

Chemistry 41c
Spring 2013
Midterm Exam Practice Material

Sample problems & answer key.

Disclaimer: These sample questions relate most closely to the chapters covered thus far in 41c: 18 (organometallics), 19, 20, 21, and 22. However, there are instances in which 41a/b chemistry is required to solve a problem. The length of this document does not imply the length of the actual midterm. It will be no longer than four pages of problems.

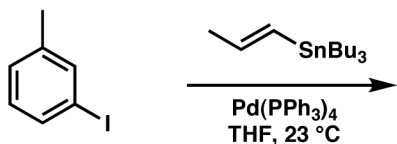
Chem 41c Quiz 1

Stoltz, Spring 2010
April 9, 2010

You have 25 min to take this quiz. It is closed note, closed book, and no collaboration is allowed. Please do not discuss the quiz with anyone until you receive it back graded. Place a box around your answers. There is no partial credit.

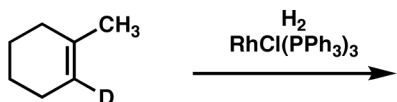
Predict the products (if any) of the following reactions: (5 points each)

1.



41c: skip questions
1 and 2.

2.



3. In the following complexes, what is the formal oxidation state of the metal, the d^n description, and the electron count? Feel free to use the periodic table in the room (no partial credit). (5 points each)

a.

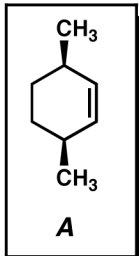


b.



Bonus (5 points)

Predict the product of the following reaction. Be sure to indicate stereochemistry in your proposed product.



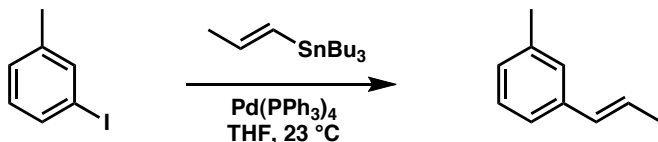
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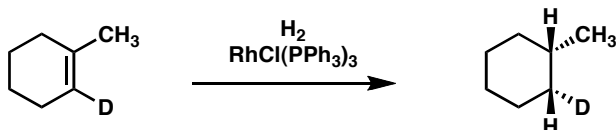
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Predict the products (if any) of the following reactions: (5 points each)

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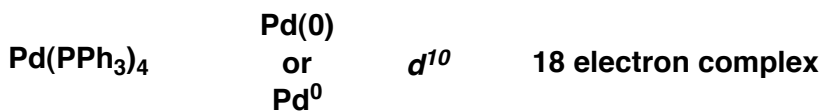
2.



41c: skip questions
1 and 2.

3. In the following complexes, what is the formal oxidation state of the metal, the d^n description, and the electron count? Feel free to use the periodic table in the room (no partial credit). (5 points each)

a.

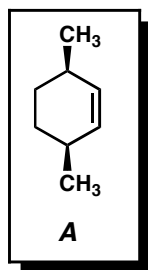
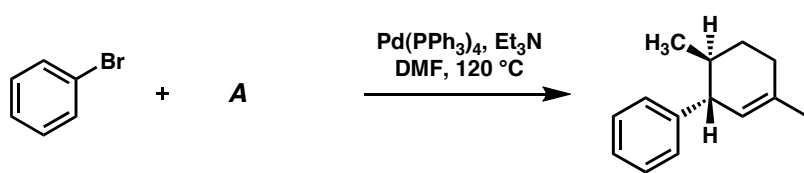


b.



Bonus (5 points)

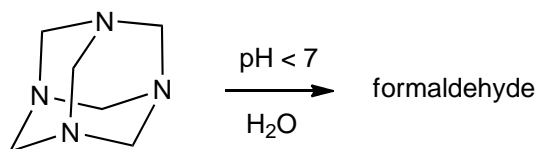
Predict the product of the following reaction. Be sure to indicate stereochemistry in your proposed product.



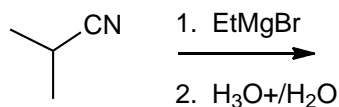
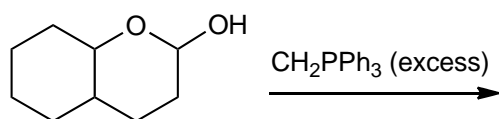
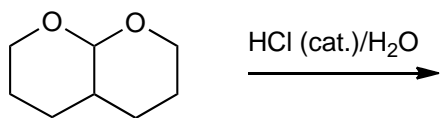
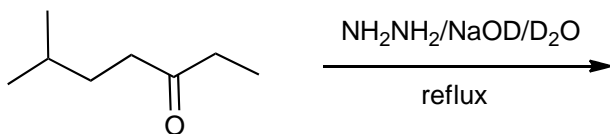
1. (a) Use a mechanism to account for the incorporation of two ^{18}O atoms into the product formed by acid-catalyzed hydrolysis of unlabeled β -propiolactam with ^{18}O -labeled water (H_2^{18}O). 12 pts



(b) Methenamine is a prodrug used for site-specific delivery of formaldehyde (an antiseptic). It is formulated in pill form that protects the molecule from the $\text{pH} < 7$ stomach environment. The pills then dissolve in the $\text{pH} > 7$ intestinal tract, where methenamine is stable. Once it is transferred to the $\text{pH} < 7$ urinary tract, Methenamine liberates 6 formaldehyde molecules. Write a mechanism to demonstrate how one formaldehyde molecule is produced. 12 pts

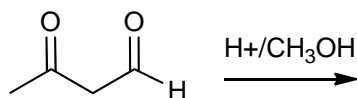


2. Predict the major product expected for each reaction shown. State "NR" if no reaction is expected. 5 pts ea



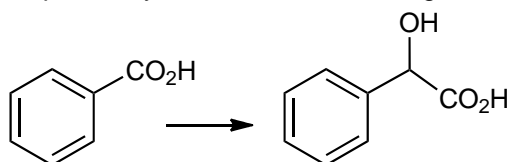
41c: skip this question

3. In acidic methanol, 3-oxobutanal is transformed into a new compound. Analyze the NMR and IR data and propose a structure for this product. (10 pts)

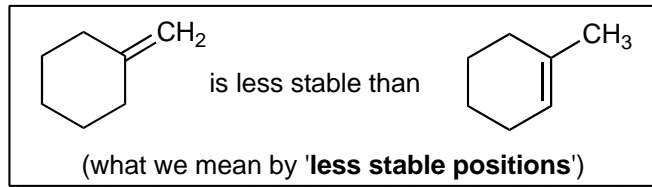
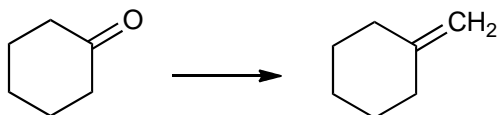


Product ^1H NMR: δ 2.19 ppm (s, 3H),
 2.75 (d, 2H), 3.38 (s, 6H), 4.89 (t, 1H);
 IR: 1715 cm^{-1}

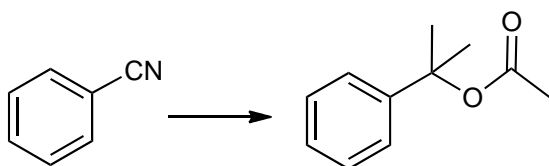
4. Propose a synthesis for the following transformation (show structures on the path, mechanisms not required). 10 pts



5. The Wittig reaction is useful for placing double bonds in **less stable positions**. For example, the following transformation can be accomplished using a Wittig reaction. (a) Show how you would use a Wittig reaction to do this (mechanisms not required). (b) Show how you do this *without* using a Wittig reaction, and explain why the Wittig reaction is a much better synthesis (the alternate route should **not** involve Wittig-type reactions like the Horner-Emmons reaction). 10 pts

