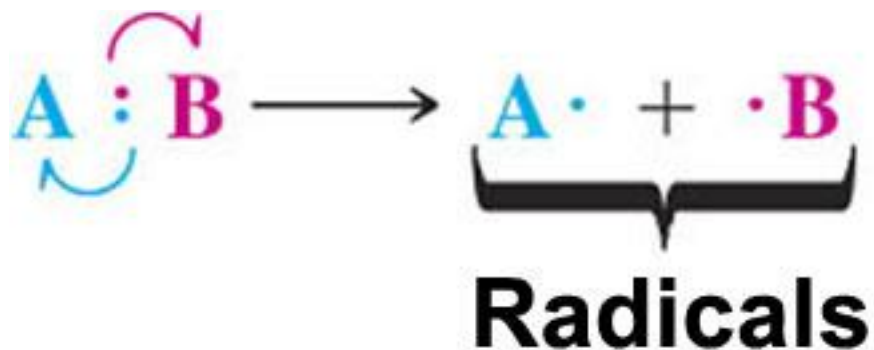


Organic Chemistry Concepts

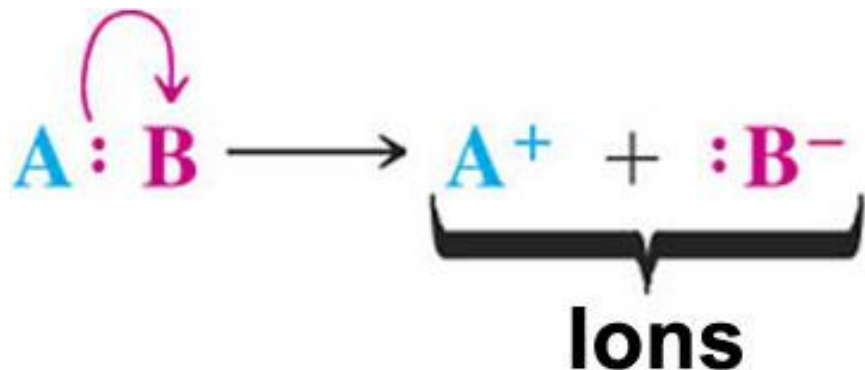
LOKT.09.051

σ -bond reactivity II

CHAPTER 7



Bond homolysis



Bond heterolysis

Homolysis: non-polar bond

Heterolysis: polar bond

Ionic reaction mechanisms



E^+ electrophile

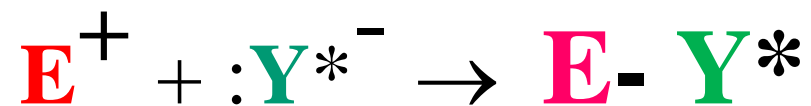
$Y:^-$ nucleophile

Sometimes **Nu:**

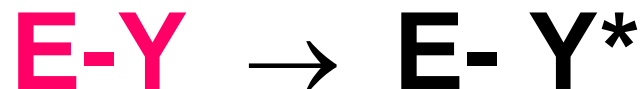


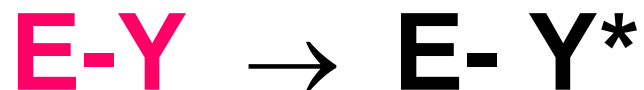
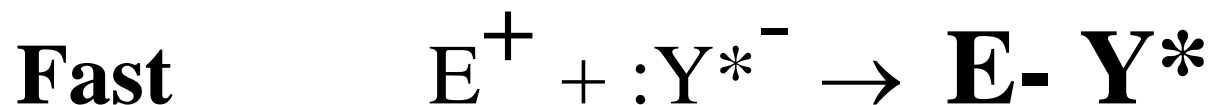
Electrophile

Nucleophile



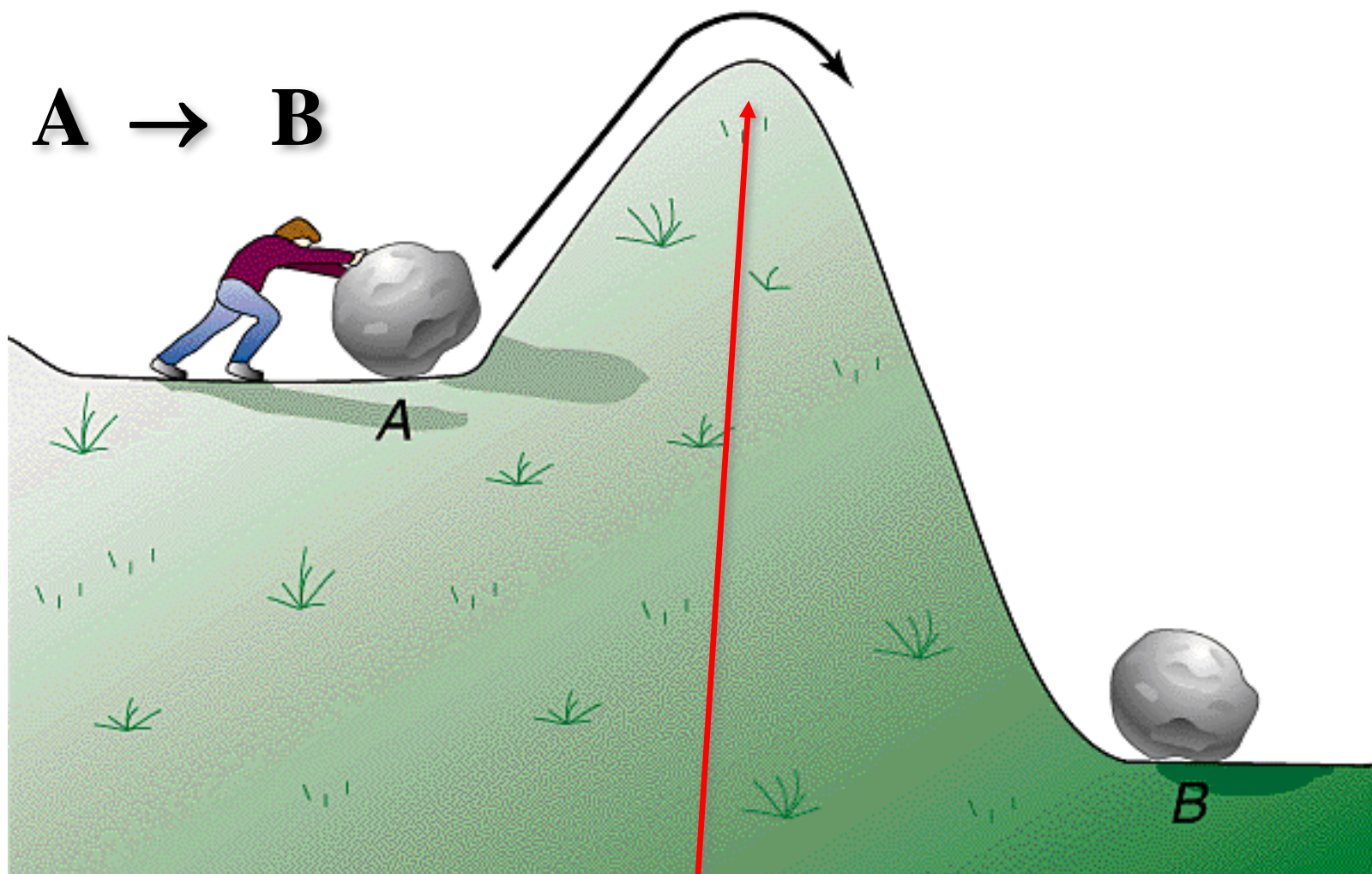
Substitution reaction





Y is “leaving group”

S_N1

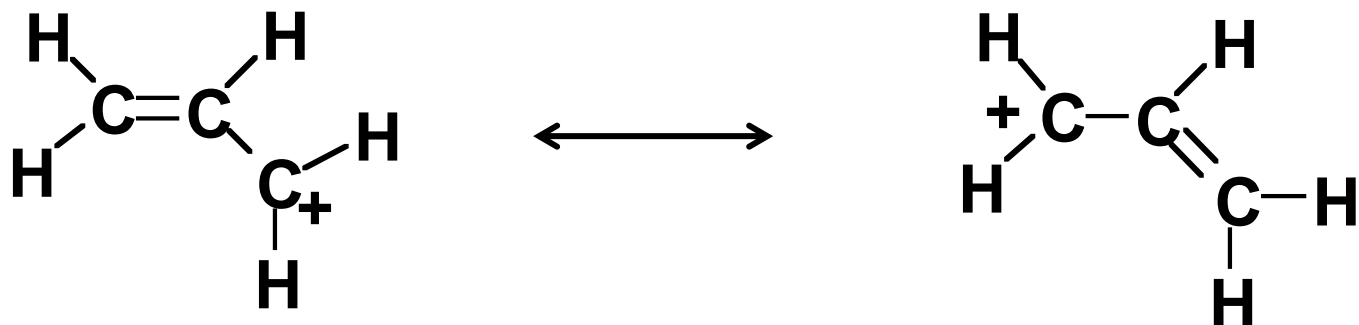


$$A \rightleftharpoons A^{\neq} \rightarrow B$$

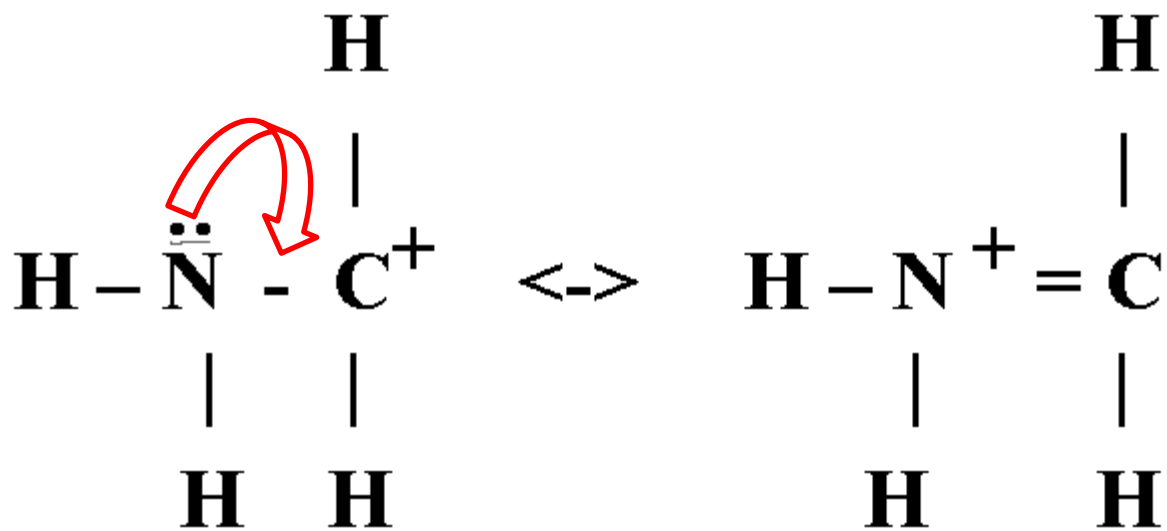
Intermediate stability:

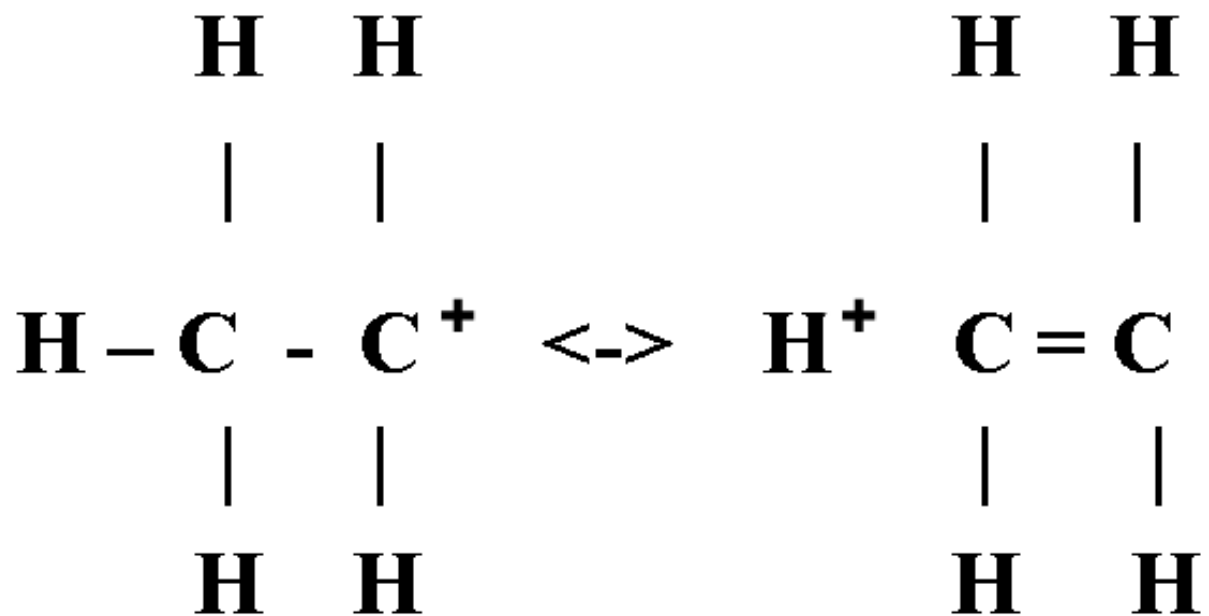
- Carbocation stabilization by resonance (π – bond)
- Resonance with +R group
- Hyperconjugation (with C-H bond)

Resonance with π -bond



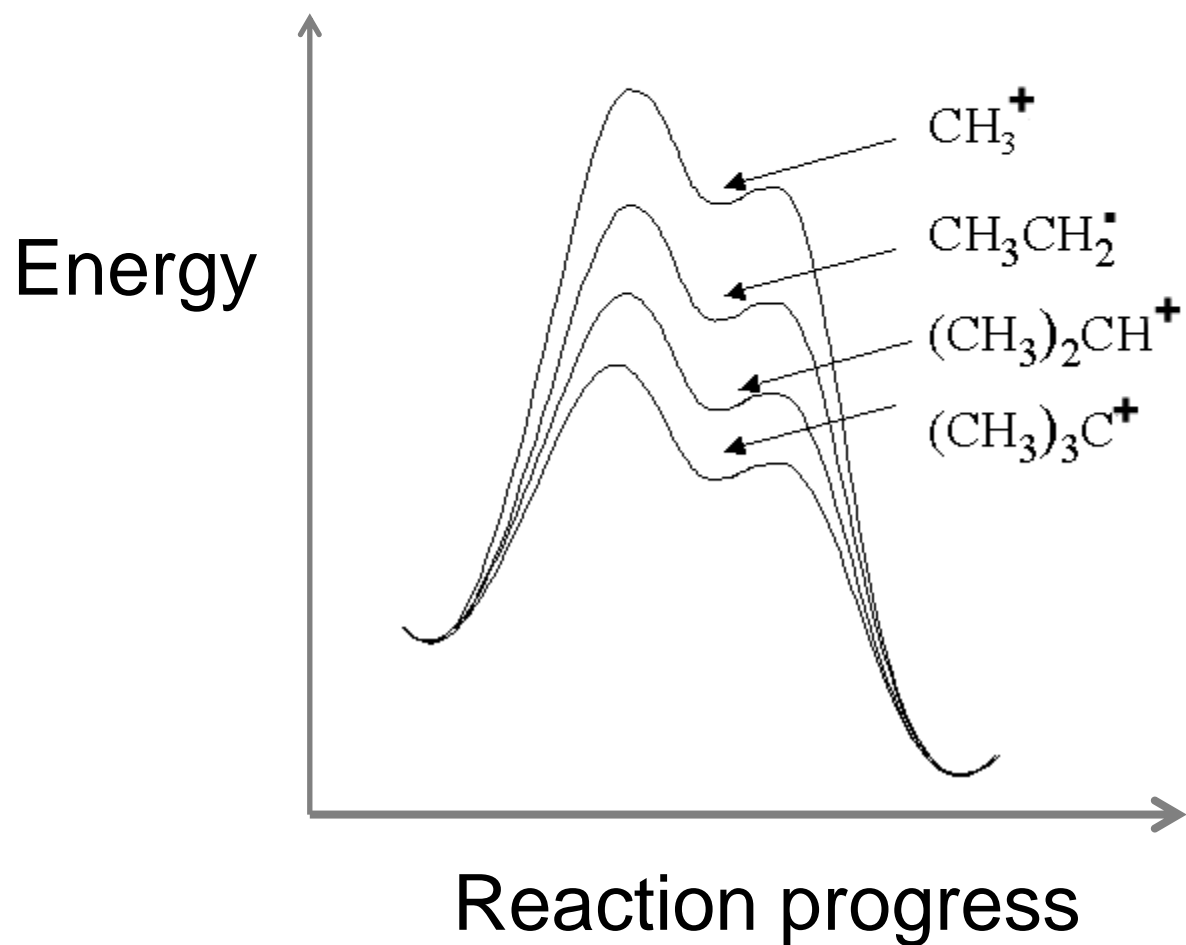
+R group



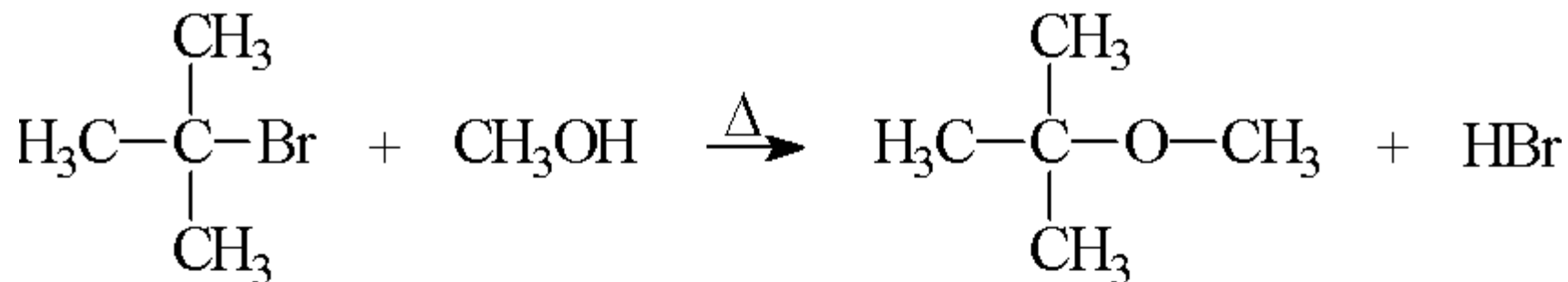


Hyperconjugation

Carbocation stability

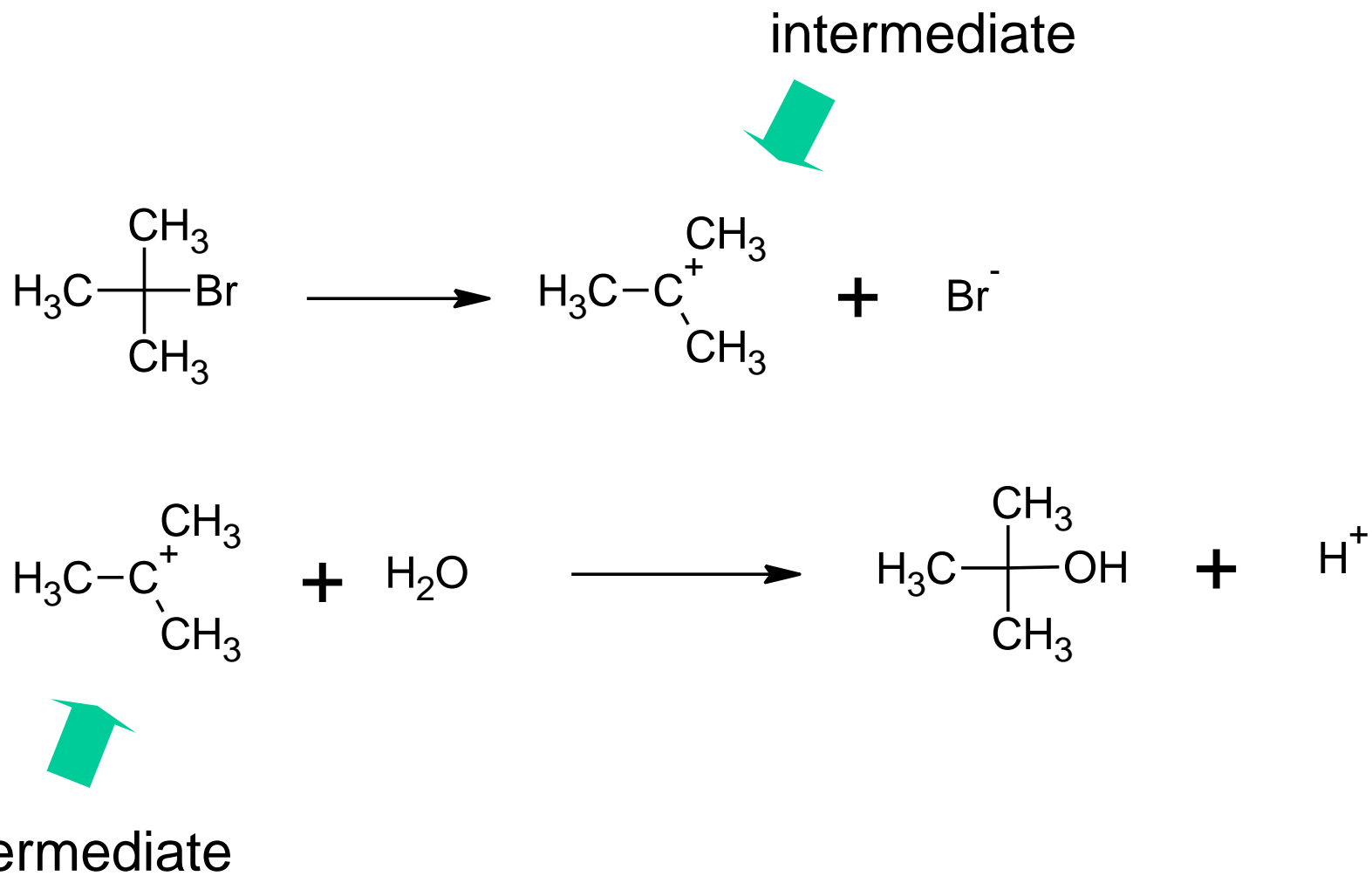


