CHM 234, Spring 2017

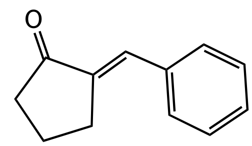
QUIZ #12   ANSWER KEY

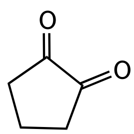
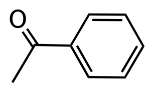
(hit the RETURN Button to return to the Main Quiz Page)

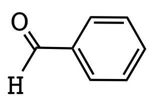
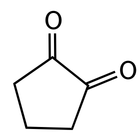
QUESTION 1

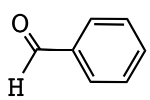
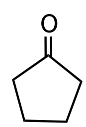
MC34r

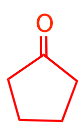
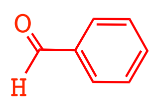
The following Aldol condensation product was formed by reaction of an enolate anion and a carbonyl compound in the presence of heat. Identify the structure that provided the enolate anion and the structure that was the Lewis acid (electrophile) in the enolate addition step.



A  → Enolate  = Electrophile/ Lewis acid

B  → Enolate  = Electrophile/ Lewis acid

C  → Enolate  = Electrophile/ Lewis acid

D  → Enolate  = Electrophile/ Lewis acid

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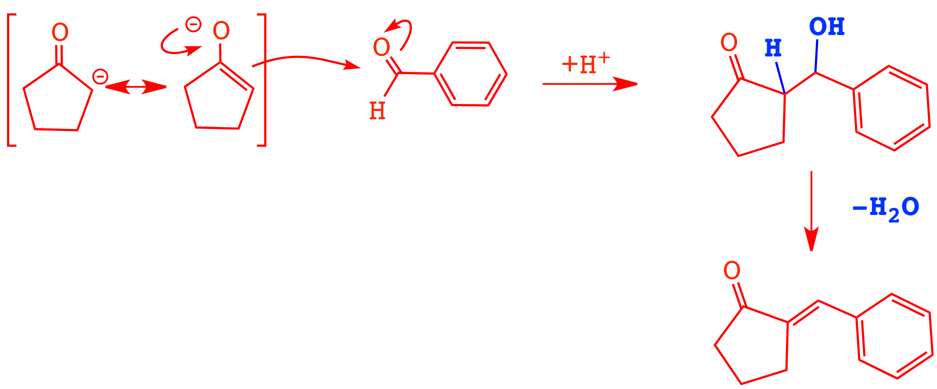
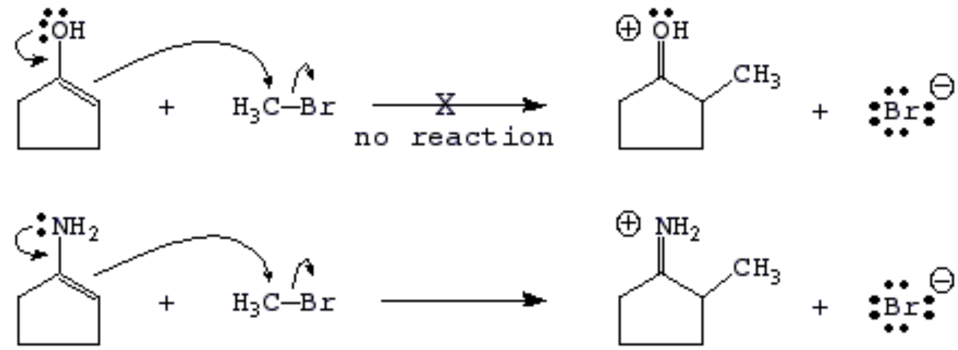


QUESTION 2

MC34n

Which is the most correct statement?



A an enol is a stronger nucleophile than an enamine because oxygen is more electronegative than nitrogen

B an enol is a weaker nucleophile than an enamine because oxygen is more electronegative than nitrogen

C an enol is a stronger nucleophile than an enamine because oxygen is less electronegative than nitrogen

D an enol is a weaker nucleophile than an enamine because oxygen is less electronegative than nitrogen

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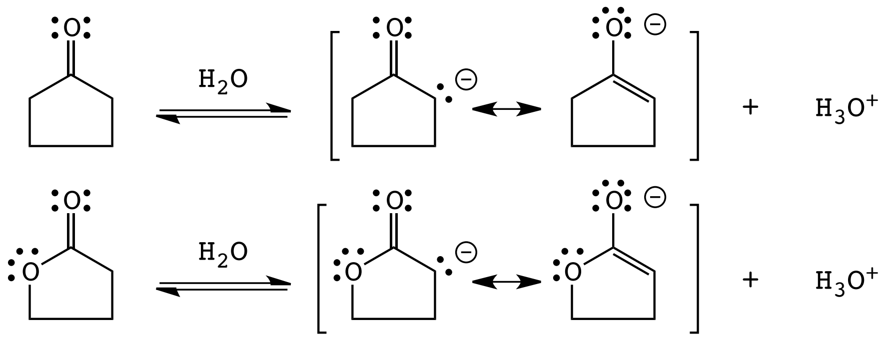
oxygten is more electronegative than nitrogen, the non-bondong electrons on oxygen are thus lower in energy, they are less donating to the C=C bond, which is thus less reactive, the enol is a weaker nucleohile, sufficiently weak that it will not do an SN2 reaction with an alkyl halide, this reaction DOES occur for the more nucleophilic enamone however

QUESTION 3

MC34m

Whish is the most correct statement?



A an ester is a stronger Bronsted acid than a ketone because the oxygen in the α-position to the C=O bond is electron donating

B an ester is a stronger Bronsted acid than a ketone because the oxygen in the α-position to the C=O bond is electron withdrawing

C an ester is a weaker Bronsted acid than a ketone because the oxygen in the α-position to the C=O bond is electron donating

D an ester is a weaker Bronsted acid than a ketone because the oxygen in the α-position to the C=O bond is electron withdrawing

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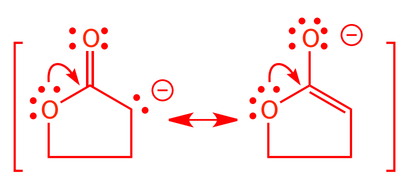
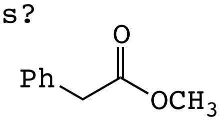


the oxygen is electron donating and thus destabilizes the anion in the 3 atom π-system, makes the anion harder to form, makes the conjugate base of the ester a stronger base, makes the ester a weaker Bronsted acid

QUESTION 4

MC34k

How many enolizable hydrogens does the following structure possess?



A 0

B 1

C 2

D 3

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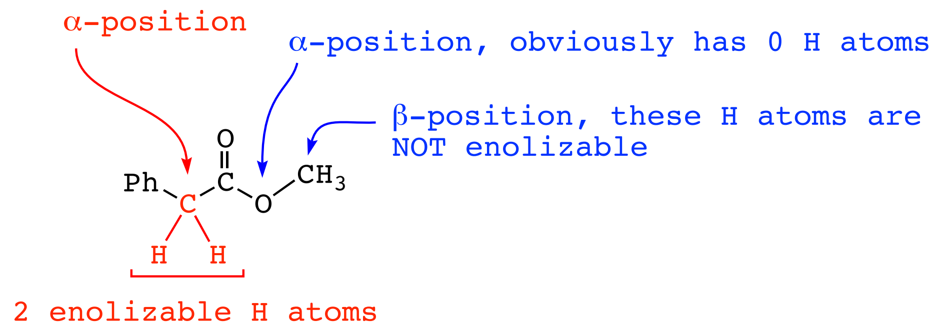
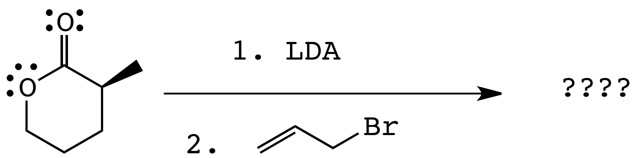
enolizable hydrogens are those in the α-position, i.e. directly adjacent to the carbonyl group (C=O bond)



QUESTION 5

MC34g

Which best characterizes the product of the following reaction sequence?

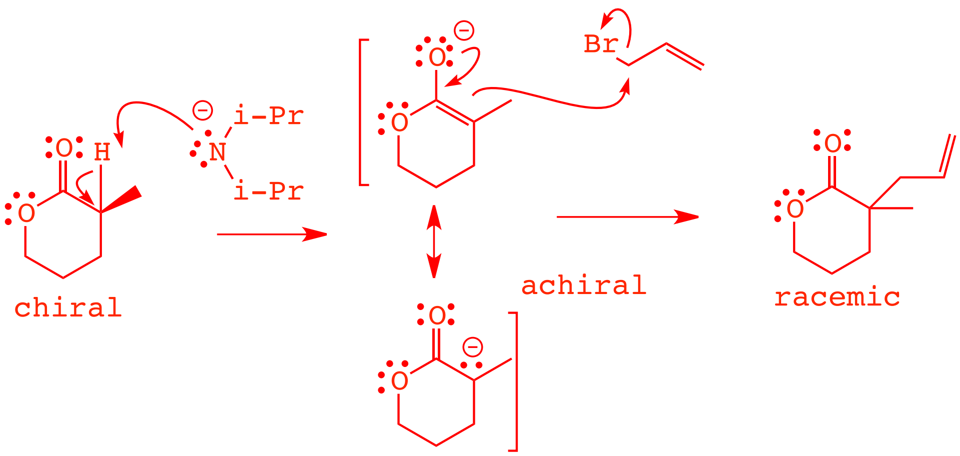


A Chiral

B Achiral

C Meso Compound

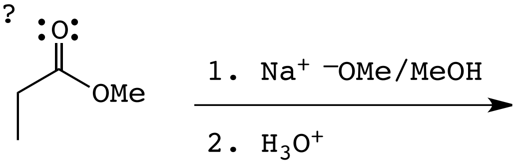
D Racemic Mixture

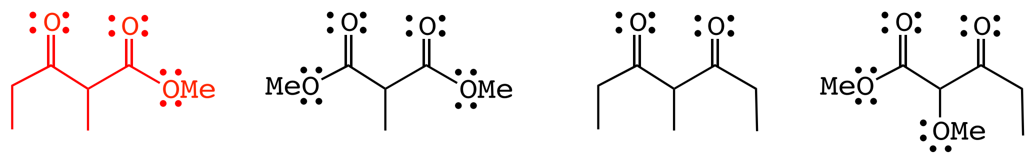


QUESTION 6

MC34p

Which is the product of the Calisen reaction of the following ester?





A B C D

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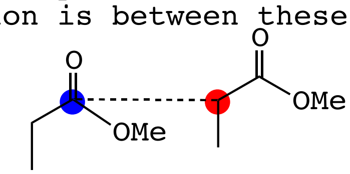
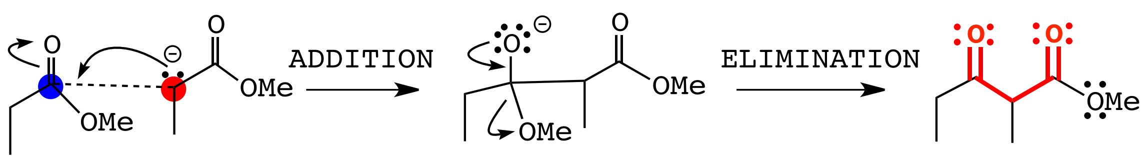
in the Claisen reaction, the nucleophilic carbon is indicated in red and the electrophilic carbon in blue, the critical C-C bond forming reaction is between these 2 carbons



the nucleophile is derived from the enolate anion of the ester, but the key point that ADDITION/ELIMINATION occurs, in common with all string nucleophile additions to esters (Grignards, acetylides, hydrides etc.)

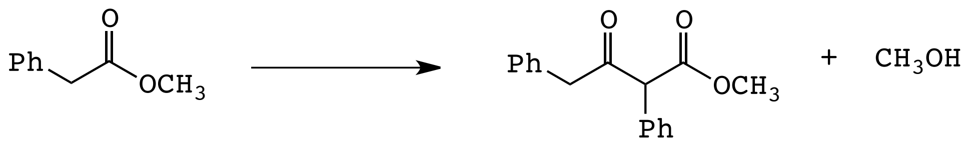


not included above is the deprotonation step that makes teh Claisen reaction irreversible, but for the presnt purposes the key structural feature of the Claisen product is the **β-dicarbonyl shown in red above**

QUESTION 7

MC34j

Using the provided bond dissociation energies, which is the enthalpy of the following reaction? (hint, calculate the energy cost of breaking the relevant bonds and calculate the energy gain from making the relevant bonds. I am not going to tell you if a positive enthalphy of reaction is endothermic or exothermic, you are supposed to know that by now!)



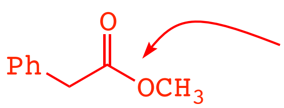
Bond	BDE (kcal/mol)
C—C	85
C—O	91
RO—H	102
C—H	99

A 9 kcal/mol

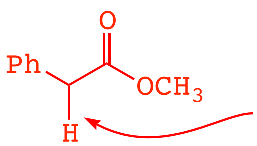
B 3 kcal/mol

C -9 kcal/mol

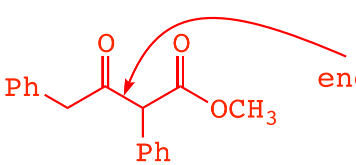
D -3 kcal/mol



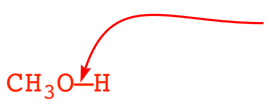
costs 91 kcal/mol to break this bond



costs 99 kcal/mol to break this bond



energy gain making this bond 85 kcal/mol



energy gain making this bond 102 kcal/mol

total enthalphy cost = (91 + 99) = 190 kcal/mol

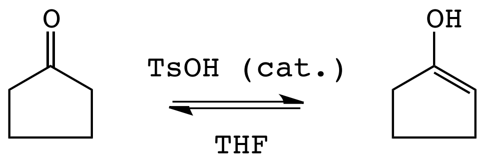
total enthalphy gain = (85 + 102) = 187 kcal/mol

reaction costs 3 kcal/mol overall, therefore the reaction is ENDOTHEMRMIC, thus reaction enthalpy is POSITIVE 3 kcal/mol

QUESTION 8

MC341

Which best describes the following equilibrium?



A equilibrium lies of the left because the C=O bond is stronger than the C=C bond

B equilibrium lies on the right because the C=O bond is stronger than the C=C bond

C equilibrium lies of the left because the C=C bond is stronger than the C=O bond

D equilibrium lies on the right because the C=C bond is stronger than the C=O bond