## Chem 3719 Klein Chapter Practice Problems



Dr. Peter Norris, 2018

## Klein Chapter 1 Problems : Review of General Chemistry

1. Draw viable structures for molecules with the following molecular formulae. Remember that each atom has a "standard" valence when forming neutral molecules, for example halogens and H are monovalent, O is divalent, N is trivalent, and C is tetravalent. Each of the molecules has only single bonds between atoms.
a. $\mathrm{CH}_{3} \mathrm{Cl}$
b. $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{~F}$
c. $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}$
d. $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{Br}$
e. $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{Cl}_{2}$
f. $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{~F}_{3}$
g. $\mathrm{C}_{3} \mathrm{Br}_{8}$
h. $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{BrCl}$
2. Draw Lewis formula structures for molecules with the following molecular formulae. Show all single bonds as single lines and any lone pairs where appropriate.
a. $\mathrm{CH}_{3} \mathrm{NH}_{2}$
b. $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$
c. $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{Cl}$
d. $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}$
3. Draw structures for the following molecules that include any formal charges and lone pairs where needed. Each of the molecules has either single bonds or double bonds between atoms and there may be ionic bonds involved in some of the structures.
a. $\mathrm{CH}_{3} \mathrm{NO}_{2}$
b. $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{ONa}$
c. $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NHLi}$
d. $\mathrm{CH}_{3} \mathrm{CHN}_{2}$
4. Indicate the hybridization of each of the $\mathrm{C}, \mathrm{N}$, and O atoms in the following molecules.
a.

b.

c.

5. Draw a structural formula for each of the following molecules and then, using the $\delta+/ \delta$ - convention, label any dipoles that are present each molecule.
a. $\mathrm{CH}_{3} \mathrm{OH}$
b. $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$
c. $\mathrm{CH}_{3} \mathrm{CHCl}_{2}$
d. $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}$

## Klein Chapter 1 Problems: Review of Gen Chem - Answers

1. "Draw viable structures for molecules with the following molecular formulae. Remember that each atom has a "standard" valence when forming neutral molecules, for example halogens and $H$ are monovalent, $O$ is divalent, $N$ is trivalent, and $C$ is tetravalent. Each of the molecules has only single bonds between atoms."
a. $\mathrm{CH}_{3} \mathrm{Cl}$
b. $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{~F}$
c. $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}$
d. $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{Br}$






e. $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{Cl}_{2}$
f. $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{~F}_{3}$
g. $\mathrm{C}_{3} \mathrm{Br}_{8}$
h. $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{BrCl}$




or



2. "Draw Lewis formula structures for molecules with the following molecular formulae. Show all single bonds as single lines and any lone pairs where appropriate."
a. $\mathrm{CH}_{3} \mathrm{NH}_{2}$
b. $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}$
c. $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{Cl}$
d. $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}$





3. "Draw structures for the following molecules that include any formal charges and lone pairs where needed. Each of the molecules has either single bonds or double bonds between atoms and there may be ionic bonds involved in some of the structures."
a. $\mathrm{CH}_{3} \mathrm{NO}_{2}$
b. $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{ONa}$
c. $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NHLi}$
d. $\mathrm{CH}_{3} \mathrm{CHN}_{2}$




4. "Indicate the hybridization of each of the $C, N$, and $O$ atoms in the following molecules."
a.


$$
\begin{aligned}
& \text { Red }=s p^{3} \\
& \text { Blue }=s p^{2}
\end{aligned}
$$

b.

Red $=s p^{3}$
Blue $=$ sp $^{2}$
c.


$$
\begin{aligned}
& \text { Red }=s p^{3} \\
& \text { Blue }=s p^{2}
\end{aligned}
$$

5. "Draw a structural formula for each of the following molecules and then, using the $\delta+/ \delta$ - convention, label any dipoles that are present each molecule."
a. $\mathrm{CH}_{3} \mathrm{OH}$
b. $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}$
c. $\mathrm{CH}_{3} \mathrm{CHCl}_{2}$
d. $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{NH}_{2}$





## Klein Chapter 2 Problems : Molecular Representations

1. Turn each of the following "bond-line" structures into more expanded representations in which each of the C, O , and H atoms are shown.
a.

b.

c.

2. From Table 2.1 in the Klein text, identify all of the functional groups present in the following molecules.
a.

b.

c.

d.

