Alcohols, Phenols & Ethers - 13

Preparation of Ethers (R-O-R') Alkoxyalkane

① By Dehydration of Alcohols:
with Conc H_2SO_4

$$CH_3-CH_2-OH \xrightarrow[140^\circ C\ (413K)]{Conc\ H_2SO_4} CH_3-CH_2-O-CH_2-CH_3$$

Note: At different Temperature, different product is formed.

$$CH_3-CH_2-OH \xrightarrow[170^\circ C\ (443K)]{Conc\ H_2SO_4} CH_2=CH_2$$

$$CH_3-CH_2-OH \xrightarrow[25^\circ C\ (298K)]{Conc\ H_2SO_4} CH_3-CH_2-O-SO_3H$$

$$CH_3-CH_2-OH \xrightarrow[0^\circ C\ (273K)]{Conc\ H_2SO_4} \left[CH_3-CH_2-\overset{+}{O}(H)-H\right] SO_3H^{\ominus}$$

All given Temperatures are for ethanol. For higher alcohols lower Temp is required

→ Proceeds through SN^2 Mechanism
* No carbocation * Attack from rear side
* Less steric Carbon * $1^\circ > 2^\circ > 3^\circ$

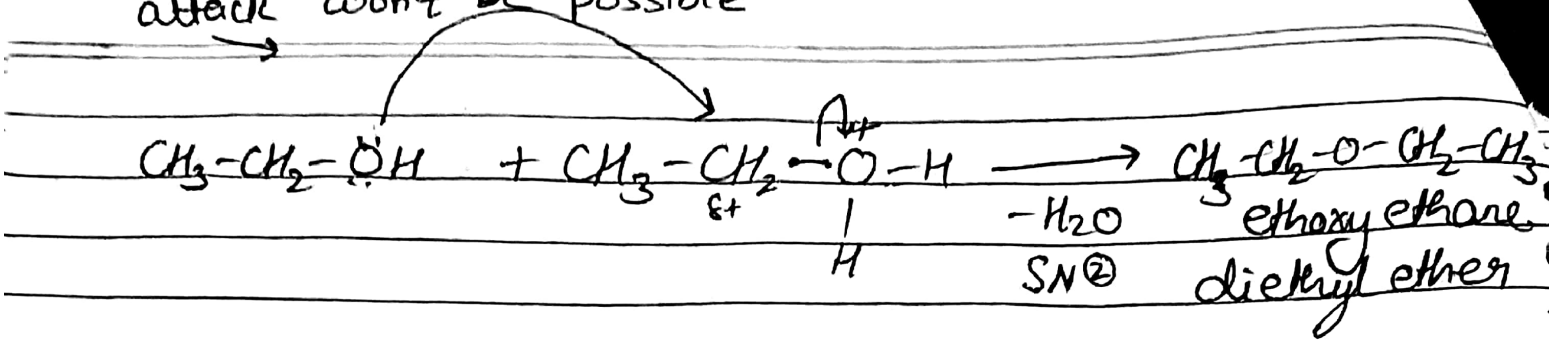
Mechanism:

$$CH_3-CH_2-\ddot{O}H \xrightarrow[Conc\ H_2SO_4]{H^+} CH_3-CH_2-\overset{+}{O}(H)-H$$

443K

Protonated alcohol

Alcohol should be 1°, as in case of 2° or 3° there will steric hinderance (crowding) & this attack won't be possible



Remember

① CH_3-CH_2-OH

- Conc H_2SO_4, 140°C (413K) → $CH_3-CH_2-O-CH_2-CH_3$ ethoxyethane
- Conc H_2SO_4, 170°C (443K) → $CH_2=CH_2$ ethene

② with Al_2O_3

CH_3-CH_2-OH

- Al_2O_3, 250°C → $CH_3-CH_2-O-CH_2-CH_3$
- Al_2O_3, 350°C → $CH_2=CH_2$

② By Williamson Synthesis:

$$R_1X + R_2\bar{O}\overset{+}{N}a \xrightarrow[\text{ether}]{\text{dry}} R_1-O-R_2 + NaX$$

alkyl halide — Sodium alkoxide

$$CH_3Br + C_2H_5\bar{O}\overset{+}{N}a \xrightarrow[\text{ether}]{\text{dry}} CH_3-O-C_2H_5 + NaBr$$

This reaction also proceeds through $SN^{②}$ Mechanism

Mechanism:

$$C_2H_5\overset{+}{O}Na \longrightarrow \underset{\text{(Nucleophile)}}{C_2H_5\bar{O}} + \overset{+}{Na}$$

$$C_2H_5\bar{O} + \underset{\delta+}{CH_3}-\overset{\delta-}{Br} \longrightarrow C_2H_5-O-CH_3 + Br^{\ominus}$$

Note: Alkyl halide should be primary (1°)

In case of 2° or 3° alkyl halide, there will be steric hinderance & hence this attack of $R\bar{O}$ is difficult.

$$CH_3-I + CH_3\overset{+}{O}Na \xrightarrow[\text{ether}]{\text{dry}} CH_3-O-CH_3 + NaI$$

$$\underset{\text{alkyl halide}}{A} + \underset{\text{Sodium alkoxide}}{B} \xrightarrow[\text{ether}]{\text{dry}} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O-CH_3$$

Find A & B.

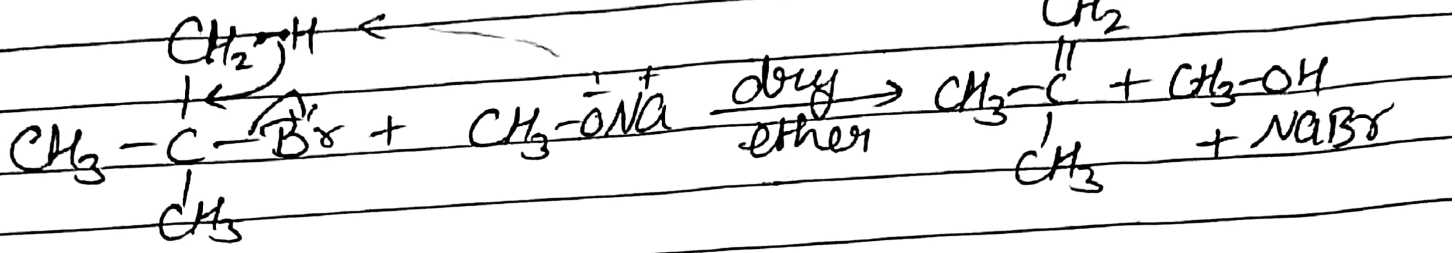
A → Should be 1°

$$CH_3-Br + CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-ONa \longrightarrow \checkmark$$

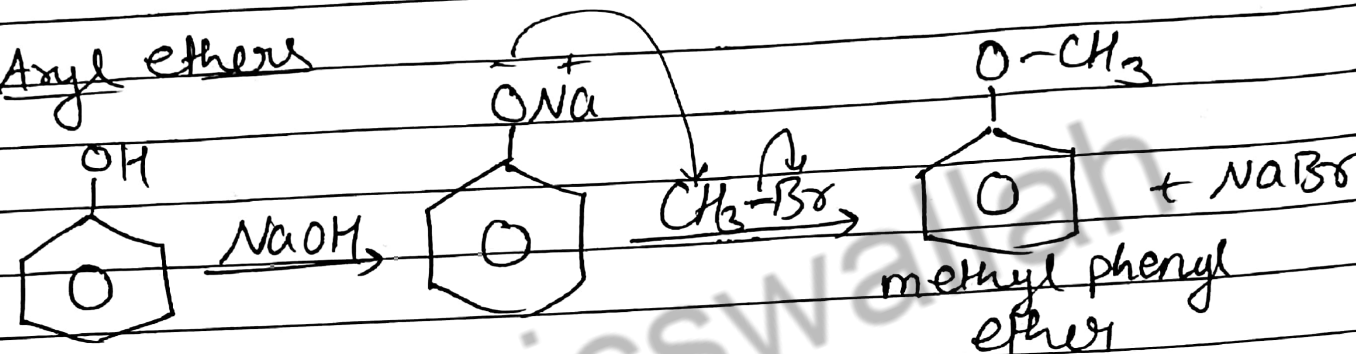
B

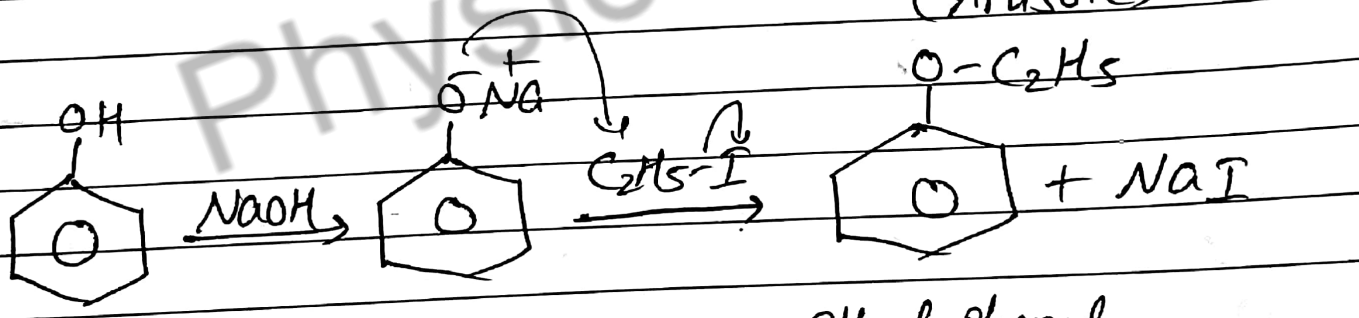
if $CH_3-ONa + CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br \xrightarrow{X}$ Elimination occurs. (next page)

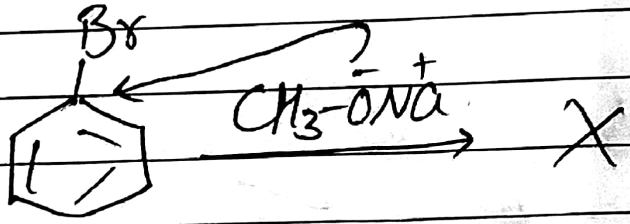
In case we take 3° Alkyl halide, elimination occurs forming alkene.



Aryl ethers







→ Aryl halides do not show SN② due to partial double bond character at C—Br