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Organic Chemistry

Third Edition

David Klein

Chapter 6

Chemical Reactivity and Mechanisms

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Chapter 6

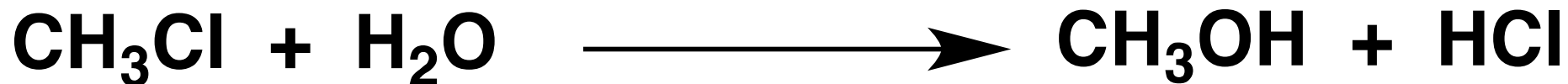
Please note:

If your clicker system can only hold 5 multiple choice answers, we have provided 'alternate answers' for those questions in which the author originally had more than 5 choices. These answers appear on the slides with a green background.

If your clicker system can hold more than 5 multiple choice answers, please delete the slides with the green backgrounds, and use the original answers the author has listed.

Section: 6.1

1. What is the sign, magnitude of ΔH° , and is the reaction exothermic or endothermic?



- a. - 37, endothermic
- b. - 37, exothermic
- c. + 37, endothermic
- d. + 37, exothermic

Section: 6.1

1. Answer is: C

Response:

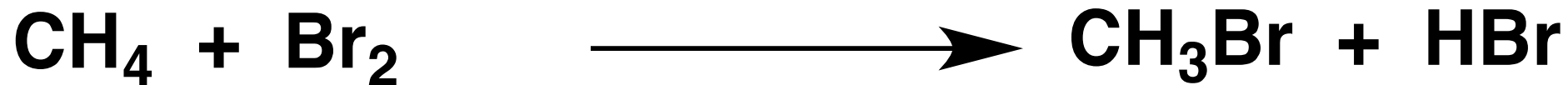
Bonds broken	kJ/mole	Bonds formed	kJ/mole
CH ₃ —Cl	+ 351	CH ₃ —OH	- 381
H—OH	+ 498	H—Cl	- 431

Sum = + 37 kJ/mol

For more examples of this type of problem, see SkillBuilder 6.1.

Section: 6.1

2. What is the sign, magnitude of ΔH° and is the reaction exothermic or endothermic?



- a. - 34, endothermic
- b. - 34, exothermic
- c. + 34, endothermic
- d. + 34, exothermic

2. Answer is: B

Response:

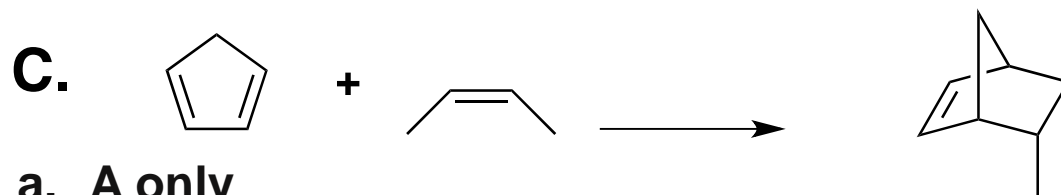
Bonds broken	kJ/mole	Bonds formed	kJ/mole
CH₃—H	+ 435	CH₃—Br	- 293
Br—Br	+ 192	H—Br	- 368

Sum = - 34 kJ/mol

For more examples of this type of problem, see SkillBuilder 6.1.

Section: 6.2

3. Which of the following have a negative ΔS ?



- a. A only
- b. B only
- c. A and B
- d. A and C
- e. B and C

3. Answer: d

When a reaction where all components are in the same phase has a decrease in entropy, the system has become more ordered by two or more molecules reacting to form a fewer number of products, or by an open chain molecule forming a ring, so there is more order in the system. In this example, only in A and C would there be a decrease in freedom of motion. See conceptual checkpoint 6.3 for more examples.

Section: 6.3

4. Which of the following will be spontaneous?

1. A reaction where $\Delta H = -400$ kJ/mole, $\Delta S = 300$ J/mol·K and $T = 300$ Kelvin.
 2. A reaction where $\Delta H = -200$ kJ/mole, $\Delta S = -500$ J/mol·K and $T = 500$ Kelvin.
 3. A reaction where $\Delta H = +100$ kJ/mole, $\Delta S = 400$ J/mol·K and $T = 400$ Kelvin.
 4. A reaction where $\Delta H = +200$ kJ/mole, $\Delta S = -300$ J/mol·K and $T = 600$ Kelvin.
- a. 1 and 2
 - b. 1 and 3
 - c. 1 and 4
 - d. 2 and 3
 - e. 2 and 4

4. Answer: b

Response: For a reaction to be spontaneous the overall entropy change must be positive. By rearrangement, a proxy for this change in ΔS_{tot} is the Gibbs Free energy, ΔG . The Gibbs free energy expression $\Delta G = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$ must be negative for a reaction to be spontaneous, and only A, with a ΔG of -490 kJ/mole and C, with a ΔG of -60 kJ/mole, meet that criteria.

