Answers to Practice Test Questions 11 Organic Reactions

Hydroxide (*OH⁻*) is the better nucleophile.
The oxygen of hydroxide is more electron rich (compared to the oxygen of water) due to its negative charge. This makes it a better electron pair donor, or nucleophile.



Product is chiral. You may draw either enantiomer, but the two Cl must be trans.

(c)



Product is not chiral.

(d)



Product is not chiral.





Product is not chiral.

(b) If HCl were used as the acid, chloride ion (Cl^{-}) would be present in solution and would compete with the water to act as a nucleophile. This would result in addition of HCl to some of the alkene molecules and addition of H₂O to other alkene molecules, generating a mixture of products:



(b) The alkenes will react with HCl.
In each case, the alkene is protonated, giving the more stable carbocation. Cl⁻ then attacks that carbocation. Thus, the H attaches to the C with more H while the Cl attaches to the C with fewer H (Markovnikov's rule).



Product is chiral. You may draw either enantiomer.



Product is chiral. You may draw either enantiomer.

Product is chiral. You may draw either enantiomer.

Product is not chiral.

(c) The alkenes will react with Br_2 . In all cases, the two atoms of Br add to opposite sides of the double bond. In some cases, this gives a CH_2Br group (not a chirality center). In some cases, this creates a chirality center.



Product is chiral. You may draw either enantiomer.

Product is not chiral. (You may need to build a model to find the mirror plane.)

Product is chiral. You may draw either enantiomer.

Product is chiral. You may draw either enantiomer.



(b) There are many acceptable answers to this question. Since there are two degrees of unsaturation and you are only allowed one C = C bond, your answer must contain one ring. Any one of the molecules shown below is acceptable:



(c) For the sake of space, one representative answer is shown. Your answer must use the alkene you drew in part (b) as the reactant. Note that the two Br add to opposite sides of the double bond. If that is detectable in the product, it must be clearly shown.



Product is chiral. You may draw either enantiomer. (d) For the sake of space, one representative answer is shown. Your answer must use the alkene you drew in part (b) as the reactant. Note that the alkene is protonated, giving the more stable carbocation. Water then attacks that carbocation (and is then deprotonated). Thus, the H attaches to the C with more H while the OH attaches to the C with fewer H (Markovnikov's rule).



Product is not chiral.

6.

(a) This is a substitution reaction.

Elimination is not possible because there is only one carbon atom in CH_3Br so we do not have "neighbouring carbon atoms, one with H attached and one with a leaving group attached".



(b) This is an addition reaction.*Add the OH to the more highly substituted carbon.*





The observed product forms from the carbocation on the left. The product in the box would have to form from the carbocation on the right. The carbocation on the left is significantly more stable than the carbocation on the right for two reasons:

- It is more highly substituted. (There are two carbon atoms attached to C^+ in the carbocation on the left. There is only one carbon atom attached to C^+ in the carbocation on the right.)
- The carbocation on the left is resonance-stabilized. The positive charge is delocalized over four carbon atoms. (In other words, the positive charge is shared by four atoms.) This is preferable to the carbocation on the right in which the positive charge is localized on just one carbon atom. The relevant resonance structures are shown below.



8. (a)



(b) The first step in the addition of *HBr* to an alkene is protonation of the alkene, forming a carbocation. This is possible because *HBr* is a strong acid.
HF is not a strong enough acid to protonate the alkene, so no carbocation is formed. As such, the reaction does not proceed.



Product is chiral. You may draw either enantiomer. You may choose any ONE of the three double bonds (since they are all equivalent), but the two Br atoms must be added trans across that double bond.

iii.





(b) Markovnikov's rule states that, when adding *HX* to an alkene or alkyne, add the H to the carbon that already has more H attached.

Markovnikov's rule usually works because, when you follow it, you generate the more substituted carbocation which is usually the more stable carbocation intermediate. As seen below, following Markovnikov's rule when adding HCl to 1-butene gives a secondary carbocation (two C attached to C^+ . If Markovnikov's rule was not followed, the carbocation would be primary (only one C attached to C^+).



carbocation formed when following Markovnikov's rule

10.

(a)



(b) The carbon atom will be electrophilic. The oxygen atom will be nucleophilic.



(c) To make the product shown in the box, the reaction would have to proceed via the carbocation intermediate shown below:



This primary carbocation intermediate is less substituted (and therefore less stable) than the tertiary carbocation intermediate shown in part (b). As such, its formation is not favoured.



Calculated pictures for the allyl cation are shown because adding methyl groups at each end of the pi system complicates the MOs slightly. The allyl pictures are accurate enough to predict the behavior of this cation (and are all a first year student would be expected to predict). Note that the pi system (the set of connected atoms that are not tetrahedral) includes only the middle three carbon atoms of this cation.

(c) The electrons from Br^{-} will be accepted by the LUMO of the carbocation.

The LUMO has lobes on the two terminal C of the π system but not on the central C.

So, the Br will bond to one of the terminal C of the π system. Either way, the same product is obtained:



Product is chiral. You may draw either enantiomer.