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**Academic Honesty Policy.** Academic honesty is strictly enforced on quizzes, exams, and other aspects of this course. Academic dishonesty will result in a failing grade in the class and a letter in the student's file. Activities constituting academic dishonesty include:

**Cheating**
- Copying from others during an examination.
- Communicating exam answers with other students during an examination.
- Offering another person's work as one's own.
- Taking an examination for another student or having someone take an examination for oneself.
- Tampering with an examination after it has been corrected, then returning it for more credit.
- Using unauthorized materials, prepared answers, written notes, or concealed information during an examination.

**Dishonest Conduct**
- Stealing or attempting to steal an examination or answer key from the instructor.
- Allowing another student to copy off of one's own work during a test.

**Collusion**
- Any student who knowingly or intentionally helps another student perform any of the above acts is subject to discipline for academic dishonesty.

I understand and will abide by this academic honesty policy: ____________________________ (signature)

Seat: _______
1. Fill in the blanks from among the choices provided. If you believe that more than one choice is valid, choose the best answer. (30 points)

a. An acid with a pKₐ of 4.76: _____________
   choices: HCl, NH₃, CF₃COOH, CH₃CH₂OH, CH₃COOH, H₂O

b. An ionic compound: _____________
   choices: BF₃, Et₂O, CCl₄, CH₄, CH₂=CH₂, NaOCH₃

c. A Lewis acid: _____________
   choices: BF₃, Et₂O, CCl₄, CH₄, CH₂=CH₂, NaOCH₃

d. A typical value of a bond dissociation energy: _____________
   choices: 1 kcal/mol, 3 kcal/mol, 10 kcal/mol, 30 kcal/mol, 100 kcal/mol, 300 kcal/mol

e. A typical energy barrier to rotation about a carbon-carbon single bond: _____________
   choices: 1 kcal/mol, 3 kcal/mol, 10 kcal/mol, 30 kcal/mol, 100 kcal/mol, 300 kcal/mol

f. A chiral molecule: _____________________________
   choices: 3-bromopentane, cis-1,3-dichlorocyclopentane, 2-chlorohexane, 2,3-dimethylbutane, methylycyclohexane, 1-propanol

g. A typical carbon-carbon bond length: _____________
   choices: 0.5 Å, 1.5 Å, 3 Å, 5 Å, 10 Å, 15 Å (Note: Å = angstrom)

h. A good reactant in an SN1 reaction: _____________________________
   choices: iodobenzene, 1-chloro-1-methylycyclohexane, 2-fluorobutane, CH₂=CHBr, 1-bromohexane, chlorocyclobutane

i. A good reactant in an SN2 reaction: _____________________________
   choices: iodobenzene, 1-chloro-1-methylycyclohexane, 2-fluorobutane, CH₂=CHBr, 1-bromohexane, chlorocyclobutane

j. A good reactant in an E1 reaction: _____________________________
   choices: iodobenzene, 1-chloro-1-methylycyclohexane, 2-fluorobutane, CH₂=CHBr, 1-bromohexane, chlorocyclobutane
2. Write the missing reactants, reagents, and products in the boxes. If NO REACTION OCCURS, write N.R. (18 points)
3. Diethyl malonate can be prepared from chloroacetic acid in the four-step synthesis shown below. (23 points)

a. Complete the synthesis by filling in the missing reagents in step 1, step 2, and step 4.

\[
\begin{align*}
\text{chloroacetic acid} & \quad \text{step 1:} \quad \text{Na}^+ \quad \text{Na}^+ \quad \text{H}_2\text{O} \\
\text{Na}^+ \quad \text{Na}^+ \quad \text{H}_2\text{O} & \quad \text{step 2:} \quad \text{Na}^+ \quad \text{Na}^+ \\
\text{Na}^+ \quad \text{Na}^+ & \quad \text{DMSO} \\
\text{diethyl malonate} & \\
\end{align*}
\]

b. Diethyl malonate is relatively acidic. Draw the three most important resonance structure for its conjugate base. Make sure to show all charges and lone pairs of electrons.

\[
\text{diethyl malonate} \quad \overset{\text{NaOEt}}{\longrightarrow} \quad \overset{\text{NaOEt}}{\longrightarrow} \quad \overset{\text{NaOEt}}{\longrightarrow}
\]

c. The conjugate base of diethyl malonate is a good nucleophile. Use the template below to write a curved-arrow mechanism for its generation (step 1) and subsequent reaction with benzyl bromide (step 2). Make sure to show all charges and lone pairs of electrons that are directly involved in the reaction. (You do not need to rewrite all resonance structures of the conjugate base of diethyl malonate.)

\[
\begin{align*}
\text{step 1:} & \quad \text{O} \quad \text{O} \\
\text{O} \quad \text{O} & \quad \text{Br} \quad \text{Ph} \\
\end{align*}
\]
4. Kemp's triacid (cis,cis-1,3,5-trimethycyclohexane-1,3,5-tricarboxylic acid) adopts a chair conformation in which the three methyl groups are in equatorial positions and the three carboxylic acid groups are in axial positions. (25 points)

Build a model of this molecule with your Darling (Molecular Visions) molecular models.

a. What is the distance in centimeters between the carbon atoms of two of the methyl groups? _______ cm

b. What is the distance in centimeters between the carbon atoms of two of the carboxylic acid groups? _______ cm

c. Draw Kemp's triacid in such a manner as to clearly illustrate the chair conformation of the cyclohexane ring and the correct positions of the methyl and carboxylic acid groups.

d. How many stereoisomers are there of 1,3,5-trimethycyclohexane-1,3,5-tricarboxylic acid (including Kemp's triacid shown above)? _______

e. Draw skeletal structure(s) of the additional stereoisomer(s).

f. What word best describes the relationship of the additional stereoisomer(s) to Kemp's triacid? ___________________
5. One of the two stereoisomers of 2-bromo-1,3-dimethylcyclohexane shown below readily undergoes elimination upon treatment with potassium tert-butoxide. (10 points)

a. Write the products of the elimination reaction in the boxes.

\[
\begin{array}{c}
\text{H}_3\text{C} \quad \text{Br} \\
\text{CH}_3
\end{array}
\quad \text{OR}
\quad
\begin{array}{c}
\text{H}_3\text{C} \\
\text{Br} \quad \text{CH}_3
\end{array}
\xrightarrow{\text{KO-}}
\begin{array}{c}
\text{t-Bu} \\
\text{t-BuOH}
\end{array}
\]

b. Circle the stereoisomer that reacts readily.

c. Explain why that stereoisomer reacts readily while the other does not.

6. Two constitutional isomers equilibrate as shown below. (20 points)

\[
\begin{array}{c}
\text{Br}
\end{array}
\xrightarrow{\text{heat}}
\begin{array}{c}
\text{Br}
\end{array}
\]

a. Write a curved-arrow mechanism for this reaction. Make sure to show all intermediates, charges, and lone pairs of electrons. Also, make sure to draw important resonance structures where appropriate.

b. Do you expect the reaction to be endothermic, exothermic, or neither? ________________

Why? ______________________________________________________________________________________

c. Draw an energy diagram for this reaction. Clearly label the reactant, product, intermediate(s), and transition state(s).
7. Explain the following with words, equations, or structures. (18 points)

a. An undergraduate research student wants to convert a sample of enantiomerically pure \((R)\)-1-chloro-1-deuterododecane to enantiomerically pure \((S)\)-1-deutero-1-iodododecane and proposes to do so by treatment with an excess of sodium iodide dissolved in acetone. His research advisor agrees that only \(S\)\(_{N2}\) displacement will occur under the reaction conditions, but thinks that the resulting 1-deutero-1-iodododecane will not be enantiomerically pure and that the enantiomeric purity of the 1-deutero-1-iodododecane will decay with increasing exposure to the sodium iodide solution. Explain the research advisor's thinking.

\[
\text{HCl} \quad \text{D} \quad (R)\text{-1-chloro-1-deuterododecane} \quad \text{H} \quad (S)\text{-1-deutero-1-iodododecane}
\]

Note: Deuterium (D) is an isotope of hydrogen with 1 proton and 1 neutron. It is sometimes referred to as "heavy hydrogen."

b. Another undergraduate research student attempts to recrystallize a sample of enantiomerically pure \((S)\)-1-bromo-2,2-dimethyl-1-phenylpropane from hot acetone. To her dismay, the optical rotation of her recrystallized product is substantially less than that of her original sample. After repeated attempts, the crystals she obtains are racemic 1-bromo-2,2-dimethyl-1-phenylpropane. Explain the racemization.

\[
\text{Br} \quad (S)\text{-1-bromo-2,2-dimethyl-1-phenylpropane}
\]

c. Both \textit{cis}-2-butene and \textit{trans}-2-butene undergo an addition reaction with bromine, but the 2,3-dibromobutane produced from \textit{cis}-2-butene has a different melting point and boiling point than the 2,3-dibromobutane produced from \textit{trans}-2-butene. Explain the difference between the 2,3-dibromobutane products.

\[
\text{cis-2-butene} \quad \text{trans-2-butene} \quad \text{CH}_3\text{-CHBr-CHBr-CH}_3 \quad \text{2,3-dibromobutane}
\]
8. The pinacol rearrangement occurs when pinacol (2,3-dimethylbutane-2,3-diol) is treated with a strong acid (e.g., H₂SO₄) and results in the formation of pinacolone (3,3-dimethyl-2-butanone). (12 points)

![Pinacol rearrangement reaction](image)

The mechanism of the pinacol rearrangement involves four steps. In the first step, pinacol is protonated. In the second step, a leaving group leaves. The third step (which has been drawn for you) is called a Wagner-Meerwein rearrangement or a 1,2-methyl shift. In the final step, a proton is lost.

Use the template below to write a curved-arrow mechanism for the pinacol rearrangement. Make sure to show all intermediates, charges, and lone pairs of electrons.

![Curved-arrow mechanism for pinacol rearrangement](image)