

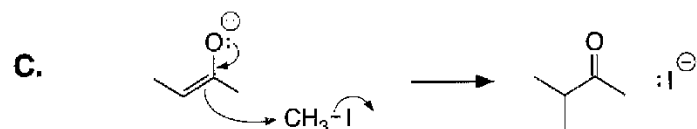
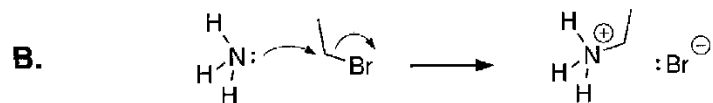
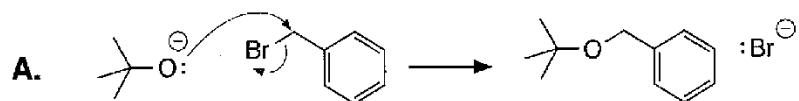
STUDY OF REACTION MECHANISM: SUBSTITUTION REACTIONS



Types of Nucleophilic Substitution Reactions



NUCLEOPHILIC SUBSTITUTION BIMOLECULAR REACTIONS (S_N2)



1. Kinetic Evidence

$$\text{Rate} = k[\text{RX}][\text{Y}]$$

$$\text{Rate} = k[\text{RX}] \quad \text{If nucleophile is in excess e.g. solvent (Pseudo-First Order Reaction)}$$



$$\text{rate} = k_2[\text{MeSNa}][\text{MeI}]$$

If [MeSNa] is constant, the equation becomes

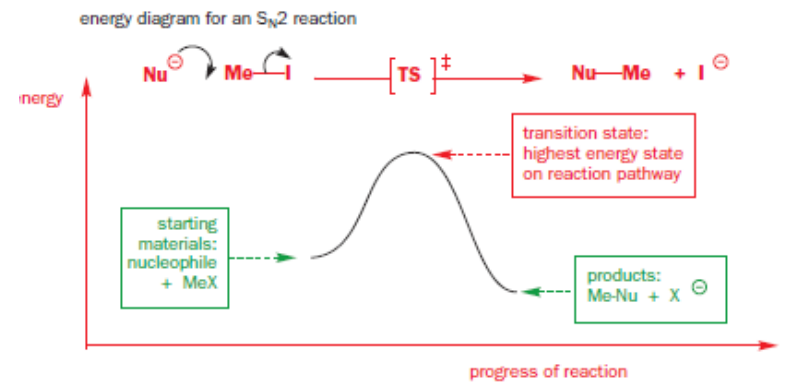
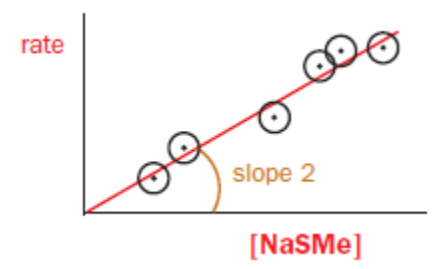
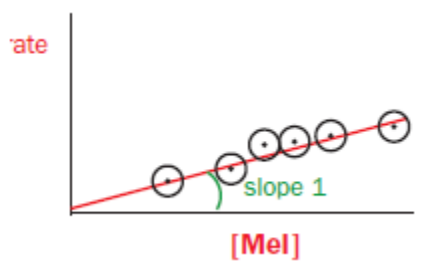
$$\text{rate} = k_a[\text{MeI}] \quad \text{where } k_a = k_2[\text{MeSNa}]$$

If [MeI] is constant, the equation becomes

$$\text{rate} = k_b[\text{MeSNa}] \quad \text{where } k_b = k_2[\text{MeI}]$$

If you examine the graphs you will see that the slopes are different because

$$\text{slope 1} = k_a = k_2[\text{MeSNa}], \quad \text{but } \text{slope 2} = k_b = k_2[\text{MeI}]$$

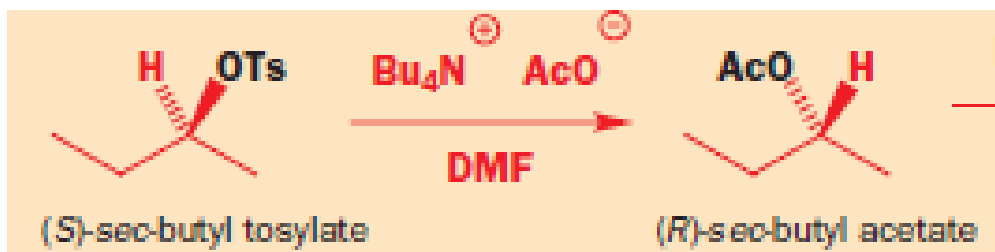
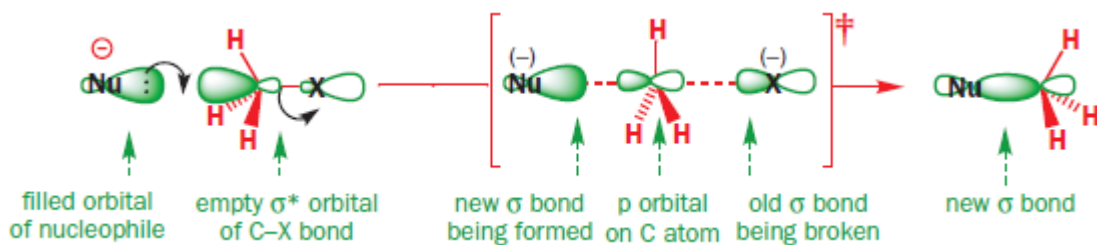
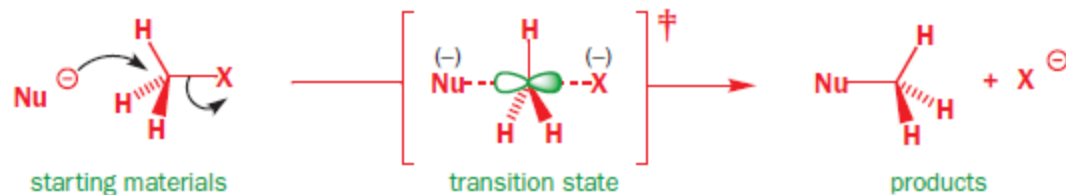


The rate of S_N2 reaction depends upon

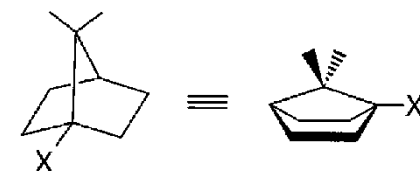
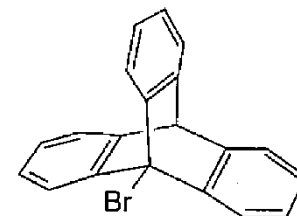
- (i) The nucleophile
- (ii) The carbon skeleton (Structure of substrate)
- (iii) The leaving group

2. Stereochemical Evidence

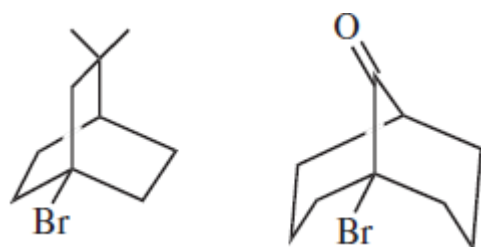
- Inversion of Configuration occurs*



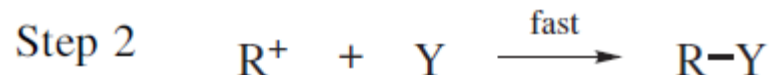
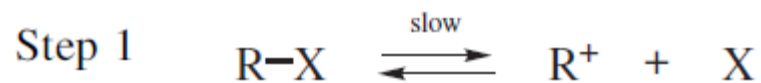
Reactants with impossible S_N2 approach trajectories



3. S_N2 reactions cannot occur at bridgehead

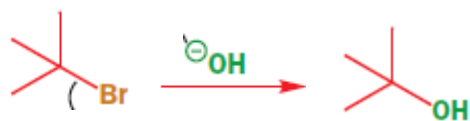


NUCLEOPHILIC SUBSTITUTION UNIMOLECULAR REACTIONS (S_N1)



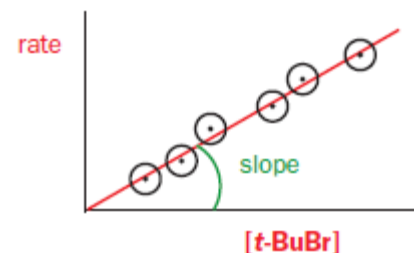
1. Kinetic Evidence

$$\text{Rate} = k[\text{RX}]$$

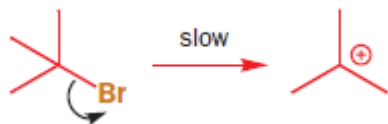


$$\text{rate} = k_1[\text{t-BuBr}]$$

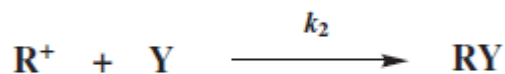
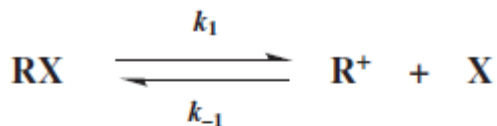
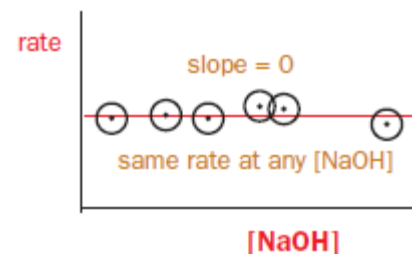
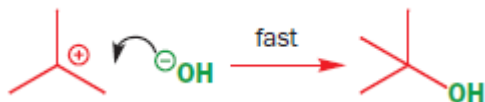
The rate of S_N1 reaction depends upon
 (i) The carbon skeleton (Structure of substrate)
 (ii) The leaving group



