1. (24%, 2% each) Single choice.

1). A sample of compound X is subjected to elemental analysis and the following percentages by weight are found: 39.97% C, 6.73% H, and 53.30% O. The molecular weight of X is 90. What is the empirical formula of X? (a) C₆H₁₀O₅, (b) C₃H₄O₂, (c) C₄H₁₆O₂, (d) C₅H₆O₂, (e) CH₂O.

2). When methanol (CH₃OH) acts as a base, its conjugate acid is _____. (a) "CH₂OH, (b) CH₂O⁺, (c) CH₄OH, (d) CH₃OH₂⁺, (e) CH₄O⁺.

3). Triethylamine [(CH₃CH₂)₃N] is a molecule in which the nitrogen atom is ____ hybridized and the CNC bond angle is _____. (a) sp², >109.5° (b) sp², <109.5° (c) sp³, >109.5° (d) sp³, <109.5° (e) sp, 109.5°.

4). Which of the following correctly lists the conformations of cyclohexane in order of increasing energy? (a) chair < twist < boat < half-chair, (b) chair < boat < half-chair < twist, (c) chair < twist < half-chair < boat, (d) half-chair < boat < twist < chair, (e) half-chair < twist < boat < chair.

5). Which of the following compounds whose chiral center labeled with a star has the R configuration? (a) A and C only (b) B, C and D (c) A, B and D (d) A and B only (e) All of the above.

![Chemical Structures](image)

6). Rank the following compounds in order of increasing boiling point: (A) (CH₃)₂N, (B) CH₃CH₂CH₂-OH, (C) CH₃-NH—CH₂CH₃, (D) CH₃CH₂CH₂-NH₂, and (E) CH₃-O—CH₂CH₃.

(a) A<C<E<D<B (b) A<E<C<D<B (c) A<E<D<C<B (d) E<A<C<D<B (e) E<D<A<C<B.

7). Which of the following compounds are chiral?

![Chemical Structures](image)

(a) A and B (b) B and C (c) B, C and D (d) A and D (e) A, D and E.

8). Which of the following statements about crown-ethers is wrong: (a) they allow inorganic salts to dissolve in nonpolar organic solvents, (b) 18-crown-6 was discovered by J.-M Lehn (a Nobel Prize winner in 1987), (c) 18-crown-6 is used to enhance the basicity of potassium tert-butoxide, (d) the fluoride ion of a potassium fluoride solution in acetonitrile can be a good nucleophile if 18-crown-6 is added, (e) 12-crown-4 can solvate lithium ion strongly.
9. Which of the following compounds are not likely to be aromatic?

(a) \[\text{C}_5\text{H}_4\text{O}\]  (b) \[\text{C}_5\text{H}_5\text{N}\]  (c) \[\text{C}_5\text{H}_4\text{O}\]  (d) \[\text{C}_5\text{H}_4\text{N}\]  (e) \[\text{C}_5\text{H}_4\text{N}_2\]

10. Rank the following aromatic compounds in order of increasing resonance energy: (A) benzene, (B) pyrrole, (C) furan, (D) thiophene, and (E) pyridine. (a) E < D < C < B < A, (b) C < B < E < D < A, (c) C < E < D < B < A, (d) E < C < B < D < A, (e) D < B < C < A < E

11. Which of the following nuclei will not have NMR signal (A) \(^{16}\text{O}\), (B) \(^{12}\text{C}\), (C) \(^{14}\text{N}\), (D) \(^{3}\text{He}\), (E) \(^{19}\text{F}\). (a) A and B (b) A, B, and C (c) B and C (d) B and D (e) D and E.

12. Which of the following reactions will be photochemically allowed based on frontier molecular orbital theory: (A) \([2+2]\), (B) \([4+2]\), (C) \([4+4]\), (D) \([1+2]\), (E) \([6+2]\). (a) A and B (b) A, B and C (c) A, C and E (d) B, C and E (e) A, C, and D.

2. (12%). Deduce the identity of the following compound from the NMR data given.
(a) \(\text{C}_4\text{H}_8\text{O}_2\) (compound A): \(^1\text{H}\) NMR, \(82.28\) (2H, multiplet), \(2.50\) (2H, triplet), \(4.35\) (2H, triplet); \(^1\text{C}\) NMR, \(\delta\) 177.81 (singlet), 68.58 (triplet), 27.70 (triplet), 22.17 (triplet).

(b) (8%) The Mass spectrum of compound B shows a weak molecular ion peak at \(m/z\) 73 and a base peak at \(m/z\) 44. Compound B has following IR and \(^1\text{H}\) NMR spectra. The NMR singlet at \(\delta 1.16\) disappears when the sample is shaken with \(\text{D}_2\text{O}\). Propose a structure for compound B and explain all the key spectra features.
3. (14%) Show how you would accomplish the following synthetic conversion in good yields. You may use alcohols with four or fewer carbon atoms, cyclopentanols, benzyl alcohol, and any necessary solvents and reagents that you need.
   (a) Acetylene \[ \rightarrow \rightarrow \text{Pentanal} \quad (4\%) \]
   (b) Benzaldehyde \[ \rightarrow \rightarrow \text{through 1,3-dithiane} \quad (4\%) \]
   (c) Use malonic ester synthesis \[ \rightarrow \rightarrow \text{COOH} \quad (6\%) \]

4. (5%, 1% each) Draw the structure of the following compounds.
   (a) $\delta$-aminononanoic acid
   (b) (1R, 2S, 3S)-1,2-dibromo-3-ethylcyclohexane
   (c) iso-butyl tosylate
   (d) N-methylimidazole
   (e) phenyl acetoacetate

5. (10%) The Mannich reaction involves several acid-catalyzed equilibria. Like the aldol condensation, the success of the Mannich reaction depends on being able to generate both nucleophilic and electrophilic carbons in the reaction mixture at the same time. Please try to draw a mechanism that account for the following Mannich reaction.

6. (5%) Glyceraldehyde ($C_3H_6O_3$) is an aldotriose. Natural occurring glyceraldehyde is a dextrorotatory compound. When the pure (+)-glyceraldehyde was incubated in alkaline solution, the solution gradually lost its optical property. Why? Propose a mechanism to explain this observation.

7. (10%) The following reaction may not happen if the $X$ is not chosen properly. You need to give two different $X$ residues, so that the reactions (1) will and (2) will not take place. Be sure to give detailed explanation for both cases.

Note: $X$ could be halides, acetate or tosylate
8. (20%, 2% each) Give the major product of the following reactions

(a) \[
\begin{align*}
\text{O}_3 & \rightarrow S(CH_3)_2 & & \text{NaOH} \\
& & & \text{heat}
\end{align*}
\]

(b) \[
\begin{align*}
\text{POCl}_3 & \rightarrow \text{Pyridine} \\
& & \text{OCH}_2\text{CH}_2\text{OD} & D^+ & \rightarrow \text{NaBD}_4 & CD_2\text{OD} & \rightarrow D_2\text{O}^+
\end{align*}
\]

(c) \[
\begin{align*}
\text{CHO} & \rightarrow \text{NaBD}_4 & CD_2\text{OD} & \rightarrow D_2\text{O}^+
\end{align*}
\]

(d) \[
\begin{align*}
1. \text{PhCO}_2\text{H} & \rightarrow 2. \text{CH}_3\text{ONa, CH}_3\text{OH}
\end{align*}
\]

(e) \[
\begin{align*}
\text{OsO}_4 & \rightarrow \text{H}_2\text{SO}_4 & \rightarrow \text{H}_2\text{O}
\end{align*}
\]

(f) \[
\begin{align*}
\text{CH}_3\text{C} & \rightarrow \text{CH}_3\text{H}_2 & \rightarrow \text{Zn(Cu)}
\end{align*}
\]

(g) \[
\begin{align*}
\text{N} & \rightarrow \text{Ag}_2\text{O} & \text{heat}
\end{align*}
\]

(h) \[
\begin{align*}
\text{N}_2\text{H}_4 & \rightarrow \text{KOH, heat} & \text{DMSO}
\end{align*}
\]

(i) Benzoquinone + \[
\begin{align*}
\text{heat}
\end{align*}
\]

(j) \[
\begin{align*}
\text{Br}_2 & \rightarrow \text{NaNH}_2 & \text{heat} & \rightarrow \text{Na/ NH}_3
\end{align*}
\]