05 DEC 2015

-: AlKyL and ARyL Halides :-

Alkyl Halide ⇒ (R-X)
(Halo alKane)

When one or more then hydrogen atom or an alkane are replaced by halozen atom/s, formation of halo-alkane will take place.

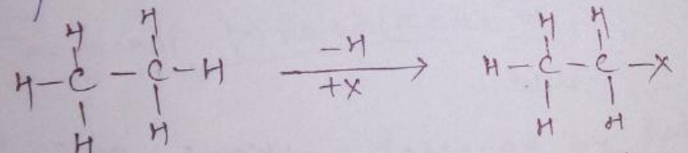
Ex-

$$\underset{\text{alKane}}{R-H} \xrightarrow[+X]{-H} \underset{\text{(halo-alkane)}}{R-X}$$

$(X = F, Cl, Br, I)$

Types of Halo-alKane/s :-

i) Mono haloalKanes ⇒ When one ~~hat~~ H- of alkane is replaced by one halozen atom. ~~of~~ Mono haloalKane will form.



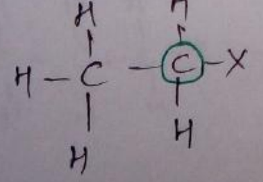
$$H_3C-CH_3 \xrightarrow[+X]{-H} H_3C-CH_2-X$$

(Mono haloalKane)

Mono haloalKane/s a for the classifyed -

i) Prymery mono haloalKane - (1°)-HaloalKane)

if halozen joining Carbon Directally attach with one -C Known as 1°- halo alKane :-

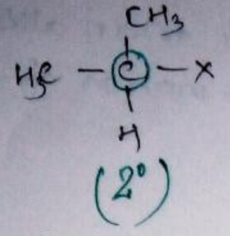


$$H_3C-CH_2-X$$

(1°)

Secondary Halo alkane (2°- Mono Haloalkane)

If halozen Cantaining Carbon directally joined with two alkyl group, Known as secondary haloalkane.

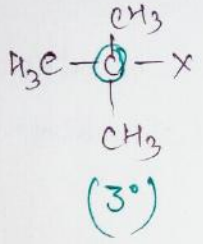


$H_3C-\overset{CH_3}{\underset{H}{C}}-X$

(2°)

Tertiary Mono Halo.alkane (3°- mono haloalkane)

When helozen Containing Carbon directally Connect with 3-C. Known as 3° Haloalkane-

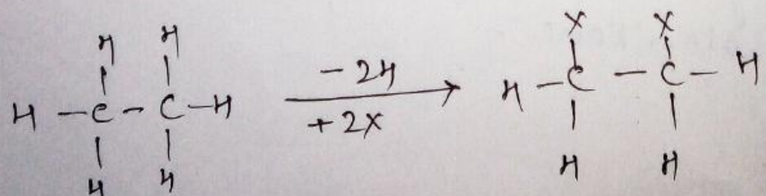


$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-X$

(3°)

Di-Halo alkane ⇒

When Two H-atom of alkane are replaced by 2-Helozen atom, formation of Di heloalkane will take place.

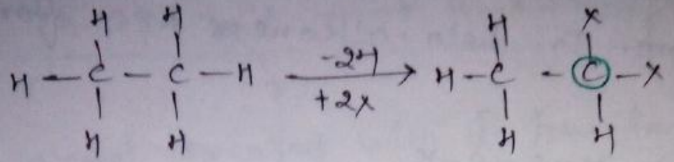


$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H \xrightarrow[+2X]{-2H} H-\overset{X}{\underset{H}{C}}-\overset{X}{\underset{H}{C}}-H$

There are following types of Di helo.alkane —

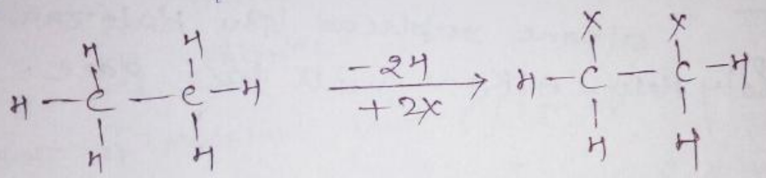
1- Geminal Diheloalkane ⇒

When - 2 -H atom af same - Carbon - are replaced by 2 - Halozen atom - Geminal Di halide form.



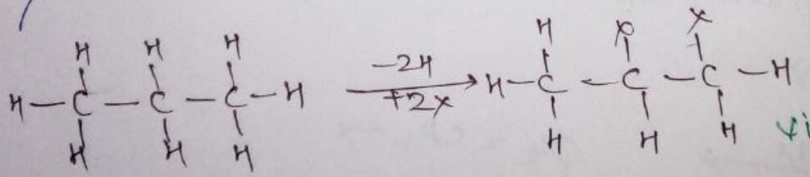
2- vicinal Di halide ⇒

When 2 - H - atom af different carbom, replaced by 2 - Helozen atom - Known as Vicinal Di halide

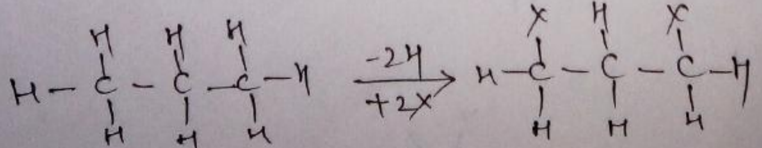


Terminal Di haloalkane ⇒

When 2 - H - atom af end - C af an alkane - Replaced by halozen atom. Known as Terminal di haloalkane



vicinal Di haloalkane

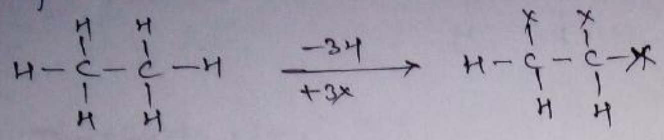


Terminal Di haloalkane

Note All terminal Di-halide's are vicinal while all vicinal Di-halide's can't be terminal.

Try Halo·Alkane →

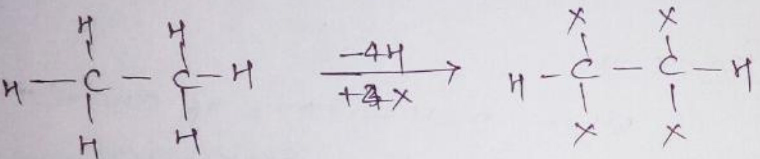
when 3-H-atom af Alkane replaced By 3-Halozan atom. Tri halo-alkane's are formed.



Ex- chloroform.

Poly Halo·alkane ⇒

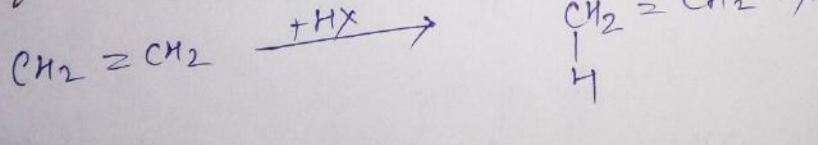
when more then 3-H atom af alkane replaced By Halozan ato formation af Poly Halo-Alkane will take place.



Ex- CCl_4

Methods of Prepration af Halo alkane ⇒

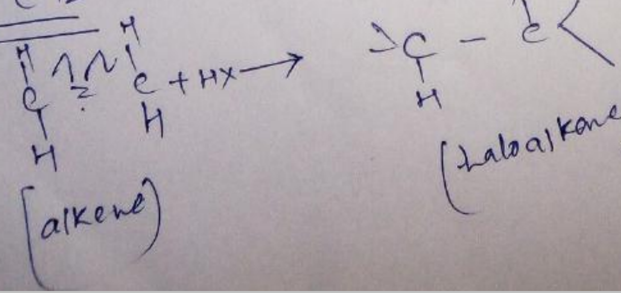
1→ from-Alkene →



$$CH_2 = CH_2 \xrightarrow{+HX} \underset{H}{\underset{|}{CH_2}} = CH_2 - X$$

$CH_2 = CH_2$

STEP-1



From -OH ⇒

$$>C=C< \xrightarrow{-OH} >\underset{H}{C}-\overset{OH}{C}<$$

STEP-1

(Ex→) $CH_3-CH_2-OH + HX \longrightarrow H_3C-CH_2-X + H_2O$

$$\boxed{R-OH + HX \longrightarrow R-X + H_2O}$$

when alcohol treated with HX the formation of Haloalkan will take place.

3

When Alcohol treated with $SOCl_2$:-

$$R-OH + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow R-Cl + HCl\uparrow + SO_2\uparrow$$

Rxn of Alcohol with PCl_5 ⇒

$$R-OH + PCl_5 \longrightarrow R-Cl + PCl + POCl_3 + HCl\uparrow$$

Rxn of Alcohol with PCl_3 →

$$3R-OH + PCl_3 \longrightarrow 3R-Cl + H_3PO_3$$

Physical Properties →

BP → The BP. of heloalkene increas with increase the molecular weight.

[BP $\propto$ molecular weight].

For Isomeric helo alkan BP $\propto \frac{1}{Branch}$.

Solubility :-

1) heloalkanes are less soluble in water becoz the Possibility of H-Bonding not takes place.

Chemical Properties ⇒

Helo alkanes show following type of chemical properties -

i) Neocuphilic Substitution Rxn

ii) Rxn with metal.

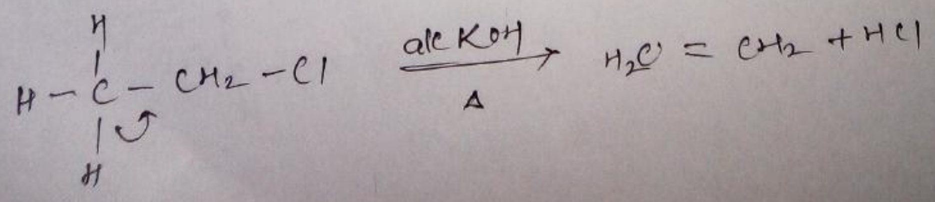
3) Readuction.

4) elimenation Rxn.