Step-I



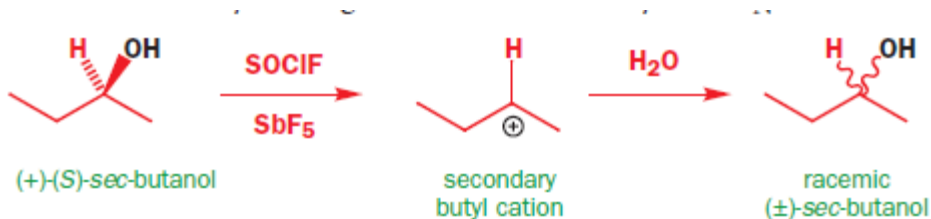
Step-II



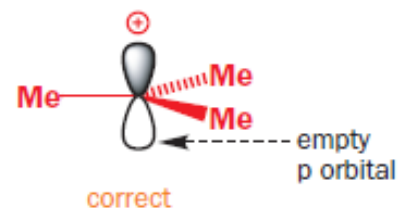
$$\text{Rate} = \frac{k_1 k_2 [\text{RX}][\text{Y}]}{k_{-1} [\text{X}] + k_2 [\text{Y}]}$$

- If other than first step is the slow step then S_N1 reactions may show complex kinetics.
- The complex kinetics can be treated by Steady State Approximation for example.

2. Stereochemical Evidence

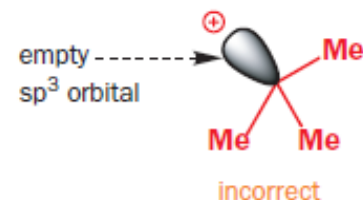


planar structure for the t-butyl cation

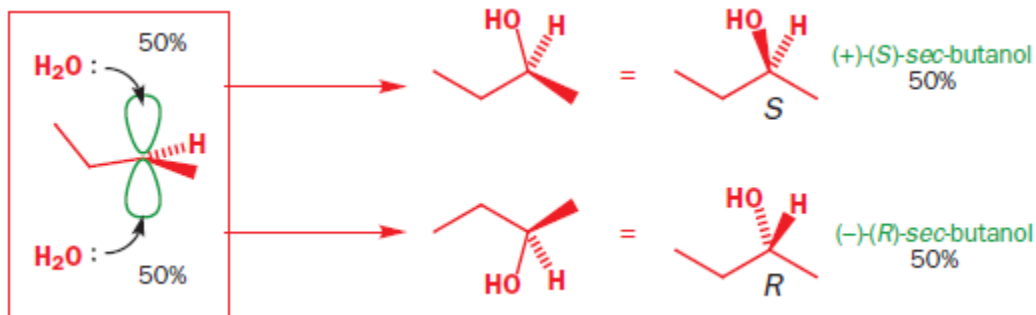


less repulsion between bonding pairs of electrons

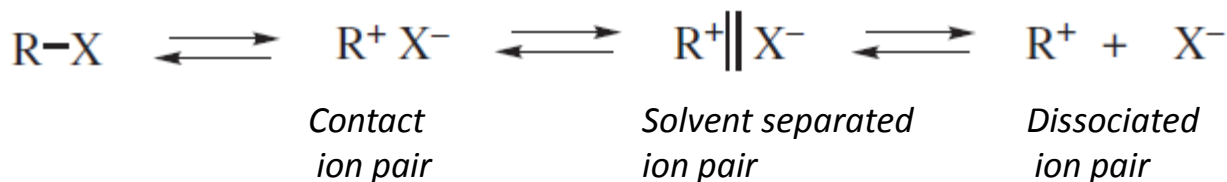
tetrahedral structure for the t-butyl cation



more repulsion between bonding pairs of electrons



Ion Pairs in S_N1 Mechanism



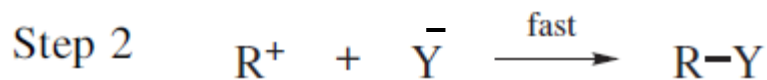
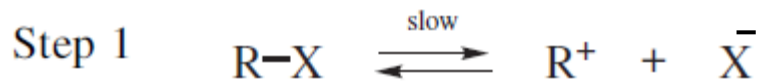
- Complete Racemization to Partial Racemization

3. S_N1 reactions cannot occur at bridgehead



- *It is because carbocation is sp²-hybridized and therefore must be planar. However, planarity cannot be achieved at bridgehead*

