1. (3) True or False. The compound shown could be made using a malonic ester synthesis.

\[ \text{CH}_3\text{CH}_2\text{HC} = \text{CH}_2 \text{OH} \]

2. (6) In each of the following, circle the base to the right which would be the one most likely used for the starting material shown and the stated type of reaction.

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>Type of Reaction</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) CH₃CH₂CO₂Me</td>
<td>Condensation reaction with another ester</td>
<td>LDA, NaOMe, NaOH</td>
</tr>
<tr>
<td>b) CH₂(CO₂Me)₂</td>
<td>α-alkylation</td>
<td>LDA, NaOMe, NaOH</td>
</tr>
<tr>
<td>c)</td>
<td>Self condensation</td>
<td>LDA, NaOMe, NaOH</td>
</tr>
</tbody>
</table>

3. (8) Using the numbers given, assign approximate pKa values to the circled H's in each of the following molecules. pKa 5 10 15 20 35

a) 15
b) 20
c) 10
d) 35

4. (35) Provide the structures of the major organic products expected, or provide the reactants and / or reagents necessary to effect the following transformations:

a) \[ \text{NaOH} \]

b) \[ \text{Br}_2, \text{H}^+ \text{ cat.} \]
5. (7) Draw the *keto form* of the enol shown below. *Additionally*, indicate for the *enol* form at which atom it would be most likely to react with an electrophile.

![Enol and Keto Forms](image)

6. (3.5) Explain *briefly* but *clearly* why NaOEt could be used in ethanol (EtOH) as solvent.

If NaOEt acts as a base and abstracts the proton from ethanol the result is EtO⁻ - the same base and ethanol – the same solvent!

7. (3.5) Explain *briefly* but *clearly* why it is *not* necessary to use an acid catalyst for the *hydrolysis* of an acid halide.

The partial + charge on the C=O carbon atom is greater than in most other carbonyl containing compounds – making it easier for the water to attack as a nucleophile. Further, the leaving group, Cl⁻, is an excellent leaving group such that even a poor nucleophile like water can displace it.

8. (10) In each of the following examples, draw the 2 key starting materials (*not* bases or solvents) required to form the products shown using aae, malonic ester or aldol reactions.
9. (9) State whether each of the following normally would act as a nucleophile or electrophile. You need not explain your answer.

a) \( \text{O} \)

b) \( \text{O} \) [by Aldol]

10. (21) From the list given, choose the best reagent for each transformation shown. Write the appropriate letter above the reaction arrow. It is possible to use the same reagent more than once.

A. \( \text{SOCl}_2 \)  
B. \( \text{LDA then PhSeCl then H}_2\text{O}_2 \)  
C. \( \text{NaOMe then MeI then H}_3\text{O}^+ \)  
D. \( \text{MeMgBr then H}_3\text{O}^+ \)  
E. \( \text{NaOEt, EtOH} \)  
F. \( \text{LiAlH}_4 \) then \( \text{H}^+ \)  
G. \( \text{DIBAL then H}_3\text{O}^+ \)  
H. \( \text{H}_2\text{O}_2 \)  
I. \( \text{H}_3\text{O}^+ \) and heat  
J. \( \text{MeNH}_2 / \text{H}^+ \)
PhCNHCH$_3$ → PhCH$_2$NHCH$_3$

PhCONHCH$_3$ + H$_2$NCH$_3$ → PhCO$_2$H + H$_2$NCH$_3$

PhCO$_2$H → PhCOCl
11. (14) In each of the following, state whether the molecule could be made using the malonic ester, aae or aldol reactions.

a)

\[ \text{ALDOL} \]

b)

\[ \text{ALDOL} \]

c)

\[ \text{MALONIC ESTER} \]

d)

\[ \text{AAE} \]

12. (4) The first step of the hydrolysis of a nitrile under acidic conditions (H_3O^+, water) is attack by the nitrile N on the H^+. What is the second step?

The O of the water molecule attacks the C of the protonated nitrile, breaking a C-N pi bond

13. (12) Show the first complete step of the arrow-pushing mechanism for each of the following:

a)

\[ \Theta \text{OH K} \]

b)

\[ \text{Li} \text{N}^+\text{Pr}_2 \]

c)

\[ \text{H}_2\text{N} \]
14. (3) True or False. Treatment of acetoacetic ester (aae) with NaOMe gives 100% of the corresponding anion.

15. (3) True or False. Treatment of acetone with KOH gives 100% of the corresponding anion.

16. (8) From the list given, choose the best descriptor for each, overall reaction shown. It is possible to use an answer more than once or not at all.

- hydrolysis
- reduction
- oxidation
- elimination
- esterification

a) \[ \text{CH}_3\text{CN} \overset{\text{hydrolysis}}{\rightarrow} \text{CH}_3\text{CO}_2\text{H} \]

b) \[ \text{CH}_3\text{CN} \overset{\text{reduction}}{\rightarrow} \text{CH}_3\text{CH}_2\text{NH}_2 \]

c) \[ \text{CHO} \overset{\text{elimination}}{\rightarrow} \text{CH} \]

d) \[ \text{CO}_2\text{Me} \overset{\text{reduction}}{\rightarrow} \text{CHO} \]