Section: 6.4

5. Which of the following conditions will favor the formation of products?

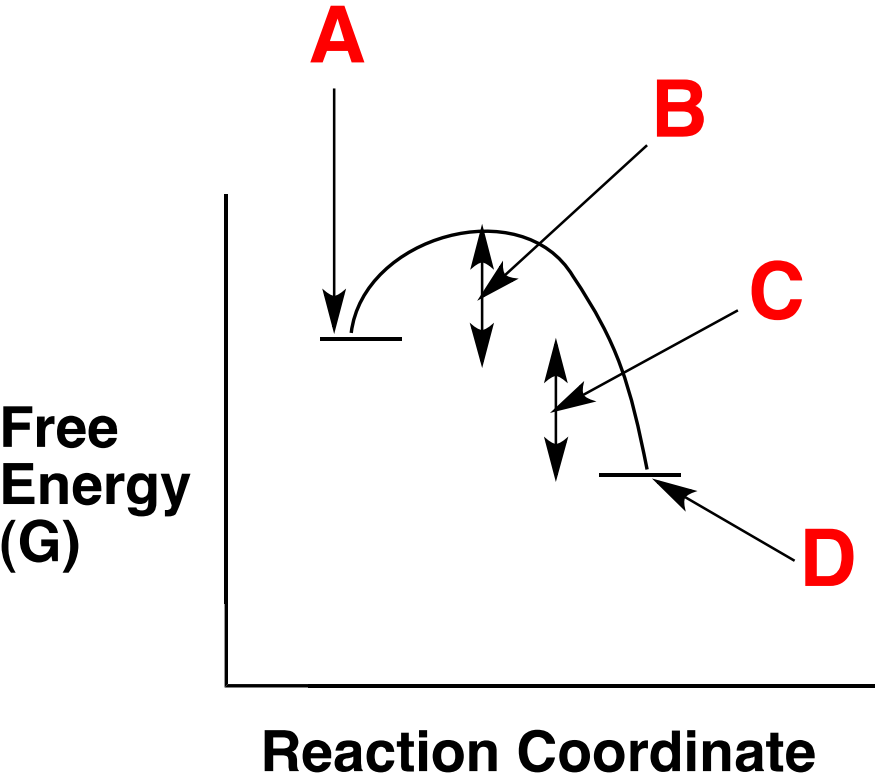
1. $\Delta G = + 175 \text{ kJ/mole}$
 2. An exothermic reaction with a positive value of ΔS
 3. $K_{\text{eq}} = 2.6$
 4. $\Delta H = -400 \text{ kJ/mole}$, $\Delta S = 200 \text{ J/mol}\cdot\text{K}$ and $T = 300 \text{ Kelvin}$.
 5. An endothermic reaction with a negative value of ΔS
 6. $K_{\text{eq}} = 0.65$
-
- a. 1, 2 and 5
 - b. 1, 4 and 6
 - c. 2, 3 and 4
 - d. 2, 4 and 5
 - e. 2, 4 and 6

5. Answer: c

Response: Only certain of the conditions shown above favor formation of the product. ΔG for a process must be negative, or the K_{eq} must be greater than 1 to show a reaction that is product favored. See conceptual checkpoint 6.6 for additional examples.

Section: 6.4

6. Identify the reactants and products on the following energy diagram



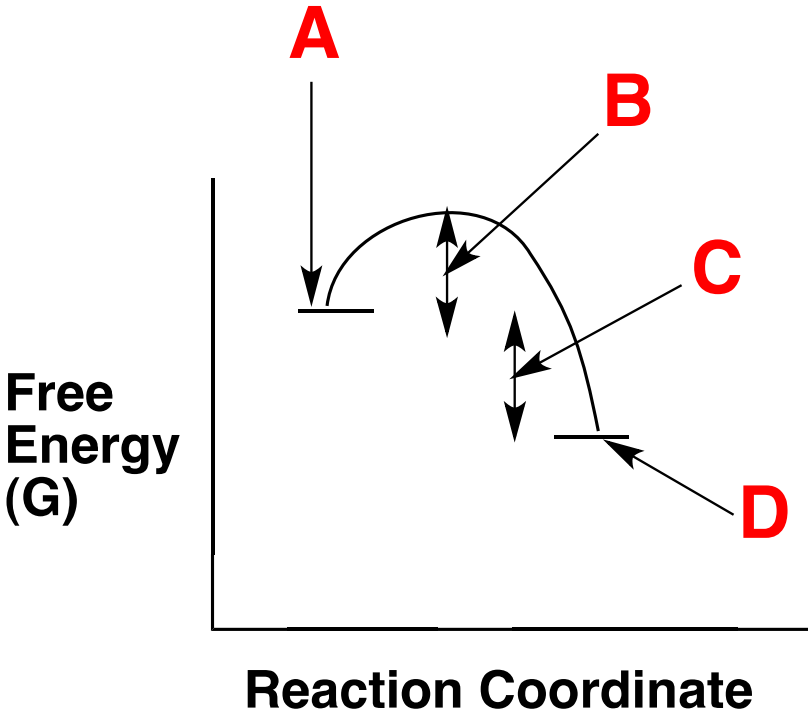
- a. A is the reactant, B is the product
- b. B is the reactant, C is the product
- c. C is the reactant, D is the product
- d. A is the reactant, C is the product
- e. A is the reactant, D is the product

6. Answer: e.

Response: See section 6.4 for further examples.

