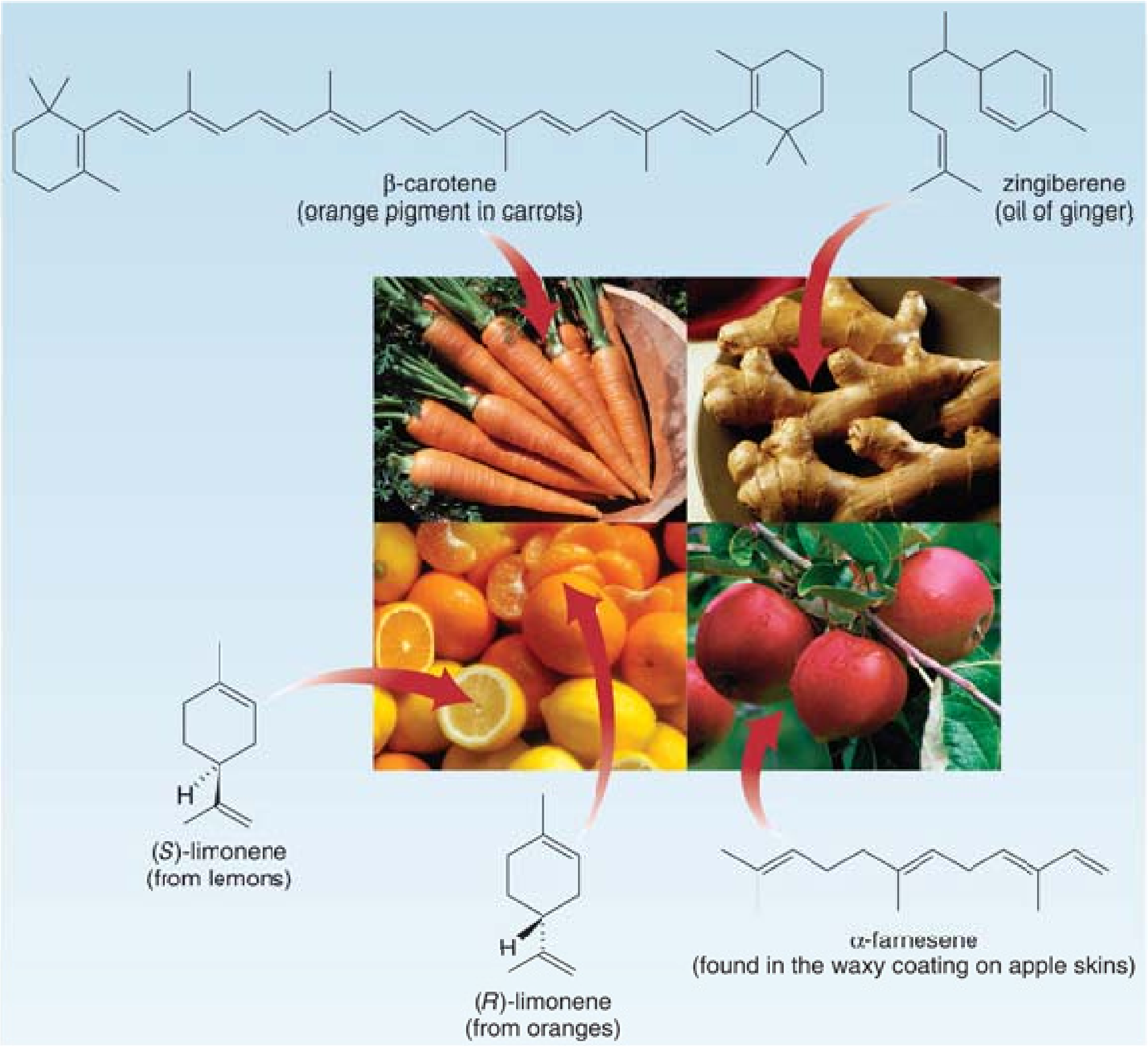
Chapter 5
Structure and Preparation of Alkenes: Elimination Reactions

Interesting Alkenes



5.1. Alkene Nomenclature

- Alkenes are hydrocarbons that contain a carbon-carbon double bond.
- Also called "olefins“.
- Characterized by molecular formula C_nH_{2n}.
- Said to be "unsaturated“.

Alkene Nomenclature

$H_2C{=}CH_2$

Ethene
or
Ethylene
(both are acceptable
IUPAC names)

$H_2C{=}CHCH_3$

Propene

(Propylene is
sometimes used
but is not an acceptable
IUPAC name)

Alkene Nomenclature

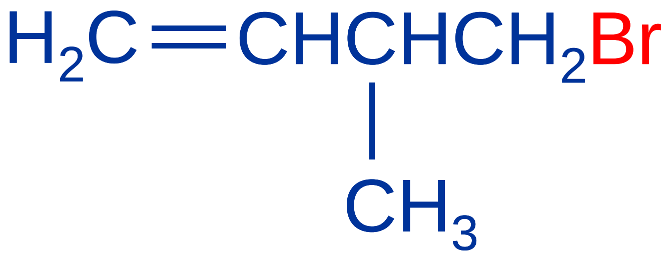
$H_2C{=}CHCH_2CH_3$ 1-Butene

1) Find the longest continuous chain that includes the double bond.

2) Replace the -ane ending of the unbranched alkane having the same number of carbons by -ene.

3) Number the chain in the direction that gives the lowest number to the doubly bonded carbon.

Alkene Nomenclature

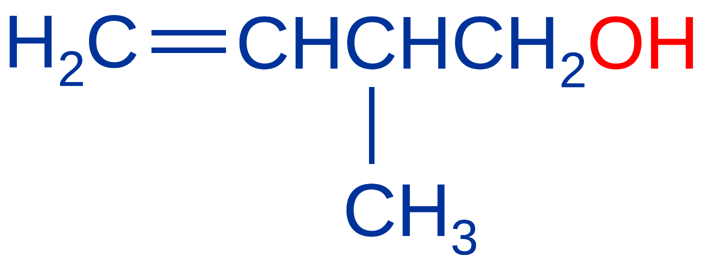


$$H_2C{=}CH\underset{\underset{CH_3}{|}}{CH}CH_2Br$$

4) If a substituent is present, identify its position by number. The double bond takes precedence over alkyl groups and halogens when the chain is numbered.

The compound shown above is: 4-bromo-3-methyl-1-butene.

Alkene Nomenclature

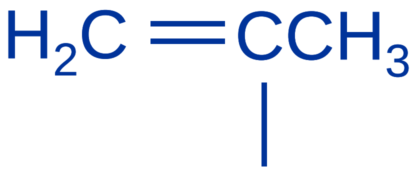


$$H_2C{=}CH\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH$$

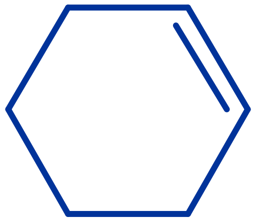
4) If a substituent is present, identify its position by number. Hydroxyl groups take precedence over the double bond when the chain is numbered.

The compound shown above is: 2-methyl-3-buten-1-ol.

Alkenyl Groups

Methylene	$H_2C=$
Vinyl	$H_2C=CH-$
Allyl	$H_2C=CHCH_2-$
Isopropenyl	 $H_2C=\underset{\vert}{C}CH_3$

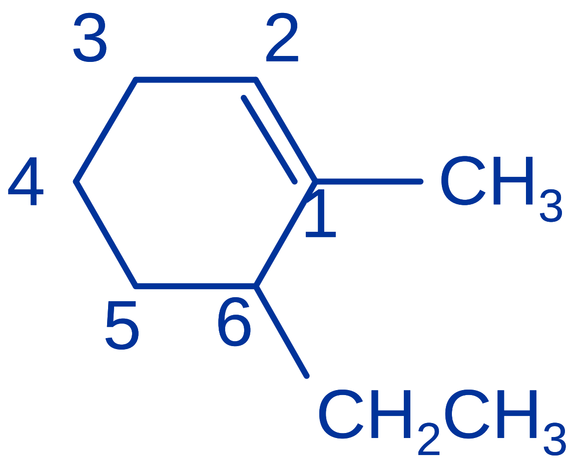
Cycloalkene Nomenclature



Cyclohexene

- Replace the -ane ending of the cycloalkane having the same number of carbons by -ene.

Cycloalkene Nomenclature



6-Ethyl-1-methylcyclohexene

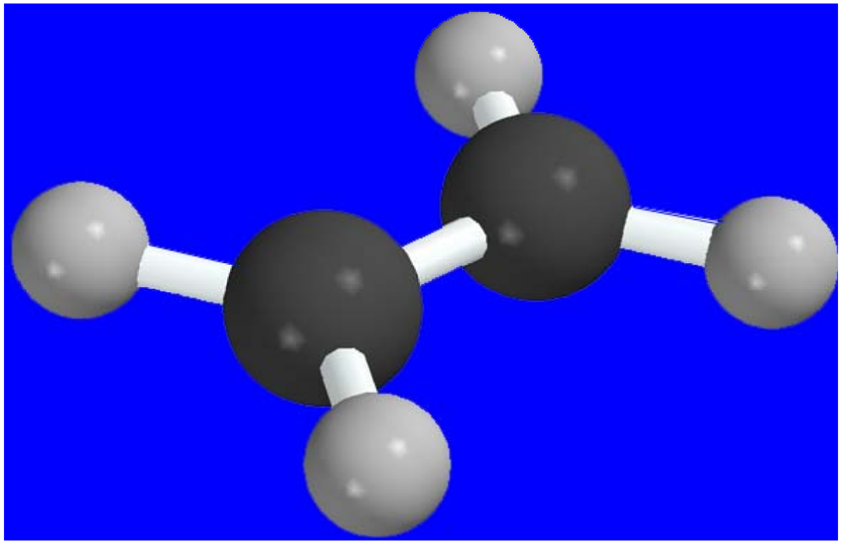
1) Replace the -ane ending of the cycloalkane having the same number of carbons by -ene.

2) Number *through* the double bond in the direction that gives the lower number to the first-appearing substituent.

5.2. Structure and Bonding in Alkenes

Structure of Ethylene

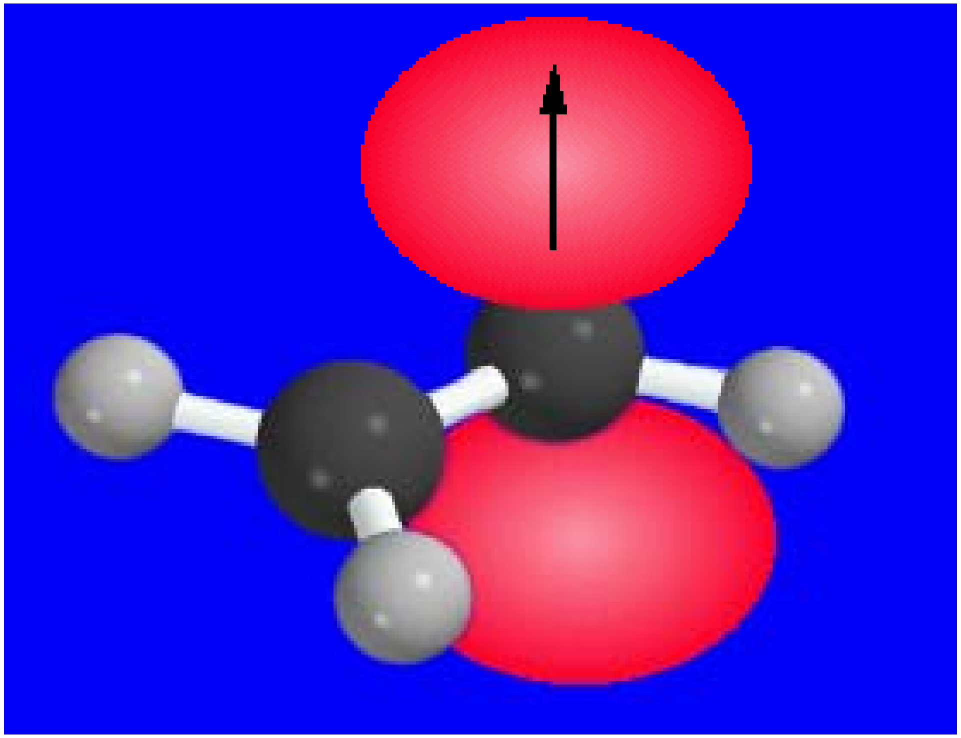
Bond angles:	H-C-H = 117°
	H-C-C = 121°
Bond distances:	C—H = 110 pm
	C=C = 134 pm



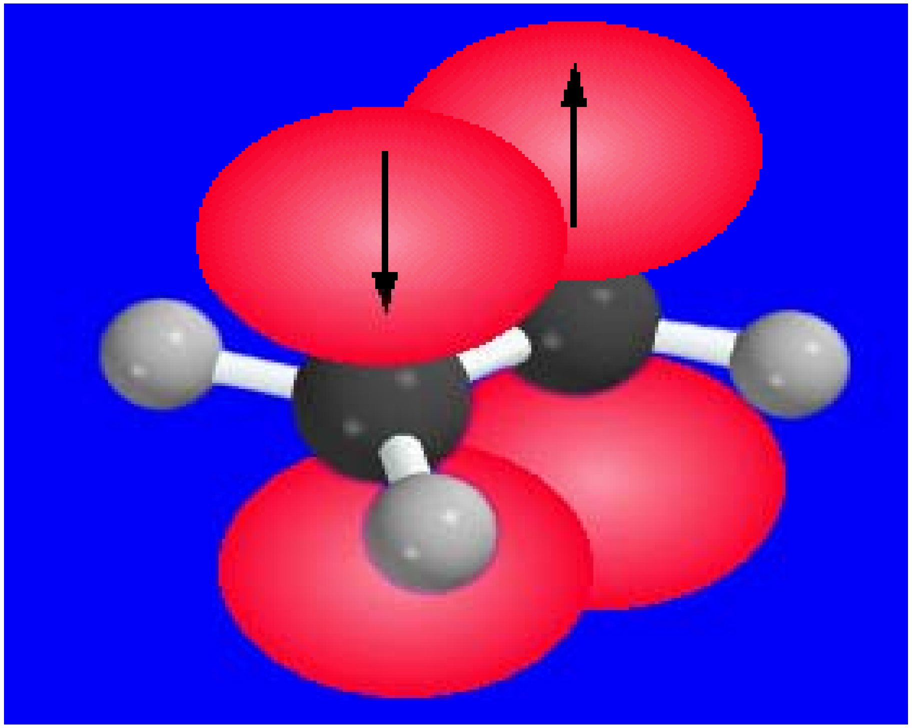
Planar

Bonding: Framework of σ bonds
Each carbon is sp^2 hybridized

Bonding in Ethylene



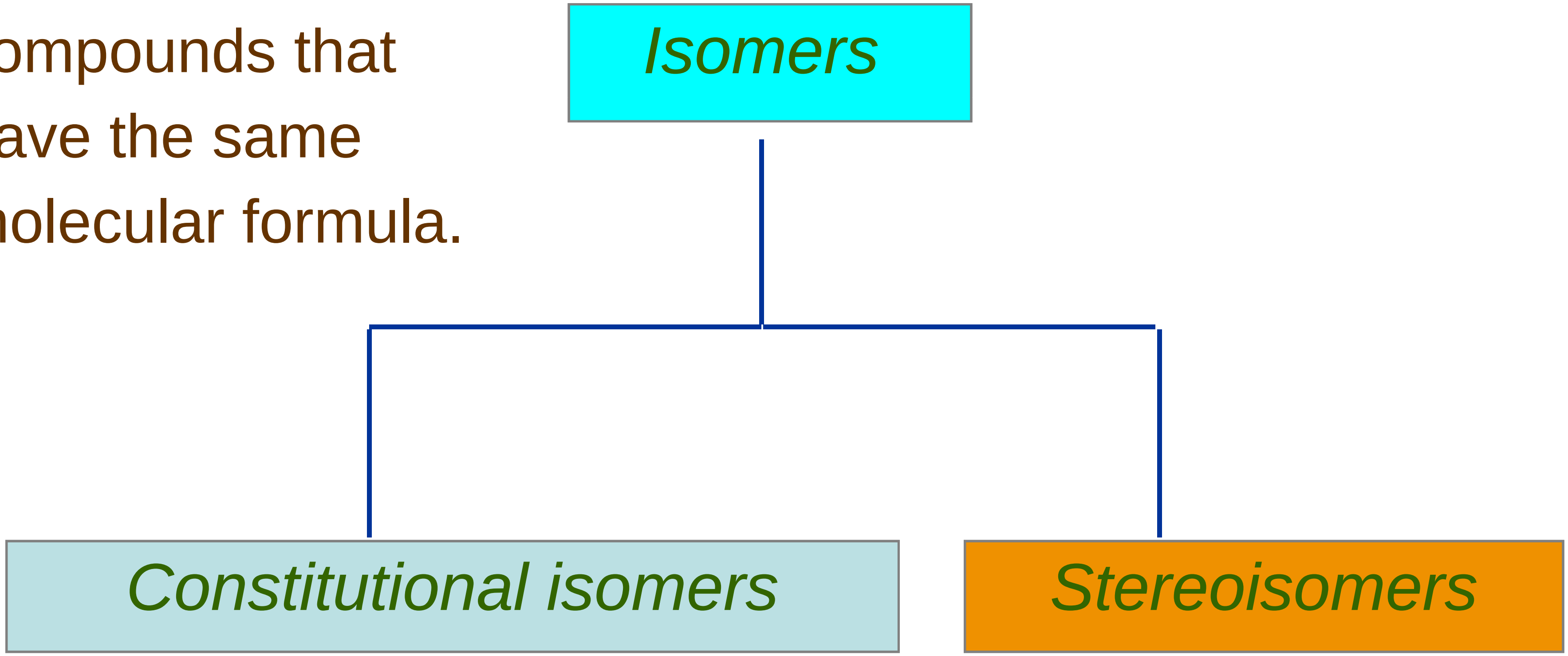
Each carbon has a half-filled *p* orbital.



Side-by-side overlap of half-filled *p* orbitals gives a π bond.

5.3. Isomerism in Alkenes

Isomers are different compounds that have the same molecular formula.



Isomers

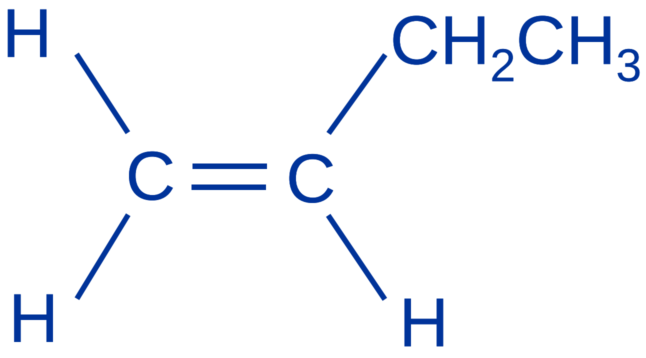
Constitutional isomers

Stereoisomers

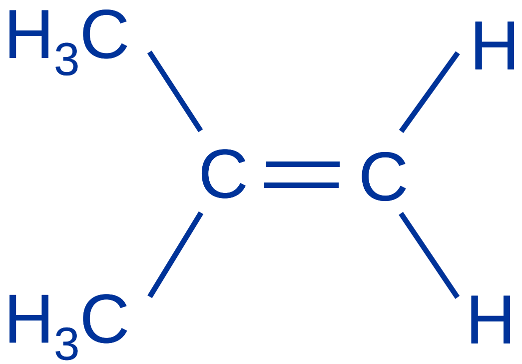
Different connectivity

Same connectivity; different arrangement of atoms in space

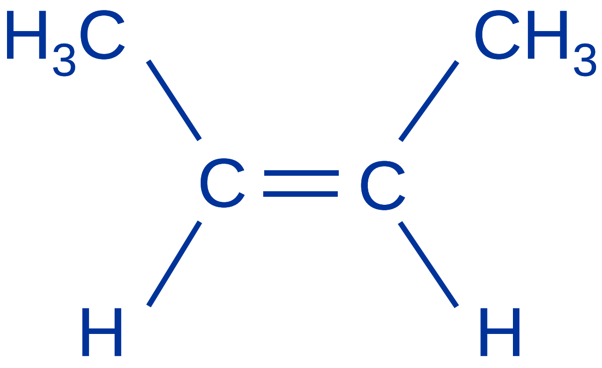
Consider the isomeric alkenes of molecular formula C_4H_8



