Chapter 7
Alkenes; Elimination Reactions

Alkenes

Alkenes contain a carbon-carbon double bond. They are named as derivatives of alkanes with the suffix "-ane" changed to "-ene". The parent alkane is the longest continuous chain that contains the double bond. The double bond is specified by the number of the first carbon in the double bond and chain containing the double bond is numbered so as to give the first carbon the lowest number.

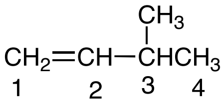
$CH_2{=}CH_2$ ethene (or ethylene)

$CH_2{=}CH{-}CH_3$ propene (or propylene)

$\underset{1}{CH_2}{=}\underset{2}{CH}{-}\underset{3}{CH_2}\underset{4}{CH_3}$ 1-butene

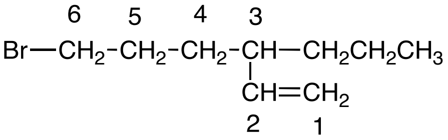
$\underset{1}{CH_3}{-}\underset{2}{CH}{=}\underset{3}{CH}{-}\underset{4}{CH_3}$ 2-butene

The double bond takes precedence over alkyl and halogen substituents.



$$\underset{1}{CH_2}{=}\underset{2}{CH}{-}\underset{3}{\overset{\overset{\displaystyle CH_3}{|}}{C}H}\underset{4}{CH_3}$$

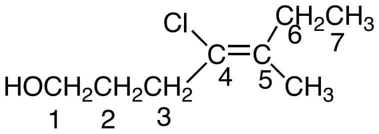
3-methyl-1-butene



$$Br{-}\overset{6}{CH_2}\text{-}\overset{5}{CH_2}\text{-}\overset{4}{CH_2}\text{-}\overset{3}{\underset{\underset{\displaystyle \underset{2}{CH}{=}\underset{1}{CH_2}}{|}}{C}H}{-}CH_2CH_2CH_3$$

6-bromo-3-propyl-1-hexene

Carbon-carbon double bonds take precedence over alkyl groups and halogens but hydroxyl groups take precedence over the double bond and so get the lowest number. The number specifying the position of the double bond is put before the number specifying the position of the hydroxyl group.



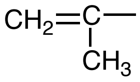
4-chloro-5-methyl-4-hepten-1-ol.
or: 4-chloro-5-methylhept-4-en-1-ol.

Some common names:

$CH_2{=}CH{-}$ vinyl group

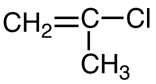
$CH_2{=}CH{-}CH_2{-}$ allyl group

$CH_2{=}CH{-}CH_2\text{-}OH$ allyl alcohol



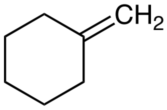
$$CH_2{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}$$

isoprenyl group



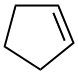
$$CH_2{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}Cl$$

When a $-CH_2$ is doubly bonded to a ring, use methylene.

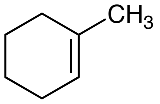


methylenecyclohexane

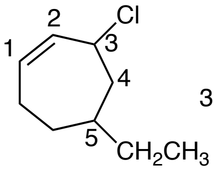
Cycloalkenes: There is no need to specify the position of the double bond since it will automatically get number one. Then number around the ring so as to give the lowest number to the substituents at the first point of difference.



cyclopentene

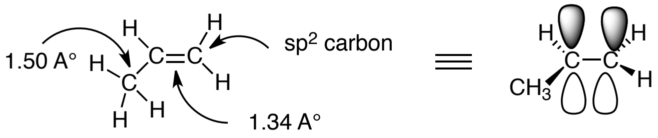


1-methylcyclohexene



3-chloro-5-methylcycloheptene

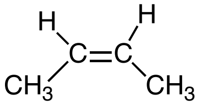
Review of Structure and Bonding



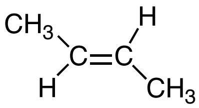
The p orbitals of the π–bond are perpendicular to the plane of the sigma framework.

Cis and *Trans* Isomerism

There is no free rotation around a carbon-carbon double bond and so alkenes can exist as *cis* or *trans* isomers.

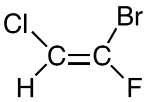


cis-2-butene



trans-2-butene

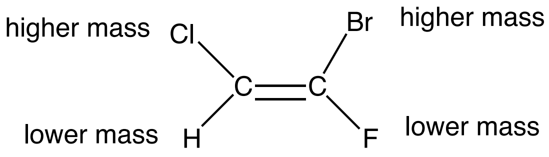
The *cis* or *trans* nomenclature is useful when the two substituents are the same or similar but what about the following?



For molecules such as this we need a new system, E or Z, that is based on the atomic number.

Rules for assigning the alkene configuration as E or Z:

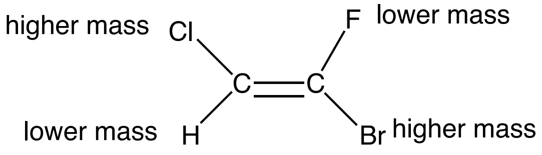
(1) Compare the atomic numbers of the substituents attached to the same carbon. Indicate which is higher and which is lower.
(2) If the two higher substituents are on the same side, this is the Z configuration (from the German zusammen which means together).
If the two higher substituents are on opposite sides, this is the E configuration (from the German entgegen which means opposite).



Z-1-bromo-2-chloro-2-fluoroethene

Compare substituents at the same carbon. Here the two higher substituents are on the same side. This is therefore the Z isomer.

For:

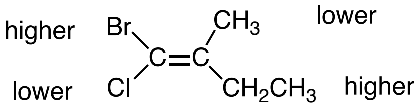


E-1-bromo-2-chloro-2-fluoroethene

Compare substituents at the same carbon. Here the two higher substituents are on opposite sides. This is therefore the E isomer.

For more complicated cases we need more rules.

(3) When two atoms are the same, compare the higher atoms attached to these atoms. Precedence is determined at the first point of difference.

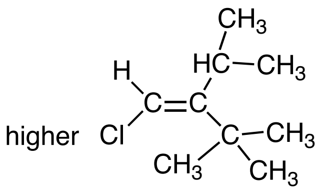


Write the ethyl group as [-C(C,H,H)]

Write the methyl group as [-C(H,H,H)]

In comparing methyl and ethyl, we see that the first two atoms are the same, both carbons. Write these down and then list the atoms that are attached to these two atoms, listing the higher atom(s) first. Now compare each of these atoms in turn. With methyl, the three substituents are all H's but with ethyl we have C, H, H. Clearly, the carbon is heavier than the hydrgoen, so the ethyl group has a higher priority than methyl. This is the E-isomer.

For:

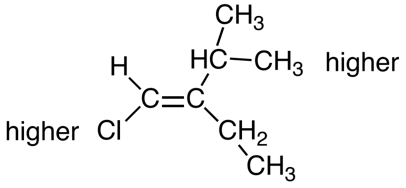


Z-isomer

-C(C,C,H)

-C(C,C,C) Higher priority, since the third C has a higher mass than H.

