α,γ-Bisdiphenylene-β-phenylallyl, an unusual example of a persistent carbon radical
Note: Problems with *italicized numbers* are more challenging.
You may want to try them last.

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CHM 321: Summary of Important Concepts

Concepts for Chapter 11: Radical Reactions

I. Nomenclature
   A. Alkyl

II. Properties
   A. sp²-hybridized
   B. Stability
      a. 3° > 2° > 1° >> CH₃
      b. resonance stabilizes radicals
   C. Functions
      1. Homolytic / homogenic bond cleavage / coupling
         a.

III. Reactions
   A. Radical substitution
      1. involves three steps: initiation, propagation, and termination
         a. initiation with heat, light, or peroxides: radicals are created
         b. propagation: one radical makes another
         c. termination: radicals are consumed

   B. Allylic halogenation

2. Selectivity
   a. Regioselectivity
      i. Chlorination is not regioselective; useful only with alkanes having
         Hs that are all the same
      ii. Bromination regioselectively brominates 3° Hs; is useful
   b. Stereoselectivity
      i. Proceeds with racemization

B. Allylic halogenation
1. Allylic substituent groups
   a. –CH$_2$CH=CH$_2$, the allyl substituent
   b. a C bonded to a C=C is an allylic C
      i. the Hs on that C are allylic Hs

2. Allylic free radicals
   a. resonance stabilization

3. Allylic halogenation is highly selective and very useful
   a. reaction conditions: NCS or NBS in CCl$_4$ + heat

C. AntiMarkinikov addition of HBr to a pi bond

1. Mechanism

\[ \text{initiation} \]

\[ \text{propagation} \]

\[ \text{termination} \]
c. termination
   i. any two radicals combine to form a neutral
1. A. For each reaction, provide either an IUPAC name for the starting material shown OR draw the correct chemical structure of the starting material named.

B. Provide structural formulas for the principal product of each reaction, and describe its stereochemical outcome. If you believe there will be no reaction given the starting material and reaction conditions, indicate so by writing "NR" for "no reaction".

a. 

\[
\begin{align*}
\text{Br}_2 & \quad \text{light} \\
300 \degree C
\end{align*}
\]

b. \( (6R)-6-(\text{chloromethyl})-2-\text{ethyl}-1-\text{nonene} \)  

\[
\text{HBr} \quad \text{hv}
\]

c. 

\[
\begin{align*}
\text{NCS} & \quad \text{CC}_2, \Lambda \\
\end{align*}
\]

2. Provide the principal organic reaction product for each of the following reactions. If you believe there will be no reaction given the starting materials and the reaction condition, indicate so by writing "NR" for "no reaction".

a. 

\[
\begin{align*}
\text{Br}_2 & \quad \text{light}
\end{align*}
\]

b. 

\[
\begin{align*}
\text{I}_2 & \quad 0 \degree C, \text{dark}
\end{align*}
\]
3. After initiation by homolysis of HBr to yield a hydrogen radical and a bromine radical, 1-pentene undergoes antiMarkovnikov addition according to these two propagation steps:

\[
\text{\begin{align*}
\text{CH}_2=CH\text{CH}_2\text{CH}_2\text{CH}_3 + \cdot \text{Br} & \rightarrow \rightarrow \cdot \text{Br} \\
\text{\text{CH}_2=CH\text{CH}_2\text{CH}_2\text{CH}_3} & + \cdot \text{Br} \rightarrow \rightarrow \text{\text{Br}} \\
\text{\text{\cdot Br} + H-\text{Br}} & \rightarrow \rightarrow \text{\text{Br}} + \cdot \text{Br}
\end{align*}}
\]

Under the reaction conditions, it is not observed to undergo Markovnikov addition. This is because one of the two propagation steps required to form a Markovnikov addition product is endothermic, and therefore disfavored:

\[
\text{\begin{align*}
\text{\cdot Br} + \text{\cdot H} & \rightarrow \rightarrow \cdot \text{H} \\
\text{\text{\cdot Br} + Br-H} & \rightarrow \rightarrow \cdot \text{H}
\end{align*}}
\]

Use the table of bond dissociation energies at right to:

a. Identify which of the two propagation steps is endothermic by placing a star (*) to its left.

b. Calculate the $\Delta H^\circ$ of that endothermic step. Show your work for full credit.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy of disassociation, $\Delta H$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C $\pi$</td>
<td>63</td>
</tr>
<tr>
<td>C=C $\sigma$</td>
<td>83</td>
</tr>
<tr>
<td>C–Br</td>
<td>70</td>
</tr>
<tr>
<td>C–H</td>
<td>98</td>
</tr>
<tr>
<td>H–Br</td>
<td>87.5</td>
</tr>
<tr>
<td>Br–Br</td>
<td>46</td>
</tr>
</tbody>
</table>
4. Provide a clear, detailed, complete, chemically correct mechanism for the following radical chlorination. Your mechanism must include labeled initiation, propagation, and one example termination steps. It must also include the two resonance isomers of the intermediate carbon radical that forms in the reaction.

\[
\text{\begin{align*}
\text{alkene} & + \text{N-Cl} \xrightarrow{\Delta} \text{Cl-alkene} & + \text{N-H}
\end{align*}}
\]
5. Radical chlorination of alkanes is not generally useful because mixtures of products often result when more than one kind of C–H bond is present in the alkane.

a. Draw skeletal structures of all the monochloro substitution products $C_6H_{13}Cl$ you might obtain by reaction of 2-methylpentane with $Cl_2$ and heat.

6. (16 points) The mechanisms of the reactions are the same, but radical monobomination, unlike radical monochlorination, is very selective: only one product forms. Consider this reaction:

\[
\text{Br} \quad \quad \text{Br} \quad \quad \Delta \quad \quad \text{Br} \quad \quad \text{H} \quad \quad \text{Br}
\]

Use curved electron half-arrows to provide a clear, correct, detailed reaction mechanism that explains how the starting materials are converted into the observed products. Clearly label the initiation, propagation and termination steps of your mechanism. The mechanism that you provide needs only to have one example of a termination step: it is not necessary to provide every possible one that can occur.
7. Consider the radical *dibromination* of bicyclo[1.1.1]pentane:

\[
\begin{align*}
\text{C}_5\text{H}_6\text{Br}_2 + 2 \text{ HBr} & \quad \xrightarrow{\Delta} \\
\text{C}_5\text{H}_6\text{Br}_2 & \quad + \quad 2 \text{ HBr}
\end{align*}
\]

a. Clearly draw structural formulas of all of the dibromobicyclo[1.1.1]pentane isomers that in theory can form from this reaction.

b. How many of the dibromobicyclo[1.1.1]pentane isomers that in theory can form from this reaction are chiral?

\[\text{________________________} \]

c. Two of the theoretical number of dibromobicyclo[1.1.1]pentane isomers are never found to form in this reaction. Draw which two and clearly explain why they are never found to form.
8. Here’s a reprise of a problem that was suggested in chapter 6: Hydrogen atoms that are on an $sp^3$-hybridized carbon that is adjacent to a double bond are called allylic hydrogens. Substitutions of these hydrogens by bromine (shown below using propene) occurs by the same reaction mechanism as the chlorination of methane:

\[
\text{\underbrace{\text{\text{\upshape \hspace{10pt} + \hspace{10pt} Br}_2}}}_{\text{heat or hv}} \rightarrow \text{\underbrace{\text{\text{\upshape \hspace{10pt} Br}}}}
\]

Provide a mechanism for this reaction, clearly indicating the initiation step(s), propagation step(s), and any termination step(s).