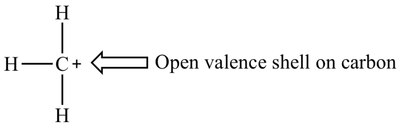
Carbocations: A Tutorial

Tutorial Contents

A. Introduction

A **carbocation** is molecule having a carbon atom bearing three bonds and a positive formal charge. Carbocations are generally unstable because they do not have eight electrons to satisfy the octet rule.

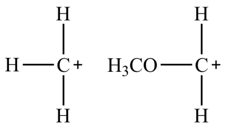


$\mathrm{H}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}+$

Open valence shell on carbon

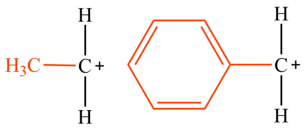
B. Carbocation Classification

In order to understand carbocations, we need to learn some basic carbocation nomenclature concerning the number of carbon groups bonded to the open valence shell carbon. A carbocation in which the open valence shell carbon is not bonded to any carbon groups is termed a **methyl carbocation**. A **primary carbocation (1^o carbocation)** is one in which there is *one* carbon group attached to the carbon bearing the positive charge. (These groups are shown in red below.) A **secondary (2^o) carbocation** is one in which there are *two* carbons attached to the carbon bearing the positive charge. Likewise, a **tertiary (3^o) carbocation** is one in which there are *three* carbons attached to the carbon bearing the positive charge.

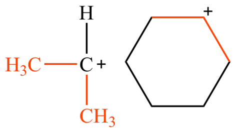


$\mathrm{H}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}+ \quad \mathrm{H_3CO}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}+$

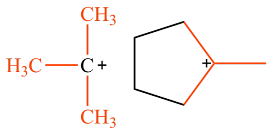
Methyl carbocations
No C–C^+ bonds



Primary (1^o) carbocations
One C–C^+ bond

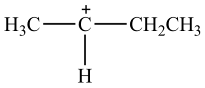


Secondary (2^o) carbocations
Two C–C^+ bonds

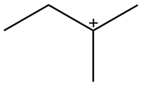


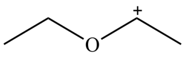
Tertiary (3^o) carbocations
Three C–C^+ bonds

Exercise 1: Label each carbocation as primary, secondary, or tertiary.

(a) 

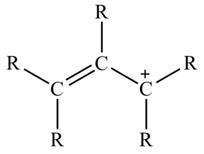
$\mathrm{H_3C}-\underset{\mathrm{H}}{\overset{+}{\mathrm{C}}}-\mathrm{CH_2CH_3}$

(b) 

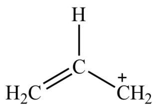
(c) 

Exercise solutions can be found at the end of this tutorial.

When the carbon bearing the positive charge is immediately adjacent to a carbon-carbon double bond, the carbocation is termed an allylic carbocation. The simplest case (all R = H) is called the allyl carbocation.

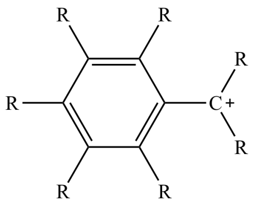


General allylic carbocation structure

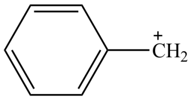


The allyl carbocation

When the carbon bearing the positive charge is immediately adjacent to a benzene ring, the carbocation is termed a benzylic carbocation. The simplest case is called the benzyl carbocation.

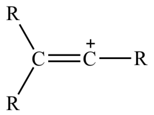


General benzylic carbocation structure

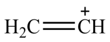


The benzyl carbocation

When the carbon bearing the positive charge is part of an alkene, the carbocation is termed a vinylic carbocation. The simplest case is called the vinyl carbocation. Note that the carbon bearing the positive charge has two attachments and thus adopts *sp* hybridization and linear geometry.