4. Mass Law Effect or Common Ion Effect

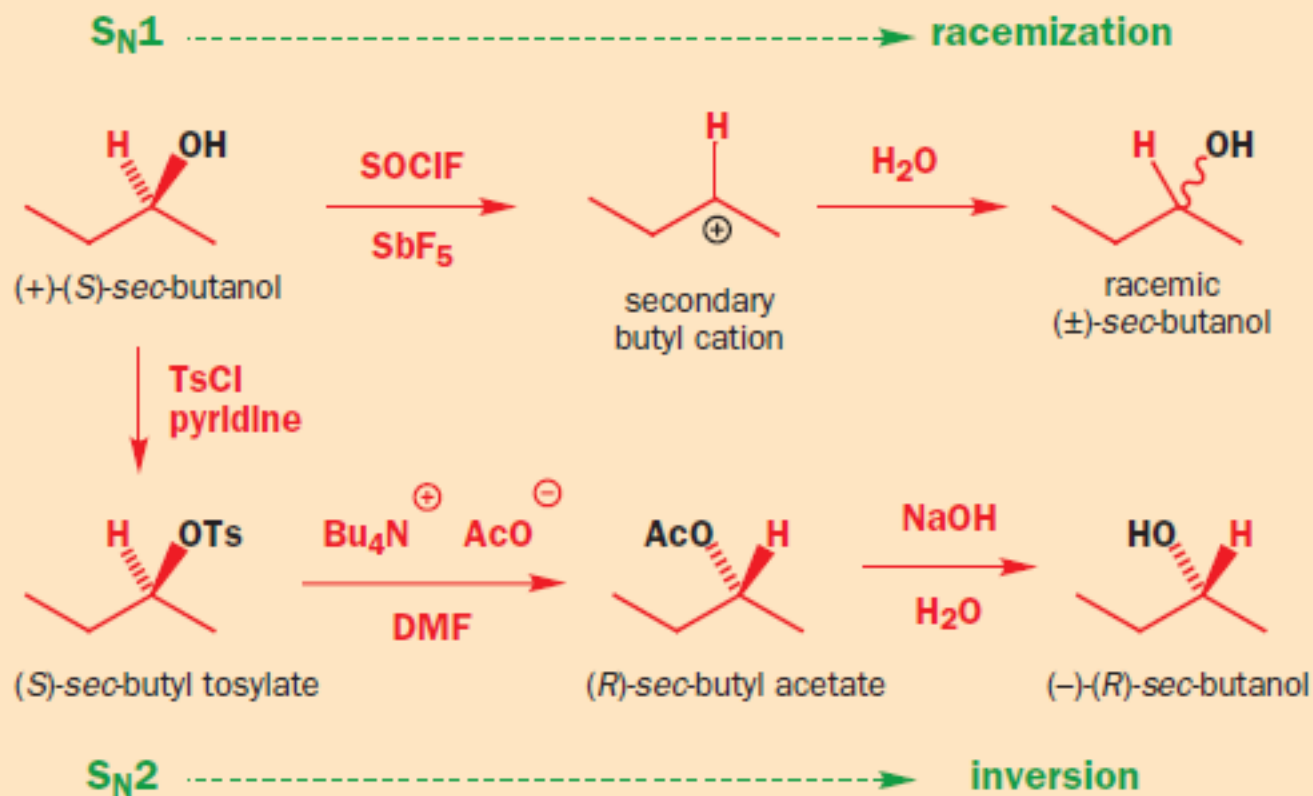


- *Adding a salt having common ion, X⁻, would push the first step in backward direction.*
- *Hence, the rate of S_N1 reaction will decrease.*

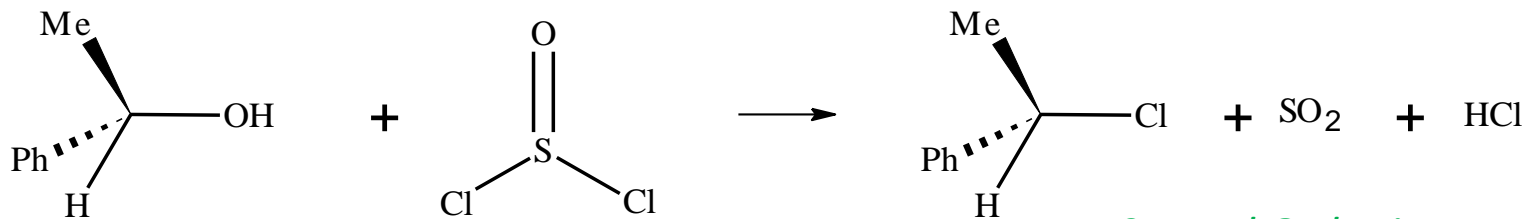
5. Salt Effect

- *Since polar ions are produced in this reaction, therefore, increase in polarity of solvent increases the rate of reaction.*
- *The ionic strength or the polarity of the medium can be increased by adding salts that don't have common ion.*

- The S_N2 reaction goes with inversion of configuration at the carbon atom under attack but the S_N1 reaction generally goes with racemization

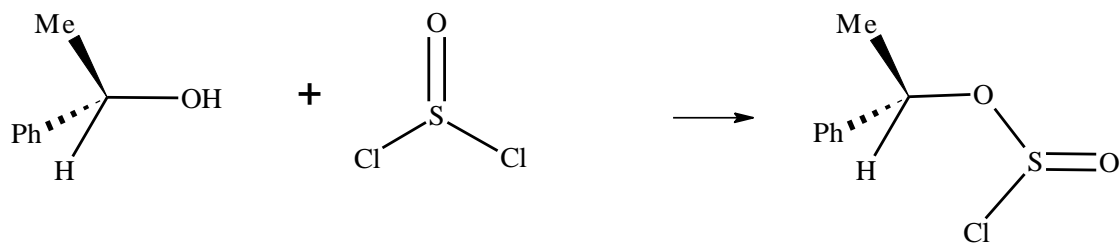


NUCLEOPHILIC SUBSTITUTION INTERNAL REACTIONS (S_Ni)

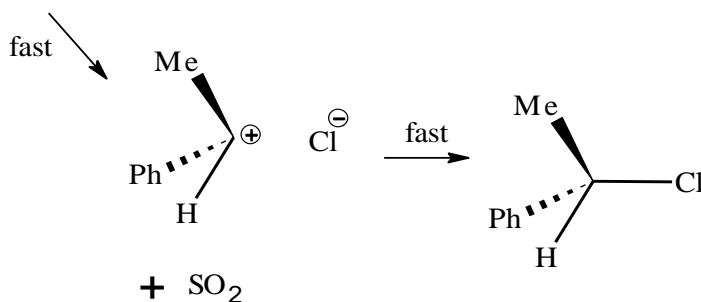
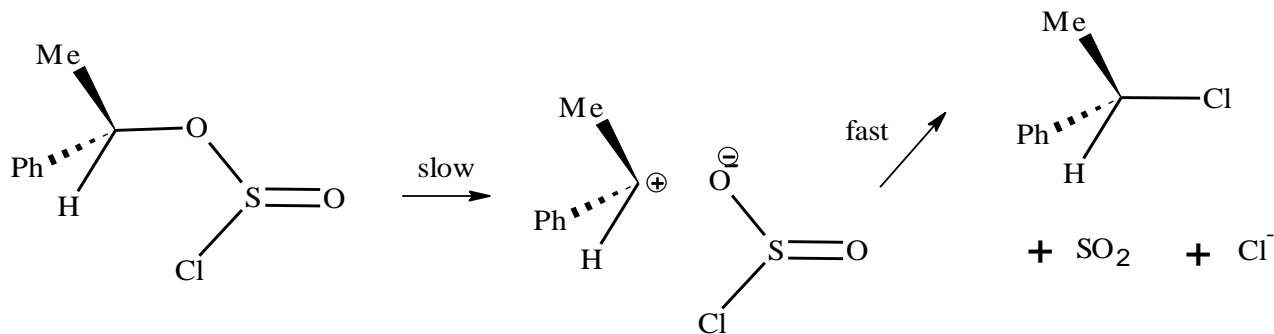


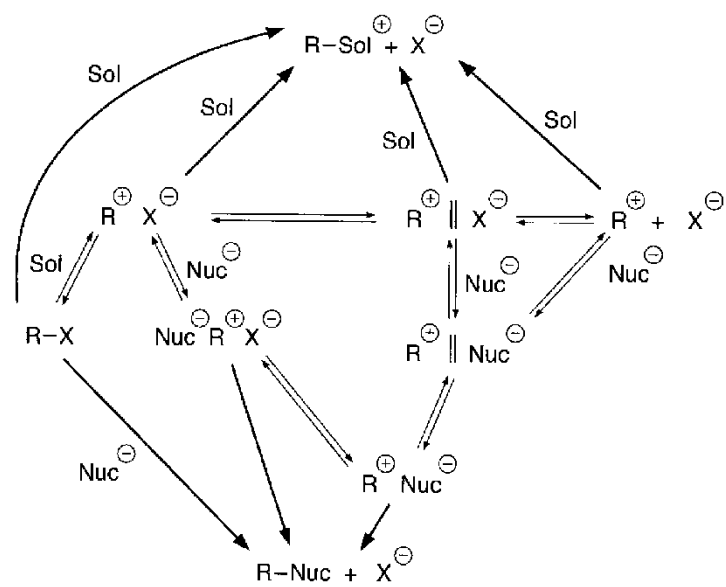
- *Second Order i.e. Rate = $k(\text{ROH})[\text{SOCl}_2]$*
- *Retention of Configuration*

• *The Mechanism*

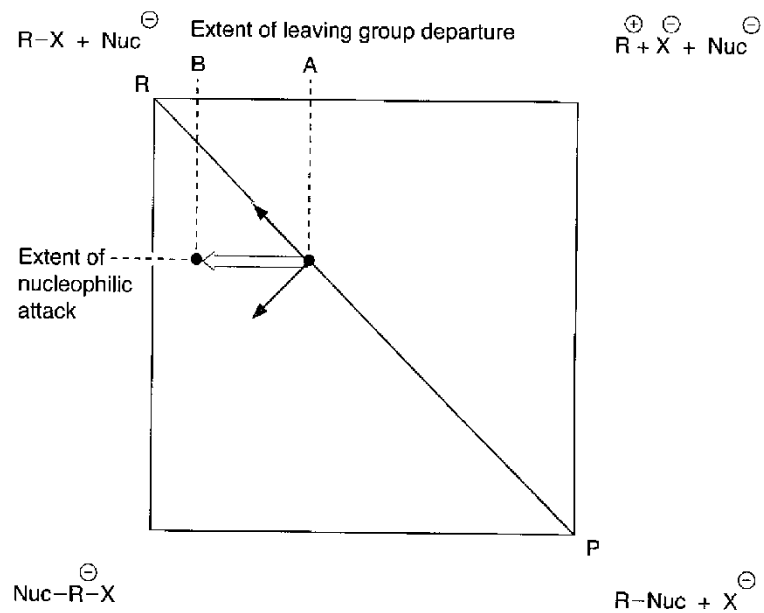


- *Reaction of ROH and SOCl_2 is second order*
- *Simple heating of ROSOCl is first order*

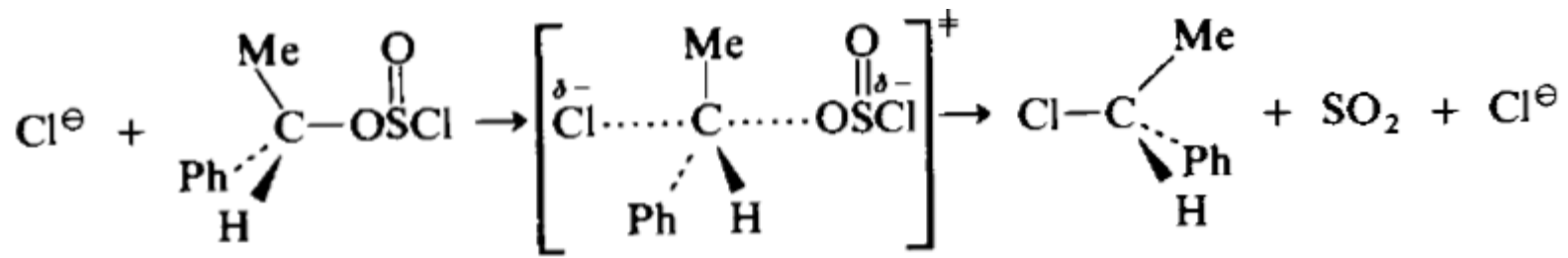




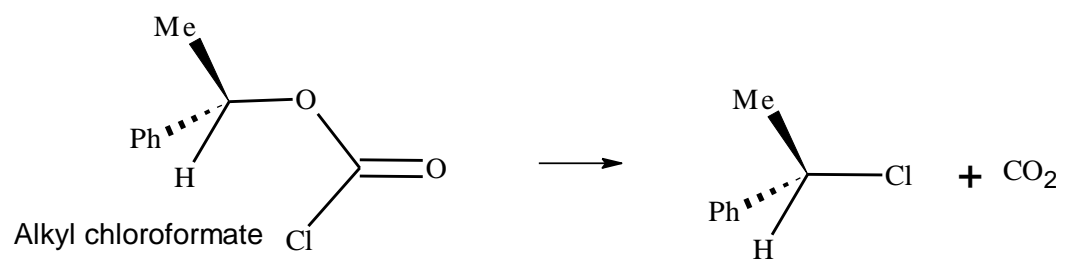
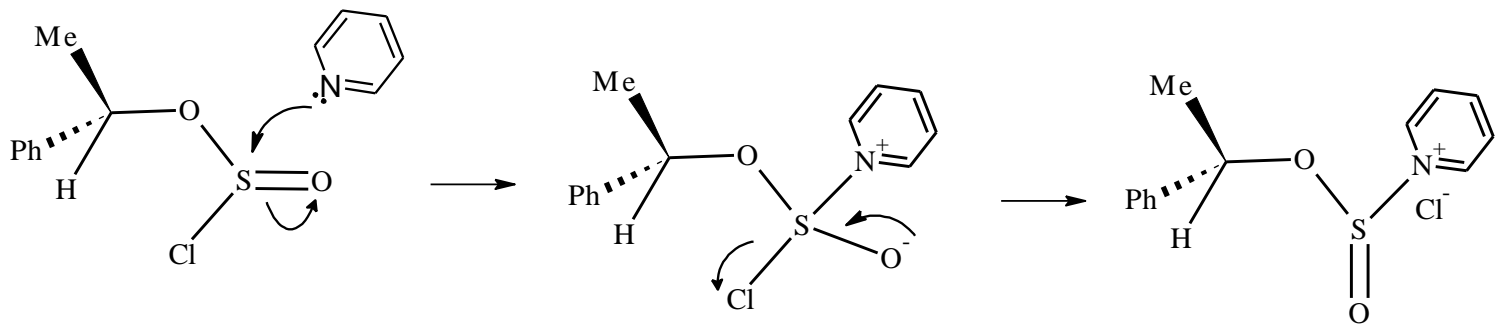
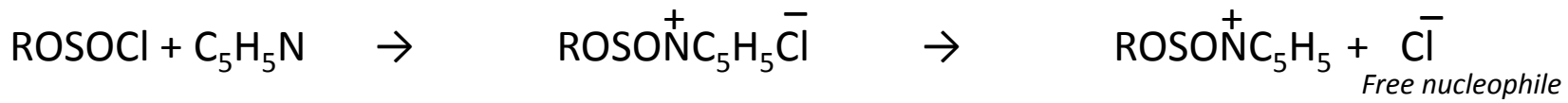
A variety of pathways for S_N2 and S_N1 reactions.



• Adding pyridine shifts the reaction to normal S_N2 mechanism.

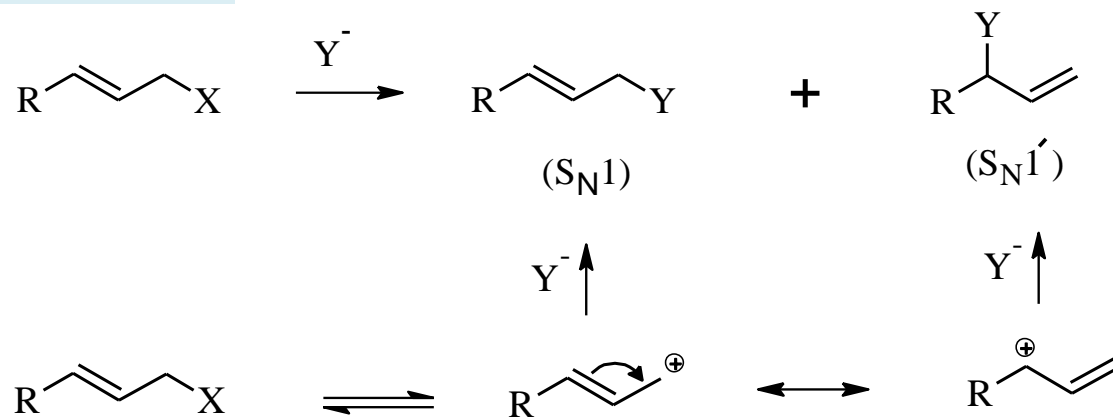


- Second Order i.e. Rate = $k(\text{ROH})[\text{SOCl}_2]$
- Inversion of Configuration

