

Alkenes and Alkynes I

Properties and Synthesis

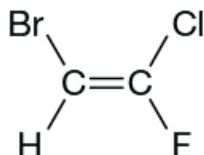
Elimination Reactions of Alkyl Halides

The (*E*)–(*Z*) System for Designating Alkene Diastereomers

- The terms *cis* and *trans* to designate the stereochemistry of alkene diastereomers (*cis*–*trans* isomers).
- **Cis-Trans System:** Useful for 1,2-disubstituted alkenes



- The *cis* and *trans* system cannot be applied on trisubstituted or tetrasubstituted alkenes, so (*E*)–(*Z*) system will be used.

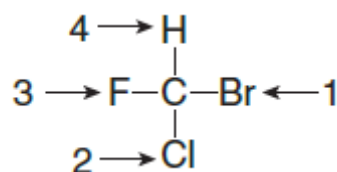


How to Use the (*E*)–(*Z*) System

Rules Needed to Assign Priority

Rule 1

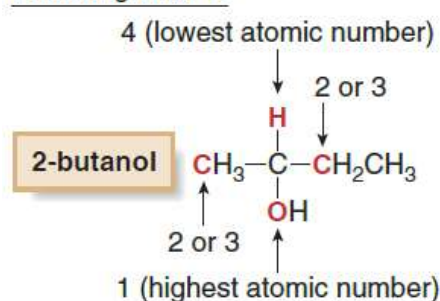
- Assign priorities (1, 2, 3, or 4) to the atoms directly bonded to the stereogenic center in order of decreasing atomic number. The atom of *highest* atomic number gets the *highest* priority (1).
- In CHBrClF, priorities are assigned as follows: Br (1, highest) → Cl (2) → F (3) → H (4, lowest). In many molecules the lowest priority group will be H.



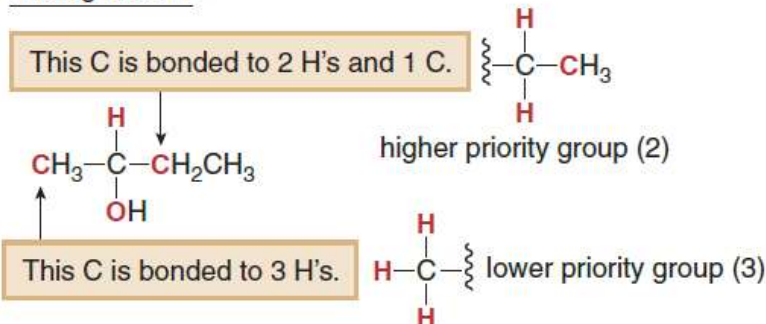
Rule 2

- If two atoms on a stereogenic center are the *same*, assign priority based on the atomic number of the atoms bonded to these atoms. *One* atom of higher atomic number determines a higher priority.

Following Rule 1:



Adding Rule 2:



Rule 3

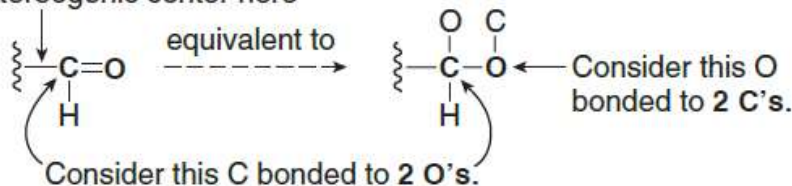
- If two isotopes are bonded to the stereogenic center, assign priorities in order of decreasing *mass* number.

	Mass number	Priority
T (tritium)	3 (1 proton + 2 neutrons)	1
D (deuterium)	2 (1 proton + 1 neutron)	2
H (hydrogen)	1 (1 proton)	3

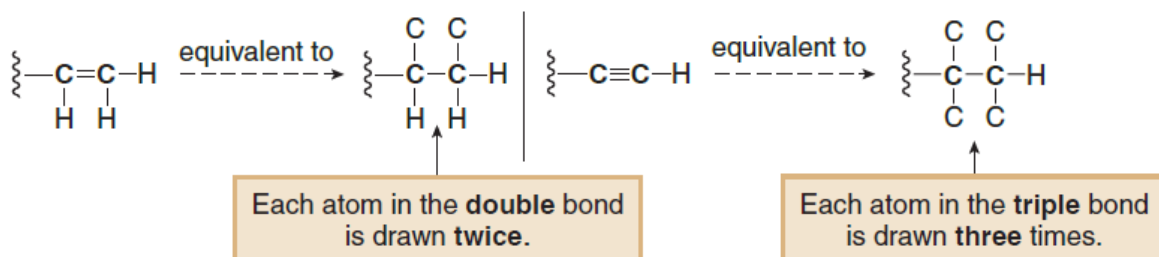
Rule 4

- To assign a priority to an atom that is part of a multiple bond, treat a multiply bonded atom as an equivalent number of singly bonded atoms.
 - **For example:** the C of a C=O is considered to be bonded to two O atoms.

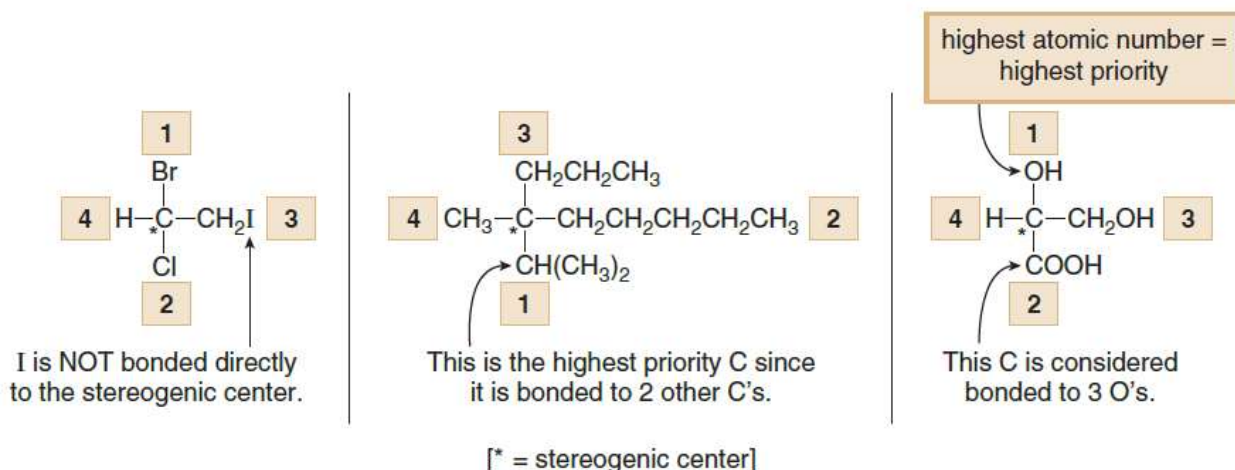
bonded to a stereogenic center here



- Other common multiple bonds are drawn below.



