

Chemistry 212 — Fall Semester 1996 Examination #3

University of Missouri—Columbia

Prof. Rainer Glaser

Wednesday, November 13, 1996

103 Schlundt Hall, 8:40 - 9:30

featuring
Carbanion Chemistry and Related Topics.

Your Name:

Herr Dr. Rainer Glaser

	Max.	Yours
Question 1 (Reactions)	25	
Question 2 (Hydroxyketones)	25	
Question 3 (Claisen et al.)	25	
Question 4 (Robinson)	25	
Total	100	

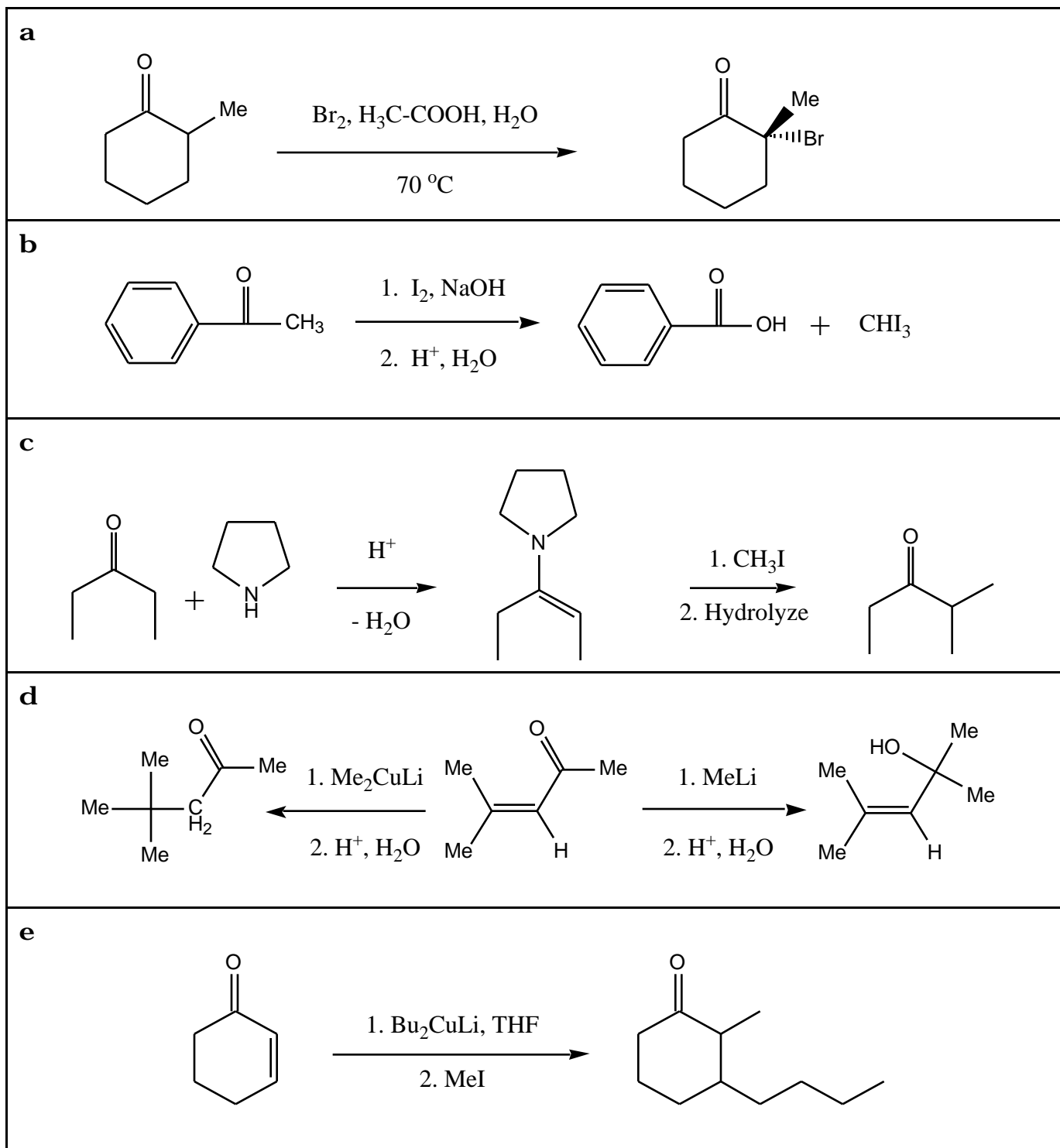


Do not turn the page until advised to do so.



Question 1. Reaction Chemistry. (25 points)

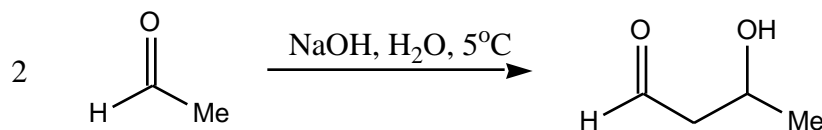
Complete the following reactions by providing the structures of starting materials, reagents, and products as needed. (5 points each reaction)



Question 2. Alpha- and Beta-Hydroxyketones. (25 points)

(a) Show overall reaction and mechanism of the aldol reaction of **acetaldehyde** at low temperature (no subsequent elimination). (4 p. for overall reaction, 6 p. for mechanism)

Overall Reaction:



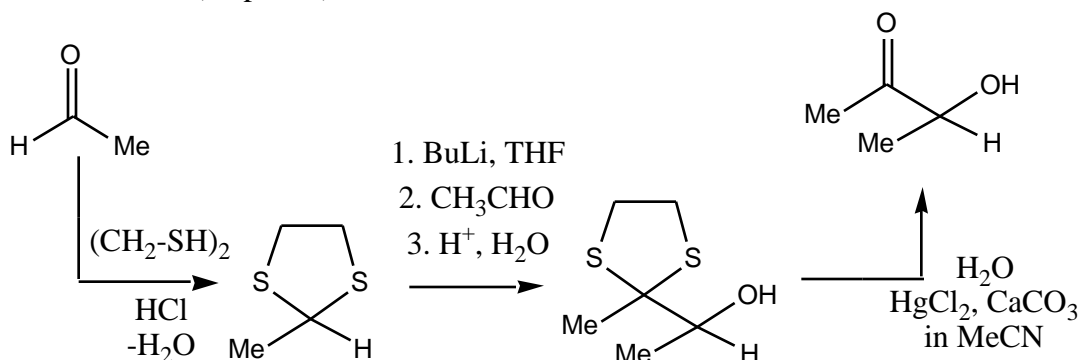
Mechanism:

Open any book for the solution

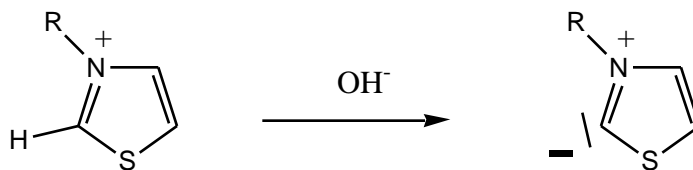
Make enolate. Enolate attacks carbonyl carbon. Alkoxide is formed and protonated.

(b) **Alpha-hydroxy isomer of the aldol product** can be prepared in two ways. **First**, use the polarity reversal method that employs dithioacetals. Show reagents needed to (a) make the dithioacetal, (b) couple the dithioacetal to aldehyde, and (c) regenerate the carbonyl. **Second**, use the thiazolium ion catalyzed coupling. In this case, only show the conversion of the thiazolium ion into the active catalyst.

Dithioacetal method: (10 points)

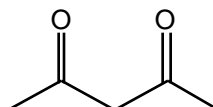
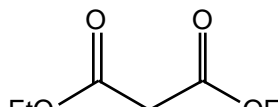
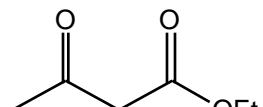


Thiazolium ion (use R at N) catalyzed coupling: (5 points)

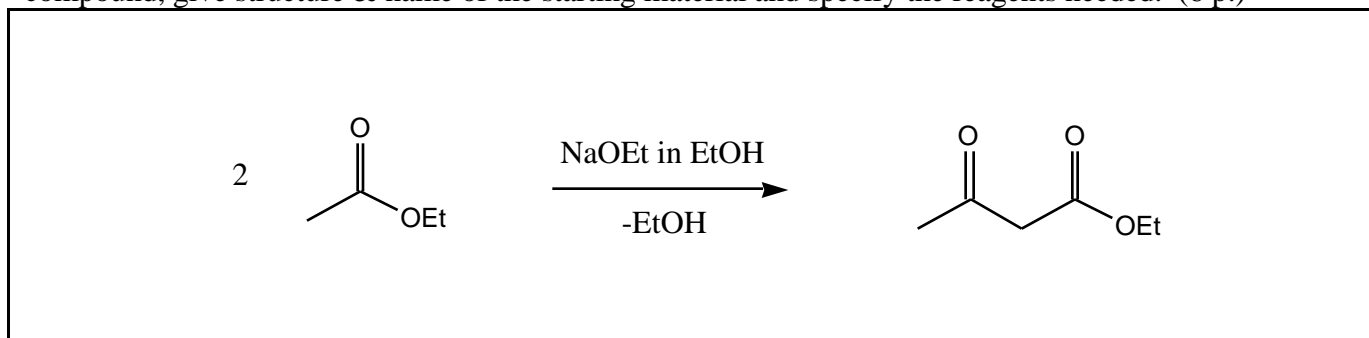


Question 3. Claisen and Dieckmann Condensations. (25 points)

(a) The structures of three important beta-dicarbonyls are shown. Give their names (trivial or IUPAC), circle the most acidic methylene group for each and give the pKa value of that methylene hydrogen. (12 p.)

I  acetylacetone 2,4-pentanedione pKa at center = 9	II  diethyl malonic acid ester diethyl propanedioate pKa at center = 13	III  ethyl acetoacetate ethyl 3-oxobutanoate pKa at center = 11
---	---	---

(b) One of the compounds shown in (a) can be made via a **Claisen Condensation**. Identify that compound, give structure & name of the starting material and specify the reagents needed. (6 p.)



(c) Define the “**Dieckmann Condensation**” and provide a simple example. Select a starting material of your choice, give reagents and product. (3 p. for definition, 4 p. for example)

Definition:

Intramolecular Claisen Condensation to make 5- and 6-membered rings.
The reaction yields a beta-carbonyl ester. Carbonyl is endocyclic, ester is not.

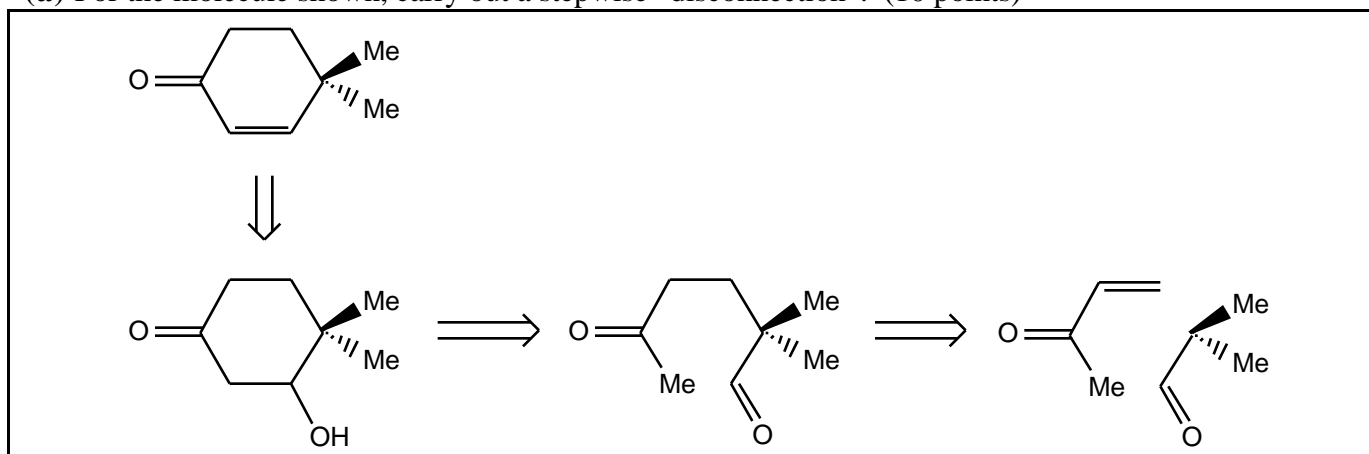
Example:

Any example that is conceptually right was considered OK.

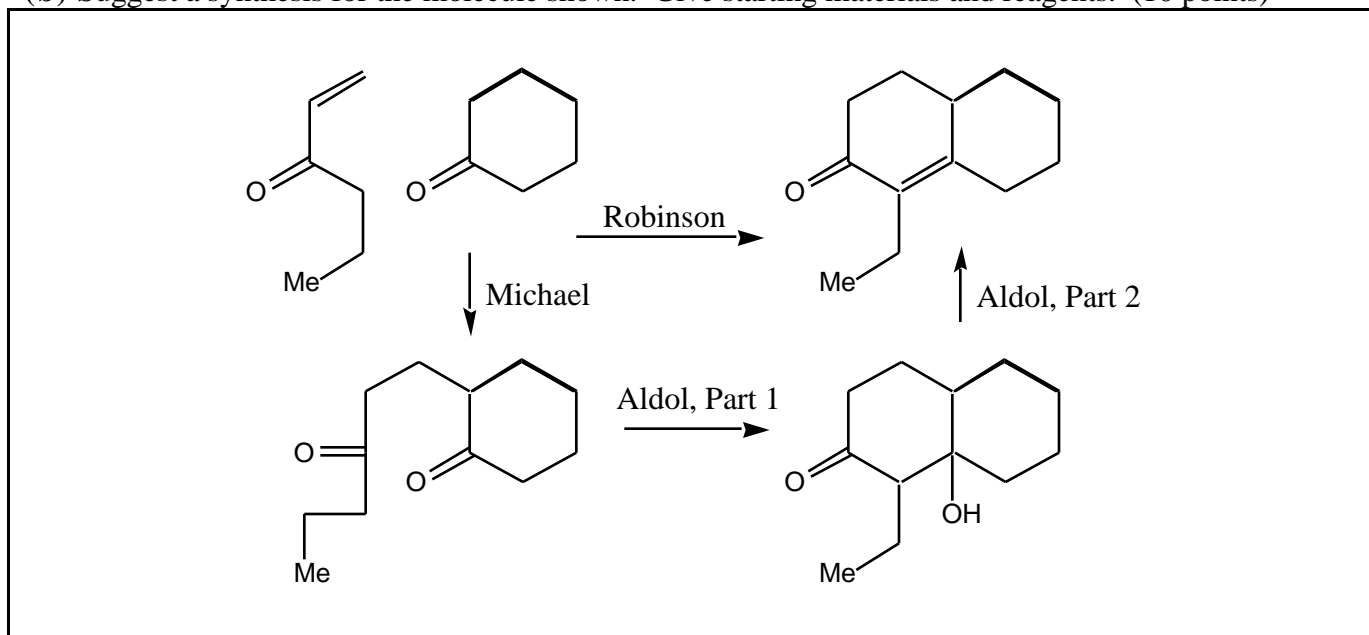
Question 4. Robinson Annulation. (25 points)

The Robinson annulation consists of a Michael reaction which is followed by an Aldol reaction. The product of a Robinson annulation is a 6-membered ring that contains an α,β-unsaturated ketone (aldehyde, ketone). (5 points)

(a) For the molecule shown, carry out a stepwise “disconnection”. (10 points)



(b) Suggest a synthesis for the molecule shown. Give starting materials and reagents. (10 points)



The End

