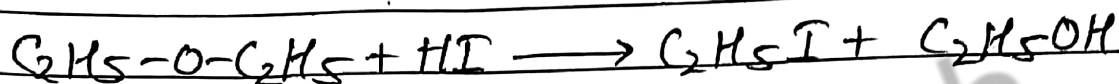
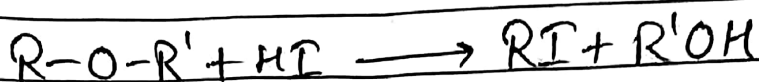


Alcohols, Phenols & Ethers - 14

Properties of Ethers (R-O-R')

① Reaction due to cleavage of C-O bond in Ethers

i) with hydroiodic acid.

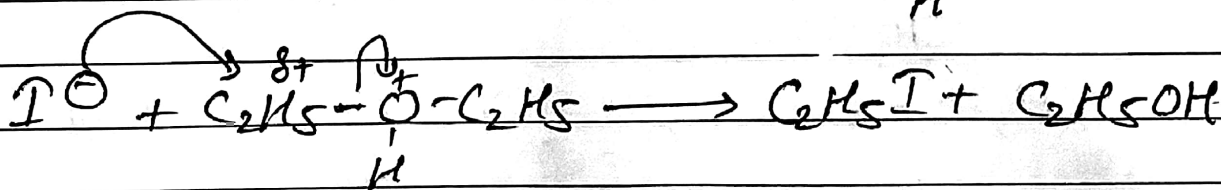
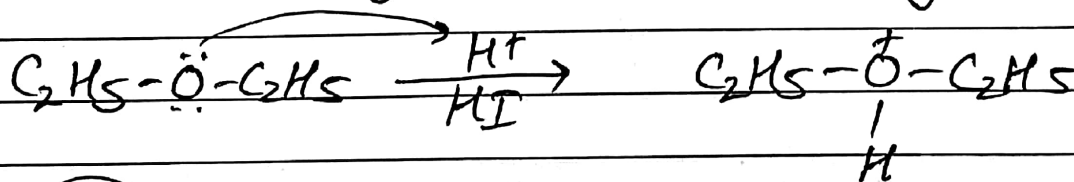


Mechanism \rightarrow occurs by both $SN^①$ & $SN^②$ Mechanism

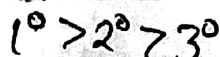
If both alkyl groups are primary $\rightarrow SN^②$

If any one of the alkyl group is tertiary $\rightarrow SN^①$

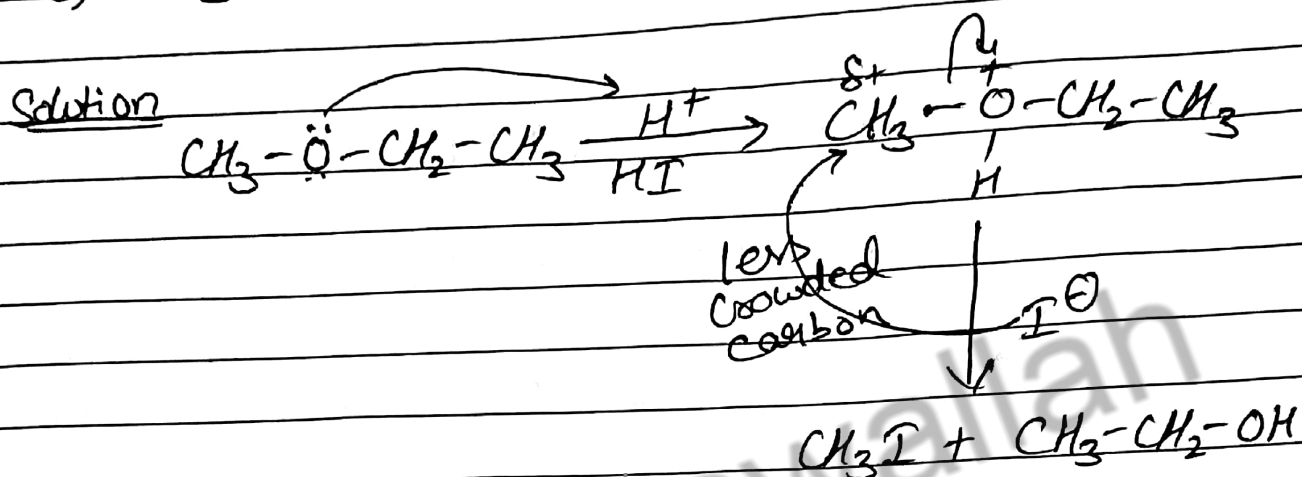
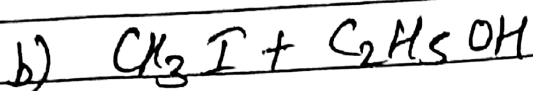
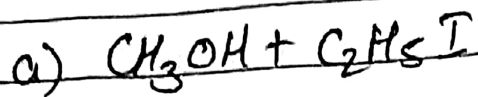
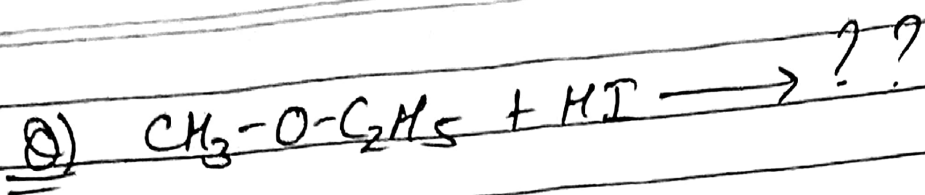
Case I: Both alkyl groups are primary $SN^②$



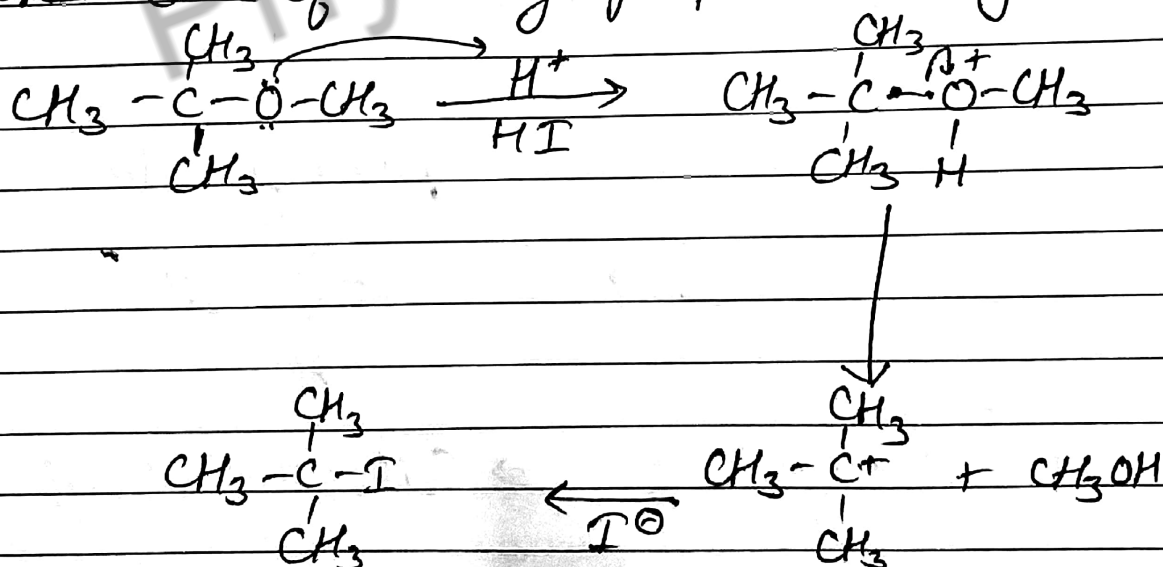
In $SN^② \rightarrow$ i) Attack occurs on less crowded carbon
(less steric hindrance)



