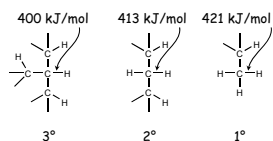
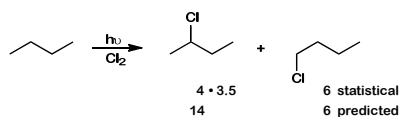


2° hydrogens are 3.5 times more reactive than 1° hydrogens.

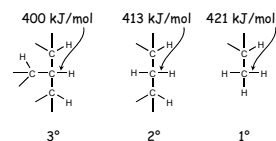


Predict the major product of the following reaction.

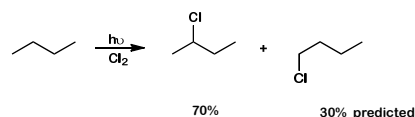


1

2° hydrogens are 3.5 times more reactive than 1° hydrogens.

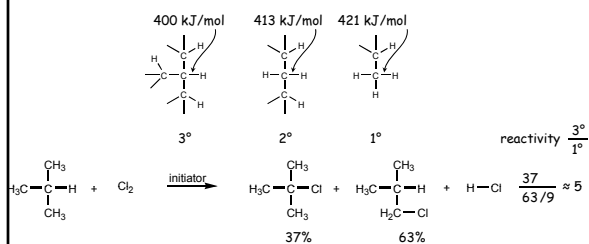


Predict the major product of the following reaction.

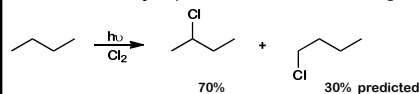


2

2° hydrogens are 3.5 times more reactive than 1° hydrogens.

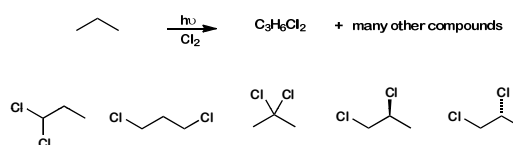


Predict the major product of the following reaction.



3

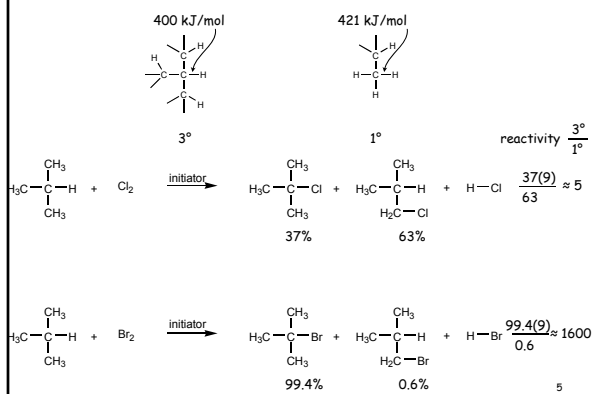
In addition to many other compounds, four isomers with the formula  $\text{C}_3\text{H}_6\text{Cl}_2$  are produced in the following reaction.



- A. Very sure this is true      D. Maybe this is false  
 B. Somewhat sure this is true      E. Somewhat sure this is false  
 C. Maybe this is true      F. Very sure this is false

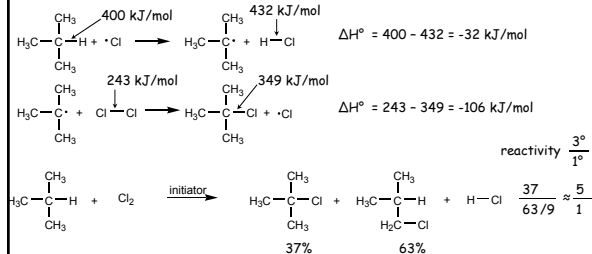
4

What is the selectivity of bromination in this reaction?



5

What is the mechanism of these reactions?



Is the first step exothermic?      A. yes      B. no

6

**What is the  $\Delta H^\circ$  for the overall reaction?**

$\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{H}-\text{Cl}$   $\Delta H^\circ = 400 - 432 = -32 \text{ kJ/mol}$   
 $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{Cl}-\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}-\text{Cl} + \cdot\text{Cl}$   $\Delta H^\circ = 243 - 349 = -106 \text{ kJ/mol}$

$\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \text{Cl}_2 \xrightarrow{\text{initiator}} \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}-\text{Cl} + \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \text{H}-\text{Cl}$

$\Delta H^\circ = -138 \text{ kJ/mol}$

**What is the difference in  $\Delta H^\circ$  of the first two steps?**

$\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{H}-\text{Cl}$   $\Delta H^\circ = 400 - 432 = -32 \text{ kJ/mol}$   
 $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{H}-\text{Cl}$   $\Delta H^\circ = 421 - 432 = -11 \text{ kJ/mol}$

$\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \text{Cl}_2 \xrightarrow{\text{initiator}} \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}-\text{Cl} + \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \text{H}-\text{Cl}$

$\Delta \Delta H^\circ = 21 \text{ kJ/mol}$

**What is the reactivity of  $3^\circ$  to  $1^\circ$  if  $\Delta \Delta H^\ddagger = 21 \text{ kJ/mol}$ ?**

$\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{H}-\text{Cl}$   $\Delta H^\circ = 400 - 432 = -32 \text{ kJ/mol}$   
 $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{H}-\text{Cl}$   $\Delta H^\circ = 421 - 432 = -11 \text{ kJ/mol}$

$A = 1$   
 $B = 5$   
 $C = 50$   
 $D = 500$   
 $E = 5000$

**transition state theory (Ch 6)**  
 $K_{eq} = 10^{21/5.7} = 10^{3.7} \approx 5000$

**Why isn't chlorination more selective?**

$\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{H}-\text{Cl}$   $\Delta H^\circ = 400 - 432 = -32 \text{ kJ/mol}$   
 $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{H}-\text{Cl}$   $\Delta H^\circ = 421 - 432 = -11 \text{ kJ/mol}$

$3^\circ \approx \frac{5}{1}$

**For a reactivity ratio of 5/1 what is the approximate  $\Delta \Delta H^\ddagger$ ?**

$\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{H}-\text{Cl}$   $\Delta H^\circ = 400 - 432 = -32 \text{ kJ/mol}$   
 $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{H}-\text{Cl}$   $\Delta H^\circ = 421 - 432 = -11 \text{ kJ/mol}$

$\Delta \Delta H^\ddagger = ?$   
 $A \sim 4$   
 $B \sim 40$   
 $C \sim 400$   
 $D \sim 0$   
 $E \sim -8$   
 $F \sim -80$

$K_{eq} = 10^{21/5.7}$   
 $K_{eq} = 10^{2/5.7} \approx 5$   
 $K_{eq} = 10^{4/5.7} \approx 5$

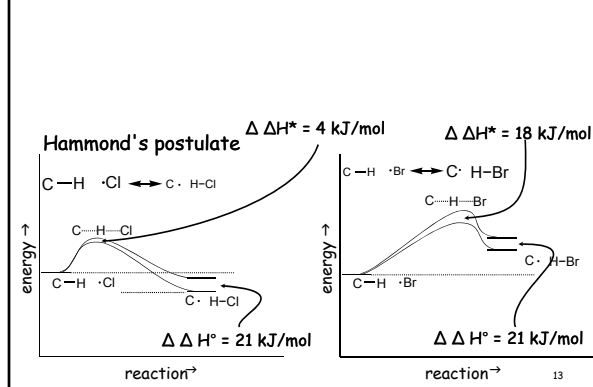
**Is the first step of bromination exothermic?**

$\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \cdot\text{Cl} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{H}-\text{Cl}$   $\Delta H^\circ = 400 - 432 = -32 \text{ kJ/mol}$   
 $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \cdot\text{Br} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{H}-\text{Br}$   $\Delta H^\circ = 400 - 366 = +34 \text{ kJ/mol}$   
 $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{H} + \cdot\text{Br} \rightarrow \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{C}\cdot + \text{H}-\text{Br}$   $\Delta H^\circ = 421 - 366 = +55 \text{ kJ/mol}$

$3^\circ \approx \frac{5}{1}$   
 $3^\circ \approx \frac{1600}{1}$

$\Delta H^\circ = +34 \text{ kJ/mol}$

Why is the  $\Delta\Delta H^\ddagger$  for bromination larger than that for chlorination?

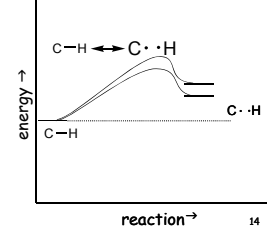
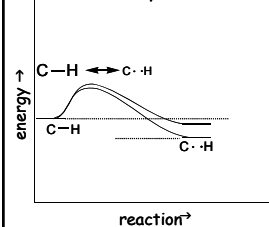


Hammond's postulate

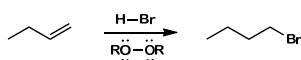
The transition state for an exothermic step resembles the reactants.

The transition state for an endothermic step resembles the products.

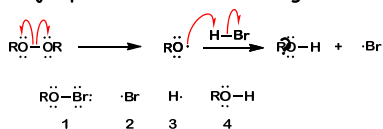
Hammond's postulate



The addition of H-Br to 1-butene in the presence of peroxides gives 1-bromobutane. Give a mechanism for this reaction consistent with this observation.



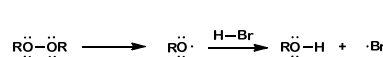
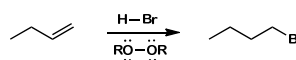
Predict the major products of the following initiation reaction.



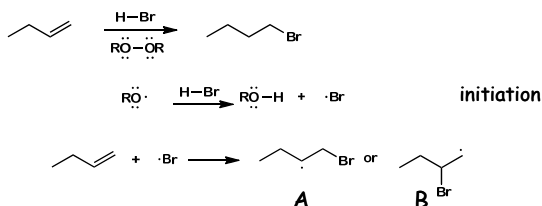
A. 1+3    B. 2+4    C. 2+3    D. 3+4    E. 1+4

15

The addition of H-Br to 1-butene in the presence of peroxides gives 1-bromobutane. Give a mechanism for this reaction consistent with this observation.

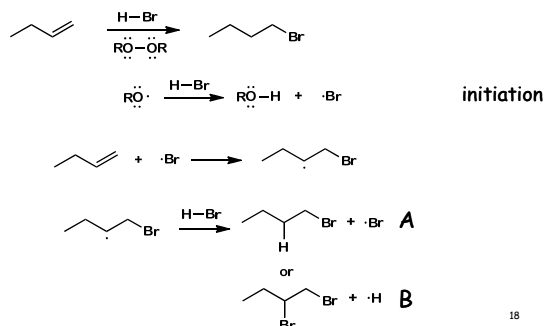


Predict the major product, A or B, of the following reaction.

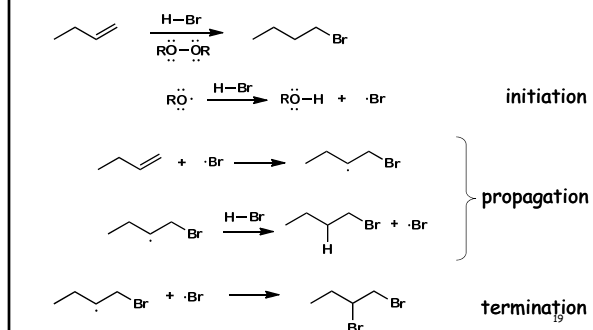


17

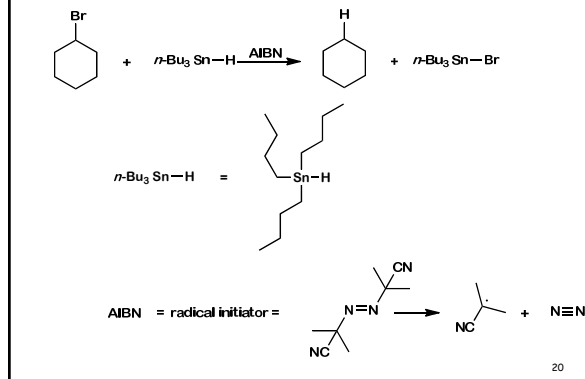
The addition of H-Br to 1-butene in the presence of peroxides gives 1-bromobutane. Give a mechanism for this reaction consistent with this observation.



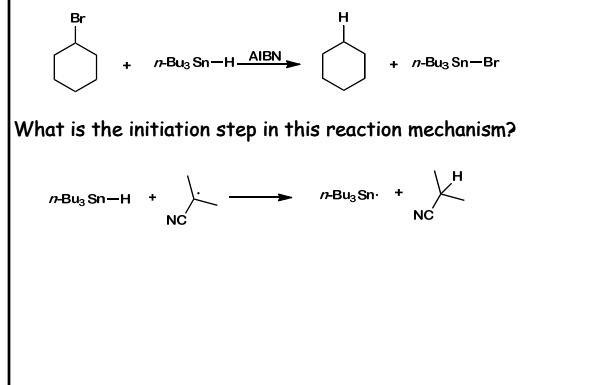
The addition of H-Br to 1-butene in the presence of peroxides gives 1-bromobutane. Give a mechanism for this reaction consistent with this observation.



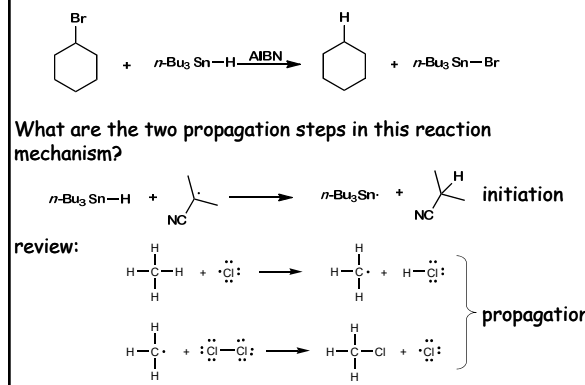
Organic bromides are easily reduced using *tri*n-butyl tin hydride in a free radical chain process.



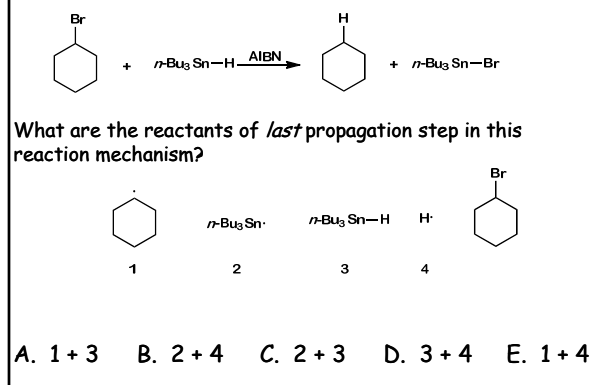
What is the mechanism of this reaction?



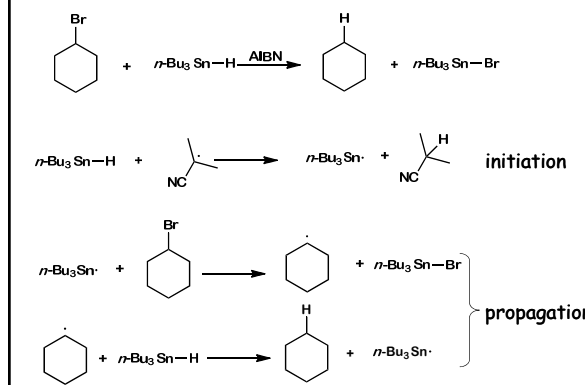
What is the mechanism of this reaction?



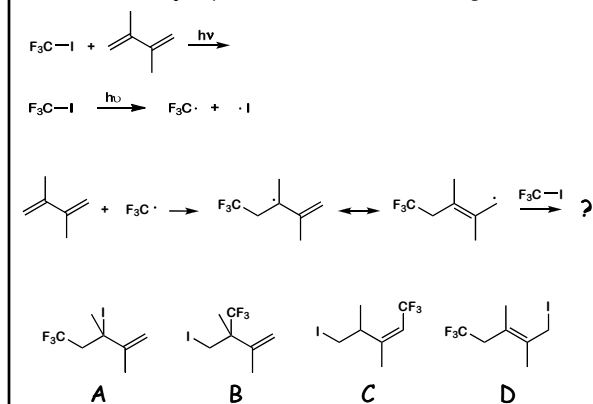
What is the mechanism of this reaction?



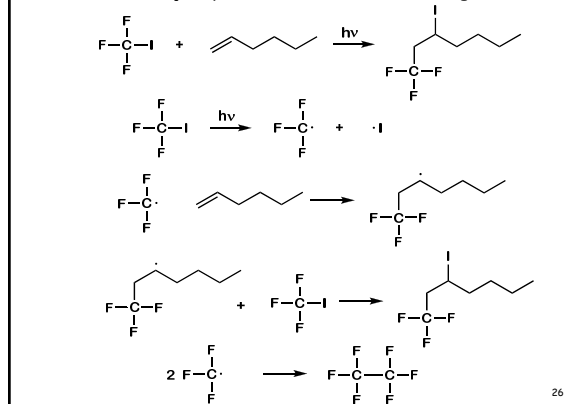
What is the mechanism of this reaction?



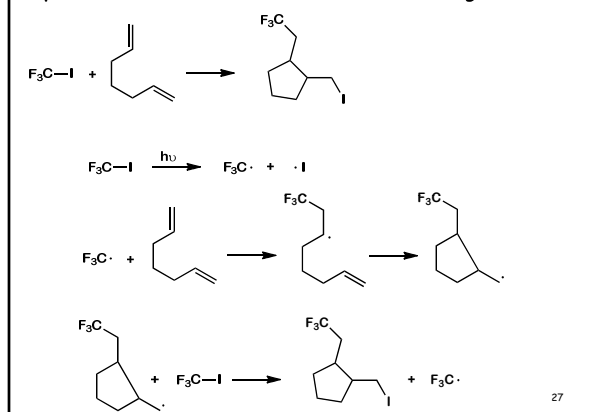
Predict the major product for the following reaction.



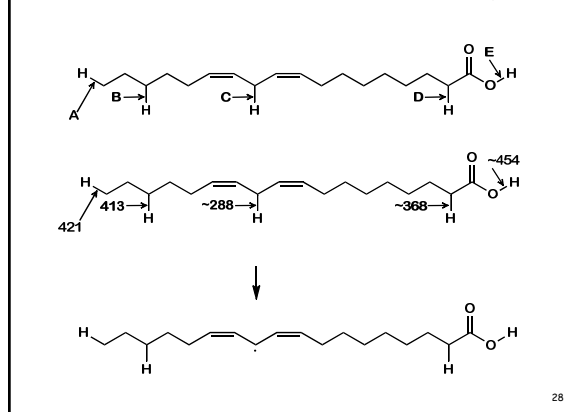
Predict the major product of the following reaction.



Propose a mechanism consistent with the following reaction.



Choose the weakest C-H bond in linoleic acid.



End of  
Material for  
Exam 3

text