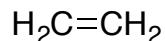


Chapter 7: Structure and Synthesis of Alkenes

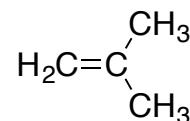
Ex: Common alkenes



ethylene
 $50 \times 10^9 \text{ lb/yr}$

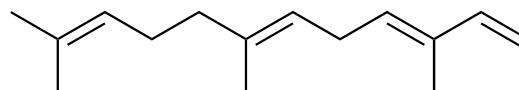


propylene
packaging, rope

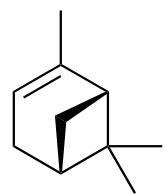


isobutylene
synthetic rubber

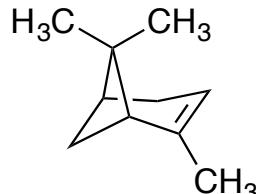
ethanol	$\text{CH}_3\text{CH}_2\text{OH}$
ethylene glycol	$\text{HOCH}_2\text{CH}_2\text{OH}$
vinyl chloride	$\text{H}_2\text{C}=\text{CH}-\text{Cl}$
polyethylene	$\dots -\left(\text{CH}_2\text{CH}_2\right)_n-\dots$



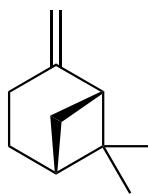
α -farnesene
waxy coating of apples



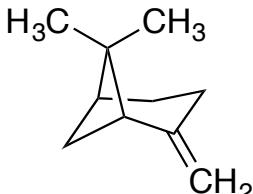
=



α -pinene
terpenoid, insect repellent



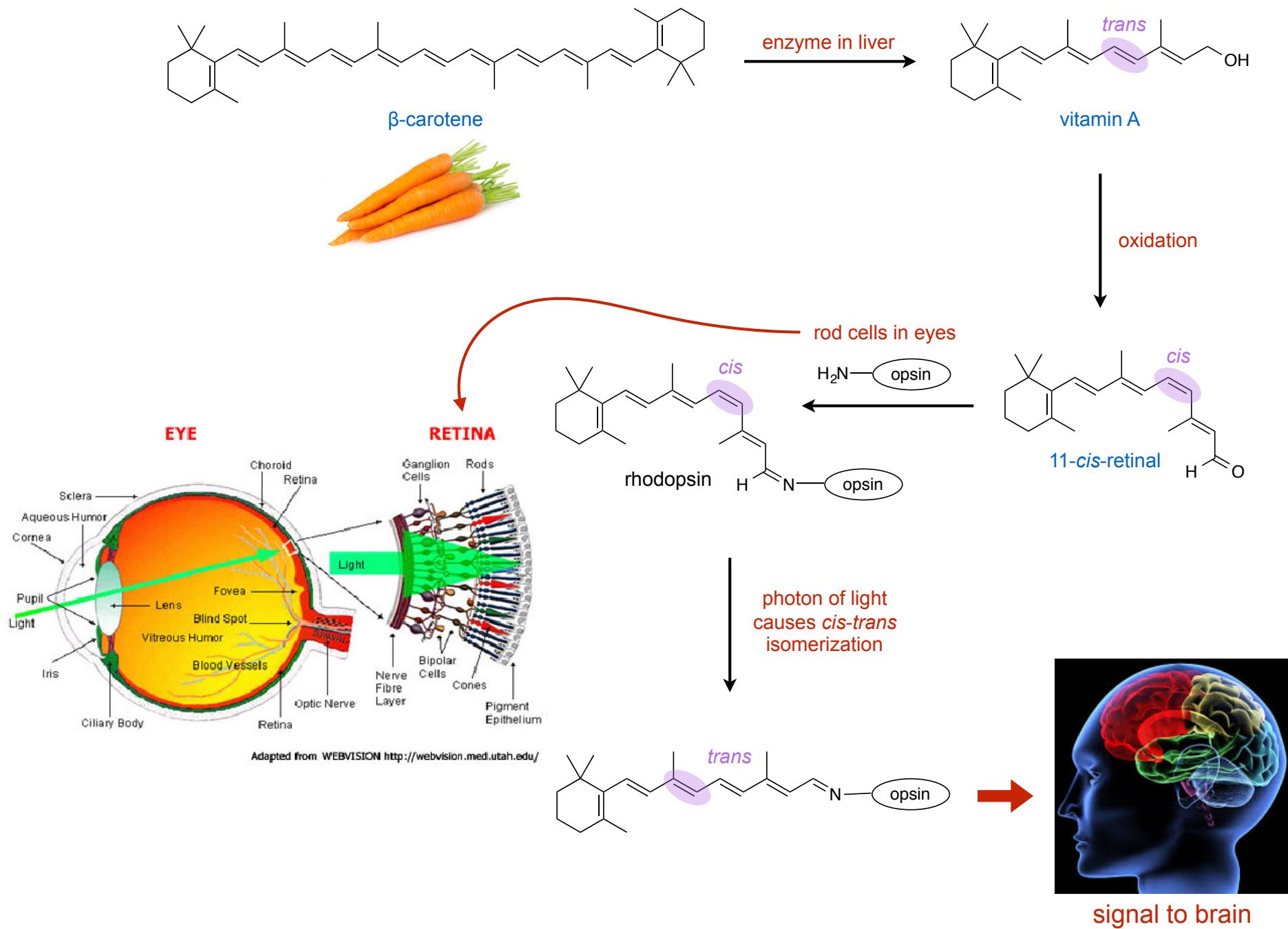
=



β -pinene

- Constituents of pine resin, major components of turpentine
- α -pinene is the most widely encountered terpenoid in nature

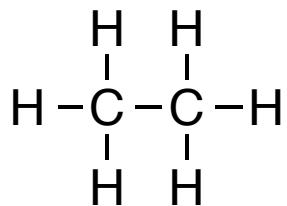
Ex: How humans detect light



Alkene

- a hydrocarbon containing a C=C double bond
- an unsaturated hydrocarbon
- an olefin (olefiant = oil forming)

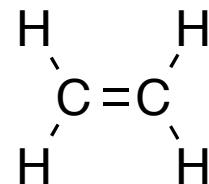
Ex:



ethane



saturated



ethene (ethylene)

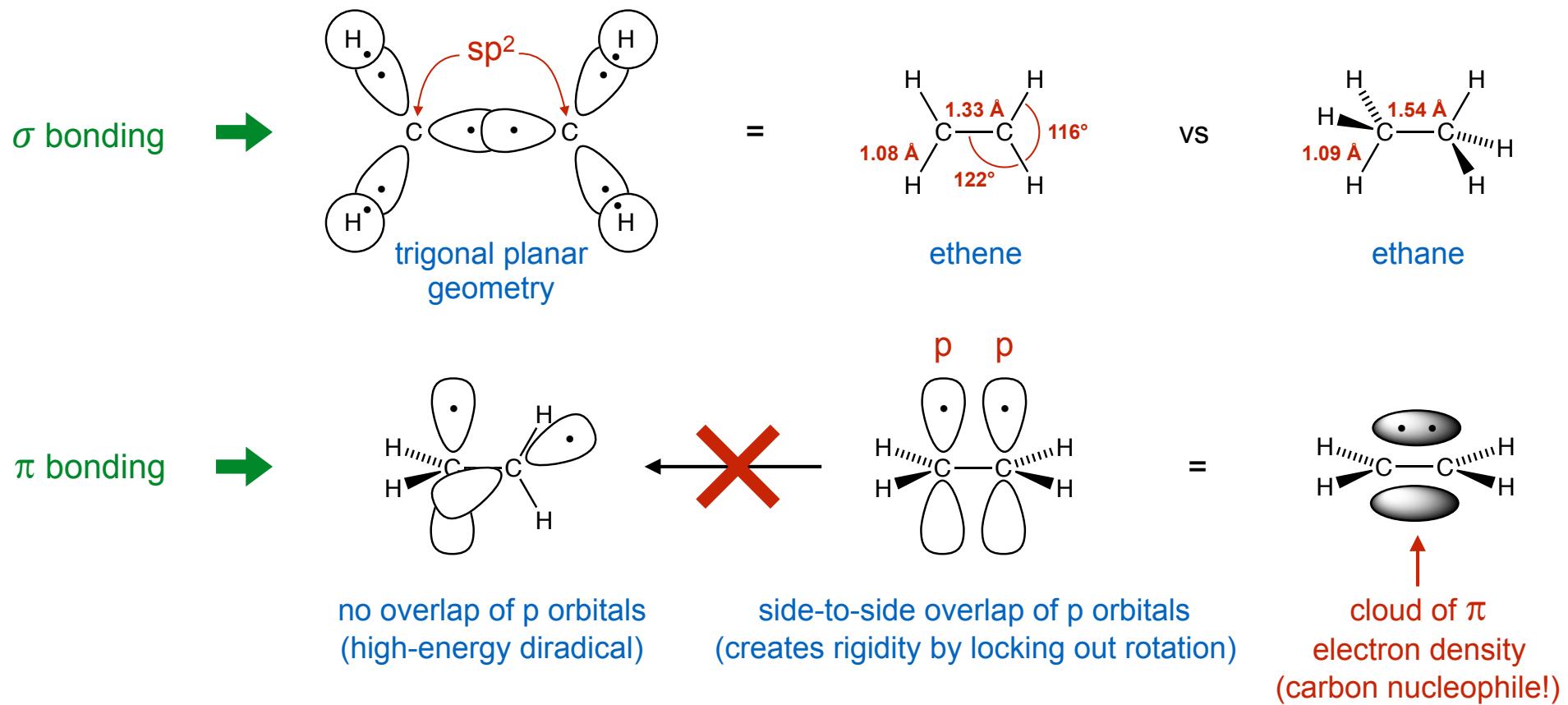


unsaturated

Q: What does unsaturated mean?

Structure of the Alkene C=C bond (7-2)

Ex: Ethene, $\text{H}_2\text{C}=\text{CH}_2$



Q: Strength of a π bond compared to a σ bond?

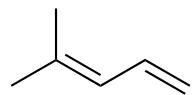
Q: Reactivity of a π bond?

	$\Delta\text{H}_{\text{bond dissociation}} (\text{kJ/mol})$
C=C double bond	611
- C-C σ bond	347
<hr/>	
π bond	264

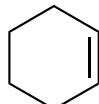
Elements of Unsaturation in Hydrocarbons (7-3)

Elements (degrees) of unsaturation - the presence of a C=C bond or ring reduces the number of H atoms by two from the formula of the corresponding saturated alkane (C_nH_{2n+2})

Ex: Isomers of C_6H_{10} with 2 elements of unsaturation



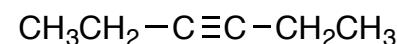
4-methylpenta-1,3-diene



cyclohexene



bicyclo[3.1.0]hexane



hex-3-yne

2 double bonds

1 ring
1 double bond

2 rings

1 triple bond



A C=C bond or ring counts as **one element (degree) of unsaturation**

A C≡C bond counts as **two elements (degrees) of unsaturation**

Q: How can knowing the number of elements of unsaturation be helpful?



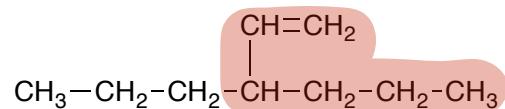
Determining molecular structure of unknown compounds from analytical data (e.g., elemental analysis)

Q: How could you determine if an unknown compound with one element of unsaturation contains a C=C bond instead of a ring?

Nomenclature of Alkenes (7-4)

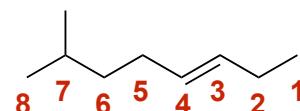
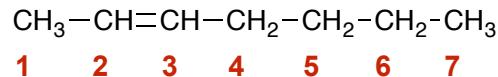
- Similar rules to those for naming alkanes
- Replace suffix -ane with -ene to indicate a C=C bond in the parent chain or ring

1. Find the longest continuous chain containing the C=C bond (parent)

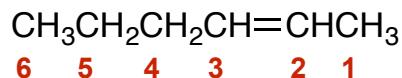


hexene

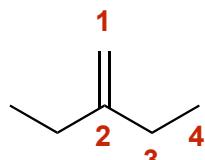
2. Number from the end closest to the C=C bond



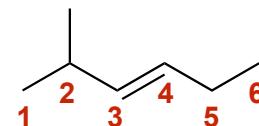
3. Number the substituents and list them alphabetically. Indicate the position of the C=C bond by the number of the first carbon atom followed by -ene. Number multiple C=C bonds the same way and use -diene, -triene, -tetraene, etc. preceded by “a”.



