

## ALPHA CARBON CHEMISTRY: ENOLS AND ENOLATES

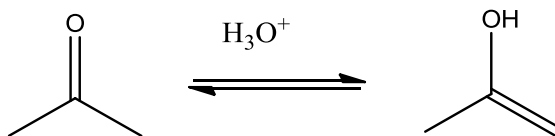
A STUDENT SHOULD BE ABLE TO:

1. Identify  $\alpha$ -carbons,  $\alpha$ -hydrogens and the bases strong enough to deprotonate them.
2. Draw the mechanisms for acid-catalyzed and base-catalyzed keto-enol tautomerization
3. Predict products of and propose syntheses using the following types of reactions.
  - Acid catalyzed halogenation of ketones at the  $\alpha$ -position
  - Hell-Volhard-Zelinski Reaction
  - Haloform reaction
  - Aldol reaction and aldol condensation. Aldol reaction products are formed without heat (room temperature or lower). Aldol condensation products occur under high temperatures or when extended conjugation within the product can be achieved.
  - Claisen condensation
  - Acetoacetic ester synthesis (alkylation at the  $\alpha$ -carbon)
  - Michael additions
4. Propose mechanisms for, and predict and interpret experimental results on the basis of mechanism, for the following reactions.
  - Keto-enol tautomerism
  - Aldol, crossed aldol, and related condensations
  - Decarboxylation of beta-keto acids
  - Claisen condensation
  - Acetoacetic ester synthesis
  - Michael additions

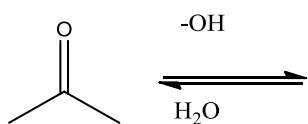
To best prepare for this module, please work Chapter 22 Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGE SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 In the following acid catalyzed tautomerization, identify the keto and enol forms.

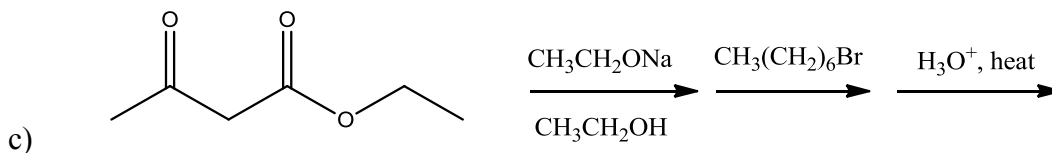
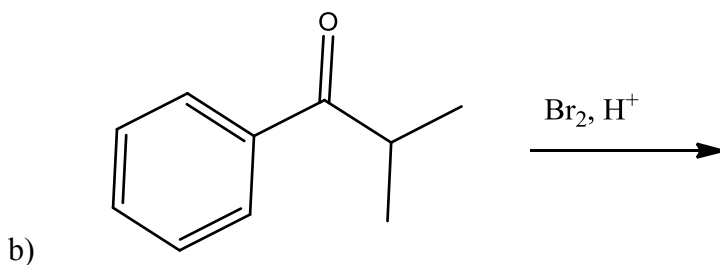
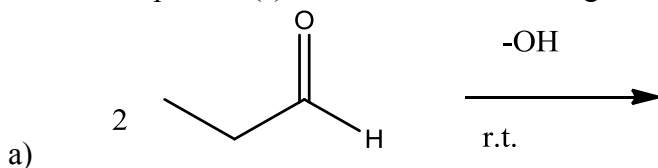


2.1 Show the mechanism for the base-catalyzed tautomerization of acetone.

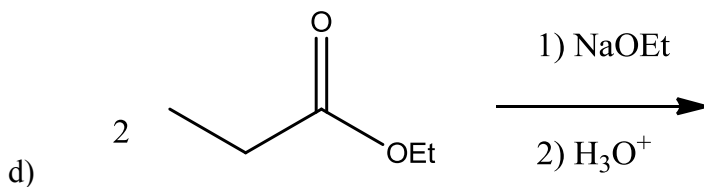


2.2 Draw the structure of the keto tautomer of phenol.

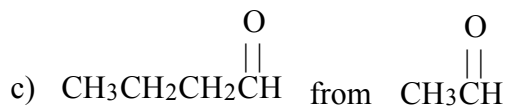
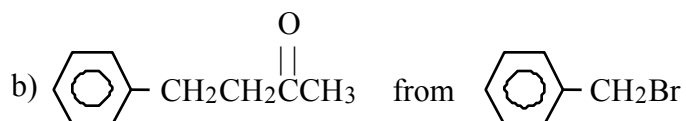
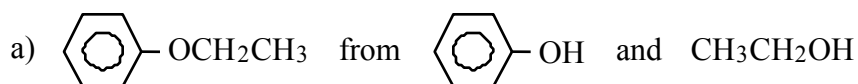
3.1 Predict the product(s) of each of the following reactions.



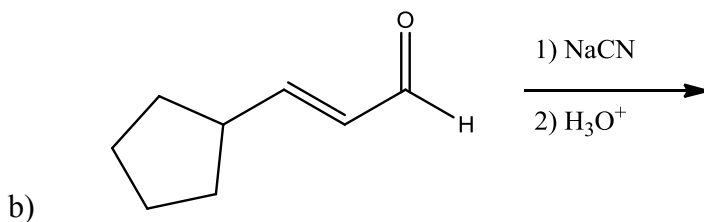
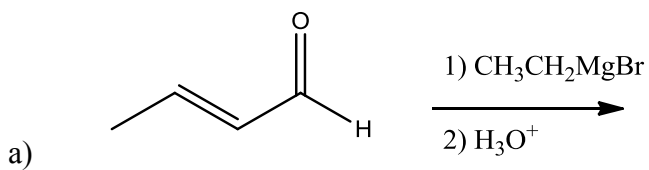
3.1



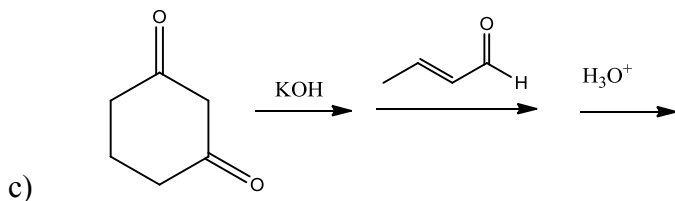
3.2 Propose a synthesis of each of the compounds shown, from the starting material(s) specified and any other needed reagents or solvents.



3.3 Predict the product of the following reactions of  $\alpha,\beta$ -unsaturated ketones

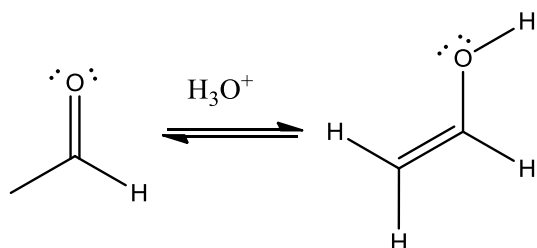


3.3

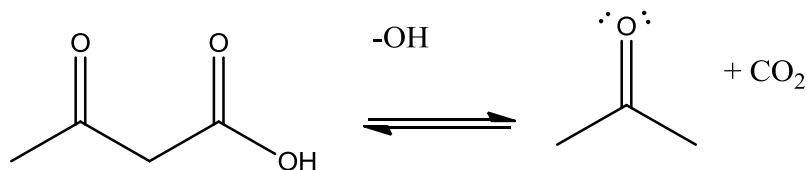


4. Propose a mechanism for each of the following reactions.

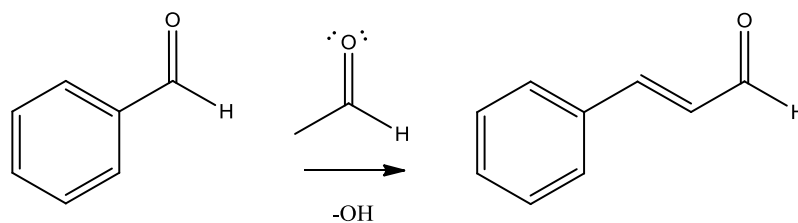
a)



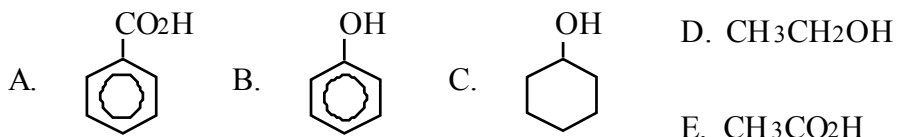
b)



c)

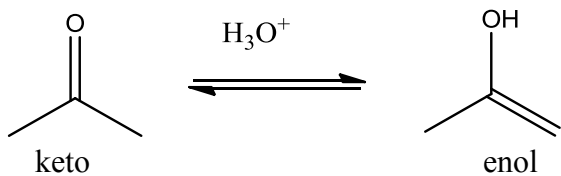


5.1 Of the following compounds: a) which one turns blue litmus red when dissolved in water? b) Which is neutral to litmus when dissolved in water? c) Which is insoluble in water but soluble in 5% NaOH (aq) and 5% NaHCO<sub>3</sub> (aq)? d) Which is insoluble in both water and NaOH (aq)?

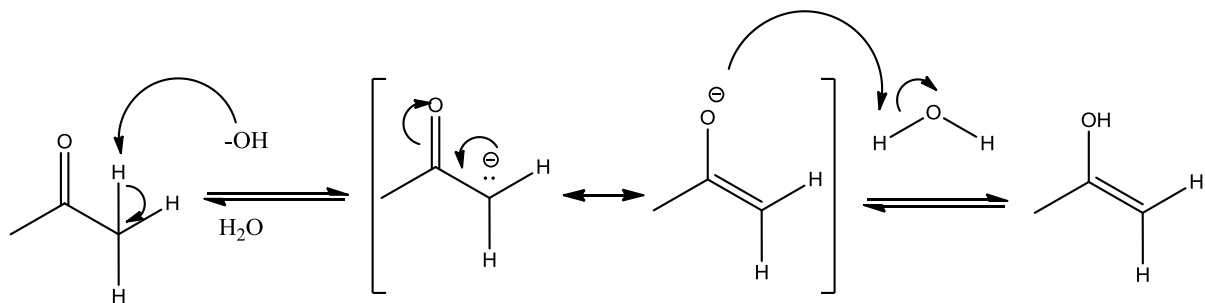


SOLUTIONS TO SAMPLE PROBLEMS:

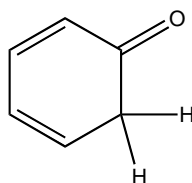
1.1



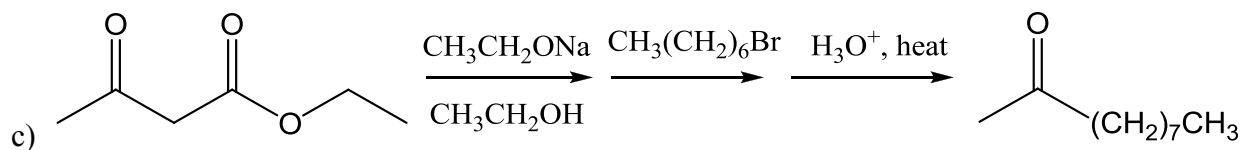
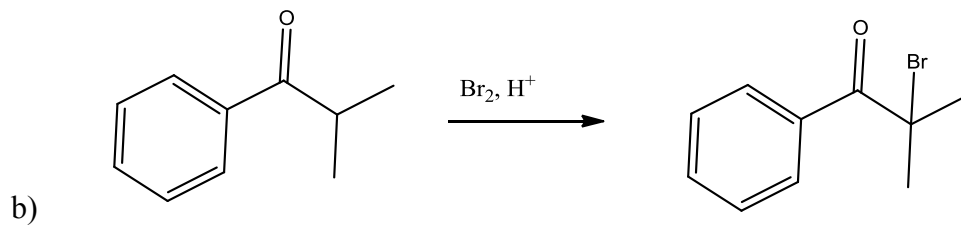
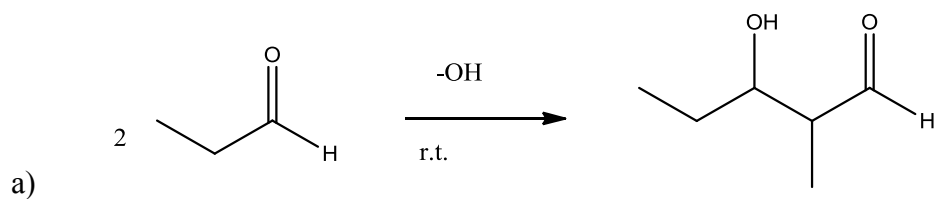
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2.2 The keto tautomer of phenol:

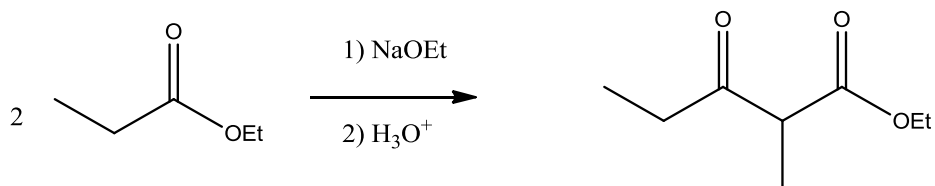


3.1 Predict the product(s):

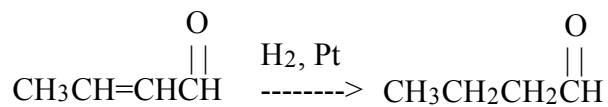
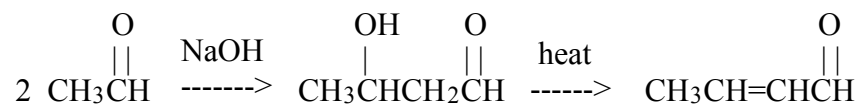
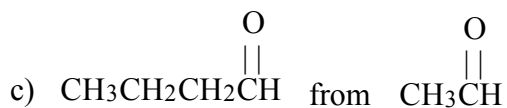
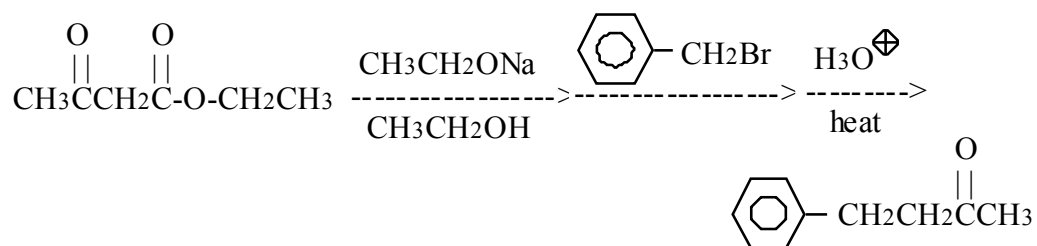
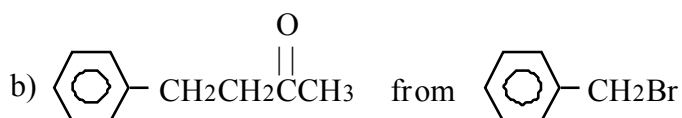
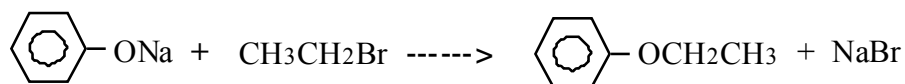
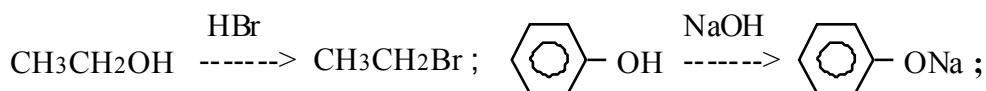
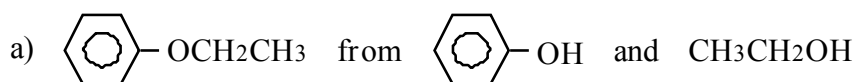


3.1

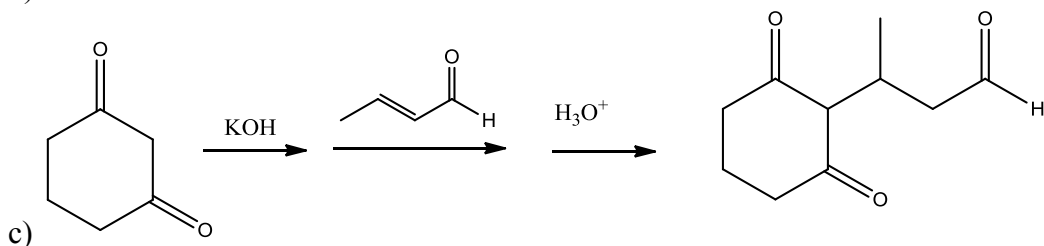
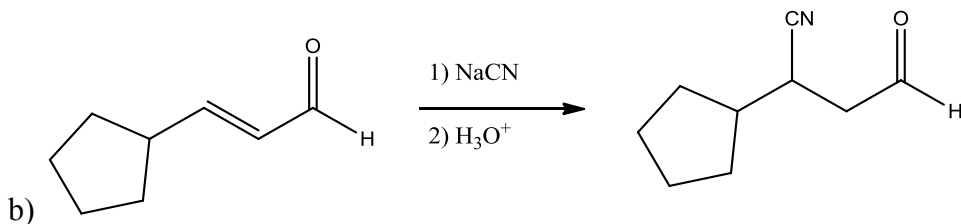
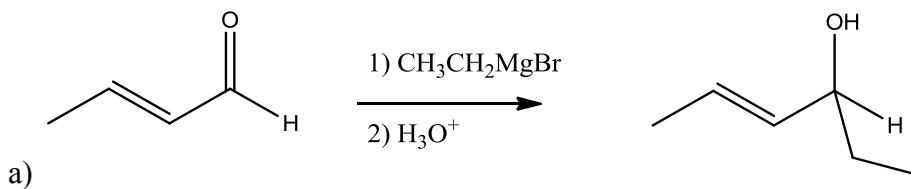
d)



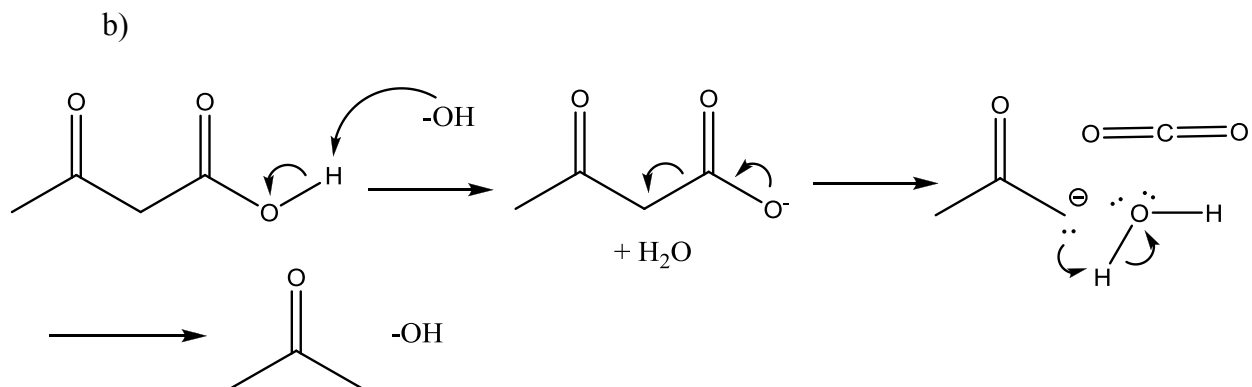
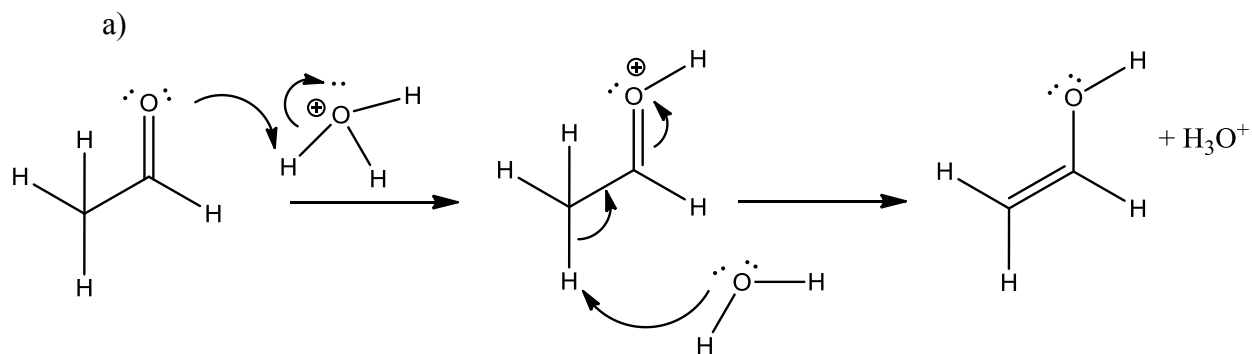
3.2 Propose a synthesis:



3.3

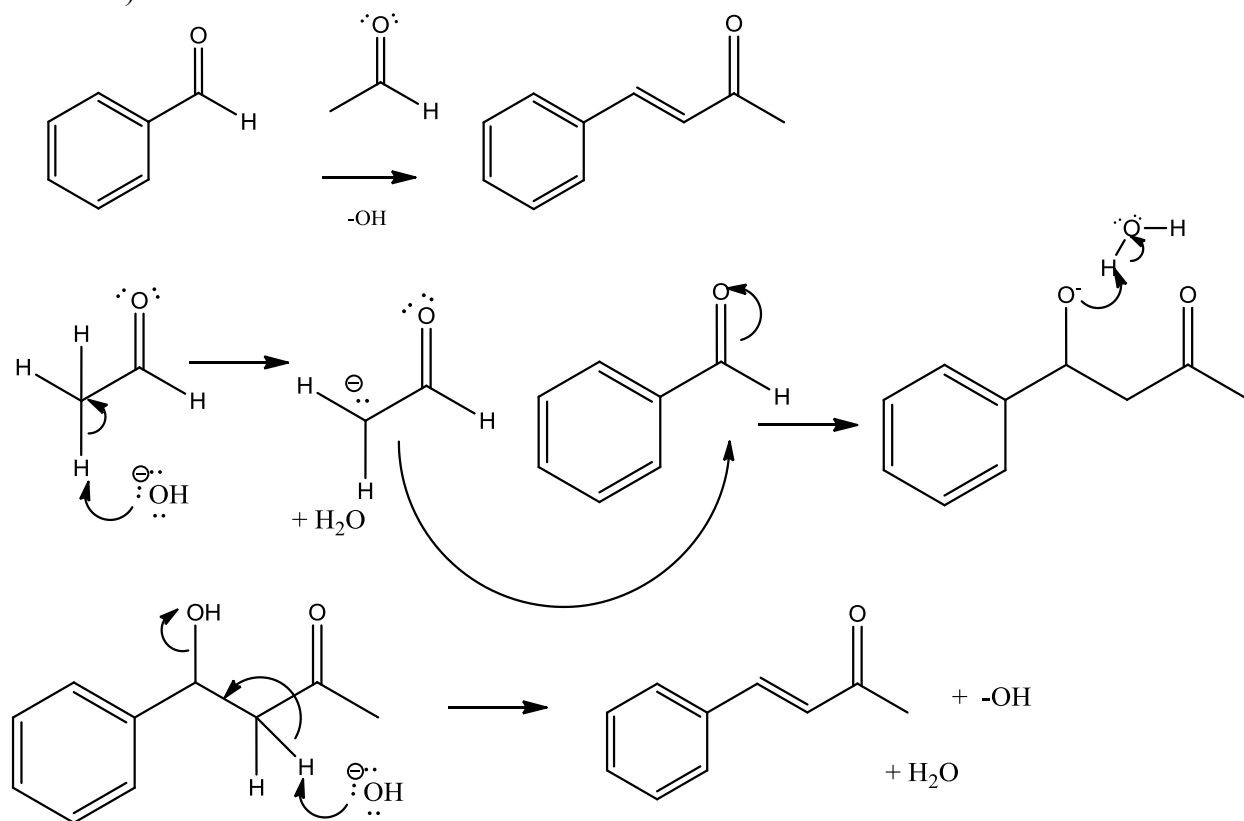


4. Mechanisms:



4.

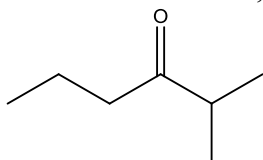
c)



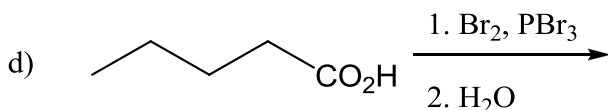
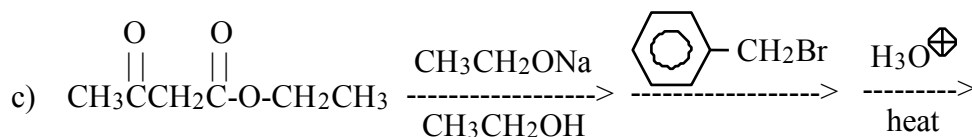
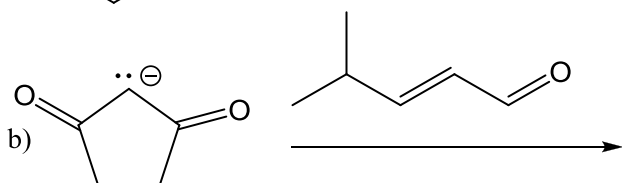
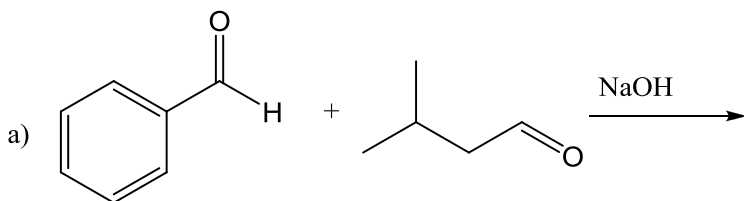
5.1

- a) E
- b) D
- c) A
- d) C

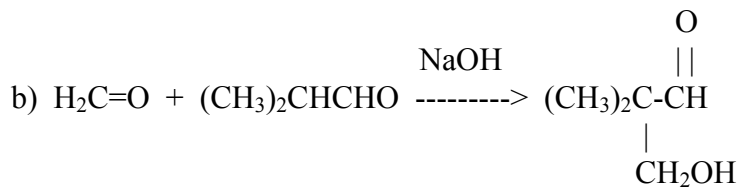
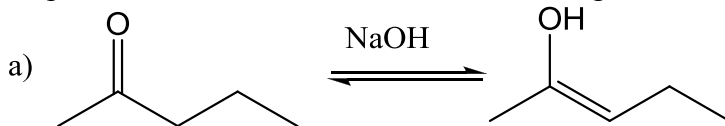
1. Circle all  $\alpha$  carbons, and draw in all  $\alpha$  hydrogens.



2. Predict the product(s) of each of the following reactions (if any):



3. Propose a mechanism for each of the following reactions:



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Eighth Drill Test (Sample B)  
Answer All Questions

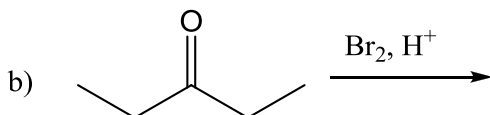
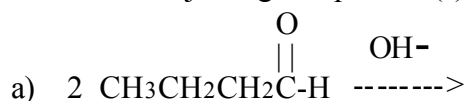
1. Circle the bases that are commonly used to generate the enolate from  $\text{CH}_3\text{CH}=\text{O}$ .

- a. NaOH      b.  $\text{CH}_3\text{ONa}$       c. NaCl      d. NaH      e.  $\text{NaNH}_2$

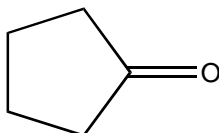
2. Which of the following compounds does not have  $\alpha$  protons?

- a.  $\text{H}_2\text{C}=\text{O}$       b.  $\text{C}_6\text{H}_5\text{CH}=\text{O}$       c.  $(\text{CH}_3)_3\text{CH}=\text{O}$       d.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{O}$

3. Predict the major organic product(s) of the following reactions.



4. Draw the enol tautomer of the ketone shown.



5. Propose a mechanism for each of the following reactions.

