

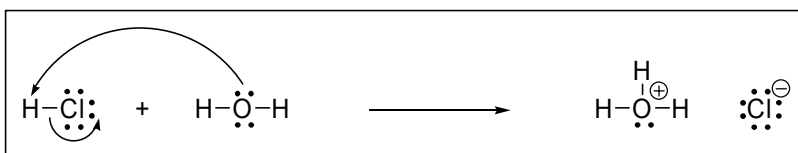
3719 Acids and Bases Worksheet

Concepts

The interaction of a protic acid with a base is the first actual chemical reaction that we study in 3719. We use it to introduce some of the fundamental concepts of **mechanism**, i.e. how to describe the **bond-breaking** and **bond-forming** events that occur as a starting material (left-hand side of the equation) is converted to product (right-hand side of the equation). Since we use acids and bases on many occasions as reagents throughout 3719 and 3720, it is important that you know what constitutes an acid or a base and what happens when the two interact.

Definitions: Acids donate protons (Bronsted definition) or accept electrons (Lewis definition)
Bases accept protons (Bronsted definition) or donate electrons (Lewis definition)

General Chem:

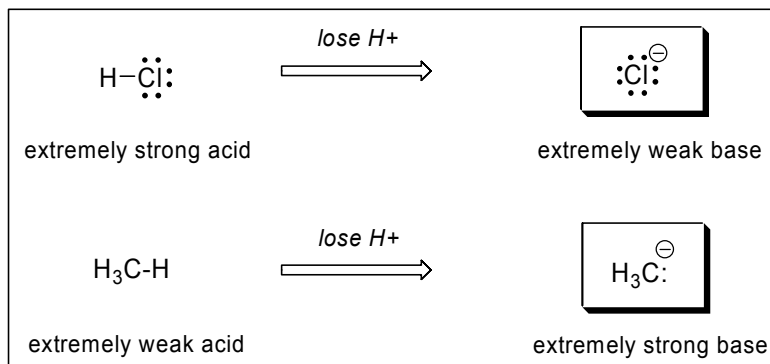


In this case HCl is the acid (proton donor), water is the base (electron donor, proton acceptor) and the arrows show the proton being transferred to generate the conjugate acid (H_3O^+) and the conjugate base (Cl^-). The strength of the acid in water is measured by the dissociation constant (K_a), the larger the K_a , the stronger the acid. In other words, the stronger the acid, the more the above reaction goes to the right. Since the values of K_a can range from very large to very small, we use the $\text{p}K_a$ scale to give us more manageable numbers ($\text{p}K_a = -\log_{10}K_a$). The $\text{p}K_a$ range for the acids we will use in Organic Chem are in the range -10 (very strong acid) to $+60$ (very weak acid).

pKa values from class:

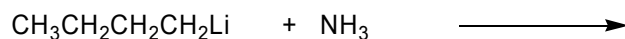
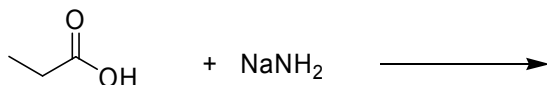
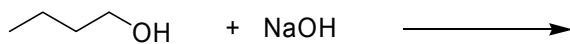
HI, HBr, HCl, H_2SO_4	-5 to -10	extremely strong acids
$\text{CH}_3\text{CO}_2\text{H}$	4.7	weaker acid
H_2O , ROH	$\sim 16-18$	weaker acids
NH_3	~ 36	<u>very weak acid</u>
CH_4	~ 60	extremely weak acid

For the most part in 3719 and 3720 we will not be using water as the base, rather we will use some organic or inorganic base which has been chosen to deprotonate the acid to a particular extent. Since we know something about relative acid strength from $\text{p}K_a$ values, we also know a lot about the relative (conjugate) base strengths:

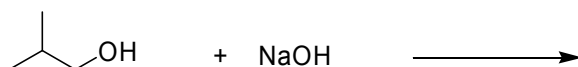
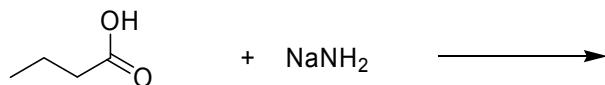
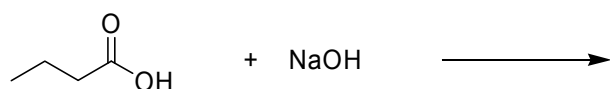


The task in Organic Chemistry is to decide what happens in terms of the equilibrium position when a particular acid is mixed with a particular base. If you understand this, then you can decide which acid or base to use in particular circumstances. The problems on the next page will give you practice with these ideas.

1. For each of the following mixtures, complete the equation, then identify the acid and base on the left and the conjugate acid and conjugate base on the right. Comparing acid and base strengths (from pK_a 's) decide whether the reaction is a) likely to happen, b) whether an equilibrium will be established and c) if equilibrium is established which side is favoured?



2. The equilibrium idea means that if the reaction is reversible there will be four species in solution at one time, the acid, the base, the conjugate acid and the conjugate base. Sometimes this is fine, but sometimes we need to choose bases that will **completely** deprotonate every molecule of acid, i.e. send the reaction completely to the right. These bases will include CH_3Li , NaNH_2 , $\text{LiN}(i\text{-Pr})_2$. Weaker bases will include NaOCH_3 , $\text{KO}t\text{Bu}$, $\text{NaOCH}_2\text{CH}_3$. For each of these bases, give the products formed when they react with H_2O , then use pK_a values to get an idea of the relative base strengths of these compounds.
3. In Chem 3720 we will study reactions based on the deprotonation of ketones such as acetone, $(\text{CH}_3)_2\text{C}=\text{O}$, which has a pK_a of ~ 19 . Given the bases $\text{LiN}(i\text{-Pr})_2$ and NaOCH_3 , decide which will be useful to completely deprotonate acetone, and which will be useful for setting up an equilibrium. Explain your choices.
4. Give the products from the following acid-base reactions and identify the acid and base on the left side, and the conjugate acid and conjugate base on the right side of the equation.

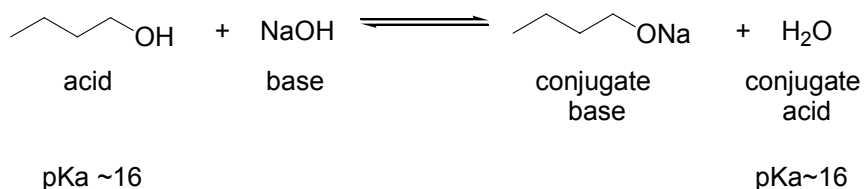


5. For each of the reactions in question 1 and question 4, which will have an equilibrium constant (K) greater than 1, close to 1, or less than 1? Explain your answers.

3719 Acids and Bases Worksheet – Answers

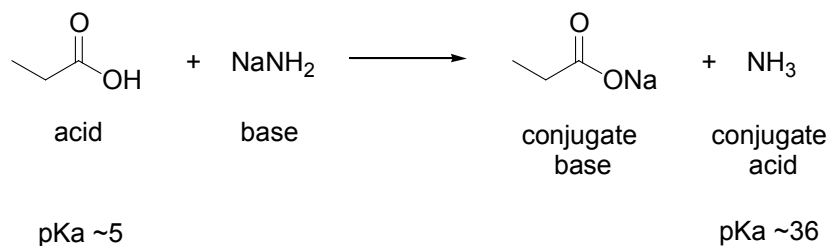
1. For this type of question you have to know the approximate pKa values discussed in class and have an idea of what they mean in terms of relative acid strength and also relative base strength.

a.



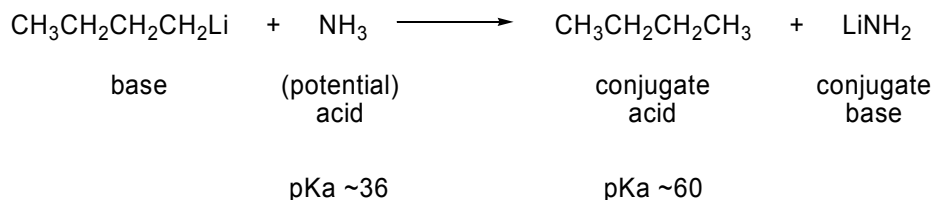
Here we have two acids of similar strengths (1-butanol on the left and H₂O on the right) and therefore two bases of similar strengths. In this situation, the forward reaction is favoured to about the same extent as the reverse reaction. Therefore a) the reaction left to right is likely to happen, b) equilibrium will be established and c) the equilibrium lies approximately in the middle (similar acid strengths, similar base strengths on both sides of the equation).

b.

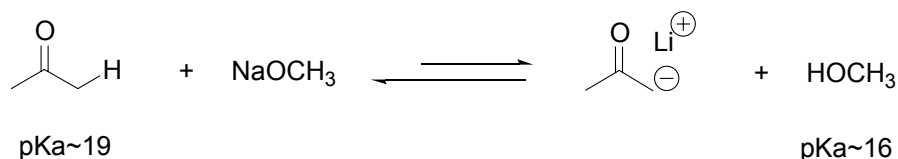


In this example we have acids of very different strength, the carboxylic acid on the left (pKa~5) is very much stronger than the ammonia on the right (pKa~36) therefore the left to right reaction is very much favoured. The reverse reaction however is unlikely to occur since the base on the right is far too weak to deprotonate such a weak acid as NH₃. Therefore a) the reaction left to right will happen, b) equilibrium will not be established and c) the right hand side is completely favoured.

c.

