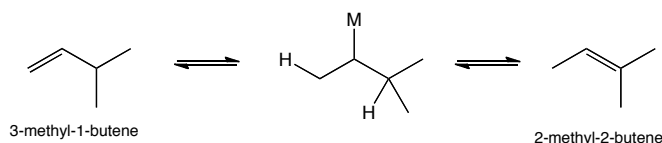


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**12-1** We need only consider the bonds undergoing change to calculate  $\Delta H$ . Bonds broken are C=C  $\pi$  (65 kcal/mole) and HO—OH (49 kcal/mole) which are replaced by two C—OH bonds (94 kcal/mole each). Thus,  $\Delta H = 65 + 49 - 2*94 = -74$  kcal/mole.

**12-2** This exercise is worked out on page 510 as "Working with Concepts".

**12-3** The steps in metal catalyzed reductions are reversible. Addition of a hydrogen to C1 and the metal to C2 leads to an intermediate which can revert to 3-methyl-1-butene by loss of a hydrogen on C1 or form 2-methyl-2-butene by loss of the hydrogen on C3.



**12-4** In looking at this exercise you might have been led to believe that there must be something that you do not understand as it borders on being trivial. The starting material contains a center of chirality that is not affected by reduction. Unless the double bond migrates during reduction by reversal of the addition stage (see answer to previous exercise) the center of chirality remains. Note that to the extent the double bond does migrate, the product will contain some of the *R* enantiomer.

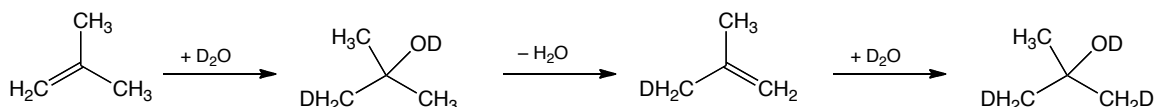
**12-5** The answer in the back of the textbook is adequate.

**12-6** In (a), (b), and (d), a new center of chirality is being formed. For (a) and (b) both enantiomers will be formed in equal amounts. The starting material for (d) already has a center of chirality. Notice that in one regiochemical sense of addition the center is preserved whereas in the other, the product as a mirror plane and there are no centers of chirality.

**12-7** Even pros have trouble drawing energy curves. Your drawing would ideally look like Figure 12-2 as there are two possible cations that can be formed here, a secondary and a tertiary.

**12-8** The answer in the back of the textbook is adequate.

**12-9** Acid catalyzed hydration of an alkene is a reversible process. Hydration of 2-methylpropene with  $D_2O$  will initially form a mono deuterio *t*-butyl alcohol. However, reversal of this reaction need not remove the deuterium and, indeed, the C—D bond is slightly stronger than is the C—H bond. Readdition of  $D_2O$  will add a second deuterium and so on.



**12-10** The answer in the back of the textbook is adequate.

**12-11** The answer in the back of the textbook is adequate.

**12-12** It is somewhat easier to deal with this question without resorting to structural drawings. Formation of a bromonium ion from cyclohexene results in a meso stereoisomer with one *R* and one *S* center of chirality at the carbons attached to bromine. Recall that the reaction of the bromonium ion with bromide ion to form the dibromide product involves the equivalent of an  $S_N2$  reaction and thus involves inversion of configuration. Thus, the *R,S* bromonium ion will form the *R,R* product if bromide ion attacks the *S* carbon whereas the *S,S* product results from attack of bromide on the *R* carbon. As bromide ion can not distinguish *R* from *S*, the rate of attack at the two carbons is identical, resulting in an equal mixture of *R,R* and *S,S*.

**12-13** Answer in the back of the textbook is adequate.

**12-14** For (a), the alkene is unsymmetrically substituted. As a result, the chlorine is on the less substituted carbon of the product. For (b), although the double bond is not symmetrical as a result of the presence of the methyl group, each carbon of the alkene has the same number of carbon substituent. Thus, a mixture of regio isomers results.

**12-15** This exercise is worked out on page 523 as "Working with Concepts".

**12-16** Answer in the back of the textbook is adequate.

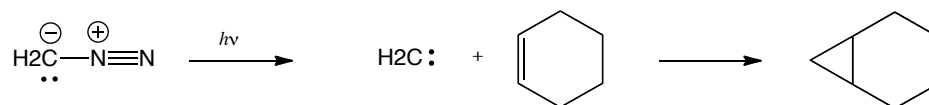
**12-17** They forgot to answer the second part of the question. The starting alkene is unsymmetrical but the  $sp^2$  carbons and the same substitution. Thus, there will be two regio isomers, just as in part (b) of Exercise 12-14.

**12-18** This exercise is worked out on page 527 as "Working with Concepts".

**12-19** Answer in the back of the textbook is adequate.

**12-20** Answer in the back of the textbook is adequate.

**12-21** Upon irradiation, diazo compounds undergo loss of nitrogen to form carbenes. Carbenes are very reactive because the carbon does not have a filled valence shell (a total of six electrons). Carbenes react with alkenes to form three-membered rings. In this case, the alkene is present in the starting diazo compound so the reaction of the carbene with the alkene is intramolecular.

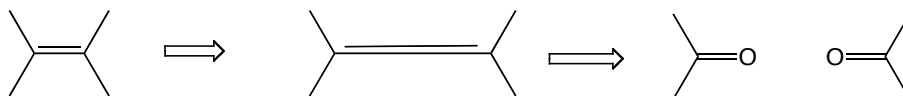


**12-22** Answer in the back of the textbook is adequate.

**12-23** The answer at the back of the textbook is adequate.

**12-24** The answer at the back of the textbook is adequate.

**12-25** To derive the two carbonyl compounds that result from ozonolysis of an alkene, we could draw the alkene with a very long double bond, erase the middle of the double bond, and then add two oxygens. To obtain the alkene starting material from the product ketones and/or aldehydes, we simply reverse this process: erase the oxygens and join the two double bonds to make one.



**12-26** The answer at the back of the textbook is adequate.

**12-27** This exercise is worked out on page 539 as "Working with Concepts".

**12-28** We can use the same technique explained in the answer to exercise **12-25** here to obtain the starting alkene---erase the two oxygens and join the two carbon together. Because the two carbonyl groups are already linked by a chain of carbon atoms, the result starting alkene will have a ring that contains the alkene (that is, both  $sp^2$  carbons of the alkene will be part of the ring).

**12-29** The answer at the back of the textbook is adequate.

**12-30** The answer at the back of the textbook is adequate.