

Carbocations

Based on a Fall 2001 Chemistry 30BH Honors project by Patricia Young

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A. Introduction

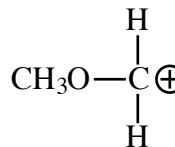
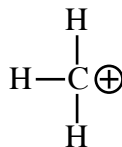
A carbocation is molecule in which a carbon atom bears three bonds and a positive charge. Carbocations are generally unstable because they do not have eight electrons to satisfy the octet rule.



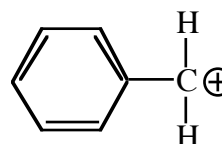
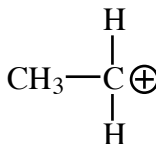
B. Carbocation Classification

In order to understand carbocations, we need to learn some basic carbocation nomenclature. A primary carbocation is one in which there is *one* carbon group attached to the carbon bearing the positive charge. A secondary carbocation is one in which there are *two* carbons attached to the carbon bearing the positive charge. Likewise, a tertiary carbocation is one in which there are *three* carbons attached to the carbon bearing the positive charge.

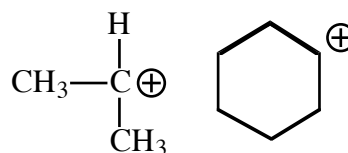
Methyl carbocations
No C-C⁺ bonds



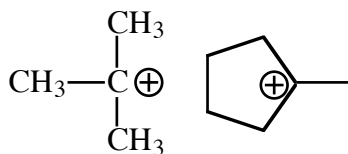
Primary (1°) carbocations
One C-C⁺ bond



Secondary (2°) carbocations
Two C–C⁺ bonds

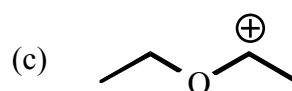
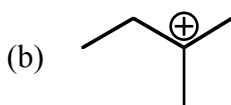
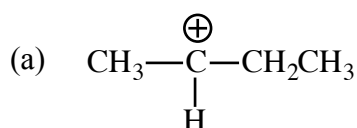


Tertiary (3°) carbocations
Three C–C⁺ bonds

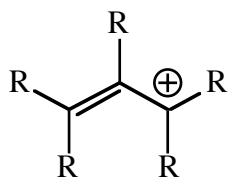


Exercise 1 Exercise solutions can be found at the end of the tutorial.

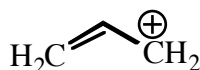
Label each carbocation as primary, secondary, or tertiary.



If 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.

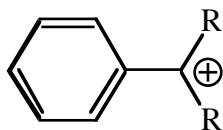


Generic allylic carbocation

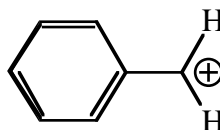


The allyl carbocation

If 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.

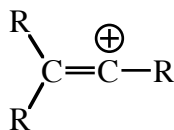


Generic benzylic carbocation

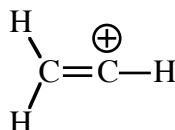


The benzyl carbocation

If 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.

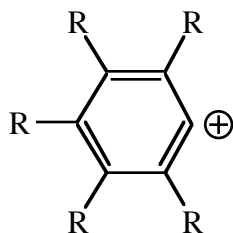


Generic vinylic carbocation

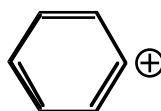


The vinyl carbocation

If 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.



Generic aryl carbocation



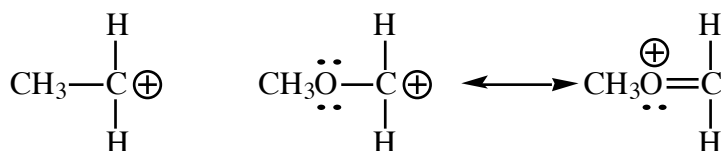
The phenyl carbocation

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 a stabilizing feature to a carbocation 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 (web.chem.ucla.edu/~harding/tutorials/tutorials.html).

Consider the following:



No resonance

Resonance

The structure 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 that has resonance and a delocalized positive charge. Charge delocalization imparts stability, so the structure with resonance is lower in energy.

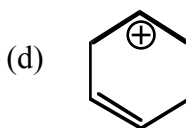
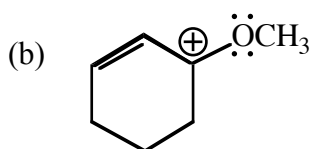
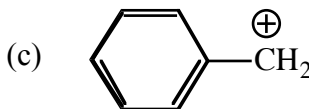
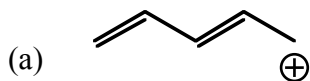
In the example shown above, an oxygen atom lone pair is involved in resonance that stabilizes a carbocation. In general, any adjacent lone pair or π bond can also be involved in resonance delocalization of a carbocation positive charge. Allylic and benzylic carbocations enjoy resonance stabilization by delocalization of the positive charge to the adjacent π bond(s). Vinylic and aryl carbocations do not enjoy resonance stabilization because their π 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.

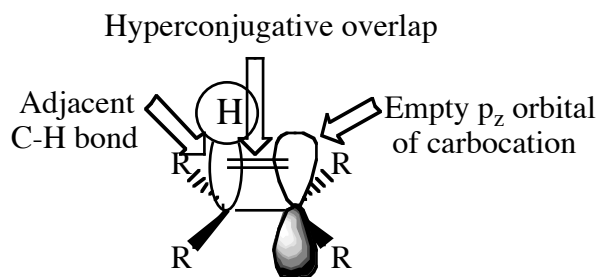
Methyl and primary carbocations without resonance are very unstable, and should never be invoked in a reaction mechanism unless no other pathway is possible. More stable carbocations (secondary or tertiary with resonance, or any carbocation with resonance) is sufficiently stable to be formed in a mechanism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

Exercise 2

Draw all significant resonance contributors for the following carbocations.



The second factor that should be considered when thinking about carbocation stability is the number of carbons attached to the carbon carrying the positive charge. We look at the number of bonding electrons that are attached to the carbocation because those bonding electrons will help in alleviating the positive charge. Bonding electrons from adjacent σ bonds may overlap with the unoccupied p orbital of the carbocation.



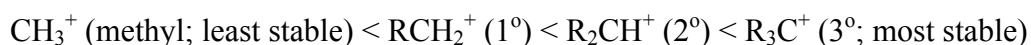
This phenomenon is termed **hyperconjugation**. Since the overlap supplies electron density to the electron-deficient carbocation carbon, we predict that increasing the number of hyperconjugative interactions increases carbocation stability. Extending this idea, we predict that increasing the number 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. 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.

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

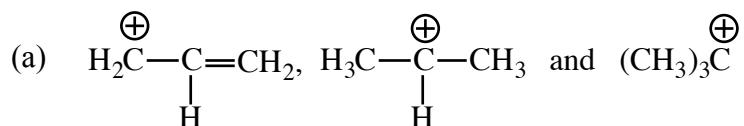
- (a) Increasing substitution increases stability.

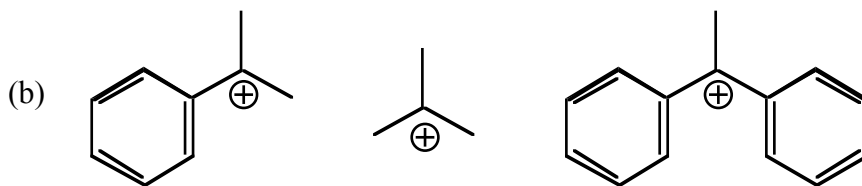


- (b) Resonance is more important than substitution. For example, a secondary carbocation without resonance is generally less stable than a primary carbocation with resonance.

