Chapter 10 - Organohalides

Give the name for each of the following alkyl halides.

1. \[
\begin{align*}
H & \quad Cl \\
C & \quad Cl \\
C & \quad H \\
Cl & \quad H
\end{align*}
\]

*Answer:* 1,1,2-trichloroethane

2. \[
\begin{align*}
\text{CHI}_3
\end{align*}
\]

*Answer:* triiodomethane

3. \[
\begin{align*}
\text{F} & \quad \text{Cl} \\
\text{F} & \quad \text{C} \\
\text{F} & \quad \text{H} \\
\text{Br}
\end{align*}
\]

*Answer:* 2-bromo-2-chloro-1,1,1-trifluoroethane

4. \[
\begin{align*}
\text{CH}_2\text{Cl}_2
\end{align*}
\]

*Answer:* dichloromethane

Draw structures corresponding to these names.

5. 3-iodopropene

*Answer:*

\[
\begin{align*}
\text{I}
\end{align*}
\]

6. *trans*-1-chloro-3-sec-butylcyclohexane

*Answer:*

\[
\begin{align*}
\text{Cl}
\end{align*}
\]

7. 1,2-dichloro-1,1,2,2-tetrafluoroethane (Cryofluorane)

*Answer:*

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{F} & \quad \text{C} \\
\text{F} & \quad \text{C} \\
\text{F} & \quad \text{F}
\end{align*}
\]
8. (S)-2-bromobutane

*Answer:*

To answer the following questions consider the reaction below:

\[
\text{C}_8H_{11} + (\text{CH}_3)_3\text{COCl} \rightarrow \text{C}_8H_{11}\text{Cl} + (\text{CH}_3)_3\text{COCl}\]

9. When propylbenzene reacts with tert-butylhypochlorite three monochlorinated products are formed in the ratios indicated. Calculate a reactivity order for each type of hydrogen atom in propylbenzene.

*Answer:*

\[
\begin{align*}
\text{Ar} - \text{CH}_2 - & = 65\% \div 2 = 32.5\% \text{ product} + 3.3 = 9.85 \\
-\text{CH}_2 - & = 25\% \div 2 = 12.5\% \text{ product} + 3.3 = 3.8 \\
-\text{CH}_3 & = 10\% \div 3 = 3.3\% \text{ product} + 3.3 = 1
\end{align*}
\]

Therefore the Relative Reactivity for CH\(_3\)CH\(_2\)ArCH\(_2\) is 1:3:8:985.

10. The reaction of propylbenzene with tert-butylhypochlorite proceeds by a radical substitution pathway. Draw the structure of the radical intermediate leading to each product.

*Answer:
11. Based on your answers to the two questions above explain why (1-chloropropyl)benzene is the major product of this reaction.

*Answer:* In question 9 we calculated that the hydrogens next to the aryl group, the benzylic hydrogens, are about 2.5 times more reactive than the methylene hydrogens and about 10 times more reactive than the methyl hydrogens. This means that the benzylic radical is more stable than a 2° or 1° radical. The reason the benzylic radical is more stable is because it is resonance stabilized. The resonance forms for the benzylic radical are:

\[
\begin{align*}
\text{benzylic radical} & \quad \leftrightarrow \quad \text{resonance form 1} \\
& \quad \leftrightarrow \quad \text{resonance form 2} \\
& \quad \leftrightarrow \quad \text{resonance form 3}
\end{align*}
\]

The 2° or 1° radicals have no other resonance forms.

12. Are any of the products of this reaction chiral? If so draw them and label the chirality center with an asterisk.

*Answer:* Yes!

\[
\begin{align*}
\text{chiral product 1} & \quad \ast \\
\text{chiral product 2}
\end{align*}
\]

13. Will the product mixture of this reaction display optical activity?

*Answer:* No, the radical intermediates for the chiral products are symmetrical and the transition states leading to chiral products are of equal energy so racemic mixtures are formed.