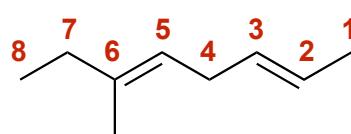
Old IUPAC → 2-hexene
New IUPAC → hex-2-ene



2-ethyl-1-butene
2-ethylbut-1-ene

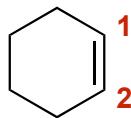


2-methyl-3-hexene
2-methylhex-3-ene

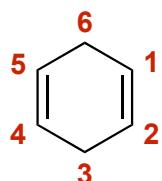


6-methyl-2,5-octadiene (not 2,5-octadiene)
6-methylocta-2,5-diene (not oct-2,5-diene)

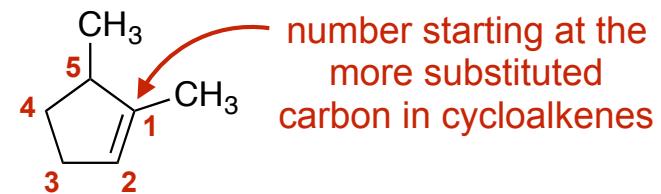
number starting at the C=C bond in cycloalkenes →



cyclohexene

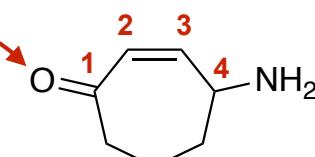


1,4-cyclohexadiene
cyclohexa-1,4-diene

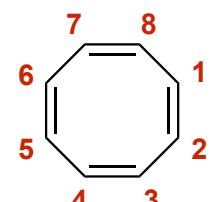


1,5-dimethylcyclopentene

most oxidized functional group takes precedence



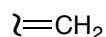
4-amino-1-cyclohept-2-enone
4-aminocyclohept-2-en-1-one



1,3,5,7-cyclooctatetraene
cycloocta-1,3,5,7-tetraene

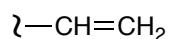
Alkenes as Substituents

Substituent

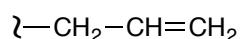


Name

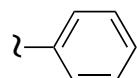
methylene



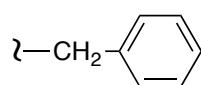
vinyl (ethenyl)



allyl (prop-2-enyl)

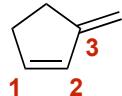


phenyl = Ph = ϕ

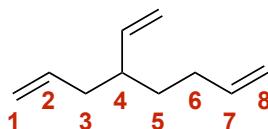


benzyl = Bn

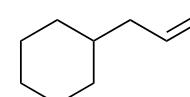
Ex:



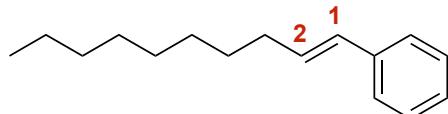
3-methylenecyclopentene



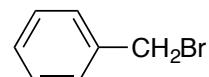
4-vinyl-1,7-octadiene
4-vinylocta-1,7-diene



allylcyclohexane (common name)
3-cyclohexylpropene (IUPAC name)

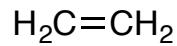


1-phenyl-1-decene
1-phenyldec-1-ene



benzyl bromide (common name)
1-bromo-1-phenylmethane (IUPAC name)

Common Names



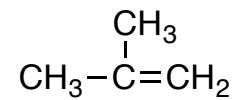
ethylene
(ethene)

precursor for polyethylene
plastics



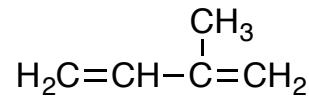
propylene
(propene)

precursor for polypropylene
plastics



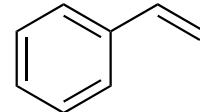
isobutylene
(2-methylpropene)

precursor for polyisobutylene
butyl rubber



isoprene
(2-methylbuta-1,3-diene)

precursor for neoprene rubber

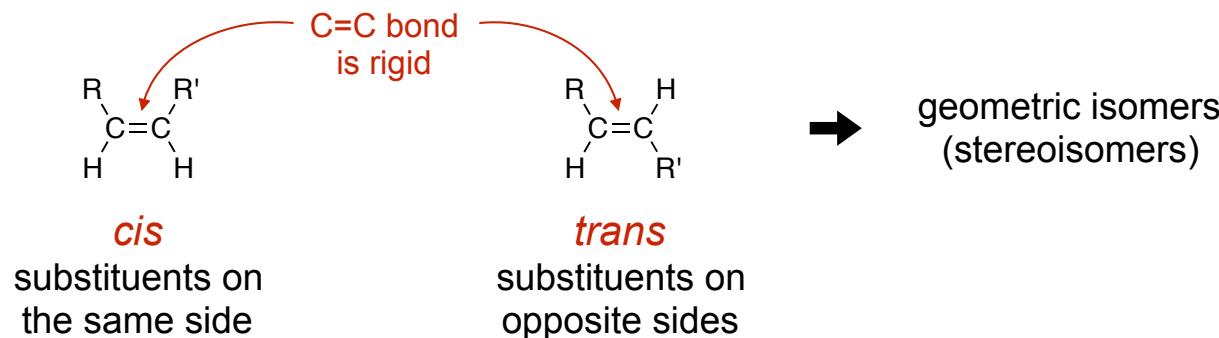


styrene
(vinylbenzene)

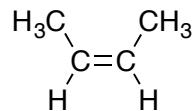
precursor for polystyrene
plastics, styrofoam

Cis-Trans Nomenclature for Isomers of 1,2-Disubstituted Alkenes (7-5)

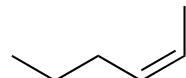
- Substituents on 1,2-disubstituted alkenes can form two different geometric isomers (stereoisomers)



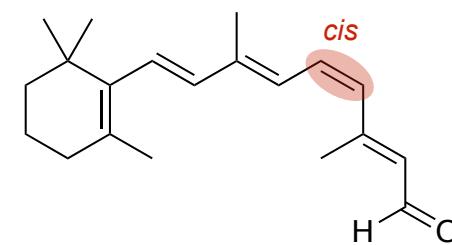
Ex:



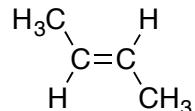
cis-but-2-ene



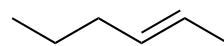
cis-hex-2-ene



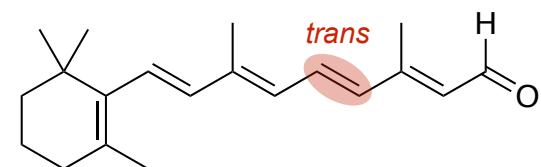
11-*cis*-retinal



trans-but-2-ene



trans-hex-2-ene

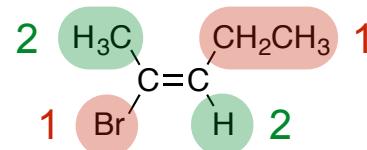


11-*trans*-retinal

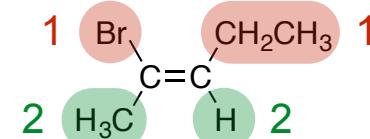
(E)-(Z) Nomenclature (7-5)

- System for indicating stereochemistry of di-, tri-, and tetra-substituted alkenes
 - Uses Cahn-Ingold-Prelog (CIP) rules to prioritize substituents on the C=C bond

Q: Why can't *cis* and *trans* be used to name these stereoisomers?

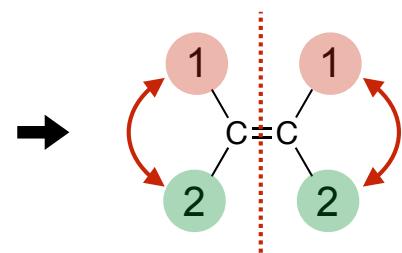


(E)-2-bromopent-2-ene

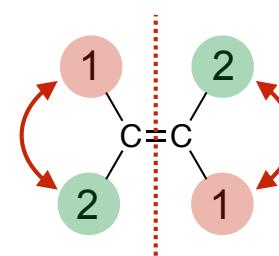


(Z)-2-bromopent-2-ene

use CIP rules to rank the two substituents on each carbon in the C=C bond

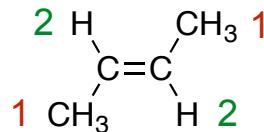


(Z)
“Zusammen”
“together”
on “Zee” same side

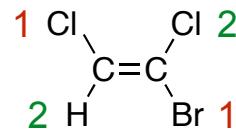


(E)
“Entgegen”
“opposite”

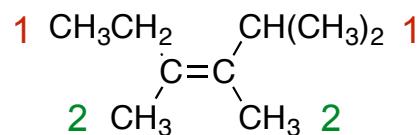
Ex: Name the following alkenes and indicate the correct stereochemistry



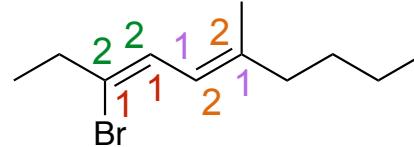
(E)-but-2-ene
trans-but-2-ene



(E)-1-bromo-1,2-dichloroethene



(Z)-2,3,4-trimethylhex-3-ene



(3Z,5E)-3-bromo-6-methyldeca-3,5-diene

Stability of Alkenes (7-8)

- Reactions that form alkenes generally give the most stable (lowest energy) alkene as the major product

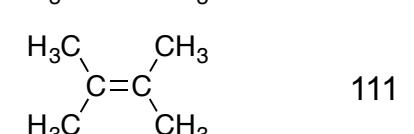
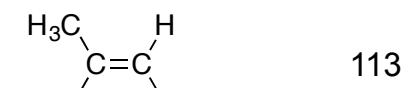
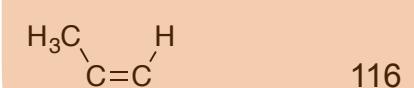
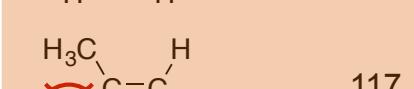
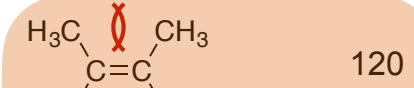
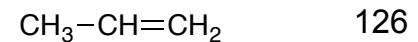
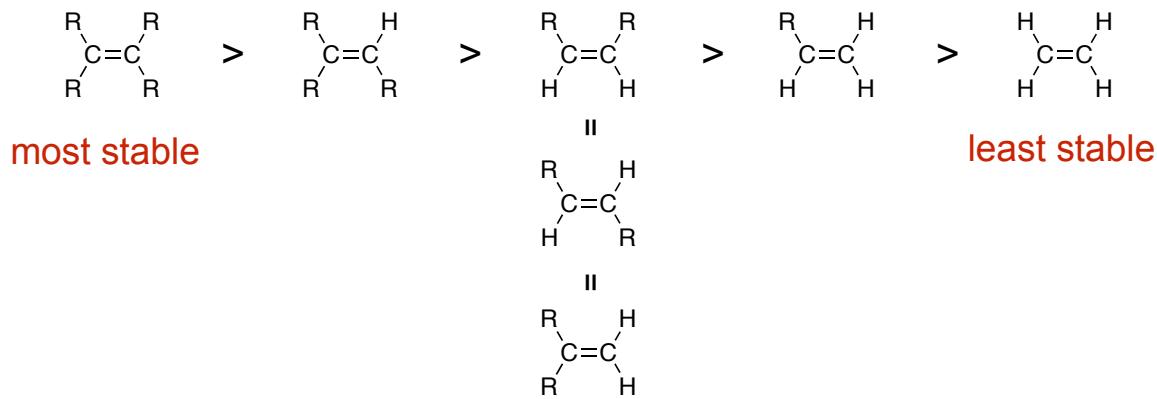
Q: How are the stabilities of alkenes determined?

Ex: Heats of hydrogenation (ΔH_{hyd})



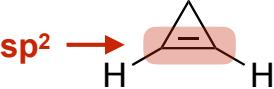
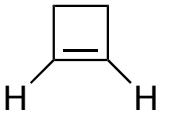
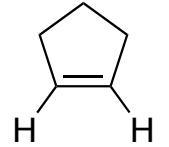
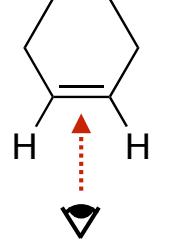
Zaitsev's Rule

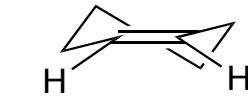
- more substituted alkenes are lower in energy (more stable)



Q: Why is knowing the relative stabilities of alkenes important?

Stability of Cycloalkenes (7-8)

<u>Cycloalkane</u>	<u>Ring Strain (kJ/mol)</u>	<u>Cycloalkene</u>	<u>Ring Strain (kJ/mol)</u>
	115		much higher
	110		128
	27		111
	0		small amount of ring strain



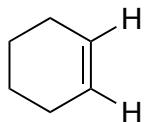
chair-like conformation

Note:

- Extra strain in cycloalkenes makes the C=C bond more reactive compare to acyclic alkenes
- Cycloalkenes with **5 or more carbon atoms** in the ring are quite stable

Cyclic *Cis*-*Trans* Isomers of Cycloalkenes

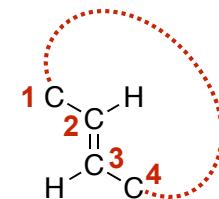
Q: Do these *cis* cycloalkenes have *trans* stereoisomers?



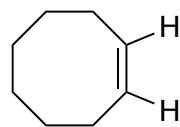
cis-cyclohexene



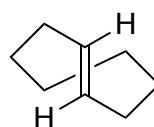
Not possible to form the *trans* isomer! Why?



two carbon atoms cannot bridge
C1 and C4 without a huge
amount of distortion and strain



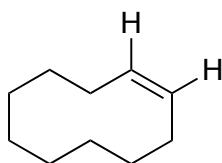
cis-cyclooctene



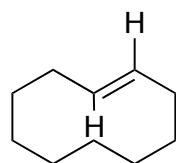
trans-cyclooctene



highly strained



cis-cyclodecene



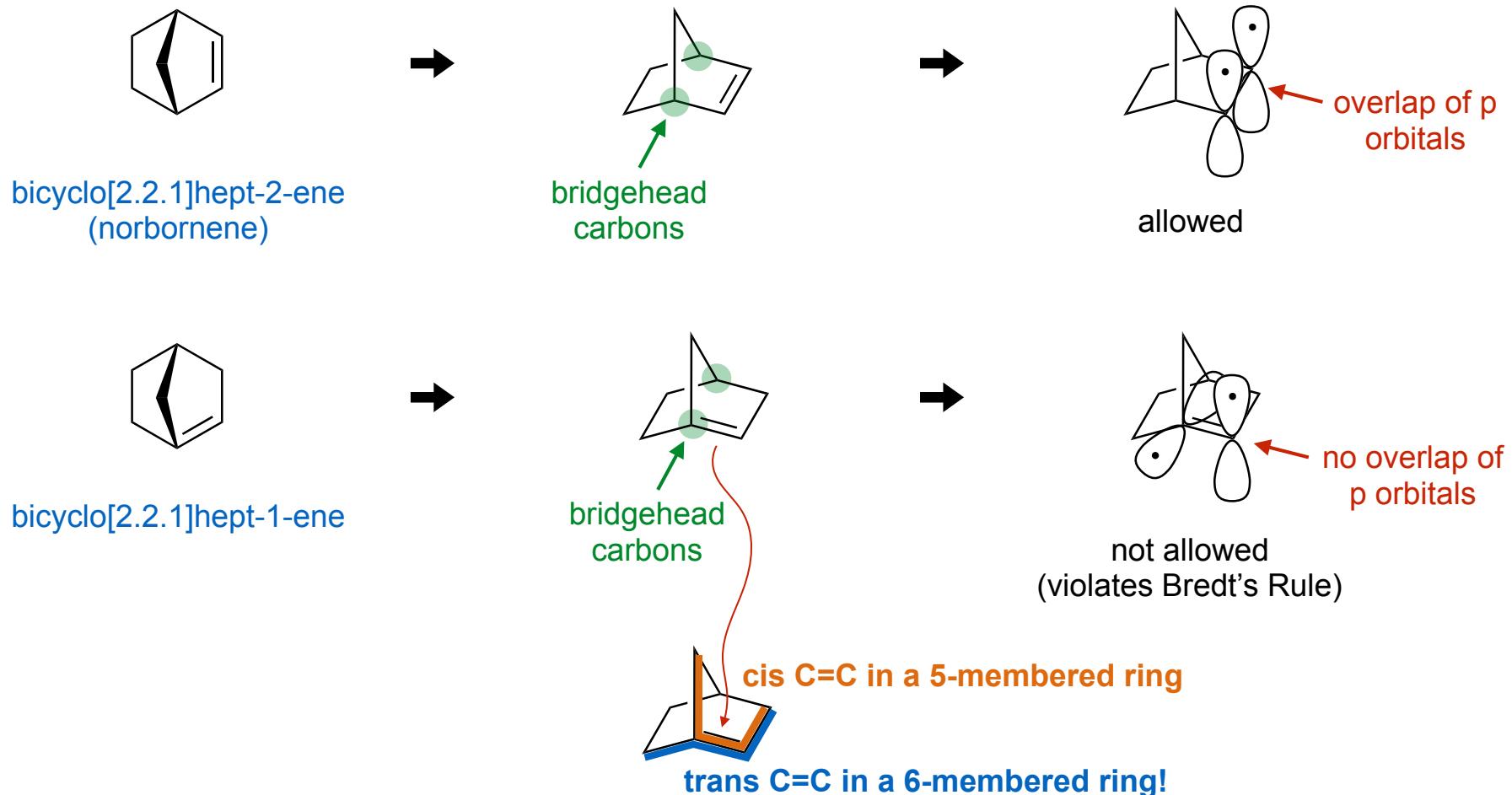
trans-cyclodecene



much less strained

Note: Cyclic alkenes require **at least 8** carbon atoms in the ring to form *cis* and *trans* isomers. Those with **10 or more** carbon atoms are almost free of strain.

