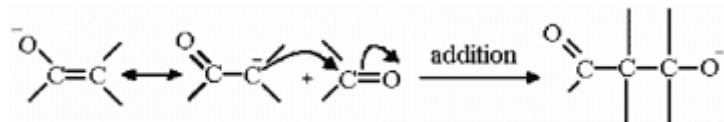


1) Show how an enolate can add to a carbonyl.

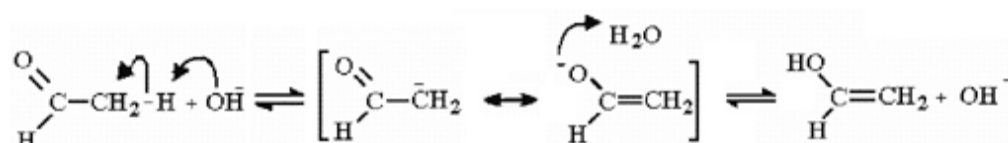
Answer:



Diff: 1

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

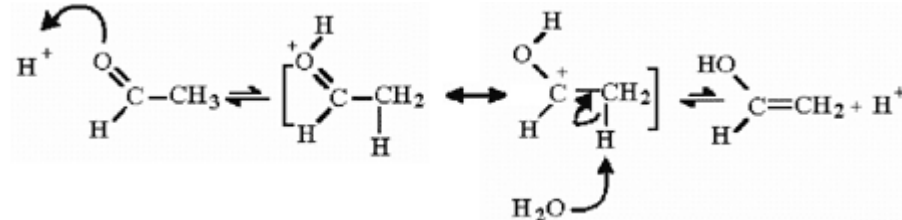
Answer:



Diff: 1

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

Answer:



Diff: 1

4) The relationship between ketones and their corresponding enols is one of:

- A) allotropes.
- B) tautomers.
- C) enantiomers
- D) diastereomers.
- E) cis-trans isomers.

Answer: B

Diff: 1

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) equal to
- C) much higher than
- D) much lower than
- E) exactly half of

Answer: D

Diff: 2

7) Which of the following reagents will quantitatively convert an enolizable ketone to its enolate salt?

- A) lithium hydroxide
- B) lithium diisopropylamide
- C) methyl lithium
- D) diethylamine
- E) pyridine

Answer: B

Diff: 1

8) The α -halogenation of cyclohexanone:

A) is catalyzed by base.

B) is slowed by the presence of acid.

C) requires one equivalent of base.

D) requires one equivalent of acid.

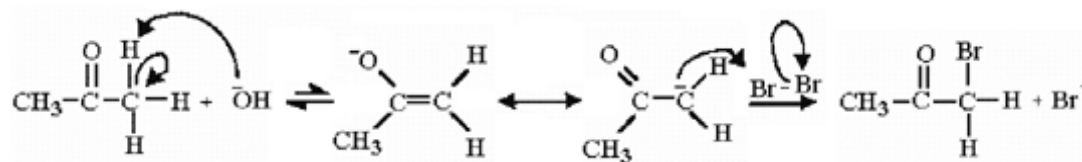
E) is catalyzed by the sodium halide salt.

Answer: C

Diff: 2

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

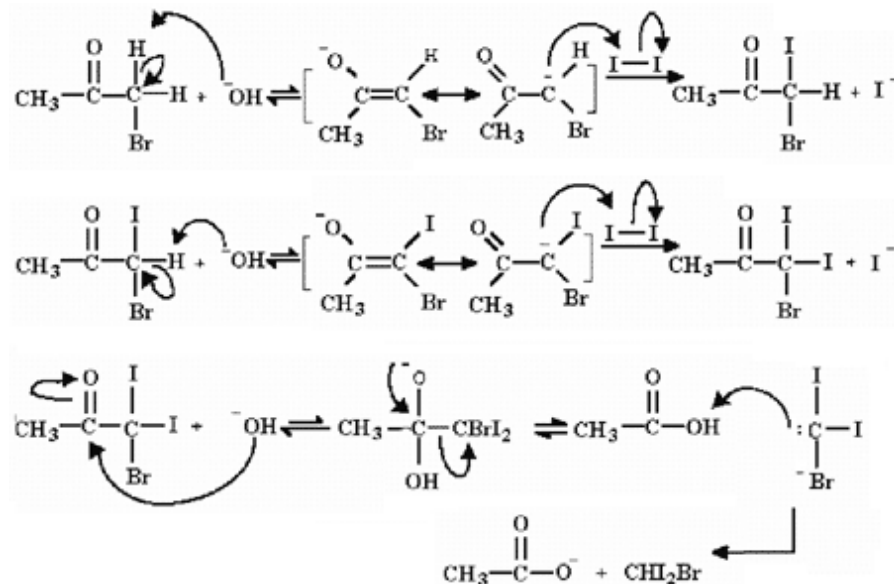
Answer:



Diff: 2

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

Answer:



Diff: 3

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) α -halogenated as well.

B) reduced to alcohols.

C) converted to the acid halide.

D) oxidized to the acid or carboxylate.

E) esterified.

Answer: D

Diff: 2

14) The Hell-Volhard-Zelinsky reaction involves:

A) the α -bromination of carboxylic acids.

B) the α -bromination of ketones.

C) the bromination of alcohols.

D) the oxidation of aldehydes to acids.

E) none of the above.

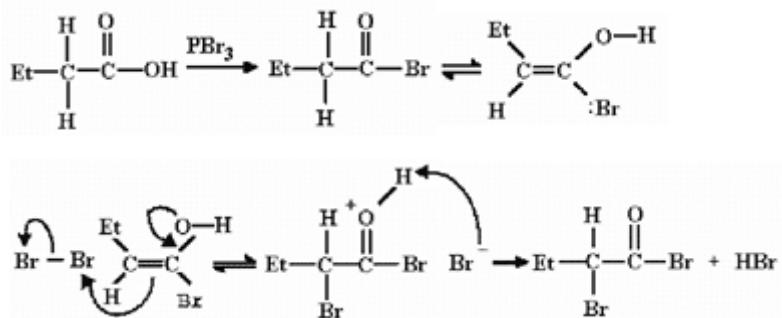
Answer: A

Diff: 1

15) Provide a mechanism for the following reaction:

butanoic acid + Br₂ + PBr₃ → 2-bromobutanoyl bromide

Answer:



Diff: 3

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

Answer: 1. PBr₃, Br₂

2. cyclohexylamine

Diff: 3

17) Which of the following will alkylate a lithium enolate most rapidly?

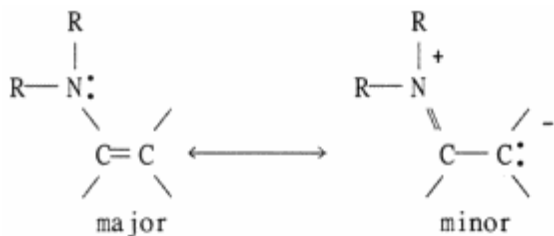
- A) methyl bromide
- B) isopropyl bromide
- C) neopentyl bromide
- D) bromobenzene
- E) 2-methylbromobenzene

Answer: A

Diff: 2

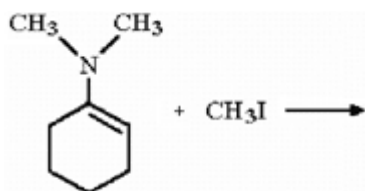
18) What are the two key resonance structures for an enamine? Label the major and minor contributors.

Answer:

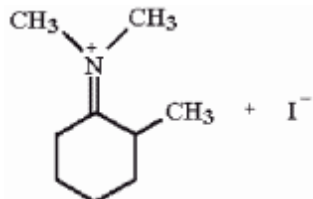


Diff: 2

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



Answer:



Diff: 2

20) Methylamine reacts with acetophenone to yield the:

- A) iminium salt.
- B) imine.
- C) acetal.
- D) amide
- E) enamine.

Answer: B

Diff: 1

21) Which of the following will react most slowly with an enamine?

- A) isopropyl chloride
- B) methyl bromide
- C) acetyl chloride
- D) benzyl chloride
- E) allyl bromide

Answer: A

Diff: 1

22) An enolate attacks an aldehyde and the resulting product is subsequently protonated. What type of reaction is this?

- A) a Fischer esterification
- B) an acid-catalyzed aldol condensation
- C) a base-mediated aldol condensation
- D) a Hell-Volhard-Zelinsky reaction
- E) a Selman-Jones reaction

Answer: C

Diff: 1

23) The aldol condensation is:

- A) an irreversible reaction.
- B) an equilibrium reaction.
- C) a tautomerization.
- D) an isomerization.
- E) a type of esterification.

Answer: B

Diff: 1

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

Answer: 2-bromocyclopentanone

Diff: 1

26) In theory a poorly planned crossed aldol reaction can produce how many different aldol regioisomers?

A) 1

B) 2

C) 3

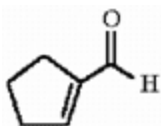
D) 4

E) 5

Answer: D

Diff: 1

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



Answer: 1. O₃

2. S(CH₃)₂

3. NaOH, Δ

Diff: 3

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

Answer: (CH₃)₃CCHO and CH₃COCH₃

Diff: 2

29) What two molecules were condensed in an aldol reaction to produce PhCH=CHCOPh?

Answer: PhCHO and PhCOCH₃

Diff: 2

30) Which of the following is least likely to undergo a smooth crossed Claisen condensation with methyl pentanoate?

A) (CH₃)₃CCO₂CH₃

B) PhCH₂CO₂CH₃

C) PhCO₂CH₃

D) HCO₂CH₃

E) (CH₃O)₂CO

Answer: B

Diff: 2

31) Which of the following is another name for the product of an aldol condensation

- A) β -hydroxyaldehyde
- B) α -hydroxyaldehyde
- C) acetal
- D) β -ketoester
- E) 1,3-dialdehyde

Answer: A

Diff: 2

32) An ylide is a molecule that can be described as a:

- A) carbanion bound to a negatively charged heteroatom.
- B) carbocation bound to a positively charged heteroatom.
- C) carbocation bound to a carbon radical.
- D) carbocation bound to a diazonium ion.
- E) carbanion bound to a positively charged heteroatom.

Answer: E

Diff: 1

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

Answer: Prepare hex-3-ene from propene as follows:

1. $\text{BH}_3 \cdot \text{THF}$
2. H_2O_2 , NaOH
3. PCC
4. $\text{CH}_3\text{CH}_2\text{CH}=\text{PPh}_3$

Prepare the ylide ($\text{CH}_3\text{CH}_2\text{CH}=\text{PPh}_3$) from propene as follows:

1. HBr , peroxides
2. PPh_3
3. BuLi

Diff: 3

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

Answer: 1. Br_2 , $h\nu$ or NBS

2. Ph_3P

Diff: 1

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

Answer: $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}=\text{PPh}_3$

Diff: 2

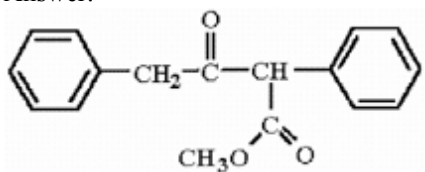
36) A Claisen condensation results in a β -ketoester. Explain why a second ester enolate does not add to this β -ketoester.

Answer: 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.

Diff: 3

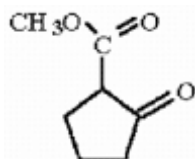
37) Provide the structure of the Claisen product in the self condensation of methyl phenylacetate.

Answer:



Diff: 2

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



Answer: 1. KMnO_4 , $-\text{OH}$, Δ

2. H^+

3. CH_2N_2 or SOCl_2 followed by CH_3OH

4. NaOCH_3

Diff: 3

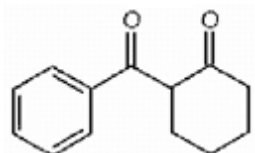
39) What two starting materials yield $\text{OHCCH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ as the crossed Claisen condensation product?

Answer: $\text{HCO}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$

Diff: 2

40) What product is formed in the crossed Claisen condensation between methyl benzoate and cyclohexanone?

Answer:



Diff: 2

41) Which of the following is most acidic?

A) acetone

B) ethyl acetate

C) malonic ester

D) acetoacetic ester

E) acetaldehyde

Answer: D

Diff: 2

42) What product results when malonic ester is treated with the following sequence of reagents:

1. $\text{NaOCH}_2\text{CH}_3$; 2. PhCH_2Br ; 3. H_3O^+ , Δ ?

Answer: $\text{PhCH}_2\text{CH}_2\text{CO}_2\text{H}$

Diff: 2

43) When compound X is heated, $\text{PhCOCH}(\text{CH}_3)_2$ and CO_2 are produced. Offer a structure for compound X.

Answer: $\text{PhCOC}(\text{CH}_3)_2\text{CO}_2\text{H}$

Diff: 3

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.

Answer: C

Diff: 1

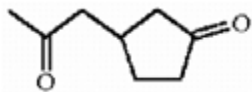
45) Which of the following is a nucleophile that does conjugate additions?

- A) $\text{CH}_2=\text{CHCHO}$
- B) $\text{CH}_2=\text{CHCN}$
- C) $\text{CH}_2=\text{CHCO}_2\text{CH}_3$
- D) $\text{CH}_3\text{CH}_2\text{MgBr}$
- E) $(\text{CH}_3)_2\text{CuLi}$

Answer: E

Diff: 1

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



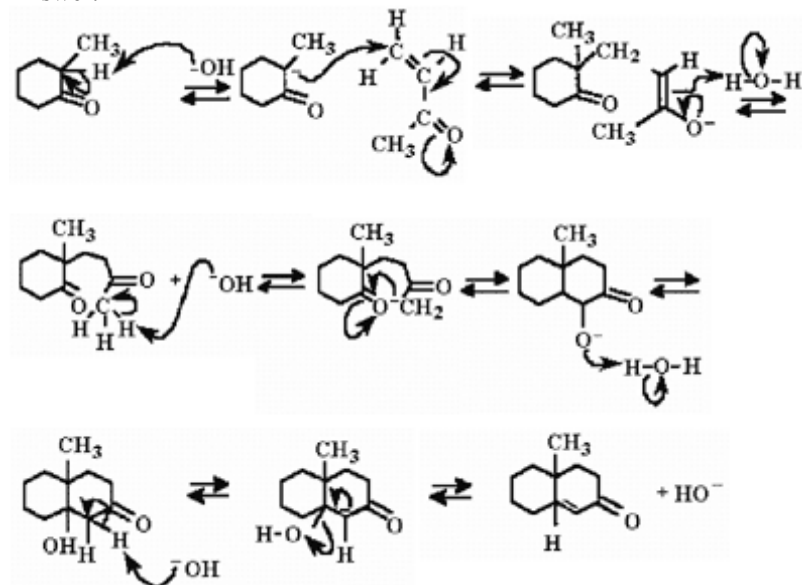
Answer: From acetoacetic ester:

1. NaOEt , EtOH
2. cyclopent-2-en-1-one
3. H_3O^+ , Δ

Diff: 3

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

Answer:



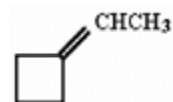
Diff: 3

48) Name the product which results when ethyl butanoate is treated with sodium ethoxide.

Answer: Ethyl 2-ethyl-3-oxohexanoate

Diff: 3

49) Provide the single reagent necessary for the conversion of cyclobutanone to the compound shown below.

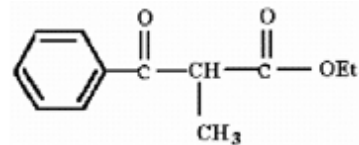


Answer: $\text{CH}_3\text{CH}=\text{PPh}_3$

Diff: 1

50) Provide the structure of the major organic product which results when $\text{PhCO}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ are heated in the presence of sodium ethoxide and the compound generated is subsequently treated with cold, dilute acid.

Answer:



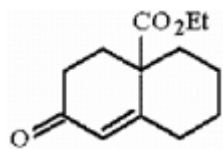
Diff: 2

51) Provide the structure of the major organic product which results when $\text{CH}_3\text{CH}_2\text{I}$ is treated with PPh_3 and the resulting salt is reacted with one equivalent of butyllithium.

Answer: $\text{CH}_3\text{CH}=\text{PPh}_3$

Diff: 1

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

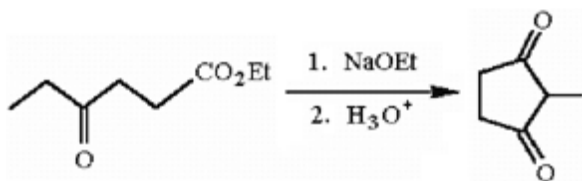


Answer: 1. NaOCH₂CH₃, CO(OCH₂CH₃)₂

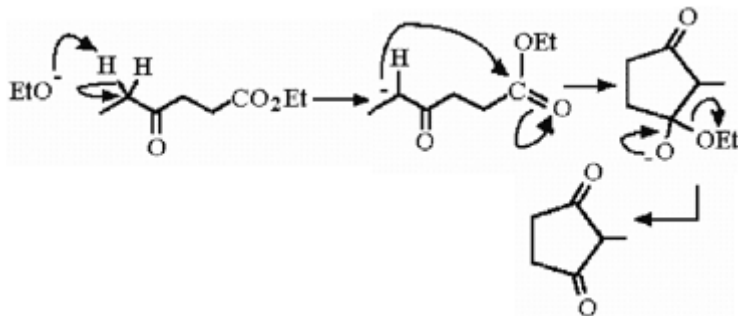
2. NaOCH₂CH₃, CH₂=CHCOCH₃

Diff: 3

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

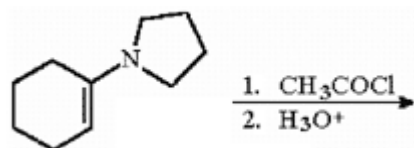


Answer:



Diff: 3

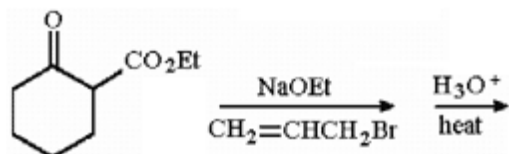
54) Provide the major organic product of the reaction shown below.



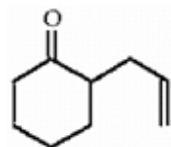
Answer: 2-acetylcyclohexanone

Diff: 2

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

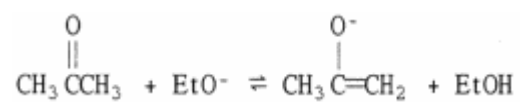


Answer:



Diff: 2

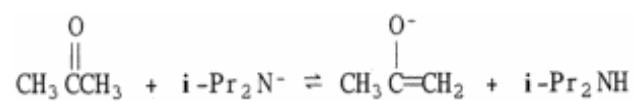
56) For the equilibrium shown below, is the K_{eq} greater or less than 1?



Answer: less than 1

Diff: 2

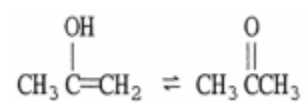
57) For the equilibrium shown below, is the K_{eq} greater or less than 1?



Answer: greater than 1

Diff: 2

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

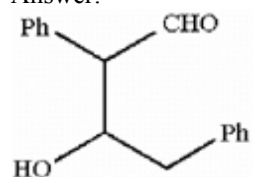


Answer: greater than 1

Diff: 1

67) Provide the structure of the major organic product which results when PhCH_2CHO is treated with NaOH .

Answer:



Diff: 2

68) What product results when an aldol is dehydrated?

- A) conjugated alkyne
- B) β -diketone
- C) β -ketoester
- D) α,β -unsaturated aldehyde
- E) β,γ -unsaturated aldehyde

Answer: D

Diff: 2

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

Answer: PhCHO and CH_3CHO

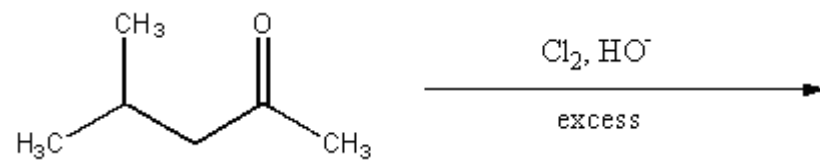
Diff: 2

70) Provide the structure of the product of the crossed Claisen condensation between $\text{PhCO}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3$.

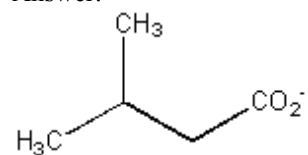
Answer: $\text{PhCOCH}(\text{CH}_3)\text{CO}_2\text{CH}_2\text{CH}_3$

Diff: 2

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

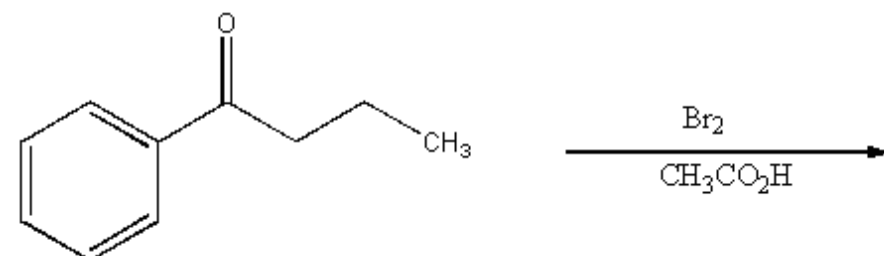


Answer:

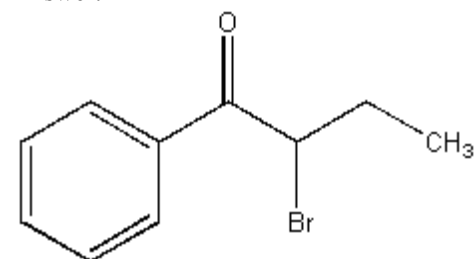


Diff: 2

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

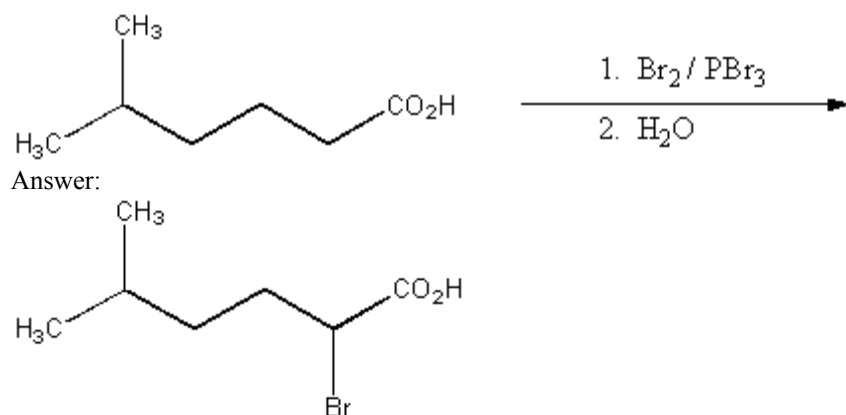


Answer:



Diff: 2

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



Diff: 2

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

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

Answer: A

Diff: 2

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

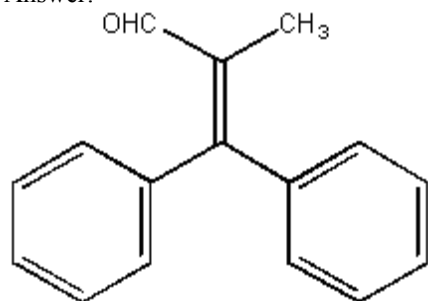
- A) enolate
- B) enol
- C) amide
- D) imine
- E) enamine

Answer: E

Diff: 2

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

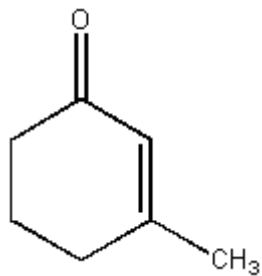
Answer:



Diff: 2

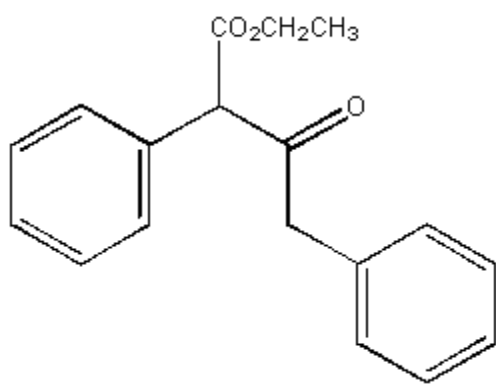
77) Provide the structure of the intramolecular aldol condensation/dehydration product that results when 2,6-heptanedione is heated in base.

Answer:

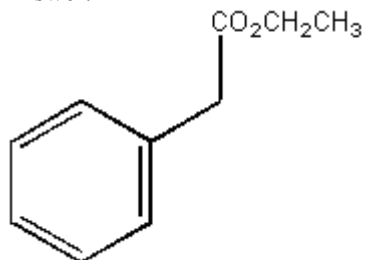


Diff: 2

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

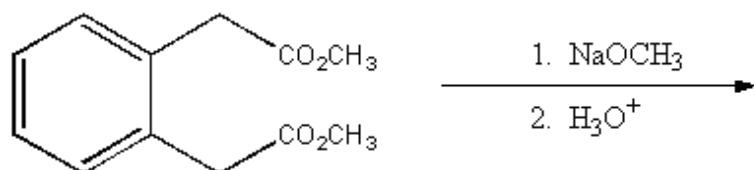


Answer:

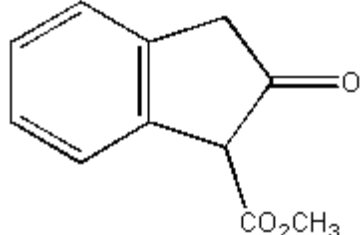


Diff: 2

79) Provide the major organic product of the following reactions.



Answer:



Diff: 2

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

Answer: ethyl acetate < acetone < ethanol < ethyl acetoacetate

Diff: 3

81) What organic compounds are produced when 2-pentanone undergoes the haloform reaction upon treatment with HO⁻ and excess Br₂?

Answer: butanoate and bromoform

Diff: 2

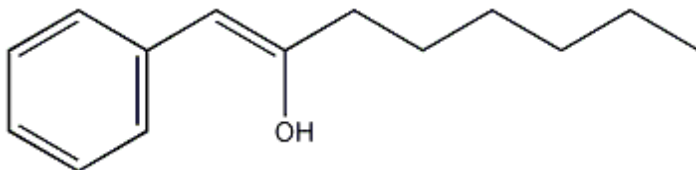
82) What species results when cyclopentanone is treated with lithium diisopropylamide at low temperature?

Answer: the lithium enolate of cyclopentanone

Diff: 2

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

Answer:



Diff: 2

84) When 2-methylcyclohexanone is treated with catalytic base in excess D₂O, how many deuterium atoms become incorporated in the organic compound?

A) 0

B) 1

C) 2

D) 3

E) 5

Answer: D

Diff: 2

85) Provide the sequence of reagents needed to convert $(\text{CH}_3\text{CH}_2\text{O}_2\text{C})_2\text{CH}_2$ to heptanoic acid.

Answer: 1. $\text{NaOCH}_2\text{CH}_3$

2. $\text{CH}_3(\text{CH}_2)_4\text{Br}$

3. H_3O^+ , D

Diff: 2

86) Provide the sequence of reagents needed to convert $(\text{CH}_3\text{CH}_2\text{O}_2\text{C})_2\text{CH}_2$ to 2,5-dimethylhexanoic acid.

