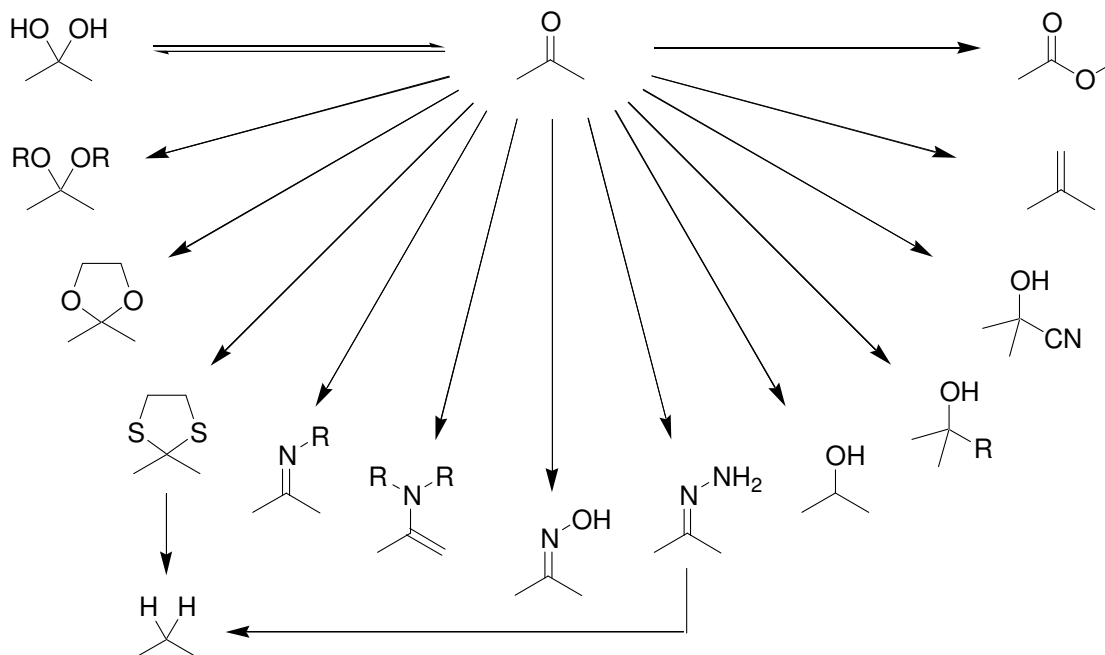


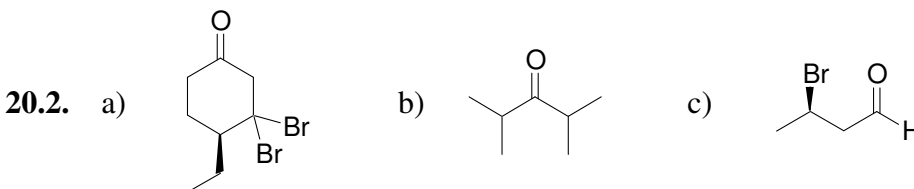
## Review of Reactions

Identify the reagents necessary to achieve each of the following transformations. To verify that your answers are correct, look in your textbook at the end of Chapter 20. The answers appear in the section entitled *Review of Reactions*.



## Solutions

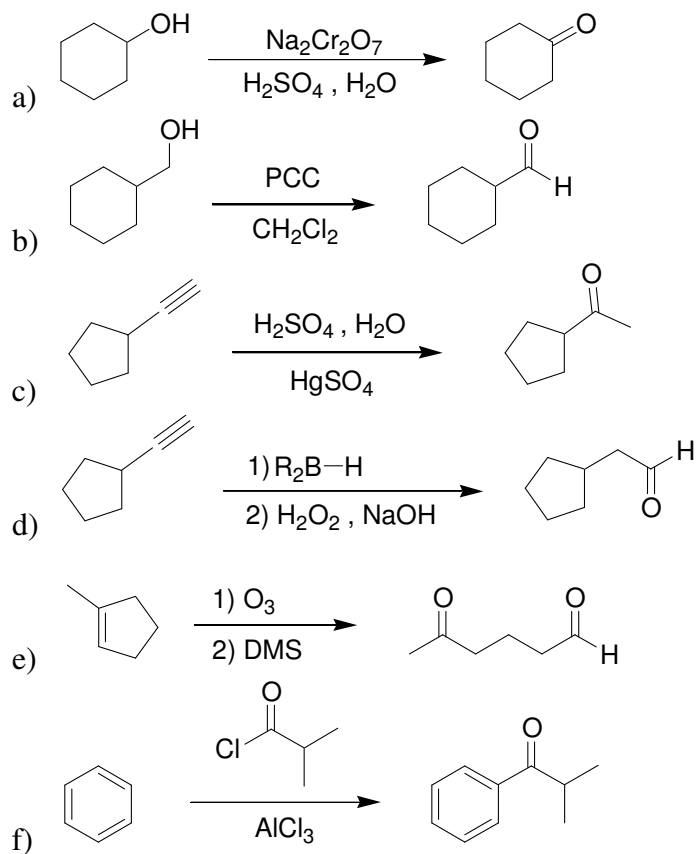
- 20.1. a) 5,5-dibromo-2,2-dimethylhexanal  
 b) (3*R*,4*S*)-3,4,5-trimethyl-2-hexanone  
 c) 2,2,5,5-tetramethylcyclopentanone  
 d) 2-propylpentanal  
 e) cyclobutanecarbaldehyde



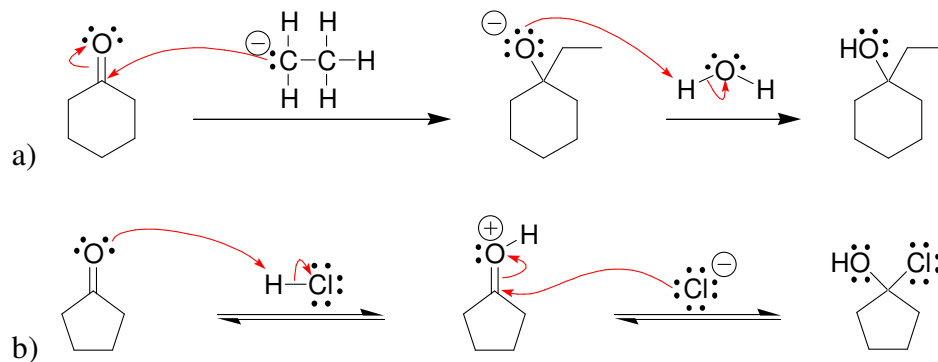
- 20.3. (1*S*,4*R*)bicyclo[2.2.1]heptan-2-one

- 20.4. a) 1,3-cyclohexanedione    b) 1,4-cyclohexanedione    c) 2,5,8-nonanetrione

## 20.5.



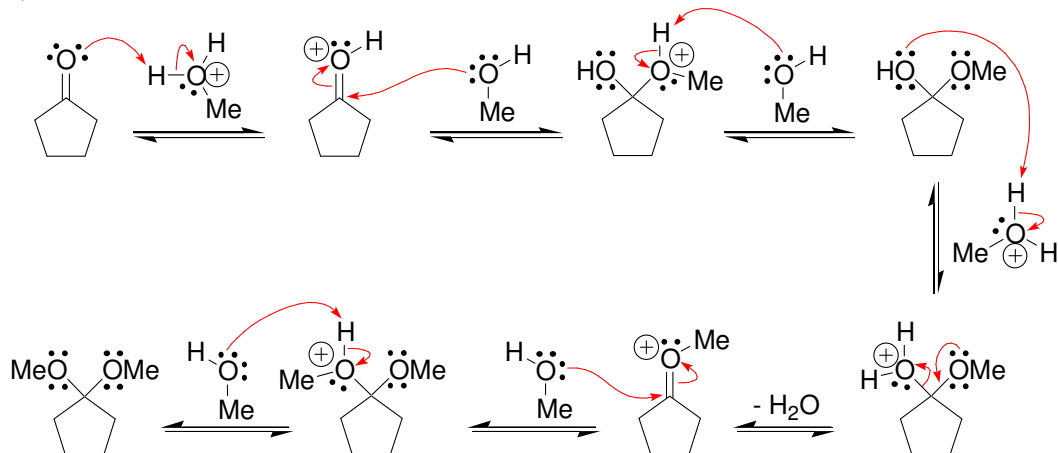
## 20.6.



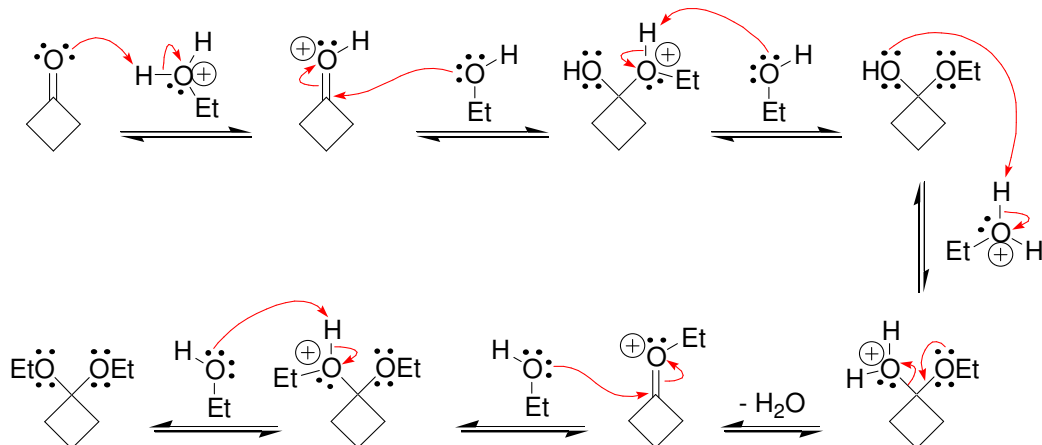
20.7. The carbonyl group in hexafluoroacetone is flanked by two very powerful electron-withdrawing groups ( $\text{CF}_3$ ). These groups withdraw electron density from the carbonyl group, thereby increasing the electrophilicity of the carbonyl group. The resulting increase in energy of the reactant causes the equilibrium to favor the product (the hydrate).

## 20.8.

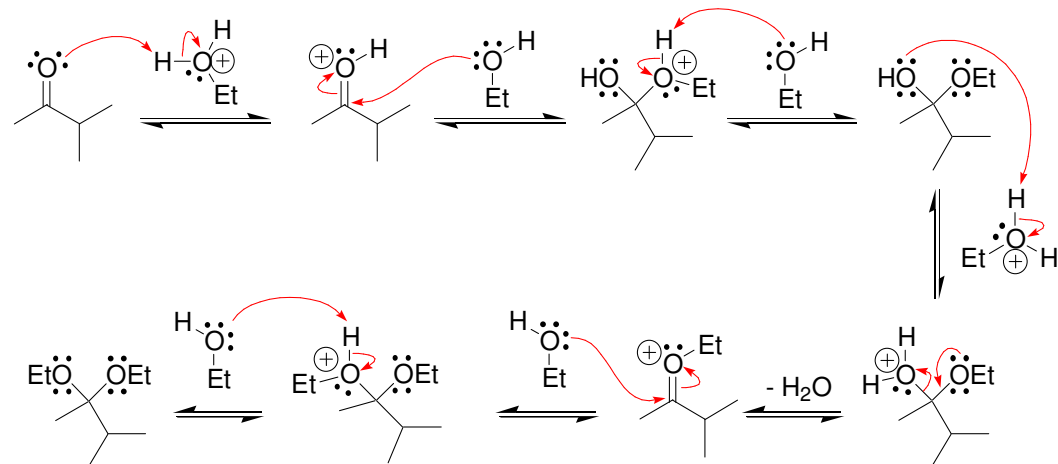
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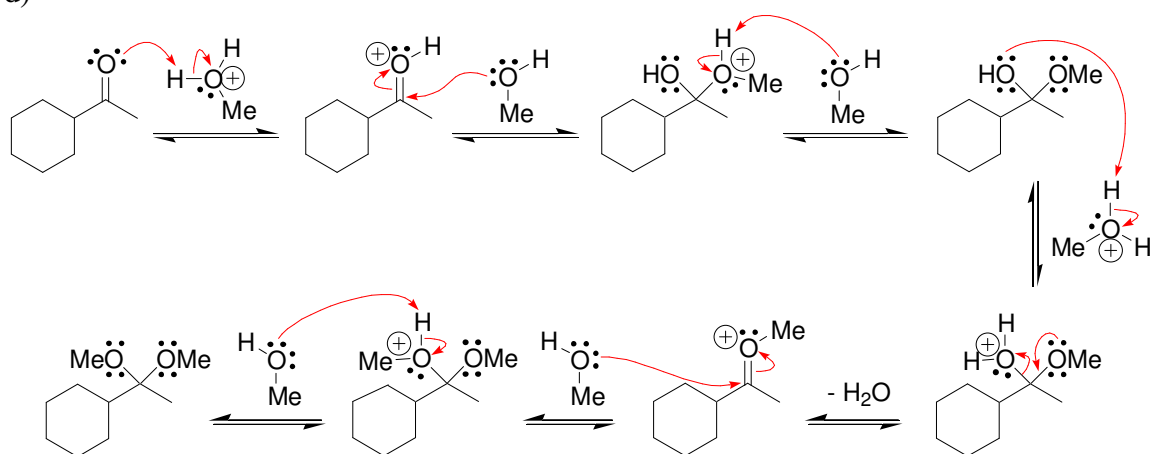
b)



c)

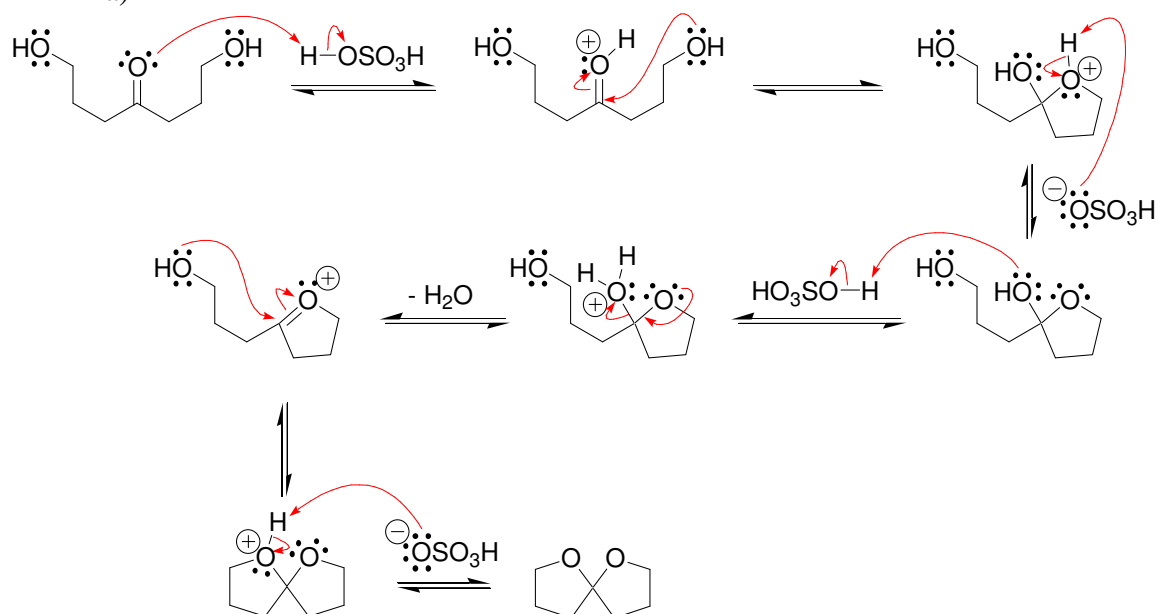


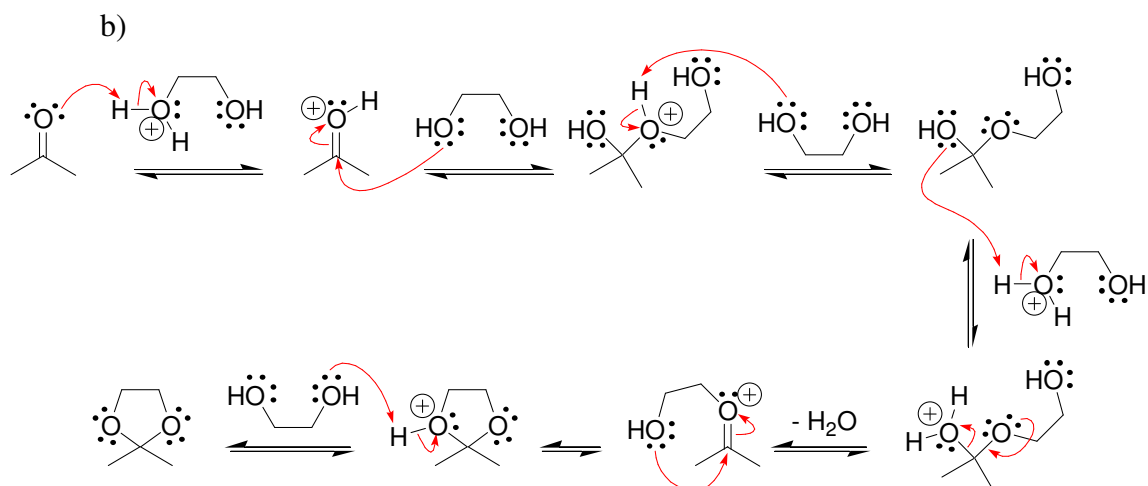
d)



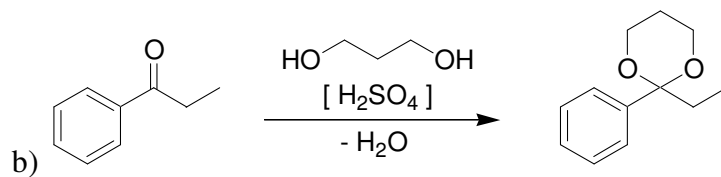
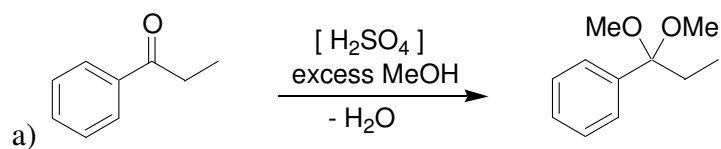
20.9.

a)

