Fill Ups & True False of Haloalkanes & Haloarenes

Fill in the Blanks

1. The halogen which is most reactive in the halogenation of alkanes under sunlight is................. . (Chlorine, bromine, iodine) (1981 - 1 Mark)

Ans: chlorine

Solution: Chlorine; because rate of formation of $^{\bullet}CH_3$ (one of the propagating steps) is high when $X^{\bullet}$ is Cl.

$CH_4 + X^{\bullet} \rightarrow {}^{\bullet}CH_3 + H - X$

2. The compound prepared by the action of magnesium on dry ethyl bromide in ether is known as .... reagent. (1982 - 1 Mark)

Ans: Grignard

Solution : Grignard (RMgX)

3. The interaction of elemental sulphur with Grignard reagent gives .... (1991 - 1 Mark)

Ans: Thioalcohol

Solution : Thioalcohol

4. Vinyl chloride on reaction with dimethyl copper gives .... (1997 - 1 Mark)

Ans : polyvinyl chloride

Solution : polyvinyl chloride

True/False

1. m-Chlorobromobenzene is an isomer of m-bromochlorobenzene. (1985 - ½ Mark)

Ans: False

Solution : False : m-Chlorobromobenzene and m-bromochlorobenzene is one and the same compound.

2. The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markovnikov's rule. (1989 - 2 Marks)

Ans: False

Solution :

$$\underset{\text{vinyl chloride}}{CH_2=CHCl+HI} \rightarrow \underset{\text{1- chloro-1-iodoethane}}{CH_3CHCl(I)}$$

This is an example of Markownikoff's rule as I^- is added at the C with less number. of H-atoms.

NOTE : anti-Markonikov's rule is applicable only to HBr, but not to HI and HCl.

Integer Type ques of Haloalkanes & Haloarenes

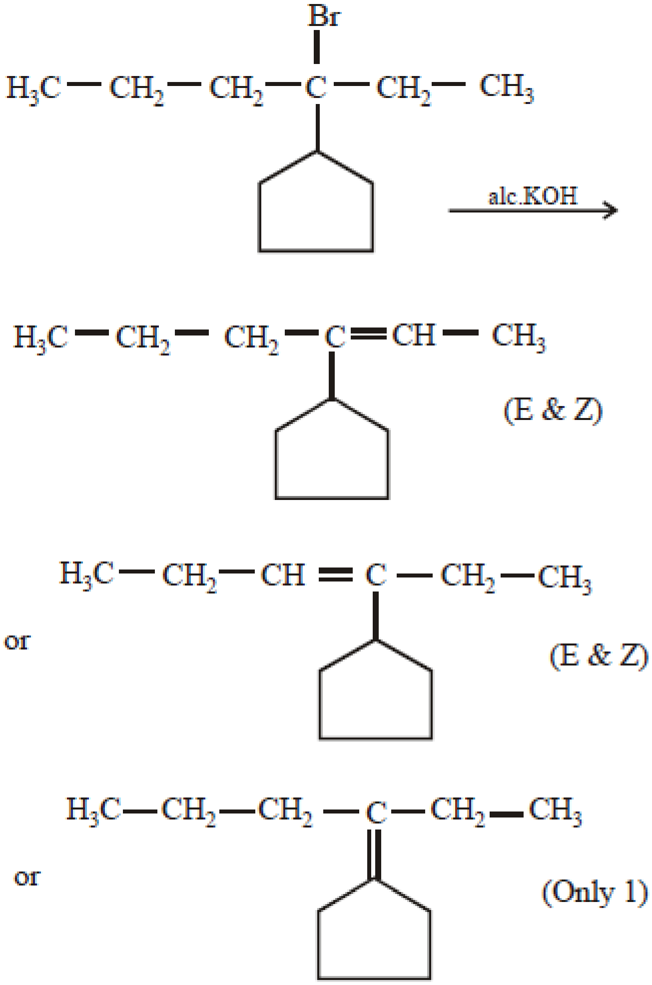
Integer Value Correct Type

1. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is (2011)

