

CH 254, Spring 2008

Name

KEY

Exam #4, 9 May 2008

(PRINT CLEARLY PLEASE!)

Marietta Schwartz, Ph.D © 2008



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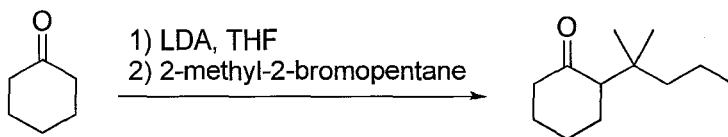
| Question # | Points Possible | Points Received |
|---------------------|-----------------|-----------------|
| 1 | 20 | |
| 2 | 15 | |
| 3 | 15 | |
| 4 | 16 | |
| 5 | 8 | |
| 6 | 8 | |
| 7 | 18 | |
| Subtotal | 100 | |
| Extra Credit | 9 | |
| Total | 109 | |

1. (20 points) Multiple Choice. For each question, circle ONE answer.

A. Which is the only one of these compounds which cannot self-condense in the presence of dilute aqueous NaOH?

- a. phenylethanal
- b. propanal
- c. 2-methylpropanal
- d. 3-methylpentanal
- e. 2,2-dimethylpropanal

B. A student proposed the following synthesis. Why did it fail?



- a. The use of LDA results in the thermodynamic product instead of the desired kinetic product.
- b. LDA is insoluble in the THF solvent so the reaction is too slow to occur at a useful rate.
- c. LDA acts as a nucleophile instead of a base in its reaction with cyclohexanone.
- d. The tertiary bromide is too sterically hindered to be attacked by the enolate.
- e. Instead of 2-methyl-2-bromopentane, 2-bromo-3-methylpentane should have been used to anticipate a cationic rearrangement that would occur.

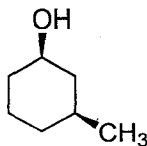
C. In the Michael reaction, addition to the α,β -unsaturated carbonyl occurs in a:

- a. 1,2-fashion
- b. 1,3-fashion
- c. 1,4-fashion
- d. 1,5-fashion
- e. Diels-Alder reaction

D. In the chromic acid oxidation of alcohols, the chromium is:

- a. reduced from Cr^{+6} to Cr^{+3}
- b. oxidized from Cr^{+6} to Cr^{+3}
- c. reduced from Cr^{+3} to Cr^{+6}
- d. oxidized from Cr^{+3} to Cr^{+6}
- e. none of the above

E. When the optically active alcohol shown here is oxidized by H_2CrO_4 , the product is:

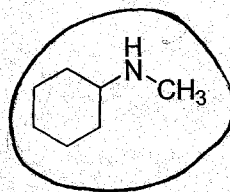
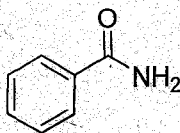
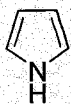
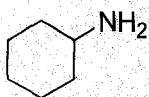
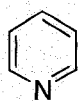


- a. a ketone which is meso and optically active
- b. an optically active ketone
- c. a racemic mixture of ketones which is optically inactive
- d. an aldehyde which is meso and optically active
- e. an acyclic carboxylic acid

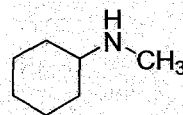
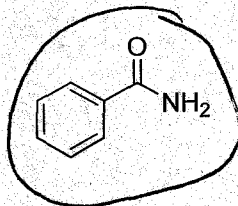
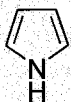
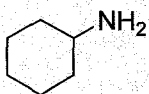
F. Which of the following reagents is not an oxidizing agent?

- a. KMnO_4
- b. CrO_3
- c. NADH
- d. PCC
- e. HIO_4

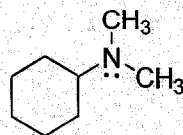
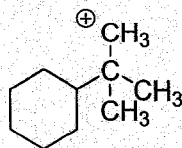
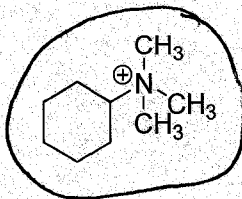
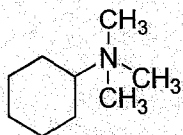
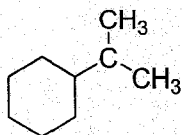
G. Which of the following is the most basic?



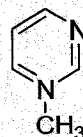
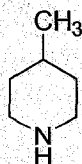
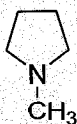
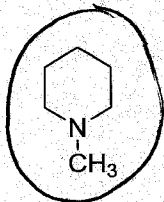
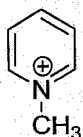
H. Which of the following is the least basic?



I. Which of the following is a quaternary ammonium ion?



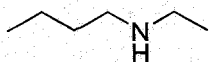
J. Which of the following is the correct structure of N-methylpiperidine?



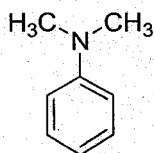
2. (15 points) Nomenclature. Name each of the following compounds using acceptable IUPAC nomenclature. Don't forget to indicate stereochemistry where appropriate.



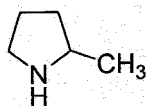
ammonia



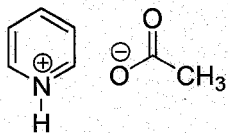
N-ethyl-1-butanamine



N,N-dimethylaniline

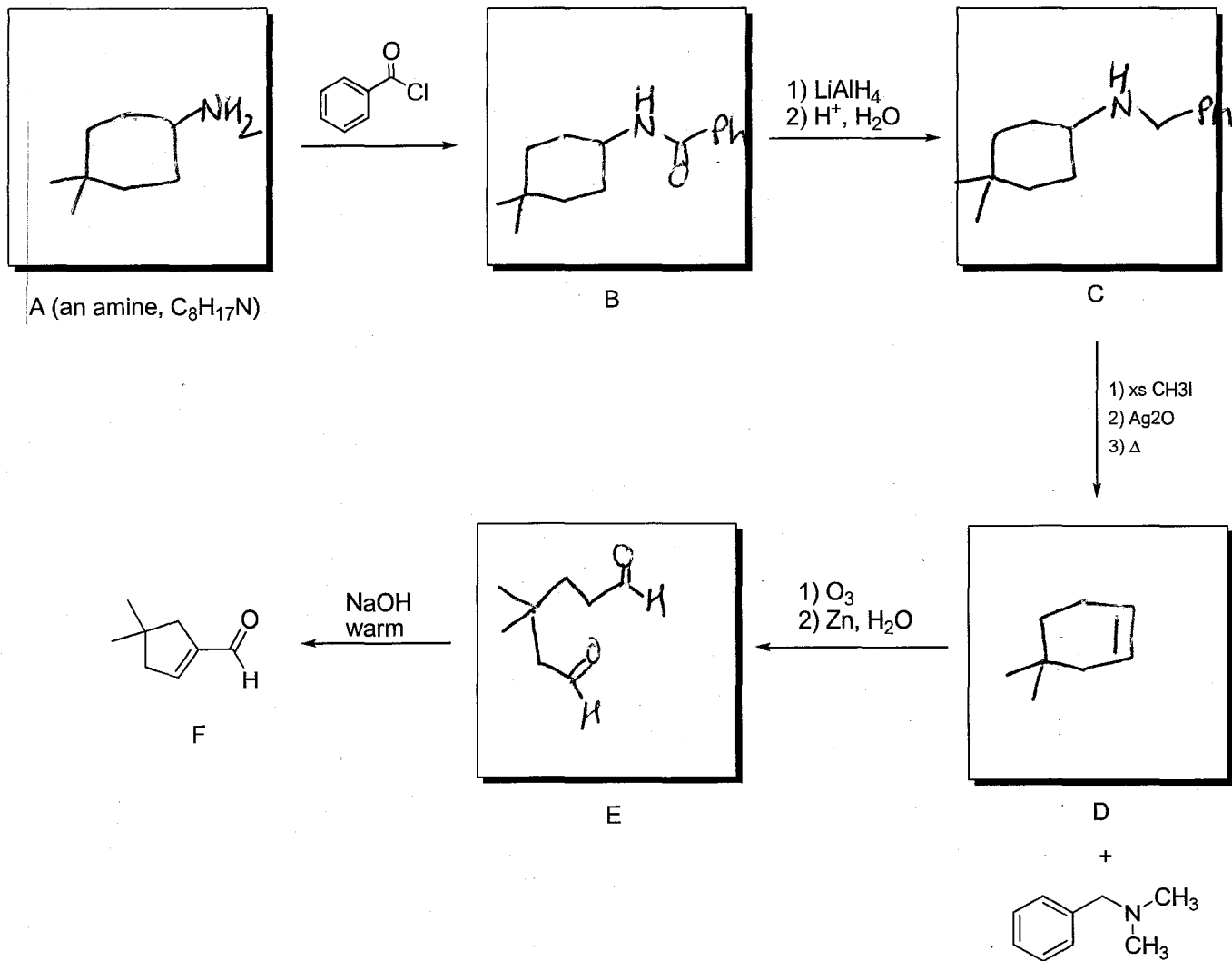


2-methylpyrrolidine



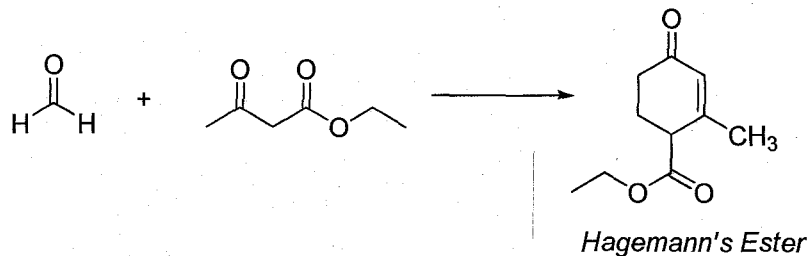
pyridinium acetate

3. (15 points) Box problem! Fill in the missing compounds so as to complete the scheme shown below.



3 pts each

4. (16 points) A compound known as *Hagemann's Ester* can be prepared by treating a mixture of formaldehyde and ethyl acetoacetate first with base and then with acid and heat. Write the structure for the product of each step.

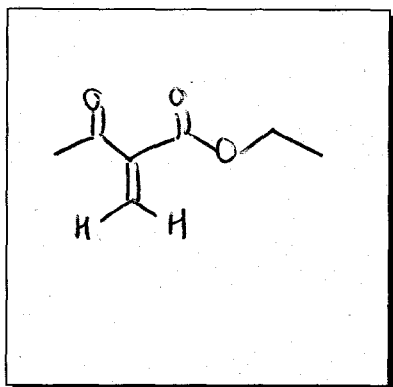


- The first step is an aldol-like condensation.
- The second step is a Michael addition.
- The third step is an intramolecular aldol condensation.
- The fourth step is a hydrolysis followed by a decarboxylation.

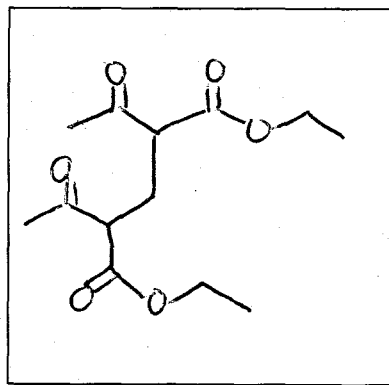
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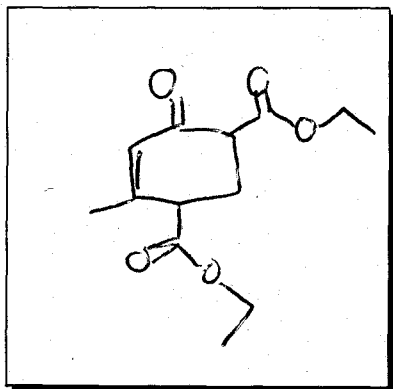
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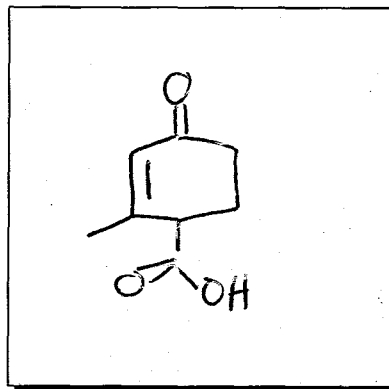
product of step (a)



product of step (b)

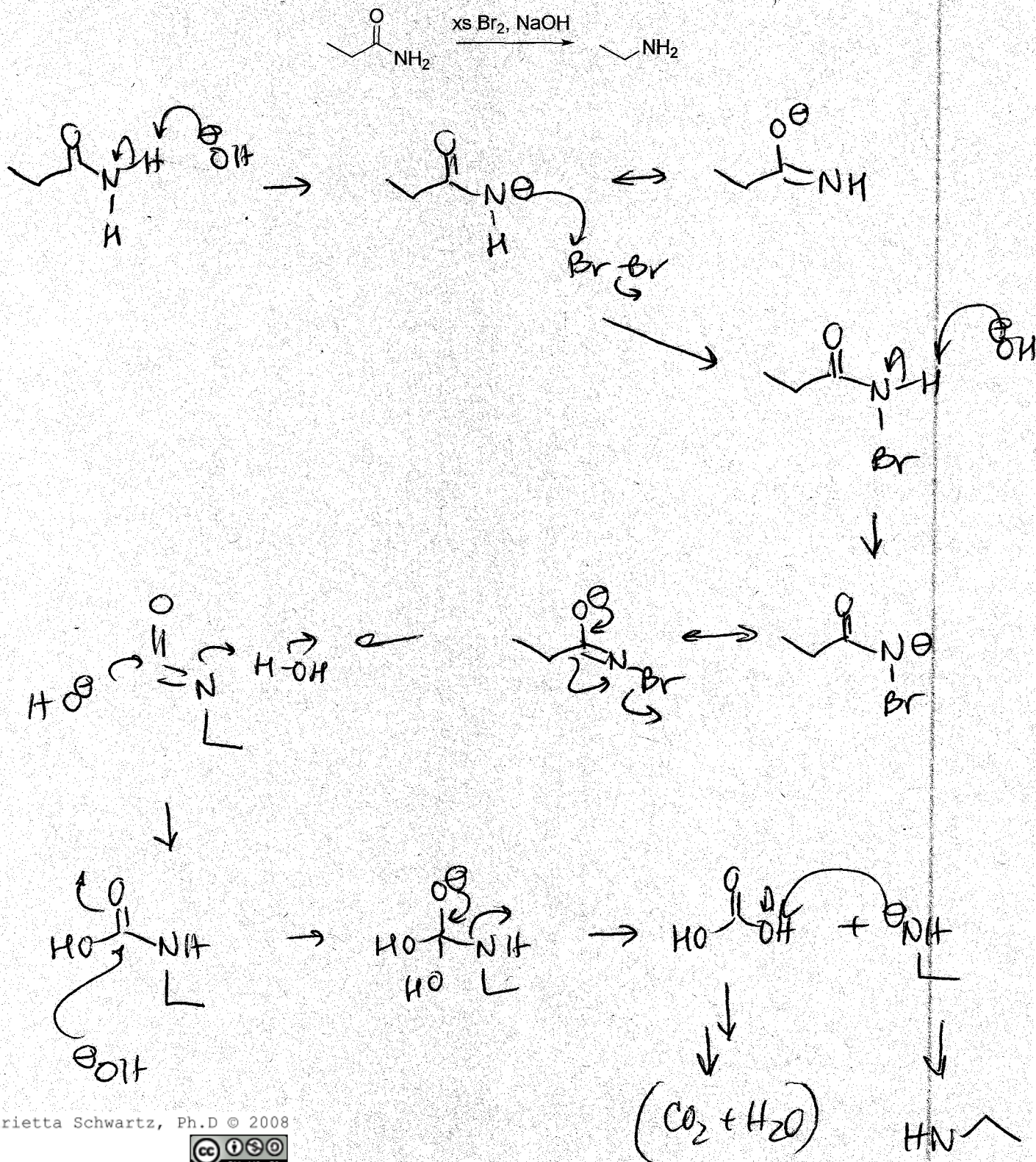


product of step (c)

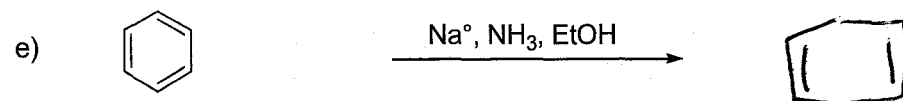
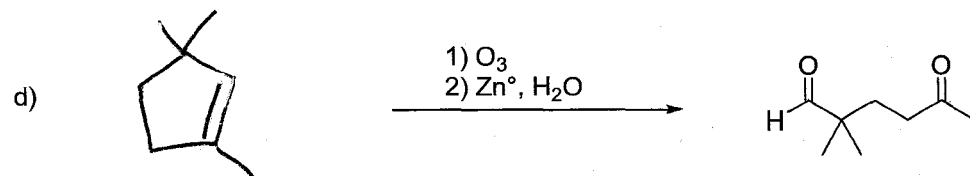
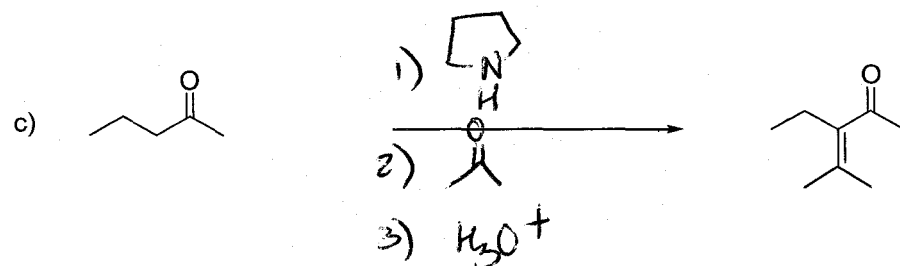
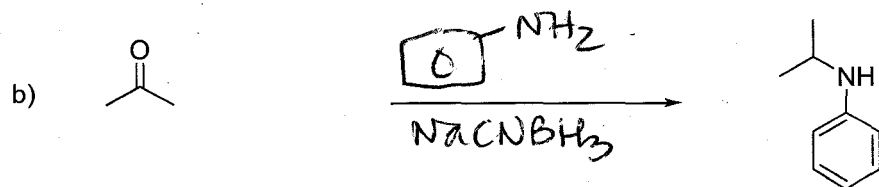
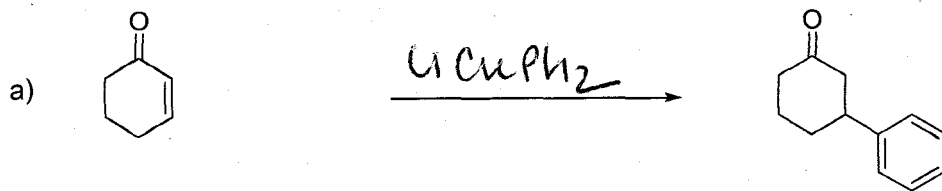


product of step (d)

5. (8 points) Provide a mechanism for the following transformation, using proper electron-pushing formalisms.

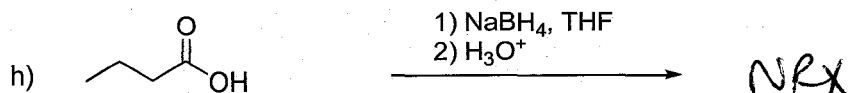
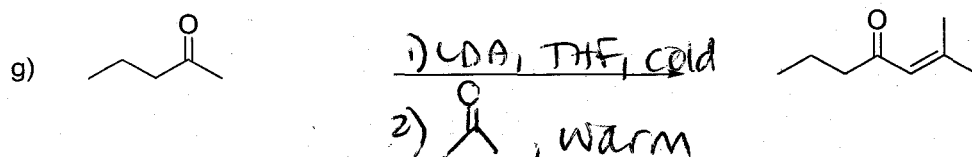
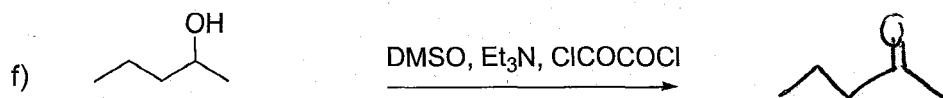


7. (18 points) Fill in the missing information so as to successfully complete each indicated reaction. (Keep in mind that "NRX" is always a viable product.) Your best five of the seven shown will be graded.



(continued on next page)

(from previous page)



Extra Credit:

1. Name the following reactions:

- C → D in Problem #3 Hofmann elimination
- E → F in Problem #3 aldol
- #5 Hofmann rearrangement
- #7c Stork
- #7e Birch reduction
- #7f Swern oxidation
- #7g aldol

2. The only member of this Texas trio who doesn't have a beard is named Beard. What's the name of the band?

ZZ Top