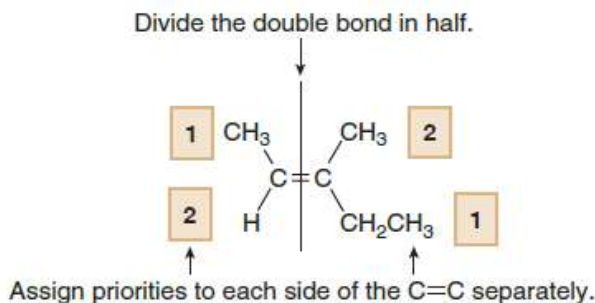
➤ **Example:**



Rules Needed to Assign the Prefixes *E* and *Z* to an Alkene

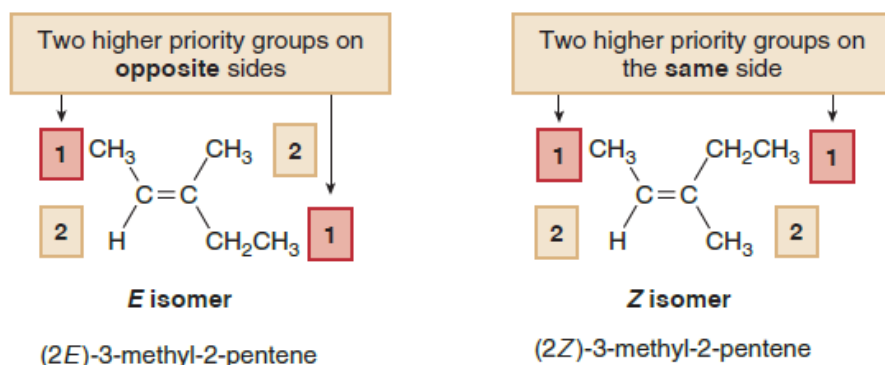
Rule 1

- Assign priorities to the two substituents on each end of the C=C by using the priority rules for *R,S* nomenclature.
- Divide the double bond in half, and assign the numbers **1** and **2** to indicate the relative priority of the two groups on each end—the higher priority group is labeled **1**, and the lower priority group is labeled **2**.



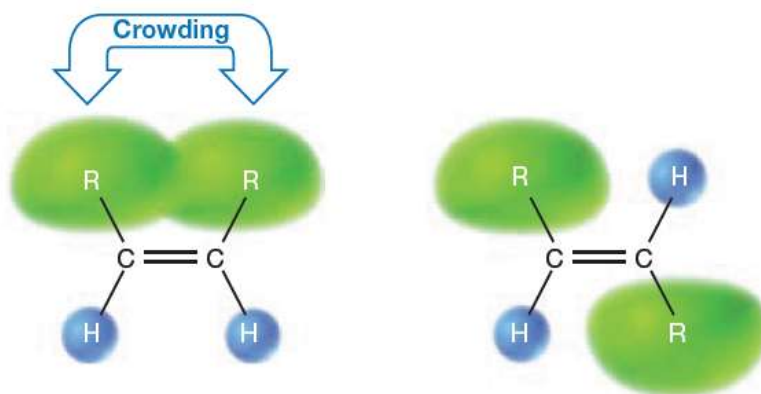
Rule 2

- Assign *E* or *Z* based on the location of the two higher priority groups (1).
- The *E* isomer has the two higher priority groups on the **opposite sides**.
 - The *Z* isomer has the two higher priority groups on the **same side**.



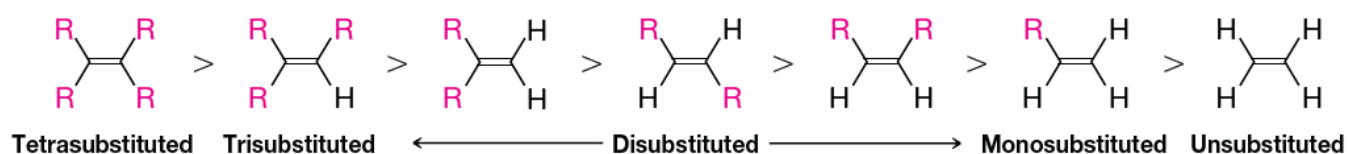
Relative Stabilities of Alkenes

- *Cis* and *trans* isomers of alkenes do not have the same stability.
 - Strain caused by crowding of two alkyl groups on the same side of a double bond makes *cis* isomers generally less stable than *trans* isomers.



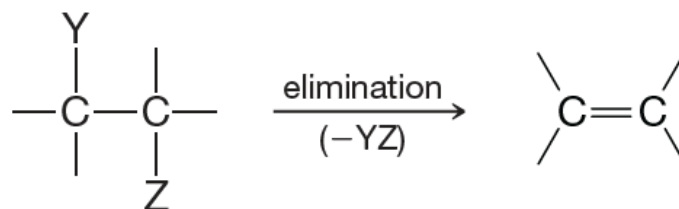
- The greater the number of attached alkyl groups (i.e., the more highly substituted the carbon atoms of the double bond), the greater is the alkene's stability.
 - This order of stabilities can be given in general terms as follows:

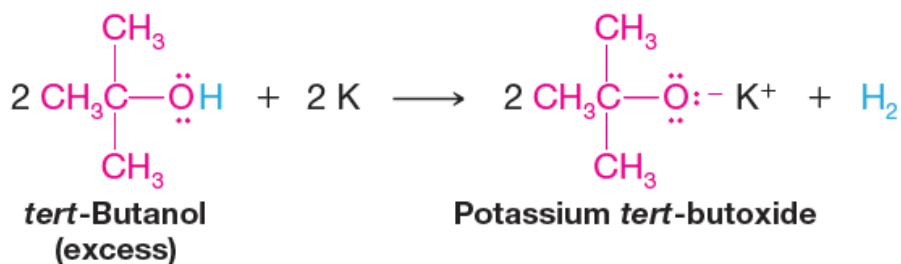
Relative Stabilities of Alkenes



Synthesis of Alkenes: Elimination Reactions

- **Elimination reactions** are the most important means for synthesizing alkenes.

