<u>Chapter 7:</u> Part 2: Substitution Reactions — SN1

- 1. The SN1 Mechanism
- 2. Factors Affecting SN1 Reactions
 - 1. The Leaving Group
 - 2. The Nucleophile
 - 3. Carbocation Intermediate
 - 4. Steric Hindrance
- 3. Stereochemistry

Alkyl halides have relatively good leaving groups -How do alkyl halides react?

$$\begin{array}{ccc}
\delta^{+} & \delta^{-} \\
RCH_{2} & X
\end{array}$$
 X= F, Cl, Br, I

an SN2 reaction....

Experimental Evidence for an S_N1 Reaction

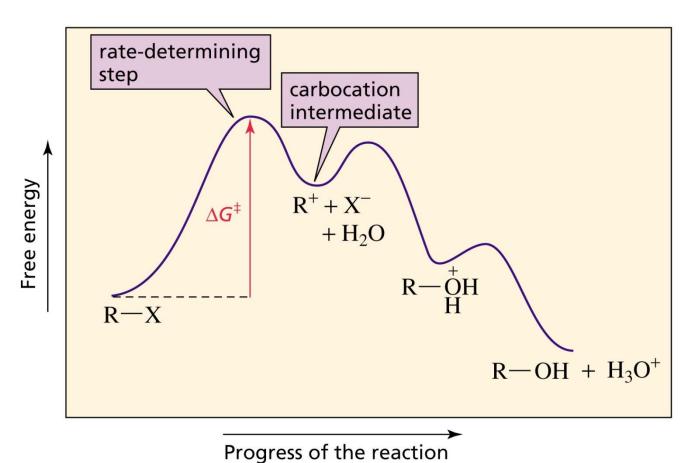
1.

2

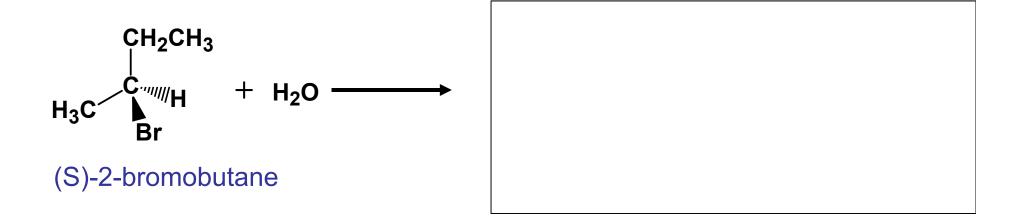
3. In the substitution of a chiral alkyl halide, a mixture of products is obtained.

The SN1 reaction: Substitution Nucleophilic *Unimolecular*

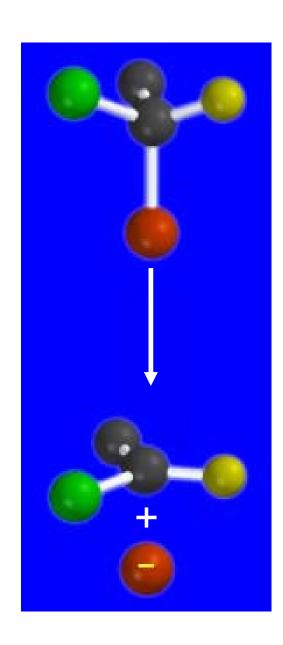
Reaction Coordinate Diagram for an S_N1 Reaction



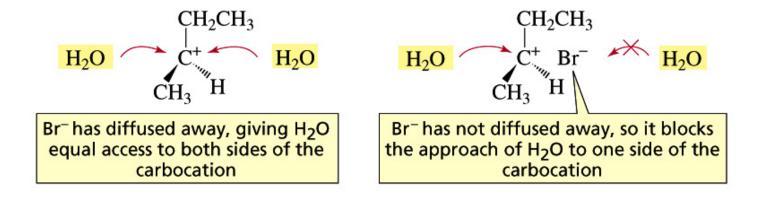
The Stereochemistry of S_N1 Reactions



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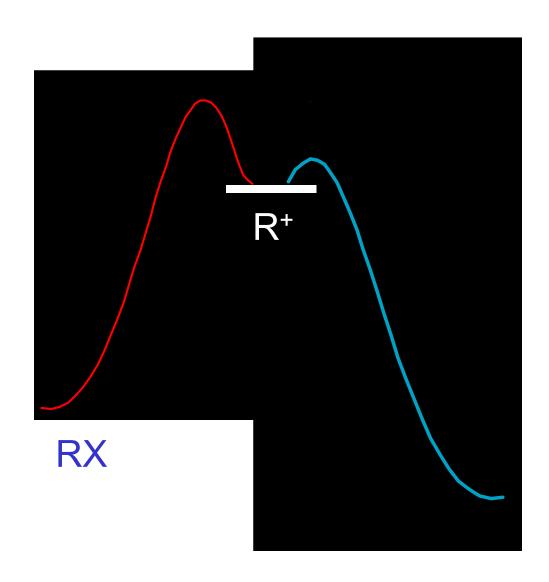


Sometimes extra inverted product is formed in an S_N1 reaction because ...



S_N1 Reactivity versus Solvent Polarity

Solvent	Dielectric	Relative
	constant	rate
acetic acid	6	
methanol	33	
formic acid	58	
water	78	

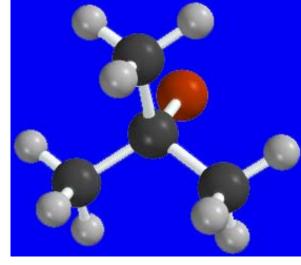


Reactivity toward substitution by the S_N1 mechanism

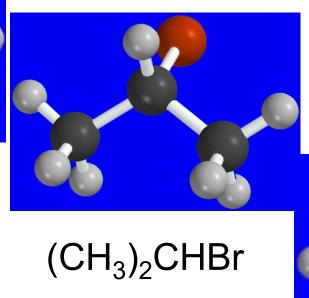
RBr solvolysis in aqueous formic acid

 Alkyl bromide 	Relative rate	
•CH ₃ Br	Methyl	1
•CH ₃ CH ₂ Br	Primary	2
•(CH ₃) ₂ CHBr	Secondary	43
•(CH ₃) ₃ CBr	Tertiary	100,000,000

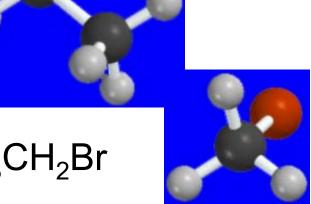
Decreasing S_N1 Reactivity



 $(CH_3)_3CBr$



CH₃CH₂Br



 CH_3Br

Finally, When a reaction forms a carbocation intermediate, always check for the possibility of a <u>carbocation</u> <u>rearrangement</u>

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\$$

Characteristics of the S_N1 mechanism

For Next Time....

FRIDAY Chapter 7: Alkenes and Eliminations (7.5-7.8)

NEXT MONDAY Chapter 7: Unimolecular Reactions (7.9-7.10)

NEXT WEDNESDAY Chapter 7: Putting it all together

Suggested Homework Problems Chapter 7

#1,3,5,16, 18, 21, 37, 41, 47, 48, 54, 56, 60, 62-65, 70, 76