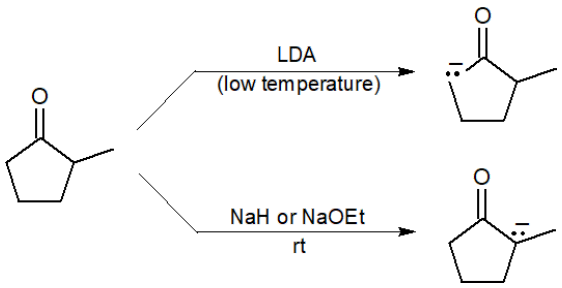
23.13: SOLUTIONS TO ADDITIONAL EXERCISES

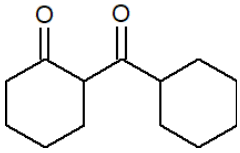
General Review

23-1



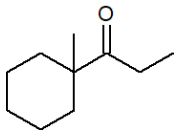
When a bulky base, such as LDA, is used, it will almost always deprotonate the least hindered position. In this case, the reaction is performed under low temperatures (to prevent the thermodynamic product from forming) and we get the kinetic product. When we use a strong base that is not bulky, it will favor deprotonating the position that will provide the most stable product at equilibrium. As a result, the enolate that forms when using NaH or NaOEt is more substituted and more stable.

23-2

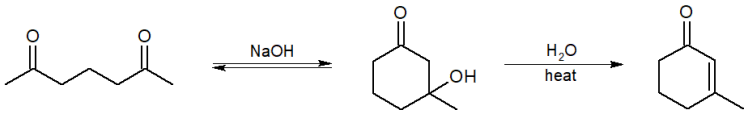


23-3 When acetophenone is halogenated at the α-position, the α-carbon becomes more acidic as a result of the electron-withdrawing halogen. This makes it more likely to go through α-halogenation again, until it no longer has any α-protons. When the base performs a nucleophilic attack on the ketone, the triiodomethyl group becomes a good leaving group. The resulting products are sodium benzoate and triiodomethane.

23-4



23-5



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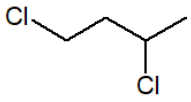
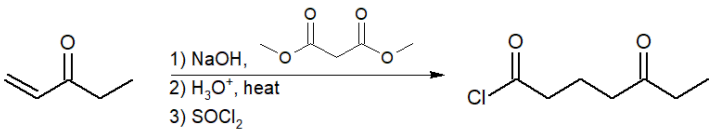


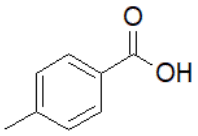
23-7



Enols and Enolate Ions

23-8:

Answer: B



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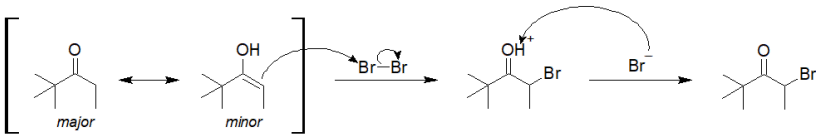

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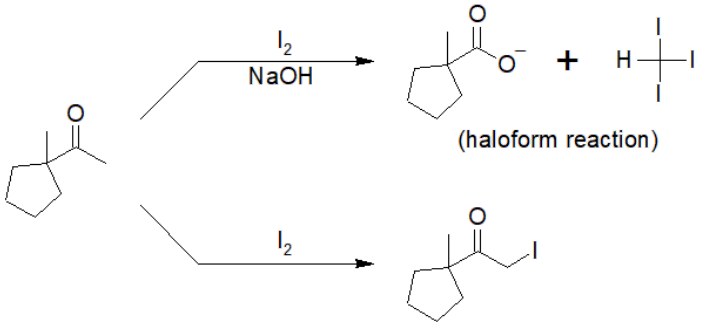
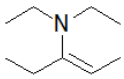


Formation and Alkylation of Enamines

23-11:

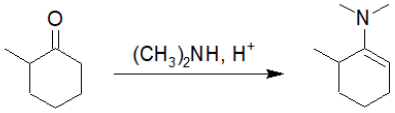
Answer: A



(2*Z*)-*N*,*N*-diethylpent-2-en-3-amine

23-12:

a)



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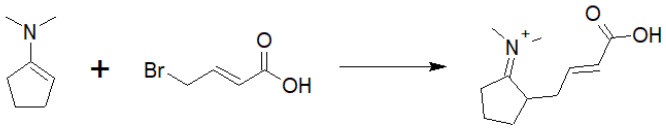