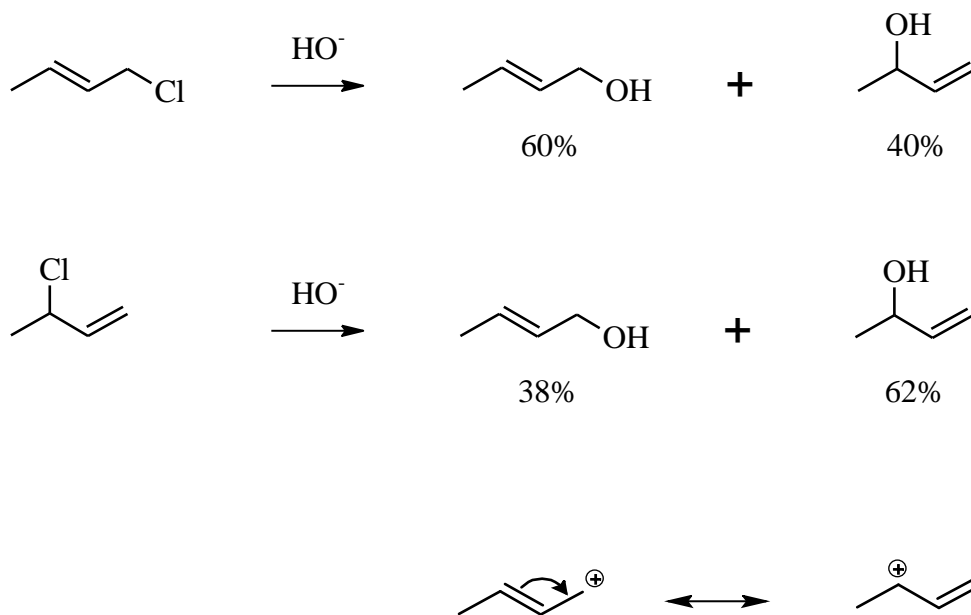


Nucleophilic Substitution at an Allylic Carbon: Allylic Rearrangements

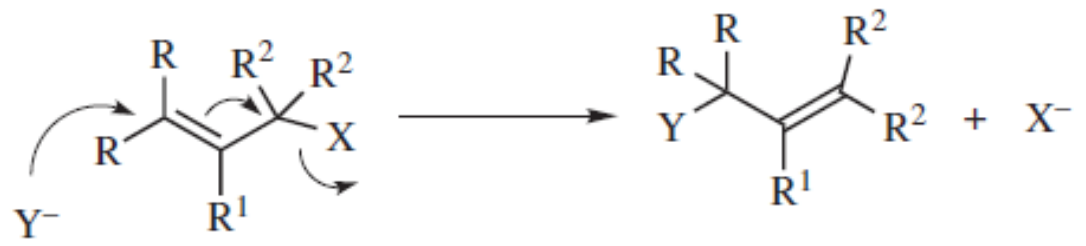
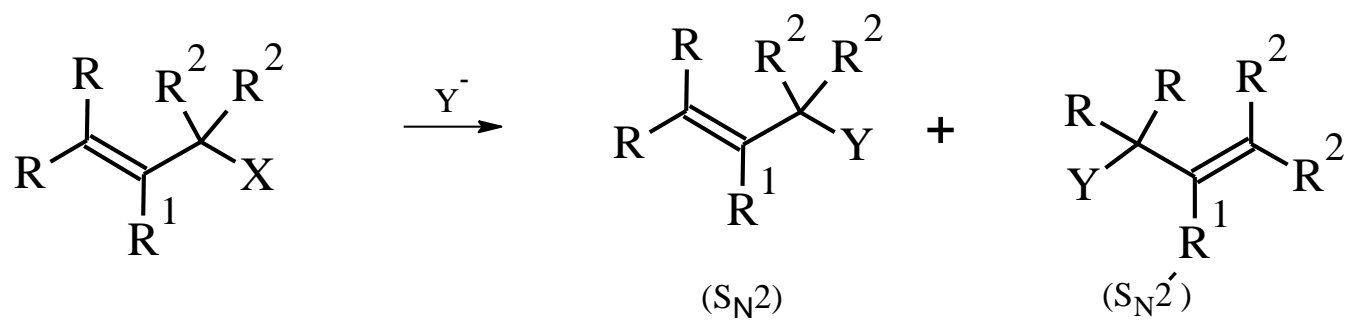
S_N1'



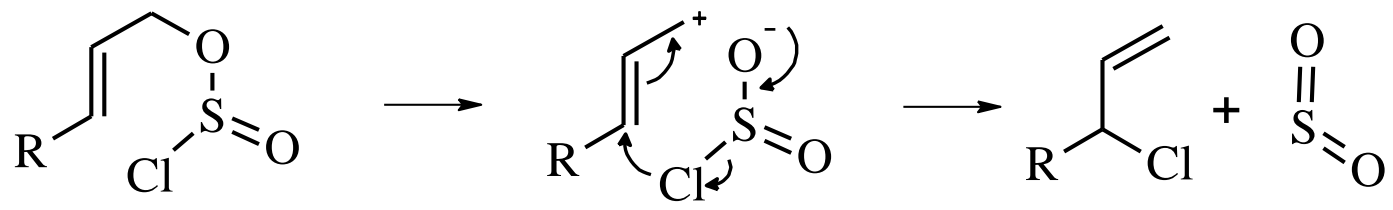
Ion Pairs in S_N1'

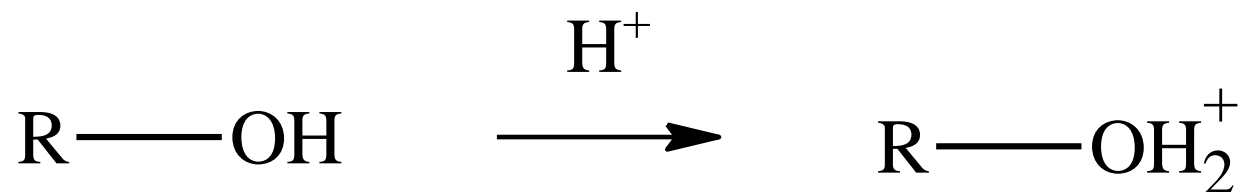


S_N2'



S_Ni'





- The First step above incorporate the symbol cA (conjugate acid)
- The next step will decide whether it is S_N1 or S_N2 mechanism