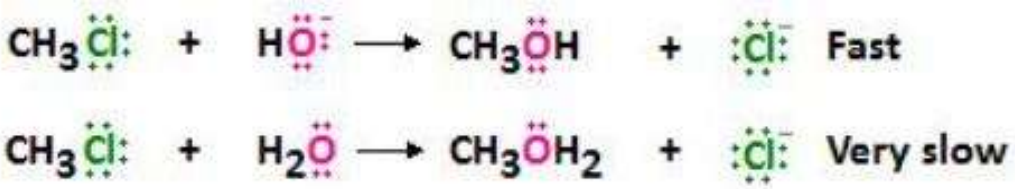
❑ Effect of Nucleophile on the Reaction Rate

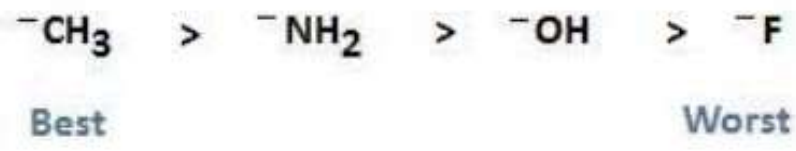
The strength of the nucleophile does not effect the reaction rate of S_N1 as the RDS does not involved the nucleophile. However in S_N2 the transition state involves the nucleophile. Greater the nucleophilicity or concentration of a nucleophile more rapid is the rate of S_N2 reaction.

Nucleophilicity depends on the following factors

❖ Anions are usually more reactive than neutrals



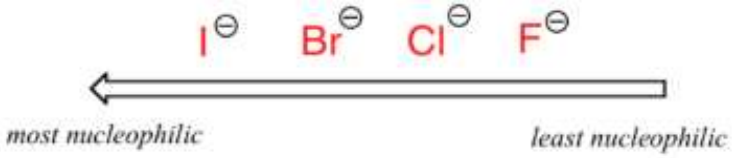
❖ When moving across a row nucleophilicity decrease from left to right.



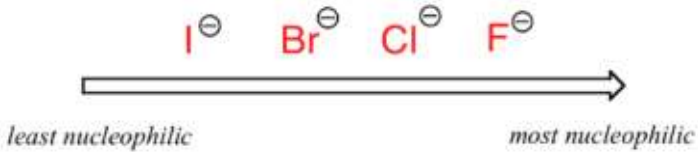
Due to increase of electronegativity

❖ Solvents and Nucleophilicity

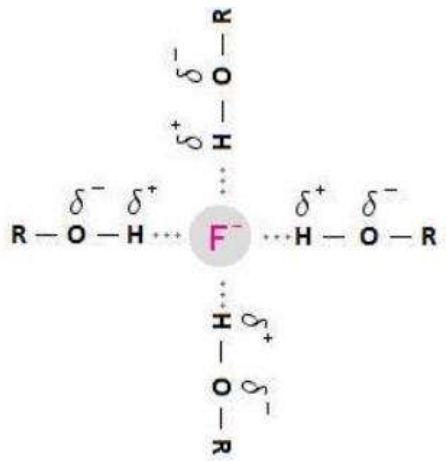
Along the column



Relative nucleophilicity in a protic solvent

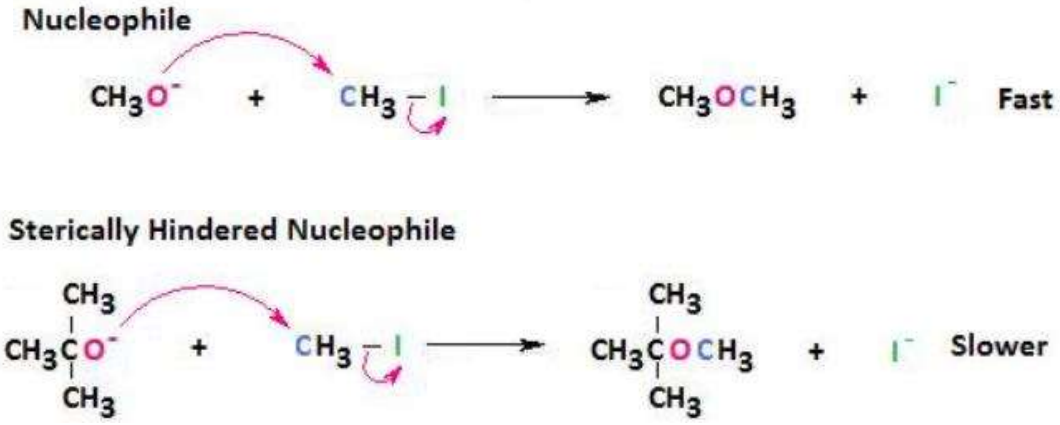


Relative nucleophilicity in a polar aprotic solvent



Smaller anions are heavily solvated than the larger anions making its electrons less avaliable