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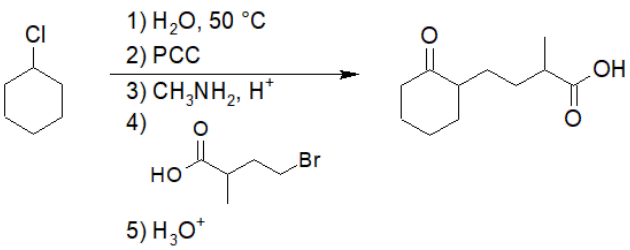
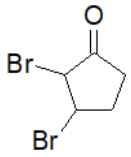


Alpha Halogenation of Ketones

23-14:



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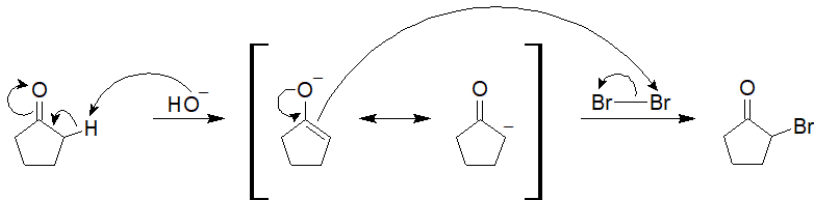
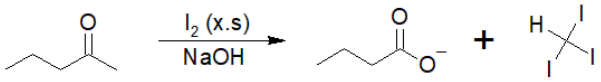


23-16:

a)



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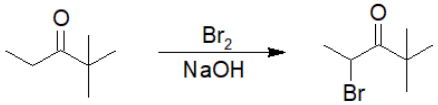

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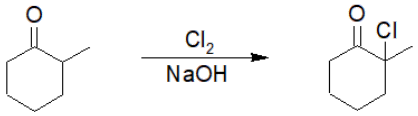
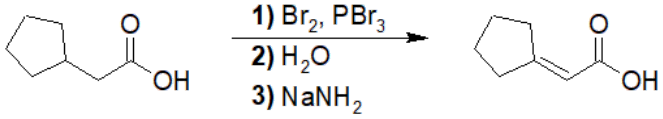


Alpha Bromination of Acids: The HVZ Reaction

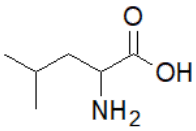
23-17:



23-18:

Answer: B

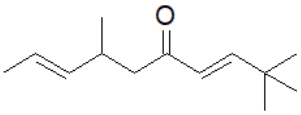
23-19:



2-amino-4-methylpentanoic acid
(also known as the amino acid Leucine)

The Aldol Condensation of Ketones and Aldehydes

23-20:



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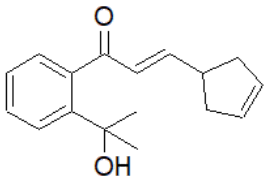

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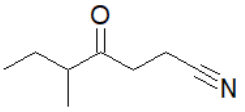
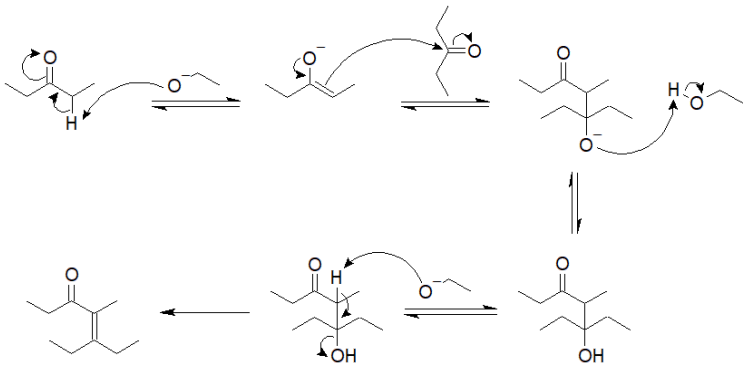


Dehydration of Aldol Products

23-23:

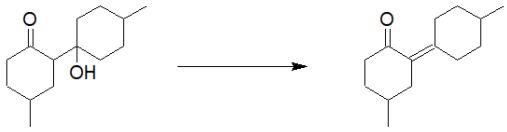
Answer: B

23-24:



23-25:

a)



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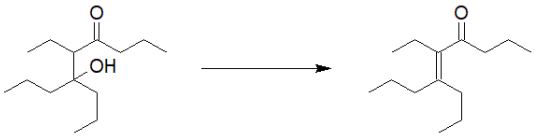

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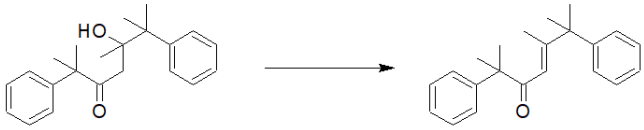
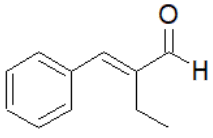


