ALKANES – STRUCTURE, PROPERTIES, AND SYNTHESIS

A STUDENT WHO HAS MASTERED THE MATERIAL IN THIS SECTION SHOULD BE
ABLE TO:

1. Predict relative boiling points of alkanes, in comparison with other alkanes and with
   compounds containing other functional groups. Intermolecular bonding type (ionic,
   hydrogen, dipole-dipole, induced dipole-induced dipole) and surface area (among isomers,
   unbranched compounds have higher surface area and higher boiling points) are important
   here.

2. Draw conformations of alkanes and cycloalkanes when given the name, and identify
   conformations when given a structure. For butane and related molecules, the important
   conformations are eclipsed and staggered (including gauche and anti). For substituted and
   unsubstituted cyclohexanes, important conformations are chair, boat, twist boat, and half
   chair.

3. Give the IUPAC names of alkanes, alkyl halides, and alcohols (open chain and cyclic) when
   given a picture of the conformation. Newman projections and bond-line formulas are
   important here.

4. Predict the relative stabilities of conformations of alkanes and cycloalkanes, and draw and
   describe the most stable conformations in these systems. Also, give or identify the types of
   strain present in different conformations in these systems, and use this information to
   explain relative stabilities. Important types of strain in conformational analysis are:
   - torsional strain (favors staggered conformations over eclipsed)
   - bond angle strain (which favors conformations with normal bond angles of 109.5° for
     sp³ atoms and 120° for sp² atoms)
   - steric strain (effects of the bulk of groups, occurring when two groups try to occupy
     the same space).

5. Given starting materials and reaction conditions, predict the products of the following
   reactions:

   Hydrogenation of alkenes and alkynes
   \[ R_2C=CR_2 + H_2/Pt, Pd, or Ni \rightarrow R_2CHCHR_2 \]
   \[ R-C≡C-R + H_2/Pt, Pd, or Ni \rightarrow RCH_2CH_2R \]

   Reduction of alkyl halides
   \[ RX + Zn + HX \rightarrow RH + ZnX_2 \]

   Halogenation of alkanes
   \[ RH + X_2 \rightarrow RX + HX \] (where X is Cl or Br; Br is more selective)

   Alkylation of terminal alkynes
   \[ R-C≡C-H + NaNH_2 \rightarrow R-C≡CNa + NH_3 \]
   \[ R-C≡CNa + R’X \rightarrow R-C≡C-R’ + NaX \]

6. Use the reactions listed in the previous objective in proposing syntheses (methods of
   preparation) of alkanes and alkyl halides.
A student who has mastered the objectives on the previous page should be able to solve the following problems and related ones:

1.1 Which of the following alkanes has the lowest boiling point? Which has the highest?
   A. \((\text{CH}_3)_2\text{CHCH}((\text{CH}_3)_2)\)  
   B. \((\text{CH}_3\text{CH}_2)_2\text{CHCH}_3\)
   C. \((\text{CH}_3)_3\text{CCH}_2\text{CH}_3\)  
   D. \(\text{CH}_3(\text{CH}_2)_4\text{CH}_3\)

1.2 Which of the following compounds has the highest boiling point? Which has the lowest?
   A. \((\text{CH}_3)_3\text{CBr}\)  
   B. \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}\)
   C. \((\text{CH}_3)_2\text{C}(\text{CH}_3)_2\)  
   D. \(\text{C}\)

2.1 Use the terms: eclipsed, staggered, gauche, anti to classify each of the following structures. Some structures may need more than one term for a full classification.

2.2 Classify each of the following structures as one of the following: chair, half chair, boat, twist boat.
3. Give the IUPAC name of each of the following compounds.

a) \( \text{CH}_3 \text{C}_-\text{H}_2\text{OH} \)

b) \( \text{CH}_3\text{CH}_3 \)

c) \( \text{CH}_3\text{C}_-\text{H}_2\text{Br} \)

d) \( \text{CH}_3\text{C}_-\text{H}_2\text{I} \)

e) \( \text{CH}_3\text{C}_-\text{H}_2\text{Cl} \)

f) \( \text{H}_3\text{C}\text{C}_-\text{H}_2\text{Cl} \)

4.1 Which of these describes the most stable conformation of butane? Which describes the least stable?
A. Eclipsed, with the methyl groups eclipsing hydrogens
B. Eclipsed, with the methyl groups eclipsing each other
C. Anti
D. Gauche

4.2 Draw the most stable conformation of each of the following:
   a) 4-methylcyclohexanol   b) methylcyclohexane   c) 1-fluoropropane   d) propane

4.3 For 1-iodo-2-methylpropane, draw:
   a) the staggered conformation(s) of lowest energy
   b) the eclipsed conformation(s) of highest energy

4.4 a) Which of these describes the most stable conformation of \( \text{cis}-3\)-isopropylcyclohexanol?
   A. The isopropyl group is equatorial and the OH is axial
   B. The isopropyl group is axial and the OH is equatorial
   C. Both substituents are equatorial
   D. Both substituents are axial

   b) Which of the choices A-D above best describes the most stable conformation of \( \text{cis}-4\)-isopropylcyclohexanol?
4.5 Underline one or more words in each set of parentheses to make each of the following sentences correct.

a) The chair form of cyclohexane is (less, more) stable than the boat form because the chair form has (less, more) (torsional, bond angle, steric) strain.

b) The “flagpole” interaction in the boat form of cyclohexane is an example of (torsional, bond angle, steric) strain.

c) The staggered form of propane is (less, more) stable than the eclipsed form because the staggered form has (less, more) (torsional, bond angle, steric, torsional and steric) strain.

d) Unstable conformations have (higher, lower) potential energy than stable ones.

5. Predict the product or products of each of the following reactions.

\[
\begin{align*}
\text{a) } & \text{CH}_3\text{CH}_2\text{C}≡\text{CH} \xrightarrow{\text{NaNH}_2, \text{light}} \\
\text{b) } & \text{(CH}_3\text{CH}_2)_3\text{CH} + \text{Br}_2 \xrightarrow{} \\
\text{c) } & \text{CH}_3 + \text{Cl}_2 \xrightarrow{\text{light}} \\
\text{d) } & \text{Br} + \text{Zn} + \text{HBr} \xrightarrow{} \\
\text{e) } & \text{CH}_3 + \text{H}_2 \xrightarrow{\text{Pd}}
\end{align*}
\]

6. Propose a synthesis of each of the following from the compound or compounds shown plus any needed inorganic reagents and solvents.

\[
\begin{align*}
\text{a) } & \text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow{} \text{H}_3\text{C} \xrightarrow{\text{H}_3\text{C}} \\
\text{b) } & \text{CH}_3\text{CH}_3 \xrightarrow{} \text{CH}_3 \xrightarrow{\text{CH}_3}
\end{align*}
\]
c) CH$_3$CH$_2$C≡CCH$_2$CH$_3$ from CH$_3$CH$_2$C≡CH and CH$_3$CH$_2$Br

d) bromocyclohexane from cyclohexene

e) CH$_3$CH$_2$CH$_2$CH$_3$ from CH$_3$C≡CH and CH$_3$Br
ANSWERS TO THE PROBLEMS:

1.1 lowest C, highest D

1.2 highest B, lowest C

2.1  a) staggered, gauche b) staggered, gauche c) eclipsed d) staggered e) staggered f) staggered, anti g) staggered, gauche h) eclipsed

2.2  a) chair b) boat c) twist boat d) half chair

3.  a) cis-3-methylcyclohexanol b) trans-1,2-dimethylcyclohexane c) 2-bromo-3-methylpentane d) 2-chloro-2-iodobutane e) 4-chloro-3,5-dimethyl-1-hexene f) 7,7-dimethylbicyclo[2.2.1]heptane

4.1 most stable C, least stable B

4.2 The most stable conformations:
   a) 4-methylcyclohexanol b) methylcyclohexane c) 1-fluoropropane d) propane

5. Predict the product or products of each of the following reactions.

   NaNH₂

   a) CH₃CH₂C≡CH  ---------->  CH₃CH₂C≡CNa

   b) (CH₃CH₂)₃CH + Br₂  ------->  (CH₃CH₂)₃CBr + HBr

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c) \[
\text{CH}_3 + \text{Cl}_2 \xrightarrow{\text{light}} \text{CH}_2\text{Cl} + \text{CH}_3 + \text{CH}_3 + \text{Cl}_2
\]

trans and cis

\[
\text{CH}_3 + \text{Cl} \xrightarrow{\text{trans and cis}} \text{CH}_2\text{Cl} + \text{Cl}
\]

\[
\text{HCl} + \text{HCl}
\]

d) \[
\text{Br} + \text{Zn} + \text{HBr} \xrightarrow{} \text{ZnBr}_2 + \text{H}_2
\]

e) \[
\text{CH}_3 + \text{H}_2 \xrightarrow{\text{Pd}} \text{CH}_3
\]

6. Synthesis:

a) \[
\text{H}_3\text{C} + \text{H}_3\text{C} + \text{H}_3\text{C} \xrightarrow{\text{from}} \text{H}_3\text{C} + \text{H}_3\text{C} + \text{H}_3\text{C}
\]

b) \[
\text{CH}_3 + \text{H}_2 \xrightarrow{\text{Ni}} \text{CH}_3 + \text{CH}_3
\]

c) \[
\text{CH}_3\text{CH}_2\text{C}=\text{CCH}_2\text{CH}_3 \xrightarrow{\text{from}} \text{CH}_3\text{CH}_2\text{C}=\text{CCH}_2\text{CH}_3 + \text{NaBr}
\]

There are two methods organic chemists use to give the answers to synthesis problems. One way is to give balanced equations, as shown here. This takes longer but gives more complete information, and is essential if you’re actually going to perform the synthesis.

\[
\text{CH}_3\text{CH}_2\text{C}=\text{CH} + \text{NaNH}_2 \xrightarrow{} \text{CH}_3\text{CH}_2\text{C}=\text{CNa} + \text{NH}_3
\]

then

\[
\text{CH}_3\text{CH}_2\text{C}=\text{CNa} + \text{CH}_3\text{CH}_2\text{Br} \xrightarrow{} \text{CH}_3\text{CH}_2\text{C}=\text{CCH}_2\text{CH}_3 + \text{NaBr}
\]

The second method is a sort of shorthand. It takes less time and space, especially for multistep synthesis, but gives less information.

\[
\text{NaNH}_2 \xrightarrow{} \text{CH}_3\text{CH}_2\text{C}=\text{CNa} \xrightarrow{} \text{CH}_3\text{CH}_2\text{C}=\text{CCH}_2\text{CH}_3
\]
d) bromocyclohexane from cyclohexene: This is a two-step synthesis.

\[
\text{H}_2 + \text{Pt} \quad \text{then} \quad \text{H}_2 + \text{Br}_2 \quad \text{light} \quad \text{Br} \quad \text{Br} + \text{HBr}
\]

shorthand version:

\[
\text{H}_2 \quad \text{Pt} \quad \text{Br}_2 \quad \text{light} \quad \text{Br}
\]

e) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \) from \( \text{CH}_3\equiv\text{CH} \) and \( \text{CH}_3\text{Br} \), a 3-step synthesis

\[
\text{CH}_3\equiv\text{CH} + \text{NaNH}_2 \quad \text{---->} \quad \text{CH}_3\equiv\text{CNa} + \text{NH}_3
\]

\[
\text{CH}_3\equiv\text{CNa} + \text{CH}_3\text{Br} \quad \text{---->} \quad \text{CH}_3\equiv\text{CCH}_3 + \text{NaBr}
\]

\[
\text{Pd} \quad \text{CH}_3\equiv\text{CCH}_3 + 2 \text{H}_2 \quad \text{---->} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]
1) Which of the following compounds has the highest boiling point?
A. \((\text{CH}_3)_4\text{C}\)  B. \((\text{CH}_3)_2\text{CHCH}_2\text{CH}_3\)  C. \((\text{CH}_3)_3\text{CCH}_2\text{CH}_3\)  D. \((\text{CH}_3)_2\text{CH(CH}_2)_2\text{CH}_3\)

2) Give the IUPAC name of:

3) Give the IUPAC name of:

4) Draw the most stable conformation of ethyl chloride.

5) Fill in the blanks. The most stable conformation of trans-1-tert-butyl-3-fluorocyclohexane has the tert-butyl group ________ and the fluorine atom ________ (axial, equatorial).

6) Predict the product or products of each of the following reactions.

   a) \(\text{light} + \text{Br}_2 \rightarrow\)

   b) \(\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3 + \text{H}_2 \rightarrow\)

   c) \((\text{CH}_3)_2\text{CBrCH}_2\text{CH}_3 + \text{Zn} + \text{HCl} \rightarrow\)

7) Propose a synthesis of cyclohexane from any other needed reagents.

8) Propose a synthesis of \(\text{CH}_2\text{CH}_2\text{CH}_3\) from \(\text{C}≡\text{CH}, \text{CH}_3\text{Br}\), and any other needed reagents.
1) Predict all of the products (organic and inorganic) of the following reactions.
   \[ \text{Ni} \]
   a) \( \text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3 + \text{H}_2 \rightarrow \)
   b) \( \text{CH}_3\text{CHBrCH}_2\text{CH}_3 + \text{Zn} + \text{HBr} \rightarrow \)
   c) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{Cl}_2 \rightarrow \)

2) It’s your first day on the job at the Gold Rush Chemical Co., and the boss tells you to make some \( 2,7\)-dimethyloctane. According to the boss, the stockroom has any chemical you might want. The boss also says that you must use up the stockroom’s excess inventory of isobutyl bromide. Show how you would perform this synthesis.

3) Draw the most stable conformation of each of these:
   a) \( \text{tert-butylcyclohexane} \)
   b) \( \text{cis-1-tert-butyl-4-methylcyclohexane} \)

4) Draw both the eclipsed and staggered conformations of 2-chloropropane in Newman projection looking down the C1-C2 bond. Indicate which is more stable, and state what kind of strain is present in the less stable conformation.

5) Give the IUPAC name of the compound shown. Also, give the name of the conformation in which the compound is drawn.

6) Which of the following has the highest boiling point?
   A. \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)
   B. \( \text{CH}_3(\text{CH}_2)_3\text{CH}_3 \)
   C. \( (\text{CH}_3)_2\text{CHCH}_2\text{CH}_3 \)
   D. \( (\text{CH}_3)_2\text{CHCH}_3 \)