Answer:

1. $\text{NaOCH}_2\text{CH}_3$

2. $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{I}$

3. $\text{NaOCH}_2\text{CH}_3$

4. CH_3I

5. H_3O^+ , D

Diff: 2

87) Provide the sequence of reagents needed to convert $(\text{CH}_3\text{CH}_2\text{O}_2\text{C})_2\text{CH}_2$ to cyclopentanecarboxylic acid.

Answer:

1. $\text{NaOCH}_2\text{CH}_3$

2. $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$

3. $\text{NaOCH}_2\text{CH}_3$

4. H_3O^+ , D

Diff: 2

88) Provide the sequence of reagents needed to convert $\text{CH}_3\text{CH}_2\text{O}_2\text{CCH}_2\text{COCH}_3$ to 7-methyl-2-octanone.

Answer:

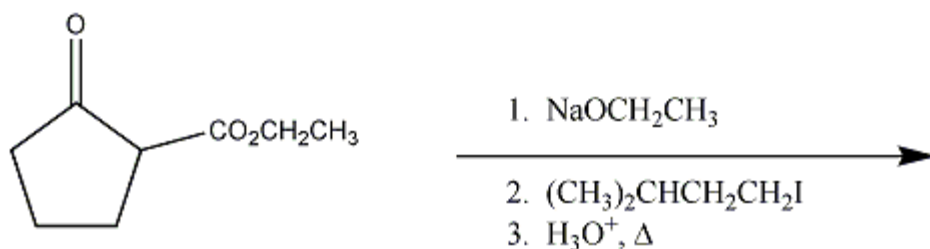
1. $\text{NaOCH}_2\text{CH}_3$

2. $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{I}$

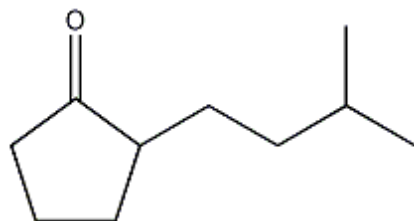
3. H_3O^+ , D

Diff: 2

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



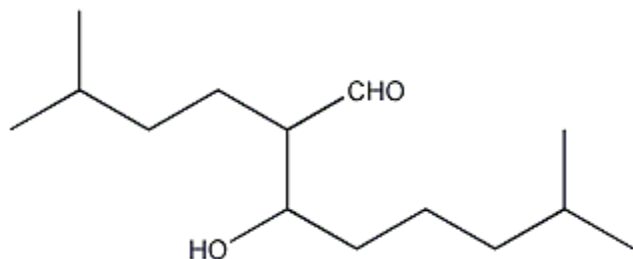
Answer:



Diff: 2

90) Provide the structure of the aldol product that results when 5-methylhexanal is treated with hydroxide.

Answer:



Diff: 2

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

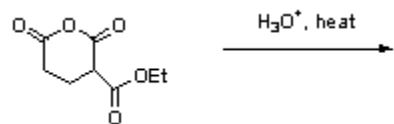


- A) Br_2 / HBr
- B) $\text{Br}_2 / \text{PBr}_3$
- C) $\text{Br}_2 / \text{NaOH}$
- D) PBr_3

Answer: A

Diff: 2

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



Answer:



Diff: 3

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



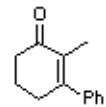
Answer: 1) I_2 / NaOH 2) $\text{CH}_3\text{OH} / \text{H}^+$ or 2) CH_2N_2

Diff: 3

94) Predict the outcome of the following reaction.



Answer:



Diff: 3

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



Answer: methyl propanoate

Diff: 2

96) Complete the following synthesis by filling in the missing reagents.

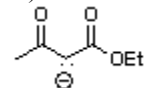


Answer: 1) NaOMe 2) benzyl bromide 3) H_3O^+ , heat

Diff: 3

97) Which of the following is the best Michael acceptor?

A)



B)



C)



D)



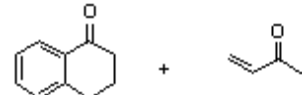
Answer: D

Diff: 3

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



Answer:



Diff: 3