3. Add any missing lone pairs to the following line structures.
a.

b.

c.

d.

4. Draw a second resonance structure for each of the following species.
a.

b.

c.

d.


## Klein Chapter 2 Problems : Molecular Representations - Answers

1. Turn each of the following "bond-line" structures into more expanded representations in which each of the $C$, $O$, and $H$ atoms are shown.
a.

b.

c.

2. From Table 2.1 in the Klein text, identify all of the functional groups present in the following molecules.
a.

b.

C.

d.

3. Add any missing lone pairs to the following line structures.
a.

b.

c.

d.

4. Draw a second resonance structure for each of the following species.
a.

b.

c.




.
d.

$\downarrow$



## Klein Chapter 3 : Acids and Bases Worksheet

## Concepts

The interaction of a protic acid with a base is the first actual chemical reaction that we study in 3719. We use it to introduce some of the fundamental concepts of mechanism, i.e. how to describe the bond-breaking and bondforming events that occur as a starting material (left-hand side of the equation) is converted to product (right-hand side of the equation). Since we use acids and bases on many occasions as reagents throughout 3719 and 3720 , it is important that you know what constitutes an acid or a base and what happens when the two interact.

Definitions: Acids donate protons (Bronsted definition) or accept electrons (Lewis definition) Bases accept protons (Bronsted definition) or donate electrons (Lewis definition)

## General Chem:



In this case HCl is the acid (proton donor), water is the base (electron donor, proton acceptor) and the green arrows show the proton being transferred to generate the conjugate acid $\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)$and the conjugate base $\left(\mathrm{Cl}^{-}\right)$. The strength of the acid in water is measured by the dissociation constant $\left(K_{\mathrm{a}}\right)$; the larger the $K_{\mathrm{a}}$, the stronger the acid. In other words, the stronger the acid, the more the above reaction goes to the right. Since the values of $K_{\mathrm{a}}$ can range from very large to very small, we use the $\mathrm{p} K_{\mathrm{a}}$ scale to give manageable numbers ( $\mathrm{p} K_{\mathrm{a}}=-\log _{10} K_{\mathrm{a}}$ ). The $\mathrm{p} K_{\mathrm{a}}$ range for acids used in Organic Chemistry are in the range -10 (very strong acid) to +50 (very weak acid).
$\mathrm{p} K_{\mathrm{a}}$ values from class (Table 3.1 in Klein text):


For the most part in 3719 and 3720 we will not be using water as the base; rather we will use some organic or inorganic base which has been chosen to deprotonate the acid to a particular extent. Since we know something about relative acid strength from $\mathrm{p} K_{\mathrm{a}}$ values, we also know a lot about the relative (conjugate) base strengths:


The task in Organic Chemistry is to decide what happens in terms of the equilibrium position when a particular acid is mixed with a particular base. If you understand this, then you can decide which acid or base to use in particular circumstances. The problems on the next page will give you practice with these ideas.

1. For each of the following mixtures, complete the equation, then identify the acid and base on the left and the conjugate acid and conjugate base on the right. Comparing acid and base strengths (from $\mathrm{p} K_{\mathrm{a}}$ values) decide whether the reaction is a) likely to happen at all, b) whether equilibrium will be established, and c) if equilibrium is established which side is favoured?



2. The equilibrium idea means that if the reaction is reversible there will be four species in solution at one time, the acid, the base, the conjugate acid, and the conjugate base. Sometimes this is what is required, but at other times we need to choose bases that will completely deprotonate every molecule of acid, i.e. send the reaction completely to the right. These bases will include $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Li}, \mathrm{NaNH}_{2}$, and $\mathrm{LiN}(i-\mathrm{Pr})_{2}$. Weaker bases will include $\mathrm{NaOH}, \mathrm{NaOCH}_{3}, \mathrm{KOtBu}$, and $\mathrm{NaOCH}_{2} \mathrm{CH}_{3}$. For each of these bases, give the products formed when they react with $\mathrm{H}_{2} \mathrm{O}$, then use $\mathrm{p} K_{\mathrm{a}}$ values to get an idea of the relative base strengths of these compounds.
3. In OChem 2 we will study reactions based on the deprotonation of ketones such as acetone, $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{O}$, which has a pKa of 19. Given the bases $\mathrm{LiN}(i-\operatorname{Pr})_{2}$ and $\mathrm{NaOCH}_{3}$, decide which one will be useful to completely deprotonate acetone, and which one will be useful for setting up an equilibrium. Explain your choices.
4. Give the products from the following acid-base reactions and identify the acid and base on the left side, as well as the conjugate acid and conjugate base on the right side of the equation.