Section: 6.5

7. Identify B and C and determine whether the reaction is endergonic or exergonic as drawn.



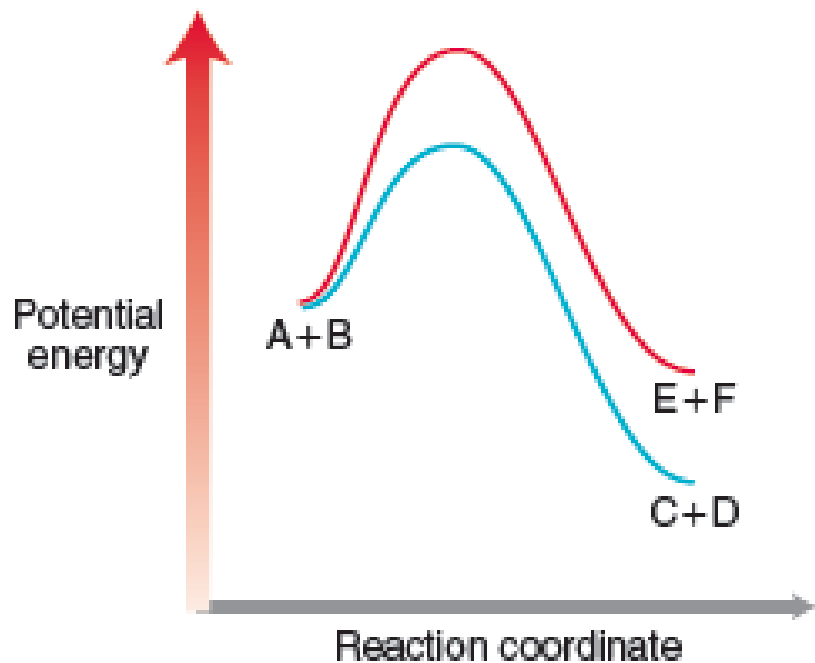
- a. B is the difference in free energy, C is the, endergonic
- b. B is the difference in free energy, C is the energy of activation, exergonic
- c. B is the energy of activation, C is the difference in free energy, endergonic
- d. B is the energy of activation, C is the difference in free energy, exergonic

7. Answer: d.

Response: The energy barrier for a reaction to occur is termed the energy of activation E_a , and the difference of overall free energy ΔG is a measure of the thermodynamic forces driving the reaction. Anytime the overall change ΔG is negative, the reaction is said to be exergonic.

Section: 6.6

8. Which are the kinetic products in the energy diagram below, and which are the thermodynamic products?



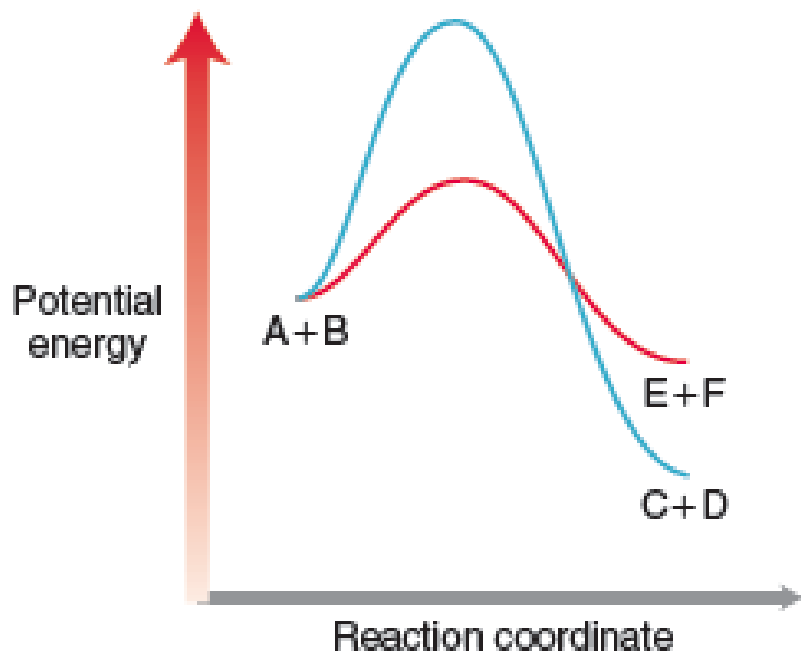
- a. C+D are thermodynamic, E+F are kinetic
- b. C+D are kinetic, E+F are thermodynamic
- c. C+D are thermodynamic and kinetic
- d. E+F are thermodynamic and kinetic

8. Answer: c.

Response: In many cases for reactions with high yields and high purity the products are both thermodynamically and kinetically favored. See conceptual checkpoint 6.7 for further examples of this type of problem.

Section: 6.6

9. Which are the kinetic products in the energy diagram below, and which are the thermodynamic products?



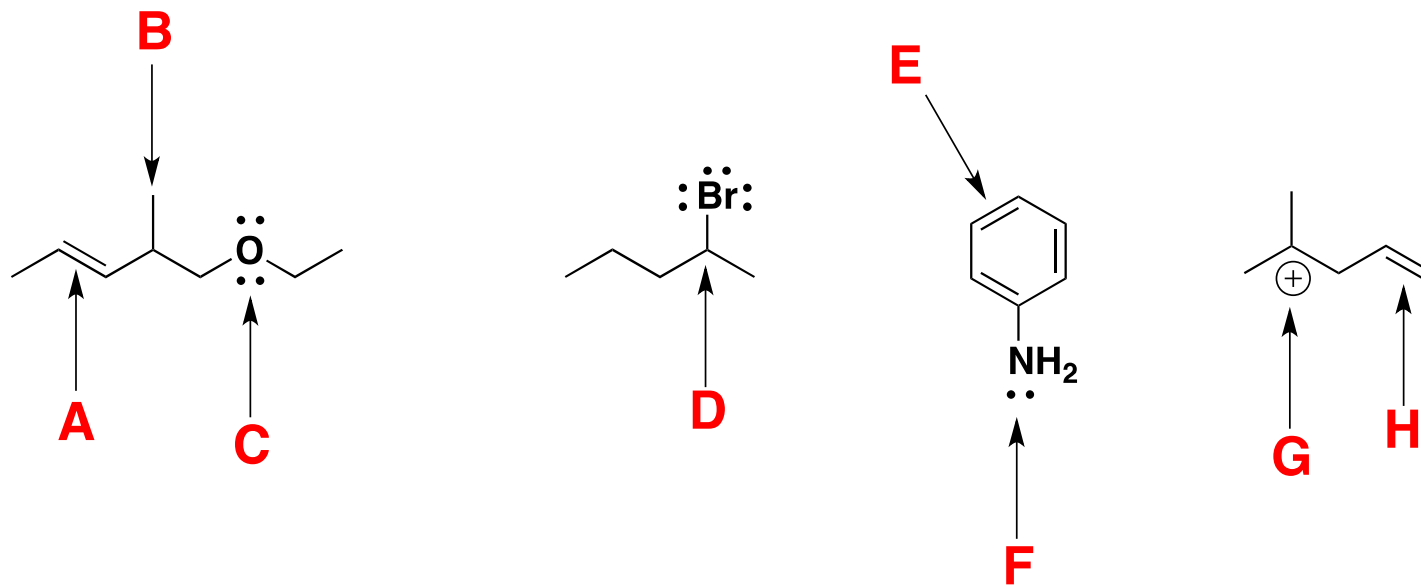
- a. C+D are thermodynamic, E+F are kinetic
- b. C+D are kinetic, E+F are thermodynamic
- c. C+D are thermodynamic and kinetic
- d. E+F are thermodynamic and kinetic

