

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

21. The product formed in the reaction of  $\text{SOCl}_2$  with white phosphorous is  
 (A)  $\text{PCl}_3$  (B)  $\text{SO}_2\text{Cl}_2$  (C)  $\text{SCl}_2$  (D)  $\text{POCl}_3$

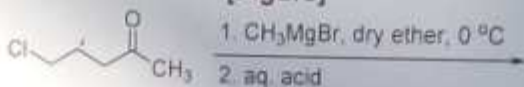
Solution: (A)

The reaction goes as follows:



22. The major product in the following reaction is

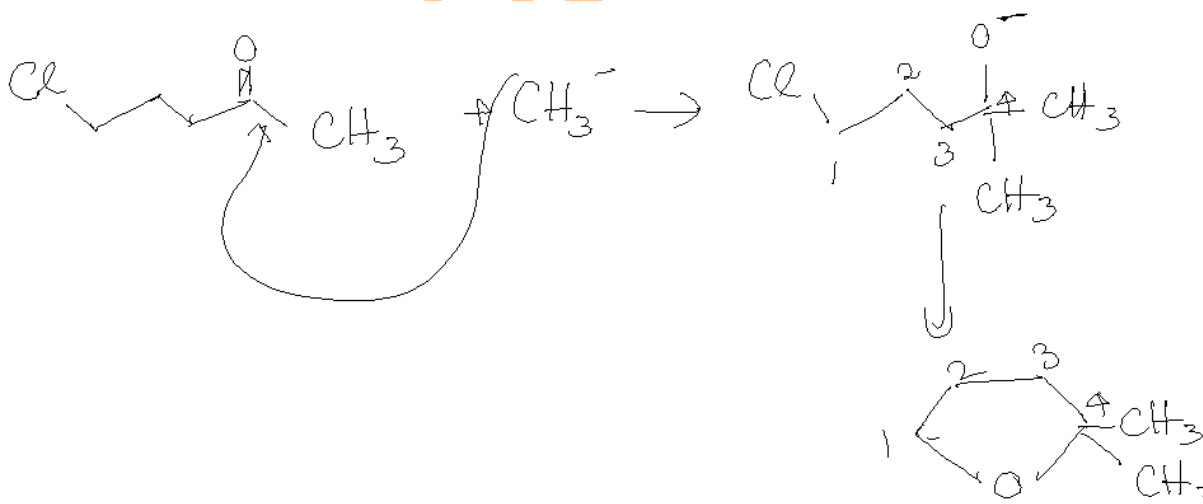
[Figure]

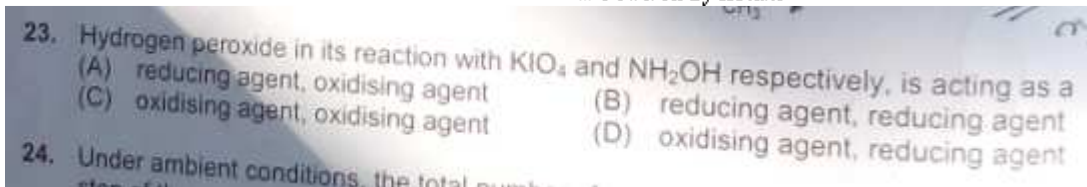


(A)  $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_3$   
 (B)  $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{C}(\text{OH})(\text{CH}_3)_2$   
 (C)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$   
 (D)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$

Handwritten notes:  $n+2-2+1=0$ ,  $m=1$

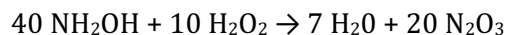
Solution: (D)



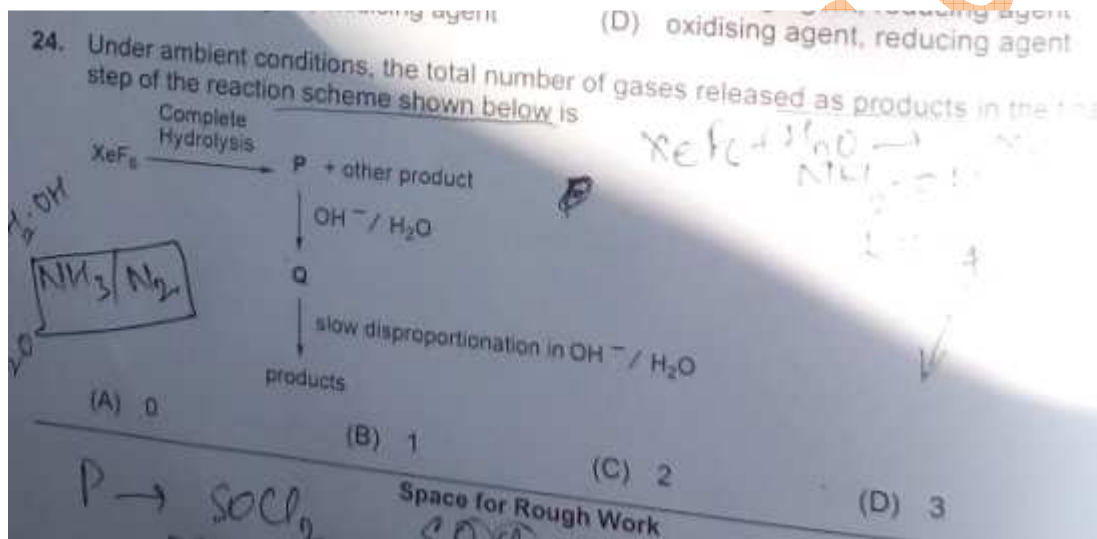


Solution: (A)

The reactions are as follows:

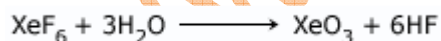


Thus it acts as: Reducing Agent in the first reaction and Oxidising Agent in the second reaction.

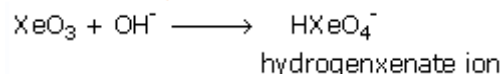


Solution: (D)

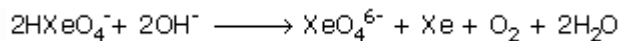
The first reaction goes as follows:



This is followed by the following reaction:

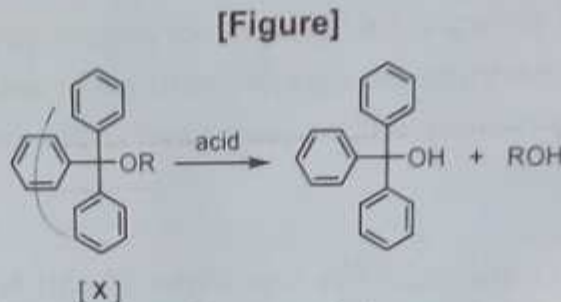


This ion when followed by further reaction gives:



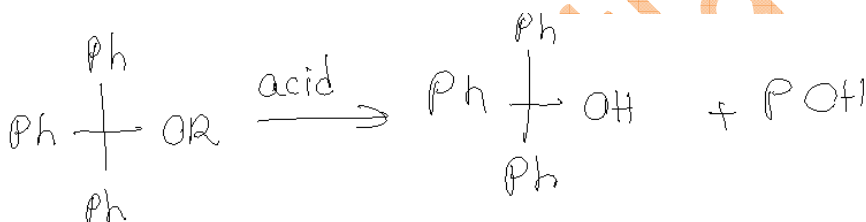
Thus three gases including water, xenon and oxygen are produced.

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



- (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)

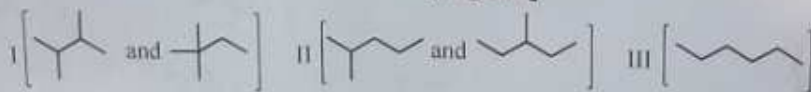


groups attached to O<sub>2</sub> should be electron donating.

So if 2 phenyl groups are replaced by 2 *para* methoxy phenyl groups, 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  $\beta$ -naphthol using dye test, it is necessary to use  
 (A) dichloromethane solution of  $\beta$ -naphthol. (B) acidic solution of  $\beta$ -naphthol.  
 (C) neutral solution of  $\beta$ -naphthol. (D) alkaline solution of  $\beta$ -naphthol.
28. Assuming  $2s-2p$  mixing is NOT operative, the paramagnetic species among the

Solution: (B)

$\beta$ -Naphthol or 2-Naphthol is identified by using a dye test using an acidic solution.

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  $M \rightarrow N$  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

Solution: (B)

$B_2$  exists in the gas phase as a paramagnetic radical.

29. For the elementary reaction  $M \rightarrow N$  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)

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:  $2x, r_2$

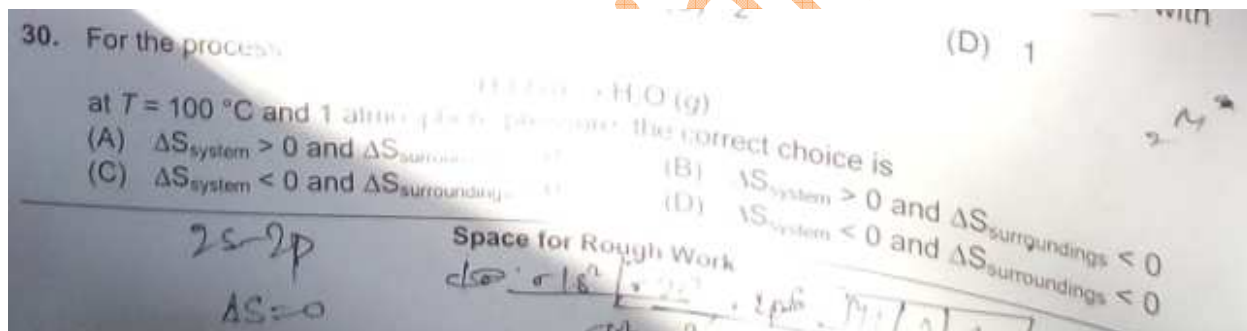
So, we get:

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

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 orderly 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**

M: HO-CH2-C#CH

1. NaNH<sub>2</sub> (excess)
2. CH<sub>3</sub>CH<sub>2</sub>I (1 equivalent)
3. CH<sub>3</sub>I (1 equivalent)
4. H<sub>2</sub>, Lindlar's catalyst

**Scheme-2**

N: CH3-C#CH

1. NaNH<sub>2</sub> (2 equivalent)
2. Br-CH<sub>2</sub>-CH<sub>2</sub>-OH
3. H<sub>3</sub>O<sup>+</sup> (mild)
4. H<sub>2</sub>, Pd/C
5. CrO<sub>3</sub>

31. The product X is

(A) CH3CO-CH2-CH=CH-CH3

(B) CH3CO-CH2-CH=CH-CH2-CH3

(C) CH3CH2O-CH2-CH=CH-CH3

(D) CH3CH2O-CH2-CH=CH-CH2-CH3

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.

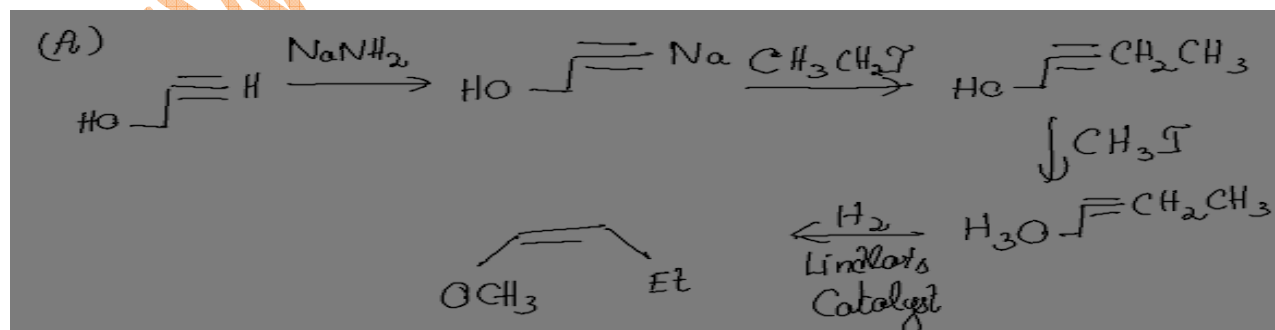
(C) It gives a positive iodoform test and is a functional isomer of X.

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

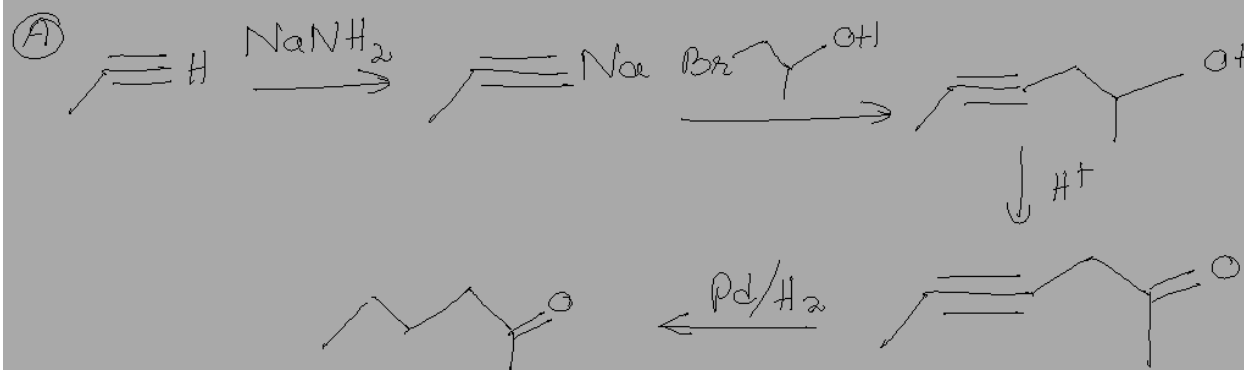
Space for Rough Work

31. Solution: (A)

The reaction goes as follows:



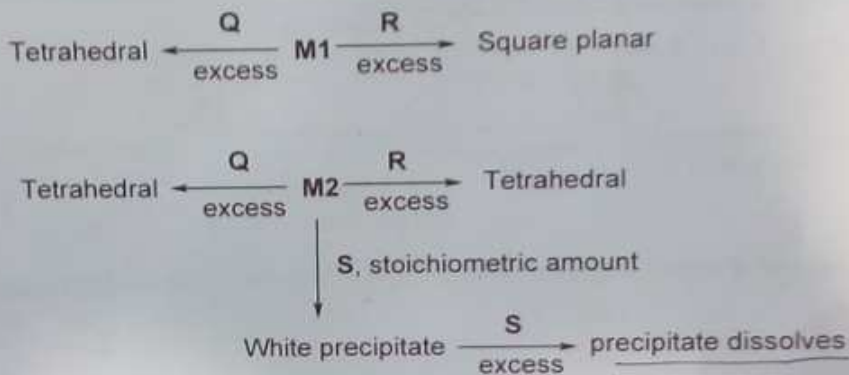
32. Solution: (A)



### 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:



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

34. Reagent **S** is  
 (A)  $\text{K}_4[\text{Fe}(\text{CN})_6]$  (B)  $\text{Na}_2\text{HPO}_4$  (C)  $\text{K}_2\text{CrO}_4$  (D) KOH

33. Solution: (B)

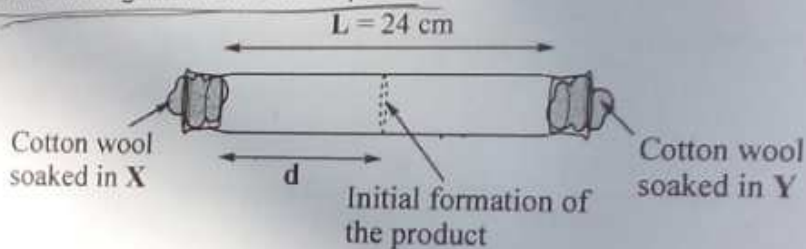
We know that  $\text{NiCl}_4^{2-}$  is tetrahedral and  $\text{NiCN}_4^{2-}$  is square planar.

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

34. Solution (B)

$\text{Na}_2\text{HPO}_4$  forms white salts the precipitate of which dissolves in excess.

X and Y are two volatile liquids with molar weights of  $10 \text{ g mol}^{-1}$  and  $40 \text{ g mol}^{-1}$  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  $L = 24 \text{ cm}$ , as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of  $300 \text{ K}$ . Vapours of X and Y react to form a product which is first observed at a distance  $d \text{ cm}$  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)

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

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

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

Hence, we have:

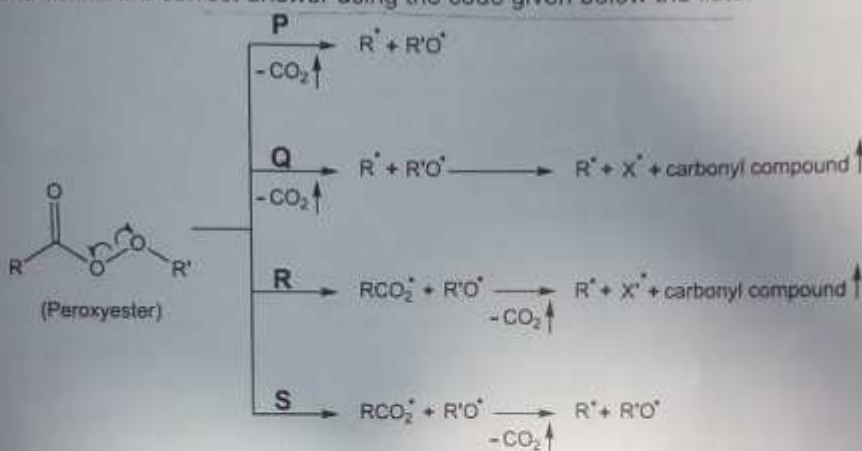
$$3d = 24 \times 2 \Rightarrow d = 16$$

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.

1, 3, R, S

2, 4  
Q, R

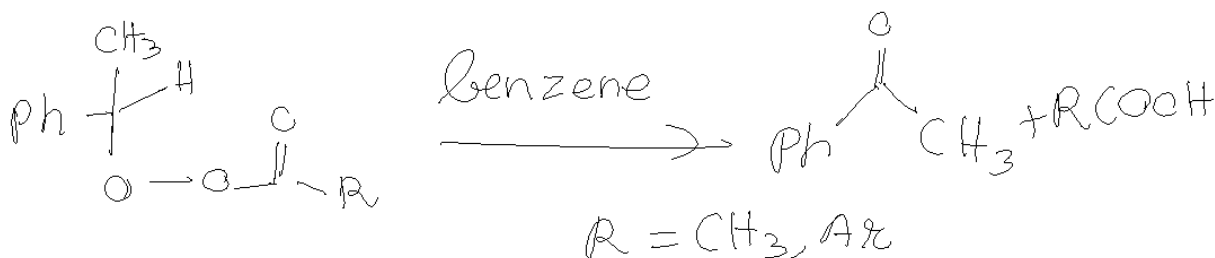
C6H5-CH2-O-CH3

Codes :

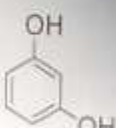
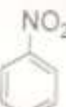

	P	Q	R	S
(A)	1	3	4	2
(B)	2	4	3	1
(C)	4	1	2	3
(D)	3	2	1	4

Solution: (B)

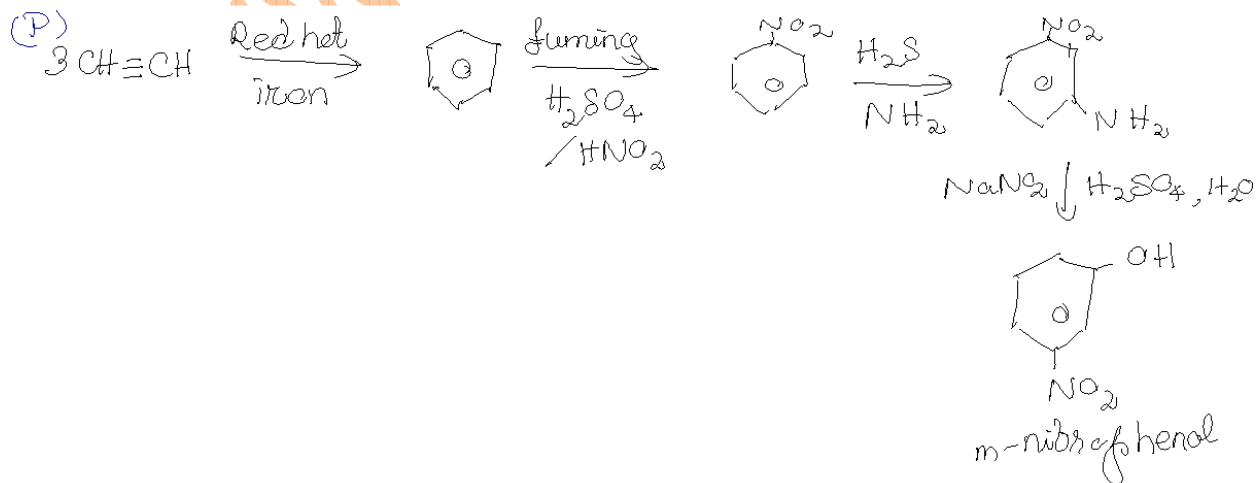
The reaction is as follows:

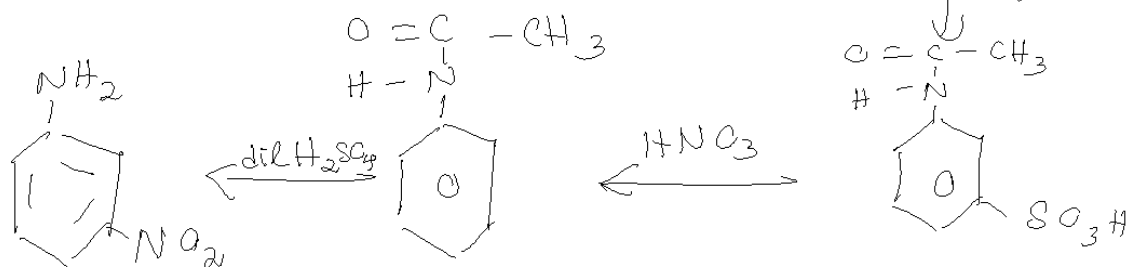
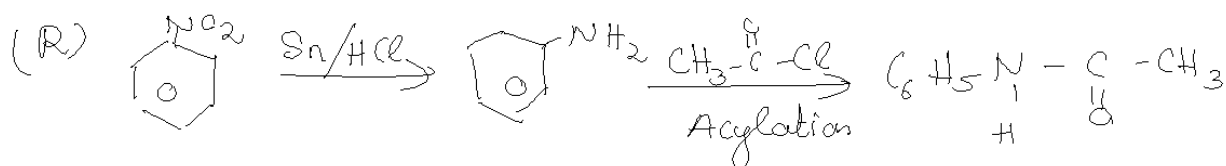
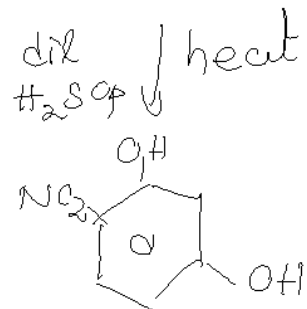
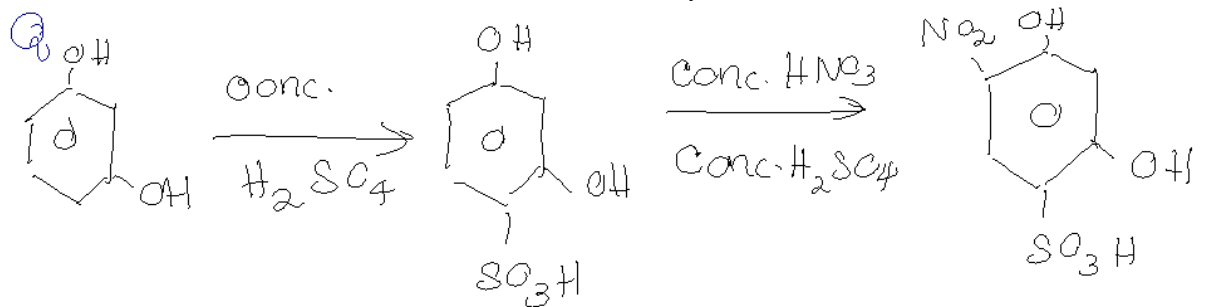


38. Match the four starting materials (P, Q, R, S) given in List I with the corresponding reaction schemes (I, II, III, IV) provided in List II and select the correct answer using the code given below the lists.

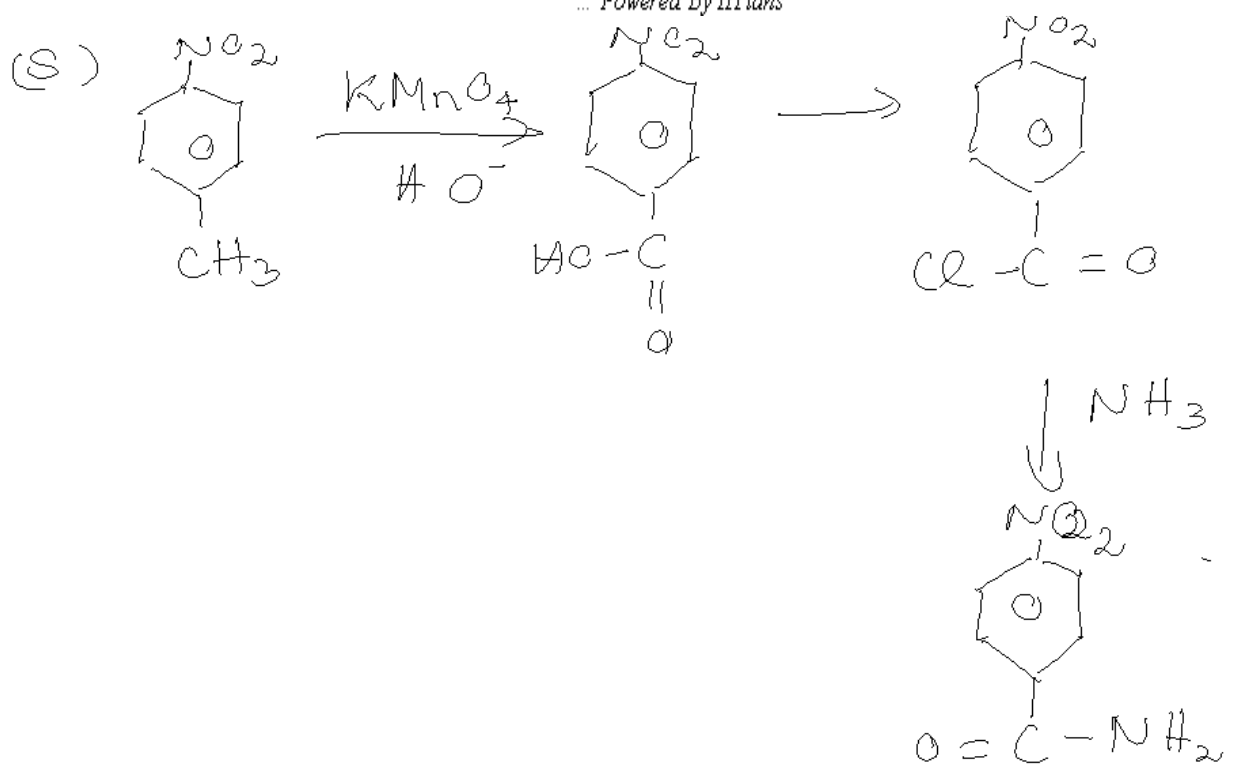
List-I	List-II																																				
<p>P. <math>\text{H}-\text{C}\equiv\text{C}-\text{H}</math></p> <p>Q. </p> <p>R. </p> <p>S. </p>	<p>1. Scheme I                      (i) <math>\text{KMnO}_4, \text{HO}^\ominus, \text{heat}</math> (ii) <math>\text{H}^\oplus, \text{H}_2\text{O}</math>                      ? <math>\xrightarrow{\text{(iii) SOCl}_2 \text{ (iv) NH}_3}</math> <math>\text{C}_7\text{H}_5\text{N}_2\text{O}_3</math></p> <p>2. Scheme II                      (i) <math>\text{Sn/HCl}</math> (ii) <math>\text{CH}_3\text{COCl}</math> (iii) conc. <math>\text{H}_2\text{SO}_4</math>                      ? <math>\xrightarrow{\text{(iv) HNO}_3 \text{ (v) dil. H}_2\text{SO}_4, \text{heat (vi) HO}^\ominus}</math> <math>\text{C}_6\text{H}_5\text{N}_2\text{O}_2</math></p> <p>3. Scheme III                      (i) red hot iron, 873 K (ii) fuming <math>\text{HNO}_3, \text{H}_2\text{SO}_4, \text{heat}</math>                      ? <math>\xrightarrow{\text{(iii) H}_2\text{S.NH}_3 \text{ (iv) NaNO}_2, \text{H}_2\text{SO}_4 \text{ (v) hydrolysis}}</math> <math>\text{C}_6\text{H}_5\text{NO}_3</math></p> <p>4. Scheme IV                      (i) conc. <math>\text{H}_2\text{SO}_4, 60^\circ\text{C}</math>                      ? <math>\xrightarrow{\text{(ii) conc. HNO}_3, \text{conc. H}_2\text{SO}_4 \text{ (iii) dil. H}_2\text{SO}_4, \text{heat}}</math> <math>\text{C}_6\text{H}_5\text{NO}_2</math></p>																																				
<p>Code :</p> <table border="0" style="display: inline-table; margin-right: 20px;"> <tr><td>(A)</td><td>P</td><td>Q</td><td>R</td><td>S</td></tr> <tr><td>(B)</td><td>1</td><td>4</td><td>2</td><td>3</td></tr> <tr><td>(C)</td><td>3</td><td>1</td><td>4</td><td>2</td></tr> <tr><td>(D)</td><td>4</td><td>1</td><td>2</td><td>1</td></tr> </table>	(A)	P	Q	R	S	(B)	1	4	2	3	(C)	3	1	4	2	(D)	4	1	2	1	<table border="0" style="display: inline-table;"> <tr><td>1</td><td>2</td><td>3</td><td>4</td></tr> <tr><td>2</td><td>3</td><td>4</td><td>1</td></tr> <tr><td>3</td><td>4</td><td>1</td><td>2</td></tr> <tr><td>4</td><td>1</td><td>2</td><td>3</td></tr> </table>	1	2	3	4	2	3	4	1	3	4	1	2	4	1	2	3
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2	3	4	1																																		
3	4	1	2																																		
4	1	2	3																																		

Solution: (C)





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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 =  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ; atomic numbers: Ti = 22; Cr = 24; Co = 27; Pt = 78)

- | List-I   | List-II   |
|--|---|
| P. $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$            | 1. Paramagnetic and exhibits ionisation isomerism       |
| Q. $[\text{Ti}(\text{H}_2\text{O})_5\text{Cl}](\text{NO}_3)_2$ | 2. Diamagnetic and exhibits <i>cis-trans</i> isomerism  |
| R. $[\text{Pt}(\text{en})(\text{NH}_3)\text{Cl}]\text{NO}_3$   | 3. Paramagnetic and exhibits <i>cis-trans</i> isomerism |
| S. $[\text{Co}(\text{NH}_3)_4(\text{NO}_3)_2]\text{NO}_3$      | 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

Handwritten notes:  $\leftarrow 2$ ,  $\leftarrow 1$ ,  $P < 3$

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. $p-d \pi$ antibonding (D) |
| Q.     | 2. $d-d \sigma$ bonding      |
| R.     | 3. $p-d \pi$ bonding         |
| S.     | 4. $d-d \sigma$ 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

Handwritten notes:  $2x + 10 - 2 = +1$ ,  $x = 3$ ,  $x - 10 - 2 = 1$

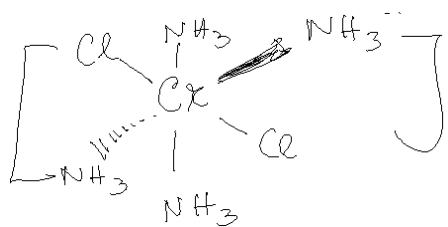
39. Solution: (B)

We have P as:  $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ .

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

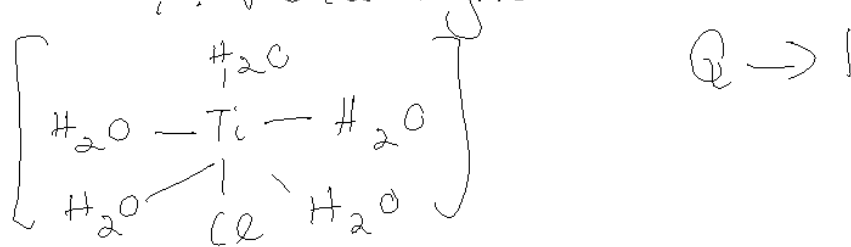


$$\Rightarrow x - 1 = 2 \quad \text{Ti: (III)}$$

$$\Rightarrow x = 3$$

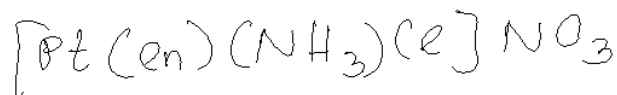
But  $\text{H}_2\text{O}$  and  $\text{Cl}_2$  are weak ligands

$\therefore$  Paramagnetic.



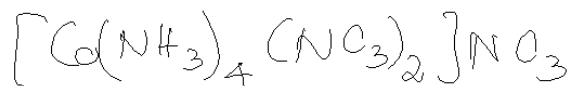
For R we have:

R  $\rightarrow$  4

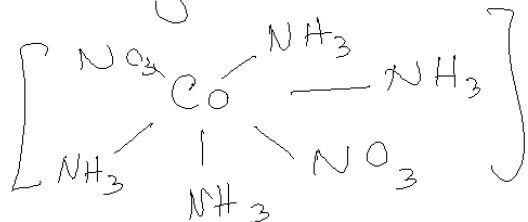


$\Rightarrow$  As  $(\text{en})$  and  $\text{NH}_3$  are strong, so it is going to show diamagnetism and exhibits ionisation isomerism

for S ;  $S \rightarrow 2$

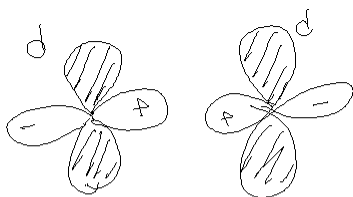


Diamagnetic & exhibits cis-trans isomerism

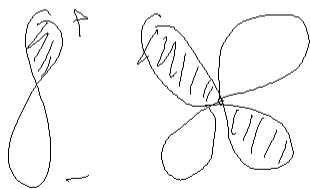


40. Solution: (C)

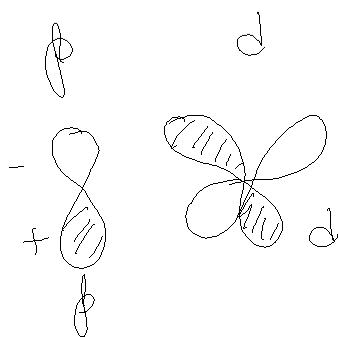
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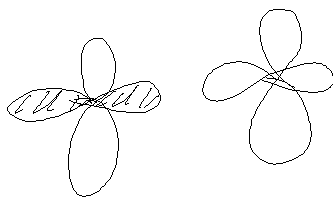
$d-d \Rightarrow$  positive overlap  
( $d-d$   $\sigma$  bond)



$p-d$  positive overlap  
( $p-d$   $\pi$  bond)



$p-d$  negative overlap  
( $p-d$   $\pi$  bond)



$d-d$  negative overlap  
( $d-d$   $\sigma$  anti bonding)

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