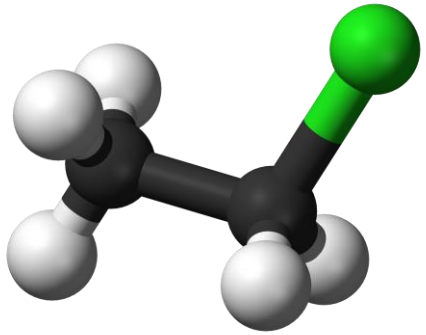
2302263 – Organic Chemistry I – Part III

Lecture 1-4

Alkyl Halides – E1 and E2 Reactions



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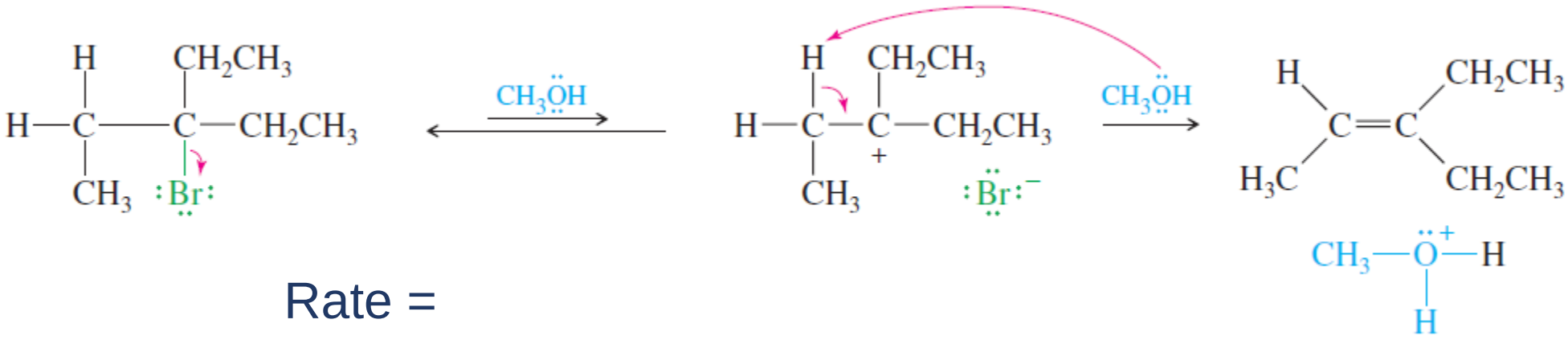
Recommended Textbook:

Chapter 6 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

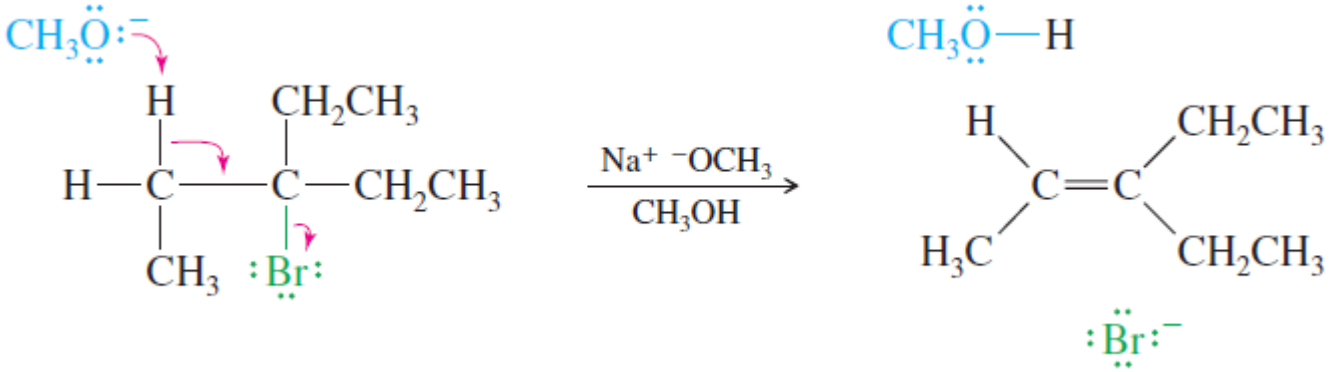
Elimination Reactions

E1



Rate =

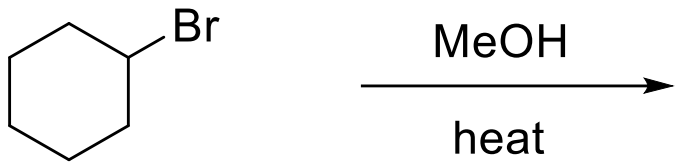
E2



Rate =

First-Order Elimination (E1)

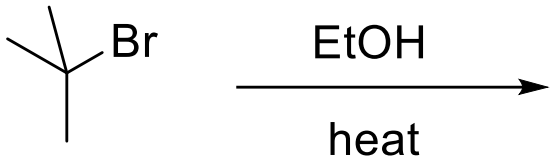
Mechanism



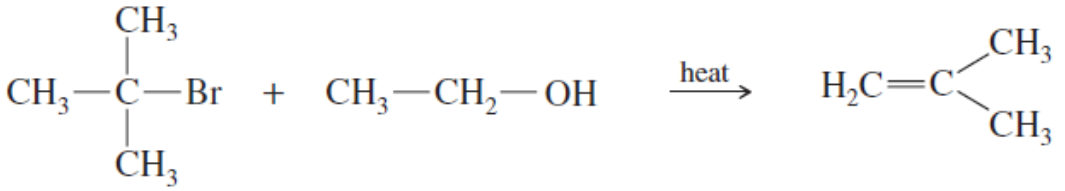
Reactivity of the Substrate in the E1: **3º** **2º** **1º**

E1: Competition with the S_N1 Reaction

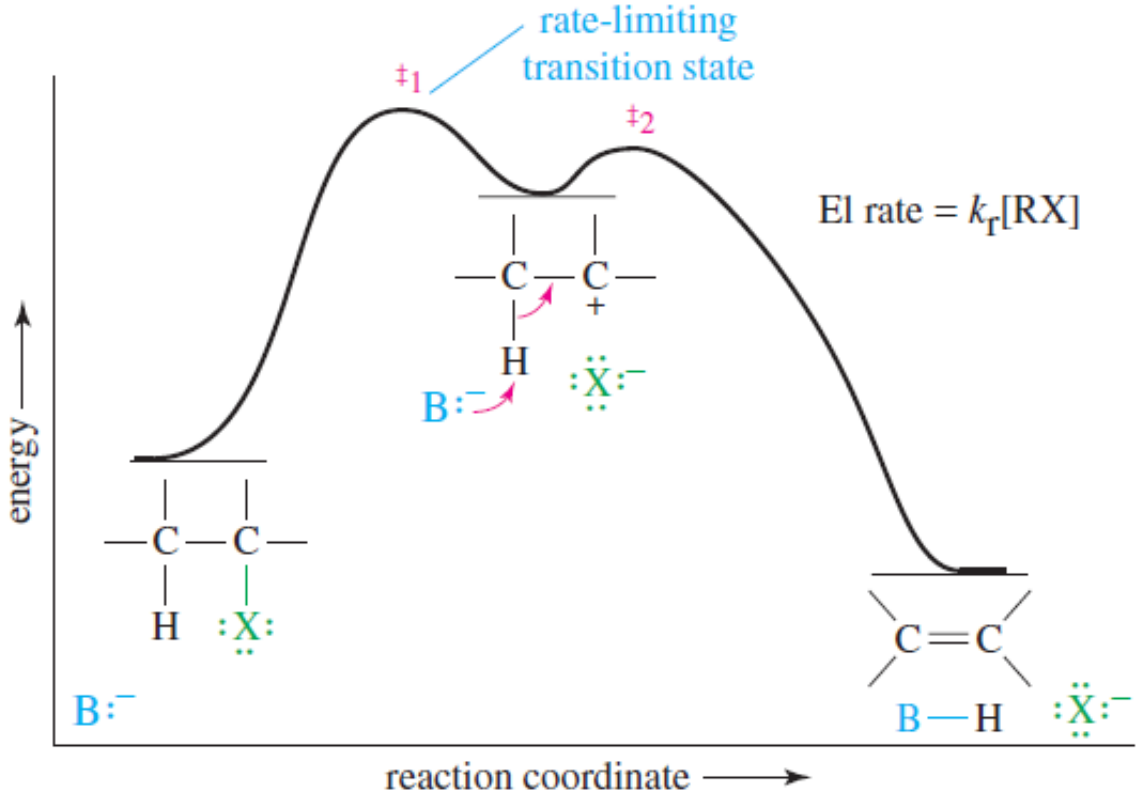
The E1 reaction almost always competes with the S_N1 reaction

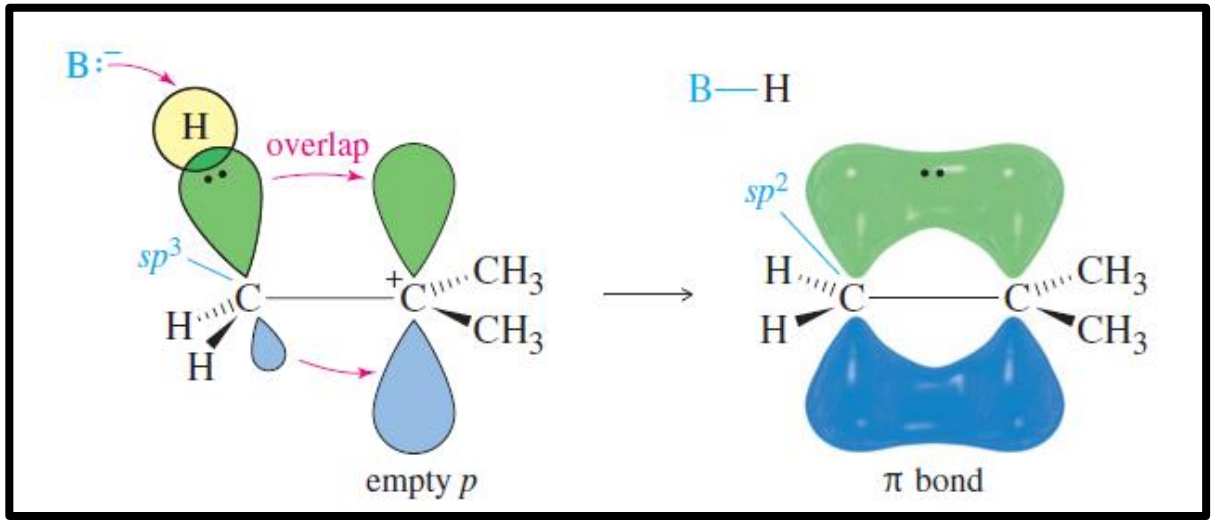


E1: Orbitals and Energetics

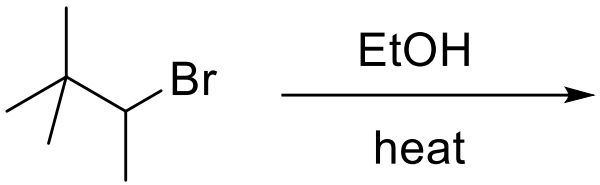


tert-butyl bromide ethanol 2-methylpropene (E1 product)

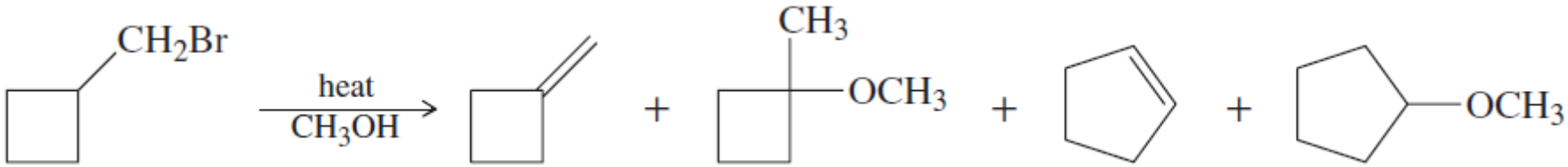




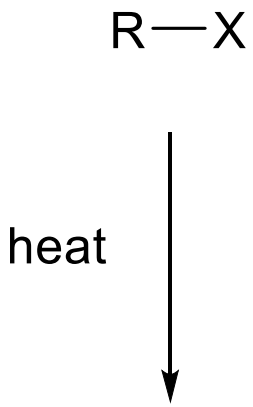
E1: Rearrangements



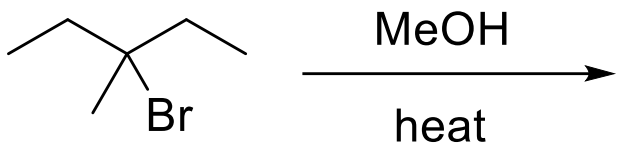
Example 1 When the following compound is heated in methanol, several different products are formed. Propose mechanisms to account for the four products shown.



Summary of Carbocation Reactions

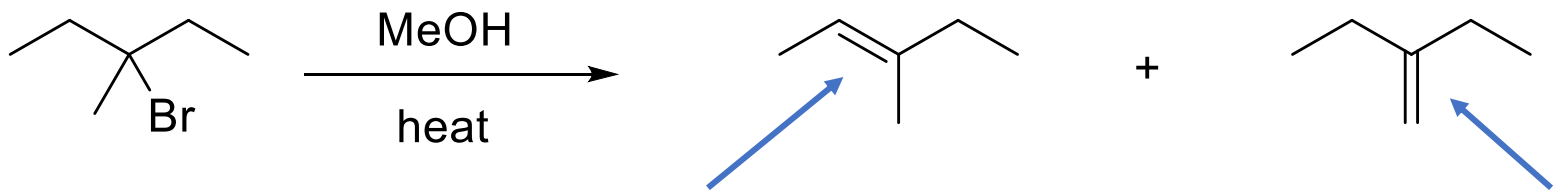


Example 2 Give the substitution and elimination products

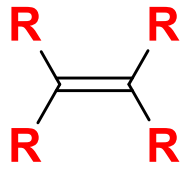


Regioselectivity of E1: Zaitsev's Rule

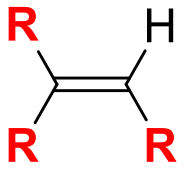
Many compounds can eliminate in more than one way, to give mixtures of alkenes.



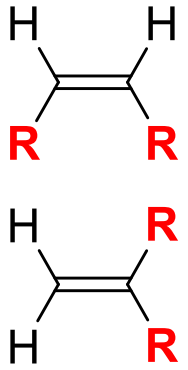
the product with the _____ substituted double bond will predominate



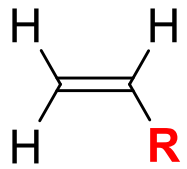
tetrasubstituted



trisubstituted

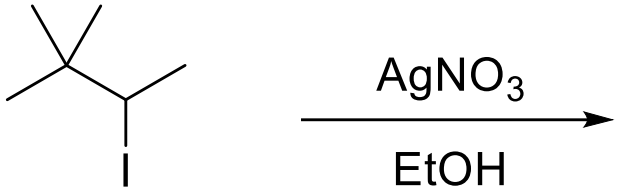


disubstituted

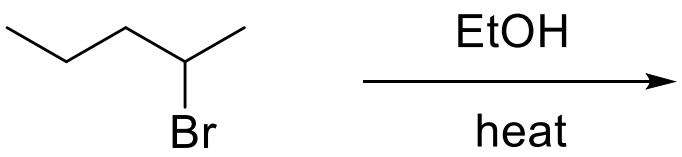


monosubstituted

Example 3 When 3-iodo-2,2-dimethylbutane is treated with silver nitrate in ethanol, three elimination products are formed. Give their structures and predict which one is the major product.



Stereochemistry of E1

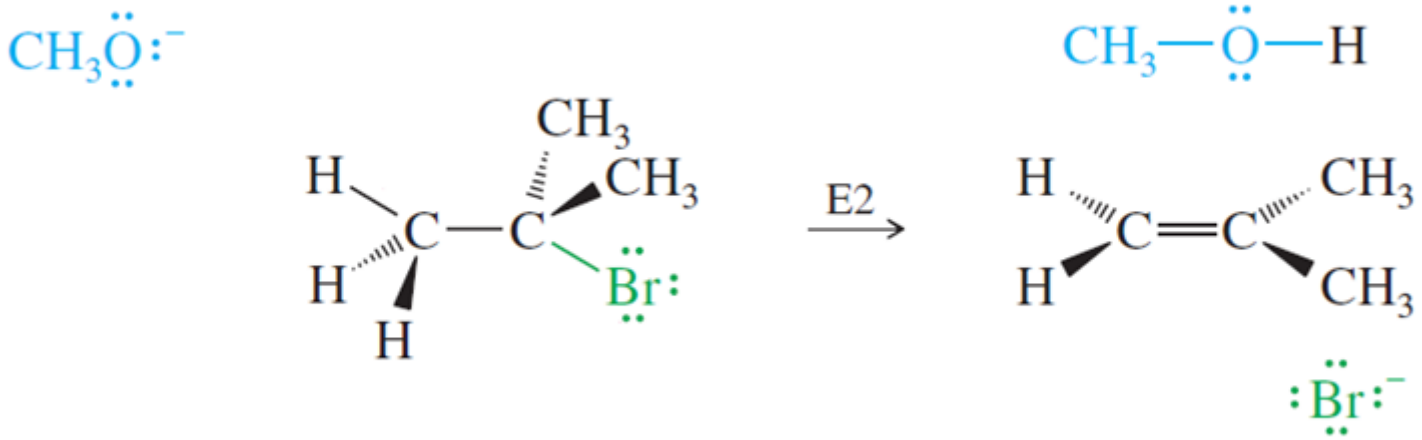


Newman projection:

Stereoselectivity:

Second-Order Elimination (E2)

Eliminations can also take place under second-order conditions with a **strong base** present.

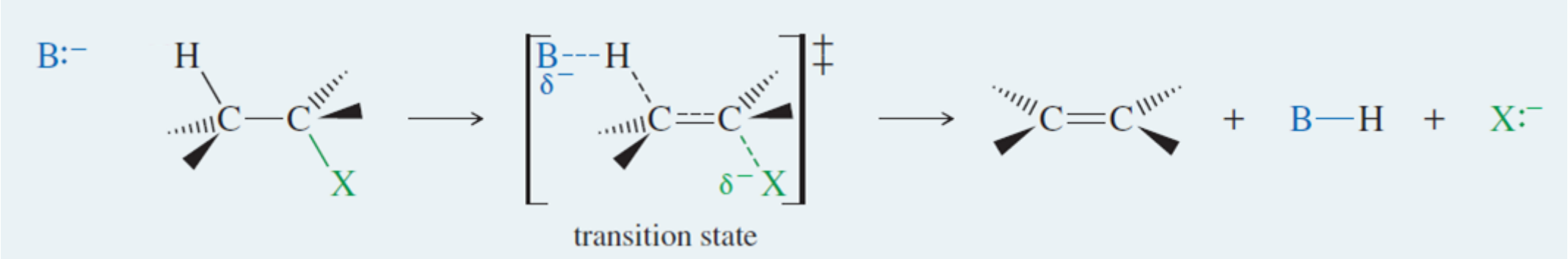


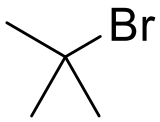
Rate =

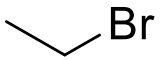
Second-Order Elimination (E2)

Mechanism

The concerted E2 reaction takes place in a **single step**. A strong base abstracts a proton on a carbon next to the leaving group, and the leaving group leaves. The product is an alkene.



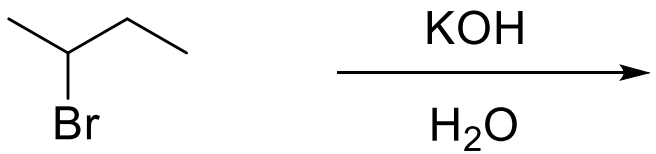


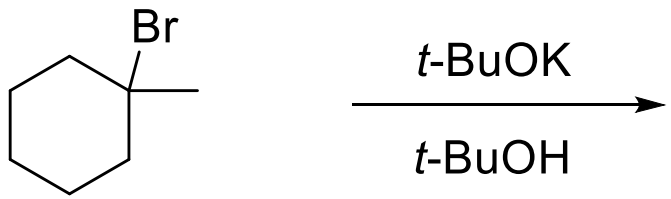


Reactivity of the Substrate in the E2: 3º 2º 1º

Reactivity of the Substrate in the S_N2: 3º 2º 1º

Regioselectivity of E2





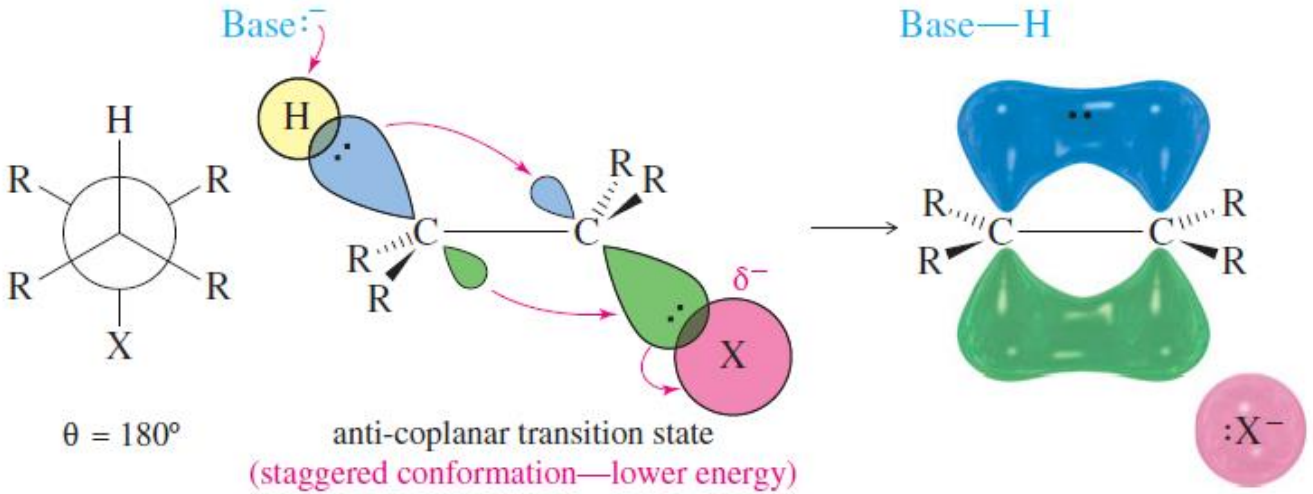
Stereochemistry of E2

Like the S_N2 reaction, the E2 follows a **concerted mechanism**

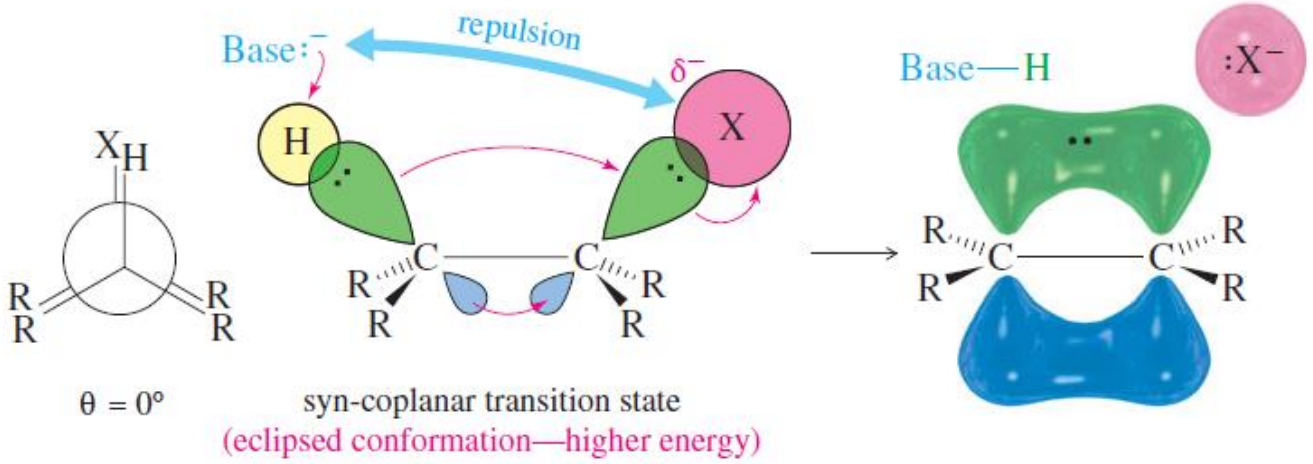
Concerted mechanisms require **specific geometric arrangements** so that the orbitals of the bonds being broken can **overlap** with those being formed and the electrons can flow smoothly from one bond to another.