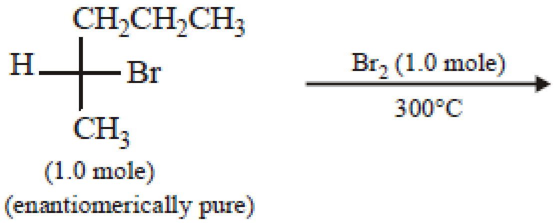
Ans: 5

Solution :

Total no. of alkenes will be = 5

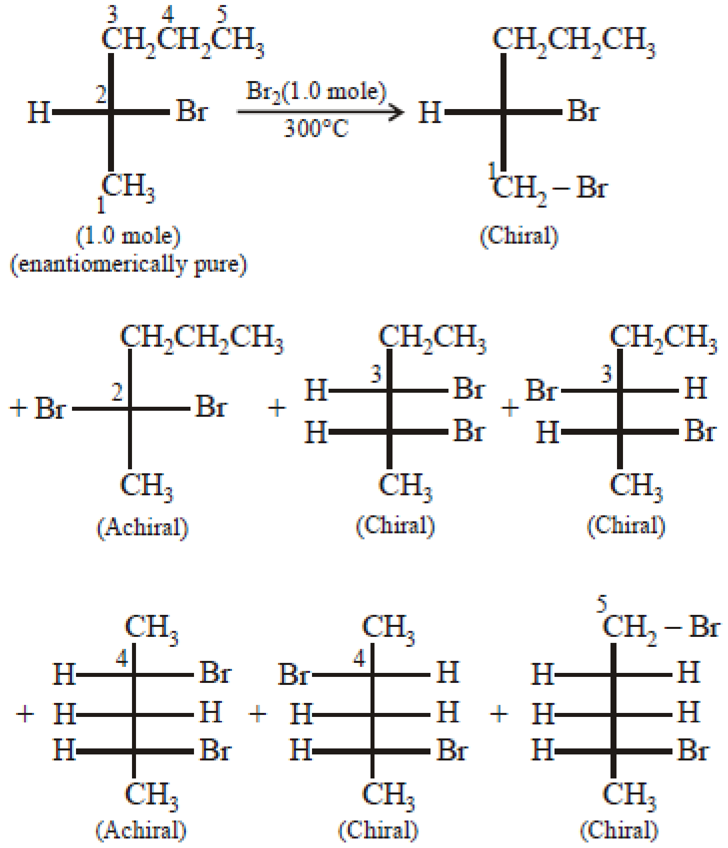


2. In the following monobromination reaction, the number of possible chiral products is (JEE Adv. 2016)



Ans: 5

Solution :



Subjective questions of Haloalkanes & Haloarenes

1. (a) Show by chemical equations only, how you would prepare the following from the indicated starting materials. Specify the reagents in each step of the synthesis.

(i) Hexachlorethane, C_2Cl_6, from calcium carbide.

(ii) Chloroform from carbon disulphide.

(b) Give one chemical test which would distinguish between C_2H_5OH from $CHCl_3$. (1979)

Solution :

(a)

(i) $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

$$C_2H_2 \xrightarrow{H_2/Ni} C_2H_6 \xrightarrow[UV]{Cl_2(excess)} CCl_3-CCl_3$$

(ii) $CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$

$$CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S$$

$$CCl_4 + 2[H] \xrightarrow{Fe/H_2O} CHCl_3 + HCl$$

(b) Carbylamines test.

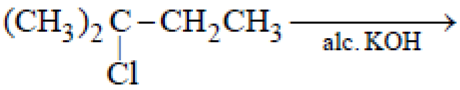
$CHCl_3$ + aq KOH + aniline (i.e. primary amine) → bad smelling isocyanides

C_2H_5OH + aq KOH + aniline → No reaction

2. Write the structural formula of the major product in each of the following cases:

(i) chloroform reacts with aniline in the presence of excess alkali (1981 - ½ Mark)

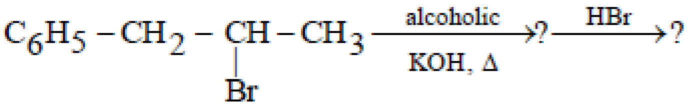
(ii) bromoethane reacts with one-half of the molar quantity of silver carbonate. (1981 - ½ Mark)

(iii) 

$$(CH_3)_2\underset{\underset{Cl}{|}}{C}-CH_2CH_3 \xrightarrow[alc.\,KOH]{}$$

(*iv*) $CH_3CH_2CHCl_2 \xrightarrow[\text{alkali}]{\text{boil}}$ *(1992 - 1 Mark)*

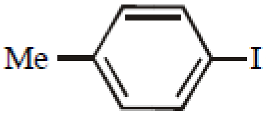
(*v*)



$C_6H_5-CH_2-\underset{\underset{\text{Br}}{|}}{CH}-CH_3 \xrightarrow[\text{KOH, }\Delta]{\text{alcoholic}} ? \xrightarrow{\text{HBr}} ?$

(1993 - 1 Mark)

(*vi*)

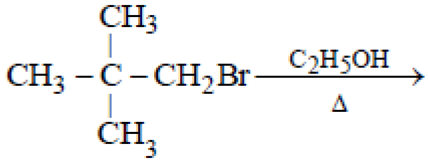


$+ \text{Cu} + \text{heat} \longrightarrow$ - - - - -

(1997 - 1 Mark)

(*vii*) $C_6H_5CH_2CHClC_6H_5 \xrightarrow[\text{heat}]{\text{alcoholic KOH}}$ 2 Products *(1998 - 2 Marks)*

(*viii*)



$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2Br \xrightarrow[\Delta]{C_2H_5OH}$

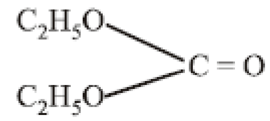
(2000 - 1 Mark)

Solution :

(*i*) $C_6H_5NH_2 + CHCl_3 \xrightarrow[\text{KOH}]{\text{alkali}} C_6H_5-N \overset{\rightarrow}{=} C$

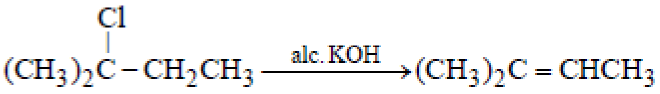
Phenyl isocyanide

(*ii*)



Diethyl carbonate

(*iii*)

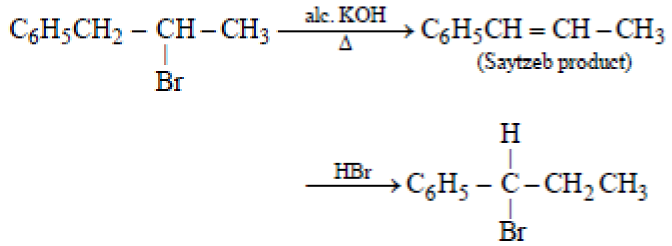


$(CH_3)_2\overset{\overset{Cl}{|}}{C}-CH_2CH_3 \xrightarrow{\text{alc. KOH}} (CH_3)_2C=CHCH_3$

(*iv*) $CH_3CH_2CHCl_2 \xrightarrow[\text{alkali}]{\text{boil}} CH_3CH_2CH(OH)_2$

$\xrightarrow[(-H_2O)]{} CH_3CH_2CHO$

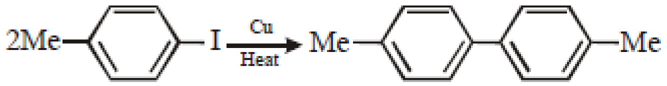
(v)



