Given the following spectral data, assign structures to the following compounds:

**Compound A:**
- Mass Spec: C₆H₁₂O₂: m/e 116(M⁺), 101, 73, 59, 57
- ¹H-NMR: δ 1.42 (s), 1.96 (s) [ratio 3:1]
- ¹³C-NMR: δ 22.3, 28.1, 79.9, 170.2
- IR: 1738 cm⁻¹ \(\rightarrow\) \(\nu\)C=O (ester)

**Compound B:**
- Mass Spec: C₄H₈O₂Cl₂
- ¹H-NMR: shown below
- ¹³C-NMR: shown below

\[
\frac{2\text{H}_2\text{O}}{2\text{Cl}} = 1 \text{ unit of unsaturation} \]

- 4 different carbons
- 2 groups of equiv H₆s
- 5 3-bond neighbors
- 4 groups of 6 equiv C's.

\(\sim 3.7\text{ppm}\)

\(4.2\text{ppm}\)

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Compound C: Mass Spec: C₅H₉OCl; m/e 122, 120 (M⁺), 93, 91, 85, 65, 63.
IR: 1720 cm⁻¹
¹H-NMR: shown below
¹³C-NMR: shown below
Deduce the structures for compounds A, B, and C from the information provided below.

The $^1$H-NMR spectrum of compound A is a singlet at 83.5 ppm.
The $^1$H-NMR spectrum of compound C is a singlet at 84.0 ppm.
The $^1$H-NMR spectrum of compound B is given below.

![NMR Spectrum of B](image)

a) Place the structures for A, B, and C on the Answer Sheet.

b) How many signals are predicted for the proton-decoupled $^{13}$C-NMR spectrum of compound B?

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c) What multiplicity (singlet, doublet, etc) is expected for the most downfield (deshielded) signal in the proton-coupled $^{13}$C-NMR spectrum?

for B:

\[ \text{\text{singlet}} \]

Thus, the most down-field $^{13}$C signal gives a singlet (under the proton-coupled mode).
Compound D ($C_8H_{10}O$) reacts with hydrogen to give a new substance, $C_9H_{12}O$. The $^1$H-NMR spectrum of D is given below (the integration numbers are provided), as well as the IR spectrum.

The integration numbers are 5 units of unsaturation and 4 units of unsat.

Most likely, a $\text{CH}_3\text{O}^-$ group is present.

The IR spectrum shows no OH's and no $\nu$C=O.

Place the structure for compound D on the Answer Sheet.

The structure shows no coupling constants from the spec.

The stereochemistry is not assignable.
Benzene ($C_6H_6$) undergoes a series of reactions to produce compound E ($C_6H_3Br_3$). The $^1$H-NMR spectrum of compound E is a singlet at $\delta 7.9$ ppm. The proton-decoupled $^{13}$C-NMR spectrum is reproduced below. In the proton-coupled spectrum, the $\delta 133$ ppm signal is a doublet, while the $\delta 122$ ppm signal remains a singlet.

Place the structure for compound E on the Answer Sheet.

units of unsaturation = 4

From the $^1$H peak at $\delta 7.9$ ppm → aromatic compd

From the proton-coupled $^{13}$C-NMR spectrum $\text{-}C_6H_3\text{-}$ only

Br (133 ppm (d))

H (122 ppm (s))

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Treating compound F (C₉H₁₂O) with CrO₃/H₂SO₄ gives a new substance, C₉H₁₀O. The proton-decoupled ¹³C-NMR spectrum shows 7 absorptions, (δ140, 135, 131, 128, 50, 20, 15 ppm) where the observed multiplicities for the proton-coupled spectrum are given next to the chemical shift values [δ140 (s), 135(d), 131(d), 128(d), 50(d), 20(i), 15(q) ppm]. The IR and ¹H-NMR spectra for compound F are shown below.

Draw the structure for compound F on the Answer Sheet.
I. A unit of unsaturation

(a) Compound A (C₄H₁₀O₃) is a common organic solvent. When it is treated with an excess of HCl, the conversion to compound B (C₄H₈Cl₂O) is observed. After neutralization and isolation, compound B is mixed with a solution of aqueous sodium hydroxide. Compound C (C₄H₈O₂) is the result. The spectroscopic data for compounds A, B, and C are given on the next three pages. What are the structures of A, B, and C?

From IR: −OH (νOH ~ 3400)

no C=O

From C, BC: two sets of equivalent carbons

NMR spectrum:

\[
\text{From } ^1H 	ext{NMR spectrum: } x - \begin{array}{c}
\text{H} \\
\text{H}
\end{array} \begin{array}{c}
\text{C} \\
\text{C}
\end{array} - \begin{array}{c}
\text{H} \\
\text{H}
\end{array} - \begin{array}{c}
\text{H} \\
\text{H}
\end{array} - \begin{array}{c}
\text{H} \\
\text{H}
\end{array} - \begin{array}{c}
\text{Y} \\
\text{Y}
\end{array} - \begin{array}{c}
\text{H} \\
\text{H}
\end{array} - \begin{array}{c}
\text{H} \\
\text{H}
\end{array} - \begin{array}{c}
\text{H} \\
\text{H}
\end{array} - \begin{array}{c}
\text{Y} \\
\text{Y}
\end{array} - \begin{array}{c}
\text{H} \\
\text{H}
\end{array} - \begin{array}{c}
\text{H} \\
\text{H}
\end{array} - \begin{array}{c}
\text{Y} \\
\text{Y}
\end{array}
\end{array}
\]

2 : 2 : 1 singlet

\[
\text{HO} - \text{O} - \text{OH}
\]

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1. (cont'd)

(b) How many equivalents of HCl are required to cause the conversion of A to B?

\[ 2\text{OH}^- \rightarrow 2\text{Cl}^- \]

2 equiv.

(c) How many mL of 5M HCl are required to cause the conversion of 150mg of A to B if a total of a five-fold excess of HCl is desired (assuming this means 5 equiv)?

\[ 0.568 \text{ mL} \]

(d) The conversion of B to C consumes two equivalents of NaOH (one to incorporate, one to deprotonate). How many grams of NaOH are required to prepare 100 mg of C if a 90% yield is expected and a stoichiometric amount (i.e., two equivalents) of base is used?

\[ 0.102 \text{ g} \]

(c) 150 mg of A = \( \frac{150 \text{ mg}}{106 \text{ mg/mmole}} \) = 1.42 mmoles

Since 2 equiv of HCl needed \( \Rightarrow 2.84 \text{ mmoles} \) HCl needed.

\[ x \text{ mL} \times \frac{5 \text{ mmoles}}{\text{mL}} = 2.84 \text{ mmoles} \]

\[ x = \frac{2.84}{5} = 0.568 \text{ mL} \]

(d) 100 mg of C = \( \frac{100 \text{ mg}}{88 \text{ mg/mmole}} \) = 1.14 mmoles

Since the yield is 90% \( \Rightarrow \frac{1.14}{0.9} = 1.27 \text{ mmoles} \) of B needed.

Since 2 equiv of NaOH needed,

1.27 mmoles \( \times 2 = 2.54 \text{ mmoles} \) of NaOH needed.

\[ 2.54 \text{ mmoles} \times \frac{40 \text{ mg}}{\text{mmole}} = 101.6 \text{ mg} \]

\[ = 0.102 \text{ g} \]
II. 3 units of unsaturation

When compound D (C₈H₁₀) reacts with chloromethane (CH₃Cl) in the presence of aluminum chloride (AlCl₃), a new compound E (C₉H₁₂) forms. What are the structures of compounds D and E? Spectra for D and E are on the next two pages.

most likely,

\[ \text{CH}_3 \text{Cl} + \text{AlCl}_3 \rightarrow \text{CH}_3 \text{AlCl}_4 \]

From IR spec:
- \( \nu \text{C} = \text{C} \)
- 2 atoms \( \nu \text{C} - \text{H} \)
- (~3100 cm\(^{-1}\))

From \(^1\text{H} \text{NMR spec}:
- 2 sets of chemically equivalent hydrogen atoms (~7 ppm)
- 3 aromatic hydrogen atoms (~2-2.5 ppm)

From \(^1\text{C} \text{NMR spec}:
- 3 sets of chemically equivalent carbon atoms

\[ \text{D} \quad \text{C}_8\text{H}_{10} \quad \text{CH}_3\text{Cl} \quad \text{AlCl}_3 \quad \text{E} \quad \text{C}_9\text{H}_{12} \]
III. (a) The synthesis of a certain molecule, C_{12}H_{22}O, (compound E), was reported along with its spectral characteristics.

IR: no absorptions above 3000 cm\(^{-1}\); strong 1720 \& 1650 cm\(^{-1}\).

NMR:
- 2.65, 1H, septet
- 1.70, 3H, singlet
- 1.53, 3H, singlet
- 1.15, 9H, singlet
- 1.07, 6H, doublet

\( \gamma \text{C}=\text{O} \rightarrow \gamma \text{C}=\gamma \text{C} \), no OH.

What is the structure of compound E?


Because of steric hindrance between the t-bu \& the olefinic methyl groups, the \( \text{C}=\text{O} \) and the \( \gamma \text{C}=\gamma \text{C} \) can't be on the same plane. Therefore, the conjugation between the \( \gamma \text{C}=\text{O} \) (ketone) two is not effectively achieved. Thus, the \( \gamma \text{C}=\text{O} \) is almost like the one for the non-conjugated ketone.
Compound F (C₄H₆O₂) is very difficult to isolate and store in a pure form. It is available commercially in the form of compound G (C₆H₁₂O₃). Compound G can be thought of as arising from the reaction of compound F with an excess of CH₃OH and a mild acid such as TsOH.

Data for Compound G only:

- Expansion of small signal at 5.469
- Integral ratios: 1:6:2:3
- 2.11 ppm: one CH₃ (most likely)
- 2.41 ppm
- 3.29 ppm
- 4.69 ppm

Assignments:
- a. 31.0 ppm
- b. 47.0 ppm
- c. 54.0 ppm
- d. 102.0 ppm
- e. 204.0 ppm

What is the structure of compound G?