For:



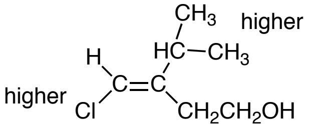
E-isomer

-C(C,C,H)

-C(C,H,H)

Higher priority since the second C has higher mass than the H.

(4) Work outward from the point of attachment, comparing all of the atoms to a particular atom before proceeding farther along the chain.



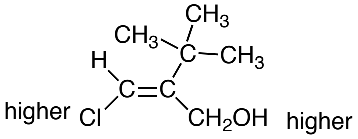
E-isomer

-C(C,C,H)

-C(C,H,H)

The oxygen does not enter into the priority scheme here since the rule is to compare all the atoms attached to a particular carbon before preceeding on. We see that the two substituents both have a C and then compare what is attached to that first carbon before proceeding on.

(5) Always evaluate the individual atoms one by one, not as a group.



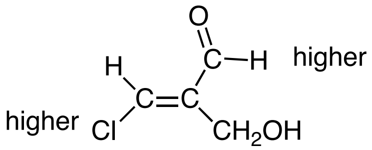
Z-isomer

-C(C,C,C)

-C(O,H,H)

Again, the first atoms are both carbons. then compare atoms are attached to these carbons, listing the higher atoms first. Oxygen has a higher mass than carbon, so the $-CH_2$ group takes priority over the *t*-butyl group.

(6) An atom that is multiply bonded to another atom is considered to be duplicated as a substituent. List it twice.

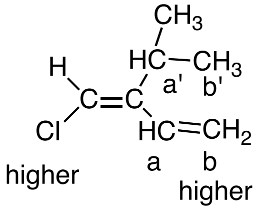


E-isomer

-C(O,O,H)

-C(O,H,H)

(7) If two atoms in the chain have the same priority, move out to the next heaviest substituent in the chain and compare the atoms that are attached to these atoms.



Z-isomer

-C(C,C,H)
a'

-C(C,C,H)
a

} same

-C(C,H,H,H)
b'

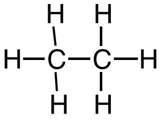
-C(C,C,H,H) higher prioity
b

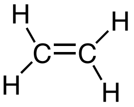
the first atoms have the same substitutent; move out on the chain and compare the next heaviest substituent.

Physical Properties

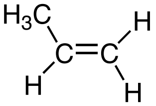
Alkenes are generally non-polar, like alkanes, and have fairly low boiling points.

Alkenes are electron deficient. They are missing two electrons as compared to alkanes.

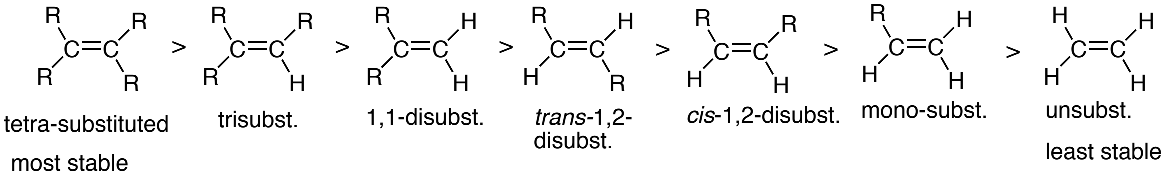

14 electrons


12 electrons

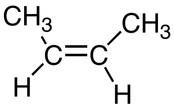
Alkyl groups donate electrons to the electron deficient alkene to help stabilize it. The alkyl group is a much better electron donor than a hydrogen.

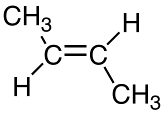


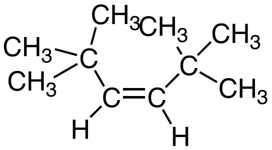
From measuring heats of combustion, we learn that alkyl substituents on a double bond help to stabilize it. The more substituted with electron donating alkyl groups, the more stable it is.

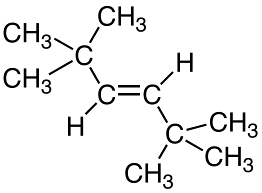


This donation of electrons by the alkyl to stabilize the double bond is called an electronic effect. There is also a steric effect due to van der Waals strain. The *cis*-isomer is slightly higher in energy than the *trans*, since the two alkyl groups are large and the electrons repel each other slightly. Note that the alkyl groups lie in the same plane and so are eclipsed in the *cis*-isomer. As the alkyl groups become larger, the steric hindrance becomes larger and the difference in energy between the *cis*- and *trans*-isomers also becomes larger.




3 KJ/mol lower in energy

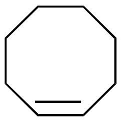



44 KJ/mol lower in energy

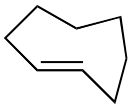
Cycloalkenes

Cyclopropene exists and is actually found in nature. It is highly strained. The smallest ring size that will contain a *trans*-double bond is eight.

cyclopropene
stable but highly strained



cis-cyclooctene

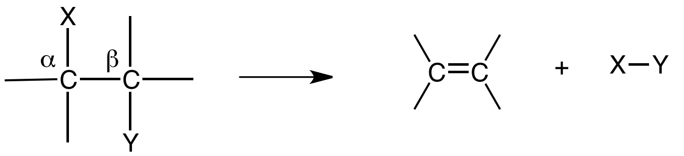


trans-cyclooctene

39 KJ/mol higher in energy than the *cis*-isomer. Not stable above -90°C.

Elimination Reactions: Preparation of Alkenes

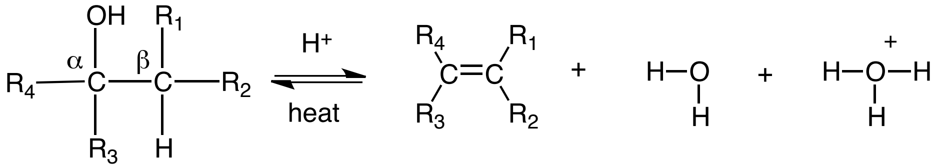
These are called β–eliminations or 1,2 eliminations.

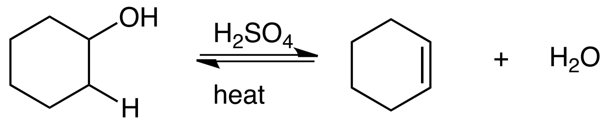


X and Y must be on adjacent carbons.

Dehydration of Alcohols

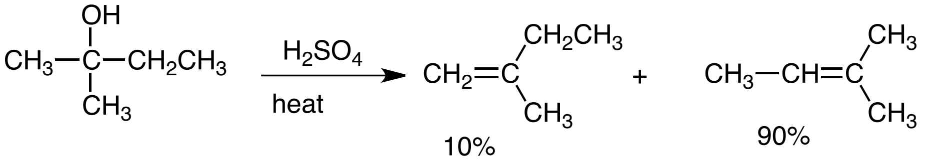
When alcohols are heated with a catalytic amount of acid, they lose water to form alkenes. The acid is not used up but is catalytic in that it speeds up the reaction and is recovered to be used again.