$+\mathrm{NaOH}$

5. For each of the reactions in question 1 and question 4 , which will have an equilibrium constant $(K)$ greater than 1, close to 1, or less than 1 ? Explain your answers.
6. Draw the structure of the conjugate base that will be formed when 1 mole of $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}$ reacts with 1 mole of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Li}$.
7. The careful choice of an appropriate solvent will play a major role in whether organic reactions will be successful. For example, reagents such as $\mathrm{CH}_{3} \mathrm{Li}$ and $\mathrm{NaNH}_{2}$ will be incompatible with solvents such as water and ethanol. Why is this?

## Klein Chapter 3 : Acids and Bases Worksheet - Answers

1. "For each of the following mixtures, complete the equation, then identify the acid and base on the left and the conjugate acid and conjugate base on the right. Comparing acid and base strengths (from $p K_{a}$ values) decide whether the reaction is a) likely to happen at all, b) whether equilibrium will be established, and c) if equilibrium is established which side is favoured?"

For this type of question you have to know the approximate $p K_{a}$ values discussed in class and have an idea of what they mean in terms of relative acid strength and also relative base strength.
a.


Here we have two acids of similar strengths (1-butanol on the left and $\mathrm{H}_{2} \mathrm{O}$ on the right) and therefore two bases of similar strengths. The forward reaction is favoured to about the same extent as the reverse reaction. Therefore a) the reaction left to right will happen, b) equilibrium will be established, and c) the equilibrium lies approximately in the middle (similar acid strengths, similar base strengths on both sides of the equation).
b.


In this example we have acids of very different strength, the carboxylic acid on the left ( $p K_{a} \sim 5$ ) is very much stronger than the ammonia on the right ( $p K_{a} \sim 38$ ) therefore the left to right reaction is very much favoured. The reverse reaction however is unlikely to occur since the base on the right is far too weak to deprotonate such a weak acid as $\mathrm{NH}_{3}$. Therefore a) the reaction left to right will happen, b) equilibrium will not be established, and c) the right-hand side is completely favoured.
c.


Here we have a situation in which the reaction will go to the right. The $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}$ is such a weak acid ( $p K a \sim 50$ ) that it is impossible to deprotonate. A 12 unit $p K_{a}$ difference between acids means that this is a completely irreversible reaction. Therefore a) the reaction from left to right will occur to give the products shown above, b) there will be no equilibrium established, and c) the right-hand side would be completely favoured in this case.
2. "The equilibrium idea means that if the reaction is reversible there will be four species in solution at one time, the acid, the base, the conjugate acid, and the conjugate base. Sometimes this is what is required, but at other times we need to choose bases that will completely deprotonate every molecule of acid, i.e. send the reaction completely to the right. These bases will include $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Li}, \mathrm{NaNH}_{2}$, and $\mathrm{LiN}(\mathrm{i}-\mathrm{Pr})_{2}$. Weaker bases will include $\mathrm{NaOH}, \mathrm{NaOCH}_{3}, \mathrm{KOtBu}$, and $\mathrm{NaOCH}_{2} \mathrm{CH}_{3}$. For each of these bases, give the products formed when they react with $\mathrm{H}_{2} \mathrm{O}$, then use $p K_{a}$ values to get an idea of the relative base strengths of these compounds."

| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Li}$ | $+\mathrm{H}_{2} \mathrm{O}$ | $\longrightarrow$ | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}$ |  | + | LiOH | completely to the right |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| very strong base | $\begin{gathered} \text { acid } \\ \mathrm{p} K_{\mathrm{a}} \sim 16 \end{gathered}$ |  | $\begin{gathered} \text { C.A. } \\ \mathrm{p} K_{\mathrm{a}} \sim 50 \end{gathered}$ |  |  | C.B. |  |
| $\mathrm{NaNH}_{2}$ | $+\mathrm{H}_{2} \mathrm{O}$ | $\longrightarrow$ | $\mathrm{NH}_{3}$ | + |  | NaOH | completely to the right |
| very strong base | $\begin{gathered} \text { acid } \\ \mathrm{p} K_{\mathrm{a}} \sim 16 \end{gathered}$ |  | $\begin{gathered} \text { C.A. } \\ \mathrm{p} K_{\mathrm{a}} \sim 38 \end{gathered}$ |  |  | $C . B$. |  |
| $\mathrm{LiN}(i-\mathrm{Pr})_{2}$ | $+\mathrm{H}_{2} \mathrm{O}$ | $\longrightarrow$ | $\mathrm{HN}(i-\mathrm{Pr})_{2}$ | + |  | LiOH | completely to the right |
| very strong base | $\begin{gathered} \text { acid } \\ \mathrm{p} K_{\mathrm{a}} \sim 16 \end{gathered}$ |  | $\begin{gathered} \text { C.A. } \\ \mathrm{p} K_{\mathrm{a}} \sim 38 \end{gathered}$ |  |  | C.B. |  |
| NaOH | $+\mathrm{H}_{2} \mathrm{O}$ |  | $\mathrm{H}_{2} \mathrm{O}$ | + |  | NaOH | equilibrium, roughly in the middle |
| strong base | $\begin{gathered} \text { acid } \\ \mathrm{p} K_{\mathrm{a}} \sim 16 \end{gathered}$ |  | $\begin{gathered} \text { C.A. } \\ \mathrm{p} K_{\mathrm{a}} \sim 16 \end{gathered}$ |  |  | C.B. |  |
| $\mathrm{NaOCH}_{3}$ | $+\mathrm{H}_{2} \mathrm{O}$ | $\xrightarrow{ }$ | $\mathrm{HOCH}_{3}$ | + |  | NaOH | equilibrium, roughly in the middle |
| strong base | $\begin{gathered} \text { acid } \\ \mathrm{p} K_{\mathrm{a}} \sim 16 \end{gathered}$ |  | $\begin{gathered} \text { C.A. } \\ \mathrm{p} K_{\mathrm{a}} \sim 16 \end{gathered}$ |  |  | C.B. |  |
| KOt-Bu | $+\mathrm{H}_{2} \mathrm{O}$ | $\rightleftharpoons$ | $\mathrm{HOt}-\mathrm{Bu}$ | + |  | NaOH | equilibrium, slightly to the right |
| strong base | $\begin{gathered} \mathrm{acid} \\ \mathrm{p} K_{\mathrm{a}} \sim 16 \end{gathered}$ |  | $\begin{gathered} \text { C.A. } \\ \mathrm{p} K_{\mathrm{a}} \sim 18 \end{gathered}$ |  |  | C.B. |  |
| $\mathrm{NaOCH}_{2} \mathrm{CH}_{3}$ | $+\mathrm{H}_{2} \mathrm{O}$ | $\cdots$ | $\mathrm{HOCH}_{2} \mathrm{CH}_{3}$ | + |  | NaOH | equilibrium, roughly in the middle |
| strong base | $\begin{gathered} \mathrm{acid} \\ \mathrm{p} K_{\mathrm{a}} \sim 16 \end{gathered}$ |  | $\begin{gathered} \text { C.A. } \\ \mathrm{p} K_{\mathrm{a}} \sim 16 \end{gathered}$ |  |  | C.B. |  |

3. 'In OChem 2 we will study reactions based on the deprotonation of ketones such as acetone, $\left(\mathrm{CH}_{3}\right)_{2} \mathrm{C}=\mathrm{O}$, which has a $p K_{a}$ of 19. Given the bases $\mathrm{LiN}(i-\mathrm{Pr})_{2}$ and $\mathrm{NaOCH}_{3}$, decide which will be useful to completely deprotonate acetone, and which will be useful for setting up an equilibrium. Explain your choices."

In this question you have to set up the equation and then decide whether the base employed is indeed strong enough to completely deprotonate the acid, i.e. send the reaction completely to the right.


Here (above) we have a very powerful base (very weak conjugate acid) and this reaction will proceed all the way over to the right, i.e. all of the acid molecules will be deprotonated.


In this case (above) we are using a weaker base and even though the left to right reaction is possible, the right to left is also now possible. Equilibrium will be established here which will favour the side that contains the weaker conjugate base, in this case the left hand side. The main consequence of using this type of base here is that we now have some of all four species in solution at once.
4. "Give the products from the following acid-base reactions and identify the acid and base on the left side, as well as the conjugate acid and conjugate base on the right side of the equation."

5. "For each of the reactions in question 1 and question 4, which will have an equilibrium constant (K) greater than 1, close to 1, or less than 1? Explain your answers."

1a) $K \sim 1$ since acids and bases on each side are of similar strengths;
1b) No equilibrium since the acid and very strong base on the left will send the reaction completely to the right, $K>1$;

1c) No equilibrium since the acid and very strong base on the left will send the reaction completely to the right, $K>1$;

4a) $K>1$ since the stronger acid and base on the left will favour the reaction to the right;
4b) No equilibrium since the reaction will go completely to the right, $K>1$;
4c) No equilibrium since the reaction will go completely to the right, $K>1$.
6. "Draw the structure of the conjugate base that will be formed when 1 mole of $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}$ reacts with 1 mole of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Li}$."


The more acidic carboxylic acid proton $(p K a \sim 5)$ will be removed before the less acidic alcohol proton ( $p K a \sim 16$ )
7. "The careful choice of an appropriate solvent will play a major role in whether organic reactions will be successful. For example, reagents such as $\mathrm{CH}_{3} \mathrm{Li}$ and $\mathrm{NaNH}_{2}$ will be incompatible with solvents such as water and ethanol. Why is this?"

These reagents are very powerful bases so they will be rapidly protonated by the solvents in question and destroyed:



## Klein Chapter 4 Problems: Alkanes \& Cycloalkanes

1. Provide accurate names for each of the following alkanes. You may use either IUPAC or trivial names for any substituents within these molecules.
a.

b.

c.

d.

2. Draw Newman projections for each of the following situations.
a. The highest energy conformation of 3-methylnonane along the C-4 - C-5 bond axis
b. The lowest energy conformation of trans-1-isopropyl-2-propylcyclohexane along the $\mathrm{C}-1-\mathrm{C}-2$ axis
c. The lowest energy conformation of 7-ethyl-2,3,8-trimethyldecane along the C-5-C-6 bond axis
3. Draw appropriate diagrams for each of the following situations and explain your choices.
a. The most stable chair conformation of 1,3-di-tert-butylcylcohexane
b. The less stable chair conformation of trans-1-isopropyl-4-methylcyclohexane
c. The less stable isomer of 1,2-di-isopropylcyclobutane
4. Indicate which species/conformation is more stable in each of the following situations and give a few words of explanation for your choices.
a.

or

b.

or

c.

or

d.


## Klein Chapter 4 Problems: Alkanes \& Cycloalkanes - Answers

1. Provide accurate names for each of the following alkanes. You may use either IUPAC or trivial names for any substituents within these molecules.


4,5-diethyl-3,7,7-trimethylundecane
c.


3-(4-ethyl-3-methylheptyl)-1,1dimethylcyclopentane
b.

cis-(1-sec-butyl)-3-(nonan-2-yl)cyclohexane
d.


1,5-diethyl-3,3-dimethyl-4-pentyl-
bicyclo[4 1 0]heptane bicyclo[4.1.0]heptane
2. Draw Newman projections for each of the following situations.
a. The highest energy conformation of 3-methylnonane along the C-4-C-5 bond axis

b. The lowest energy conformation of trans-1-isopropyl-2-propylcyclohexane along the C-1-C-2 axis

c. The lowest energy conformation of 7-ethyl-2,3,8-trimethyldecane along the C-5-C-6 bond axis


7-ethyl-2,3,8-trimethyldecane

substituents anti
3. Draw appropriate diagrams for each of the following situations and explain your choices.
a. The most stable chair conformation of 1,3-di-tert-butylcylcohexane

both large groups are equatorial, thereby avoiding any bad 1,3-diaxial interactions that would occur in the other ring-flipped chair conformation
b. The less stable chair conformation of trans-1-isopropyl-4-methylcyclohexane

c. The less stable isomer of 1,2-di-isopropylcyclobutane

both large groups are axial, thereby causing the destabilizing 1,3-diaxial interactions that would not be present in the ring-flipped chair conformation
4. Indicate which species/conformation is more stable in each of the following situations and give a few words of explanation for your choices.
a.