❖ Sterically Hindered Nucleophiles React More Slowly

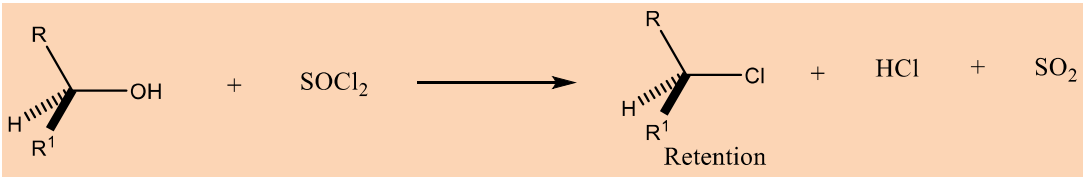


Difference between S_N2 and S_N1

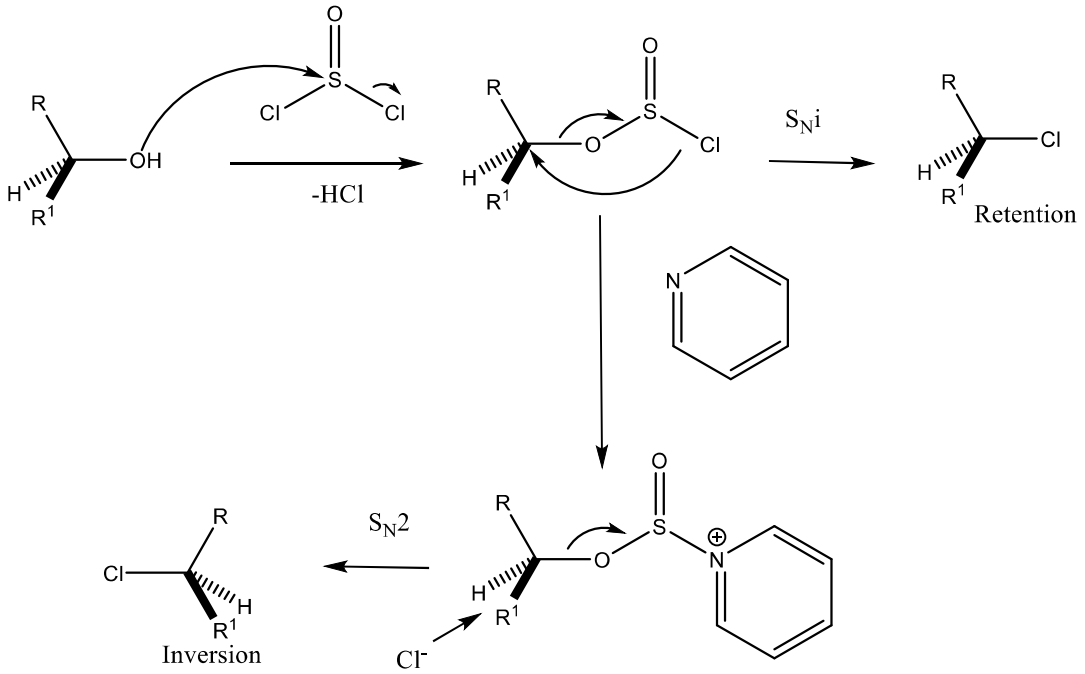
	S_N2	S_N1
Molecularity	Bimolecular	Unimolecular
Order	Second Order	First Order
Alkyl halide	$CH_3X > 1^o > 2^o > 3^o$	$CH_3X < 1^o < 2^o < 3^o$
Nucleophile	Strong	Not Important (usually weak)
Leaving Group	Good One	
Stereochemistry	Inversion	Inversion + Retention
Rearrangements	No	Yes

S_Ni Reactions (Substitution nucleophilic, internal)

S_Ni or Substitution Nucleophilic intramolecular stands for a specific but not often encountered nucleophilic aliphatic substitution reaction mechanism

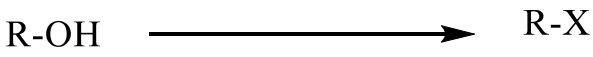


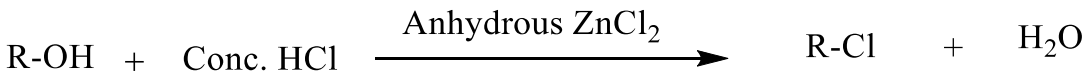
Mechanism



Preparation of alkyl halide

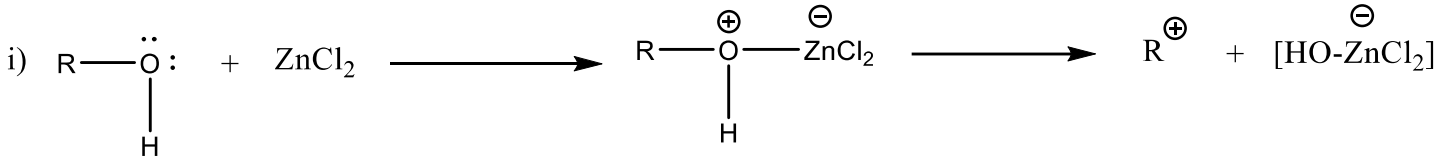
❑ *From alcohol*

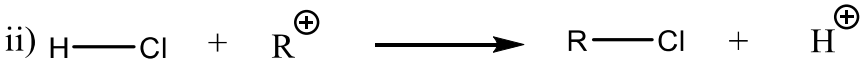


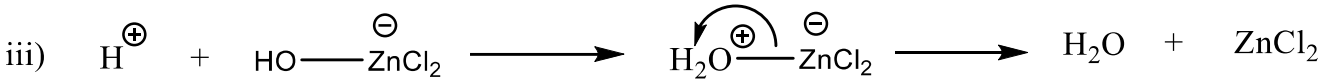


A mixture of **$ZnCl_2$** and Conc **HCl is known as Lucas reagent**

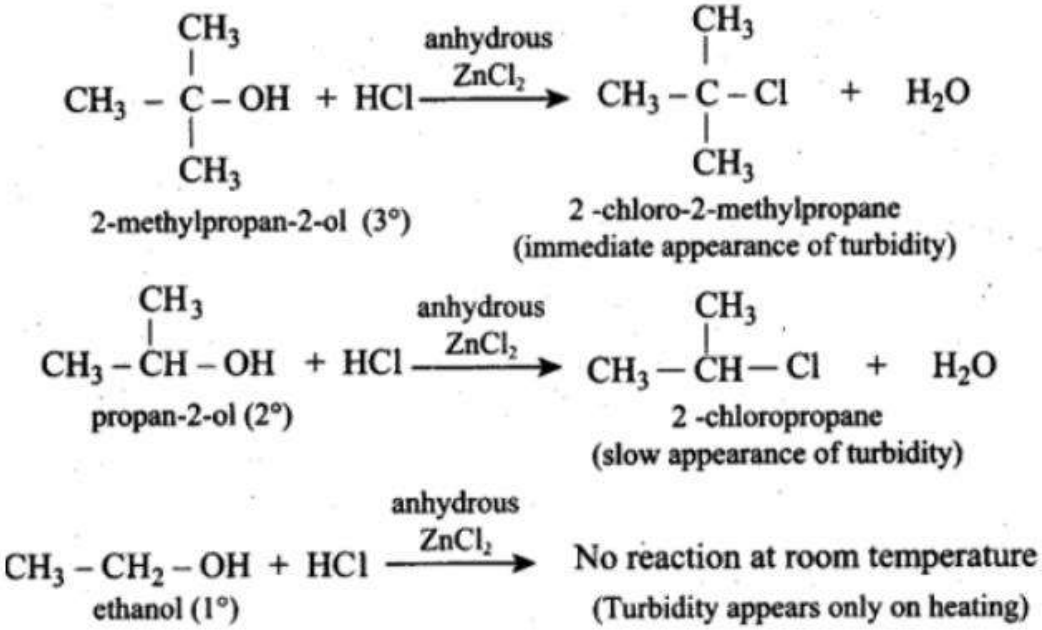
Mechanism







- *Reactivity order- $3^o > 2^o > 1^o$*
- *Lucas test is use to distinguish Primary, Secondary and Tertiary alcohols.*



- *Alkyl bromides can be obtained by heating alcohol with KBr in presence of excess of Conc. H_2SO_4 or by refluxing the alcohol with constant boiling HBr (40%) in presence of a little conc. sulphuric acid.*

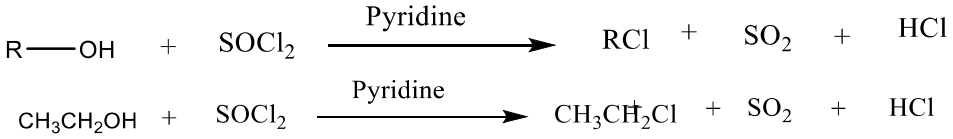
$$CH_3CH_2OH + HBr \xrightarrow[\Delta]{KBr/Conc.H_2SO_4} CH_3CH_2Br + KHSO_4 + H_2O$$

- *The mixture of KBr and conc. H_2SO_4 is not used in case of secondary and tertiary alcohols to prevent their dehydration.*