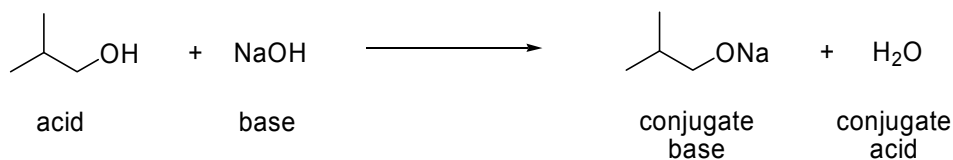
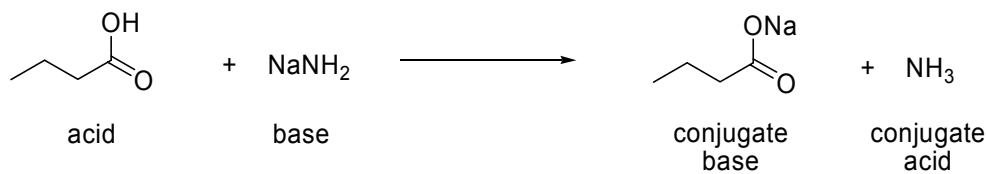
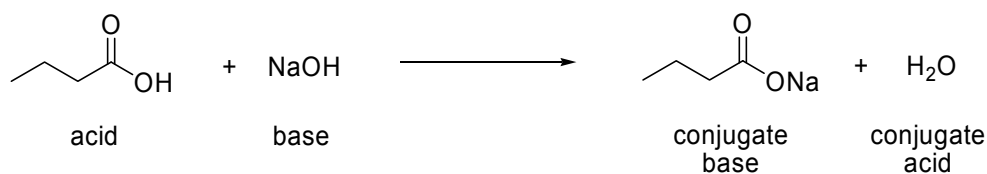


Here we have a situation in which the reaction will go to the right. The CH₄ is such a weak acid (pKa~60) that it is nigh on impossible to deprotonate. A 24 unit pKa difference between acids means a completely irreversible reaction. Therefore a) the reaction left to right will occur to give the products shown above, b) there will be no equilibrium established and c) the right-hand side would be completely favoured in this case.



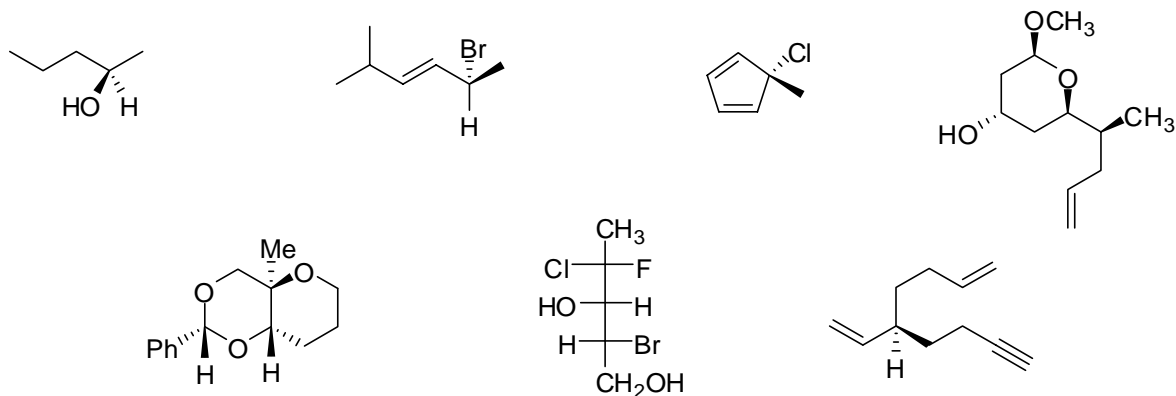
In this case we are using a weaker base and even though the left to right reaction is possible, the right to left is also now possible. Equilibrium will be established here which will favour the side that contains the weaker conjugate base, in this case the left hand side. The main consequence of using this type of base here is that we now have some of all four species in solution at once.

4. The bases will be those species capable of donating electrons, the acids will have protons capable of being removed.

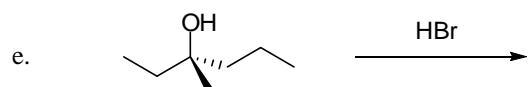
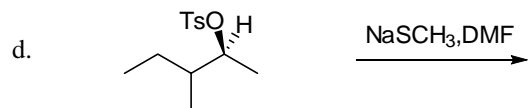
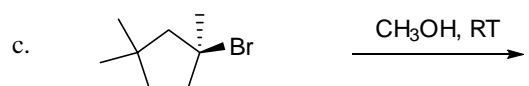
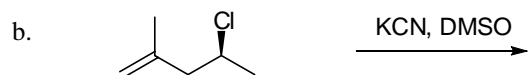
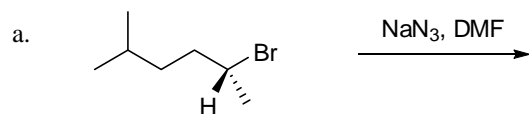


5. 1a) $K \sim 1$ since acids and bases on each side are of similar strengths;
 1b) No equilibrium since the strong acid and very strong base on the left will send the reaction completely to the right (i.e. $K \gg 1$).
 1c) No equilibrium since the strong acid and very strong base on the left will send the reaction completely to the right (i.e. $K \gg 1$).
 4a) $K > 1$ since the stronger acid and base on the left will favour the reaction to the right.
 4b) No equilibrium since the good acid and very strong base on the left will send the reaction completely to the right (i.e. $K \gg 1$).
 4c) $K \sim 1$ since acids and bases on each side are of similar strengths.

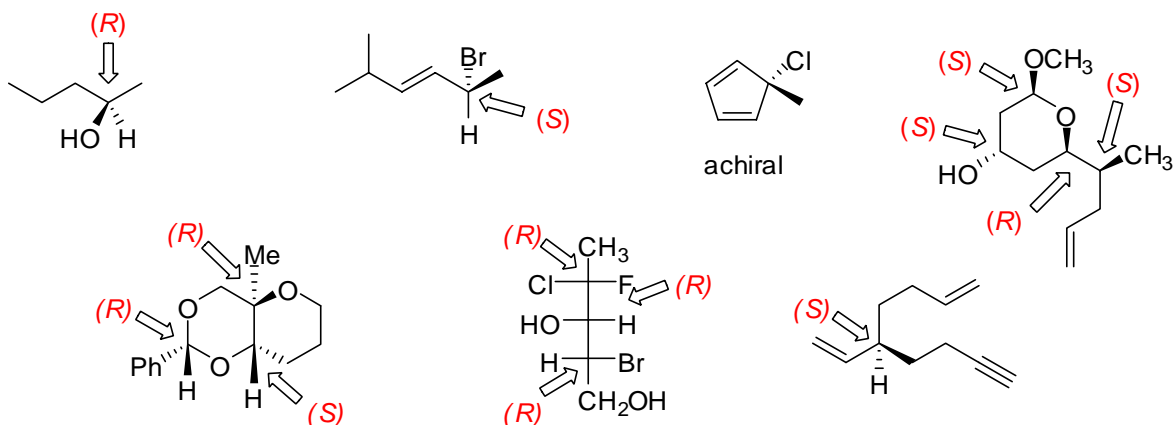
1. (From Chapter 7) For each of the following molecules, identify any stereogenic centers and label them as having either the (*R*) or (*S*) configuration.



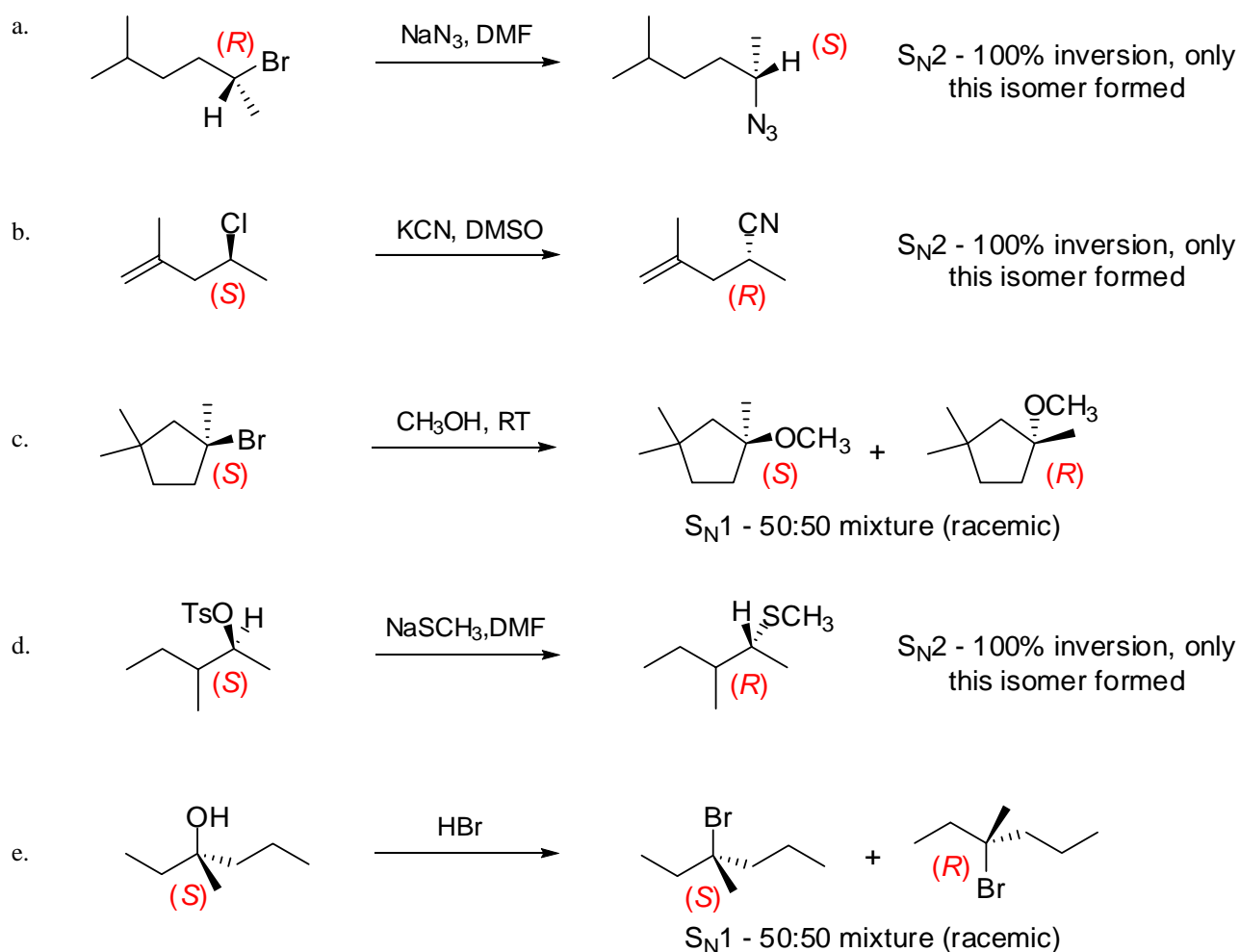
2. (From Chapter 8) Each of the following reactions has stereochemical implications in terms of the products formed. For each; draw the expected organic products, indicate how much of each stereoisomer is formed, and label any stereogenic centers in the starting materials and products as either the (*R*) or (*S*) configuration.



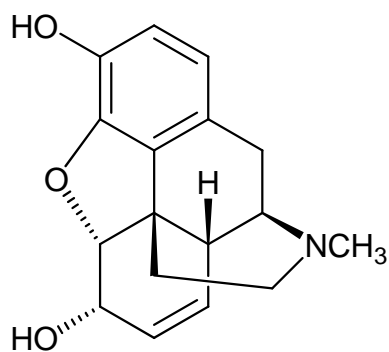
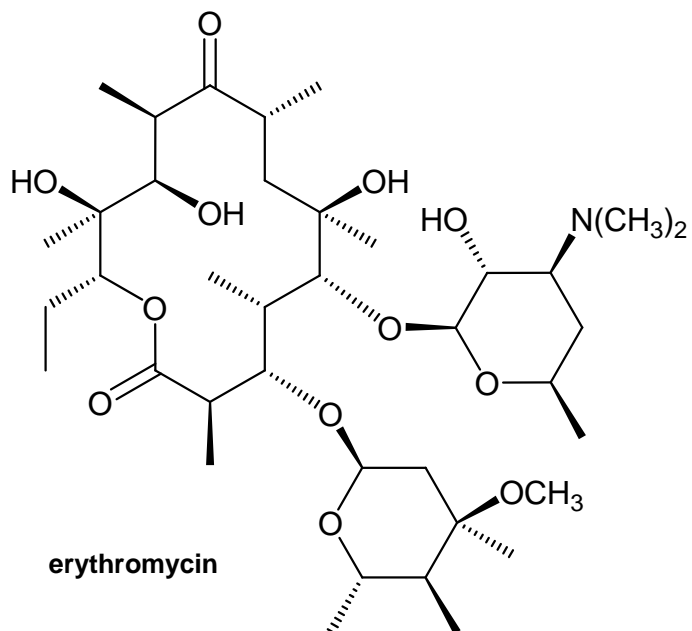
1. For each of the following molecules, identify any chiral centers and label them as being either (*R*) or (*S*).



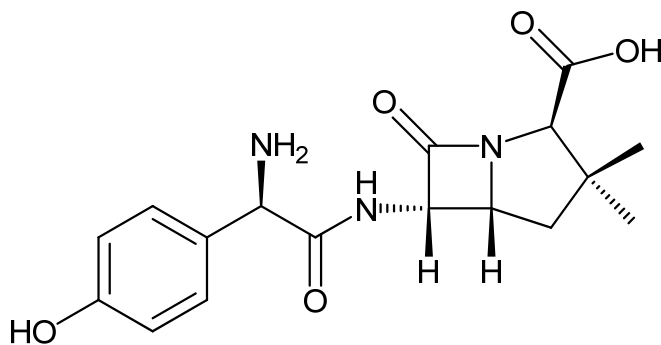
2. Each of the following reactions has stereochemical implications in terms of the products formed. For each: draw the expected organic products, indicate how much of each stereoisomer is formed, and label the chiral centers as being either (*R*) or (*S*).



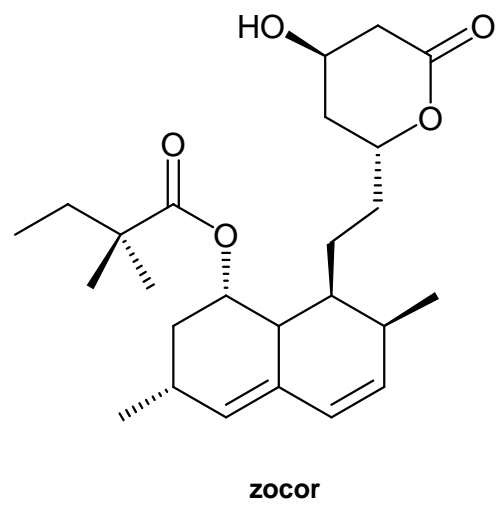
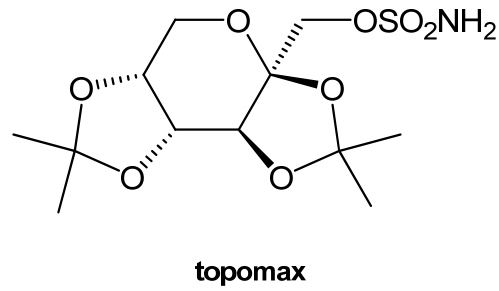
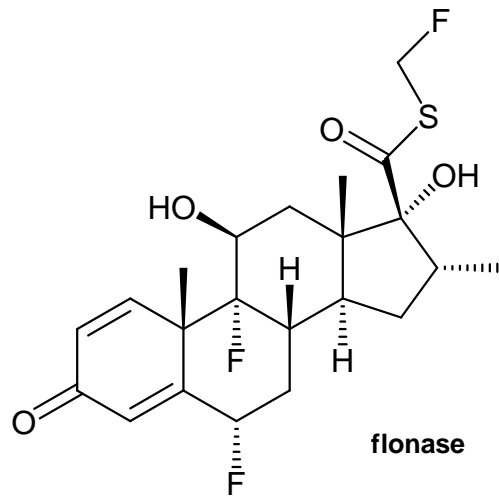
1. For each of the following pharmaceutical compounds, identify all stereogenic (i.e. all asymmetric carbon atoms) and label the configuration of each as being either (*R*) or (*S*).



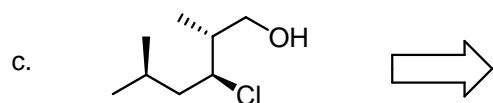
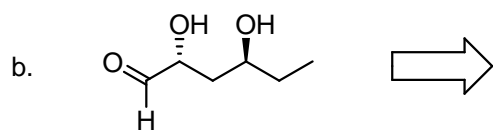
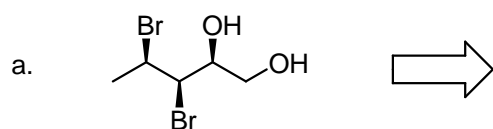
morphine



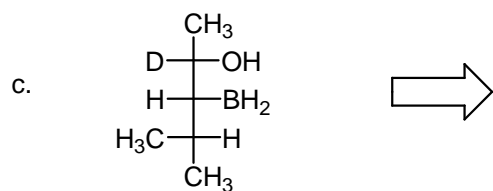
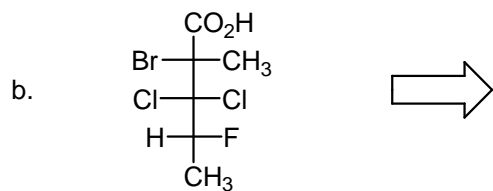
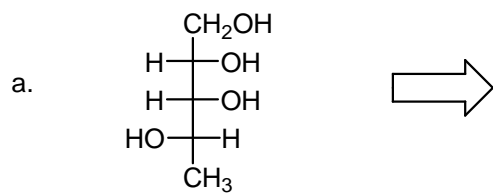
amoxicillin



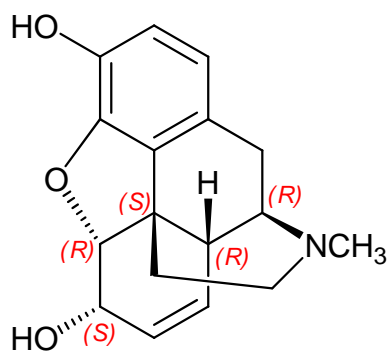
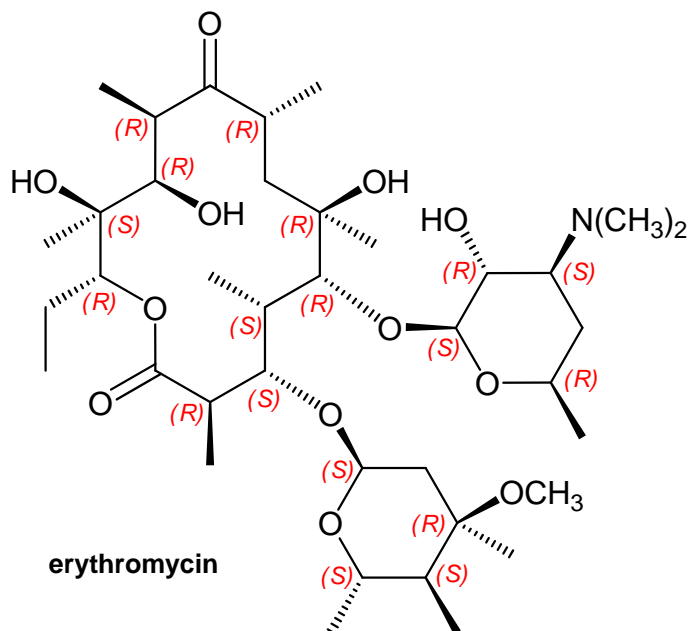
2. Convert the following “wedge-dash” depictions into Fischer projections.



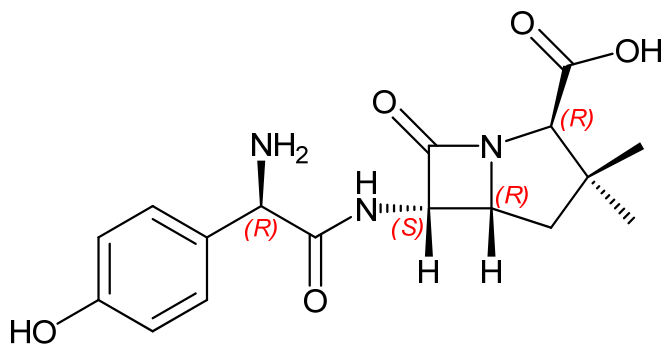
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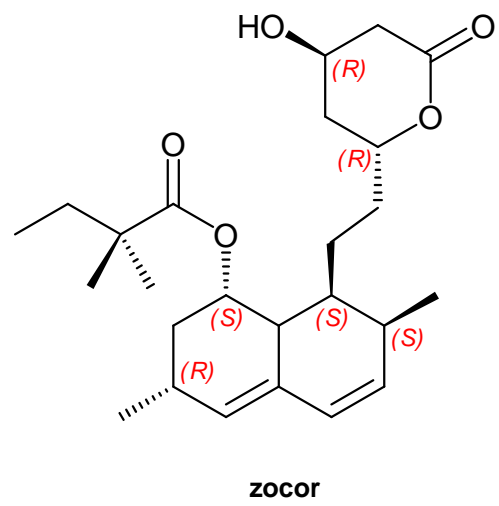
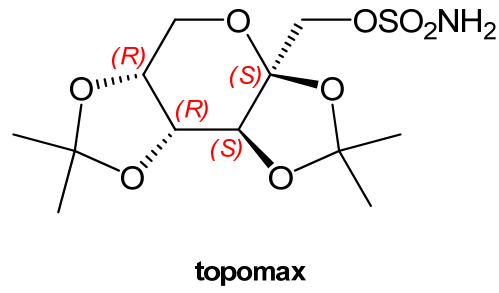
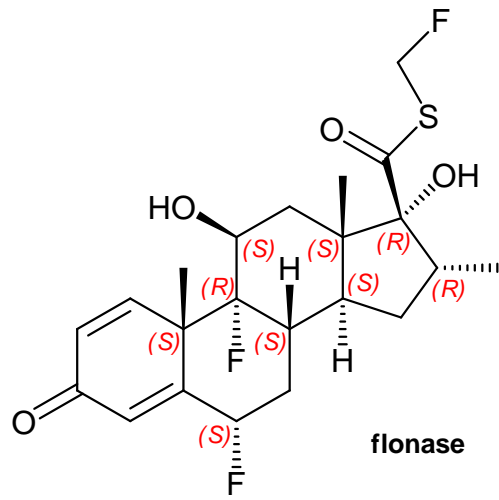
1. For each of the following pharmaceutical compounds, identify all stereogenic (i.e. all asymmetric carbon atoms) and label the configuration of each as being either (*R*) or (*S*).



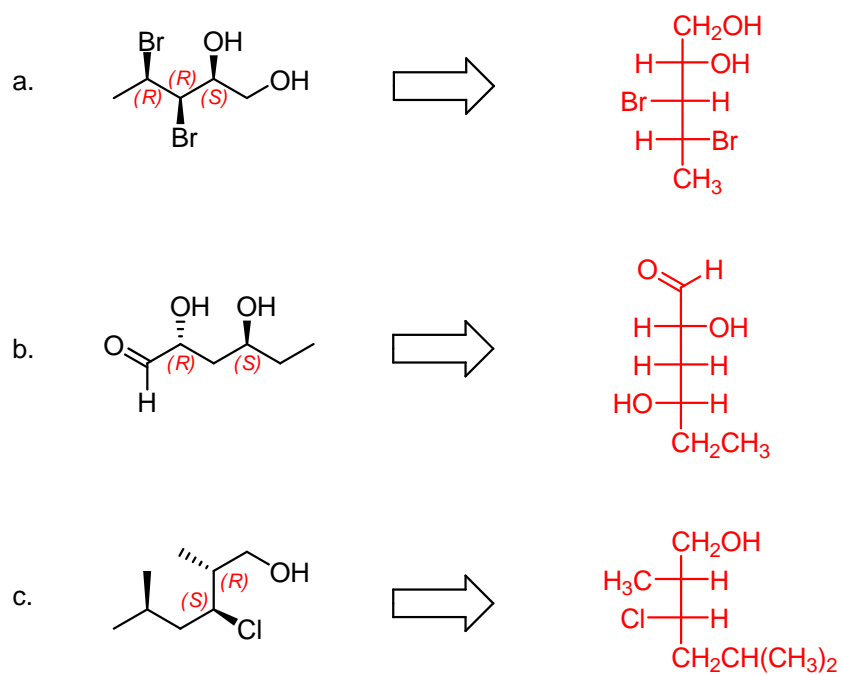
morphine



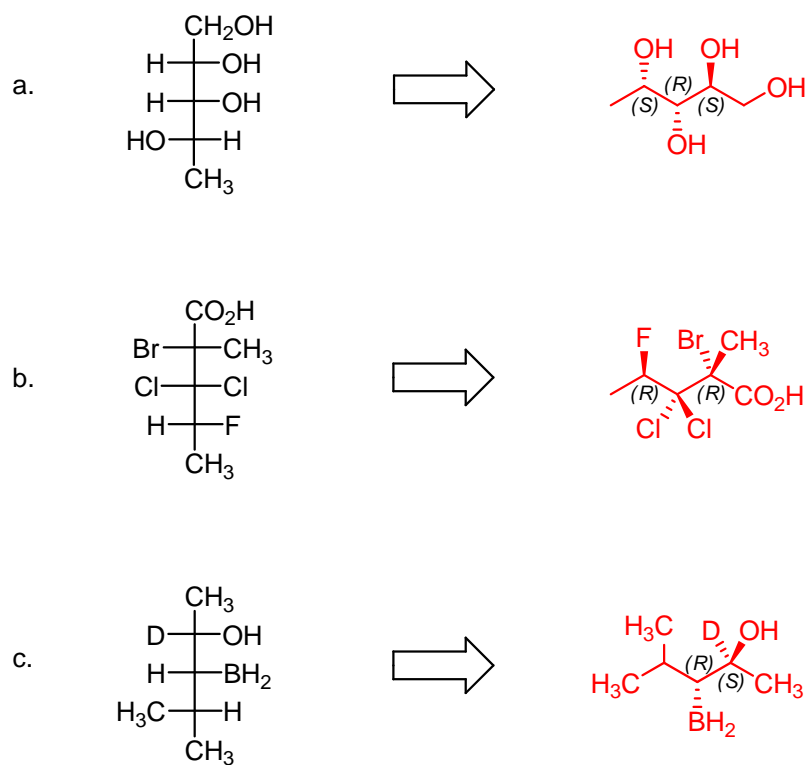
amoxicillin



2. Convert the following “wedge-dash” depictions into Fischer projections.



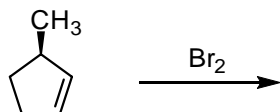
3. Convert the following Fischer projections into “wedge-dash” depictions.



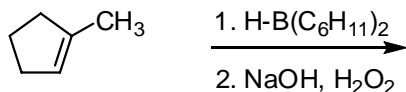
Mechanism and Stereochemistry

Note: These problems are quite challenging and are meant to “bring it all together” in terms of the mechanism and stereochemistry ideas seen thus far in Chemistry 3719 – if you can do these then you really are on top of the material. If you don’t get the idea initially, at least use these problems as a way to start reading the material in more depth (notes *and* book) and begin putting the ideas from Chapters 4, 5, 6, 7, and 8 together (mechanism *and* stereochemistry).

1. Give all of the possible dibromide products from the following reaction and a mechanism for their formation. Label each stereocenter in those products as being either (*R*) or (*S*); how many unique products are actually formed here?



2. Give the major expected products from each step of the following reaction sequence. To do this you must remember that the alkene is flat and has two “faces” onto which the H-BR₂ reagent may add; with this in mind, how many organoborane products do you expect *as major products* from the first step, and how many alcohols do you expect *as major products* from the second step? Label any stereocenters that are formed in each of the reaction steps as being either (*R*) or (*S*) and, if you get more than one product in each step, use this (*R*)/(*S*) information to relate the products in each step (are they enantiomers, diastereomers, or completely unrelated?)

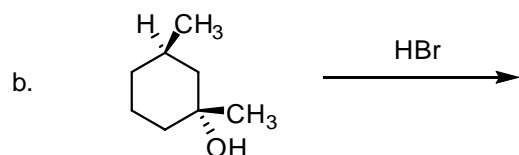
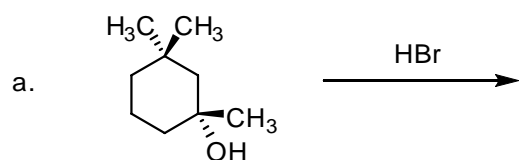


3. The mechanism for the ozonolysis of an alkene involves the initial concerted, *syn*, addition of O₃ to the alkene followed by the initial product (the molozonide) breaking apart, and then reforming, to give the ozonide product. There are two initial molozonide products possible here; draw them, identify any stereocenters, label them as being (*R*) or (*S*), and then relate the molozonides as being either enantiomers or diastereomers (remember that the alkene is flat and has two faces). Using one of the two malozonides, complete the ozonolysis mechanism to show the formation of the ozonide.

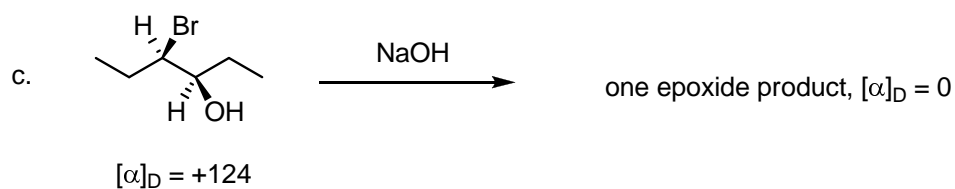
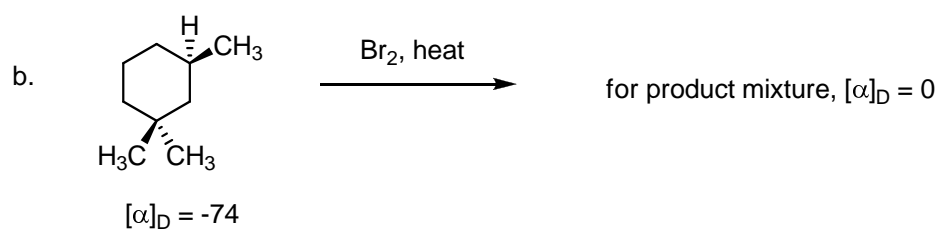
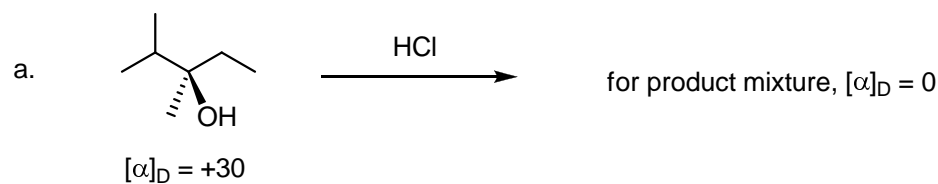


4. The above problems focused on the idea that addition to an alkene may result in stereoisomeric products; addition from “above” the double bond (i.e. to the “top” face of the alkene) gives one stereoisomer, whereas addition from “below” (i.e. to the “bottom” face) gives the other stereoisomer. The outcome of these reactions, in terms of stereoisomerism seen within the products, is a direct result of the mechanism that operates in the reaction. Since carbocations and radicals are flat, this idea also plays a role in their chemistry. The following questions are related to those reactions.

The following reactions both result in more than one substitution product; draw those products, then label the configuration of any stereocenters within the products. How are the products related to each other in part a.)? How are the products related to each other in part b.)? Explain the differences in the stereochemical outcomes of the two reactions.

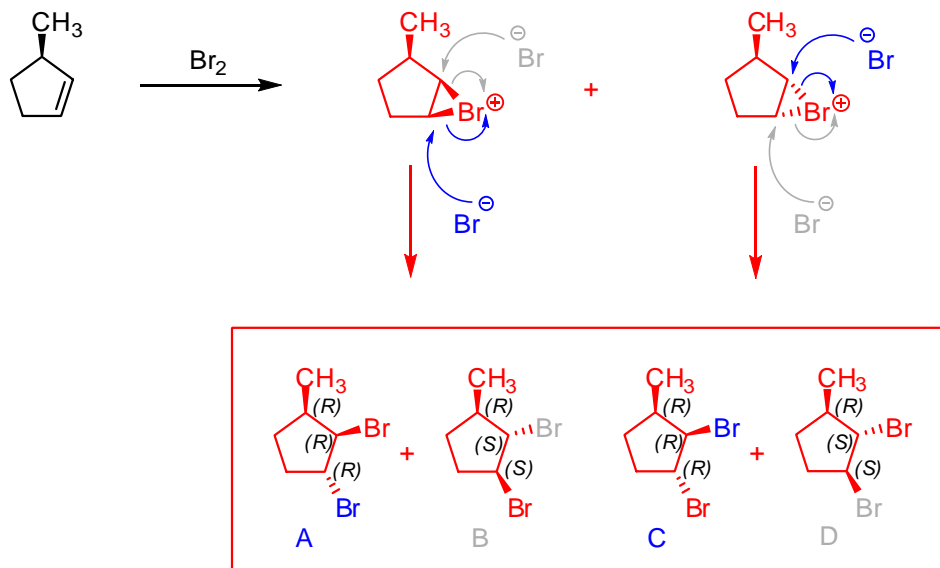


5. The reactions below begin with optically active starting materials yet the organic product(s) from each reaction are optically inactive (i.e. $[\alpha]_D = 0$). Consider each of the reactions and, importantly, the mechanism that is operating in each case in order to explain each stereochemical outcome. In other words, what are the products, how are they formed, and why is the optical rotation of the product(s) 0° in each case?



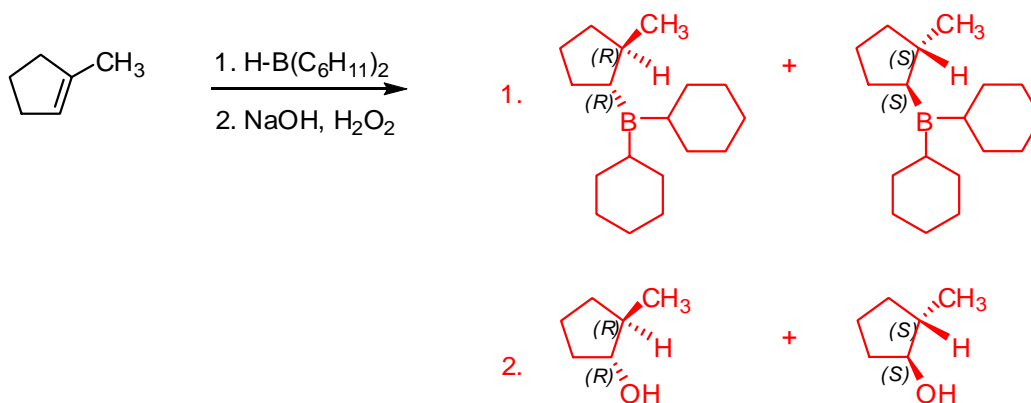
Mechanism and Stereochemistry - Key

1. Give all of the possible dibromide products from the following reaction and a mechanism for their formation. Label each stereocenter in those products as being either (*R*) or (*S*); how many unique products are actually formed here?



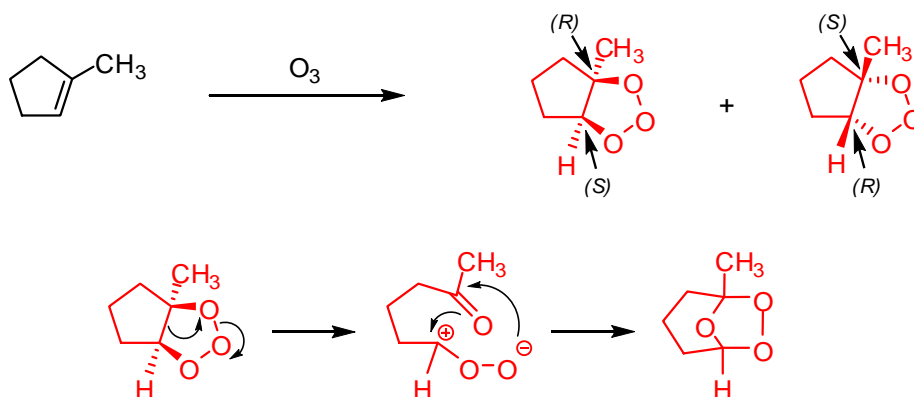
Since the mechanism is an *anti addition*, the initial Br adds to either the “top” or “bottom” face of the alkene, i.e. on the same side as the CH_3 group (“top”) or opposite the CH_3 group (“bottom”) to give two possible *bromonium ion* intermediates as shown. The Br anion (the nucleophile) then attacks from the opposite face to give the *trans* stereochemistry for the Br substituents. Seeing that there are two different products possible from each situation (A and B, C and D) you are then able to label each stereocenter as being either (*R*) or (*S*); you will then see that A = C and B = D so there are actually only two stereoisomeric products formed in this reaction.

2. Give the major expected products from each step of the following reaction sequence. To do this you must remember that the alkene is flat and has two “faces” onto which the H-BR_2 reagent may add; with this in mind, how many organoborane products do you expect from the first step, and how many alcohols from the second step? Label any stereocenters that are formed in each of the reaction steps as being either (*R*) or (*S*) and, if you get more than one product in each step, use this (*R*)/(*S*) information to relate the products in each step (are they enantiomers, diastereomers, or completely unrelated?)



This reaction involves the *syn* addition of the H from H-BR₂ to the more crowded C of the alkene, and the BR₂ portion to the less crowded C of the alkene to give one major *regioisomeric* product. By adding this H-BR₂ reagent to the alkene we generate two new chiral C atoms; depending upon whether the H-BR₂ adds to the top or bottom face of the alkene, those new stereocenters will either be (*R*) or (*S*) and thus you have the formation of stereoisomers. Looking at the products above from step 1; if H-BR₂ adds from “below” the alkene the CH₃ group is pushed “up” and the isomer shown is formed; this happens to be (*R*)/(*R*) at the two new chiral centers. If H-BR₂ adds from “above” the alkene the CH₃ group is pushed “down” and the second isomer shown is formed; this happens to be (*S*)/(*S*) at the two new chiral centers. Since the two newly formed stereocenters have the opposite configuration in each case, these two products are *enantiomers*. In the second reaction you have to remember that the stereochemistry of the C-B bond is retained when the C-O bond is formed in each case. So, the first product from step 1 gives the first product shown from step 2 with the stereochemistry retained (i.e. below the plane with C-O being a dashed bond just as C-B was). The second product from step 1 likewise gives the product of *stereochemical retention*, i.e. the second product from step 2. These two alcohol products are also related as *enantiomers*.

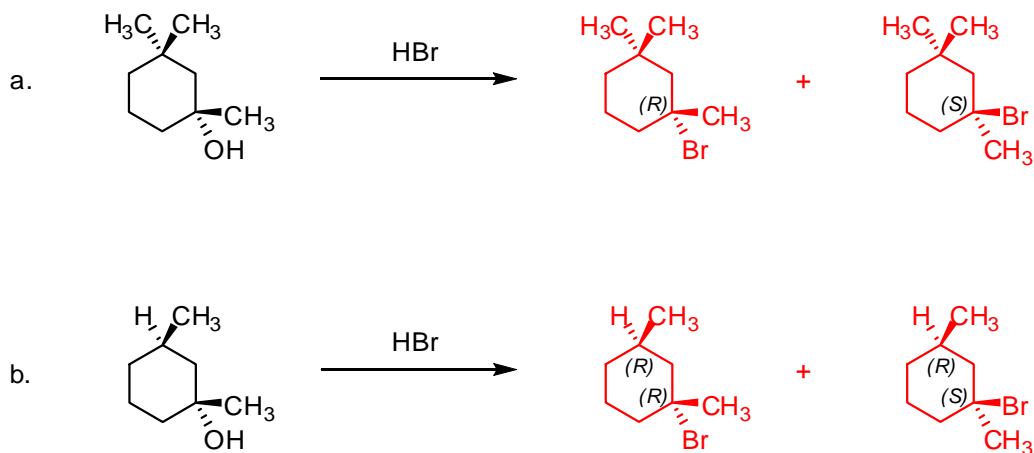
3. The mechanism for the ozonolysis of an alkene involves the initial concerted, *syn*, addition of O₃ to the alkene followed by the initial product (the molozonide) breaking apart, and then reforming, to give the ozonide product. There are two initial molozonide products possible here; draw them, identify any stereocenters, label them as being (*R*) or (*S*), and then relate the molozonides as being either enantiomers or diastereomers (remember that the alkene is flat and has two faces). Using one of the two malozonides, complete the ozonolysis mechanism to show the formation of the ozonide.



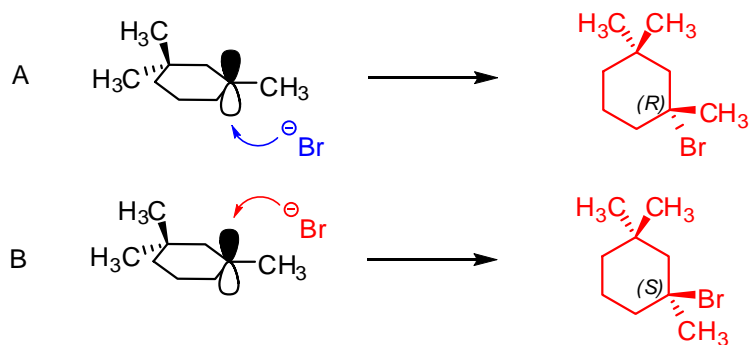
Since the first step in the ozonolysis reaction is a *syn addition* to the alkene, the O₃ may bond either to the “top” face of the alkene or the “bottom” face of the alkene, *but not both*. In this example this will result in two different, stereoisomeric, products as shown. Both of these molozonide intermediates will then collapse as shown above, with the unstable intermediate thus formed recombining to give the ozonide product.

4. The above problems focused on the idea that addition to an alkene may result in stereoisomeric products; addition from “above” the double bond (i.e. to the “top” face of the alkene) gives one stereoisomer, whereas addition from “below” the double bond (i.e. to the “bottom” face) gives the other stereoisomer. The outcome of these reactions, in terms of stereoisomerism in the products, is a direct result of the mechanism that operates in the reaction. Since carbocations and radicals are flat, this idea also plays a role in their chemistry. The following questions are related to those reactions.

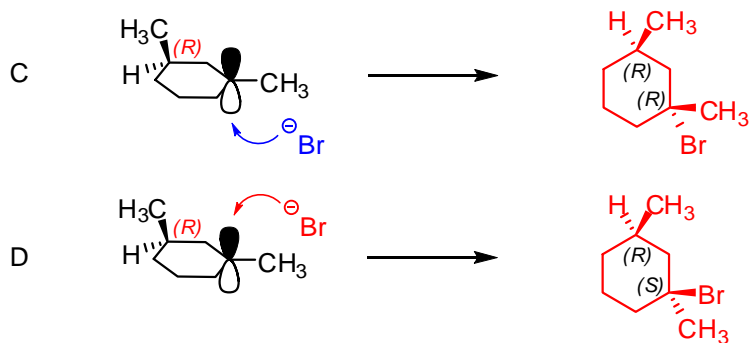
The following reactions both result in more than one substitution product; draw those products, then label the configuration of any stereocenters within the products. How are the products related to each other in part a.)? How are the products related to each other in part b.)? Explain the differences in the stereochemical outcomes of the two reactions.



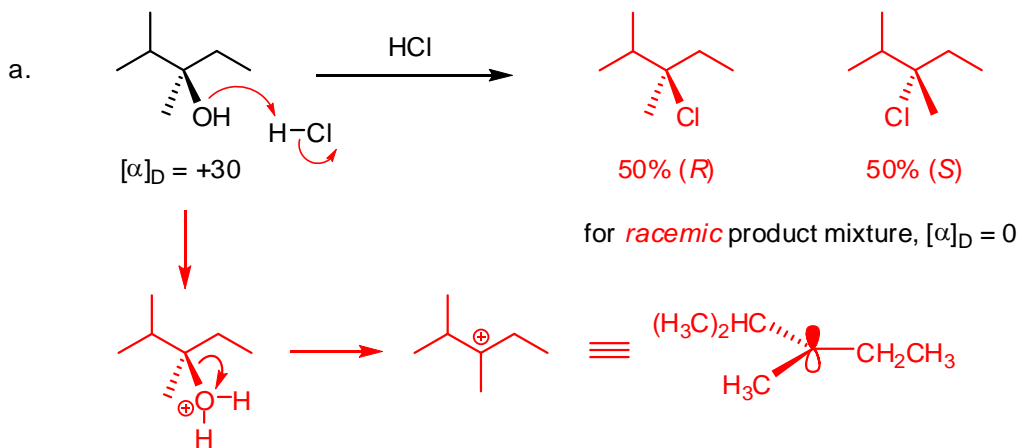
These are both S_N1 reactions in which the OH group first gets protonated by the HBr; then the water leaving group breaks away to form a *tertiary carbocation*. The carbocation is an sp^2 hybridized carbon atom with three (different) alkyl groups attached and an empty p orbital. Since the p orbital is symmetrical (i.e. the top lobe is the same as the bottom lobe), the Br anion (nucleophile) may add from either side. Attack from underneath (pathway A below) gives the (*R*) isomer; attack from above (pathway B below) gives the (*S*) isomer. The products from this reaction are therefore related as *enantiomers*. Note that the other substituted carbon (the one with the two CH_3 groups attached) is **not** a chiral center.



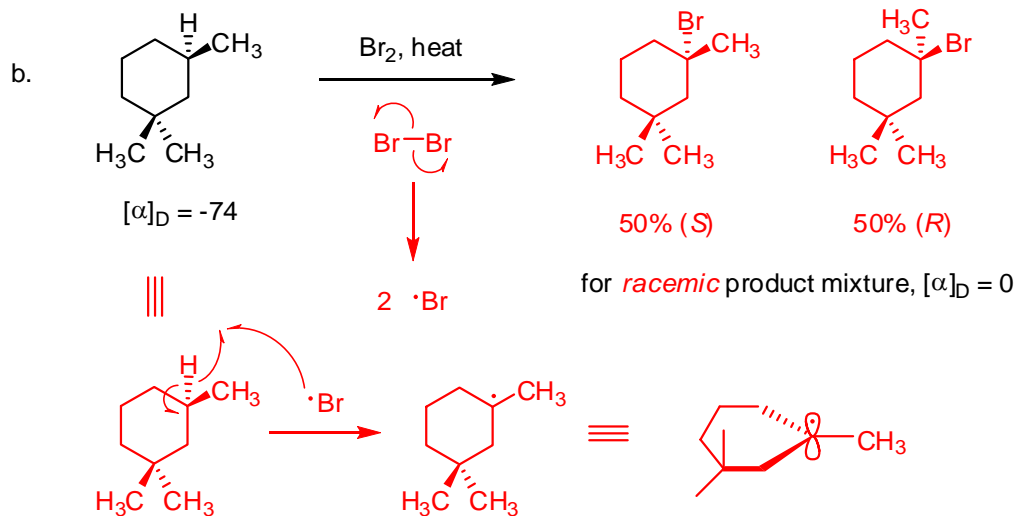
The second reaction is very similar with the added twist of a chiral center already in the starting material. That chiral center *does not change* during this reaction; therefore the products will both have one (*R*) stereocenter and either a second (*R*) center (see pathway C) or an (*S*) center (see pathway D). The products are definitely stereoisomers but they are no longer related as enantiomers; they are *diastereoisomers*.



5. The reactions below begin with optically active starting materials yet the organic product(s) from each reaction are optically inactive (i.e. $[\alpha]_D = 0$). Consider each of the reactions and, importantly, the mechanism that is operating in each case in order to explain each stereochemical outcome. In other words, what are the products, how are they formed, and why is the optical rotation of the product(s) 0° in each case?

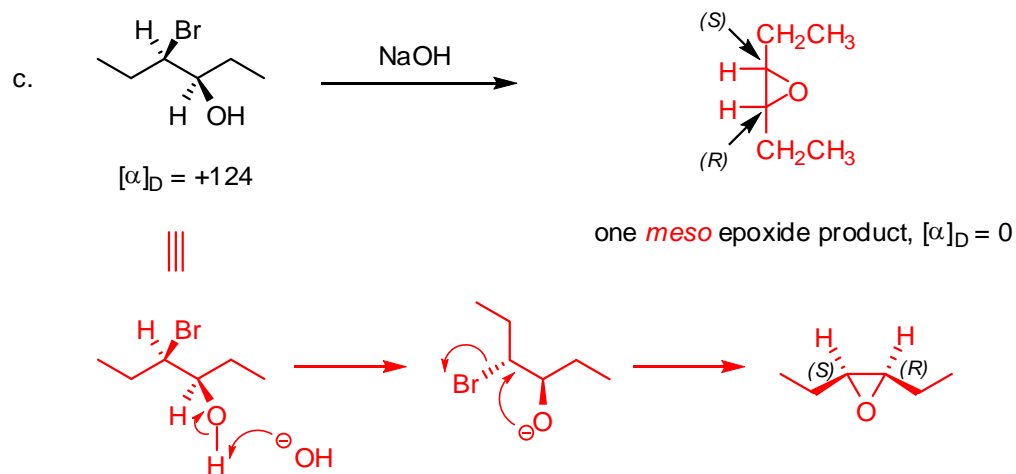


In this $\text{S}_{\text{N}}1$ reaction, the powerful acid (HCl) first protonates the OH group, which generates a good leaving group. When water breaks away the α -carbon rehybridizes, from sp^3 to sp^2 , and consequently changes shape from tetrahedral to trigonal planar (i.e. flat). In the “side-on” depiction of the carbocation (above) it is obvious that the top lobe of the (symmetrical) p orbital is just as accessible as the bottom lobe. The chloride anion will now behave as a nucleophile by donating electrons (note this is also acting as a Lewis base) to the carbocation. Since there is an equal chance of the chloride anion attacking from the top or bottom of the carbocation, two products are formed; one is the (*R*) enantiomer, the other the (*S*) enantiomer. Since these products are formed in (approximately) equal amounts, and their (equal but opposite) optical rotations will cancel each other out, we have a racemic mixture with a net retention of 0° .



This reaction involves free radicals with one of the key propagation steps being the abstraction of H by a Br atom (radical). Since a Br atom is quite selective (much more so than a Cl atom) in terms of the type of H that it will abstract, the removal of the single 3° H from the starting material, to leave a 3° carbon radical, is expected. This results in the carbon going from sp^3 to sp^2 hybridization, and consequently changing shape from tetrahedral to trigonal planar (i.e. flat). In the “side-on” depiction of the radical (above) it can be seen

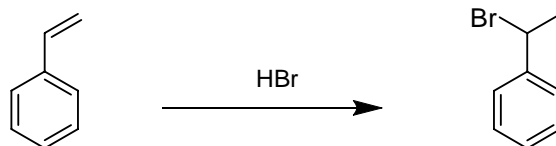
that the top lobe of the (symmetrical) p orbital is just as accessible as the bottom lobe, therefore the subsequent reaction with Br₂ may occur at either face (with equal likelihood) to produce equal amounts of the (*R*) and (*S*) enantiomers. Again, this constitutes a racemic mixture for which the overall optical rotation will be 0°.