14. In the discussion on relative reactivity of alkane hydrogens towards radical chlorination, we showed that the relative rate of 2° to 1° hydrogen atom abstraction is 3.5 : 1 for butane. Calculate the relative amounts of 1-chloropropane and 2-chloropropane obtained the radical chlorination of propane, using this relative rate of reactivity.

\[
\text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow{\text{Cl}_2 \text{ light}} \text{CH}_3\text{CH}_2\text{CH} - \text{Cl} \quad + \quad \text{Cl}_2
\]

*Answer:* Propane has six 1° hydrogens, so 6 × 1 = 6; and two 2° hydrogens, so 2 × 3.5 = 7. The percentage of 1-chloropropane is therefore 6/13 or 46% and the percentage of 2-chloropropane is 7/13 or 54%.
Consider the reaction below to answer the following questions.

\[ \text{CH}_3 \text{CH} = \text{CHCH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{hv}} \text{CH}_3 \text{CH} = \text{CHCH}_2\text{CH}_3 \quad \text{and} \quad \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_3 \]

15. Draw all the monochlorination products of methylcyclopentane (ignore stereoisomers).

*Answer:*

\[ \text{CH}_2\text{Cl} \quad \text{CH}_3 \quad \text{CH}_2\text{Cl} \quad \text{CH}_3 \quad \text{CH}_2\text{Cl} \quad \text{CH}_3 \]

16. Label the chirality centers in the monochlorination products of methylcyclopentane with an asterisk.

*Answer:*

\[ \text{CH}_2\text{Cl} \quad \text{CH}_3 \quad \text{CH}_2\text{Cl} \quad \text{CH}_3 \quad \text{CH}_2\text{Cl} \quad \text{CH}_3 \] * * *

17. Tell whether radical chlorination of methylcyclopentane is an oxidation or a reduction process.

*Answer:*

In the radical chlorination of methylcyclopentane a C-H bond is broken and a C-Cl bond is formed, so the process is an organic oxidation.

Consider the reaction below to answer the following questions.

\[ \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{NBS}} \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_3 \quad \text{and} \quad \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_3 \]

18. Place asterisks(*) at all *allylic* positions in compound A.

*Answer:*

\[ \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_3 \]

19. Draw the resonance forms of the allylic radical intermediate that accounts for the formation of B and C.

*Answer:*

\[ \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_3 \quad \text{and} \quad \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_3 \]

\[ \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_3 \quad \text{CH}_3\text{CH} = \text{CHCH}_2\text{CH}_3 \]
20. D and E, below, are minor products in this reaction. Explain why.

\[ \text{BrCH}_2\text{CH} \equiv \text{CHCH}_2\text{CH}_3 + \text{CH}_2 \equiv \text{CHCH}_2\text{CH}_2\text{CH}_3 \]

\[ \text{D} \quad \text{E} \]

**Answer:** Products D and E are formed from the other allylic radical, whose resonance forms are shown below.

\[ \text{CH}_2\text{CH} \equiv \text{CHCH}_2\text{CH}_3 \quad \xleftarrow{\text{1° allylic}} \quad \text{CH}_2 \equiv \text{CHCH}_2\text{CH}_2\text{CH}_3 \quad \xrightarrow{\text{2° allylic}} \]

This allylic radical forms more slowly than the radical for products A and B because it has some 1° character, and thus, is less stable. The allylic radical intermediate for products A and B is 2° allylic.

Choose the best reagent or sequence of reagents from the list provided below for carrying out the following transformations. Place the letter of your response to the left of the reaction.

- a. PBr$_3$
- b. HCl (gas), ether
- c. 1. Mg, ether
- d. SOCl$_2$, pyridine
- e. HBr (gas), ether
- f. 1. Mg, ether
- 2. D$_2$O
- 2. NBS

21. _____

**Answer:** e

22. _____

**Answer:** c

23. _____

**Answer:** d
Provide structures for the reactants, intermediates, or products, as indicated, in the following reactions. Draw the structures in the boxes provided.

24.

\[
\text{CH}_3\text{CH}_2\text{I} \quad \xrightarrow{1. \text{ Li, pentane}} \quad \text{CH}_3\text{I} \\
\quad \xrightarrow{2. \text{ CuI}} \quad (\text{CH}_3\text{CH}_2)_2\text{CuLi} \\
\]

**Answer:**

\[
\text{CH}_3\text{CH}_2\text{I} \quad \xrightarrow{1. \text{ Li, pentane}} \quad (\text{CH}_3\text{CH}_2)_2\text{CuLi} \\
\quad \xrightarrow{2. \text{ CuI}} \quad \text{CH}_3\text{CH}_2\text{CH}_3 \\
\]

25.

\[
\square \quad \xrightarrow{\text{SOCl}_2, \text{ pyridine}} \quad \text{Cl} \\
\]

**Answer:**

\[
\square \quad \xrightarrow{\text{SOCl}_2, \text{ pyridine}} \quad \text{Cl} \\
\]

26.

\[
\text{CH}_2=\text{CH}_2 \quad \xrightarrow{\text{NBS}}, \text{CCl}_4 \quad + \\
\]

**Answer:**

\[
\text{CH}_2=\text{CH}_2 \quad \xrightarrow{\text{NBS}}, \text{CCl}_4 \quad + \\
\]

\[
\text{CH}_2=\text{CH}_2 \quad \xrightarrow{\text{NBS}}, \text{CCl}_4 \quad + \\
\]

\[
\text{CH}_2=\text{CH}_2 \quad \xrightarrow{\text{NBS}}, \text{CCl}_4 \quad + \\
\]
27. \[
\begin{align*}
\text{OH} & \quad \xrightarrow{\text{HCl, ether}} \quad \begin{aligned}
\text{Cl} & \\
& \\
\end{aligned}
\end{align*}
\]

**Answer:**

\[
\begin{align*}
\text{OH} & \quad \xrightarrow{\text{HCl, ether}} \quad \begin{aligned}
\text{Cl} & \\
& \\
\end{aligned}
\end{align*}
\]

28. \[
\begin{align*}
\text{Br} & \quad \xrightarrow{\text{ether}} \quad \begin{aligned}
\text{CH}_3\text{CH}_3 & \\
& \\
\end{aligned}
\end{align*}
\]

**Answer:**

\[
\begin{align*}
\text{Br} & \quad \xrightarrow{\text{ether}} \quad \begin{aligned}
\text{CH}_3\text{CH}_3 & \\
& \\
\end{aligned}
\end{align*}
\]

29. \[
\begin{align*}
& \quad \xrightarrow{\text{1. NBS, CCl}_4, \text{2. KOH, ethanol}} \quad \begin{aligned}
& \\
& \\
\end{aligned}
\end{align*}
\]

**Answer:**

\[
\begin{align*}
& \quad \xrightarrow{\text{1. NBS, CCl}_4, \text{2. KOH, ethanol}} \quad \begin{aligned}
& \\
& \\
\end{aligned}
\end{align*}
\]
Propose a synthesis of each of the following compounds from the given starting material and any inorganic reagents necessary.

30.

\[
\begin{align*}
\text{Br} & \quad \text{Mg} \quad \text{ether} \\
\end{align*}
\]

Answer:

\[
\begin{align*}
\text{Br} & \quad \text{Mg} \quad \text{ether} \\
\end{align*}
\]

31.

\[
\begin{align*}
P\text{Br}_3 & \quad \text{ether} \\
\end{align*}
\]

Answer:

\[
\begin{align*}
P\text{Br}_3 & \quad \text{ether} \\
\end{align*}
\]

32.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3\text{CHCH} & \quad \text{from} \quad \text{CH}_3\text{CHCH}_2\text{OH} \\
\text{CH}_2 & \\
\end{align*}
\]

Answer:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3\text{CHCH}_2\text{OH} & \quad \text{PBr}_3 \quad \text{ether} \quad \text{KOH} \quad \text{ethanol} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3\text{CHCH}_2\text{Br} & \quad \text{CH}_3\text{CHCH} \\
\end{align*}
\]
33. 

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{Br} \\
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\end{align*}
\]

**Answer:**

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Br} \\
\text{H}_3\text{C} & \quad \text{Li} \\
\text{H}_3\text{C} & \quad \text{Li} \\
\text{H}_3\text{C} & \quad \text{CuLi} \\
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\end{align*}
\]

34. Identify the reagents a and b in the following scheme.

**Answer:** a = NBS, hv    b = KOH, ethanol

Label each transformation below as:

a. an oxidation  
b. a reduction  
c. neither an oxidation nor a reduction

Place the letter corresponding to the correct answer in the blank to the left of the transformation.

35. 

**Answer:** a

36. 

**Answer:** c
37. \[ \text{Answer: } b \]

38. \[ \text{Answer: } a \]

39. Rank the following compounds in order of increasing oxidation level. Place the number rank (1 = lowest; 4 = highest) in the blank below the structure.

\[ \text{Answer: } 4 \quad 1 \quad 3 \quad 2 \]