M2 $\xrightarrow{S,\ \text{stoichiometric amount}}$ White precipitate $\xrightarrow[\text{excess}]{S}$ precipitate dissolves

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

CHEMISTRY

33. Solution: (B)

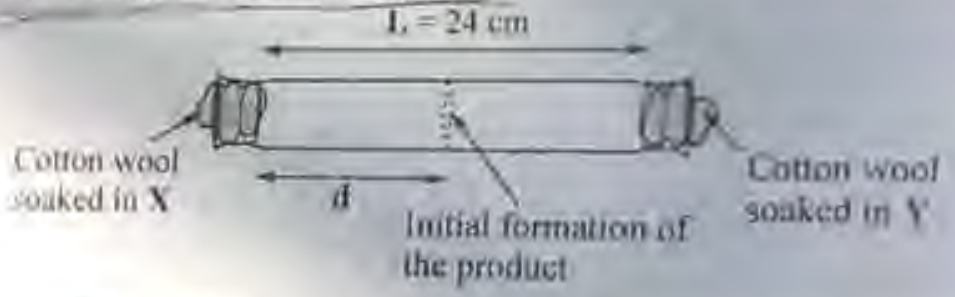
We know that $NiCl_4^{2-}$ is tetrahedral and $NiCN_4^{2-}$ is square planar.

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
(D) increased collision frequency of X 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:

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

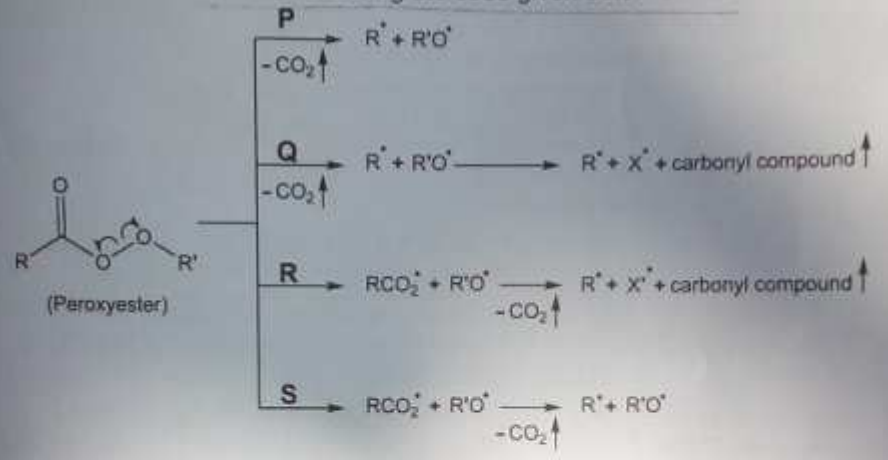
Hence, we have:

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

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

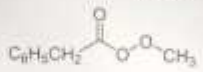
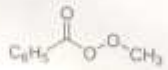
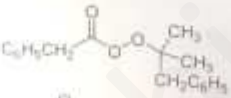
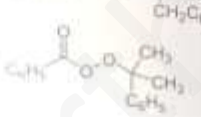
P. Pathway P

Q. Pathway Q

R. Pathway R

S. Pathway S

List-II

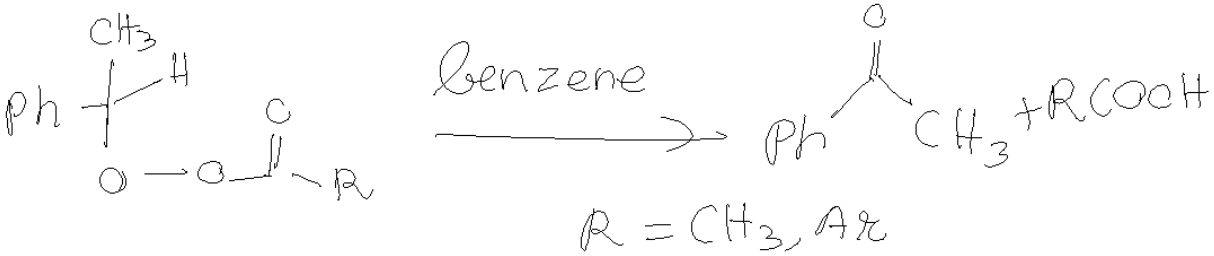
1. 
2. 
3. 
4. 