Exercise 3

Rank the relative stability of the three carbocations in each set.





In vinylic carbocations, 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.

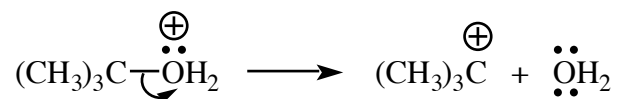
Similar reasoning explains why an aryl carbocation is less stable than a typical secondary alkyl carbocation such as cyclohexyl carbocation.

Because of their reduced stability, vinyl and aryl carbocations are not often encountered.

D. Carbocation Formation

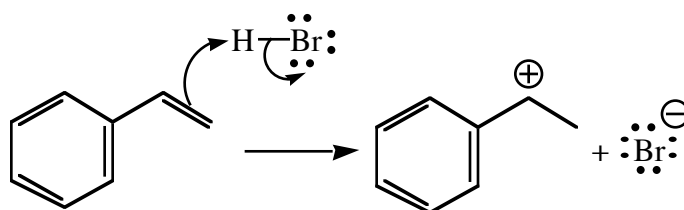
Even though carbocations can be found in many organic reaction mechanisms, most carbocations are formed by one of only two basic mechanism steps: ionization of a carbon - leaving group bond or electrophilic addition to a π bond.

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 leaving group ionization affords a carbocation, for example, the S_N2 reaction.

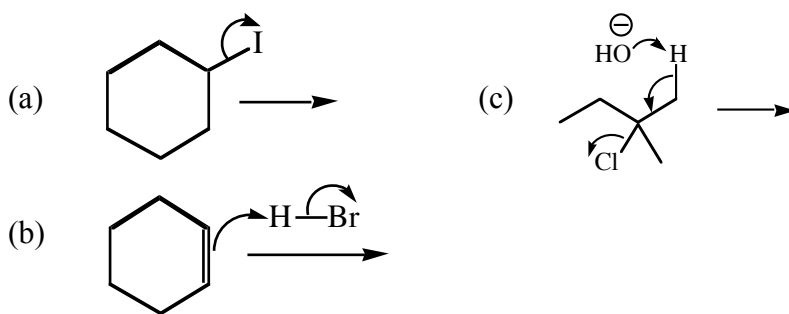
Electrophilic Addition to a π Bond. When an electrophile attacks a π bond, the π electron pair may form a new σ bond to the electron-deficient atom of the electrophile. (Not all additions to π bonds involve electrophiles or carbocations.) The other π bond carbon no longer shares the π electron pair, resulting in a carbocation. This addition is indicated with a curved arrow starting at the π bond and ending at the electron deficient atom of the electrophile. More powerful electrophiles or the formation of more stable carbocations result in lower activation energy and faster addition. Electrophilic addition to a π bond is illustrated by the reaction of HBr (an electrophile) with styrene (PhCH=CH_2). Note that the more stable carbocation (secondary with resonance) is formed. This is a key mechanistic feature of Markovnikov's Rule.



Electrophilic addition to a π 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

Suggest the products of each mechanism step.

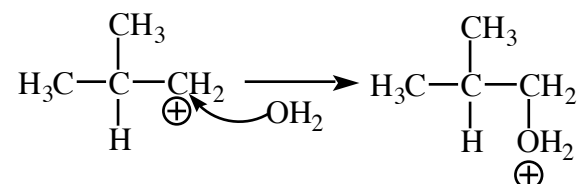


E. Three Fates of a Carbocation

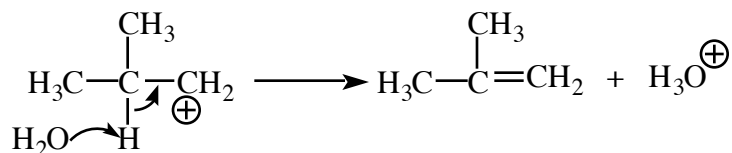
Now we consider how carbocations behave in reaction mechanisms. Generally speaking, carbocations are unstable due to their open octets and positive charges. Thus, their reactions will be strongly influenced by filling the octet of the carbon bearing the positive charge, or at least making this positive 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) lose a proton to form a π bond, and (c) rearrange. **Note in each case that the carbon bearing the open octet gains a pair of electrons thus completing its octet.**