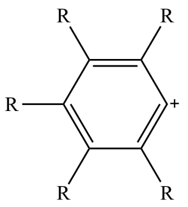


General vinylic carbocation structure

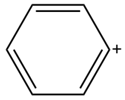


The vinyl carbocation

When the carbon bearing the positive charge is part of a benzene ring, the carbocation is termed an aryl carbocation. The simplest case is called the phenyl carbocation.



General aryl carbocation structure



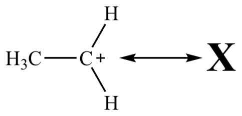
The phenyl carbocation

C. Carbocation Stability

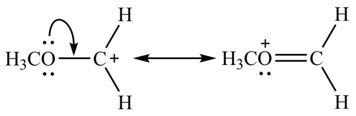
The stability of carbocations is dependent on a few factors. The first factor to look at when deciding the stability of a carbocation is resonance. Resonance is (usually) a carbocation-stabilizing feature because it delocalizes the positive charge and creates additional bonding between adjacent atoms. Decreasing the electron deficiency increases the stability.

Having trouble with resonance? Consult the resonance tutorials on the course web site (http://web.chem.ucla.edu/~harding/tutorials/tutorials.html).

Consider the following:



Lacks resonance.
A less stable carbocation.



Has resonance delocalization of the open valence shell. *A more stable carbocation.*

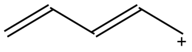
The primary carbocation on the left does not have any resonance contributors in which electrons are donated to the carbon with the open octet. Compare this with the carbocation on the right, which has resonance and a delocalized positive charge. Charge delocalization imparts stability, so the structure with resonance is lower in energy.

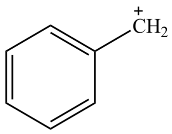
In the example shown above, an oxygen atom lone pair is involved in resonance that stabilizes a carbocation. In general, any adjacent lone pair or carbon-carbon π bond can also be involved in resonance delocalization of a carbocation positive charge. Allylic and benzylic carbocations enjoy resonance stabilization by delocalization of the positive charge to the adjacent pi bond(s). Vinylic and aryl carbocations do not enjoy resonance stabilization because their pi electron clouds are perpendicular to the vacant *p* orbital of the carbocation. (Recall that resonance requires the interacting orbitals to be parallel so they can overlap. Without overlap there can be no resonance.)

Note the influence of inductive effect versus resonance on the energies of these molecules. The oxygen atom that is bonded to the carbocation on the right is more electronegative than the corresponding hydrogen atom in the left-hand structure. We would think that the inductive effect would pull electron density away from the carbocation, making it higher in energy. **In actuality, resonance usually (but not always) outweighs other factors.** In this case, carbocation stabilization by resonance electron donation is a more significant factor than carbocation destabilization by inductive electron withdrawal.

Methyl and primary carbocations without resonance are very unstable, and should never be invoked in a reaction mechanism unless no other pathway is possible. More stable carbocations (secondary or tertiary with resonance, or any carbocation with resonance) is sufficiently stable to be formed in a mechanism under reasonable reaction conditions.

Exercise 2: Draw all significant resonance contributors for the following carbocations.

(a)


(b)


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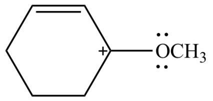

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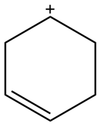
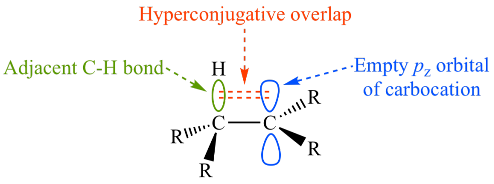


A second factor that should be considered when thinking about carbocation stability is the number of carbon groups attached to the carbon carrying the positive formal charge. Bonding electrons in sigma bonds adjacent to the open valence shell carbon can delocalize the positive charge to some extent by overlapping with the unoccupied *p* orbital of the carbocation:



This phenomenon is termed **hyperconjugation**. Since the overlap supplies electron density to the electron-deficient carbocation carbon, we predict that increasing the number of hyperconjugative interactions increases carbocation stability. Extending this idea, we predict that increasing the number of bonds adjacent to the carbocation by increasing the number of alkyl groups attached to the carbocation carbon results in an increase in carbocation stability. For example, a tertiary carbocation should be more stable than a secondary carbocation. This prediction is accurate.

Our simple prediction suggests that any adjacent bonding electron pair will participate in carbocation hyperconjugation. However, only C–H and C–C bonds provide a significant level of increased stability.

When considering the importance of hyperconjugation versus resonance as the more important stabilizing feature, resonance usually wins out. One functional group that provides resonance stabilization provides more stabilization than one carbon group. For example, a primary carbocation with resonance is more stable than a secondary carbocation without resonance. A secondary carbocation with resonance is usually more stable than a tertiary carbocation without resonance. Of course a primary carbocation with two resonance-stabilizing substituents is more stable than a secondary carbocation without resonance. However, two carbon substituents sometimes do (and sometimes do not) provide more stabilization than a single resonance-providing functional group.

The **general rules for carbocation stability** can be summarized as follows.

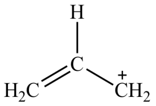
(a) Increasing substitution increases stability.

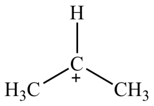
CH_3^+ (methyl; least stable) < RCH_2^+ (1°) < R_2CH^+ (2°) < R_3C^+ (3°; most stable)

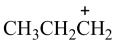
(b) Resonance is more important than substitution. For example, a secondary carbocation without resonance is generally less stable than a primary carbocation with resonance.

Exercise 3: Rank the relative stability (most stable to least stable) of the carbocations in each set.

(a)

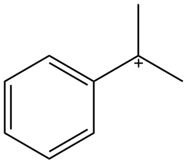


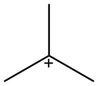


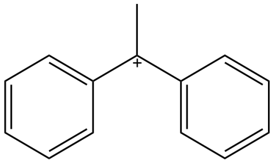


$CH_3CH_2\overset{+}{C}H_2$

(b)







In a vinylic carbocation, the positive charge is assigned to a carbon with *sp* hybridization. How does this influence the carbocation's stability? An *sp* orbital has more *s* character than an sp^2 orbital. Electrons in an *s* orbital are closer to the nucleus and therefore more tightly held than electrons in a *p* orbital. This can be taken to mean that the electronegativity of carbon increases with increasing *s* character. Thus: *sp* carbon (most *s* character; most electronegative) > sp^2 > sp^3 (least *s* character; least electronegative). Electronegativity is a measure of electron attraction. So the stability of a cation is influenced by the electronegativity of the atom bearing the positive charge. The more electronegative the atom the less stable the cation. A vinylic carbocation carries the positive charge on an *sp* carbon, which is more electronegative than an sp^2 carbon of an alkyl carbocation. Therefore a primary vinylic carbocation is less stable than a primary alkyl carbocation.

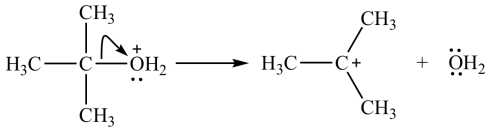
Similar reasoning explains why an aryl carbocation is less stable than a typical secondary alkyl carbocation such as cyclohexyl carbocation.

Because of their (generally) low stability, vinyl and aryl carbocations are not often encountered.

D. Carbocation Formation

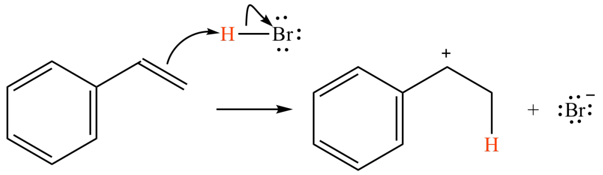
Even though carbocations can be found in many organic reaction mechanisms, most carbocations are formed by one of only two basic mechanism steps: ionization of a carbon - leaving group bond or electrophilic addition to a pi bond.