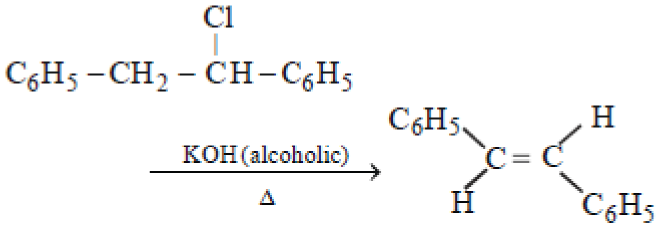
$$C_6H_5CH_2-\underset{\displaystyle Br}{\underset{|}{C}}H-CH_3 \xrightarrow[\Delta]{\text{alc. KOH}} \underset{\text{(Saytzeb product)}}{C_6H_5CH=CH-CH_3} \xrightarrow{HBr} C_6H_5-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}-CH_2CH_3$$

[NOTE : $C_6H_5CH_2\overset{+}{C}HCH_3$ and $C_6H_5\overset{+}{C}HCH_2CH_3$ carbocations are formed on addition of HBr on $C_6H_5CH=CHCH_3$, the latter being benzylic carbocation, is stabilised due to resonance and hence Br^- adds on it forming $C_6H_5CHBr.CH_2CH_3$ as the final product.]

(vi)



(vii)

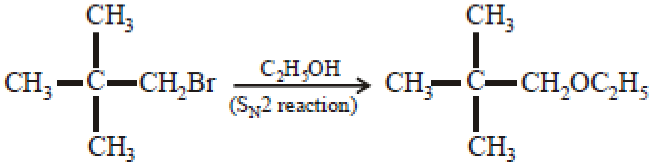


$$C_6H_5-CH_2-\overset{\displaystyle Cl}{\overset{|}{C}}H-C_6H_5 \xrightarrow[\Delta]{\text{KOH (alcoholic)}}$$

cis and *trans* - Stilbene

(*trans* is major)

(viii)



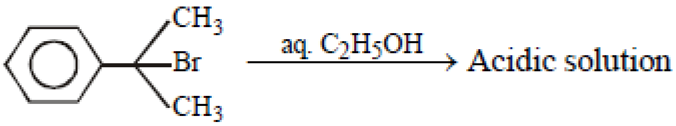
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2Br \xrightarrow[(S_N2\text{ reaction})]{C_2H_5OH} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2OC_2H_5$$

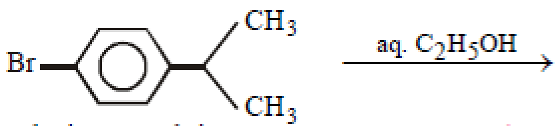
3. Give reasons for the following :

(i) 7-Bromo-1, 3, 5-cycloheptatriene exists as ionic compound, while 5-bromo-1, 3-cyclopentadiene does not ionise even in presence of Ag+ ion. Explain.

(2004 - 2 Marks)

(ii)





Neutral solution.

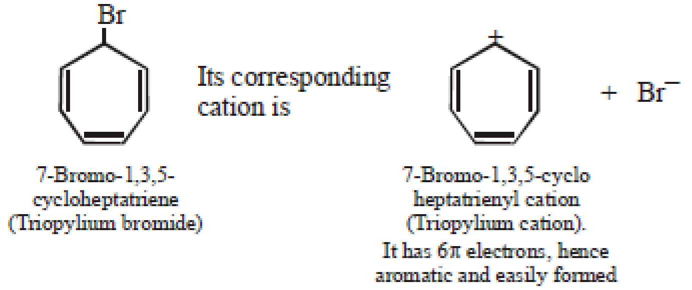
Explain. **(2005 - 1 Mark)**

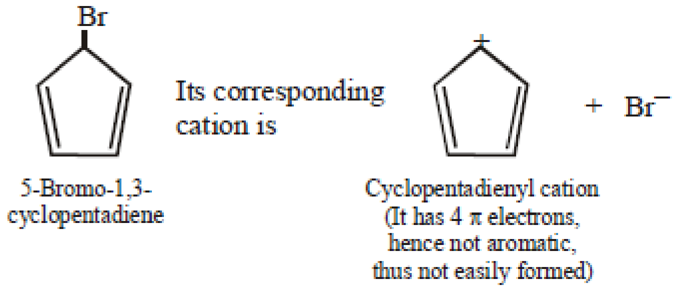
Solution:

(i) TIPS/Formulae:

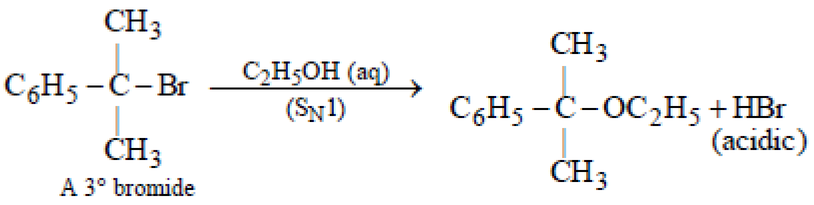
7-Bromo-1,3,5-cycloheptatriene is aromatic whereas

5-Bromo-1,3-Cycloheptadiene is non aromatic.



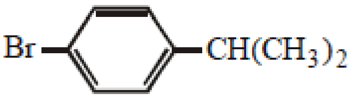


(ii) **NOTE** : The former halide is a 3° halide, hence it undergoes S_N1 reaction forming HBr, as one of the products, which make solution acidic



$$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow[(S_N1)]{C_2H_5OH\,(aq)} C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-OC_2H_5+\underset{(acidic)}{HBr}$$

A 3° bromide



is an aryl halide so it does not undergo nucleophilic substitution reactions. Hence the solution will remain neutral.

4. State the conditions under which the following preparation are carried out. Give the necessary equations which need not be balanced :

(i) Lead tetraethyl from sodium-lead alloy (1983 - 1 Mark)

(ii) Methyl chloride from aluminium carbide (1983 - 1 Mark)

solution :

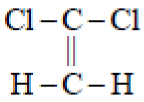
(i) $4C_2H_5Br + 4(Na\text{–}Pb) \xrightarrow{\text{dry ether}} Pb(C_2H_5)_4 + 4NaBr + 3Pb$

(ii) $Al_4C_3 \xrightarrow{H_2O} CH_4 \xrightarrow[\text{sun light}]{Cl_2} CH_3Cl$

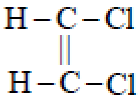
5. Write the structure of all the possible isomers of dichloromethane. Which of them will have zero dipole moment? (1985 - 2 Marks)

Solution :

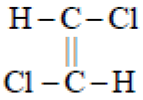
Dichloroethene exists in three isomeric forms.



1, 1–dichloroethene

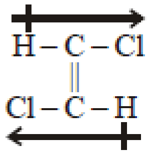


(*cis*)–1, 2–dichloroethene



(*trans*)–1, 2–dichloroethene

trans-1, 2-Dichloroethene has zero dipole moment.



6. What happens when excess chlorine is passed through boiling toluene in the presence of sunlight?(1987 - 1 Mark)

Solution :

$$C_6H_5CH_3 \xrightarrow[\text{UV Light}]{Cl_2} C_6H_5CH_2Cl \xrightarrow{Cl_2} C_6H_5CHCl_2 \xrightarrow{Cl_2} \underset{\text{Benzotrichloride}}{C_6H_5CCl_3}$$

NOTE : This follows free radical mechanism.]