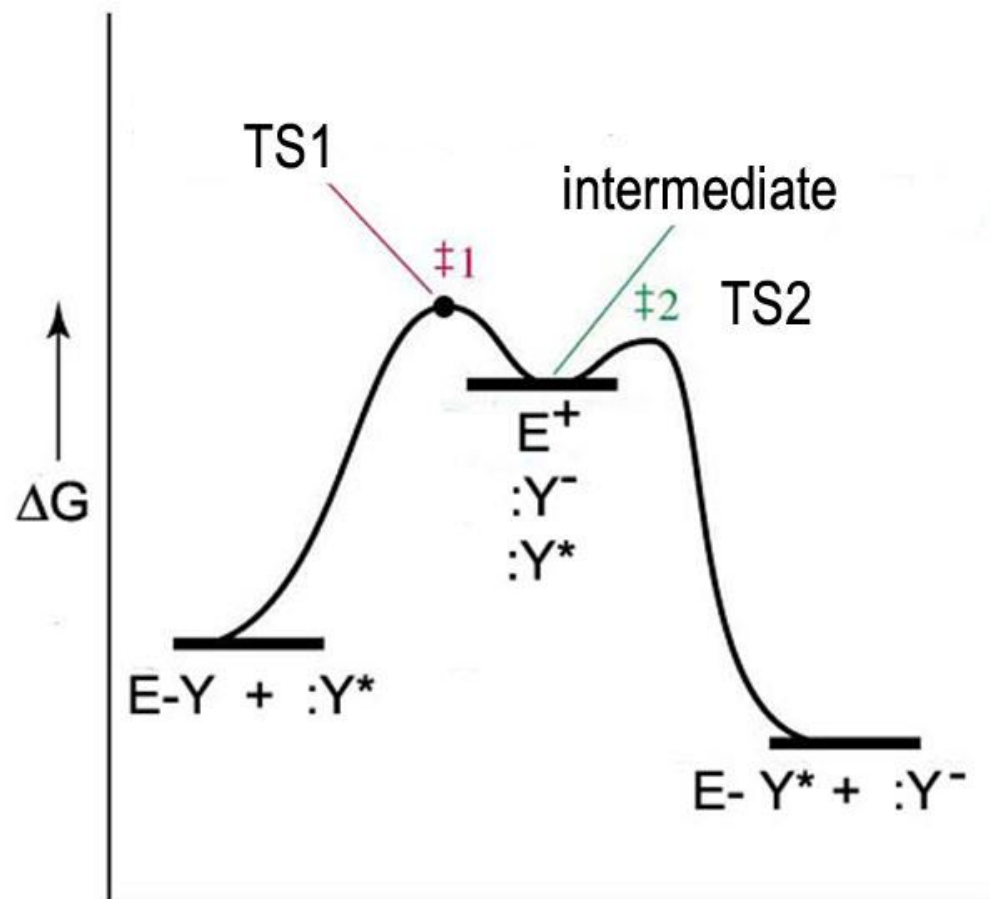
Nucleophilic substitution reaction S_N1



$$v = k[(\text{CH}_3)_3\text{CBr}]$$

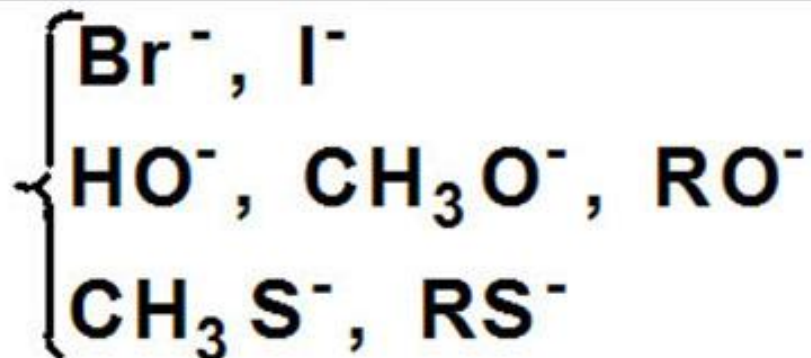
S_N1



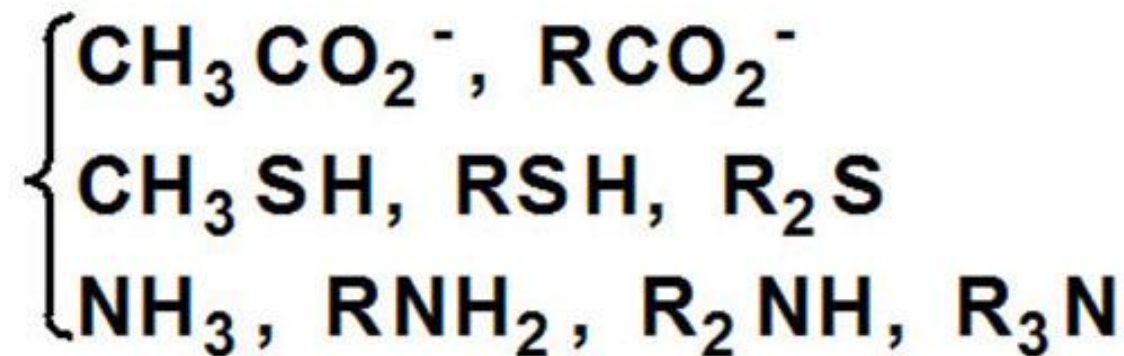


List of nucleophiles

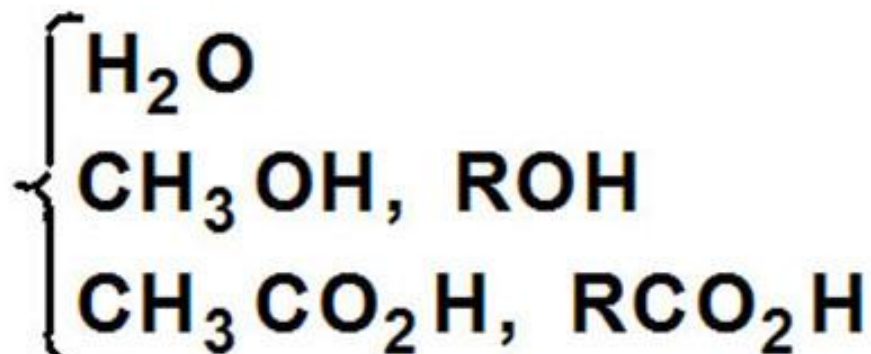
Excellent



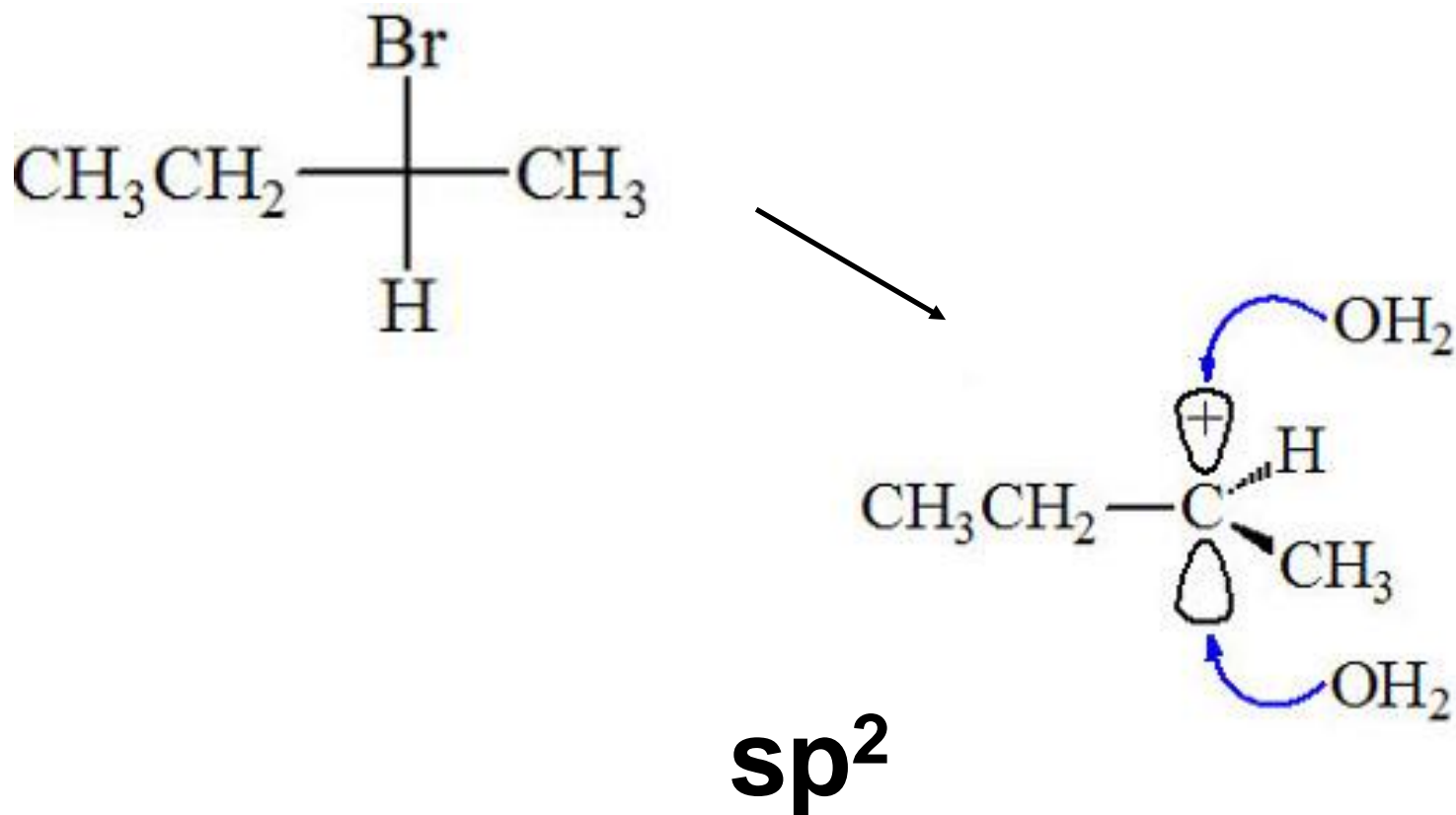
Very good



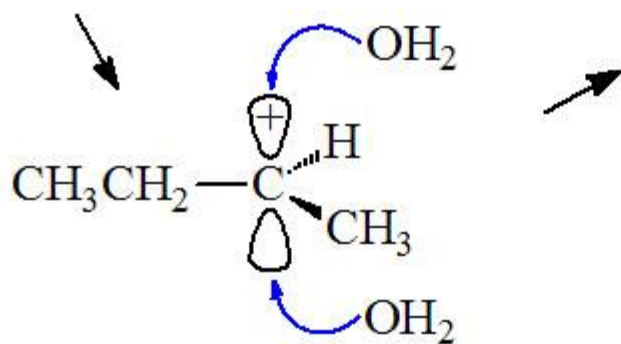
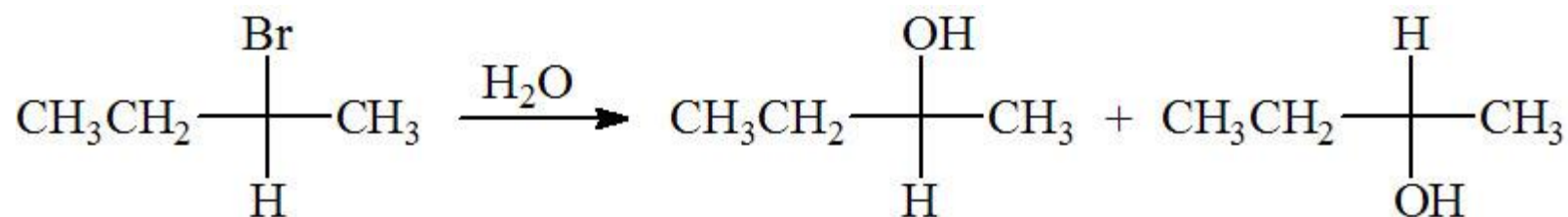
Good



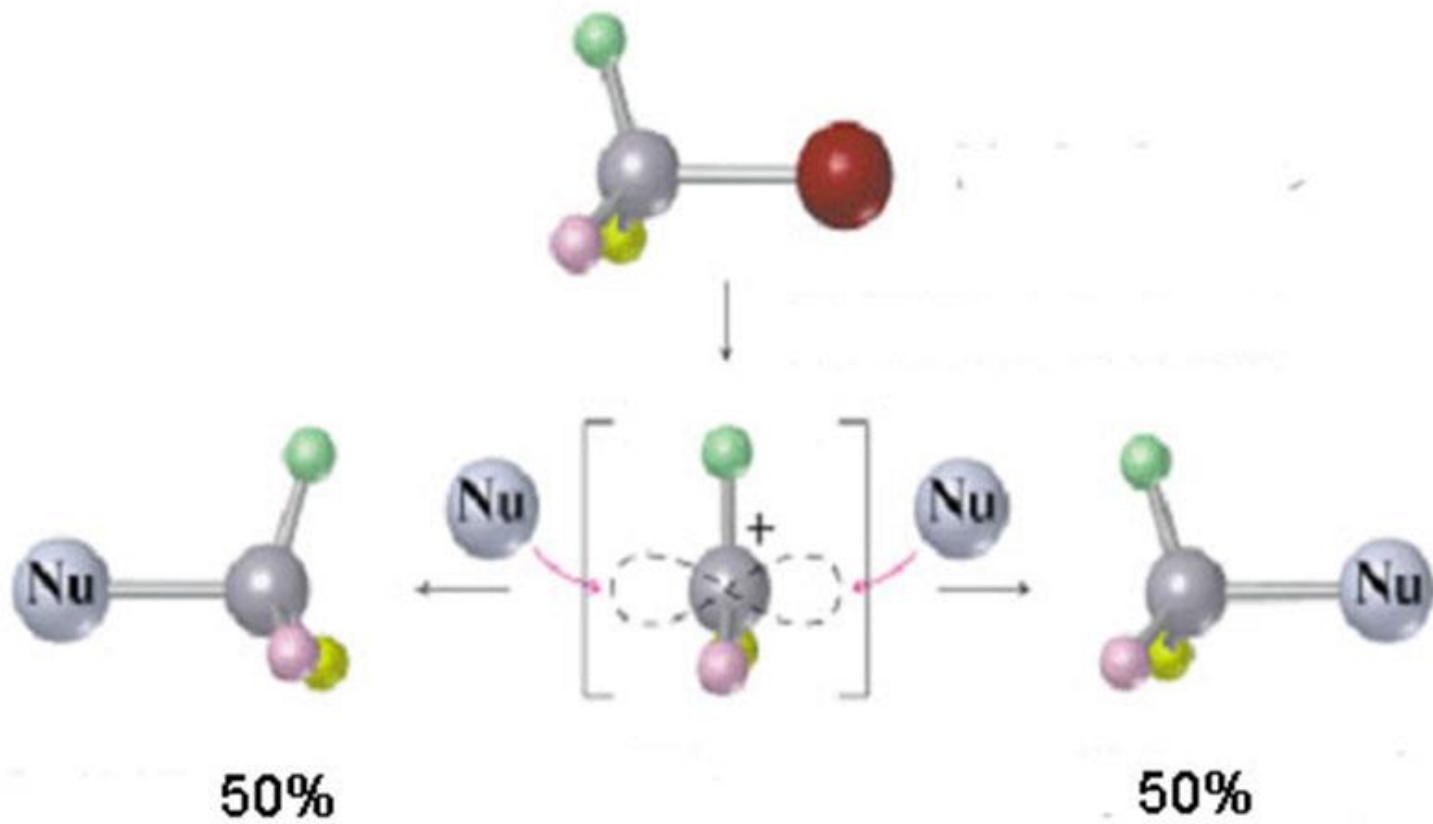
Carbocation structure

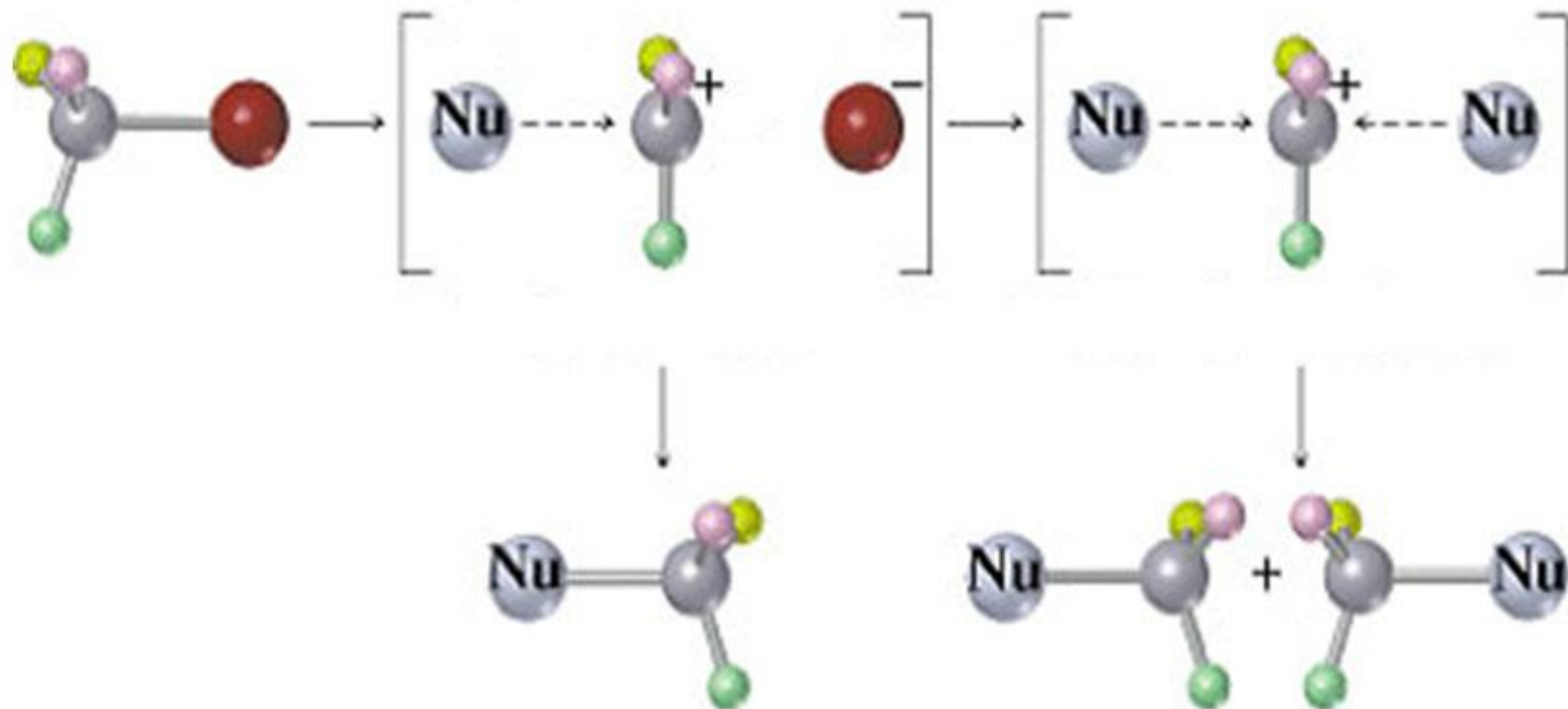


Racemate formation in S_N1 reaction



sp²

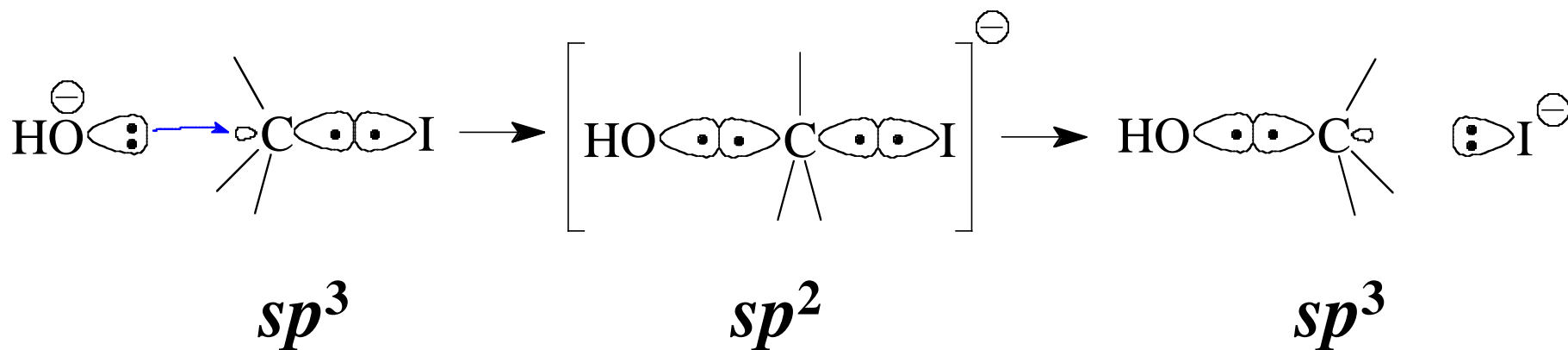
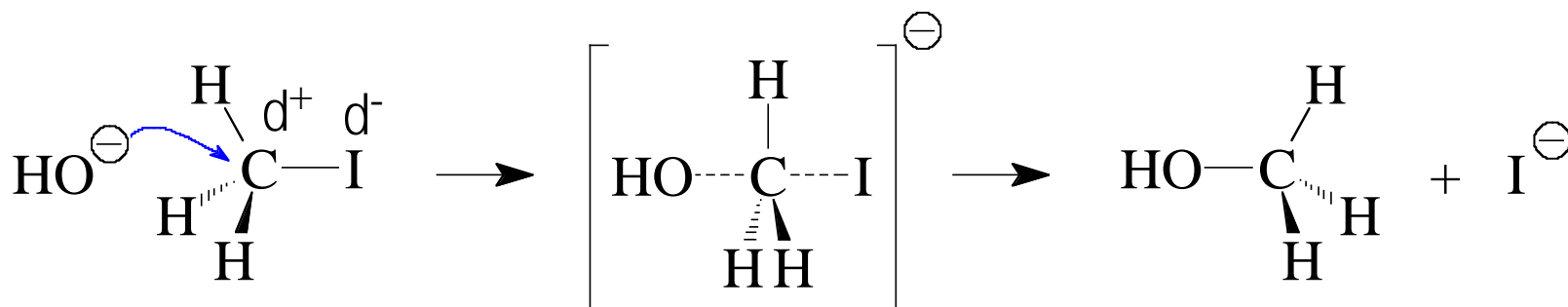




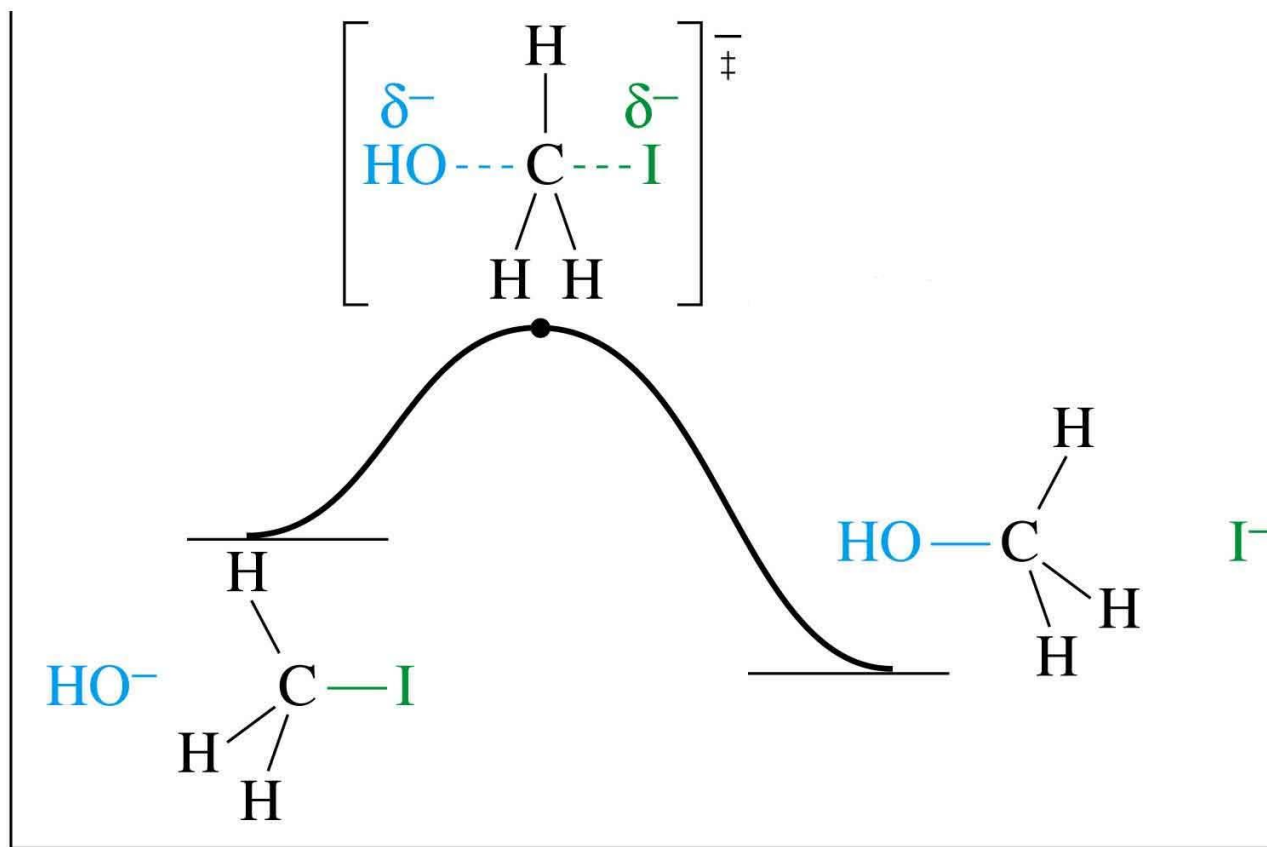
Inversion

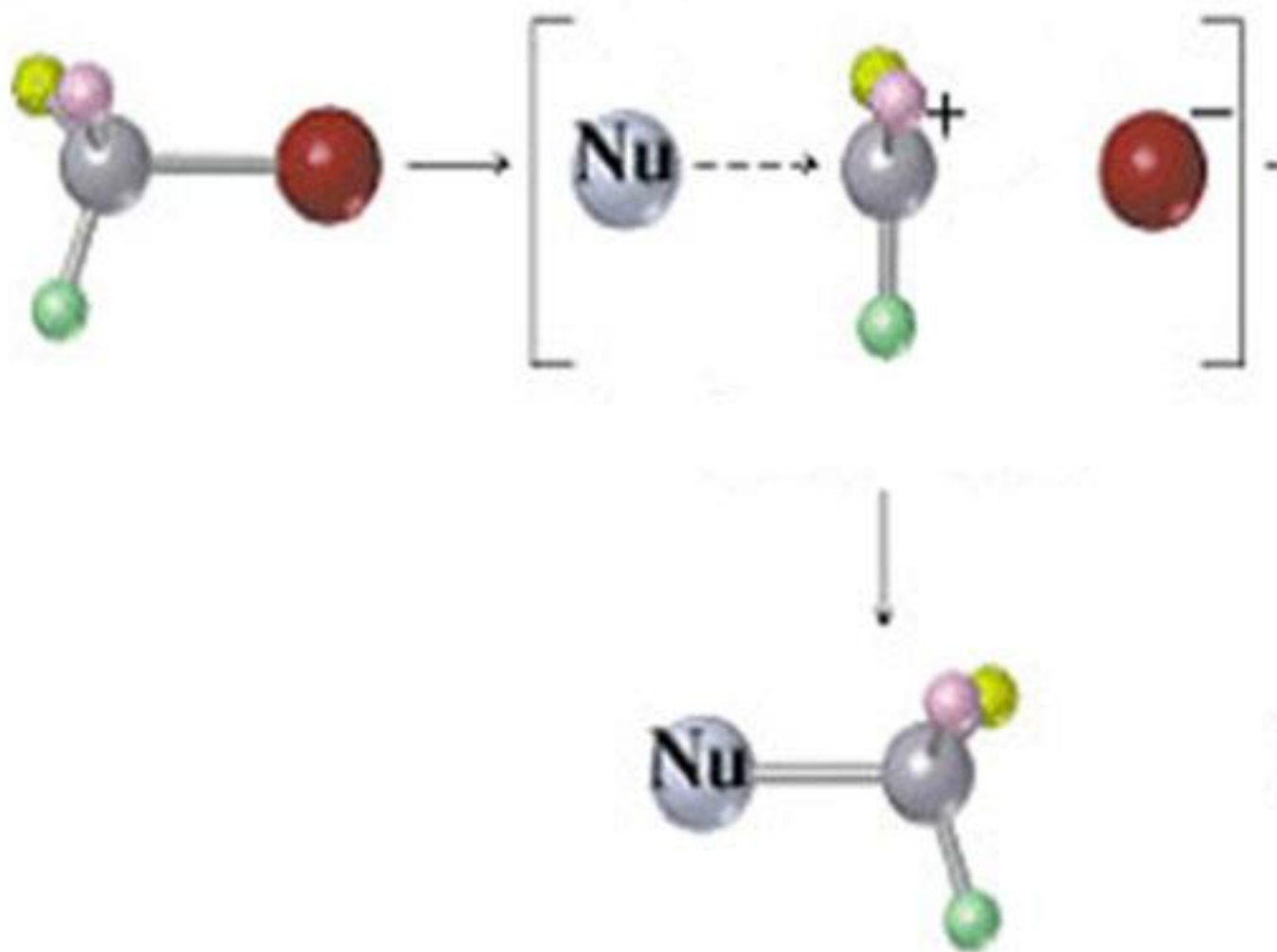
Racemate

Nucleophilic substitution reaction S_N2



Transition state



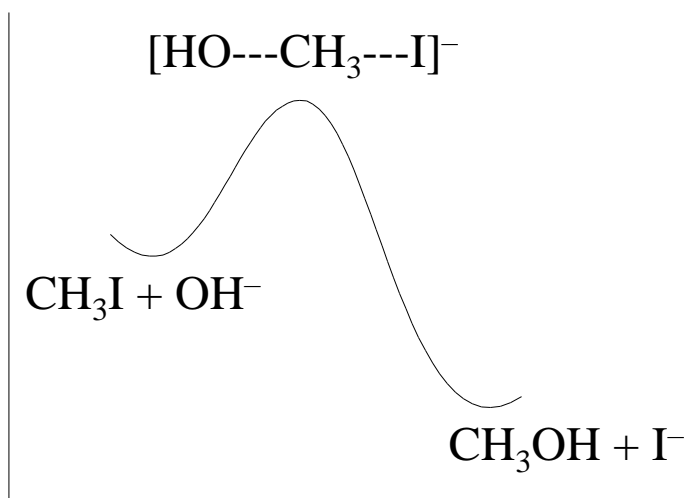


Inversion

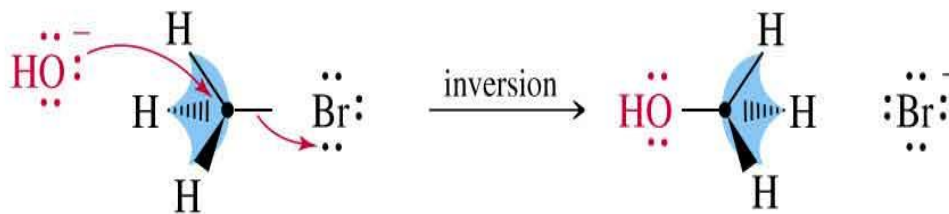
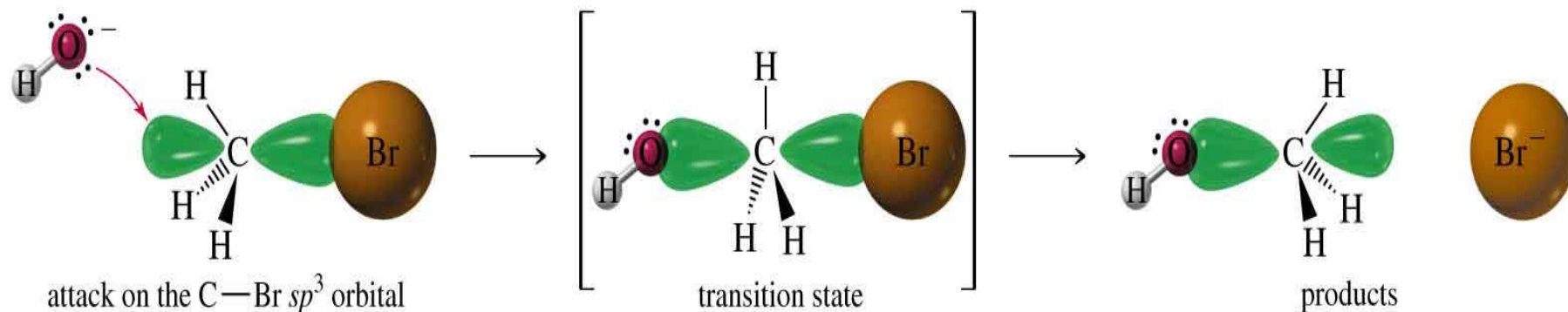
Different kinetics, different stereochemistry



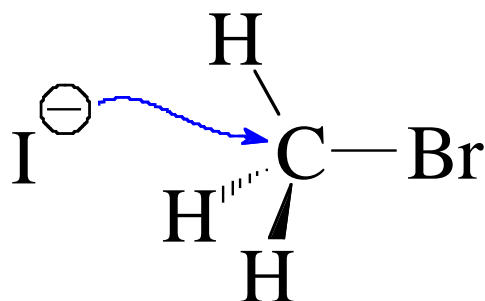
$$v = k[\text{CH}_3\text{I}][\text{OH}^-],$$



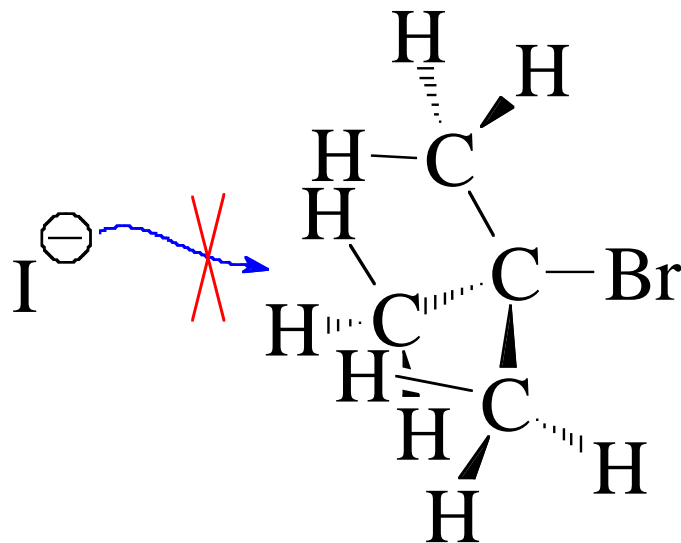
Stereochemical inversion



Steric hindrances



Good reaction



Hindered reaction

List of nucleophiles in S_N2 reactions

Excellent: I^- , HS^- , RS^- , H_2N^-

Very good: Br^- , HO^- , RO^- , CN^- , N_3^-

Good: NH_3 , Cl^- , F^- , RCO_2^-

Satisfactory: H_2O , ROH

Bad: RCO_2H

CHAPTER 7