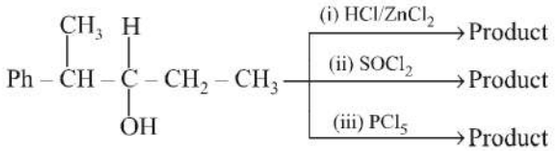
Haloalkanes and Haloarenes

1. Find the sum of total number of structural and configurational isomers of a bromo compound, C_5H_9Br, formed by the addition of HBr to 2-pentyne respectively.

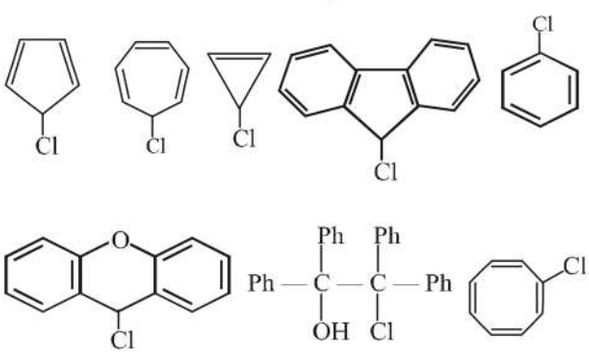
2. 

(Optically pure single stereoisomer)

Find the sum of total number of isomeric chlorides obtained in these reactions (consider only the major products).

3. How many total number of alkenes are possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH?

4. How many of the following compounds will give white precipitate with aqueous $AgNO_3$?



5. 2-Bromopentane is heated with KOH in alcoholic and aqueous medium respectively. Find the total number of products.

6. In the following sequence of reactions

$$CH_3 - Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow[ether]{LiAlH_4} C$$

How many sp^3 hybridized atoms are present in product C.

7. $$CH_3CH_2Cl \xrightarrow{NaCN} X \xrightarrow{Ni/H_2} Y \xrightarrow[anhydride]{Acetic} Z$$

Find the sum of carbon and hydrogen atoms in product Z.

8. Consider the following reaction.

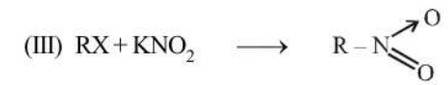
$$C_2H_5I \xrightarrow{Alc.\ KOH} X \xrightarrow{Br_2} Y \xrightarrow{KCN} Z$$

How many CN group are present in product Z?

9. How many following reactions are correct?

(I) $RX + AgCN \longrightarrow RNC$

(II) $RX + KCN \longrightarrow RCN$

(III) $RX + KNO_2 \longrightarrow$ 

(IV) $RX + AgNO_2 \longrightarrow R–O–N=O$

10. In the following sequence of reactions

$$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[ether]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$$

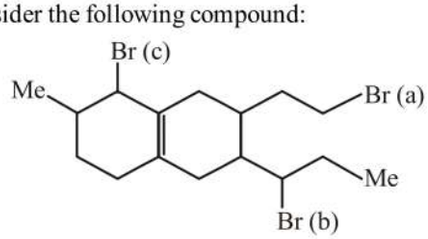
Find the number of –OH group in compound D.

11. Find the total number of lone pair in compound Z which is formed as follows:

$$CH_3CH_2CH_2Br \xrightarrow{aq.\ NaOH} X \xrightarrow{Al_2O_3} Y \xrightarrow{Cl_2/H_2O} Z$$

12. An organic compound A with molecular formula C_4H_9Br on treatment with alcoholic KOH gave two isomeric compounds B and C with the formula C_4H_8. On ozonolysis, B gave only one product CH_3CHO while C gave two different products. Find the sum of carbon atoms in compound A, B and C.

13. Consider the following compound:



How many following statements are correct?

(I) Loss of Br (a) atom in dehydrobromination reaction results in the formation of the most reactive double bond towards hydrogenation reaction.

(II) Removal of Br (c) atom results in the formation of the most stable carbocation.

(III) The above compound contains five asymmetric C atoms.

(IV) The above compound does not show geometrical isomers.

14. IUPAC name of DDT is 2,2-*bis* (*p*-chlorophenyl)-1,1,1-trichloroethane. How many reactive chlorine atoms are there in the compound?

15. How many methylanilines are formed when 3-methylchlorobenzene is treated with sodamide in liquid ammonia?

SOLUTIONS

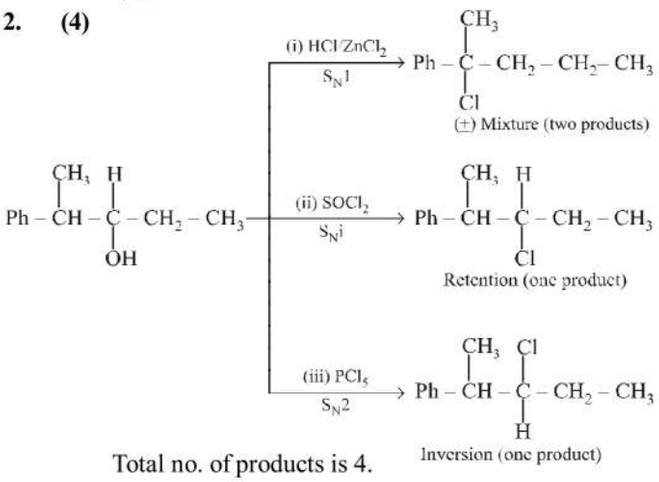
1. **(6)** Addition of HBr to 2-pentyne gives two structural isomers (I) and (II)

$$CH_3-C\equiv C-CH_2CH_3 \xrightarrow{HBr}$$

$$\underset{(I)}{CH_3C(Br)=CHCH_2CH_3}+\underset{(II)}{CH_3CH=C(Br)CH_2CH_3}$$

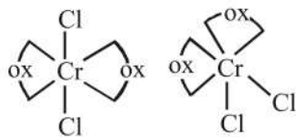
Each one of these will exist as a pair of geometrical isomers. Thus, there are two structural and four configurational isomers. Hence, total number of isomers is 6.

2. **(4)**

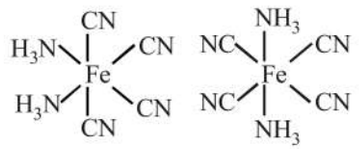


Total no. of products is 4.

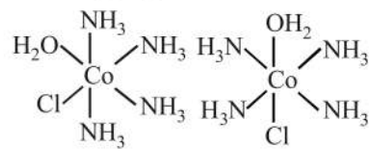
$[CrCl_2(C_2O_4)_2]^{3-}$



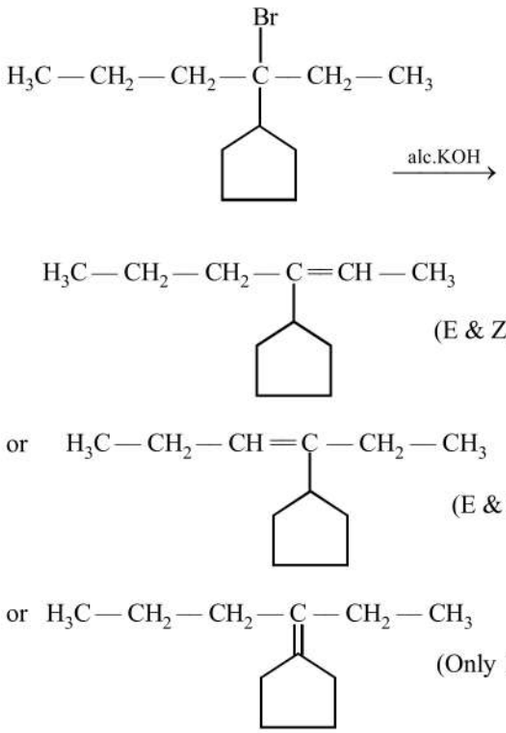
$[Fe(NH_3)_2(CN)_4]^-$



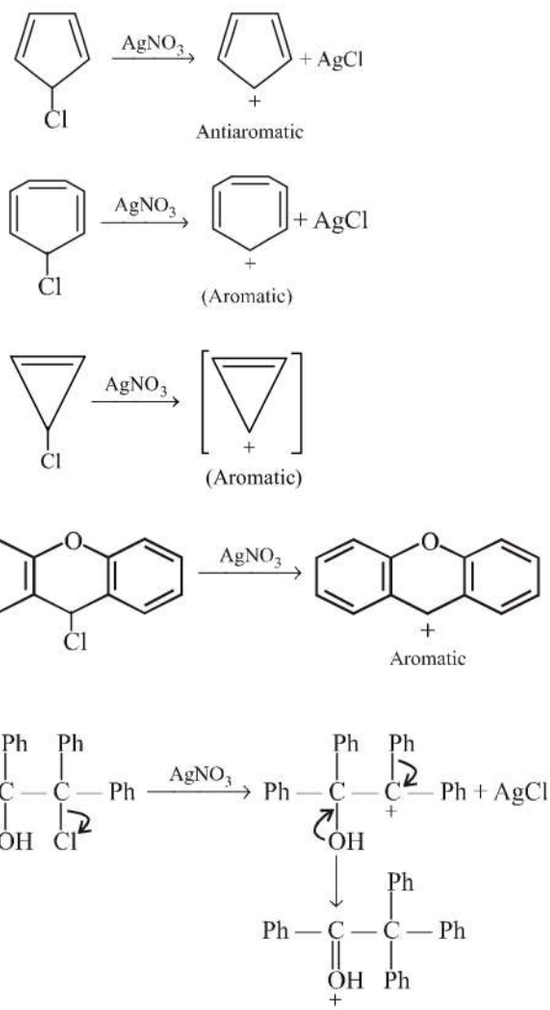
$[Co(NH_3)_4(H_2O)Cl]^{2+}$



3. **(5)** Total no. of alkenes will be = 5



4. **(5)**



5. **(5)** $CH_3-\underset{\text{2-Bromopentane}}{\overset{\overset{Br}{|}}{CH}}-CH_2-CH_2-CH_3 \xrightarrow{KOH\ (aq.)}$

$CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-CH_2-CH_3$

(±) mixture (two products)

$CH_3-\overset{\overset{Br}{|}}{CH}-CH_2-CH_2-CH_3$

2-Bromopentane

$\downarrow KOH\ (alc.)$

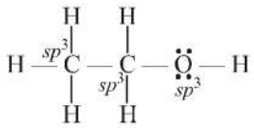
$CH_2=CH-CH_2-CH_2-CH_3 \ +$

$CH_3-CH=CH-CH_2CH_3$ (E & Z)

Hence, 5 products will formed.

6. **(3)** $CH_3-Br \xrightarrow{KCN} \underset{(A)}{CH_3-CN} \xrightarrow{H_3O^+}$

$\underset{(B)}{CH_3-COOH} \xrightarrow{LiAlH_4} \underset{\substack{(C)\\ \text{Ethyl alcohol}}}{CH_3-CH_2-OH}$



7. **(16)** $CH_3CH_2Cl \xrightarrow{NaCN} \underset{(X)}{CH_3CH_2CN} + HCN$

$\downarrow Ni/H_2$

$CH_3COOH + CH_3CH_2CH_2NHCOCH_3 \xleftarrow{(CH_3CO)_2O} \underset{(Y)}{CH_3CH_2CH_2NH_2}$

(Z)

8. **(2)** $C_2H_5I \xrightarrow{alc.\ KOH} CH_2=CH_2 \xrightarrow{Br_2}$

$BrCH_2-CH_2Br \xrightarrow{KCN} CNCH_2.CH_2CN$

9. **(2)** (I) $RX + AgCN \longrightarrow RNC$ (correct)

(II) $RX + KCN \longrightarrow RCN$ (correct)

(III) $RX + KNO_2 \longrightarrow RNO_2$ (wrong)

When haloalkanes is treated with potassium nitrite (KNO_2), alkyl nitrite is formed as major product because since the bond between K–O is ionic in nature, the negative charge on oxygen serves as an attacking site.

$R–X + KNO_2 \longrightarrow RONO + KX$

(IV) $RX + AgNO_2 \longrightarrow RONO$ (wrong)

On treating haloalkanes with silver nitrite (Ag–O–N = O), nitroalkanes is formed because since the bond between Ag–O is covalent, the lone pair on nitrogen acts as an attacking site for nucleophilic substitution.

$RX + AgNO_2 \longrightarrow R–NO_2 + AgX$

10. **(1)** $CH_3CH_2OH \xrightarrow{P+I_2} \underset{(A)}{CH_3CH_2I}$

$\xrightarrow[Ether]{Mg} \underset{(B)}{CH_3CH_2MgI} \xrightarrow{HCHO}$

$H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OMgI \xrightarrow{H_2O} H-\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{H}{|}}{C}}-OH$

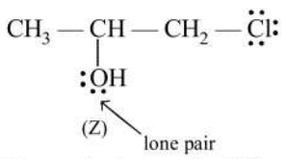
(C) (D)

n–propylalcohol

11. **(5)** $CH_3CH_2CH_2Br \xrightarrow{aq.\ KOH}$

$\underset{(X)}{CH_3CH_2CH_2OH} \xrightarrow[heat]{Al_2O_3}$

$\underset{(Y)}{CH_3CH=CH_2} \xrightarrow{Cl_2/H_2O} \underset{(Z)}{CH_3CHOHCH_2Cl}$



(Z) lone pair

Hence, the lone pair of electron in Z is 5.

12. **(12)** The compound A is a haloalkane which undergoes dehydrohalogenation with alcoholic KOH to form two isomeric alkenes B and C. Since B upon ozonolysis gave only one product, *i.e.*, CH_3CHO, B is expected to be 2-butene ($CH_3CH=CHCH_3$). Since C gave different products on ozonolysis, it must be a position isomer of 2-butene, *i.e.*, 1-butene. The entire sequence of reaction is as follows:

$CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_3 \xrightarrow{alc.\ KOH}$

2–Bromobutane(A)

$\underset{\text{2- Butene (B)}}{CH_3CH=CHCH_3} + \underset{\text{1- Butene (C)}}{CH_3CH_2CH=CH_2}$

$\downarrow$ Ozonolysis $\qquad\qquad \downarrow$ Ozonolysis

$\underset{\text{(1 product)}}{2CH_3CHO} \qquad \underset{\text{(2 products)}}{CH_3CH_2CHO + HCHO}$

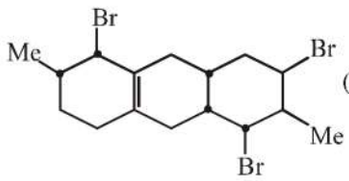
Thus, compound A, B & C contains total 12 carbon atoms.

13. (3)

(I) Loss of Br (a) would give less-substituted alkene (more reactive, less stable).

(II) Removal of Br (c) would give more stable 2° allylic C^+.

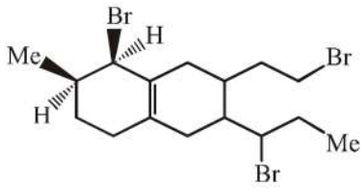
(III)



(•) Marked are positive asymmetric C atoms

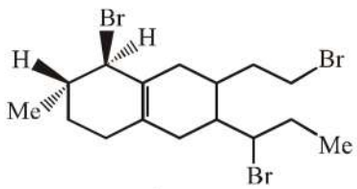
Statements (a), (b), and (c) are correct.

(IV) Statement (d) is wrong, since the compound shows geometrical isomerism.



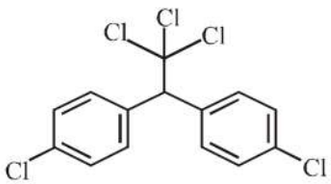
cis

and



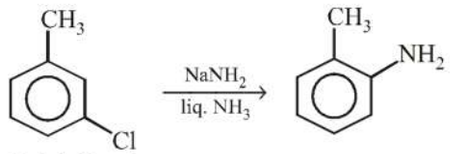
trans

14. (3)



The chlorine atoms which is not directly attached to the ring, will be more reactive.

15. (3)



3–Methyl chloro-benzene