7. What effect should the following resonance of vinyl chloride have on its dipole moment? (1987 - 1 Mark)

$$CH_2=CH-Cl \longleftrightarrow \overset{-}{C}H_2-CH_2=Cl^{+}$$

Solution :

TIPS/Formulae : Resonance decreases the dipole moment of vinyl chloride ($CH_2 = CHCl$). The positive charge on Cl and a negative charge on C (developed by resonance) oppose each other and hence diminish the electronegativity of Cl and thus polarity (and dipole moment) of the bond. The dipole moments of vinyl chloride and chlorobenzene are 1.4D and 1.7D respectively, while the dipole moment of alkyl halides is 2–2.2D.

8. An organic compound X, on analysis gives 24.24 per cent carbon and 4.04 per cent hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound X may be represented by two isomeric structures, Y and Z. Y on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound while Z on similar treatment gives ethanal. Find out the molecular formula of X and give the structures of Y and Z. (1989 - 4 Marks)

Solution :

$$\%\text{ of Cl in X} = \frac{35.5 \times 2.9}{143.5} \times 100 = 71.72\%$$

Empirical formula of (X)

Element	%	Relative no. of atoms	Simplest ratio
C	24.24	2.02	1
H	4.04	4.04	2
Cl	71.72	2.02	1

∴ Empirical formula of (X) is CH_2Cl

Since X has two isomers Y and Z; both react with KOH(aq).

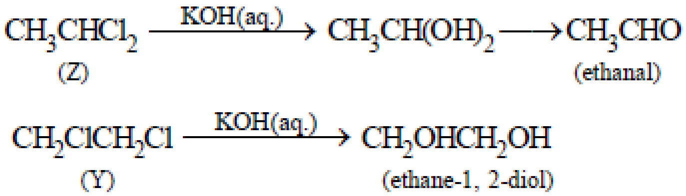
Y $\xrightarrow{\text{KOH(aq.)}}$ dihydroxy compound i.e. 2Cl atoms on adjacent carbon

Z $\xrightarrow{\text{KOH(aq.)}}$ CH_3CHO i.e. Z should have 2Cl atoms on one C atom

Thus Z should be CH_3CHCl_2 (1, 1-dichlorethane) and

Y should CH_2ClCH_2Cl (1, 2-dichloroethane)

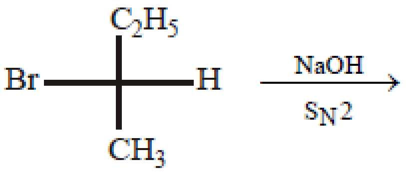
Reactions :



$$\underset{(Z)}{CH_3CHCl_2} \xrightarrow{\text{KOH(aq.)}} CH_3CH(OH)_2 \longrightarrow \underset{\text{(ethanal)}}{CH_3CHO}$$

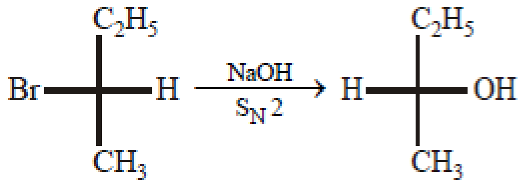
$$\underset{(Y)}{CH_2ClCH_2Cl} \xrightarrow{\text{KOH(aq.)}} \underset{\text{(ethane-1, 2-diol)}}{CH_2OHCH_2OH}$$

9. Draw the stereochemical structures of the products in the following reaction : (1994 - 4 Marks)



Solution:

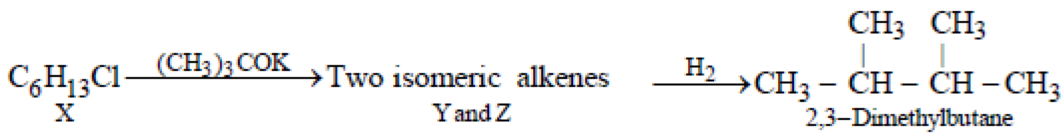
S_N2 reaction leads to inversion in configuration



10. An alkyl halide, X, of formula $C_6H_{13}Cl$ on treatment with potassium tertiary but oxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structures of X, Y and Z. (1996 - 3 Marks)

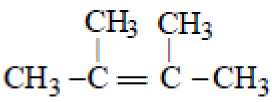
Solution :

Summary of the given facts

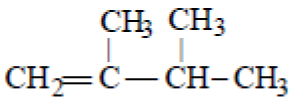


$$\underset{X}{C_6H_{13}Cl} \xrightarrow{(CH_3)_3COK} \underset{Y \text{ and } Z}{\text{Two isomeric alkenes}} \xrightarrow{H_2} \underset{2,3\text{–Dimethylbutane}}{CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{CH_3}{\overset{|}{C}H}-CH_3}$$

The two isomeric precursors of (Y and Z) of 2, 3-dimethylbutane

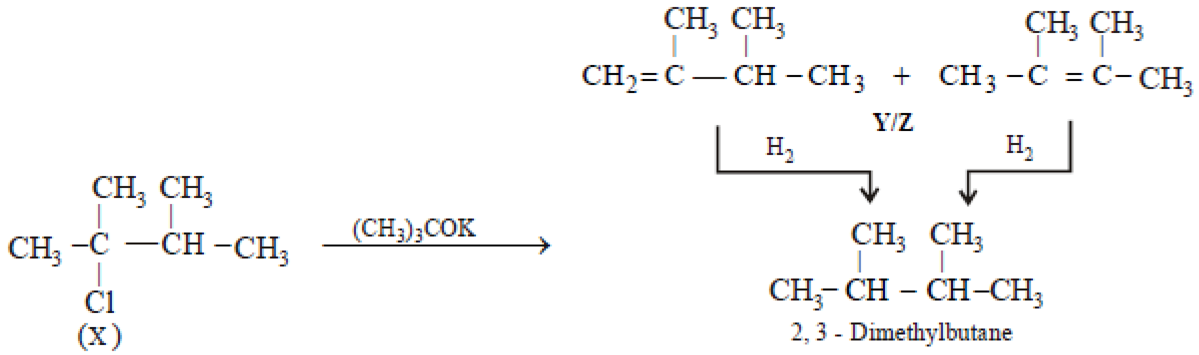


$$CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3$$



$$CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{C}H}-CH_3$$

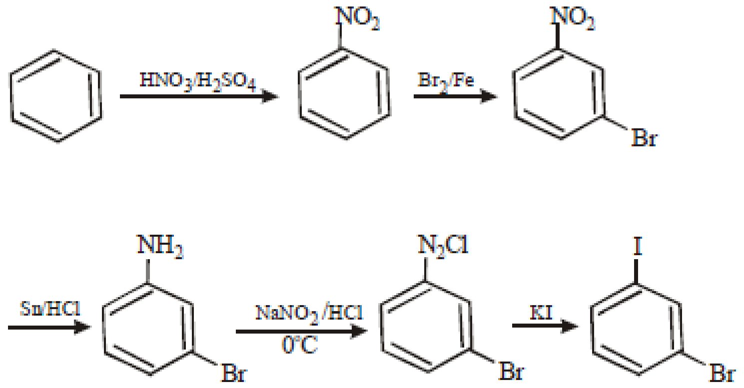
Hence the precursor of Y & Z should have following structure which explains all the given facts



$$\underset{(X)}{CH_3-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{CH_3}{\overset{|}{C}H}-CH_3} \xrightarrow{(CH_3)_3COK} \underset{Y/Z}{CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{C}H}-CH_3 + CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3} \xrightarrow{H_2} \underset{2,3\text{ - Dimethylbutane}}{CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{CH_3}{\overset{|}{C}H}-CH_3}$$

11. How will you prepare m-bromoiodobenzene from benzene (in not more than 5-7 steps)? (1996 - 2 Marks)

Solution :



12. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic (A). The organometallic reacts with ethanal to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1–bromo–1–methylcyclopentane (C). Write the structures of (A), (B) and explain how (C) is obtained from (B). (2001 - 5 Marks)

Solution :