Having the two large groups on opposite sides of the ring will avoid destabilizing interactions
c.


The right-hand conformation has only one $\mathrm{CH}_{3}-\mathrm{CH}_{3}$ gauche interaction as opposed to two on the left
b.


Both of the large substituents will be able to be in axial positions thereby avoiding 1,3-diaxial problems
d.


Both of the large substituents will be able to be as far away as possible from each other when in the anti orientation

## Klein Chapter 5 Problems: Stereoisomerism

1. Identify any chiral carbons in the following molecules and, using the Cahn-Ingold-Prelog rules, label their configuration as either $R$ or $S$.
a.

b.

c.

d.

2. Within each of the following pairs of molecules, identify the relationship between them as being either enantiomers, diastereomers, or identical.
a.
 and

b.

and

c.

3. Convert each of the following structures as directed.
a.

b.

c.

4. Identify all the chiral carbon atoms in cholesterol (below) and label them as either the $R$ or $S$ configuration.


## Klein Chapter 5 Problems : Stereoisomerism - Answers

1. Identify any chiral carbons in the following molecules and, using the Cahn-Ingold-Prelog rules, label their configuration as either $R$ or $S$.
a.

b.

c.

d.

2. Within each of the following pairs of molecules, identify the relationship between them as being either enantiomers, diastereomers, or identical.
a.

b.

c.

3. Convert each of the following structures as directed.
a.

b.

c.




4. Identify all the chiral carbon atoms in cholesterol (below) and label them as either the $R$ or $S$ configuration.

$1=(S)$
$2=(R)$
$3=(S)$
$4=(S)$
$5=(S)$
$6=(R)$
$7=(R)$
$8=(R)$

## Klein Chapter 6 Problems : Reactivity \& Mechanisms

1. In each of the following situations, indicate whether the reactions are favoured or disfavoured in terms of enthalpic and entropic factors in the Gibbs free energy equation (Table 6.1 might help here).
a.

b.

c.

d.

2. Draw a mechanistic interpretation (using curved arrow(s) to show bonds forming and breaking), and then an approximate transition state (including partial electron-densities) for each of the following events.
a.

b.

c.

d.



3. Draw curved arrows to describe each of the steps in the following reaction mechanism, and then label those steps as being one of the four types discussed in class, i.e. nucleophilic attack, loss of a leaving group, proton transfer, or rearrangement. Then draw a transition state for each step within the mechanism, and finally indicate which step is rate-determining and the molecularity (unimolecular, bimolecular, etc.) of that step.



## Klein Chapter 6 Problems : Reactivity \& Mechanisms - Answers

1. In each of the following situations, indicate whether the reactions are favoured or disfavoured in terms of enthalpic and entropic factors in the Gibbs free energy equation (Table 6.1 might help here).
a.

Enthalpically favoured - swapping weak $\pi$ and $\mathrm{Br}-\mathrm{Br}$ bonds for new $\sigma$ bonds Entropically disfavoured - two molecules becoming one so less disorder
b.

Enthalpically disfavoured - swapping strong $\sigma$ bonds for weaker $\pi$ bond
Entropically favoured - one molecule is becoming two so more disorder
c.

Enthalpically favoured - swapping weak $\pi$ and $H-H$ bonds for new $\sigma$ bonds
Entropically disfavoured - two molecules becoming one so less disorder
d.

Enthalpically favoured - swapping weak $\mathrm{Br}-\mathrm{Br}$ bond for stronger $\sigma$ bonds Entropically neutral - two molecules are converting to two so little change
2. Draw a mechanistic interpretation (using curved arrow(s) to show bonds forming and breaking), and then an approximate transition state (including partial electron densities) for each of the following events.
a.

b.

: Br :

c.

d.




3. Draw curved arrows to describe each of the steps in the following reaction mechanism, and then label those steps as being one of the four types discussed in class, i.e. nucleophilic attack, loss of a leaving group, proton transfer, or rearrangement. Then draw a transition state for each step within the mechanism, and finally indicate which step is rate-determining and the molecularity (unimolecular, bimolecular, etc.) of that step.


## Transition states:

A.

$B$.

C.

D.


## Klein Chapter 7 Problems: Nucleophilic Substitution \& Elimination

1. Provide each of the following alkyl halides with acceptable names. You may use either the functional class or substitutive nomenclature as appropriate. Be sure to assign the configurations of any chiral centers.
a.

b.

c.

d.

2. Draw detailed mechanisms for the following reactions that use "curved arrows" to show the breaking and forming of bonds and identify the mechanism that is operating.
a.

b.

c.

d.

3. Provide the products expected to be formed under each of the following sets of conditions.
a.

b.

c.

d.

4. Provide each of the following alkene-containing molecules with acceptable names. Be careful to assign the configurations of any chiral centers ( $R$ or $S$ ) and double bonds ( $E$ or $Z$ ).
a.

b.

C.

d.

5. Draw detailed mechanisms for the following reactions that use "curved arrows" to show the breaking and forming of bonds and identify the mechanism that is operating.
a.

b.

c.


d.

6. Provide the products expected to be formed under each of the following sets of conditions.
a.

b.

c.

d.


## Klein Chapter 7 Problems : Nucleophilic Substitutions \& Eliminations

1. Provide each of the following alkyl halides with acceptable names. You may use either the functional class or substitutive nomenclature as appropriate. Be sure to assign the configurations of any chiral centers.
a.

(3S,7S,8R)-7-chloro-3-fluoro-4,4,8-
trimethyldecane
b.

7-ethyl-6,6-difluoro-2methylundecane
c.

d.

(1S,3R,5R)-1-bromo-3-(( $R$ )-sec-butyl)-5-
butylcyclohexane
(1S,2R,4R)-1-chloro-4-iodo-2-(2-methyl-pentan-2-yl)cyclopentane
2. Draw detailed mechanisms for the following reactions that use "curved arrows" to show the breaking and forming of bonds and identify the mechanism that is operating.
a.

c.

$S_{N} 2$ - backside attack on simple methyl electrophile
b.


$$
\begin{aligned}
& S_{N} 2 \text { - inversion of stereochemistry } \\
& \text { during concerted substitution }
\end{aligned}
$$

d.


3. Provide the products expected to be formed under each of the following sets of conditions.
a.



(+/-) racemic mixture
b.

c.


d.

4. Provide each of the following alkene-containing molecules with acceptable names. Be careful to assign the configurations of any chiral centers $(R$ or $S)$ and double bonds ( $E$ or $Z$ ).
a.

( $6 S, 7 S, 8 R, E$ )-1-bromo-6-chloro-3,7-diethyl-8-methyldec-2-ene
b.

(1R,3S,5R)-1-((E)-but-1-en-1-yl)-3-ethyl-5-fluorocyclohexane
c.

(4R,5R,Z)-5-ethyl-3-iodo-4-propyloct-2-ene
d.

(1R,2S,3S,4R)-1-bromo-3-butyl-4-ethyl
-2-(prop-1-en-2-yl)cyclopentane
5. Draw detailed mechanisms for the following reactions that use "curved arrows" to show the breaking and forming of bonds and identify the mechanism that is operating.
a.


E2 with small base favours the trisubstituted (Zaitsev) product
b.




E1 with acid favours
the trisubstituted (Zaitsev) product


$\stackrel{ }{-\mathrm{H}_{2} \mathrm{O}}$

c.


E2 with large base favours the less-substituted (Hofmann) product
d.


E1 with migration to the tetrasubstituted
(Zaitsev) product


6. Provide the products expected to be formed under each of the following sets of conditions.
a.


b.


c.


d.


## Klein Chapter 8 Problems : Addition Reactions

1. Draw detailed mechanisms for the following reactions that use "curved arrows" to show the breaking and forming of bonds and identify the mechanism that is operating.
a.

b.

c.



d.

2. Provide the major and minor products expected to be formed under each of the following sets of conditions.
a.

b.

c.

d.

3. Provide the reagents and conditions required to facilitate the following synthetic conversions.
a.


b.

c.

d.


## Klein Chapter 8 Problems: Addition Reactions - Answers

1. Draw detailed mechanisms for the following reactions that use "curved arrows" to show the breaking and forming of bonds and identify the mechanism that is operating.
a.

b.

c.



syn add'n
Hydroboration-oxidation via concerted addition followed by concerted rearrangement




migration with retention


Electrophilic anti addition of $\mathrm{Br}_{2}$ via the bromonium ion which accounts for formation of only trans products
2. Provide the major and minor products expected to be formed under each of the following sets of conditions.
a.

1.

b.

achiral
c.

d.

3. Provide the reagents and conditions required to facilitate the following synthetic conversions.
a.

racemic
c.

b.

d.


## Klein Chapter 9 Problems: Alkynes

1. Draw detailed mechanisms for the following reactions that use "curved arrows" to show the breaking and forming of bonds and identify the mechanism that is operating.
a.

b.

c.



d.

 $\mathrm{H}_{2} \mathrm{O}_{2}$
2. Provide the major and minor products expected to be formed under each of the following sets of conditions.
a.

b.

c.

d.

3. Provide complete names for the following alkyne-containing molecules, including any $R / S$ or $E / Z$ descriptors.
a.

c.

b.

d.


## Klein Chapter 09 Problems: Alkynes - Answers

1. Draw detailed mechanisms for the following reactions that use "curved arrows" to show the breaking and forming of bonds and identify the mechanism that is operating.
a.

b.

c.



||trap cation



2. Provide the major and minor products expected to be formed under each of the following sets of conditions.
a.

b.

C.

d.

3. Provide complete names for the following alkyne-containing molecules, including any $R / S$ or $E / Z$ descriptors.
a.

(2R,7S)-2-bromo-7-chlorooct-4-yne
c.

(2R,3S)-3-ethynyl-2-isopropyl-1,1dimethylcyclopentane
b.

$(3 S, 4 R)$-4-ethynyl-3-fluorocyclohex-1-ene
d.

(S,E)-4-iodo-3,3-dimethylhept-5-en-1-yne

## Klein Chapter 10 Problems : Radical Reactions

1. Draw detailed mechanisms for the following reactions that use "curved arrows" to show the breaking and forming of bonds and any important resonance structures. Then identify the mechanism that is operating.
a.

b.

c.

d.

2. Provide the major products expected to be formed under each of the following sets of conditions.
a.

b.

c.

d.

3. Draw all of the possible resonance structures for the following radicals.
a.

b.

c.

d.


## Klein Chapter 10 Problems : Radical Reactions - Answers

1. Draw detailed mechanisms for the following reactions that use "curved arrows" to show the breaking and forming of bonds and any important resonance structures. Then identify the mechanism that is operating.
a.

b.


c.

d.


2. Provide the major products expected to be formed under each of the following sets of conditions.
a.

anti-Markovnikoff addition
b.


Cl radical is unselective so significant amounts of each product will be formed

c.

d.


racemic
mixture
3. Draw all of the possible resonance structures for the following radicals.
a.


b.

c.

d.


## Klein Chapter 11 Problems: Synthesis

1. Provide the major products formed from each step in the following reaction sequences. Be careful to include any changes in stereochemistry that may occur.
a.


b.

c.


d.


2. Give a sequence of reagents that would affect the following synthetic conversions. Each problem requires at least two synthetic steps.
a.

b.

C.

d.

racemic
3. In each of the following problems, draw a starting material that could be used as a suitable precursor in the conversion to the given product.
a.

c.


racemic
b.

d.


## Klein Chapter 11 Problems : Synthesis - Answers

1. Provide the major products formed from each step in the following reaction sequences. Be careful to include any changes in stereochemistry that may occur.
a.

$\xrightarrow[\substack{\text { 3. } \mathrm{HBr}, \mathrm{H}_{2} \mathrm{O}_{2}}]{\substack{\text { 1. } \mathrm{NBS}, \text { heat } \\ \text { 2. } \mathrm{NaOCH}_{3}, \mathrm{THF}}}$
2. 


2.

3.

4.

racemic
b.

1.

2.

3.

2.

3.

c.

d.


1.

2.

3.

4.

2. Give a sequence of reagents that would affect the following synthetic conversions. Each problem requires at least two synthetic steps.
a.


b.

c.

d.


Bromination/E2/Hydroboration-Oxidation
3. In each of the following problems, draw a starting material that could be used as a suitable precursor in the conversion to the given product.
a.

epoxidation \& acid-catalyzed opening
c.


Radical halogenation \& E2
b.

alcohol activation \& $S_{N} 2$ inversion
d.

$S_{N} 1$ \& Hofmann E2

