• Points to remember in Alcohol

S_N1 reaction :

$$R\text{–}OH \xrightarrow{H^{\oplus}} R-\overset{\oplus}{O}H_2 \xrightarrow{-H_2O} \overset{\oplus}{R} \xrightarrow{X^{\ominus}} R - X(\text{R may rearrange})$$

Reactivity of HX : HI > HBr > HCl

Reactivity of ROH : allyl, benzyl > 3° > 2° > 1° (Carboocation)

e.g. CH_3CHCH_3 (OH) — Isopropyl alcohol $\xrightarrow[\text{or NaBr, } H_2SO_4]{\text{conc. HBr}}$ $\xrightarrow{\text{reflux}}$ CH_3CHCH_3 (Br) — Isopropyl bromide

S_N2 reaction :

$$ROH + PCl_5 \longrightarrow RCl + POCl_3$$
$$ROH + PCl_3 \longrightarrow RCl + H_3PO_3$$
$$ROH + SOCl_2 \xrightarrow{\text{Pyridine}}$$

Williamson's synthesis :

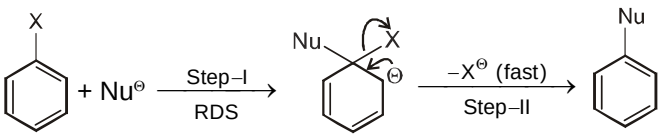
It is the reaction in which sodium or potassium alkoxide is heated with an alkyl halide (S_N2).

$$R_1O^- + R^2\text{–}X \rightleftharpoons R^{\delta-}_{1}O.....R^2.....X^{\delta-} \longrightarrow R^1OR^2 + X^-(g)$$

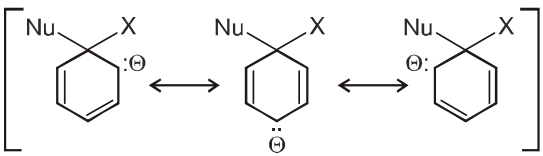
This method is particularly useful for preparing mixed ethers.

Nucleophilic Aromatic Substitution of aryl halides(S_N2Ar):

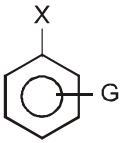
- An electron withdrawing group at ortho or para positions with respect to a good leaving groups are necessary conditions for S_N2Ar.



Intermediate ion is stabilized by resonance. and are stable salts called Meisenheimer salts.



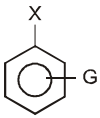
- A group that withdraws electrons tends to neutralize the negative charge of the ring and this dispersal of the charge stabilizes the carbanion.



G withdraws electrons : stabilizes carbanion, activates the Ar-S_N2 reaction.

($-\overset{+}{N}(CH_3)_3$, $-NO_2$, $-CN$, $-SO_3H$, $-COOH$, $-CHO$, $-COR$, $-X$)

- A group that releases electrons tends to intensify the negative charge, destabilizes the carbanion, and thus slows down reaction.



G ($-NH_2$, $-OH$, $-OR$, $-R$)releases electrons : destabilizes carbanion, deactivates the Ar-S_N2 reaction.

Element effect :

Reactivity order towards S_N2Ar with different halogens

Ar-F > Ar-Cl > Ar-Br > Ar-I