CHEM 343 – Principles of Organic Chemistry II – Summer 2014

Instructor: Paul J. Bracher

Quiz #3

Monday, July 21st, 2014

10:30 a.m. (in class)

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

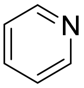
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded.
- You may use any resources you wish and collaborate with others.
- Your quiz answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		28
II		21
III		21
IV		30
TOTAL		100

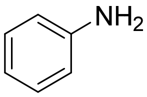
Questions, Required Information, Supplementary Information

Problem I. Multiple choice (28 points total; +4 points for a correct answer, +1 point for an answer intentionally left blank, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

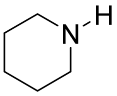
(1) C Which of the following compounds is the strongest Brønsted–Lowry base?



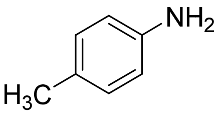
(a)



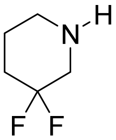
(b)



(c)



(d)



(e)

It helps to approach the problem of determining the strongest base by analyzing which of the lone pairs is the most electron-rich and available to complex with a proton. Choices (b) and (d) are relatively weak bases because the lone pair is conjugated with the aromatic ring. Choice (a) is also a relatively weak base because the lone pair is in an sp^2 orbital vs. sp^3 orbitals for choices (c) and (e). Orbitals with more *s* character place the electron density of the lone pair closer to the nucleus, where it is less available to act as a base. In comparing choices (c) and (e), (e) is a weaker base because the highly electronegative fluorine atoms remove electron density from the nearby nitrogen atom by an inductive effect.

(2) D For which of the following reactions would HCl not serve the role of a catalyst in aqueous solution?

- (a) hydrolysis of 2,2-dimethoxypropane (the dimethyl acetal of acetone)
- (b) hydrolysis of ethyl acetate (an ester)
- (c) isomerization of acetone to its enol tautomer
- (d) hydrolysis of *N*,*N*-dimethylacetamide (a tertiary amide)
- (e) hydrolysis of acetic anhydride (an acid anhydride)

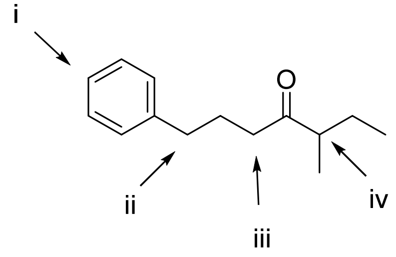
Aqueous acid will effect all of these transformations, but for the hydrolysis of an amide, HCl serves as a stoichiometric reagent rather than a catalyst. One of the products of this reaction, an amine, is a good base and will consume one equivalent of HCl.

(3) A Which of the following sets of reagents will generate the highest yield of a <u>secondary</u> amide from 1 millimole (1 mmol) of benzoyl chloride (an acid chloride)?

(a) 1 mmol of $CH_3CH_2NH_2$ + 1 mmol of pyridine
(b) 1 mmol of $CH_3CH_2NH_2$ + 1 mmol of NH_3
(c) 2 mmol of $CH_3CH_2NH_2$ + 1 mmol of NH_3
(d) 1 mmol of $(CH_3)_2NH$
(e) 2 mmol of $(CH_3)_2NH$

Choices (d) and (e) will produce tertiary amides. The mixture of amines in choices (b) and (c) will produce a mixture of primary and secondary amides. The ethylamine in choice (a) will produce a secondary amide, while the pyridine is incapable of forming a stable amide but will be able to serve as the stoichiometric base required to neutralize the HCl byproduct such that the ethylamine's lone pair remains free to react.

(4) D Which of the labeled carbon atoms on compound (**A**) has the most acidic hydrogen atom in the molecule?



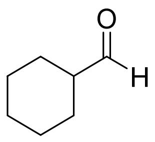
A

(a) i
(b) ii
(c) iii
(d) iv
(e) compound **A** has no hydrogen atoms

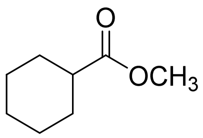
α-hydrogens (next to carbonyl groups) on carbon atoms with more alkyl groups are more acidic. You can explain this difference by the increased stability resulting from extra alkyl-group substitution of the C=C bond in the corresponding enolate.

(5) C

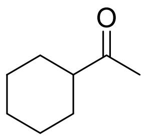
Which of the following compounds will react with excess aqueous I_2 and NaOH to form a yellow precipitate?



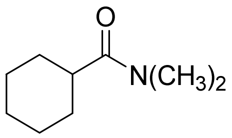
(a)



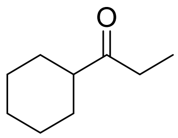
(b)



(c)



(d)

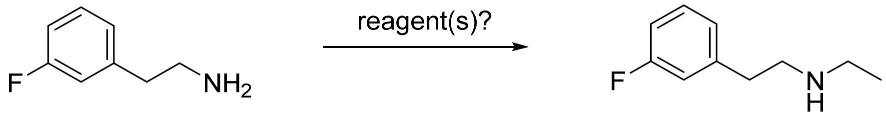


(e)

This is the classic iodoform test for methyl ketones. The yellow precipitate is iodoform (CHI_3).

(6) E

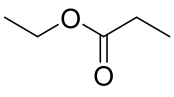
Which of the following reagents is/are the best choice to effect the conversion drawn below?



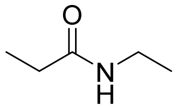
(a) CH_3I
(b) CH_2CH_3I
(c) CH_2CH_3I, pyridine
(d) CH_2O (2 eq.)
(e) CH_3CHO, $NaBH_3CN$

Note that alkylation of amines by an S_N2 reaction is not reliable unless you desire to exhaustively alkylate (to form a quaternary ammonium salt) or you use a large excess of the starting amine (and can easily purify the product amine from all of the unreacted starting material at the end of the reaction).

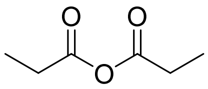
(7) C Rank the following molecules in order of thermodynamic stability toward hydrolysis from <u>most-to-least</u> stable. (The most stable compound is listed first in each answer choice.)



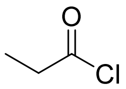
B



C



D



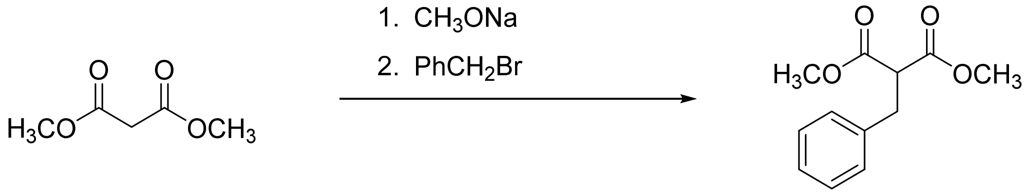
E

(a) **B** > **C** > **D** > **E**
(b) **C** > **B** > **E** > **D**
(c) **C** > **B** > **D** > **E**
(d) **C** > **E** > **B** > **D**
(e) **D** > **E** > **B** > **C**

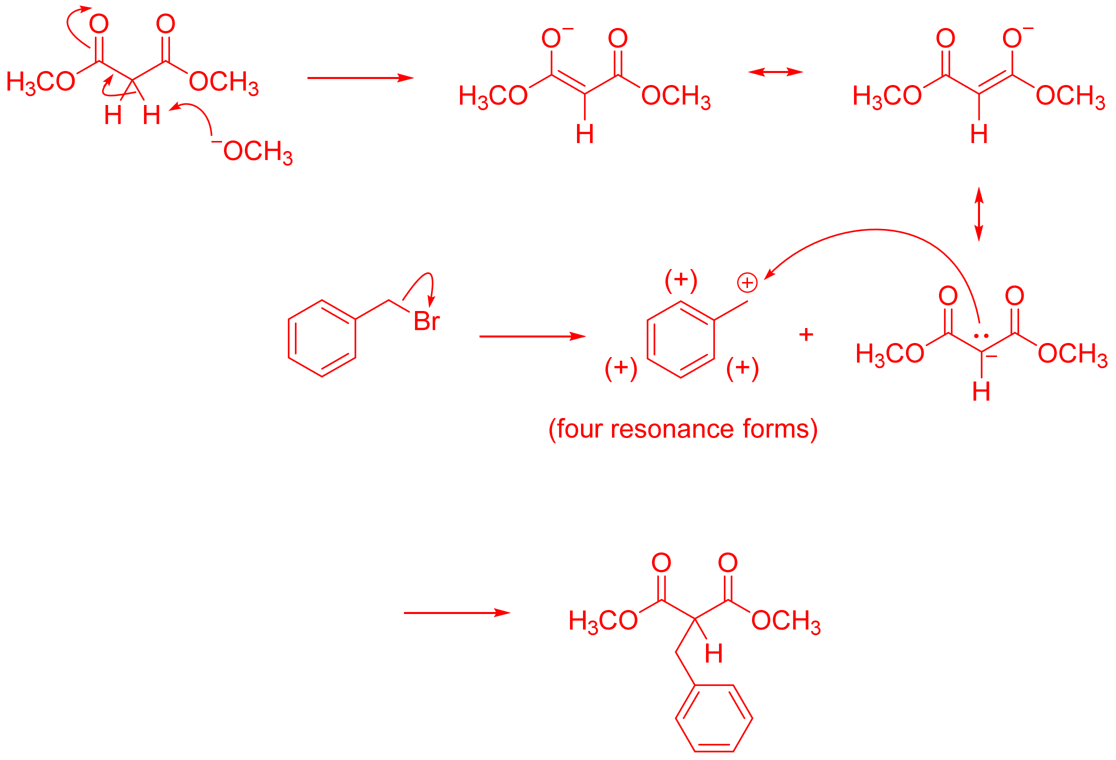
In general, amides are more stable than esters, which are more stable than acid anhydrides, which are more stable than acid chlorides.