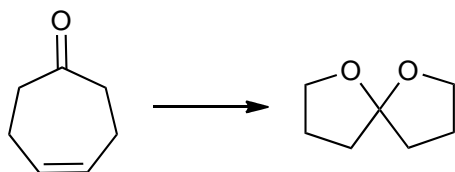


6. Propose an efficient synthesis of the following compound (mechanisms not required). 10 pts

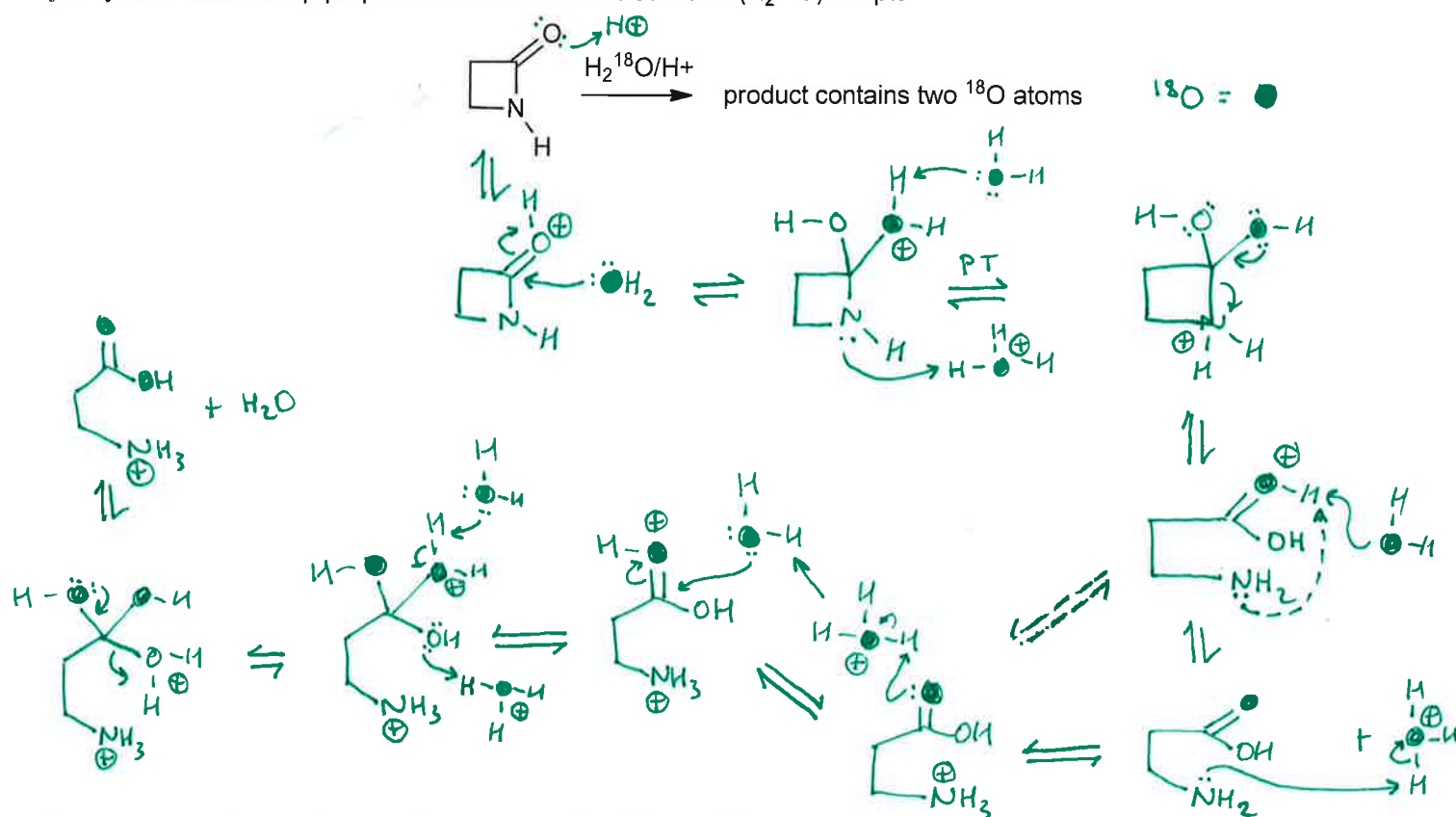


7. A carboxylic acid with formula C₅H₁₀O₂ is treated with thionyl chloride to give compound **A**. Compound **A** has only one signal in its NMR spectrum. Draw the structure of the product that is formed when **A** is treated with a methanol/pyridine mixture. 6 pts

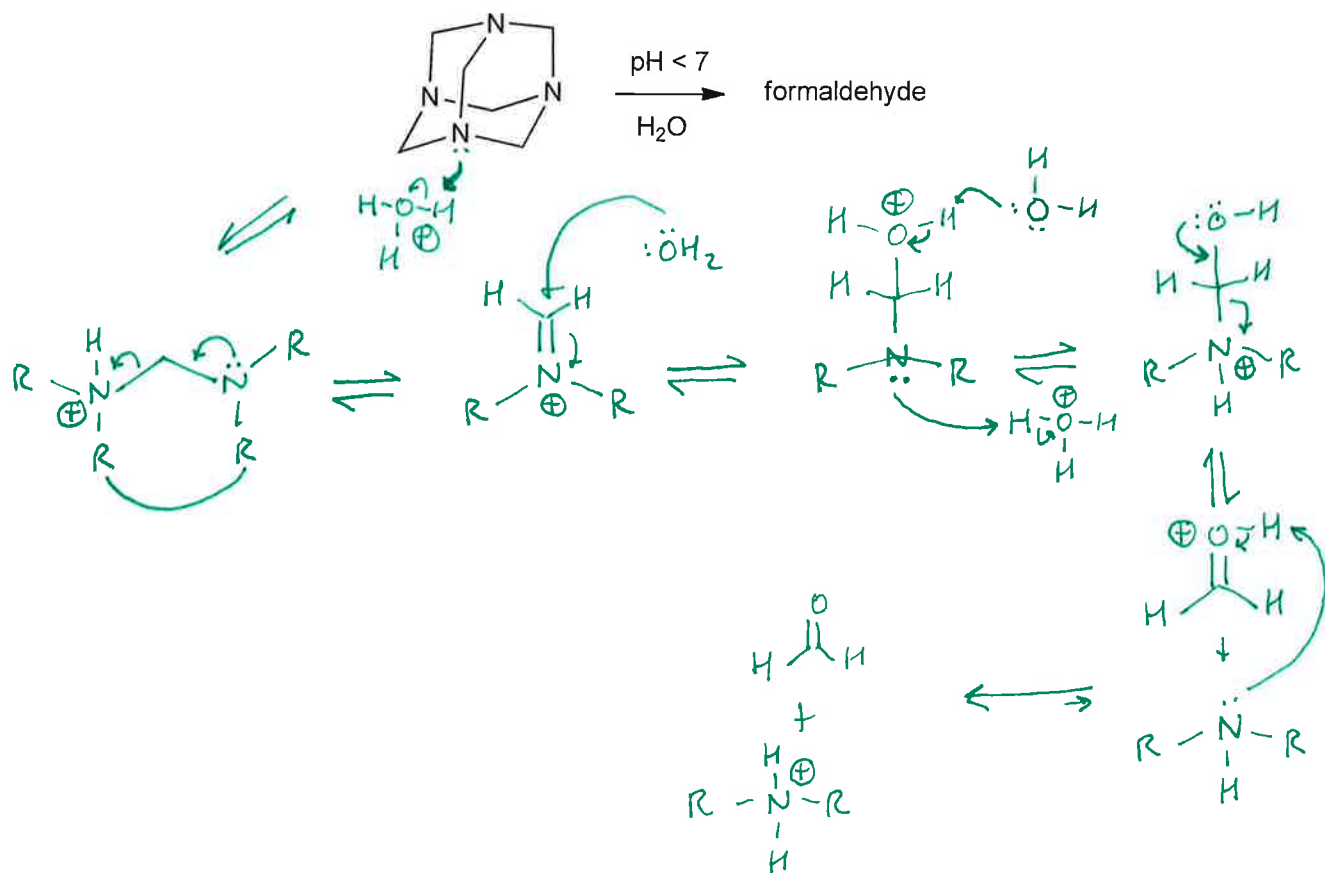
8. Propose a synthesis for the following transformation (show structures on the path, mechanisms not required). 10 pts



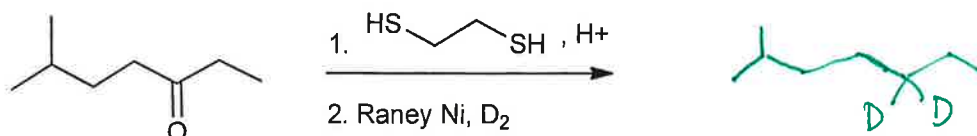
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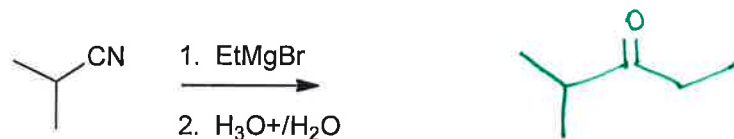
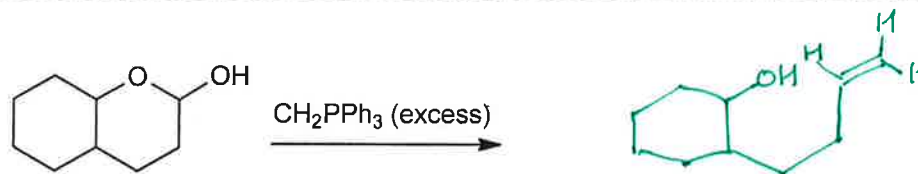
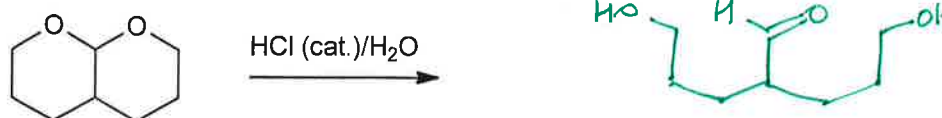
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2. Predict the major product expected for each reaction shown. State "NR" if no reaction is expected. 5 pts ea

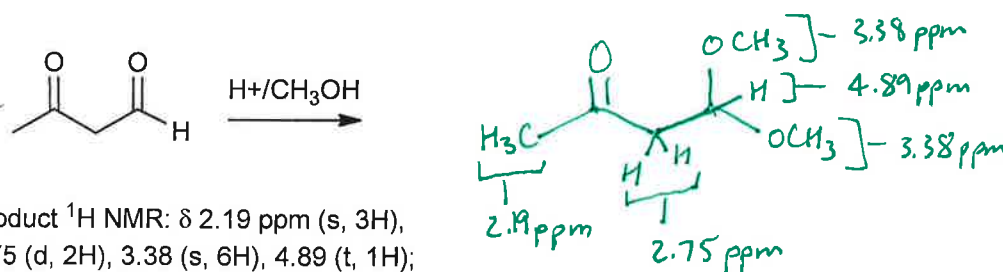


41c: Wolff-Kishner
with NH₂NH₂/
D₂O/NaOD



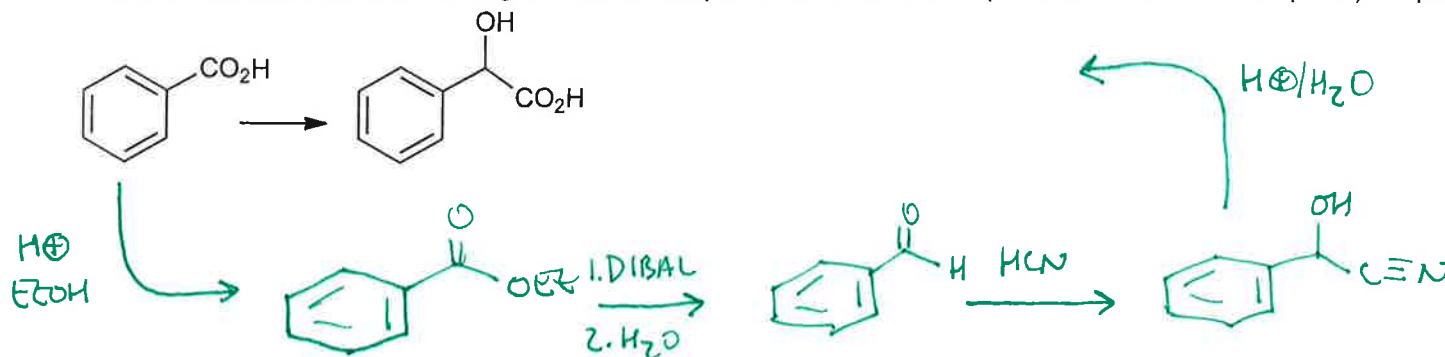
41c: skip this
question

3. In acidic methanol, 3-oxobutanal is transformed into a new compound. Analyze the NMR and IR data and propose a structure for this product. (10 pts)

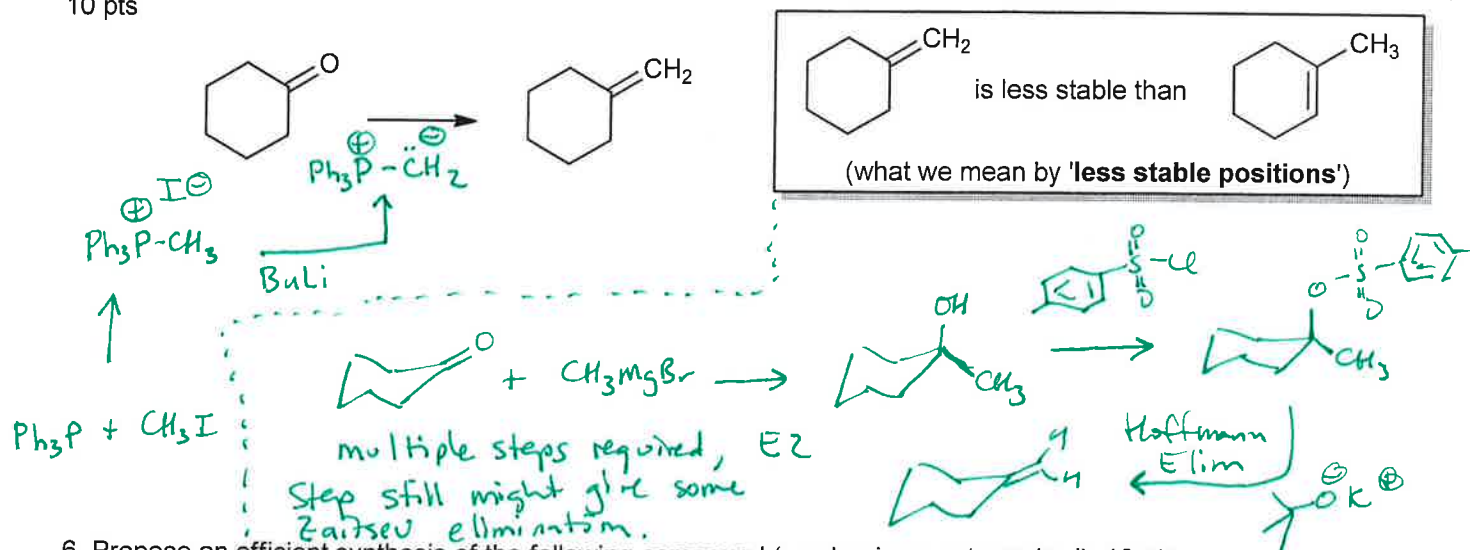


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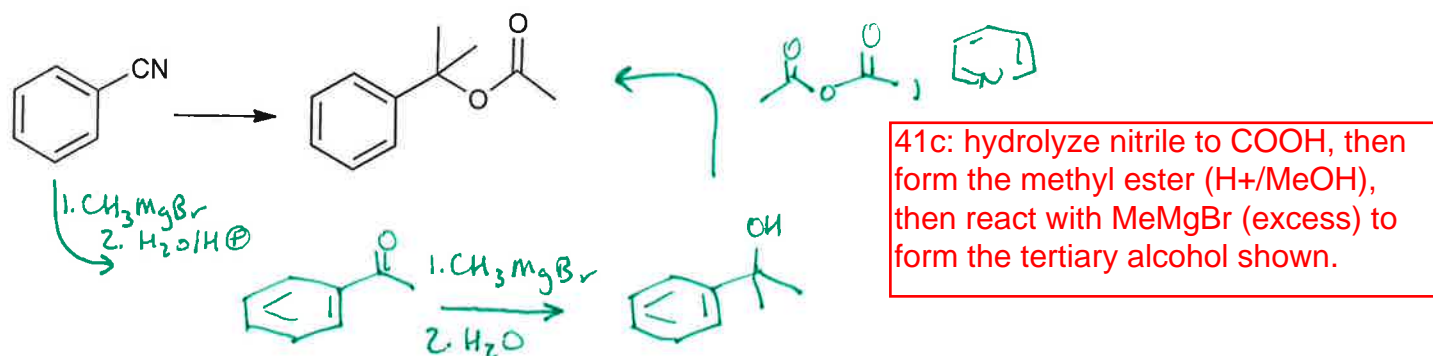
4. Propose a synthesis for the following transformation (show structures on the path, mechanisms not required). 10 pts



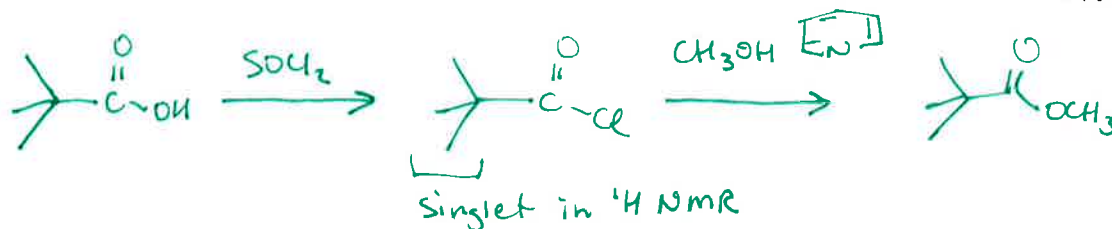
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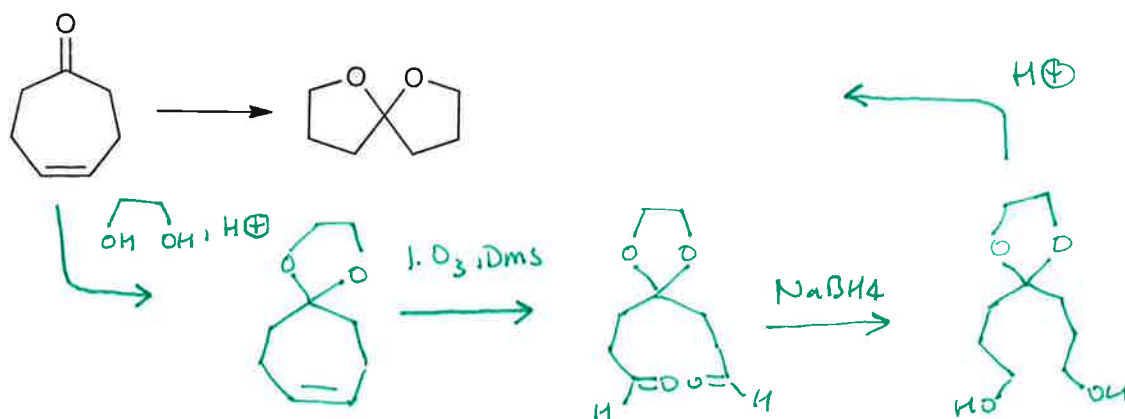
6. Propose an efficient synthesis of the following compound (mechanisms not required). 10 pts



7. A carboxylic acid with formula $C_5H_{10}O_2$ is treated with thionyl chloride to give compound **A**. Compound **A** has only one signal in its NMR spectrum. Draw the structure of the product that is formed when **A** is treated with a methanol/pyridine mixture. 6 pts

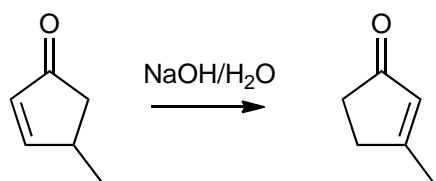
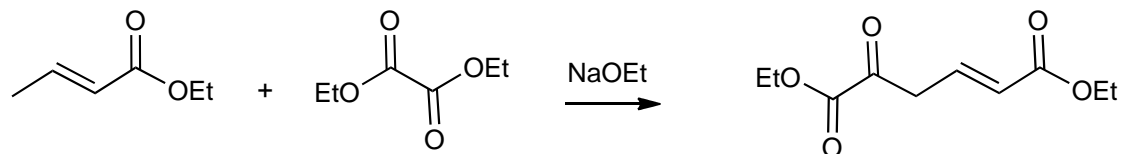


8. Propose a synthesis for the following transformation (show structures on the path, mechanisms not required). 10 pts

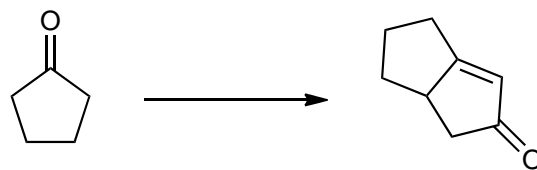
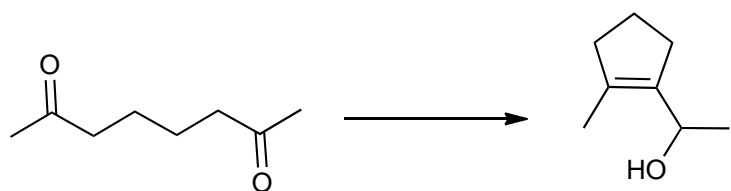
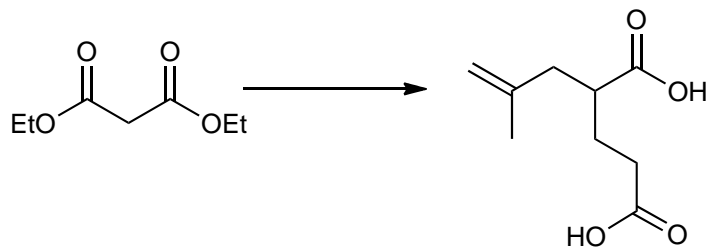
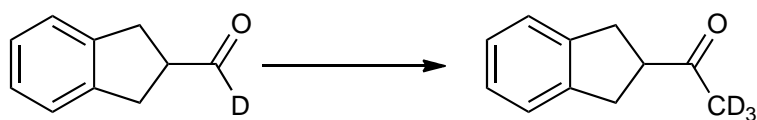


1. Write a stepwise mechanism for each of the following reactions. (10 pts each)

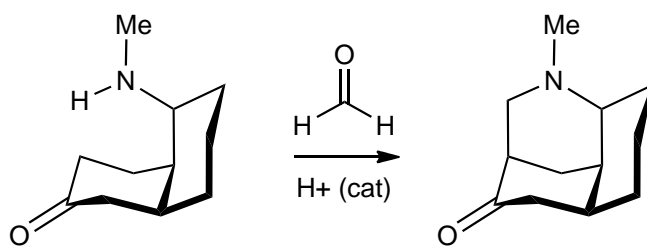
2



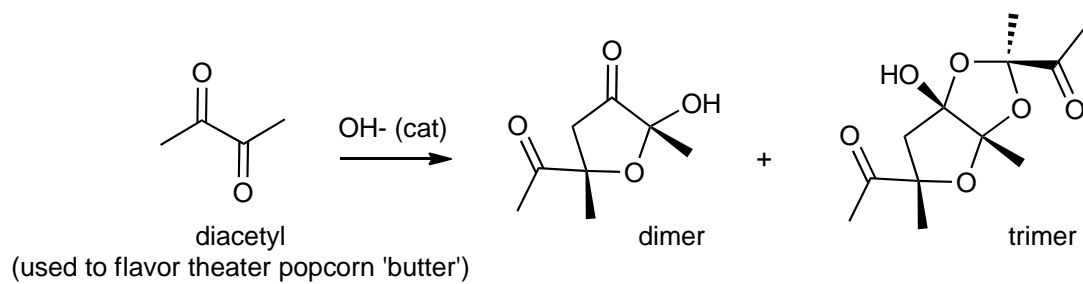
2. Show how each of the following transformations could be accomplished by listing the required reagents, and their sequence, over the arrow. Mechanisms are not required. (5 pts each)



3. Write a mechanism that accounts for the following reaction sequence. (15 pts)

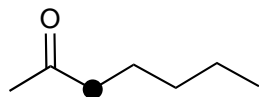


4. Write a mechanism that accounts for the base-catalyzed (OH^-) formation of dimers and trimers from diacetyl. (15 pts)



5. Show me what your chalkboard would look like after you give a brief lecture on the **directed aldol reaction**. Please note: this is not an essay question. 15 pts

6. Propose a malonic ester or acetoacetic ester synthesis of ^{13}C -labelled 2-heptanone, shown below. Provide a mechanistic analysis to demonstrate a complete understanding of your proposal. 15 pts

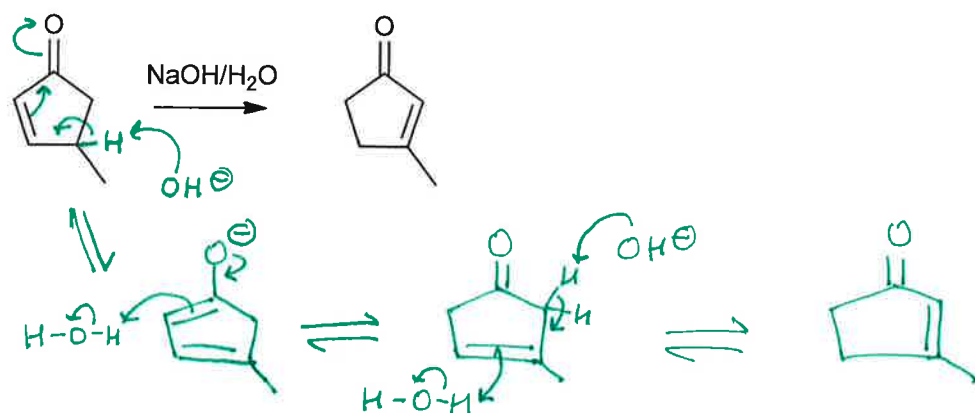
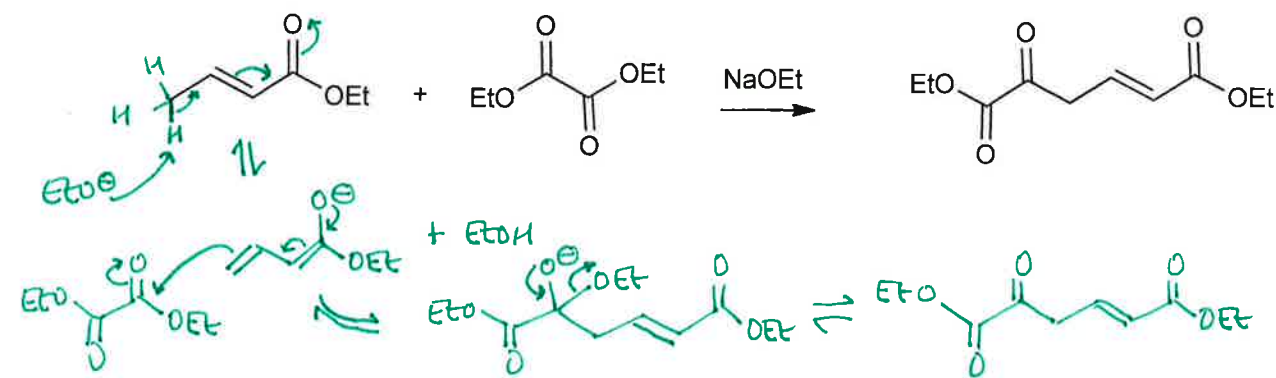


● = ^{13}C isotope

1. Write a stepwise mechanism for each of the following reactions. (10 pts each)

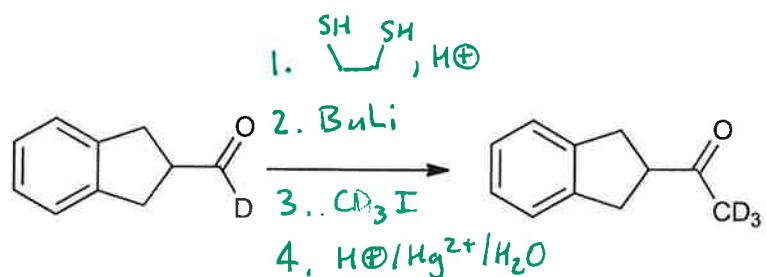
2

Assigned 19.30



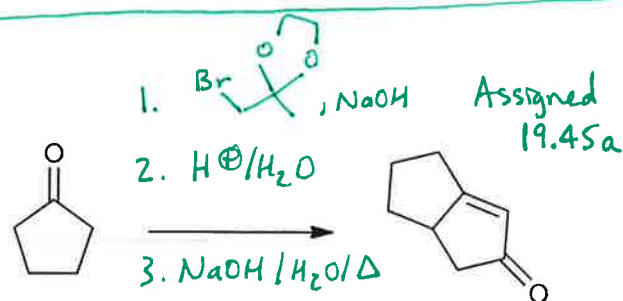
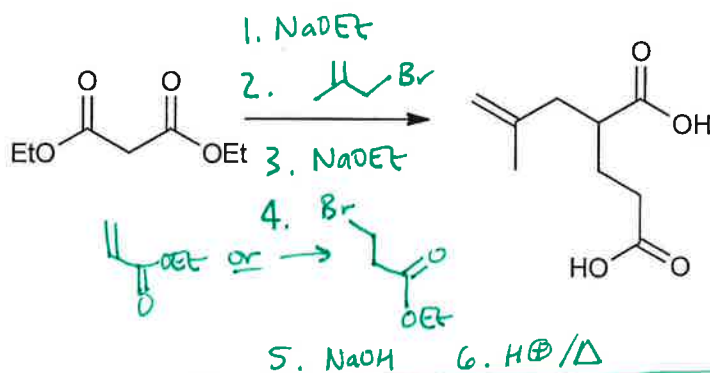
Assigned 18.20 c

2. Show how each of the following transformations could be accomplished by listing the required reagents, and their sequence, over the arrow. Mechanisms are not required. (5 pts each)



OR

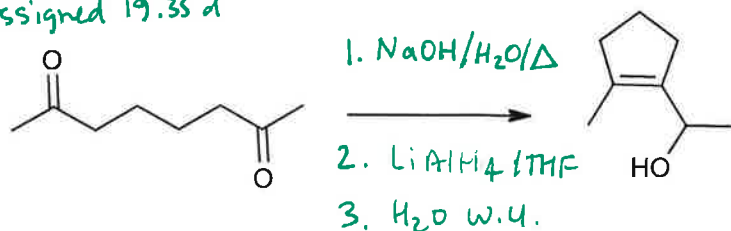
1. CD_3MgI
 2. Jones Cr^{VI} oxidation
 H_2CrO_4



Assigned 19.45a

41c: the Grignard/Jones route would be appropriate, based upon our coverage.

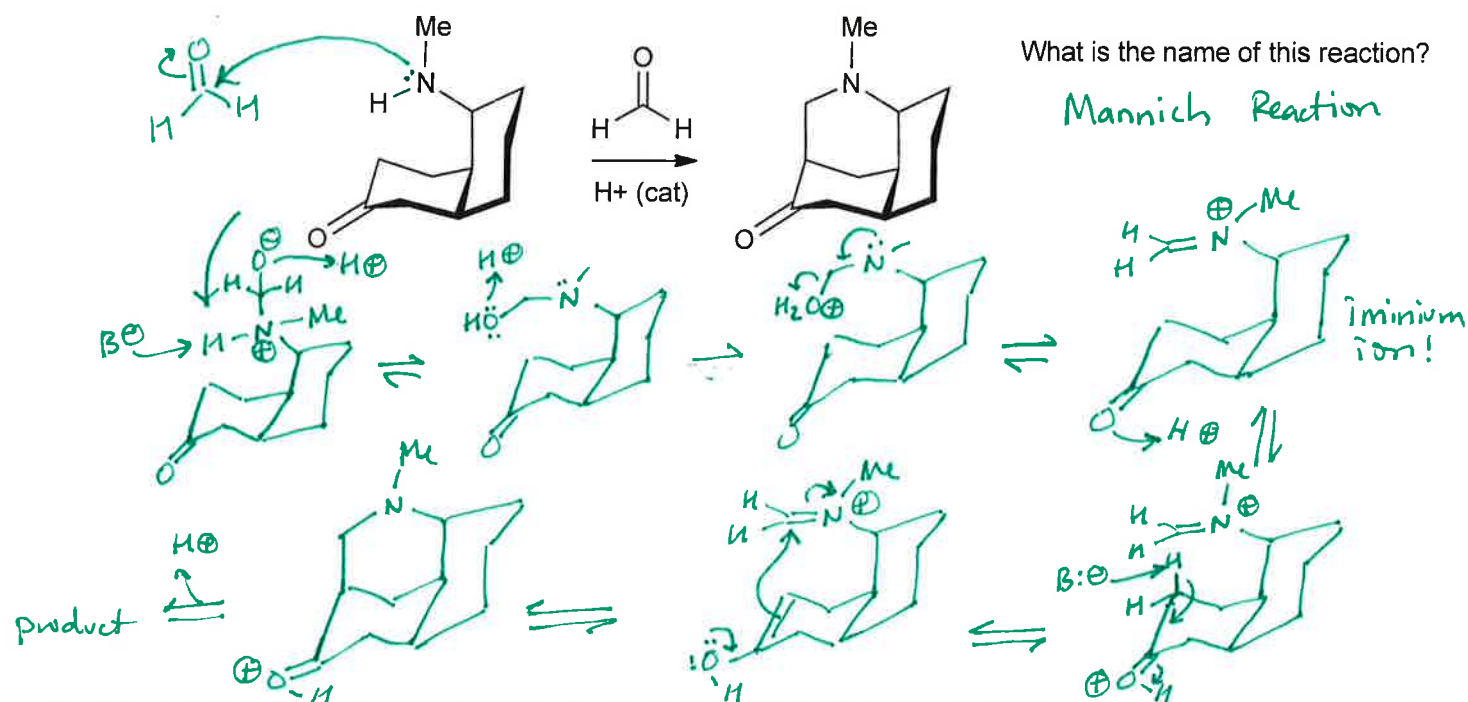
Assigned 19.35d



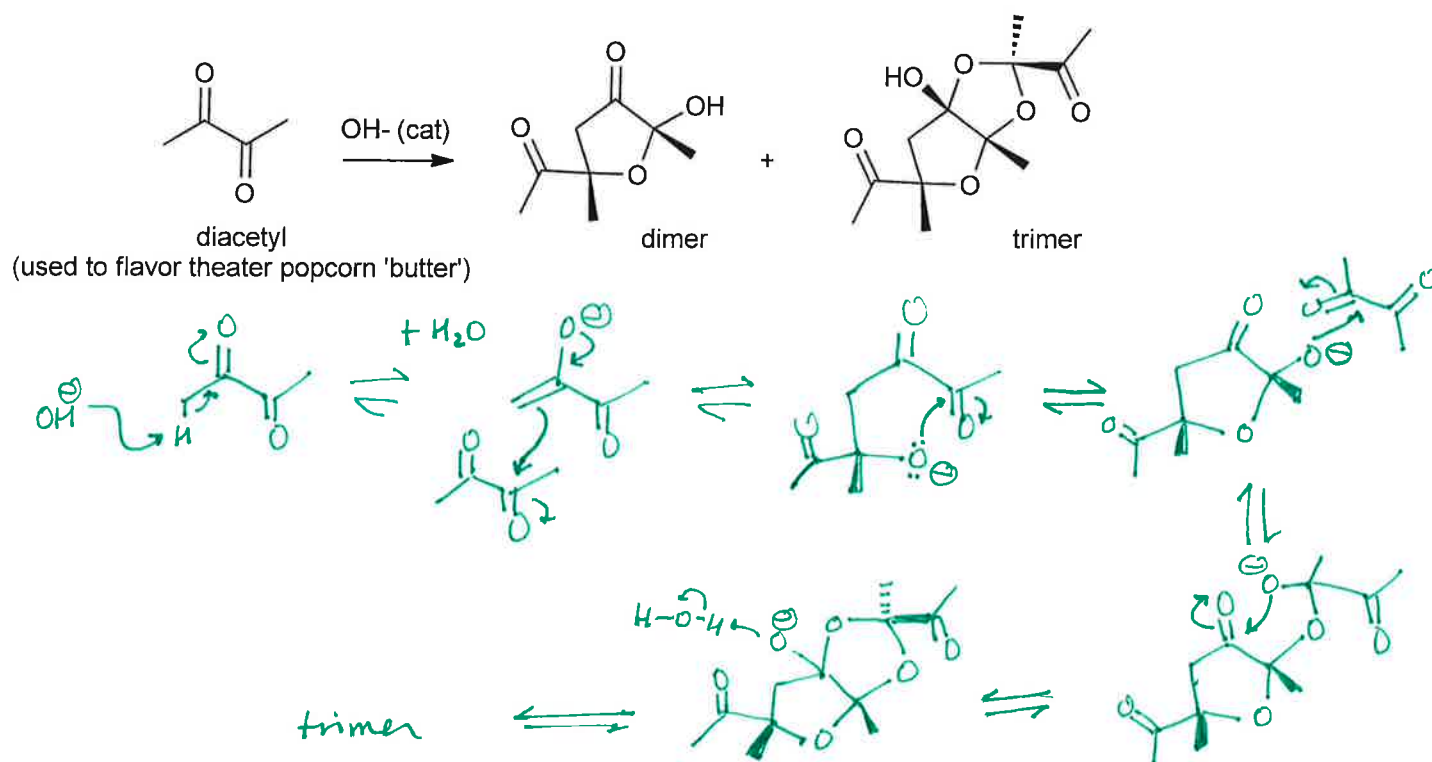
41c: we didn't learn this reaction by name, but the mechanism does not fall too far outside our coverage.
 Note: the species "B:-" is shorthand for a weak base.

3. Answer the question and write a mechanism that accounts for the following reaction sequence. (15 pts)

5

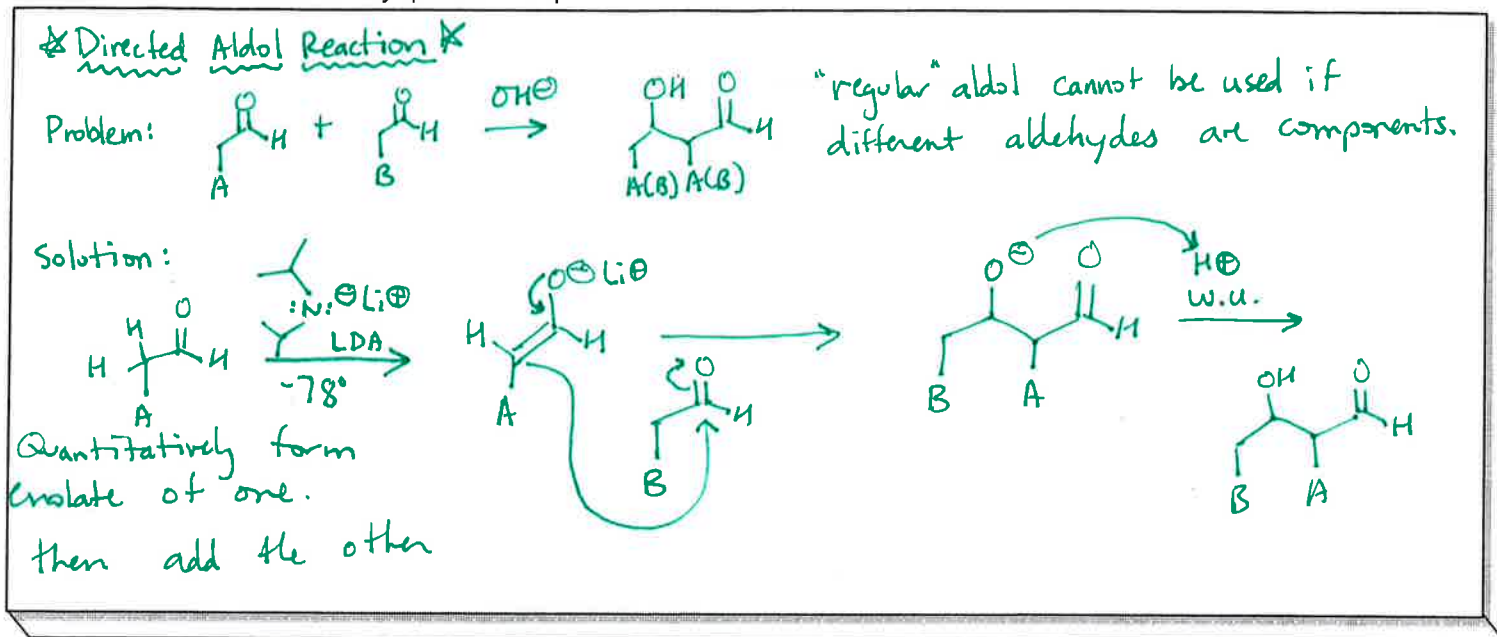


4. Write a mechanism that accounts for the base-catalyzed (OH^-) formation of dimers and trimers from diacetyl. (15 pts)



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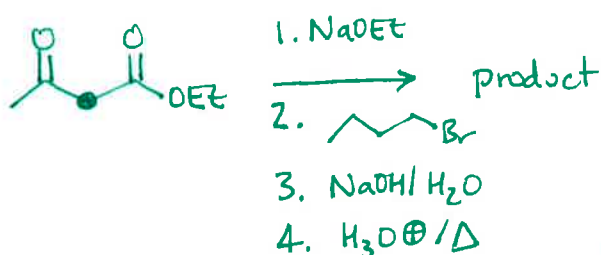
4



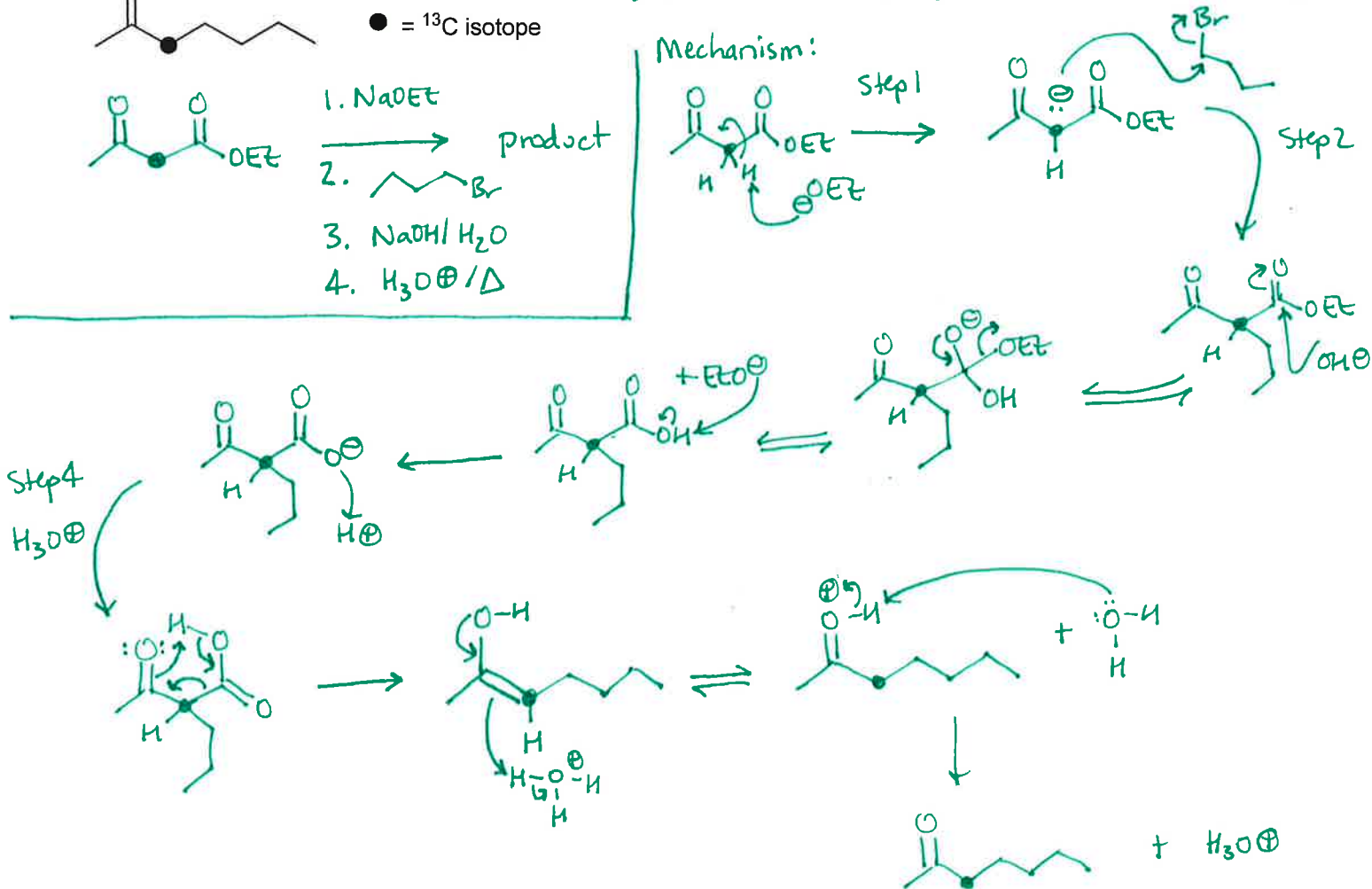
6. Propose a malonic ester or acetoacetic ester synthesis of ^{13}C -labelled 2-heptanone, shown below. Provide a mechanistic analysis to demonstrate a complete understanding of your proposal. 15 pts



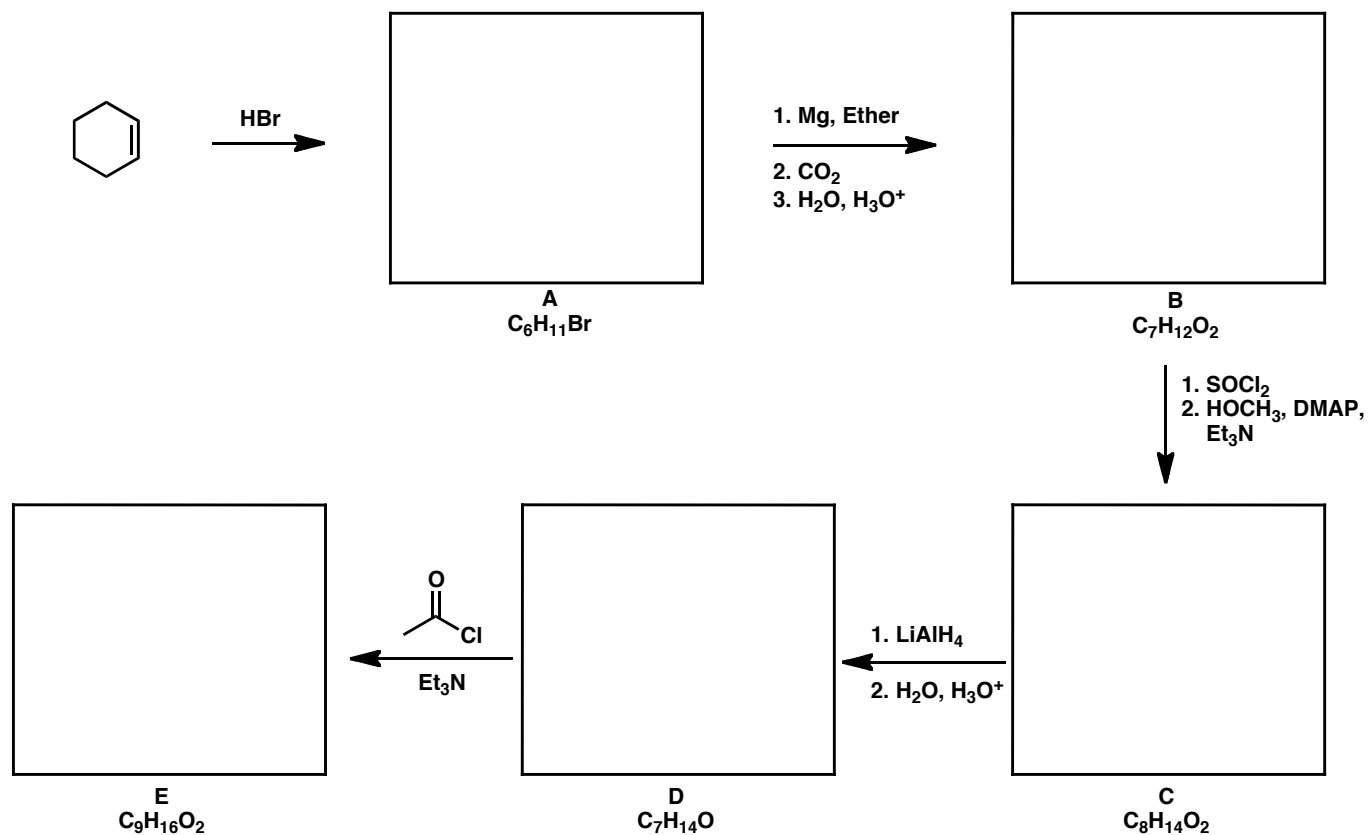
substituted ketone requires acetoacetic ester synthesis



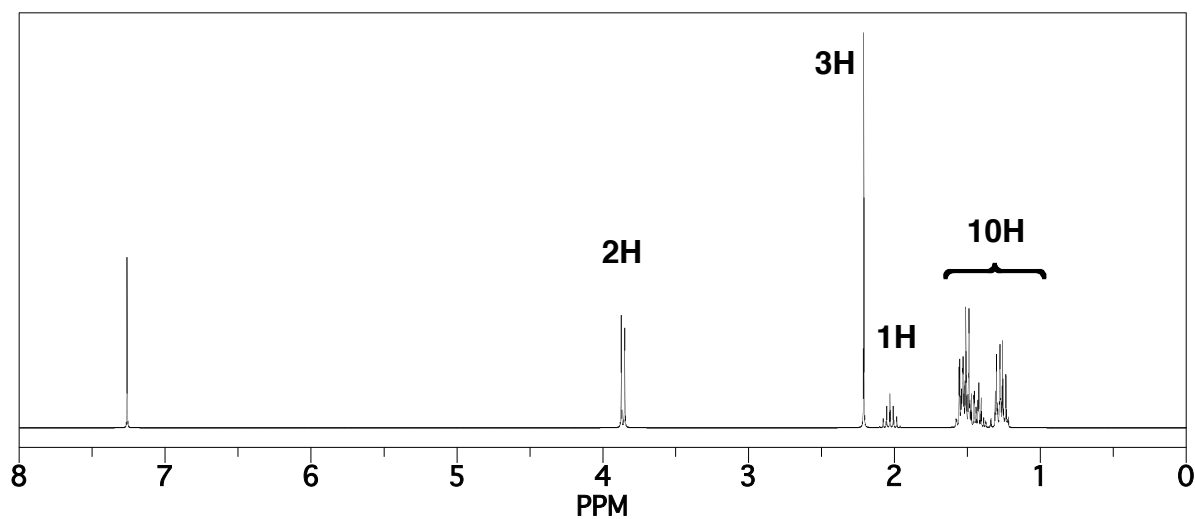
Mechanism:



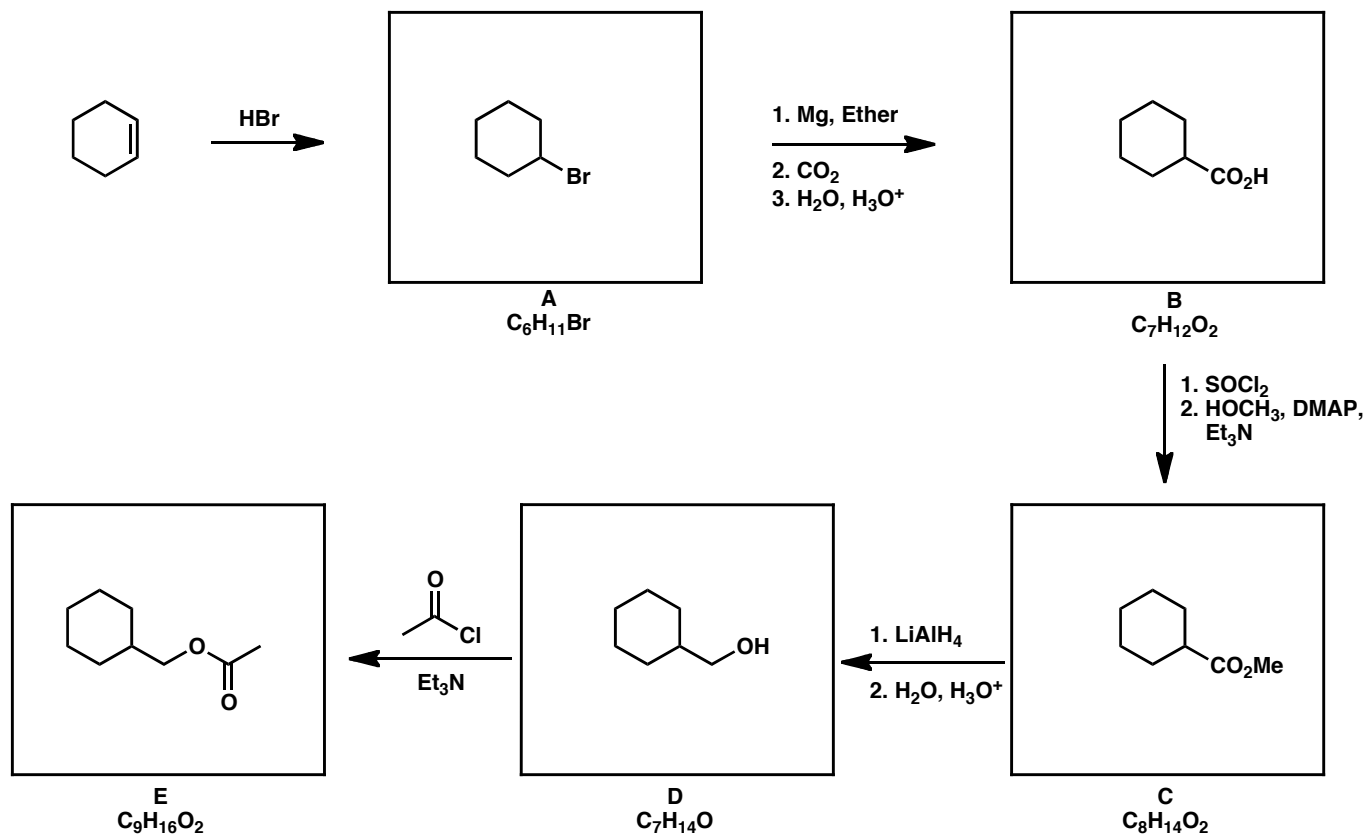
3. Provide the missing products in this multi-step synthesis scheme (15 points).



Hint: Below is the ^1H NMR spectrum of compound **E** acquired in CDCl_3 .



3. Provide the missing products in this multi-step synthesis scheme (15 points).



Hint: Below is the ¹H NMR spectrum of compound E acquired in CDCl₃.

