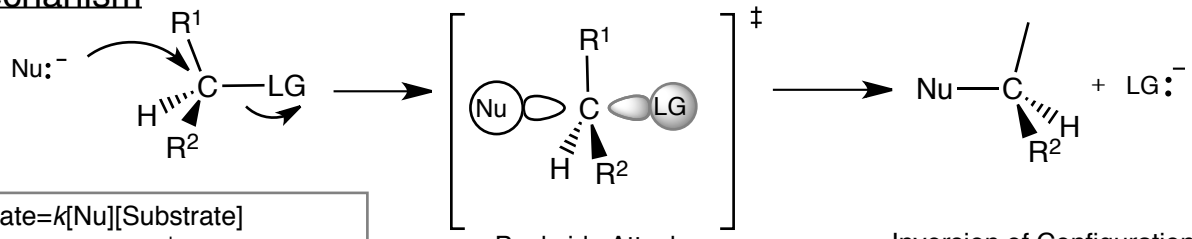
S_N1 and S_N2 mechanisms

S_N2 mechanism

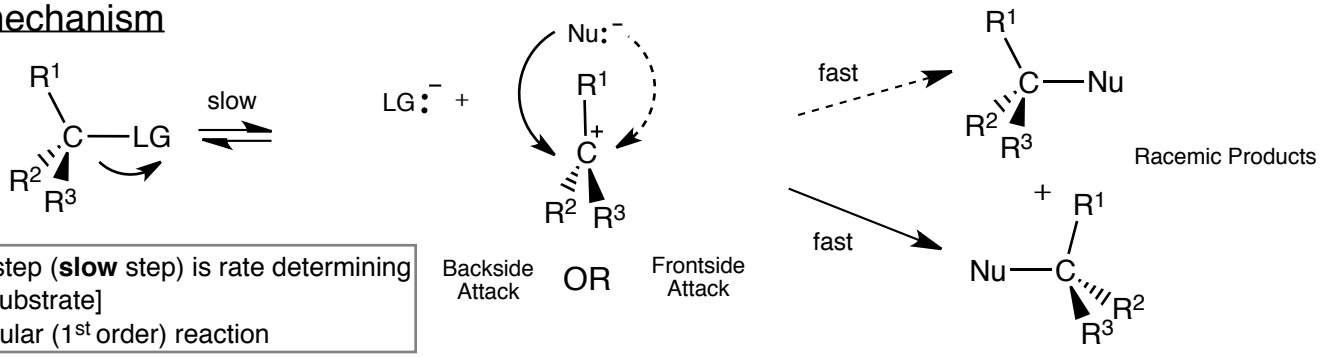


Rate=*k*[Nu][Substrate]
Bimolecular (2nd order) reaction

Backside Attack

Inversion of Configuration

S_N1 mechanism



The first step (**slow** step) is rate determining
Rate=*k*[Substrate]
Unimolecular (1st order) reaction

Backside Attack OR Frontside Attack

Nucleophiles

Excellent Nucleophiles: CN^- , HS^-, I^-
Good Nucleophiles: OH^-, Br^-, N_3^-, NH_3, NO_2^-
Fair Nucleophiles: Cl^-, CH_3COO^-, F^-, CH_3OH, H_2O

Negatively charged nucleophiles are more reactive than neutral nucleophiles:
Ex: ^-OH is a better nucleophile than H_2O

Nucleophilicities parallel basicities if the nucleophilic atom is the same size:
Ex: $RO^- > HO^- >> RCO_2^- > ROH > H_2O$

In protic solvents, larger atoms are better nucleophiles:

Nucleophilicity in polar **protic** solvents:
$I^- > Br^- > Cl^- > F^-$

Nucleophility in **aprotic** solvents:
$F^- > Cl^- > Br^- > I^-$

Leaving Group

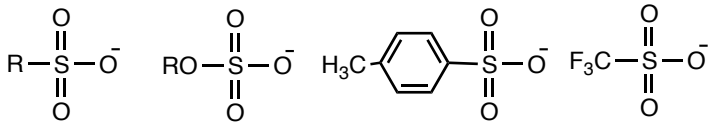
In general, weak bases make good leaving groups:

I^- > Br^- > Cl^- > F^-

weak base
good leaving group

strong base
poor leaving group

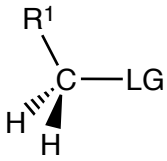
Alkanesulfonate, alkylsulfate and triflate ions also make good leaving groups:



alkanesulfonate ion | alkyl sulfate ion | tosylate ion | triflate ion

Substrates

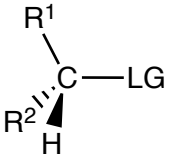
1°



Always S_N2

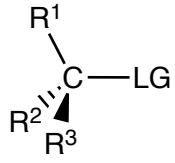
(Due to less sterically hindered substrates and instability of primary carbocations)

2°



- S_N2 if strong Nu and polar aprotic solvent
- S_N1 if weak Nu and polar protic solvent

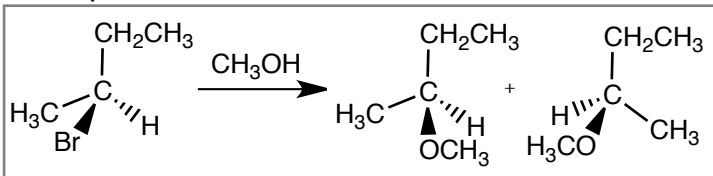
3°



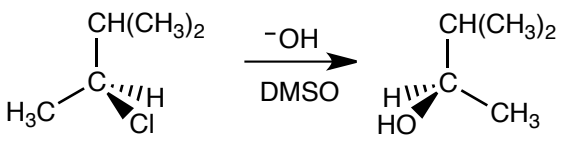
Always S_N1

(*Due to stability of tertiary carbocations and steric hindrance of backside attack*)

Examples



Since it is a *weak nucleophile* and a p*rotic solvent*, this reaction will be **S_N1** with a *racemic* product



Since it is a *strong nucleophile* and an ap*rotic solvent*, this reaction will be **S_N2** with an *inversion of configuration*