Capture a nucleophile. The 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 an electron pair is accepted and a new covalent bond is formed. By definition, a species that donates a pair of electrons to form a new covalent bond is a nucleophile. Because carbocations are very reactive, even weak nucleophiles such as water can be captured with ease.

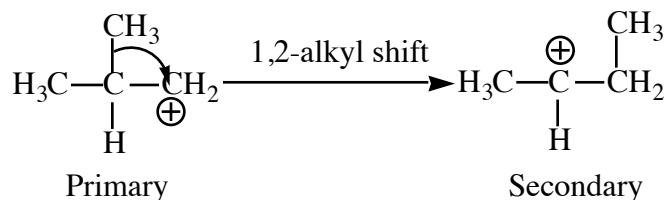


Lose a proton to form a π bond. Accepting an electron pair from an adjacent bond to a hydrogen atom neutralizes the positive charge or fills the open octet and forms a new π bond. (The carbocation carbon now has four bonds and a full octet, so its formal charge is zero.) The hydrogen atom must be removed 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.

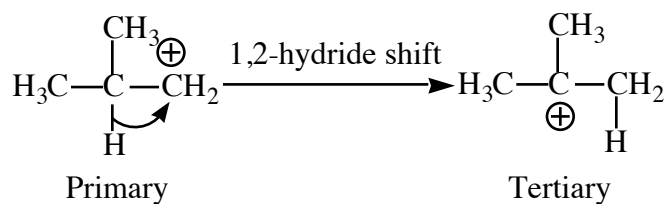


When carbocation deprotonation can lead to more than one product, the more stable product is major.

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.



Shift of a hydrogen atom is called a 1,2-hydride shift. Hydride ion = H^- .



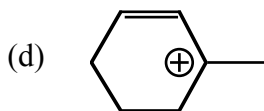
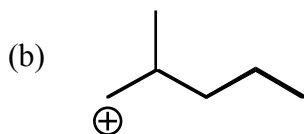
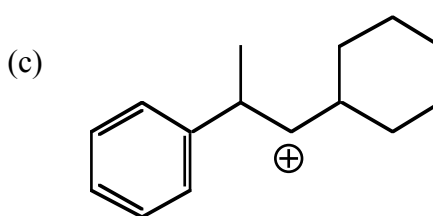
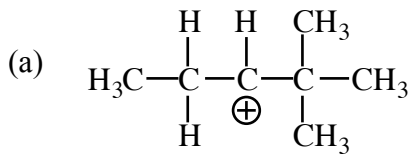
Of these two examples, hydride shift leads to a tertiary carbocation whereas alkyl shift leads to a secondary carbocation. Because a tertiary carbocation is more stable than a secondary carbocation, the hydride shift is favored in preference to the alkyl shift.

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.

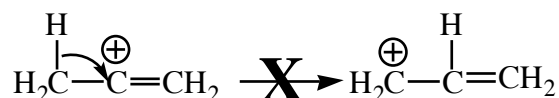
The most common carbocation rearrangements involve a carbocation rearranging into a more stable carbocation, such as $2^\circ \rightarrow 3^\circ$ with resonance. (So use these rearrangements with impunity.) Rearrangements that transform a carbocation into another of apparently equal stability are less common, but they do occur. (So before invoking this kind of 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 best rearrangement. Include curved arrows.



