7-1 We can see from table 7-1 that the most reactive alkyl halides in solvolysis reactions are tertiary and the least are primary. In this exercise, we are comparing the reactivity of a primary with a tertiaryalkyl halide in a solvolysis reaction. The tertiary wins hands down. The discussion in the answer inthe textbook of steric hindrance in the primary halide is not relevent to this reaction as water is a poor nucleophile for second order substitution reactions.

7-2 The key to an exercise of this type is to first identify the bond changes in the reaction. Then, we find the total energy of the bonds that are broken and find the difference with the total of the energies of the bonds made. Notice that no sign is implied in the result of this calculation. The sign of ΔH is most easily determined by remembering that the change in energy is negative if the bonds made are stronger than the bonds broken.

Bonds broken   Bonds made

C—Br   71   C—OH   96

H—OH   119   H—Br   87
         190   183
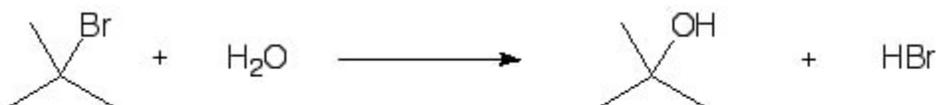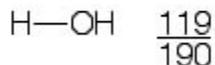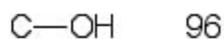
$$\Delta H = 190 - 183 = +7 \text{ kcal/mole}$$

There is no practical way to actually run this reaction as detailed in the exercise. The reaction of HBr with H_2O is very exothermic and will drive the reaction to the right. Even if only one equivalent of water is used, the reaction will proceed to 50% conversion, consuming half of the water for reaction with the product HBr. Again, another example of a poorly though thru exercise as the implication is that the conversion of an alkyl bromide to an alcohol is not energetically practical. Nothing could be further from the truth.

7-3 That this sample of 3-bromo-3-methylhexane is optically active indicates that there is more of one enantiomer present than the other. In a solvolysis reaction, an intermediate carbocation is produced by loss of the leaving group (in this case, bromide ion). Carbocations bear only three substituents and thus the positively charged carbocation is no longer a stereocenter. With no other nucleophile present, the carbocation reacts with the bromide ion to reform the alkyl bromide. However, addition of the bromide ion to either side of the cation is equally likely, resulting in a racemic mixture of 3-bromo-3-

methylhexane.

7-4 This exercise is worked out on page 257 as "Working with Concepts".

7-5 Unlike the example in exercise 7-3, the cation that results from loss of chloride ion has two different sides and addition of water will occur at different rates. Addition to one side leads to a product alcohol where the OH group is cis to the methyl group whereas addition to the other side results in the trans isomer.
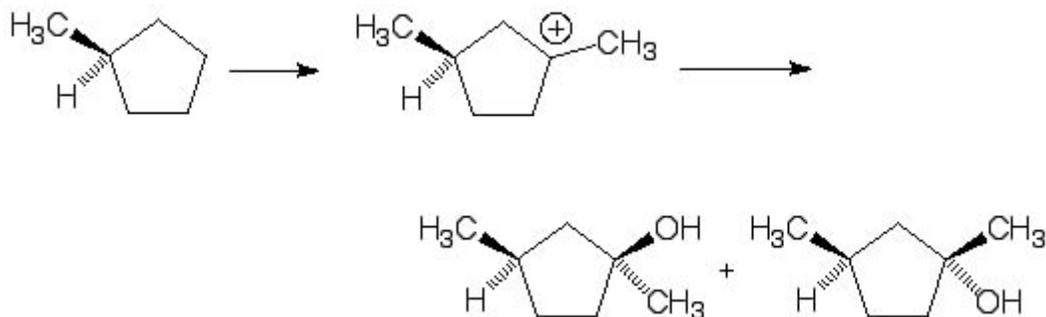
7-6 This exercise is worked out on page 259 as "Working with Concepts".

7-7 Aqueous ammonia is not really ammonium hydroxide as we call it but rather ammonia dissolved in water. Thus, the two major nucleophilic species present are ammonia and water and we would predict the former to be more nucleophlic. The product is thus the amine.

7-8 This exercise is worked out on page 262 as "Working with Concepts".

7-9 We expect reactions of secondary substrates in water to at least partially follow first order pathways involving carbocation intermediates. Thus, we expect loss of stereochemical purity.

7-10 This exercise clearly points out the weakness that is inherent in first order reactions. Although simple in appearance, the reaction of a tertiary alkyl bromide with water in a solvolysis reaction can lead to multiple products. Why does the exercise use aqueous ethanol? Because a simple alkylbromide such as 2-bromo-2-methylpropane is not soluble in water by itself. However, the addition of ethanol not only increases solubility but also adds another nucleophile that can add to the intermediate carbocation. Thus, both an alcohol resulting from reaction with water and an ether resulting from reaction with ethanol are produced. In addition, some of the carbocation reacts by loss of a proton toform an alkene product.

7-11 The reagent, hydroxide ion, is both a nucleophile and a base. Reaction of this small nucleophile with a primary alkyl halide will result in substitution to the virtually

exclusion of elimination. With a tertiary alkyl halide, only elimination will be observed. This exercise has a secondary alkyl halide, bromocyclohexane, as the reactant. We expect both substitution and elimination. At this stage in your development as an organic chemist, you do not have sufficient background to predict which reaction will predominate.
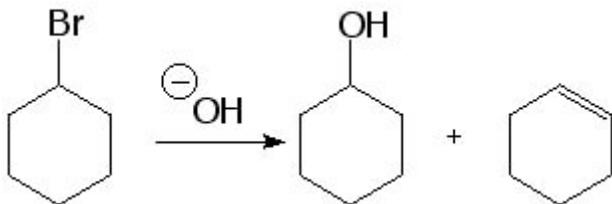
7-12 An E2 elimination reaction requires that there be a leaving group on one carbon and a hydrogenatom on an adjacent carbon atom. Only ethyl iodide and 2-chloro-2-methylpropane fit these two requirements for an E2 reaction. In methyl iodide, there is no carbon adjacent to that bearing the leaving group, and for 2-chloro-2-methylpropanethere is no hydrogen on the carbon adjacent to that bearing chlorine.

7-13 Here we have an example of a starting material that has two functional groups: a secondary alkyl chloride and a secondary alkyl iodide. We know that iodide ion is a significantly better leaving group than is chloride ion (Table 6-4).

7-14 This exercise is worked out on page 270 as "Working with Concepts".

7-15 E2 reactions are greatly favored when the leaving group and the hydrogen atom being removed are in an anti peri planar arrangement. However, with the isomer shown of hexachlorocyclohexane in the favored conformation with all chlorine atoms equatorial, there are no hydrogen atoms in the correction position for elimination. Thus, elimination can only occur from another conformation. Although the chair conformation with all chlorine atoms axial has the required orientation of hydrogen atoms and the chlorine leaving groups, this will be a very high energy conformation. Elimination will thus occur from one of the boast conformations.

7-16 (a) The key here is that basicity decreases proceeding down a column of the periodic table. Thus, trimethylphosphine is less basic than is trimethylamine and the latter gives more elimination.
(b) In this comparison, it is steric hindrance that determines which gives a greater amount of elimination. The presence of two isopropyl groups on the nitrogen significantly interferes with substitution.
(c) As with part (a) the difference here is that iodide is below chloride in the periodic table and thus is less basic. All other factors being equal, the less basic the nucleophile, the more substitution there is compared with elimination.

7-17 Substitution involves the reaction of a nucleophile with a substrate to produce a

product plus the anion of the leaving group. Thus, the same number of products are produced as starting materials consumed. On the other hand, in an elimination reaction, a base removes a proton to form the conjugate acid of the base, a leaving group is lost, *and* an alkene product is formed. Thus, elimination produces three products and consumes two starting materials. Entropy favors the products and the higher the temperature, the greater is the influence of entropy.
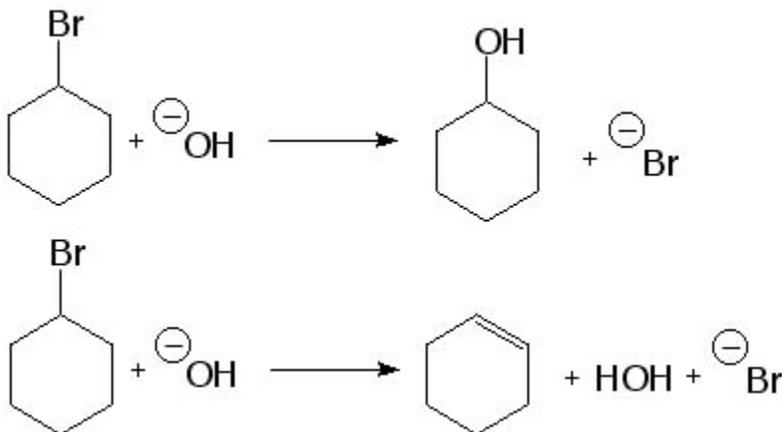
7-18 The first two examples use relatively good and unhindered nucleophiles. Thus, substitution predominates. The last example employs the most common sterically hindered base that is used to favor elimination reactions.
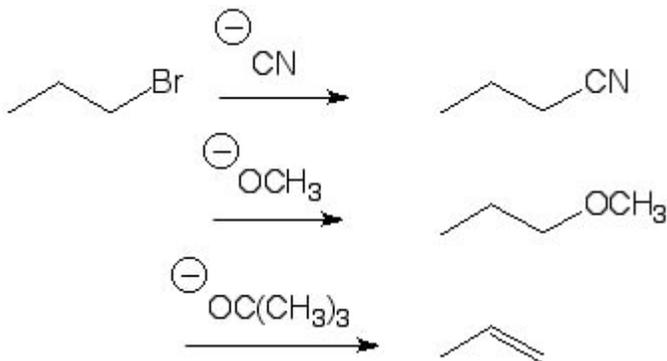
7-19 Here we are dealing with a relatively hindered substrate. As a result, the direction of the reaction toward substitution or elimination will be determined by the nucleophile. A good nucleophile that is a weak base will favor substitution (iodide ion in this case) whereas a strong base (methoxide ion) will favor elimination.

7-20 From Table 7-4 on the same page in the textbook as this exercise, we can see the fate of a secondary alkyl halide (next to last row). For 2-bromopropane, the reactions with NaSCH3 (b) andNaOCH2CH3 (c) are straightforward---these are a weakly basic, good nucleophile (b) which givessubstitution and a strongly basic, unhindered nucleophile which gives predominantly elimination. Restassured that the textbook has provided you no way of answering (a) where the poor nucleophilecolumn predicts: "slow, S_N1, E1" for secondary alkyl halides. An answer of either one, the other, orboth is

perfectly appropriate.

7-21 Again, we can use Table 7-4. For (a) we have a tertiary alkyl bromide and a poor nucleophile and we expect both substitution and elimination by first order pathways. For (b), we have a tertiary alkylchloride with a strongly basic, unhindered nucleophile and thus predict elimination (second order)will dominate.

7-22 Polar solvents with only weak bases favor first order reactions whereas second order reactions are favored with strong bases. For (a), we have a polar medium but only a weak base/nucleophile for the first reaction whereas a strong base is present for the second reaction. Thus, E1 predominates for the first and E2 is favored for the second. Part (b) is a poor question. That E2 will predominate for thefirst reaction is clear from the presence of a strong base. But in part (b), we have a polar medium butno nucleophile. Notice that the book does not provide an answer for (b)!!