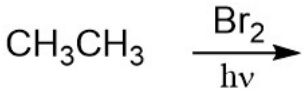
Chapter 10 Radical Reactions

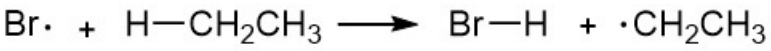
1 Predict the major product for the following reaction.

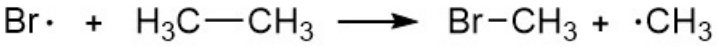


Provide a mechanism for the monobromination of ethane.
Begin with an initiation step, and then use propagation steps until the product is formed.

Consider: why does the bromine radical abstract a H atom not a CH_3 group?
Estimate ΔH for competing propagation steps...

bond broken bond formed





BDE (kcal/mol)	C-H 98	H-Br 88	C-C 90	C-Br 68

******Therefore, free-radical halogenation always replaces a H atom with a Cl or Br atom******

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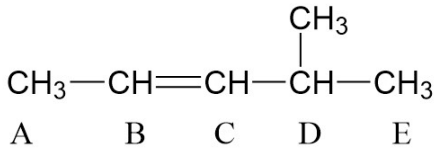
2 In the compound shown, which hydrogen is most easily abstracted in a free radical bromination reaction?



3 Predict the major product(s) for each reaction. Consider both regiochemistry and stereochemistry.

**** Bromination occurs at most substituted carbon, chlorination forms all possible products ****

Consider: why is bromination more selective than chlorination?
See ΔH for the H atom abstraction step for both...

bond broken bond formed

$$Br\cdot + H{-}CH_2CH_3 \longrightarrow H{-}Br + \cdot CH_2CH_3$$

$$Cl\cdot + H{-}CH_2CH_3 \longrightarrow H{-}Cl + \cdot CH_2CH_3$$

BDE (kcal/mol)	C–H 98	H–Br 88	H–Cl 103	*H-F 135*	*H-I 71*

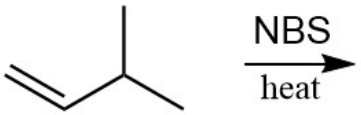
****The first propagation step for bromination is *endothermic*** so it is slow and the transition states leading to the different intermediates (1°/2°/3°) are significantly different (primary is over 1600 times slower than tertiary).

****For chlorination, this step is *exothermic*** so it is fast and does not discriminate about which hydrogen is abstracted. The transition states for chlorination at 1°/2°/3° sites are not significantly different, so the reaction rates are similar (primary is one-fourth the rate of tertiary).

Thermodynamic considerations (strengths of bonds formed and bonds broken) also explain why **reactions with F_2 and I_2 are not useful. Fluorination releases too much energy (explosive) and iodination forms very weak bonds so it is too endothermic and unfavorable.

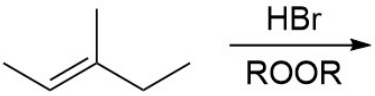
Predict the TWO products expected:

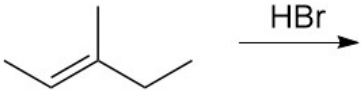
4

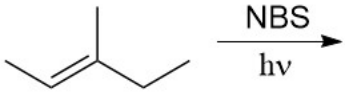


5

Predict the major products for the following reactions.

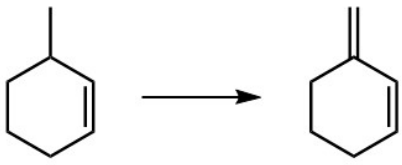




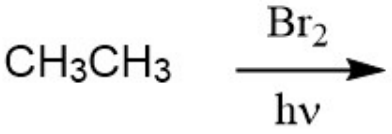


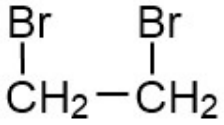
6

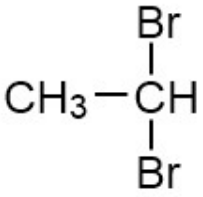
Transform the given starting material to desired TM.

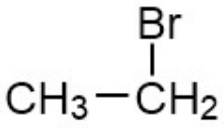


1a Predict the major product of the following reaction.



A) 

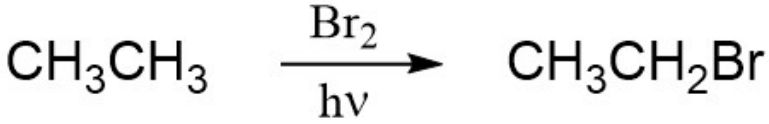
C) 

B) 

D) No Reaction

1b

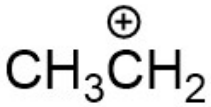
Which of the following is a likely intermediate in the mechanism for the reaction below?

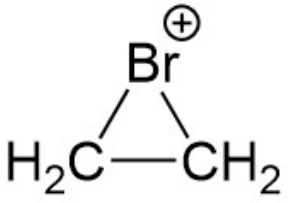


A) 

D) 

B) 

C) 

E) 

3 The following reaction gives a mixture of products. Describe the mixture.

A) Three constitutional isomers (all are chiral).

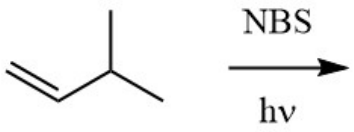
B) Four constitutional isomers (three are chiral).

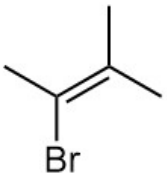
C) Four constitutional isomers (two are chiral).

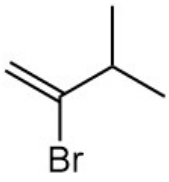
D) Five constitutional isomers (three are chiral).

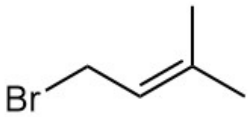
E) Five constitutional isomers (two are chiral).

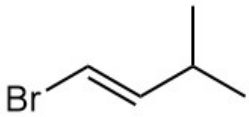
4 Which of the following is one of the two expected products for the given reaction?

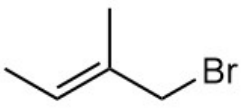


A) 

C) 

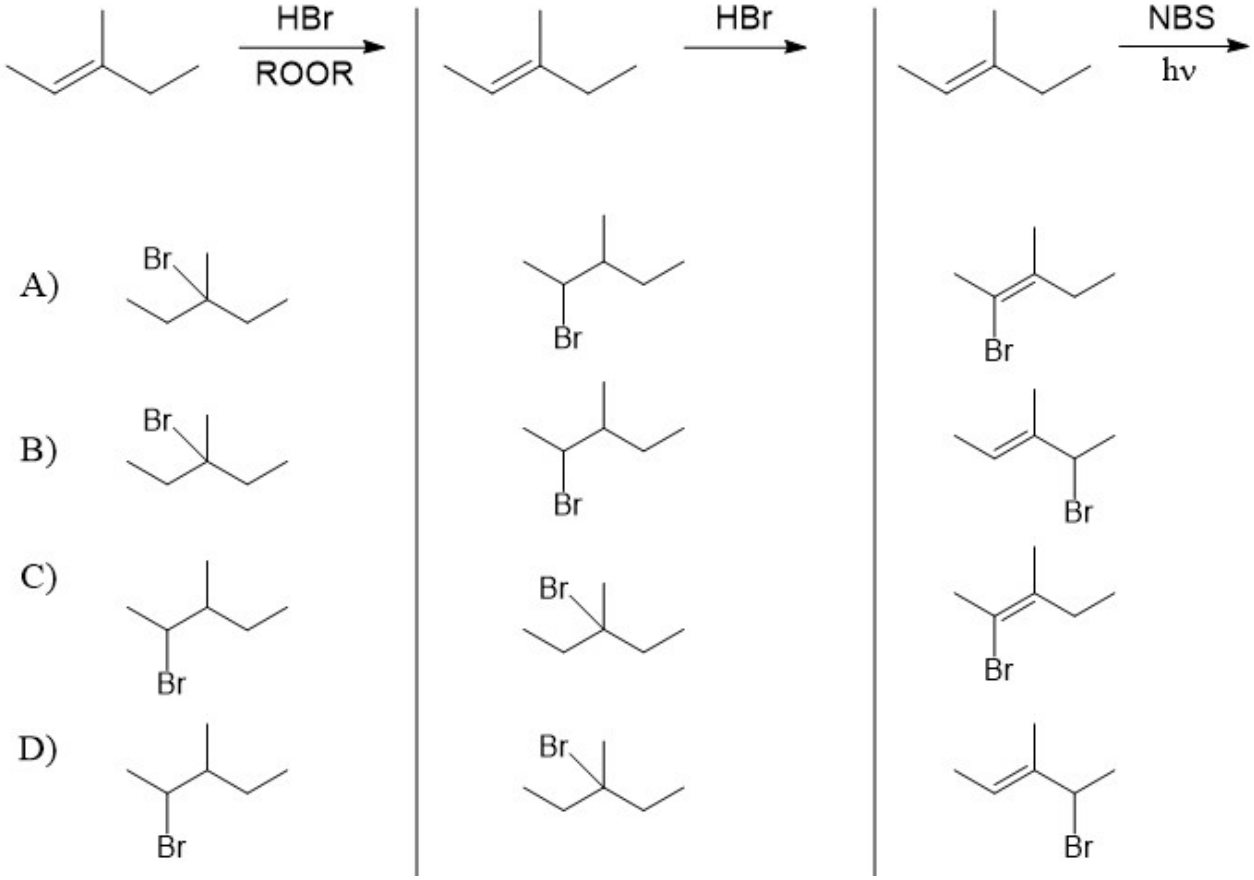
B) 

D) 

E) 

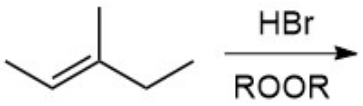
Predict the major products for the following reactions.

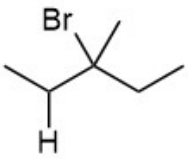
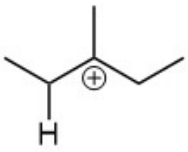
5a

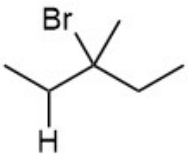
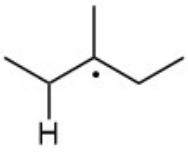


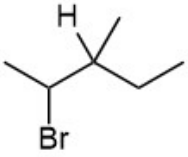
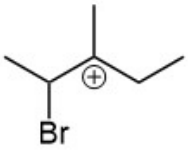
5b

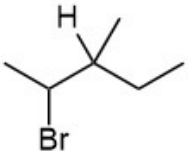
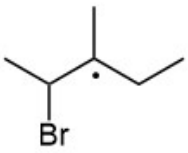
Predict the major product and briefly explain.

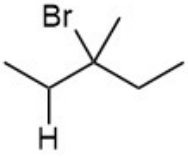


A)  because  is more stable

B)  because  is more stable

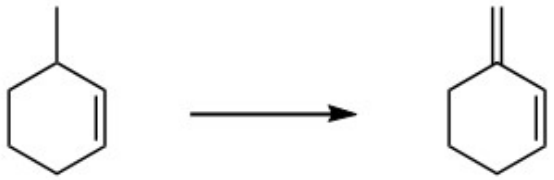
C)  because  is more stable

D)  because  is more stable

E) 

because Dr. Markovnikov told me so

6 Which reagents would be best to achieve the following synthesis?



A) 1) NBS, hν
2) NaOEt

C) 1) NBS, hν
2) *t*-BuOK

B) 1) Br_2, hν
2) NaOEt

D) 1) Br_2, hν
2) *t*-BuOK