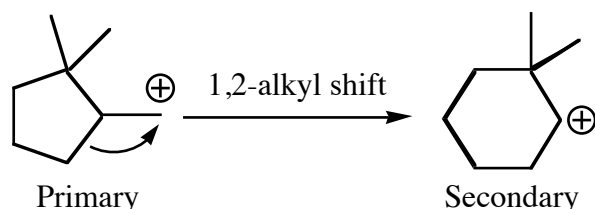
Vinyllic carbocations *generally do not rearrange, even if they can become more stable*. For example, the rearrangement shown below does not occur, even though a secondary carbocation would rearrange to become a more stable allylic carbocation (primary with resonance).



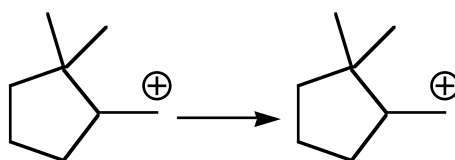
This resistance to rearrangement is probably due to orbital alignment restrictions during the rearrangement transition state.

E. Rearrangement Causing a Change in Ring Size

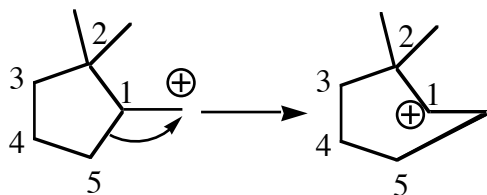
Rearrangement may lead to a change in ring size. For example:



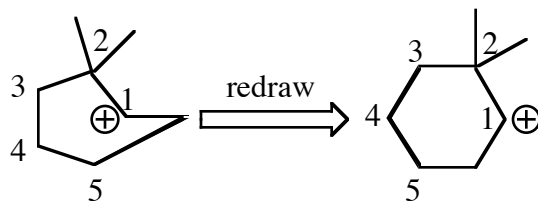
The driving force for this rearrangement is formation of a more stable secondary carbocation from a less stable primary carbocation. What often puzzles students is how to draw the structure of the product. Here is a little trick that might help. Begin by redrawing the starting structure:



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.

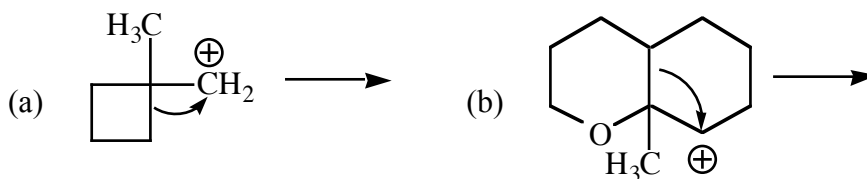


Now redraw the rearranged product to make it look better, using the numbering scheme to keep the substituent positions in order.



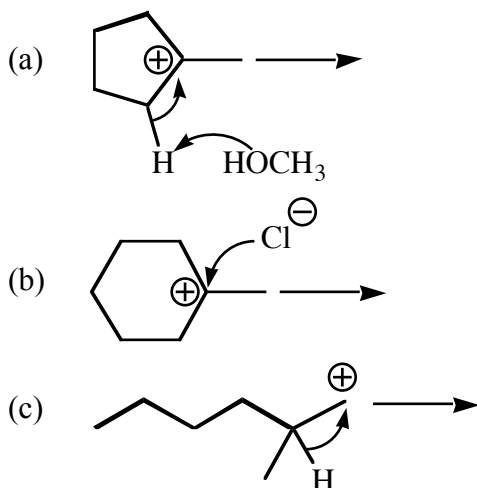
Exercise 6

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



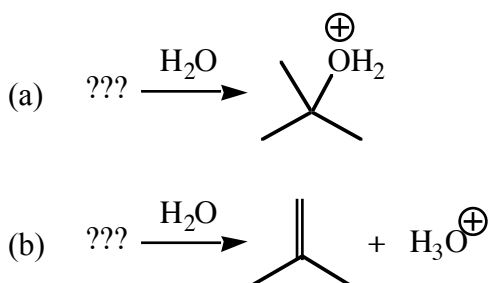
Exercise 7

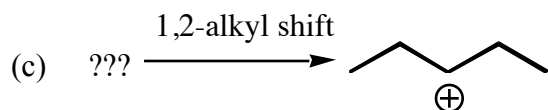
Draw the products based on the curved arrows. Name the carbocation fate illustrated.



Exercise 8

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





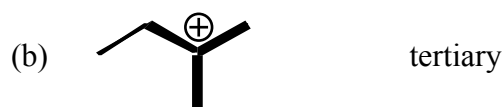
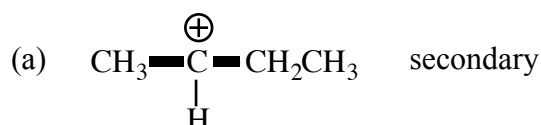
Exercise 9

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

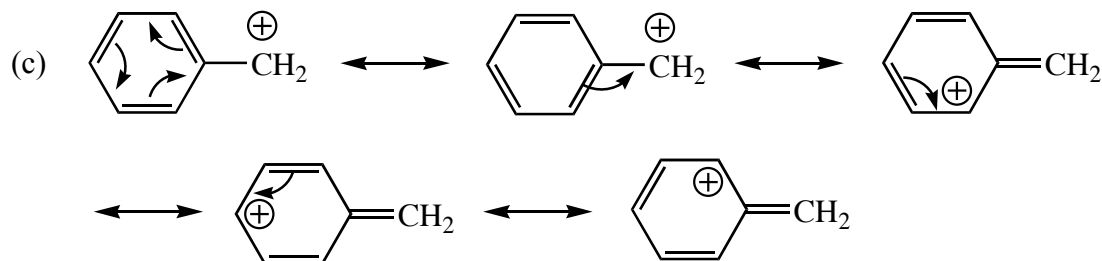
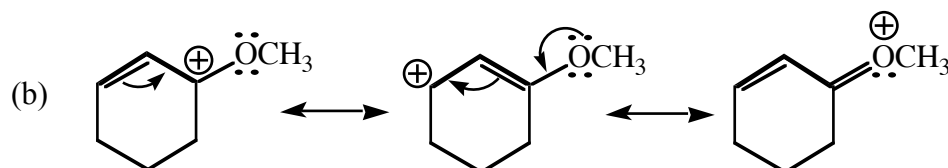
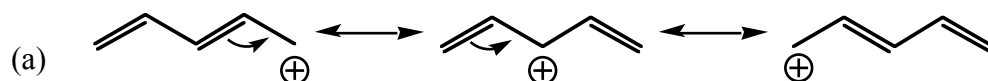
Exercise Solutions

Exercise 1

The carbon-carbon bonds that determine the carbocation type are shown in bold.



Exercise 2



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

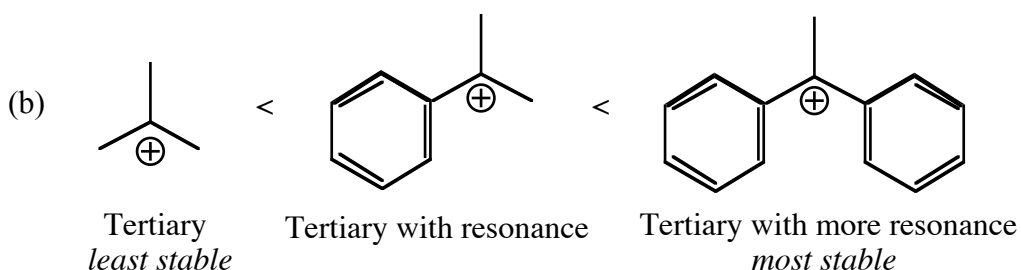
Exercise 3

Use the general carbocation stability rules:

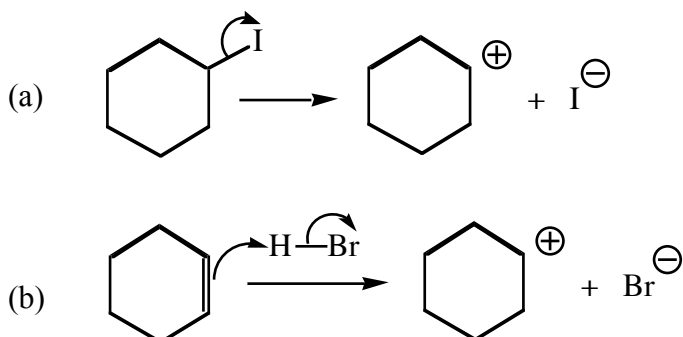
(i) Methyl (least stable) < 1° < 2° < 3° (most stable), and

(a) $\text{H}_3\text{C}-\overset{\oplus}{\text{C}}(\text{H})-\text{CH}_3 < \text{H}_2\text{C}=\overset{\oplus}{\text{C}}(\text{H})-\text{CH}_2 < (\text{CH}_3)_3\overset{\oplus}{\text{C}}$

Secondary *least stable* Primary with resonance Tertiary *most stable*



Recall that if the curved arrow starts at a bond, that bond is broken. A curved arrow that points from 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.



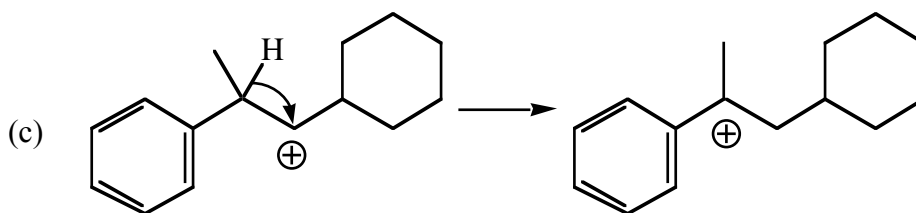
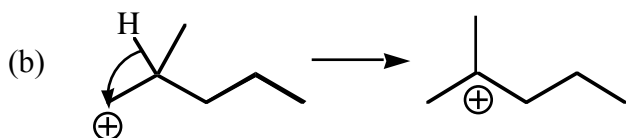
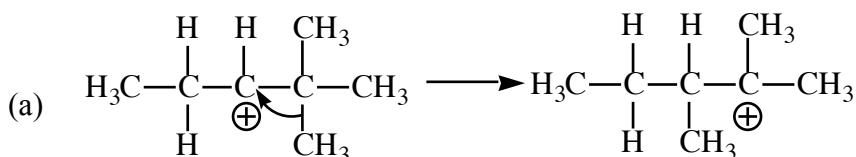
(c) 

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electron pair gained from scission of the adjacent C–H bond. The carbon that starting with the leaving group never has an open octet.

Exercise 5

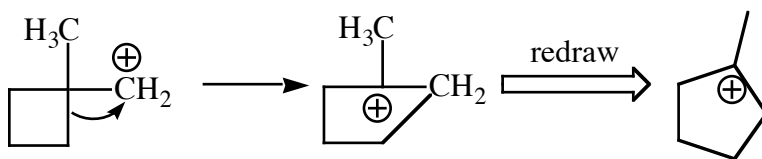
The best rearrangement will provide the greatest increase in stability. For example, a carbocation that can rearrange into a secondary or tertiary carbocation will preferentially rearrange into the tertiary carbocation because (everything else being equal) a tertiary carbocation is more stable than a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



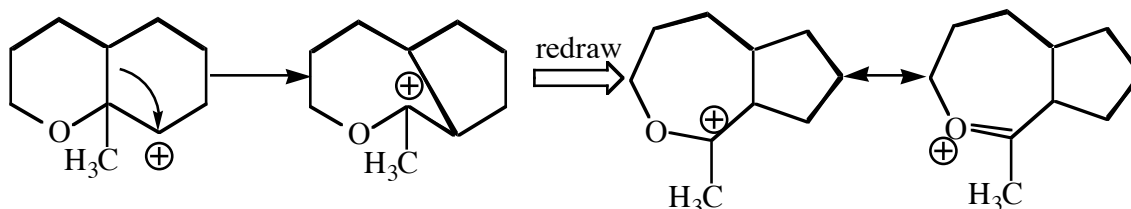
(d) This carbocation is tertiary with resonance, and cannot gain greater stability by rearrangement.

