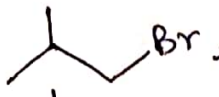
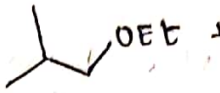
Williamson's Ether Synthesis

It is a widely used method for ether synthesis both symmetrical & asymmetrical.

Let us understand using few examples:-

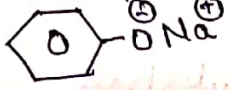
(1)  + EtO^-Na^+ ⟶  + $NaBr^-$ → leaving grp

alkyl halide (isobutyl bromide) — Nucleophile Sodium ethoxide — (ethyl isobutyl ether)

Order of Good leaving grp:- $I^- > Br^- > Cl^- > F^-$

⇒ the rxn proceeds via S_N2 reaction

⇒ the alkyl halide is a primary alkyl halide i.e. Unhindered

(2) $CH_3CH_2CH_2Br$ +  ⟶ $CH_3CH_2CH_2-O-C_6H_5 + Br^-$

Ethyl bromide — Sodium phenoxide

(3)  + $CH_3O^-Na^+$ ⟶ ✗ Ether syn not possible

aryl halide — nucleophile

C–Br bond is difficult to cleave.

sp^2

Rxn (3) shows the limitation of the synthesis

If you want to prepare ~~aromatic ethers~~ ethers with aryl grps then you need to opt rxn (2) not (3)

(4) $CH_3-CH(CH_3)-Br$ + $NaO^-C(CH_3)_2CH_3$ ⟶ $CH_3-CH=CH_2$ + $CH_3-C(CH_3)_2-O^-H^+$

steric hinderance in nucleophile

Elimination pdt — Major

~~Not~~ Substitution — Minor

Reaction (4) shows the second limitation of ether synthesis.

Since alkyl halide is 2° & Nucleophile is sterically hindered so elimination is favoured at the place of substitution.

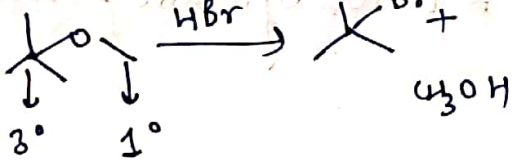
Cleavage of Ethers using HI

On heating with concentrated acids (HI especially) the ether linkages break to form alcohol or phenol & an alkyl halide

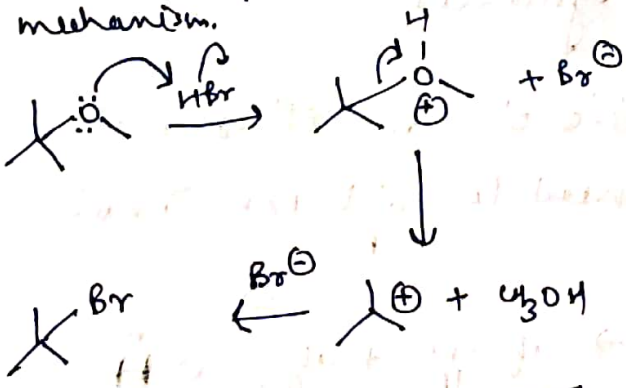
$$R-O-R' + HX \xrightarrow{373K} R-X + R'-OH$$

mechanism:- depending upon substrate

SN^1

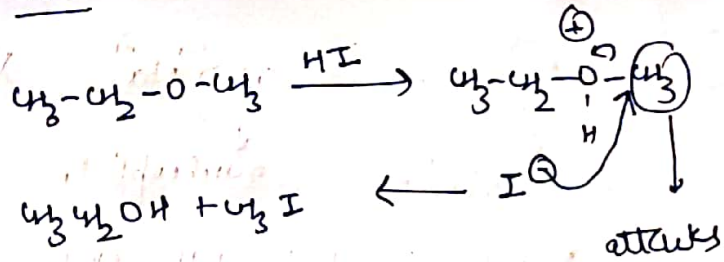
Ex 

If there is a 3° grp in ether the cleavage occurs by SN^1 mechanism.

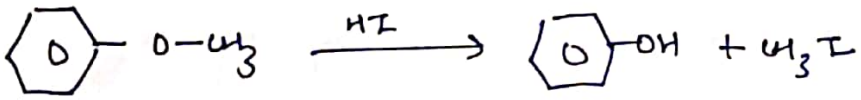


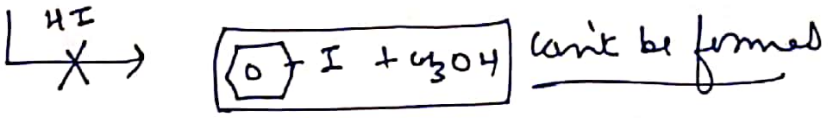
CH_3Br + KOH Not formed

SN^2

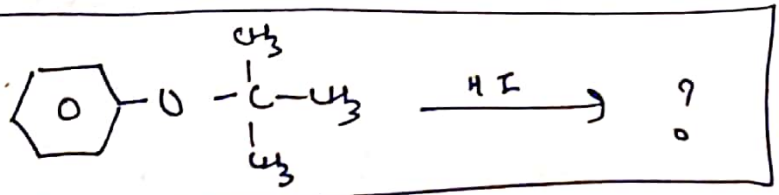


Special case





$\because$ C–O bond is a partial double bond in this compound



complete & watsapp.