**Final Exam**  **Chem 3045x**  **Wednesday, Dec. 20, 2000**

**Instructions:** This is an open book examination. You may use the course text and the solution manual during the course of the examination. Please **print** your name and social security number on the front page of the examination. Be sure to allot your time in a manner that is related to the point value of the question. Be sure to show your reasoning wherever possible for partial credit.

All material to be graded must be on one of the pages of the exam with your name and social security number on the front page. If you need more space than is available on the page with the questions, use the back page of the previous page and label the number of the question on that page.

*Correlation tables for IR, $^1$H NMR and $^{13}$C NMR are attached on the last page of the exam.*

Your Name: ________________________________

Your Soc. Sec. Number: ________________________________

Time for the exam: three hours.

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Total: 300 Points
1. (10 Points). One member of each pair of the isomeric alcohols shown below reacts faster with HCl than the other to form an alkyl chloride. Draw the structure of the compound from each of the following pairs that is converted more rapidly to the corresponding alkyl chloride on treatment with HBr. Indicate briefly the reasoning for your choice.

(a) 1-butanol or 2-butanol

HCl is $S_N^1$ conditions. Secondary carbonium ion formed faster

(b) 1-methylcyclopentanol or cyclohexanol

[Diagram showing tertiary carbonium ion - faster vs. secondary carbonium ion - slower]
2. (20 Points) Menthol and neomenthol are constitutional isomers possessing the same Lewis structure A, shown below. Menthol is the most stable stereoisomer possessing the Lewis structure A and neomenthol is the next most stable stereoisomer possessing the Lewis structure A.

(a) Draw a structure which clearly shows the axial and equatorial positions of the substituents in menthol. (Hint: A hydroxy group is a smaller group than a methyl group.)

(b) Are the hydroxy and methyl groups cis or trans to each other in menthol?

Cis-both down

d) Are the hydroxy and methyl groups cis or trans to each other in neomenthol?

trans
3. (20 Points) Treatment of either of the 1,2-bromoalcohols A or B with HCl results in formation of the 1-bromo-2-chloro cyclopentane, C. The rate of reaction of A to form C is much faster than the rate of reaction of B to form C. The reaction proceeds through a common reactive intermediate. Draw the structure of this intermediate. Explain the reason that A forms C faster than B forms C.
4. (20 Points) Suggest plausible syntheses starting with the indicated organic molecules. More than one synthetic step may be required. You may use any inorganic reagents you require in any step.
5. (20 points). Describe the structural relationship between the following pairs as one of the following constitutional isomers, enantiomers, diastereomers, meso forms, diastereomers or identical.

- Identical
- Enantiomer
- Diastereomers
- Identical
6. (10 Points). Use Hückel theory to explain why the following hydrocarbon possesses an unusually large dipole moment for a hydrocarbon. Which ring possesses the negative dipole and which possesses the positive dipole?

7. (20 Points). Define a rule for aromaticity and then draw a circle around the structures A-E that are aromatic according to your rule.

Definition of aromaticity: closed, planar, conjugated cyclic hydrocarbon with $4n+2 \pi$ electrons

8. (10 Points). Treatment of the allylic alcohol A with acid causes it to rearrange to the isomer B. Suggest a plausible mechanism for the rearrangement.
9. (20 Points) Suggest a plausible structure for \( \text{C}_4\text{H}_8 \) (A) and \( \text{C}_{10}\text{H}_{16} \) (B) based on the indicated reactions. Be sure to indicate pertinent stereochemistry in the structures you suggest.

(A) \( \text{C}_4\text{H}_8 \) \( \xrightarrow{\text{Cl}_2} \) \( \text{C}_4\text{H}_8 \)

(B) \( \text{C}_{10}\text{H}_{16} \)

10. (20 Points) Which of the following compounds, if any, are chiral? Explain your reasoning for full credit.
11. (20 Points) Compound A (C\textsubscript{7}H\textsubscript{13}Br) is a tertiary bromide. On treatment with sodium ethoxide in ethanol, A is converted to a hydrocarbon B (C\textsubscript{7}H\textsubscript{12}). Ozonolysis of B gives C as the only product. Deduce the structures of A and B.