We see that tertiary alcohols react faster than secondary, which react faster than primary alcohols. (3° > 2° > 1°)

With unsymmetrical alcohols, we see that the more substituted alkene is usually formed as the major product. This is called Zaitsev's rule. The β–hydrogen is removed from the carbon with the least number of hydrogens so as to form the alkene that has more alkyl substituents. The alkene which has the more electron donating alkyl groups is the more stable alkene.



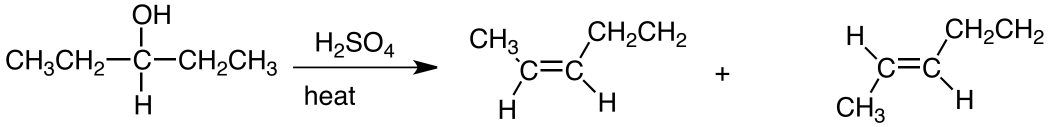
10% disubstituted double bond

90% trisubstituted double bond; more stable

When there are two possible products of a reaction and one is formed in greater amounts, we say that this reaction is regioselective.

When two stereoisomers are possible and one of them is formed in greater amounts, we call this reaction stereoselective as in the following example. We see that the *trans*-isomer is the major product because it is more stable.

This is a general trend: usually in acidic condition, when the reaction is reversible, the major product will be the more stable product.



cis-2-pentene (25%)

trans-2-pentene (75%)

Mechanism

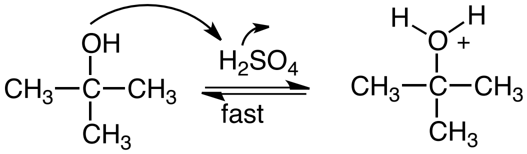
There are two mechanisms that occur, depending on the substrate. With tertiary substrates we see the E1 mechanism that involves a carbocation and is analogous to the S_N1 mechanism with tertiary alcohols. With primary substrates we see the E2 mechanism that does not involve a carbocation and is analogous to the S_N2 reaction.

With secondary alcohols we usually see the E1 mechanism with the carbocation intermediate.

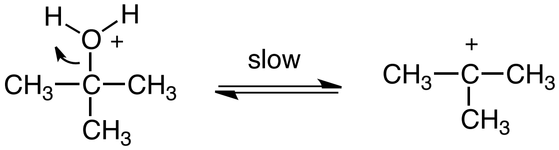
E1 Mechanism

The E1 mechanism is observed with tertiary alcohols and is similar to the $S_N1$reaction of tertiary alcohols with hydrogen halides. Both reactions are catalyzed by acid and both involve a carbocation intermediate. The E1 reaction occurs in three steps, like the S_N1 reaction. The first two steps of the E1 and S_N1 reactions of tertiary alcohols are identical. It is the third step that is different.

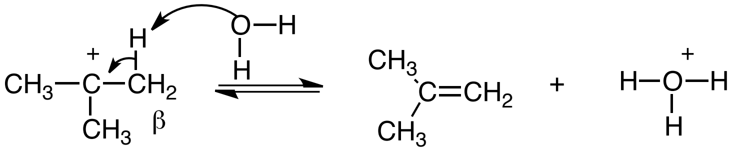
Step 1: We have rapid protonation of the alcohol oxygen. This makes it into a good leaving group.



Step 2: We have formation of a carbocation by loss of water. This is the slow, rate determining step. It is slow (endothermic) because a bond is cleaved but no bond is formed.



Step 3: This step is a relatively fast acid-base reaction in which a β–proton is remove by water acting as a base. The two electrons that were in the β C-H bond go to form the π–bond of the alkene.

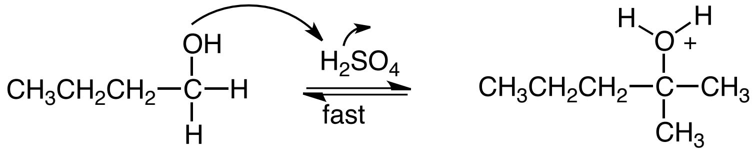


It is important to note that each of these steps is reversible. In the next chapter we will see the reverse reaction, the hydration of the alkene to give the alcohol. Both the forward dehydration reaction and the hydration reaction are very important reactions. In the dehydration reaction under discussion here, we drive the equilibrium in favor of alkene formation by removing the water as it forms. As we will see, in the hydration reaction, to add water to the double bond, we use an excess of water.

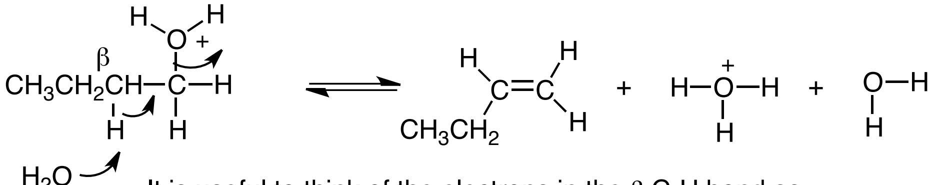
E2 Mechanism

With primary alcohols we have the E2 mechanism. The "2" indicates that the reaction is bi-molecular in the rate determining step. There are two steps overall.

Step 1: The first step is the same as in the first step of the E1 reaction. It is the reversible protonation of the alcohol oxygen to make it into a good leaving group.



Step 2: There is no carbocation intermediate. The primary carbocation that would be involved is too high in energy and so we get removal of the β–proton and loss of the water occurring at the same time in one step.

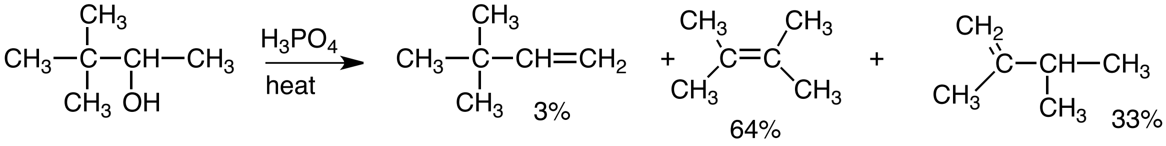


It is useful to think of the electrons in the β C-H bond as helping to push out the departing water as the π–bond forms.

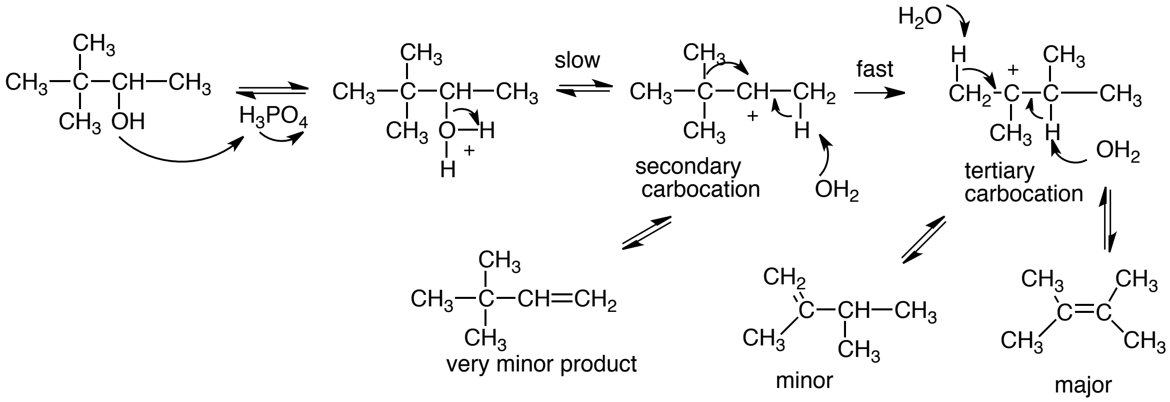
Rearrangement Reactions

As a general rule, whenever we see carbocation intermediates, the carbon skeleton will rearrange either through the shift of an alkyl group or a hydride. This shift occurs so as to form a more stable carbocation intermediate. If such rearrangement is possible it will occur and it is very rapid.

For example:

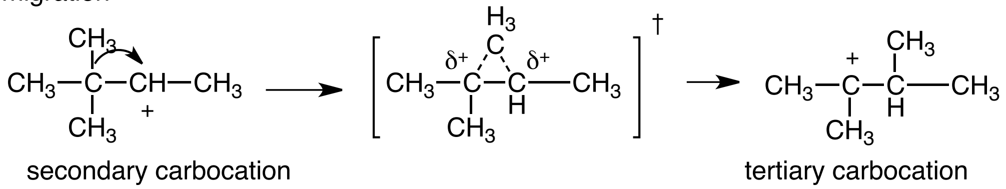


Here we see a methyl group migration that changes a secondary carbocation into a more stable tertiary carbocation.

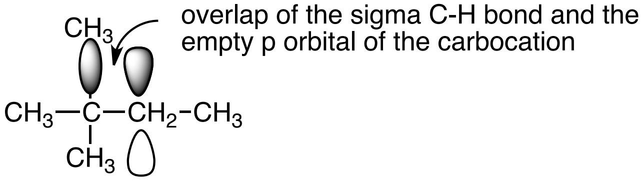


In the transition state for the methyl migration, the methyl group is partially bonded to both carbon atoms.

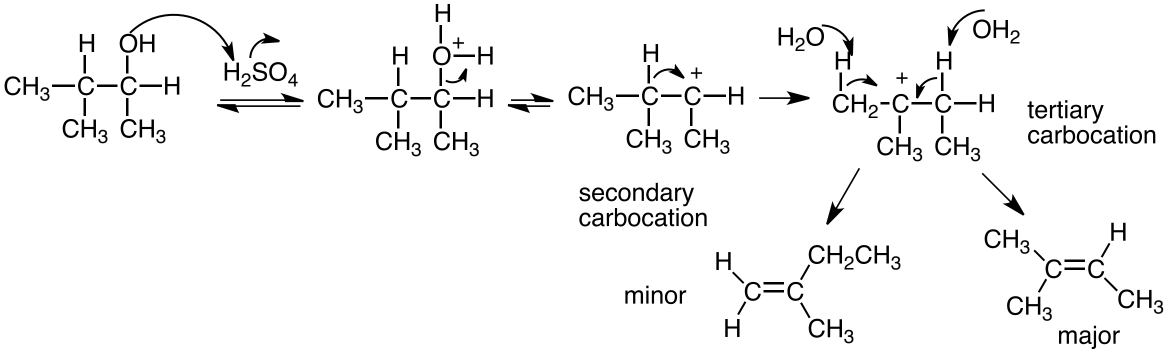
Methyl group migration



These rearrangements reactions are very fast. There is a small energy barrier to the migration. The empty p orbital of the carbocation overlaps with the adjacent C-H sigma bond.

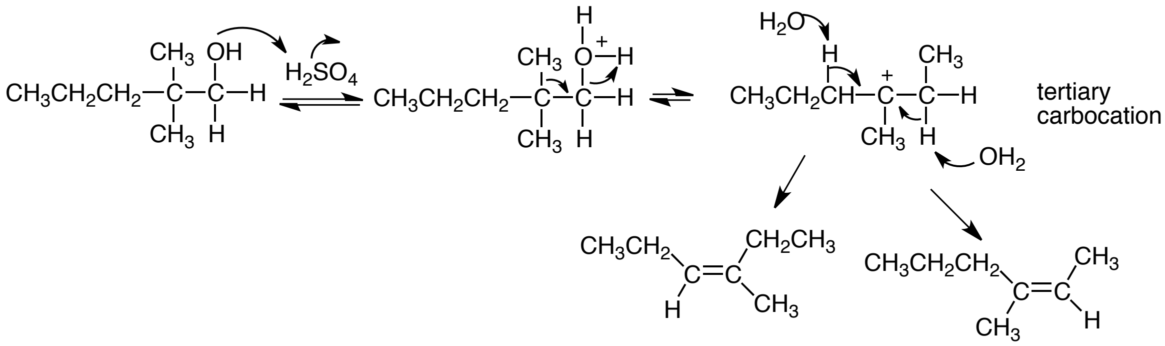


We can also have migration of a hydride with its two electrons.

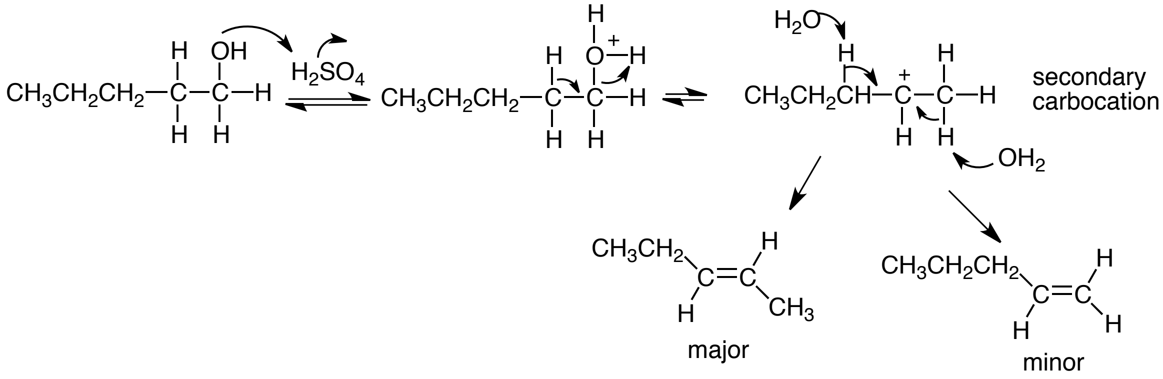


With primary alcohols, we do not see a carbocation but there can still be rearrangements. The migration of the alkyl group or hydride occurs at the same time as loss of the protonated alcohol.

methyl migration

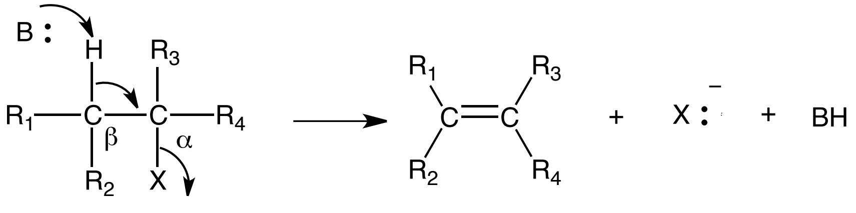


Hydride migration

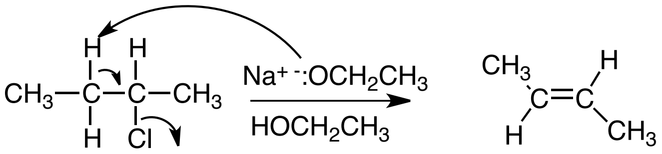


Dehydrohalogenation

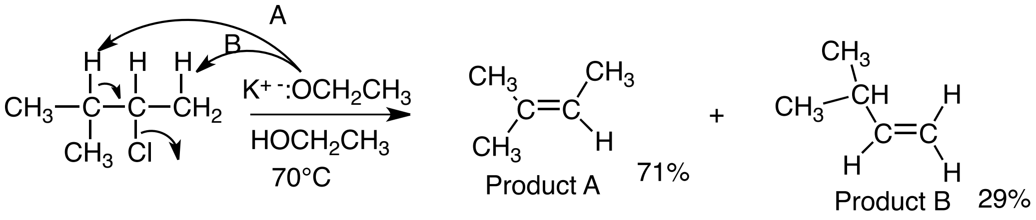
Dehydrohalogenation occurs in basic conditions with loss of H-X to make an alkene.



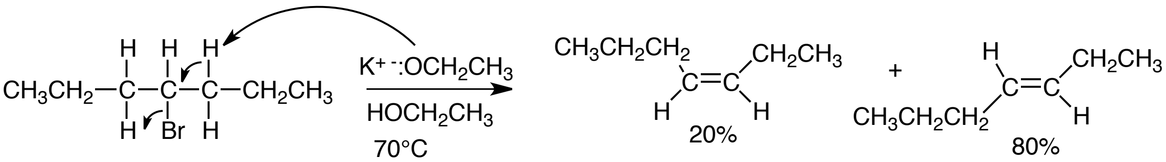
A relatively strong base such as sodium ethoxide ($NaOCH_2CH_3$) in ethanol as the solvent is needed to remove the β-hydrogen.



We usually form the more substituted alkene according to Zaitsev's rule.



And the *trans* or E-alkene is also usually favored since it is lower in energy due to the fact that it is less hindered.



Mechanism for Dehydrohalogenation

This is an E2 reaction. Some experimental facts:

(1) The reaction follows second order kinetics, meaning there are two reactive species in the transition state that participate in the reaction.

Rate = k [alkyl halide] [base]

(2) The rate increases with decreasing strength of the R-X bond.

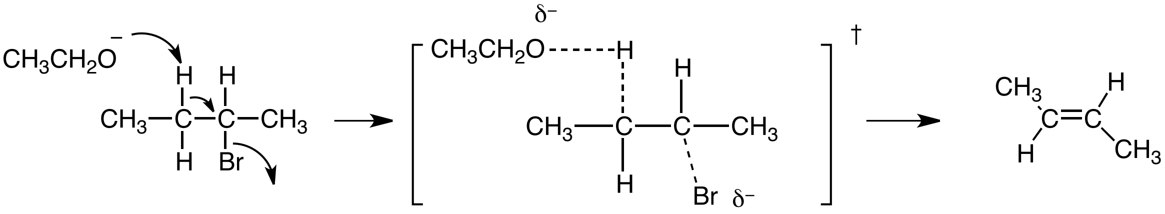
Rate R—I > R—Br > R—Cl > R—F

weakest C-X bond;
fastest elimination reaction

strongest C-X bond;
slowest elimination reaction

Four things happen all at once
(1) Formation of a new bond between the base, B, and the β-hydrogen.
(2) Breaking of the β C-H bond.
(3) Formation of the new carbon-carbon double bond.

(4) Breaking of the C-X bond.

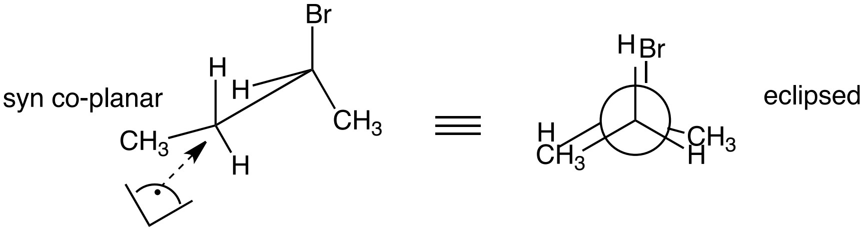


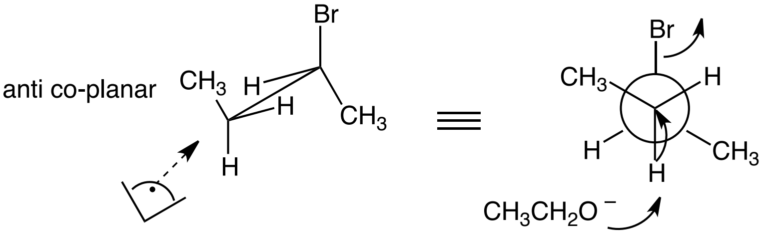
There is a partial double bond in the transition state. Since the double bond that has more electron donating alkyl groups is lower in energy, it forms faster than the less substituted double bond. A good way to think of this reaction is that the two electrons in β C-H bond, move to from the new π–portion of the double bond and push out the two electrons in the C-Br bond.

Anti-Elimination.

There is also a geometrical requirement in the elimination reaction. The two main orbitals involved – the β C-H bond and the C-X bond to the leaving group – must be in the same plane. In for the two electrons to move from the β C-H bond to form the new π–bond and kick out the C-Br electrons, the electrons must be also to interact with each other. As we know, these electrons are confined to their orbitals, so in order for these electrons to interact the orbitals must overlap in space. They must be co-planar.

There are two ways this can happen. The leaving group X and the β C-H can be syn co-planar or anti co-planar. In the syn co-planar conformation, all of the bonds are eclipsed. This is higher in energy than the anti cop-planar conformation in which all the bonds are staggered.

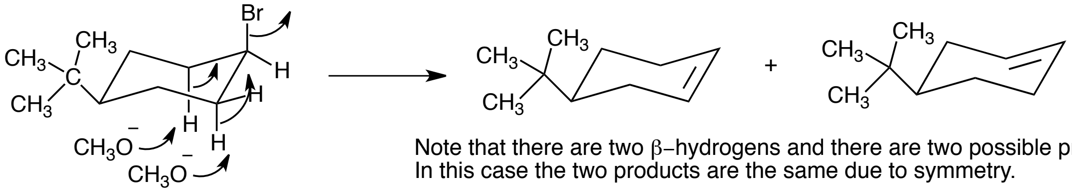




staggered conformation, much lower in energy than the eclipsed conformation of the syn co-planar conformation.

Therefore, in cyclohexane rings, the leaving group must be axial and there must also be an axial proton in the β–position.

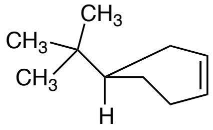
Cis-1-bromo4-*t*-butylcyclohexane undergoes elimination rapidly because there is an axial bromine in the low energy conformation which places the large *t*-butyl group in the equatorial position. Note that there are two β–hydrogens and that elimination of either one can occur and so there are two possible products. In this case, however, due to symmetry, the two possible products are the same molecule.



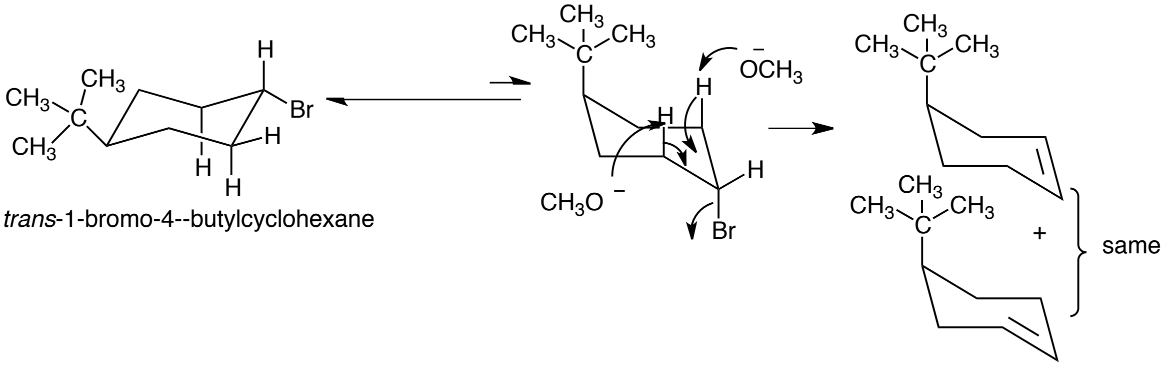
cis-1-bromo-4--butylcyclohexane

Note that there are two β–hydrogens and there are two possible products. In this case the two products are the same due to symmetry.

Note also that when we put a double bond into the chair conformation of cyclohexane, the chair becomes distroted due to the 120° angles around the sp^2 carbons.



But we see that the *trans*-isomer undergoes elimination very slowly since the low energy conformation has an equatorial *t*-butyl group and an equatorial bromine. In order for elimination to occur, the molecule must undergo a ring flip that puts the bromine in the axial position and the *t*-butyl group would also be in an axial position. This is a very high energy conformation and there will be a low concentration of this species present at any given time. Again, there are two β-hydrogens, leading to two possible products. Again, in this case, due to symmetry, the products are the same.



trans-1-bromo-4--butylcyclohexane

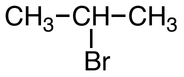
Isotope Effects

Using a deuterium instead of hydrogen can give information on the mechanism of a reaction. Deuterium undergoes the same reactions as hydrogen but the rates of the reaction may be different.

A carbon-deuterium is ~12 KJ/mol stronger than a carbon-hydrogen bond. Therefore, there is a slightly greater activation energy for breaking a C-D bond than for a C-H bond. Therefore the rate constant for a step in which a C-D bond is broken is smaller for for a C-H bond.

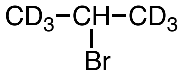
This is called a kinetic isotope effect where the rate of the reaction using hydrogen (K_H) is greater than the rate when using a deuterium (K_D) by a factor of 3-8 (K_H/K_D= 3-8).

For an E2 reaction, in which a C-H bond (or a C-D) bond is broken in the rate determining step, there is a kinetic isotope effect of 6.7.



$CH_3{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}CH_3$

versus



$CD_3{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}CD_3$

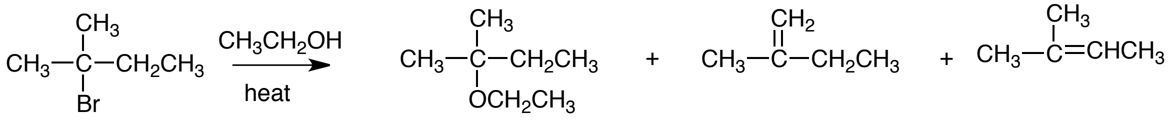
$K_H/K_D = 6.7$

E1 Mechanism

Just the substitution reaction can occur in one step (S_N2) or two steps (S_N1), the elimination reaction also can occur by means of two different mechanisms. As discussed above, the E2 mechanism is bimolecular and occurs in one step. The E1 reaction is analogous to the S_N1 mechanism and occurs in two steps by means of a carbocation intermediate.

We see the E1 mechanism when we have a tertiary substrate and a weak base. Very often the base is the solvent (an alcohol or water) and we call this a solvolysis reaction. Very often we see a combination of E1 and S_N1 reactions occurring together.

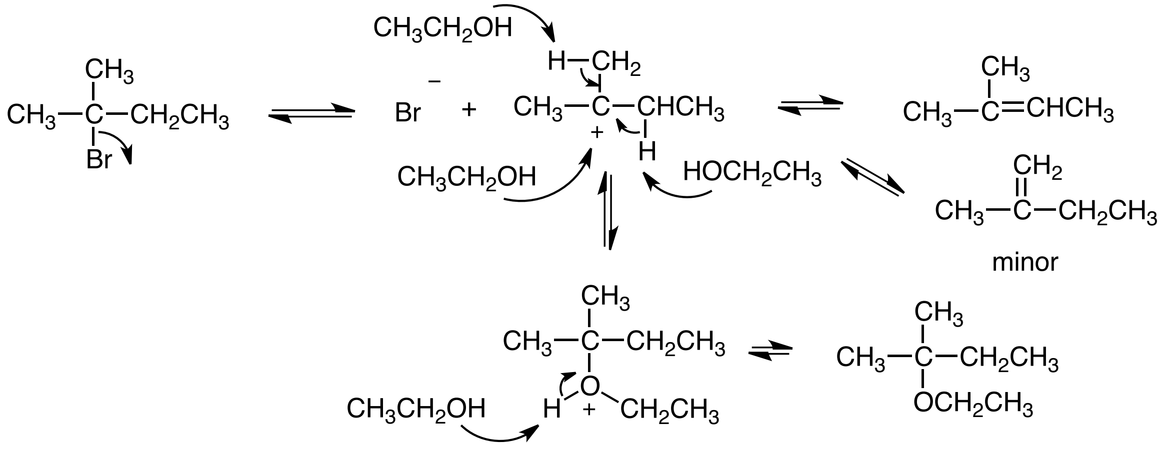
For example:



The mechanism: The first step is the formation of a carbocation. This is a unimolecular step. The bromine leaves to form a carbocation that is stabilized by the solvent. Now the solvent ethanol can attack the carbocation directly in an S_N1 reaction or it can act as a base to remove an α–proton to form an alkene. Two α–protons are available. The major alkene product will be the more substituted alkene in accordance with Zaitsev's rule, since it is the more stable product.

The proportion of substitution will depend on the substrate, the base and the reaction conditions but usually there is a mixture of both products. Higher temperature favors elimination, since it has the higher activation energy.

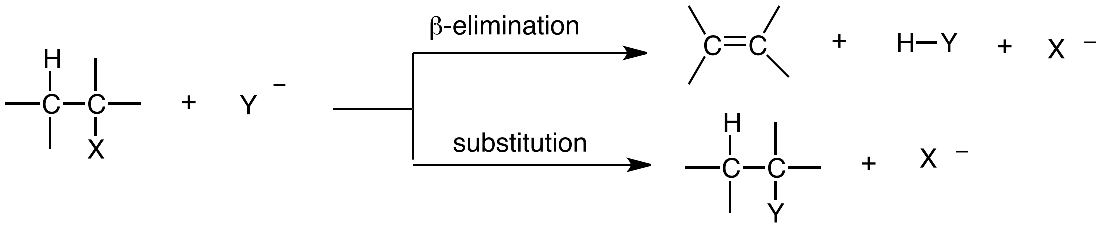
Note also that rearrangements can occur in E1 conditions, since there is a carbocation intermediate.



E1 reactions are not too useful synthetically. If the elimination product is the desired goal, then a strong base is generally used so as to favor the E2 mechanism.

Substitution Versus Elimination

Many good nucleophiles are also strong bases and so we often see a competition between substitution and elimination.

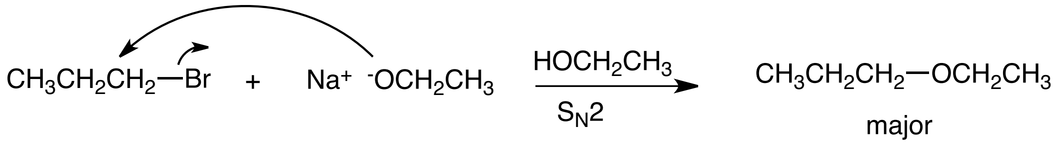


How can we predict which reaction will occur?
There are two important factors:
(1) The structure of the alkyl halide substrate
(2) The basicity of the anion

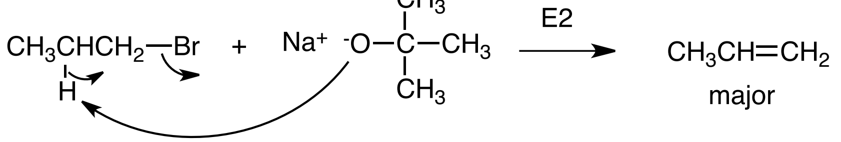
In general, the more hindered the substrate and the more hindered the nucleophile, the more elimination is favored over substitution and the more basic the nucleophile, the more elimination is favored over substitution.

With Primary (1°) Substrates:

Substitution is favored over elimination, even with strong bases such as RO^- and HO^- except with very hindered nucleophiles such as *t*-butoxide.

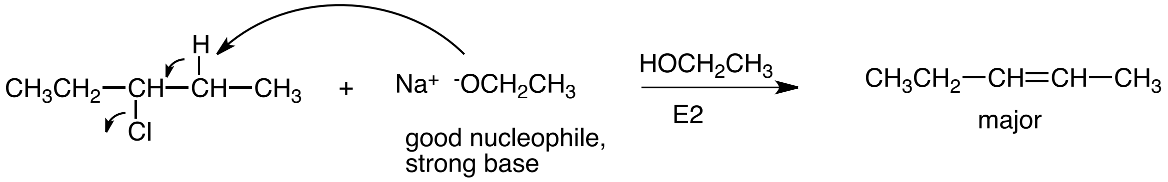


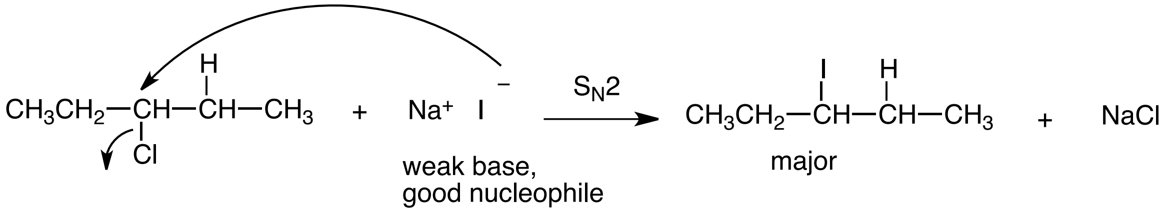
BUT:



With Secondary (2°) Substrates:

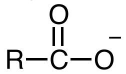
We see mainly elimination except with nucleophiles that are relatively weak bases.





Other examples of species that are good nucleophiles but relatively weak bases and so give mainly S_N2 reactions with secondary substrates are:

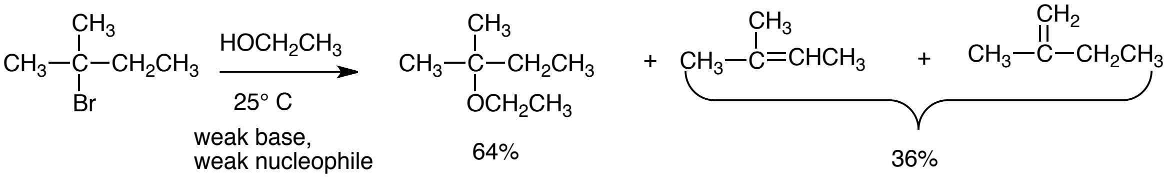
I^- Br^- Cl^- RS^- HS^- $N{\equiv}C:^-$

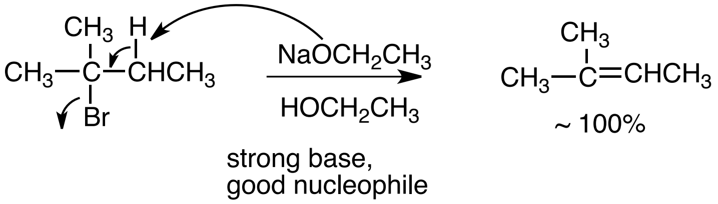


$R-\overset{\overset{O}{\|}}{C}-O^-$ N_3^- R_3N

With tertiary (3°) Substrates:

Elimination reactions are favored with strong bases such as RO^- and HO^-. In solvolysis conditions and with weak bases, there is a combination of competing S_N1 and E1 reactions. Substitution generally prevails over elimination but there is always a mixture of the two products.





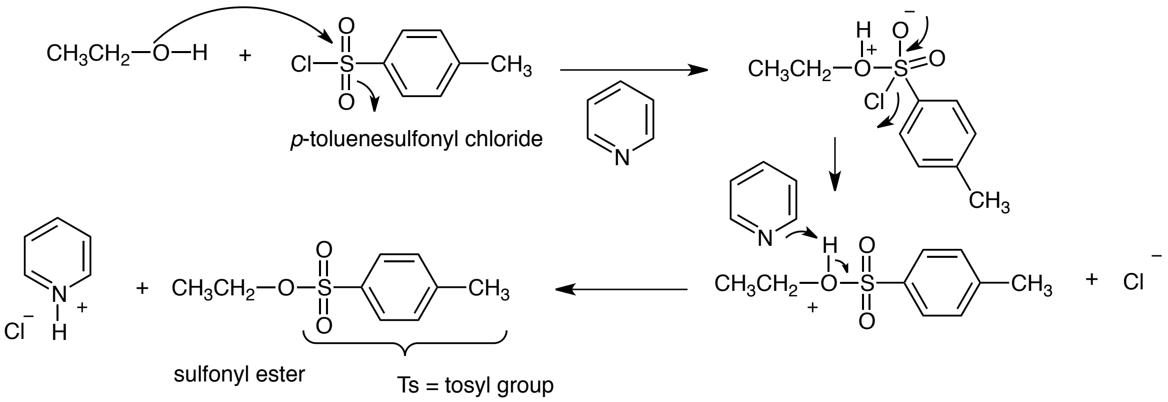
Increasing the reaction temperature will tend to favor elimination over substitution. In elimination reactions we are breaking two relatively strong sigma-bonds and forming one sigma-bond and a relatively weaker π–bond.