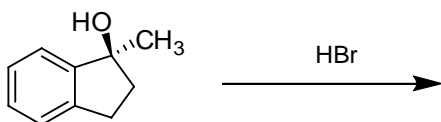
This reaction is the equivalent of an “internal” S_N2; the hydroxide will deprotonate the OH group on the starting material, thereby making an alkoxide nucleophile. The Br, which will serve as a leaving group, must be aligned in the opposite direction to allow backside attack to occur; therefore the displacement will occur from the conformation shown above. This results in the formation of the *meso* product in which the (*S*) stereocenter is mirrored internally by the (*R*) stereocenter; this is the *meso* situation where the rotation of each center cancels each other out and the overall rotation is seen to be 0°.

Typical Exam Questions on Chapter 10 and Chapter 11 Material

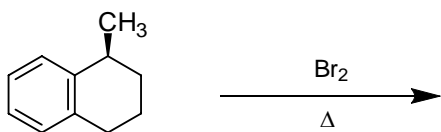
1. Give a complete mechanism, using arrows to represent the movement of electrons, for the following reaction. Show all resonance structures that are possible for any intermediates that might be formed. Why is this the only organic product formed?



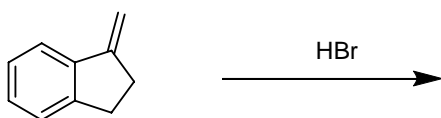
2. The following reaction results in a mixture of alkyl halide products for which $[\alpha]_D = \text{zero}$. Give the expected products then explain this result in terms of the mechanism operating during the reaction, as well as the structure of the intermediate that is formed. Include all important resonance structures for the intermediate(s).



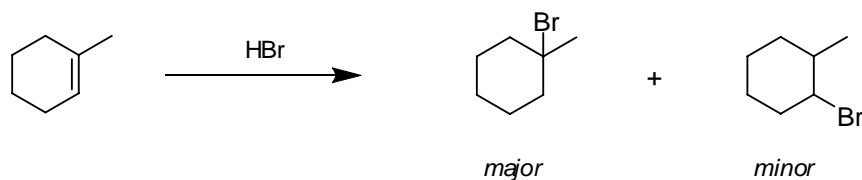
3. Give the expected organic products from the following reaction and a value for the optical rotation of the product mixture. Explain the optical rotation outcome by drawing a detailed mechanism that includes all important resonance structures for any intermediate(s) that is/are formed along the way.



4. Two major organic products are formed under the conditions below. Provide their structures, give an indication of how much of each is formed, and then a detailed mechanism (including any important resonance structures) that explains why, for the product mixture, $[\alpha]_D = \text{zero}$.



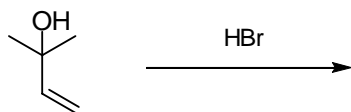
5. Explain the *regiochemical* outcome, i.e. the major/minor product distribution, for this reaction in terms of the mechanism operating.



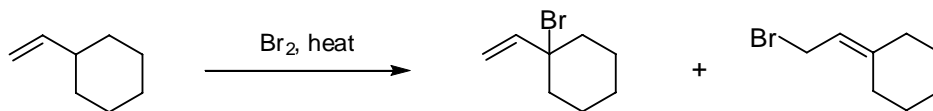
6. Rank the following carbocations in descending order of relative stability (most stable = **3**, least stable = **1**). Explain your choices in terms of the factors contributing to stabilization in each case.



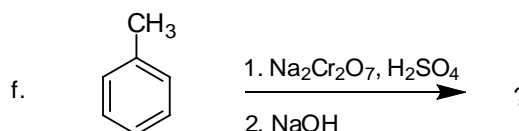
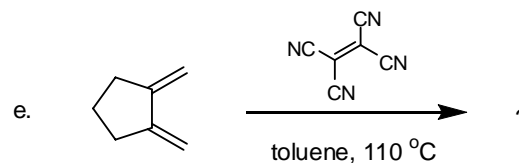
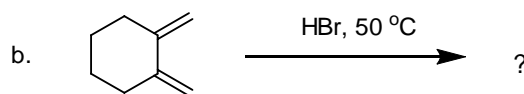
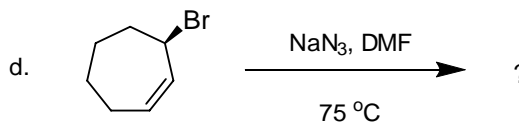
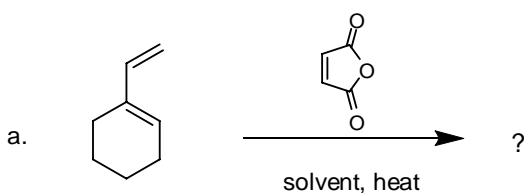
7. The following reaction gives two possible substitution products. Give structures for these products followed by a mechanistic explanation (push arrows to show how bonds are formed and broken) that explains the formation of both products. Which is the major product and why?



8. Give a complete mechanism that shows all possible steps that lead to the two products in the following reaction. Include structures of any intermediates that are formed and explain which of the two products is expected to be major.

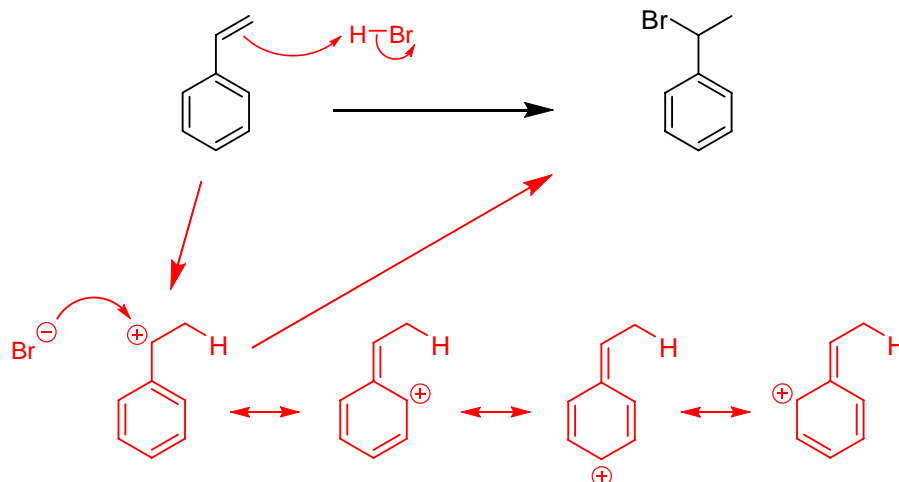


9. Give the expected products from the following reactions. Be careful when issues of stereochemistry or regiochemistry arise.



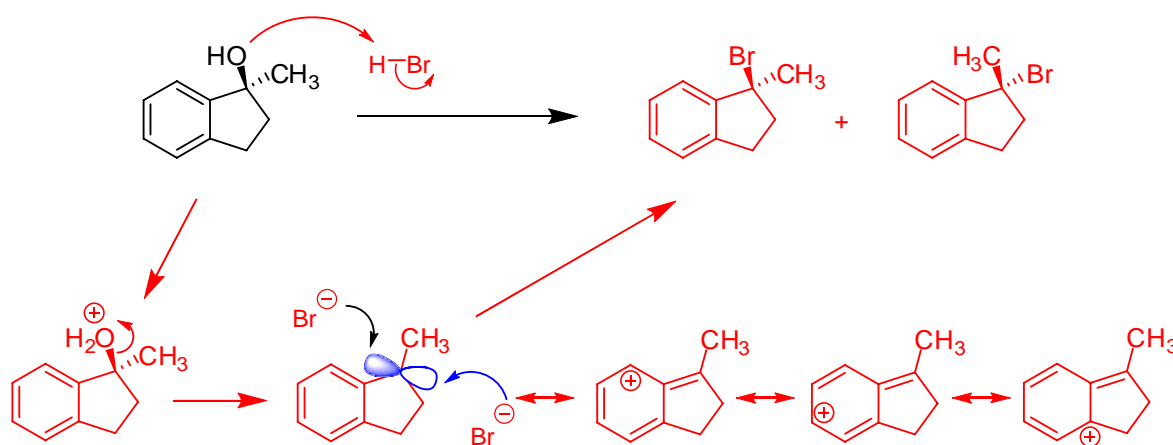
Typical Exam Questions on Chapter 10 and Chapter 11 Material – Answer Key

1. Give a complete mechanism, using arrows to represent the movement of electrons, for the following reaction. Show all resonance structures that are possible for any intermediates that might be formed. Why is this the only organic product formed?



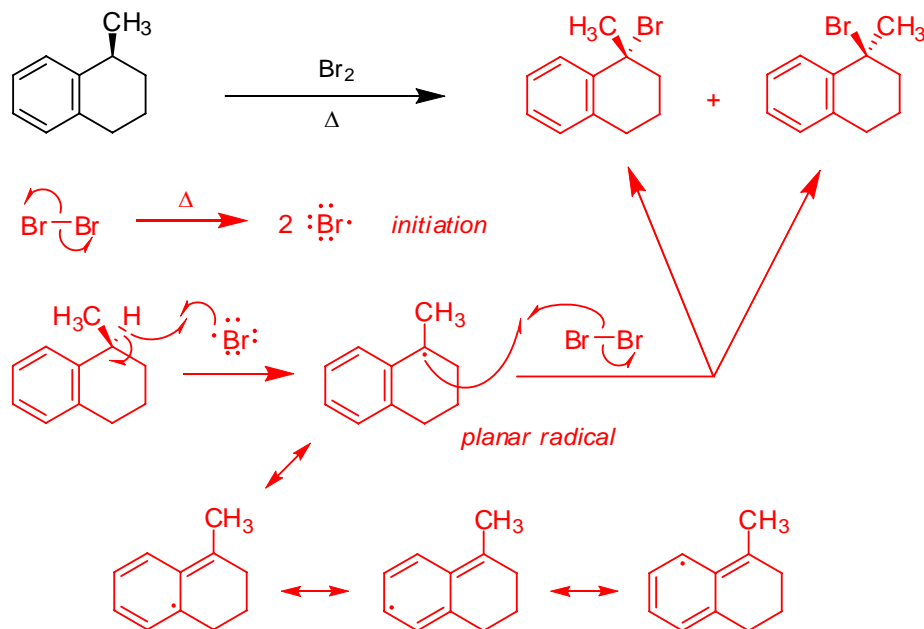
The initial addition of the proton is based on the Markovnikoff idea where the major product will result from the more stable intermediate, in this case a secondary benzylic carbocation as opposed to the alternative primary carbocation. Even though the positive charge is delocalized around the benzene ring, the bromine anion only bonds with the benzylic carbon because the (quite stable) benzene ring is then retained in the product.

2. The following reaction results in a mixture of alkyl halide products for which $[\alpha]_D = 0$. Give the expected products then explain this result in terms of the mechanism operating during the reaction, as well as the structure of the intermediate that is formed. Include all important resonance structures for the intermediate(s).



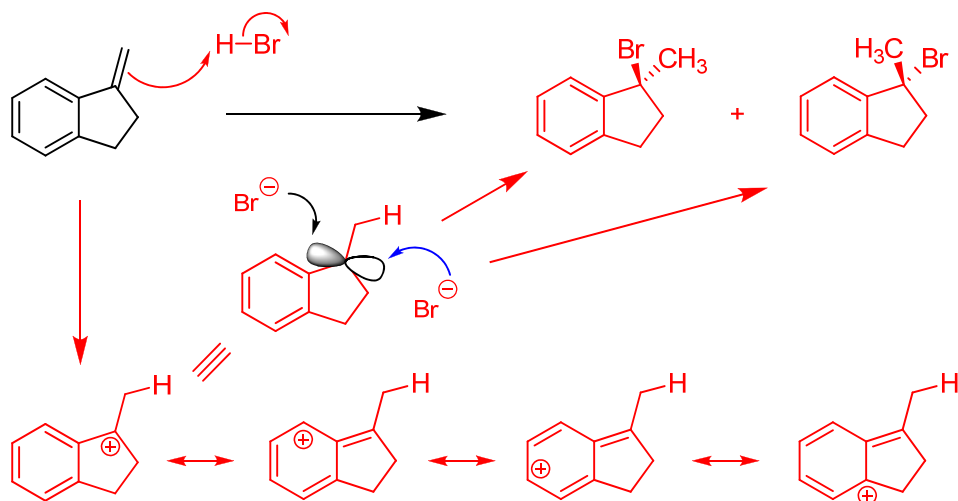
This is an S_N1 reaction at a benzylic carbon. Protonation allows the H_2O to leave and give a tertiary benzylic carbocation, which is flat and has three different groups attached to it. When the Br adds it may do so from either face to give an ~50:50 mixture of the enantiomeric products shown, which explains the optical rotation data.

3. Give the expected organic products from the following reaction and a value for the optical rotation of the product mixture. Explain the optical rotation outcome by drawing a detailed mechanism that includes all important resonance structures for any intermediate(s) that is/are formed along the way.



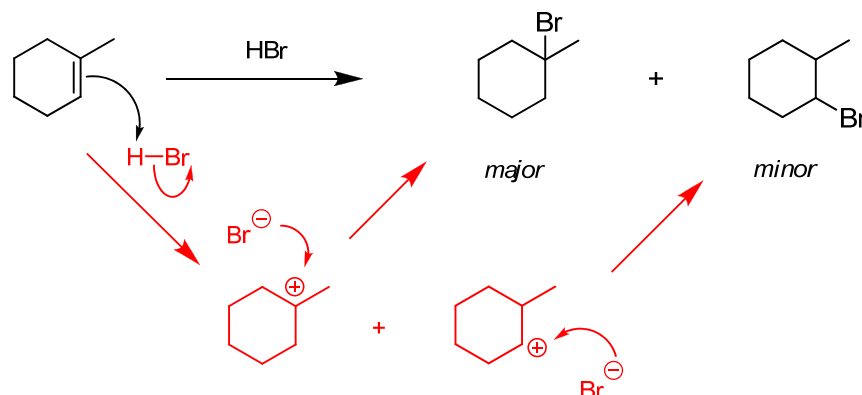
The benzylic H is abstracted preferentially since the carbon radical that remains is not only tertiary but also stabilized by delocalization through the benzene ring. Since the carbon radical is flat and has three different groups attached, the Br atom in the second propagation step will attach from either above or below the plane of the radical to give the enantiomeric products shown. Since there is approximately equal probability of attack at either face of the radical a racemic mixture of products will result and thus $[\alpha]_D = \text{zero}$.

4. Two major organic products are formed under the conditions below. Provide their structures, give an indication of how much of each is formed, and then a detailed mechanism (including any important resonance structures) that explains why, for the product mixture, $[\alpha]_D = \text{zero}$.



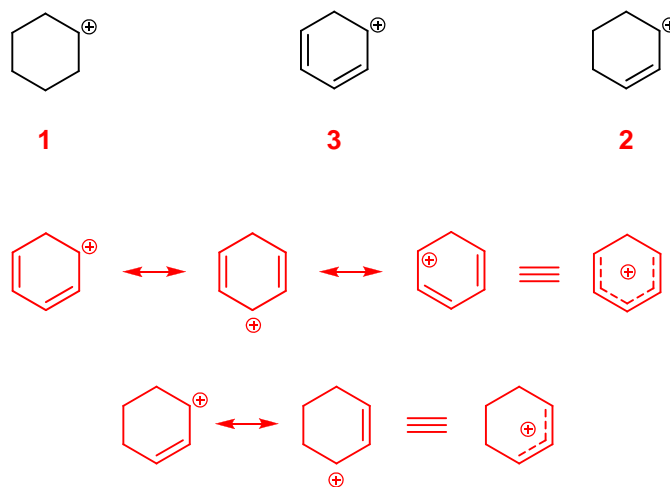
Racemic mixture formed because the flat carbocation may be attacked from above or below with equal likelihood. Optical rotations of the thus-formed enantiomers cancel.

5. Explain the *regiochemical* outcome, i.e. the major/minor product distribution, for this reaction in terms of the mechanism operating.



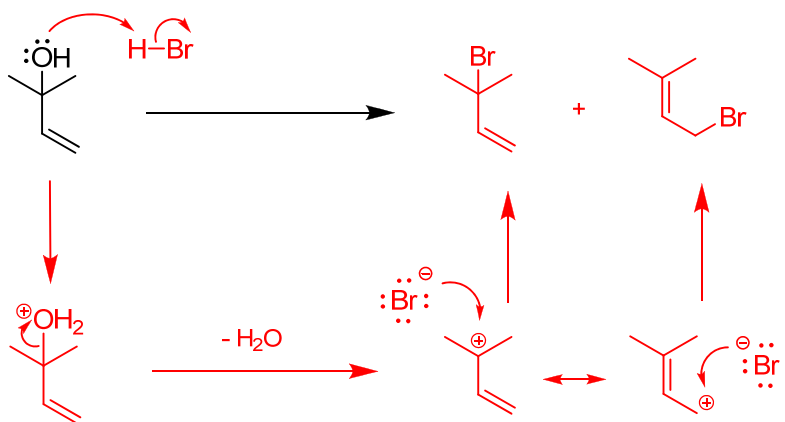
Two isomers are possible here depending upon how the initial addition of the proton occurs. Formation of the tertiary carbocation will be favoured over the alternative secondary carbocation since the tertiary carbocation will be stabilized more by donation of electron density from (more) adjacent sigma bonds (i.e. hyperconjugation). This is a classic Markovnikoff process with the major regioisomer being formed *via* the more stable carbocation.

6. Rank the following carbocations in descending order of relative stability (most stable = **3**, least stable = **1**). Explain your choices in terms of the factors contributing to stabilization in each case.



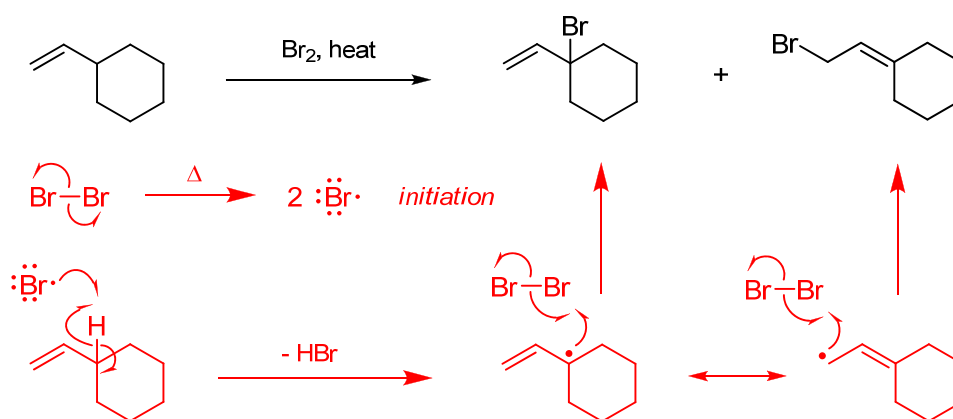
The least stable carbocation (labeled **1** above) is simply secondary and so is stabilized only by the effects of hyperconjugation. The carbocation of intermediate stability (labeled **2** above) is secondary *and* allylic and is therefore stabilized by hyperconjugation as well as delocalization (see resonance structures above). The most stabilized carbocation (see **3** above) is able to spread the electron deficiency (i.e. the positive charge) over more atoms which makes it the most stabilized of the three systems.

7. The following reaction gives two possible substitution products. Give structures for these products followed by a mechanistic explanation (push arrows to show how bonds are formed and broken) that explains the formation of both products. Which is the major product and why?



This S_N1 reaction is similar to the 1,2- versus 1,4-addition of HBr to a conjugated diene in that an allylic carbocation is formed that is able to delocalize its charge over two carbons that are not equivalent. Charge is shared between a tertiary and a primary carbon so most of the charge will be on the tertiary carbon (more significant resonance form). Br anion then attacks the carbocation and, if the reaction is kept cold (to discourage the reverse reaction), the tertiary bromide will be the major product. If the reaction is warmed up the reverse reaction (i.e. the Br breaking back off from the product to give the allylic carbocation again) will be possible and equilibrium will be established with the more highly substituted alkene (i.e. the primary bromide) will likely be the major product.

8. Give a complete mechanism that shows all possible steps that lead to the two products in the following reaction. Include structures of any intermediates that are formed and explain which of the two products is expected to be major.



In this free radical halogenation reaction the Br radical will abstract the tertiary allylic H atom to generate the carbon radical shown. The radical is stabilized by delocalization and can then react with Br_2 at either the primary carbon or the tertiary carbon. More of the electron deficiency will be at the tertiary carbon and that will lead to the major product. These reactions are run in non-polar solvents, which will suppress the loss of the Br as a leaving group and thus prevent an equilibrium being established.

9. Give the expected products from the following reactions. Be careful when issues of stereochemistry or regiochemistry arise.