Problem II. Mechanism (21 points).

(1) (15 points) Draw a sensible mechanism for the following reaction. Remember to use proper "curved arrow notation" to account for the redistribution of electrons in the making and breaking of bonds. Show all significant resonance forms that account for the stability of the intermediates in the reaction.



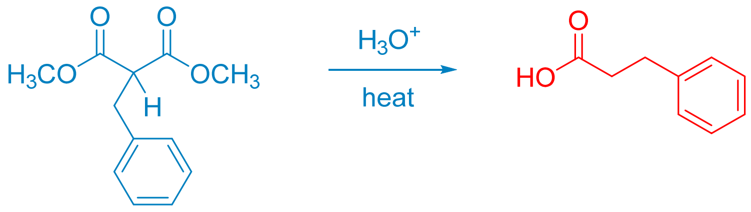
F **G**



(four resonance forms)

- Note: It's ok to show the alkylation as a classic S_N2 reaction as well, rather than an attack of the enolate on a carbocation

(2) (6 points) What product will form if compound **G** is heated in hot aqueous acid?

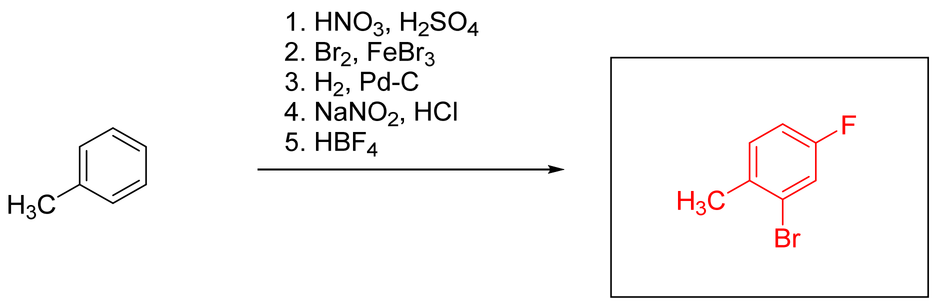


G

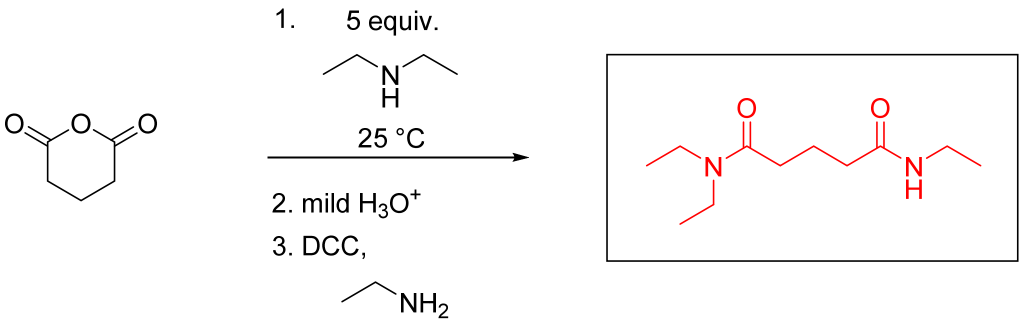
- These conditions will hydrolyze the esters and cause one of the groups to decarboxylate.

Problem III. Reactions (21 points). The following chemical reactions are missing their starting materials, products, or reagents. Write the missing compounds into the empty boxes below, as appropriate. For missing products, draw the single organic product that you expect to be produced in the highest yield among all of the possibilities. In some cases, there will be more than one correct answer that will merit full credit.

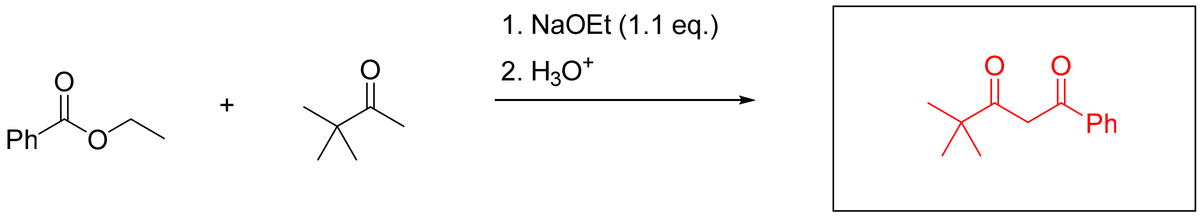
(1) (7 points)



(2) (7 points)

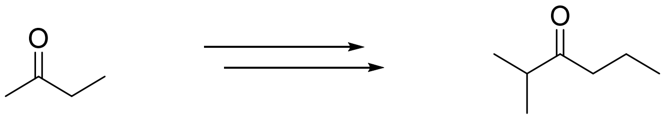


(3) (7 points)

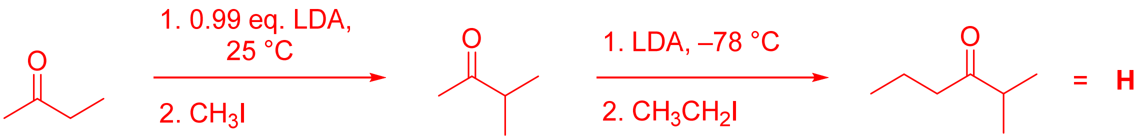


Problem IV. Synthesis (30 points). Design efficient synthetic routes for compounds **H** and **J** from the indicated starting materials and any other reagents you wish, but be sure to follow the constraints listed!

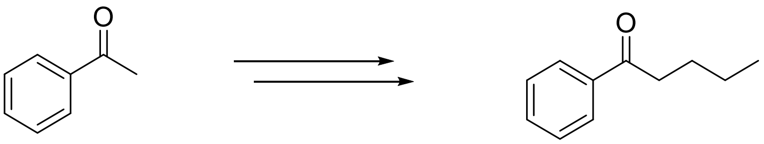
(1) (15 points) Synthesize compound **H** from the indicated starting material using LDA as your only base.



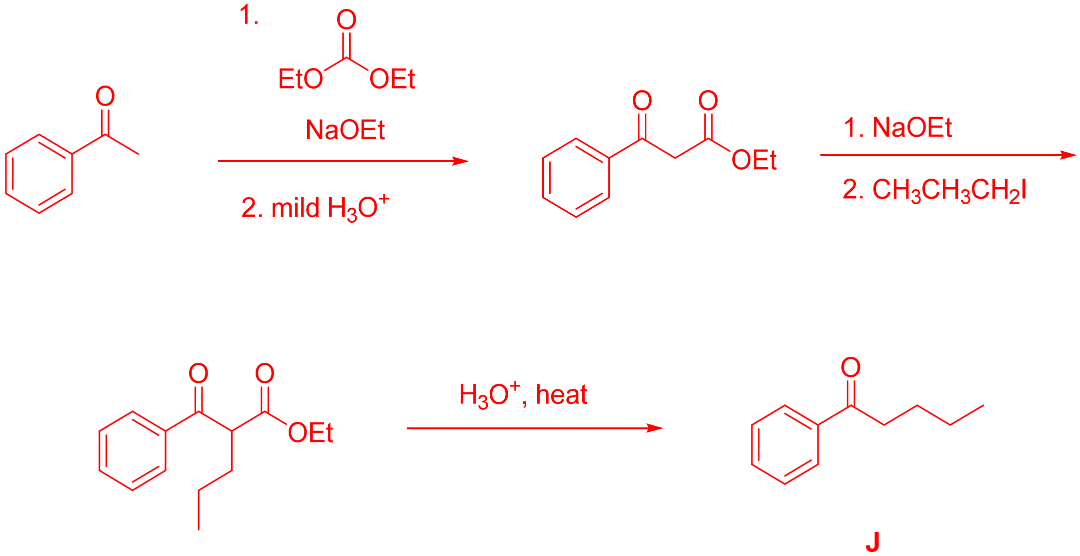
H



(2) (15 points) Synthesize compound **J** using no base stronger than sodium ethoxide (NaOEt). Hint: you might want to use diethyl carbonate (EtOCOOEt) as a reagent.



J



J