Alcohols, Phenols & Ethers - 04

Preparation of Alcohols - 3

From Grignard's Reagent with Carbonyl Compound & From Amines

① Grignard's Reagent ($R-MgX$) with Carbonyl Compound $\left(-\overset{O}{\overset{\|}{C}}-\right)$

Nucleophilic Addition of $R-MgX$ takes place on $-\overset{O}{\overset{\|}{C}}-$ followed by hydrolysis gives alcohol.

$$H-\overset{\overset{\delta-}{O}}{\overset{\|}{\underset{\delta+}{C}}}-H + CH_3\overset{\delta-}{\}}\overset{\delta+}{MgBr} \xrightarrow{\text{dry ether}} H-\underset{CH_3}{\overset{\overset{\delta-}{O}\overset{\delta+}{MgBr}}{\overset{|}{\underset{|}{C}}}}-H \xrightarrow[\text{hydrolysis}]{H^+/H_2O}$$

Formaldehyde / methanal

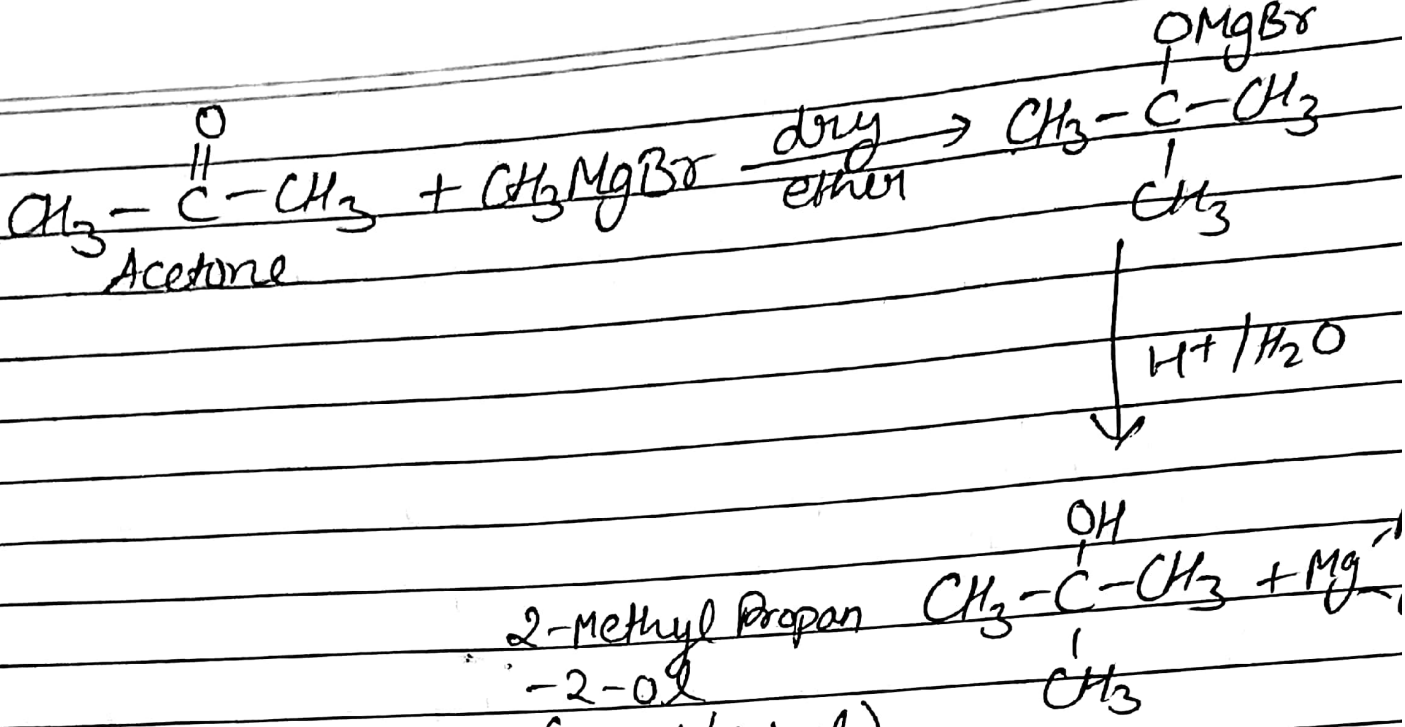
$$H-\underset{CH_3}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-H + Mg\overset{Br}{\underset{OH}{}}$$

Ethanal (1° Alcohol) — Hydroxy Magnesium bromide

$$CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3MgBr \xrightarrow{\text{dry ether}} CH_3-\underset{H}{\overset{OMgBr}{\overset{|}{\underset{|}{C}}}}-CH_3 \xrightarrow[\text{hydrolysis}]{H^+/H_2O}$$

Acetaldehyde / ethanal

Propan-2-ol ($2°$ Alcohol) $CH_3-\underset{}{\overset{OH}{\overset{|}{\underset{|}{C}}}}H-CH_3 + Mg\overset{Br}{\underset{OH}{}}$



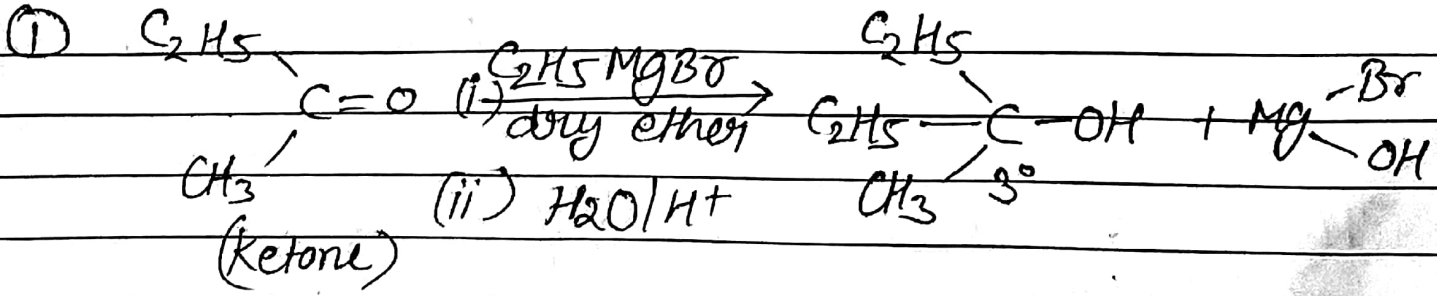
2-Methyl Propan-2-ol
(3° Alcohol)

(i) Formaldehyde ⟶ 1° Alcohol

(ii) Acetaldehyde or any other aldehyde ⟶ 2° Alcohol

(iii) Acetone or any Ketone ⟶ 3° Alcohol

Questions

(1) 

(2) $CH_3-\overset{O}{\overset{\|}{C}}-H$ (Aldehyde) $\xrightarrow[\text{dry ether}]{(i)\ C_6H_5MgBr}$ $\xrightarrow{(ii)\ H_2O/H^+}$ $H-\underset{C_6H_5}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH + Mg^{Br}_{OH}$ (2°)

(3) $CH_3-\overset{O^{\delta-}}{\overset{\|}{C^{\delta+}}}-H \xrightarrow[\text{dry ether}]{(i)\ CH_3MgBr}$ (ii) NH_4Cl

CH_3^-/Mg^+Br

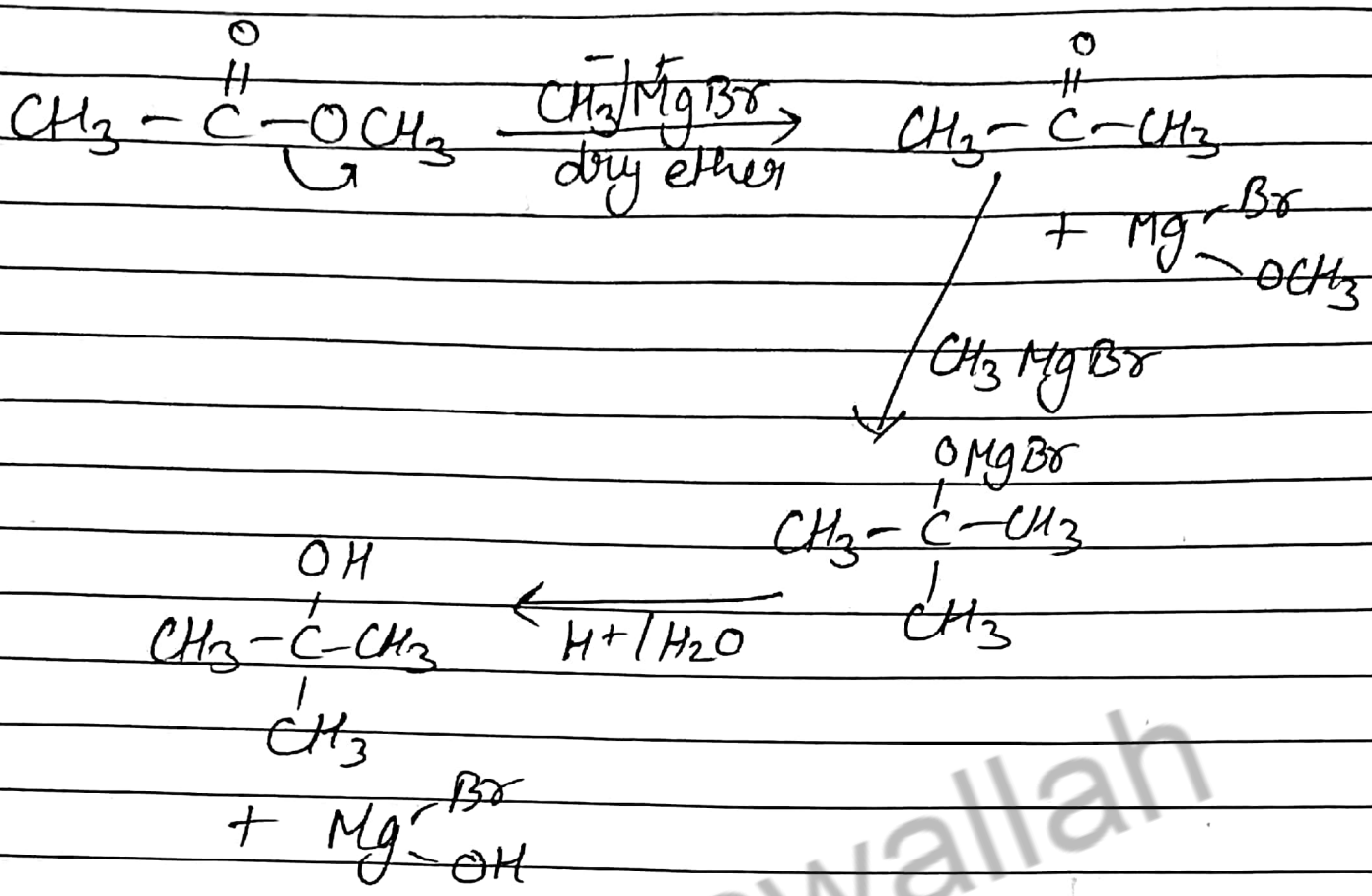
$CH_3-\underset{|}{\overset{O^-Mg^+Br}{\overset{|}{C}}}-CH_3 \xrightarrow[\text{gives } H^+]{NH_4^+Cl^-} CH_3-\underset{|}{\overset{OH}{\overset{|}{C}}}-CH_3 + NH_3 + Mg^{Br}_{Cl}$

Note: Similar Reaction occurs with Acid derivatives when R-MgX is in excess

$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{dry ether}]{CH_3^-/Mg^+Br} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + Mg^{Br}_{Cl}$

$\xrightarrow{CH_3MgBr}$

$CH_3-\underset{CH_3}{\overset{OMgBr}{\overset{|}{C}}}-CH_3 \xrightarrow{H^+/H_2O} CH_3-\underset{CH_3}{\overset{OH}{\overset{|}{C}}}-CH_3 + Mg^{Br}_{OH}$



② From Amines (1° Amines) : Action of HNO_2 (Nitrous Acid) OR ($NaNO_2 + HCl$)

$$\overset{+}{R}/\overset{-}{NH_2} + H\bar{O}/\overset{+}{N}O \longrightarrow R-OH + N_2 + H_2O$$

$$C_2H_5NH_2 + HONO \longrightarrow C_2H_5OH + N_2 + H_2O$$

$$CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_3 + HONO \longrightarrow CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + N_2 + H_2O$$

Note: Methyl Amine (CH_3NH_2) do not give this reaction

Trick To remember

$$R-\underset{HO}{\overset{H}{\underset{|}{\overset{|}{N}}}}-\underset{NO}{\overset{H}{\underset{|}{\overset{|}{N}}}} \longrightarrow ROH + N_2 + H_2O$$

$$C_2H_5-\underset{HO}{\overset{H}{\underset{|}{\overset{|}{N}}}}-\underset{NO}{\overset{H}{\underset{|}{\overset{|}{N}}}} \longrightarrow C_2H_5OH + N_2 + H_2O$$