

## FREE RADICAL REACTIONS

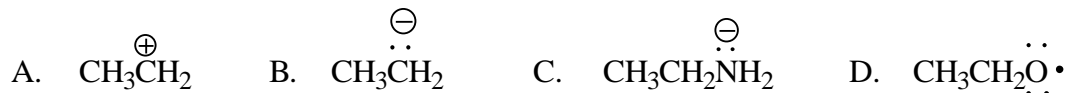
A STUDENT SHOULD BE ABLE TO:

1. Define, recognize, and give examples of: homolytic cleavage (homolysis), heterolytic cleavage, free radical, exothermic and endothermic reactions.
2. Given homolytic bond dissociation energies (enthalpies), calculate heats (enthalpies) of reaction. Bond forming is an exothermic process ( $\Delta H$  is negative); bond breaking is endothermic ( $\Delta H$  is positive). The heat of reaction equals the sum of the bond dissociation enthalpies of the bonds broken minus the sum of the enthalpies of the bonds formed.
3. Predict the relative stabilities of free radicals and the relative rates of reactions that give rise to free radicals. The order of free radical stabilities is:  
allylic  $>$   $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\cdot$   
Relatively stable species are relatively easy to form (and difficult to destroy).
4. Draw resonance structures for radicals.
5. Predict the product(s) of free radical reactions. Important reactions include:  
Halogenation of alkanes.  $\text{I}_2$  does not react, the order of reactivity is  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2$ , and the order of selectivity is  $\text{Br}_2 > \text{Cl}_2 > \text{F}_2$ . Stereochemistry of reactions (these occur via a planar intermediate) is important.  
Anti-Markovnikov addition of hydrogen bromide to alkenes and alkynes.  
Free radical polymerization of alkenes.
6. Propose mechanisms for free radical reactions, and predict and explain experimental results using a knowledge of these mechanisms. Important reactions include:  
Halogenation of alkanes  
Anti-Markovnikov addition of HBr  
Free radical polymerization of alkenes  
Important concepts include:  
Energy of activation (effect of temperature changes)  
For reactions in which bonds are both broken and formed,  $E_{\text{act}}$  must be greater than both zero and  $\Delta H$ .  
Collision frequency (effects of temperature and concentration)  
Initiation, propagation, and termination steps
7. Propose synthesis using free radical reactions, and any other reactions studied in the course so far.

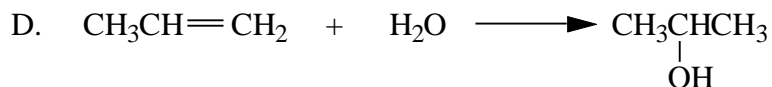
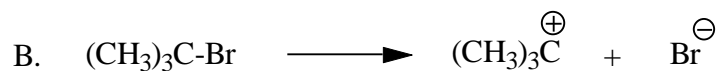
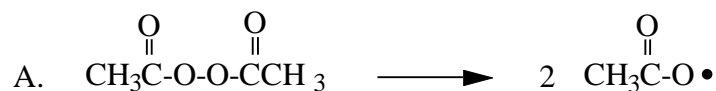
To best prepare for this module, please work Chapter 11 Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGE SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

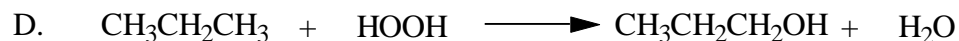
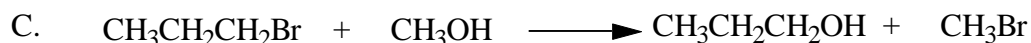
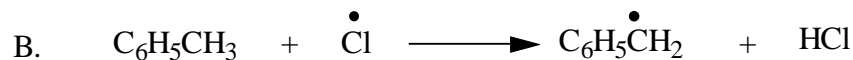
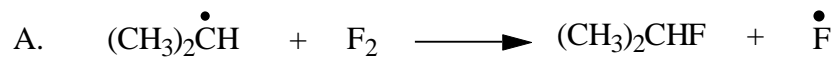
1.1 Which of the following is a free radical?