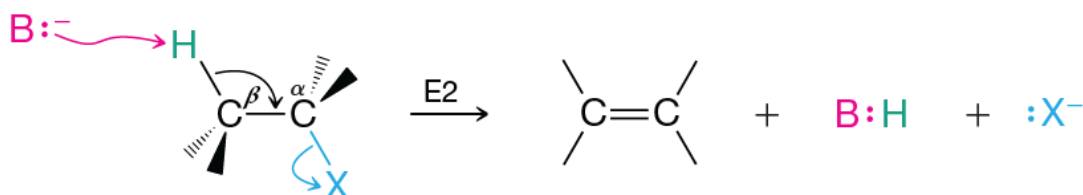




Mechanisms of Dehydrohalogenations

The E2 Reaction

- In an E2 mechanism, a base removes a β hydrogen from the β carbon as the double bond forms and a leaving group departs from the α carbon.

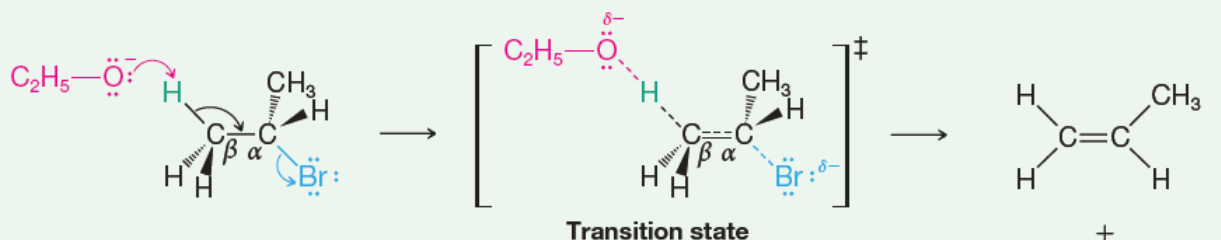


- The reaction is second order overall: **Rate** = $k[\text{CH}_3\text{CHBrCH}_3][\text{C}_2\text{H}_5\text{O}^-]$.
- The reaction is **bimolecular**.

Reaction



Mechanism



The basic ethoxide ion begins to remove a proton from the β carbon using its electron pair to form a bond to it. At the same time, the electron pair of the β C—H bond begins to move in to become the π bond of a double bond, and the bromine begins to depart with the electrons that bonded it to the α carbon.

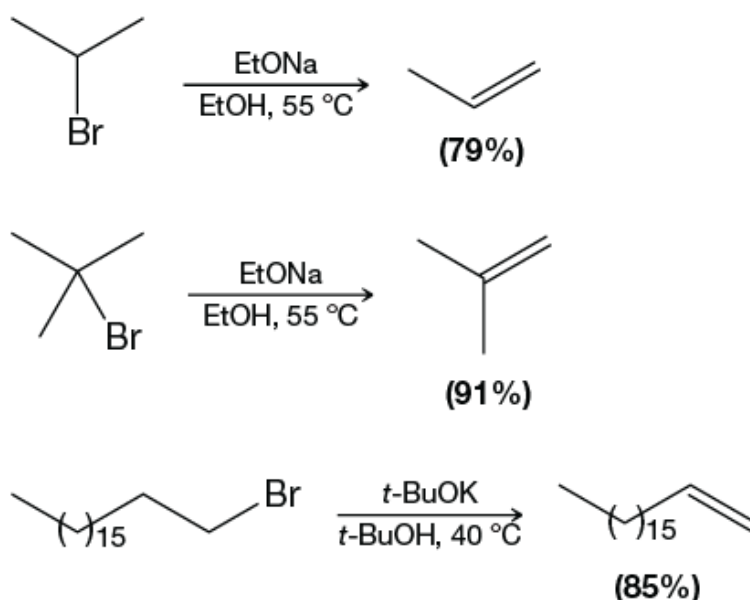
Partial bonds in the transition state extend from the oxygen atom that is removing the β hydrogen, through the carbon skeleton of the developing double bond, to the departing leaving group. The flow of electron density is from the base toward the leaving group as an electron pair fills the π bonding orbital of the alkene.

At completion of the reaction, the double bond is fully formed and the alkene has a trigonal planar geometry at each carbon atom. The other products are a molecule of ethanol and a bromide ion.

Zaitsev's Rule: Formation of the More Substituted Alkene Is Favored with a Small Base

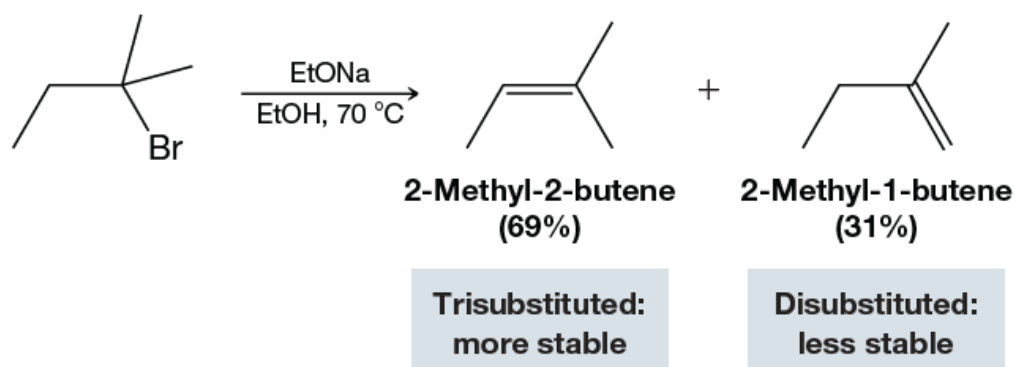
➤ Dehydrohalogenations where only a single elimination product was possible.

➤ **Examples:**



- The ratio depends on the **stability of the alkene** produced and the **nature of the base**.

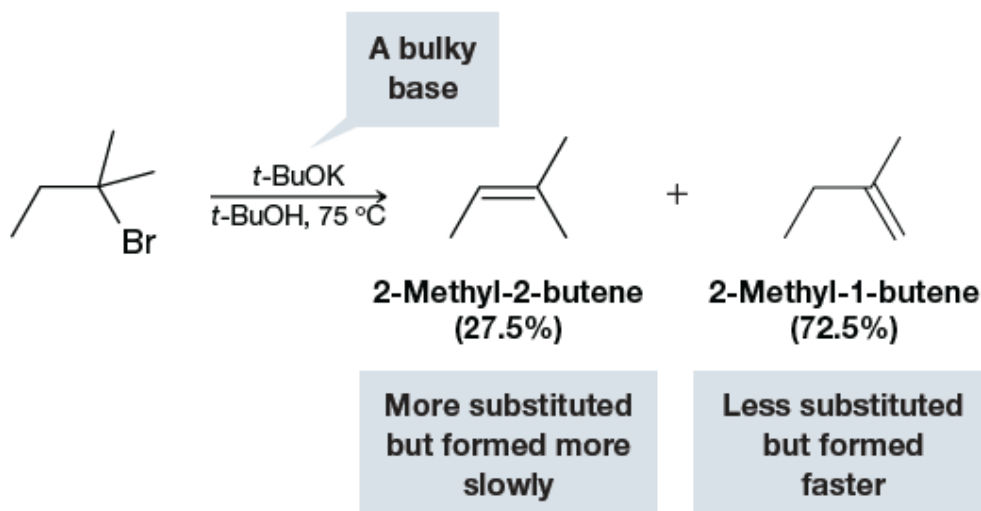
➤ **Zaitsev's Rule:** states that in an elimination reaction the major product is the more stable alkene with the more highly substituted double bond.



Hofmann Rule: Formation of the Less Substituted Alkene Using a Bulky Base

➤ **Hofmann rule:** states that the major product in Hofmann eliminations and other similar elimination reactions is the less stable alkene (or the alkene featuring a lesser substituted double bond).

- **For example:** Carrying out dehydrohalogenations with a bulky base such as potassium *tert*butoxide (*t*-BuOK) in *tert*-butyl alcohol (*t*-BuOH) favors the formation of the **less substituted alkene**.

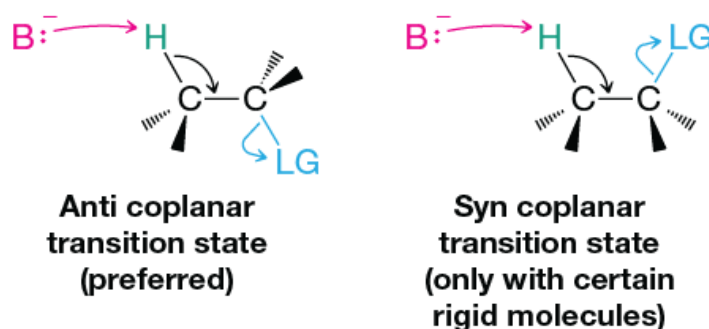


Zaitsev's Rule vs Hofmann Rule

	Zaitsev Rule	Hofmann Rule
Definition	an empirical rule that determines the final product of a particular reaction as the most substituted product.	an empirical rule that determines the final product of a particular reaction as the least substituted product.
Final Product	Majority is the most substituted product	Majority is the least substituted product
Reaction	Elimination from β carbon having most hydrogen substitutes	Elimination from α carbon having the least hydrogen substitutes

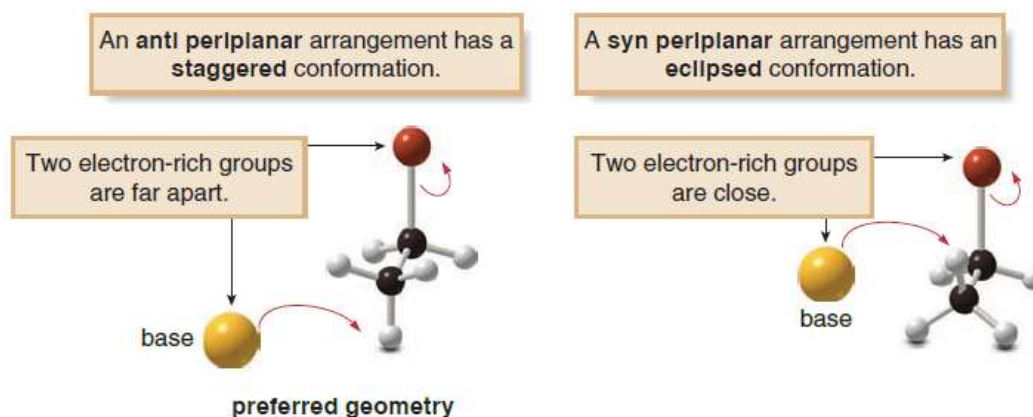
The Stereochemistry of E2 Reactions: The Orientation of Groups in the Transition State

- The five atoms involved in the transition state of an E2 reaction (including the base) must be **coplanar**, that is, lie in the same plane.



- The **anti coplanar** conformation is the preferred transition state geometry.

- The **syn coplanar** transition state occurs only with rigid molecules that are unable to assume the anti arrangement.
 - **The reason:** the anti coplanar transition state is staggered (and therefore of lower energy), while the syn coplanar transition state is eclipsed.

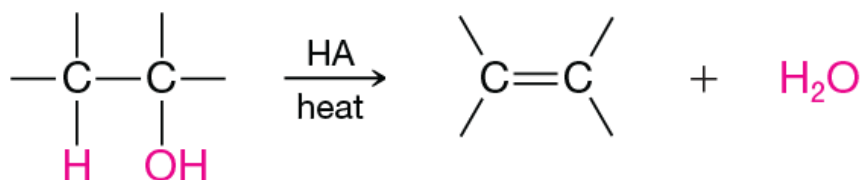


NB

- The H and X atoms can be oriented on the same side of the molecule. This geometry is called **syn periplanar**.
- The H and X atoms can be oriented on opposite sides of the molecule. This geometry is called **anti periplanar**.

Elimination of Alcohols: Acid-Catalyzed Dehydration

- Most alcohols undergo **dehydration** (lose a molecule of water) to form an alkene when heated with a strong acid.

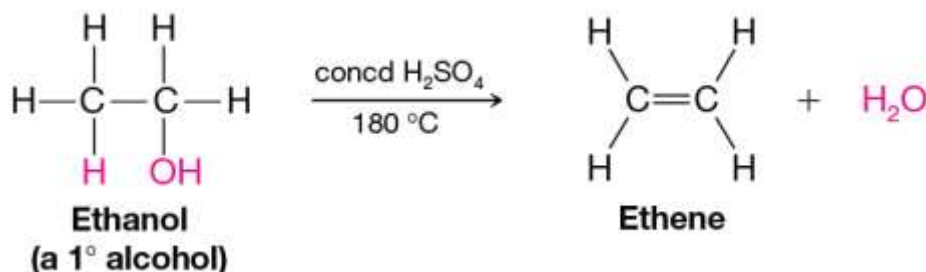


- The reaction is an **elimination** and is favored at higher temperatures.
- The most commonly used acids in the laboratory are Brønsted acids—proton donors such as sulfuric acid and phosphoric acid.
- The most commonly used acids in the industrial, gas-phase dehydrations are Lewis acids such as alumina (Al₂O₃).
- Alcohol dehydration follows an **E1** mechanism with **secondary** and **tertiary** alcohols.
 - **Primary** alcohols can follow an **E2** mechanism or undergo rearrangement.