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)

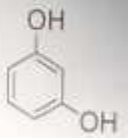
The reaction is as follows:

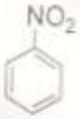


38. Match the four starting materials (**P**, **Q**, **R**, **S**) given in **List I** with the corresponding reaction schemes (**I**, **II**, **III**, **IV**) provided in **List II** and select the correct answer using the code given below the lists.

List-I

P. $H-C\equiv C-H$

Q. 

R. 

S. 

List-II

1. Scheme I

(i) $KMnO_4$, $HO^{\ominus}$, heat (ii) $H^{\oplus}$, H_2O
(iii) $SOCl_2$ (iv) NH_3
? ⟶ $C_7H_6N_2O_3$

2. Scheme II

(i) Sn/HCl (ii) CH_3COCl (iii) conc. H_2SO_4
(iv) HNO_3 (v) dil. H_2SO_4, heat (vi) $HO^{\ominus}$
? ⟶ $C_6H_6N_2O_2$

3. Scheme III

(i) red hot iron, 873 K (ii) fuming HNO_3, H_2SO_4, heat
(iii) $H_2S.NH_3$ (iv) $NaNO_2$, H_2SO_4 (v) hydrolysis
? ⟶ $C_6H_5NO_3$

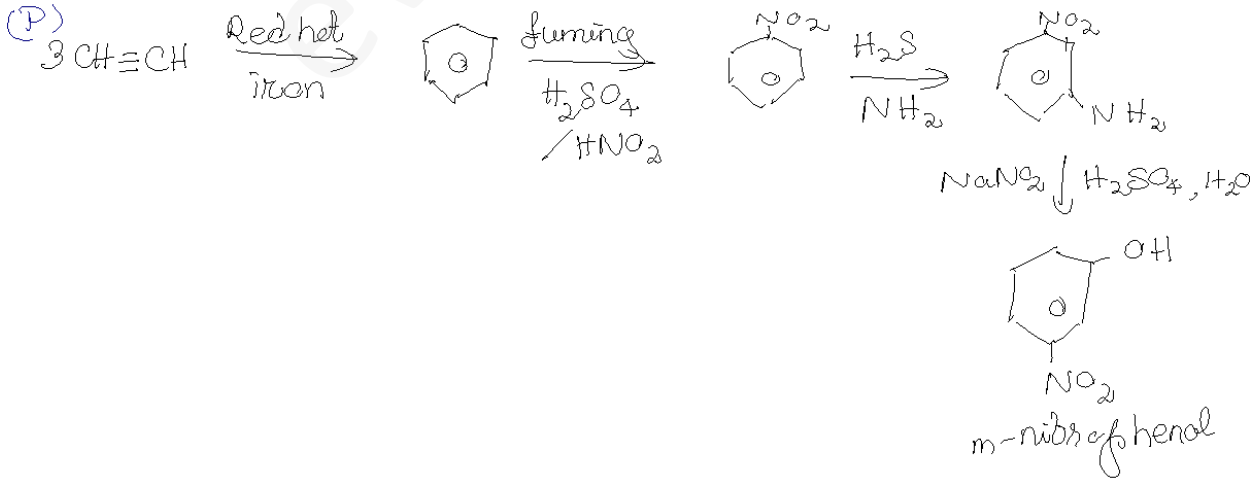
4. Scheme IV

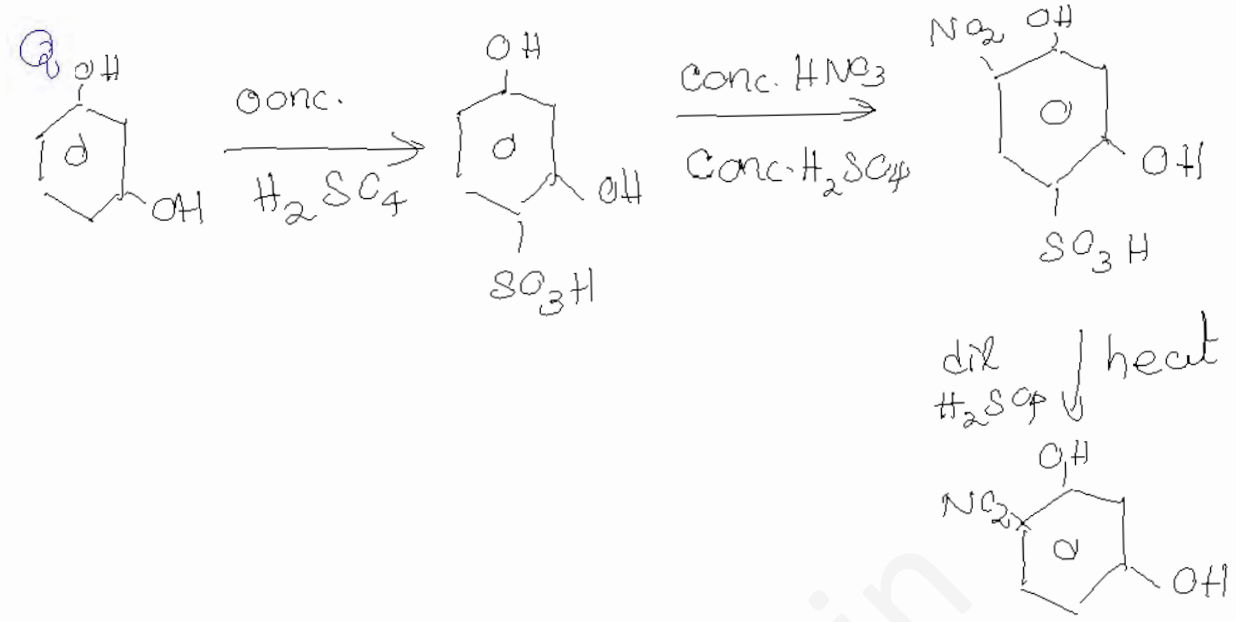
(i) conc. H_2SO_4, 60 °C
(ii) conc. HNO_3, conc. H_2SO_4 (iii) dil. H_2SO_4, heat
? ⟶ $C_6H_5NO_4$

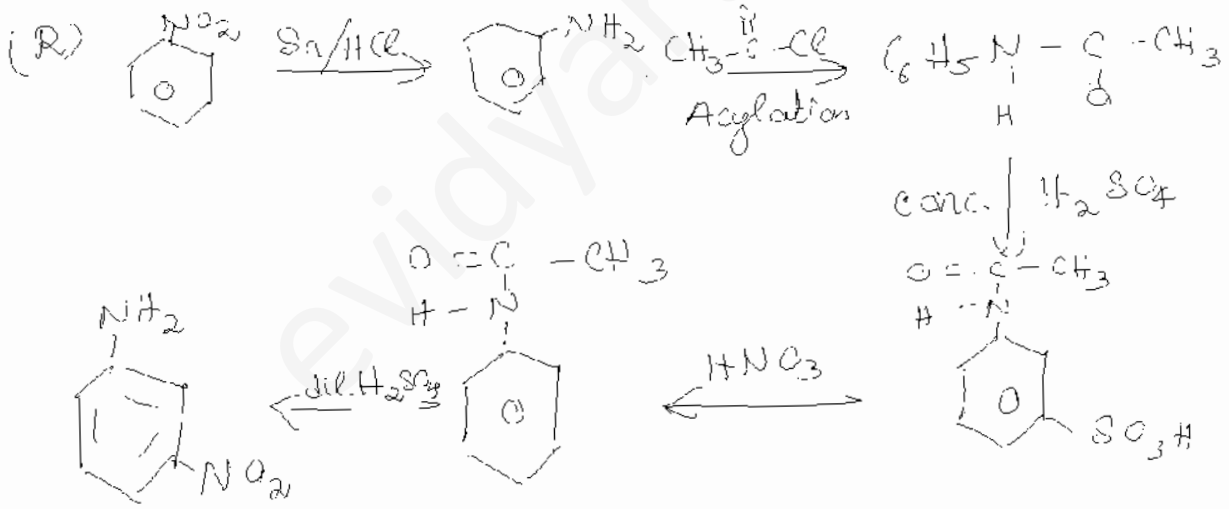
Code :

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

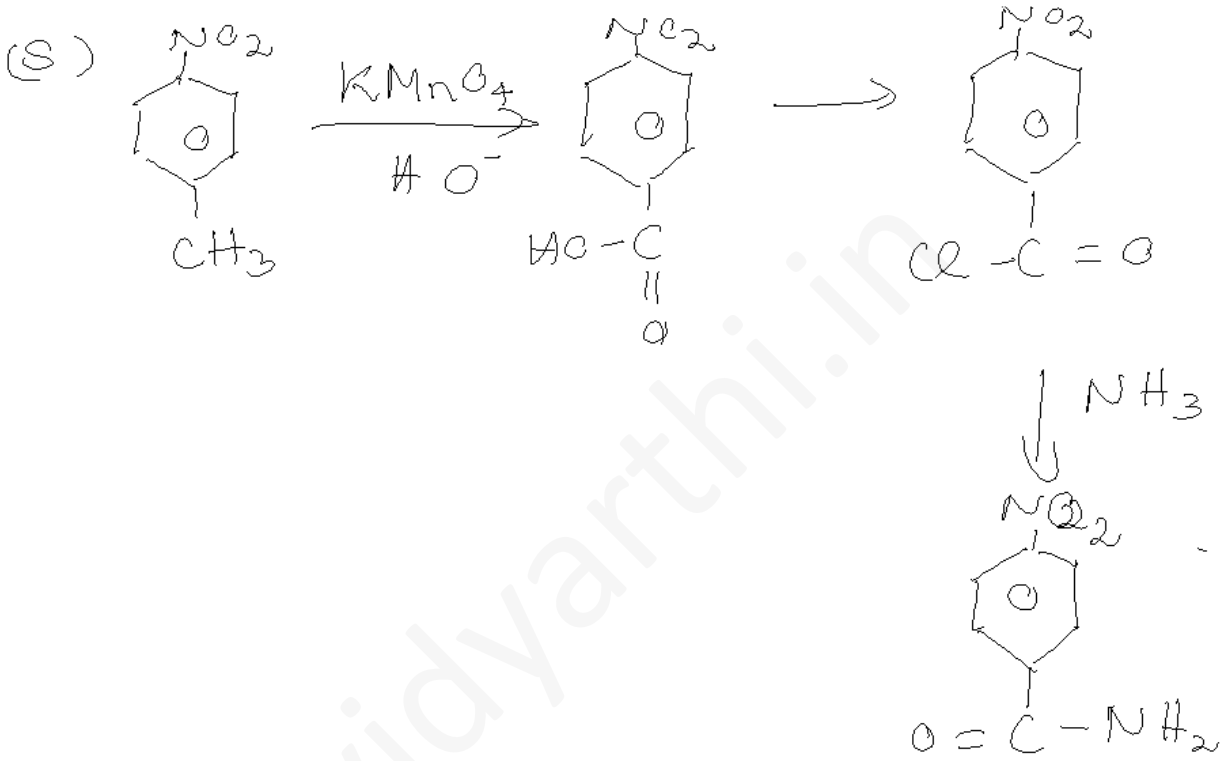
Solution: (C)







(c)



39. Match each coordination compound in **List-I** with an appropriate pair of characteristics from **List-II** and select the correct answer using the code given below the lists.
{en = $H_2NCH_2CH_2NH_2$; atomic numbers: Ti = 22; Cr = 24; Co = 27; Pt = 78}

List-I	List-II
P. $[Cr(NH_3)_4Cl_2]Cl$	1. Paramagnetic and exhibits ionisation isomerism
Q. $[Ti(H_2O)_5Cl](NO_3)_2$	2. Diamagnetic and exhibits *cis-trans* isomerism
R. $[Pt(en)(NH_3)Cl]NO_3$	3. Paramagnetic and exhibits *cis-trans* isomerism
S. $[Co(NH_3)_4(NO_3)_2]NO_3$	4. Diamagnetic and exhibits ionisation isomerism

Code :

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

40. Match the orbital overlap figures shown in **List-I** with the description given in **List-II** and select the correct answer using the code given below the lists.

List-I	List-II
P. 	1. $p-d$ π antibonding
Q. 	2. $d-d$ σ bonding
R. 	3. $p-d$ π bonding
S. 	4. $d-d$ σ antibonding

Code :

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

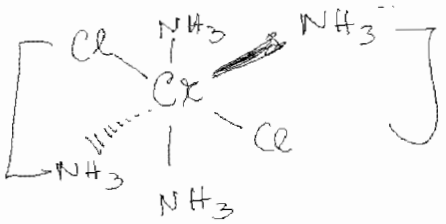
39. Solution: (B)

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

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:



Q

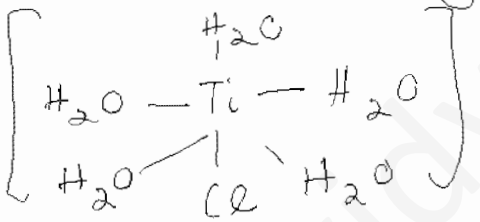
$[Ti(CH_2O)_5Cl](NO_3)_2$

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

$\Rightarrow x = 3$

But H_2O and Cl_2 are weak ligands

$\therefore$ Paramagnetic



Q → 1

R → 4

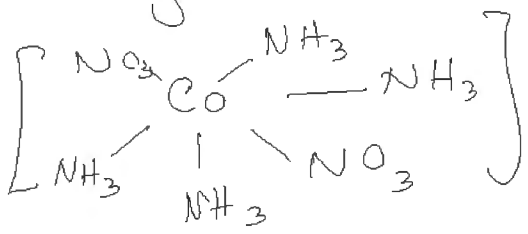
$[Pt(en)(NH_3)Cl]NO_3$

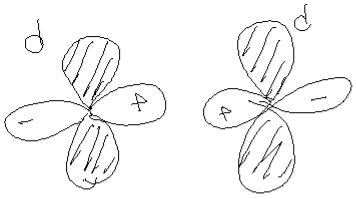
⇒ As (en) and NH_3 are strong, so it is going to show diamagnetism and exhibits ionisation isomerism

for S ; S → 2

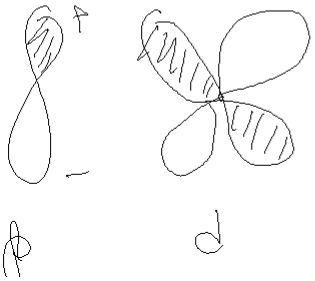
$[Co(NH_3)_4(NO_3)_2]NO_3$

Diamagnetic & exhibits cis-trans isomerism

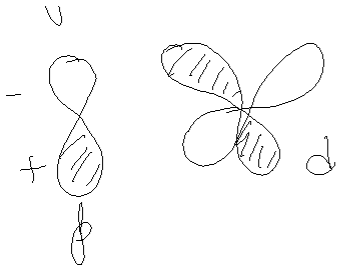




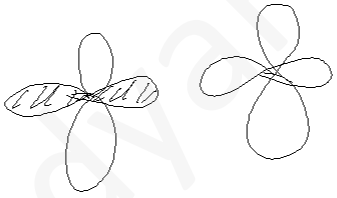
d-d ⇒ positive overlap
(d-d σ bond)



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)