1.2 Which of the following is a homolytic cleavage?



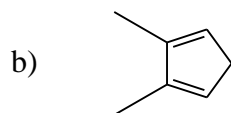
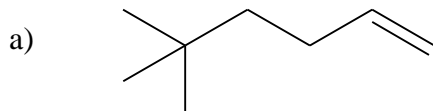
2. Calculate the value of  $\Delta H$  for each of the following reactions using the table of bond dissociation energies in your textbook.



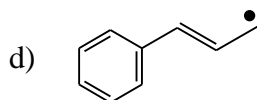
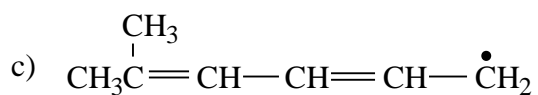
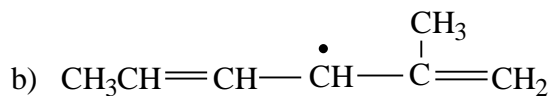
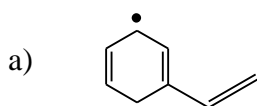
3.1 Which of the following free radicals is the most stable? Which is the least stable?



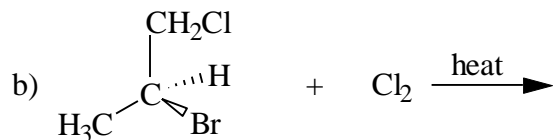
3.2 Identify the weakest C-H bond in each of the following compounds. Which are the strongest?



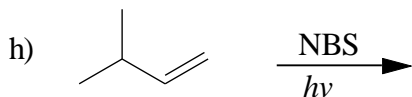
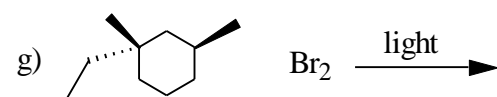
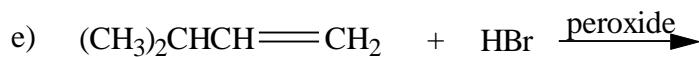
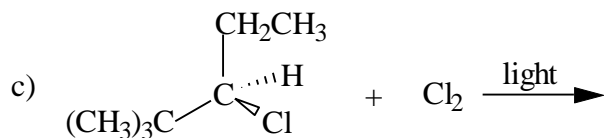
4. Draw all resonance structures for the following radicals, and make sure to show the necessary fishhook arrows.



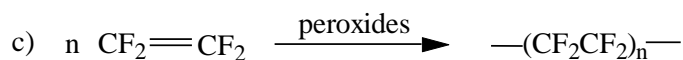
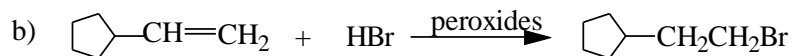
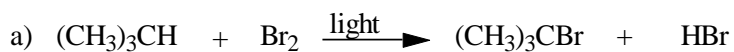
5. Predict the product(s) of each of the following reactions. Indicate stereochemistry where appropriate.



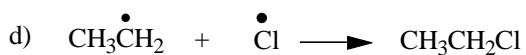
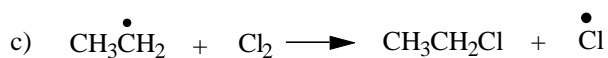
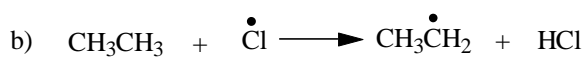
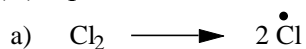
5.



6.1 Propose a mechanism for each of the following reactions.



6.2 For which of the following reactions is  $E_{\text{act}}$  (A) equal to zero, (B) greater than zero, and (C) equal to  $\Delta H$ ?



