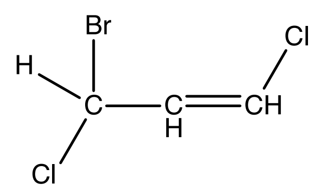
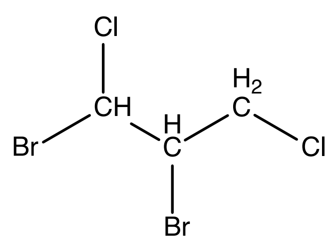
Chemistry 2000 answers for review problems on organic chemistry, acids and bases

1. (a) Yes: the mirror image of this molecule is different from the molecule itself.

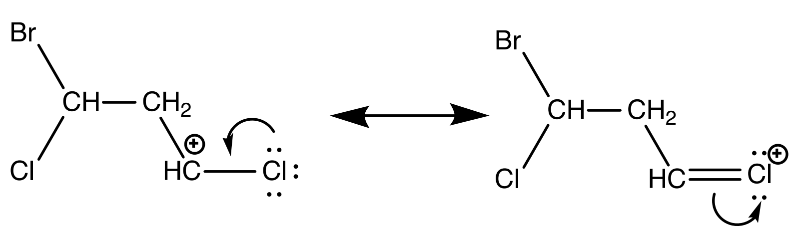
   (b) i. The product of the first addition is the following:

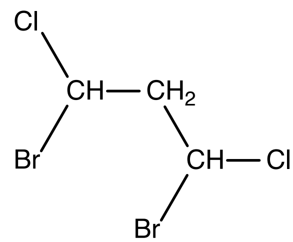
   ii. The product of the second addition is trickier. If you put the positive charge on the central carbon, you have a secondary carbocation which, based on what we learned in class, ought to be more stable than the alternative. If you decide that this is the more stable carbocation, then you would get the following product:

   However, in the terminal carbocation, you can resonance-delocalize the charge to the chlorine atom:

   Although this is not a "good" resonance structure (positive charge on electronegative atom), it will contribute somewhat to stability of the cation. If you decide that this is the better carbocation, then the product is



I do not know which of the two products would be formed if you actually tried this experiment. Moreover, while we tend to emphasize simple cases in class where there is one preferred product, it's possible in this case that the two carbocations have similar stability, and that both products are formed. Since there isn't one obvious right answer, what I would really want to see on a question like this would be

A. awareness of at least one issue related to the stability of carbocations, and

B. correct electron pushing to get the products.

2. (a) 9.00

   (b) The second K_b, associated with the equilibrium

$$HSO_3{}^- + H_2O \rightleftharpoons H_2SO_3 + OH^-,$$

   is smaller than the first K_b. (This is always the case because of the reduced negative charge of the protonated base.) Moreover, by Le Chatelier's principle, the hydroxide ion generated by the first equilibrium would shift the second equilibrium towards the reactants, i.e. prevent this second equilibrium from being a significant source of hydroxide.

3. (a) 3.64

   (b) i. The reactions of $H_2PO_4^-$ as an acid and as a base can both be written as reactions of this amphoteric species with water. If you look at these reactions, since they have the same reactants and both have two products, you can compare the equilibrium constants directly. Thus, $H_2PO_4^{2-}$ will react as an acid if $K_a(H_2PO_4^-) > K_b(H_2PO_4^-)$.

ii. $K_a(HPO_4^{2-})$ is necessarily smaller than $K_a(H_2PO_4^-)$. Moreover, the protons generated by the dissociation of $H_2PO_4^-$ cause the dissociation

$$HPO_{4(aq)}{}^{-2} \rightleftharpoons H^+_{(aq)} + PO_{4(aq)}{}^{3-}$$

to shift towards the reactants (Le Chatelier's principle).

4. Yes, but this reaction will not go to completion, i.e. an equilibrium will be reached with significant amounts of each acid/conjugate base pair.

5. Each of these acids is a stronger acid than acetic acid due to an inductive effect of the halogen. However, chlorine is more electronegative, so this inductive effect will be stronger, and therefore chloroacetic acid will be the stronger acid.