Stability of Bridged Bicyclic Alkenes: Bredt's Rule

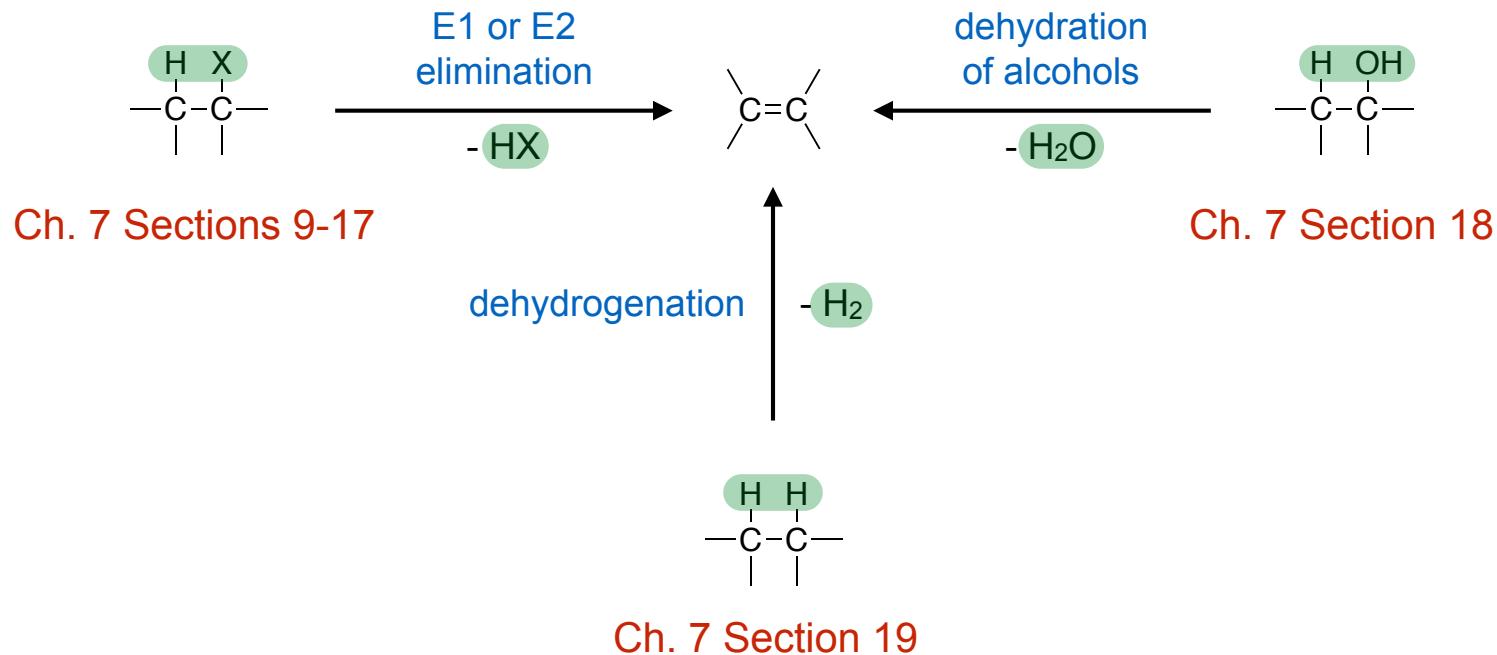


Bredt's Rule - Bridged bicyclic compounds cannot have a C=C bond at a bridgehead carbon unless one ring has at least 8 carbon atoms

Synthesis of Alkenes

Q: How are alkenes synthesized?

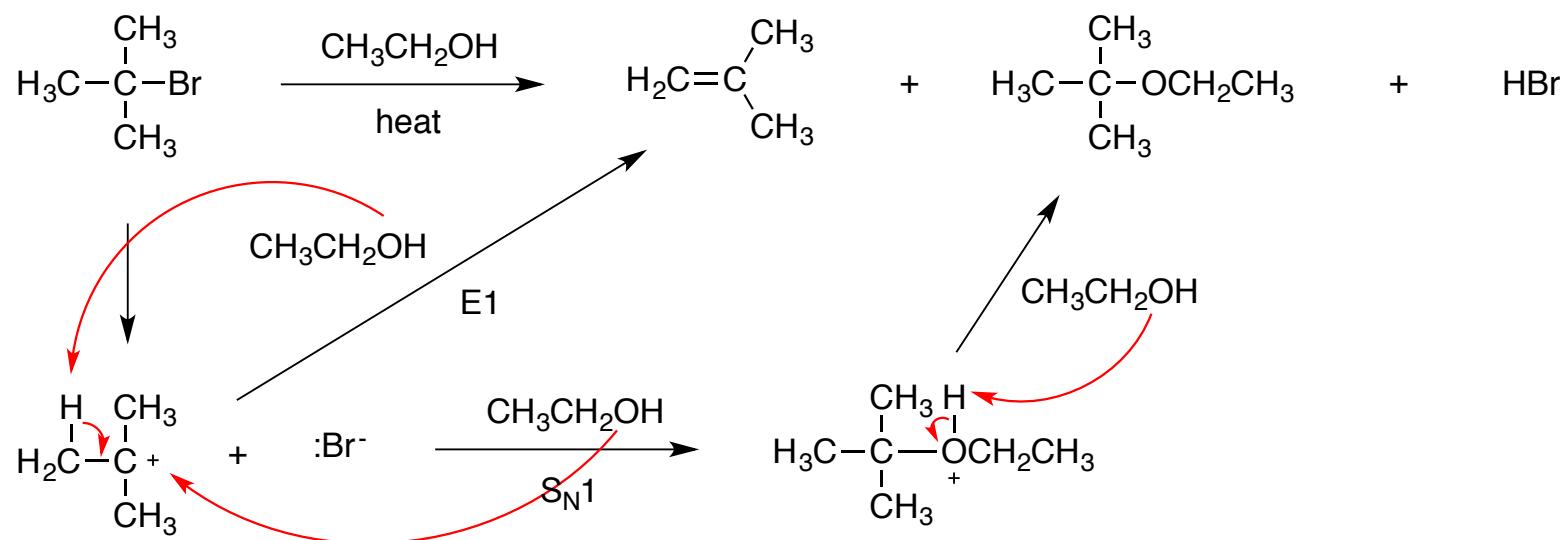
Q: What organic functional groups can be converted into alkenes?



Note: You will learn additional methods to prepare alkenes from other organic functional groups

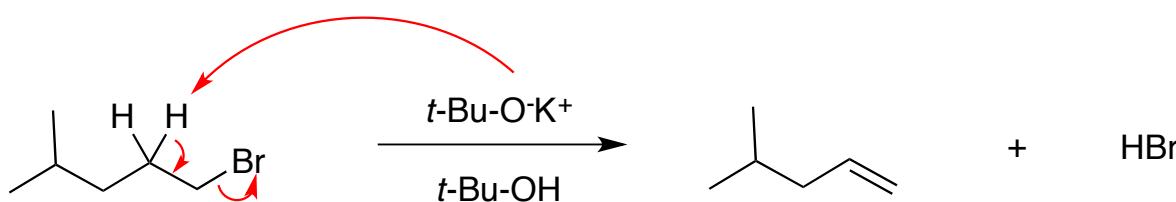
Synthesis of Alkenes by Elimination of HX from Alkyl Halides (7-9)

Ex: E1 Elimination



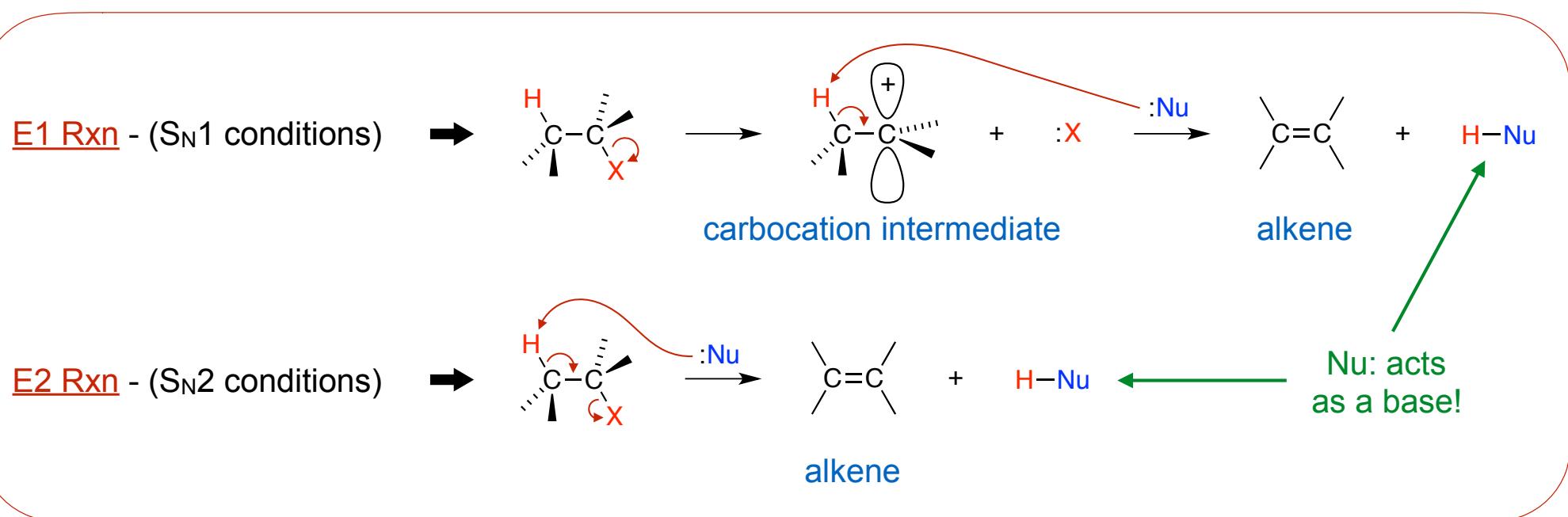
Distribution of products depends on relative rates at which the products form and their relative stabilities

Ex: E2 Elimination

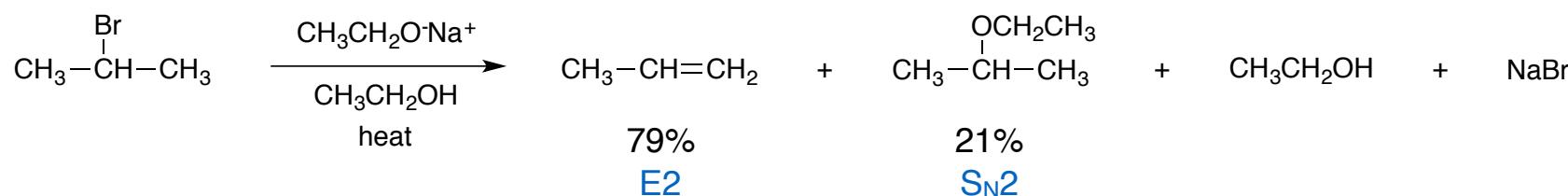
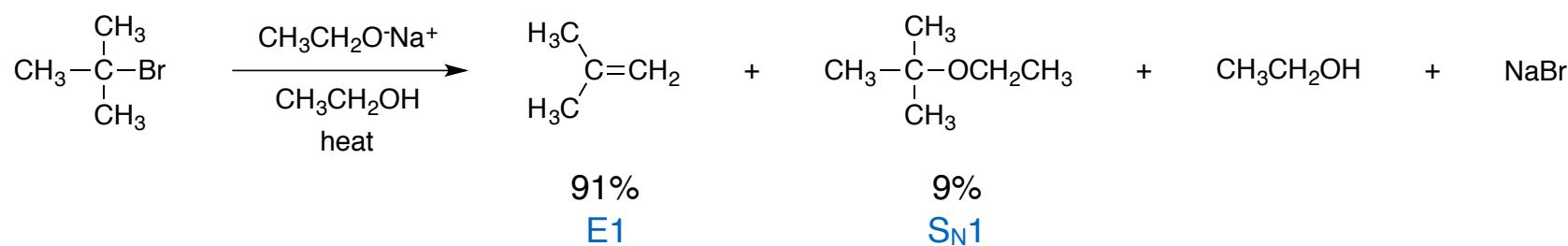


Elimination Reactions

- Elimination produces alkenes
 - Elimination reactions always compete with substitution reactions

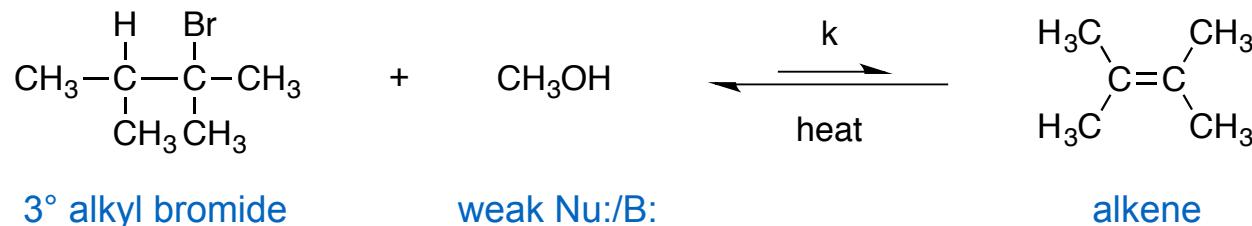


Ex:



First-Order Elimination: The E1 Reaction (7-10)

Ex:

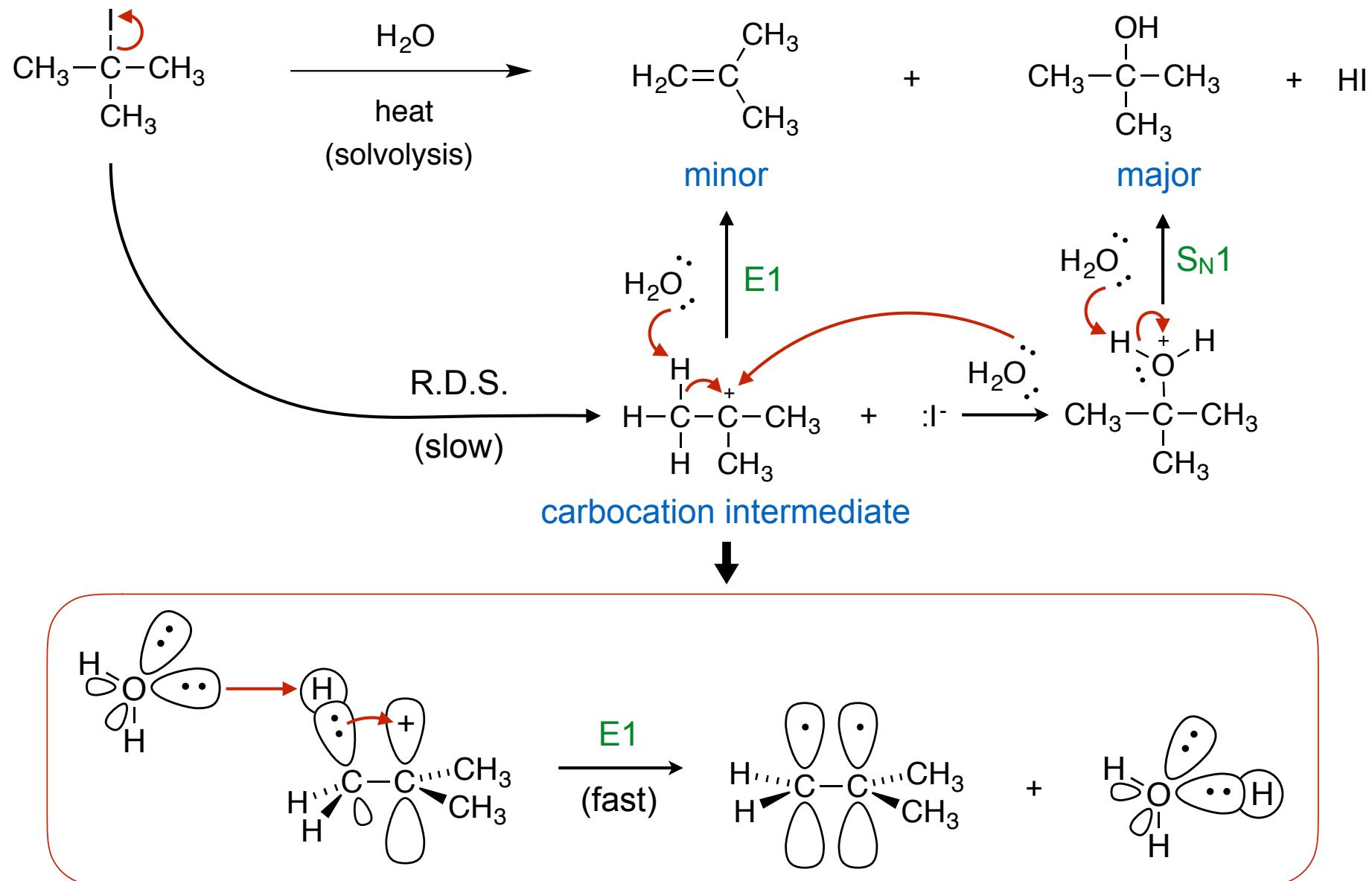


Experimental Observations

- When [CH₃OH] is doubled → rxn rate remains constant
 - When [R-Br] is doubled → rxn rate doubles
- } Rxn rate = k[R-Br] → 1st-order rxn

E1 → Elimination, 1st-order

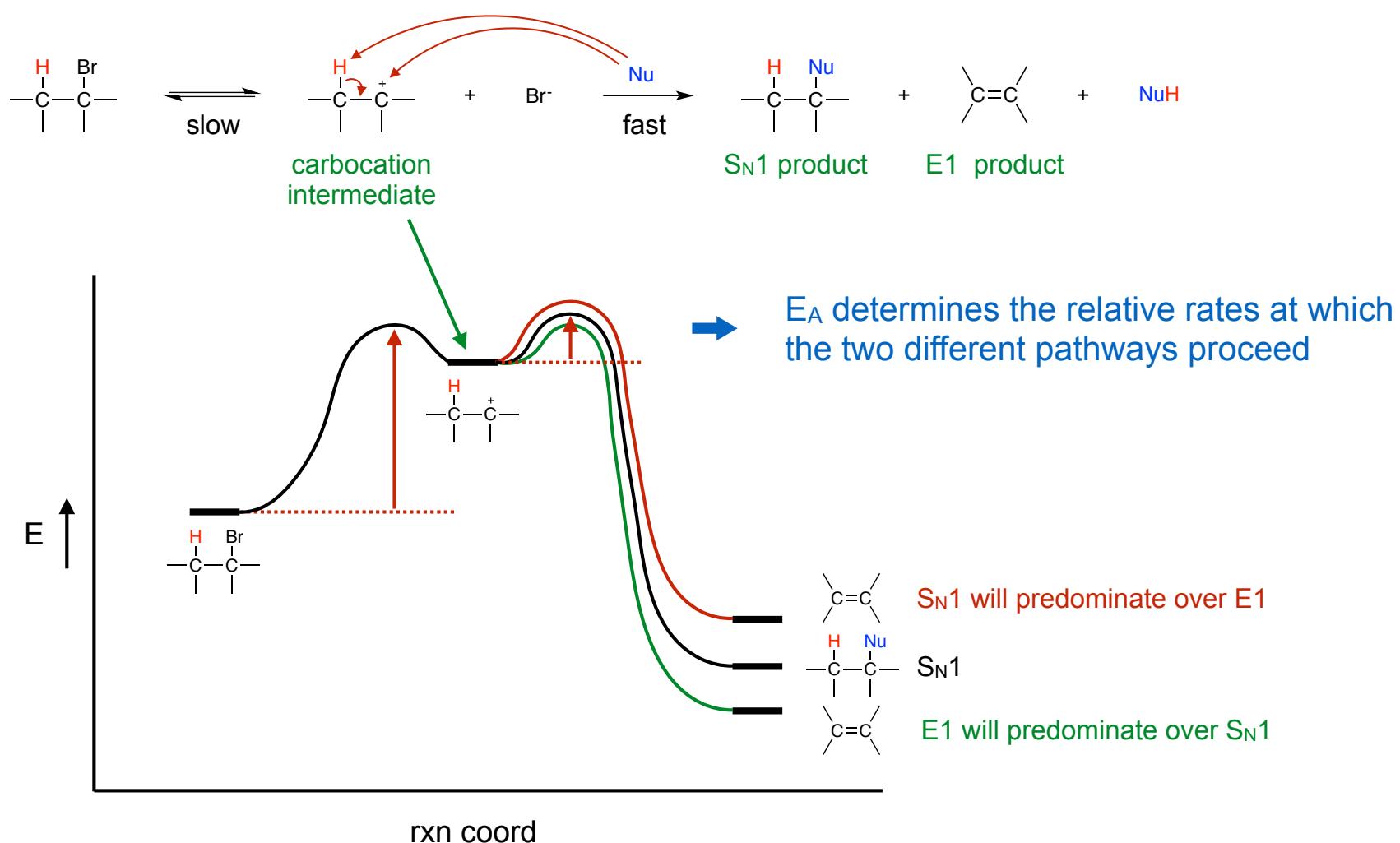
Ex:



Q: Why is E1 elimination always possible when carrying out S_N1 substitution?

→ E1 and S_N1 reactions both proceed via a carbocation intermediate!

Q: Which first-order pathway— S_N1 or $E1$ —will predominate to form the major product?



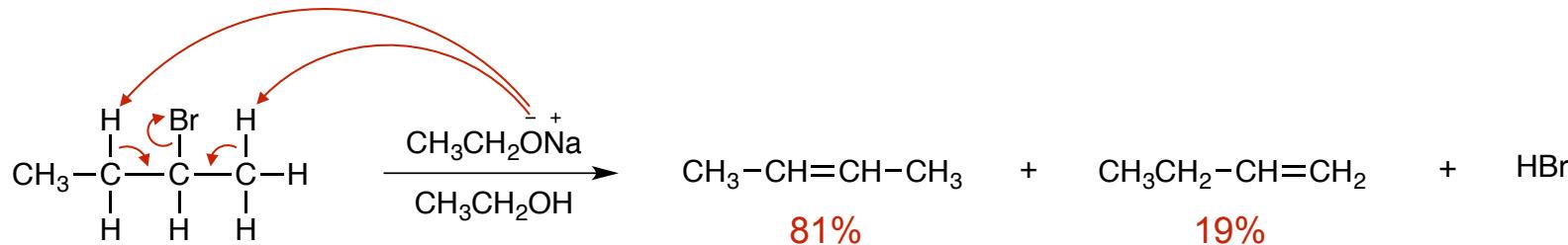
Carbocations often react via both S_N1 and $E1$ pathways simultaneously giving mixtures of products

- S_N1 and $E1$ reactions with alkyl halides generally are not used for organic synthesis if more selective/efficient synthetic approaches are available

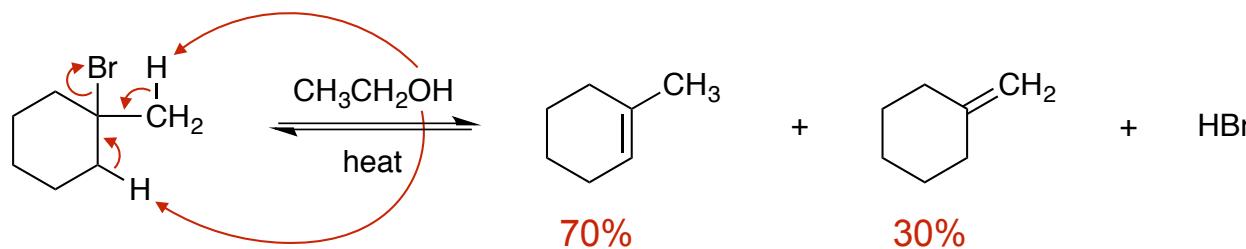
Zaitsev's Rule (7-11)

Elimination reactions favor formation of alkenes that are more highly substituted

Ex:

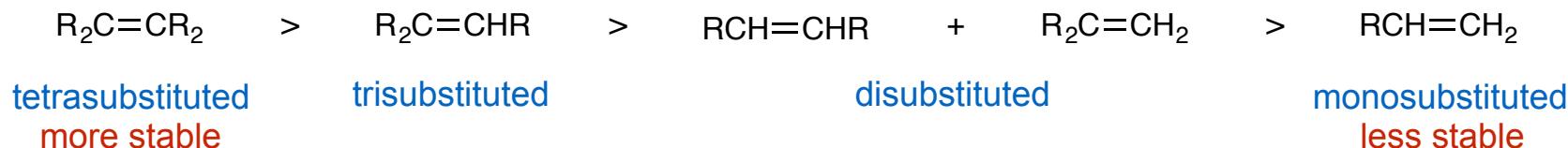


Ex:

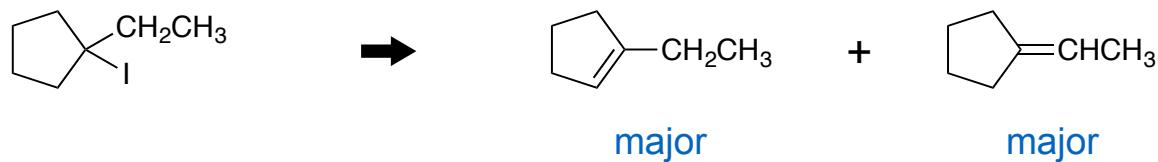
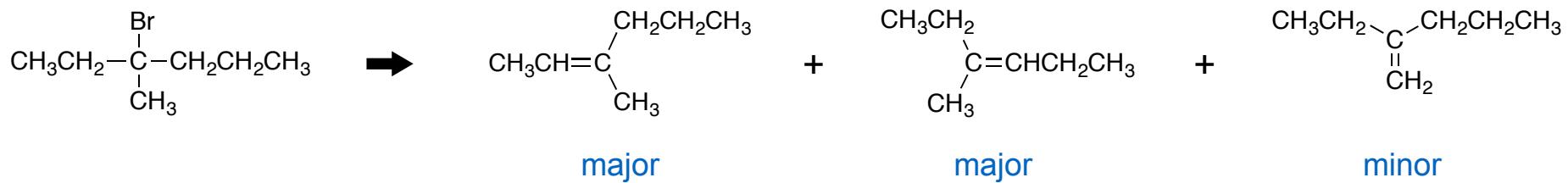
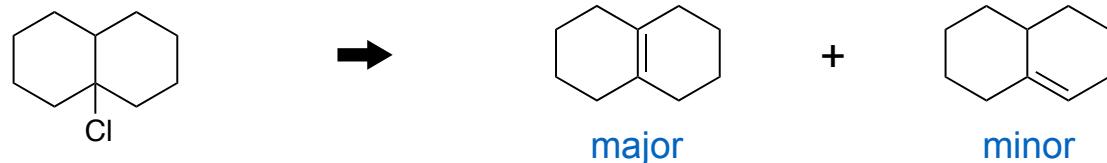


Zaitsev's Rule - The most substituted alkene predominates in elimination reactions

- Alkyl groups are electron donating and lower the energy of alkenes by contributing electron density to the π bond (i.e., more alkyl substituents = greater stability)



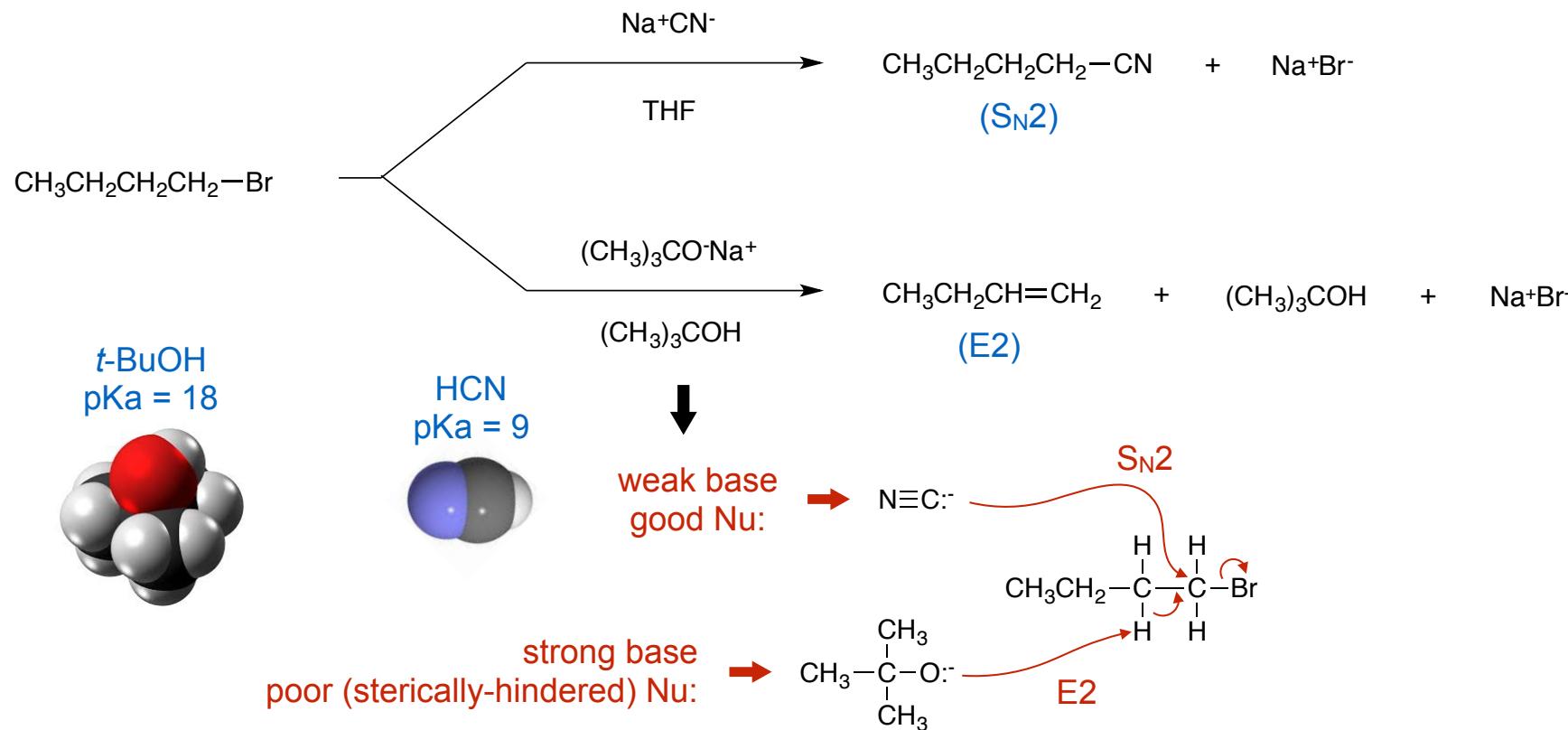
Q: What are the possible products of E1 elimination? Major product?



Second-Order Elimination: The E2 Reaction (7-12)

- E2 elimination always competes with S_N2 substitution with 1° and 2° alkyl halides (S_N2) when the nucleophile is a **strong base**, especially when the nucleophile is a **large, sterically-hindered base**
- E2 elimination occurs with 3° alkyl halides (S_N1) when the nucleophile is a strong base

Ex:

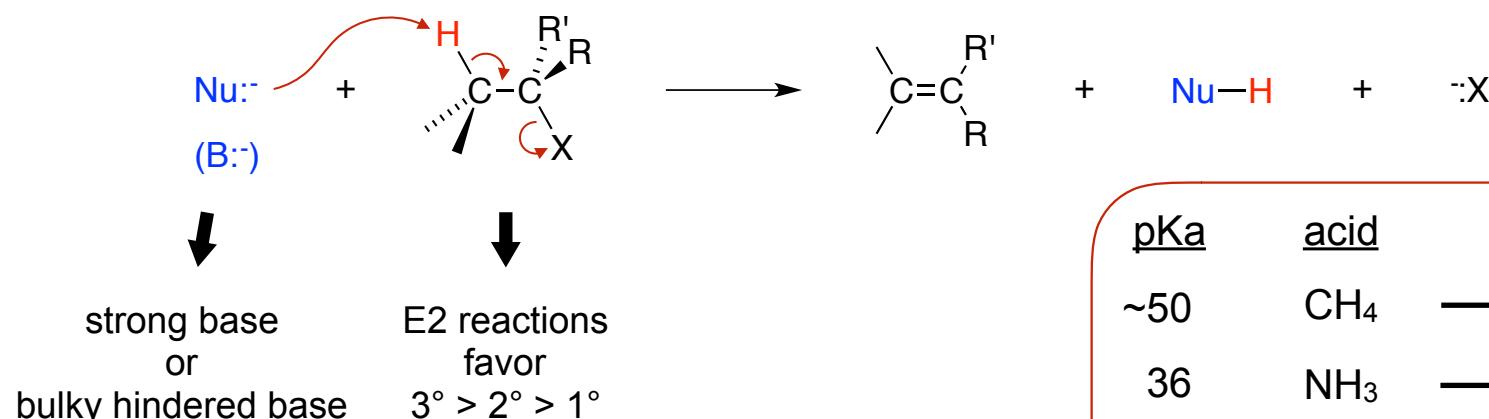


Experimental Observations

- When $[(\text{CH}_3)_3\text{CO}^-\text{Na}^-]$ is doubled \rightarrow rxn rate doubles
 - When $[\text{R}-\text{Br}]$ is doubled \rightarrow rxn rate doubles
- $\left. \right\} \text{Rxn rate} = k[\text{R}-\text{Br}][(\text{CH}_3)_3\text{CO}^-\text{Na}^-] \rightarrow \text{2nd-order rxn}$

E2 → Elimination, 2nd-order

General Reaction for E2 Elimination



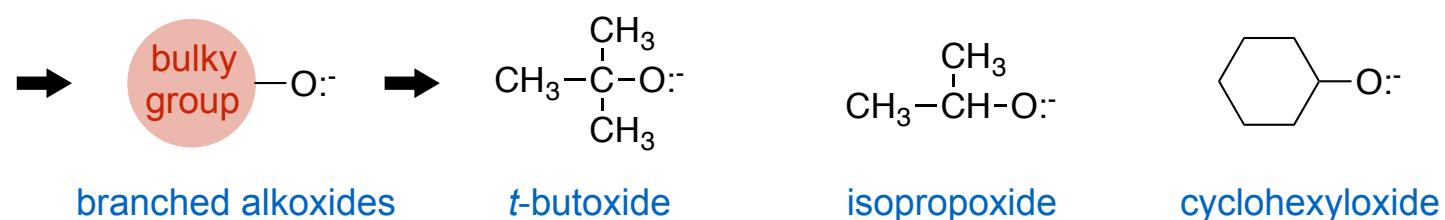
Q: What are strong bases or bulky sterically hindered bases?

<u>pKa</u>	<u>acid</u>	<u>conj. base</u>
~50	CH ₄	→ :CH ₃ ⁻ + H ⁺
36	NH ₃	→ :NH ₂ ⁻ + H ⁺
16	H ₂ O	→ :OH ⁻ + H ⁺
3.5	HF	→ :F ⁻ + H ⁺

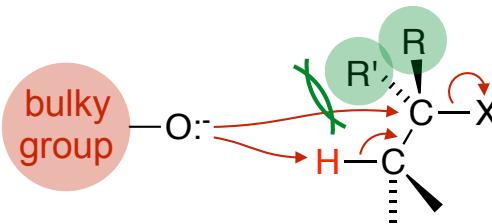
strong bases that are conjugate
bases of weak acids



sterically hindered bases that
are poor nucleophiles



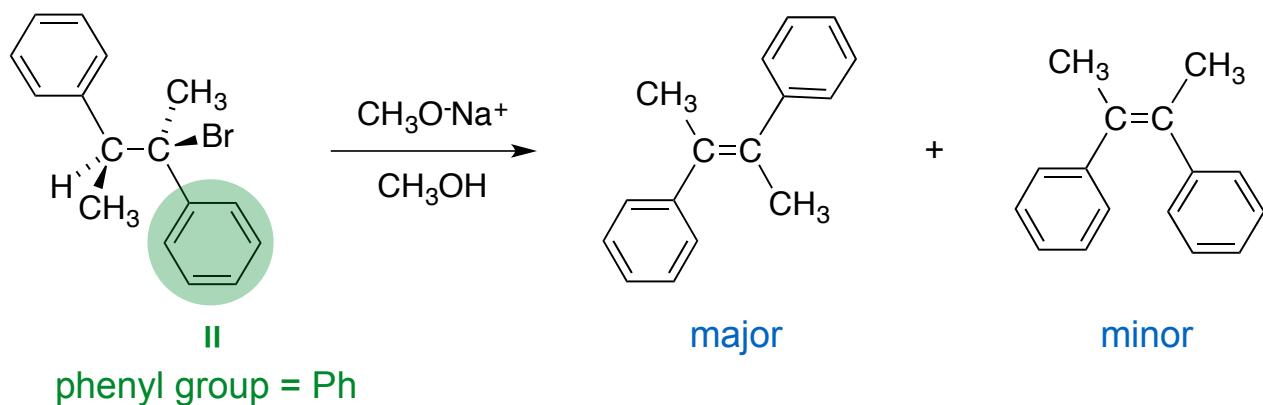
**bulky group biases inhibits substitution
& biases approach to favor elimination**



Stereochemistry of E2 Reactions (7-14)

- E2 reactions require *anti*-coplanar or *syn*-coplanar geometry of H and X for elimination to occur
- Elimination from *anti*-coplanar or *syn*-coplanar conformations of H and X gives two alkenes with opposite stereochemistry

Ex:

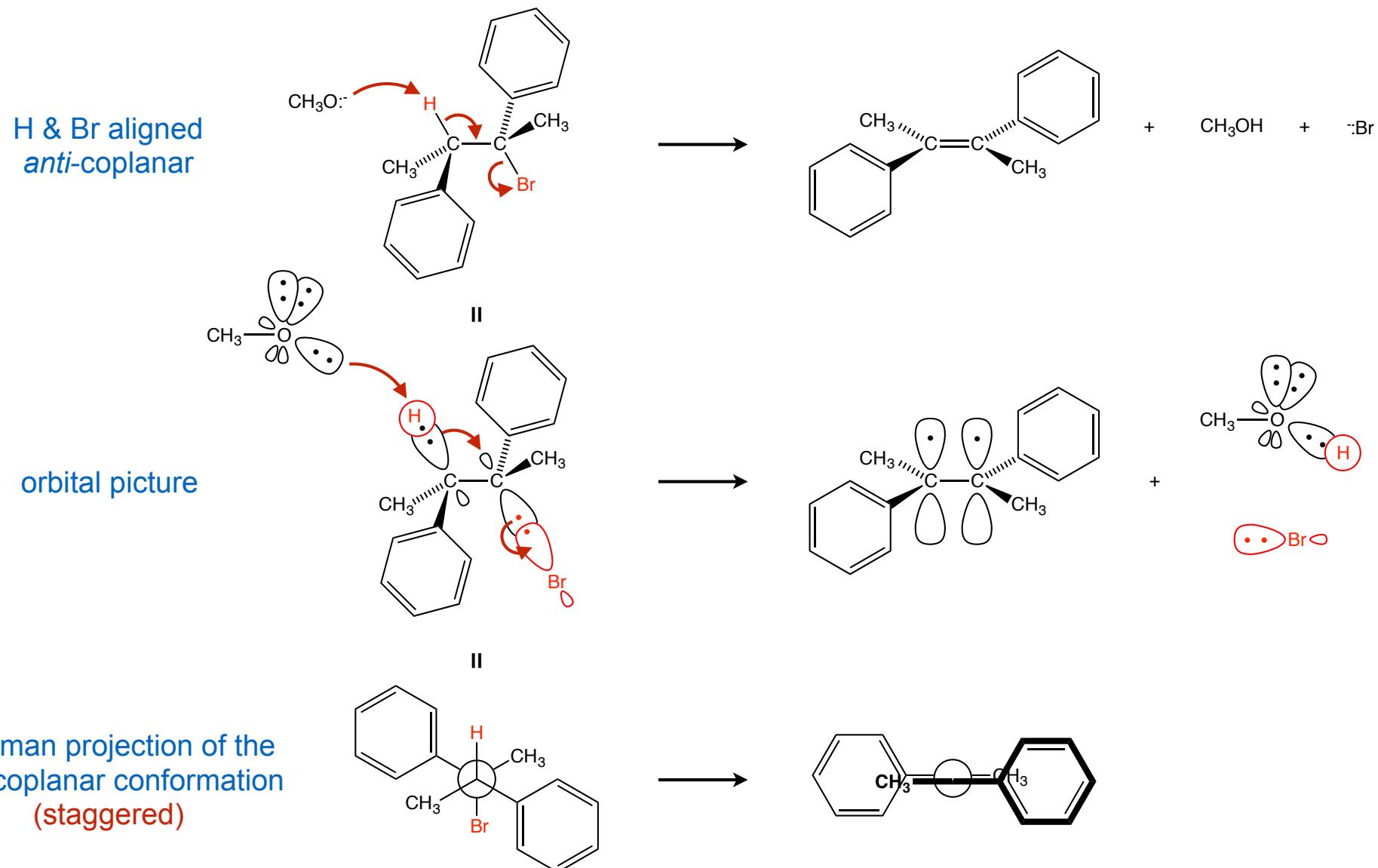


Q: Why is one alkene favored over the other?

→ Examine the conformations required for E2 reactions to occur

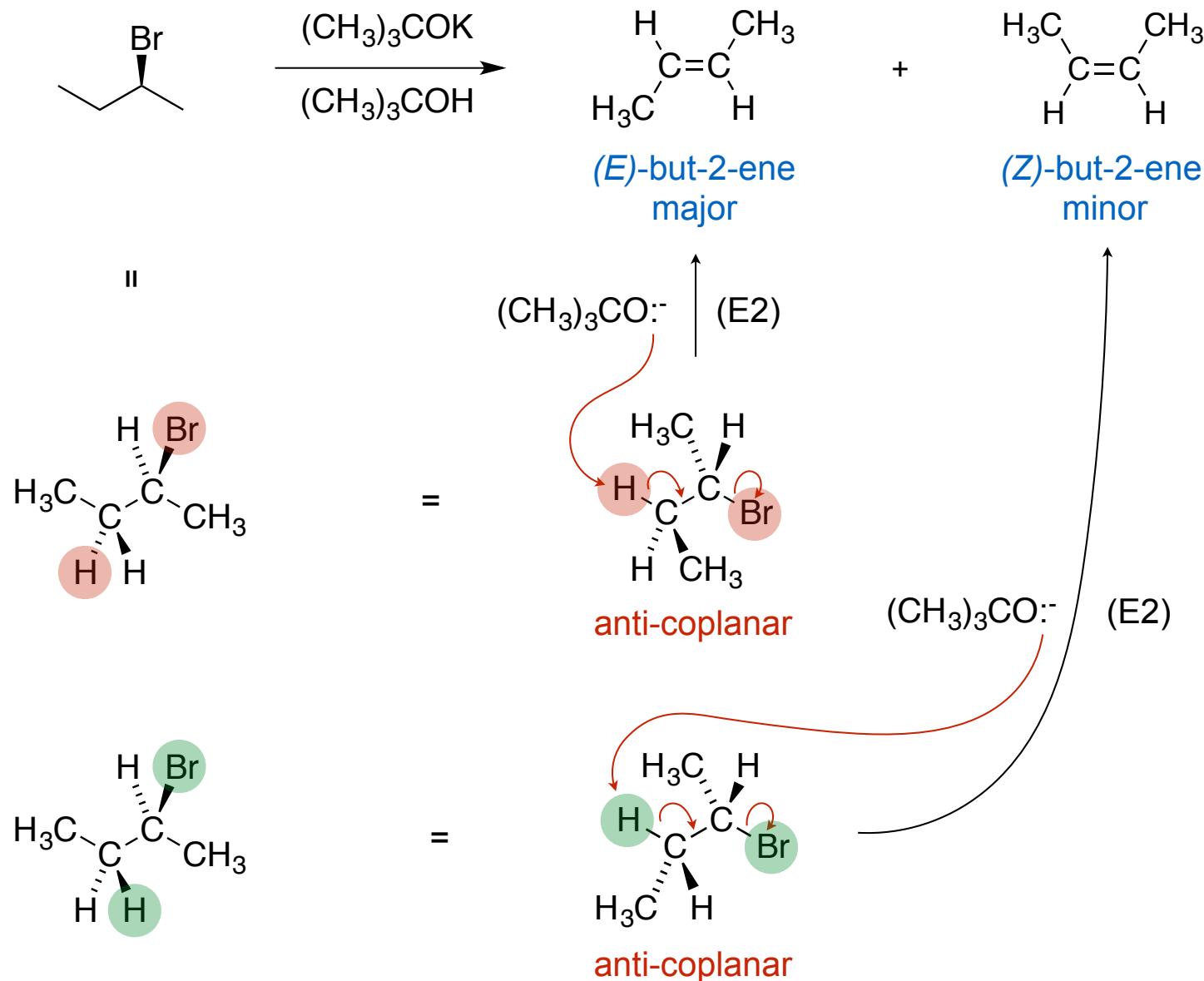
Anti-Coplanar Conformation

- When H and X are *anti* to each other (torsion angle of H-C-C-X, $\theta = 180^\circ$)
- The *anti*-coplanar conformation aligns the sp^3 -hybridized orbitals coplanar allowing a π bond to form



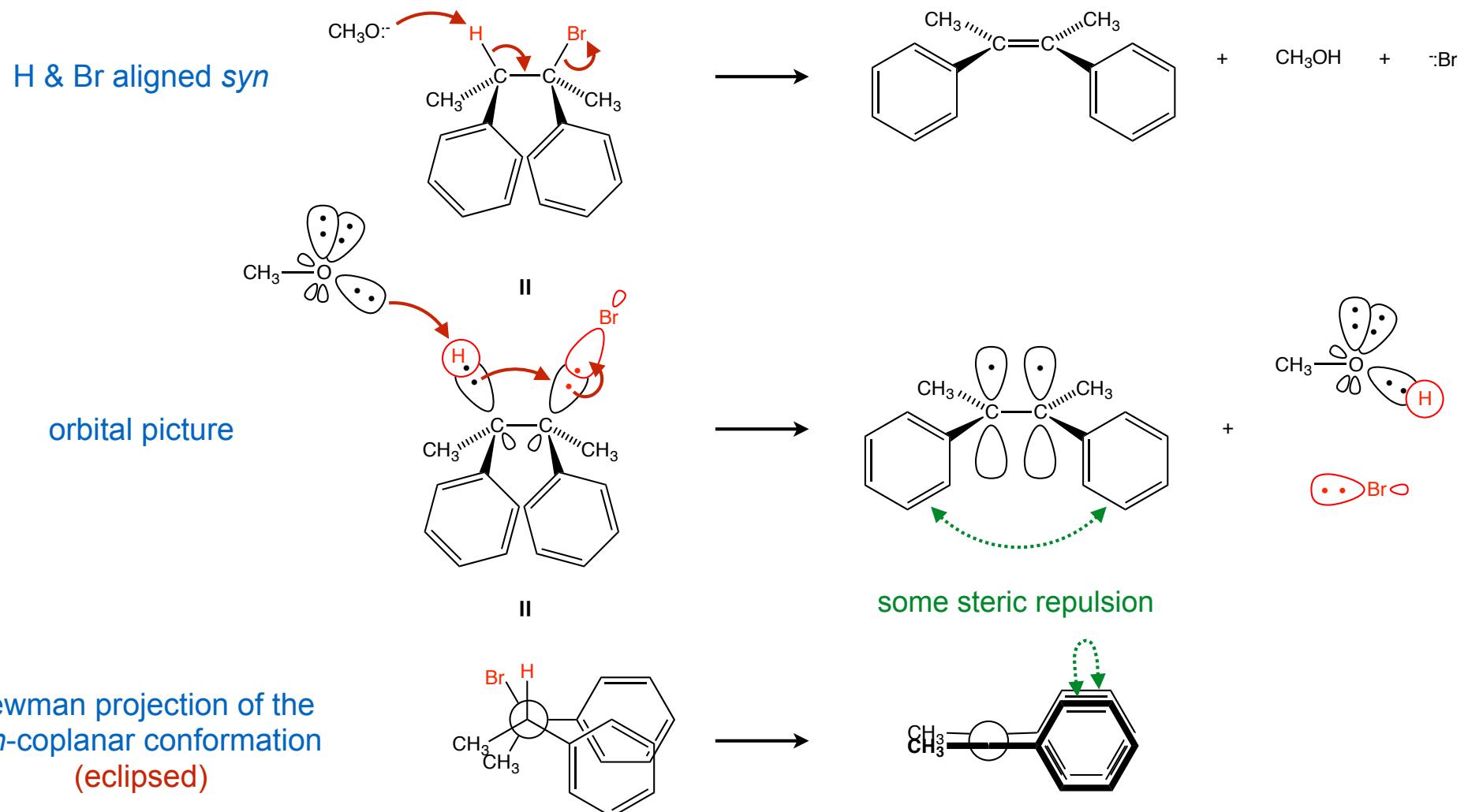
Q: What is the major product of the reaction below?

Ex:

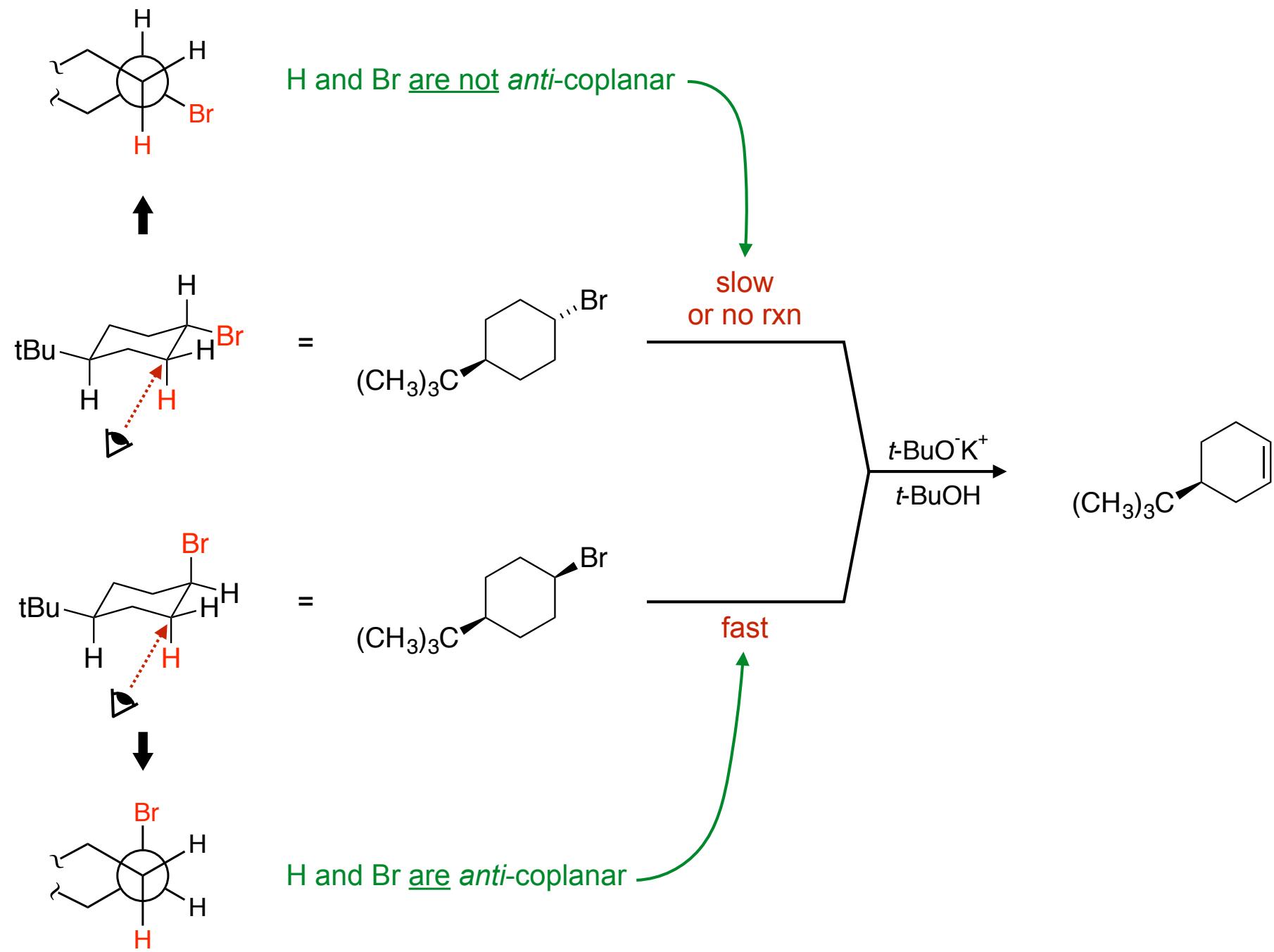


Syn-Coplanar Conformation

- When H and X are *syn* to each other (torsion angle of H-C-C-X, $\theta = 0^\circ$)
- The *syn-coplanar conformation* aligns the sp^3 -hybridized orbitals coplanar allowing a π bond to form
- Higher energy than the *anti-coplanar conformation* due to eclipsing interactions



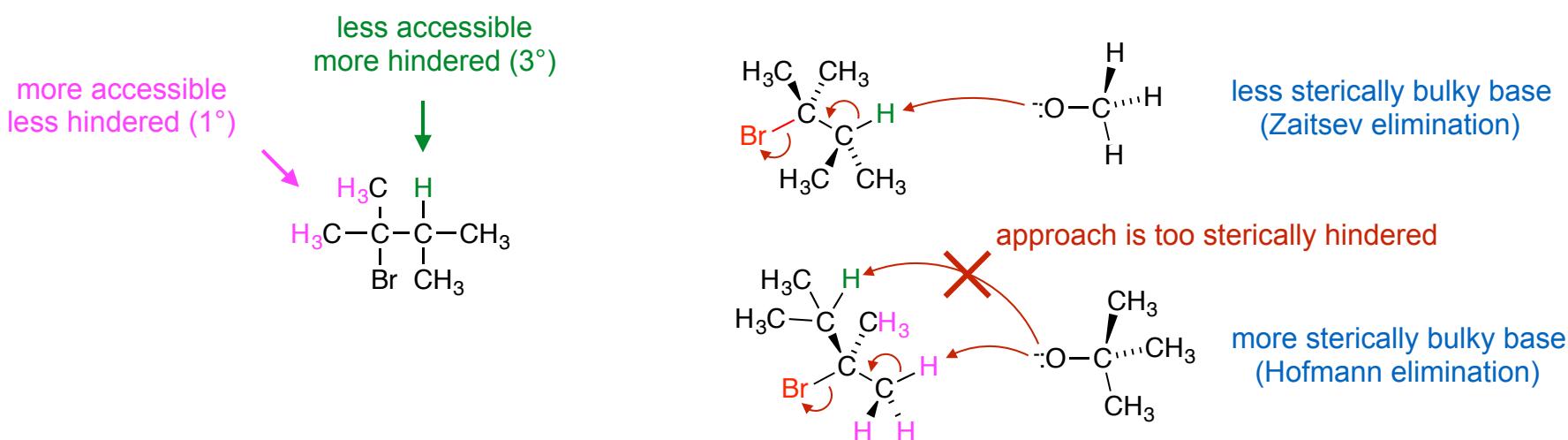
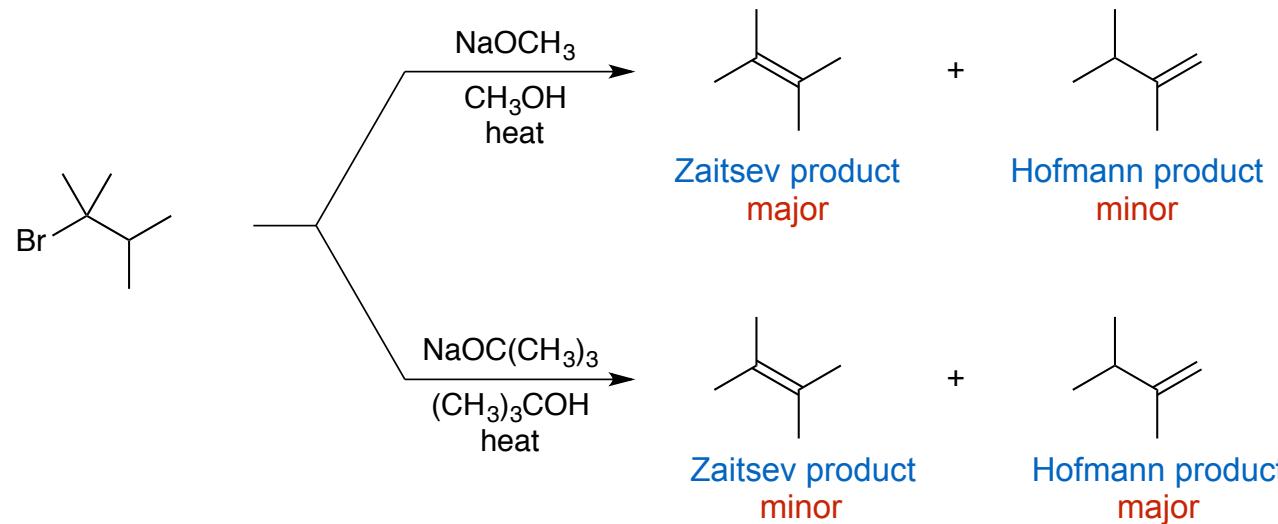
Q: Which E2 reaction will proceed at the faster rate?



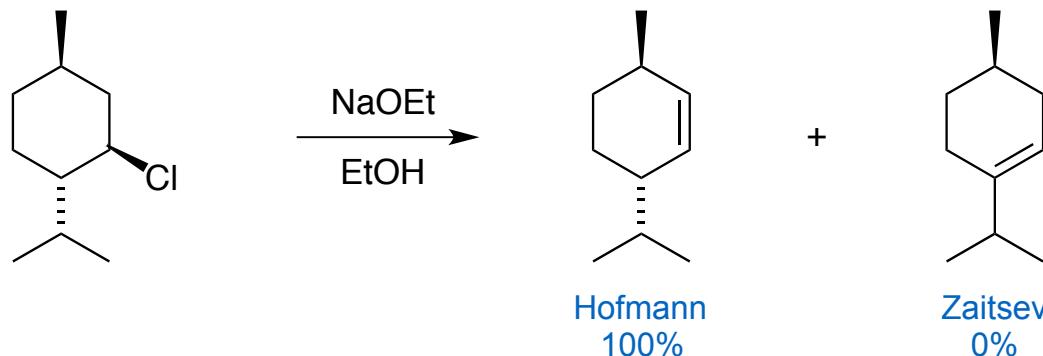
Zaitzev vs Hofmann Products with Bulky Bases (7-13)

- Bulky bases can often form less-substituted alkenes called **Hofmann products**
- Bulky bases will abstract a proton to form a less-substituted alkene (**Hofmann product**) if steric hindrance prevents the base from abstracting a proton leading to the more-substituted alkene (**Zaitsev product**)

Ex:

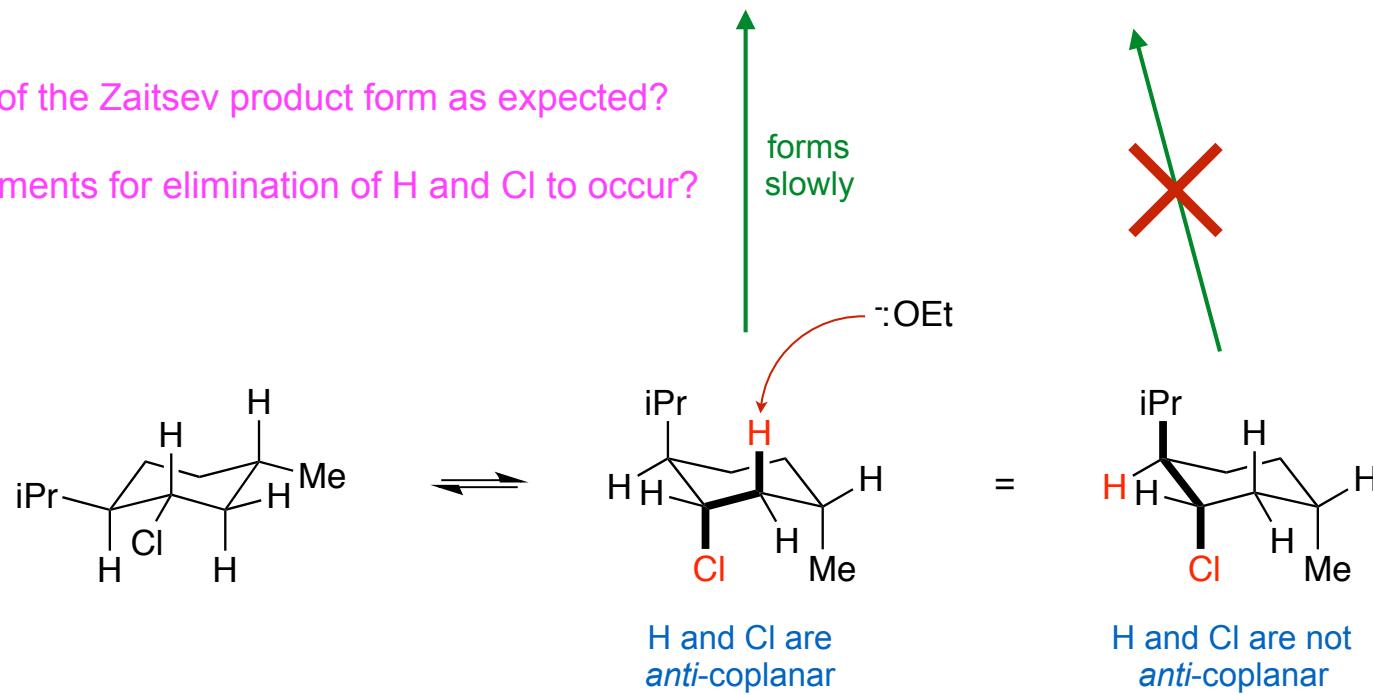


Ex: E2 reaction where Hofmann elimination predominates



Q: Why doesn't any of the Zaitsev product form as expected?

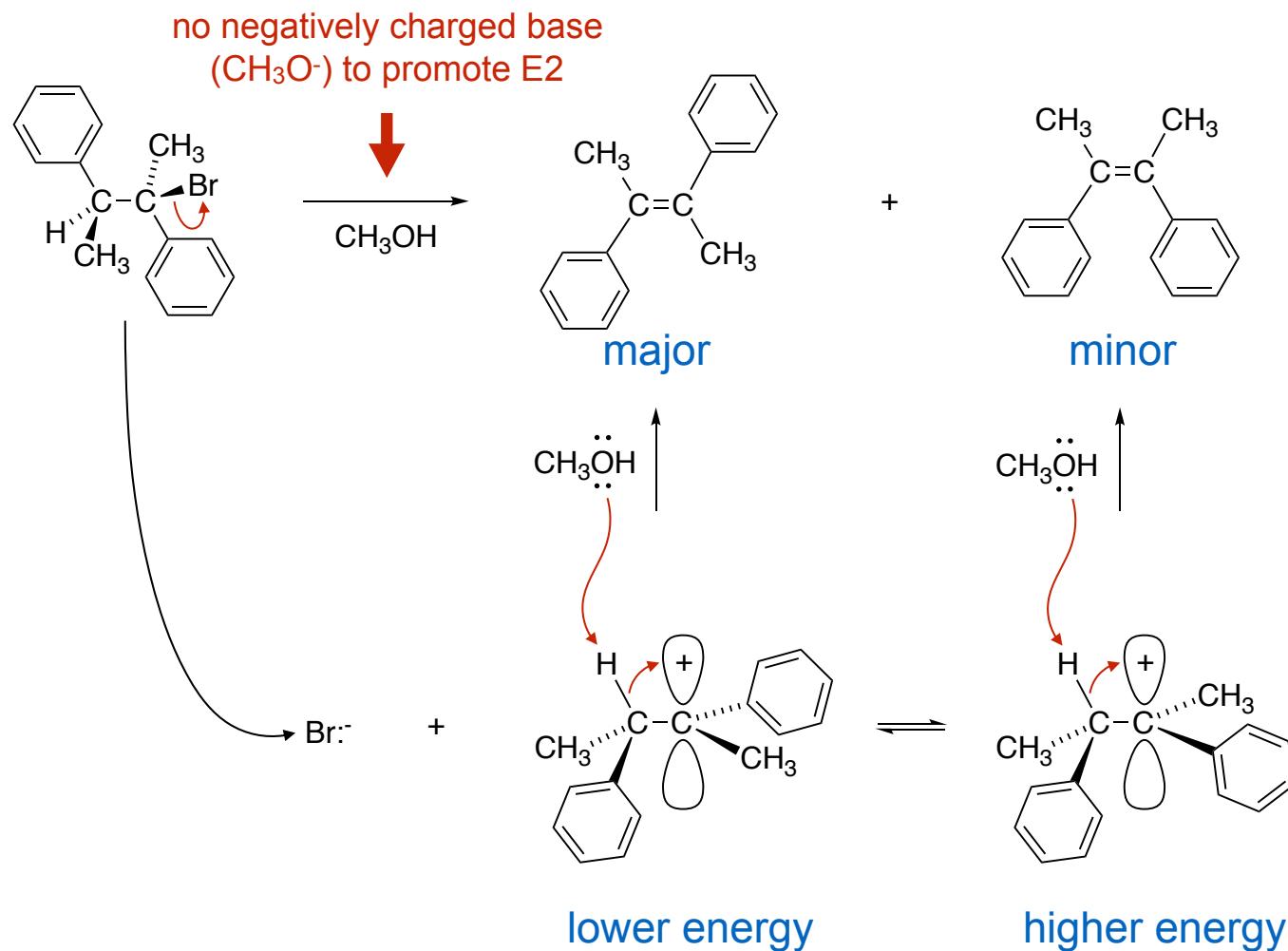
Q: Structural requirements for elimination of H and Cl to occur?



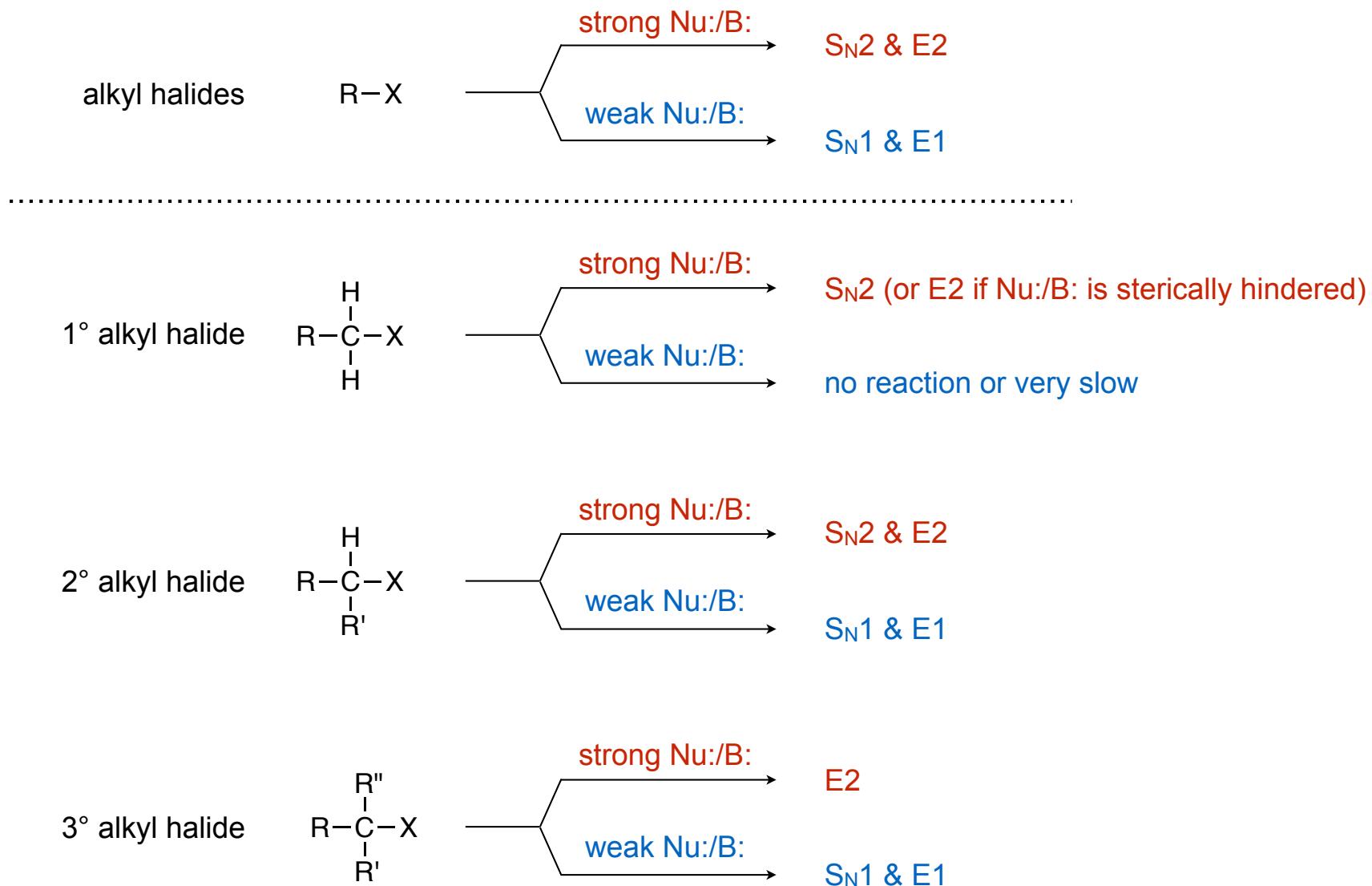
Q: Why does the Hoffman alkene form slowly and in very low overall yield?

Stereochemistry of E1 Reactions

- E1 reactions proceed through carbocations with the conformation that is lowest in energy
- Conformations that are lowest in energy are those that minimize electronic repulsion



Predicting Substitution & Elimination Reactions



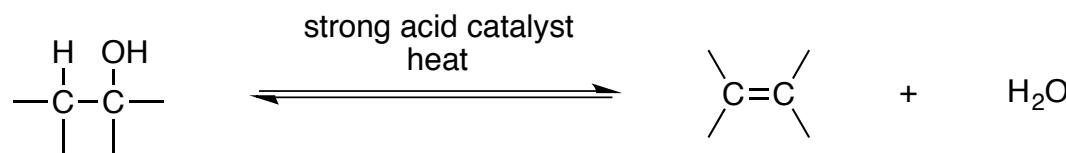
substitution: promoted by good nucleophiles that are weak bases \rightarrow Br^- , I^- , $-SH$, $-CN$, etc.

elimination: promoted by bulky, strong bases \rightarrow $(CH_3)_3CO^-$, $(CH_3)_2CHO^-$, etc.

