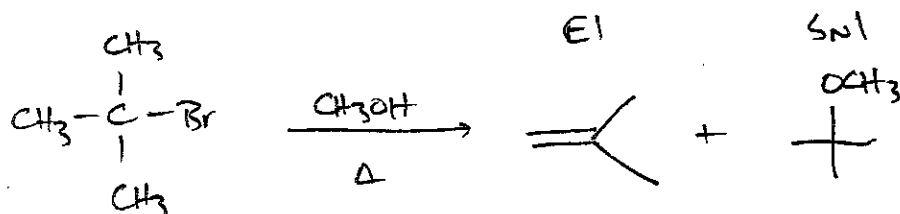


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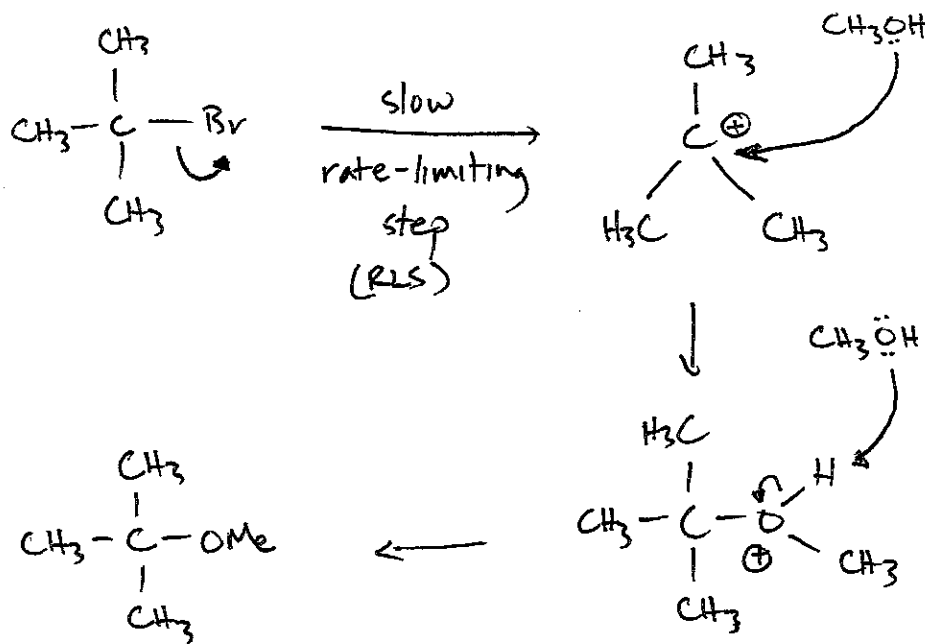
• Last lecture:  $S_N2$  vs  $E2$  reactions

- Anti elimination
- Factors determining reaction mechanism



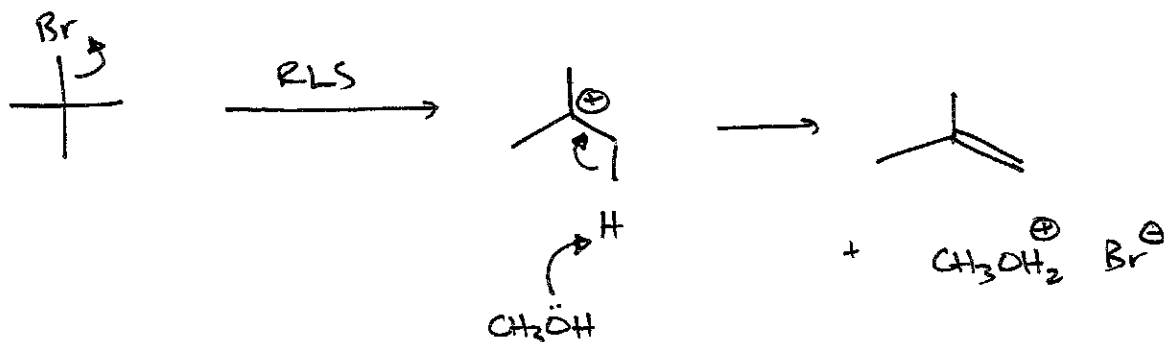
Kinetic analysis: 1<sup>st</sup> order reaction

•  $S_N1$  mechanism:

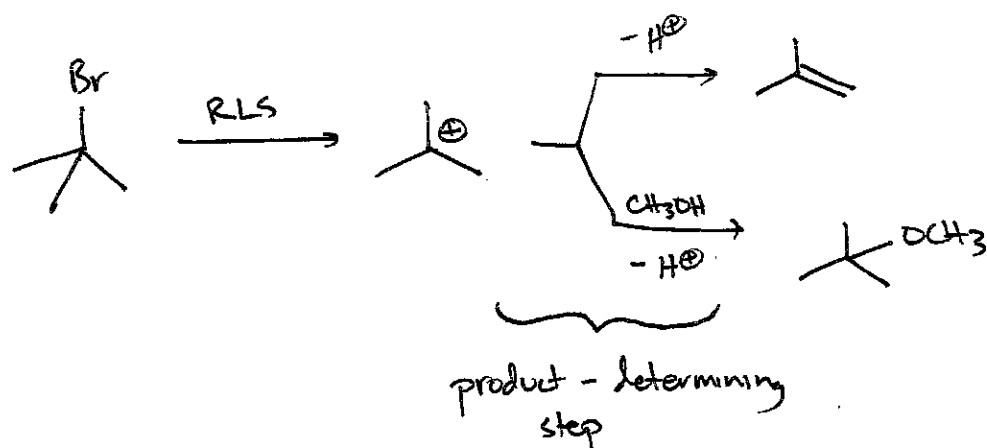


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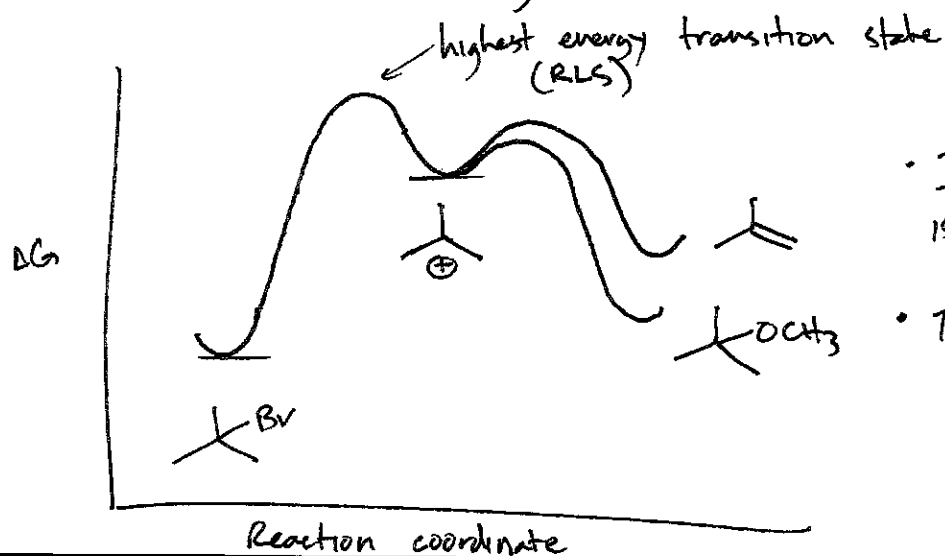
• E1:



• Overall process:



• Reaction coordinate diagram



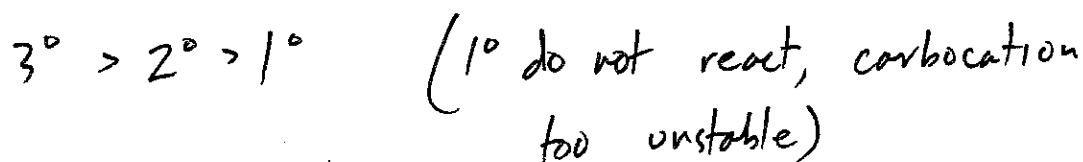
• Intermediate carbocation is formed in E1/SN1

• This does not occur for E2/SN2

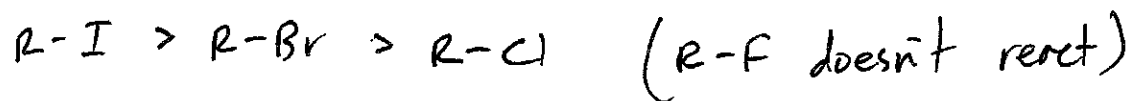
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Impact of key reaction parameters on  $S_N1/E1$  reactivity

1) Alkyl halide structure

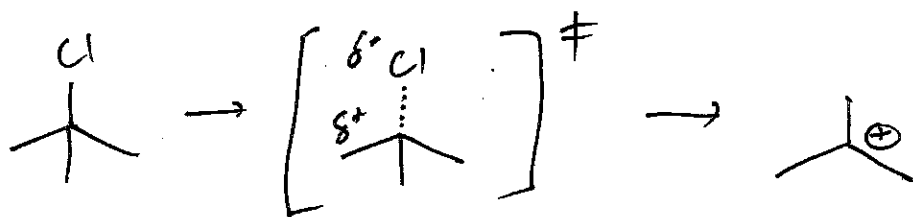


2) Better leaving group  $\rightarrow$  better reactivity for  $E1/S_N1$



3) Solvent effects:  $S_N1/E1$  is strongly favored by polar protic solvents ( $H_2O$ ,  $R-OH$ )

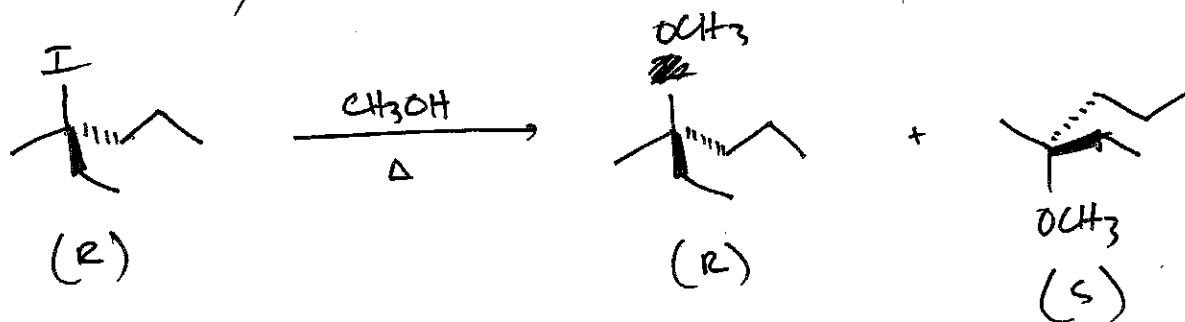
Rationale: consider rate-determining TS



transition state stabilized by polar protic solvents (can stabilize the  $\delta^+$ ,  $\delta^-$  more easily)

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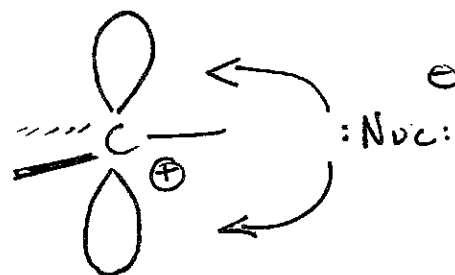
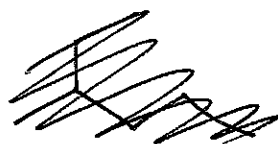
• Stereochemistry



Racemic mixture

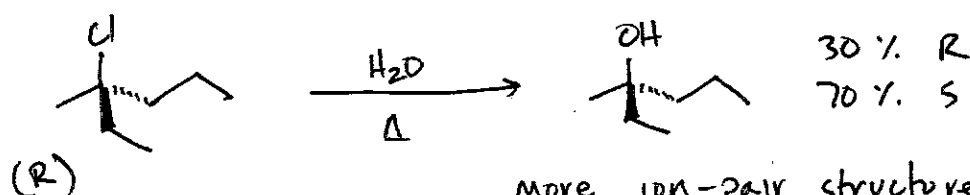
• Mechanistic rationale

- Nucleophile can attack either face of the carbocation. This results in the formation of both enantiomers

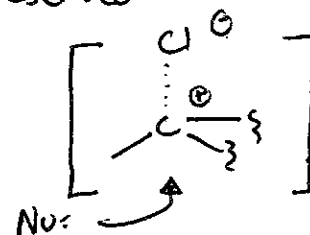


empty p-orbital

• Sometimes the stereochemical information is preserved



more ion-pair structure in intermediate



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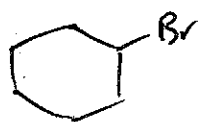
• Compare  $S_N2/S_N1/E2/E1$  (p 42) 9.7 summary)

- Rules of thumb: •  $1^\circ$  alkyl halides  $\rightarrow$  no  $S_N1/E1$   
 $\rightarrow$  usually  $S_N2$ , but  $E2$   
 can occur with strong, bulky  
 base ( $\text{K}^\oplus \text{O}^\ominus \text{---}$ )

•  $3^\circ$  alkyl halide: No  $S_N2$  (due to sterics)  
 - can have  $E2$  with strong base  
 - polar protic solvent +  $\Delta$  can give  $E1/S_N1$

•  $2^\circ$  alkyl halides: all mechanisms possible

•  $E2$  elimination in cyclic systems: anti orientation needed  
 for  $E2$ !



substrate for  $E2$   
 with  $\text{NaOEt}$

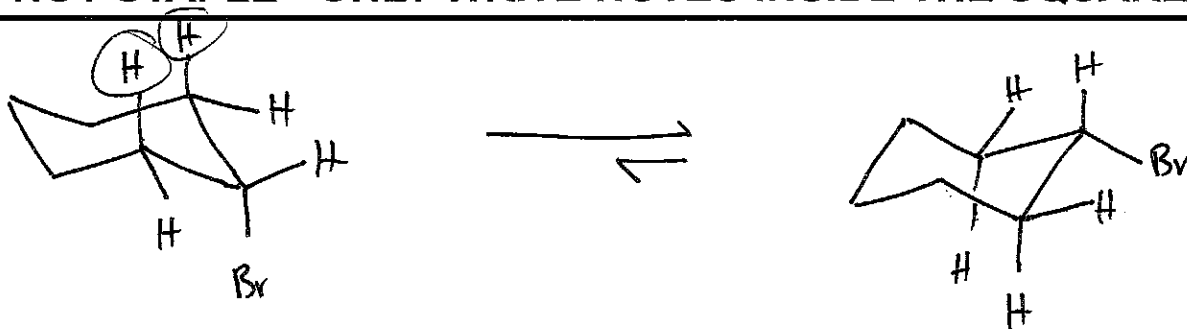
•  $E2$  only possible if both  
 $\text{Br}/\text{H}$  are axial

Course 343 Lecturer Hackenberger

Day \_\_\_\_\_ Date 11/11/2013

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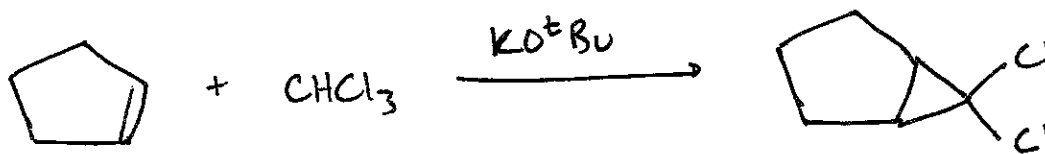


circled H's can be deprotonated for E2 rxn

• cannot undergo E2 rxn  
- no anti-H

• E2 rxn occurs from minor chair conformer

• Carbenes



Accepted reaction mechanisms