In practical terms, if an elimination reaction is desired, use strong E2 conditions (high temperature and a hindered strong base).

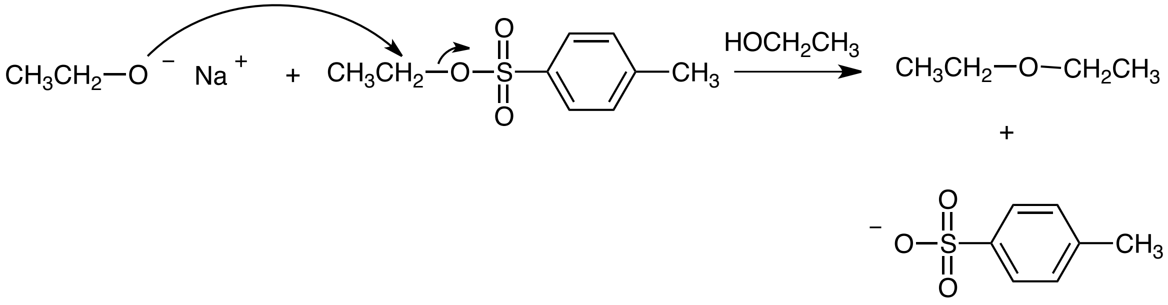
To favor a substitution reaction, use lower temperature, an unhindered nucleophile and an unhindered substrate.

Sulfonate Esters

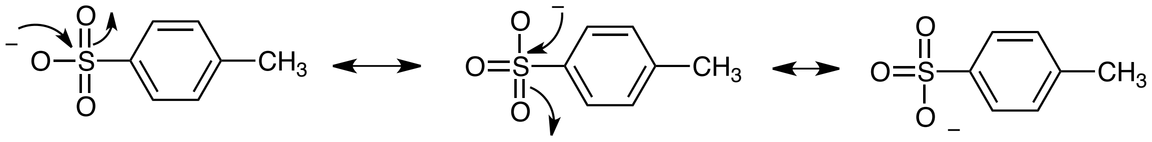
Alkyl sulfonates esters are also very good leaving groups, similar in leaving group ability to halogens. They are prepared from alcohols by reaction with a sulfonyl chloride. A common sulfonyl chloride is *p*-toluene sulfonyl chloride. Generally a mild, non-nucleophilic base such as pyridine or triethyl amine is used to neutralize the HCl that is formed in the reaction.



The sulfonyl ester can then be attacked by strongly basic nucleophiles to give substitution products with loss of the tosyl group.

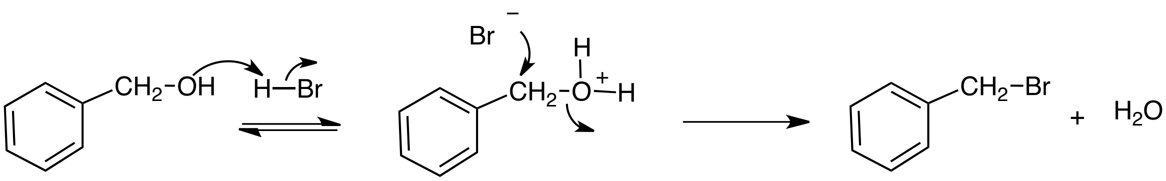


The tosyl group is a very good leaving group, equivalent to a halogen, because it forms a resonance-stabilized anion that is a weak base. Remember, by definition, a good leaving group is a weak base.



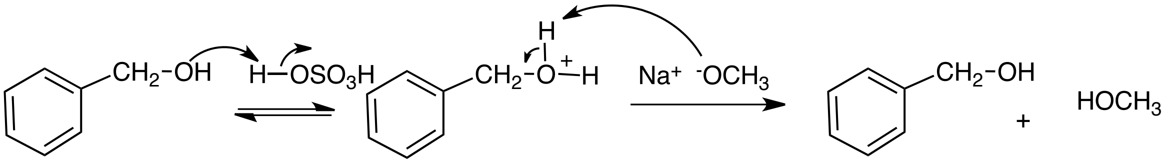
The (-) charge is spread out over all three oxygens and is thereby stabilized.

Note that the overall effect of making the alcohol into the tosylates is to convert the OH group into a good leaving group under mild, non-acidic conditions. As we have learned, we can convert the OH group into a good leaving group by protonation but this restricts the nucleophiles we can use to those that are very weakly basic such as the halogens.

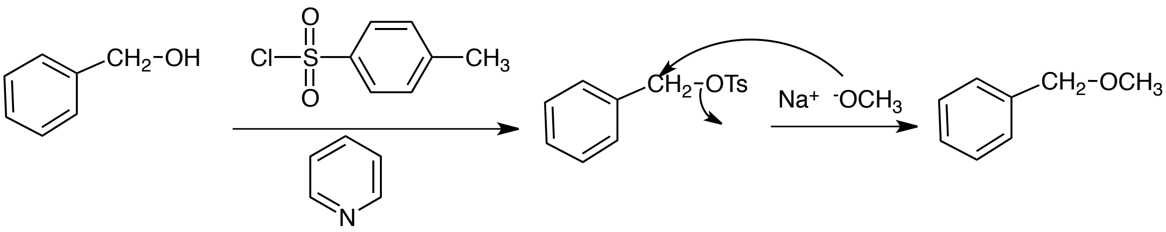


The Br$^-$ is a very weak base and will not deprotonate the oxygen.

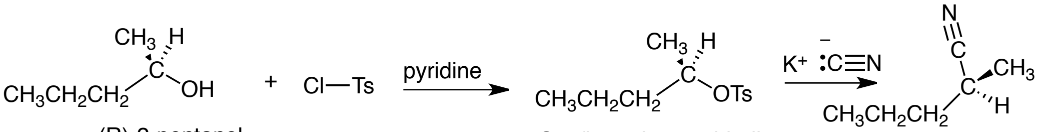
If we tried to do this same type of reaction with a more basic nucleophile like CH_3O^-, we would simply deprotonate the hydroxyl group in an acid-base reaction rather than a substitution reaction. Recall that the fastest reactions are always the proton transfer reactions.



So, if we first make the tosylates we can safely react it with the basic sodium methoxide and get an excellent yield of the substitution product.



Note that the stereochemistry of the C-O bond does not change when the tosylates is made but it does undergo inversion in the subsequent S_N2 reaction.



(R)-2-pentanol

Configuration at chirality center is still (R).

(S)- configuration at chirality center.