7. Propose synthesis of the given products from the indicated starting material, and using any other necessary reagents.

a) cyclohexene from cyclohexane

b)  $\text{CH}_3\text{CH}_2\text{CHOHCH}_2\text{OH}$  from  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

c) 2-bromo-3-methylbutane from 2-methylbutane

SOLUTIONS TO SAMPLE PROBLEMS:

1.1 D

1.2 A

2. a)  $-285 \text{ kJ mol}^{-1}$

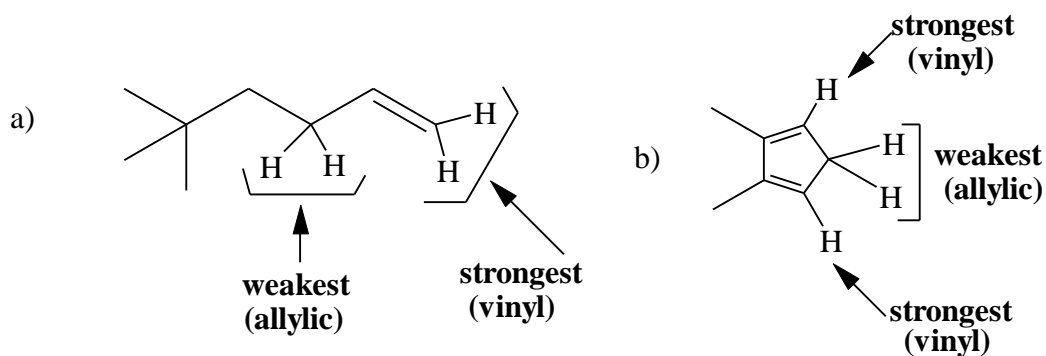
b)  $-75 \text{ kJ mol}^{-1}$

c)  $-8 \text{ kJ mol}^{-1}$

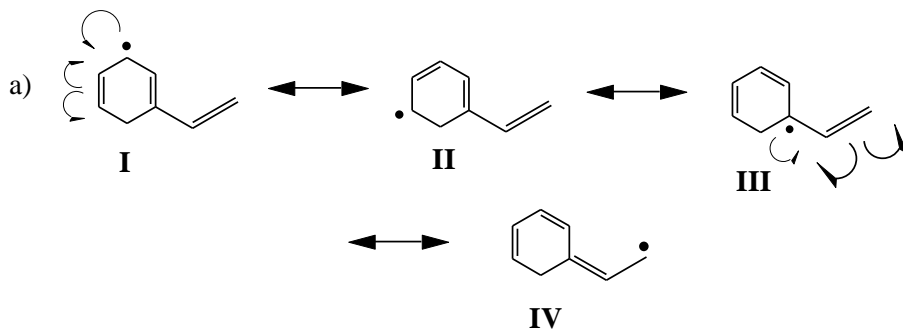
d)  $-256 \text{ kJ mol}^{-1}$

3.1 most stable: A; least stable C

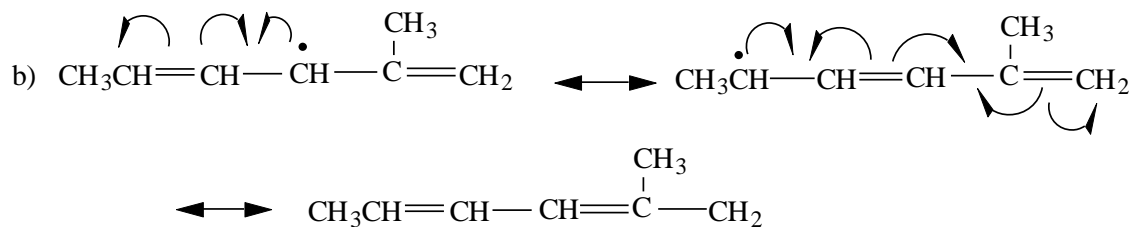
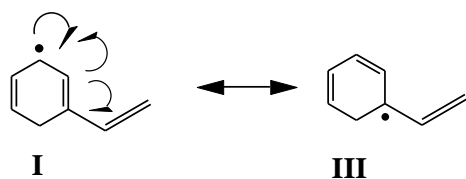
3.2



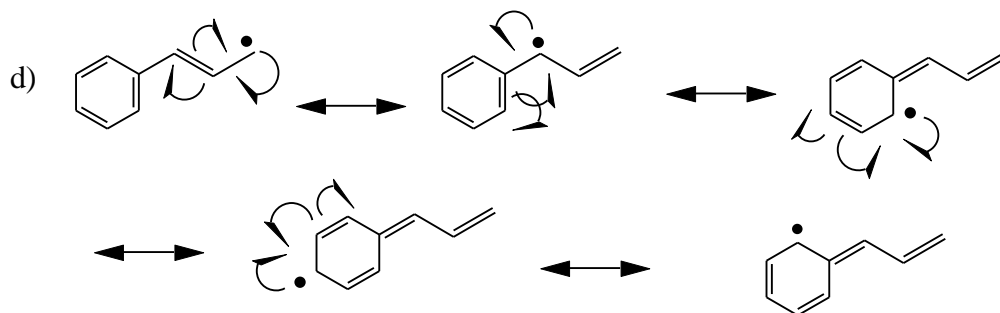
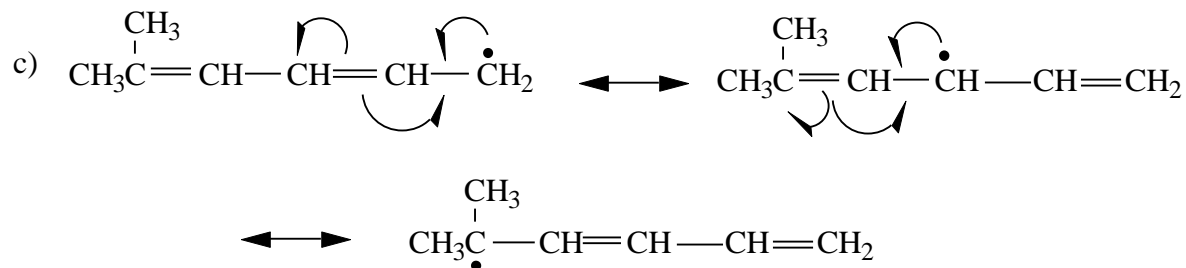
4. Draw all resonance structures.



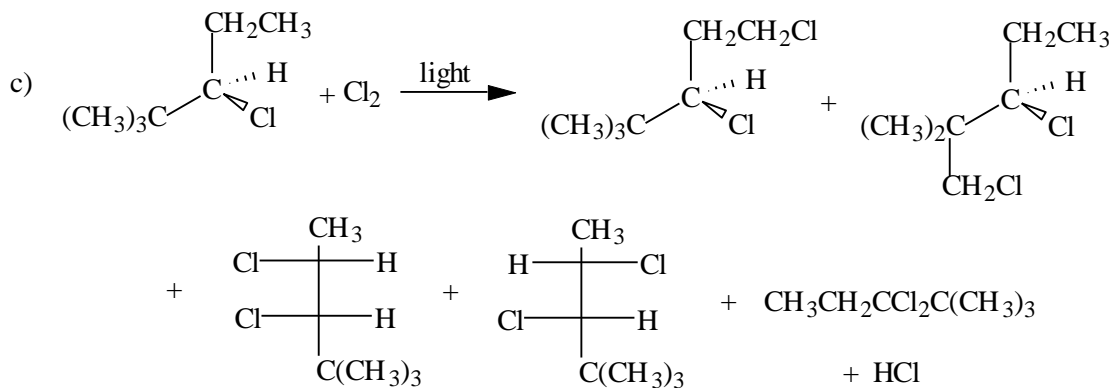
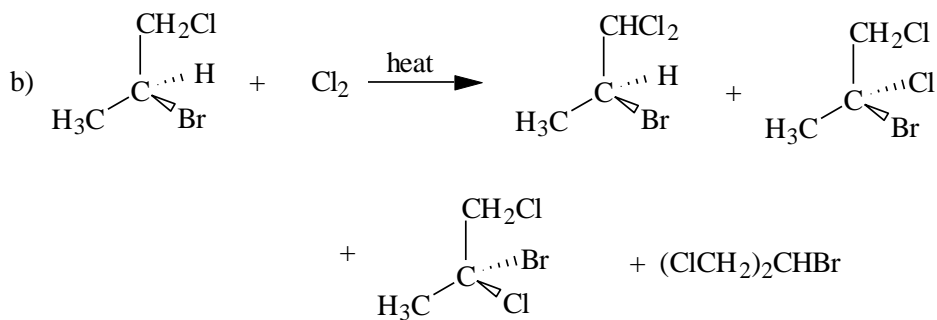
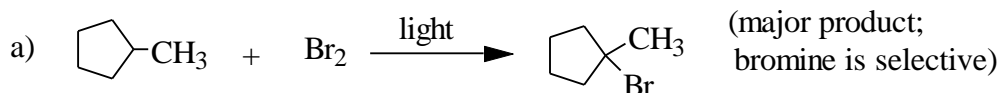
Note: structure I gives structure III by moving the arrows as shown below.