A (C\textsubscript{7}H\textsubscript{13}Br) \xrightarrow{\text{CH}_3\text{CH}_2\text{O}^-} B (C\textsubscript{7}H\textsubscript{12}) \xrightarrow{1. \text{O}_3} \xrightarrow{2. \text{H}_2\text{O}, \text{Zn}} C

\[ \text{Br} \xrightarrow{\text{EtO}^-} \text{C} \]
12. **(20 Points)** Treatment of neomenthyl chloride A with strong base results in a rapid reaction to produce B as the major product, while treatment of methyl chloride C results in a very slow reaction to produce D as the major product. Suggest a plausible mechanistic interpretation of these results. A chlorine atom possesses a smaller van der Waals diameter than a methyl group.

![Chemical structures](image)

**13. (20 Points)** Consider that the infrared carbonyl stretching frequencies of the three compounds A, B, and C are quite different. Based on your knowledge of resonance theory and infrared spectroscopy, predict which will have the highest carbonyl stretching frequency.
frequency and which will have the lowest carbonyl stretching frequency. Explain your reasoning.

Stretching frequency determined by bond strength. More single bond character, weaker bond. Resonance destabilizes NO$_2$ ketone more than H ketone. CH$_3$O stabilizes resonance structure, which has more single bond character.
14. (20 Points). Suggest a plausible synthesis of the following compounds starting from benzene. Any inorganic reagents may be employed.

\[ \text{CH}_3\text{Cl} \quad \text{AlCl}_3 \]
\[ \text{CO}_2\text{H} \quad \text{Br} \]
\[ \text{NO}_2 \]
1) \text{Br}_2/\text{FeBr}_3
2) \text{KMnO}_4

\[ \text{CH}_3 \quad \text{Cl} \quad \text{AlCl}_3 \]
\[ \text{Zn}/\text{HCl} \]

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

1) \text{Br}_2/\text{FeBr}_3
15. (20 Points). Draw the structure of the major product you would expect to result then the indicated starting material is treated with the indicated reagents.

- 

16. (20 Points). Draw a Lewis structure consistent with the following NMR spectra and molecular compositions.
(a) Molecular composition $\text{C}_8\text{H}_{18}$; 1H NMR consists of a singlet at $\delta = 0.9 \text{ ppm}$

\[
\text{CH}_3 \text{CH} \text{CH}_3 \\
\text{CH} \text{CH}_3 \text{CH}_3 \\
\text{CH}_3 \text{CH} \text{CH}_3 \\
\text{CH}_3
\]

(b) Molecular composition $\text{C}_8\text{H}_8$; 1H NMR consists of a singlet at $\delta = 5.8 \text{ ppm}$

\[
\text{C}_8\text{H}_8
\]

(c) Molecular composition $\text{C}_2\text{H}_3\text{Cl}_3$; 1H NMR consists of a singlet at $\delta = 2.7$

\[
\text{H}_3\text{C} - \text{CCl}_3
\]

(d) Molecular composition $\text{C}_3\text{H}_5\text{Br}$; $^{13}\text{C}$ NMR consists of three signals at $\delta = 33 \text{ ppm}$ (triplet), $\delta = 118 \text{ ppm}$ (triplet) and $\delta = 134 \text{ ppm}$ (doublet).

\[
\text{Br}
\]

(e) Molecular composition $\text{C}_3\text{H}_5\text{Br}$; $^{13}\text{C}$ NMR spectrum consists of two signals at $\delta = 12 \text{ ppm}$ (triplet) and $17 \text{ ppm}$ (doublet).

\[
\text{Br}
\]
17. (20 Points. 10 Points for each spectrum) Suggest a structure that is consistent with the IR, 1H NMR and 13C NMR spectra shown on the following pages for the molecular compositions $A = C_5H_{10}O_2$ and $B = C_3H_7Br$. Indicate briefly how each structure is consistent with each spectrum. The number of protons responsible for each signal is indicated next to the signal on the spectrum.

The suggested structure for $A$ is

My reasoning for suggesting the structure for $A$: 
The suggested structure for B is

My reasoning for suggesting the structure for B: