Structure and Preparation of Alkenes: Elimination Reactions

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Alkene Nomenclature

First identify the longest continuous chain that includes the double bond.

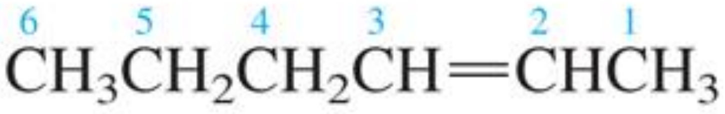
Replace the *-ane* ending of the corresponding unbranched alkane with *-ene*.

Number the chain in the direction that gives the lowest number to the first carbon of the alkene.

$H_2\overset{1}{C}=\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3$

1-Butene

But-1-ene



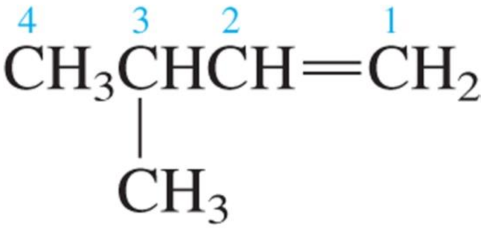
$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H=\overset{2}{C}H\overset{1}{C}H_3$

2-Hexene

Hex-2-ene

Alkene Nomenclature

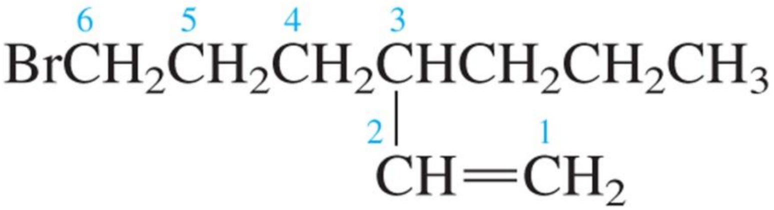
Alkenes take precedence over alkyl- and halo-substituents when numbering the carbons.



$CH_3\underset{\substack{|\\ CH_3}}{C}HCH{=}CH_2$

3-Methyl-1-butene
3-Methylbut-1-ene

The longest contiguous carbon chain including the alkene takes precedence over a longer chain that does not include the alkene.

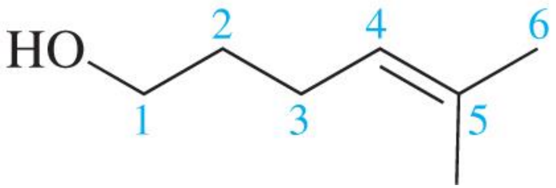


$BrCH_2CH_2CH_2\underset{\substack{|\\ CH{=}CH_2}}{C}HCH_2CH_2CH_3$

6-Bromo-3-propyl-1-hexene
6-Bromo-3-propylhex-1-ene

Alkene Nomenclature

Hydroxyl groups outrank alkenes and the compound is numbered so that the carbon with the –OH attached gets the lowest number. The suffix is –*enol* and the locant for the alkene precedes the –en and the locant for the –OH precedes the –ol.



5-Methyl-4-hexen-1-ol
5-Methylhex-4-en-1-ol

Common Names

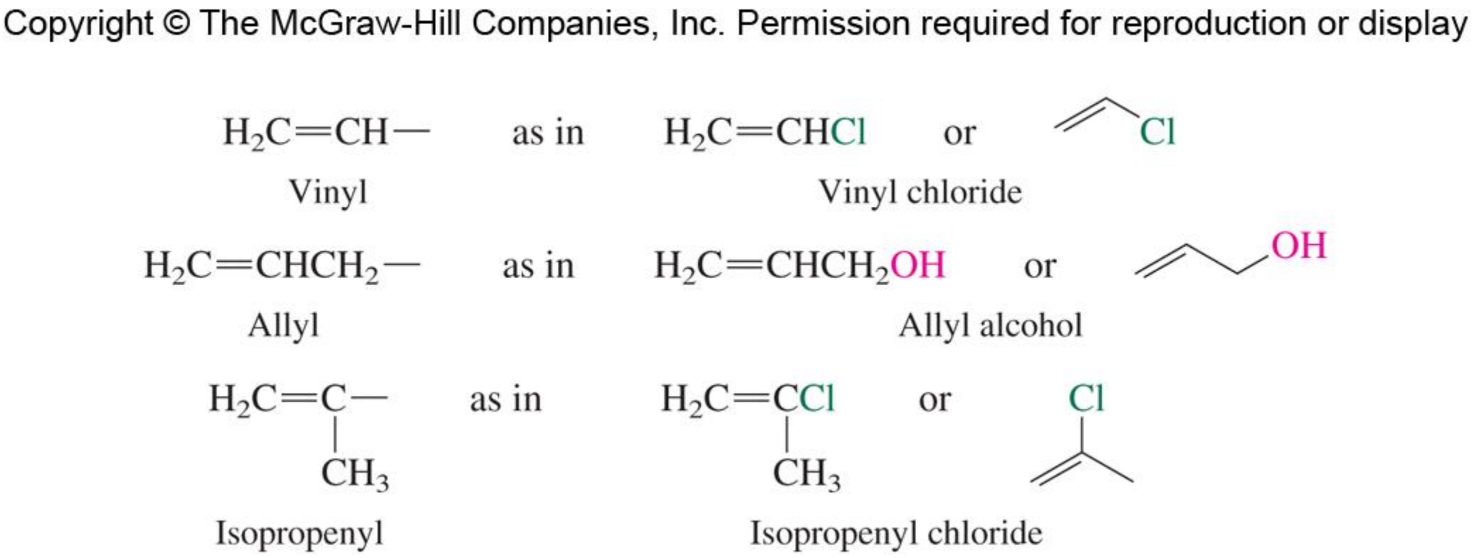
Some common names are acceptable.

$H_2C{=}CH_2$

IUPAC name: **ethene**
Common name: ethylene

$CH_3CH{=}CH_2$

IUPAC name: **propene**
Common name: propylene



$H_2C{=}CH-$ as in $H_2C{=}CHCl$ or
Vinyl — Vinyl chloride

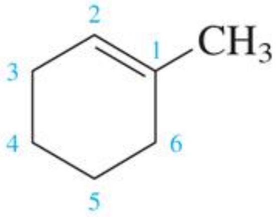
$H_2C{=}CHCH_2-$ as in $H_2C{=}CHCH_2OH$ or
Allyl — Allyl alcohol

$H_2C{=}\underset{CH_3}{\underset{|}{C}}-$ as in $H_2C{=}\underset{CH_3}{\underset{|}{C}}Cl$ or
Isopropenyl — Isopropenyl chloride

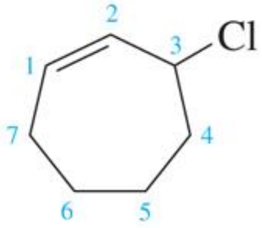
Naming Cycloalkenes

Change corresponding cycloalkane name suffix from –ane to -ene. No substituents: no locant. With alkyl and halo substituents number the alkene carbons 1 and 2 so that the substituent has the lowest number.

Cyclopentene



1-Methylcyclohexene



3-Chlorocycloheptene
(not 1-chloro-2-cycloheptene)

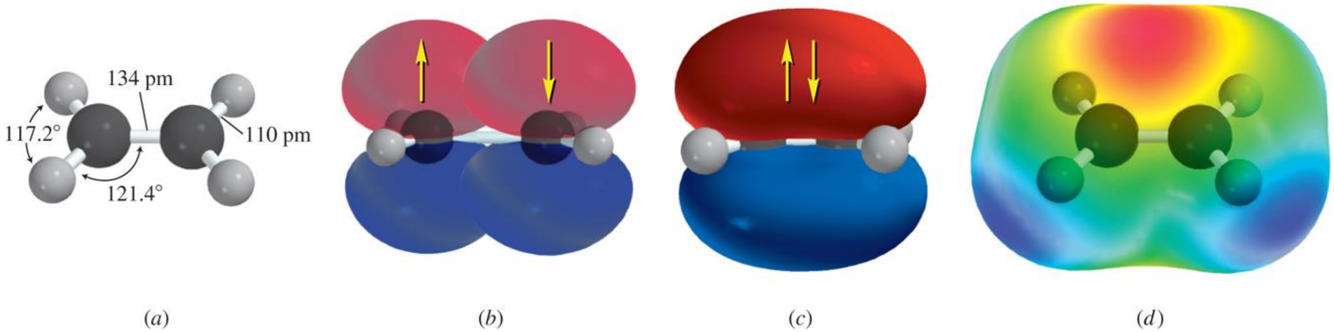
Structure and Bonding in Alkenes

sp^2 Hybridized Carbons

Alkene carbons are *sp*^{2} hybridized and alkenes are planar (a).

The alkene has one σ-bond and one π-bond (c) formed by overlap of the *p* orbitals (b).

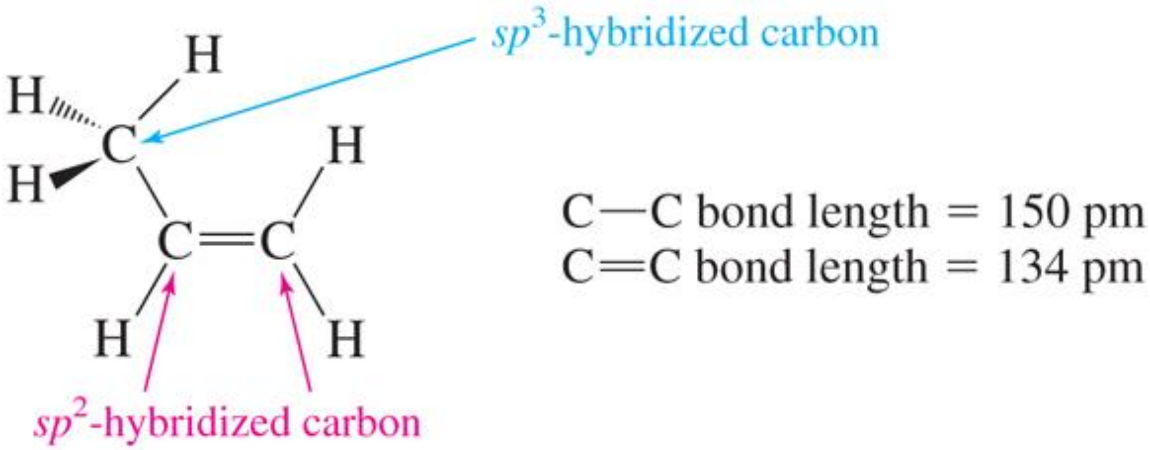
The electrostatic potential map shows the high electron density shown as red above (and below) the C-C bond (d).



Bond Strength

The C=C double bond is stronger and shorter than a single bond.

The π bond is weaker than a σ bond.

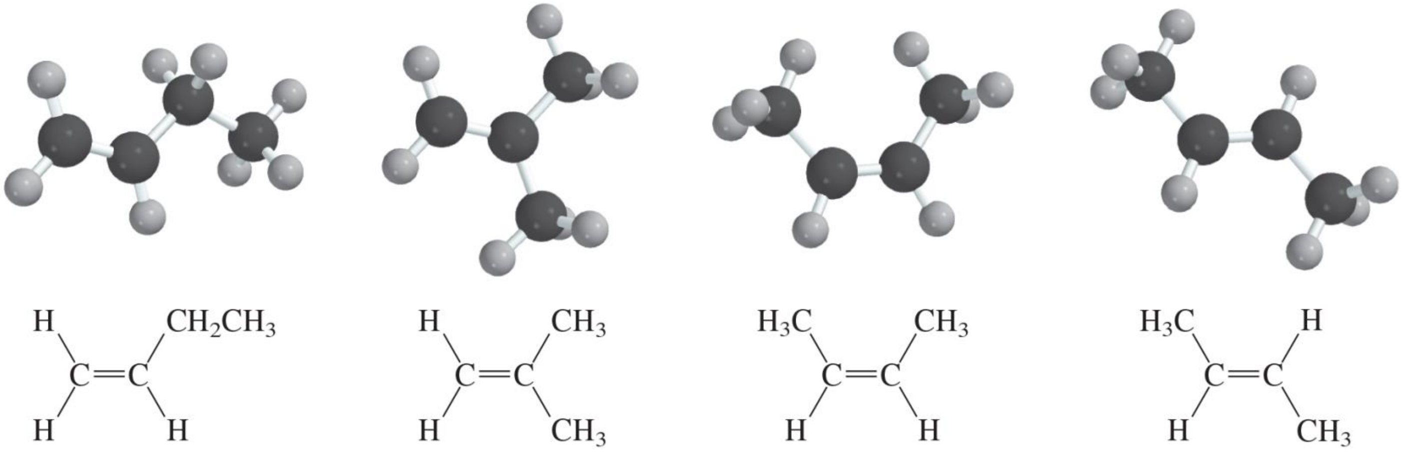


C—C bond length = 150 pm
C=C bond length = 134 pm

Isomerism in Alkenes

Isomers of C_4H_8

The four isomers are:



1-Butene 2-Methylpropene *cis*-2-Butene *trans*-2-Butene

1-Butene is a constitutional isomer of the other three.

Cis- and *trans*-2-butene are stereoisomers: same connectivity but a different arrangement in space.

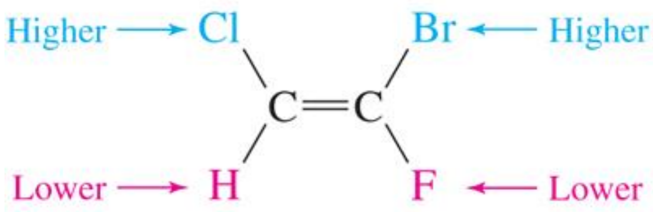
Cis and Trans Isomers

Rotation about double bonds is restricted so interconversion or rotation about a double bond is not possible.

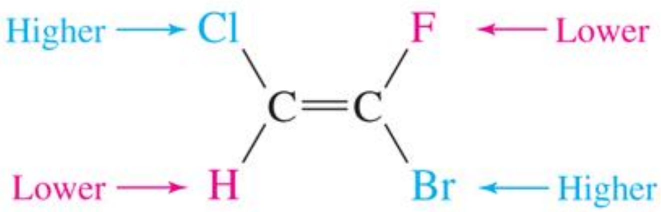
Naming Stereoisomeric Alkenes by the E–Z Notational System

E-Z Nomenclature

Some alkenes are too complex to name using cis or trans. For these alkenes the E-Z system is used.



Z configuration
Higher ranked substituents (Cl and Br)
are on same side of double bond



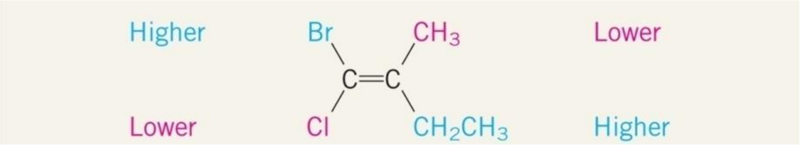
E configuration
Higher ranked substituents (Cl and Br)
are on opposite sides of double bond

The two atoms directly connected to each alkene are compared. The atom with higher atomic number has higher priority. The position of the high priority groups are compared. If they are on the same side the compound is (Z) – otherwise it is (E).

E-Z Nomenclature

This system is the Cahn-Ingold-Prelog system.

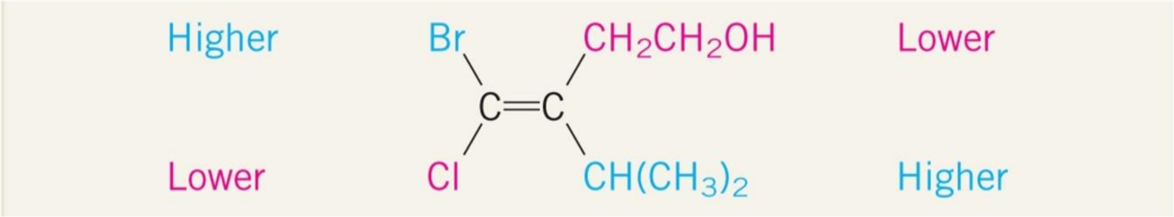
When two atoms directly attached to the same carbon of the double bond are identical, compare the atoms attached to these two on the basis of their atomic numbers. Precedence is determined at the first point of difference:



Compare the atoms connected to the two carbons on the right and ethyl [– C(C,H,H)] outranks methyl [– C(H,H,H)]

E-Z Nomenclature

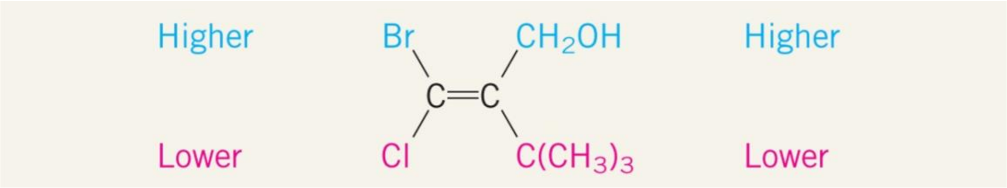
Compare the atoms directly connected to the two carbons on the right and – $CH(CH_3)_2$ [– C(C,C,H)] outranks – CH_2CH_2OH [– C(C,H,H)].



The oxygen is NOT considered because the first point of difference was reached with the first carbon. The O is on the second carbon.

E-Z Nomenclature

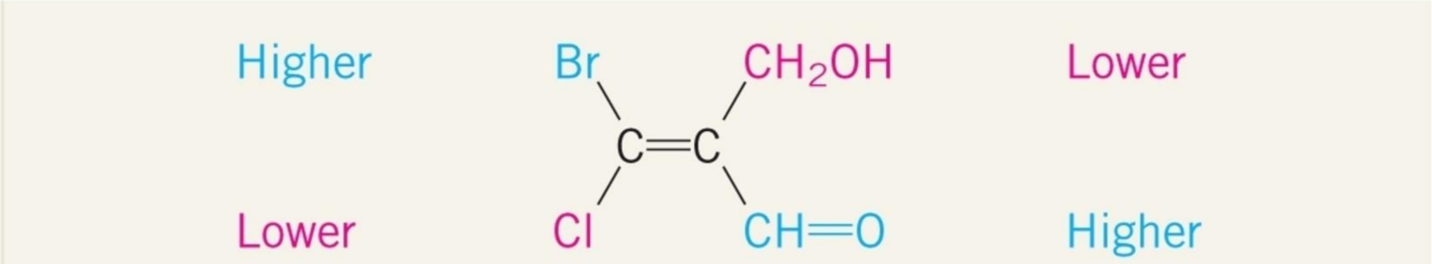
Compare the atoms directly connected to the two carbons on the right one by one, never as a group. Because oxygen has a higher atomic number than carbon, – CH_2OH [– C(O,H,H)] outranks – $C(CH_3)_3$ [– C(C,C,C)].



The oxygen IS the first point of difference.

E-Z Nomenclature

A multiply bonded atom is considered as two bonds to that atom. The group – CH = O [– C(O,O,H)] outranks – CH_2OH [– C(O,H,H)]



Physical Properties of Alkenes

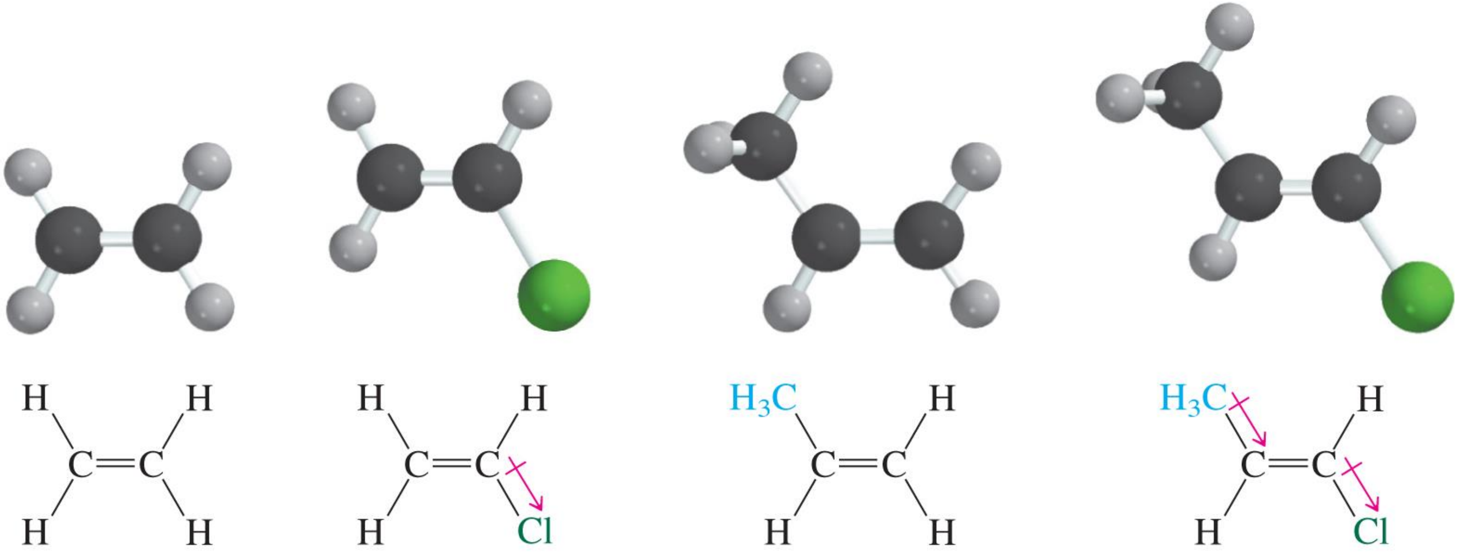
- Alkenes resembles alkanes in most of their physical propertied.
- Alkenes up to 4 C atoms are gases at room temperature.
- Alkenes are insoluble in water.
- Dipole moment for most alkenes is very small.

Dipole Moments

Molecular dipole moment = sum of bond dipole moments.

Vinyl chloride has a dipole towards the more electronegative chlorine.

Trans-1-chloropropene dipole moment > vinyl chloride dipole moment therefore the methyl group is electron donating.



Ethylene
$\mu = 0$ D

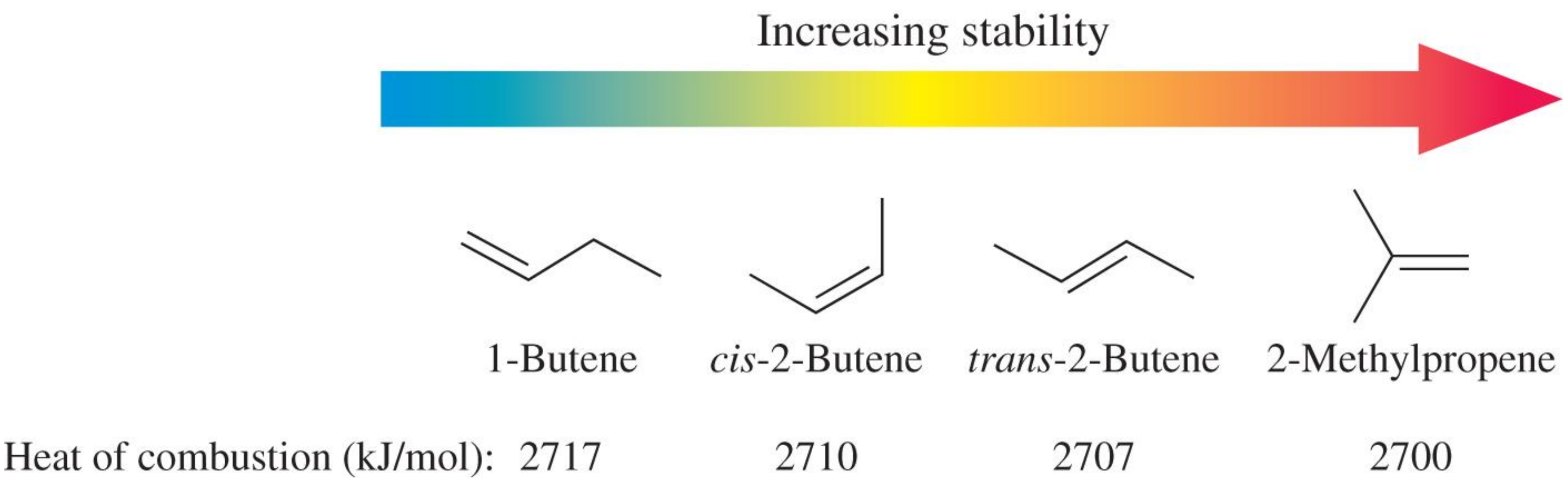
Vinyl chloride
$\mu = 1.4$ D

Propene
$\mu = 0.3$ D

trans-1-Chloropropene
$\mu = 1.7$ D

Stability of Alkenes

The heat of combustion of alkenes can be used to determine relative stabilities. Alkenes with the lowest heat of combustion are most stable.



Stability of Alkenes

The most important factors governing alkene stability are:

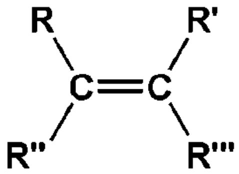
1. Degree of substitution of C=C (an electronic effect);
2. van der Waals strain in the cis stereoisomer (a steric effect)
3. Chain branching increases stability.

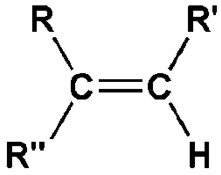
Highly substituted double bonds are more stable than isomers with less substituted double bonds.

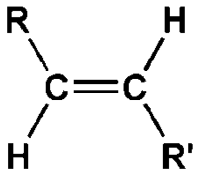
Trans alkenes are more stable than the cis stereoisomers.

Stability of Alkenes

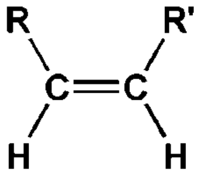
The general trend is: more substituted alkenes are more stable than less substituted alkenes.


tetrasubstituted

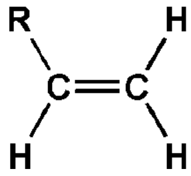

trisubstituted

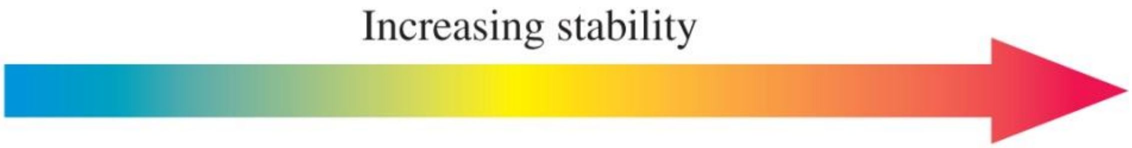

disubstituted

trans


disubstituted

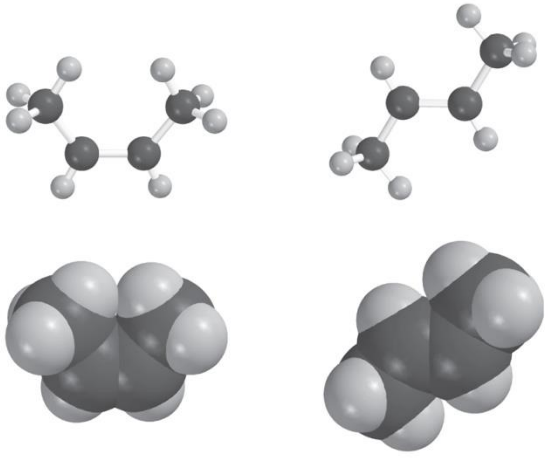
cis


monosubstituted



Stability of Alkenes

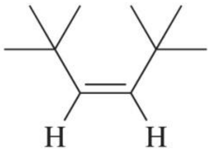
Trans alkenes are more stable than the cis stereoisomers.
Steric strain between the methyl groups in the cis isomer.



cis-2 Butene

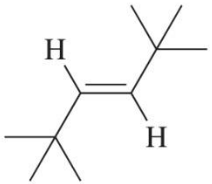
trans-2 Butene

With larger groups the effect is more pronounced.



cis-2,2,5,5-Tetramethyl-3-hexene
(less stable)

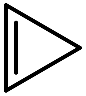
Energy difference =
44 kJ/mol
(10.5 kcal/mol)



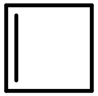
trans-2,2,5,5-Tetramethyl-3-hexene
(more stable)

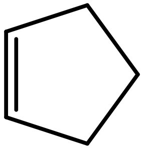
Cycloalkenes

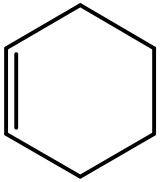
Cyclopropene has the most strained of the cycloalkenes because the *sp*^{2} hybridized carbon prefers a bond angle of 120^o. Cyclobutene has less ring strain and the other larger rings have negligible ring strain.



cyclopropene



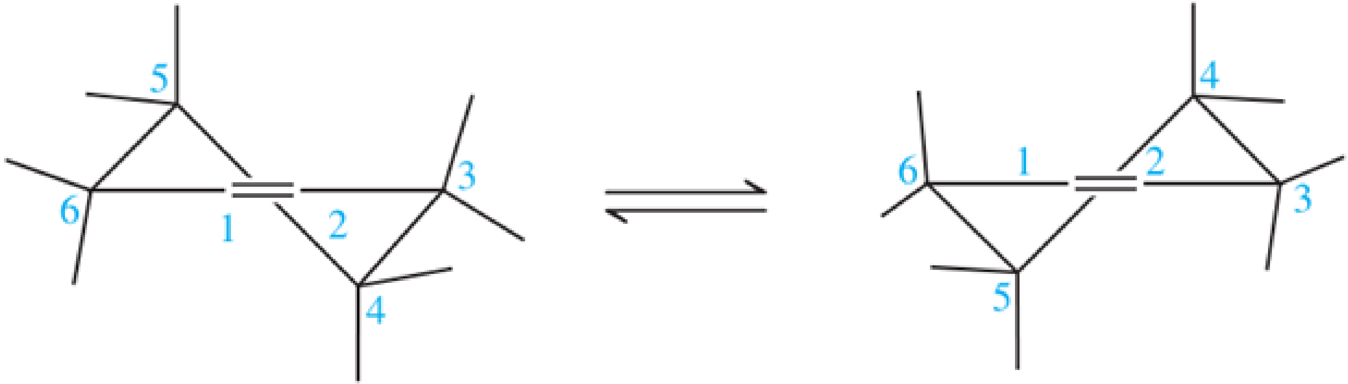




cyclohexene

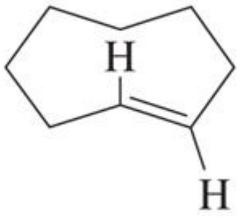
Cyclohexene

Cyclohexene exists as a half-chair.



Cyclooctene

Cyclooctene can exist as either a cis or trans isomer. Smaller cycloalkenes can only have an alkene with a cis conformation .



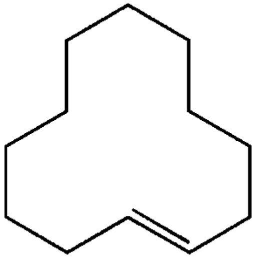
(*E*)-Cyclooctene
(*trans*-cyclooctene)
Less stable

Energy difference =
39 kJ/mol (9.2 kcal/mol)

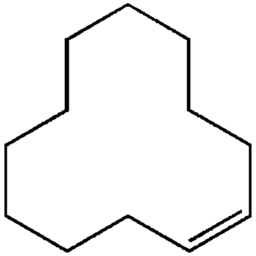
(*Z*)-Cyclooctene
(*cis*-cyclooctene)
More stable

Cyclododecene

Cis and *trans*-cyclododecene are almost equal in stability.



trans-Cyclododecene



cis-Cyclododecene

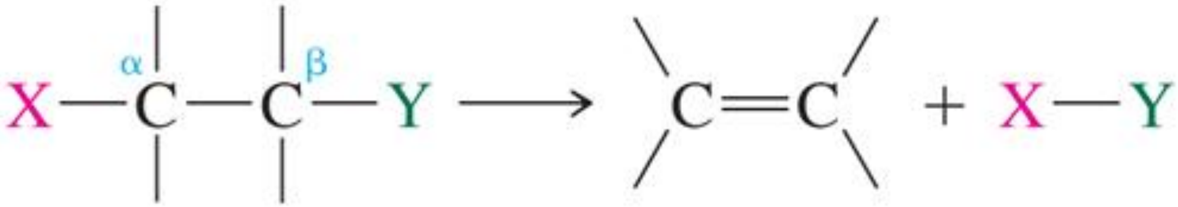
When there are more than 12 carbons in the ring, *trans*-cycloalkenes are more stable than *cis*.

Preparation of Alkenes: Elimination Reactions

- Dehydrogenation
- Dehydration of alcohols
- Dehydrohalogenation of alkyl halides

Elimination

The elimination of two substituents from adjacent carbons (α and β) forms alkenes.



The process is β-elimination.

Dehydrogenation of Alkanes

The elimination where X=Y=H is dehydrogenation. This is a high temperature industrial process.

$$\mathrm{CH_3CH_3} \xrightarrow{750^\circ\mathrm{C}} \mathrm{H_2C{=}CH_2} + \mathrm{H_2}$$

Ethane	Ethylene	Hydrogen

$$\mathrm{CH_3CH_2CH_3} \xrightarrow{750^\circ\mathrm{C}} \mathrm{CH_3CH{=}CH_2} + \mathrm{H_2}$$

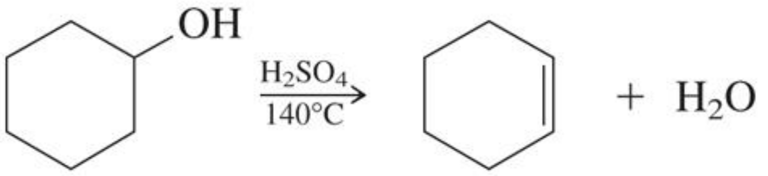
Propane	Propene	Hydrogen

Dehydration of Alcohols

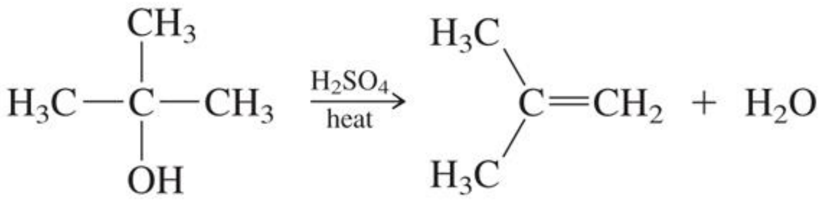
The elimination where X=OH and Y=H is dehydration.
Catalyzed by strong acids.

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

Ethyl alcohol Ethylene Water



Cyclohexanol Cyclohexene (79−87%) Water


$$(CH_3)_3COH \xrightarrow[heat]{H_2SO_4} (H_3C)_2C{=}CH_2 + H_2O$$

2-Methyl-2-propanol 2-Methylpropene (82%) Water

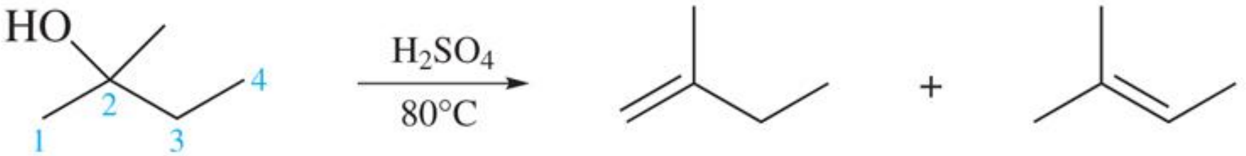
Regioselectivity in Alcohol Dehydration: The Zaitsev Rule

Regioselectivity

Selective reaction: when one product is preferentially formed.

Regioselective reactions proceed preferentially in one direction.

Dehydration of 2-methyl-2-butanol is regioselective forming the more substituted alkene.



2-Methyl-2-butanol

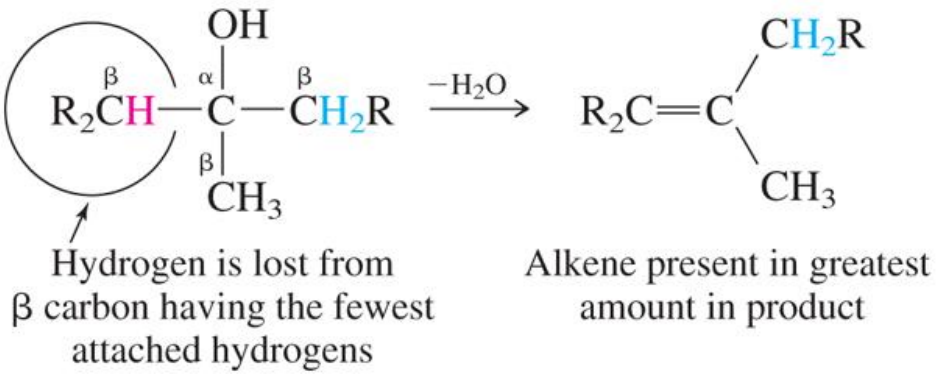
2-Methyl-1-butene (10%)

2-Methyl-2-butene (90%)

Zaitsevs Rule

Zaitsevs rule states that the alkene formed in greatest amount is the one that corresponds to removal of the hydrogen from the β carbon having the fewest hydrogens.

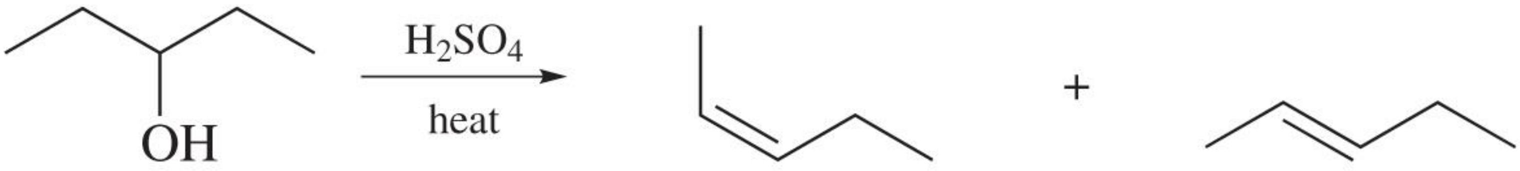
Alternatively it is stated that β elimination reactions of alcohols yield the most highly substituted alkene as the major product.



Stereoselective Dehydration

A *stereoselective* reaction yields one stereoisomer in preference to another.

Dehydration normally favors the more stable trans stereoisomer.



3-Pentanol

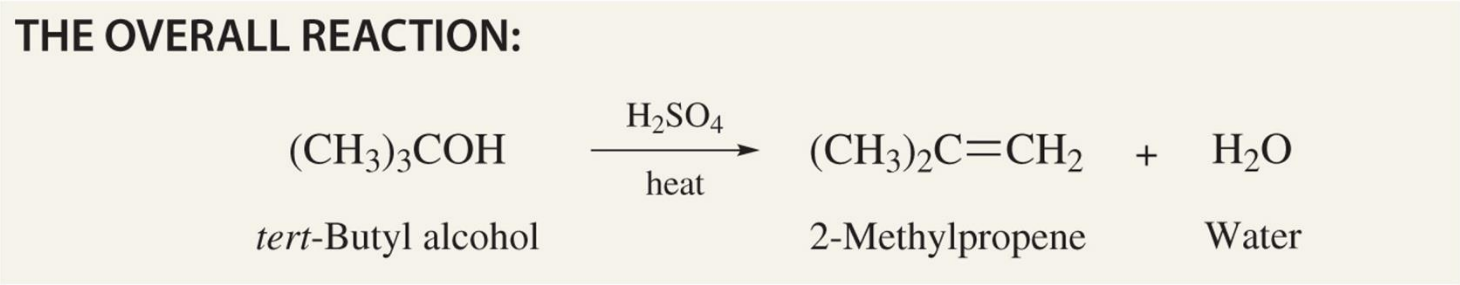
cis-2-Pentene (25%)
(minor product)

trans-2-Pentene (75%)
(major product)

The E1 and E2 Mechanisms of Alcohol Dehydrogenation

E1 Mechanism of Dehydration

The mechanism must describe the step-by-step formation of the products according to the reaction equation. The acid, written above the reaction arrow, is a catalyst in the reaction.



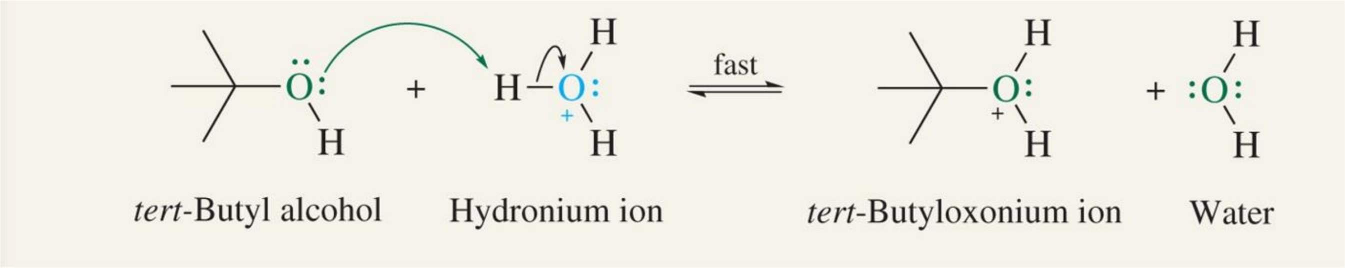
THE OVERALL REACTION:

$$(CH_3)_3COH \xrightarrow[\text{heat}]{H_2SO_4} (CH_3)_2C{=}CH_2 + H_2O$$

tert-Butyl alcohol — 2-Methylpropene — Water

E1 Mechanism: Step 1

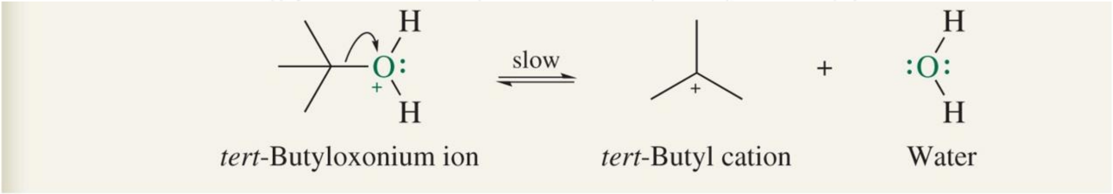
Step 1. Protonation.



This is an acid-base reaction in which the alcohol is protonated by the strong acid catalyst. The sulfuric acid dissolved in water forms hydronium ion.

E1 Mechanism: Step 2

Step 2. Dissociation.

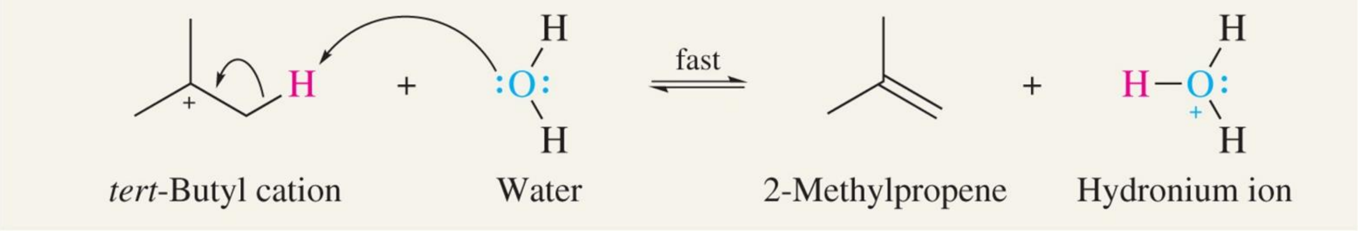


The C-O bond breaks to form water (a very stable molecule) and a fairly stable tertiary carbocation.

This is the rate determining step. Since it is a unimolecular reaction the reaction is termed E1: a first order elimination reaction.

E1 Mechanism: Step 3

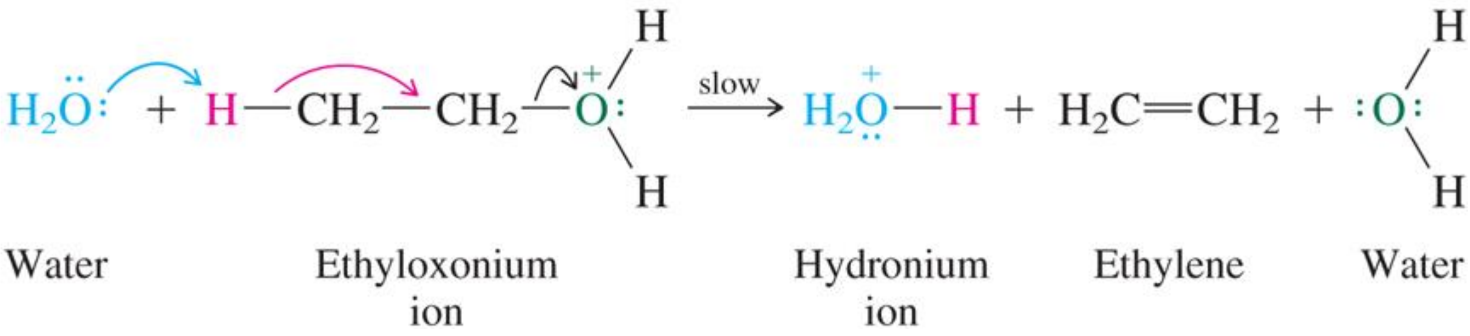
Step 3. Deprotonation.



The water acts as a base and abstracts a proton from the carbocation. This reforms the acid catalyst.

E2 Mechanism of Dehydration

Primary cations are unstable so primary alcohols cannot react by the same mechanism. The second and third steps are replaced by a concerted reaction:



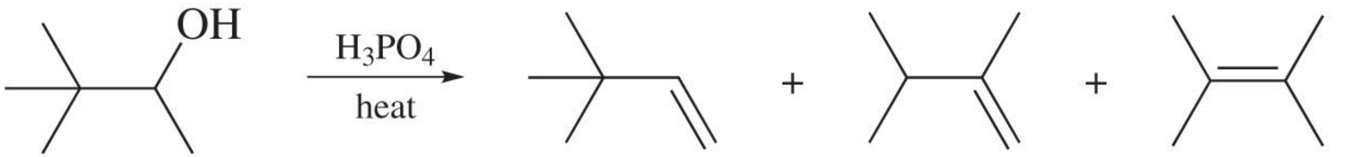
$$H_2\ddot{O}: + H{-}CH_2{-}CH_2{-}\overset{+}{O}H_2 \xrightarrow{slow} H_2\overset{+}{O}{-}H + H_2C{=}CH_2 + :\ddot{O}H_2$$

This is the rate determining step. Since it is a bimolecular reaction the reaction is termed E2: a second order elimination reaction.

Rearrangements in Alcohol Dehydrogenation

Rearrangements

A reaction in which the connectivity of the atoms changes is a rearrangement. In this example the two major products have a different carbon skeleton to the starting alcohol.



3,3-Dimethyl-2-butanol

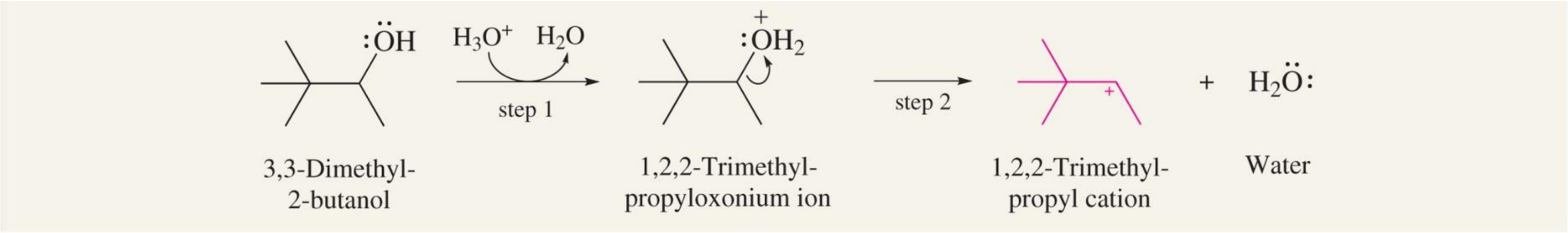
3,3-Dimethyl-1-butene (3%)

2,3-Dimethyl-1-butene (33%)

2,3-Dimethyl-2-butene (64%)

Mechanism of Rearrangement: Steps 1 and 2

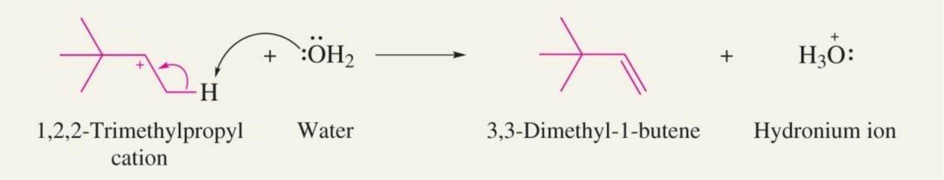
The first two steps will be exactly the same resulting in the formation of a secondary carbocation. Abbreviated as:



Remember that a secondary carbocation is more stable than a primary carbocation but less stable than a tertiary carbocation.

Mechanism of Rearrangement: Step 3

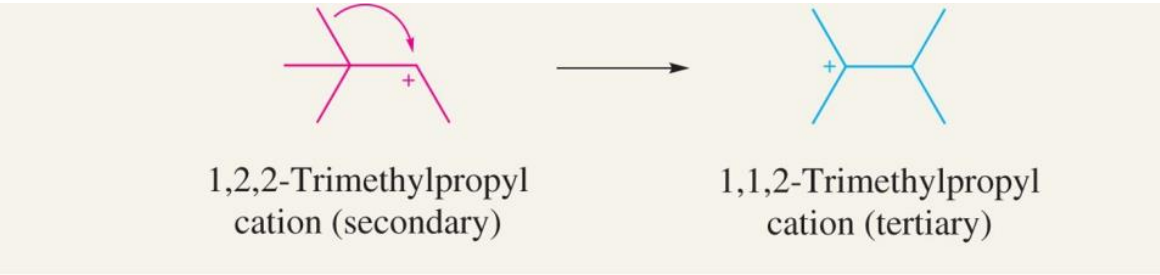
Step 3: Deprotonation (minor pathway).



The secondary cation may be deprotonated to form an alkene. This is the minor pathway based on products formed. This means that there is a more favorable pathway.

Mechanism of Rearrangement: Step 3'

Step 3': Methyl shift.

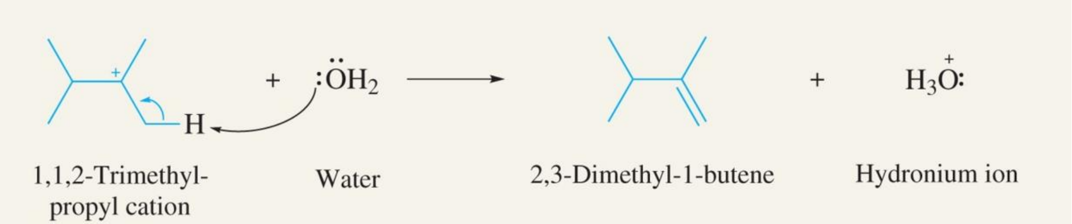


A methyl group migrates over to form a more stable tertiary cation.

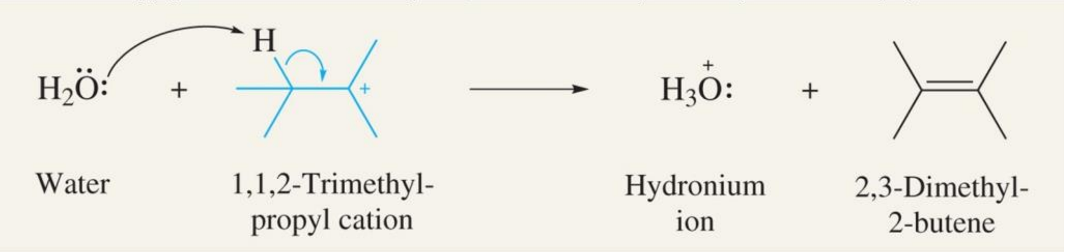
This is the major pathway since the two major products have the same carbon skeleton as the tertiary cation and must both be formed from this tertiary cation.

Mechanism of Rearrangement: Step 4 & 4’

Step 4: Deprotonation.



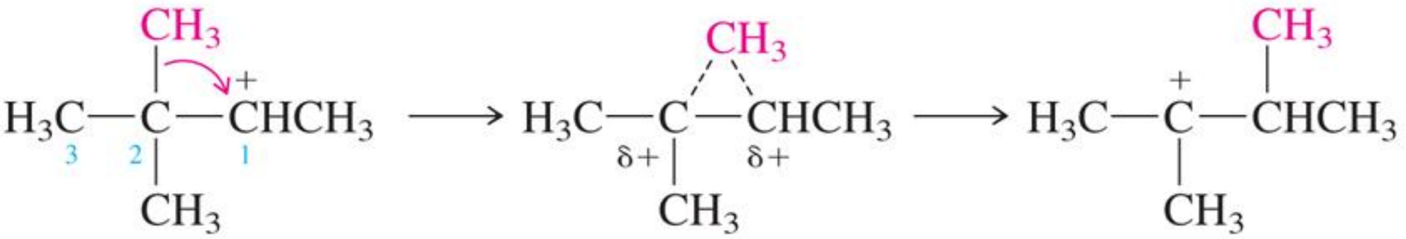
Step 4’: Deprotonation.



A hydrogen can be abstracted from either of the adjacent carbons to form two isomeric alkenes.

Carbocation Rearrangement

Carbocations will rearrange if they can form a more stable cation. The shift proceeds through a three center transition state.



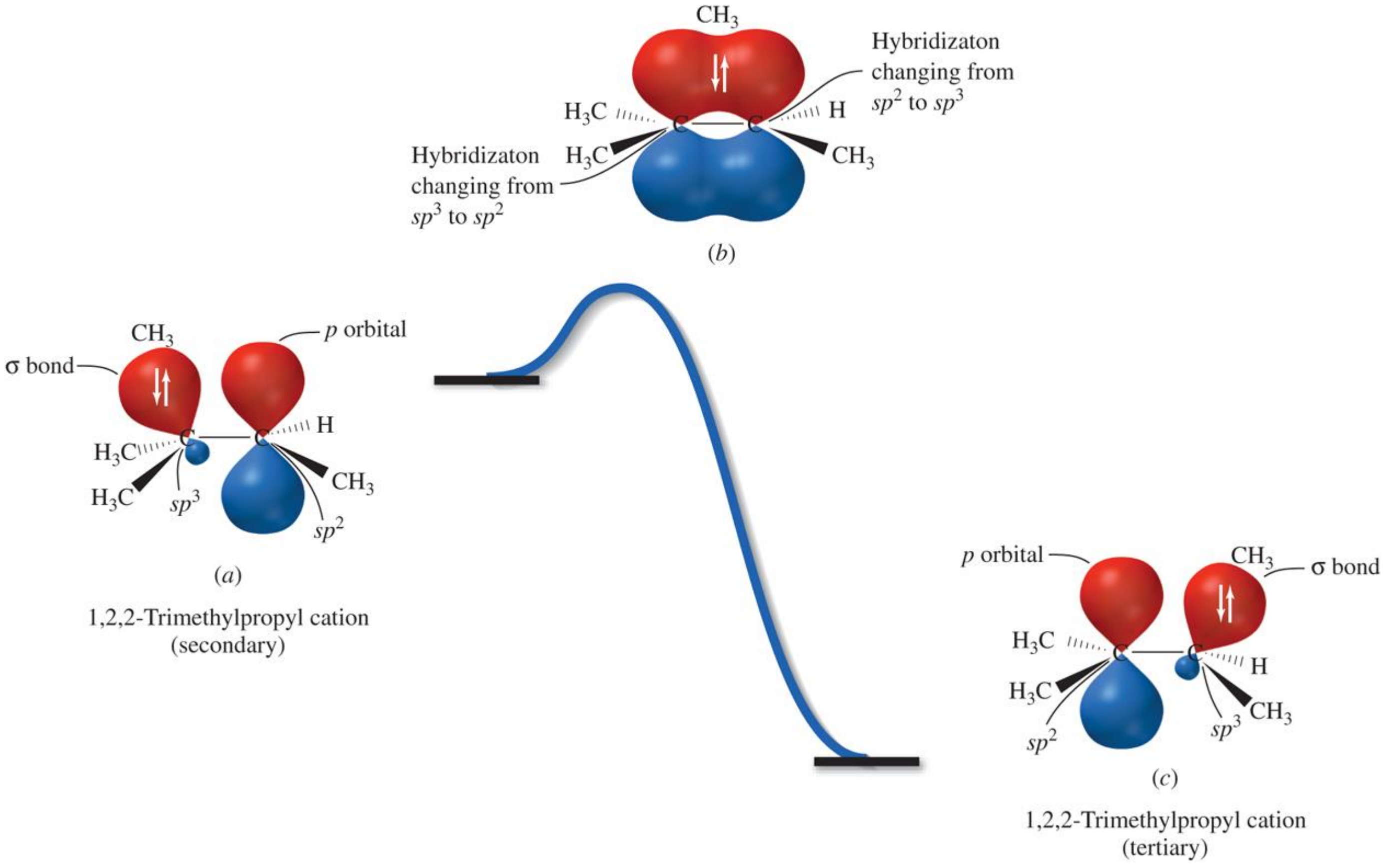
1,2,2-Trimethylpropyl cation (secondary, less stable)

Transition state for methyl migration (dashed lines indicate partial bonds)

1,1,2-Trimethylpropyl cation (tertiary, more stable)

Carbocation Rearrangement

Orbital representation of a methyl shift.



(*a*)

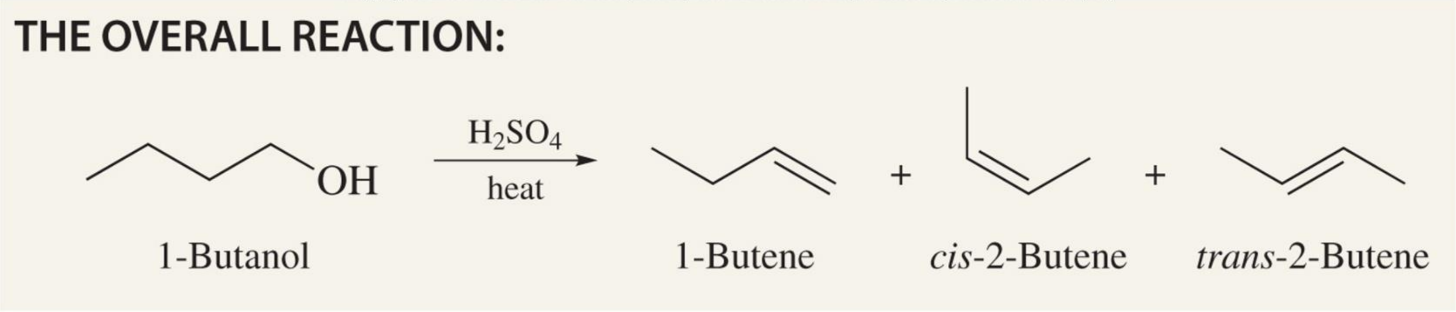
1,2,2-Trimethylpropyl cation
(secondary)

(*c*)

1,2,2-Trimethylpropyl cation
(tertiary)

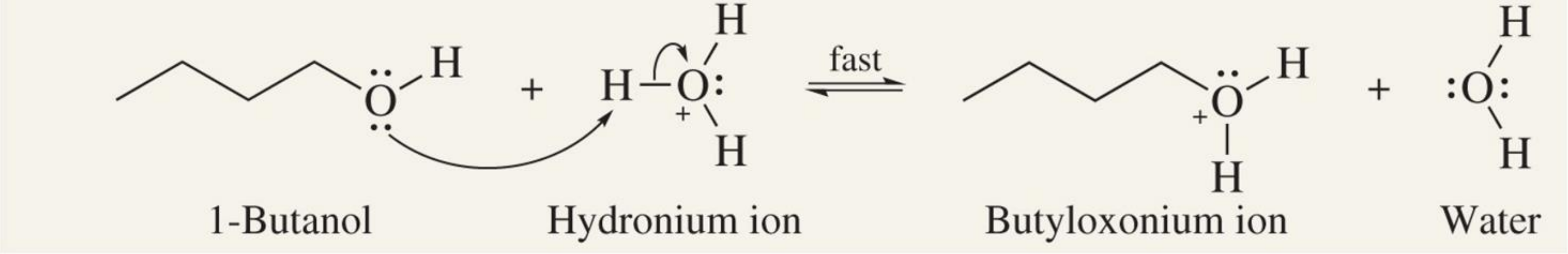
Hydride Shift

Cation rearrangements also involve shift of other alkyl groups as well as hydride, for example:



Mechanism of the Hydride Shift

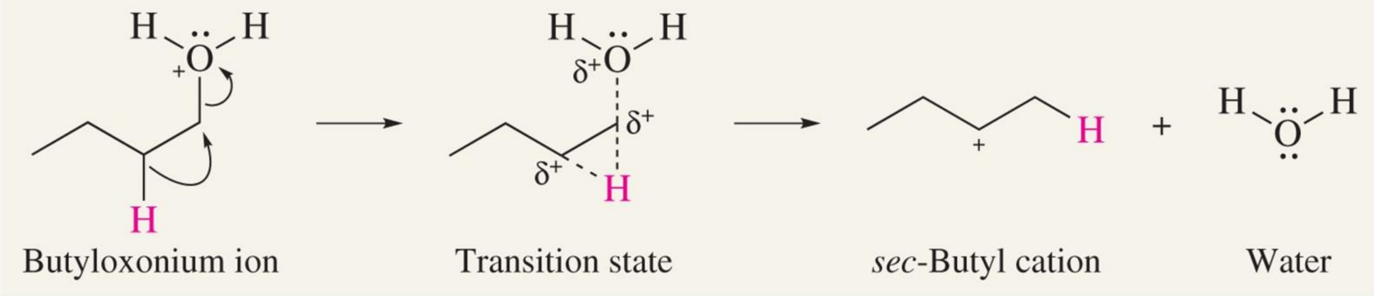
Step 1: Protonation.



The standard acid-base protonation of an alcohol is the first step of the reaction.

Mechanism of the Hydride Shift

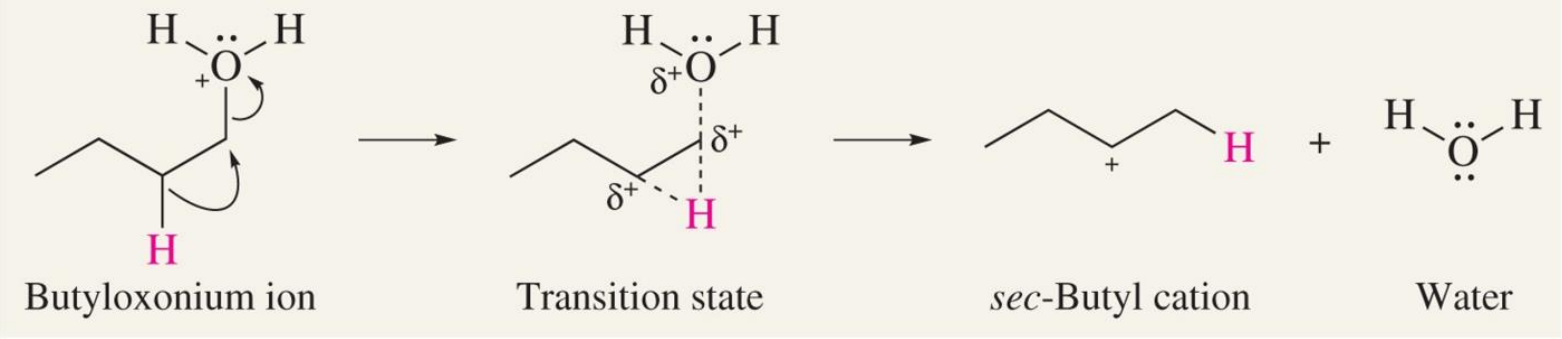
Step 2: Deprotonation (minor pathway).



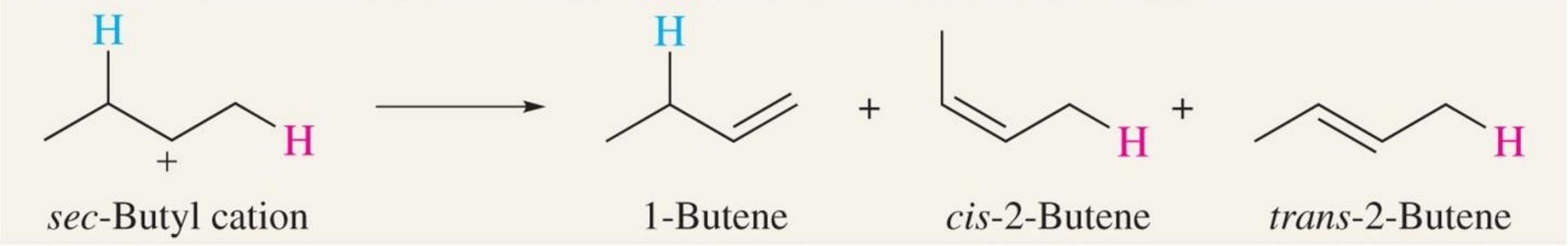
This pathway cannot explain all the products formed.

Mechanism of the Hydride Shift

Step 2’: Hydride shift.



Step 3’: Deprotonation.



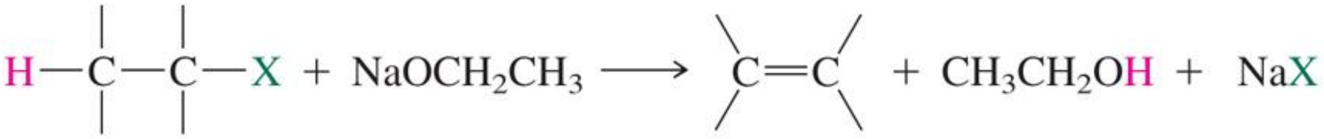
This pathway accounts for all the products formed.

Dehydrohalogenation of Alkyl Halides

E2 Dehydrohalogenation

Dehydrohalogenation is loss of a H and halogen from an alkyl halide. This is a β-elimination reaction. A strong base like sodium ethoxide ($NaOCH_2CH_3$) is needed.

General equation:



The rate is dependent on the concentration of the base and the alkyl halide so it is termed an E2 reaction.

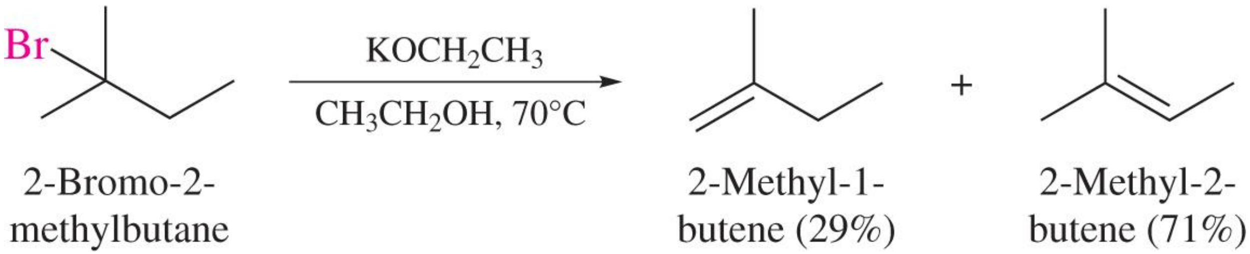
Dehydrohalogenation

For primary alcohols a strong but more hindered base is preferred.

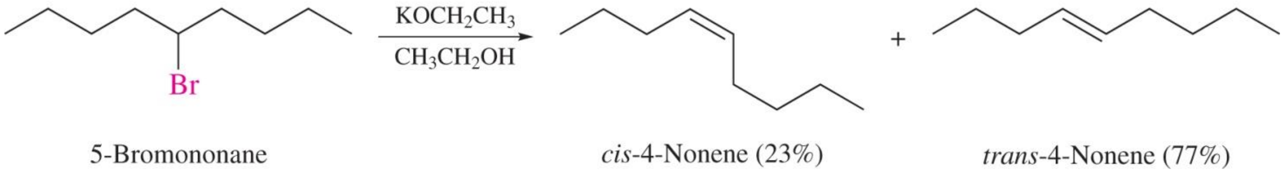
$$\underset{\text{1-Chlorooctadecane}}{CH_3(CH_2)_{15}CH_2CH_2Cl} \xrightarrow[\text{DMSO, 25°C}]{KOC(CH_3)_3} \underset{\text{1-Octadecene (86\%)}}{CH_3(CH_2)_{15}CH{=}CH_2}$$

Selectivity of Dehydrohalogenation

Dehydrohalogenation follows the Zaitsev rule. The more substituted alkene is preferentially formed.

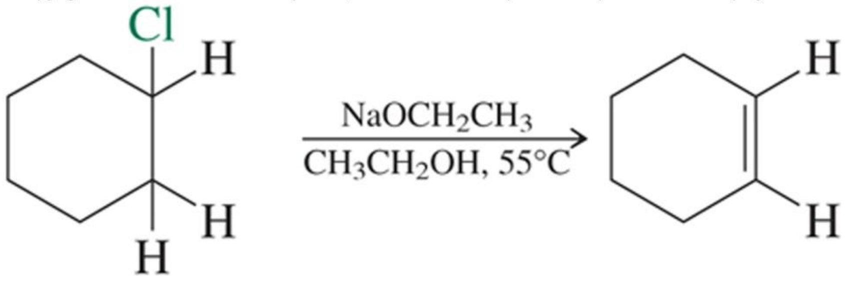


The reaction is also stereoselective preferentially forming the more stable trans stereoisomer.



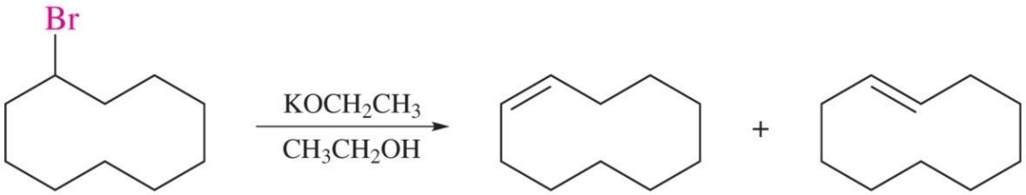
Formation of cycloalkenes

Dehydrohalogenation of cycloalkyl halides leads to cycloalkenes. Cis cyloalkenes are formed if the ring has 10 or fewer C atoms. Larger ring sizes give a mixture of cis and trans



Cyclohexyl chloride

Cyclohexene
(100%)



Bromocyclodecane

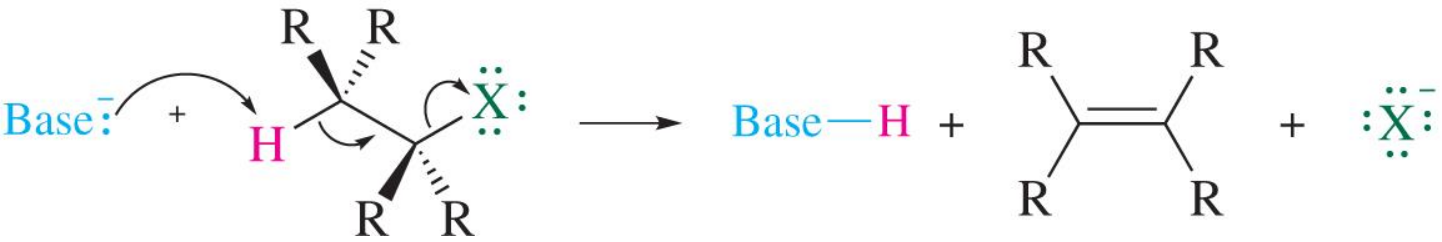
cis-Cyclodecene
(*Z*)-cyclodecene
(85%)

trans-Cyclodecene
(*E*)-cyclodecene
(15%)

The E2 Mechanism of Dehydrohalogenation of Alkyl Halides

Mechanism of Dehydrohalogenation

Kinetic studies were used to develop the mechanism for dehydrohalogenation.



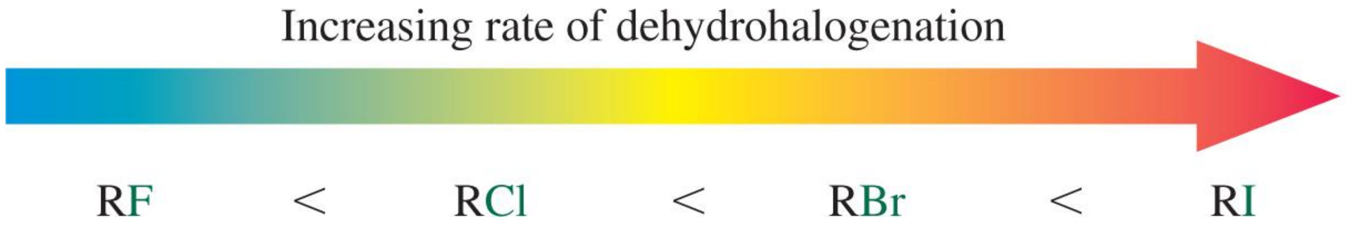
The reaction is a bimolecular reaction and the rate is defined as:

$$\text{Rate} = k[\text{Alkyl halide}][\text{Base}]$$

The Leaving Group

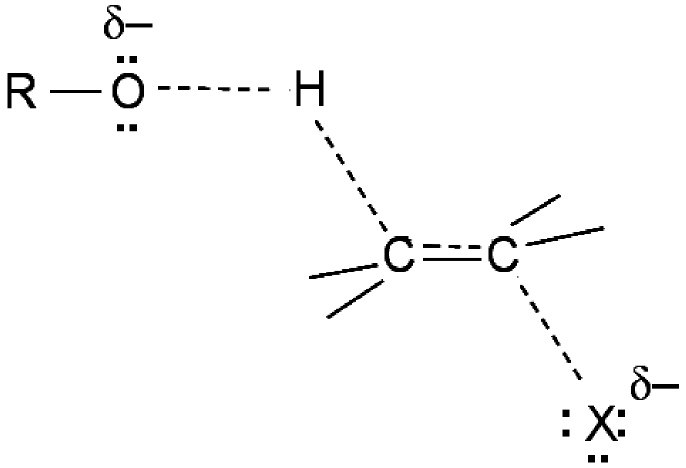
The halide anion that leaves the alkyl halide is known as the leaving group.

The choice of halogen affects the rate constant for this reaction in the order below. The C-I bond is weakest and iodide is the best leaving group. Fluoride is not a good leaving group.



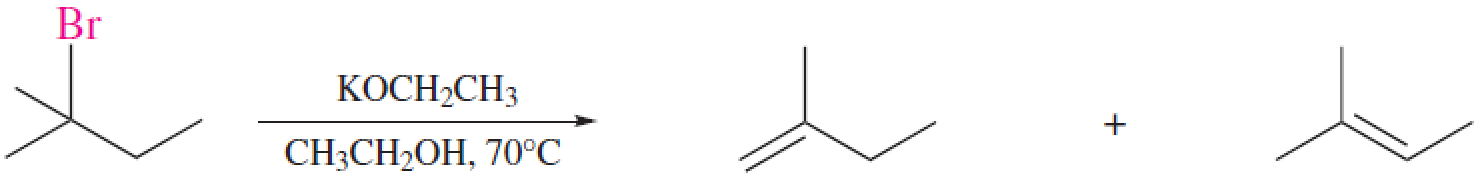
The Transition State in Dehydrohalogenation

In the transition state bonds are partially made and partially broken. The base has partially abstracted the proton and the alkene is partially formed and the halide bond is partially broken.

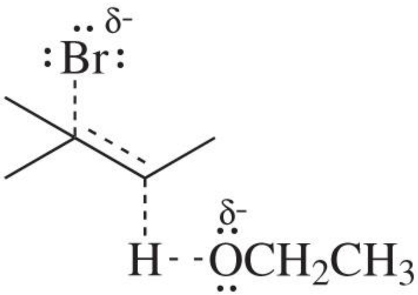


The Transition State in Dehydrohalogenation

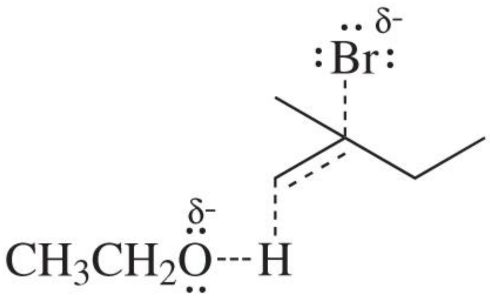
In this reaction



there are two distinct transition states :



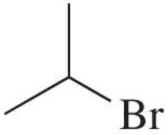
is lower energy than



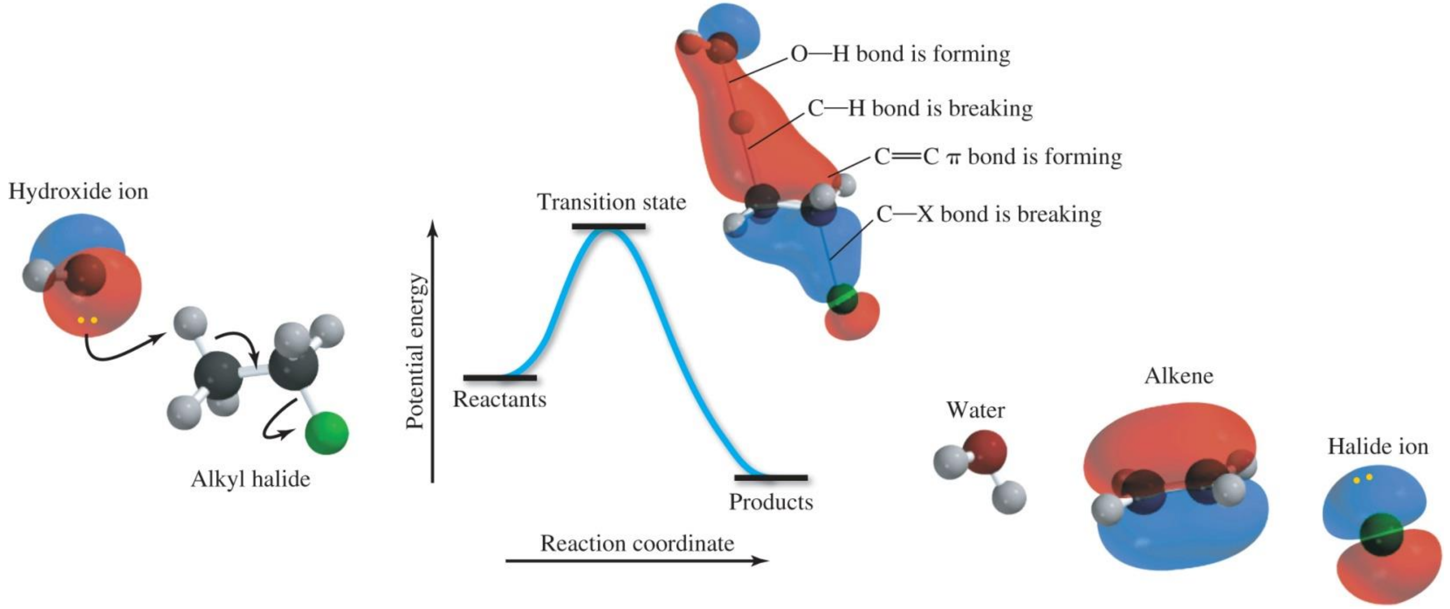
The second transition state is more stable because it is more substituted.

The Transition State in Dehydrohalogenation

More substituted transition states are more stable so the reactions that form more substituted alkenes have lower activation energy and are therefore faster.

			
Alkyl halide	Ethyl bromide	Isopropyl bromide	2-Bromo-2-methylbutane
Relative E2 rate (sodium ethoxide, ethanol, 55°C)	1	6	42

Potential Energy Graph for E2 Elimination



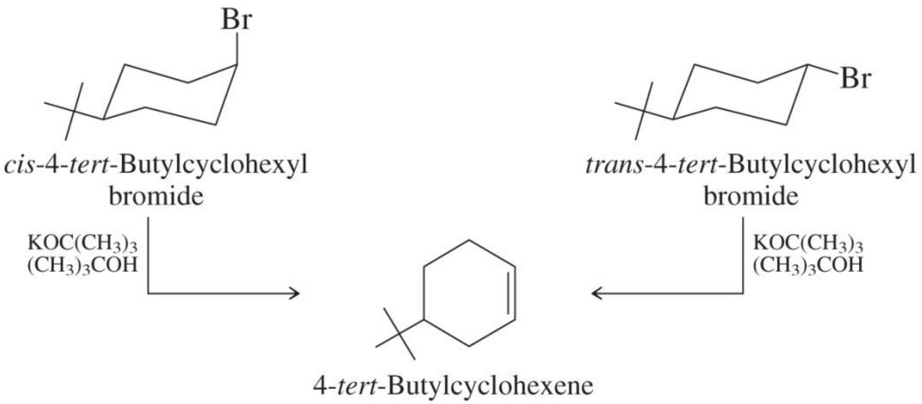
Anti Elimination in E2 Reactions:
Stereoelectronic Effects

Stereochemical Insights

The cis and trans isomers below give the same product.

BUT, the cis isomer reacts 500 times faster than the trans.

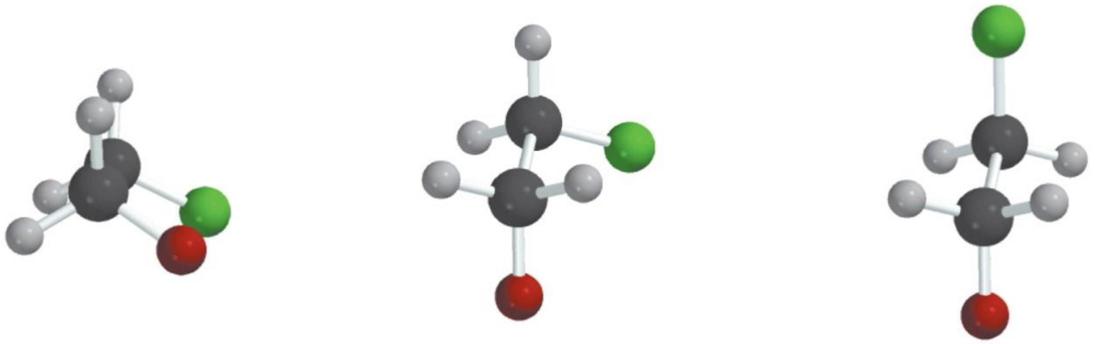
Perhaps an axial Br reacts faster?



Remember that the large t-butyl group will be equatorial.

Stereochemical Insights

These and other studies suggest that the hydrogen atom and the bromine should have an anti arrangement.



Syn coplanar
Eclipsed conformation
C—H and C—X bonds aligned

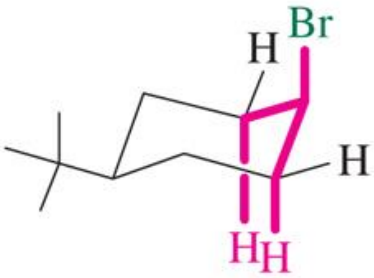
Gauche
Staggered conformation
C—H and C—X bonds not aligned

Anti coplanar
Staggered conformation
C—H and C—X bonds aligned

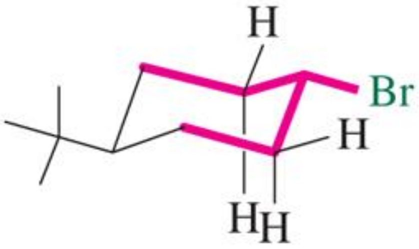
Favored arrangement.

Stereochemical Insights

The cis conformation has H’s that are anti coplanar while the trans compound does not.



cis-4-*tert*-Butylcyclohexyl bromide
(faster E2 rate:
H and Br are anti coplanar)

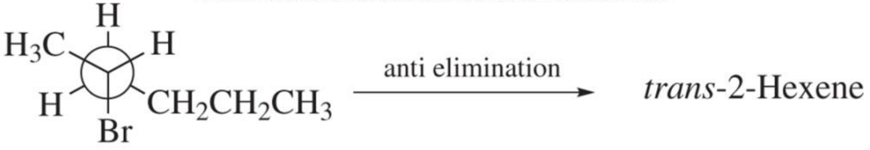


trans-4-*tert*-Butylcyclohexyl bromide
(slower E2 rate:
no H atoms anti to Br)

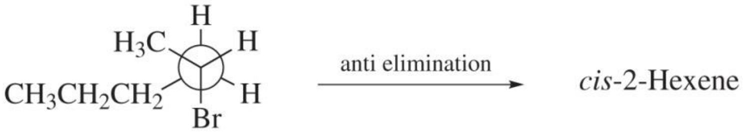
Newman Projections of Reactive Conformations

Compare the possible conformations for dehydrohalogenation of 2-bromohexane.

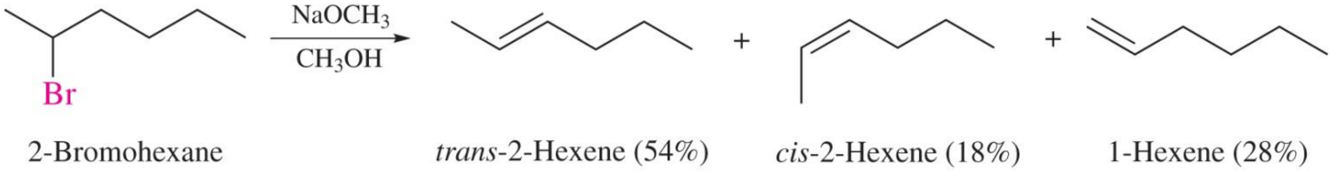
More stable conformation



Less stable conformation



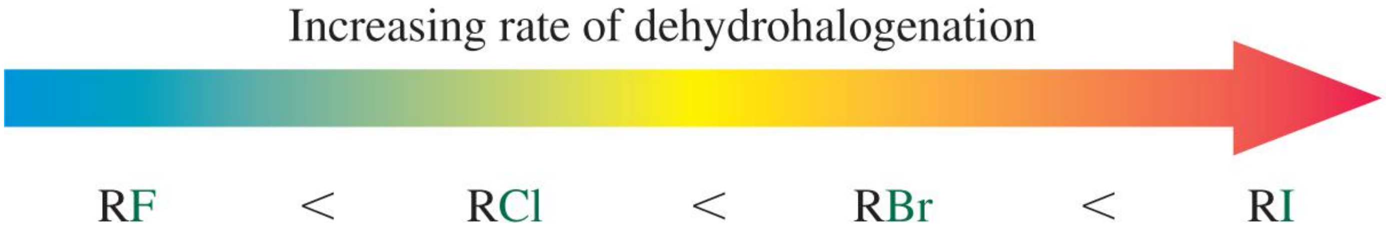
The major product is formed from the more stable conformation.



The Leaving Group

The halide anion that leaves the alkyl halide is known as the leaving group.

The choice of halogen affects the rate constant for this reaction in the order below. The C-I bond is weakest and iodide is the best leaving group. Fluoride is not a good leaving group.



Isotopes Effects And The E2 Mechanism

Deuterium Isotope Effects and Mechanism

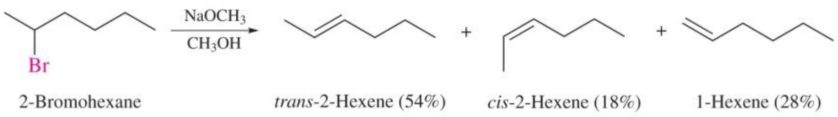
A C-D bond is ≈12 kJ/mol stronger than a C-H bond.

Therefore the rate constant k for an elementary step where C-D breaks is smaller than for a C-H bond.

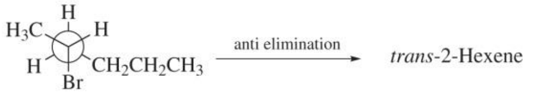
The difference in rate is expressed as a ratio k_H/k_D, and is a kinetic isotope effect.

Because it compares ^2H to ^1H, it is called a deuterium isotope effect.

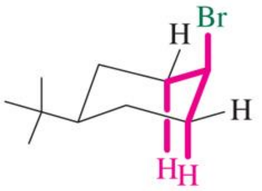
If the C-H bond breaking step is rate determining then k_H/k_D should be in the range 3-8.



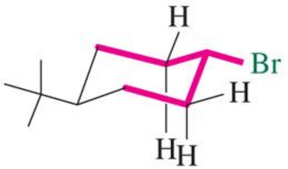
Anti elimination from the more stable staggered conformation gives the major product.



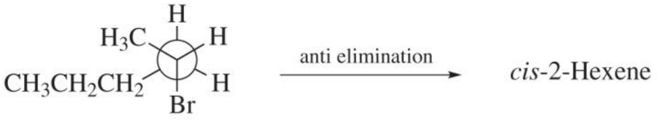
more stable conformation



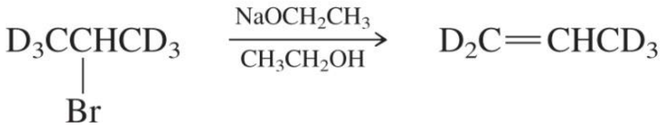
cis-4-*tert*-Butylcyclohexyl bromide
(faster E2 rate:
H and Br are anti coplanar)



trans-4-*tert*-Butylcyclohexyl bromide
(slower E2 rate:
no H atoms anti to Br)

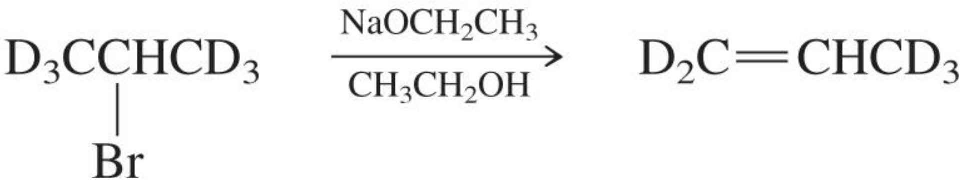


less stable conformation



$$\underset{\mathrm{Br}}{\mathrm{D_3CCHCD_3}} \xrightarrow[\mathrm{CH_3CH_2OH}]{\mathrm{NaOCH_2CH_3}} \mathrm{D_2C{=}CHCD_3}$$

Deuterium Isotope Effects and Mechanism



$$\mathrm{D_3C\underset{\underset{Br}{|}}{C}HCD_3} \xrightarrow[\mathrm{CH_3CH_2OH}]{\mathrm{NaOCH_2CH_3}} \mathrm{D_2C{=}CHCD_3}$$

For this reaction the ratio $k_H/k_D = 6.7$

Therefore the hydrogen is removed in the rate determining step (RDS) not after.

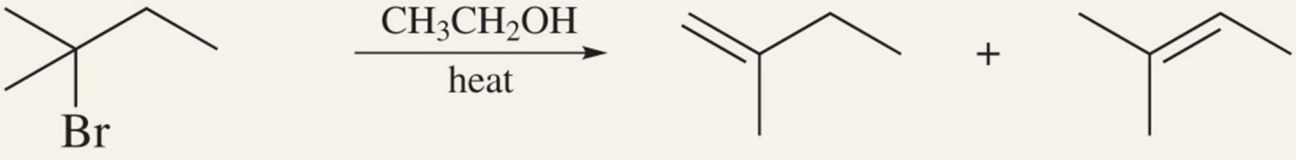
The mechanism must be E2.

The E1 Mechanism of Dehydrohalogenation of Alkyl Halides

E1 vs E2

The E2 elimination is a concerted reaction. In contrast the E1 reaction has a step by step mechanism. The reaction equation “looks” similar.

THE OVERALL REACTION:



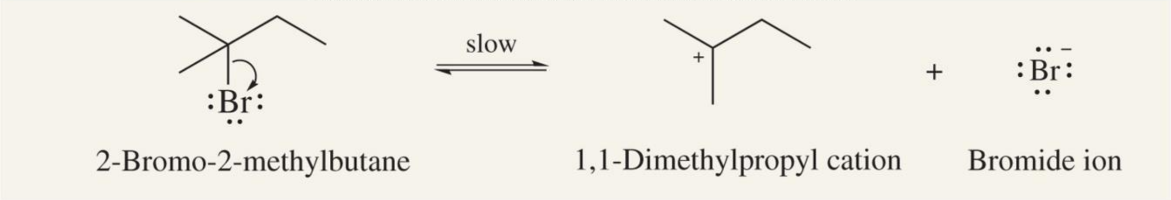
2-Bromo-2-methylbutane

2-Methyl-1-butene (25%)

2-Methyl-2-butene (75%)

The E1 Dehydrohalogenation

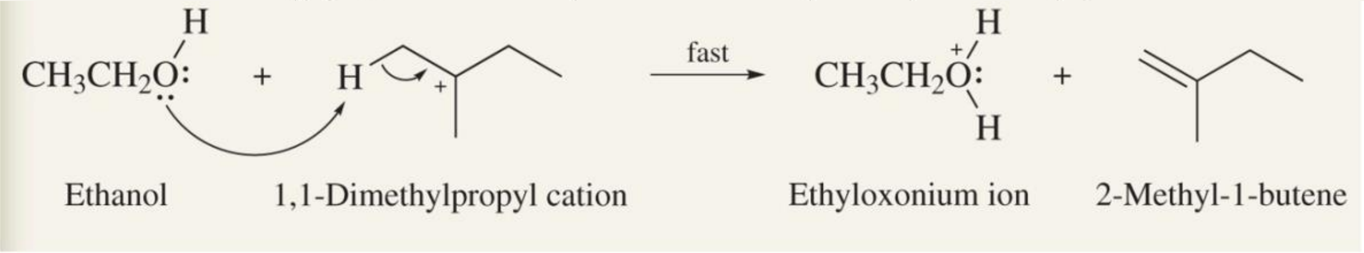
Step 1. Ionization.



The first step is the slow ionization of the alkyl halide. Since a carbocation is formed this will not happen with a primary alkyl halide. This is the slow rate determining step. It is unimolecular so the reaction is termed E1.

The E1 Dehydrohalogenation

Step 2. Deprotonation (of a primary H).



Step 2’. Deprotonation (of a secondary H).

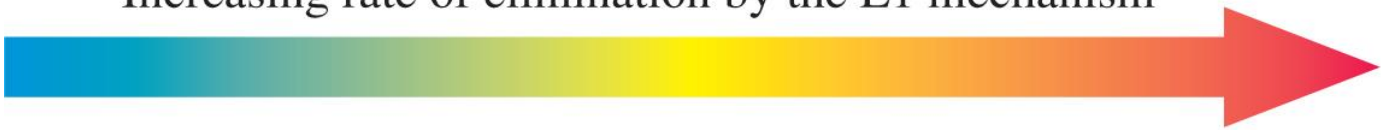
The second step is similar to step 3 in the E1 dehydration of alcohols.

E1 vs E2

The E1 elimination generally only occurs with a tertiary alkyl halide with a weak base (not charged). The rate of an E1 reaction is given by:

$$\text{Rate} = k[\text{alkyl halide}]$$

Increasing rate of elimination by the E1 mechanism



RCH_2X < R_2CHX < R_3CX

Primary alkyl halide
slowest rate of
E1 elimination

Tertiary alkyl halide
fastest rate of
E1 elimination