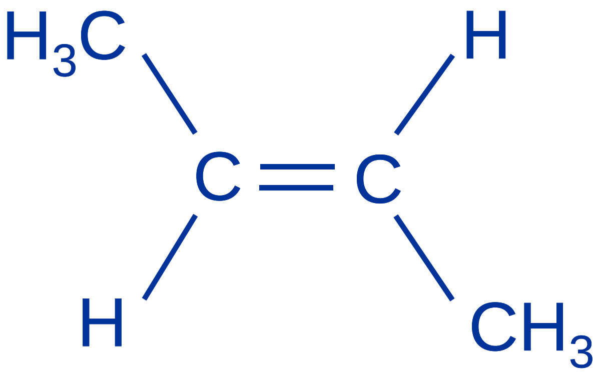
1-Butene



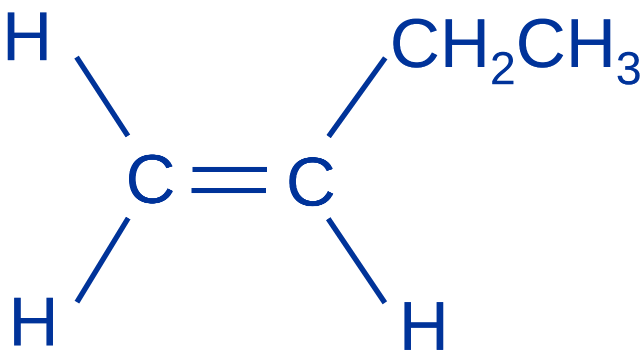
2-Methylpropene



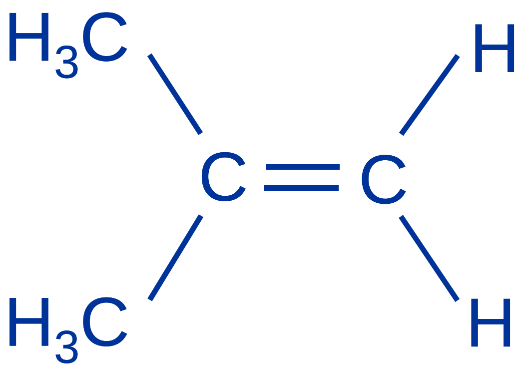
cis-2-Butene



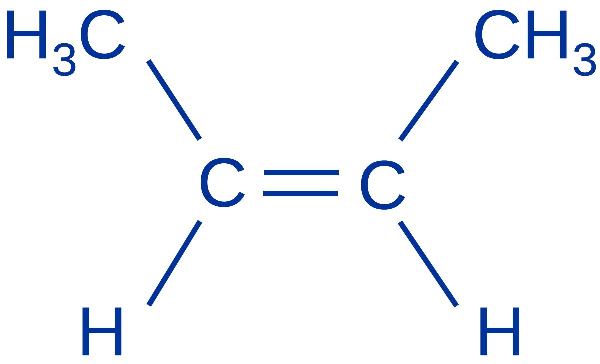
trans-2-Butene



1-Butene

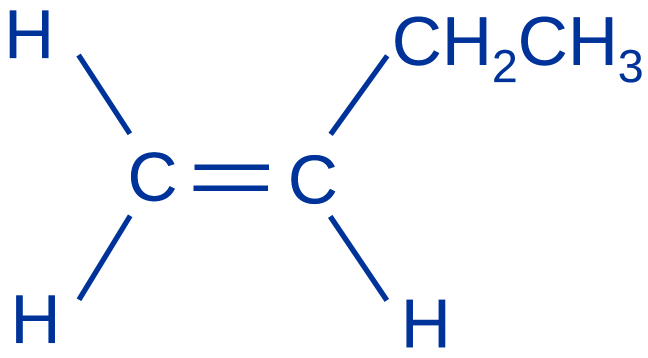


2-Methylpropene

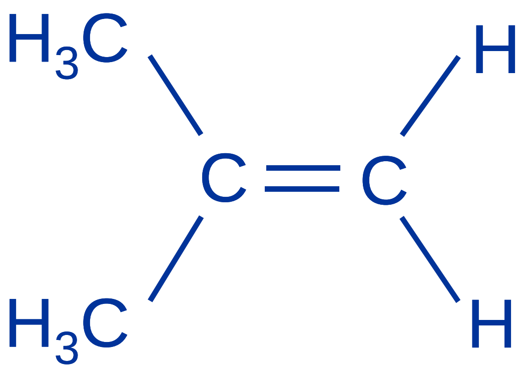


cis-2-Butene

Constitutional isomers

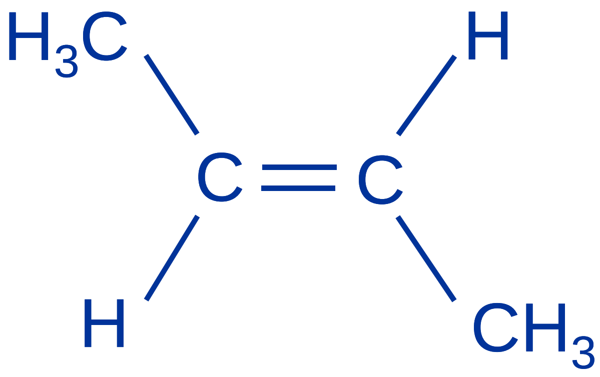


1-Butene



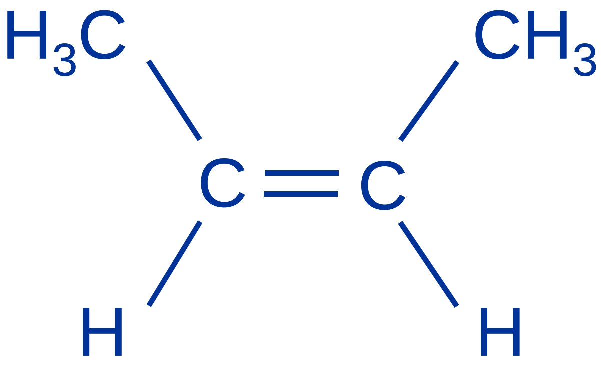
2-Methylpropene

Constitutional isomers

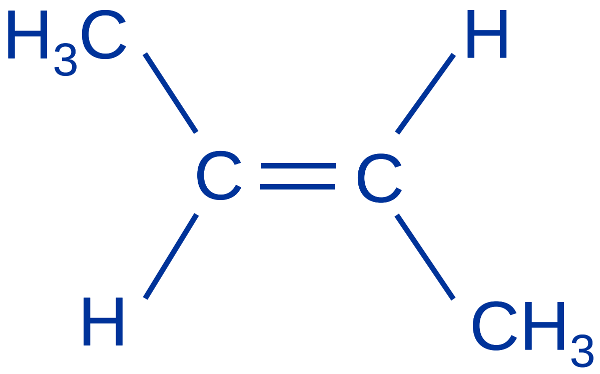


trans-2-Butene

Stereoisomers

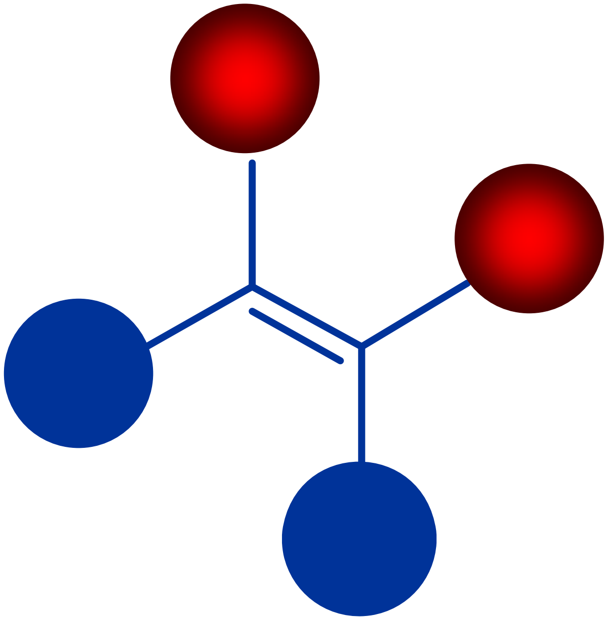


cis-2-Butene

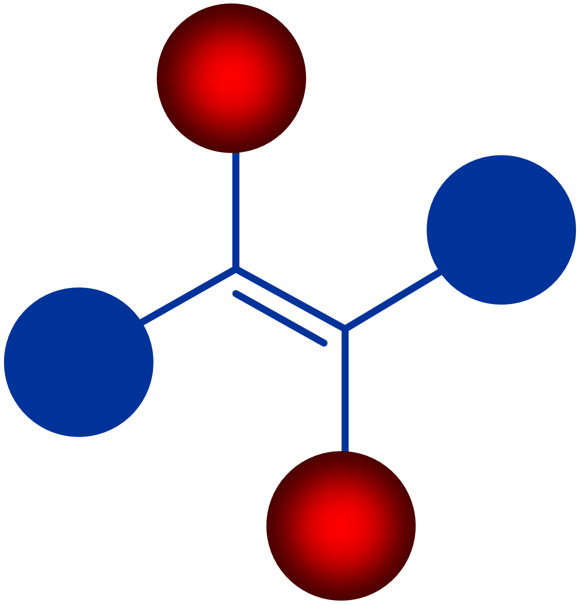


trans-2-Butene

Stereochemical Notation



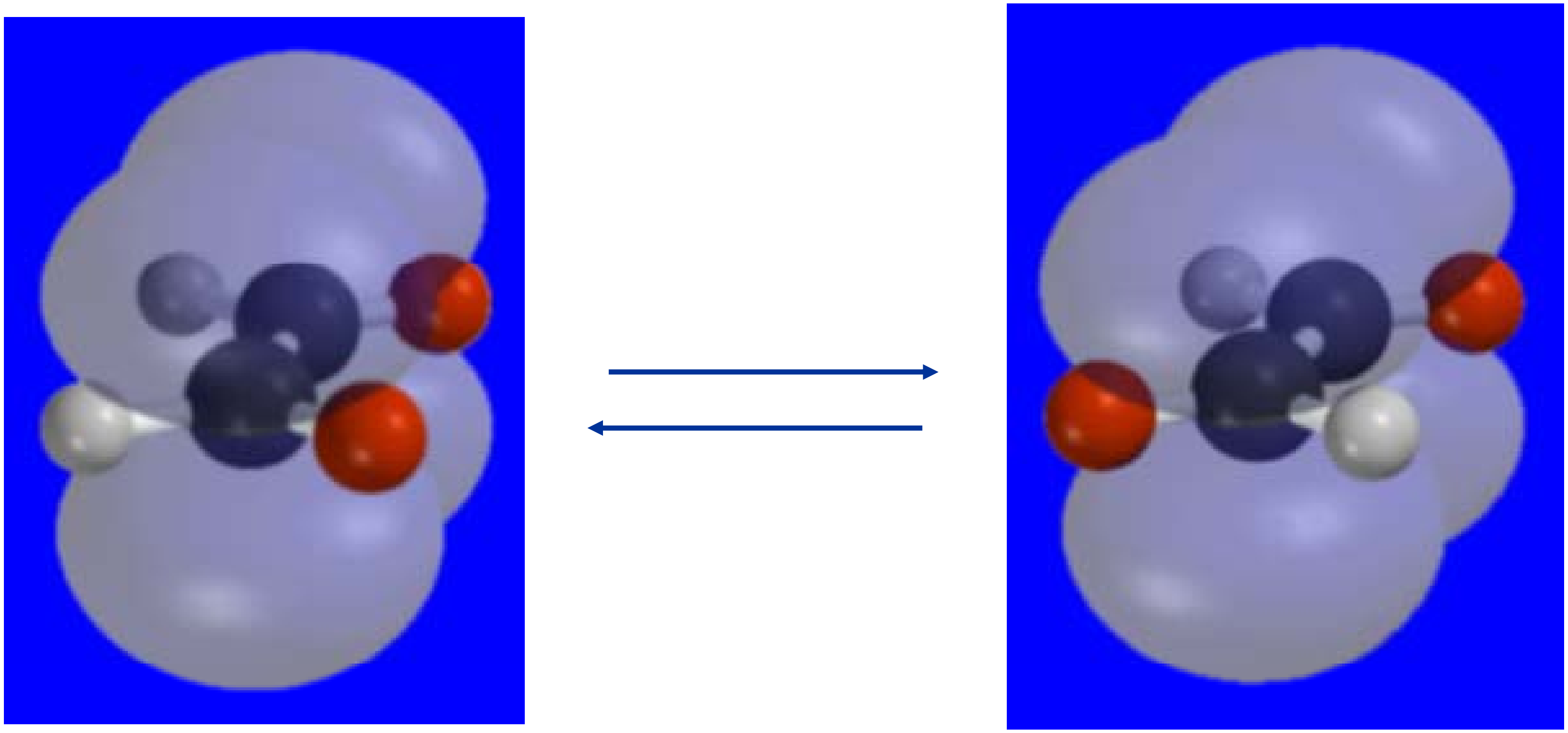
cis (identical or analogous substitutents on same side)

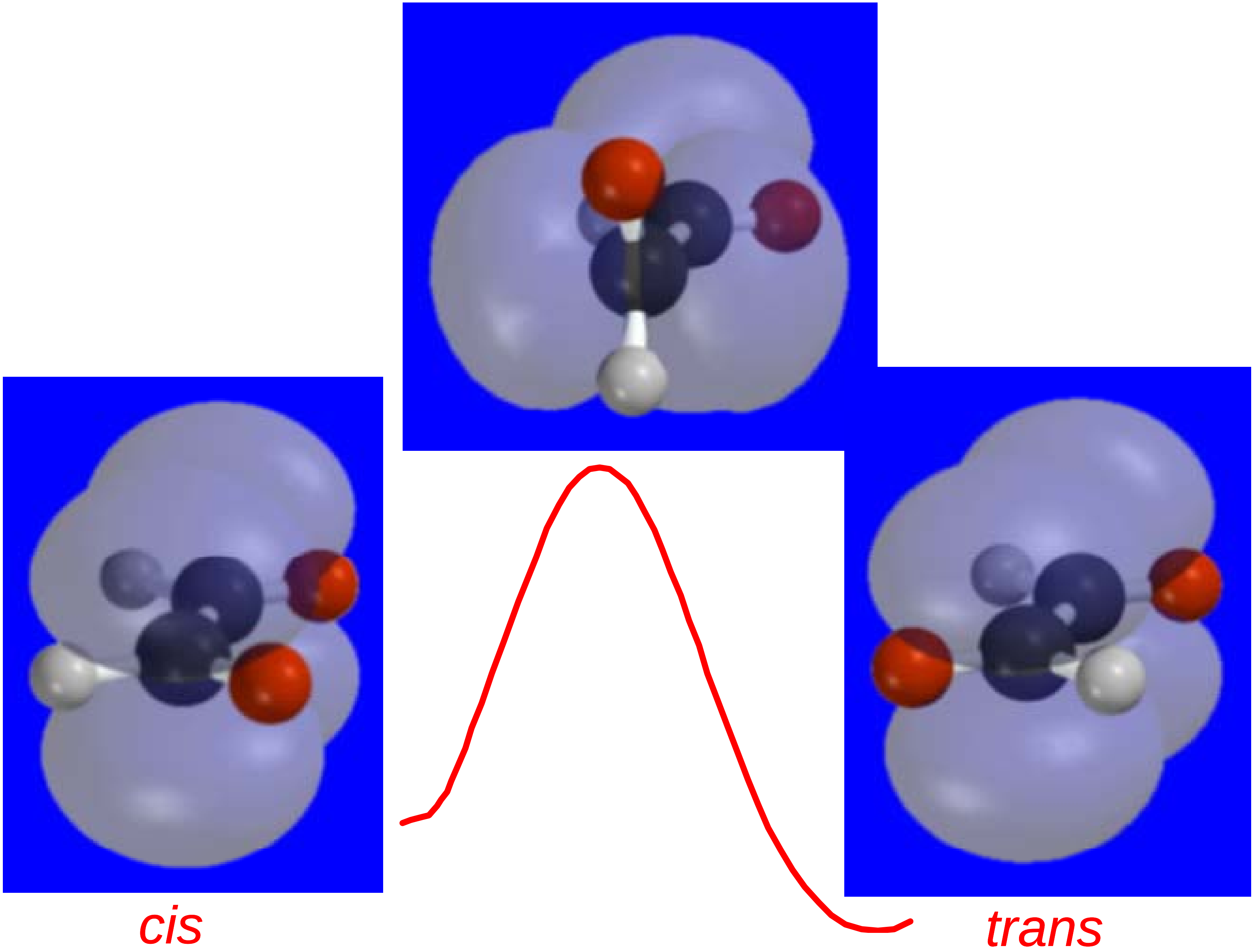


trans (identical or analogous substituents on opposite sides)

Isomerism

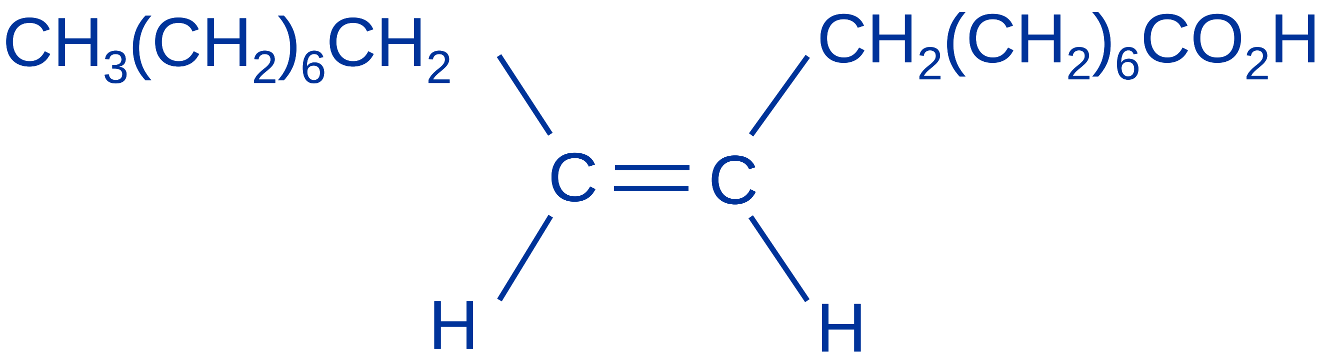
- Interconversion of stereoisomeric alkenes does not normally occur. Requires that π component of double bond be broken.




cis
trans

5.4. Naming Steroisomeric Alkenes by the E-Z Notational System

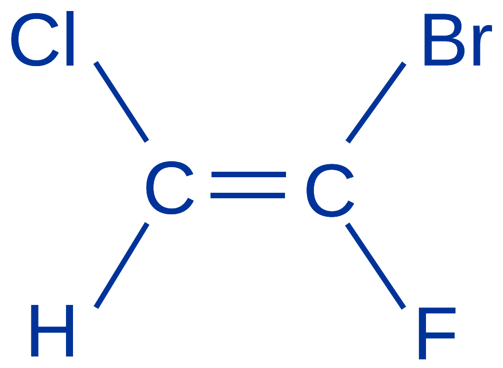
Stereochemical Notation



Oleic acid

- *cis* and *trans* are useful when substituents are identical or analogous (oleic acid has a *cis* double bond).
- *cis* and *trans* are ambiguous when analogies are not obvious.

Example

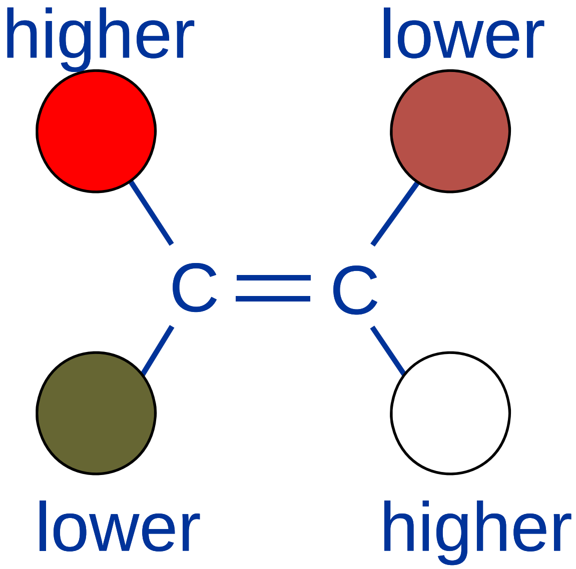


What is needed:

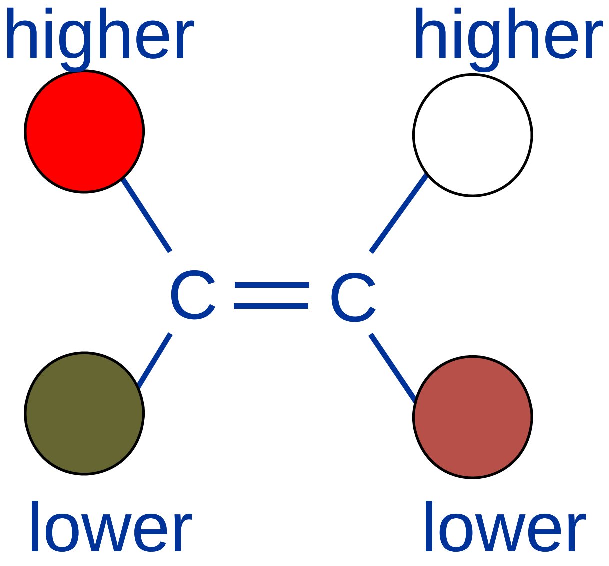
1) Systematic body of rules for ranking substituents.
2) New set of stereochemical symbols other than *cis* and *trans*.

The E-Z Notational System

E : higher ranked substituents on *opposite* sides.
Z : higher ranked substituents on *same* side.



Entgegen

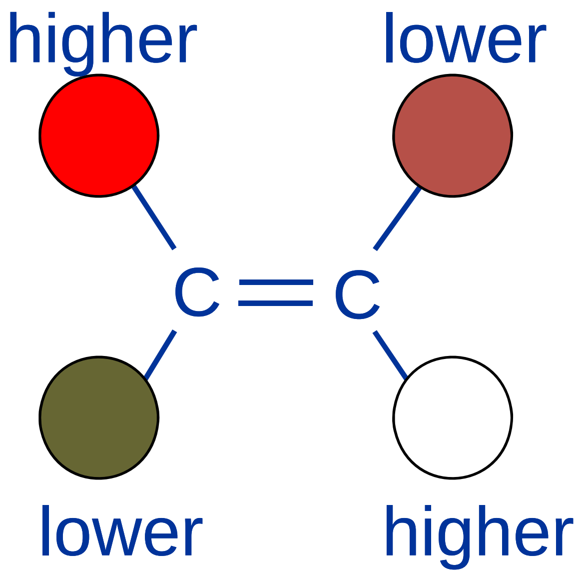


Zusammen

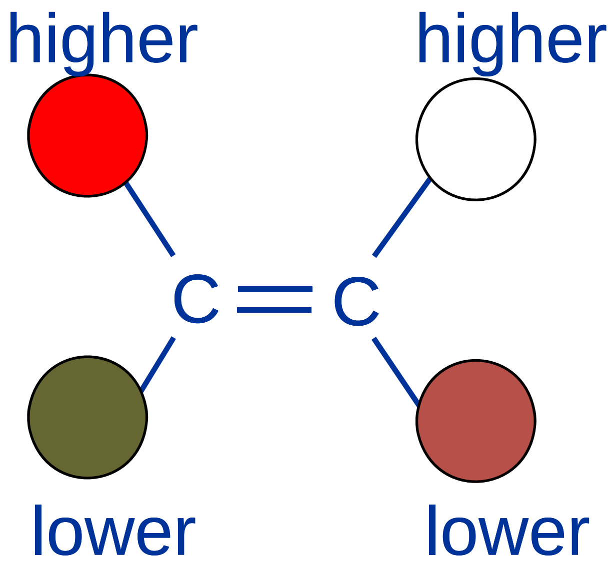
The E-Z Notational System

Question: How are substituents ranked?

Answer: They are ranked in order of decreasing atomic number.



Entgegen



Zusammen

The Cahn-Ingold-Prelog (CIP) System

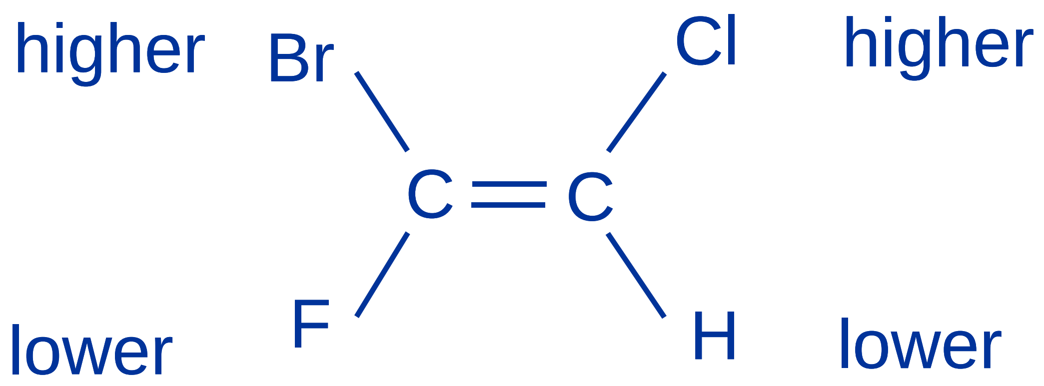
- The system that we use was devised by
  R. S. Cahn
  Sir Christopher Ingold
  Vladimir Prelog

- The rules for ranking groups were devised in connection with a different kind of stereochemistry but have been adapted to alkene stereochemistry.

Table 5.1. CIP Rules

(1) Higher atomic number outranks lower atomic number.

Br > F Cl > H



(*Z*)-1-Bromo-2-chloro-1-fluoroethene

Table 5.1. CIP Rules

(2) When two atoms are identical, compare the atoms attached to them on the basis of their atomic numbers. Precedence is established at the first point of difference.

$—CH_2CH_3$ outranks $—CH_3$

$—C(\underset{\uparrow}{C},H,H)$ $—C(\underset{\uparrow}{H},H,H)$

Table 5.1. CIP Rules

(3) Work outward from the point of attachment, comparing all the atoms attached to a particular atom before proceeding furtheralong the chain.

—$CH(CH_3)_2$ outranks —CH_2CH_2OH

—C(C,C,H) —C(C,H,H)

Table 5.1. CIP Rules

(4) Evaluate substituents one by one. Don't add atomic numbers within groups.

—CH_2OH outranks —$C(CH_3)_3$

—C(O,H,H) —C(C,C,C)

Table 5.1. CIP Rules

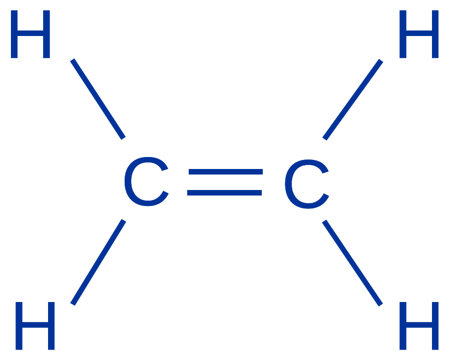
(5) An atom that is multiply bonded to another atom is considered to be replicated as a substituent on that atom.

$—CH{=}O$ outranks $—CH_2OH$

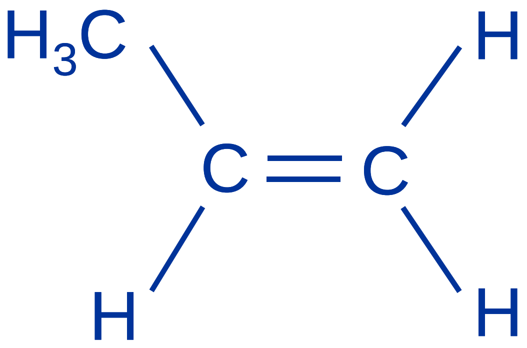
$—C(O,\underset{\uparrow}{O},H)$ $\qquad$ $—C(O,\underset{\uparrow}{H},H)$

5.5. Physical Properties of Alkenes

Dipole moments



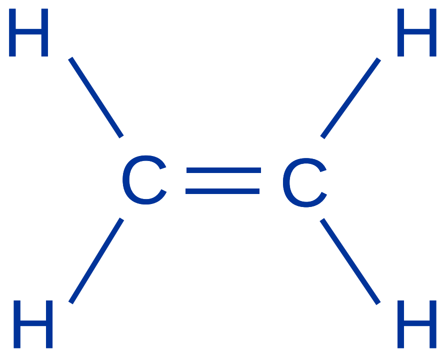
$\mu = 0$ D



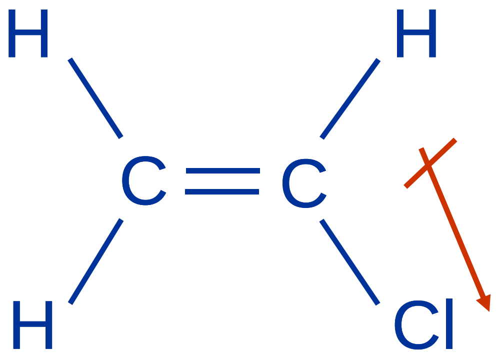
$\mu = 0.3$ D

- ➢ What is direction of dipole moment?
- ➢ Does a methyl group donate electrons to the double bond, or does it withdraw them?

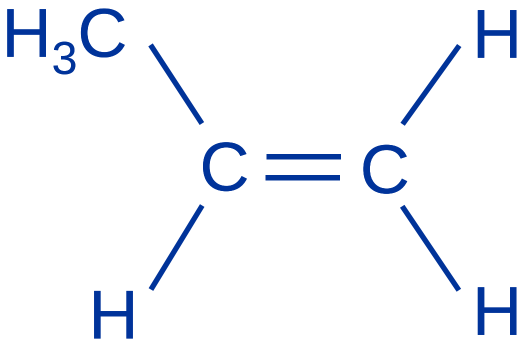
Dipole moments



$\mu = 0\ D$



$\mu = 1.4\ D$

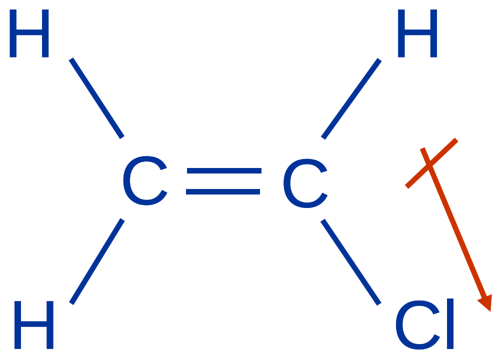


$\mu = 0.3\ D$

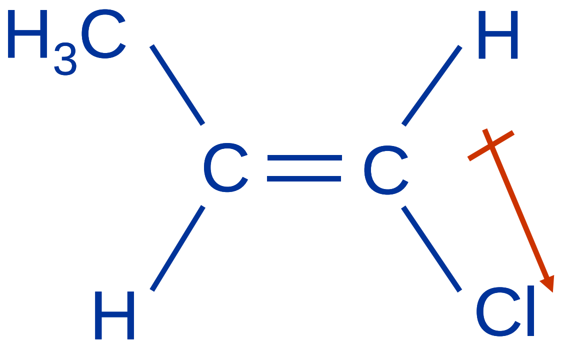
- ➢ Chlorine is electronegative and attracts electrons.

Dipole moments

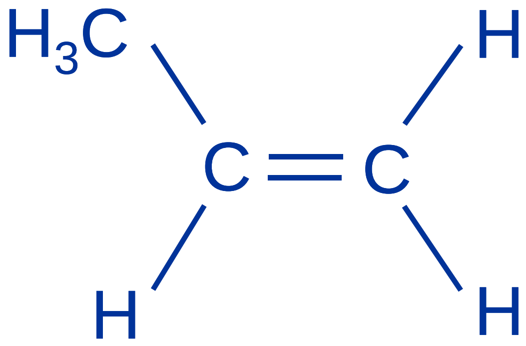
- Dipole moment of 1-chloropropene is equal to the sum of the dipole moments of vinyl chloride and propene.



$\mu = 1.4$ D

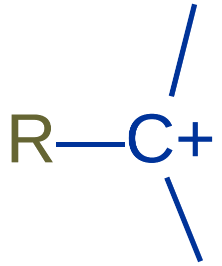


$\mu = 1.7$ D

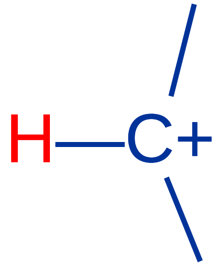


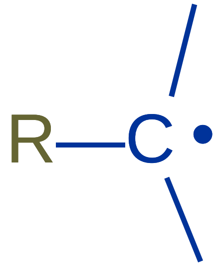
$\mu = 0.3$ D

Alkyl groups stabilize sp^2 hybridized carbon by releasing electrons

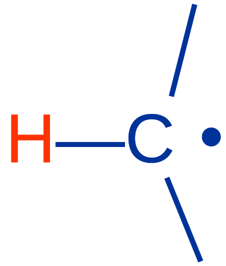


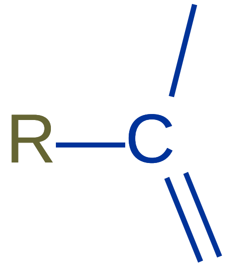
is more stable than



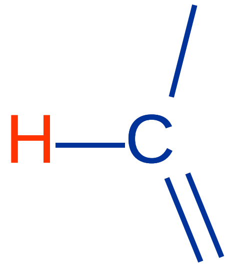


is more stable than



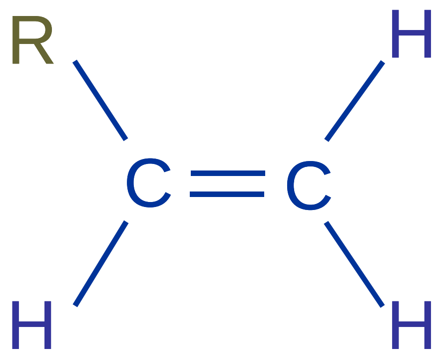


is more stable than

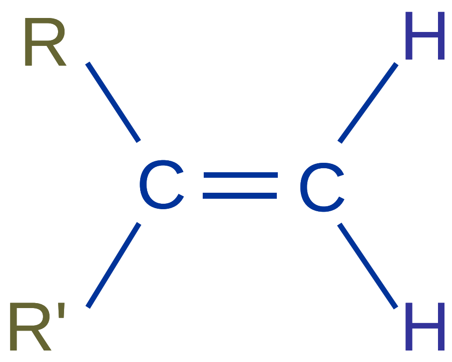


5.6. Relative Stabilities of Alkenes

- Double bonds are classified according to the number of carbons attached to them.

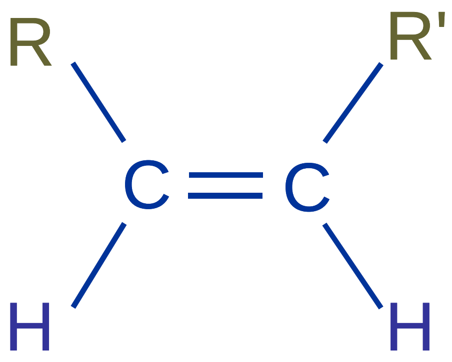


monosubstituted



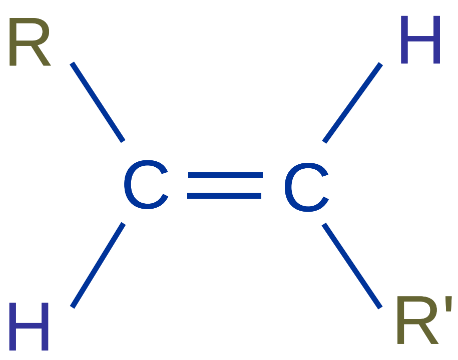
R & R’ are called geminal groups

disubstituted



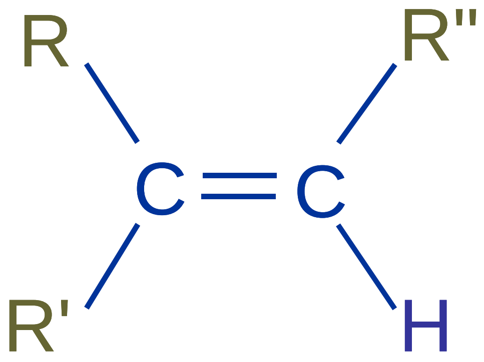
R & R’ are called vicinal groups

disubstituted

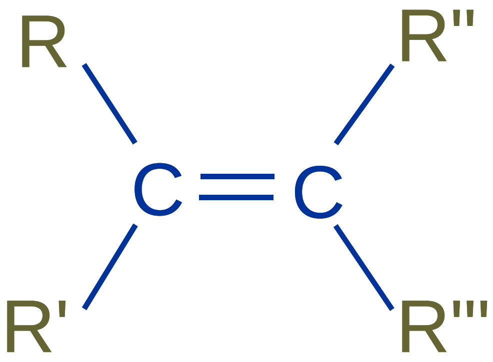


disubstituted

- Double bonds are classified according to the number of carbons attached to them.



trisubstituted



tetrasubstituted

Substituent Effects on Alkene Stability

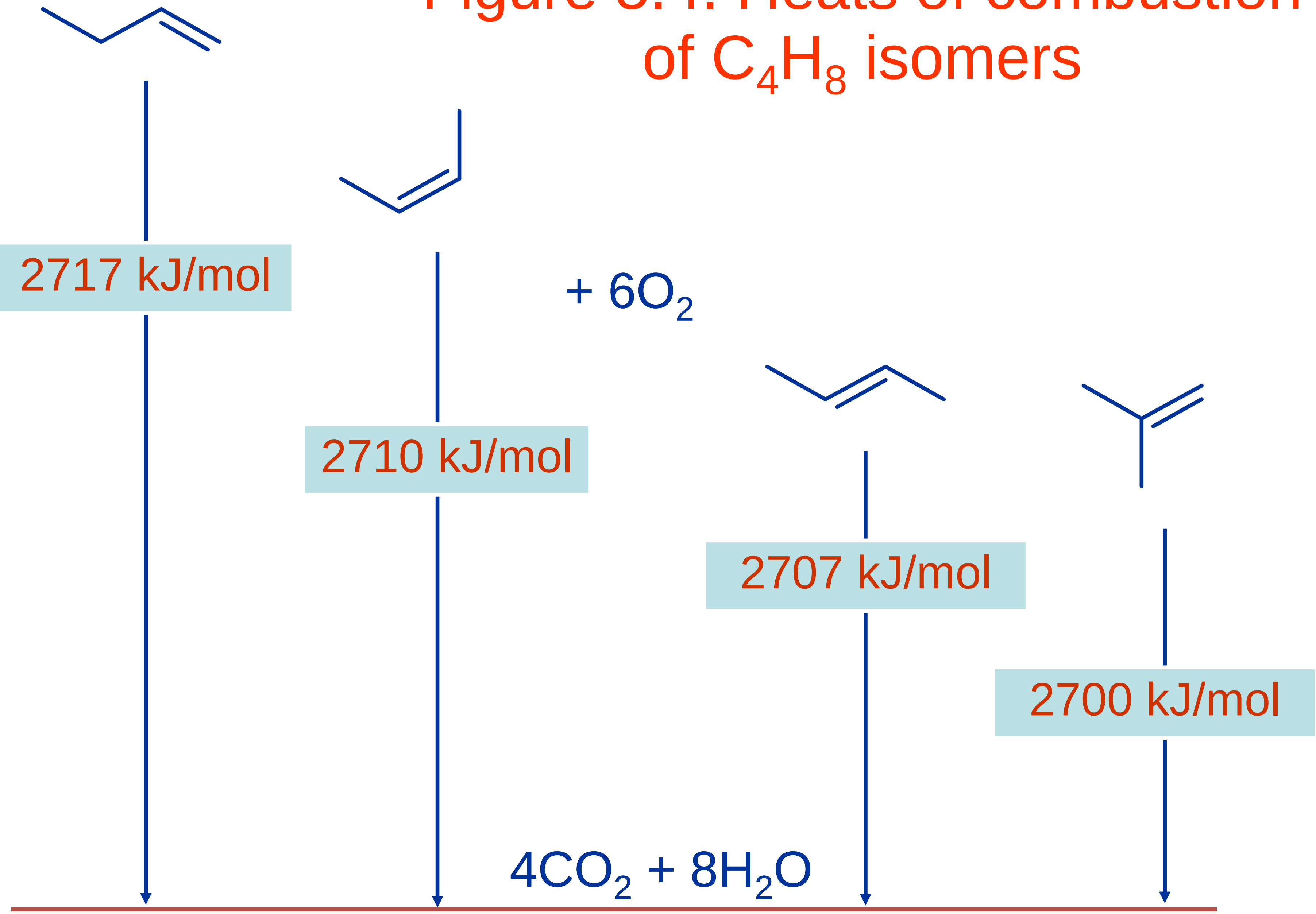
➢ Electronic

- Disubstituted alkenes are more stable than monosubstituted alkenes.

➢ Steric

- *trans* alkenes are more stable than *cis* alkenes.

Figure 5.4. Heats of combustion of C_4H_8 isomers



+ $6O_2$

2717 kJ/mol

2710 kJ/mol

2707 kJ/mol

2700 kJ/mol

$4CO_2 + 8H_2O$

Substituent Effects on Alkene Stability

Electronic

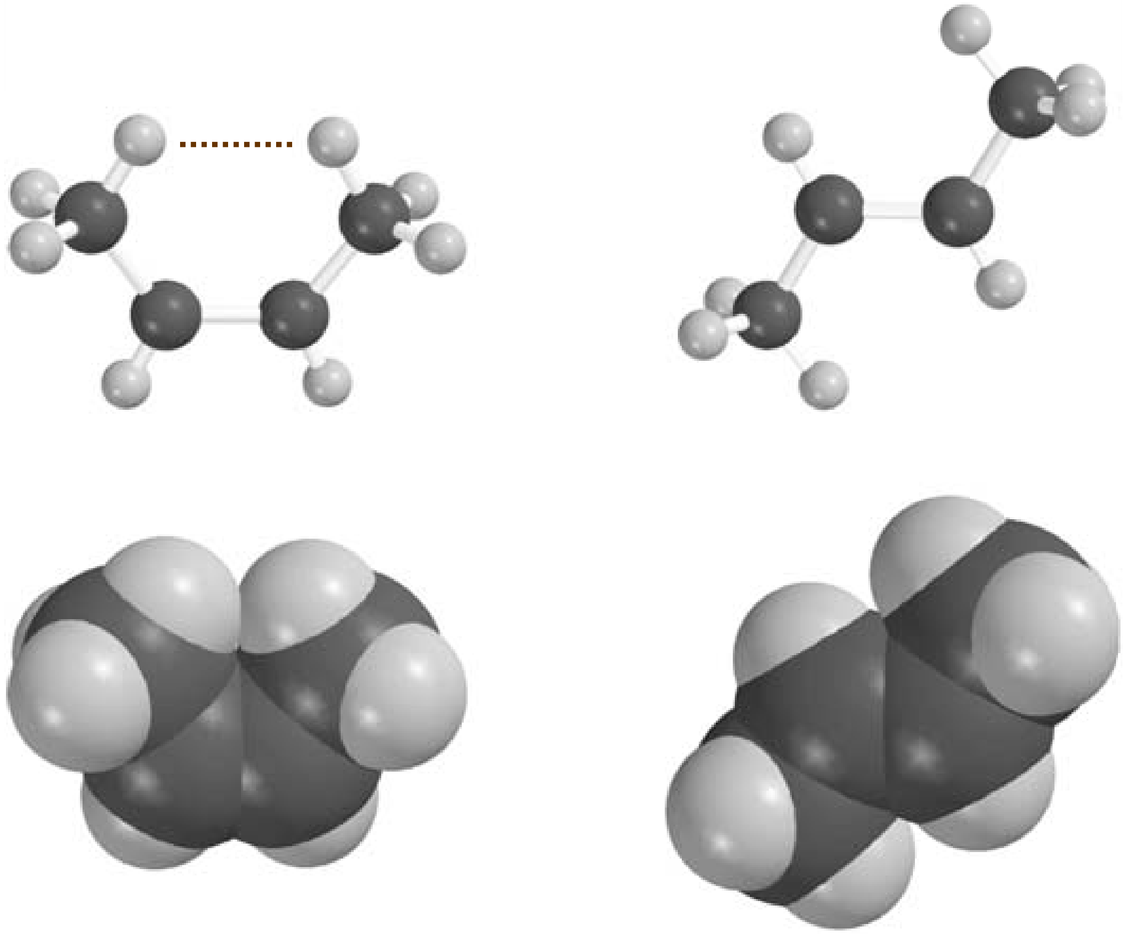
- ➢ Alkyl groups stabilize double bonds more than H.
- ➢ More highly substituted double bonds are more stable than less highly substituted ones.

Steric

- ➢ *trans* alkenes are more stable than *cis* alkenes.
- ➢ *cis* alkenes are destabilized by van der Waals strain.

Figure 5.5. *cis* and *trans*-2-Butene

van der Waals strain
due to crowding of
cis-methyl groups

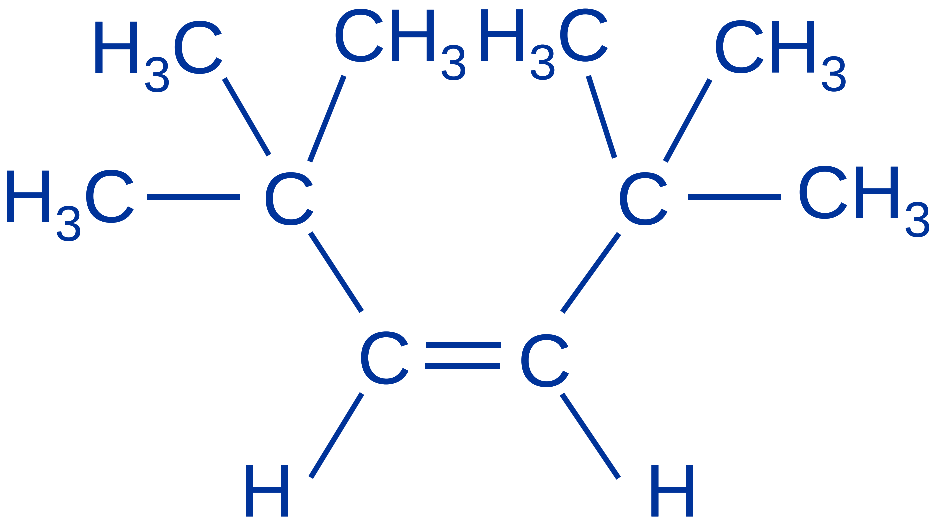


cis-2 Butene

trans-2 Butene

van der Waals Strain

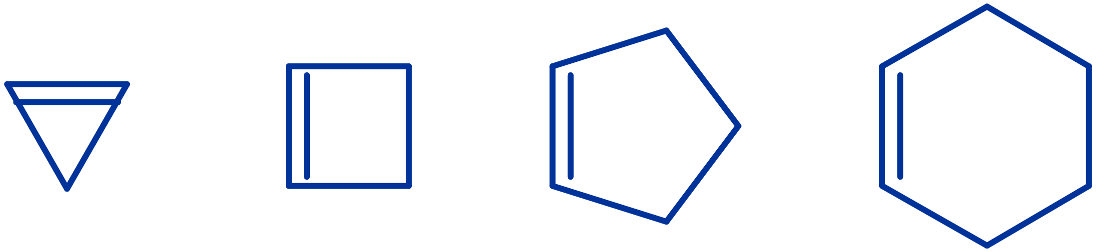
- ➢ Steric effect causes a large difference in stability between *cis* and *trans*-$(CH_3)_3CCH{=}CHC(CH_3)_3$.
- ➢ *cis* is 44 kJ/mol less stable than *trans.*



5.7. Cycloalkenes

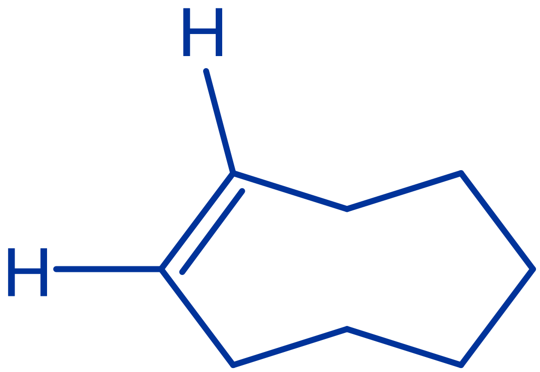
- Cyclopropene and cyclobutene have angle strain.

- Larger cycloalkenes, such as cyclopentene and cyclohexene, can incorporate a double bond into the ring with little or no angle strain.

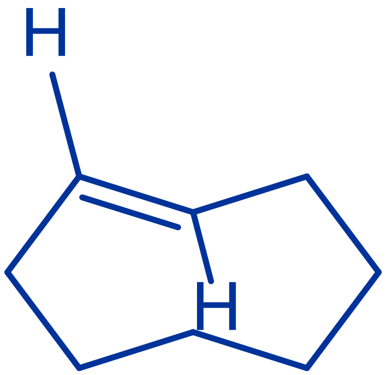


Stereoisomeric cycloalkenes

- *cis*-cyclooctene and *trans*-cyclooctene are stereoisomers.
- *cis*-cyclooctene is 39 kJ/mol more stable than *trans*-cyclooctene.



cis-Cyclooctene

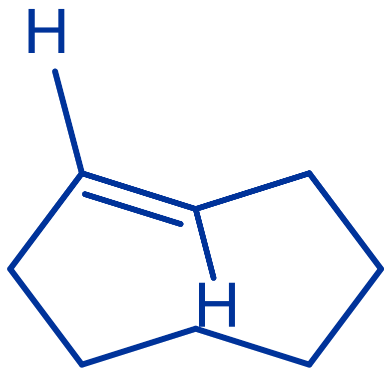


trans-Cyclooctene

Stereoisomeric cycloalkenes

- *trans*-cyclooctene is smallest *trans*-cycloalkene that is stable at room temperature.

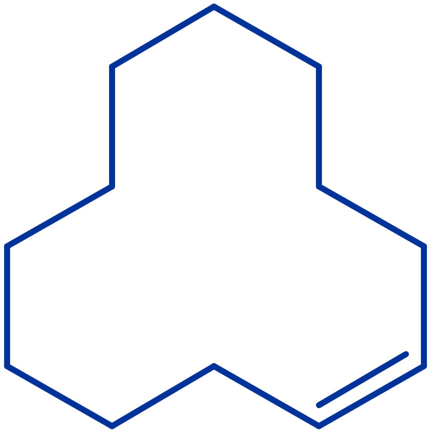
- *cis* stereoisomer is more stable than *trans* through C11 cycloalkenes.



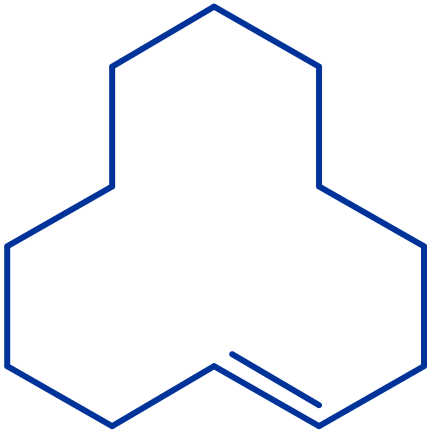
trans-Cyclooctene

Stereoisomeric cycloalkenes

- *cis* and *trans*-cyclododecene are approximately equal in stability.



cis-Cyclododecene



trans-Cyclododecene

- When there are more than 12 carbons in the ring, *trans*-cycloalkenes are more stable than *cis*.
- The ring is large enough so the cycloalkene behaves much like a noncyclic one.

5.8. Preparation of Alkenes: Elimination Reactions

β-Elimination Reactions Overview

- Dehydrogenation of alkanes:

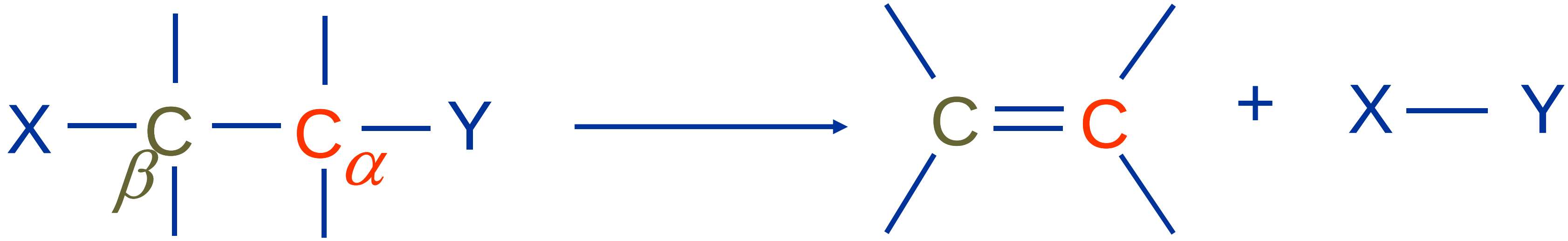
  X = Y = H

- Dehydration of alcohols:

  X = H; Y = OH

- Dehydrohalogenation of alkyl halides:

  X = H; Y = Br, etc.



Dehydrogenation

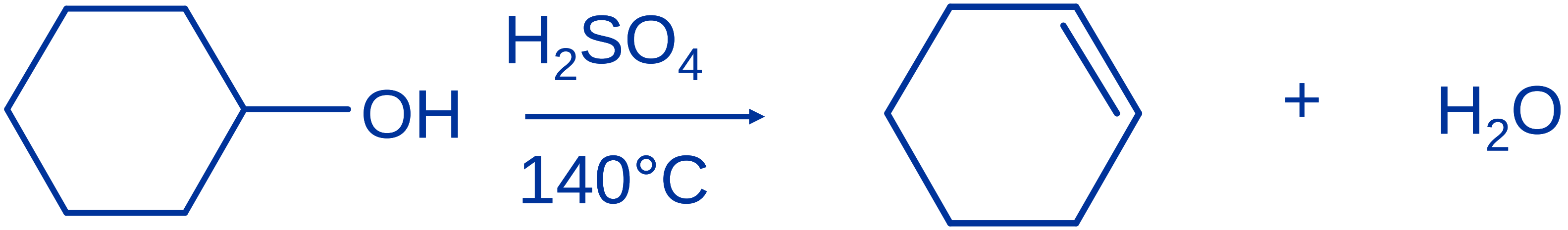
- Limited to industrial syntheses of ethylene, propene, 1,3-butadiene, and styrene.
- Important economically, but rarely used in laboratory-scale syntheses.

$$CH_3CH_3 \xrightarrow{750°C} H_2C{=}CH_2 + H_2$$

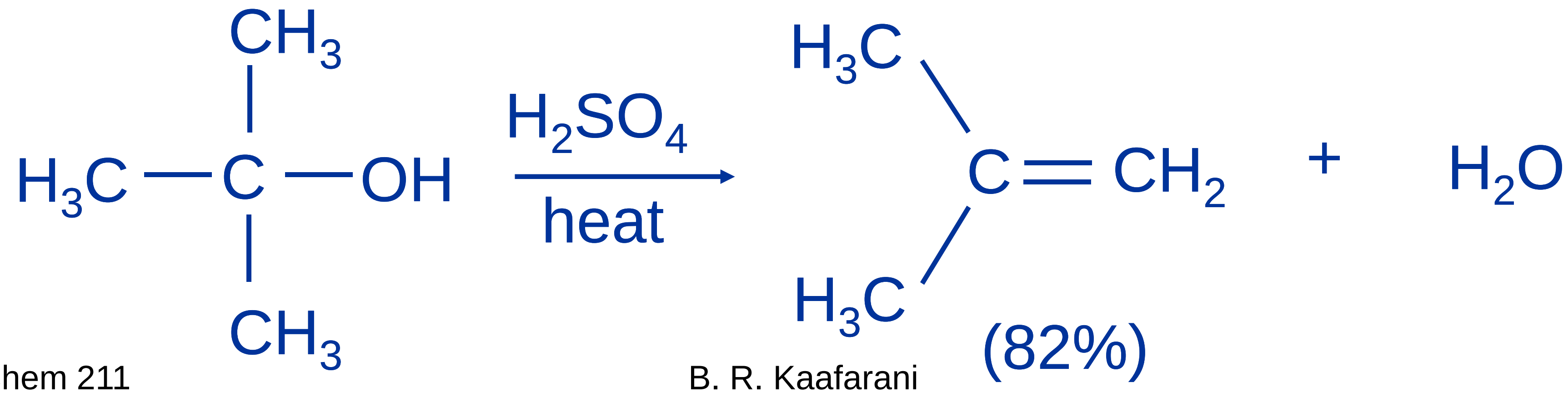
$$CH_3CH_2CH_3 \xrightarrow{750°C} H_2C{=}CHCH_3 + H_2$$

5.9. Dehydration of Alcohols

$$CH_3CH_2OH \xrightarrow[160°C]{H_2SO_4} H_2C{=}CH_2 + H_2O$$

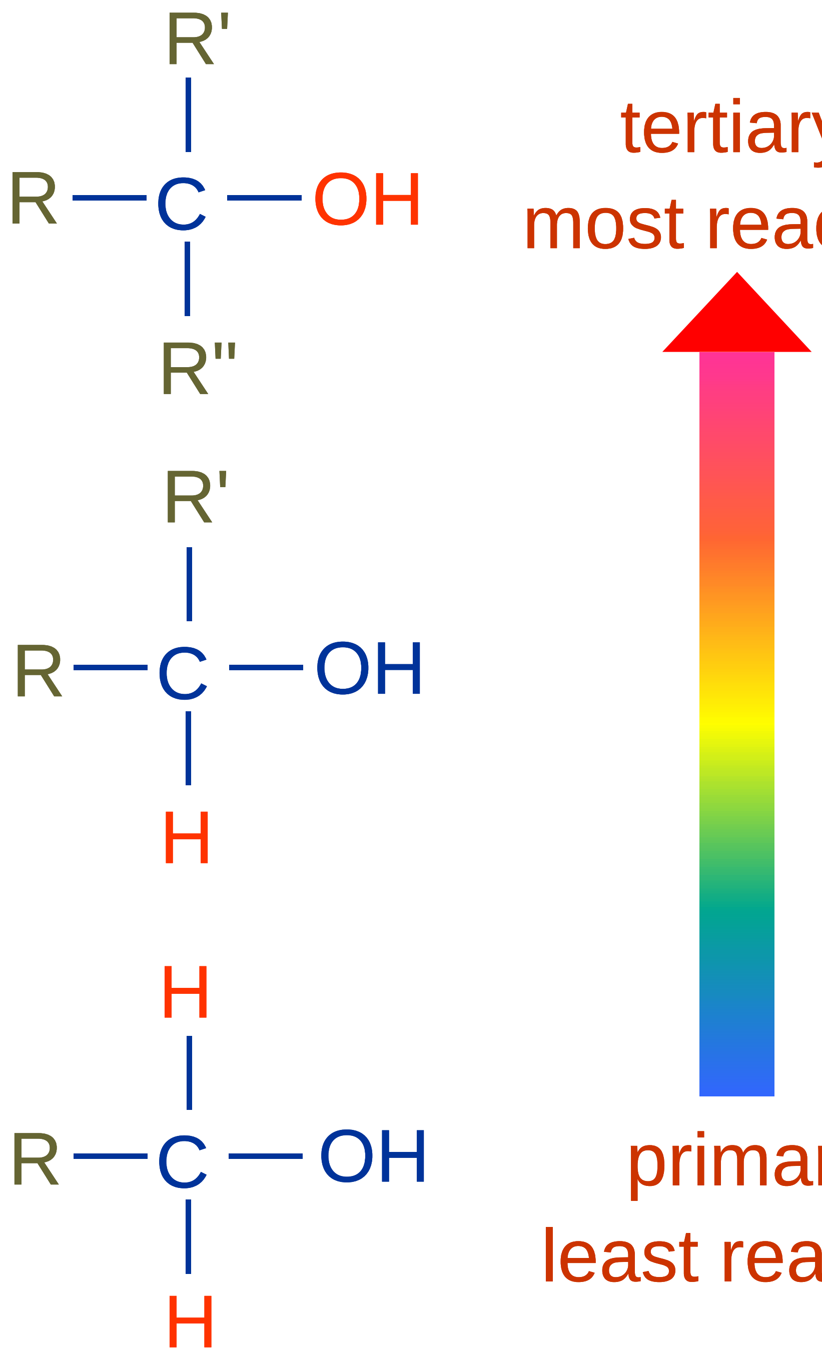


(79-87%)



(82%)

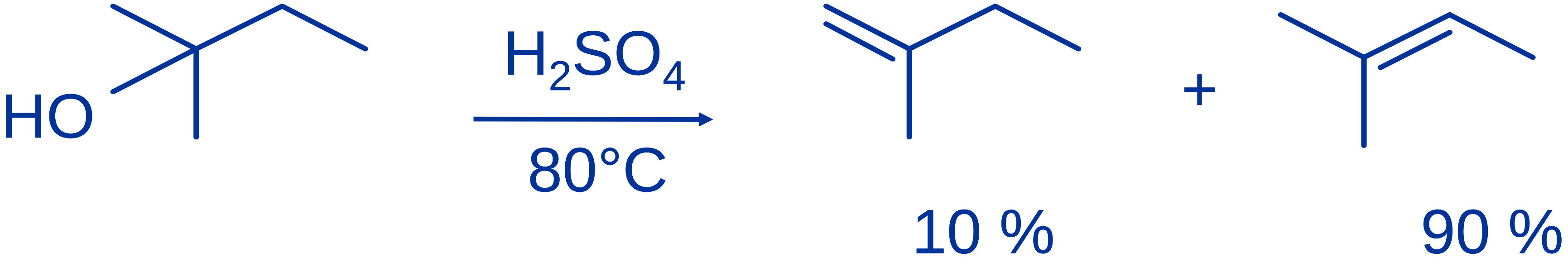
Relative Reactivity

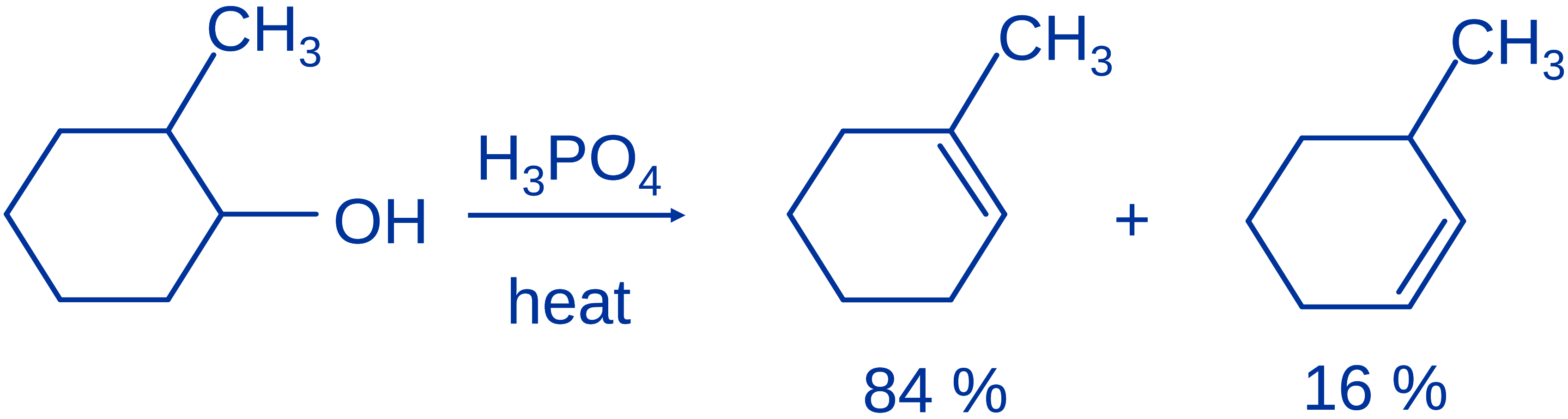


tertiary:
most reactive

primary:
least reactive

5.10. Regioselectivity in Alcohol Dehydration: The Zaitsev Rule

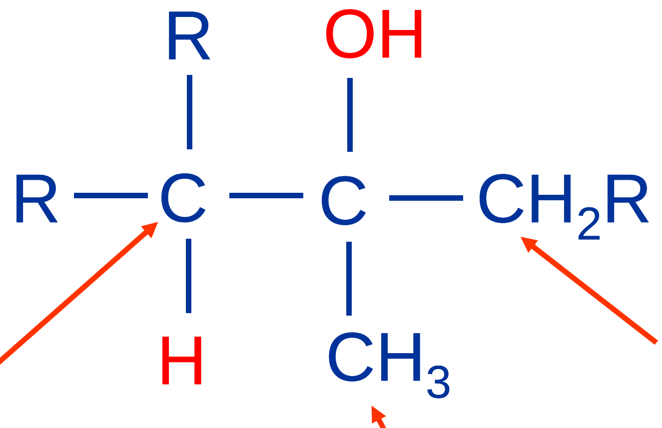




- A reaction that can proceed in more than one direction, but in which one direction predominates, is said to be regioselective.

The Zaitsev Rule

- When elimination can occur in more than one direction, the principal alkene is the one formed by loss of H from the β carbon having the fewest hydrogens.



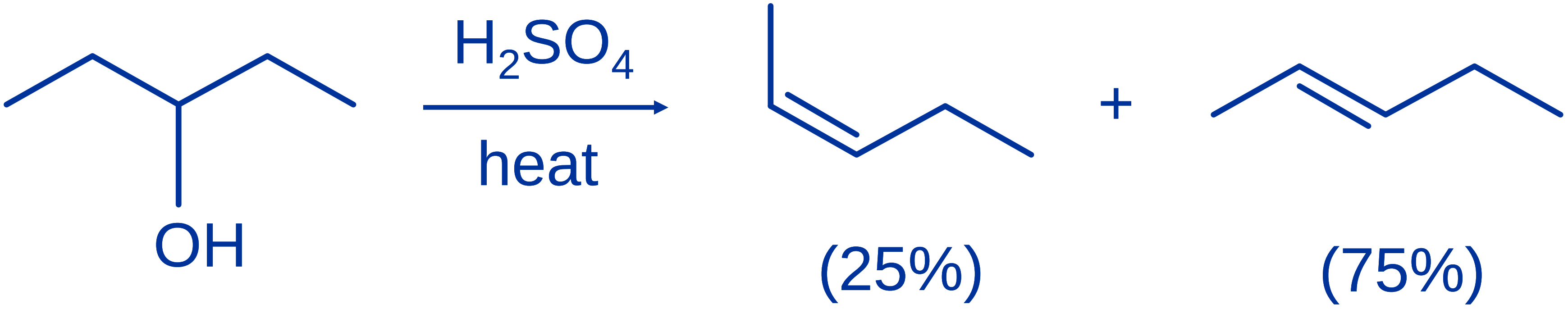
$$R-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2R$$

only one proton on this β carbon

two protons on this β carbon

three protons on this β carbon

5.11. Stereoselectivity in Alcohol Dehydration



- A stereoselective reaction is one in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amounts than any other.

5.12

The E1 and E2 Mechanisms of Alcohol Dehydration

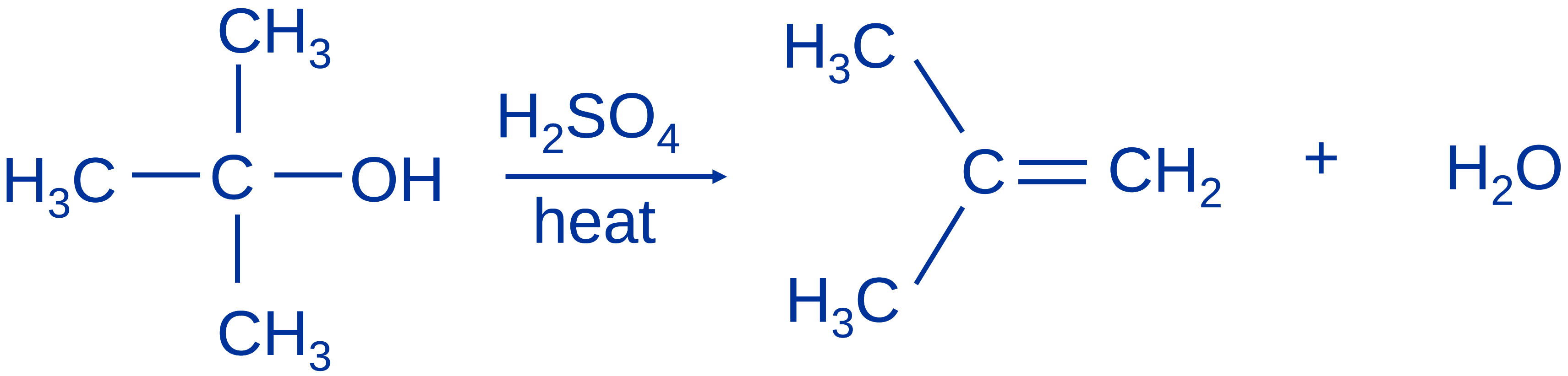
A connecting point...

- The dehydration of alcohols and the reaction of alcohols with hydrogen halides share the following common features:

1) Both reactions are promoted by acids.
2) The relative reactivity decreases in the order tertiary > secondary > primary

- These similarities suggest that *carbocations* are intermediates in the acid-catalyzed dehydration of alcohols, just as they are in the reaction of alcohols with hydrogen halides.

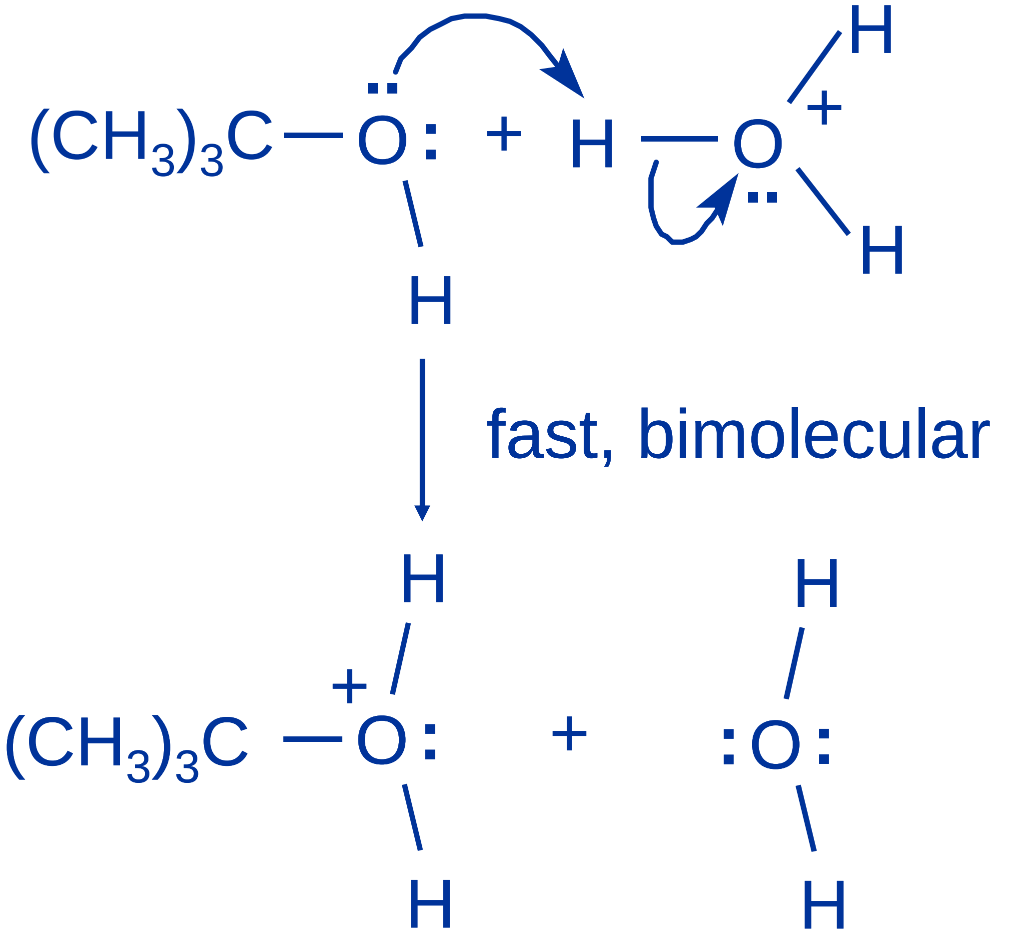
Dehydration of *tert*-Butyl Alcohol



- First two steps of mechanism are identical to those for the reaction of *tert*-butyl alcohol with hydrogen halides.

Mechanism

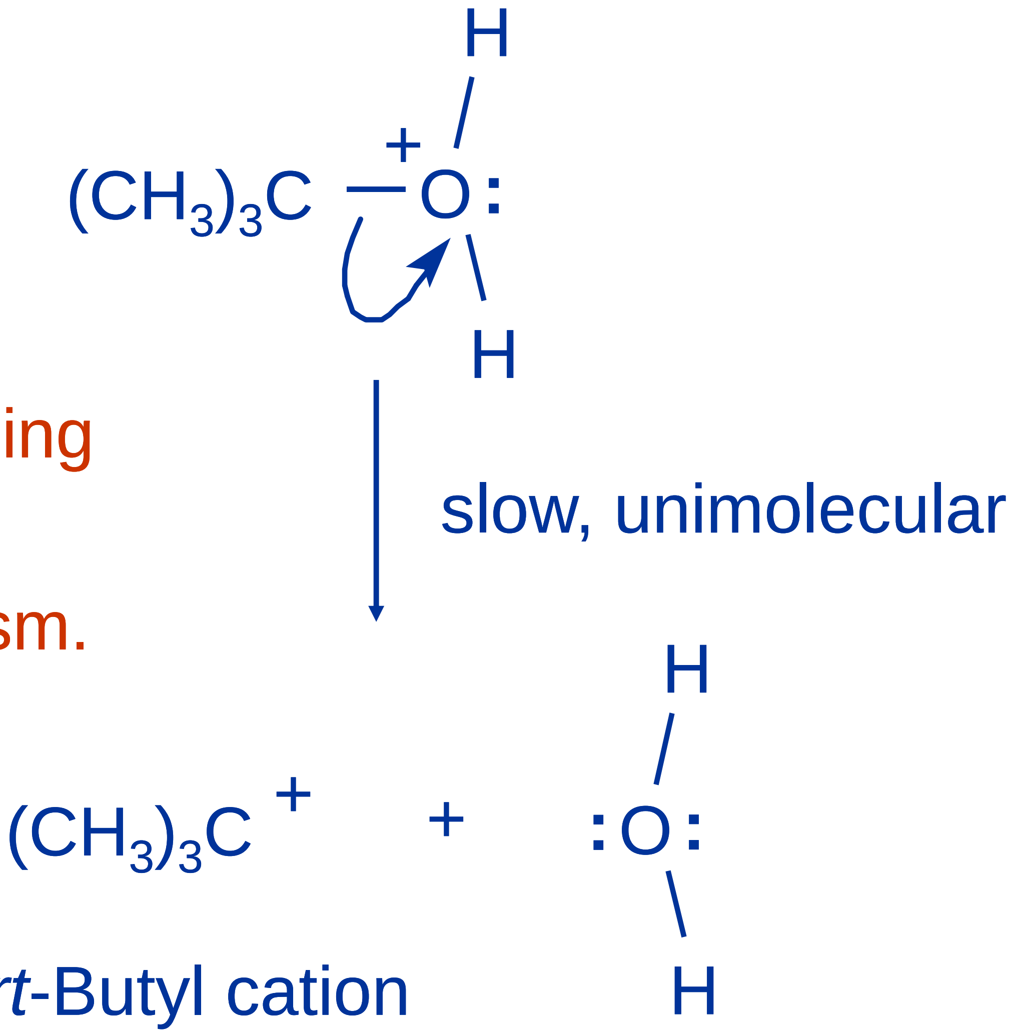
Step 1: Proton transfer to *tert*-butyl alcohol.



tert-Butyloxonium ion

Mechanism

Step 2: Dissociation of *tert*-butyloxonium ion to carbocation.

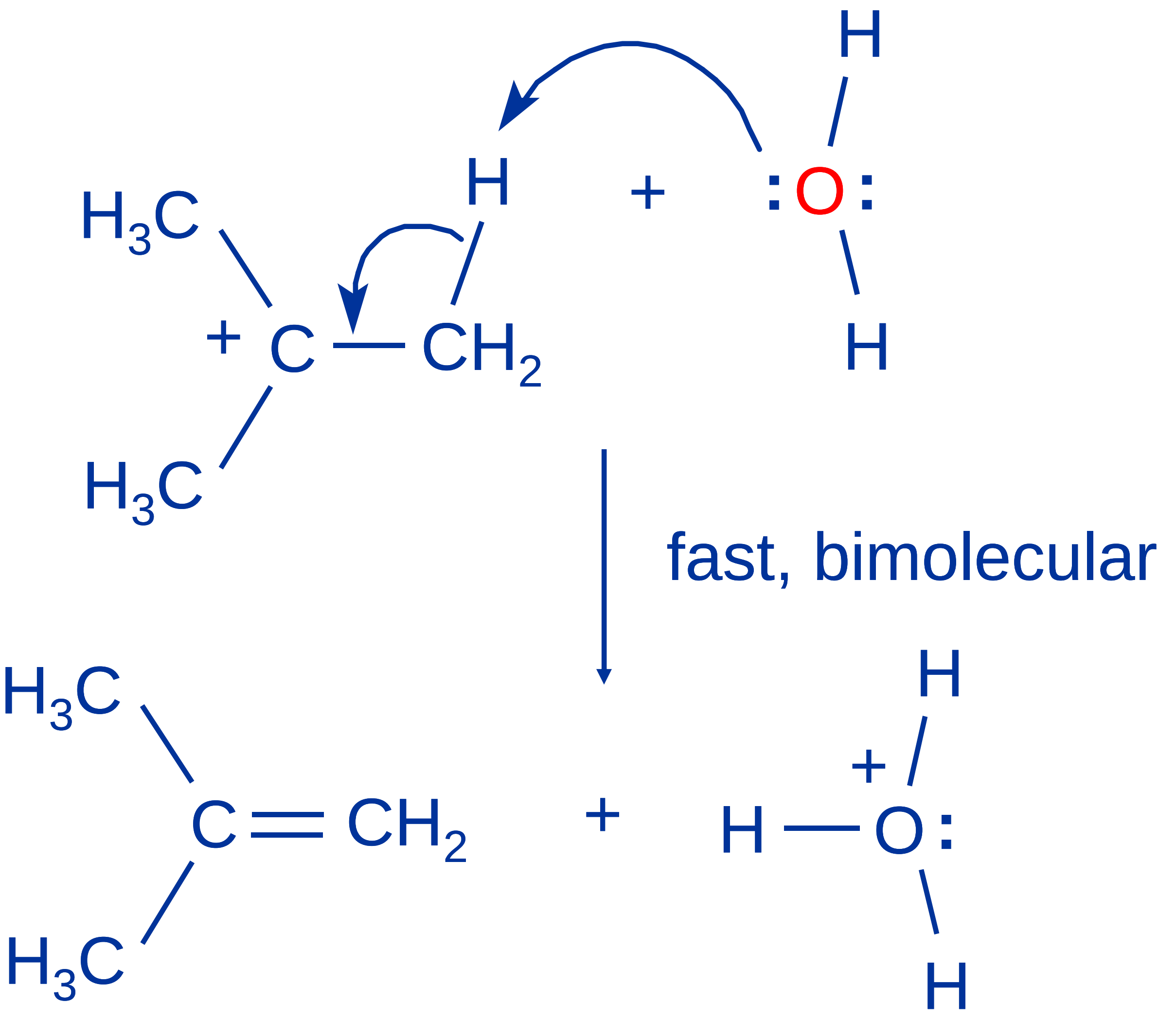


tert-Butyl cation

- Because rate-determining step is unimolecular, this is called the E1 mechanism.

Mechanism

Step 3: Deprotonation of *tert*-butyl cation.



Carbocations

- Are intermediates in the acid-catalyzed dehydration of tertiary and secondary alcohols.

- Carbocations can:
  - React with nucleophiles.
  - Lose a β-proton to form an alkene.

Dehydration of Primary Alcohols

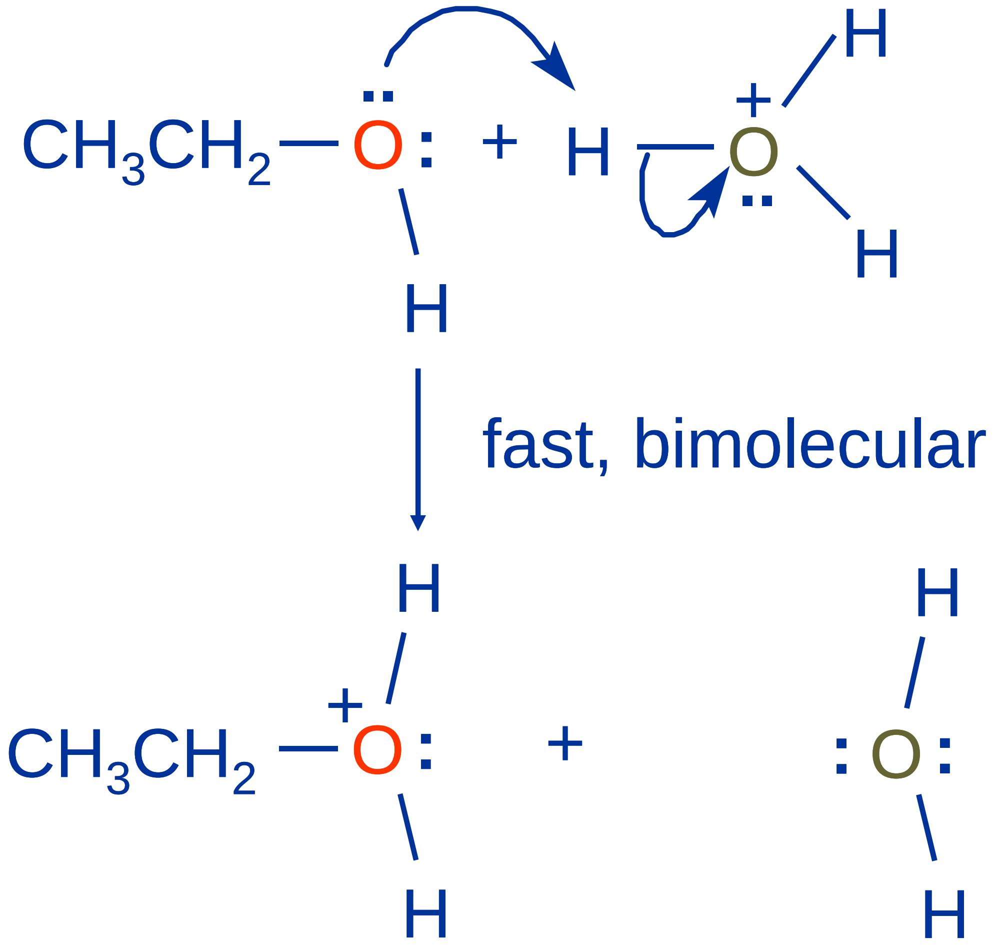
$$CH_3CH_2OH \xrightarrow[160^\circ C]{H_2SO_4} H_2C{=}CH_2 \quad + \quad H_2O$$

- *Avoids* carbocation because primary carbocations are too unstable.

- Oxonium ion loses water and a proton in a bimolecular step.

Mechanism

Step 1: Proton transfer from acid to ethanol.

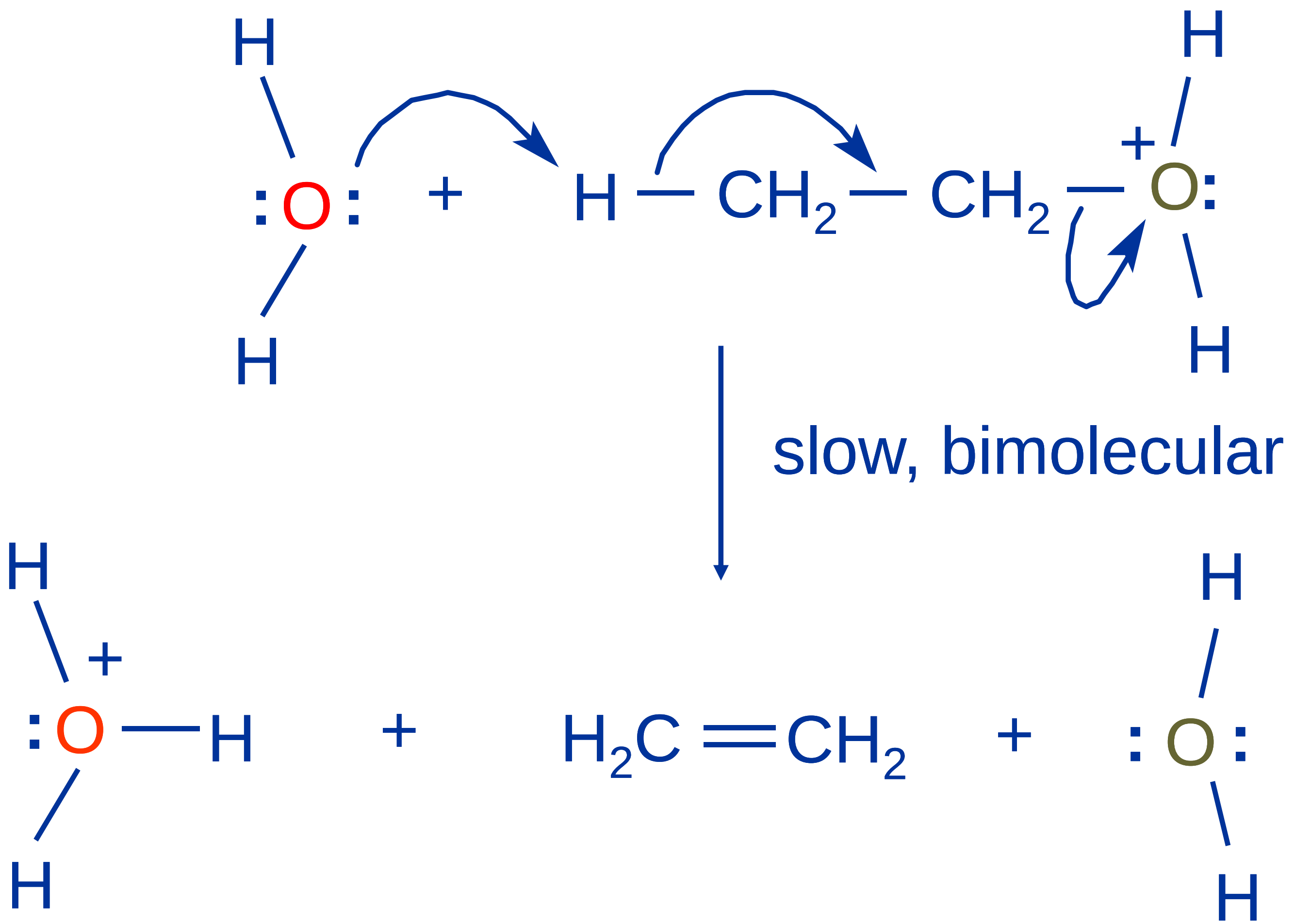


fast, bimolecular

Ethyloxonium ion

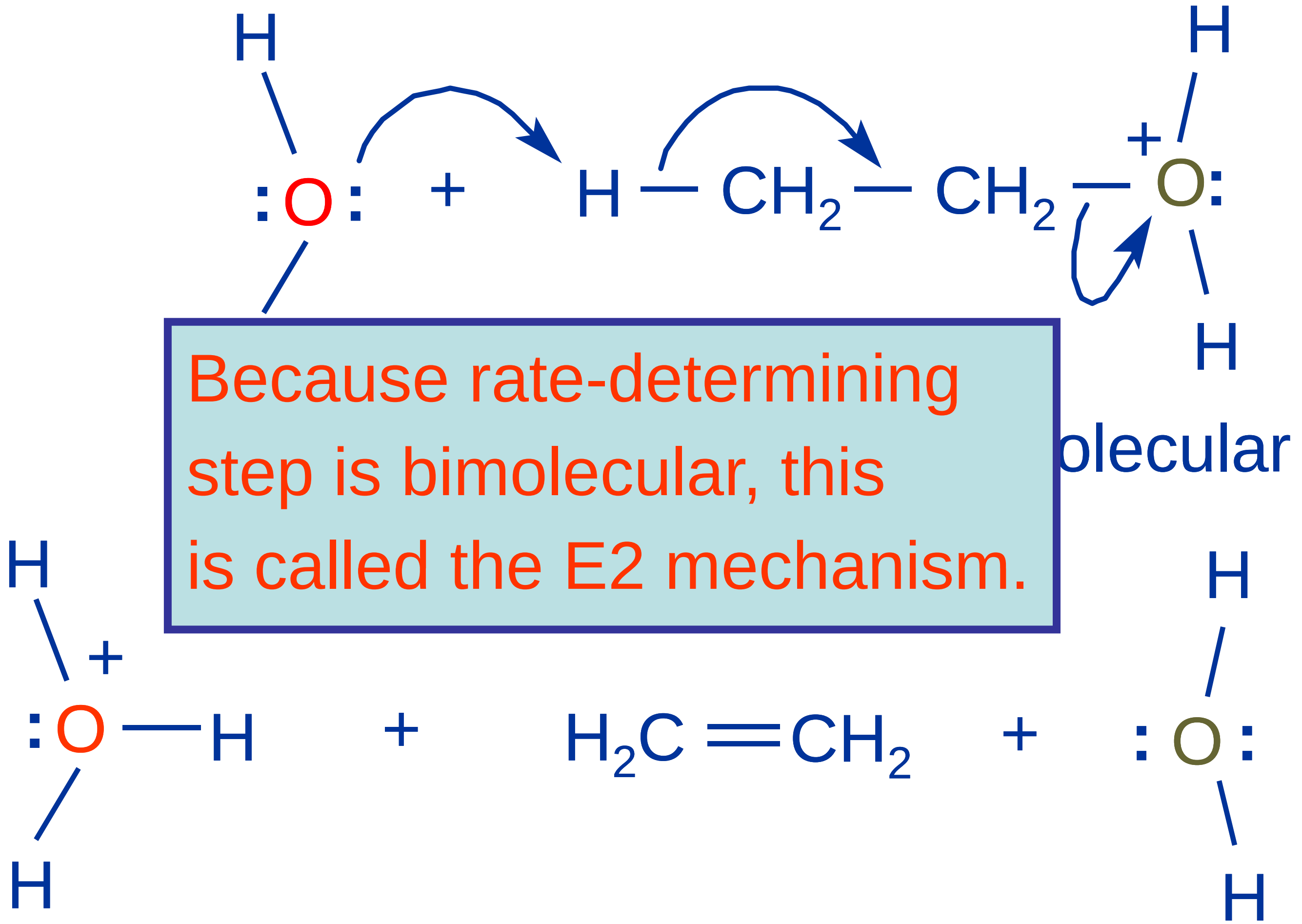
Mechanism

Step 2: Oxonium ion loses both a proton and a water molecule in the same step.



Mechanism

Step 2: Oxonium ion loses both a proton and a water molecule in the same step.



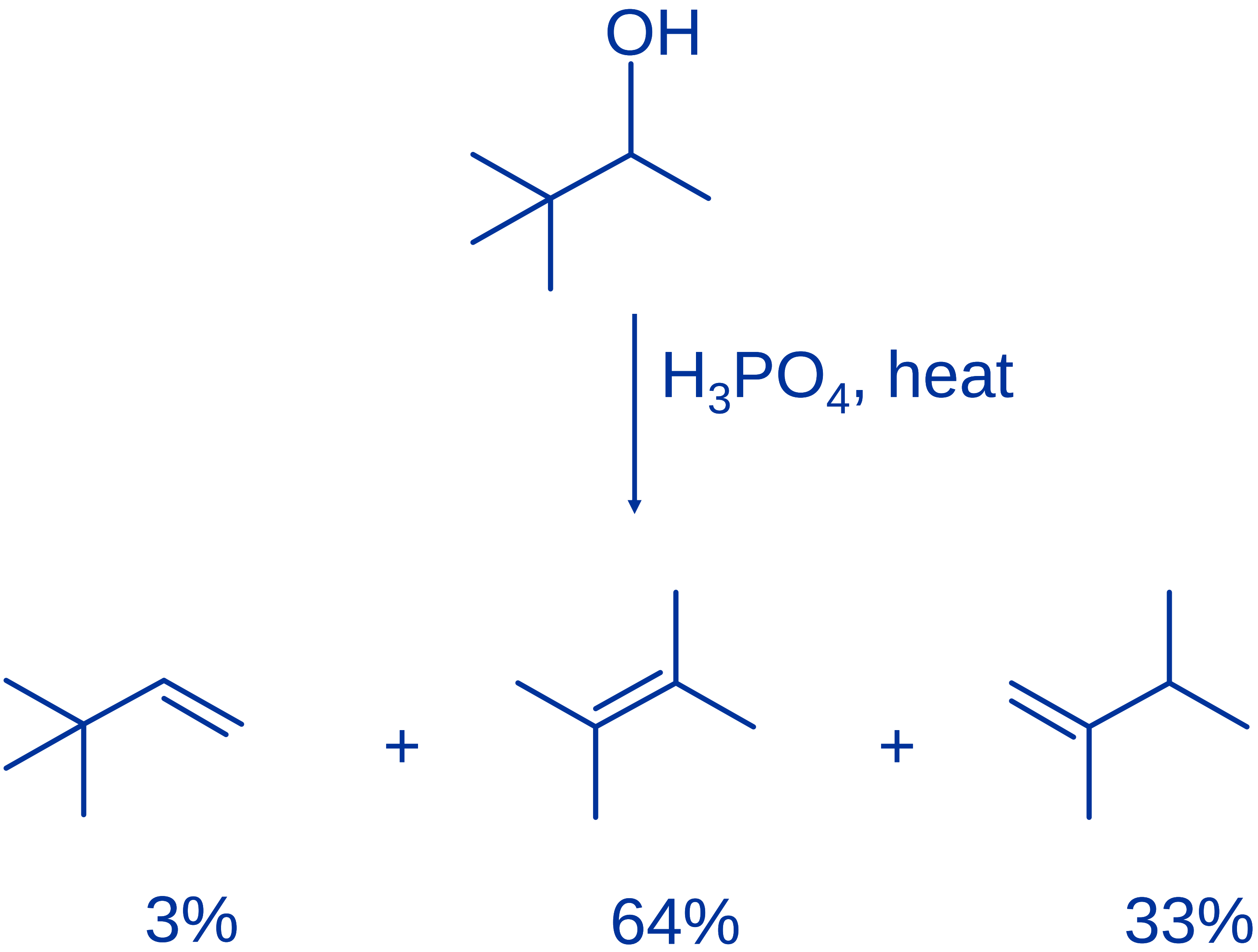
Because rate-determining step is bimolecular, this is called the E2 mechanism.

olecular

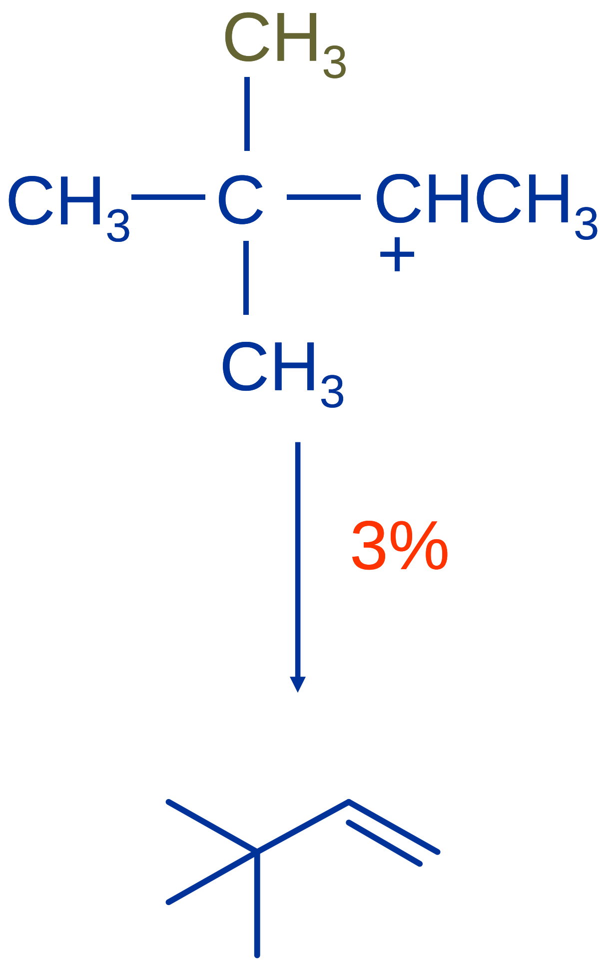
5.13. Rearrangements in Alcohol Dehydration

- Sometimes the alkene product does not have the same carbon skeleton as the starting alcohol.

Example

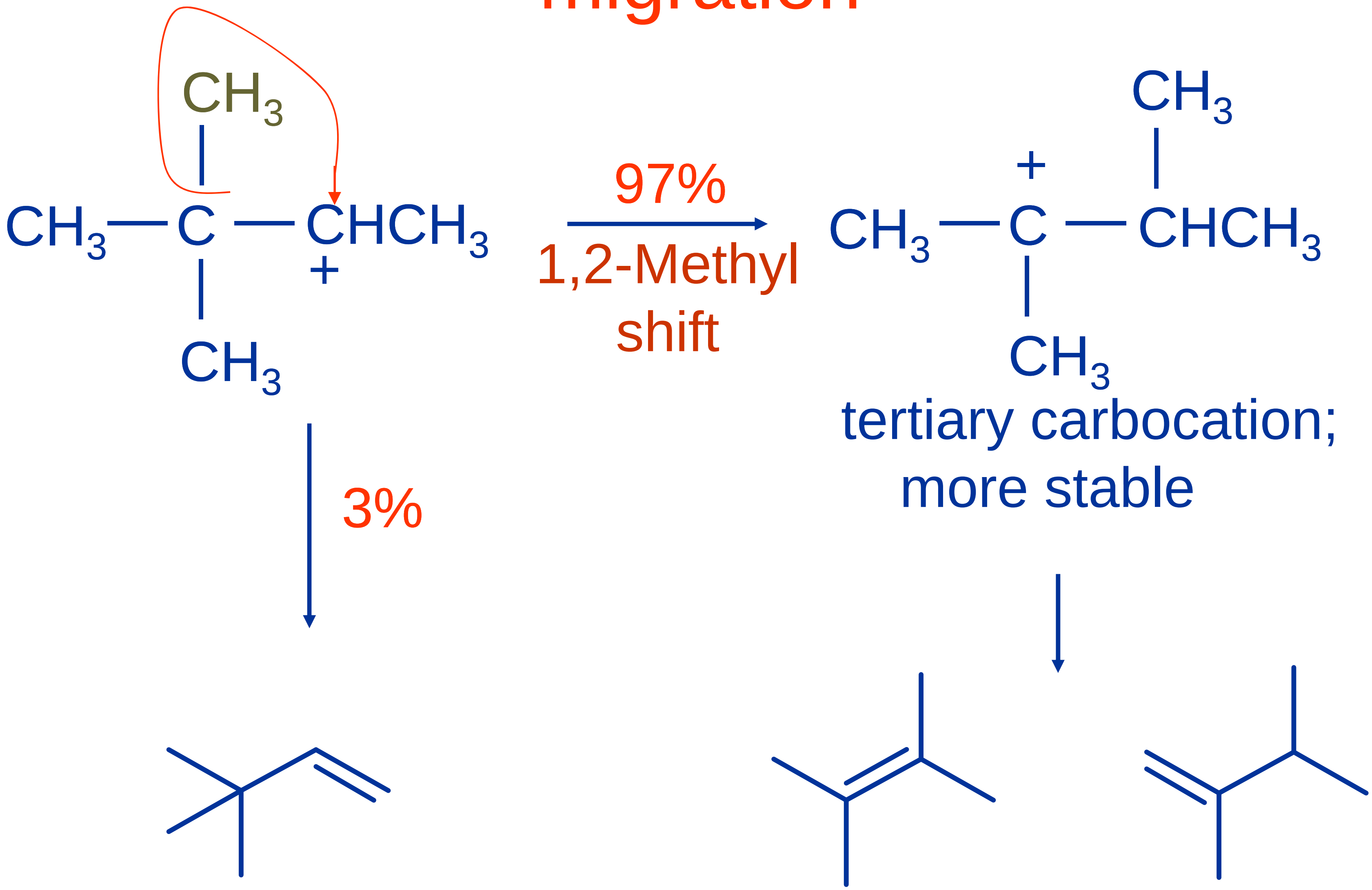


Rearrangement involves alkyl group migration


$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\overset{+}{C}HCH_3$$

- Carbocation can lose a proton as shown.
- Or it can undergo a methyl migration.
- CH_3 group migrates with its pair of electrons to adjacent positively charged carbon.

Rearrangement involves alkyl group migration



tertiary carbocation; more stable

Another rearrangement

$CH_3CH_2CH_2CH_2OH$

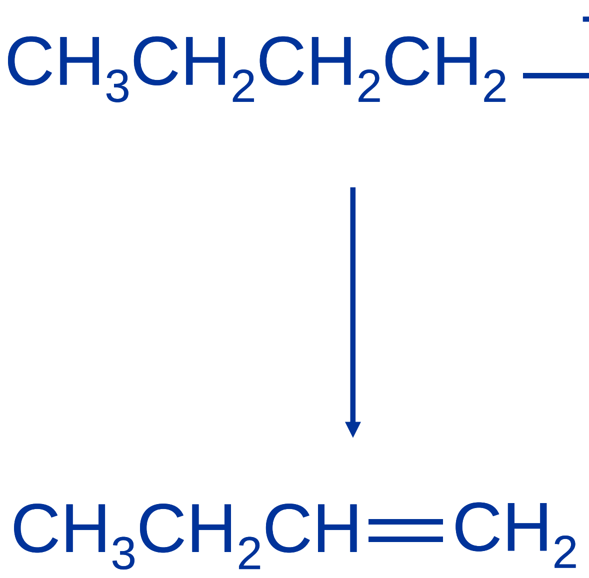
$\downarrow$ H_3PO_4, heat

$CH_3CH_2CH{=}CH_2$ + $CH_3CH{=}CHCH_3$

12%

mixture of *cis* (32%)
and *trans*-2-butene (56%)

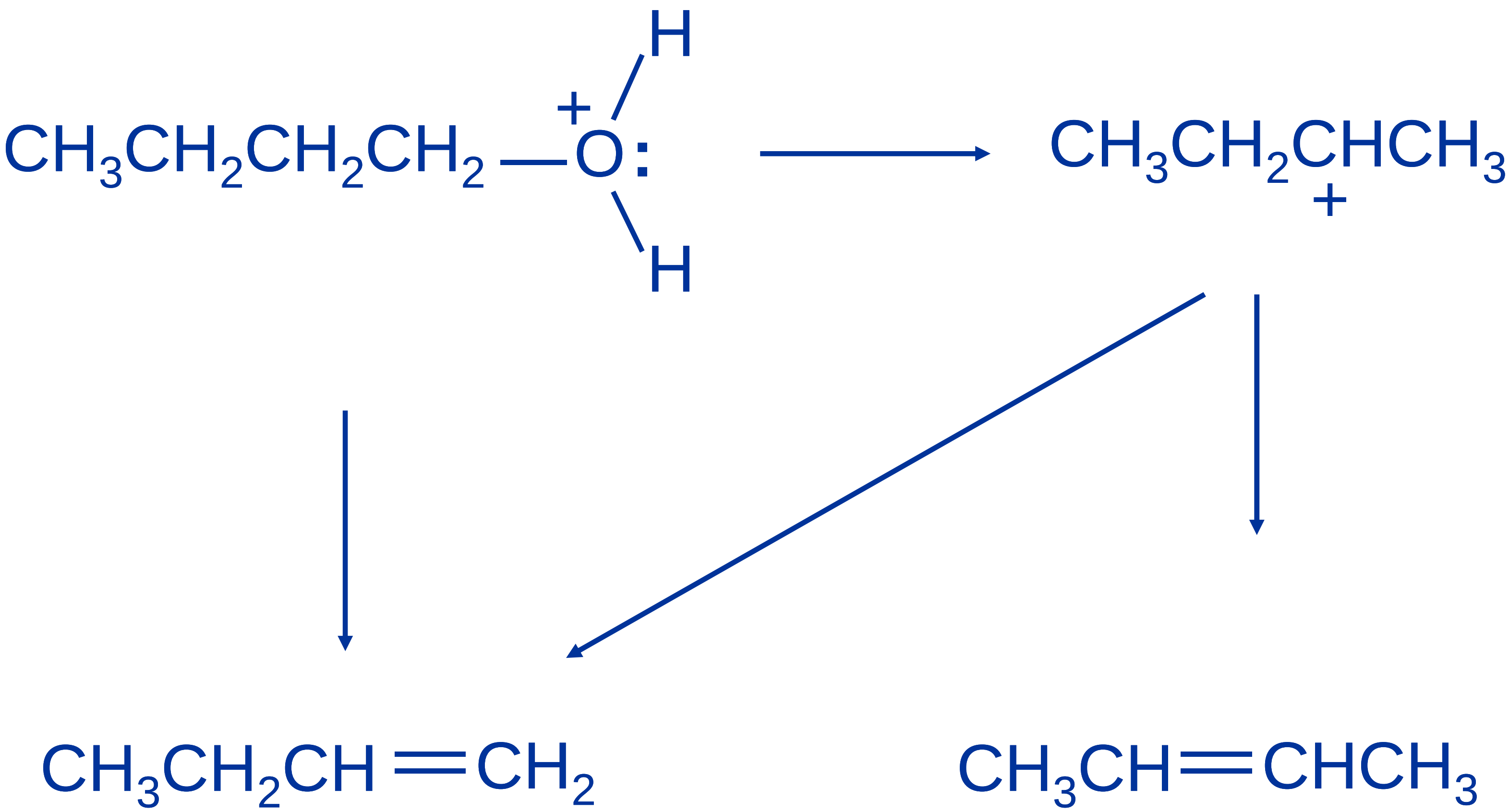
Rearrangement involves hydride shift



- Oxonium ion can lose water and a proton (from C-2) to give 1-butene.
- Does not give a carbocation directly because primary carbocations are too unstable.

- Hydrogen migrates with its pair of electrons from C-2 to C-1 as water is lost.
- Carbocation formed by hydride shift is secondary.

Rearrangement involves hydride shift



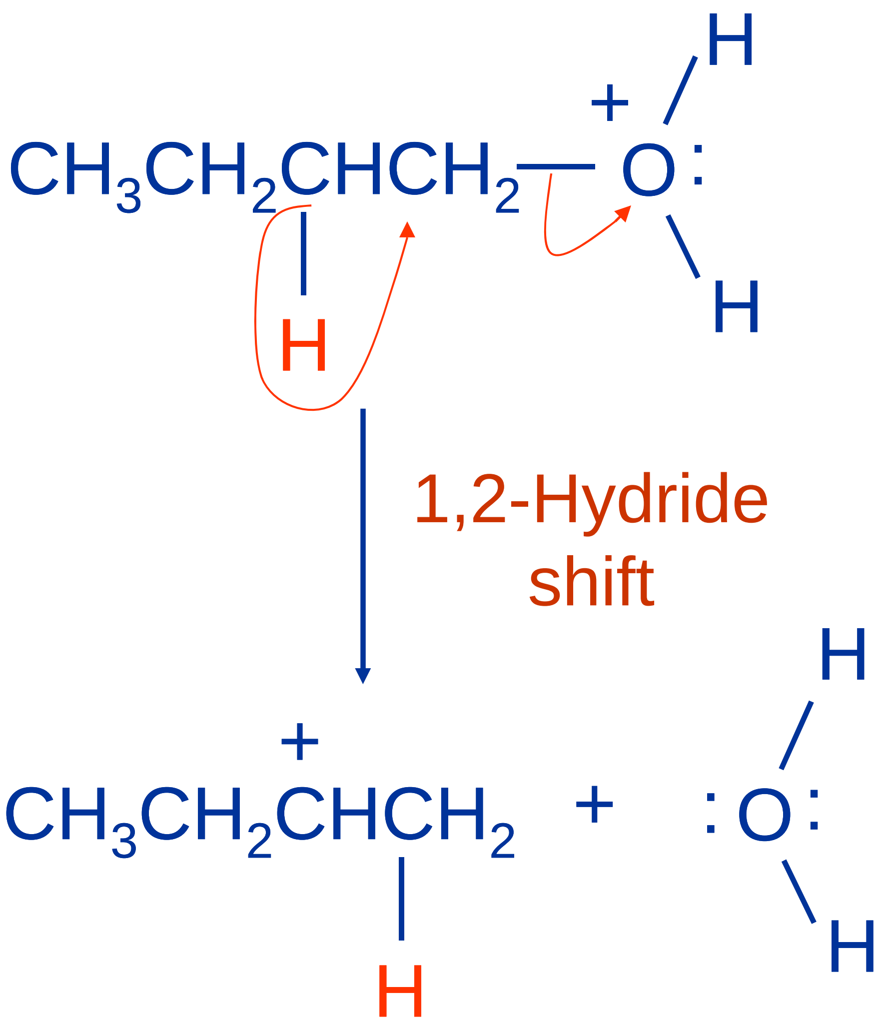
$$CH_3CH_2CH_2CH_2-\overset{H}{\underset{H}{\overset{+}{O}}}: \longrightarrow CH_3CH_2\underset{+}{C}HCH_3$$

$$CH_3CH_2CH{=}CH_2$$

$$CH_3CH{=}CHCH_3$$

mixture of *cis*
and *trans*-2-butene

Hydride Shift



$$CH_3CH_2\underset{\displaystyle H}{\underset{|}{C}}HCH_2-\overset{+}{O}H_2 \xrightarrow{\text{1,2-Hydride shift}} CH_3CH_2\overset{+}{C}H\underset{\displaystyle H}{\underset{|}{C}}H_2 + H_2O$$

1,2-Hydride shift

Carbocations can...

- React with nucleophiles.
- Lose a proton from the β-carbon to form an alkene.
- Rearrange (less stable to more stable).

5.14. Dehydrohalogenation of Alkyl Halides

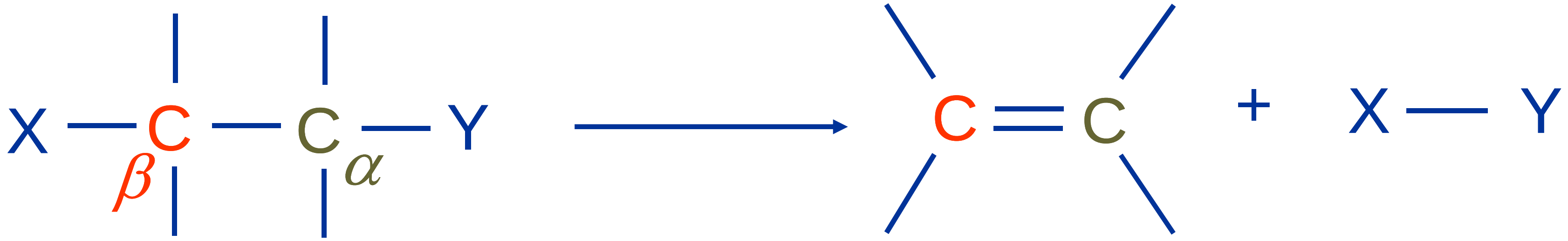
β-Elimination Reactions Overview

- Dehydrogenation of alkanes:

  X = Y = H. Industrial process; not regioselective.
- Dehydration of alcohols:

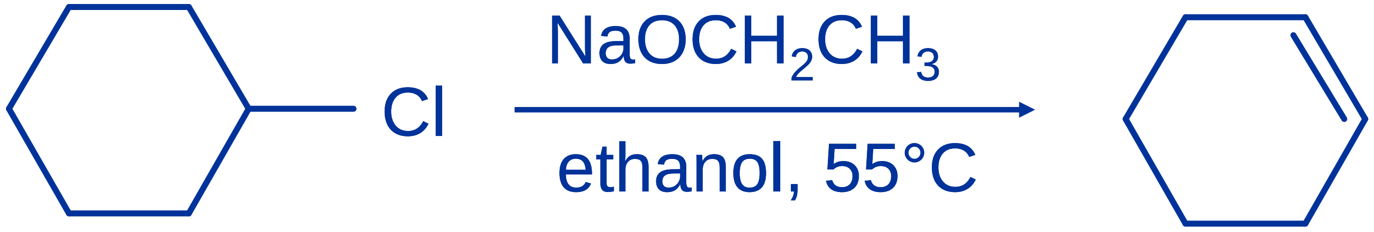
  X = H; Y = OH. Acid-catalyzed.
- Dehydrohalogenation of alkyl halides:

  X = H; Y = Br, etc. Consumes base.



Dehydrohalogenation

- This is a useful method for the preparation of alkenes.



(100 %)

likewise, $NaOCH_3$ in methanol, or KOH in ethanol.

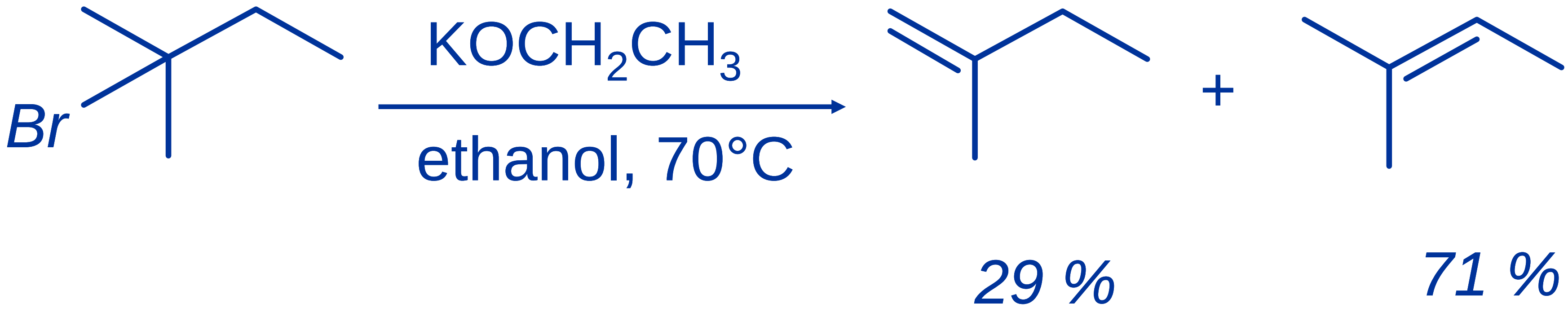
Dehydrohalogenation

- When the alkyl halide is primary, potassium *tert*-butoxide in dimethyl sulfoxide is the base/solvent system that is normally used.

$$CH_3(CH_2)_{15}CH_2CH_2Cl \xrightarrow[\text{dimethyl sulfoxide}]{KOC(CH_3)_3} CH_3(CH_2)_{15}CH=CH_2$$

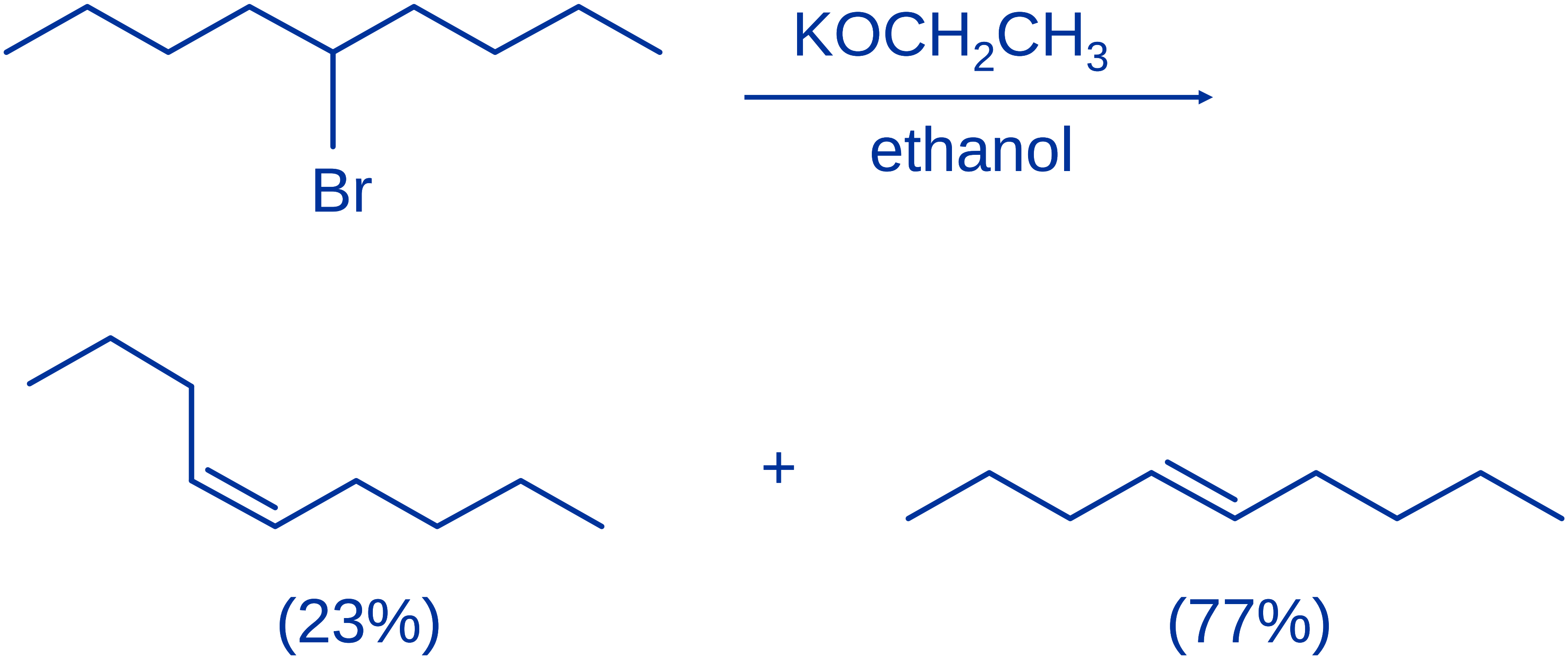
(86%)

Regioselectivity



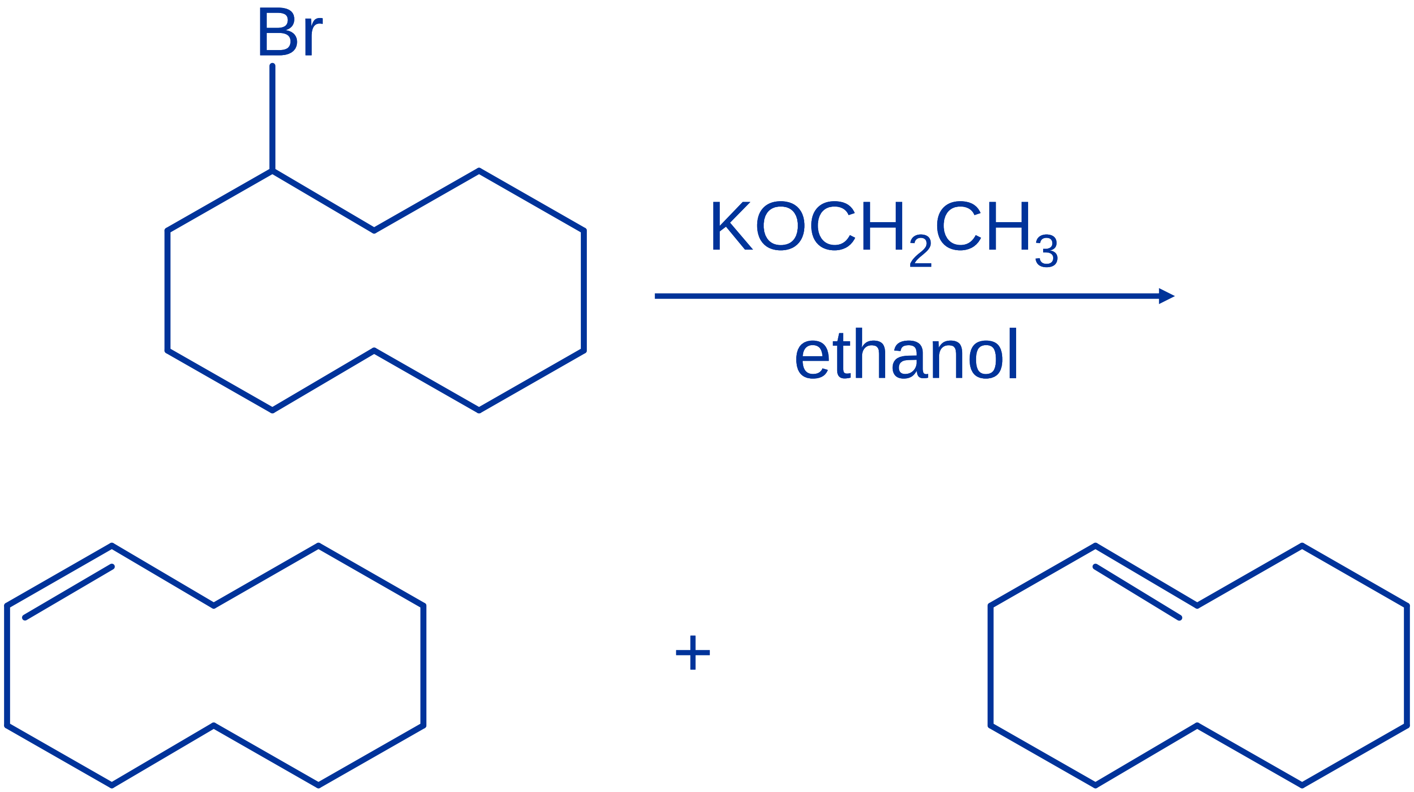
- *Follows Zaitsev's rule:*
- *More highly substituted double bond predominates.*

Stereoselectivity



More stable configuration
of double bond predominates

Stereoselectivity



(85%) (15%)

More stable configuration
of double bond predominates

5.15. Mechanism of the Dehydrohalogenation of Alkyl Halides: The E2 Mechanism

Facts

(1) Dehydrohalogenation of alkyl halides exhibits second-order kinetics

first order in alkyl halide

first order in base

rate = k[alkyl halide][base]

This implies that rate-determining step involves both base and alkyl halide; i.e., it is bimolecular.

(2) Rate of elimination depends on halogen

weaker C—X bond; faster rate

rate: RI > RBr > RCl > RF

This implies that carbon-halogen bond breaks in the rate-determining step.

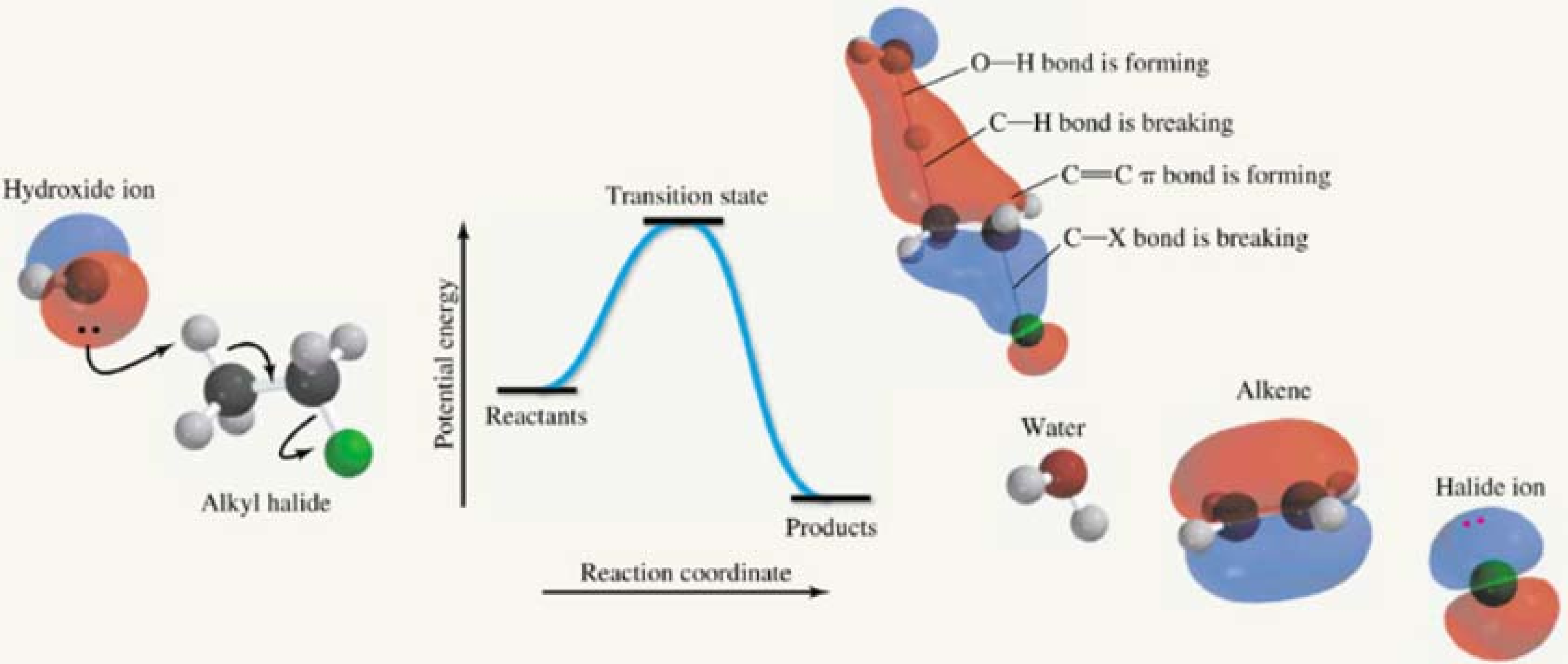
The E2 Mechanism

- Concerted (one-step) bimolecular process.
- Single transition state.

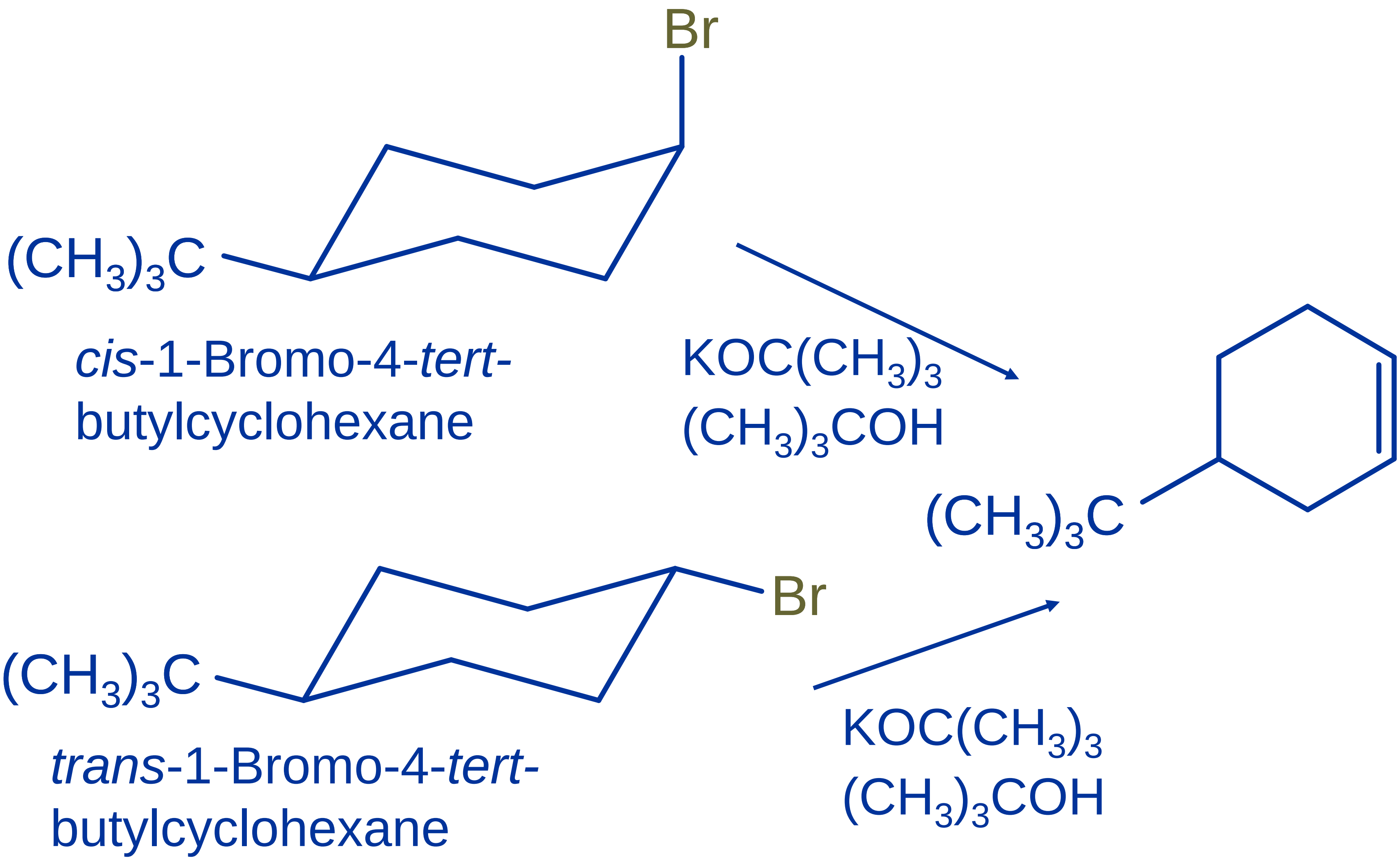
  C—H bond breaks.

  π component of double bond forms.

  C—X bond breaks.



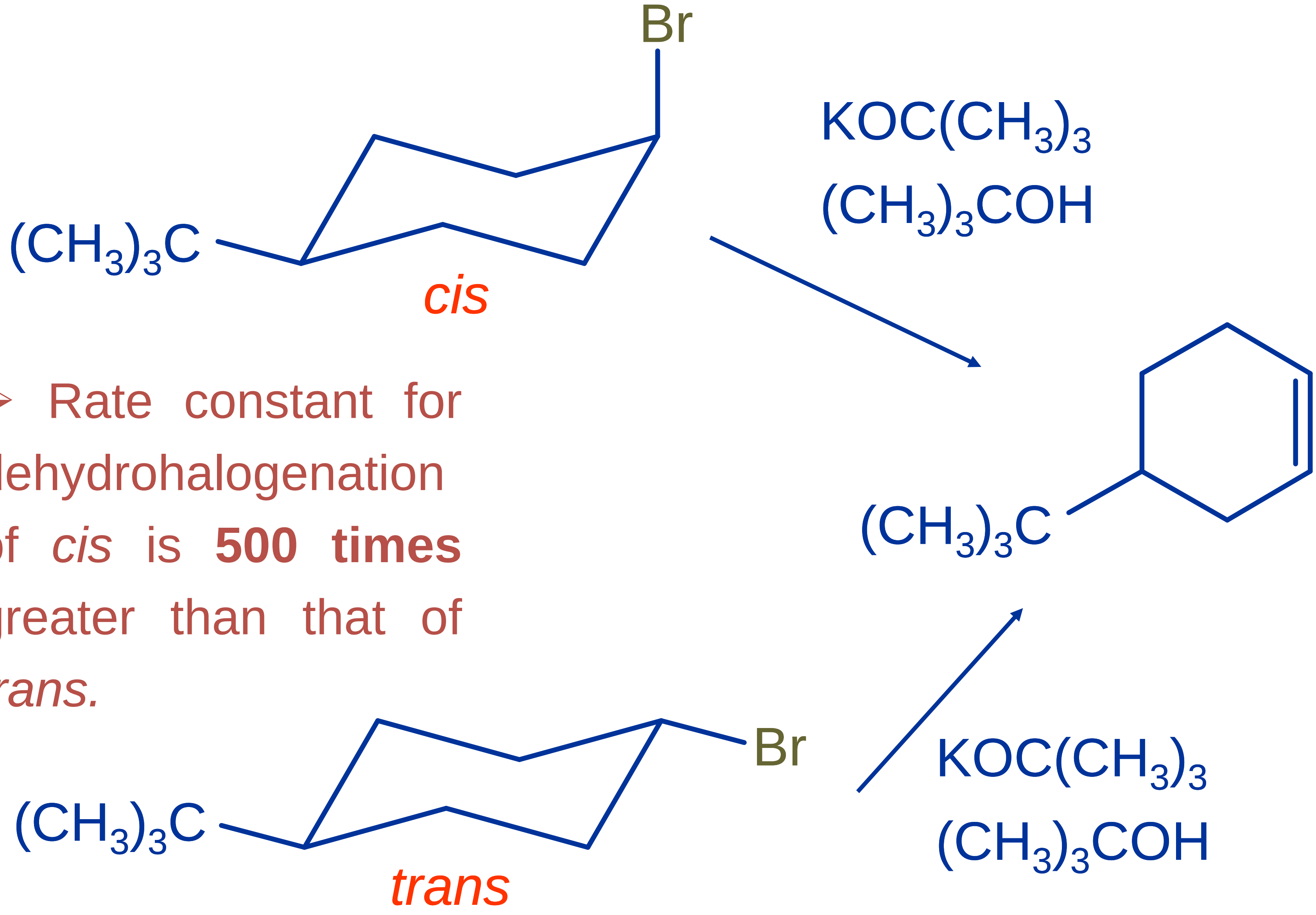
5.16. *Anti* Elimination in E2 Reactions Stereoelectronic effect



cis-1-Bromo-4-*tert*-butylcyclohexane

trans-1-Bromo-4-*tert*-butylcyclohexane

Stereoelectronic effect



cis

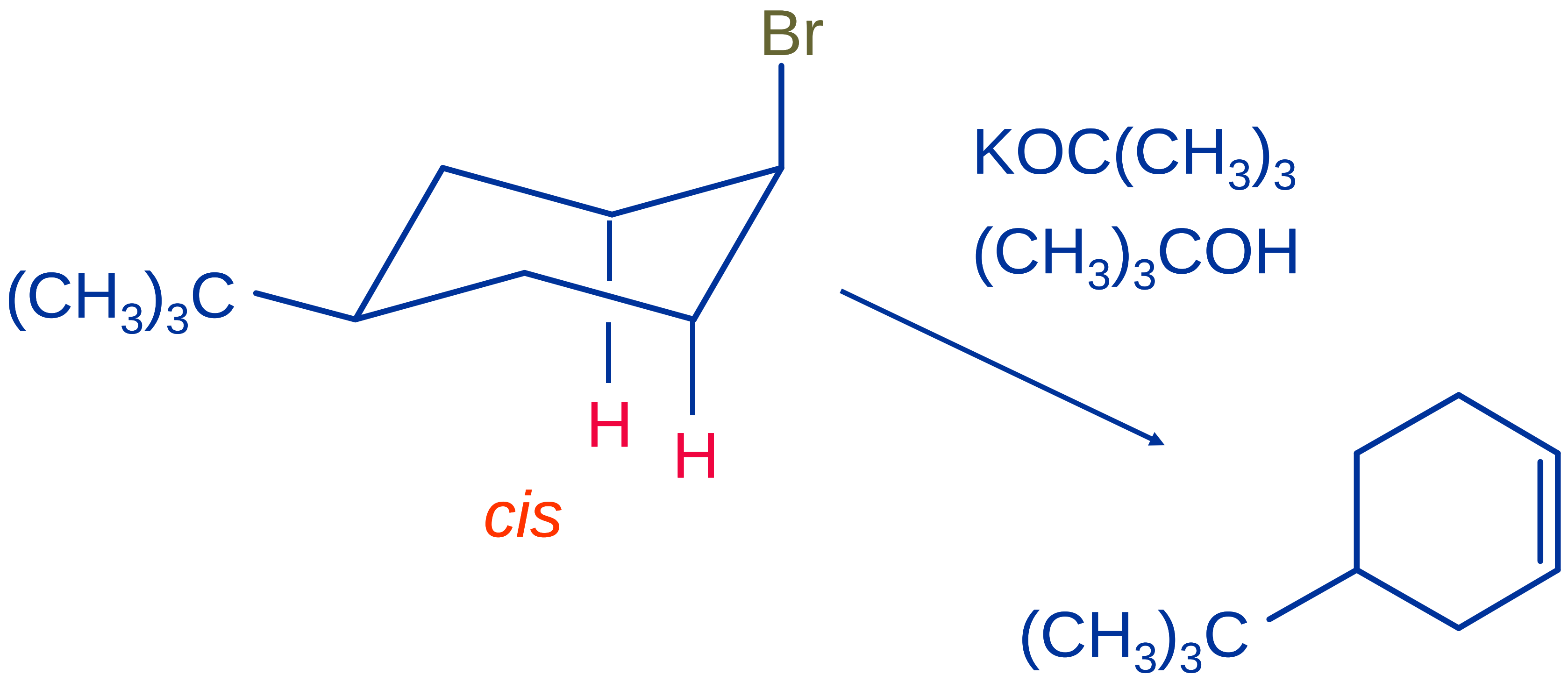
$KOC(CH_3)_3$
$(CH_3)_3COH$

trans

$KOC(CH_3)_3$
$(CH_3)_3COH$

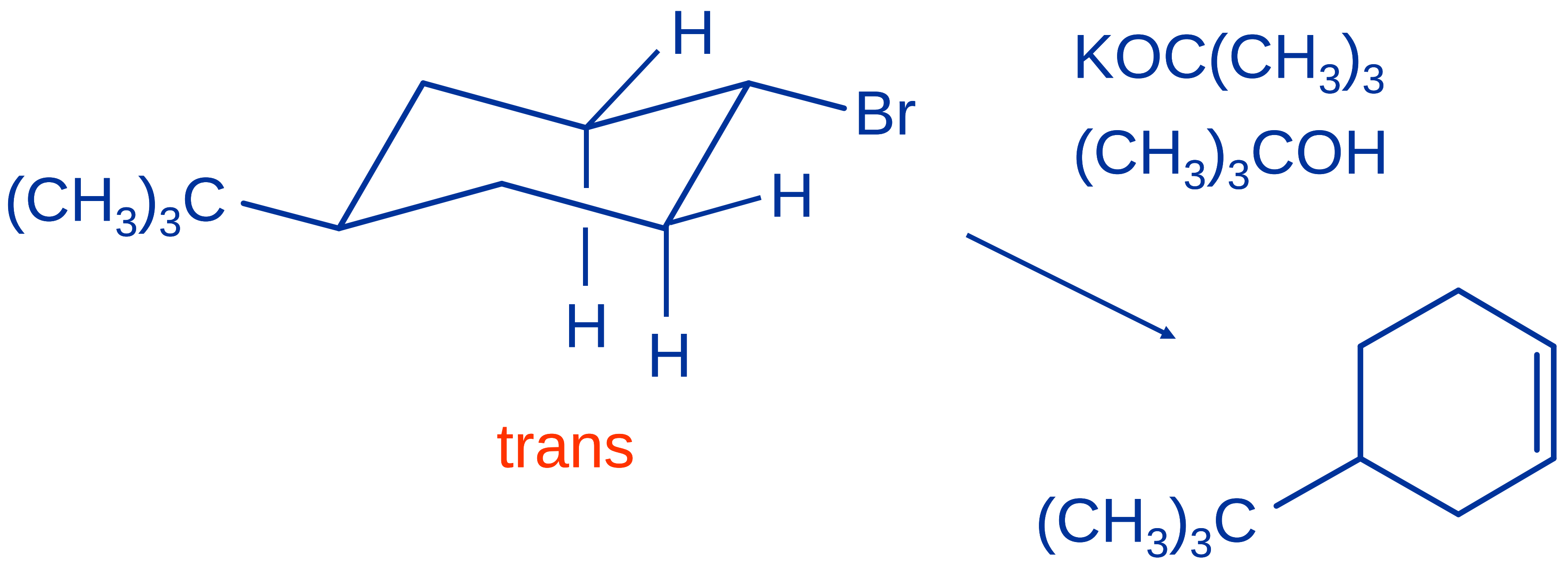
- Rate constant for dehydrohalogenation of *cis* is **500 times** greater than that of *trans.*

Stereoelectronic effect



- H that is removed by base must be *anti* coplanar to Br.
- Two *anti* coplanar H atoms in *cis* stereoisomer.

Stereoelectronic effect



trans

- H that is removed by base must be *anti* coplanar to Br.
- No *anti* coplanar H atoms in *trans* stereoisomer; all vicinal H atoms are gauche to Br.

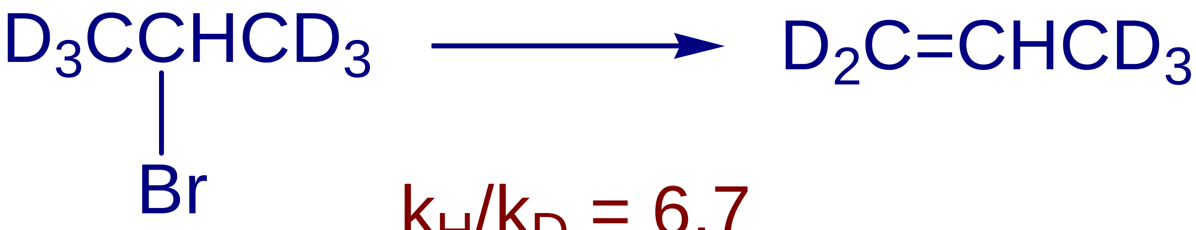
Stereoelectronic effect

- An effect on reactivity that has its origin in the spatial arrangement of orbitals or bonds is called a stereoelectronic effect.

- The preference for an *anti* coplanar arrangement of H and Br in the transition state for E2 dehydrohalogenation is an example of a stereoelectronic effect.

5.17. Isotope Effects and the E2 Mechanism

- A C-D bond is ≈12 kJ/mol stronger than a C-H bond.
- The activation energy for breaking a C-D bond is greater than for breaking a C-H bond.
- The rate constant k for an elementary step where C-D breaks is smaller than for a C-H bond.
- The difference in rate is expressed as a ratio k_H/k_D, and is a kinetic isotope effect.
- Because it compares ^2H to ^1H, it is called a deuterium isotope effect.
- In E2 mechanism, a base removes a proton from a β carbon. The mechanism should exhibit a deuterium isotope effect.

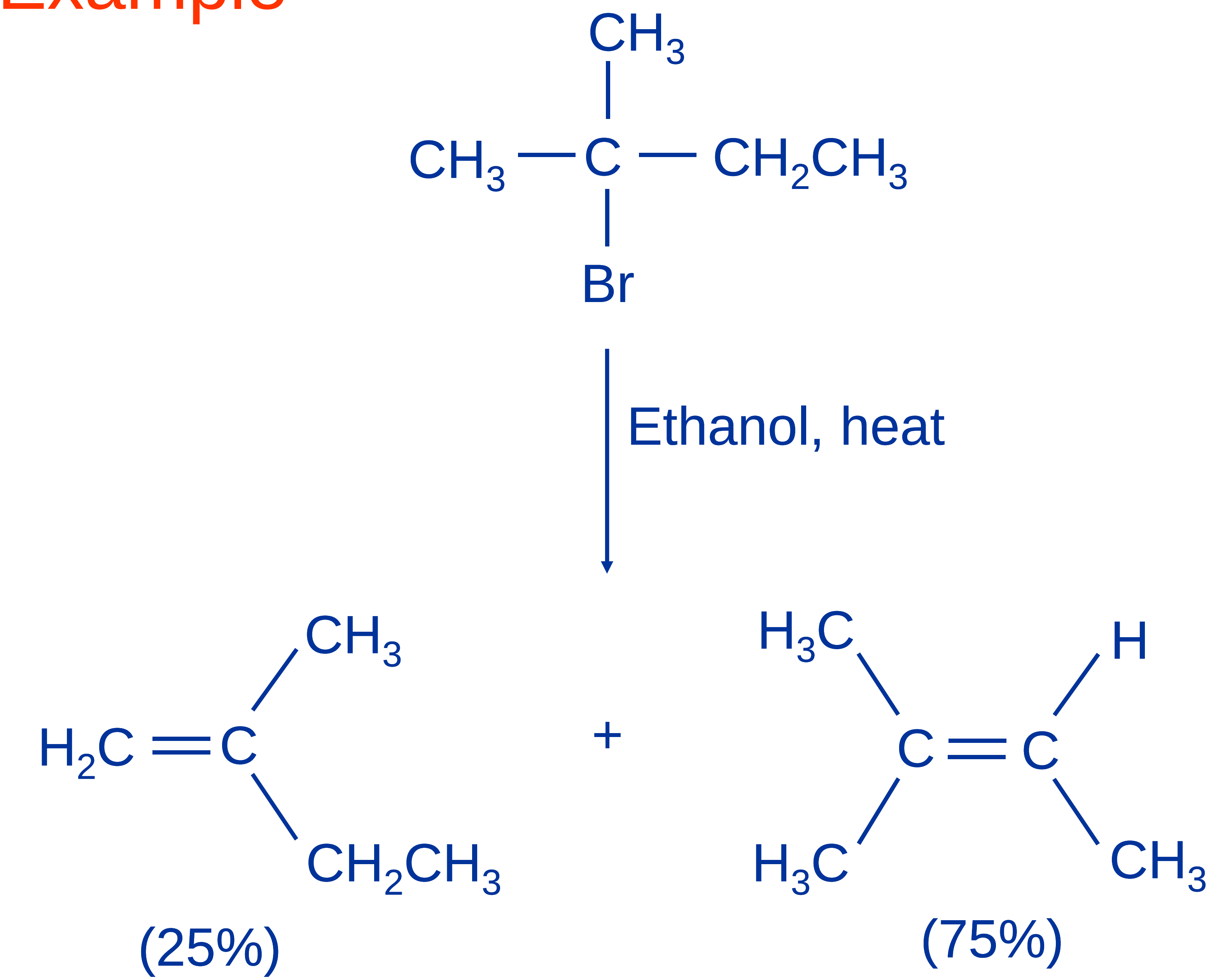


$$D_3C\underset{\substack{|\\ Br}}{C}HCD_3 \longrightarrow D_2C{=}CHCD_3$$

$k_H/k_D = 6.7$

5.18. The E1 Mechanism of Dehydrohalogenation of Alkyl Halides

Example


CH_3
CH_3
C
CH_2CH_3
Br
Ethanol, heat
CH_3
H_2C
C
CH_2CH_3
(25%)
+
H_3C
H
C
C
H_3C
CH_3
(75%)

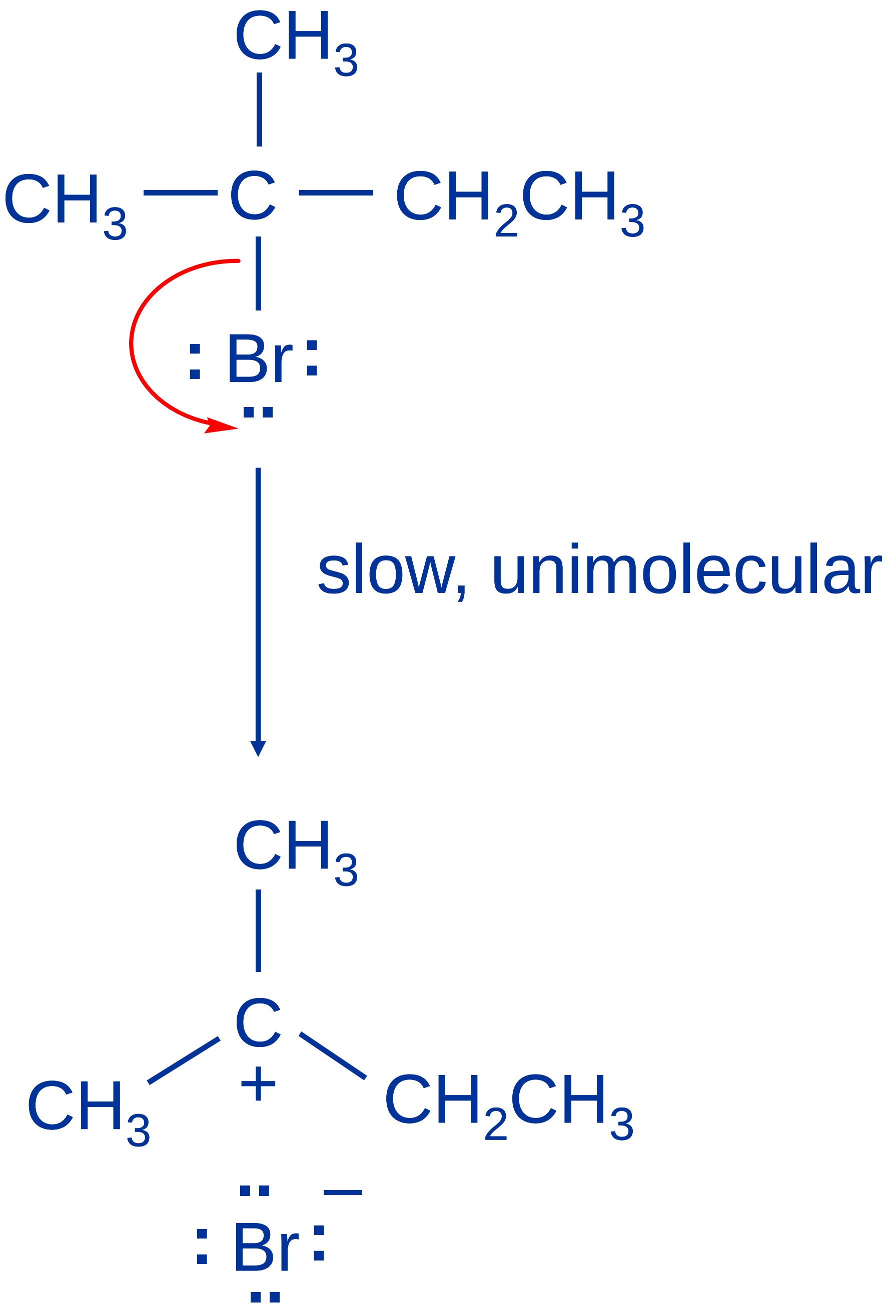
The E1 Mechanism

1. Alkyl halides can undergo elimination in absence of base.

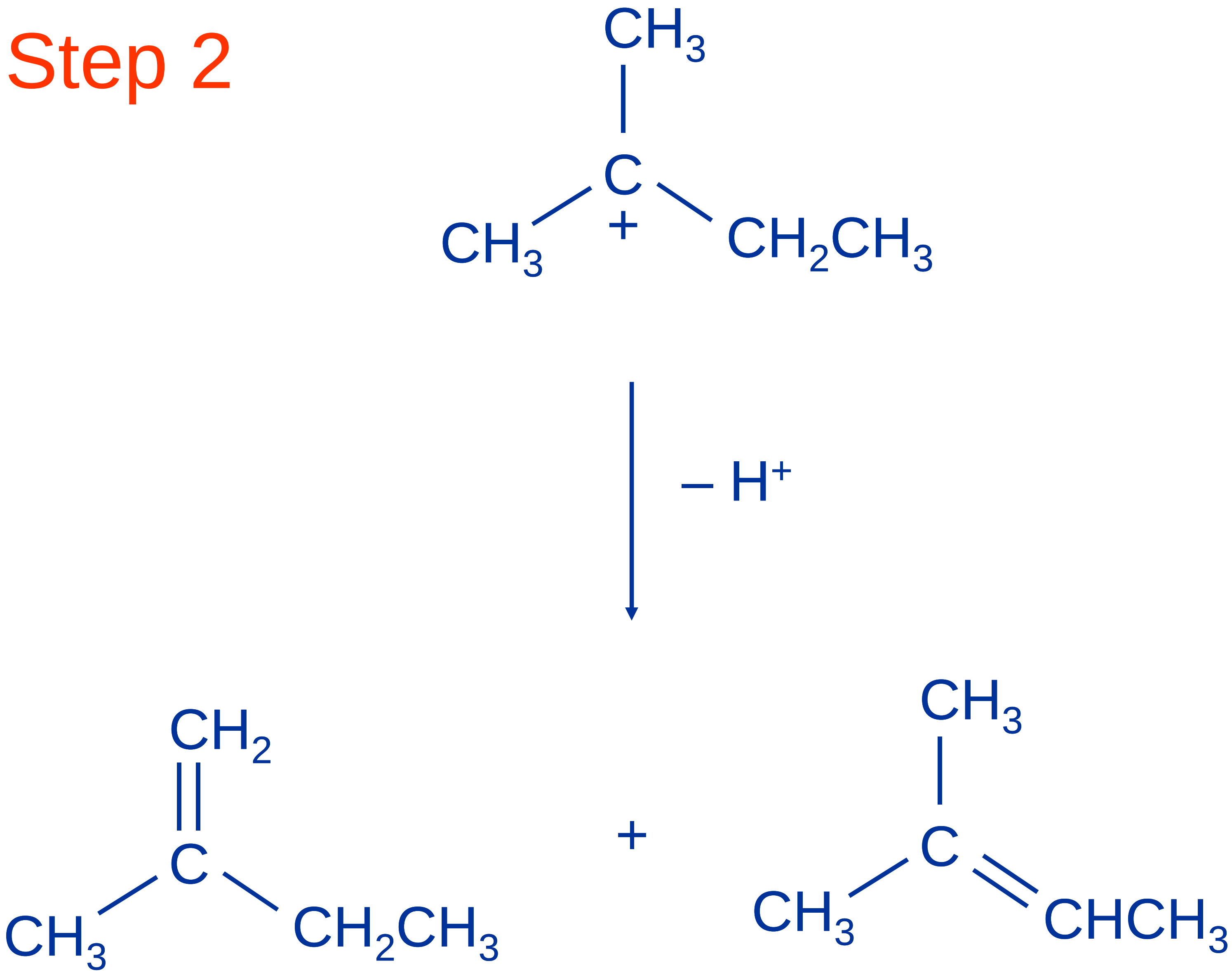
2. Carbocation is intermediate.

3. Rate-determining step is unimolecular ionization of alkyl halide.

Step 1



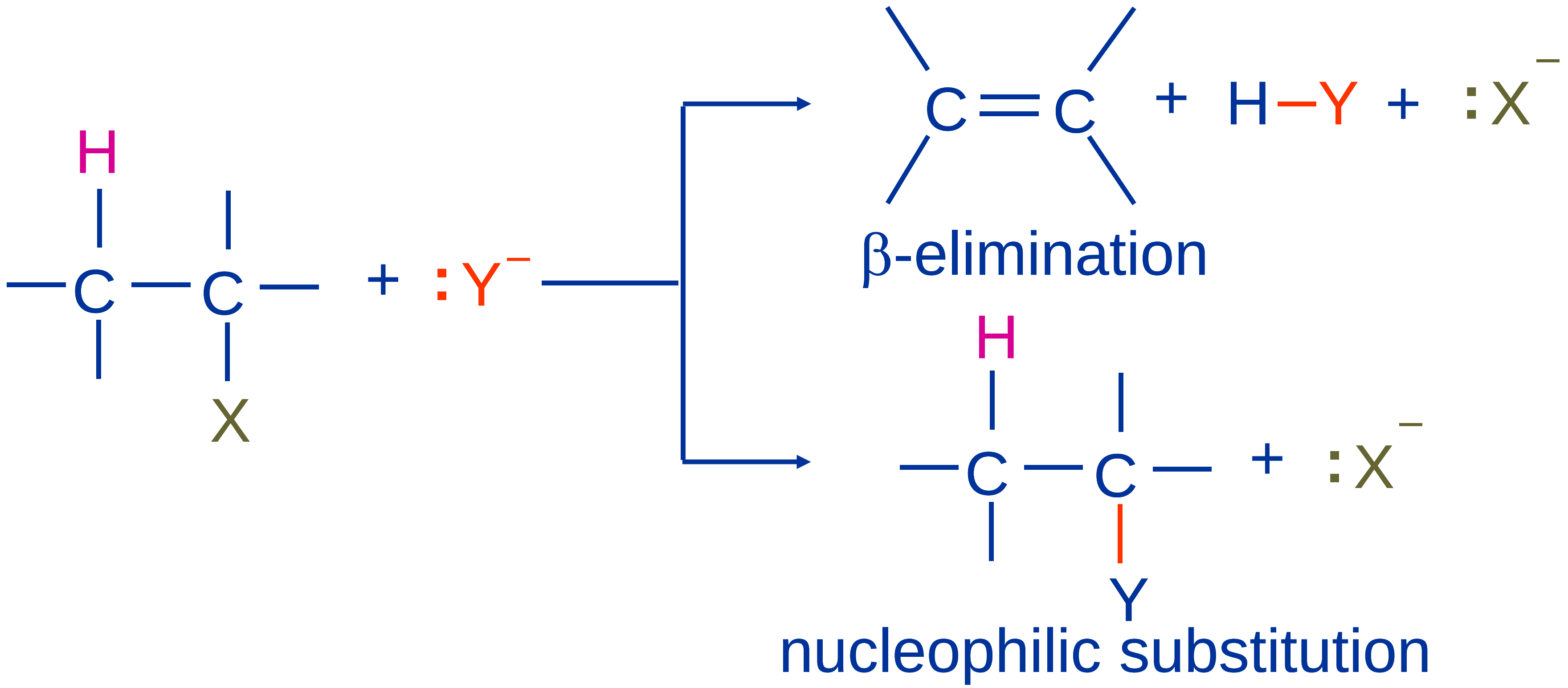
Step 2



8.11. Substitution and Elimination as Competing Reactions

Two Reaction Types

- Alkyl halides can react with Lewis bases by nucleophilic substitution and/or elimination.
- How can we tell which reaction pathway is followed for a particular alkyl halide?

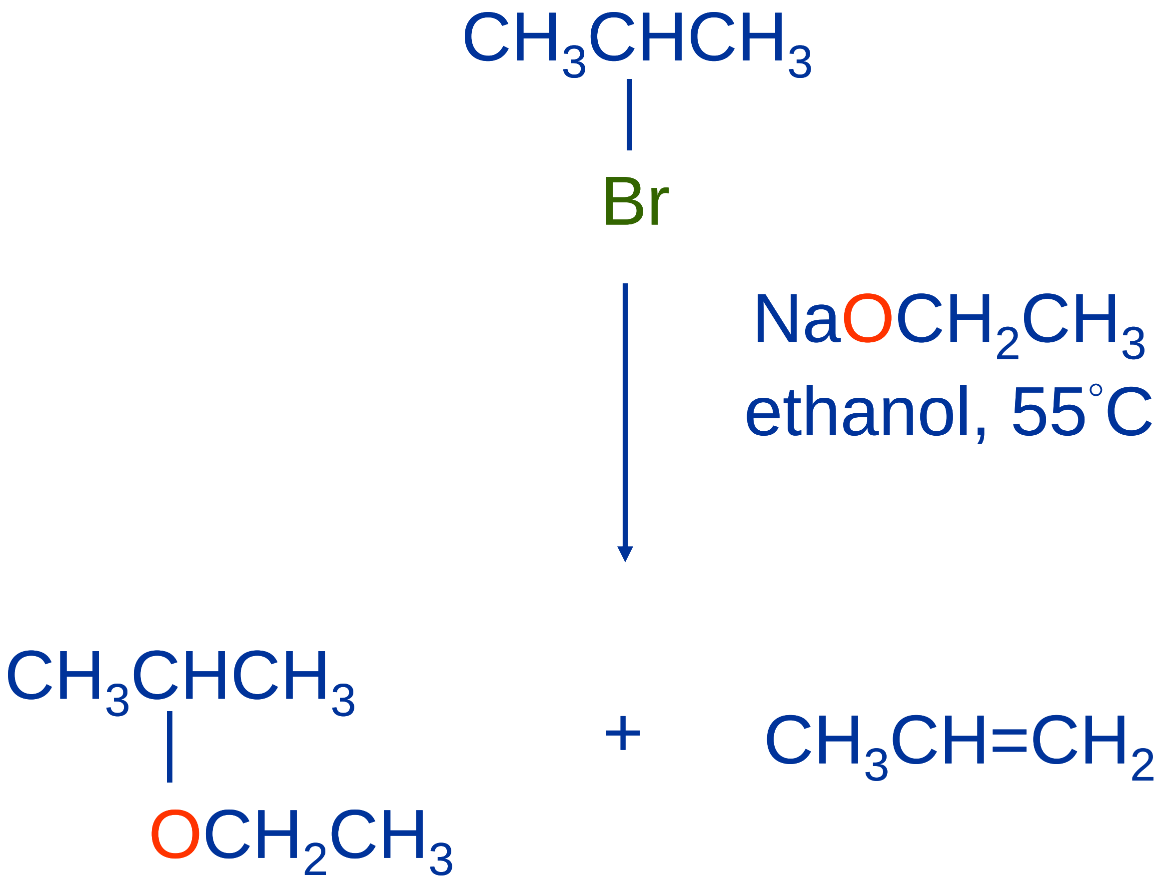


Elimination versus Substitution

- The most import factors are the ***structure of the alkyl halide*** and ***the basicity of the anion***.

- The major reaction of a secondary alkyl halide with an alkoxide ion is elimination by the E2 mechanism.

Example



$$\mathrm{CH_3\underset{\substack{|\\ Br}}{C}HCH_3} \xrightarrow[\text{ethanol, }55^{\circ}\text{C}]{\mathrm{NaOCH_2CH_3}} \mathrm{CH_3\underset{\substack{|\\ OCH_2CH_3}}{C}HCH_3} + \mathrm{CH_3CH{=}CH_2}$$

(13%) (87%)

Figure 8.8

S_N2

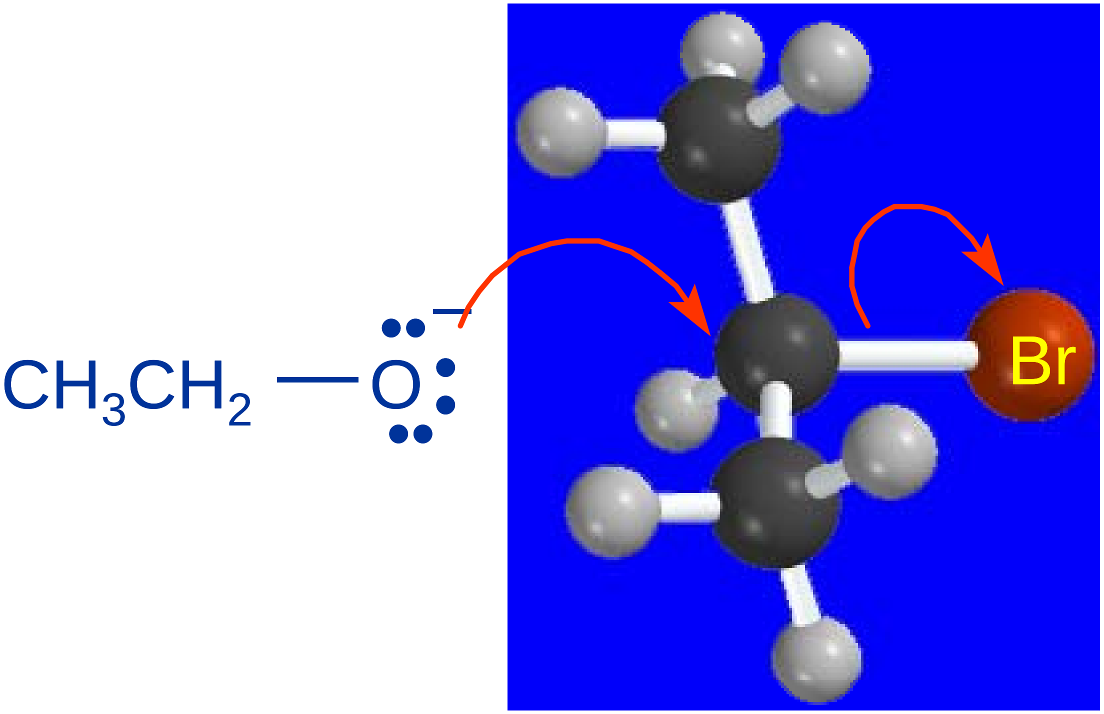
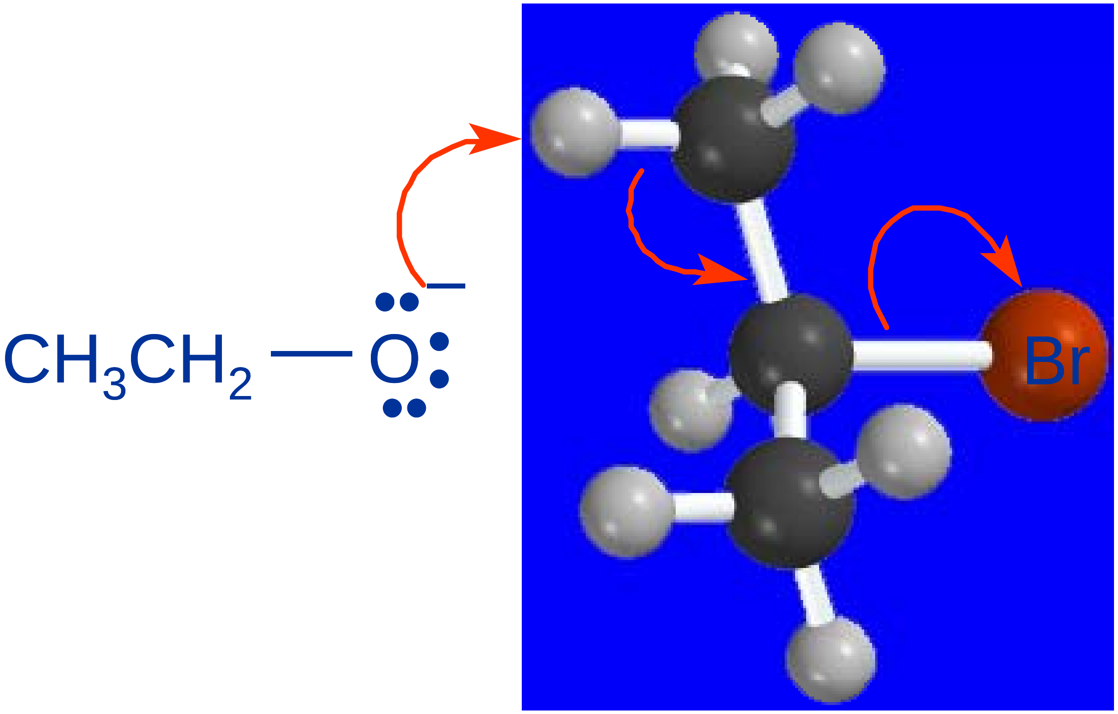

$CH_3CH_2—\ddot{\underset{\cdot\cdot}{O}}:^-$

Figure 8.8

E2



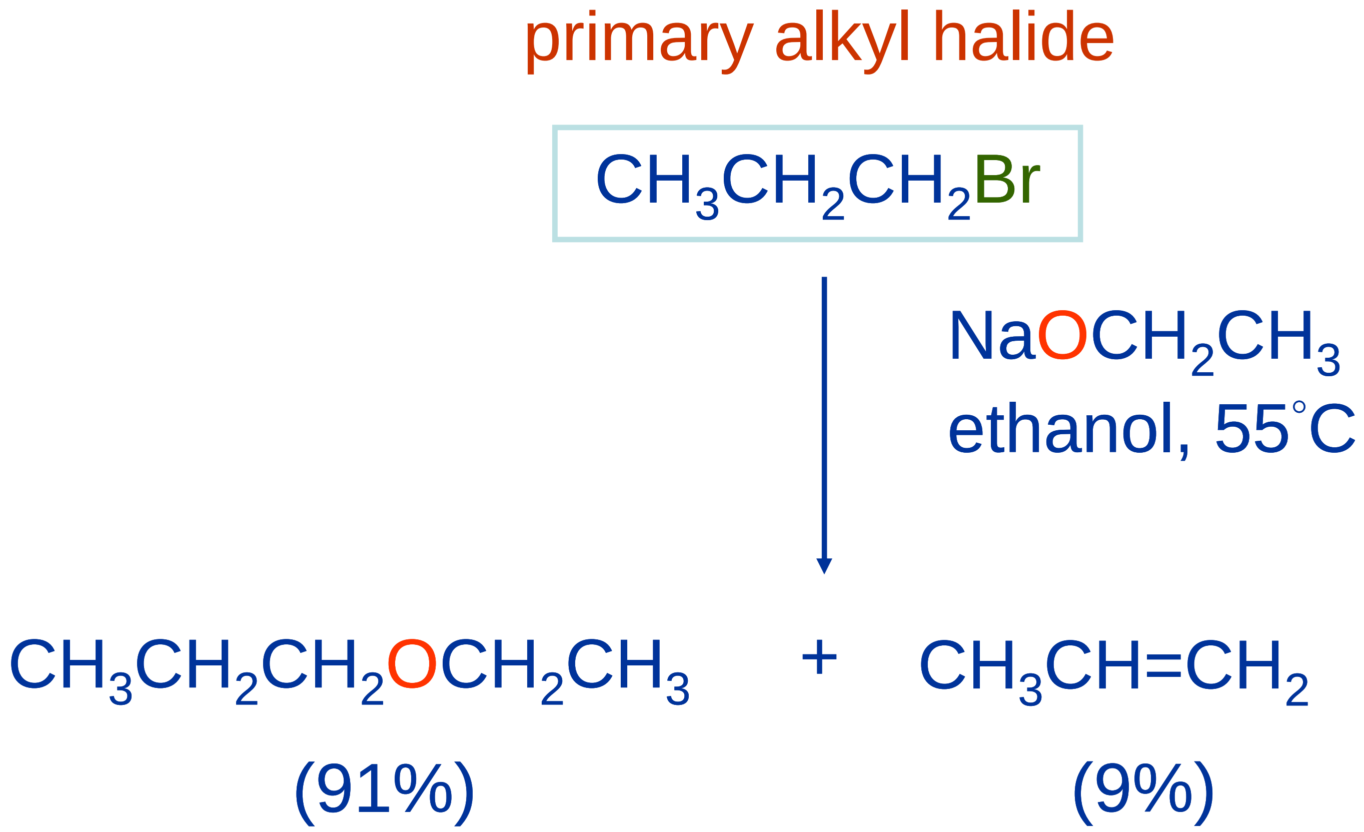
When is substitution favored?

➢ Given that the major reaction of a secondary alkyl halide with an alkoxide ion is elimination by the E2 mechanism, we can expect the proportion of substitution to increase with:

1) Decreased crowding at the carbon that bears the leaving group.

Uncrowded Alkyl Halides

- Decreased crowding at carbon that bears the leaving group increases substitution relative to elimination.



primary alkyl halide

$\boxed{CH_3CH_2CH_2Br}$

$NaOCH_2CH_3$

ethanol, 55°C

$CH_3CH_2CH_2OCH_2CH_3 \quad + \quad CH_3CH{=}CH_2$

(91%) (9%)

But a crowded alkoxide base can favor elimination even with a primary alkyl halide.

primary alkyl halide + bulky base

$CH_3(CH_2)_{15}CH_2CH_2Br$

$$\Big\downarrow \; \boxed{KOC(CH_3)_3} \quad \textit{tert}\text{-butyl alcohol, } 40^\circ C$$

$CH_3(CH_2)_{15}CH_2CH_2OC(CH_3)_3 \quad + \quad CH_3(CH_2)_{15}CH{=}CH_2$

(13%) (87%)

When is substitution favored?

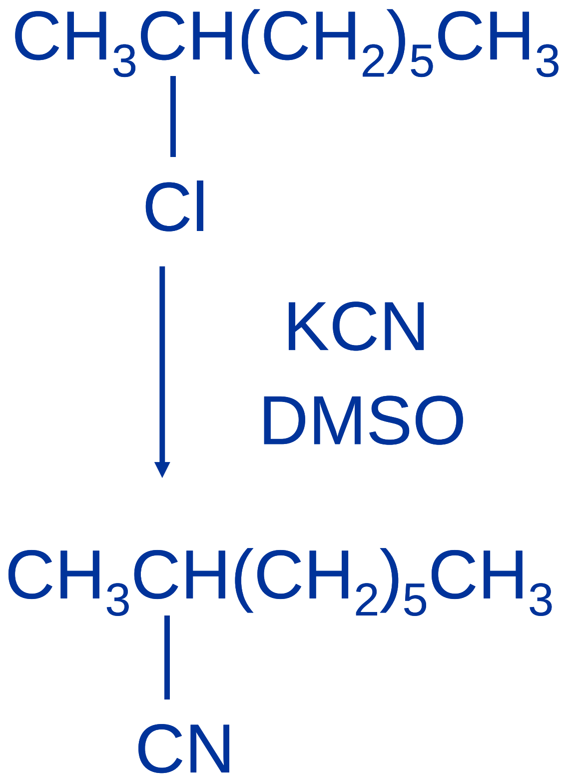
- Given that the major reaction of a secondary alkyl halide with an alkoxide ion is elimination by the E2 mechanism, we can expect the proportion of substitution to increase with:

1) Decreased crowding at the carbon that bears the leaving group.
2) Decreased basicity of the nucleophile.

Weakly Basic Nucleophile

- Weakly basic nucleophile increases substitution relative to elimination.

secondary alkyl halide + weakly basic nucleophile



$$CH_3\underset{\displaystyle Cl}{\underset{|}{C}}H(CH_2)_5CH_3 \xrightarrow[DMSO]{KCN} CH_3\underset{\displaystyle CN}{\underset{|}{C}}H(CH_2)_5CH_3$$

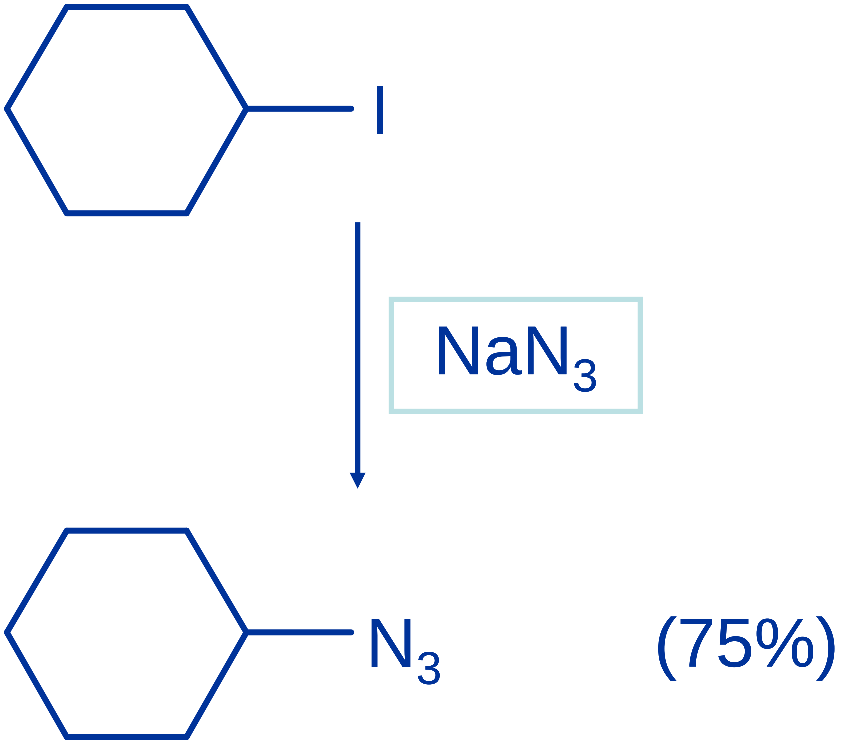
pK_a (HCN) = 9.1

(70%)

Weakly Basic Nucleophile

- Weakly basic nucleophile increases substitution relative to elimination.

secondary alkyl halide + *weakly basic nucleophile*

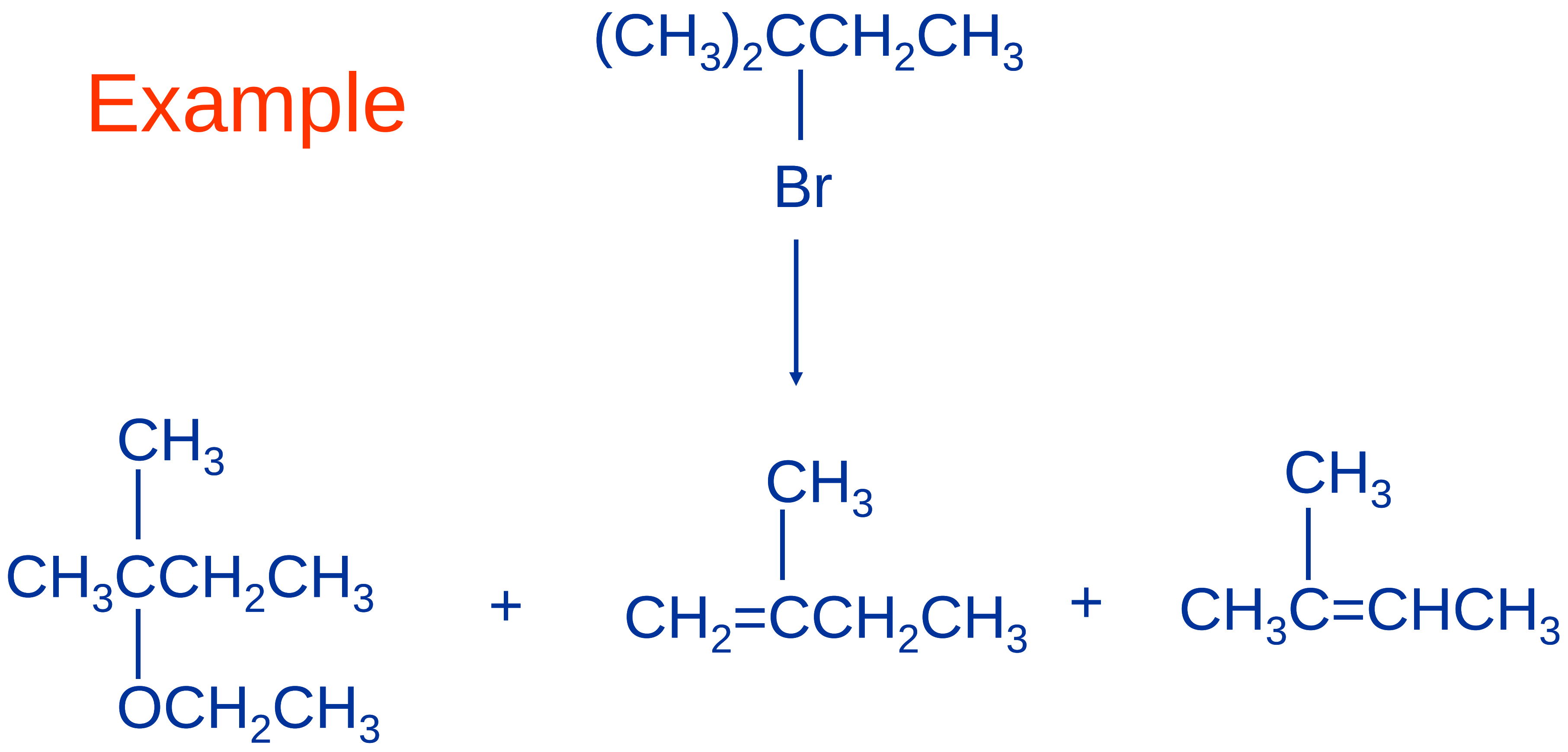


pK_a (HN_3) = 4.6

Tertiary Alkyl Halides

- Tertiary alkyl halides are so sterically hindered that elimination is the major reaction with all anionic nucleophiles. Only in solvolysis reactions does substitution predominate over elimination with tertiary alkyl halides.

Example



$$(CH_3)_2\underset{\underset{\displaystyle Br}{|}}{C}CH_2CH_3 \longrightarrow CH_3\underset{\underset{\displaystyle OCH_2CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_2CH_3 + CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}CH_2CH_3 + CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CHCH_3$$

ethanol, 25°C

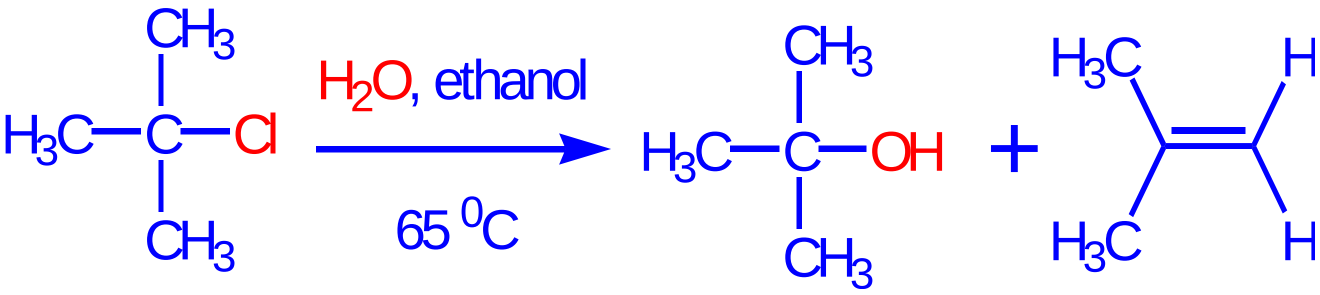
64% 36%

2*M* sodium ethoxide in ethanol, 25°C

1% 99%

E1 Reactions

- E1 eliminations begin with the same unimolecular dissociation we saw in the S_N1 reaction, but the dissociation is followed by loss of a proton from the intermediate carbocation rather than by substitution.



Summary of Substitution and Elimination

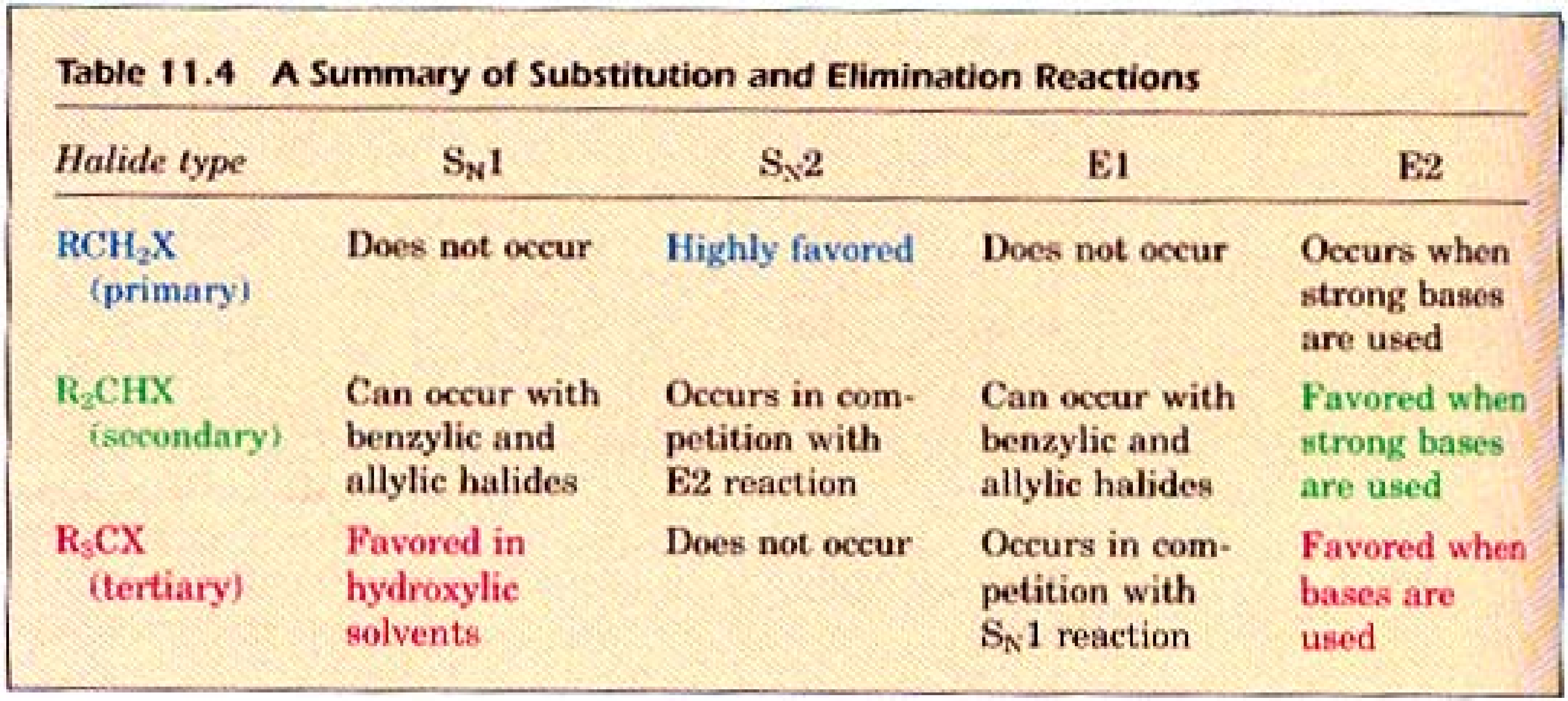


Table 11.4 A Summary of Substitution and Elimination Reactions

Halide type	S_N1	S_N2	E1	E2
RCH_2X (primary)	Does not occur	Highly favored	Does not occur	Occurs when strong bases are used
R_2CHX (secondary)	Can occur with benzylic and allylic halides	Occurs in competition with E2 reaction	Can occur with benzylic and allylic halides	Favored when strong bases are used
R_3CX (tertiary)	Favored in hydroxylic solvents	Does not occur	Occurs in competition with S_N1 reaction	Favored when bases are used

Summary of Substitution and Elimination

1. Primary alkyl halides: S_N2 substitution results if a good nucleophile such as RS^-, I^-, CN^-, NH_3, or Br^- is used. E2 elimination takes place if a strong, bulky base such as *tert*-butoxide is used.

$$CH_3CH_2CH_2CH_2Br \xrightarrow[\text{THF/HMPA}]{\text{NaCN}} CH_3CH_2CH_2CH_2CN$$

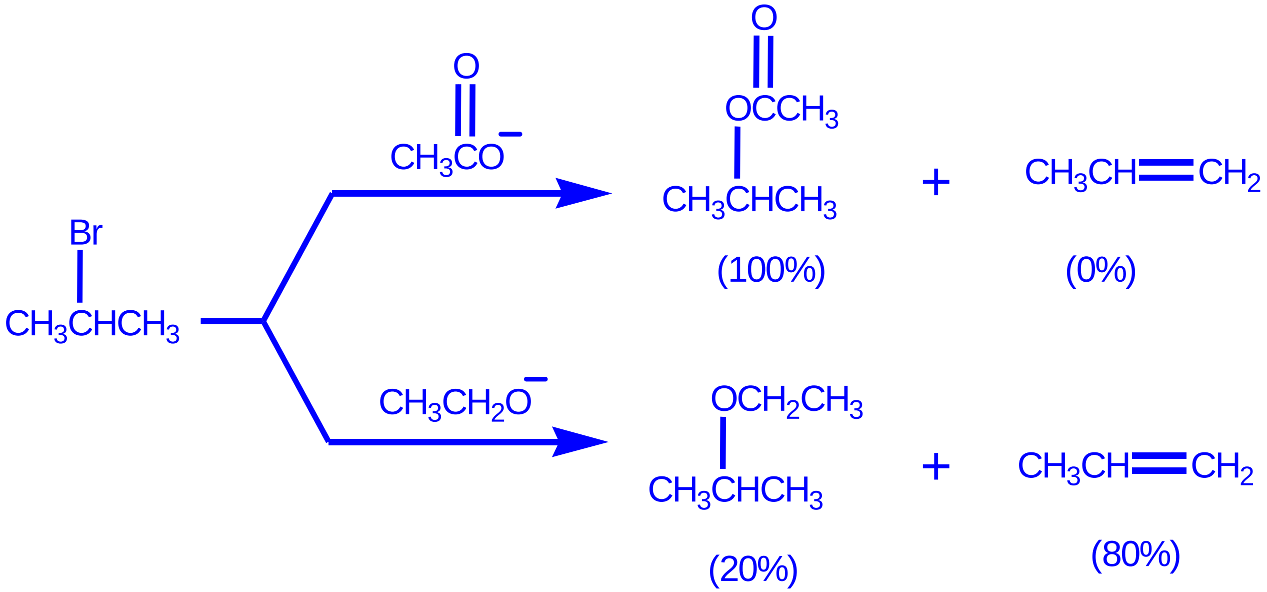
(90%)

$$CH_3CH_2CH_2CH_2Br \xrightarrow{(CH_3)COK} CH_3CH_2CH{=}CH_2$$

(85%)

Summary of Substitution and Elimination

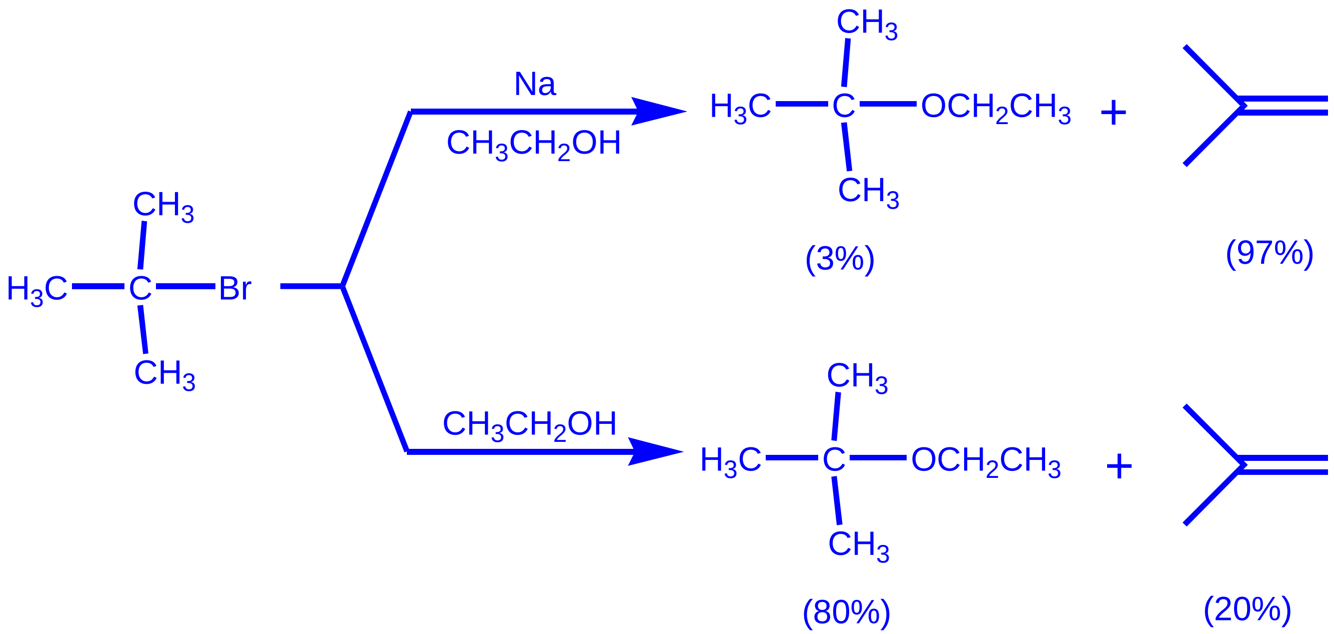
2. Secondary alkyl halides: S_N2 substitution and E2 elimination occur in competition, often leading to a mixture of products. If a weakly basic nucleophile is used in a polar aprotic solvent , S_N2 substitution predominates. If a strong base such as $CH_3CH_2O^-$, OH^-, or NH_2^- is used E2 elimination predominates.



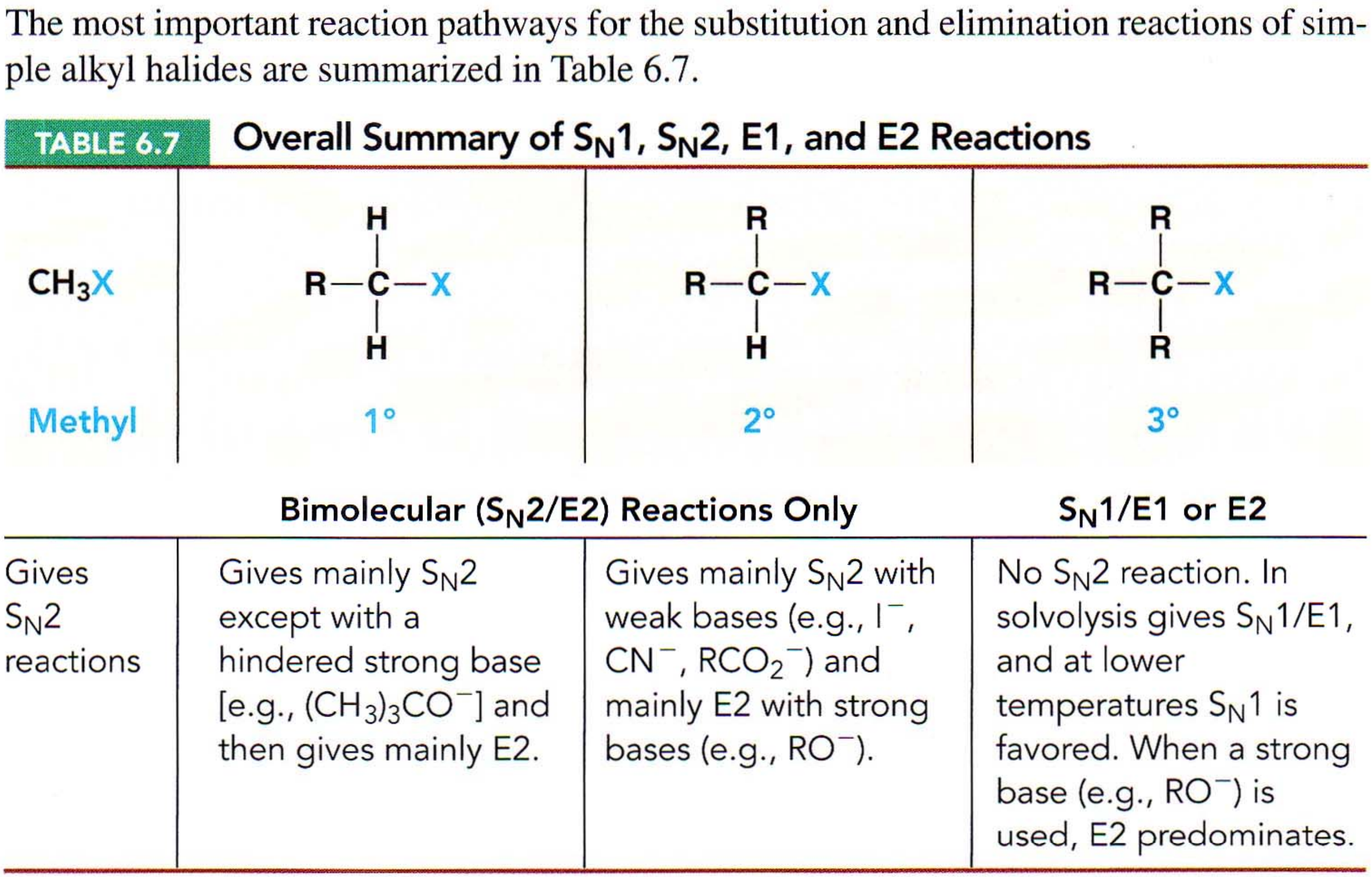
- Secondary alkyl halides, particularly allylic and benzylic ones, can also undergo S_N1 and E1 reactions if weakly basic nucleophiles are used in protic solvents such as ethanol or acetic acid.

Summary of Substitution and Elimination

3. Tertiary halides: E2 elimination occurs when a base such as OH^- or RO^- is used. By contrast, reaction under nonbasic conditions (heating) in pure ethanol) leads to a mixture of products resulting from both S_N1 substitution and E1 elimination.



Summary of Substitution and Elimination



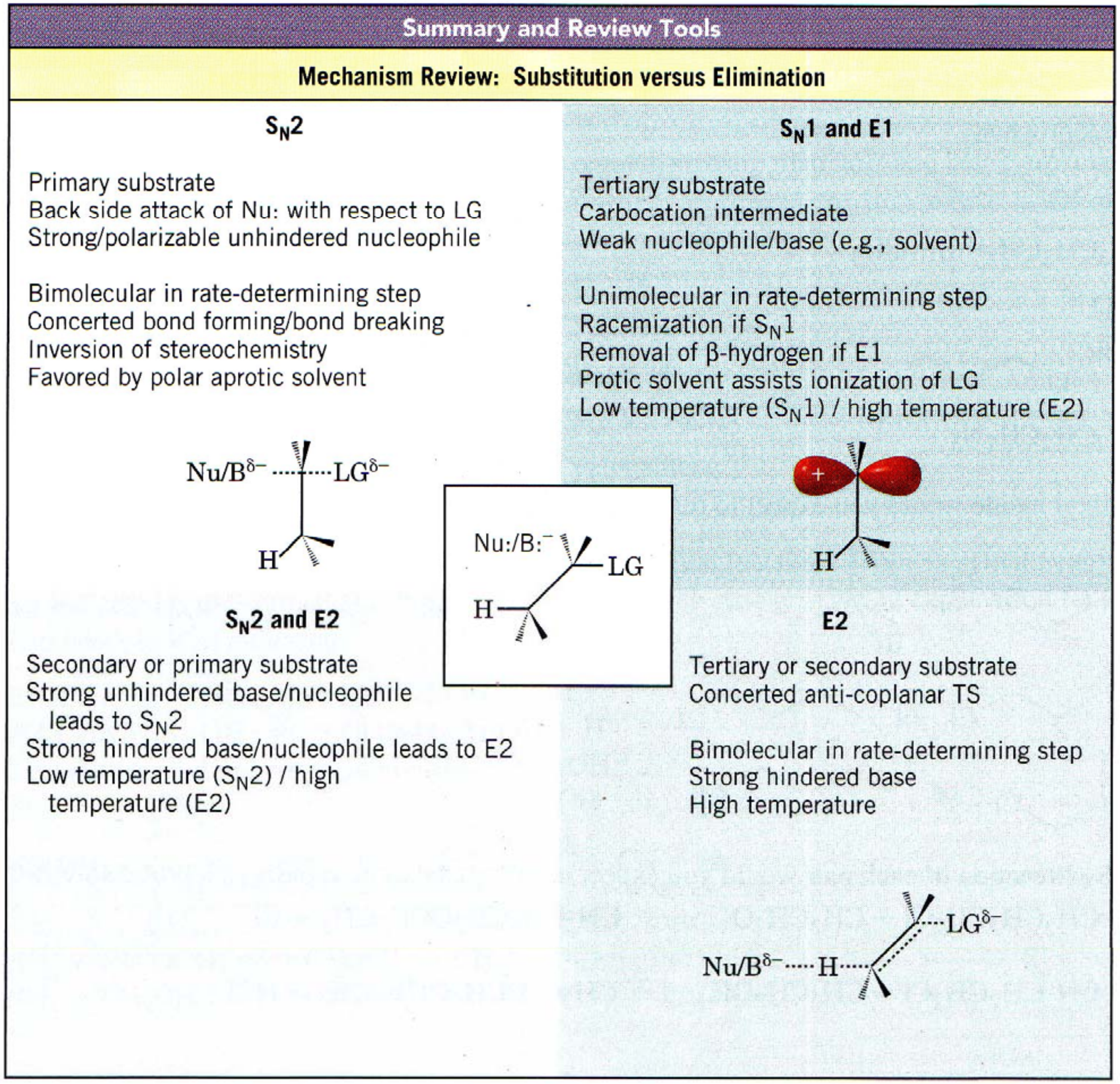
The most important reaction pathways for the substitution and elimination reactions of simple alkyl halides are summarized in Table 6.7.

TABLE 6.7 **Overall Summary of S_N1, S_N2, E1, and E2 Reactions**

CH_3X Methyl	$R-\overset{H}{\underset{H}{C}}-X$ 1°	$R-\overset{R}{\underset{H}{C}}-X$ 2°	$R-\overset{R}{\underset{R}{C}}-X$ 3°
Bimolecular (S_N2/E2) Reactions Only			**S_N1/E1 or E2**
Gives S_N2 reactions	Gives mainly S_N2 except with a hindered strong base [e.g., $(CH_3)_3CO^-$] and then gives mainly E2.	Gives mainly S_N2 with weak bases (e.g., I^-, CN^-, RCO_2^-) and mainly E2 with strong bases (e.g., RO^-).	No S_N2 reaction. In solvolysis gives S_N1/E1, and at lower temperatures S_N1 is favored. When a strong base (e.g., RO^-) is used, E2 predominates.

Solomons

Summary of Substitution and Elimination



Summary and Review Tools

Mechanism Review: Substitution versus Elimination

S_N2

Primary substrate
Back side attack of Nu: with respect to LG
Strong/polarizable unhindered nucleophile

Bimolecular in rate-determining step
Concerted bond forming/bond breaking
Inversion of stereochemistry
Favored by polar aprotic solvent

S_N1 and E1

Tertiary substrate
Carbocation intermediate
Weak nucleophile/base (e.g., solvent)

Unimolecular in rate-determining step
Racemization if S_N1
Removal of β-hydrogen if E1
Protic solvent assists ionization of LG
Low temperature (S_N1) / high temperature (E2)

S_N2 and E2

Secondary or primary substrate
Strong unhindered base/nucleophile leads to S_N2
Strong hindered base/nucleophile leads to E2
Low temperature (S_N2) / high temperature (E2)

E2

Tertiary or secondary substrate
Concerted anti-coplanar TS

Bimolecular in rate-determining step
Strong hindered base
High temperature

Solomons