Preparation of Haloalkanes and Haloarenes

Preparation of Haloalkanes :

(1) From Alcohol (2) From alkanes

(3) From Alkenes (4) By halogen exchange.

(I) From Alcohol :

(A) By rxn with HX (X = Cl, Br, I)

(B) By rxn with PX_3 or PX_5 (X = Cl, Br, I)

(C) By rxn with $SOCl_2$ (thionyl chloride)

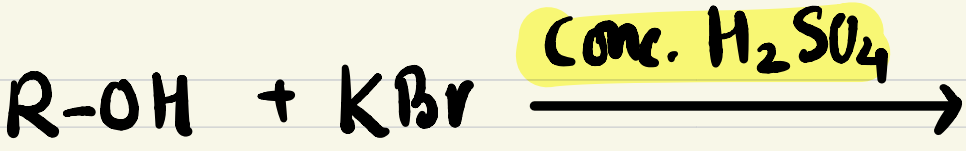
(A) Alcohol + HX :

$$R\text{-}OH + HCl \xrightarrow{\text{anhyd. } AlCl_3} R\text{-}Cl + H_2O$$

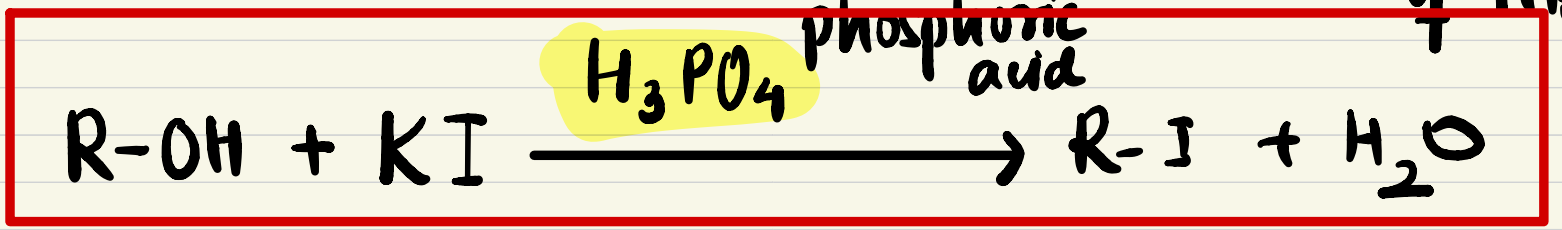
Next Cl

R-Cl : liq.

H_2O : liq.



$KBr + H_2SO_4 \longrightarrow HBr + KHSO_4$ in situ generation of HBr



* For preparation of R-I from KI (or NaI) we use H_3PO_4 instead of conc. H_2SO_4

Strong Oxidising agent.

$KI + H_2SO_4 \longrightarrow HI + KHSO_4$

$HI \xrightarrow{H_2SO_4} I_2$

(B) $R-OH + PX_3$

$R-OH + PX_5$

PBr_3 & PBr_5 — Unstable

PCl_5 is stable & PCl_3 is also stable

$SOBr_2$, SOI_2 — do not exist

$$R-OH + PCl_3 \longrightarrow \underset{\text{liq.}}{R-Cl} + \underset{\text{liq.}}{H_3PO_3}$$

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

$$R-OH \xrightarrow{(Br_2 + P_4)} R-Br + HBr + POBr_3$$

(C) $$R-OH + SOCl_2 \longrightarrow \underset{\text{liq.}}{R-Cl} + HCl_{(g)} + SO_{2(g)}$$

Best method to prepare alkyl halide from alcohol.

to remember.

(II) From Alkanes: Free radical substitution reaction

Chlorination of methane:

$$CH_4 + Cl_2 \xrightarrow{\text{sunlight (or } h\nu)} \boxed{CH_3Cl} + HCl$$

good amount

Bromination of methane:

$$CH_4 + Br_2 \xrightarrow{h\nu} \boxed{CH_3Br} + HBr$$

good amount

Iodination of methane:

$$CH_4 + I_2 \underset{}{\overset{h\nu}{\rightleftharpoons}} \boxed{CH_3I} + HI$$

yield is very low → why? iodination of alkane is a reversible reaction

How to carry out iodination of alkanes? By using strong O.A like HIO_3 or HNO_3

or How to make high yield?

$$HIO_3 + HI \longrightarrow I_2 + H_2O$$

only one type C-atom ⇒ one type of H-atom.

Ex1: $CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$ [1 Rx]

only one type of C-atom ⇒ only one type of H-atom.

Ex2: $\overset{a}{CH_3}-\overset{a}{CH_3} + Cl_2 \xrightarrow{h\nu} CH_3-CH_2-Cl + HCl$ [1 Rx]

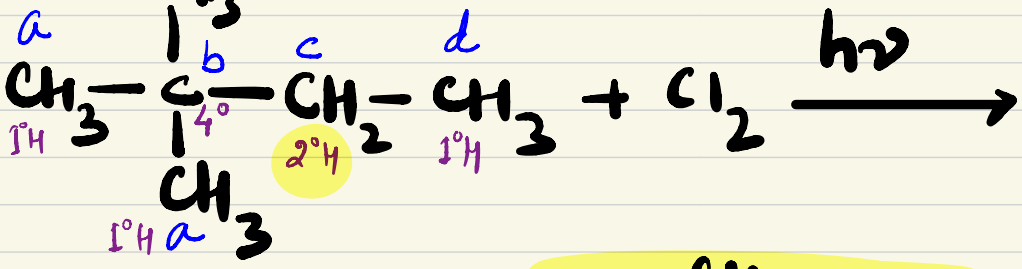
Ex3: $\overset{a}{CH_3}-\overset{b}{CH_2}-\overset{a}{CH_3} + Cl_2 \xrightarrow{h\nu} CH_3-\underset{Cl}{CH}-CH_3 + CH_3-CH_2-CH_2-Cl + HCl$

(major) (minor)

two types of C-atoms ⇒ two type of H-atoms.

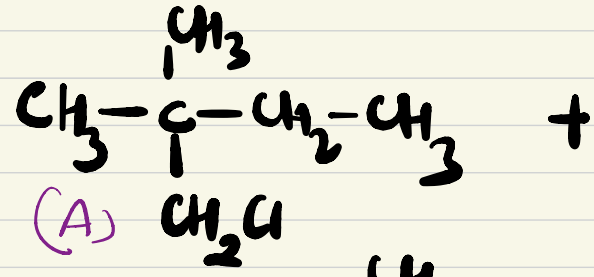
[2 Rx]

Ex4:

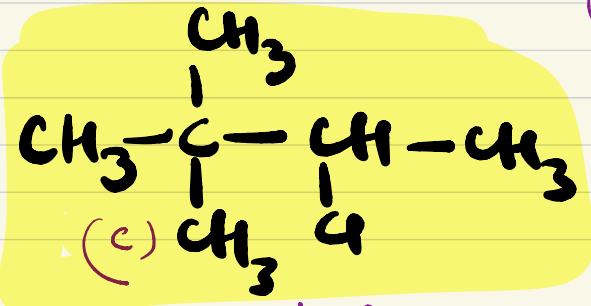


4 types of C-atoms & 3 types of H-atoms.

$\xrightarrow{h\nu}$

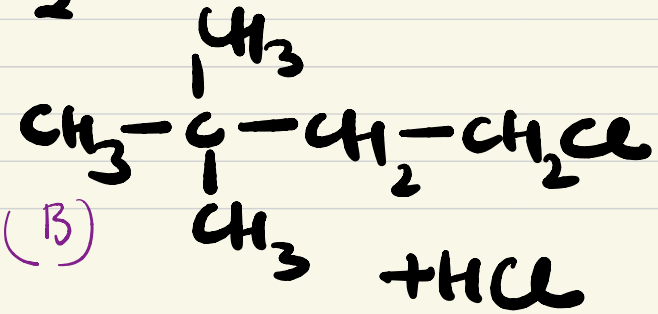


(A)



(major)

+



(B)

+ HCl

[3 Rx]

In the above situations, how to find out the major product? ⇒ More reactive H gets substituted by Halogen gives the major product.

* Reactivity of H-atoms : 3°H > 2°H > 1°H.

* $C_5H_{10}(A) + Cl_2 \longrightarrow$ Single monochlorinated product.

Write the str. of A & its IUPAC name.