Exercise 6

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

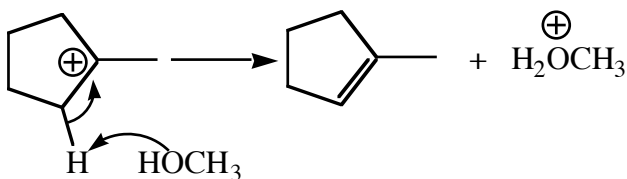


(b) The rearranged carbocation is secondary with resonance whereas the starting carbocation is secondary.

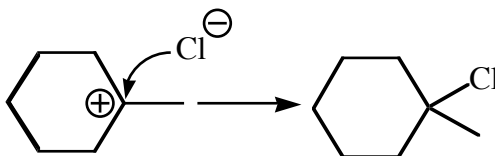


Exercise 7

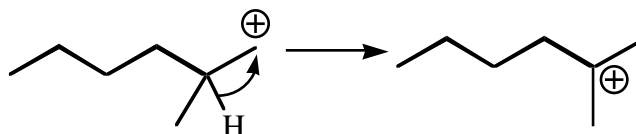
(a) Lose proton, form π bond.



(b) Capture nucleophile.

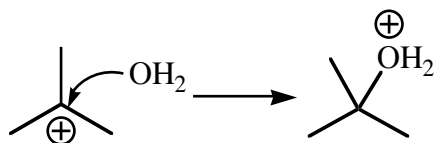


(c) Rearrange.

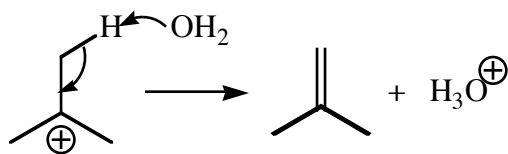


Exercise 8

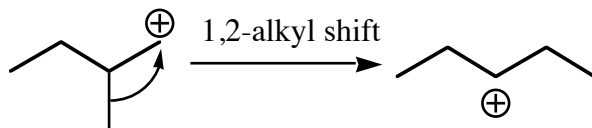
(a)



(b)



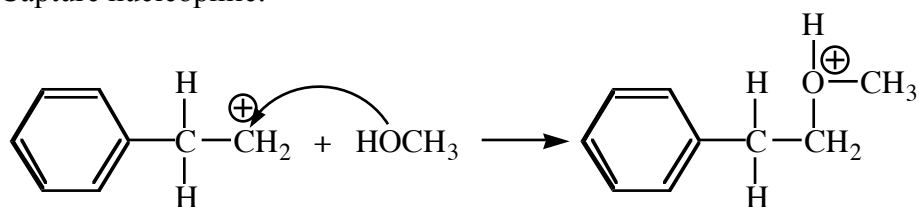
(c)



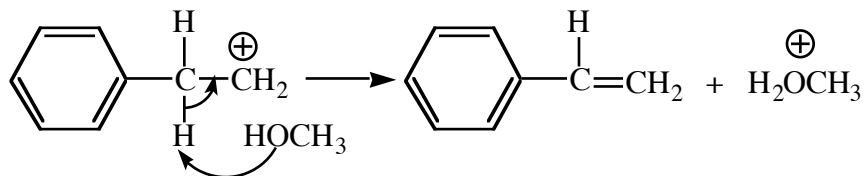
Exercise 9

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

Capture nucleophile:



Lose proton, form π bond:



Rearrange:

