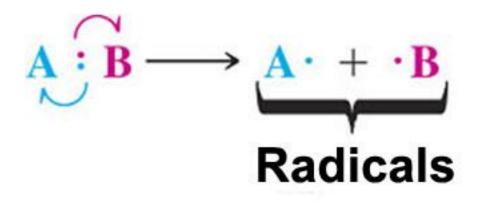
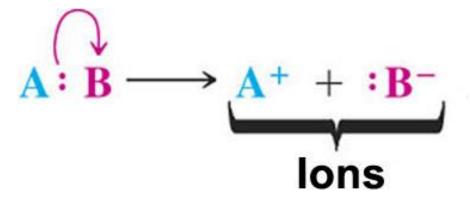
Organic Chemistry Concepts LOKT.09.051

σ-bond reactivity II

CHAPTER 7



Bond homolysis

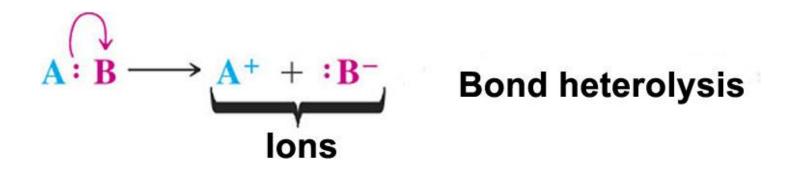


Bond heterolysis

Homolysis: non-polar bond

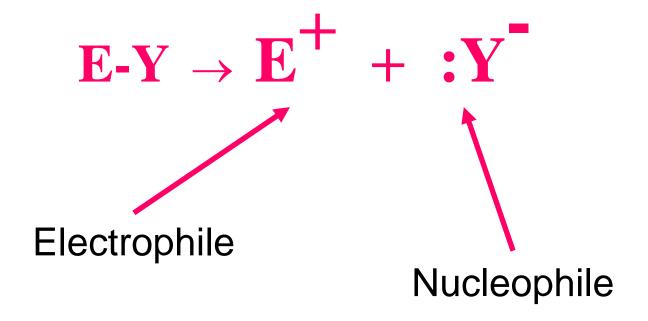
Heterolysis: polar bond

Ionic reaction mechanisms



- E⁺ electrophile
- Y: nucleophile

Sometimes Nu:



$$\mathbf{E}^{+} + : \mathbf{Y}^{*} \rightarrow \mathbf{E}^{+} + : \mathbf{Y}^{*}$$

$$\mathbf{E}^{+} + : \mathbf{Y}^{*} \rightarrow \mathbf{E}^{-} \mathbf{Y}^{*}$$

Substitution reaction

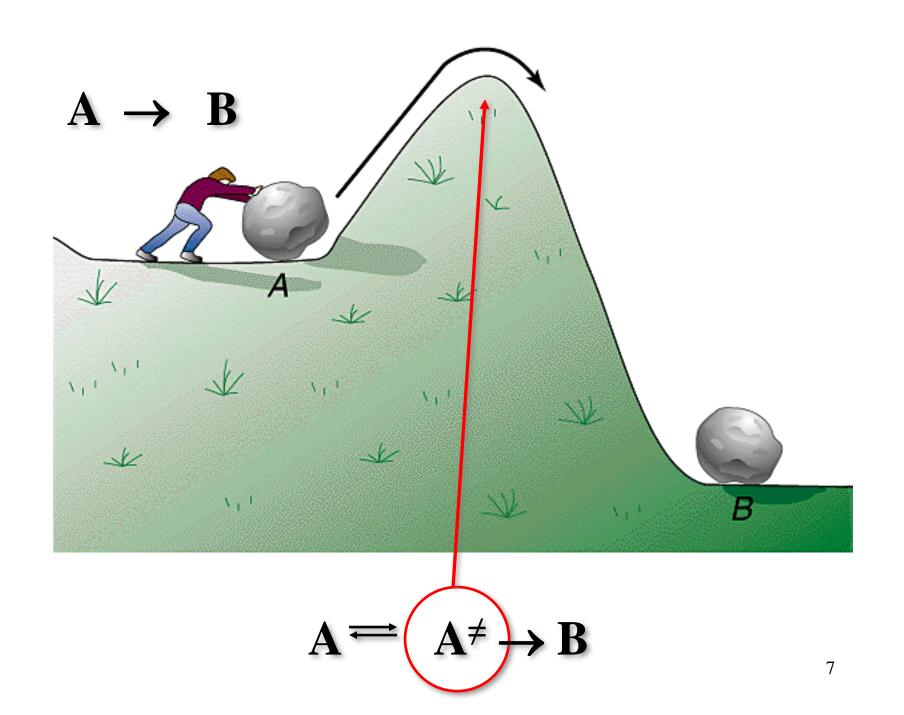
$$E-Y \rightarrow E-Y^*$$

Slow
$$\mathbf{E} - \mathbf{Y} \rightarrow \mathbf{E}^+ + : \mathbf{Y}^-$$
Fast $\mathbf{E}^+ + : \mathbf{Y}^- \rightarrow \mathbf{E} - \mathbf{Y}^*$

$$E-Y \rightarrow E-Y^*$$

Y is "leaving group"

S_N1



Intermediate stability:

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

Resonance with π -bond

+R group

$$H \longrightarrow H$$

$$H - N - C^{+} \longleftrightarrow H - N^{+} = C$$

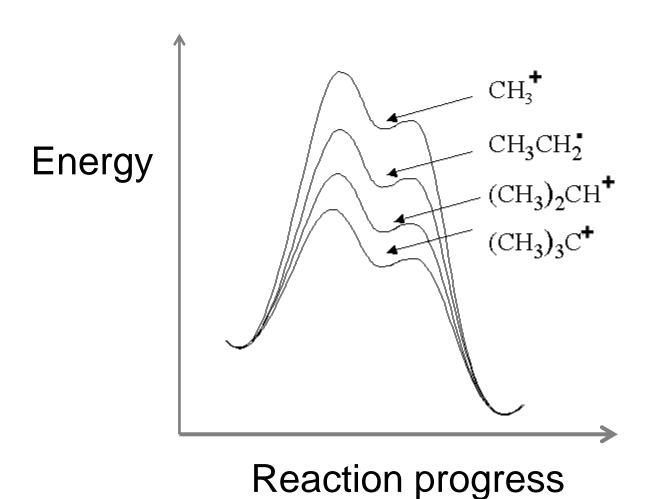
$$H \rightarrow H$$

$$H \rightarrow H$$

$$H H H H H H H$$
 $| H H H H$
 $| H H H$
 $| H H H$
 $| H H H$

Hyperconjugation

Carbocation stability



12

Nucleophilic substitution reaction $S_N 1$

$$v = k[(CH_3)_3CBr]$$

 $S_{\rm N}1$.

intermediate

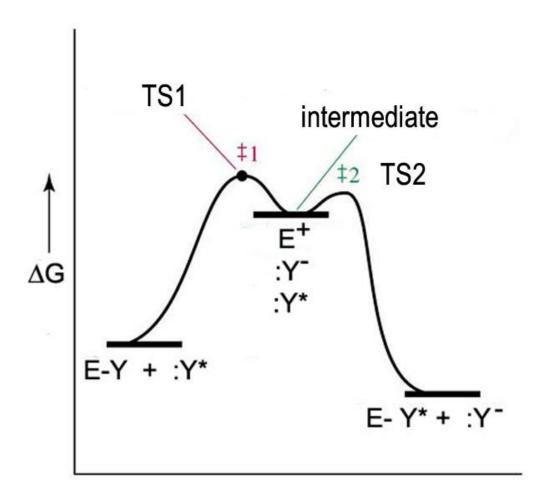


$$H_3C$$
 H_3C
 CH_3
 H_3C
 CH_3
 CH_3
 CH_3

$$H_3C-C^{+}$$
 $+$ H_2O \longrightarrow $H_3C \xrightarrow{CH_3}$ $+$ H^+ CH_3



intermediate



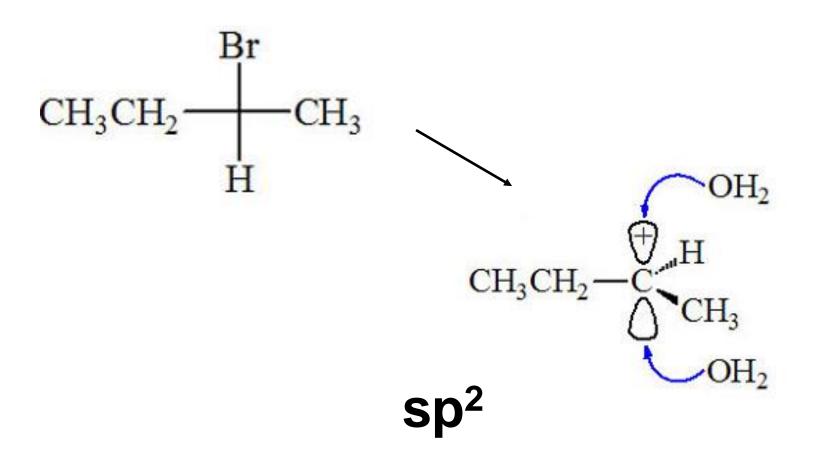
List of nucleophiles

$$\begin{cases} Br^{-}, \ I^{-} \\ HO^{-}, \ CH_{3}O^{-}, \ RO^{-} \\ CH_{3}S^{-}, \ RS^{-} \end{cases}$$

$$\begin{cases} CH_{3}CO_{2}^{-}, \ RCO_{2}^{-} \\ CH_{3}SH, \ RSH, \ R_{2}S \\ NH_{3}, \ RNH_{2}, \ R_{2}NH, \ R_{3}N \end{cases}$$

$$\begin{cases} H_{2}O \\ CH_{3}OH, \ ROH \\ CH_{3}CO_{2}H, \ RCO_{2}H \end{cases}$$

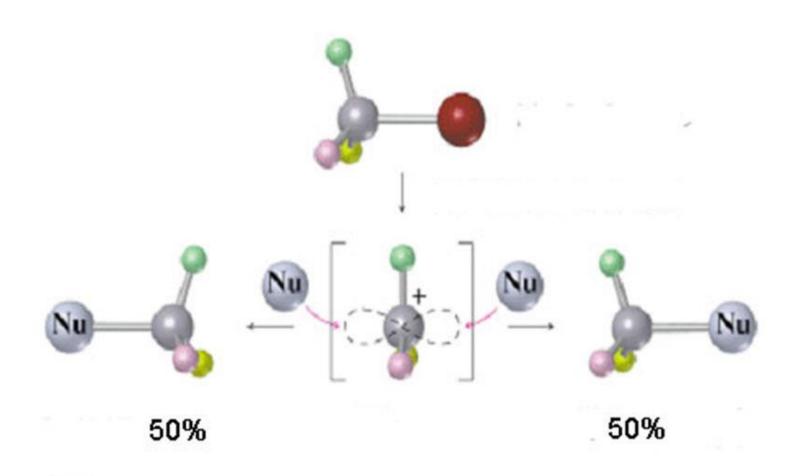
Carbocation structure

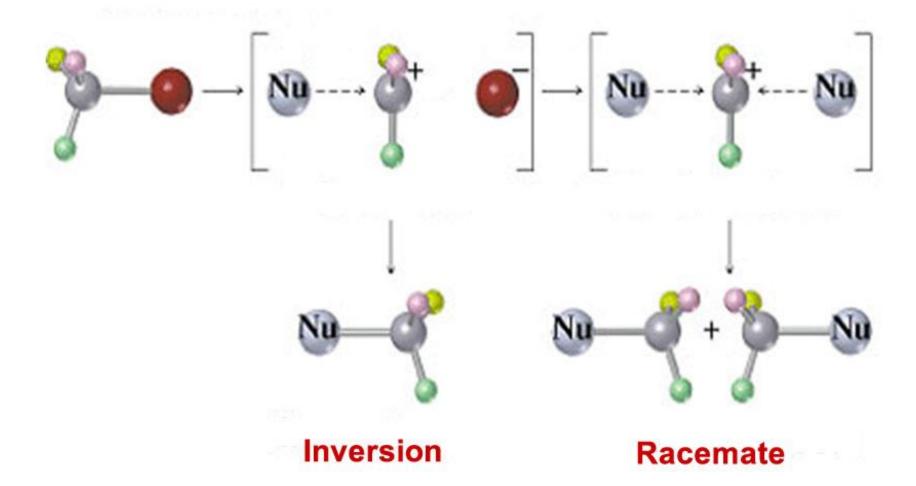


Racemate formation in S_N1 reaction

$$CH_{3}CH_{2} \xrightarrow{H_{2}O} CH_{3}CH_{2} \xrightarrow{H_{2}O} CH_{3}CH_{2} \xrightarrow{H_{2}O} CH_{3}$$

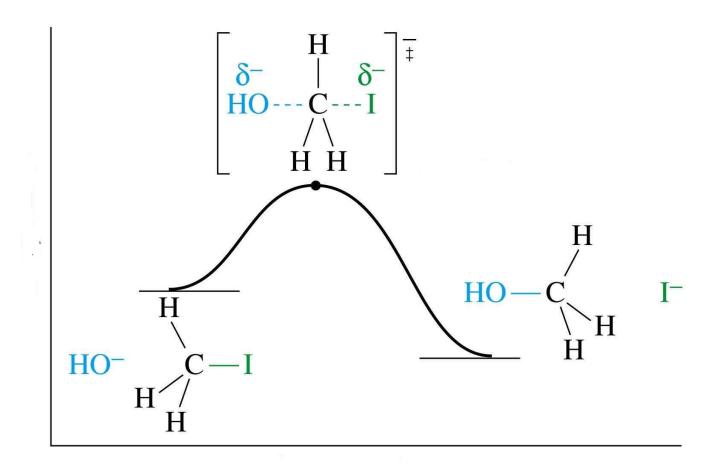
$$CH_{3}CH_{2} \xrightarrow{CH_{3}CH_{2}} CH_{3}$$

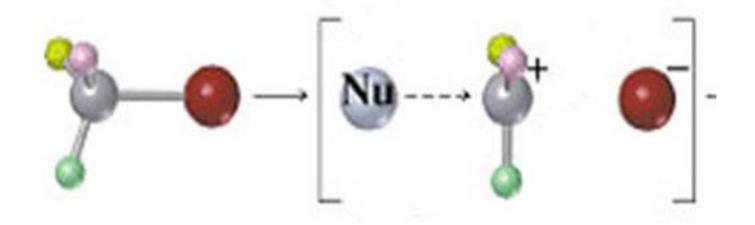


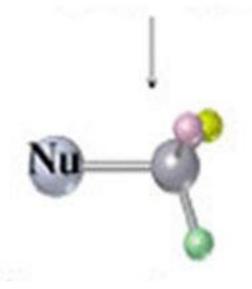


Nucleophilic substitution reaction S_N^2

21







Inversion

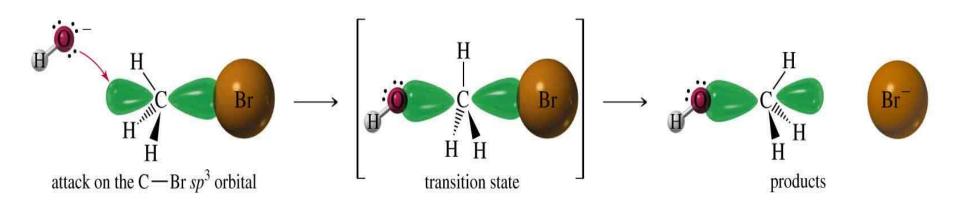
Different kinetics, different stereochemistry

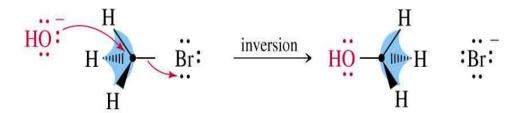
$$CH_3I + OH^- \rightarrow CH_3OH + I^-$$

 $v = k[CH_3I][OH^-],$

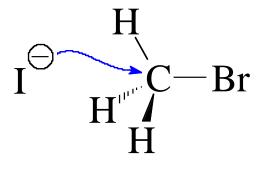
$$[HO---CH_3---I]^ CH_3I + OH^ CH_3OH + I^-$$

Stereochemical inversion





Steric hindrances



Good reaction

Hindered reaction

List of nucleophiles in $S_N 2$ reactions

Excellent: I-, HS-, RS-, H₂N-

Very good: **Br**⁻, **HO**⁻, **RO**⁻, **CN**⁻, **N**₃⁻

Good: **NH**₃, **Cl**⁻, **F**⁻, **RCO**₂⁻

Satisfactory: H₂O, ROH

Bad: RCO₂H

CHAPTER 7