- *Alkyl halides may be obtained by refluxing alcohol with excess of 57% HI. These can also be obtained by heating alcohol with KI in presence of phosphoric acid.*

$$CH_3CH_2OH + HI \xrightarrow{Heat} CH_3CH_2I + H_2O$$

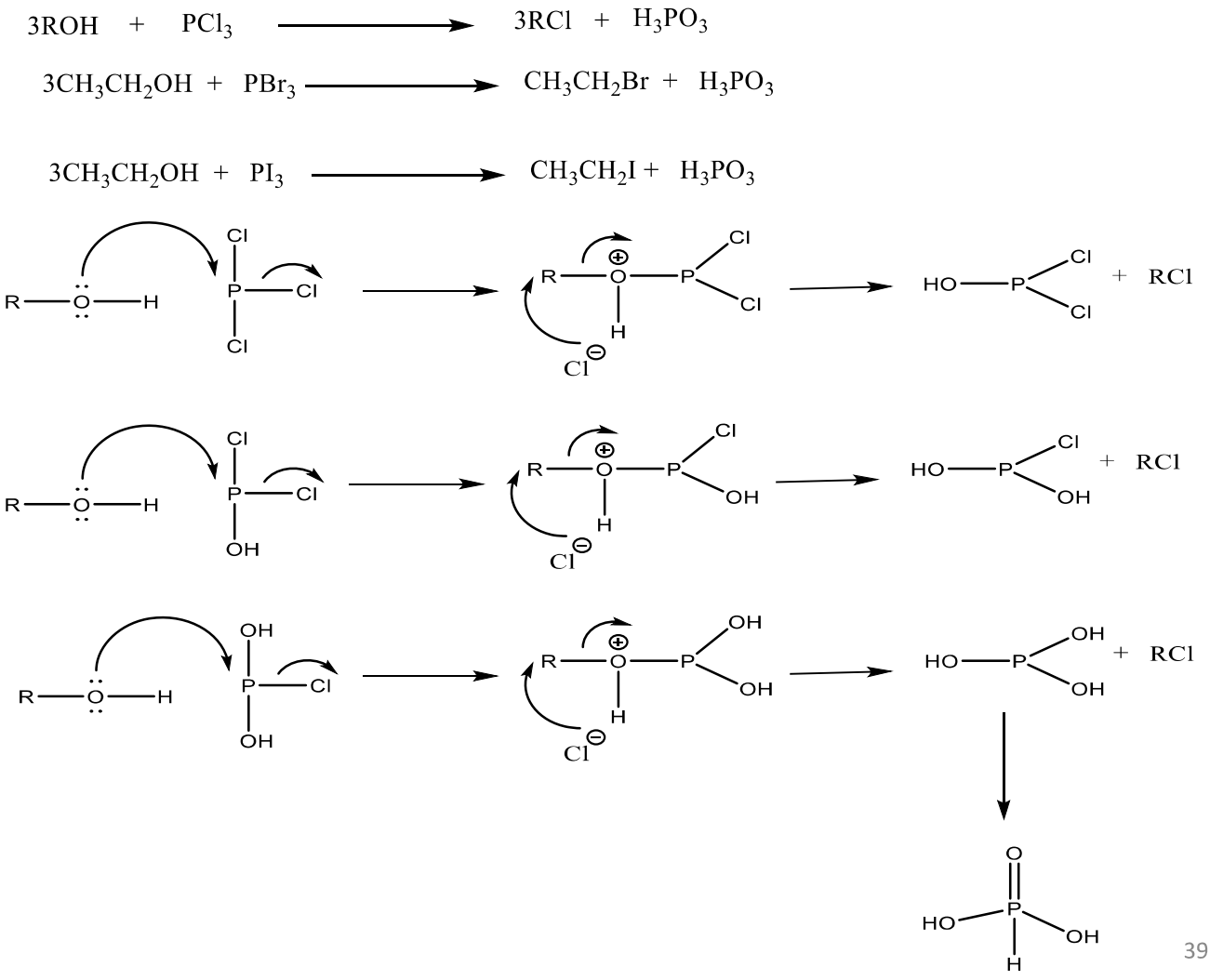
Reaction of alcohol with thionyl chloride (Drazen's Process)



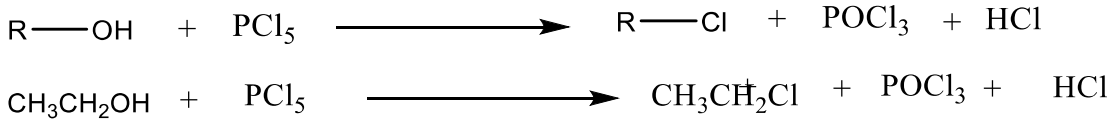
Mechanism

Already discussed

Reaction with Phosphorous trihalides



Reaction with phosphorous pentachloride



Mechanism