9. Answer: a.

Response: See conceptual checkpoint 6.7 for further examples of this type of problem.

Section: 6.7

10. Identify the nucleophilic centers in the following molecules.



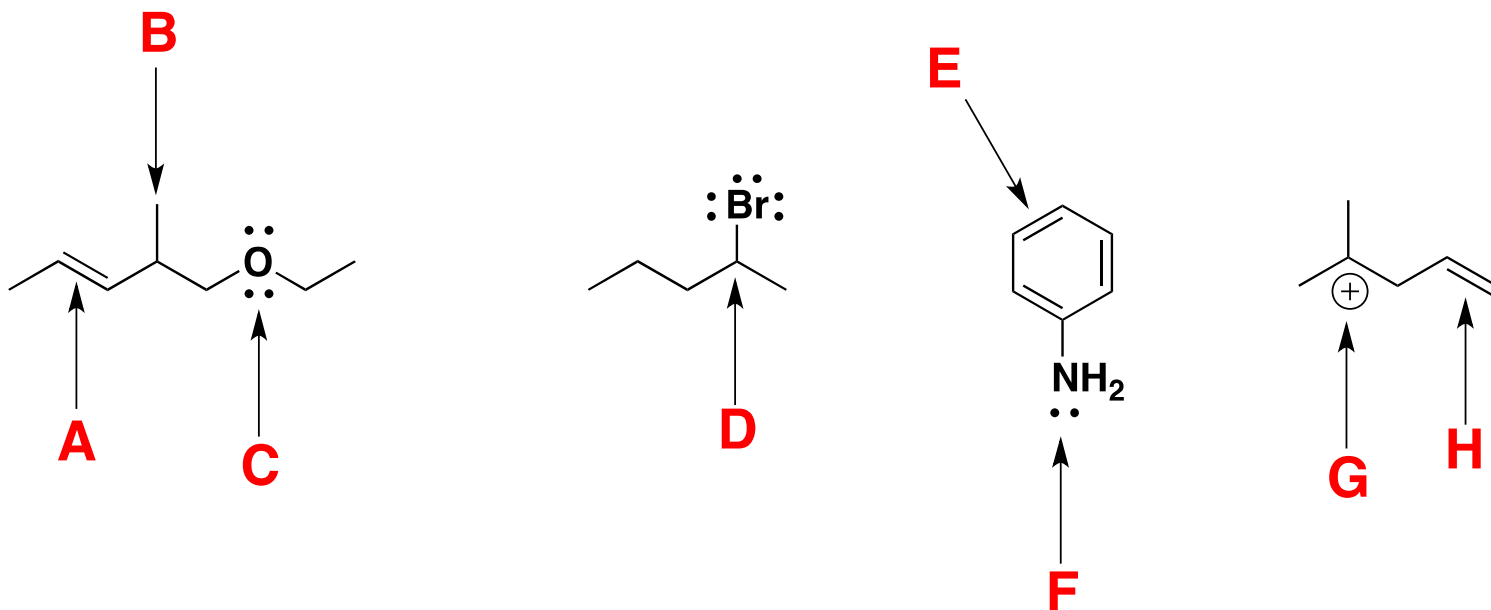
- a. A, C, D, E and F
- b. B, D and G
- c. D and G
- d. A, C, E, F and H
- e. A, B, C, E, F and H

10. Answer: d.

Response: See table 6.3 for a summary of typical nucleophilic centers. Any portion of a molecule with electron rich regions such as a lone pair or a Π bond can act as a nucleophile. Anytime a negative formal charge is associated with an atom it will act as a nucleophile.

Section: 6.7

11. Identify the electrophilic centers in the following molecules.



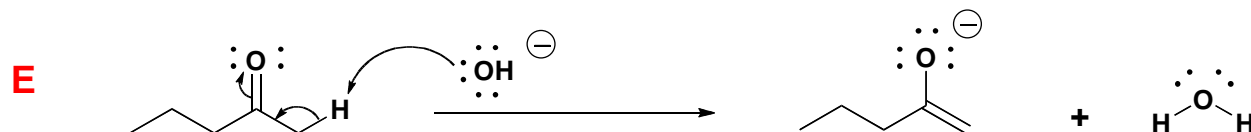
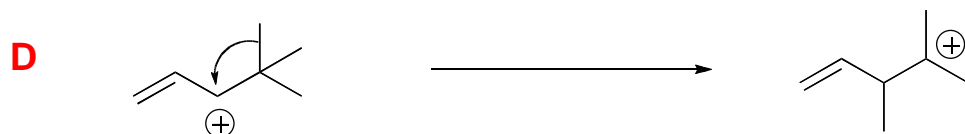
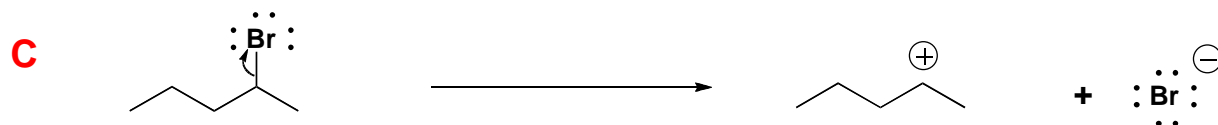
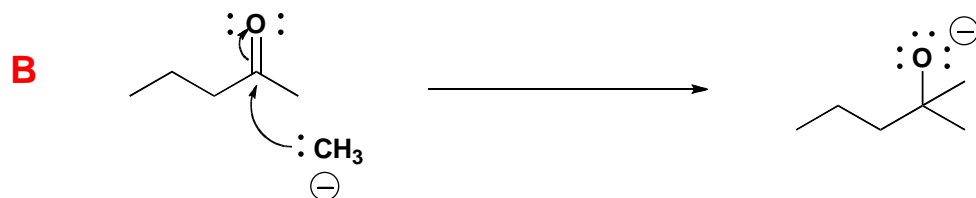
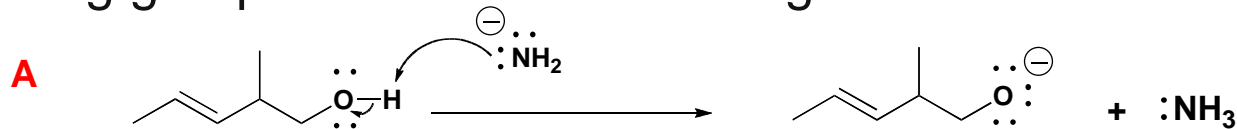
- a. A, C, D, E and F
- b. B, D and G
- c. D and G
- d. A, C, E, F and H
- e. A, B, C, E, F and H

11. Answer: c.

Response: See table 6.3 for a summary of typical electrophilic centers. Any portion of a molecule with electron deficient regions can act as a electrophile. Anytime a positive formal charge is associated with an atom it will act as a electrophile. For further practice see SkillBuilder 6.2.

Section: 6.8

12. Identify the arrow-pushing pattern(s) associated with loss of a leaving group utilized in the following.



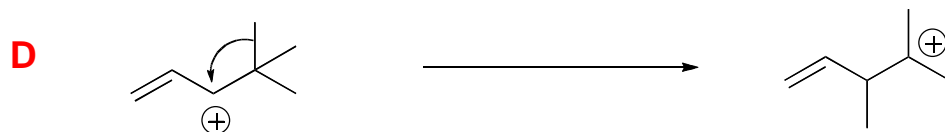
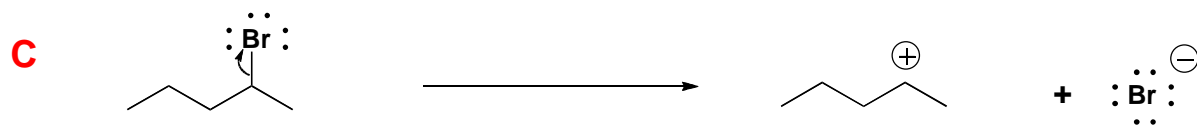
- a. A
- b. B
- c. C
- d. D
- e. E

12. Answer: c

Response: For more examples of this type of problem, see SkillBuilder 6.3.

Section: 6.8

13. Identify the arrow-pushing pattern(s) associated with nucleophilic attack utilized in the following.



- a. A
- b. B
- c. D
- d. A and B
- e. B and E

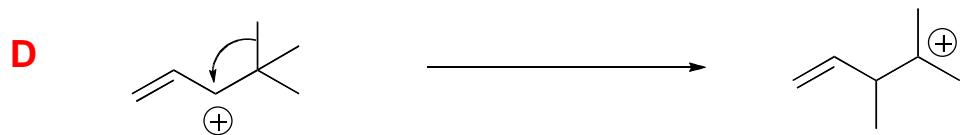
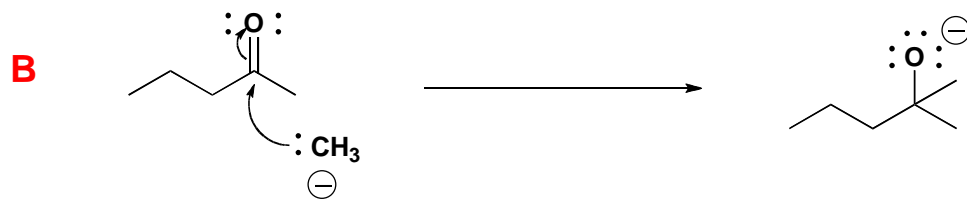
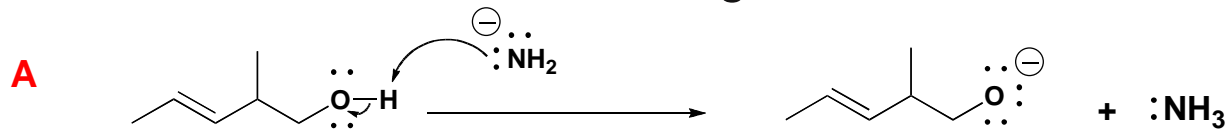
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13. Answer: b

Response: For more examples of this type of problem, see SkillBuilder 6.3.

Section: 6.8

14. Identify the arrow-pushing pattern(s) associated with proton transfers utilized in the following.



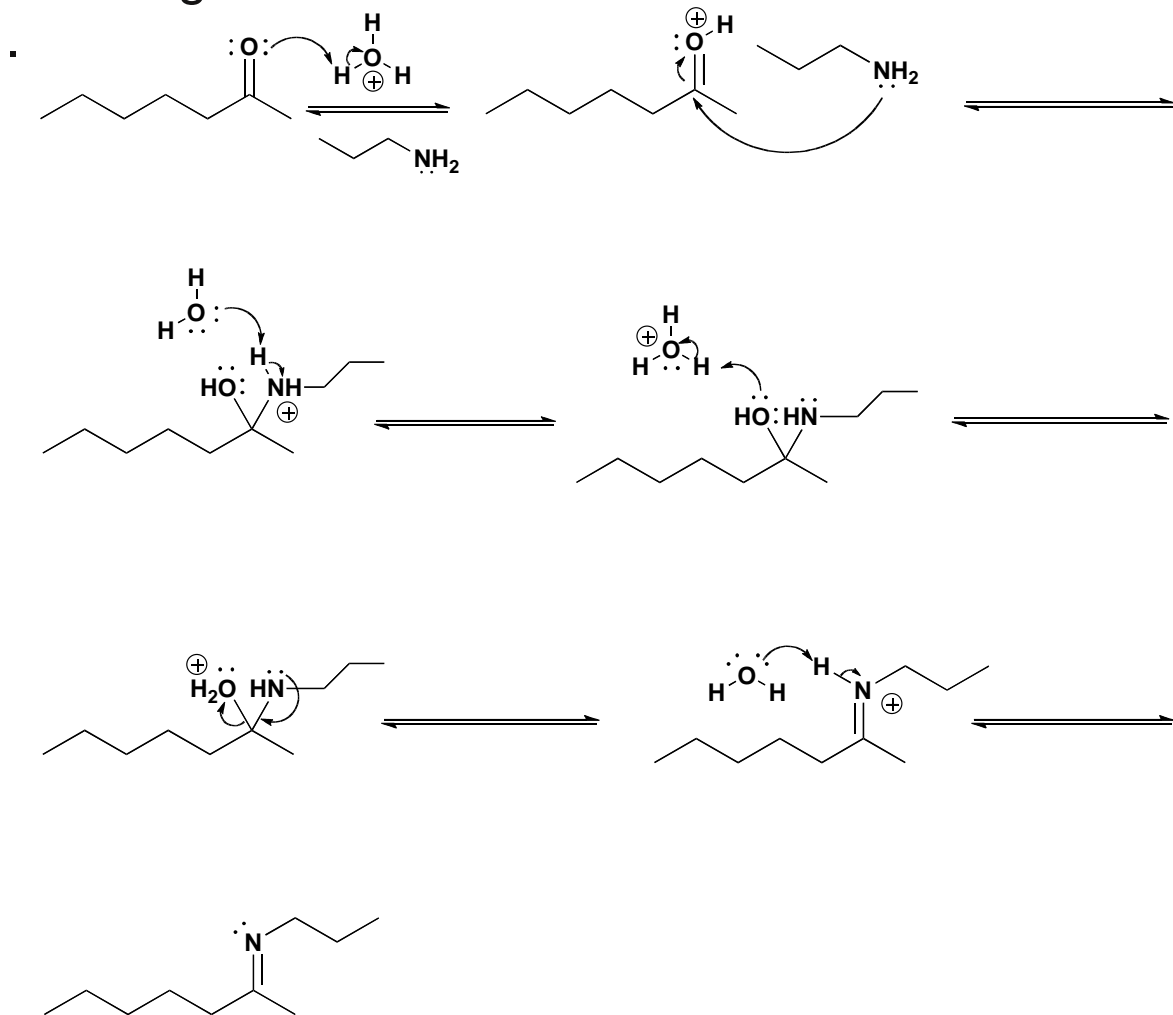
- a. A
- b. B
- c. D
- d. A and B
- e. A and E

14. Answer : e

Response: For more examples of this type of problem, see SkillBuilder 6.3.

Section: 6.9

15. For the following multistep reaction, read the curved arrows and identify the sequence of arrow-pushing patterns where 1 is the loss of a leaving group, 2 is nucleophilic attack, 3 is proton transfer, and 4 is a rearrangement.



a. 2, 3, 1, 3, 1, 3

b. 1, 3, 3, 3, 1, 3

c. 3, 2, 3, 3, 1, 3

d. 1, 3, 3, 3, 1, 1

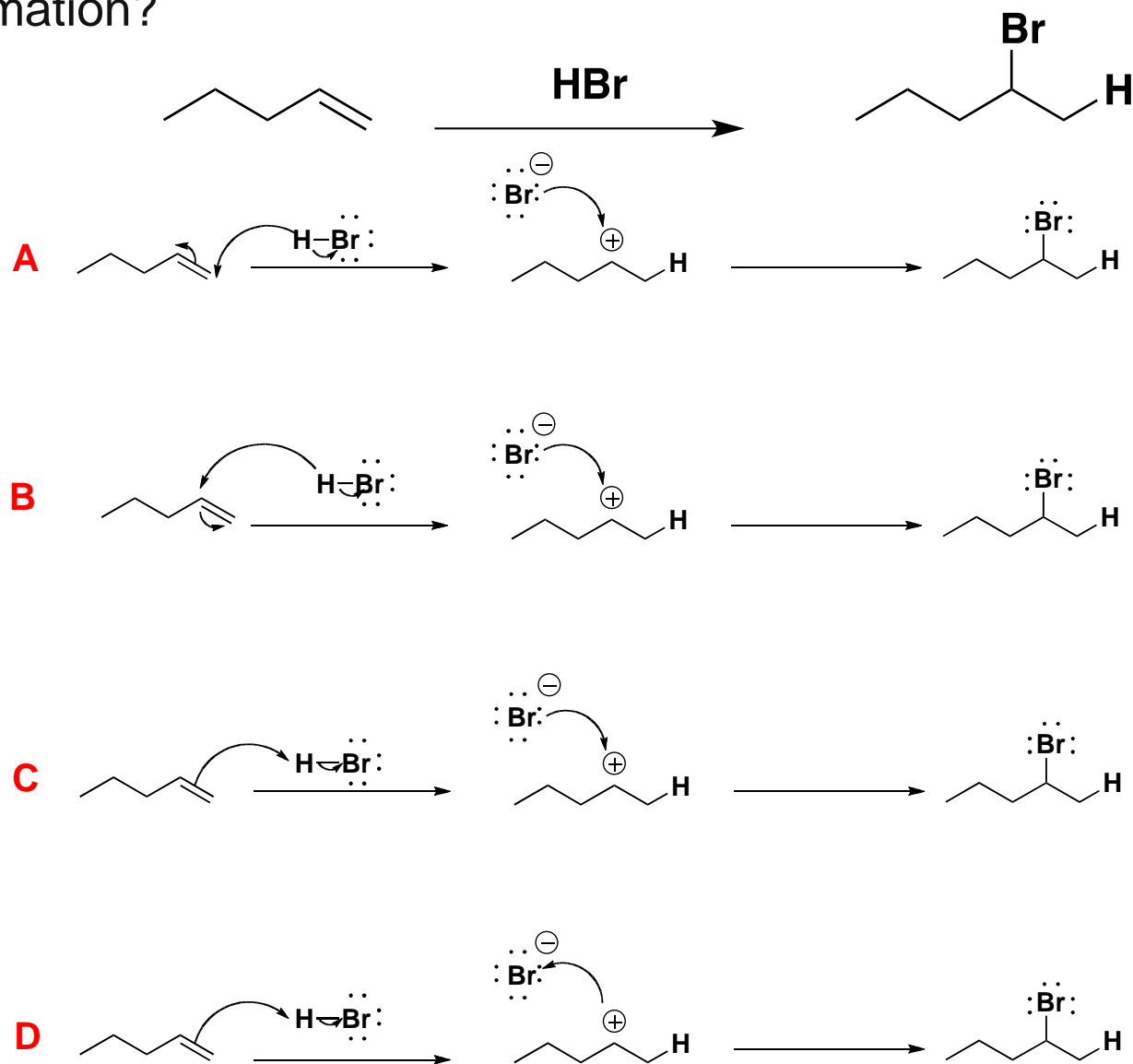
e. 3, 2, 3, 3, 1, 1

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15. Answer: c

Response: For more examples of this type of problem, see SkillBuilder 6.4

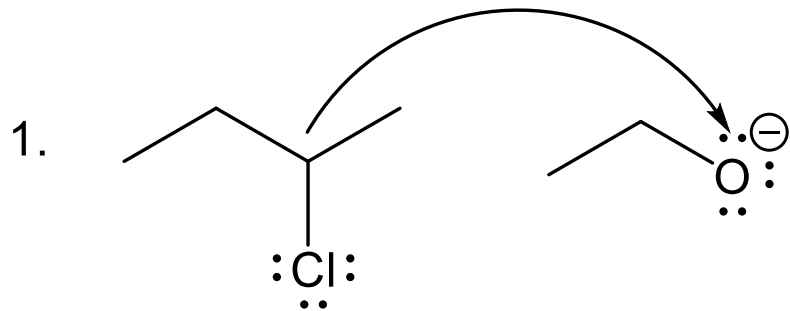
16. Which represents the correct arrow-pushing for the following transformation?



16. Answer is: c.

Response: For more examples of this type of problem, see SkillBuilder 6.5.

17. Which of the following curved arrow transformations do not follow the rules for curved arrow drawings?



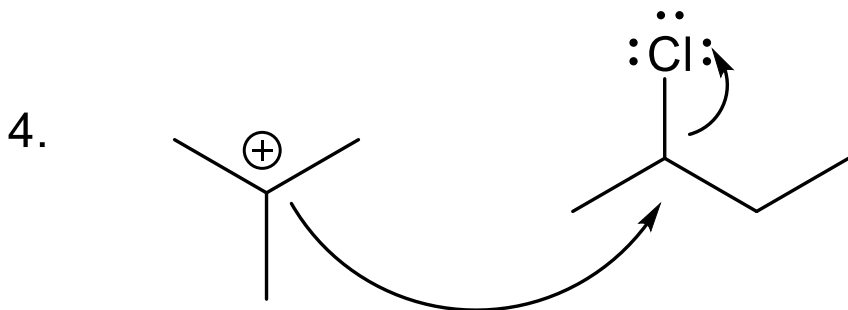
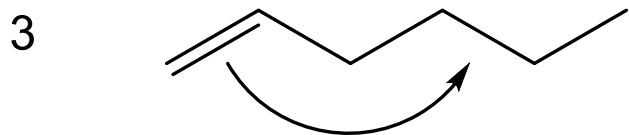
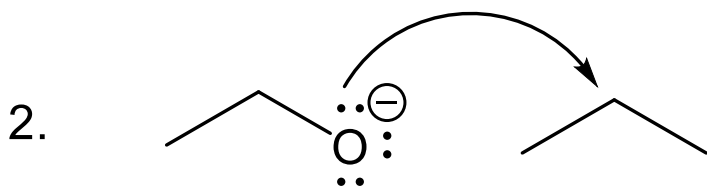
a. 1 and 2

b. 1 and 3

c. 2 and 3

d. 2, 3, and 4

e. All of them

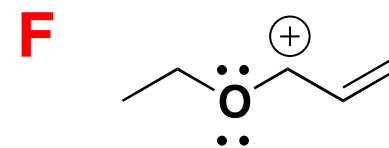
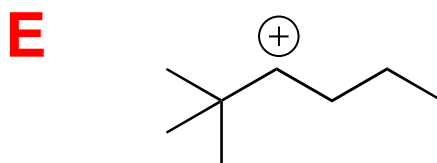
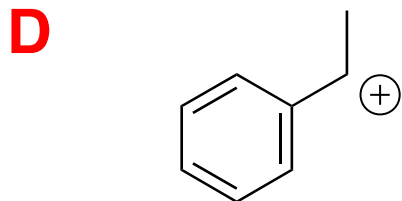
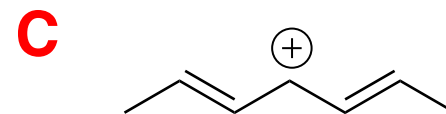
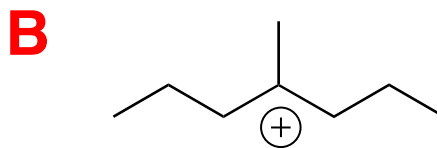
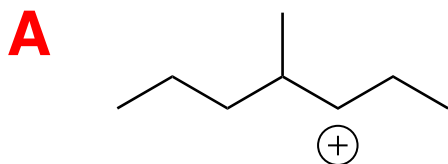


17. Answer is: e.

Response: None of these patterns are acceptable. 1 does not start at a lone pair or bond and goes to a location of high electron density, in 2 the arrow would form a 5 center carbon, in 3 the new bond would violate the octet rule for 2 carbons, and the shift is too great, and in 4, the arrow starts at a positive charge.

Section: 6.11

18. Which of the following carbocations will rearrange?



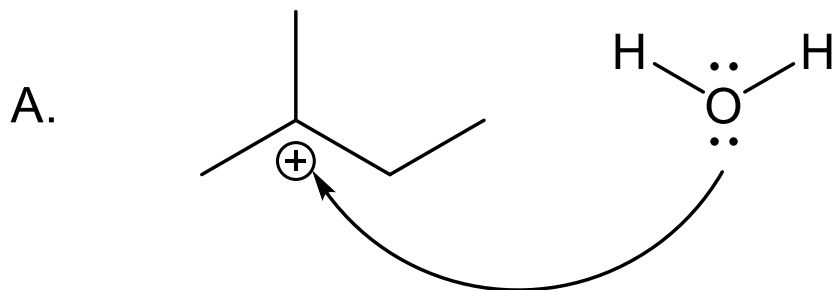
- a. A and B
- b. A and C
- c. B and C
- d. A and E
- e. B and E

18. Answer: D

Response: For more examples of this type of problem, see SkillBuilder 6.6.

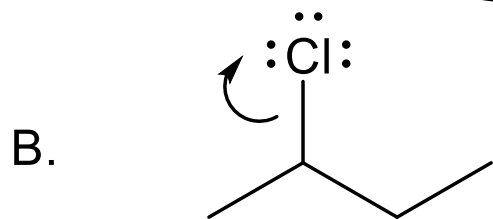
Section: 6.12

19. Which of the following curved arrow mechanistic steps would you expect to be irreversible?



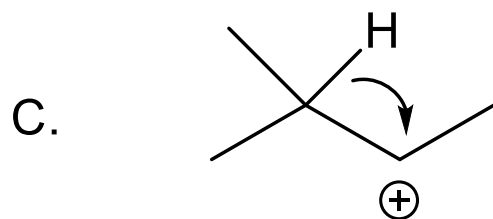
a. A only

b. B only

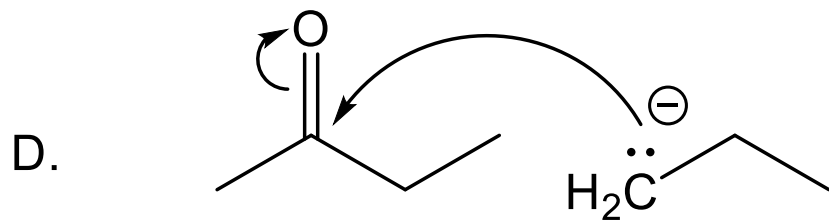


c. A and C

d. B and D



e. C and D



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19. Answer: e.

Response: Example A has a nucleophile that is also a good leaving group, so the step is reversible, while example D uses a nucleophile that is a poor leaving group, so it is irreversible. Example C involves a Carbocation shift, which are normally drawn as irreversible. Example B has a leaving group which can also act as a nucleophile.