1. Carbon-carbon bonds are not easily broken. Which bond in the following compound would be the *least* difficult to break homolytically?



2. Which of the following molecules would not be a product of one of the propagation steps involved in free-radical halogenation?



3. Predict the major product of the following reaction.



4. On the basis of your knowledge of the reaction of halogens with alkanes, decide which product you would *not* expect to be formed in *even small quantities* in the bromination of ethane?

A. BrCH2CH2BrB. CH3CH2CH2BrC. CH3CHBr2D. CH3CH2CH2CH2CH3E. BrCH2CH2CH2CH2Br

5. Consider the following tertiary carbon radical. What orbital does the radical (single unpaired electron) occupy?



6. What is the major product of the following reaction?



9. Predict the *major* product of the following reaction.



E. The reaction does not take place.

10. Which of the following molecules has six tertiary hydrogen atoms?



11. What is the major product of the following reaction?



12. Predict the *major* product of the following reaction.



13. Why is it that iodine does not do free-radical halogenations?

- A. Light cannot homolytically cleave the I—I bond as it does for Br₂ and Cl₂.
- B. The iodine radical is too unreactive to abstract hydrogen atoms from even tertiary carbons.
- C. Carbon radicals will not abstract an iodine atom from I₂.
- D. Iodine is far too reactive and typically explodes in the presence of organic compounds.
- E. Iodine atoms recombine faster than the other halogens and thus terminate the reaction too rapidly.

14. Predict the *major* product of the following reaction.



15. Consider the result of a free-radical halogenation of an alkane, using the interhalogen compound Br—Cl. On the basis of what you know of the mechanism of this type of halogenation, decide which of the following statements would be true of the process? (Assume that Br—Cl cannot disproportionate to Br₂ and Cl₂ under the reaction conditions.)

A. Halogenation would occur and create a carbon-chlorine bond with the selectivity typically observed for chlorination.

B. Halogenation would occur and create a carbon-chlorine bond with the selectivity typically observed for bromination.

C. Halogenation would occur to create a carbon-bromine bond with the selectivity typically observed for chlorination.

D. Halogenation would occur to create a carbon-bromine bond with the selectivity typically observed for bromination.

E. Roughly equal amounts of bromination and chlorination would occur, with a selectivity intermediate between the two.

16. The product of free-radical halo-genation reactions is an alkyl halide. The major amount of this halide forms during the second step of propagation. However, you should be aware that one possible termination step also forms alkyl halides. Why does the majority of the alkyl halide product come from the propagation step and not the termination step?

A. At any given time during the reaction, the concentration of both the alkyl radical and the halide radical is high enough that they can readily come together to form alkyl halides during propagation.

B. At any given time during the reaction, the concentration of both the alkyl radical and the halide radical is so low that the chance of each of them finding the other to form alkyl halides during a termination step is very small.

C. The initiation step converts 100% of the halogen to halide radicals through a light- or heatinduced homolytic bond cleavage. This step ensures that there is always a high concentration of halide radical present for reactivity in a propagation step.

D. The second step of propagation (combination of an alkyl radical with a halide radical) is highly endothermic and therefore takes place very rapidly.

E. Once the alkyl halide forms during a termination step, the carbon-halogen bond is broken in a homolytic fashion and the newly generated carbon radical goes back into a propagation step for further reactivity.

17. Predict the major product of the following reaction.



18. When we use the word "mechanism" in describing a chemical reaction, what does this word refer to?

A. A mechanism provides insight into electron movement and bonding that takes place during a chemical transformation.

B. A mechanism provides a useful means of predicting the product(s) of chemical reactions.

C. A mechanism provides unequivocal proof of the given pathway (in terms of electron movement and bonding) that a reaction follows.

D. Both A and B are correct.

E. Both B and C are correct.

19. Predict the *major* product of the following reaction.



20. The reaction of methane with I_2 in the presence of heat or light *does not* result in the formation of methyl iodide. The most accurate reason for this is described by which of the following statements?

A. The dissociation energy for I_2 is sufficiently high (36 kcal/mol) to ensure that iodine radical (I·) is not able to form by a homolytic cleavage of I_2 .

B. A very high energy of activation is required for the abstraction of a hydrogen atom by the iodine radical (I). This energy is sufficiently high to make this step thermodynamically unfavorable.

C. The reaction of I with a C!H bond is extremely exothermic and therefore does not take place.

D. The reaction of I \cdot with a C!H bond generates sufficient energy to cause an explosion, thereby destroying any of the methyl iodide that is formed.

E. The second step of propagation (reaction of \cdot CH₃ with I₂) does not take place. Therefore, methyl iodide is not formed.