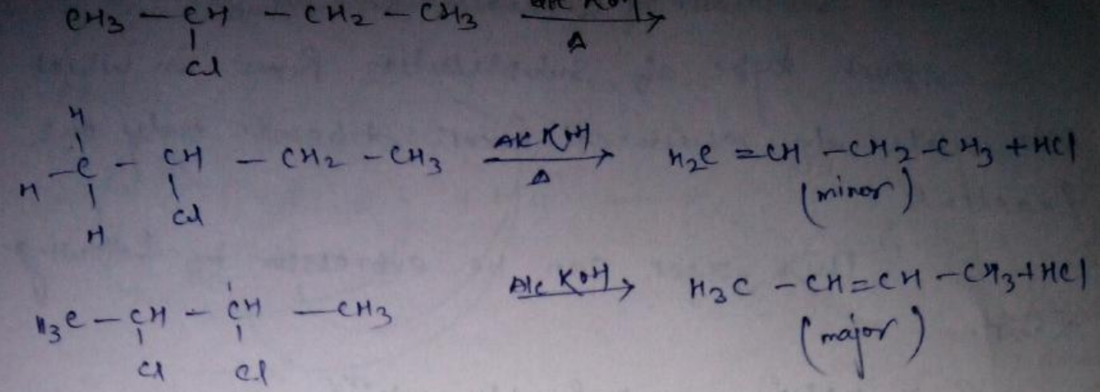
i) Elemination Rxn →

Such type of chemical Rxn in which sum atom remove from the reactant Know as elimination Rxn -

The most important elimination Rxn when helo alkane be heated ~~with~~ in the presence of Alc - KOH -



$$H-\underset{H}{\overset{H}{C}}-CH_2-Cl \xrightarrow[\Delta]{alc\,KOH} H_2C = CH_2 + HCl$$



$$CH_3-\underset{Cl}{CH}-CH_2-CH_3 \xrightarrow[\Delta]{alc\ KOH}$$

$$H-\underset{H}{\overset{H}{C}}-\underset{Cl}{CH}-CH_2-CH_3 \xrightarrow[\Delta]{Alc\ KOH} H_2C=CH-CH_2-CH_3+HCl \ (minor)$$

$$H_3C-\underset{Cl}{CH}-\underset{Cl}{CH}-CH_3 \xrightarrow{Alc\ KOH} H_3C-CH=CH-CH_3+HCl \ (major)$$

Rxn with Metal ⇒

i) wurtz Rxn

ii) Coerey House Rxn-

#iii) Formation of Grignard Reagent ⇒

$$R-X+Mg \xrightarrow{dry\ ether} R-MgX$$

$(X=Cl, Br, I)$ (grignared reagent)

Readuction of Alkyl Hedide Rxn ⇒

$$R-X+2[H] \xrightarrow[\substack{(i)\ LiAlH_4 \\ (ii)\ Na+C_2H_5OH \\ (iii)\ HI\ /\ Red\ P}]{} R-H+HX$$

Imp

$Nu^\ominus$ Substitution Rxn ⇒

x

when the $X^\ominus$ ($Nu^\ominus$) of haloalKane is replaced by another $Nu^\ominus$, Known as substitution Rxn.

On the Basis of Rate of Rxn there are two type's of $Nu^\ominus$ Substitution Rxn-

i) S_N1 ($Nu^{\ominus}$ Substitution unimolecular Rxn) –

Such type of Substitution Rxn in which the rate of chemical Rxn dipends only one Reactent.

This rxn can be expression by following Rxn.

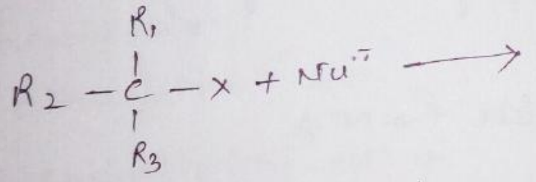
$$R-X + Nu^{-} \longrightarrow R-Nu + X^{-}$$

rate $\propto [R-X]$

This Rxn goes through following mechenism.

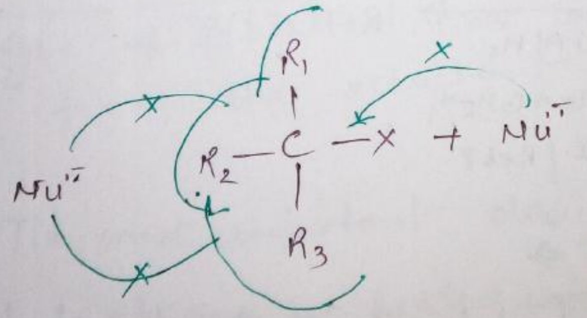
$$R-X + Nu^{-} \longrightarrow R-Nu + X^{-}$$

rate $\propto [R-X]$

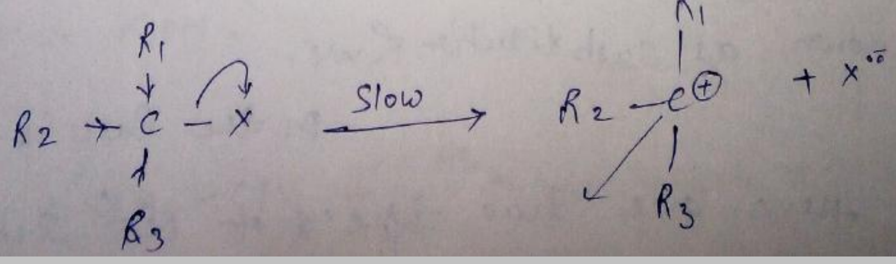


$$R_2-\overset{R_1}{\underset{R_3}{C}}-X + Nu^{-} \longrightarrow$$

STEP-1

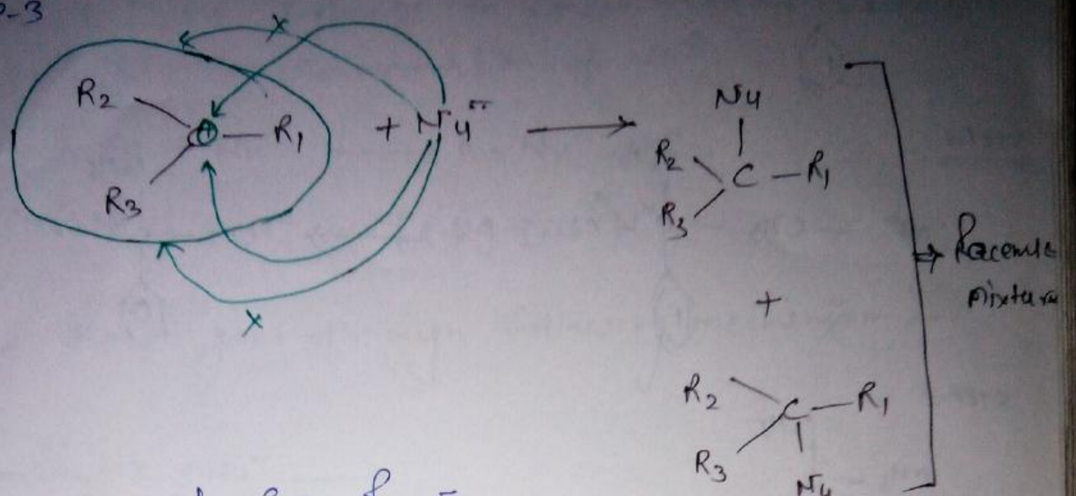


So –



STEP-2 Carbocation rearrangement -

STEP-3

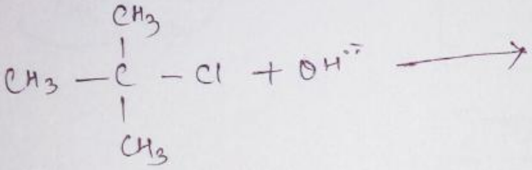


The order of S_N1 Rxn

will be 3° Heloalkane, 2° > 1° > CH_3-X.

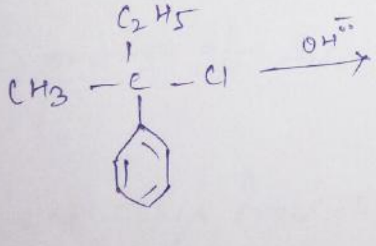
Question

i)



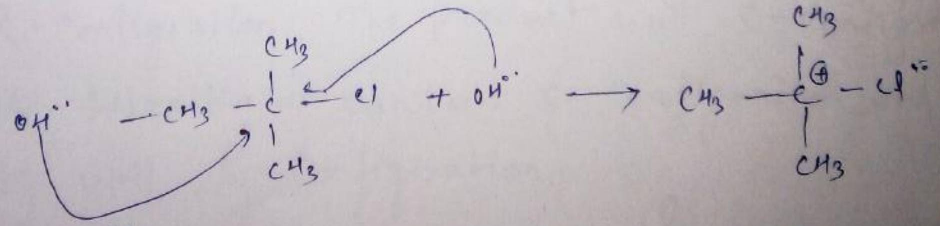
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl + \ddot{O}H^- \longrightarrow$

ii)



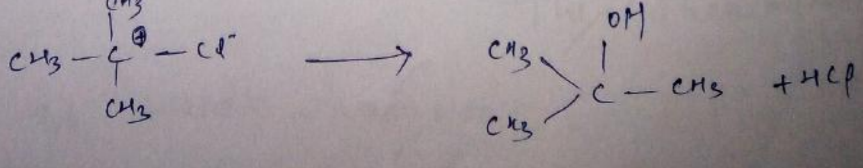
i)

STEP-I



$\ddot{O}H^- \quad -CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl + \ddot{O}H^- \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{C}}}-\ddot{Cl}^-$

STEP-2.



$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{C}}}-Cl^- \longrightarrow (CH_3)_2\overset{OH}{C}-CH_3 + HCl$

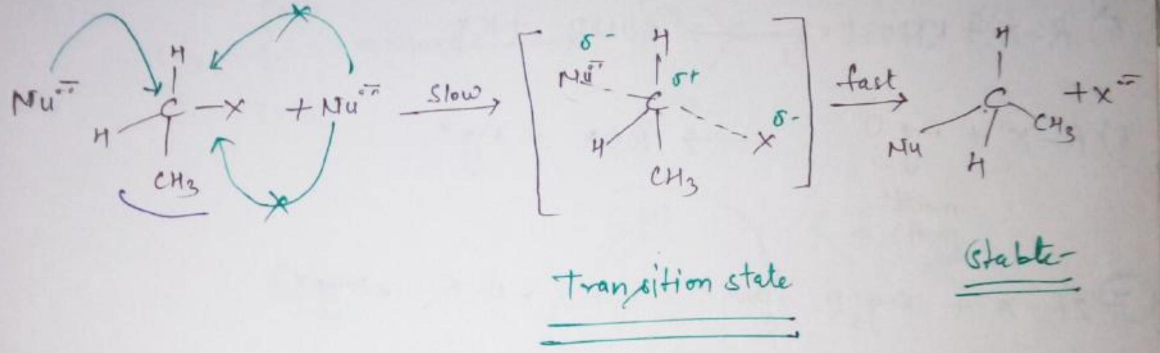
S_{N_2} ⇒ such type of $Nu^\ominus$ substitution Rxn in which the Rate of Rxn Depents on Consentration of heloalKane as well as the consentration of $Nu^\ominus$.

$$R-X + Nu^{\cdot\cdot} \longrightarrow R-Nu^{\cdot\cdot} + X^{\cdot\cdot}$$

$$\text{Rate of rxn} \propto [R-X]\,[Nu^{\cdot\cdot}]$$

This rxn goes through following mechenism –

$$CH_3-\overset{\delta+}{CH_2}-X + Nu^{\cdot\cdot} \longrightarrow$$



* The order of S_{N_2} Rxn given by heloalKane will be.

NOTE - IN This Process if heloalkane are Cantain ~~are~~ R-Configration, The product will S-Configration and if heloalkane cantain S- Configration the Product will R. Configration. This Phenominun as Known as walden inversion.

[3° — S_{N_1} 2° - S_{N_1} or S_{N_2} all of these]
1° — S_{N_2}

$1^\circ - S_N2$	$2^\circ \rightarrow S_N1$ or S_N2	$3^\circ - S_N1$	is given by.

* The most important substitution Rxnr ARE ⇒

i) $R-X \cdot \xrightarrow[(aq)]{KOH} R-OH - KX$

2) $R-X + KCN \xrightarrow{C_2H_5OH} R-CN + KX$

3) $R-X + AgCN \longrightarrow RNC + Ag.X$

4) $R-X + AgNO_2 \longrightarrow R-NO_2 + AgX$

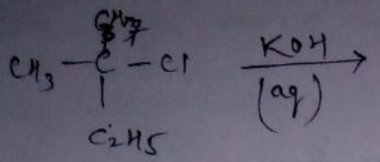
5) $R-X + KNO_2 \longrightarrow RONO + KX$

6) $R-X + Ag_2O \longrightarrow ROH + AgX$

moist
(नमी)

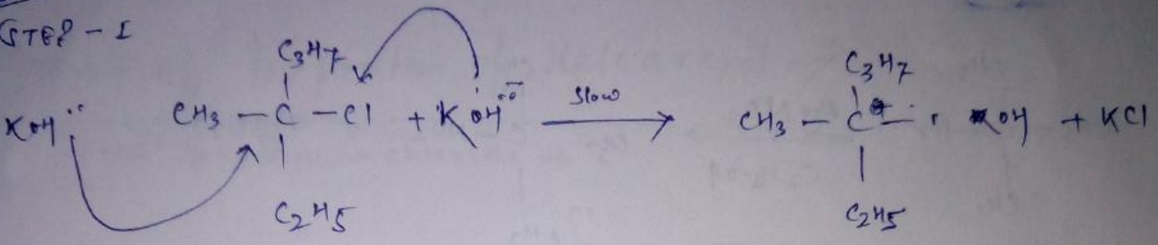
⑦ $2R-X + Ag_2O$ (dry) $\longrightarrow R-O-R + 2AgX$

Solve this Rxn with mechanism:→

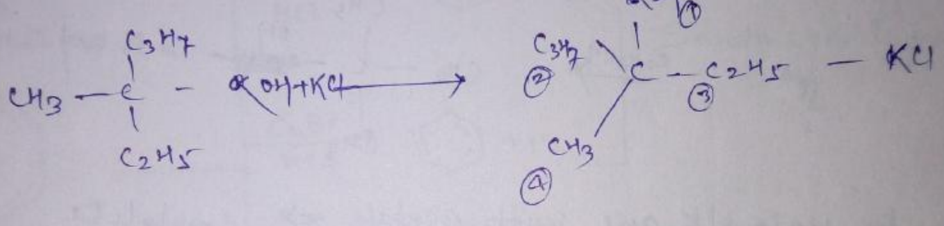


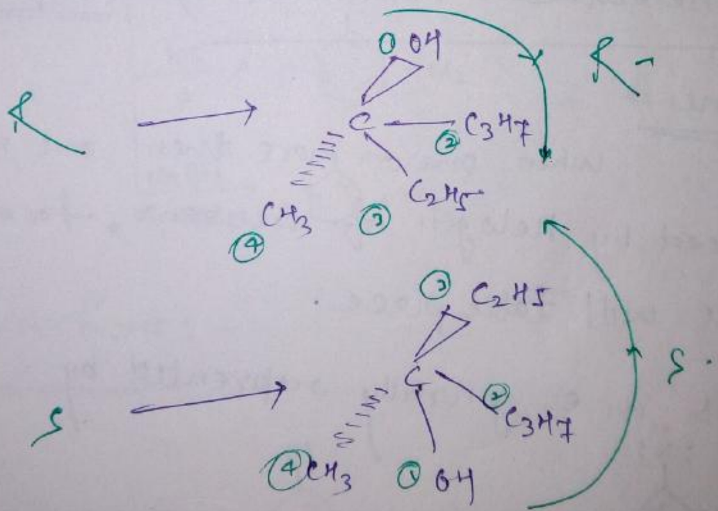
solve

STEP - I



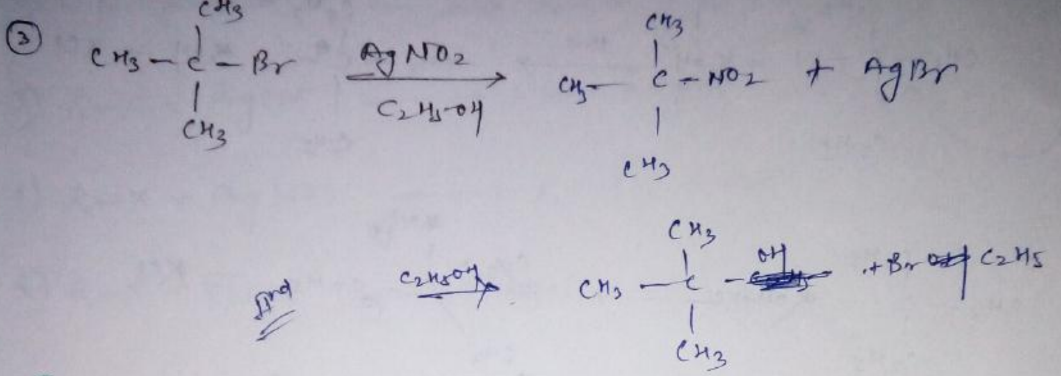
STEP-2





① $CH_3-Br \xrightarrow[alc]{KCN} CH_3-CN + KBr$

② $CH_3-CH_2-Br \xrightarrow[moist]{Ag_2O} CH_3-CH_2-OH + AgBr$

③ 

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br \xrightarrow[C_2H_5-OH]{AgNO_2} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-NO_2 + AgBr$

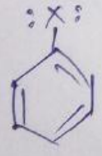
IIIrd $\xrightarrow{C_2H_5OH} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + Br \quad C_2H_5$

Rear of Heloalkane with metal → complete

Helo Arenes ⇒

when one or more then one Hydrogen are replaced by Helogen of Benzene, formation of Heloarenes will take place.

Heloarenes are genrally reprented by.



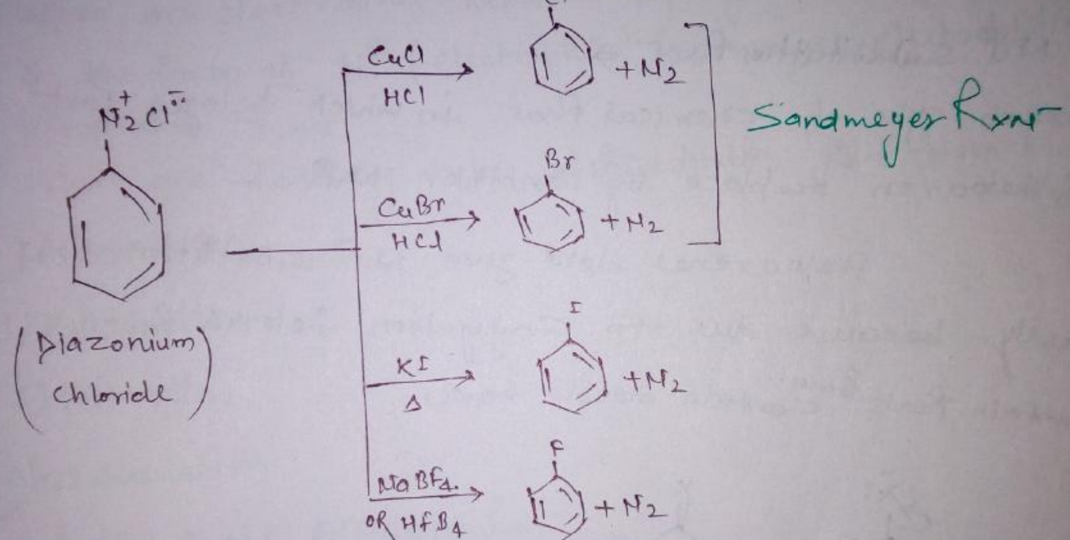
when helogen present in Benzene Ring Know as mono heloarenes. when two helozen is present in Benzene ring Konow as dihelo arenes.

When 3- Helozen present in Benzene ring Known try ring. more then 3-Helogen present known as Poly heloarenes.

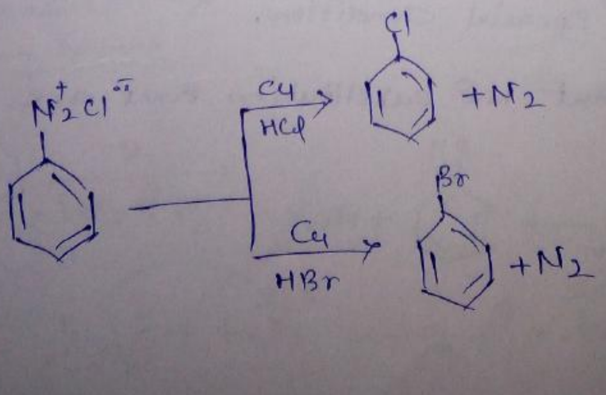
Here X - will F, Cl, Br, I.

Method of Prepration of Heloarenes →

i) from Diazonium chloride ⇒



Gattermann Rxn :-



Chemical Properties ⇒

ChlroBenzene and BromoBenzene give following Types of chemical properties —

1) $Nu^\ominus$ Substitution Rxn

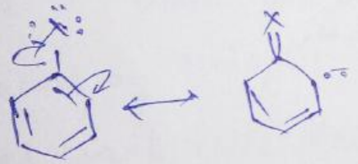
2) Electrophilic Substitution Rxn

3) Rxn with metal

(1) $Nu^\ominus$ Substitution Rxn ⇒

Such Type of chemical Rxn in which helogen Part of hetoaren replace by another $Nu^\ominus$.

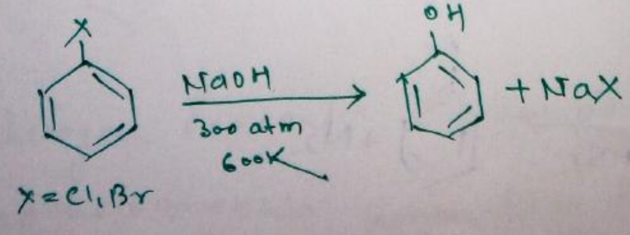
Heloarenes dont give $Nu^\ominus$ substitution rxn easily. because due to Conjugation helozen Part Cantain Part Partial Cantain double Bond.



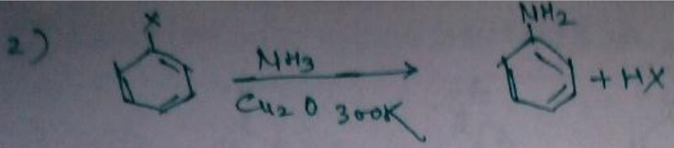
There for the $Nu^\ominus$ Substitution Rxn of heloarenes carry out by help of Special Condition.

Some most important $Nu^\ominus$ substitution Rxn are

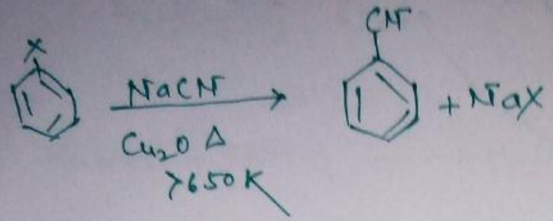
1)



2)



3)



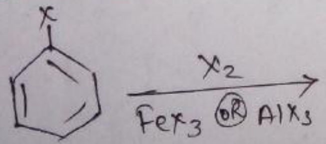
② Electrophilic Substitution Rxn

When an electrophil Replaced hydrogen from heloarenes in the form of $H^{\oplus}$ (electrophile) known as electrophilic Substitution Rxn.

There are following types of $E^{\oplus}$ Substitution Rxn given by helo arenes :-

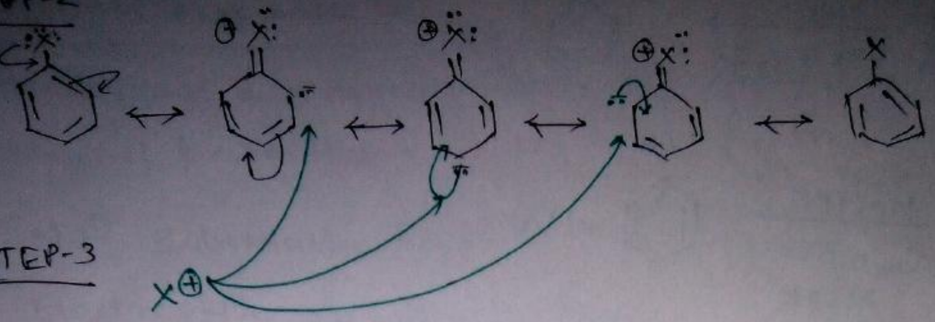
1) Helozination
2) Nitration
3) Sulphonation
4) fridel Craft Alkylation Rxn
5) fridel craft Acielation Rxn

1) Helozination ⇒



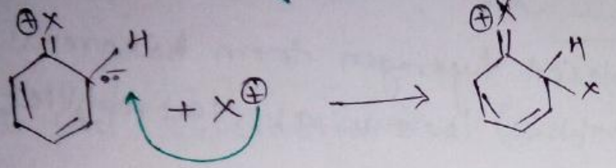
STEP-1- $:\ddot{X}-\ddot{X}: + FeX_3 \longrightarrow X^{\oplus} + FeX_4^{\ominus}$

STEP-2

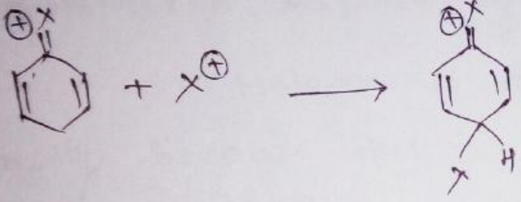


STEP-3

a) ortho attack

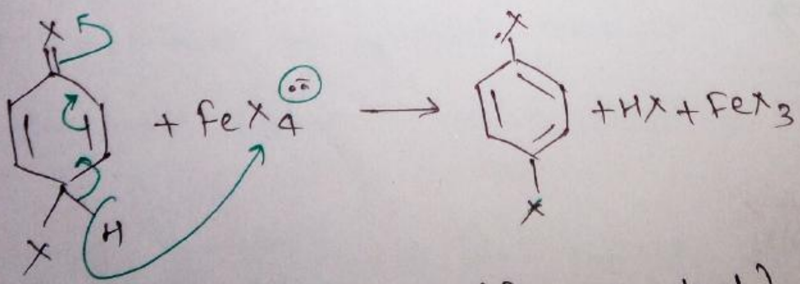


ⓑ Para attack -



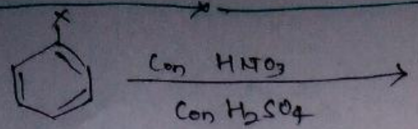
STEP-4

(ortho product)



(Para product)

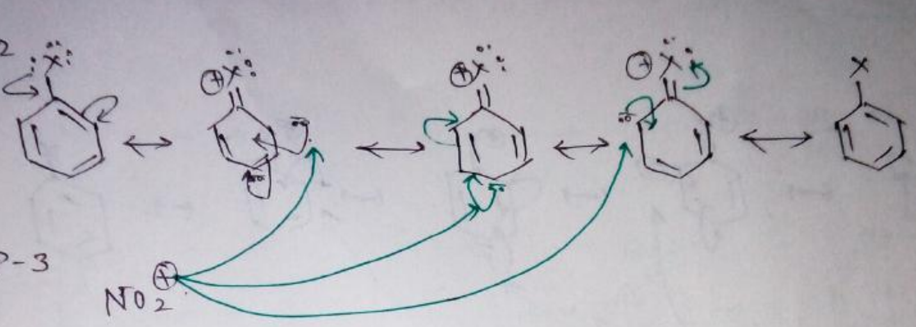
2) Nitration of ChloroBenzene ⇒



STEP-1

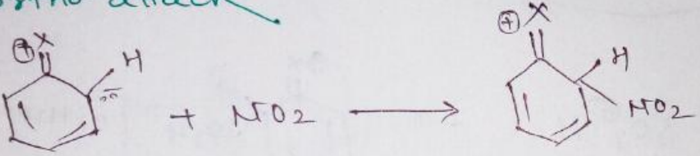
$$HONO_2 + HHSO_4 \longrightarrow H_2O + \overset{\oplus}{N}O_2 + HSO_4^{\ominus}$$

STEP-2

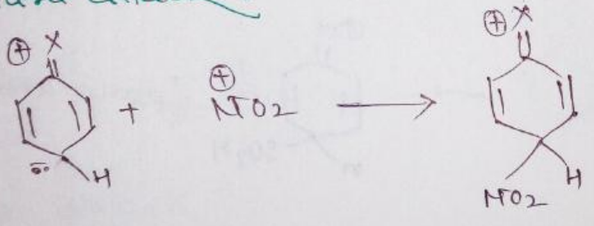


STEP-3

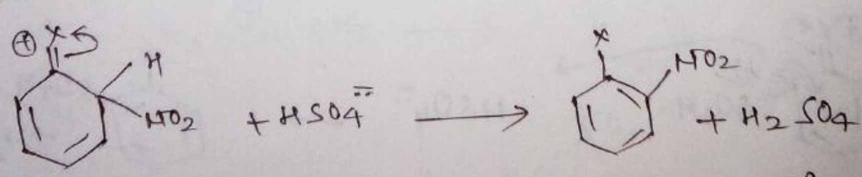
a) ortho-attack



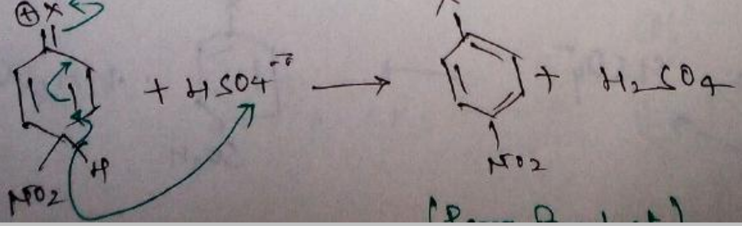
b) Para attack.



STEP- 4

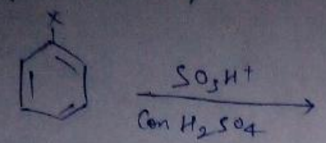


(ortho product)

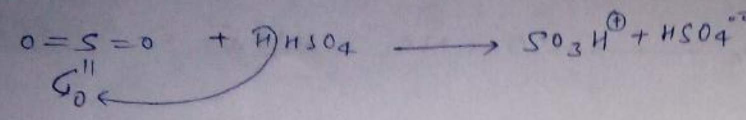


(Para Product)

Sulphonation ⇒

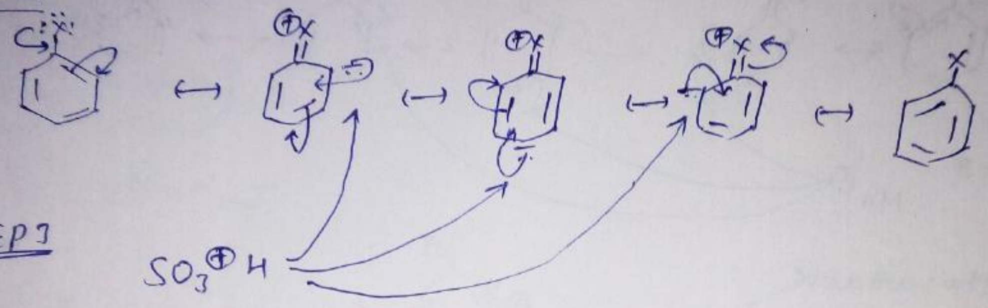


STEP-1



$$SO_3 + H_2SO_4 \longrightarrow SO_3H^{\oplus} + HSO_4^{-}$$

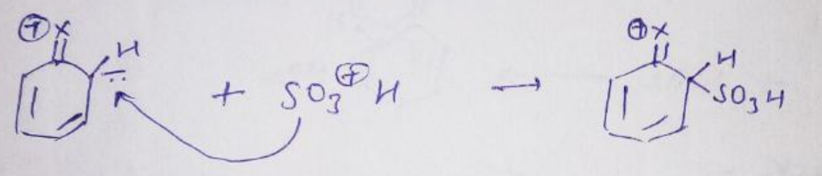
STEP-2



STEP 3

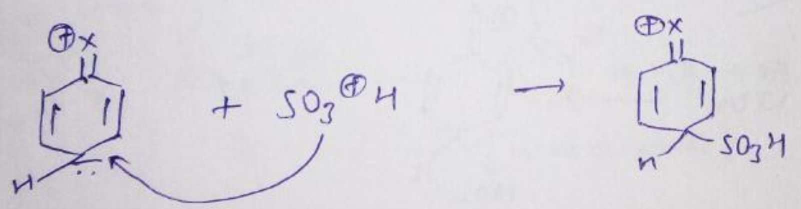
$SO_3^{\oplus}H$

(a)



(ortho attack)

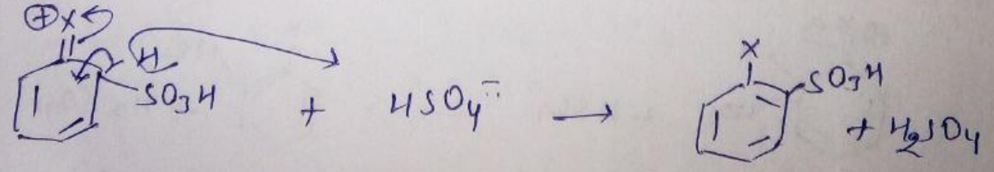
(b)



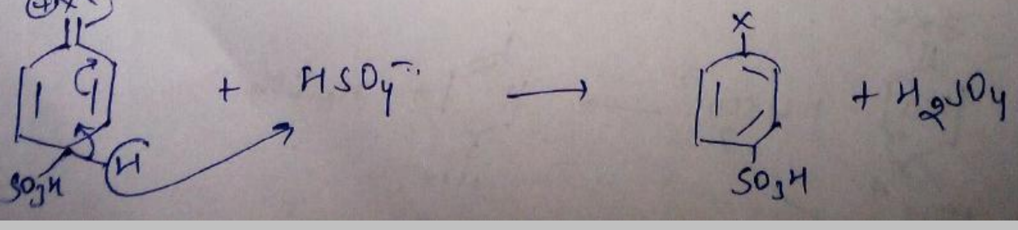
(para attack)

STEP 4

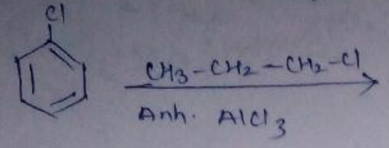
(a)



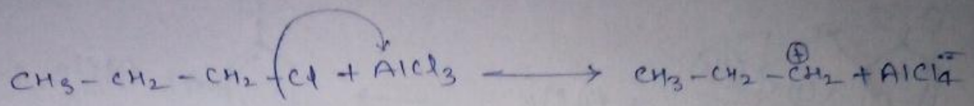
(b)



* Fridel Craft Alkylation Rxn →

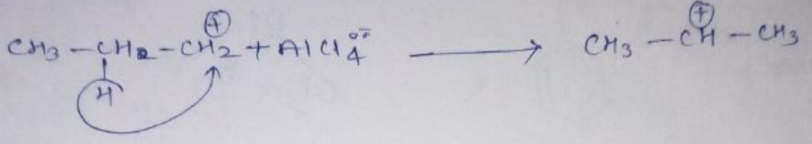


STEP-1



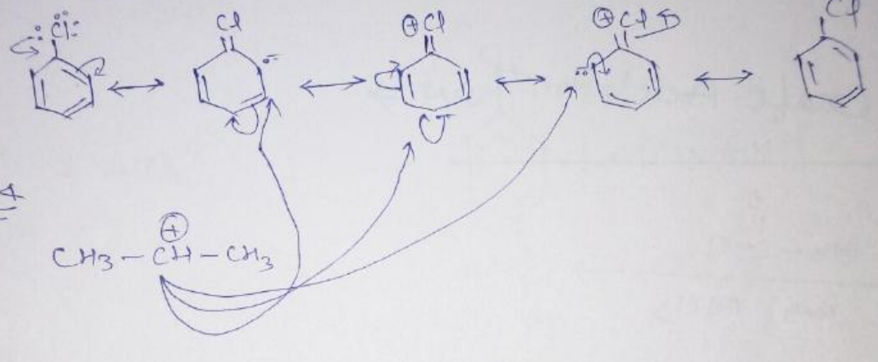
$CH_3-CH_2-CH_2-Cl + AlCl_3 \longrightarrow CH_3-CH_2-\overset{+}{C}H_2 + AlCl_4^{-}$

STEP-2

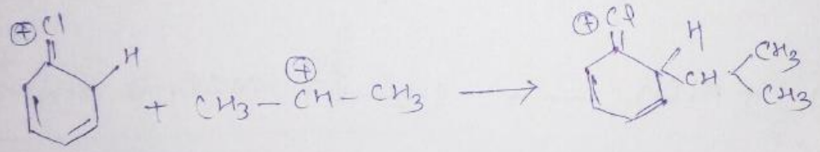


$CH_3-CH_2-\overset{+}{C}H_2 + AlCl_4^{-} \longrightarrow CH_3-\overset{+}{C}H-CH_3$

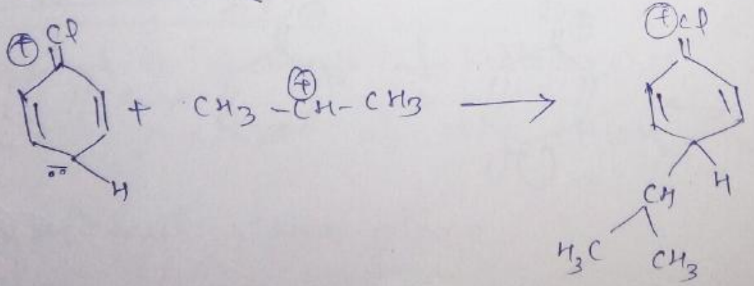
STEP-3



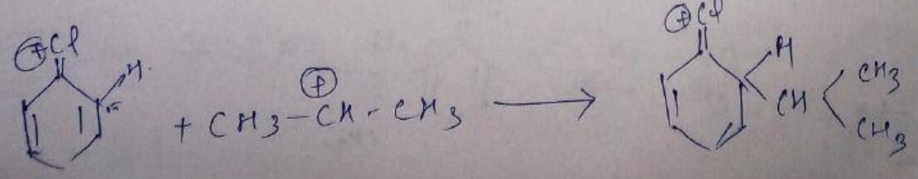
STEP - 4



Para attack

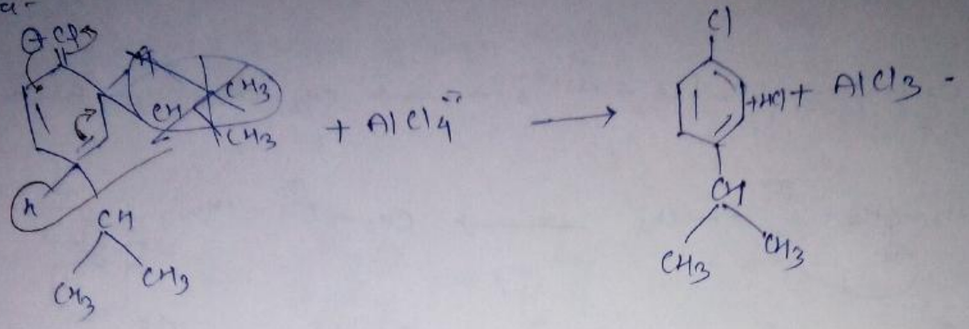


ortho attack

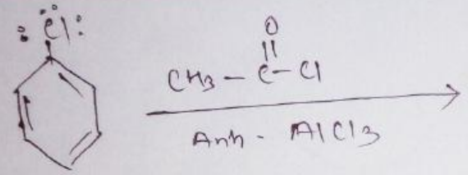


STEP-5 ortho-

Para-

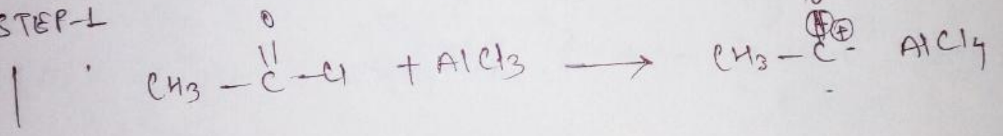


Foridal Craft Acielation Rxn ⇒



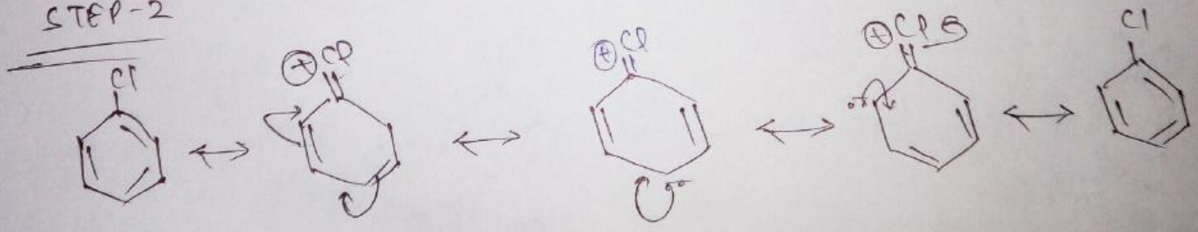
$CH_3-\overset{O}{\overset{||}{C}}-Cl \xrightarrow[\text{Anh - AlCl}_3]{}$

STEP-1

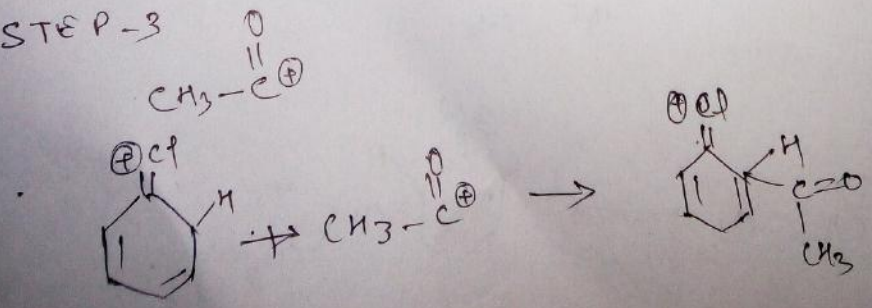


$CH_3-\overset{O}{\overset{||}{C}}-Cl + AlCl_3 \longrightarrow CH_3-\overset{O}{\overset{\oplus}{C}}\ AlCl_4$

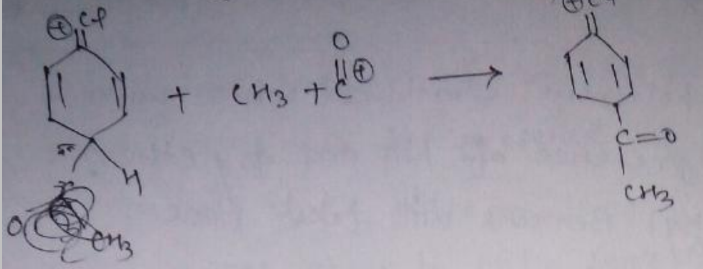
STEP-2



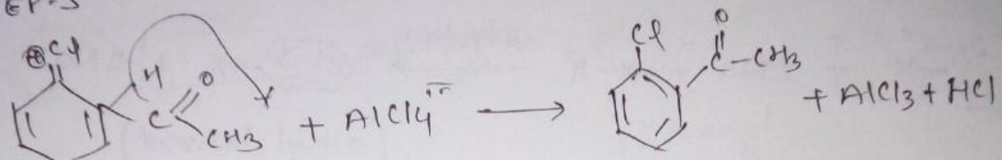
STEP-3

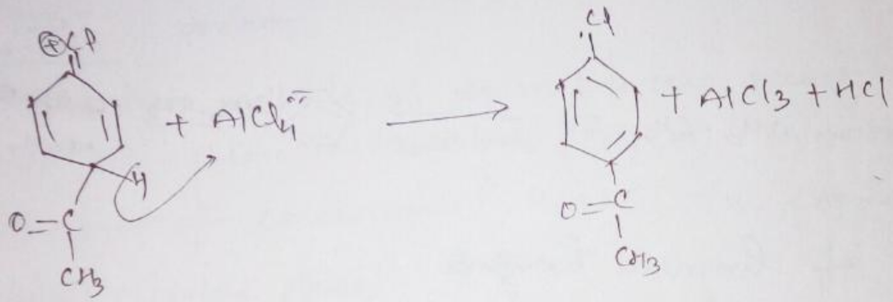


Para attack -



STEP-5

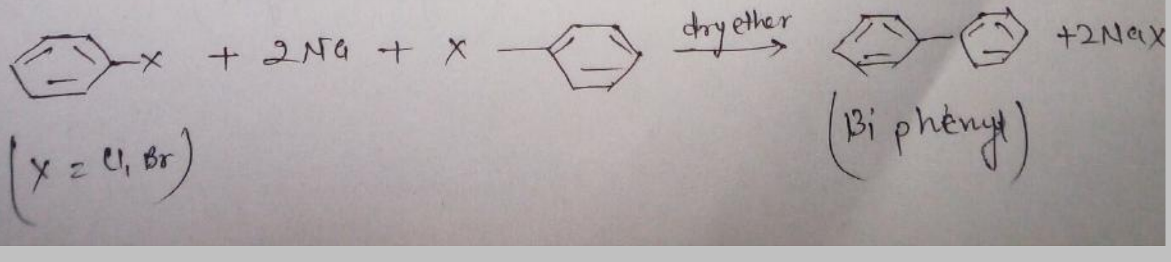




Rxn with Metal ⇒

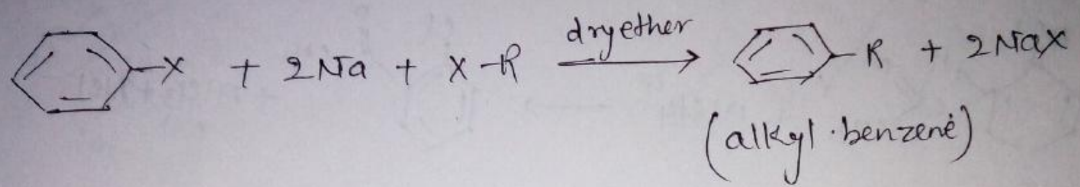
Fittig Rxn

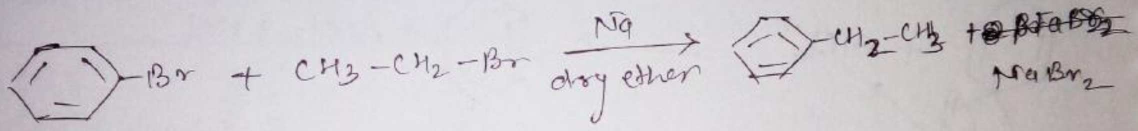
when two molicule of heloarenes react with Na in the presence of dry ether, The formation of ~~by~~ biphinyl take place.



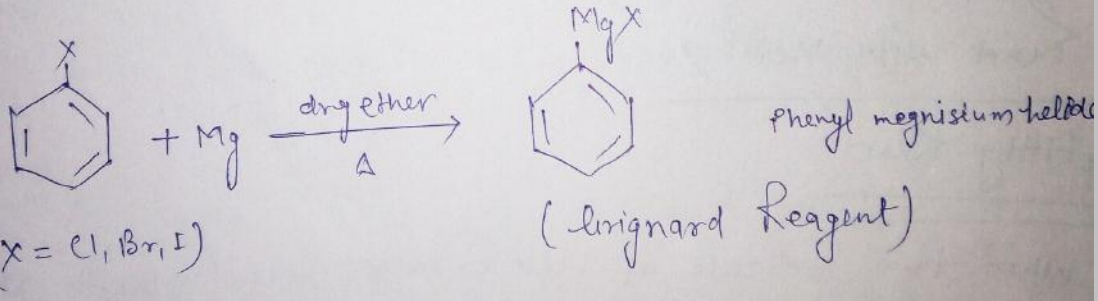
* Wurtz fittig Rxn ⇒

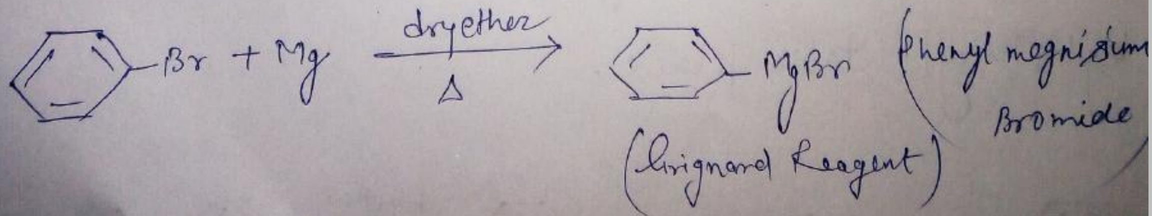
When one molecule of heloarene combined which with Alkyl helide in the presence of Na and dry ether, The formation of Alkyl Benzene will take place.





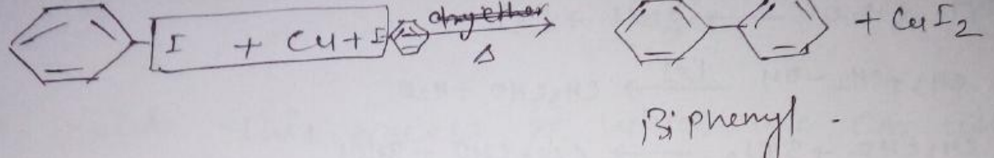
Formation of Grignard Reagents





#ULLMANN RXN ⇒

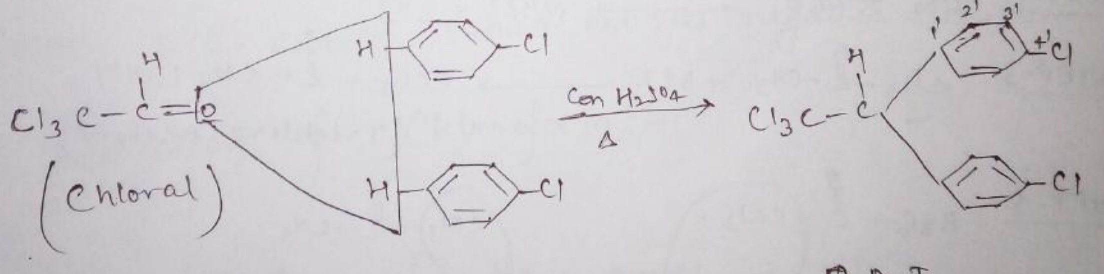
When two molicule of a Ioido Benzene  Combined with each other in the presence of Cu, The formation of bi phenyl take place –
This reaxn given by only Ioido Benzene –



Bi phenyl.

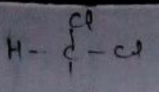
DDT कीटनाशक

When two mollcule of Chloro Benzene react with a molicule of tri-chloro Accetaldihide (CCl_3CHO) (chloral) in the presence of Consdrtrated H_2SO_4, The formation of D.D.T. take place.



D.D.T

2,2-bis(4'-Chlorophenyl)-1,1,1-tri chloro ethane

chloroform :→  $H-\overset{Cl}{\underset{Cl}{C}}-Cl$ 1, 1,1- trichloro methane

Method of Preparation :-

labourtery :-

from Alcohol :-

$$CH_3CH_2OH \xrightarrow{CaOCl_2+H_2O}$$

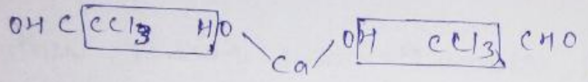
STEP-1 $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$

STEP-2 $Cl_2 + H_2O \longrightarrow 2HCl + [O]$

STEP-3. $CH_3-CH_2-OH \xrightarrow{[O]} CH_3CHO + H_2O$

STEP-4 $CH_3CHO + 3Cl_2 \longrightarrow CCl_3CHO + 3HCl$

(Trichloro acetelalihyro chloro)

STEP 5  $OHC\boxed{CCl_3 \quad H}O \diagdown Ca \diagup O\boxed{H \quad CCl_3}CHO \rightarrow (HCOO)_2Ca + 2CHCl_3$

(Calcium format)

from Acetone

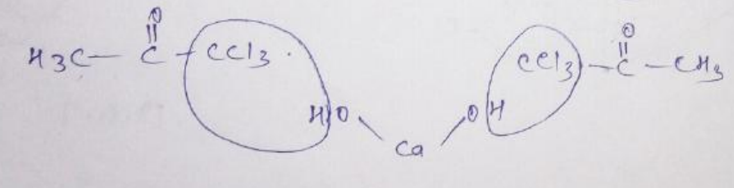
$$CH_3COCH_3 \xrightarrow{CaOCl_2+H_2O}$$

STEP-1 $CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$

STEP-2 $Cl_2 + H_2O \longrightarrow 2HCl + [O]$

STEP-3 $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 3Cl_2 \longrightarrow CCl_3-\overset{O}{\overset{\|}{C}}-CH_3 + 3HCl$

(Trichloro Acetone)

STEP-4 

$$H_3C-\overset{O}{\overset{\|}{C}}-CCl_3 \quad HO \diagdown Ca \diagup OH \quad CCl_3-\overset{O}{\overset{\|}{C}}-CH_3$$

$$\longrightarrow (CH_3COO)_2Ca + 2CHCl_3$$

Physical Properties :-

1- it is sweet smelling colourless liquid.

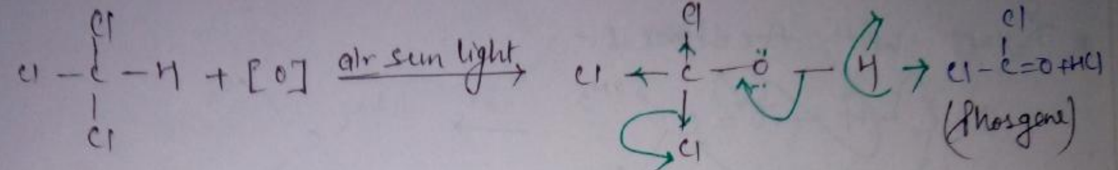
2- it is insolible in water.

3- Highly solivle in organic Solvent

4- it is use as an anesthetic ; बेहोशी।

Cheimistry Properties :-

Oxydation → when chloroform contact into the air and sun light . decomposs its hell and form a poistions gas phosgene.



$$Cl-\overset{Cl}{\underset{Cl}{C}}-H + [O] \xrightarrow{\text{air sun light}} Cl-\overset{Cl}{\underset{Cl}{C}}-\ddot{O}-H \rightarrow Cl-\overset{Cl}{C}=O + HCl$$

(Phosgene)

To avoide this process by which we can use chloroform for a long time, following 3 precautions we will use.

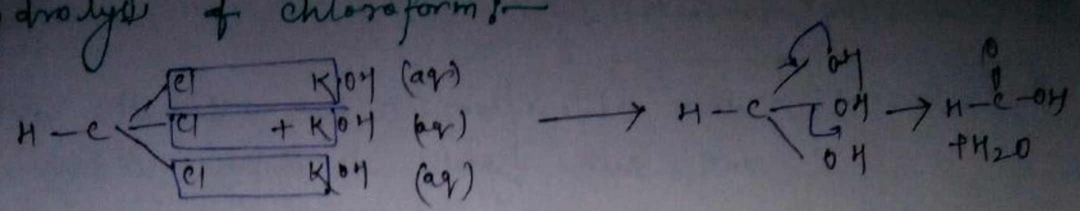
1) stored Chloroform in dark brown cloured bottle.
2) fill chloroform in to the bottle upto brim. due to which posebilities of air neglected.
3) Add 1 % C_2H_5OH which act as negative Catlist.

Reduction of Chloroform :-

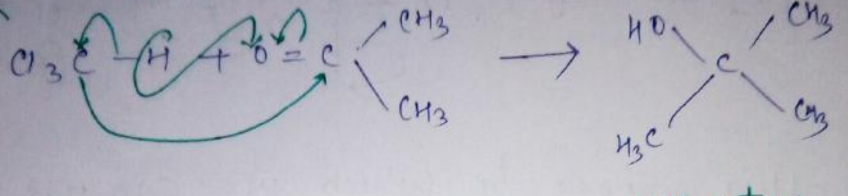
$$CHCl_3 + 2[H] \xrightarrow[HCl]{Zn} CH_2Cl_2 + HCl$$

Dichloro Methene

Hydrolysis of chloroform :-



Rxn with Acetone :-



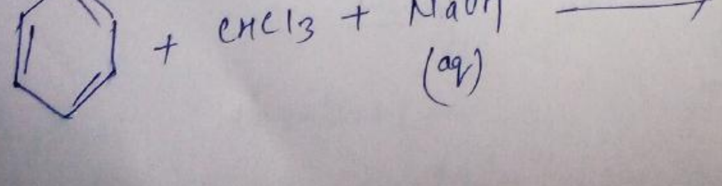
chlorotene
(hypnotic drugs)

Nitration of chloroform ⇒

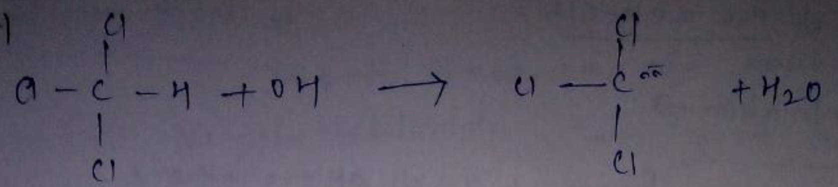
$Cl_3C-H + HONO_2 \longrightarrow Cl_3C-NO_2 + H_2O$

Chloropicrin
⇓
(Insectiside)

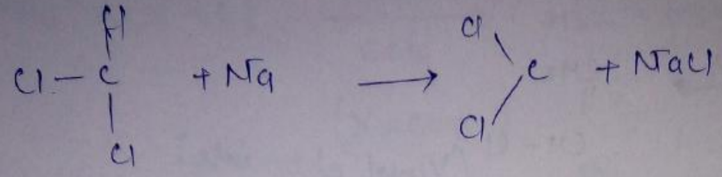
Imp Reimer tiemann Reaction :-



STEP-1



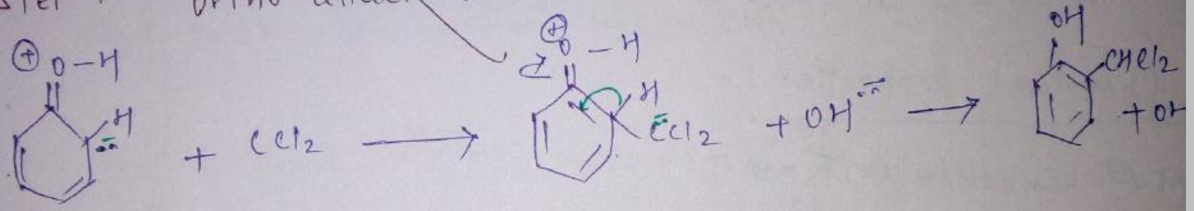
STEP-2



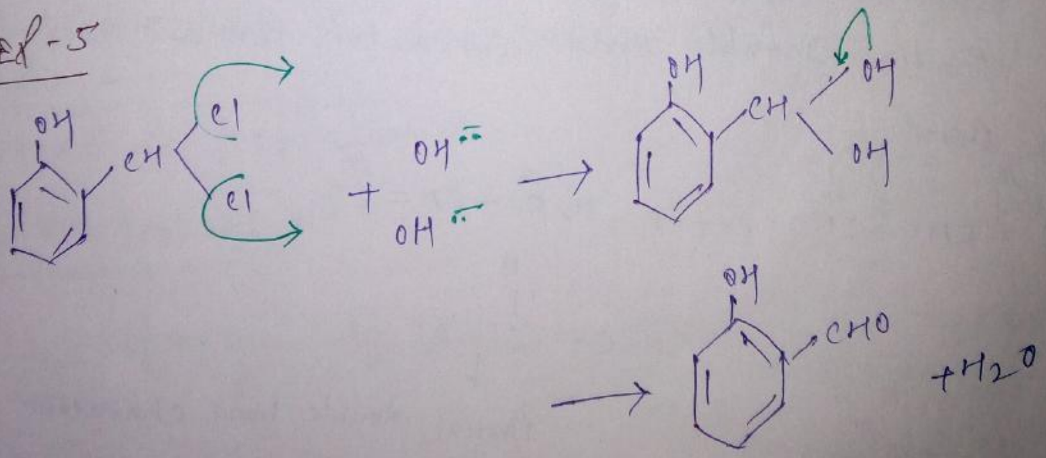
STEP-3

Phenol Resonance :-

STEP-4 -- Ortho attack .



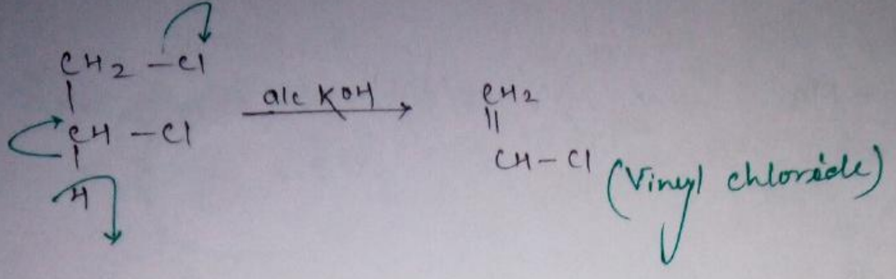
STEP-5



Vinyl chloride ⇒ $H_2C=CH-\ddot{Cl}:$

Method of Prebration ⇒

From 1,2-di chloro ethane.



$$CH_2Cl-CH_2Cl \xrightarrow{alc\ KOH} CH_2=CH-Cl$$

(Vinyl chloride)

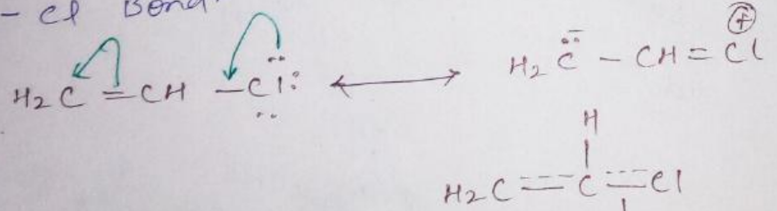
2) From ethyne :- $CH\equiv CH$

$$H-C\equiv C-H + HCl \longrightarrow H_2C=CH-Cl$$

Chemical properties :-

$Nu^\ominus$ Substitution Rxn :-

Vinyl chloride does not give $Nu^\ominus$ Substitution Rxn becoz Partial Double bond Corrector Present in C-Cl Bond.



$$H_2C=CH-\ddot{Cl}: \longleftrightarrow H_2\overset{\cdot\cdot}{\bar{C}}-CH=\overset{\oplus}{Cl}$$

Partial double bond character

↓

difficult to break C-Cl Bond

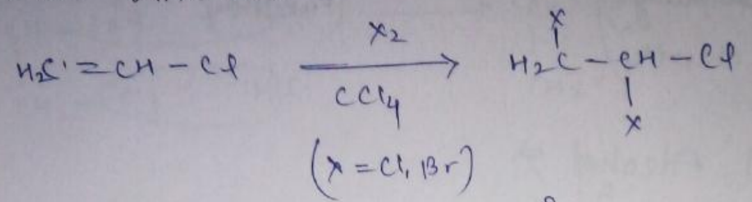
↓

hence not give neucleophilic Sub- Rxn -

II- Addition RxN ⇒

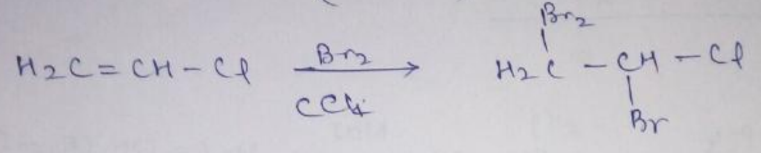
Due to presence of double Bond Correcton vinyle chloride can give addition RxN.

i) RxN with Helozen :-



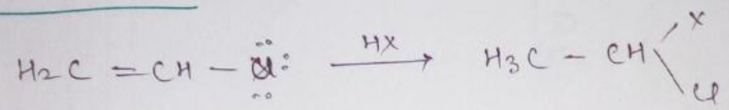
$$H_2C=CH-Cl \xrightarrow[CCl_4]{X_2} H_2\overset{X}{C}-\underset{X}{CH}-Cl$$

$(X = Cl, Br)$

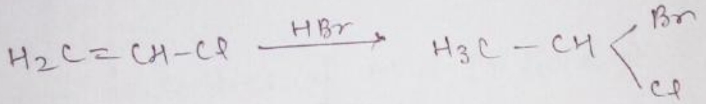


$$H_2C=CH-Cl \xrightarrow[CCl_4]{Br_2} H_2\overset{Br_2}{C}-\underset{Br}{CH}-Cl$$

RxN with HX :-



$$H_2C=CH-\ddot{\underset{..}{Cl}}: \xrightarrow{HX} H_3C-CH\begin{smallmatrix}X\\Cl\end{smallmatrix}$$



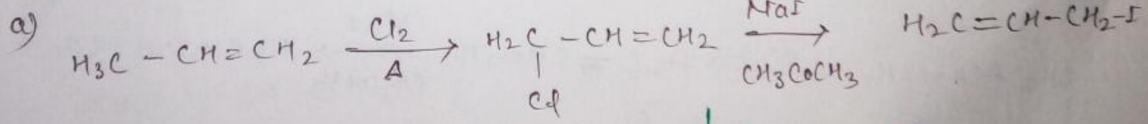
$$H_2C=CH-Cl \xrightarrow{HBr} H_3C-CH\begin{smallmatrix}Br\\Cl\end{smallmatrix}$$

Allyl ~~A~~ Ioidide ⇒ $(H_2C=CH-CH_2-I)$

method of Prebration ⇒

i) from Propene ⇒ ⓪③

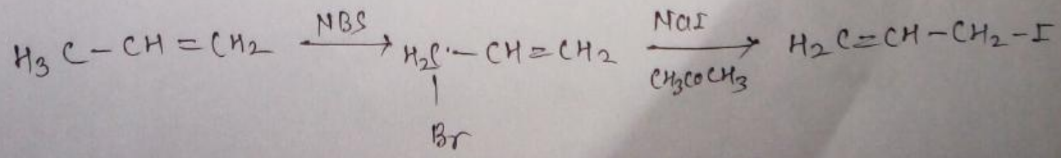
a)



$$H_3C-CH=CH_2 \xrightarrow[\Delta]{Cl_2} H_2\underset{Cl}{C}-CH=CH_2 \xrightarrow[CH_3COCH_3]{NaI} H_2C=CH-CH_2-I$$

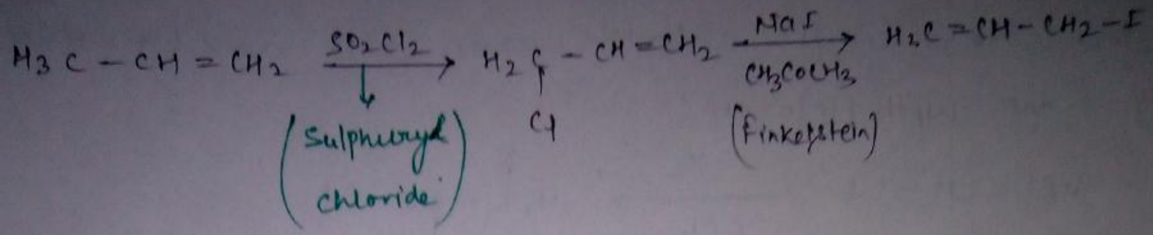
(Finkelstein)

b)



$$H_3C-CH=CH_2 \xrightarrow{NBS} H_2\underset{Br}{C}-CH=CH_2 \xrightarrow[CH_3COCH_3]{NaI} H_2C=CH-CH_2-I$$

(c) from SO_2Cl_2 (Sulphurile chloride)



$$H_3C-CH=CH_2 \xrightarrow{SO_2Cl_2} H_2\underset{Cl}{\underset{|}{C}}-CH=CH_2 \xrightarrow[CH_3COCH_3]{NaI} H_2C=CH-CH_2-I$$

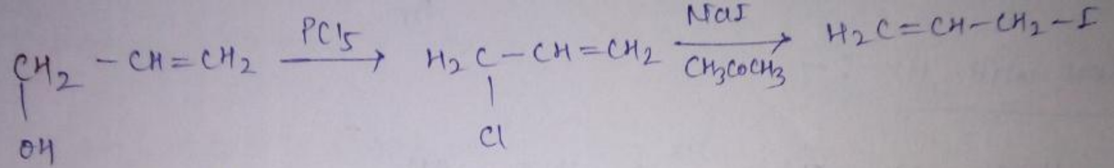
(Sulphuryl chloride)

(Finkelstein)

ethod)

II- From Allyl Alcohol ⇛

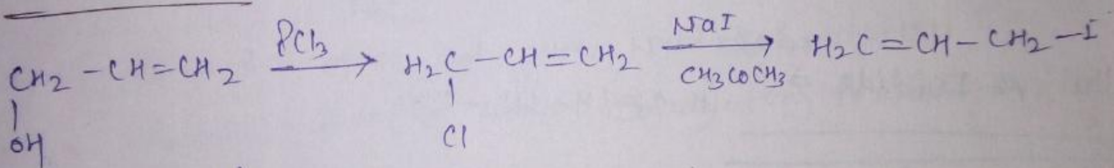
a) From PCl_5



$$\underset{OH}{\underset{|}{CH_2}}-CH=CH_2 \xrightarrow{PCl_5} H_2\underset{Cl}{\underset{|}{C}}-CH=CH_2 \xrightarrow[CH_3COCH_3]{NaI} H_2C=CH-CH_2-I$$

(allyl alcohol)

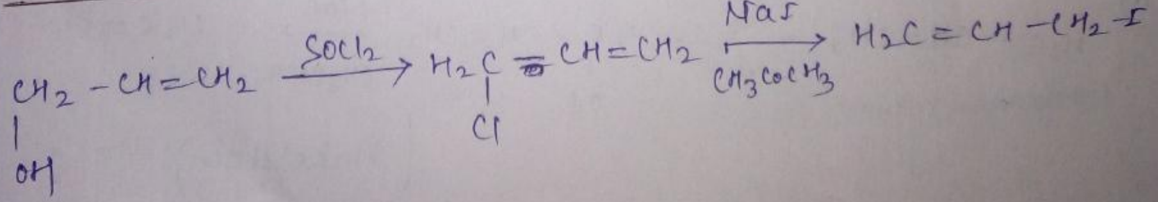
B) From PCl_3



$$\underset{OH}{\underset{|}{CH_2}}-CH=CH_2 \xrightarrow{PCl_3} H_2\underset{Cl}{\underset{|}{C}}-CH=CH_2 \xrightarrow[CH_3COCH_3]{NaI} H_2C=CH-CH_2-I$$

(allyl alcohol)

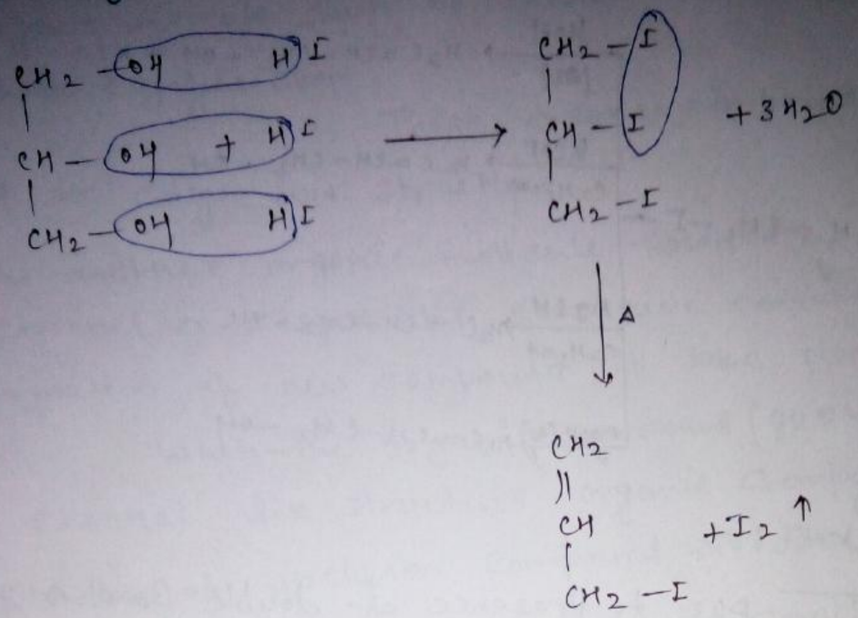
c) From $SOCl_2$ Rxn



$$\underset{OH}{\underset{|}{CH_2}}-CH=CH_2 \xrightarrow{SOCl_2} H_2\underset{Cl}{\underset{|}{C}}\cancel{=}CH=CH_2 \xrightarrow[CH_3COCH_3]{NaI} H_2C=CH-CH_2-I$$

Imp-

From Glycerine (Glycerol) (ग्लिसरॉल)



$$CH_2(OH)-CH(OH)-CH_2(OH) + 3HI \longrightarrow CH_2I-CHI-CH_2I + 3H_2O$$

$$CH_2I-CHI-CH_2I \xrightarrow{\Delta} CH_2=CH-CH_2-I + I_2\uparrow$$

Chemical Properties of Allyl Ioidide ⇒

i) $Nu^{\ominus}$ Sub- Rxn :-

$H_2C =$

Allyl he Ioide can give $Nu^{\ominus}$ Sub- Rxn becoz the process of Conjugated is not posible -

$H_2C=CH-CH_2-\ddot{\underset{\cdot\cdot}{I}}:$

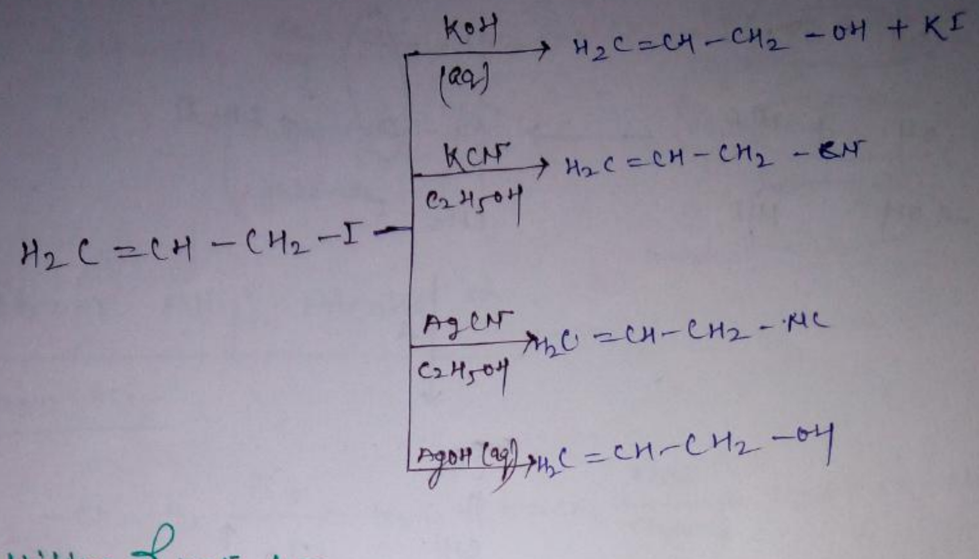
↓

Singl Bond

↓

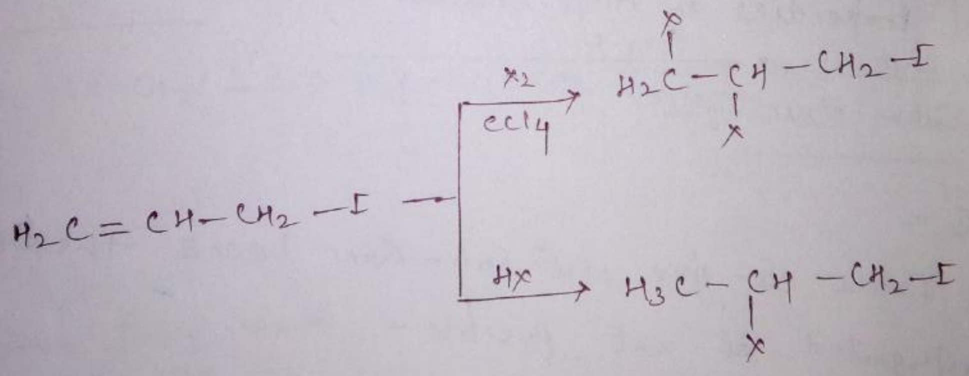
Can give nucleophilic Sub- Rxn

The most important Sub- Rxn are ⇒



Addition Rxn :-

Due to presence of double Bond Allyl Ioidide can give addition Rxn.



inclusion Compound and chlotherates :-

imp Organic molicule Such as Urea, Thio Urea, quinol ~~urea~~ have crystlyne shap.

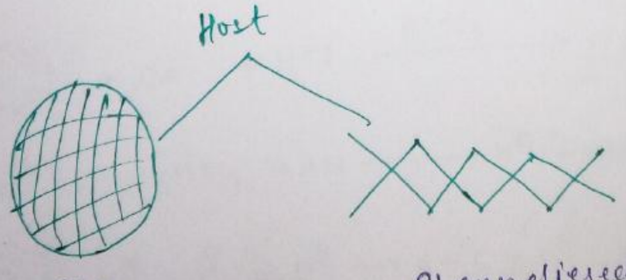
These organic compound have channelied or casge live structure.

The another organic molicule trapped by these channel or casged like structure containing compond formation of new compound will take place.

When the organic compound (guest) trapped by channel lie structure organic compound (oste) formation of inclusion Compound will take place for Example Urea form inclusion complexes by trapping the guasst molicule (n-alkane).

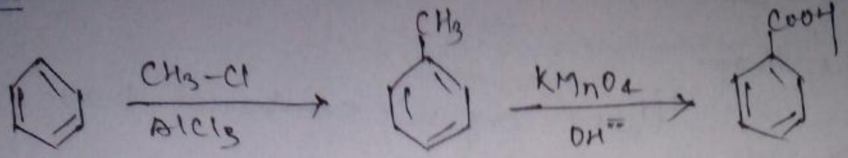
When organic compound (guasst) trapped by cage like structure organic compound (HOst) formation of Chlatherates. will take place.

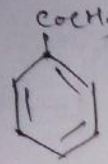
Qunol form chlatherates by trapping inered gas into its cavities.



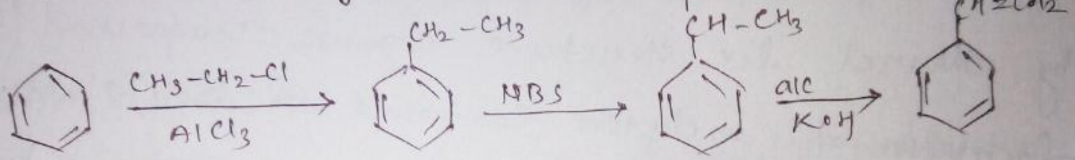
Question previous year.

2015



 - hint - friedal craft Rxn.

Benzene to vinyle Benzene.



ab sulute → erliverst system R, S. >

skew, sttagard-, gouss-

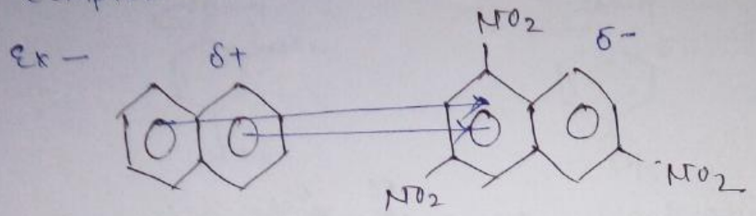
Quel-
(04)

Charged transfer Complex :—

Some e⊖ rich molicule combined with e⊖ deficient molicule, due to which formation af complex will take place.

This complex is known as charge transfer Complex –

Ex –



Sulphonation of Benzene is ~~ruible~~ ~~siuble~~ process is becoz SO_3 is non.polar. molicular and dissociation by H_2SO_4 is weak.

$O=\overset{O}{\overset{\|}{S}}=O + H\,HSO_4 \rightleftharpoons$

Give the Reaⁿ b/w ethanol and bleaching powder –

This is chloroform method –

⑦


$+ CO + HCl \xrightarrow{AlCl_3}$

STEP-1 $AlCl_3 + HCl \longrightarrow H^{\oplus} + AlCl_4^{\ominus}$

STEP-2 $H^{\oplus}\ \ \ddot{C} \equiv O^{\oplus} \longrightarrow H-C \equiv O^{\oplus} \longrightarrow H\overset{\oplus}{C}O = \overset{\oplus}{C}HO$

STEP-3 Resonace – attacking.

| |