Synthesis of Alkenes by Dehydration of Alcohols (7-18)

- A commonly used method to prepare alkenes

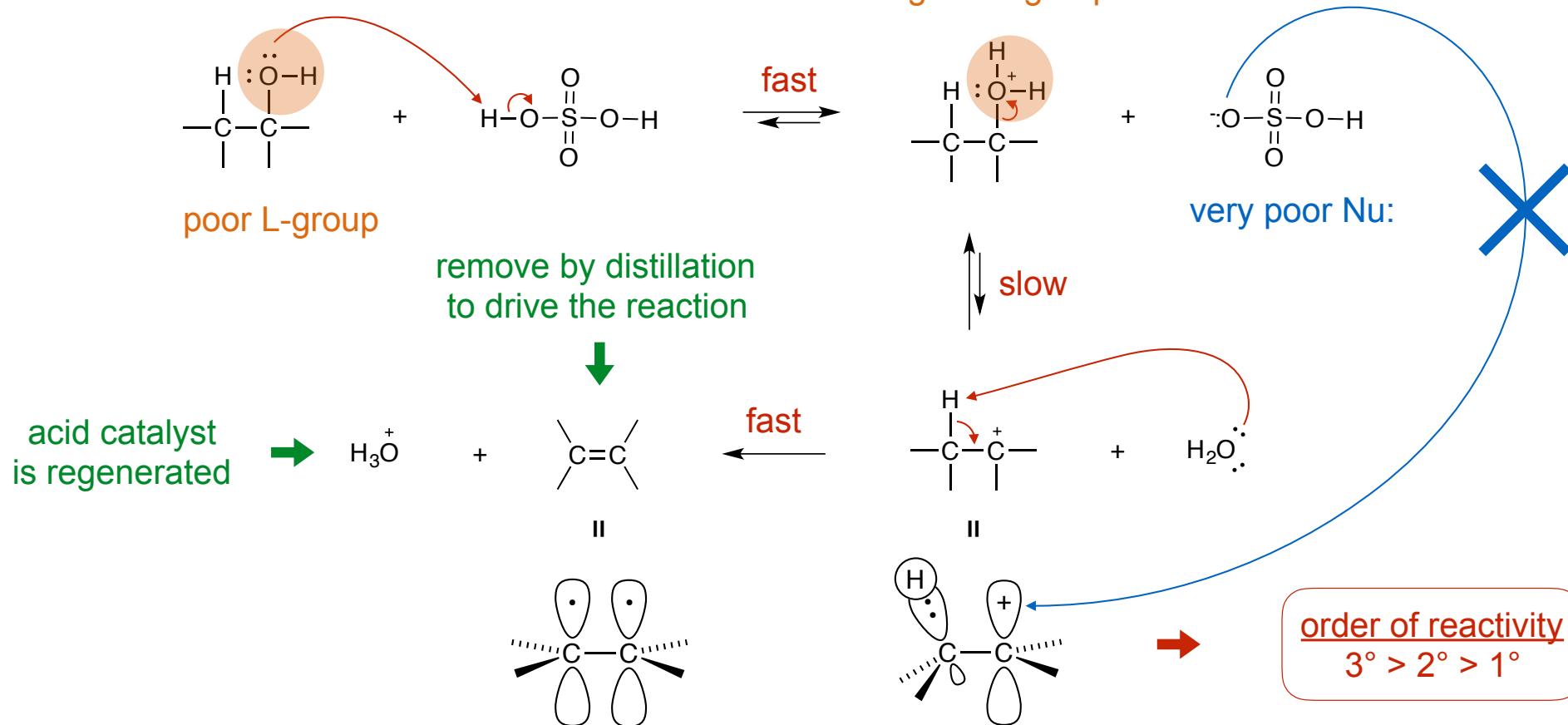
General Rxn



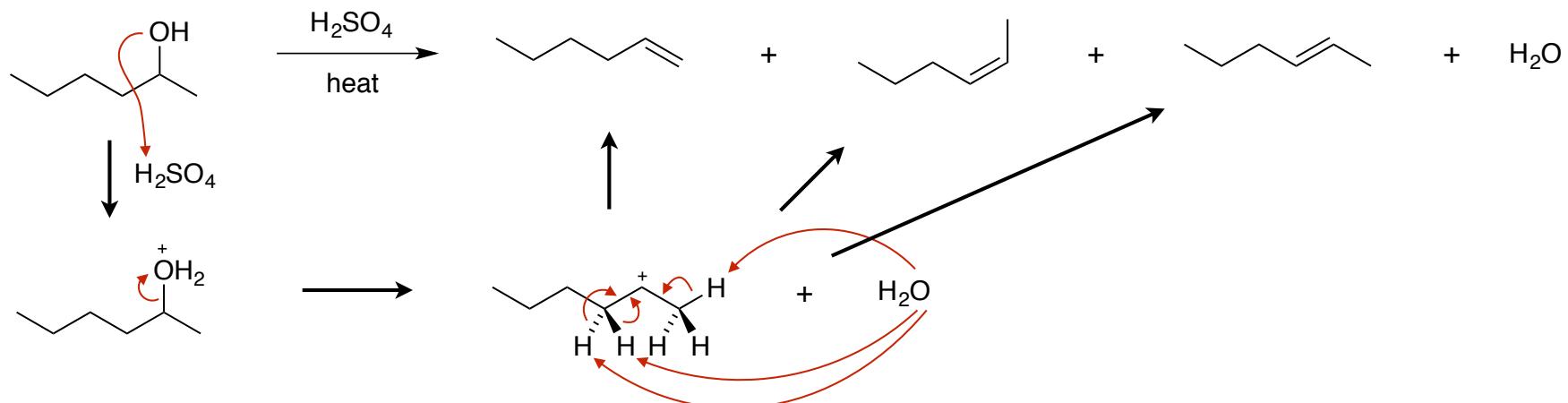
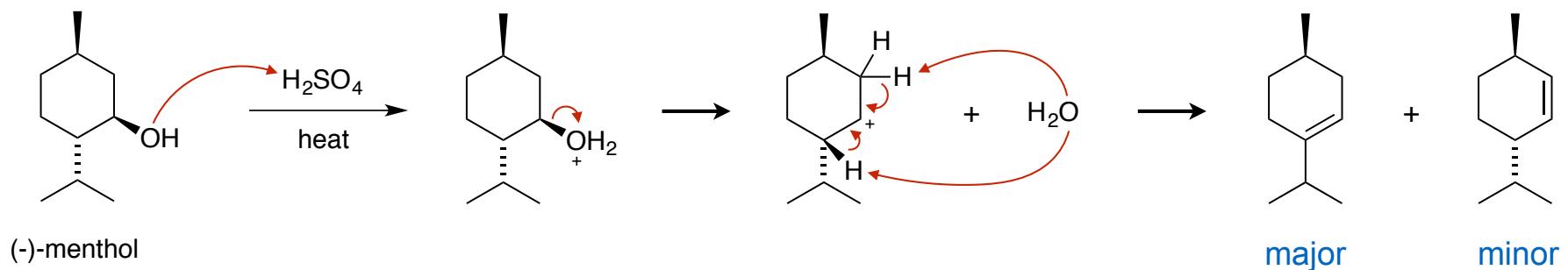
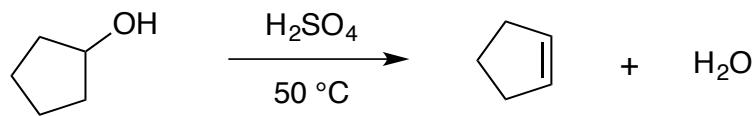
<u>Strong Acids</u>	<u>pKa</u>
H_2SO_4	-10
H_3PO_4	2

Q: What role does the acid catalyst play?

Mechanism



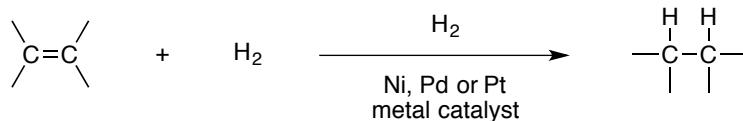
Ex:



Synthesis of Alkenes by Dehydrogenation of Alkanes (7-11)

General Rxns

Hydrogenation



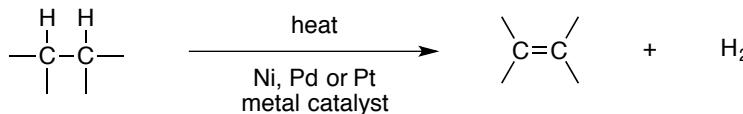
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$\Delta H^\circ = -(80-120) \text{ kJ/mol}$ (favorable)

$\Delta S^\circ = -125 \text{ J/K-mol}$ (disfavored)

Hydrogenation rxns are exergonic and favored at RT

Dehydrogenation

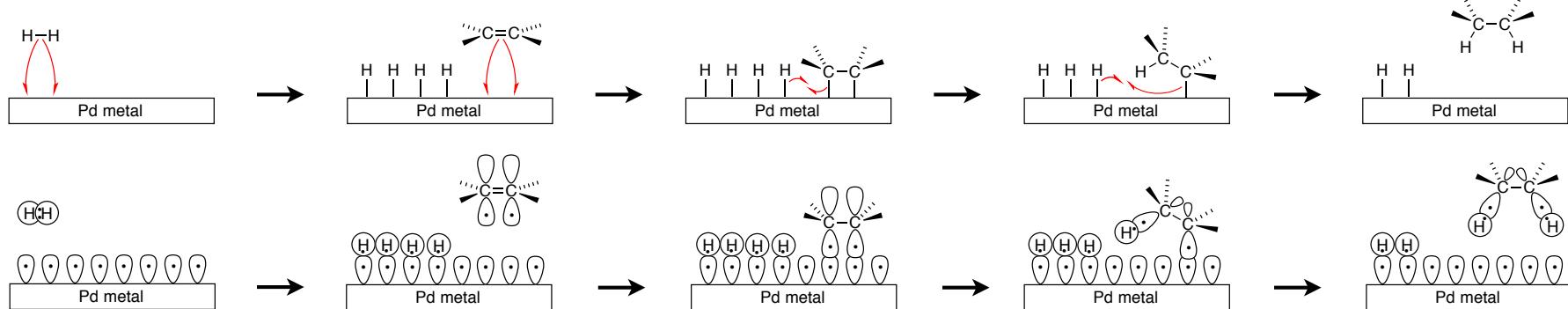


$\Delta H^\circ = +(80-120) \text{ kJ/mol}$ (disfavored)

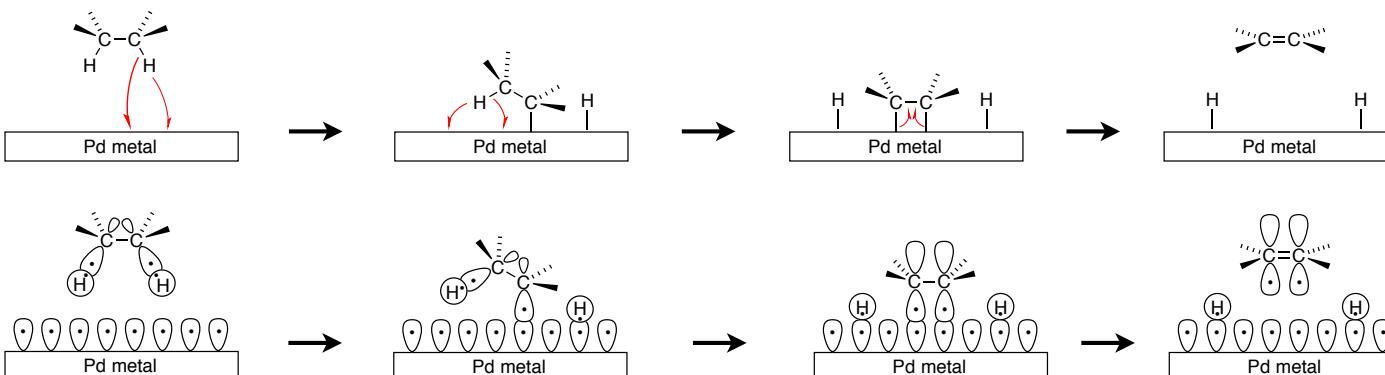
$\Delta S^\circ = +125 \text{ J/K-mol}$ (favorable)

Dehydrogenation rxns are endergonic and disfavored at RT, but favored at high T due to favorable entropy (ΔS°)

Mechanism of Hydrogenation



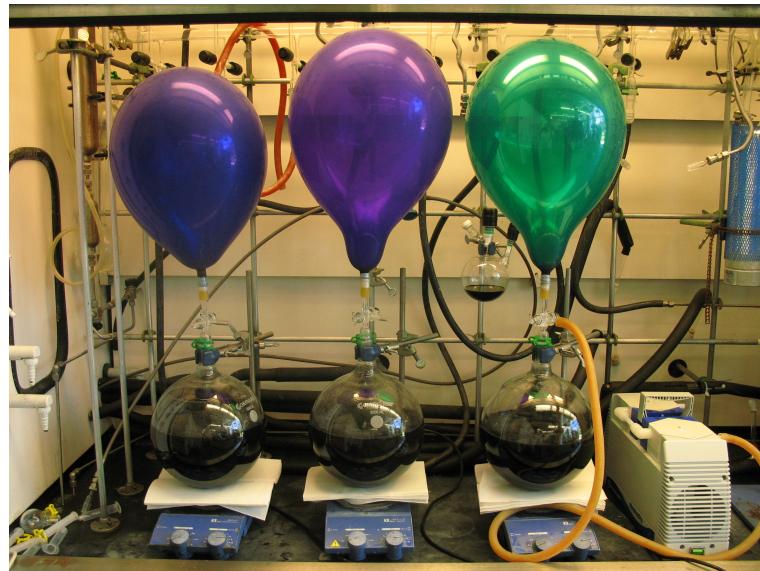
Mechanism of Dehydrogenation



Q: Setups used for hydrogenation and dehydrogenation?



5% Pd metal dispersed
on particles of carbon
(Pd/C)



low-pressure hydrogenation in a flask

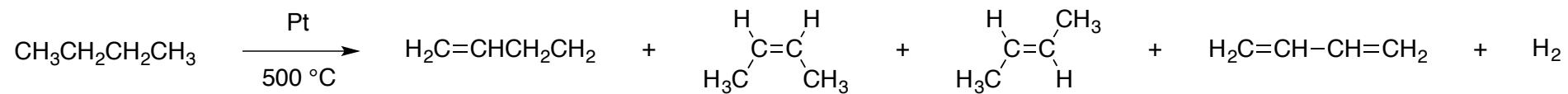


high-pressure hydrogenation
(Parr shaker)



industrial setup for dehydrogenation

Ex: Catalytic Dehydrogenation of Butane



Dehydrogenation generally is not regioselective and produces mixtures of different alkenes