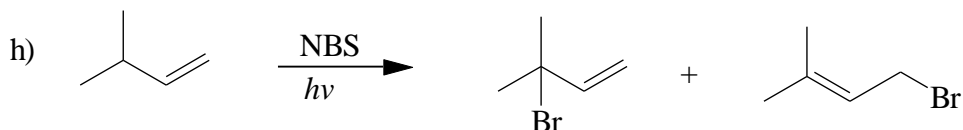
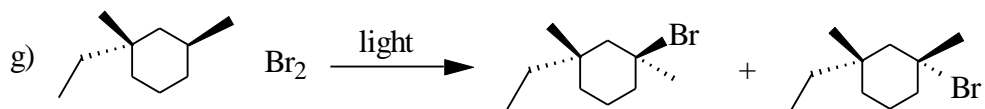
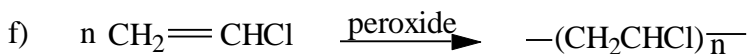
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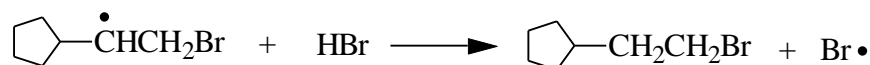
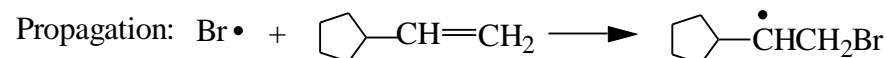
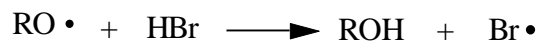
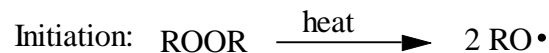
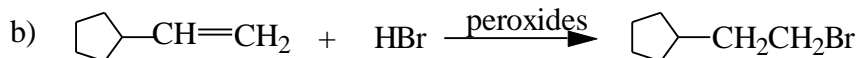
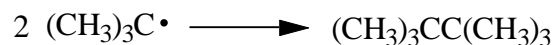
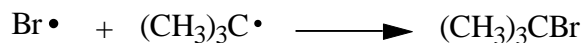
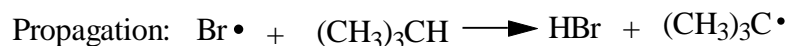
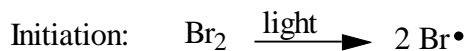
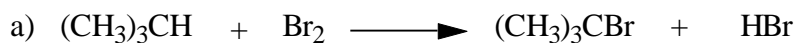
5. Predict the product(s):



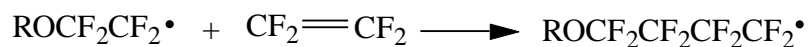
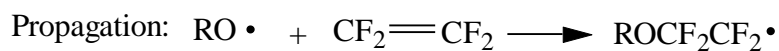
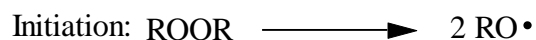
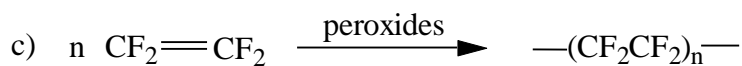
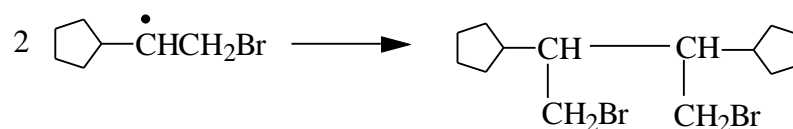
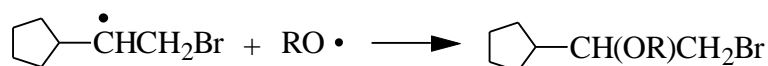
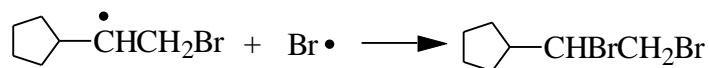
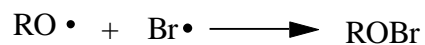
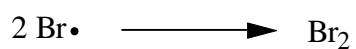
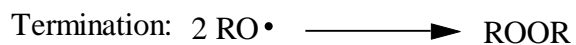
5.



6.1 Propose a mechanism for each of the following reactions.



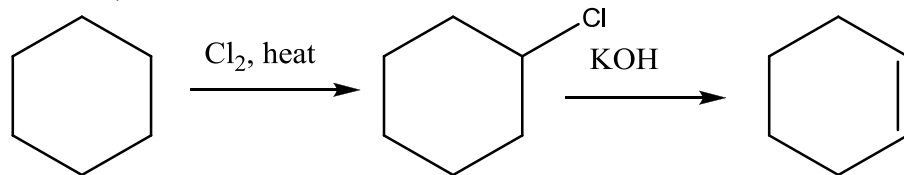
6.1 b) (continued)



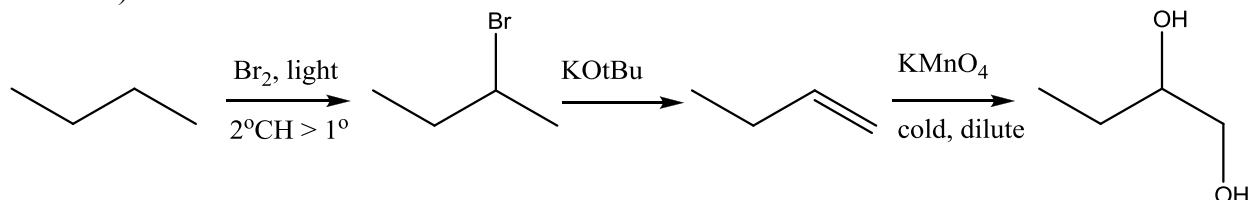
etc.

- 6.2  $E_{\text{act}} = 0$ : d  
 $E_{\text{act}} > 0$ : a, b, c  
 $E_{\text{act}} = \Delta H$ : a

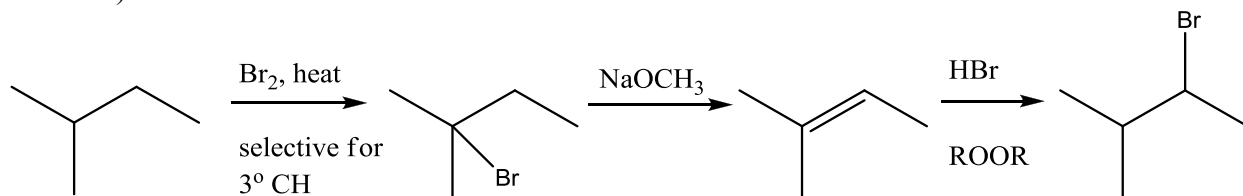
7. a)



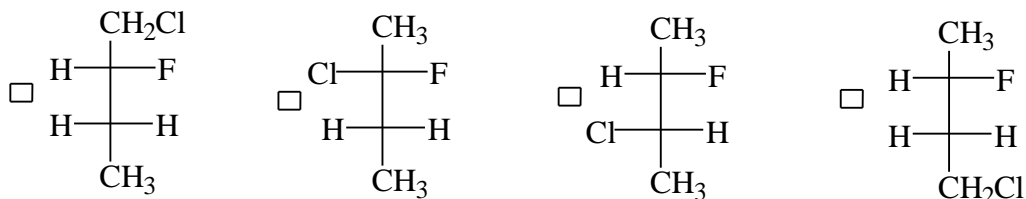
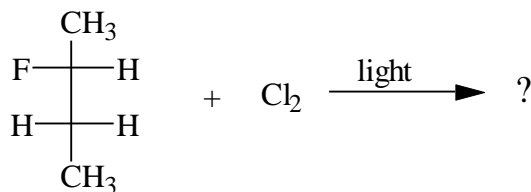
b)



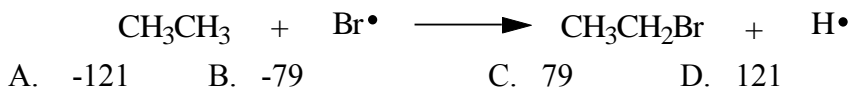
c)



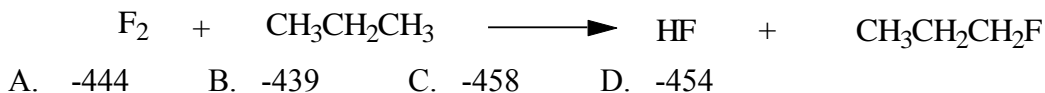
1. Which of the following compounds is a product of the reaction shown?



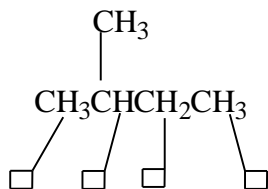
2. What is  $\Delta H$  in  $\text{kJ mol}^{-1}$  for the process shown? Some bond dissociation energies in  $\text{kJ mol}^{-1}$  are:  $\text{CH}_3-\text{CH}_3$ , 368;  $\text{CH}_3\text{CH}_2-\text{H}$ , 410;  $\text{CH}_3\text{CH}_2-\text{Br}$ , 289.



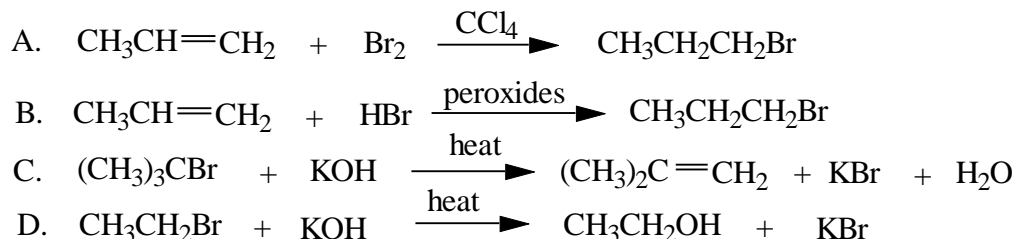
3. What is  $\Delta H$  in  $\text{kJ mol}^{-1}$  for the reaction shown? Some bond dissociation energies in  $\text{kJ mol}^{-1}$  are:  $\text{CH}_3\text{CH}_2\text{CH}_2-\text{H}$ , 410;  $(\text{CH}_3)_2\text{CH}-\text{H}$ , 395;  $\text{F}-\text{F}$ , 159;  $\text{CH}_3\text{CH}_2\text{CH}_2-\text{F}$ , 444;  $(\text{CH}_3)_2\text{CH}-\text{F}$ , 439;  $\text{H}-\text{F}$ , 569.



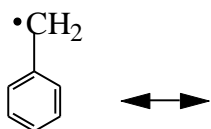
4. Which of the indicated hydrogen s reacts most RAPIDLY with  $\text{Cl}_2$  in the presence of light?



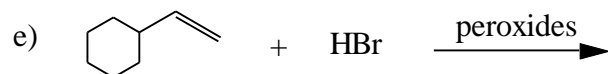
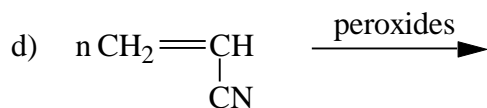
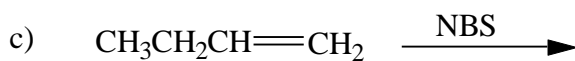
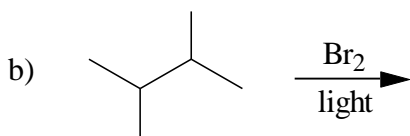
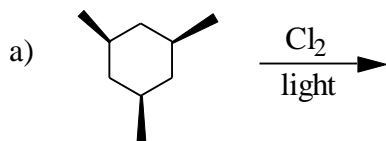
5. Which of the following reactions proceeds by way of a free radical mechanism?



6. Draw all resonance structures for the following radical.



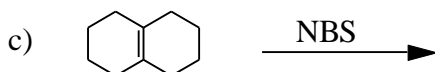
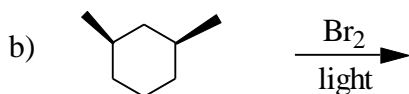
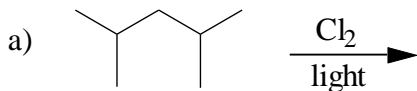
7. Predict the product(s) of each of the following reactions. Indicate stereochemistry where appropriate.



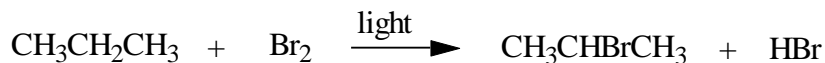
8. Propose a mechanism for the following reaction.



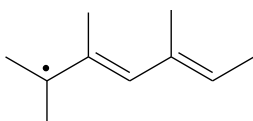
1. Predict the product(s) of each of the following reactions. Indicate stereochemistry where appropriate.



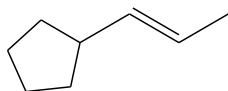
2. What is  $\Delta H$  in  $\text{kJ mol}^{-1}$  for the process shown? Some bond dissociation energies in  $\text{kJ mol}^{-1}$  are:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-H}$ , 410;  $(\text{CH}_3)_2\text{CH-H}$ , 397;  $\text{CH}_3\text{CH}_2\text{-CH}_3$ , 356;  $\text{Br-Br}$ , 192;  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-Br}$ , 289;  $(\text{CH}_3)_2\text{CH-Br}$ , 285;  $\text{H-Br}$ , 368.



3. Draw all resonance structures for the following radical.

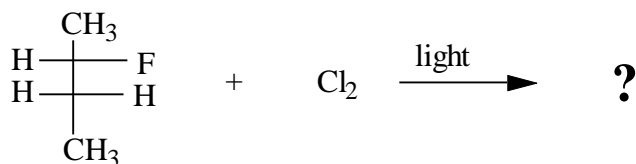


4. Identify the strongest and the weakest C-H bonds the following compound.



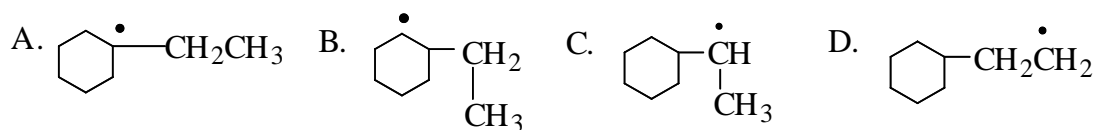
5. Which of the following gas phase reactions would have the  $E_{\text{act}}$  equal to the  $\Delta H^\circ$ ?
- A.  $\text{Cl}-\text{Cl} \longrightarrow 2 \text{Cl}\cdot$
- B.  $2\text{Cl}\cdot \longrightarrow \text{Cl}-\text{Cl}$
- C.  $\text{Cl}\cdot + \text{CH}_4 \longrightarrow \text{CH}_3\cdot + \text{HCl}$
- D.  $\text{CH}_3\cdot + \cdot\text{CH}_3 \longrightarrow \text{CH}_3\text{CH}_3$
- E.  $\text{CH}_3\cdot + \text{Cl}-\text{Cl} \longrightarrow \text{CH}_3-\text{Cl} + \cdot\text{Cl}$

6. Which of the following **IS NOT** a product of the reaction shown?



- A.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}-\text{C}-\text{F} \\ | \\ \text{H}-\text{C}-\text{Cl} \\ | \\ \text{CH}_3 \end{array}$     B.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{F}-\text{C}-\text{Cl} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{CH}_3 \end{array}$     C.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{F}-\text{C}-\text{H} \\ | \\ \text{Cl}-\text{C}-\text{H} \\ | \\ \text{CH}_3 \end{array}$     D.  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{Cl}-\text{C}-\text{F} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{CH}_3 \end{array}$

7. Which of the following free radicals is the **LEAST** stable?



8. Propose a mechanism for each of the following reactions.