2 possible conformations:

Anti-periplanar



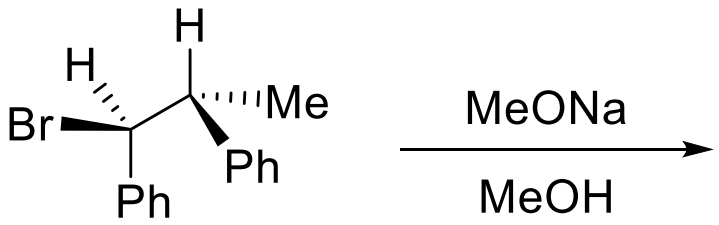
Syn-periplanar



Stereospecific

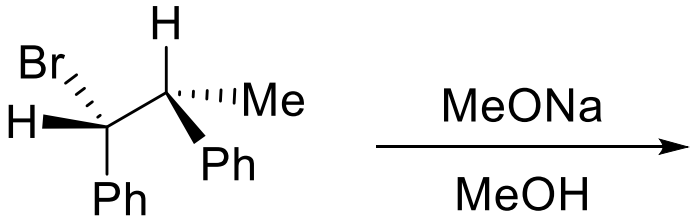
Stereochemistry of E2

Example 4 Predict the outcome of the following reaction



MeONa

MeOH

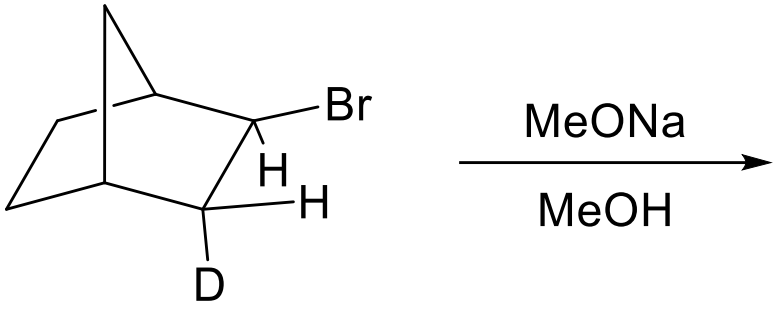


MeONa

MeOH

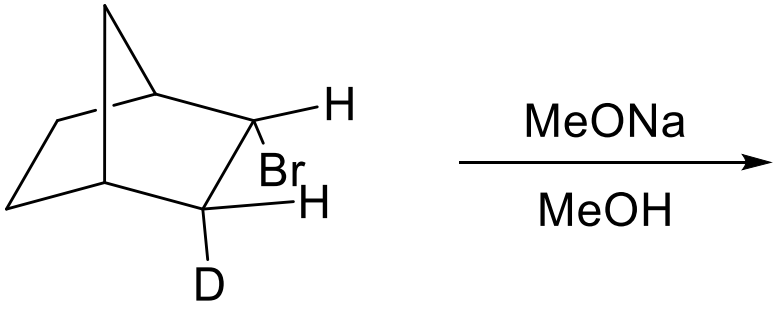
Stereochemistry of E2

Example 4 Predict the outcome of the following reaction



MeONa

MeOH



MeONa

MeOH

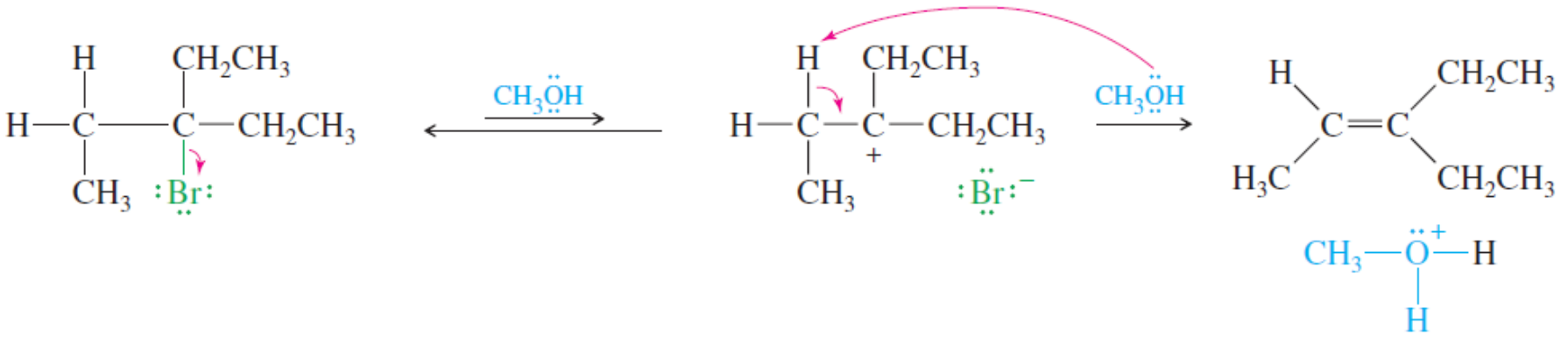
Comparison of E1 vs. E2 Reactions

1) Kinetic

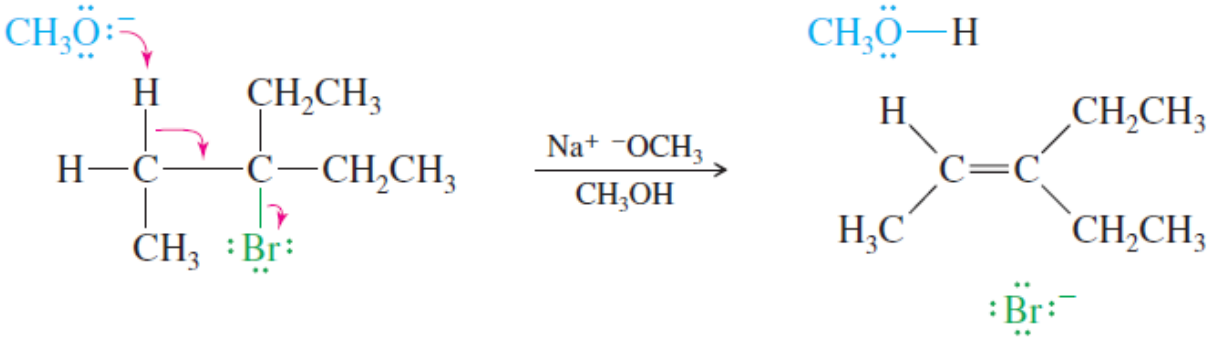
2) Base

3) Solvent

E1



E2

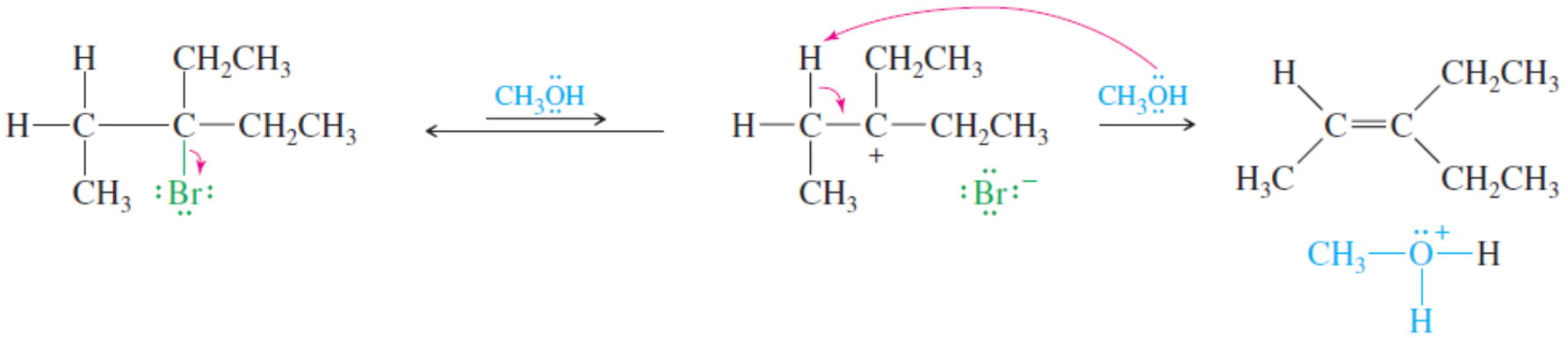


Comparison of E1 vs. E2 Reactions

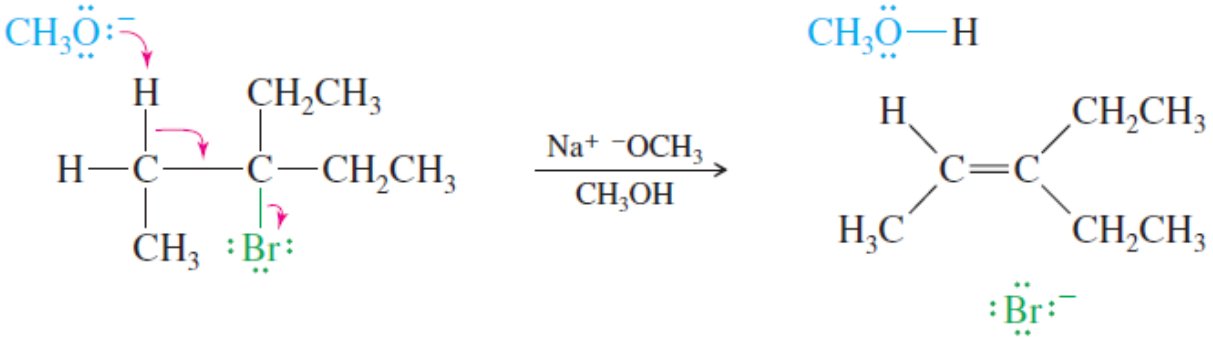
4) Substrate

5) Rearrangements

E1



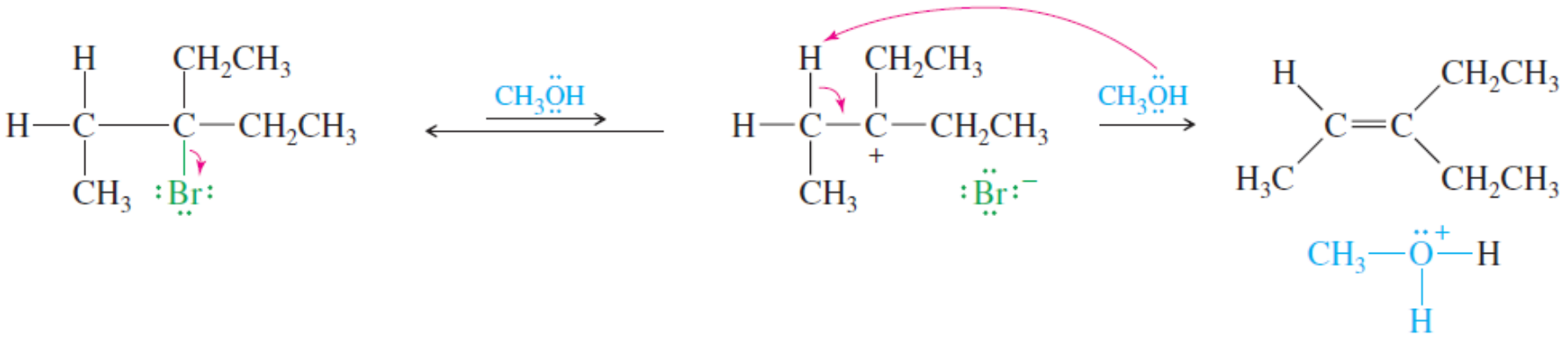
E2



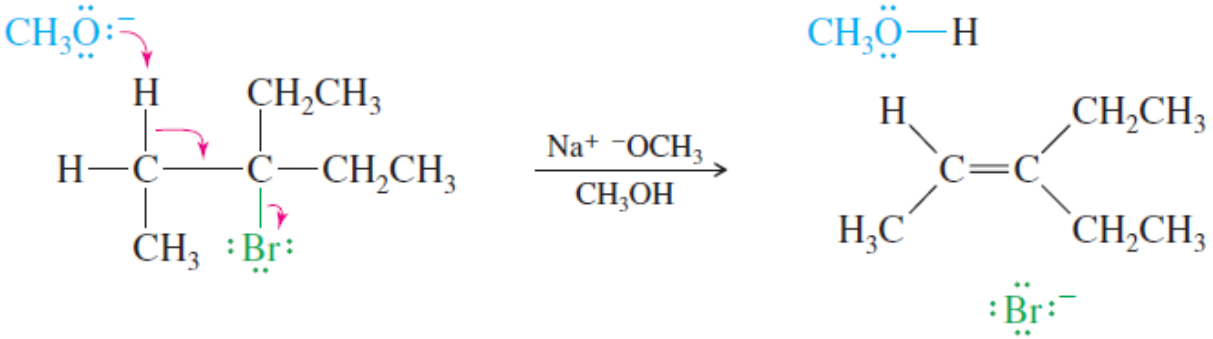
Comparison of E1 vs. E2 Reactions

6) Regioselectivity

E1



E2



7) Stereochemistry

Comparison of E1 vs. E2 Reactions

SUMMARY Elimination Reactions

	E1	E2
Promoting factors		
base	weak bases work	strong base required
solvent	good ionizing solvent	wide variety of solvents
substrate	$3^\circ > 2^\circ$	$3^\circ > 2^\circ > 1^\circ$
leaving group	good one required	good one required
Characteristics		
kinetics	first order, $k_r[RX]$	second order, $k_r[RX][B:^-]$
orientation	most substituted alkene	most substituted alkene
stereochemistry	no special geometry	coplanar transition state required
rearrangements	common	impossible