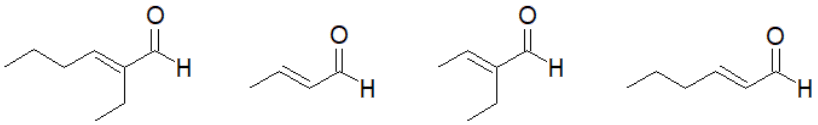
Crossed Aldol Condensations

23-26:



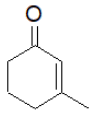
23-27:

23-28:



Aldol Cyclizations

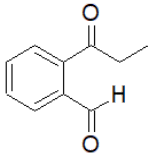
23-29:



3-methylcyclohex-2-en-1-one

23-30:

a)



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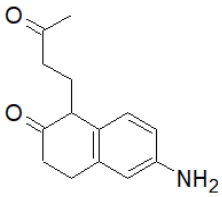
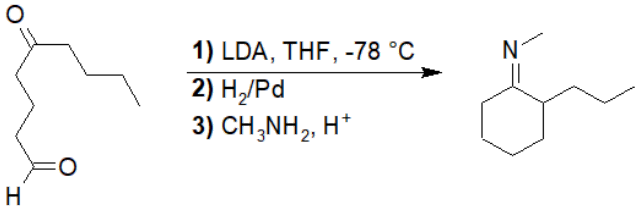


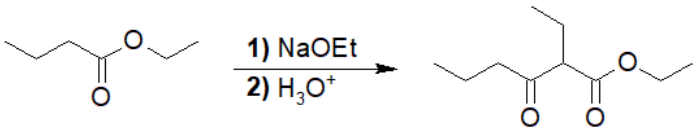
23-31:

Several answers possible. One plausible method of synthesis:



Claisen Condensations

23-32:



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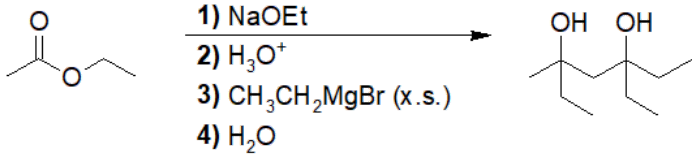
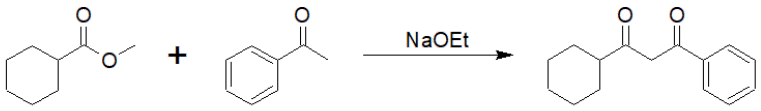


23-34:

a)



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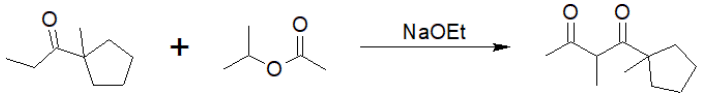
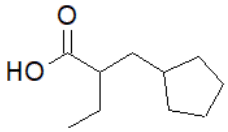


Syntheses Using *β*-Dicarbonyl Compounds

23-35:



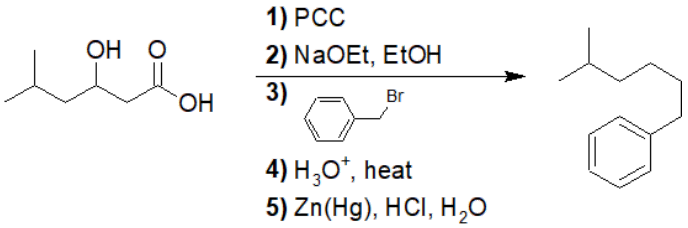
2-(cyclopentylmethyl)butanoic acid

23-36:

Answer: B

23-37:

Possible route of synthesis:

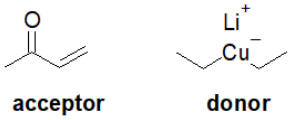


Conjugate Additions: The Michael Reaction

23-38:

Michael acceptors are generally α,β-unsaturated ketones; however, aldehydes or acid derivatives can also function as acceptors. Michael donors are weak bases/strong nucleophiles.

a)

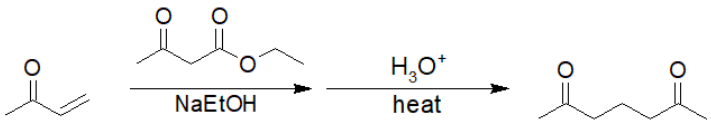


acceptor **donor**

b)

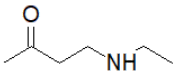
donor **acceptor**

23-39:



23-40

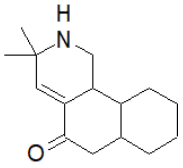
Answer: C



4-(ethylamino)butan-2-one

The Robinson Annulation

23-41:



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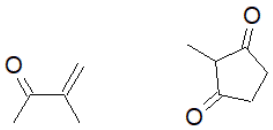

acceptor donor

23-43: