SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

1) Show how an enolate can add to a carbonyl.  

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

2) Provide a detailed, stepwise mechanism for the base-catalyzed enolization of acetaldehyde.

3) Provide a detailed, stepwise mechanism for the acid-catalyzed enolization of acetaldehyde.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

4) The relationship between ketones and their corresponding enols is one of:
   A) allotropes.  
   B) diastereomers.  
   C) tautomers.  
   D) enantiomers  
   E) cis-trans isomers.

5) (S)-2-Methylbutanal _________ upon sitting in an acidic or a basic aqueous solution.
   A) esterifies  
   B) hydrolyzes  
   C) inverts completely to the R configuration  
   D) racemizes  
   E) irreversibly forms the hydrate.

6) When a ketone and its enol are in equilibrium, under most conditions the concentration of the enol is ________ the concentration of the ketone.
   A) slightly higher than  
   B) exactly half of  
   C) much higher than  
   D) much lower than  
   E) equal to.

7) Which of the following reagents will quantitatively convert an enolizable ketone to its enolate salt?
   A) lithium hydroxide  
   B) diethylamine  
   C) methylithium  
   D) pyridine  
   E) lithium diisopropylamide.

8) The α-halogenation of cyclohexanone:
   A) requires one equivalent of acid.  
   B) requires one equivalent of base.  
   C) is catalyzed by the sodium halide salt.  
   D) is slowed by the presence of acid.  
   E) is catalyzed by base.
SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

9) Provide a detailed, stepwise mechanism for the α-bromination of acetone in base.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

10) Which of the following ketones will give a positive iodoform test?
   A) 3-hexanone
   B) cyclohexanone
   C) 2-hexanone
   D) 4-heptanone
   E) 2-methyl-3-pentanone

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

11) Provide a detailed, stepwise mechanism for the formation of acetate and bromodiiodomethane from bromoacetone, hydroxide and iodine.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

12) What is the carbon nucleophile which attacks molecular bromine in the acid-catalyzed α-bromination of a ketone?
   A) a carbocation
   B) an acetylide
   C) an enol
   D) an enolate
   E) a Grignard reagent

13) When aldehydes are subjected to the same conditions that α-halogenate ketones (i.e., X_2 and aqueous acid or base), they are:
   A) reduced to alcohols.
   B) oxidized to the acid or carboxylate.
   C) converted to the acid halide.
   D) α-halogenated as well.
   E) esterified.

14) The Hell-Volhard-Zelinsky reaction involves:
   A) the α-bromination of carboxylic acids.
   B) the bromination of alcohols.
   C) the α-bromination of ketones.
   D) the oxidation of aldehydes to acids.
   E) none of the above.

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

15) Provide a mechanism for the following reaction:

   butanoic acid + Br_2 + PBr_3 → 2-bromobutanoyl bromide
ESSAY. Write your answer in the space provided or on a separate sheet of paper.

16) Provide the sequence of synthetic steps required to produce N-cyclohexyl-2-bromopropanamide from propanoic acid.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

17) Which of the following will alkylate a lithium enolate most rapidly?
   A) methyl bromide
   B) 2-methylbromobenzene
   C) isopropyl bromide
   D) bromobenzene
   E) neopentyl bromide

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

18) What are the two key resonance structures for an enamine? Label the major and minor contributors.

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

19) What iminium salt is produced in the reaction shown below?

20) Methylamine reacts with acetophenone to yield the:
   A) imine.
   B) enamine.
   C) amide
   D) iminium salt.
   E) acetal.

21) Which of the following will react most slowly with an enamine?
   A) benzyl chloride
   B) isopropyl chloride
   C) methyl bromide
   D) acetyl chloride
   E) allyl bromide
22) An enolate attacks an aldehyde and the resulting product is subsequently protonated. What type of reaction is this?  
A) a Selman-Jones reaction  
B) an acid-catalyzed aldol condensation  
C) a Fischer esterification  
D) a base-mediated aldol condensation  
E) a Hell-Volhard-Zelinsky reaction

23) The aldol condensation is:  
A) an irreversible reaction.  
B) a tautomerization.  
C) an isomerization.  
D) a type of esterification.  
E) an equilibrium reaction.

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

24) What compound is produced in the reaction of cyclopentanone with Br2 in acetic acid?  

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

25) Which of the following could result from the dehydration of a self-aldol condensation product?  
A) 4-methyl-5-hexen-2-one  
B) 4-methyl-3-penten-2-one  
C) 4-methyl-4-hexen-2-one  
D) 4-methyl-4-penten-2-one  
E) 3-methyl-4-penten-2-one

26) In theory a poorly planned crossed aldol reaction can produce how many different aldol regioisomers?  
A) 1  
B) 2  
C) 3  
D) 4  
E) 5

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

27) Provide the sequence of steps necessary to synthesize the compound shown below from cyclohexene.

28) What two molecules were condensed in an aldol reaction to produce (CH3)3CCH=CHCOCH3?

29) What two molecules were condensed in an aldol reaction to produce PhCH=CHCOPh?
MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

30) Which of the following is least likely to undergo a smooth crossed Claisen condensation with methyl pentanoate?
   A) \((\text{CH}_3)_3\text{CCO}_2\text{CH}_3\)
   B) \(\text{HCO}_2\text{CH}_3\)
   C) \(\text{PhCO}_2\text{CH}_3\)
   D) \(\text{PhCH}_2\text{CO}_2\text{CH}_3\)
   E) \((\text{CH}_3\text{O})_2\text{CO}\)

31) Which of the following is another name for the product of an aldol condensation
   A) \(\beta\)-hydroxyaldehyde
   B) 1,3-dialdehyde
   C) \(\beta\)-ketoester
   D) \(\alpha\)-hydroxyaldehyde
   E) acetal

32) An ylide is a molecule that can be described as a:
   A) carbocation bound to a positively charged heteroatom.
   B) carbocation bound to a diazonium ion.
   C) carbanion bound to a negatively charged heteroatom.
   D) carbocation bound to a carbon radical.
   E) carbanion bound to a positively charged heteroatom.

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

33) Propose a Wittig reaction-based synthesis of hex-3-ene using propene as the only carbon source and any other reagents necessary.

34) Through what sequence of steps can toluene be converted into \(\text{PhCH}_2\text{PPh}_3^+\text{Br}^-\)?

35) Provide the preferred reagent pair to synthesize 3-ethylpent-2-ene via a Wittig reaction.

36) A Claisen condensation results in a \(\beta\)-ketoester. Explain why a second ester enolate does not add to this \(\beta\)-ketoester.

37) Provide the structure of the Claisen product in the self condensation of methyl phenylacetate.

38) Starting with cyclohexene and employing a Dieckmann cyclization show how the compound below can be prepared.

39) What two starting materials yield \(\text{OHCCH}_2\text{CO}_2\text{CH}_2\text{CH}_3\) as the crossed Claisen condensation product?
40) What product is formed in the crossed Claisen condensation between methyl benzoate and cyclohexanone?

MUTLIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

41) Which of the following is most acidic?
   A) malonic ester
   B) ethyl acetate
   C) acetaldehyde
   D) acetone
   E) acetoacetic ester

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

42) What product results when malonic ester is treated with the following sequence of reagents: 1. NaOCH₂CH₃; 2. PhCH₂Br; 3. H₃O⁺, Δ?

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

43) When compound X is heated, PhCOCH(CH₃)₂ and CO₂ are produced. Offer a structure for compound X.

MUTLIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

44) In the Michael reaction, addition to the α,β-unsaturated carbonyl occurs in a:
   A) 1,2-fashion.
   B) 1,3-fashion.
   C) 1,4-fashion.
   D) 1,5-fashion.
   E) Diels-Alder reaction.

45) Which of the following is a nucleophile that does conjugate additions?
   A) CH₂=CHCHO
   B) (CH₃)₂CuLi
   C) CH₃CH₂MgBr
   D) CH₂=CHCN
   E) CH₂=CHCO₂CH₃

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

46) Provide a synthesis of the compound shown below from cyclopent-2-en-1-one and acetoacetic ester.

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

47) Provide a detailed, stepwise mechanism for the Robinson annulation reaction between 2-methylcyclohexanone and methyl vinyl ketone.

48) Name the product which results when ethyl butanoate is treated with sodium ethoxide.
49) Provide the single reagent necessary for the conversion of cyclobutanone to the compound shown below.

50) Provide the structure of the major organic product which results when PhCO₂CH₂CH₃ and CH₃CH₂CO₂CH₂CH₃ are heated in the presence of sodium ethoxide and the compound generated is subsequently treated with cold, dilute acid.

51) Provide the structure of the major organic product which results when CH₃CH₂I is treated with PPh₃ and the resulting salt is reacted with one equivalent of butyllithium.

52) Provide the sequence of synthetic steps necessary to convert cyclohexanone into the compound shown below.

53) Provide a detailed, stepwise mechanism for the transformation shown below.

54) Provide the major organic product of the reaction shown below.

55) Provide the major organic product of the reaction shown below.

56) For the equilibrium shown below, is the K<sub>eq</sub> greater or less than 1?

\[
\text{CH}_3\text{CCH}_3 + \text{EtO}^- \rightleftharpoons \text{CH}_3\text{C} \equiv \text{CH}_2 + \text{EtOH}
\]
57) For the equilibrium shown below, is the $K_{eq}$ greater or less than 1?

\[
\begin{array}{c}
\text{CH}_3\text{CCH}_3 + \text{i-Pr}_2\text{N}^- \rightleftharpoons \text{CH}_3\text{C}==\text{CH}_2 + \text{i-Pr}_2\text{NH}
\end{array}
\]

58) For the equilibrium shown below, is the $K_{eq}$ greater or less than 1?

\[
\begin{array}{c}
\text{OH}
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3\text{C}==\text{CH}_2 \rightleftharpoons \text{CH}_3\text{CCH}_3
\end{array}
\]

59) Name the aldol produced when butanal is treated with NaOH.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

60) The reaction of LDA with acetophenone produces:

A) halogenation.
B) an enolate.
C) an ylide.
D) alkylation.
E) an enol.

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

61) What name is given to the alpha substitution of a carbonyl compound where the electrophilic component is another carbonyl compound?

62) Disregarding stereoisomers, how many different enols can phenylacetone form?

A) 0  B) 4  C) 2  D) 3  E) 1

63) Disregarding stereoisomers, how many different enols can the $\beta$-diketone \text{CH}_3\text{COCH}_2\text{COCH}_2\text{CH}_3 form?

A) 0  B) 3  C) 1  D) 2  E) 4

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

64) Provide the structure of lithium diisopropylamide.

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

65) Why is the acid-catalyzed halogenation of ketones generally preferred over the base-promoted halogenation?
MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

66) In the iodoform reaction, a methyl ketone is converted to the __________ upon treatment with excess iodine and hydroxide.
   A) acyl iodide
   B) aldehyde
   C) primary alkyl iodide
   D) primary amide
   E) carboxylate

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

67) Provide the structure of the major organic product which results when PhCH₂CHO is treated with NaOH.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

68) What product results when an aldol is dehydrated?
   A) α,β-unsaturated aldehyde
   B) β-ketoester
   C) β,γ-unsaturated aldehyde
   D) β-diketone
   E) conjugated alkyne

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

69) What two organic starting materials are required to produce cinnamaldehyde (PhCH=CHCHO) via a crossed aldol condensation followed by dehydration?

ESSAY. Write your answer in the space provided or on a separate sheet of paper.

70) Provide the structure of the product of the crossed Claisen condensation between PhCO₂CH₂CH₃ and CH₃CH₂CO₂CH₂CH₃.

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

71) Provide the major organic product of the following reaction.
72) Provide the major organic product of the following reaction.

```
O
\[
\text{Ph} \quad \text{CH}_3
\]
\[
\text{Br}_2 \quad \text{CH}_3\text{CO}_2\text{H}
\]
```

73) Provide the major organic product of the following reaction.

```
\[
\text{H}_3\text{C} \quad \text{CH}_3
\]
\[
\text{CO}_2\text{H} \quad 1. \text{Br}_2 / \text{PBr}_3
\]
\[
2. \text{H}_2\text{O}
\]
```

**MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.**

74) What type of product results when 3-pentanone is treated with LDA (lithium diisopropylamide) at low temperature?

A) enolate  
B) amide  
C) enamine  
D) enol  
E) imine

75) What type of product results when 3-pentanone reacts with dimethylamine?

A) enamine  
B) enol  
C) amide  
D) imine  
E) enolate

**SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.**

76) Provide the structure of the product which results from the base-catalyzed condensation followed by dehydration between benzophenone and propanal.

```
\[
\text{Ph} \quad \text{CH}_3
\]
\[
\text{CO}_2\text{CH}_2\text{CH}_3
\]
```

77) Provide the structure of the intramolecular aldol condensation/dehydration product that results when 2,6-heptanedione is heated in base.

```
```

78) Provide the structure of the ester that would undergo self-condensation to yield the \(\beta\)-ketoester shown below.

```
\[
\text{Ph} \quad \text{CH}_3
\]
\[
\text{CO}_2\text{CH}_2\text{CH}_3
\]
```
79) Provide the major organic product of the following reactions.  

\[
\begin{array}{c}
\text{CO}_2\text{CH}_3 \\
\text{CO}_2\text{CH}_3 \\
\end{array}
\xrightarrow{1. \text{NaOCH}_3}
\xrightarrow{2. \text{H}_3\text{O}^+}
\begin{array}{c}
\text{CH}_2\text{CH}_3 \\
\end{array}
\]

80) Arrange the following compounds in order of increasing acidity: acetone, ethyl acetoacetate, ethyl acetate, and ethanol.  

81) What organic compounds are produced when 2-pentanone undergoes the haloform reaction upon treatment with HO^- and excess Br_2?  

82) What species results when cyclopentanone is treated with lithium diisopropylamide at low temperature?  

83) Provide the structure of the more stable enol tautomer of 1-phenyl-2-octanone.  

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.  

84) When 2-methylcyclohexanone is treated with catalytic base in excess D_2O, how many deuterium atoms become incorporated in the organic compound?  
A) 5  
B) 3  
C) 0  
D) 2  
E) 1  

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.  

85) Provide the sequence of reagents needed to convert (CH_3CH_2O_2C)CH_2 to heptanoic acid.  

86) Provide the sequence of reagents needed to convert (CH_3CH_2O_2C)CH_2 to 2,5-dimethylhexanoic acid.  

87) Provide the sequence of reagents needed to convert (CH_3CH_2O_2C)CH_2 to cyclopentanecarboxylic acid.  

88) Provide the sequence of reagents needed to convert CH_3CH_2O_2CCH_2COCH_3 to 7-methyl-2-octanone.  

89) Provide the major organic product of the following reaction sequence.  

\[
\begin{array}{c}
\text{CO}_2\text{CH}_3 \\
\end{array}
\xrightarrow{1. \text{NaOCH}_2\text{CH}_3}
\xrightarrow{2. (\text{CH}_3)_2\text{CHCHCH}_2\text{I}}
\xrightarrow{3. \text{H}_3\text{O}^+, \Delta}
\begin{array}{c}
\text{CH}_2\text{CH}_3 \\
\end{array}
\]
90) Provide the structure of the aldol product that results when 5-methylhexanal is treated with hydroxide.

MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

91) Which set of reagents would best accomplish the following transformation?

A) Br₂ / NaOH  B) Br₂ / PBr₃  C) PBr₃  D) Br₂ / HBr

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

92) Draw the major organic product resulting from the reaction conditions shown below.

93) Complete the following short synthesis by providing the necessary sequence of reagents.

94) Predict the outcome of the following reaction.

95) What additional starting material is needed to complete the following transformation?

96) Complete the following synthesis by filling in the missing reagents.
MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question.

97) Which of the following is the best Michael acceptor?
A) \[
\begin{array}{c}
\text{N} \\
\text{H}
\end{array}
\]  
B) \[
\begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\]  
C) \[
\begin{array}{c}
\text{NO}_2
\end{array}
\]  
D) \[
\begin{array}{c}
\text{O} \\
\text{O}_2\text{C}
\end{array}
\]  

SHORT ANSWER. Write the word or phrase that best completes each statement or answers the question.

98) Predict the starting materials necessary for the following Robinson annulation.

\[ \text{starting materials} \xrightarrow{\text{OH}^- \text{ heat}} \text{product} \]
Answer Key
Testname: ENOL_ALL

1)

2)

3)

4) C
5) D
6) D
7) E
8) B
9)

10) C
11)
Answer Key
Testname: ENOL_ALL

12) C
13) B
14) A
15)

16) 1. PBr₃, Br₂
    2. cyclohexylamine
17) A
18)

19)

20) A
21) B
22) D
23) E
24) 2-bromocyclopentanone
25) B
26) D
27) 1. O₃
    2. S(CH₃)₂
    3. NaOH, Δ
28) (CH₃)₃CCCHO and CH₃COCH₃
29) PhCHO and PhCOCH₃
30) D
31) A
32) E
33) Prepare hex-3-ene from propene as follows:
   1. BH₃·THF
   2. H₂O₂, NaOH
   3. PCC
   4. CH₃CH₂CH≡PPh₃

   Prepare the ylide (CH₃CH₂CH≡PPh₃) from propene as follows:
   1. HBr, peroxides
   2. PPh₃
   3. BuLi

34) 1. Br₂, hv or NBS
     2. Ph₃P

35) CH₃CH₂COCH₂CH₃ and CH₃CH≡PPh₃

36) The product β-ketoester is in enolate form. The production of this resonance stabilized enolate is what drives the Claisen condensation. A second ester enolate will not add to the nonelectrophilic product enolate.

37) ![Diagram](image1)

38) 1. KMnO₄, -OH, Δ
     2. H⁺
     3. CH₂N₂ or SOCl₂ followed by CH₃OH
     4. NaOCH₃

39) HCO₂CH₂CH₃ and CH₃CO₂CH₂CH₃

40) ![Diagram](image2)

41) E
42) PhCH₂CH₂CO₂H
43) PhCOC(CH₃)₂CO₂H
44) C
45) B

46) From acetoacetic ester:
   1. NaOEt, EtOH
   2. cyclopent-2-en-1-one
   3. H₃O⁺, Δ
47) Ethyl 2-ethyl-3-oxohexanoate
48) CH₃CH=Ph₃
50) CH₃CH=Ph₃
52) 1. NaOCH₂CH₃, CO(OCH₂CH₃)₂
  2. NaOCH₂CH₃, CH₂=CHCOCH₃
53) 2-acetylcyclohexanone
54) less than 1
55) greater than 1
56) greater than 1
59) 2-ethyl-3-hydroxyhexanal
60) B
61) Carbonyl condensation
62) C
63) E
64) [(CH$_3$)$_2$CH]$_2$N$^-$ Li$^+$
65) Multiple halogenation is a frequent problem in the base-promoted halogenation.
66) E
67)

68) A
69) PhCHO and CH$_3$CHO
70) PhCOCH(CH$_3$)CO$_2$CH$_2$CH$_3$
71)

72)

73)

74) A
75) A
80) ethyl acetate < acetone < ethanol < ethyl acetoacetate
81) butanoate and bromoform
82) the lithium enolate of cyclopentanone
83) 84) B
Answer Key
Testname: ENOL_ALL

85) 1. NaOCH₂CH₃
    2. CH₃(CH₂)₄Br
    3. H₃O⁺, D
86) 1. NaOCH₂CH₃
    2. (CH₃)₂CHCH₂CH₂I
    3. NaOCH₂CH₃
    4. CH₃I
    5. H₃O⁺, D
87) 1. NaOCH₂CH₃
    2. BrCH₂CH₂CH₂CH₂Br
    3. NaOCH₂CH₃
    4. H₃O⁺, D
88) 1. NaOCH₂CH₃
    2. (CH₃)₂CHCH₂CH₂CH₂I
    3. H₃O⁺, D
89) 
\[
\begin{array}{c}
\text{O} \\
\text{CH} \\
\text{CH} \\
\text{CH} \\
\text{CH} \\
\end{array}
\]
90) 
\[
\begin{array}{c}
\text{CHO} \\
\text{HO} \\
\end{array}
\]
91) D
92) 
\[
\begin{array}{c}
\text{HO} \\
\text{O} \\
\end{array}
\]
93) 1) I₂ / NaOH  2) CH₃OH / H⁺ or 2) CH₂N₂
94) 
95) methyl propanoate
96) 1) NaOMe  2) benzyl bromide  3) H₃O⁺, heat
97) C
Answer Key
Testname: ENOL_ALL

98)