1. The temperature and concentration of acid required to dehydrate an alcohol depend on the structure of the alcohol substrate.

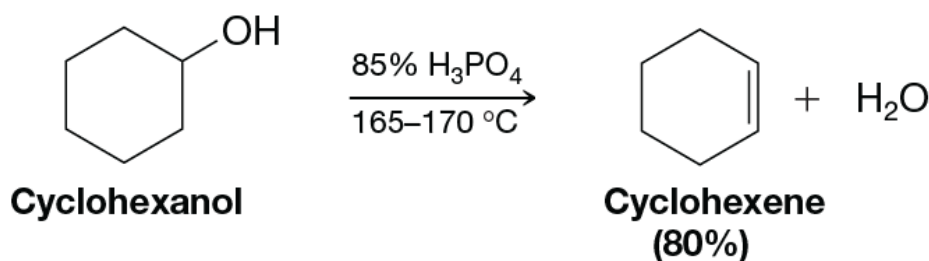
(a) **Primary alcohols:** are the most difficult to dehydrate.

- **For example:** Dehydration of ethanol requires concentrated sulfuric acid and a temperature of 180 °C:



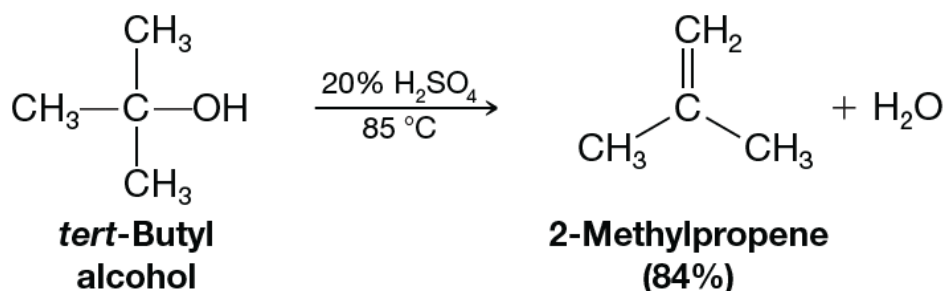
(b) **Secondary alcohols:** usually dehydrate under milder conditions.

- **For example:** Cyclohexanol dehydrates in 85% phosphoric acid at 165–170 °C:



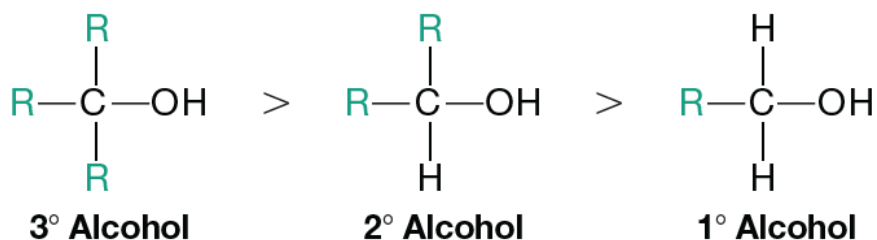
(c) **Tertiary alcohols:** are usually so easily dehydrated that relatively mild conditions can be used.

- **For example:** *tert*-Butyl alcohol dehydrates in 20% aqueous sulfuric acid at a temperature of 85 °C:



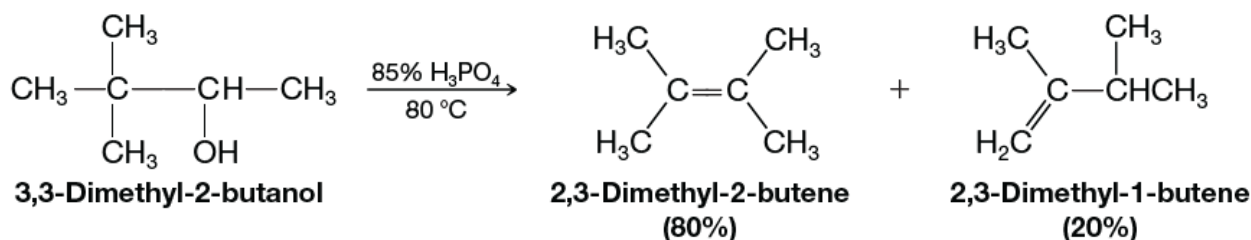
NB

- The relative ease with which alcohols undergo dehydration is $3^\circ > 2^\circ > 1^\circ$.



2. Some primary and secondary alcohols also undergo rearrangements of their carbon skeletons during dehydration.

- **For example:** Rearrangement occurs in the dehydration of 3,3-dimethyl-2-butanol.

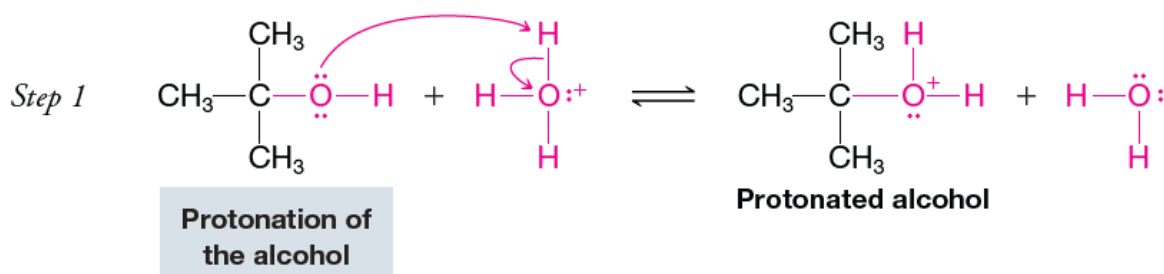


Mechanism for Dehydration of Secondary and Tertiary Alcohols: An E1 Reaction

- The mechanism is an E1 reaction in which the substrate is a protonated alcohol.
- Consider the dehydration of *tert*-butyl alcohol as an example:

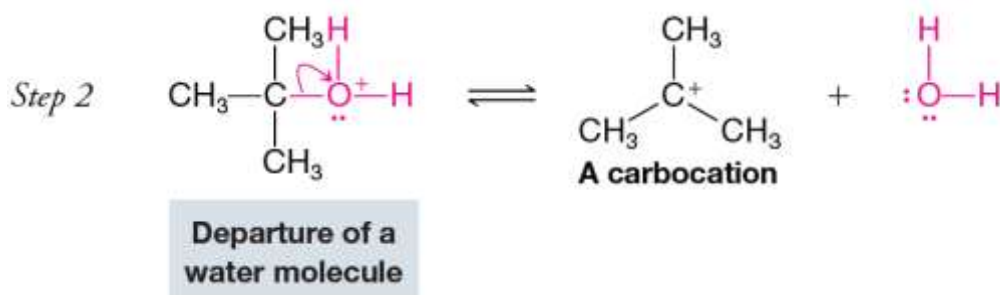
Step 1

- A proton is rapidly transferred from the acid to one of the unshared electron pairs of the alcohol.
- The presence of the positive charge on the oxygen of the protonated alcohol weakens all bonds to oxygen, including the carbon–oxygen bond.



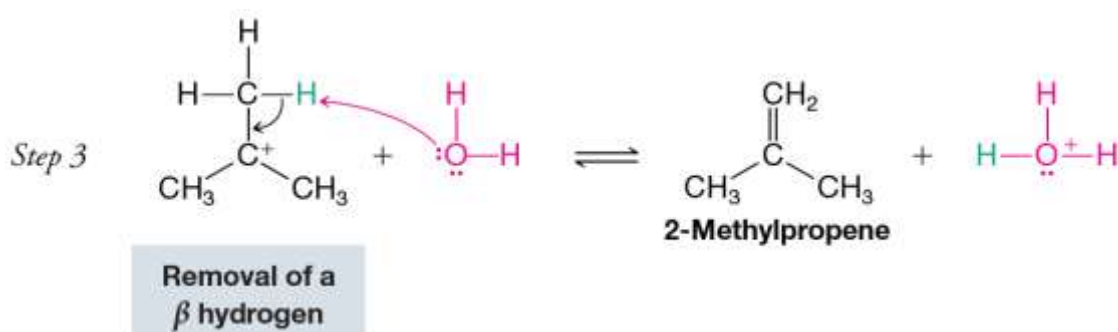
Step 2

- The carbon–oxygen bond breaks **heterolytically**.
- The bonding electrons depart with the water molecule and leave behind a carbocation.
 - The carbocation is highly reactive **because** the central carbon atom has only six electrons in its valence level, not eight.



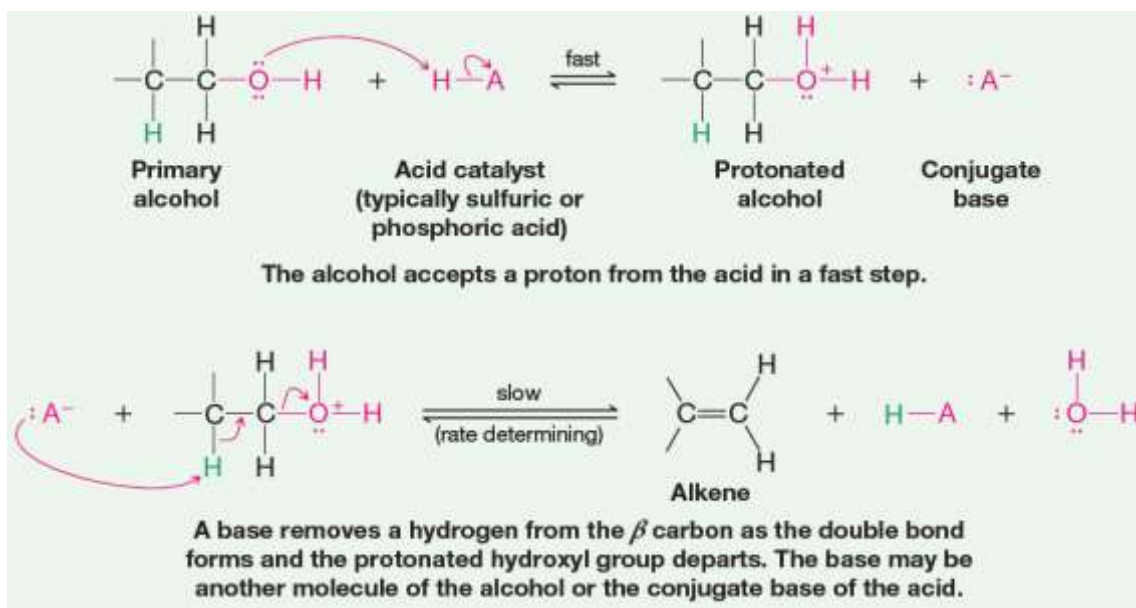
Step 3

- A water molecule removes a proton from the β carbon of the carbocation.
- The result is the formation of a hydronium ion and an alkene



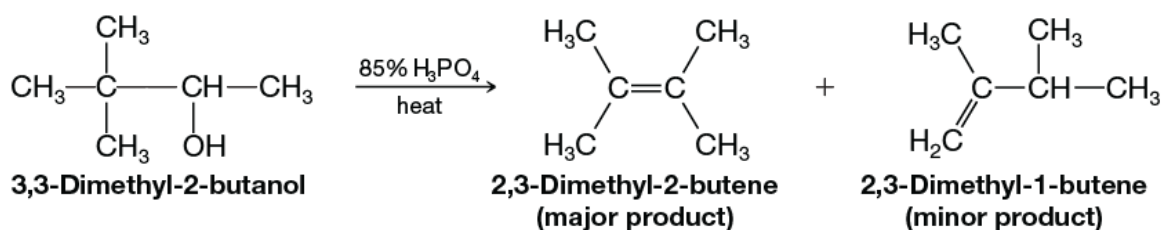
A Mechanism for Dehydration of Primary Alcohols: An E2 Reaction

- Dehydration of primary alcohols apparently proceeds through an E2 mechanism **because** the primary carbocation required for dehydration by an E1 mechanism is relatively unstable.



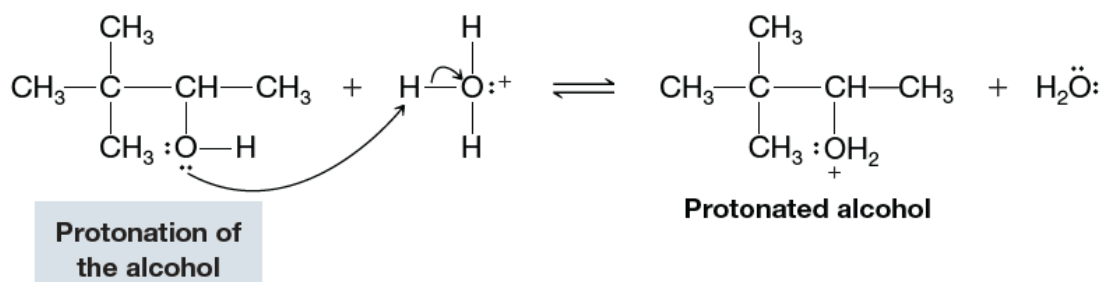
Rearrangements during Dehydration of Secondary Alcohols

Consider the **rearrangement** that occurs when 3,3-dimethyl-2-butanol is dehydrated:



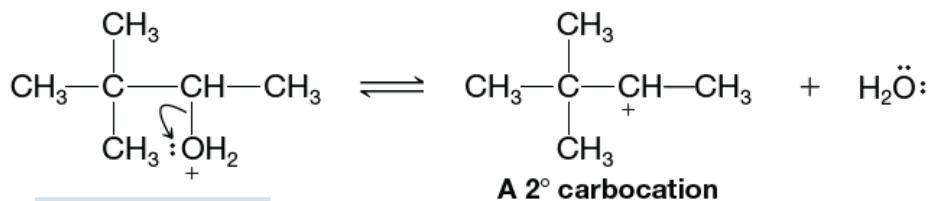
Step 1: The first step of this dehydration is the formation of the protonated alcohol in the usual way:

Step 1



Step 2: In the second step the protonated alcohol loses water and a secondary carbocation forms:

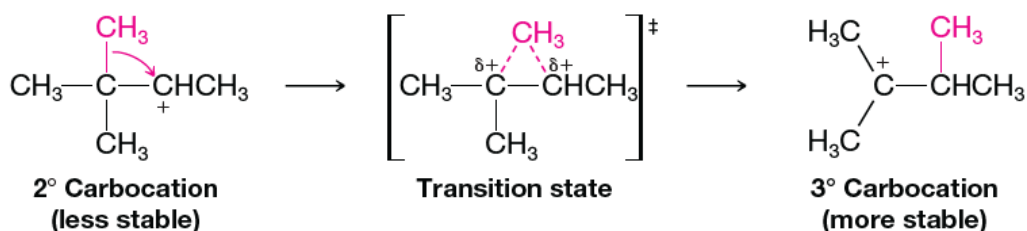
Step 2



Departure of a water molecule

Step 3: Now the rearrangement occurs. **The less stable, secondary carbocation rearranges to a more stable tertiary carbocation:**

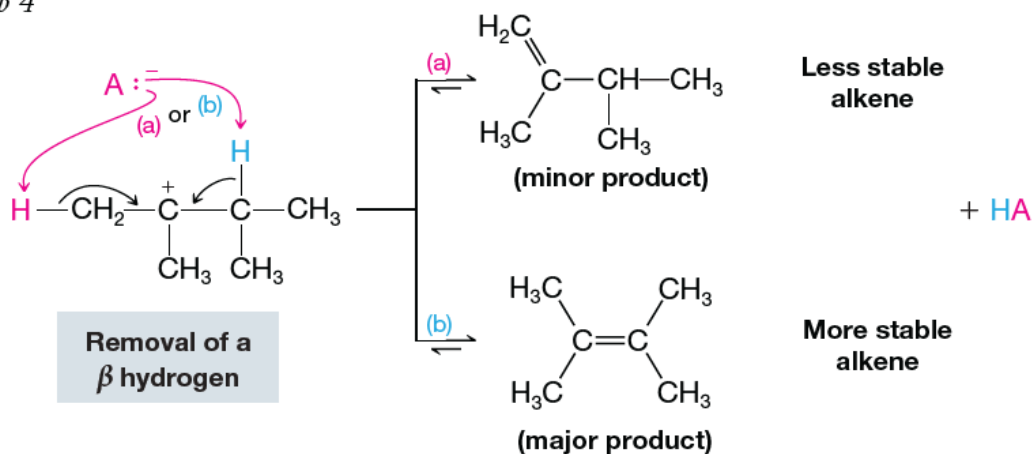
Step 3



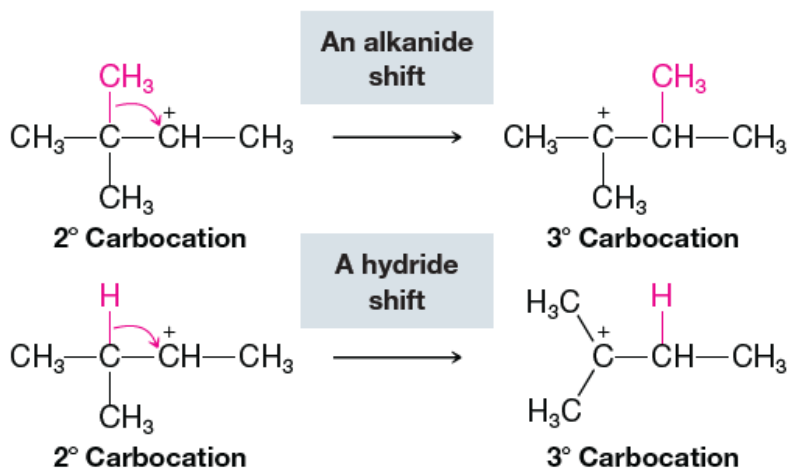
Rearrangement by migration of a methyl group

Step 4: The final step of the reaction is the removal of a proton from the new carbocation (by a Lewis base in the reaction mixture) and the formation of an alkene. This step, however, can occur in two ways:

Step 4



- The more favored product is dictated by the stability of the alkene being formed.
 - The conditions for the reaction (heat and acid) allow **equilibrium to be achieved** between the two forms of the alkene, and **the more stable alkene is the major product because it has lower potential energy.**
- Other common examples of carbocation rearrangements



Synthesis of Alkynes: Elimination Reactions

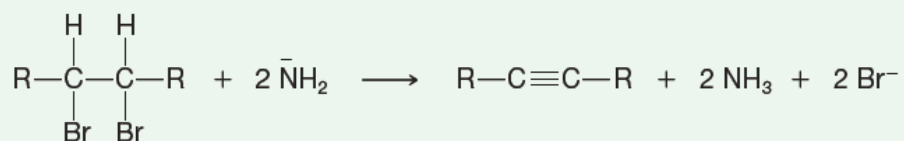
Dehydrohalogenation of Vicinal Dihalides

- A vicinal dibromide can be synthesized by addition of bromine to an alkene.
- The *vic*-dibromide can then be subjected to a double dehydrohalogenation reaction with a strong base to yield an alkyne.

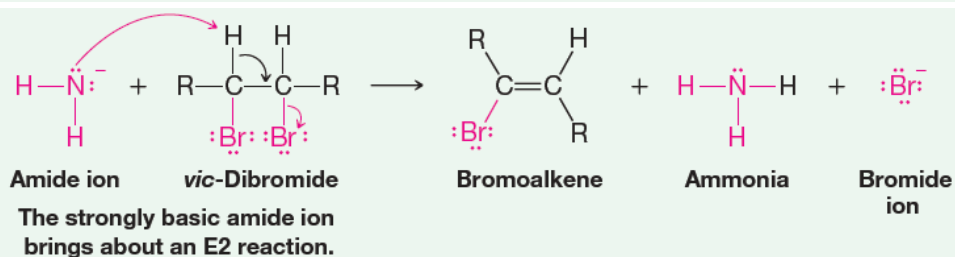


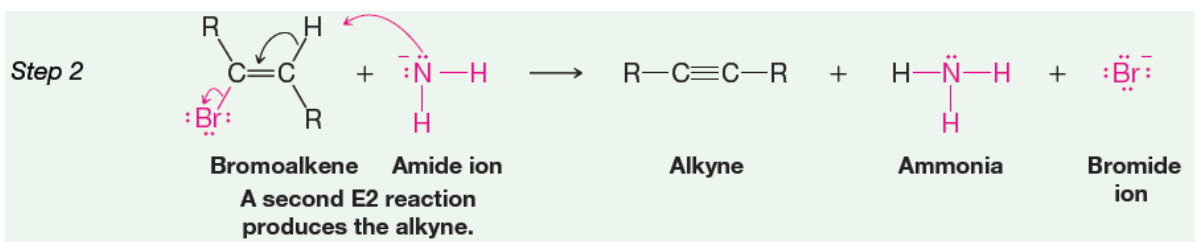
Mechanism for the Reaction

Reaction



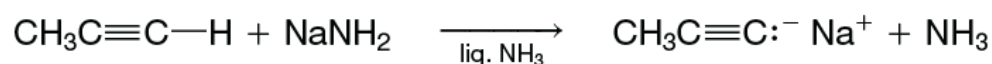
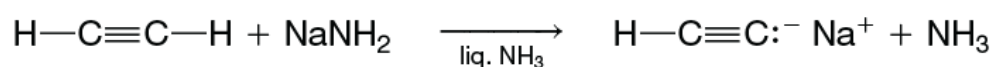
Step 1





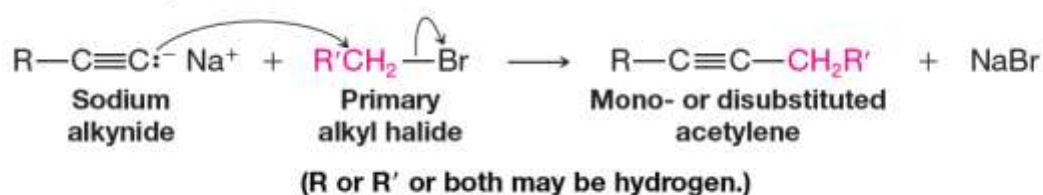
Terminal alkynes can be converted to nucleophiles for carbon-carbon bond formation

- The acetylenic proton of ethyne or any terminal alkyne can be removed with a strong base such as sodium amide (NaNH_2). The result is an alkynide anion.

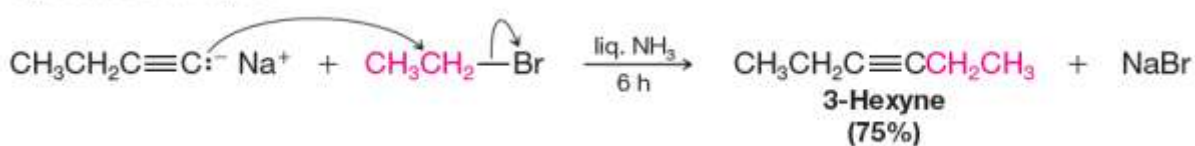


- Alkynide anions are useful nucleophiles for carbon-carbon bond forming reactions with alkyl halides.
 - The primary alkyl halide causes an $\text{S}_{\text{N}}2$ reaction.

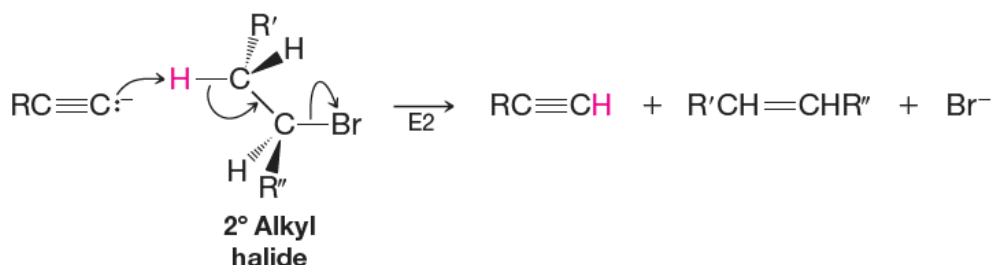
General Example



Specific Example



- The secondary and tertiary alkyl halides causes an E2 reaction.



Solved Example: Outline a synthesis of 4-phenyl-2-butyne from 1-propyne.

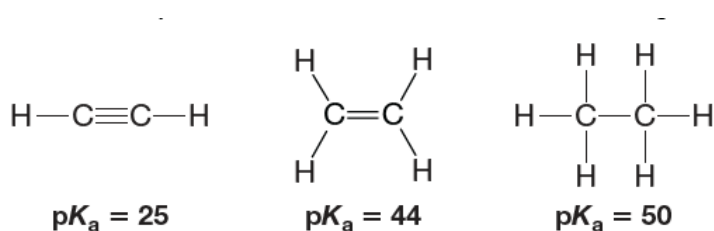
Solution:



The Acidity of Terminal Alkynes

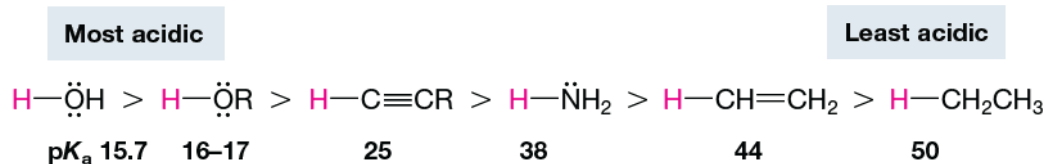
- The hydrogen bonded to the carbon of a terminal alkyne, called an **acetylenic hydrogen atom**, is considerably more acidic than those bonded to carbons of an alkene or alkane.

A terminal alkyne is
~10²⁰ times more
acidic than an
alkene or alkane.



- The order of basicity of their anions is opposite that of their relative acidity:

Relative Acidity



Relative Basicity