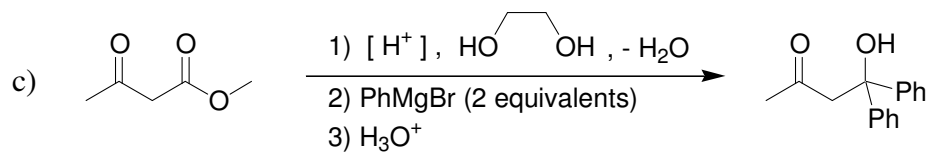
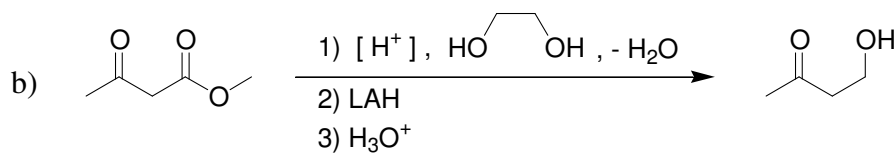
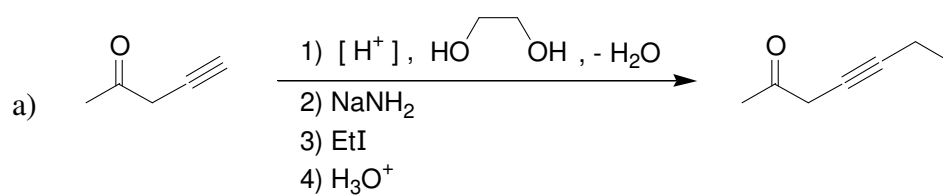


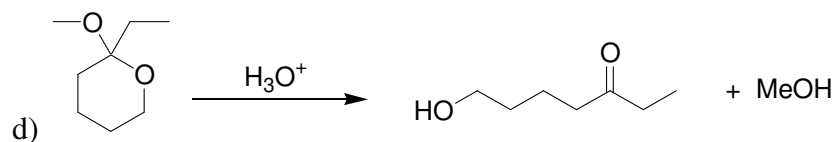
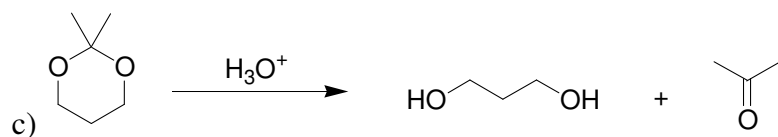
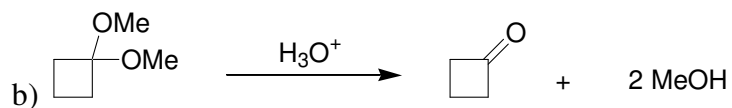
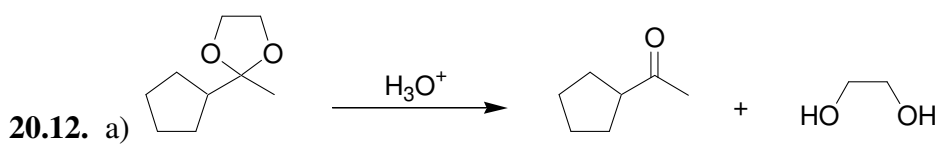


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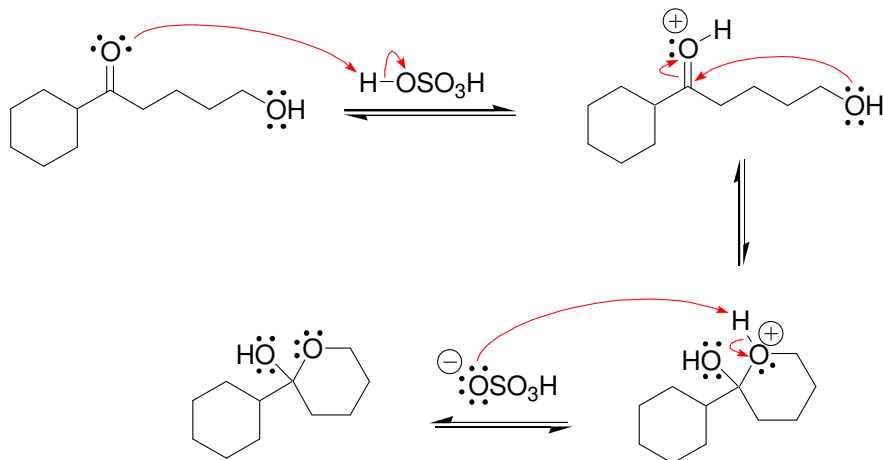


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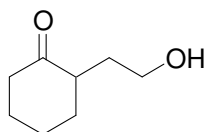




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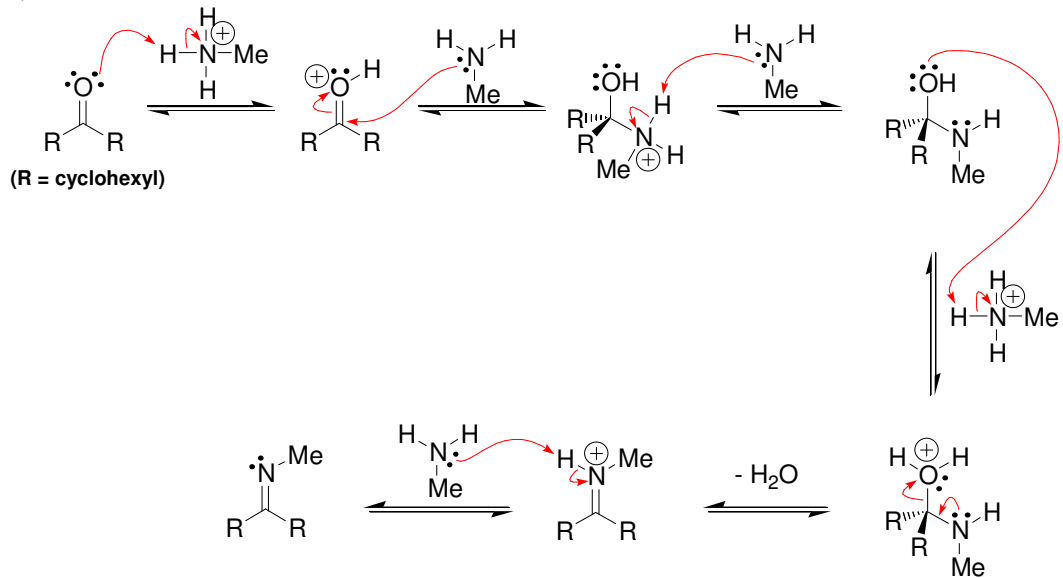


20.14.

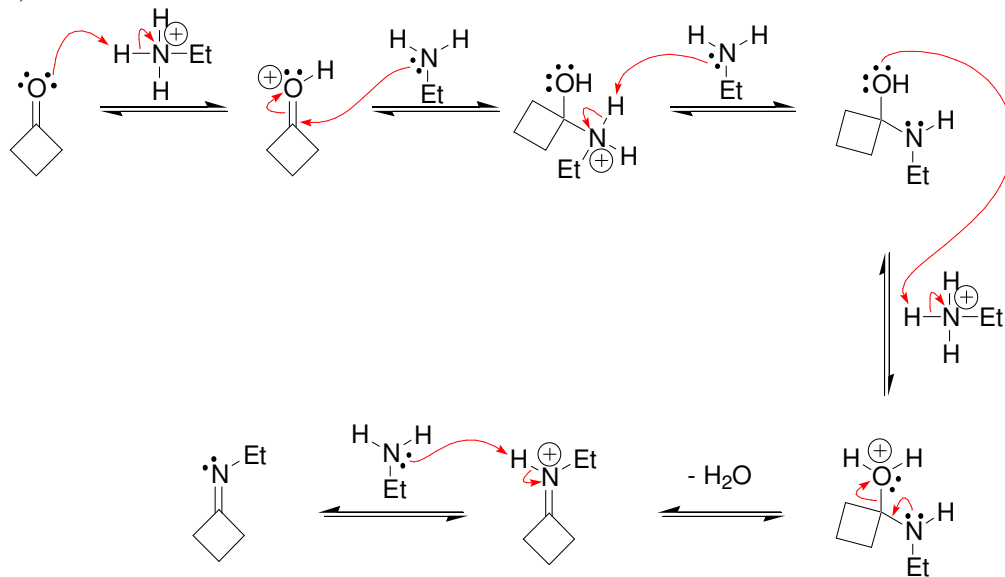


**20.15. Note:** For each of the mechanisms shown below, the first two steps can be reversed (first the amine attacks the carbonyl group, and then the tetrahedral intermediate is protonated). It would be wise to check your lecture notes to determine if your instructor has a strong preference for this alternate sequence of steps.

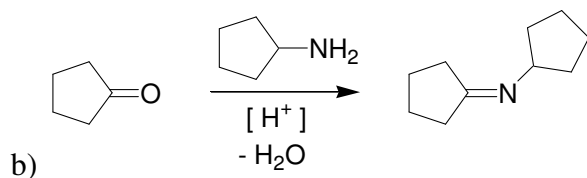
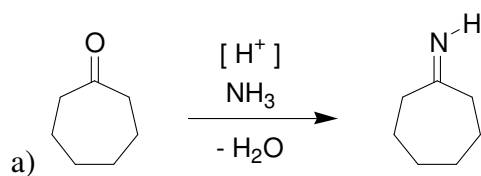
a)



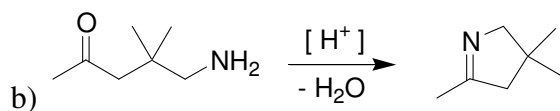
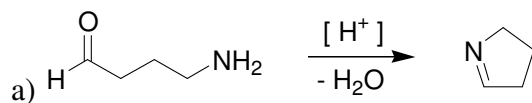
b)



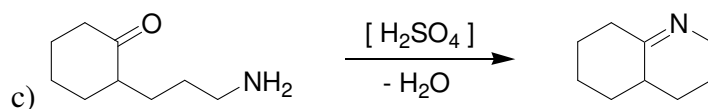
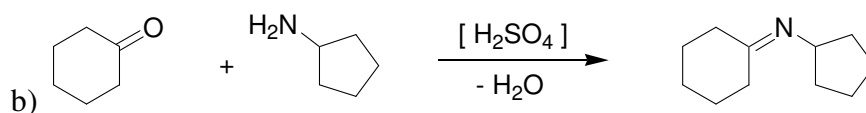
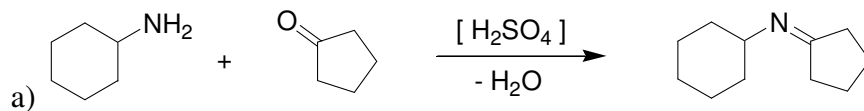
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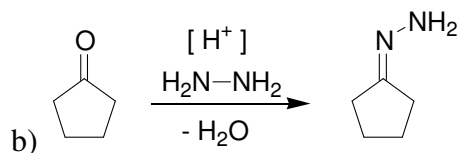
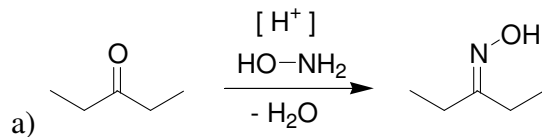
## 20.17.



## 20.18.

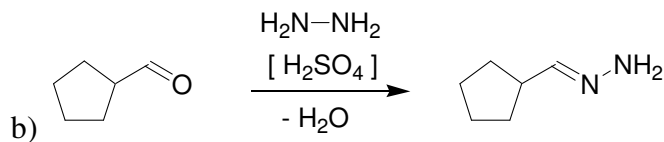
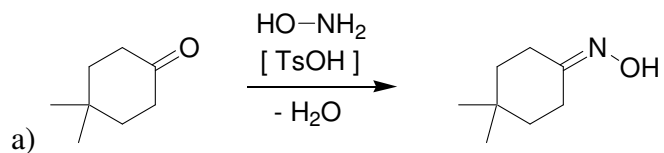


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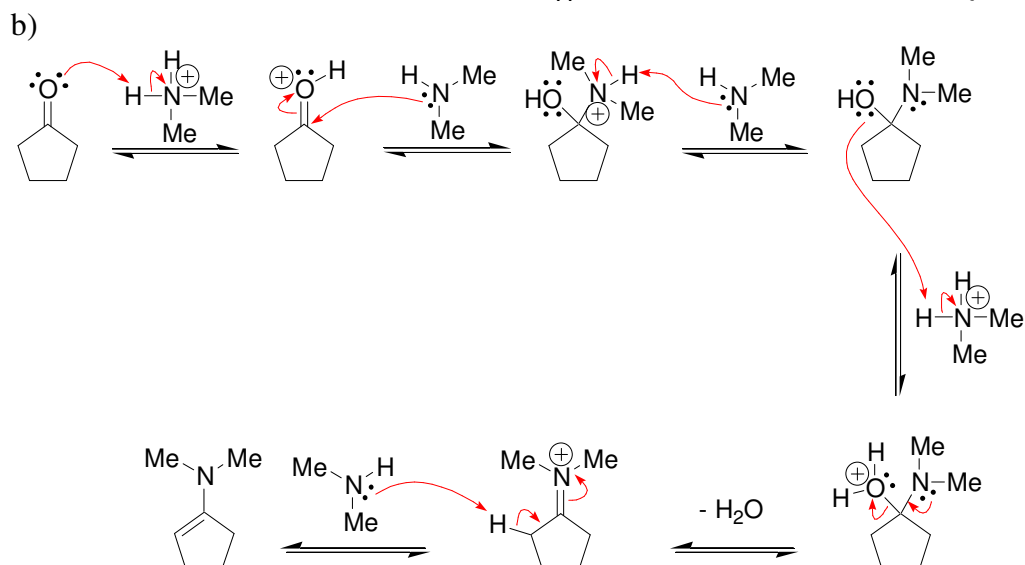
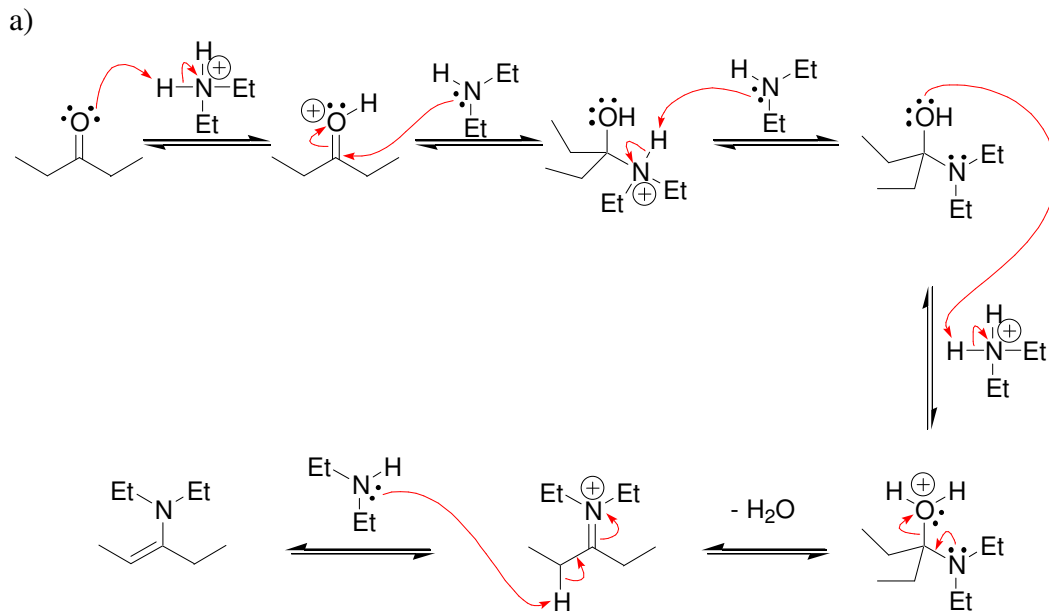




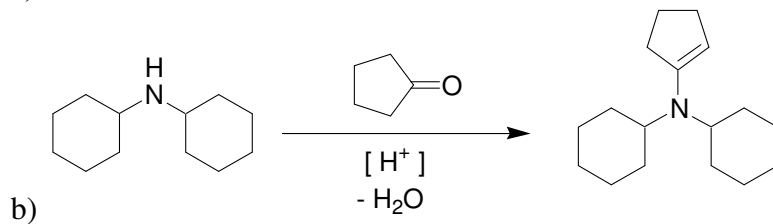
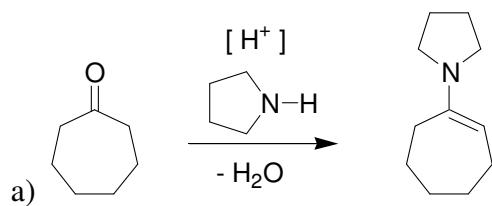
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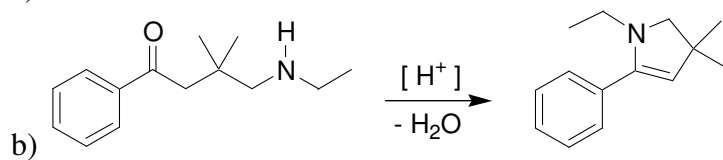
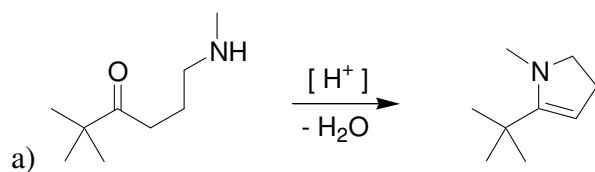
**20.21.** Note: For each of the mechanisms shown below, the first two steps can be reversed (first the amine attacks the carbonyl group, and then the tetrahedral intermediate is protonated). It would be wise to check your lecture notes to determine if your instructor has a strong preference for this alternate sequence of steps.



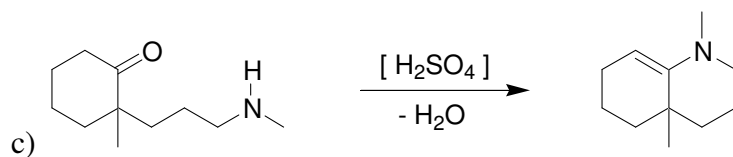
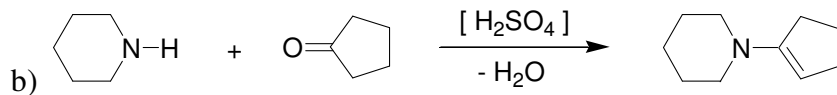
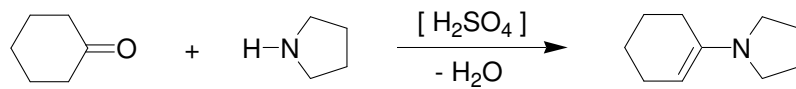
## 20.22.



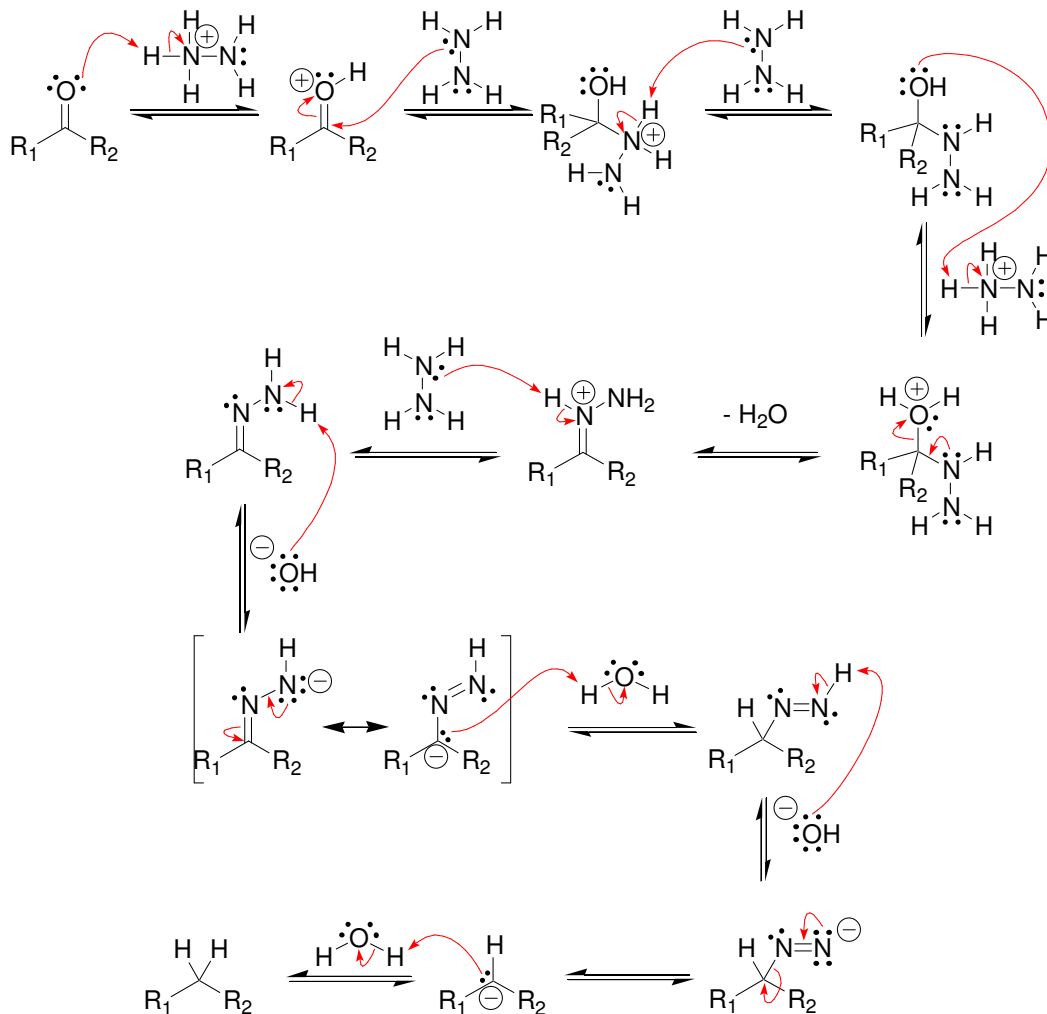
## 20.23.



## 20.24.

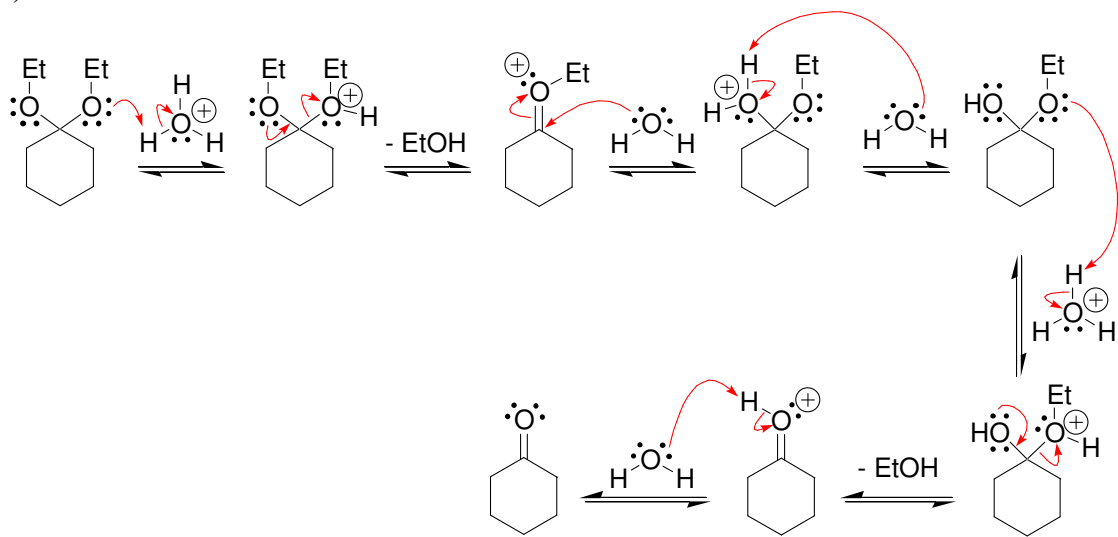


**20.25.** Note: *The first two steps of this mechanism can be reversed (first the amine attacks the carbonyl group, and then the tetrahedral intermediate is protonated). It would be wise to check your lecture notes to determine if your instructor has a strong preference for this alternate sequence of steps.*

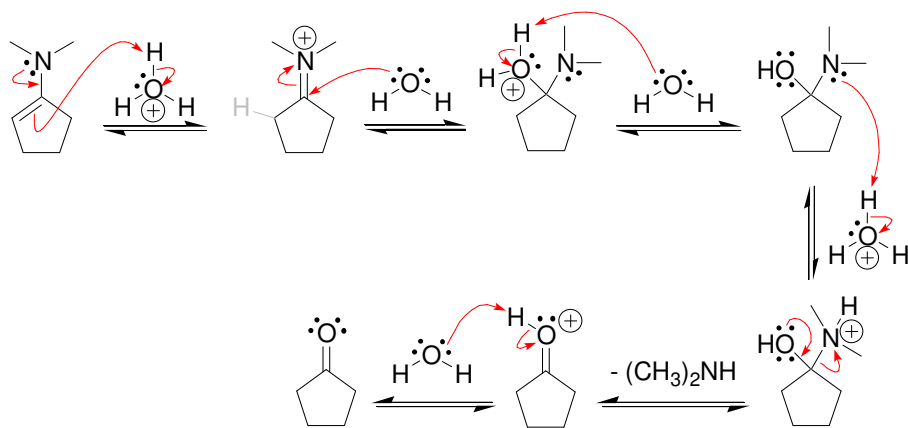


## 20.26.

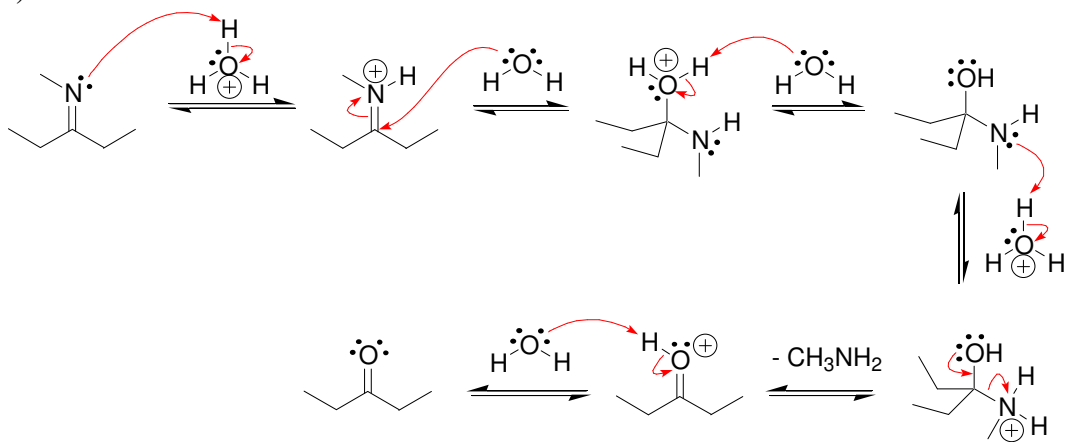
a)

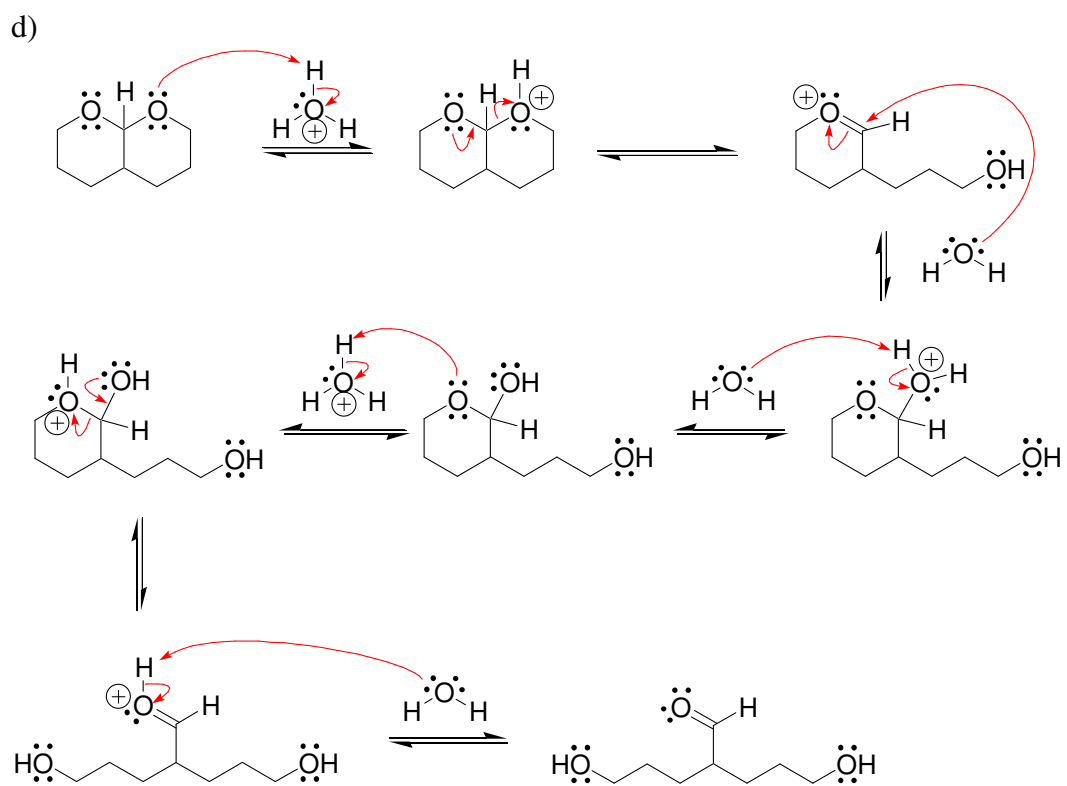


b)

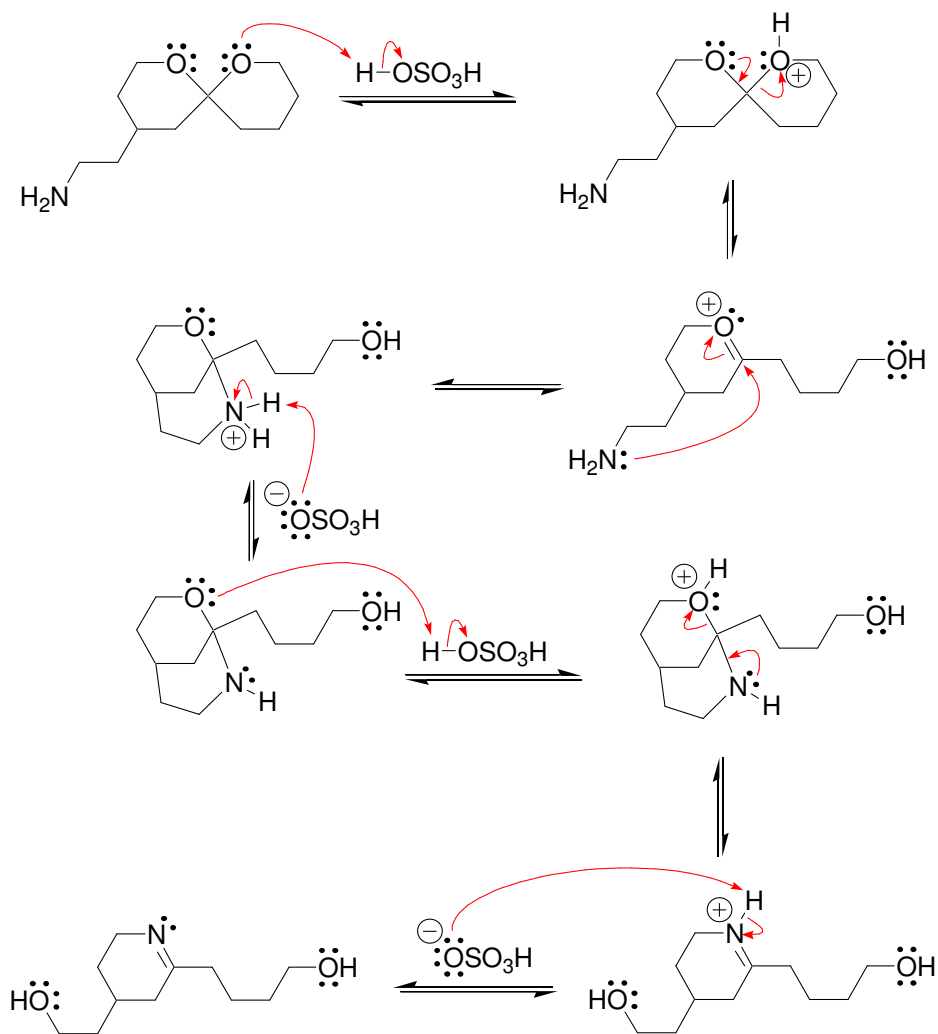


c)

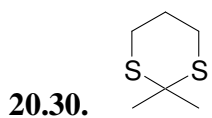
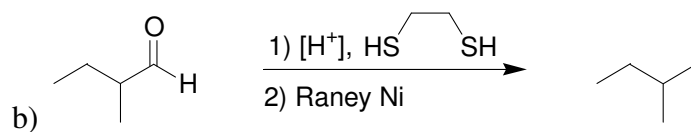
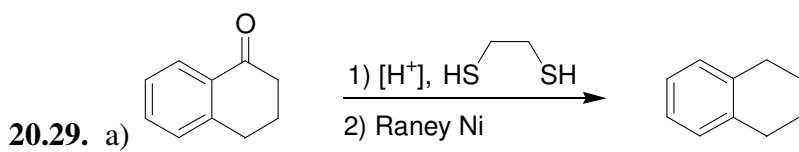
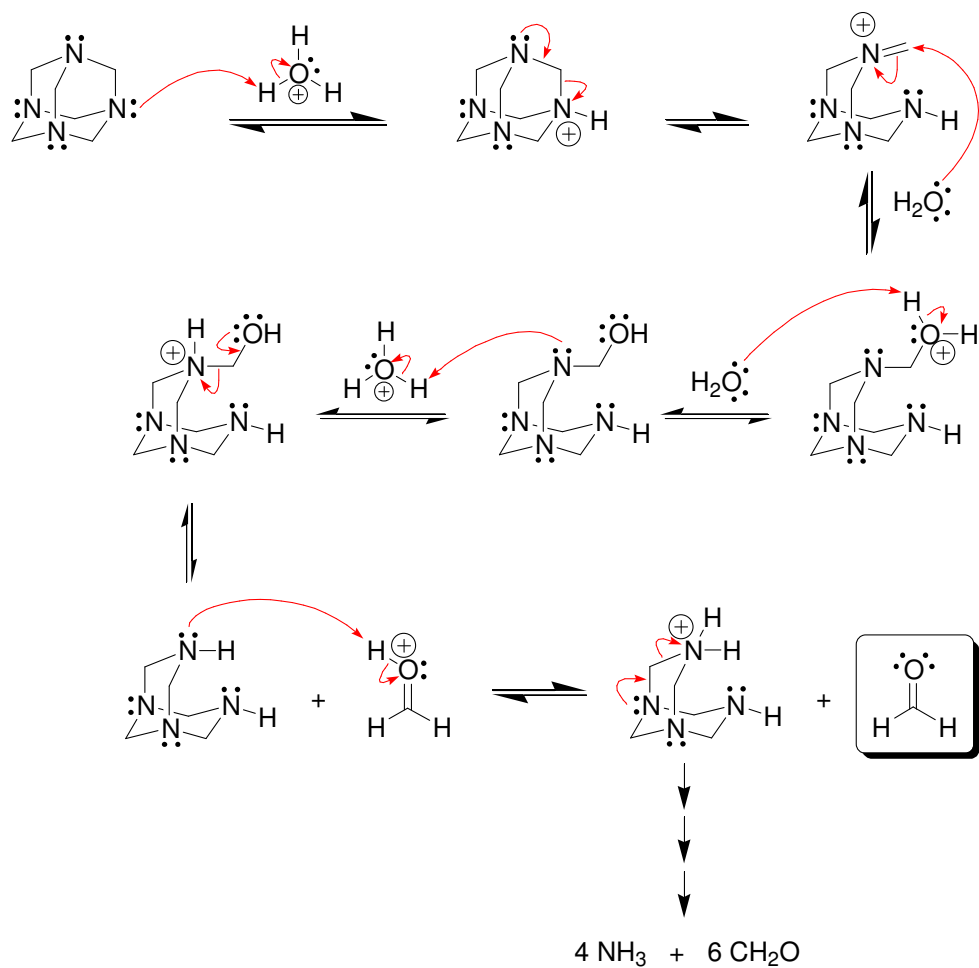




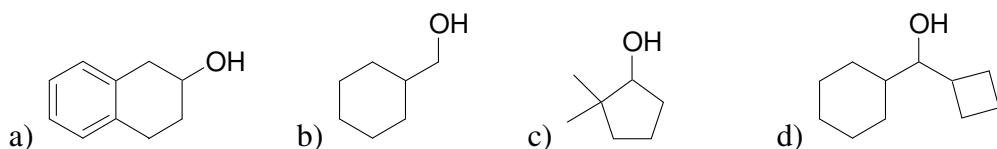
## 20.27.



20.28.

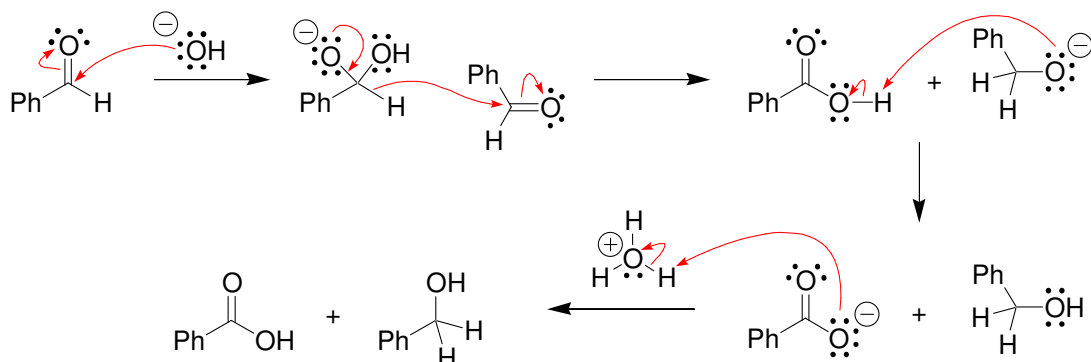


## 20.31.



## 20.32.

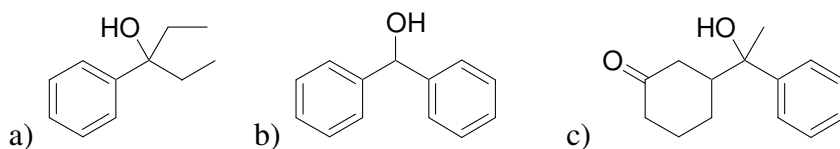
a) Below is a mechanism for the Cannizzaro reaction. After a hydroxide ion attacks one molecule of benzaldehyde, the resulting tetrahedral intermediate functions as a hydride delivery agent to attack another molecule of benzaldehyde, giving a carboxylic acid and an alkoxide ion. The alkoxide ion then deprotonates the carboxylic acid, generating a more stable carboxylate ion. This carboxylate ion is then protonated when an acid is added to the reaction mixture.



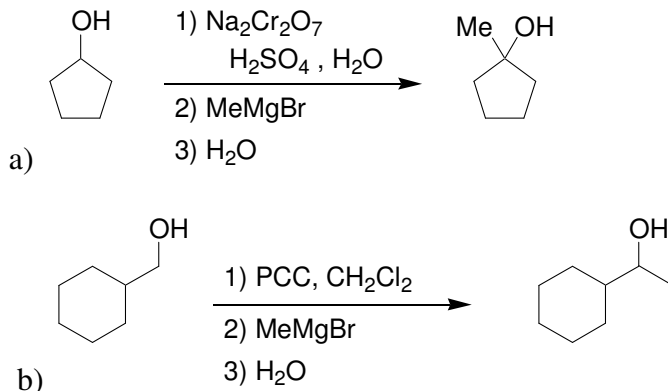
b) The function of  $\text{H}_3\text{O}^+$  in the second step is to serve as a proton source to protonate the resulting carboxylate ion.

c) Water is only a weak acid ( $\text{p}K_a = 15.74$ ), and is not sufficiently strong to serve as a proton source for a carboxylate ion ( $\text{p}K_a$  of  $\text{PhCOOH}$  is 4.21). See section 3.5 for a discussion of this topic.

## 20.33.

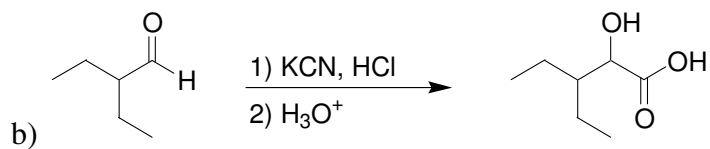
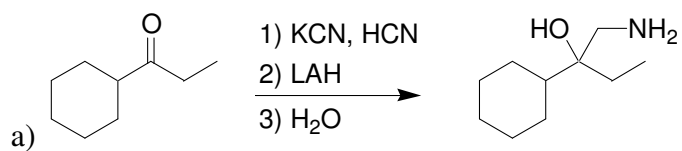


## 20.34.

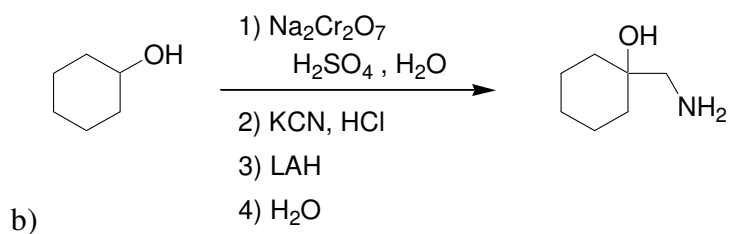
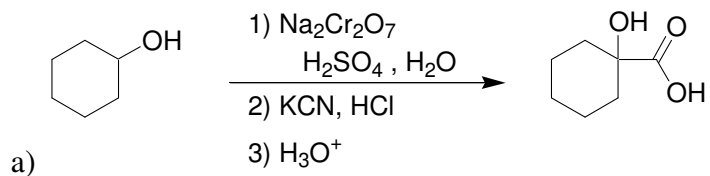




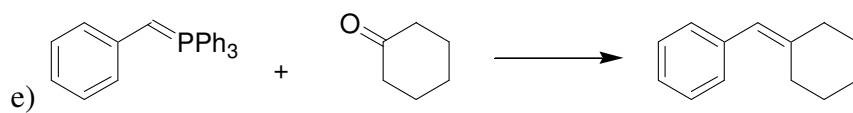
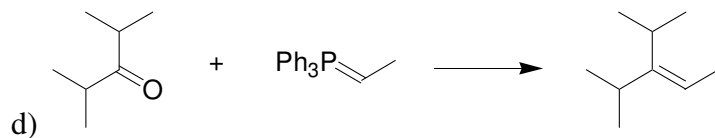
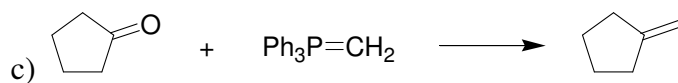
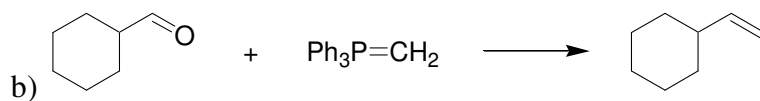
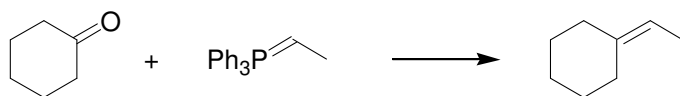
20.35.



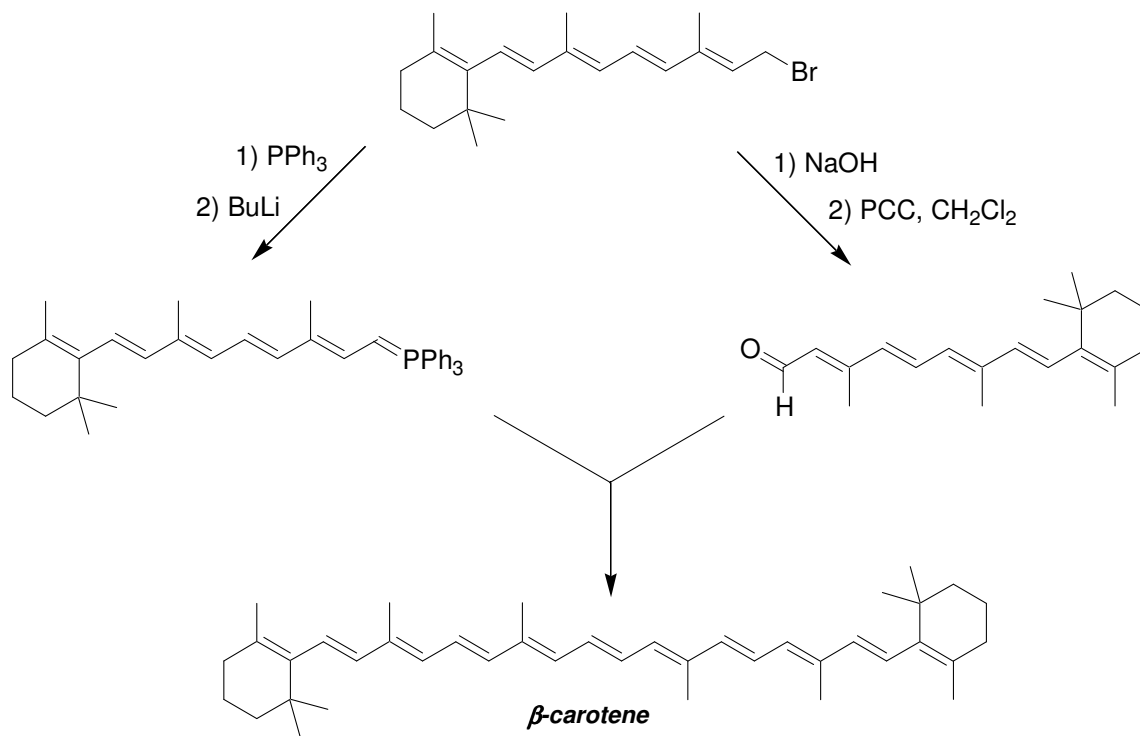
20.36.



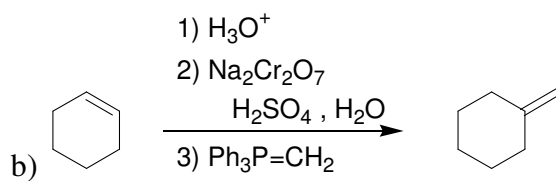
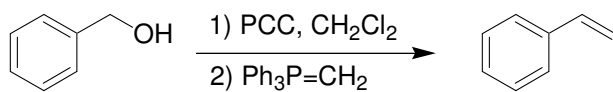
20.37. a)



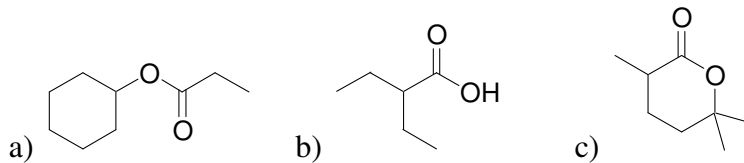
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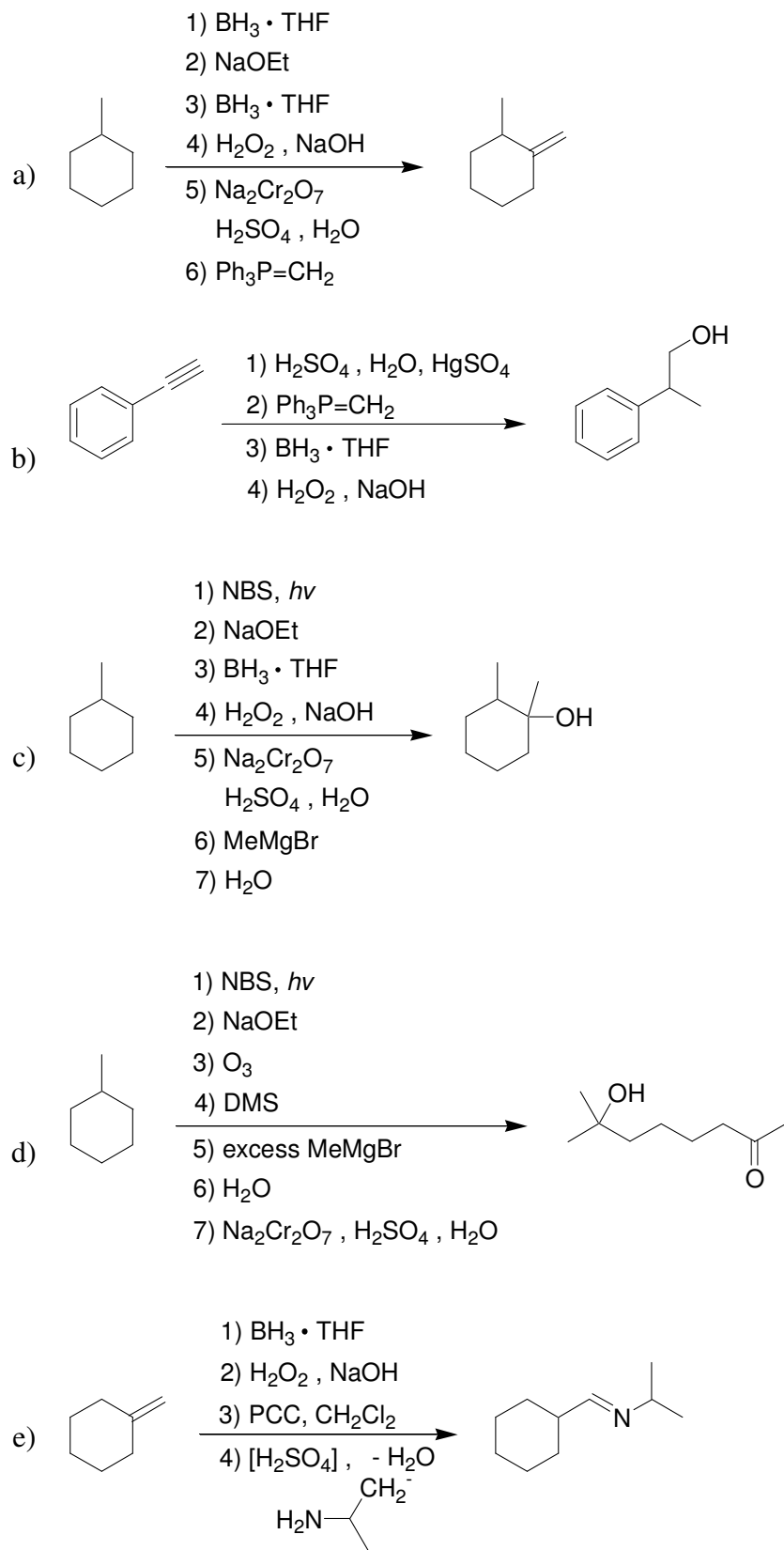
## 20.39. a)

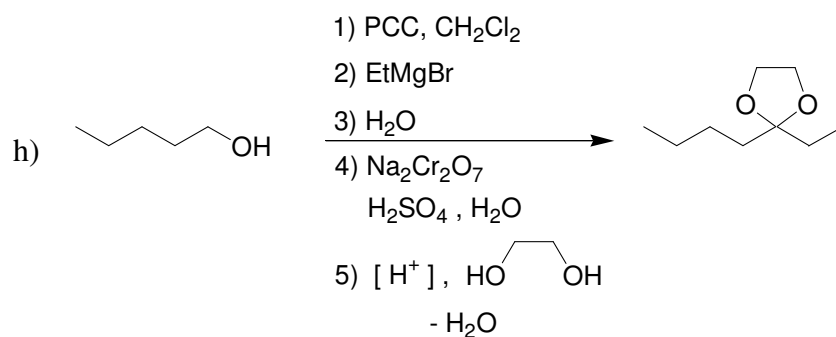
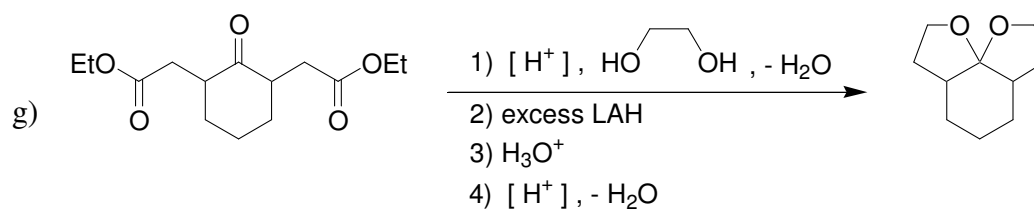
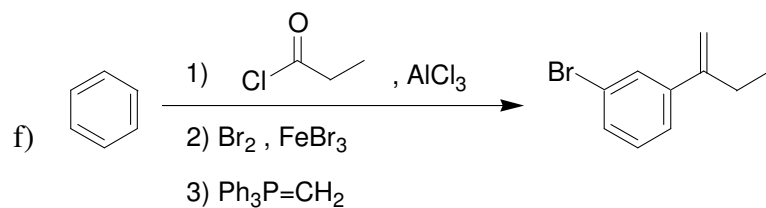


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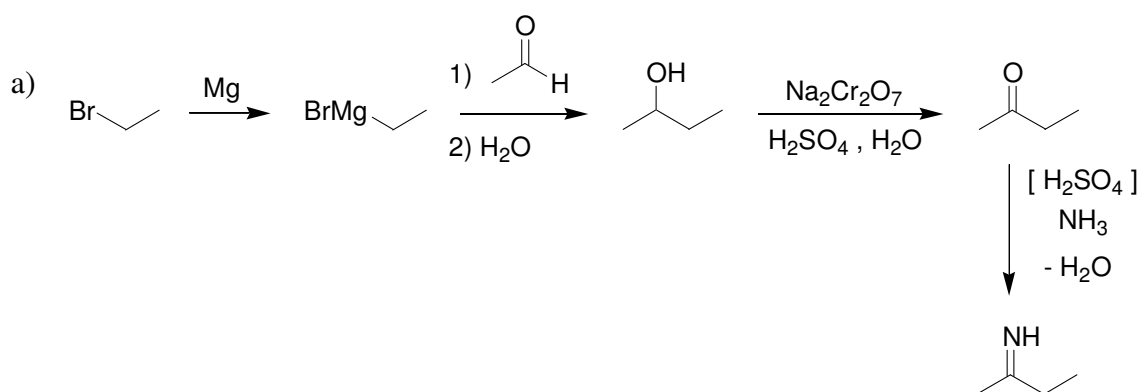


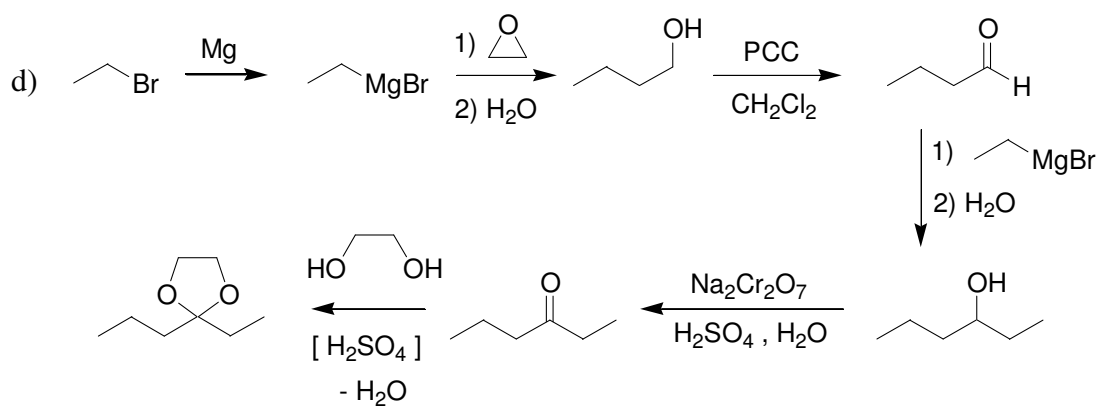
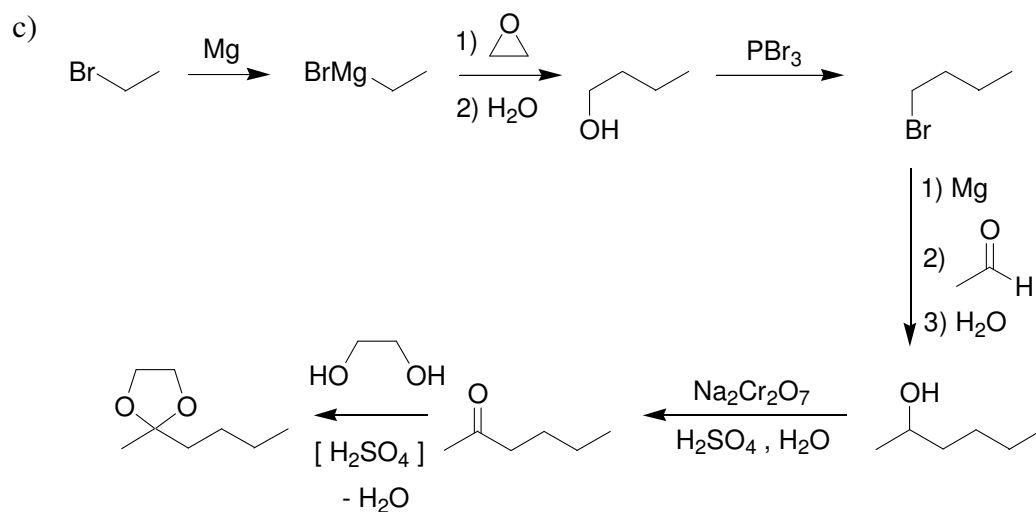
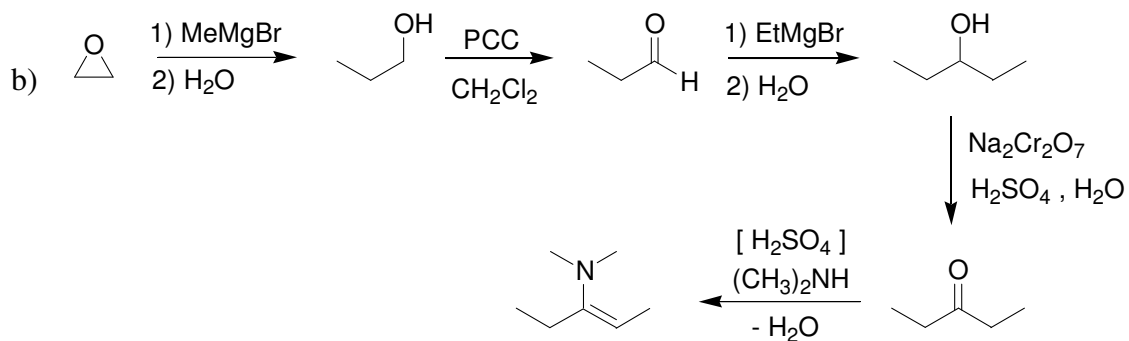
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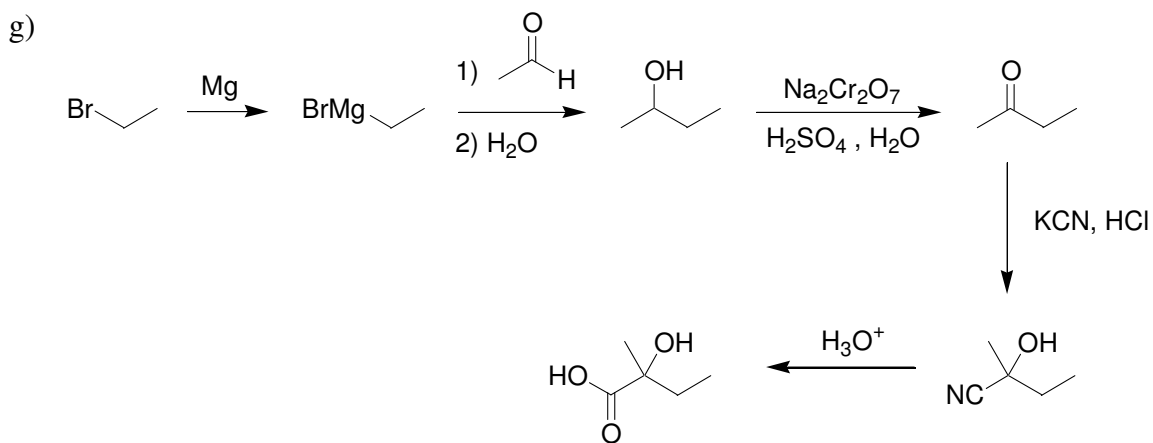
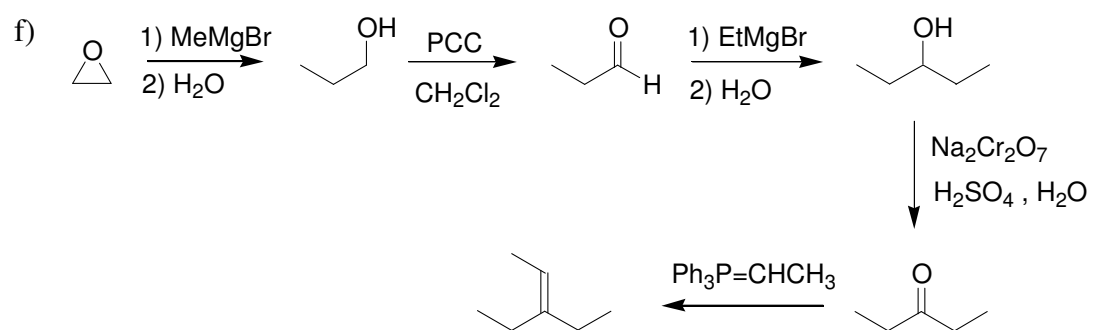
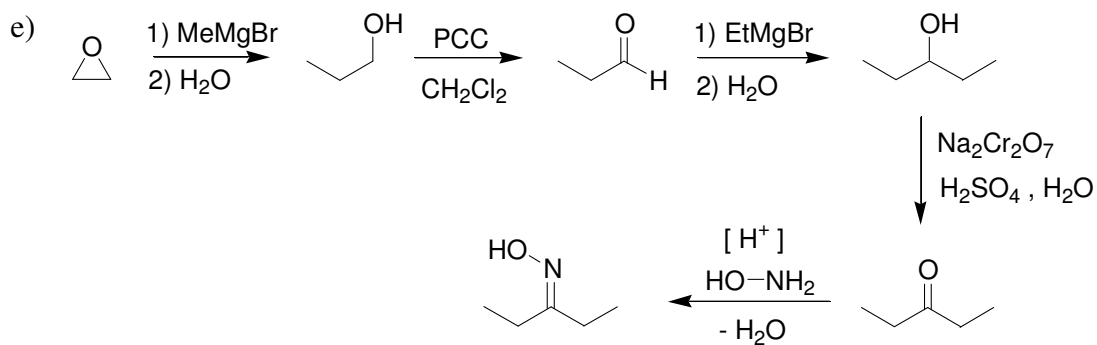


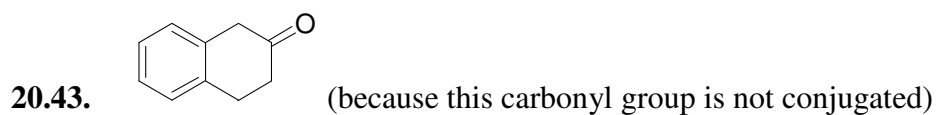
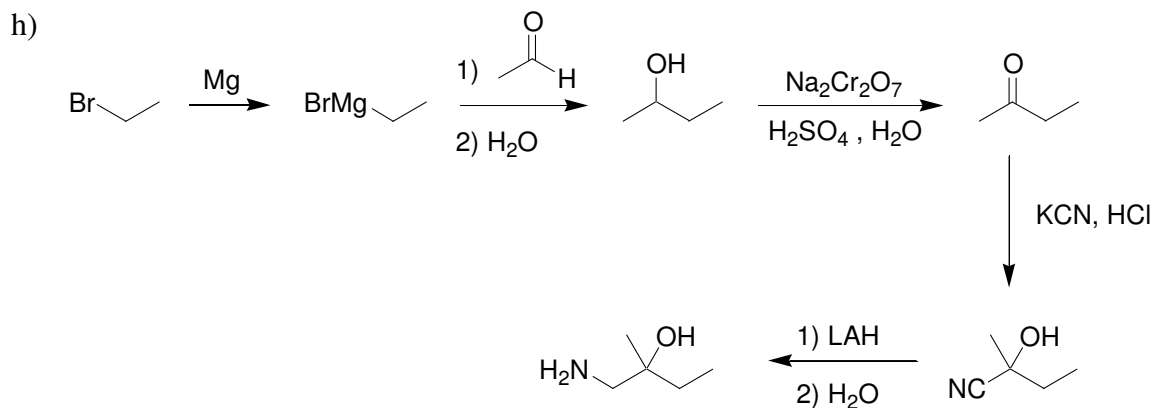


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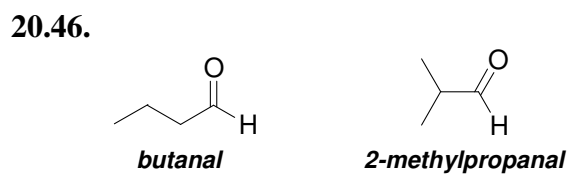
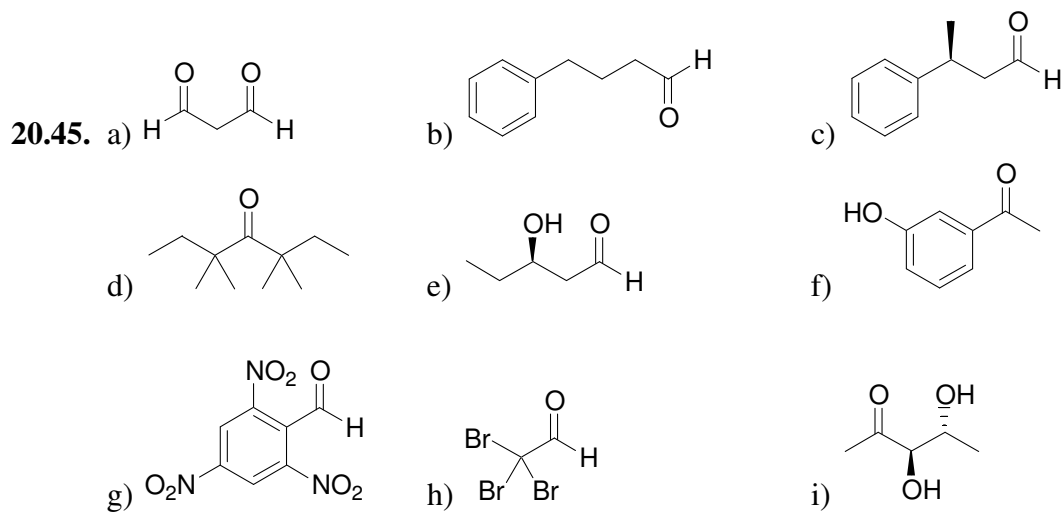




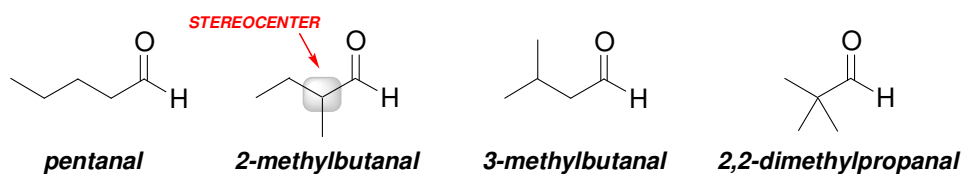




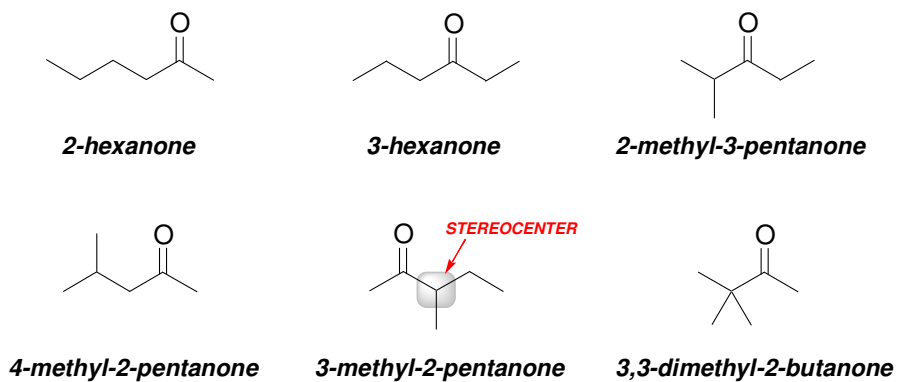
- 20.44. a) (2*S*,3*R*)-3-methyl-2-propylcyclopentanone  
 b) cyclohexanecarbaldehyde  
 c) 3-methyl-2-butenal  
 d) (*S*)-4-methyl-3-hexanone



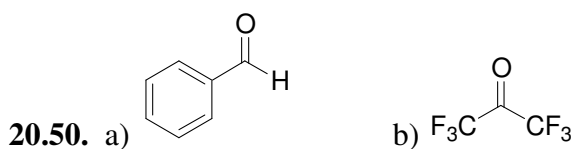
20.47.



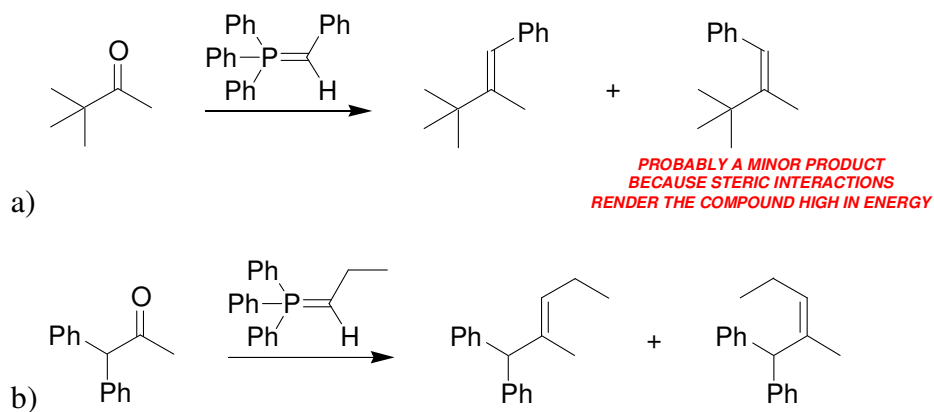
20.48.



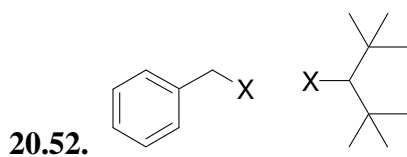
20.49. The carbonyl group of a ketone will never appear at C-1 because if it would did, the compound would be called an aldehyde rather than a ketone.



20.51

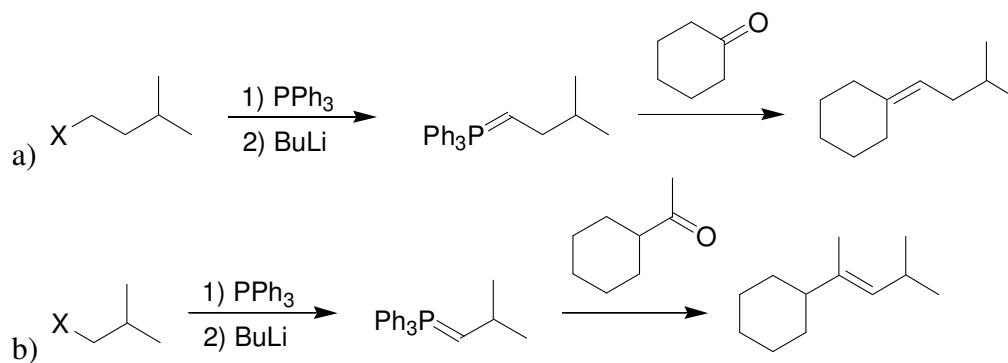




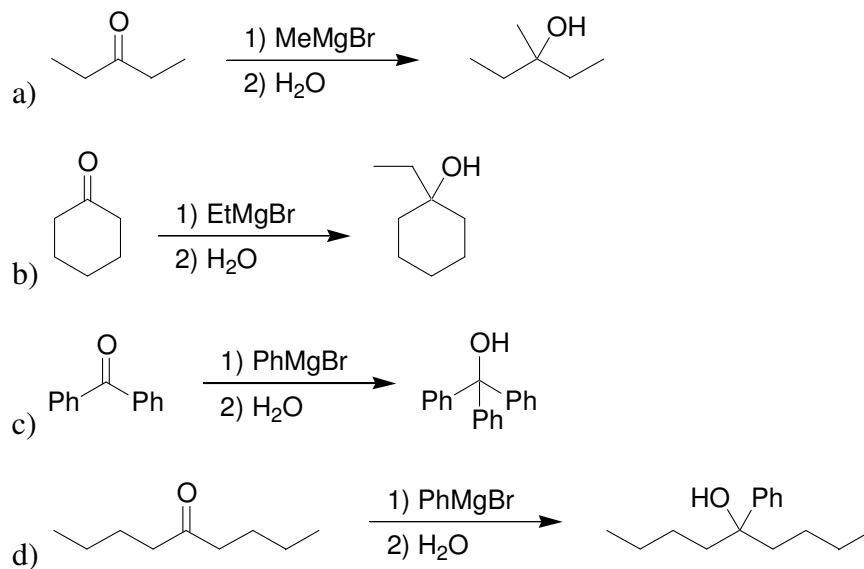


The latter alkyl halide above will be more difficult to convert into a Wittig reagent, because it is too sterically hindered to undergo  $S_N2$  attack.

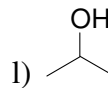
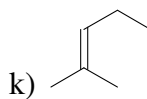
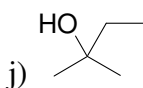
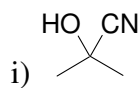
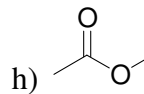
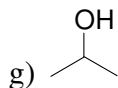
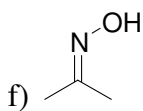
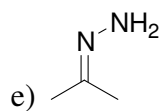
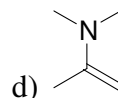
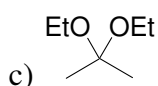
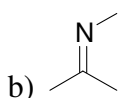
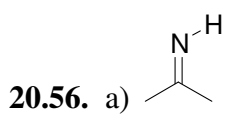
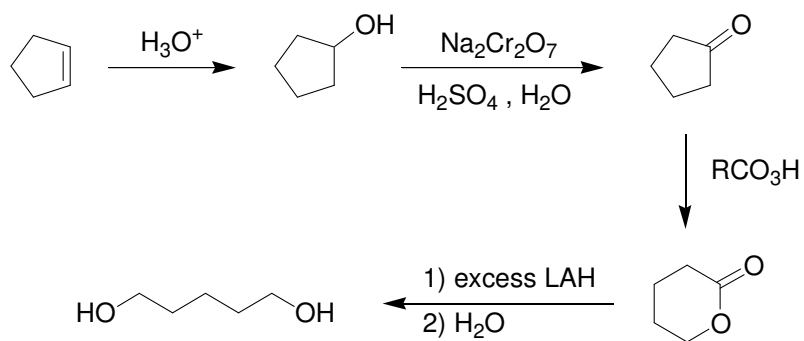
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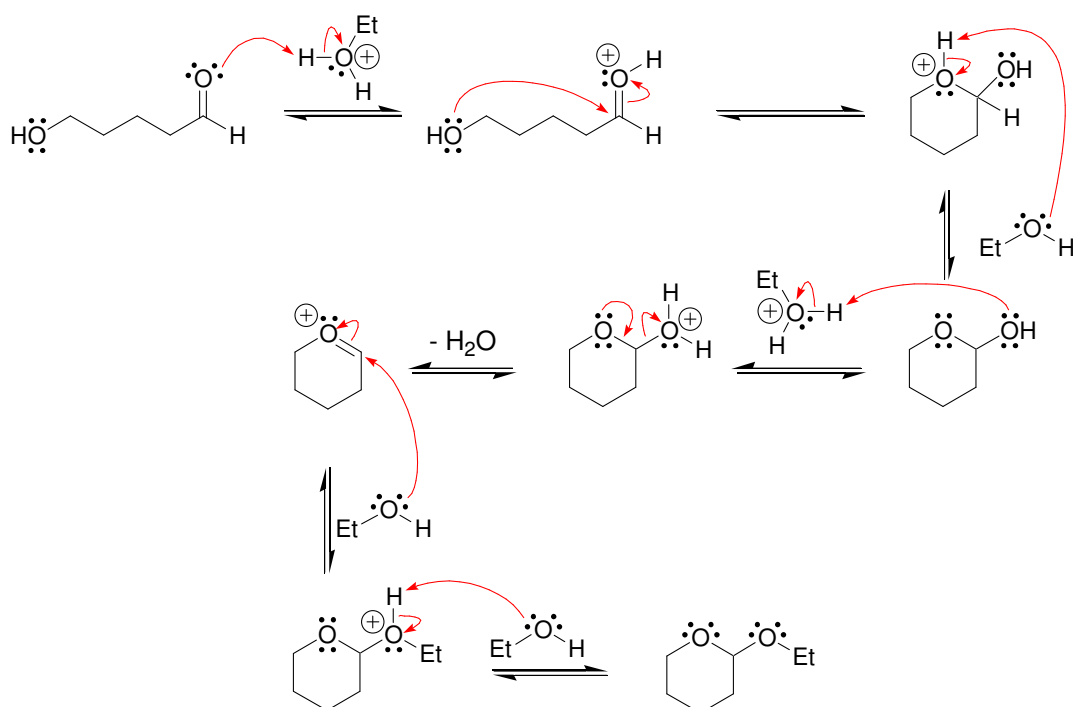
20.54.



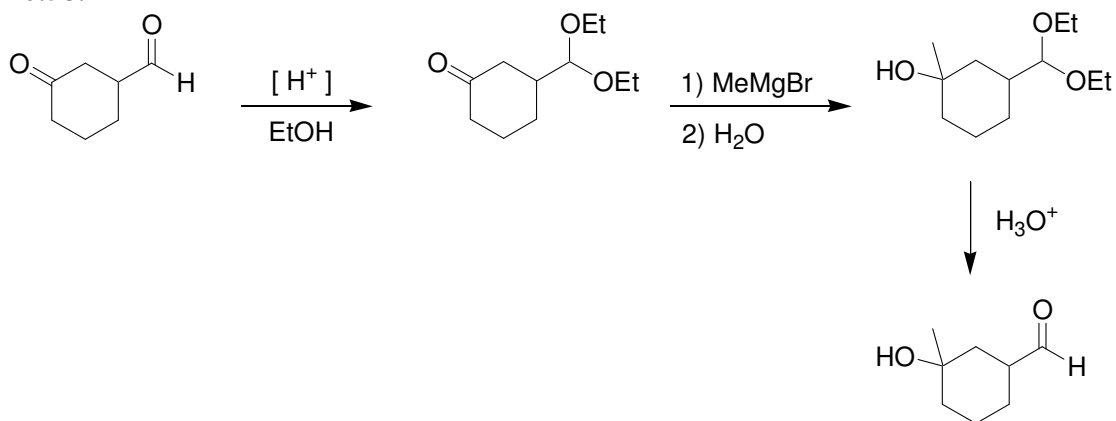
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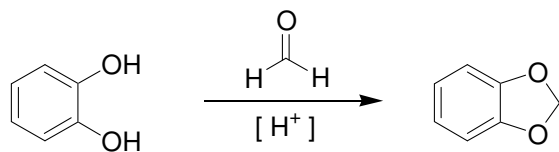
20.57.



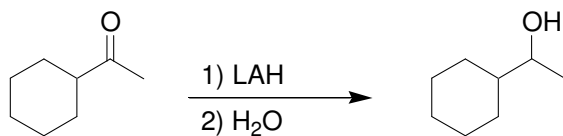
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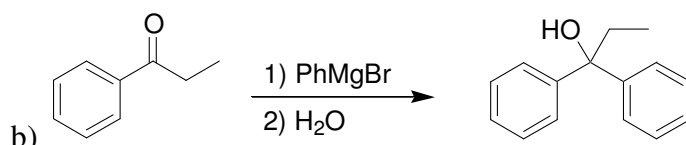
20.59.



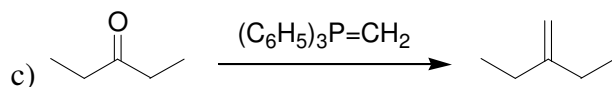
20.60. a)



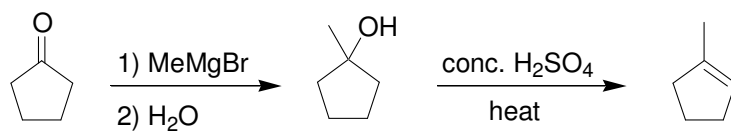
b)



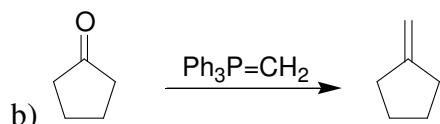
c)

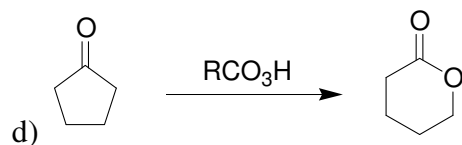
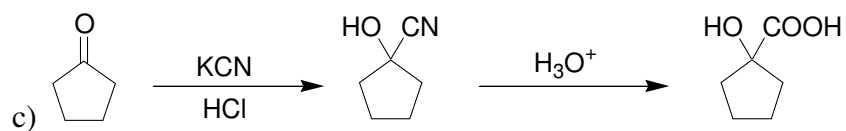


20.61. a)

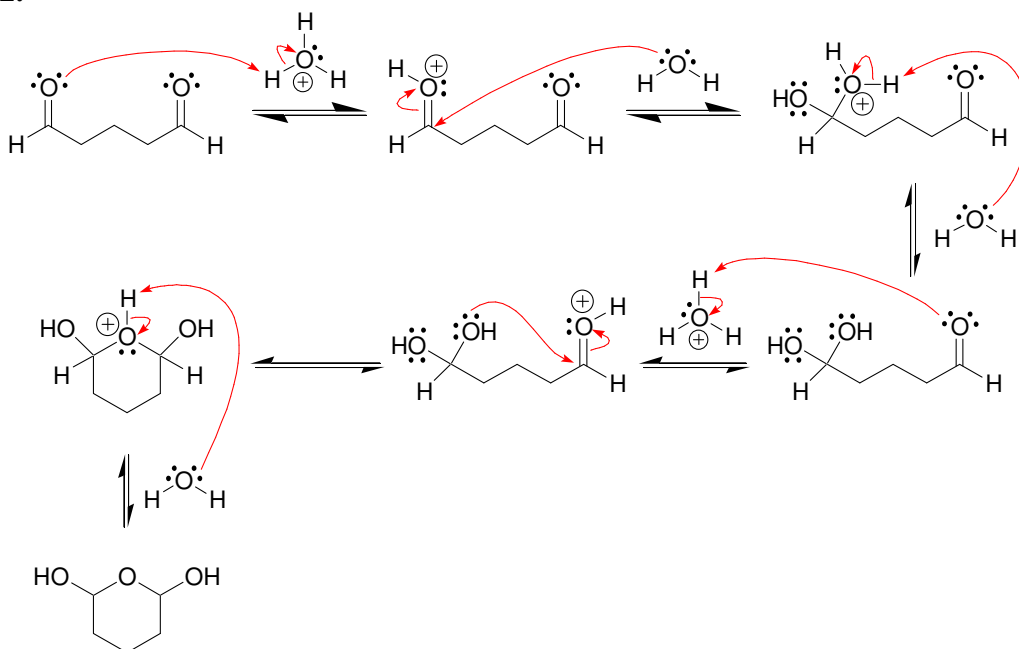


b)

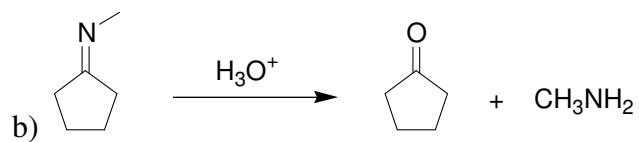
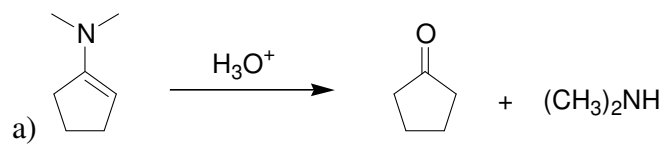


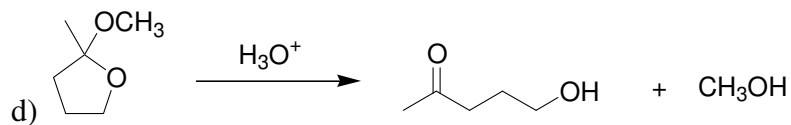
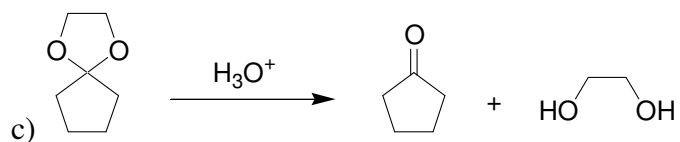


## 20.62.

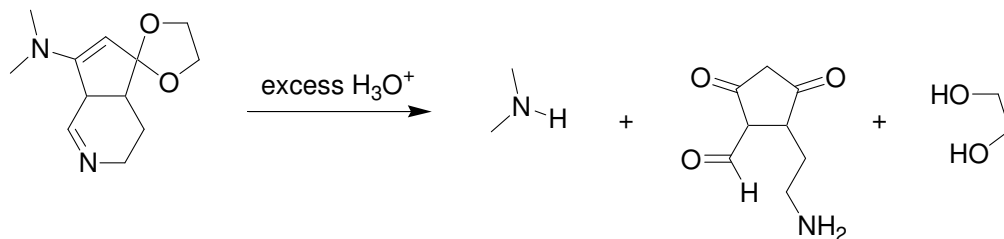


## 20.63.

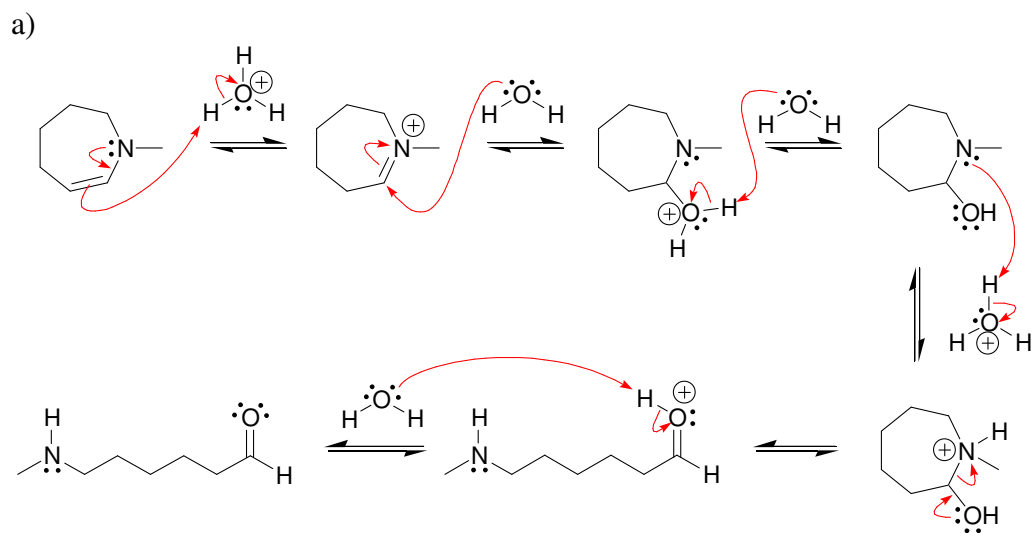




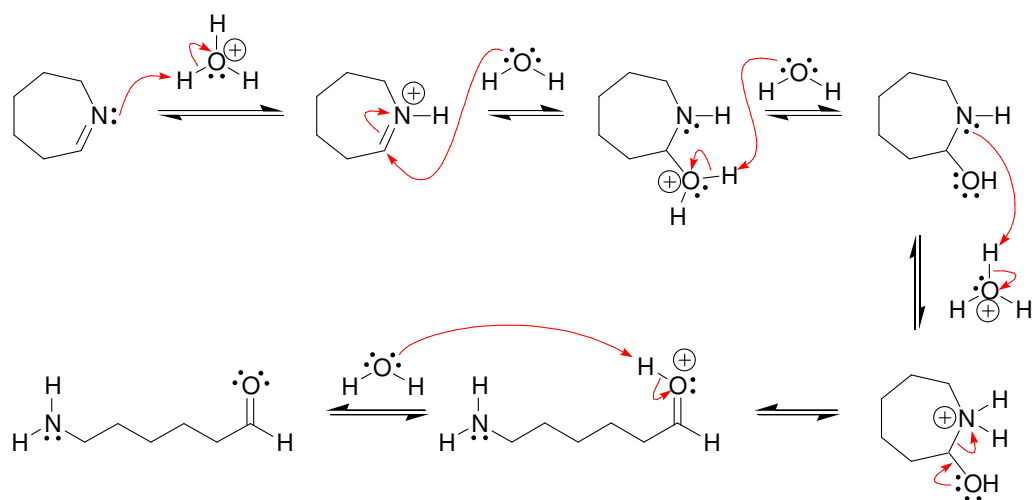
20.64.



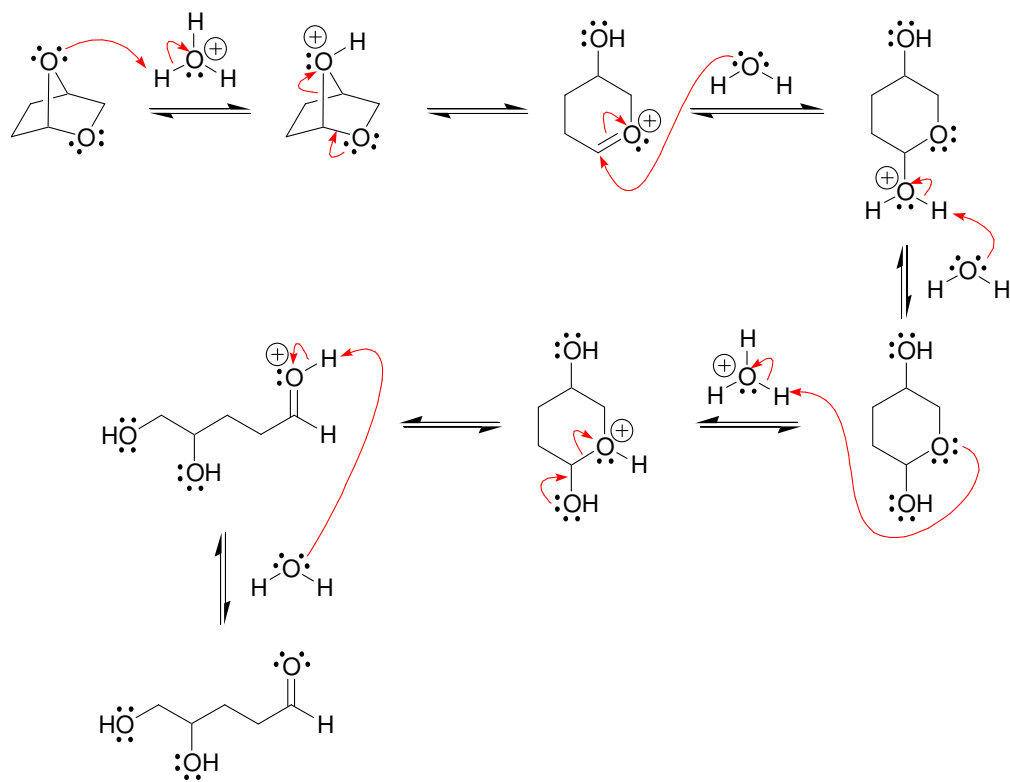
20.65.



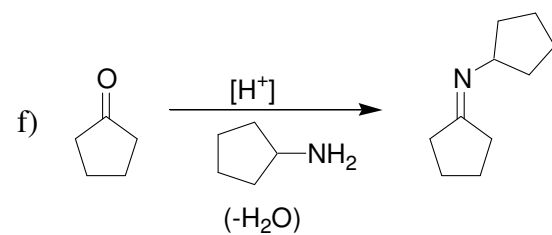
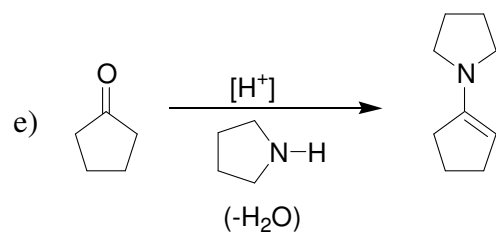
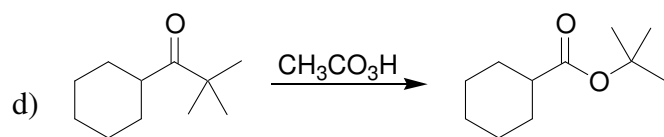
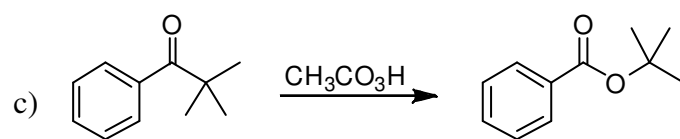
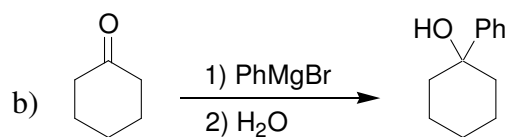
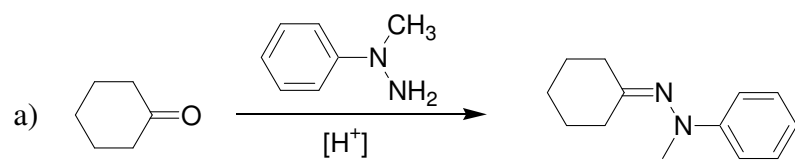
b)



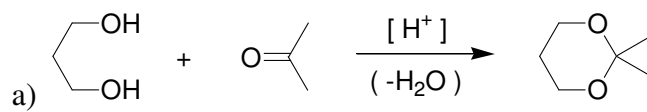
c)

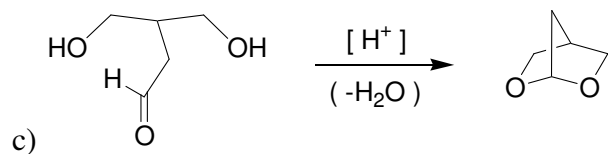
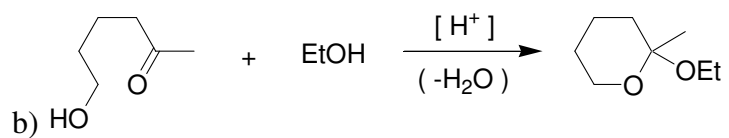


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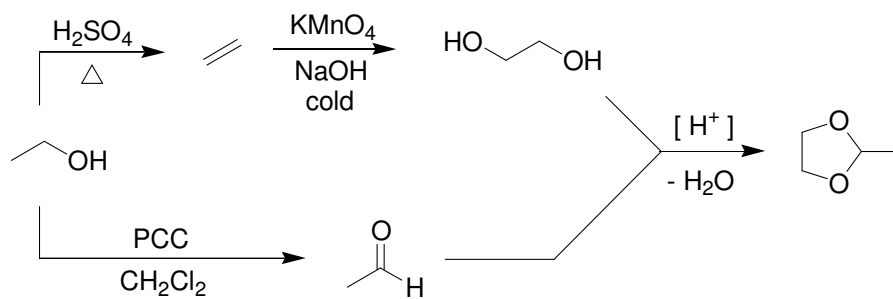


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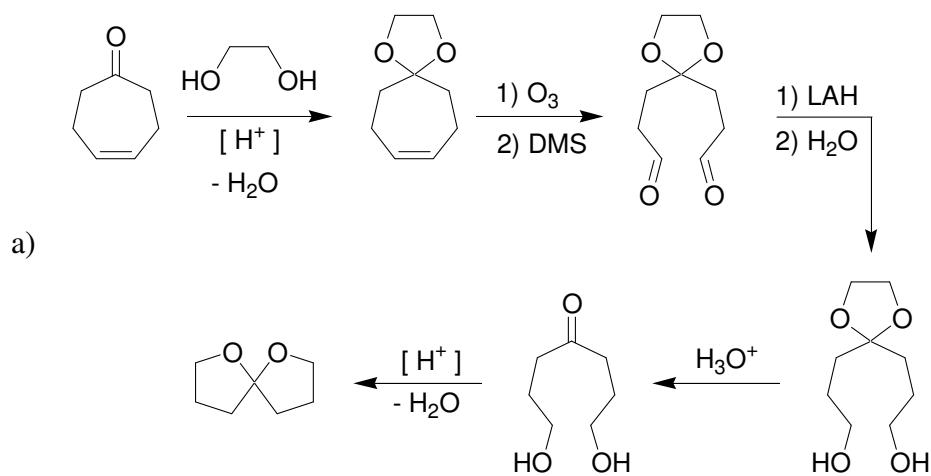




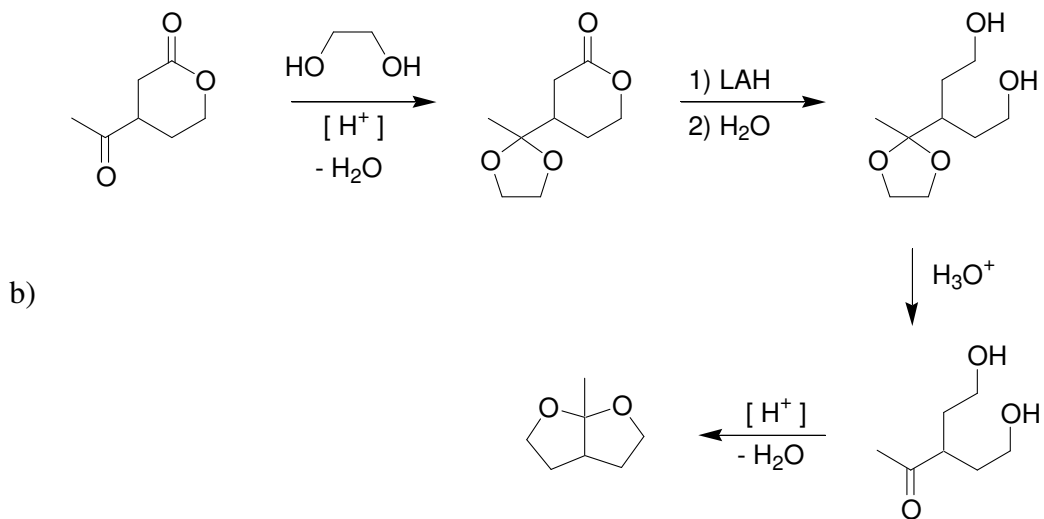
20.68.



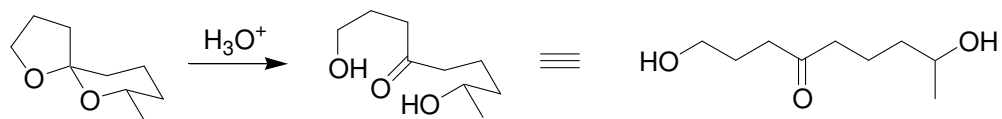
20.69.



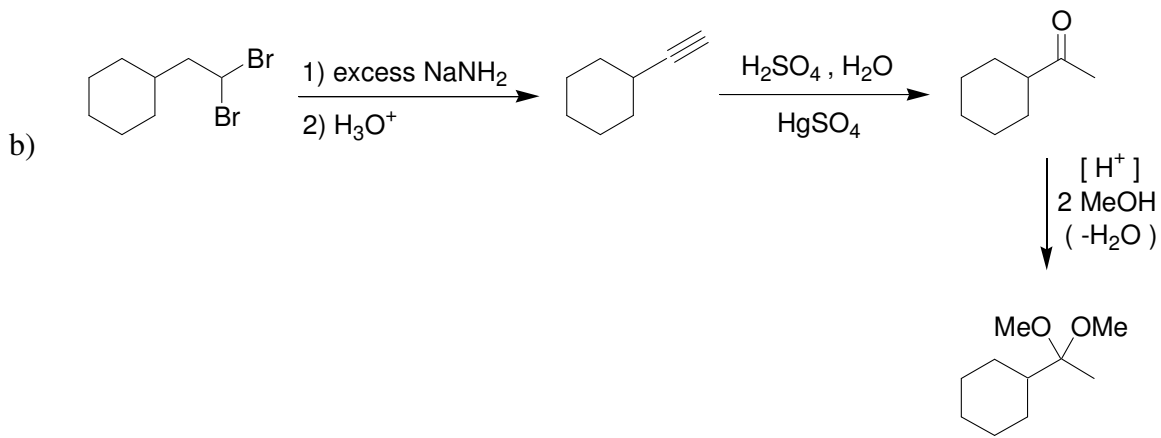
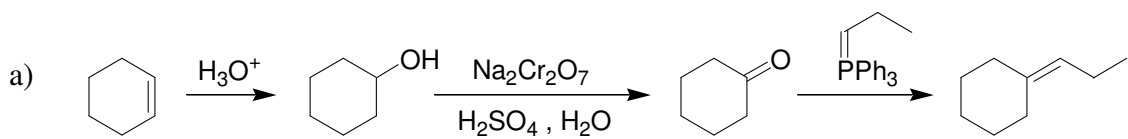


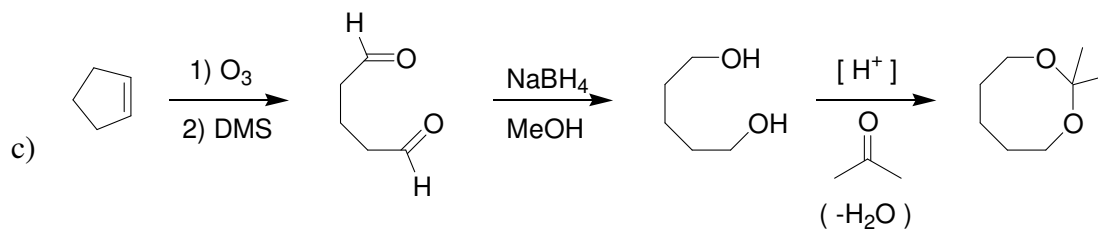


20.70.

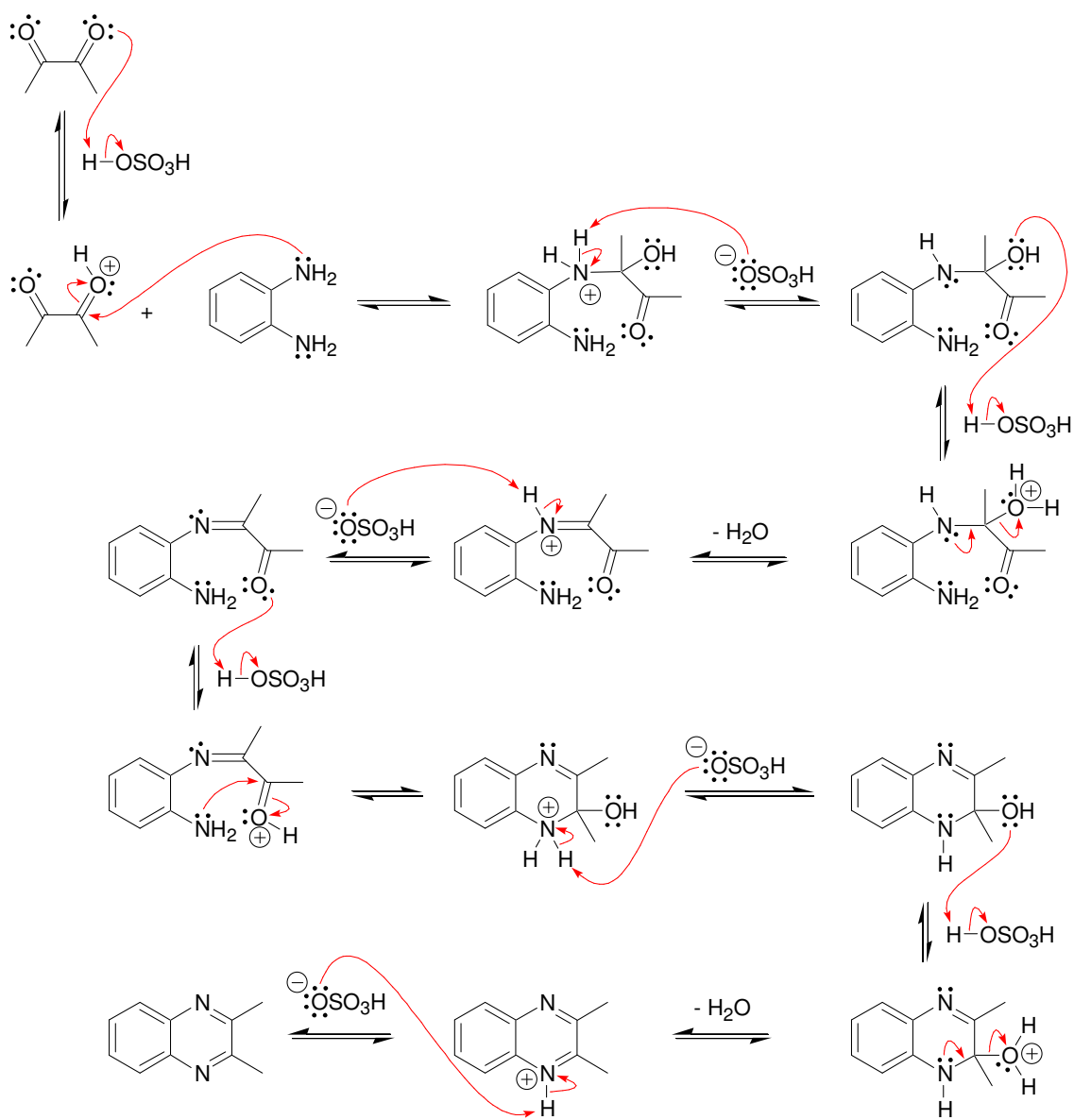


20.71.





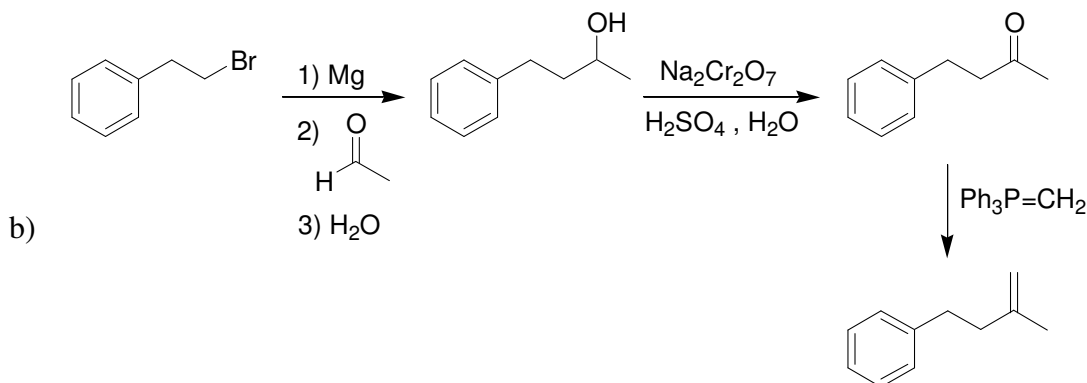
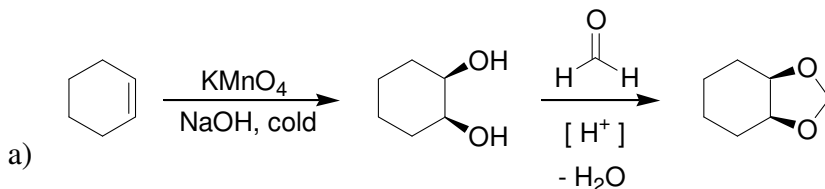
## 20.72.

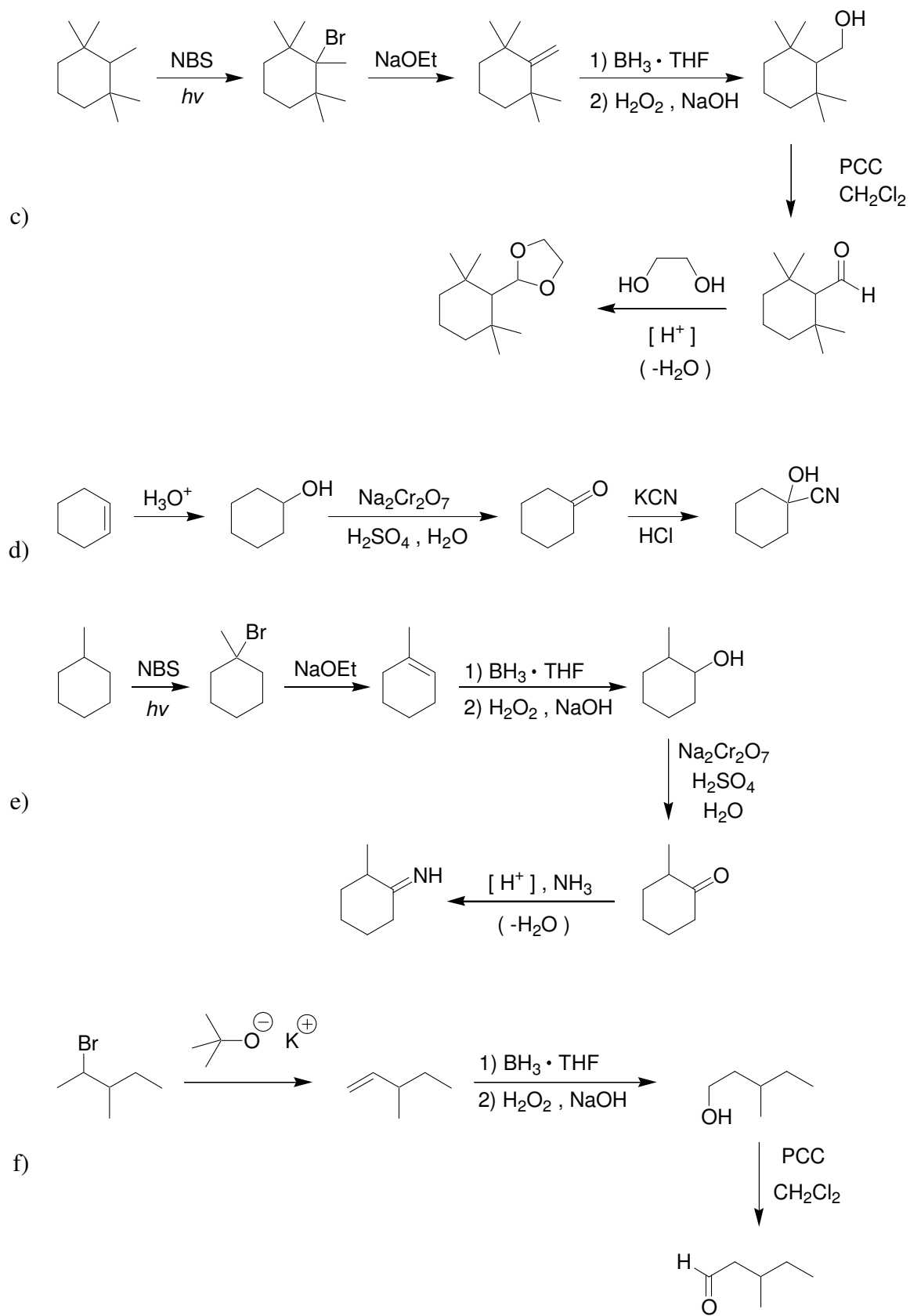


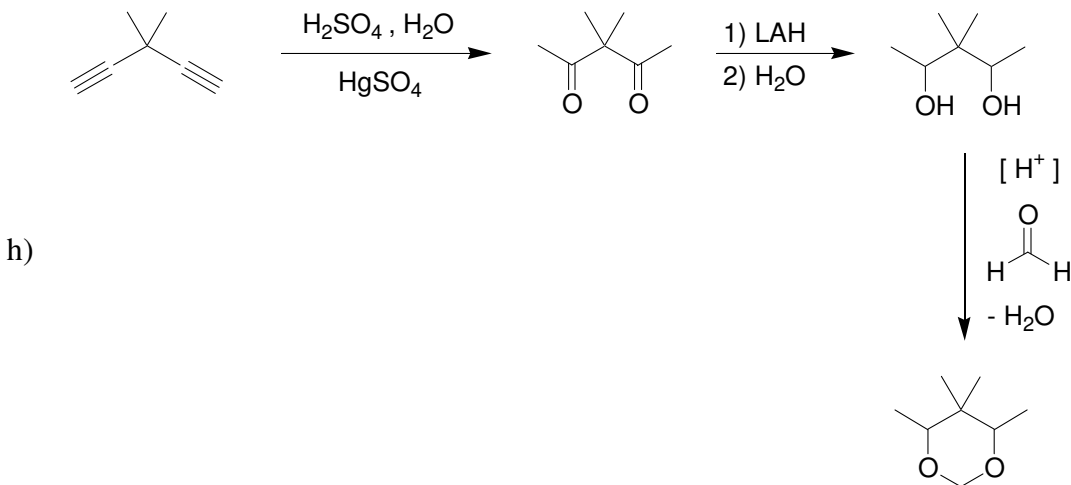
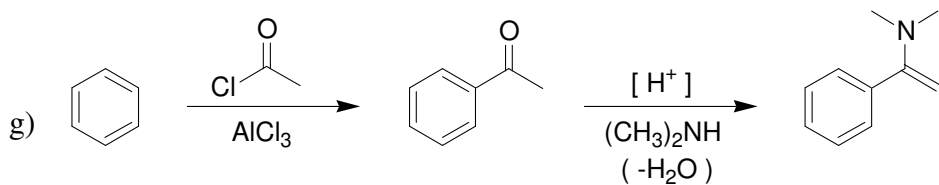
**20.73.** Cyclopropanone exhibits significant ring strain, with bond angles of approximately  $60^\circ$ . Some of this ring strain is relieved upon conversion to the hydrate, because an  $sp^2$ -hybridized carbon atom (that must be  $120^\circ$  to be strain free) is replaced by an  $sp^3$ -hybridized carbon atom (that must be only  $109.5^\circ$  to be strain free). In contrast, cyclohexanone is a larger ring and exhibits only minimal ring strain. Conversion of cyclohexanone to its corresponding hydrate does not alleviate a significant amount of ring strain.

**20.74.** 1,2-dioxane has two adjacent oxygen atoms and is therefore a peroxide. Like other peroxides, it is extremely unstable and potentially explosive. 1,3-dioxane has two oxygen atoms separated by one carbon atom. This compound is therefore an acetal. Like other acetals, it is only stable under basic conditions, but undergoes hydrolysis under mildly acidic conditions. 1,4-dioxane is stable under basic conditions as well as mildly acidic conditions, and is therefore used as a common solvent.

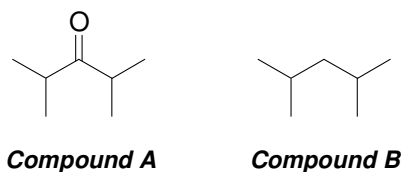
**20.75.**





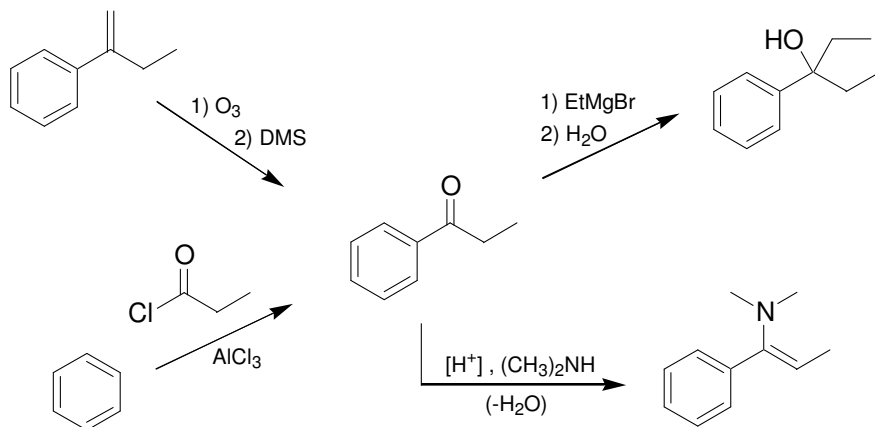


20.76.

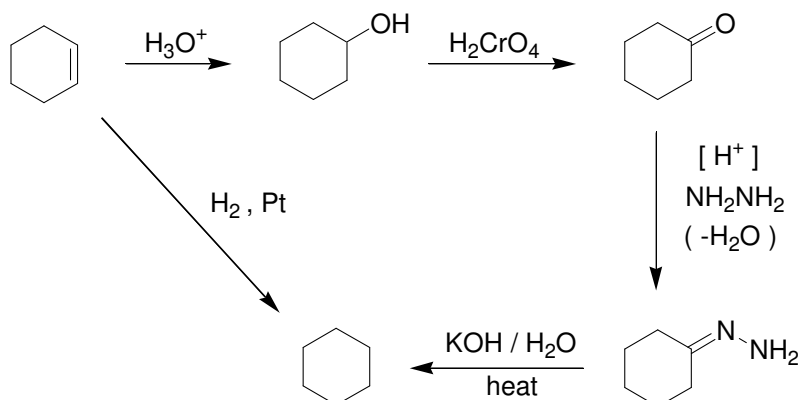


- a) Three  
 b) Three  
 c) Compound A is a ketone, while Compound B is an alkane. Therefore, Compound A will exhibit a signal at approximately  $1715\text{ cm}^{-1}$ , while Compound B will not exhibit a signal in the same region.

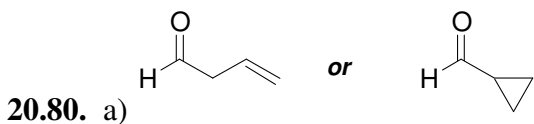
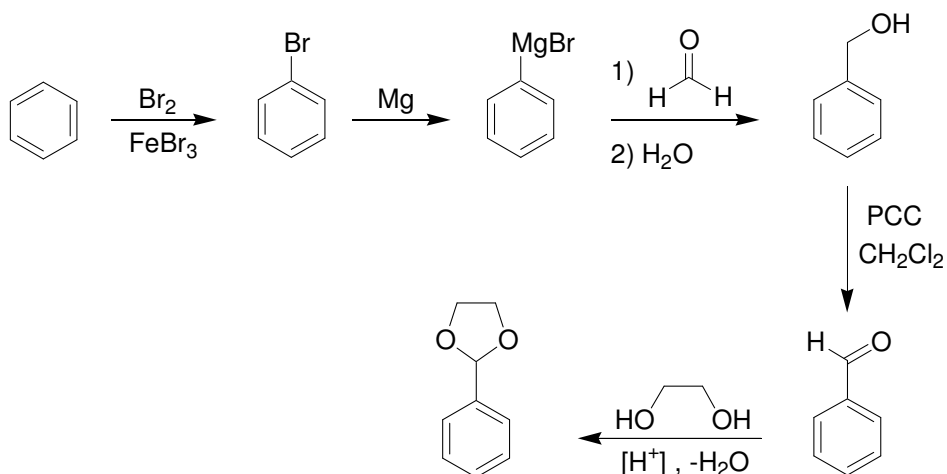
20.77.



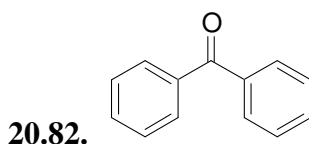
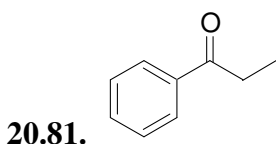
20.78.



20.79.

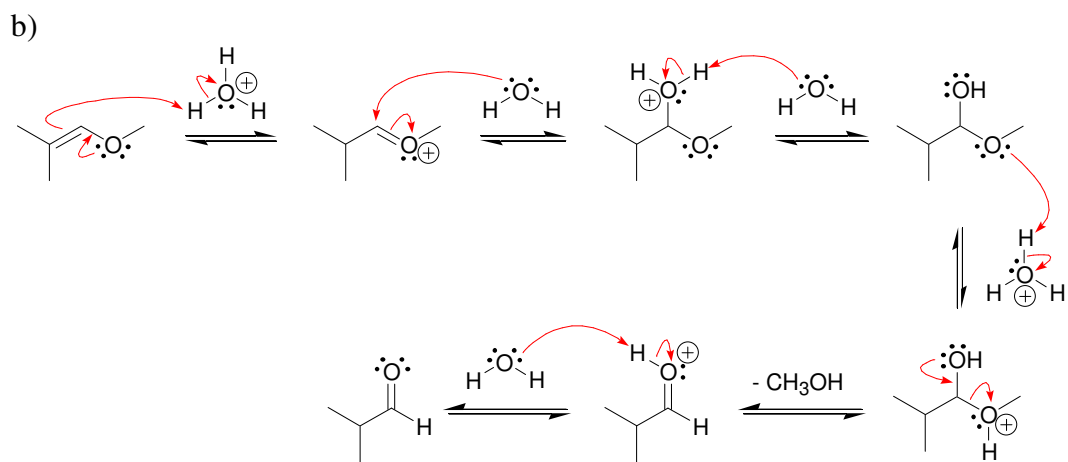
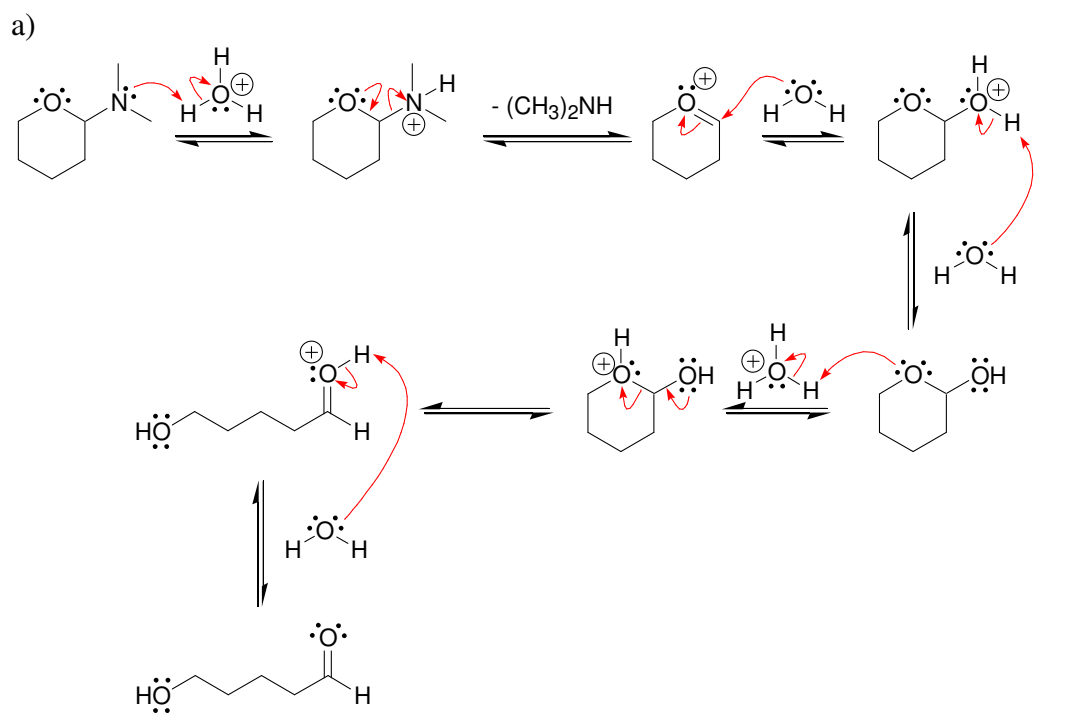


b) The first compound above would exhibit four signals in its  $^{13}\text{C}$  NMR spectrum, while the second compound would exhibit only three signals in its  $^{13}\text{C}$  NMR spectrum.



20.83. 2,2,4,4-Tetramethyl-3-pentanone

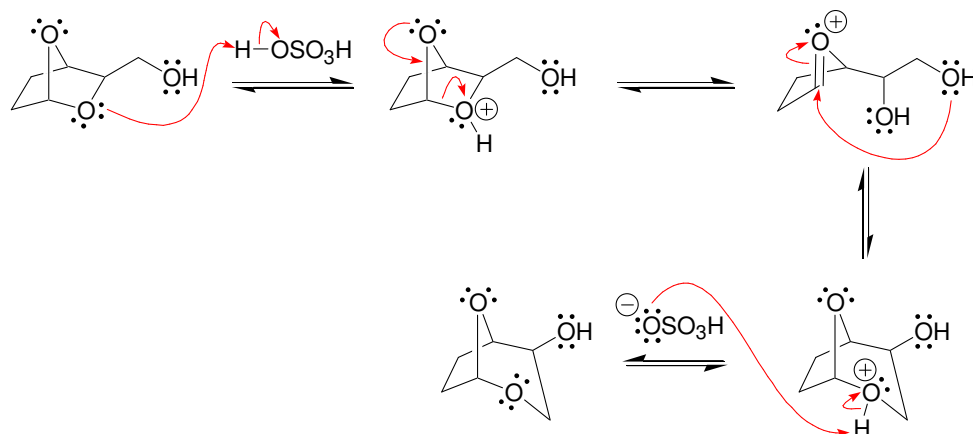
20.84.



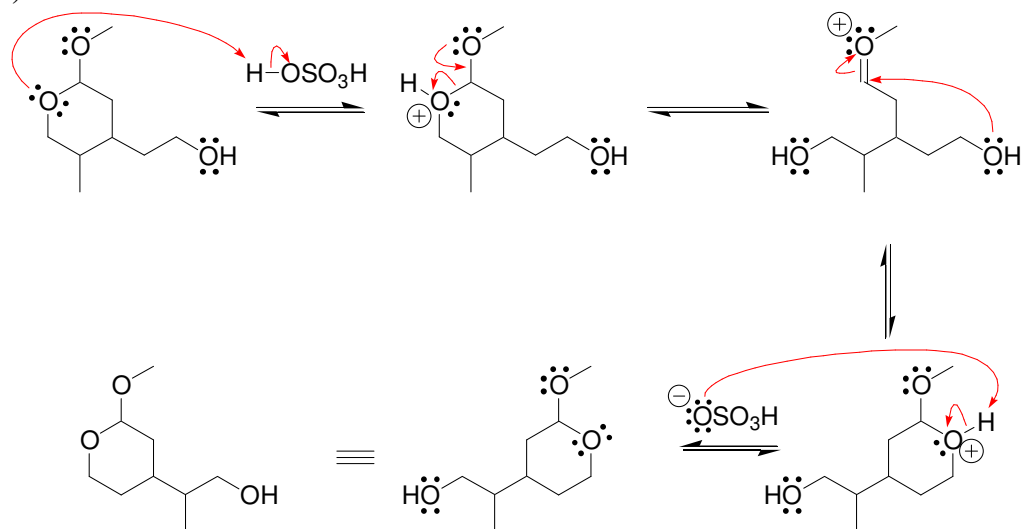




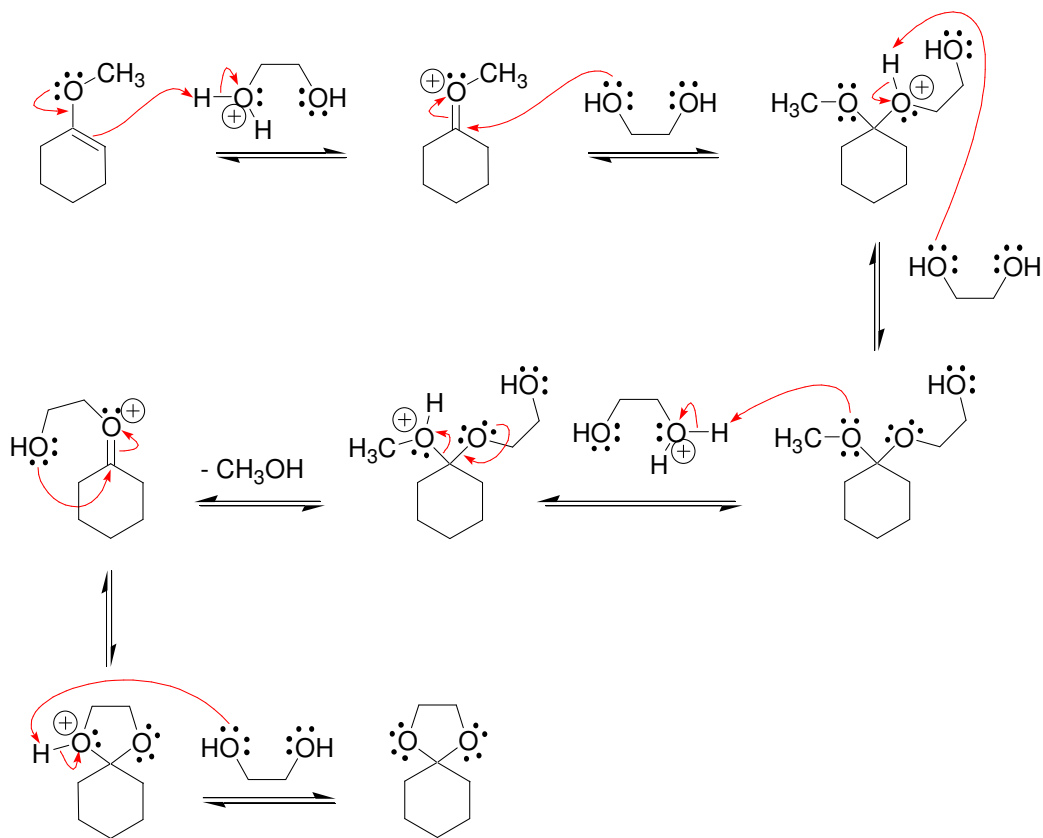
d)



e)



f)



20.85.