ii) There is NO carbocation formed



Case II: One of the alkyl group is tertiary $\text{S}_\text{N}1$



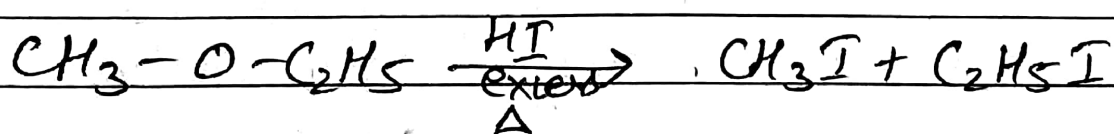
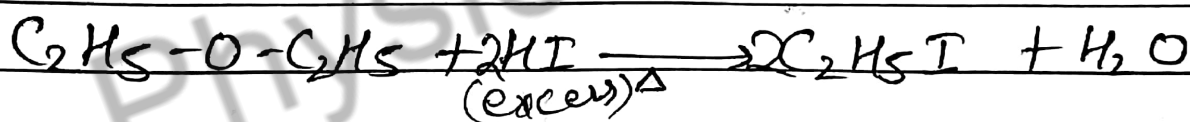
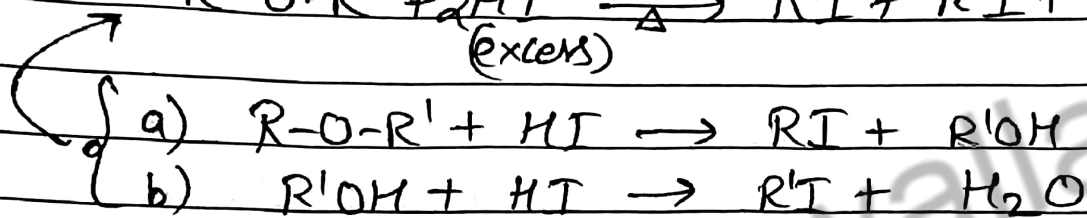
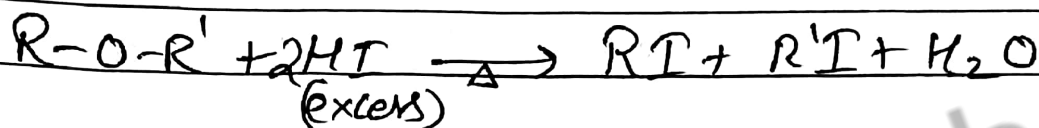
In $\text{S}_\text{N}1 \rightarrow$ Carbocation is formed & attack occurs
on more stable Carbocation
 $3^\circ > 2^\circ > 1^\circ$

If there is any secondary alkyl group, then look for other hints like solvent.

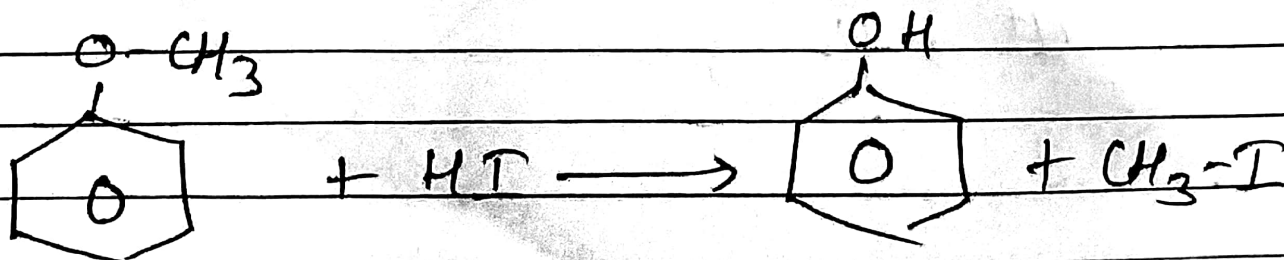
Polar protic solvent ($\text{H}_2\text{O} / \text{C}_2\text{H}_5\text{OH}$) $\rightarrow \text{SN}^{\textcircled{1}}$

Polar aprotic solvent ($\text{CH}_3-\overset{\text{O}}{\underset{\text{||}}{\text{C}}}-\text{CH}_3$) $\rightarrow \text{SN}^{\textcircled{2}}$

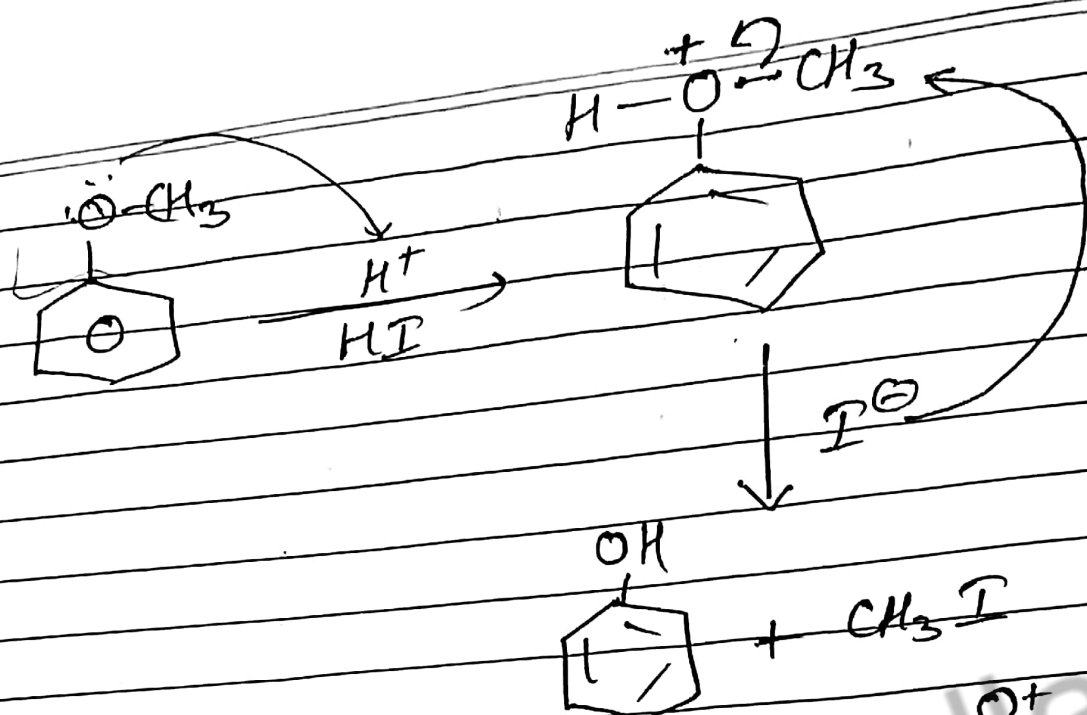
If HI is in excess & mixture is heated, then the alcohol so formed also converts to alkyl halide



In case of Alkyl Aryl ethers, Phenol and alkyl halide are formed. Phenol never changes to $\text{Ph}-\text{I}$ even on addition of excess HI

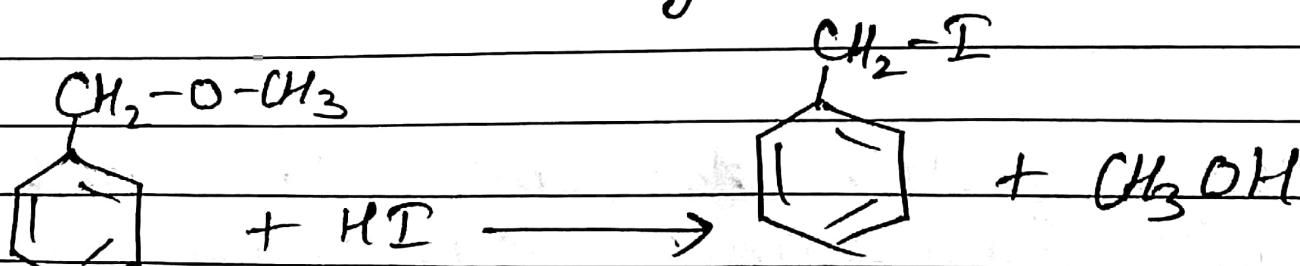


Anisole



As in the Intermediate the $\text{C}-\text{O}^+$ bond has partial double bond character due to Resonance & is difficult to break when compared to $\text{C}-\text{O}-\text{CH}_3$ bond.

In case of benzyl alkyl ethers, S_N1 is followed due to highly Resonance stabilised benzyl carbocation



② Reactions due to benzene Ring of Aryl ethers

$\Rightarrow E^+$ substitution



$-OR$ group increases e^- density in benzene Ring due to +M effect & thus Activate Benzene Ring for E^+ substitution

e^- density Increases more at ortho & para position, thus incoming E^+ attacks at ortho & para position

