CHEMISTRY 66H
Exam 2
M.T. Crimmins
March 8, 2001

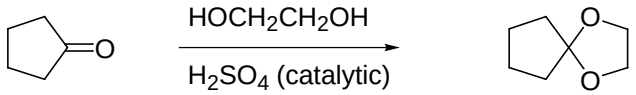
Name_____**KEY**_____

Pledge: I have neither given nor received aid on this exam.

Signature_____MTC_____

I. Predict the major organic product of the following reactions. Be sure to indicate stereochemistry where approapriate. 5 points each

1.



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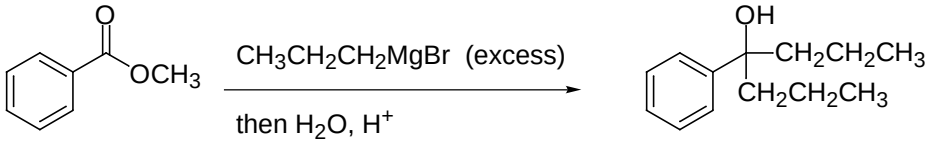

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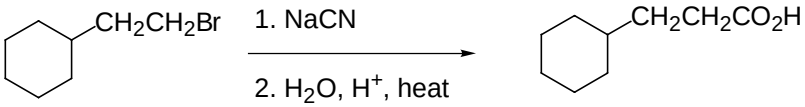

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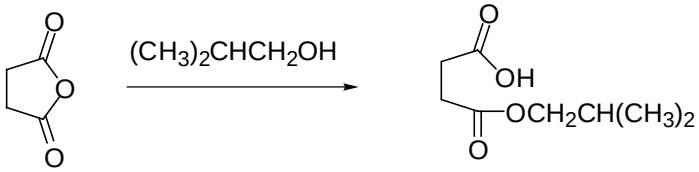

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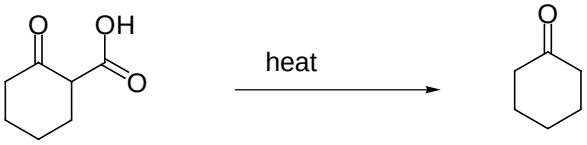

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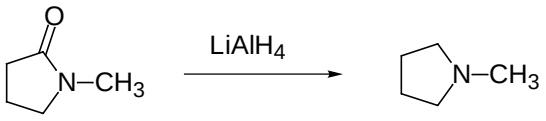

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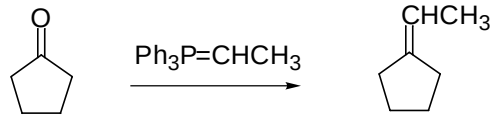

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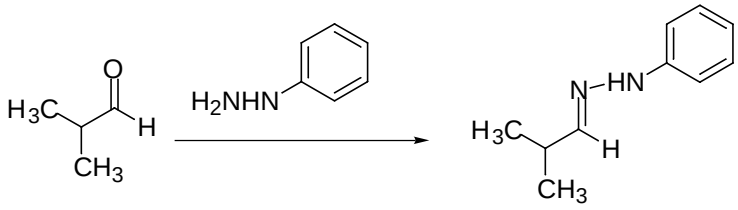

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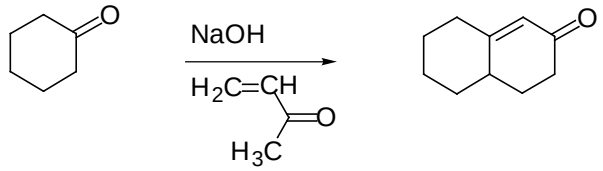

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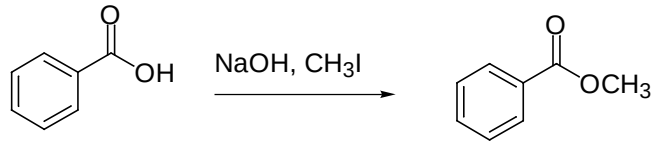
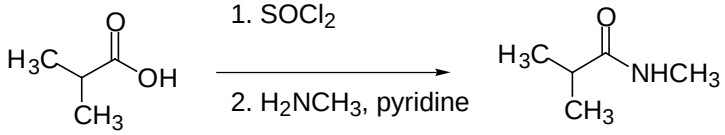


Give reagents to carry out the following transformations. Some may require more than one step. 5 points each

11.



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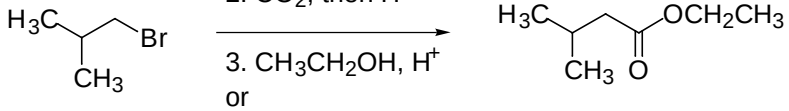
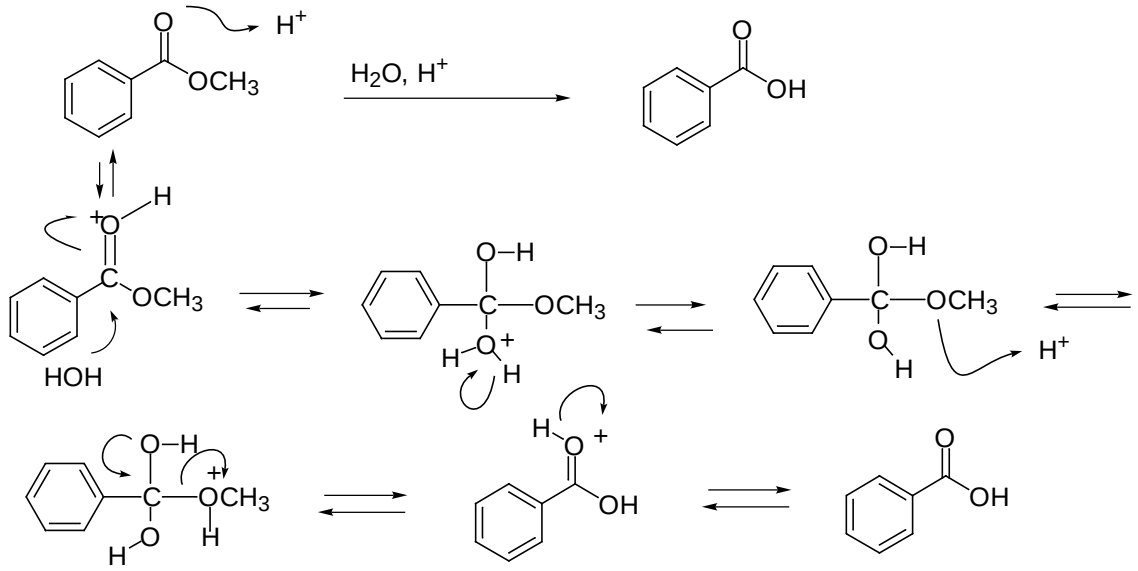


or

1. NaCN 2. H_2O, H^+, heat 3. CH_3CH_2OH, H^+

Give a stepwise, detailed mechanism with arrows and intermediates for each of the following reactions. 6 points each).

13.



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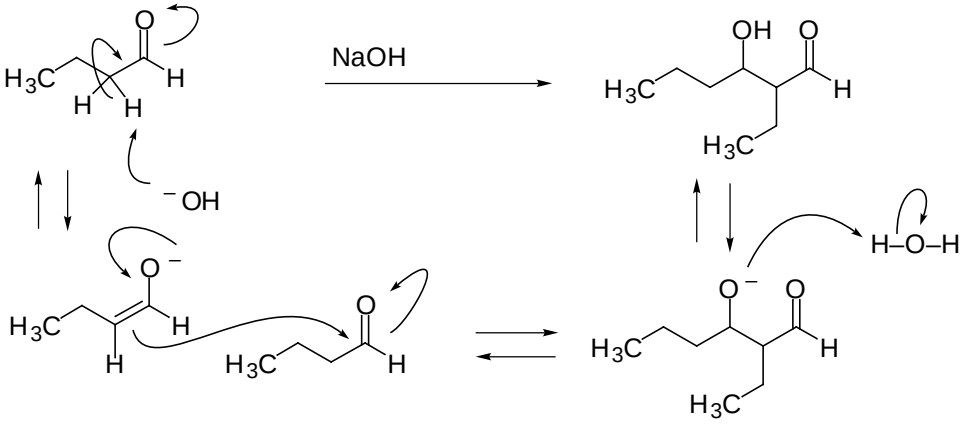

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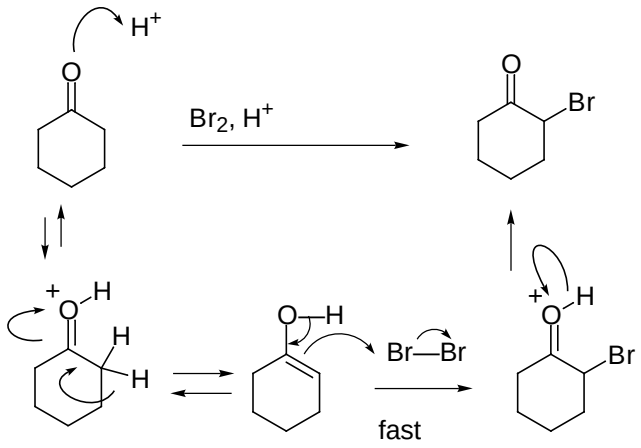
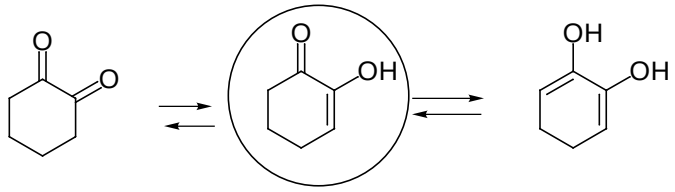
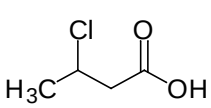


16. Draw all the possible tautomers for 1,2-cyclohexanedione. Circle the favored tautomer and briefly explain why it is favored. (6 points).

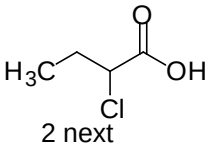


most stable because the enol OH can hydrogen bond to the other carbonyl and the enol double bond is conjugated to the C=O double bond

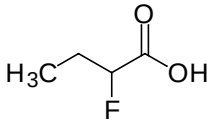
17. Rank the following acids in order of decreasing acidity (1 = most, 2 = next, 3 = least acidic) and briefly explain. (5 points).



3 least



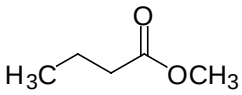
2 next



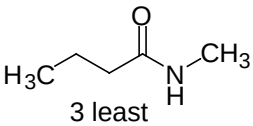
1 most

flourine is more electronegative than chlorine so has a greater inductive effect at the alpha position for stabilizing the conjugate base (carboxylate) . As the chlorine is moved further away from the baxoylic acid group, it has a lesser inductive effect and the acid is less acidic.

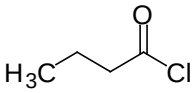
18. Rank the following in order of decreasing reactivity toward nucleophilic attack. (1 = most, 2 = next, 3 = least acidic) and briefly explain. (5 points).



2 next



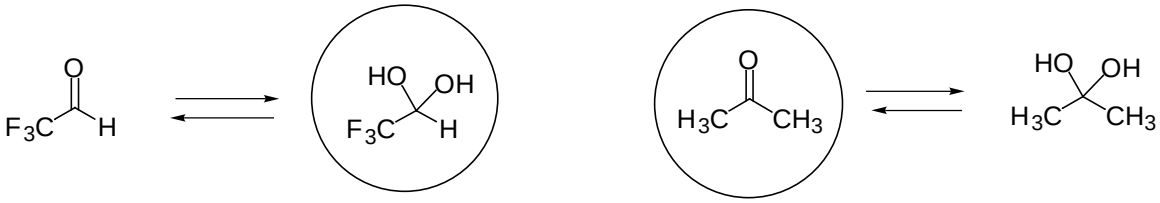
3 least



1 most

rate of attack depends on the leaving group ability (its basicity) and the positive charge on the carbonyl carbon. chloride is a weaker base than alkoxide is a weaker base than amide. also, inductively, since nitrogen is less electronegative, it donates more electron density to the carbonyl carbon through resonance donoation of its lone pair. Oxygen donates better than chlorine since its size is more similar to carbon than is chlorine.

19. Consider the reactions below. In each case, circle the species which will predominate at equilibrium and briefly explain. (6 points).



The more highly positive the carbonyl carbon, the more the hydrate is favored since the carbonyl is destabilized. Also, the more stereically hindered the carbonyl, the less favored is the hydrate do to steric interactions. So, in triflouroacetaldehyde, the hydrate is more favored because of a very electrophilic carbonyl and a relatively unhindered hydrate. Conversely, in acetone, the ketone is favored since the two methyl groups donate electron density to reduce the positive charge on the carbonyl carbon and the hydrate is sterically disfavored.