Ionization of a Carbon - Leaving Group Bond. When a bond between a carbon atom and a leaving group ionizes, the leaving group accepts the pair of electrons that used to be shared in the covalent bond. This may leave the carbon atom with an open octet, resulting in a carbocation. The ionization is indicated with a curved arrow starting at the bond and pointing to the leaving group atom that accepts the electron pair. Better leaving groups or formation of a more stable carbocation result in lower activation energy and faster ionization. Carbon - leaving group bonding ionization is illustrated using an oxonium ion:



Carbocation formation by ionization of a leaving group occurs in many organic reactions such as the S_N1 and E1 mechanisms. Not every case of leaving group ionization affords a carbocation, for example, the S_N2 reaction.

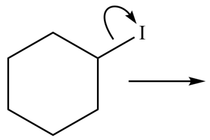
Electrophilic Addition to a Pi Bond. When an electrophile attacks a pi bond, the pi electron pair may form a new sigma bond to the electron-deficient atom of the electrophile. (Not all additions to pi bonds involve electrophiles or carbocations.) The other pi bond carbon no longer shares the pi electron pair, resulting in a carbocation. This addition is indicated with a curved arrow starting at the pi bond and ending at the electron deficient atom of the electrophile. Formation of more stable carbocations result in lower activation energy and faster addition. Electrophilic addition to a pi bond is illustrated by the reaction of HBr (an electrophile) with styrene ($PhCH{=}CH_2$). Note that the more stable carbocation (secondary with resonance instead of primary without resonance) is formed. This is a key mechanistic feature of Markovnikov's Rule.



Electrophilic addition to a pi bond occurs in many reactions of alkenes, alkynes and benzene rings. Note every addition reaction forms a carbocation, for example, catalytic hydrogenation or ozonolysis.

Exercise 4: Draw the products of each mechanism step.

(a)



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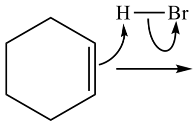

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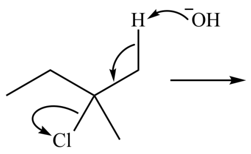
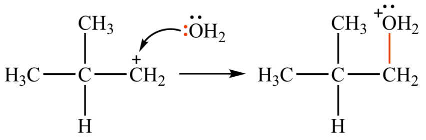


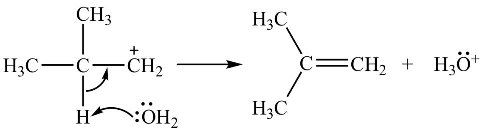
E. Three Fates of a Carbocation

Now we consider how carbocations behave in reaction mechanisms. Generally speaking, carbocations are unstable due to their open octets and positive charges. Thus, their reactions will be strongly influenced by filling the octet of the carbon bearing the positive charge, or at least making this positive charge more stable. There are three common mechanism pathways (or fates) by which carbocations may achieve this stability. These fates are (a) capture a nucleophile, (b) be deprotonated to form a pi bond, and (c) rearrangement. **Note in each case that the carbon bearing the open octet gains a pair of electrons thus completing its octet.**

Capture a nucleophile. A carbocation is electrophilic because it has a positive charge and (in most cases) a carbon atom with an open octet. The positive charge is neutralized when a nucleophile's electron pair (shown below in red) is accepted and a new covalent bond is formed. Because carbocations are very reactive, even weak nucleophiles such as water can be captured with ease.

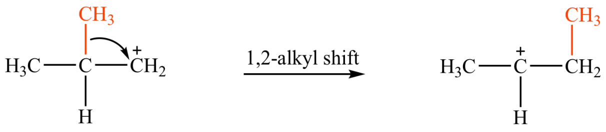


Be deprotonated to form a pi bond. Accepting an electron pair from an adjacent bond to a hydrogen atom neutralizes the positive charge or fills the open octet and forms a new pi bond. (The carbocation carbon now has four bonds and a full octet, so its formal charge is zero.) The hydrogen atom must be removed by a base, but because carbocations are generally very reactive species and very strongly driven to dispose of the positive charge even a weak base such as water or iodide ion can accomplish this deprotonation.



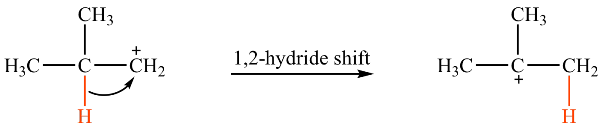
When carbocation deprotonation can lead to more than one product, the more stable product is major.

Rearrangement. The bonding electrons of a carbocation may shift between adjacent atoms to form a more stable carbocation. For example, rearrangement will occur if a secondary carbocation can be formed from a primary carbocation because a secondary carbocation is more stable than the primary carbocation. There can be two types of rearrangements. Shift of an alkyl group is called a 1,2-alkyl shift. In the following example the migrating methyl group and the associated electron pair are shown in red.



Primary carbocation Secondary carbocation

Shift of a hydrogen atom is called a 1,2-hydride shift (or a 1,2-H shift). Hydride ion = $H:^-$. In the following example the migrating hydrogen atom and the associated electron pair are shown in red



Primary carbocation Tertiary carbocation

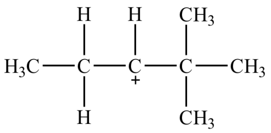
Of these two rearrangement examples, hydride shift leads to a tertiary carbocation whereas alkyl shift leads to a secondary carbocation. Because a tertiary carbocation is more stable than a secondary carbocation, the hydride shift is favored in preference to the alkyl shift.

Any C–H or C–C bond adjacent to a carbocation may shift (including C–C bonds that are part of a ring), but only C–C and C–H bonds can migrate during carbocation rearrangement.

The most common carbocation rearrangements involve a carbocation rearranging into a more stable carbocation, such as 2° → 3° with resonance. (So use these rearrangements with impunity.) Rearrangements that transform a carbocation into another of apparently equal stability are less common, but they do occur. (So before invoking this kind or rearrangement ask yourself if a better rearrangement, or some other mechanism step, is possible.) Rearrangement to a less stable carbocation is very unusual, but also does occur. (This is the pathway of last very last resort. All other reasonable options must be ruled out first.)

Exercise 5: For each carbocation, draw the most likely carbocation rearrangement. Include curved arrows.

(a)



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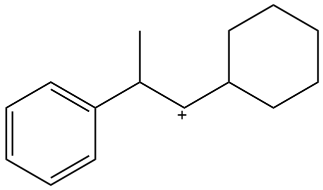

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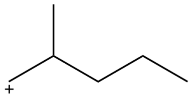

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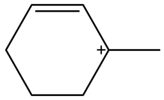
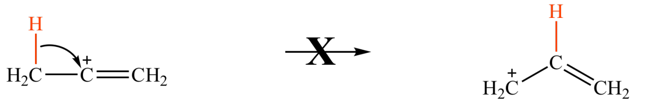


Vinylic carbocations *generally do not rearrange, even if they can become more stable*. For example, the rearrangement shown below does not occur, even though a secondary carbocation would rearrange to become a more stable allylic carbocation (primary with resonance).



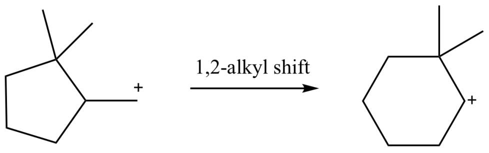
Secondary vinylic
without resonance stabilization

Primary allylic
with resonance stabilization

This resistance to rearrangement is probably due to orbital alignment restrictions during the rearrangement transition state.

E. Rearrangement Causing a Change in Ring Size

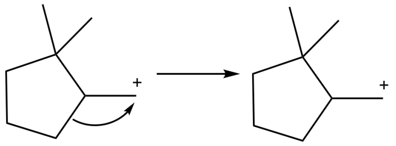
Rearrangement may lead to a change in ring size. For example:



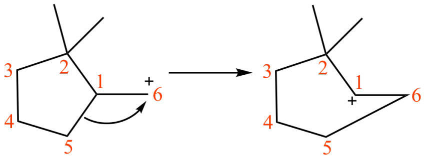
Primary

Secondary

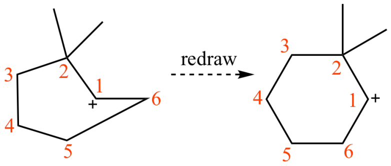
The driving force for this rearrangement is formation of a more stable secondary carbocation from a less stable primary carbocation. What might be puzzling to you is how to draw the structure of the product. Here is a little trick that might help. Begin by redrawing the starting structure along with the curved arrows:



Next, number the ring to keep track of the atoms, then make the bond changes suggested by the curved arrows, but leave the atoms in place. This may lead to a funky structure, but this will be fixed in the next step. In this case, the C1–C5 bond shifts, taking a pair of electrons from C1, leaving C1 with an open octet and a positive formal charge. The former carbocation carbon gained an electron pair, so its formal charge becomes one unit more negative (+1 to zero). The five-membered ring has expanded to a six-membered ring.

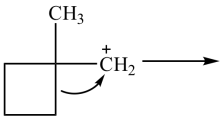


Now redraw the rearranged product to make it look better, using the numbering scheme to keep the substituent positions in order.

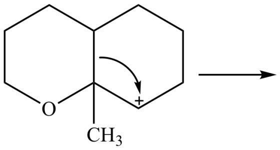


Exercise 6: Draw the rearranged carbocations based on the given curved arrows. Indicate how the carbocation stability has increased by this rearrangement.

(a)

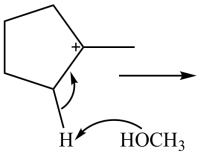


(b)

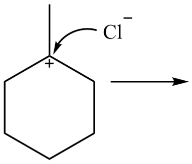


Exercise 7: Draw the mechanism step products based on the curved arrows. Name the carbocation fate illustrated.

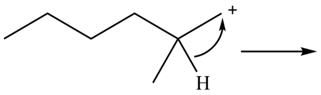
(a)



(b)

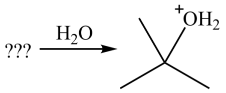


(c)

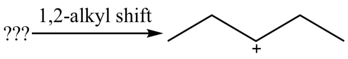


Exercise 8: Provide a carbocation to complete each reaction. Draw the curved arrows.

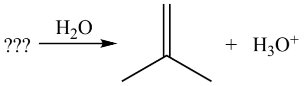
(a)



(c)



(b)

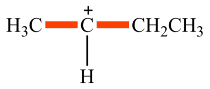


Exercise 9: Illustrate the three carbocation fates using any molecules you want. Use curved arrows and give the products.

Exercise Solutions

Exercise 1: The carbon-carbon bonds that determine the carbocation type are shown in red.

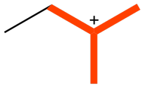
(a)



$H_3C-\underset{H}{\overset{+}{C}}-CH_2CH_3$

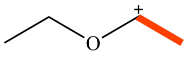
Secondary

(b)



Tertiary

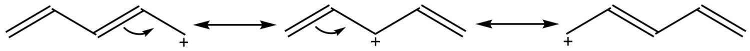
(c)



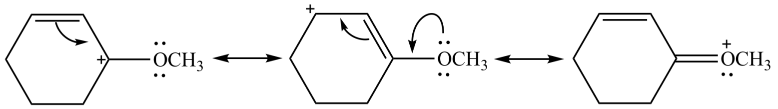
Primary

Exercise 2 *Having trouble with resonance? Consult the resonance tutorials on the course web site (http://web.chem.ucla.edu/~harding/tutorials/tutorials.html).*

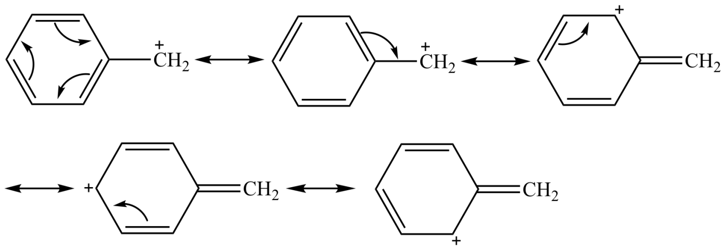
(a)



(b)



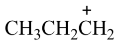
(c)



(d) No additional significant resonance contributors can be drawn for this carbocation.

Exercise 3: Use the general carbocation stability rules: (i) methyl (least stable) < 1° < 2° < 3° (most stable), and (ii) resonance is more significant than substitution pattern.

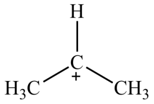
(a)



$CH_3CH_2\overset{+}{C}H_2$

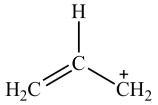
Primary
Least stable

<



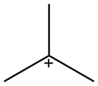
Secondary

<



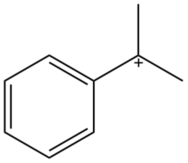
Primary with resonance
Most stable

(b)



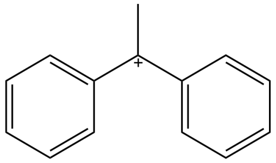
Tertiary
Least stable

<



Tertiary with resonance

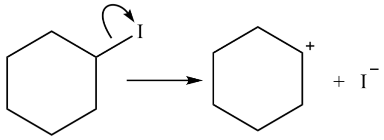
<



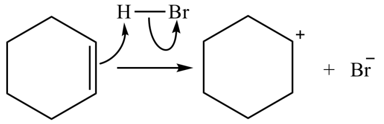
Tertiary with more resonance
Most stable

Exercise 4: Recall that if the curved arrow starts at a bond, that bond is broken. A curved arrow that points form an atom or bond to another atom or the space between two atoms indicates that those two atoms become bonded. If the atoms are already bonded then the bond order increases. For example a single bond becomes a double bond.

(a)

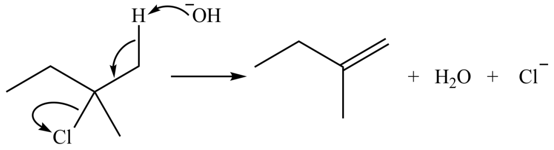


(b)



Exercises (a) and (b) show that the same carbocation (in this case cyclohexyl) can be formed by two very different reaction pathways.

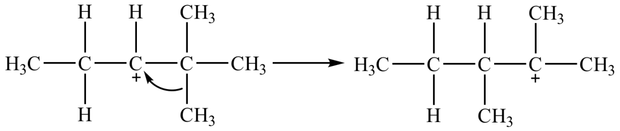
(c)



Recall that ionization of a carbon - leaving group bond does not always form a carbocation. In this case, the electron pair lost to the leaving group is replaced by the electron pair gained from scission of the adjacent C–H bond. The carbon starting with the leaving group never has an open octet.

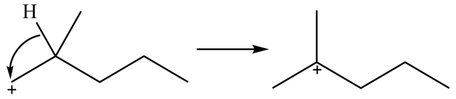
Exercise 5: The best rearrangement will provide the greatest increase in stability. For example, a carbocation that can rearrange into a secondary or tertiary carbocation will preferentially rearrange into the tertiary carbocation because (everything else being equal) a tertiary carbocation is more stable than a secondary carbocation.

