I. (9 points) Answer in the boxes below the following questions for the Grignard reagent CH$_3$-MgBr.

(1) (2 points) Is the carbon atom associated with magnesium electrophilic or nucleophilic?

[electrophilic]  [nucleophilic]  [circle one]

(2) (3 points) Explain why the Grignard reaction has to be carried out in an anhydrous solvent.

The Grignard reagent produced would be destroyed by the reaction with water present in a non-anhydrous solvent.

(3) (4 points) Write the conjugate carbon acid (i.e., C-H) of the CH$_3$-MgBr and explain why Grignard reagents are strong bases.

<table>
<thead>
<tr>
<th>structure:</th>
<th>explanation:</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-C-H</td>
<td>The pKa of CH$_4$ is ca. 50. Therefore, its conjugate base is highly basic.</td>
</tr>
</tbody>
</table>

II. (6 points) Ethyl alcohol (C$_2$H$_5$OH) quite often is present in technical-grade diethyl ether. If this grade of diethyl ether were used, what effect, if any, would the ethyl alcohol have on a Grignard reagent used? Explain using a chemical equation using methylmagnesium bromide as an example.

A Grignard reagent formed would deprotonate H of the ethyl alcohol OH.

III. (8 points) For each of the reactions below, draw in the boxes provided the structure of the expected major organic product.

(1)

\[
\begin{align*}
\text{Br} & \quad \text{Mg (1.1 mol equiv)} \quad \text{ether} \\
\text{H} & \quad \text{H$_3$C-CH$_3$ (1.1 mol equiv)} \\
\text{CH$_3$OH} & \quad \text{aq NH$_3$Cl (acidic workup)}
\end{align*}
\]

(2)

\[
\begin{align*}
\text{Br} & \quad \text{Mg (1.1 mol equiv)} \quad \text{ether} \\
\text{H} & \quad \text{H$_3$C-CH$_3$ (1.1 mol equiv)} \\
\text{CH$_3$OH} & \quad \text{aq NH$_3$Cl (acidic workup)}
\end{align*}
\]
IV. (16 points) For the following reaction sequence, draw the correct structures in the boxes provided.

\[
\text{Ph}_3\text{P} : (\text{C}_{18}\text{H}_{15}\text{P}) + \text{BrCH}_3 \xrightarrow{\text{benzene, reflux}} \text{Ph}_3\text{P} = \text{Br} \rightarrow \text{Ph}_3\text{P} = \text{CH}_3
\]

"salt"

\[
\text{NaOC}_2\text{H}_5/\text{C}_2\text{H}_5\text{OH}
\]

\[
\text{Ph}_3\text{P} = \text{CH}_3
\]

\[
\text{C}_{21}\text{H}_{19}\text{PO} (\text{ylide}) + \text{NaBr} + \text{C}_2\text{H}_5\text{OH}
\]

V (12 points) Show how many peaks you would expect to observe in the proton-decoupled \(^{13}\text{C}\) NMR spectrum of each of the following compounds. Indicate your answers in the boxes provided.

1. \[
\text{H}_3\text{C} \overset{\text{O}}{\text{CO}} \text{CH}_3
\]

2. \[
\text{S} \overset{\text{OOC}}{\text{SO}} \text{CH}_3
\]

3. \[
\text{NH}_3^+ \overset{\text{CH}_3}{\text{C}}
\]

4. \[
\text{cis} \overset{\text{COOH}}{\text{COOH}} \overset{\text{COOH}}{\text{COOH}}
\]

5. \[
\text{180° rotation}
\]

6. \[
\text{H}_3\text{C} \overset{\text{O}}{\text{O}} \text{CH}_3
\]
VI. (5 points) The proton NMR spectrum of a mixture of acetonitrile (CH$_3$C≡N), methylene chloride, (CH$_2$Cl$_2$) and benzene (C$_6$H$_6$) is integrated and results in step heights of 15, 6, and 18 mm for the signals at $\delta$ 2.10, 5.30, and 7.26 ppm, respectively. In what mole ratio are the three substances present? No explanation required. No partial credit will be given to this problem.

\[
\text{acetonitrile : methylene chloride : benzene} = \frac{15}{3} : \frac{6}{2} : \frac{18}{6} = 5 : 3 : 3
\]

VII. (8 points) For each of the reactions given below, draw in the box the structure of the expected product. Make sure to indicate the stereochemistry of the product whenever applicable.

(1)

\[
\text{OCH}_3
\]

\[
\text{CH}_2\text{Cl}_2
\]

room temperature

endo product

(2)

VIII. (10 points) Provide in the box below a step-by-step, curved-arrow mechanism for the formation of hydroxy acid 2 from diketone 1. Make sure to include the mechanism for the acidic workup as well.
IX. (16 points) Shown below are proton NMR spectra of four compounds. The compounds are among those structures given on page 6. Assign each spectrum to its compound by putting the letter corresponding to the compound in the answer box next to the spectrum. The table of characteristic proton NMR chemical shifts appears on page 11.

1. [Diagram with peak(s) intensity ratios: a : b : c = 6 : 1 : 5]

2. [Diagram with peak(s) intensity ratios: a : b : c : d = 3 : 2 : 2 : 5]

3. [Diagram with peak(s) intensity ratios: a : b : c : d = 2 : 2 : 2 : 5]

4. [Diagram with peak(s) intensity ratios: a : b : c : d = 3 : 4 : 3 : 2]
IX. (continued)

A

B

C

D

E

F

G

H

X. (15 points) On the basis of its spectroscopic information provided below, propose the structure for the compound, C₅H₁₂O. Draw the proposed structure in the box on page 7 and give a brief explanation as to how the structure is deduced from the spectroscopic information provided.

IR spectrum
(liquid film)

wave-numbers (cm⁻¹) % transmittance

13C NMR in CDCl₃

notes: Neither solvent or TMS peak(s) seen in the spectrum. The letter d or q on top of each peak denotes the splitting pattern, doublet or quartet, respectively, when the spectrum is run in the proton-coupled mode.
0 unit of unsaturation

Explanation (just assign the IR peak at 3368 cm⁻¹ and all H-1 peaks right next to the corresponding functional group/H-1 nuclei):
XI. (15 points) On the basis of its spectroscopic information provided below, propose the structure of the compound, $C_{10}H_{16}O_4$. Draw the proposed structure in the box on page 9 and give a brief explanation as to how the structure is deduced from the spectroscopic information provided. Make sure to assign all proton and C-13 NMR peaks.

![IR spectrum](image)

![20MHz carbon-13 NMR spectrum](image)

![proton-coupled C-13 NMR](image)

![proton-decoupled C-13 NMR](image)

![100MHz proton NMR spectrum](image)
XI.
(continued)

Structure:

These should show only one sp² alkene C-13 peak. => -1 point

Explanation (just assign the strongest IR peak and all H-1 and C-13 peaks right next to the corresponding functional group/H-1, C-13 nuclei):

- Units of unsaturation: 3; only 6 C-13 peaks!