

## Polar Reaction Mechanisms

### Eliminations

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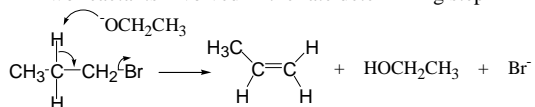
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## Elimination Reaction Mechanisms

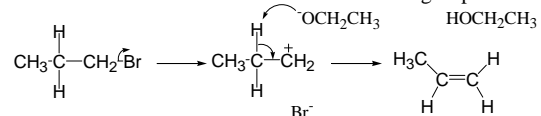
- Bimolecular (E2)

– Two reactants involved in the rate determining step



- Unimolecular (E1)

– One reactant involved in the rate determining step



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## Problem

- Draw reaction energy diagrams for both the E1 and E2 mechanisms

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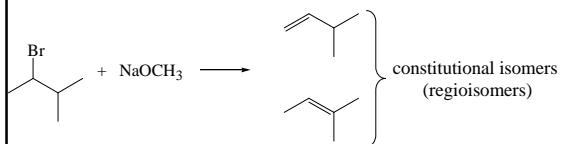
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## Regiochemistry

- Multiple products are often possible



- But are not usually formed in equal amounts
  - Small bases promote formation of most stable alkene
  - Bulky bases preferentially remove least hindered proton

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## Problem

- Given the information on the previous slide, which of the possible products will be the major product?
- If you substitute  $\text{NaOC}(\text{CH}_3)_3$  for  $\text{NaOCH}_3$ , will the major product change? (If so, what will it be?)

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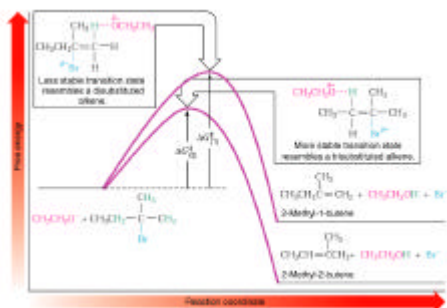
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## Energetic Rationale




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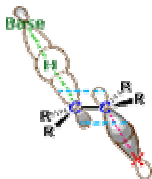
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## Stereochemical Considerations

- E1
  - The intermediate carbocation is achiral (planar)
  - Preference for alkene stereoisomers will be solely based on their relative stabilities
- E2
  - Formation of the pi bond requires overlap of the orbitals that will re-hybridize from  $sp^3$  to p
  - This requires that the hydrogen and the leaving group be planar
  - Anti-periplanar arrangement (potentially chiral) is preferred




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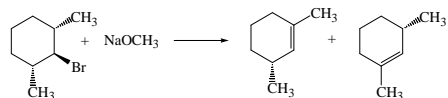
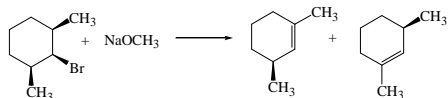
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## Problem

- One of the following E2 reactions can occur, the other cannot. Which is which and why?

– Hint: Draw a three-dimensional picture of each starting material




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## Factors Influencing Elimination Rates

- E1
  - Temperature
  - Stability of intermediate carbocation formed
  - Leaving group ability
- E2
  - Temperature
  - Stability of anti-periplanar conformation
  - Leaving group ability
  - Base strength

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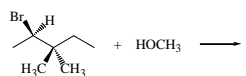
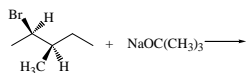
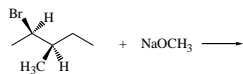
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### Problem

- Predict the mechanism (E1 vs. E2) and the major product of the following reactions.



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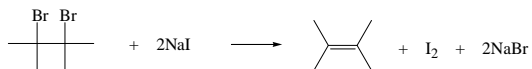
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### Problem

- Why does the following mixture undergo elimination rather than substitution?



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