(a)

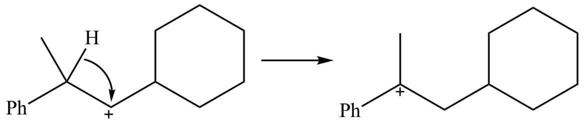


$$H_3C{-}CH_2{-}\overset{+}{C}H{-}C(CH_3)_2{-}CH_3 \longrightarrow H_3C{-}CH_2{-}CH(CH_3){-}\overset{+}{C}H{-}CH_3$$

(b)



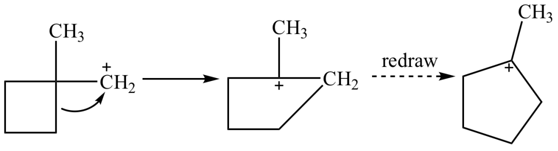
(c)



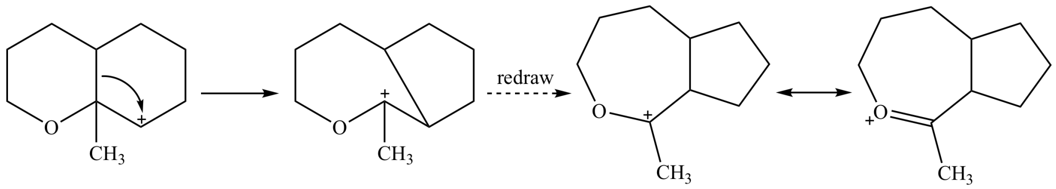
(d) This carbocation is tertiary with resonance, and cannot gain greater stability by rearrangement.

Exercise 6

(a) The rearranged carbocation is tertiary whereas the starting carbocation is primary. Rearrangement also relieves the strain associated with the cyclobutane ring.

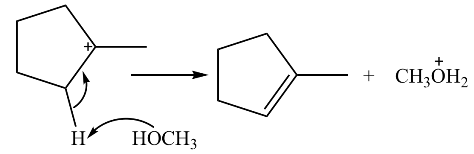


(b) The rearranged carbocation is secondary with resonance whereas the starting carbocation is secondary.

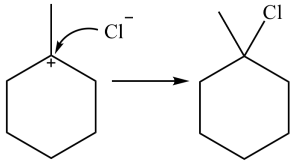


Exercise 7

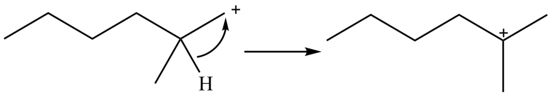
(a) Be deprotonated; form pi bond:



(b) Capture nucleophile:

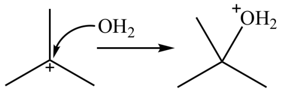


(c) Rearrangement:

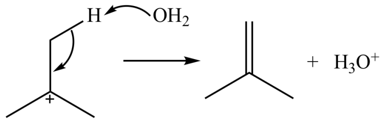


Exercise 8

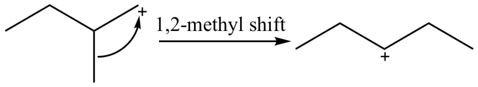
(a)



(b)

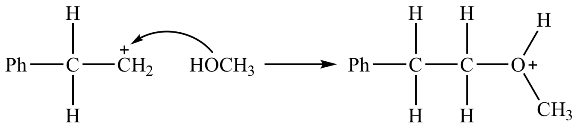


(c)

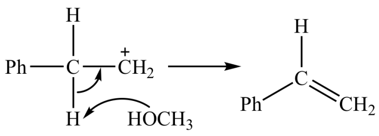


Exercise 9: Any carbocation and any other reactants are acceptable as long as the carbocation fates are accurately illustrated.

Capture nucleophile:



Be deprotonated; form pi bond:



Rearrangement: