

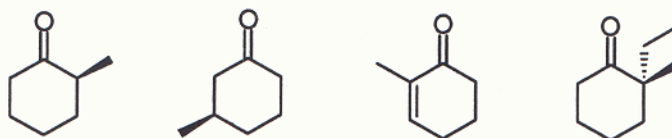
Name: \_\_\_\_\_

Chem 142  
Spring 1999  
Exam 3

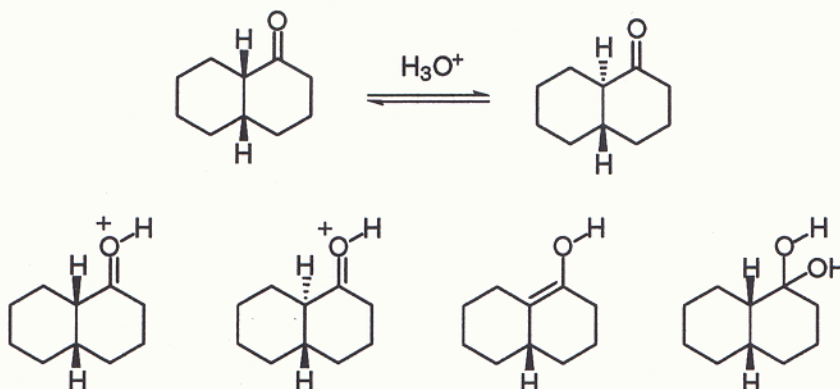
Problem	points (total)	Grader	Score: _____
_____	_____	_____	
_____	_____	_____	
_____	_____	_____	
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_____	_____	_____	

For each question in this section, circle the correct answer. Each problem is worth 3 points.

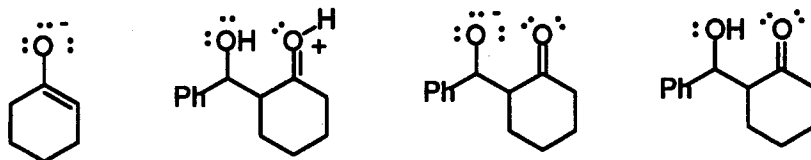
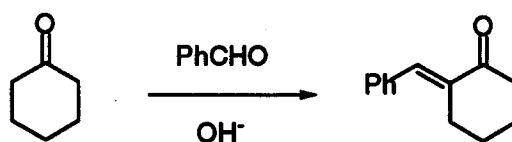
1. Which of the following would you expect to undergo base catalyzed racemization with OH<sup>-</sup>?



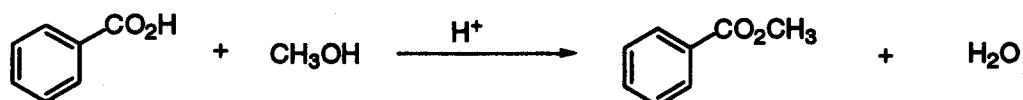
2. Which of the following is not an intermediate in the transformation shown?



3. Which is not an intermediate in the reaction shown?

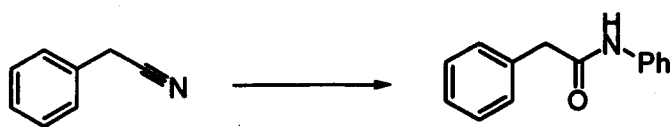


4. Which of the following statements is not true with respect to the reaction shown?



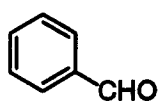
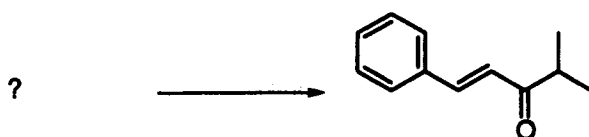
- $H^+$  can be used in catalytic amounts
- $H^+$  lowers the energy of activation of the rate determining step of the reaction
- to drive the equilibrium toward products, excess water must be added
- $H^+$  is consumed in the reaction
- more than one of the above

5. Which would be the best way to carry out the following transformation?

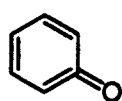


- $PhNH_2$ , heat
- 1)  $LAH$ ; 2)  $PhCOCl$
- 1)  $H_3O^+$ ; 2)  $DCC$ ,  $PhNH_2$
- 1)  $PCC$ ; 2)  $HCN$ ,  $NaCN$ ; 3)  $H^+$ ,  $H_2O$

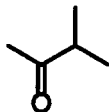
6. Which pair of reagents would afford the product shown when treated with  $OH^-$  and mild heat?



