Problem Set  Chapter 15  Answer Key

1. It’s the “tropylium” ion:

   \[
   \begin{array}{c}
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \text{H} \\
   \end{array}
   \]

   If you said the benzyl cation (C₆H₅CH₂⁺), that’s OK too: the tropylium and benzyl cations are constitutional isomers.

   It can form by the following route:

2. a.  
   
   \[
   \begin{array}{c}
   \text{CH₃} \\
   \end{array}
   \]

   b.  
   
   \[
   \begin{array}{c}
   \text{CH₃} \\
   \text{CH₃} \\
   \end{array}
   \]

3. From top to bottom, the correct matches are:
   
   F
   D
   B
   C
4. a. ![Image of compound with methyl group and chlorine]

b. ![Image of alkyne]

5. product on the left, starting material on the right.

The IR spectrum on the left has absorptions at about 3100 cm\(^{-1}\) (C\(sp^2\)-H \(\sigma\) bond stretch) and about 900 cm\(^{-1}\) (bending of two C\(sp^2\)-H \(\sigma\) bonds on a terminally disubstituted alkene); the IR spectrum on the right does not.

6. From top to bottom: B
   C
   A
   F

7. Like bromine, carbon in nature exists as two isotopes, \(^{12}\)C and \(^{13}\)C. \(m/z = 139\) represents a molecular ion that contains one \(^{13}\)C isotope of carbon; it has molecular formula \((^{12}\text{C}_9^{13}\text{C}_1\text{H}_{18})^+\).

Unlike bromine, \(^{13}\)C / \(^{12}\)C = 1.08 \%, that is, only 1 carbon atom in 100 is the heavy isotope of carbon. Since decalin has 10 carbons, the probability that any decalin molecule will have a \(^{13}\)C in it is 10 x 1.08\% = 10.8 \%. Therefore, about 10\% of the decalin molecules in a sample of decalin will be observed to have molecular ions with \(m/z = 139\), rather than 138.

A similar argument would apply for hydrogen. It also has two stable isotopes in nature, \(^1\)H and \(^2\)H. The contribution of \(^2\)H to the intensity of \(m/z = 139\) is quite small, however: \(^2\)H / \(^1\)H = 0.016 \%, so the probability that any decalin molecule will have a \(^2\)H in it is only 18 x 0.016\% = 0.288 \%.
8. Solvolysis of \textit{trans}-1-bromo-2-methylcyclopentane in water at 50 °C for 12 hours gives two products, A and B. The infrared and mass spectra of product A are shown below:

a. Clearly label two features on the IR spectrum indicating the functional group class of product A.

b. Clearly label the molecular ion ($M^+$) of the mass spectrum.

c. The fragment appearing at mass 67 suggests a loss of what functional group from the molecular ion?

\textit{methyl (CH}_3\text{)}

d. Provide a structural formula for product A.

v. Product B has molecular formula C$_6$H$_{12}$O. Provide a structural formula for product B.