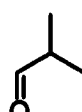
I



II



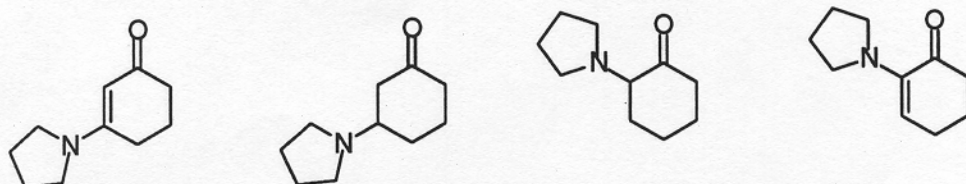
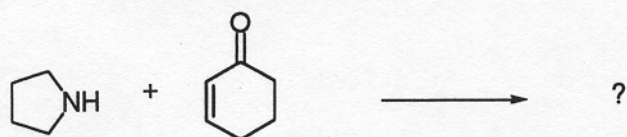
III



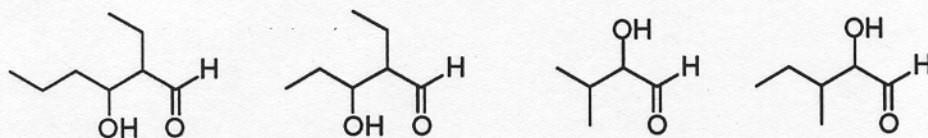
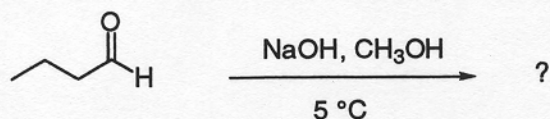
IV

- I and II
- I and III
- II and III
- II and IV

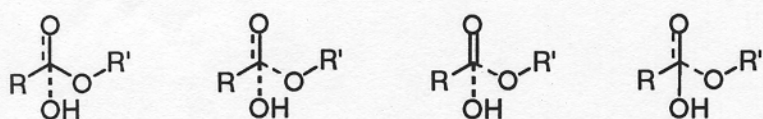
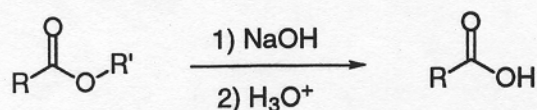
7. Which is the product of the reaction shown?



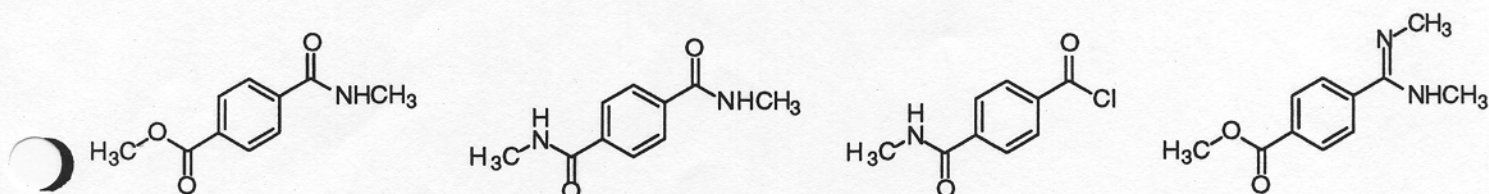
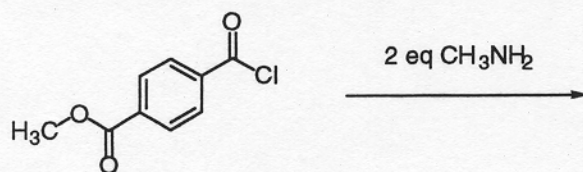
8. Which would be the major product expected for the following transformation?



9. Which of the following best represents the transition state for the rate determining step in the base promoted hydrolysis of an ester?

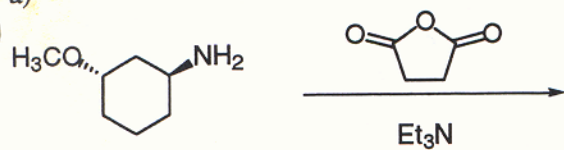


10. What would be the major product of the following transformation?

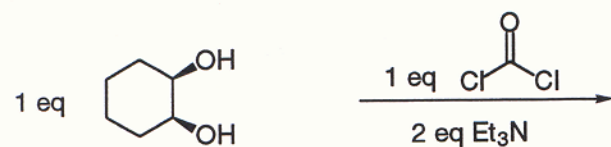


11. Provide the major product for the following reactions. (3 points each)

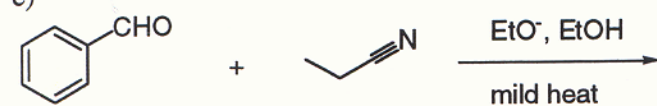
a)



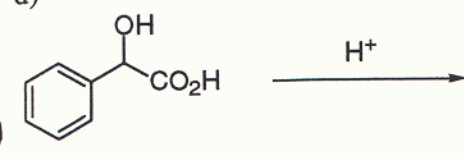
b)



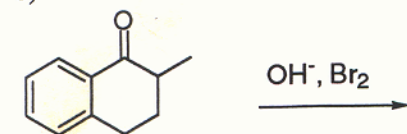
c)



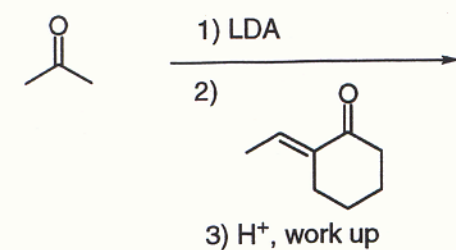
d)



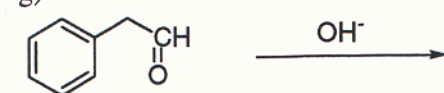
e)



f)

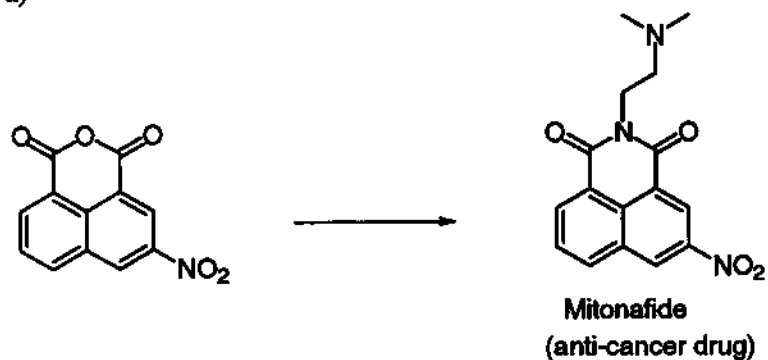


g)

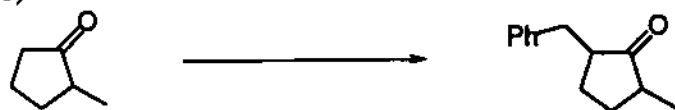


12) Provide the missing reagents necessary to accomplish the indicated transformations. Where relevant, specify the number of equivalents required. If the reagents need to be added in a specific order specify so. (3 points each)

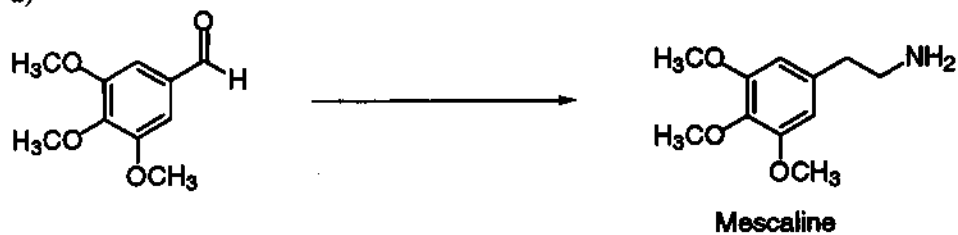
a)



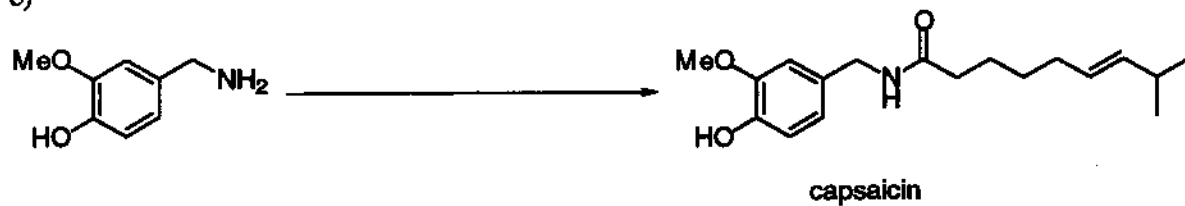
b)



d)



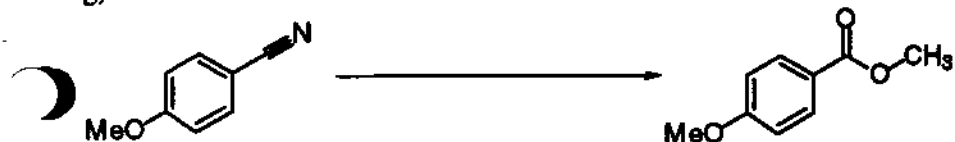
e)



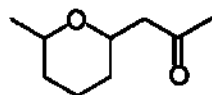
f)



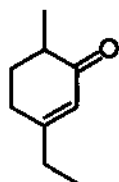
g)



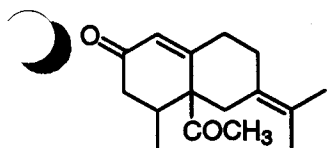
12. Provide the compound that would react through an intramolecular conjugate addition reaction to afford the compound below. (6 points)



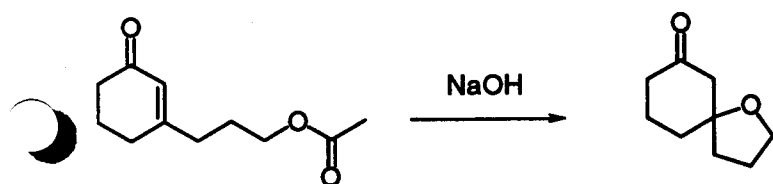
13. Provide the compound which would undergo an intramolecular aldol condensation to give the following compound. (6 points)



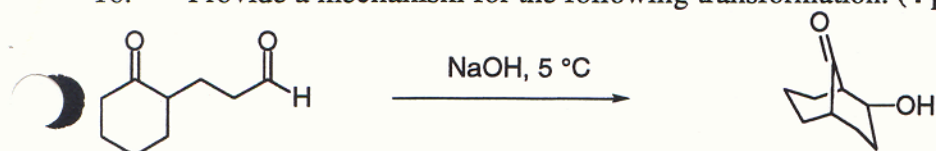
14. Provide the two compounds which would react via a robinson annulation to give the following enone. (6 points)



15. Provide a mechanism for the following transformation. (An SN2 reaction does not occur in this transformation) (6 points)

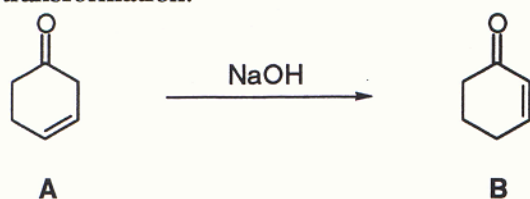


16. Provide a mechanism for the following transformation. (4 points)



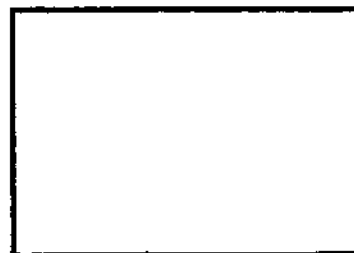
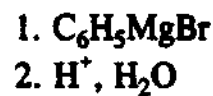
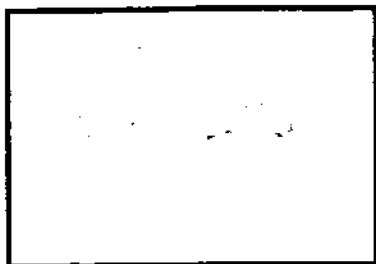
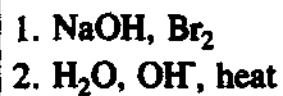
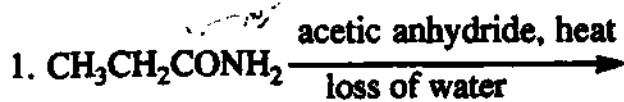
Extra Credit (6 points)

Ketones that have conjugated double bonds (**B**) are thermodynamically more stable than those that have a  $\text{CH}_2$  between the carbonyl and the double bond (**A**). Interestingly, structures like **A** readily isomerize to the thermodynamically more stable structures **B** when treated with base. Provide a mechanism for this transformation.

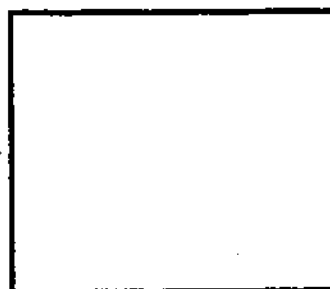
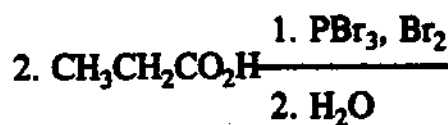




(8)

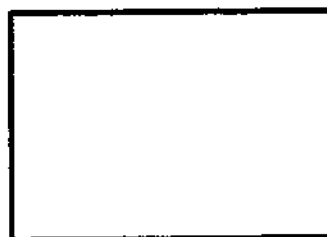
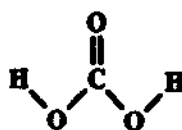


(4)



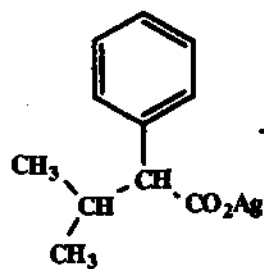
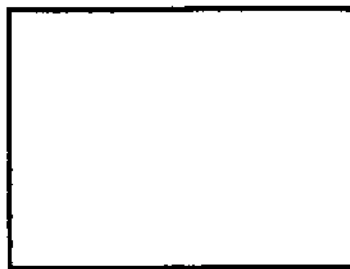
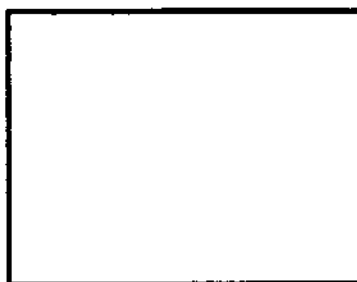
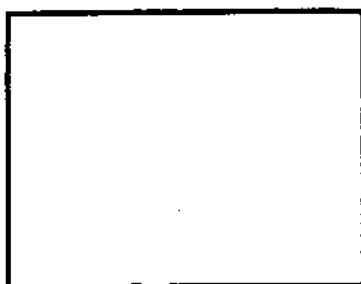
(2)

3.



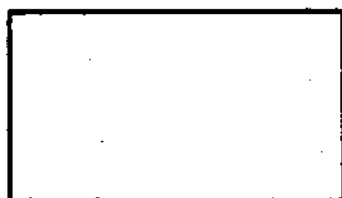
(6)

4.

Br<sub>2</sub>, CCl<sub>4</sub>, heat
 1. Mg, Et<sub>2</sub>O  
 2. CO<sub>2</sub>  
 3. H<sub>3</sub>O<sup>+</sup>
1. SOCl<sub>2</sub>2. C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>

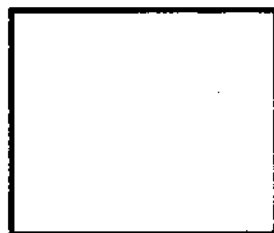
(2)

5.

C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>BrC<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub>

(4)

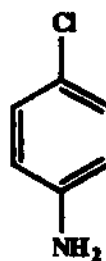
6.



ortho isomer +



para isomer

H<sub>2</sub>/Pt

(4)

7. Show the reaction product which results from treatment of a secondary amine with sodium nitrite and acid:



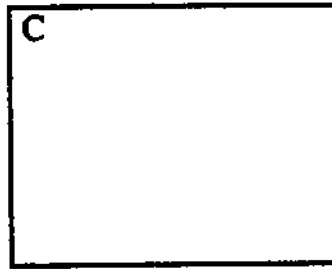
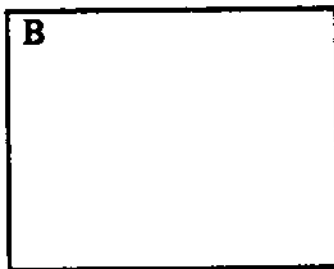
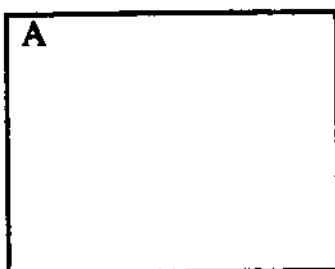
(2)

8. Name the product that results from treatment of m-aminotoluene (also called m-toluidine) with sodium nitrite and CuBr under acidic conditions.

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(8)

9. Benzene is treated with a mixture of concentrated nitric and sulfuric acids to yield a product, A, ( $C_6H_4N_2O_4$ ). A is treated with a mixture of hydrogen sulfide and ammonia in alcohol to yield B ( $C_6H_6N_2O_2$ ). B is treated with sodium nitrite and acid in the presence of CuCN to give C ( $C_7H_4N_2O_2$ ). What are the structures of A, B and C and what are the types of reactions that produce each of them (i.e., substitution, elimination, oxidation, etc...choices should not necessarily be made from this listing)




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 rxn producing A

rxn producing B

rxn producing C

(2)

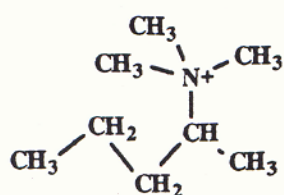
10.  $C_3H_9N$  reacts with benzenesulfonyl chloride in excess KOH to give a clear solution. Acidification of this solution yields a precipitate. What are two possible structures for  $C_3H_9N$ ?



(2)

11. What technique could you use to distinguish between the two possible structures (problem No. 10)?

(6) 12.



heat

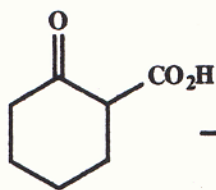
?

minor

minor

major

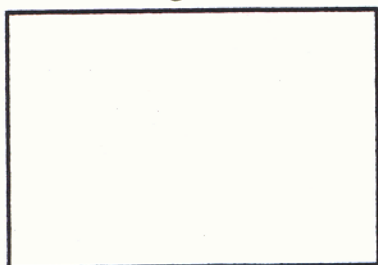
(2) 13.



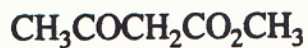
heat

(3) 14.

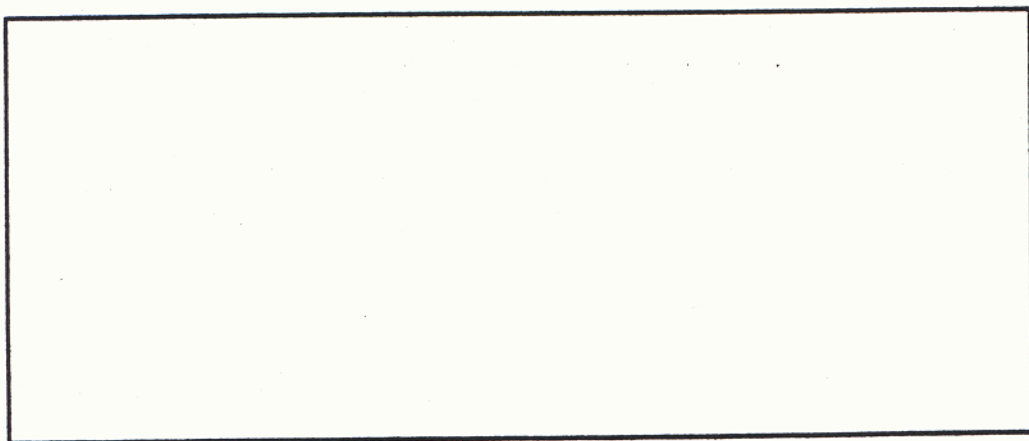
3 C starting material



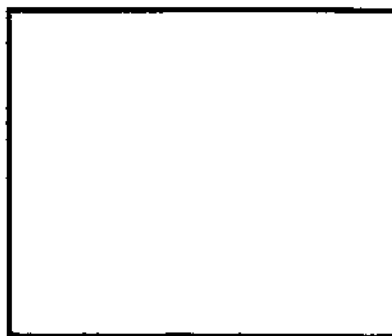
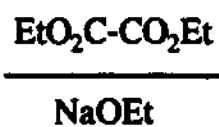
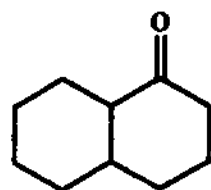
NaOCH<sub>3</sub>



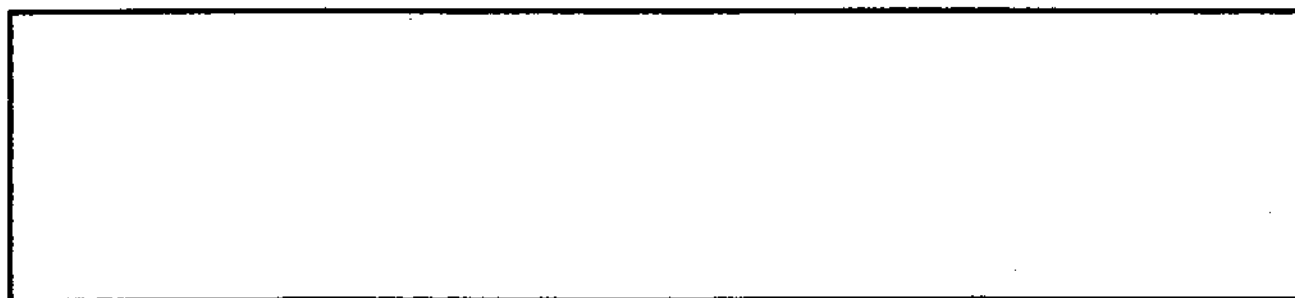
(3) 15. Show an example of a Diekmann Condensation:



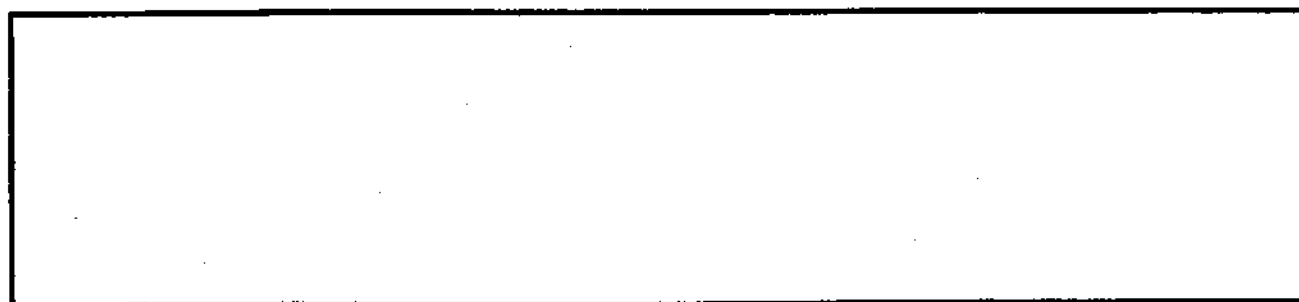
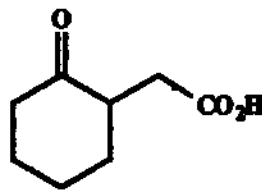
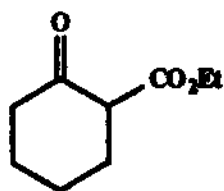
(3) 16.



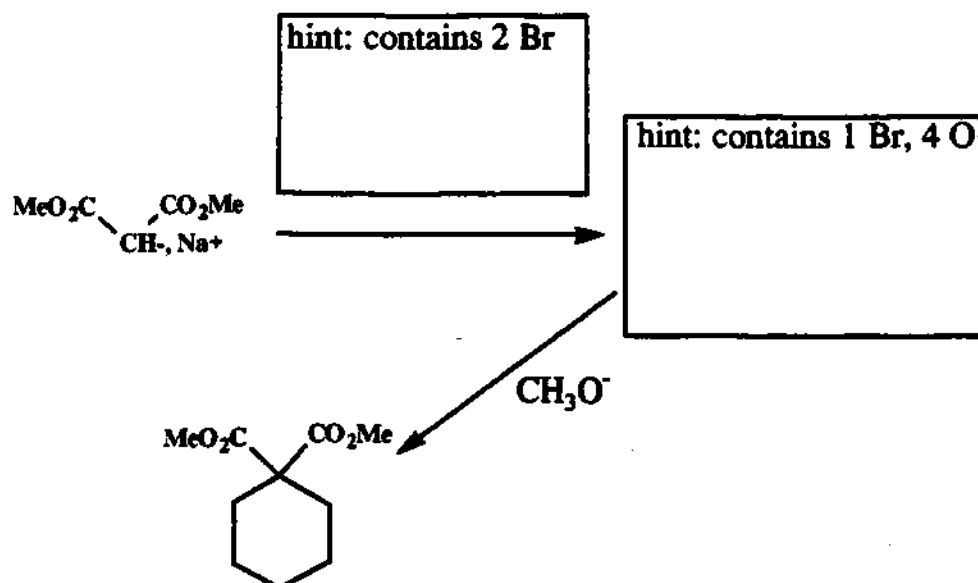
(5) 17. Show how the following sequence can be carried out:



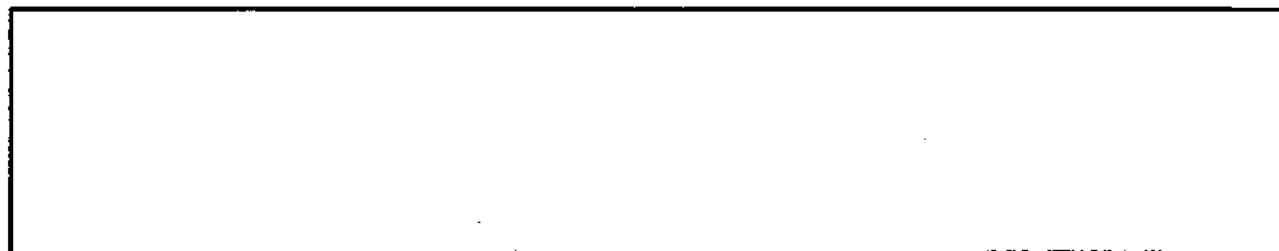
(5) 18. Show how the following conversion could be carried out:



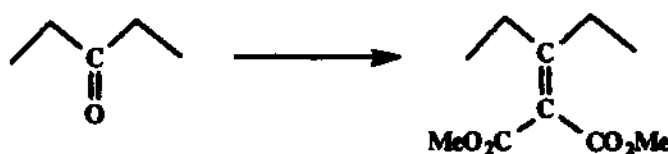
(4) 19.



- (6) 20. Benzaldehyde is treated with  $\text{HSCH}_2\text{CH}_2\text{SH}$  in the presence of an acid catalyst. The product of this reaction is treated with methyl lithium followed by addition of ethyl bromide. The resulting compound isolated with workup,  $\text{C}_{11}\text{H}_{14}\text{S}_2$ , is treated with  $\text{HgCl}_2$  in methanol and water, producing a product with seven different carbon resonances in its cmr spectrum. Its pmr spectrum shows a quartet and triplet upfield and a five proton multiplet downfield. What is the structure of this final product?

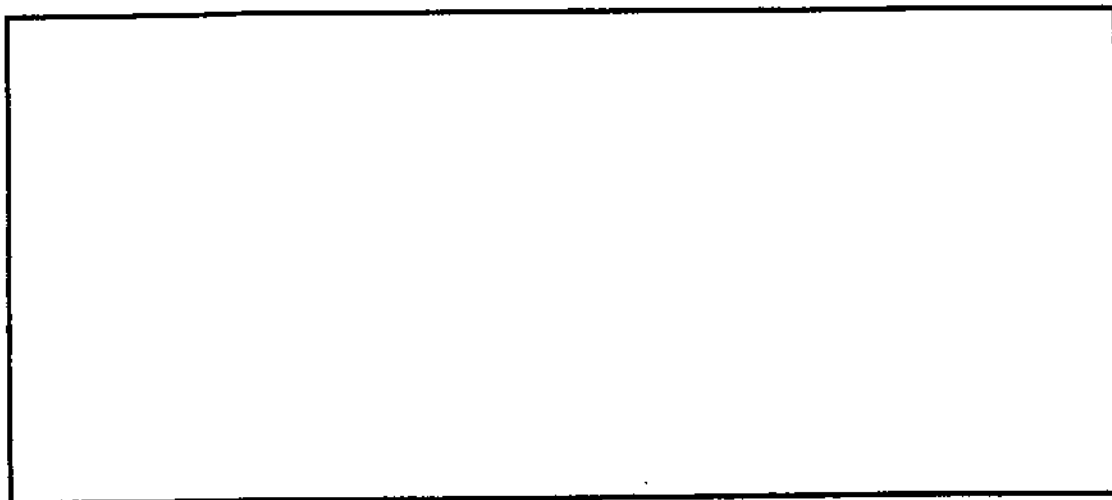
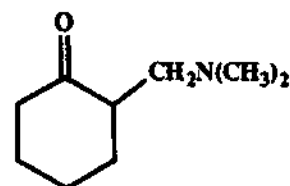


- (4) 21. Using any reagents you like show how you would carry out the following conversion: (a Knoevenagel condensation)

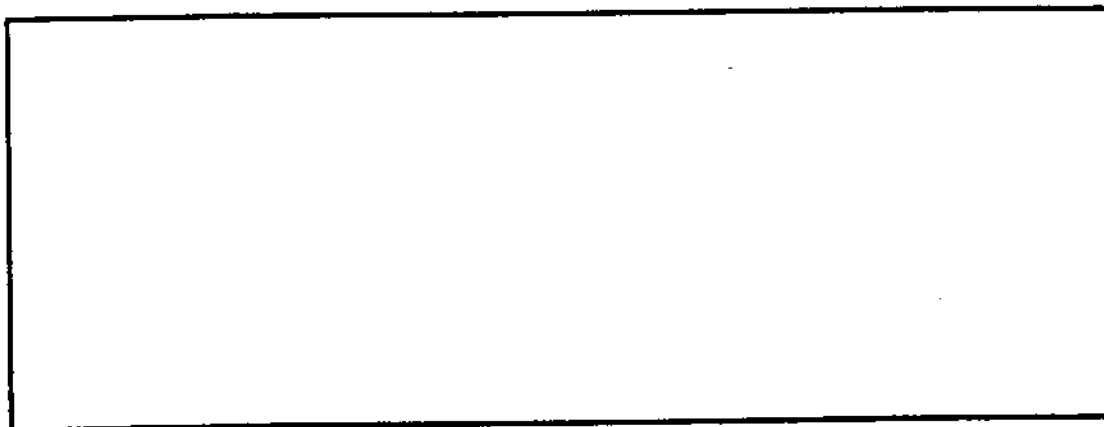


(7) 22. Show a curly arrow mechanism for the following reaction:

dimethylamine + formaldehyde + cyclohexanone  $\longrightarrow$



(3) 23. Show how you would make an enamine and how the enamine might react with acetyl chloride.



(5) 24. An unknown liquid compound upon being treated with benzene sulfonyl chloride and excess KOH in a test tube resulted in two immiscible layers. Upon addition of acid the two layers transformed into one clear solution. The unknown compound reacted with methyl bromide to give  $C_6H_{16}NBr$ , which upon treatment with  $Ag_2O$ , followed by heating, resulted in the evolution of some ethene. The unknown had a pmr showing a quartet and triplet upfield (10H) and a singlet (3H) near the quartet. What is the structure of the unknown?