國立成功大學 105 學年度碩士班招生考試試題

系　　所：臨床藥學與藥物科技研究所

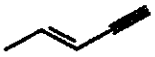
考試科目：有機化學

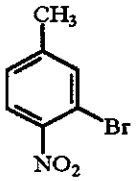
考試日期：0228，節次：2

※ 考生請注意：本試題不可使用計算機。　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

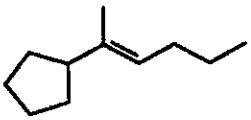
Section I - Nomenclature (1 point each)

In the space provided, give the best IUPAC name for the compound shown on the right.

1. _____ 

2. _____ *Name as a derivative of benzene.* 

3. _____ 

4. _____ 

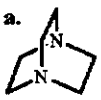
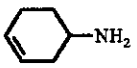
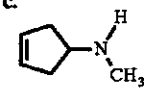
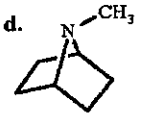
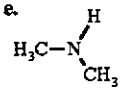
Multiple Choice and Short Answer (1 point each)

For each of the questions below, circle the letter corresponding to the most correct answer.

5. Which of the following is true regarding an S_N2 reaction:
   a. rearrangements commonly occur in polar, aprotic solvents
   b. the intermediate radical does not undergo rearrangement
   c. the most stable carbocation is always formed
   d. a and c only are both correct
   e. none of the above are correct

6. Which of the following is true regarding S_N1 reactions:
   a. concurrent E1 elimination reactions are common
   b. rearrangement of the carbocation intermediate is common
   c. the reaction is favored by polar, protic solvents
   d. a and c only are both correct
   e. a, b and c are all correct

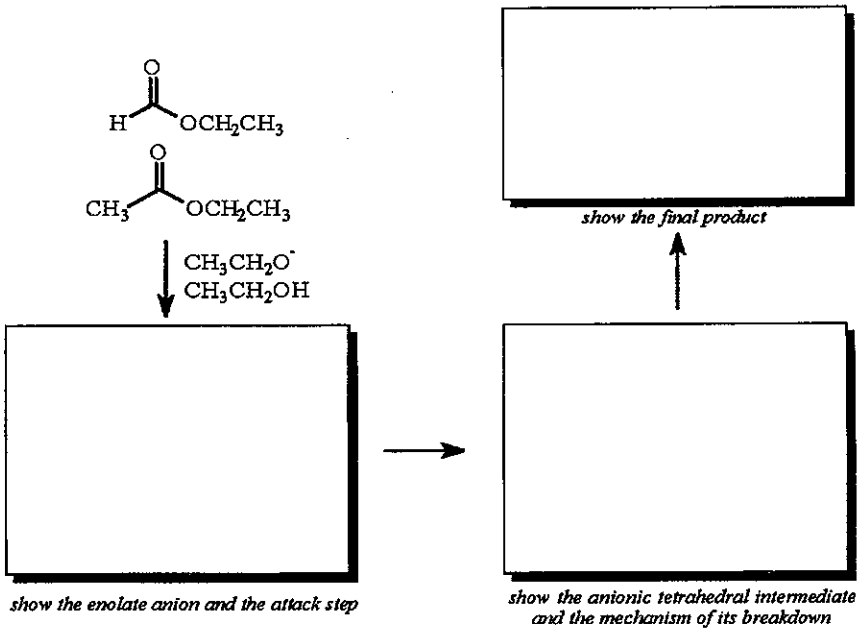
7. An unknown compound reacts with *p*-toluenesulfonic acid to form a solid which is insoluble in strong base solution. Elemental analysis indicates that the compound has two degrees of unsaturation. A structure which is consistent with these data is:

a. 
b. 
c. 
d. 
e. 

8. In the tetrahedral intermediate with three possible **anionic** leaving groups, the best leaving group will be:

a. the strongest base
b. the group having the strongest conjugate base
c. the group with the highest pK_a
d. the phenoxy group
e. the group having the weakest conjugate base

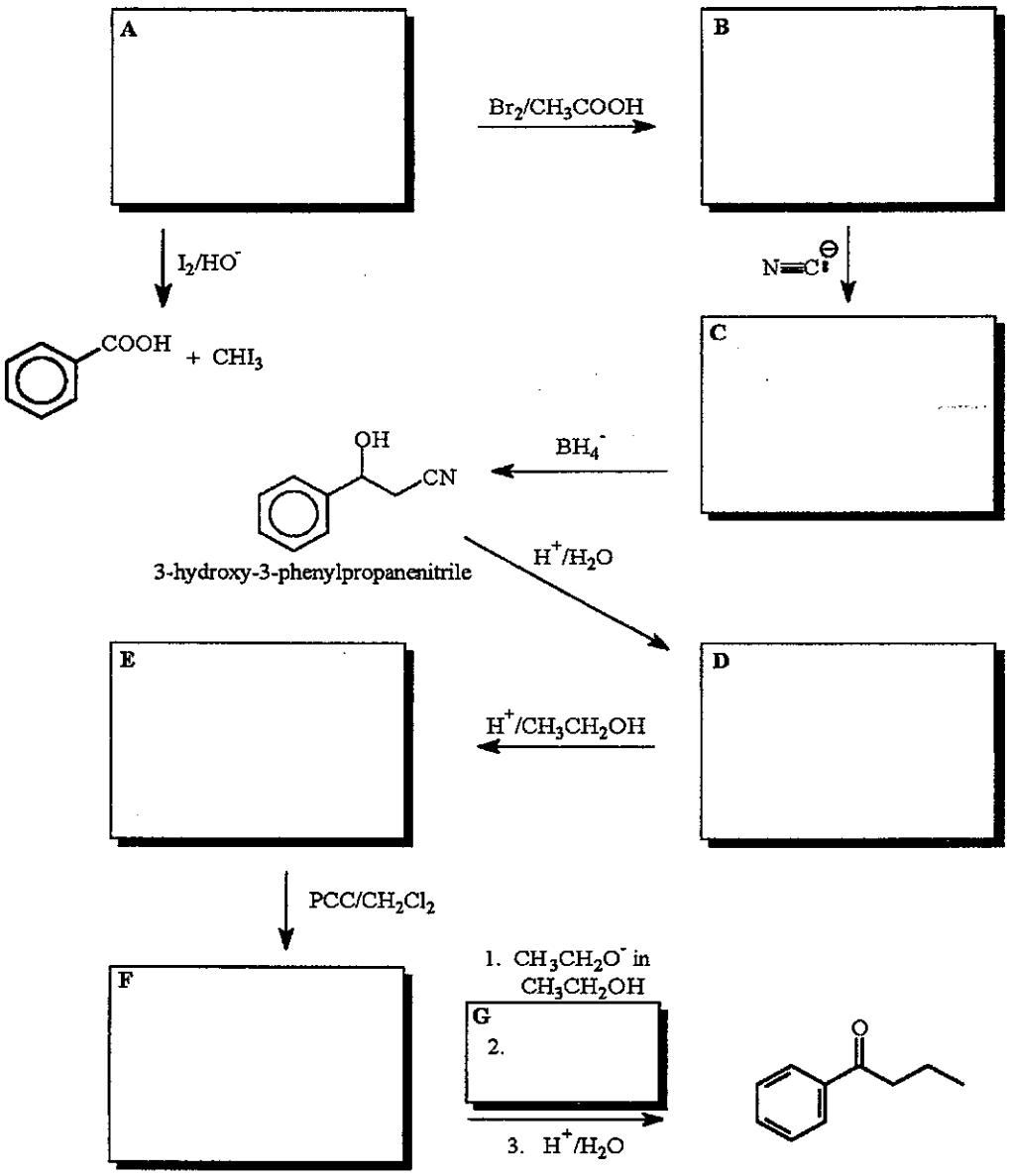
9. For the mixed Claisen condensation of ethyl acetate and ethyl formate, show the structure of the enolate anion and the mechanism of the attack step (using curved arrows to show movement of electrons). In the second box, show the structure of the anionic tetrahedral intermediate, along with the electron movement for its breakdown, and in the third box show the structure of the final condensation product. (5 points for each box)



10. The **native** ^{13}C NMR, **1-bromo-2-chlorobenzene** will have: (1.5 points)

a. six singlets
b. four singlets and two doublets
c. two singlets and four doublets
d. one singlet and two doublets
e. two singlets and two doublets

11. Compound **A** reacts with I_2 in base to give a precipitate of iodoform and form benzoic acid. **B** can be formed from **A** by reaction with Br_2 in acetic acid. Compound **B** readily undergoes reaction with cyanide anion to give **C**, which can be reduced by $NaBH_4$ to form 3-hydroxy-3-phenylpropanenitrile. Acid hydrolysis of this compound forms **D**, which, on reaction with acidic ethanol gives compound **E**. Gentle oxidation of **E** with pyridinium chlorochromate gives **F**, which, on treatment with ethoxide in ethanol followed by reaction with reagent **G** and acid hydrolysis (and decarboxylation) gives 1-phenyl-1-butanone. Selected spectral data are provided for compounds **A** and **F**. Based on the chemical and spectral information provided, suggest structures for compounds **A-G**. Also, in the spaces provided on the following page, clearly indicate the information which you obtained from each spectral source.(2.5 **points for each spectrum,** 5**points for each structure)**



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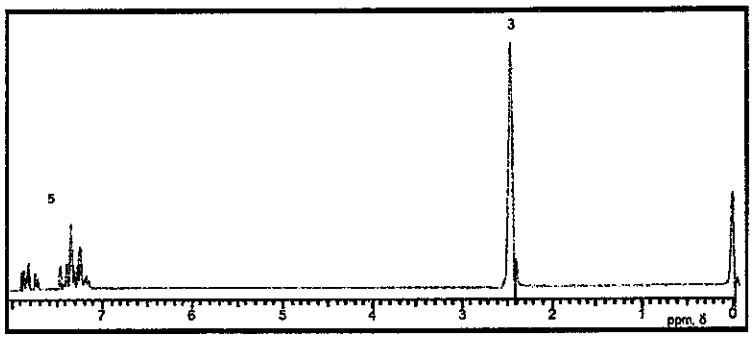
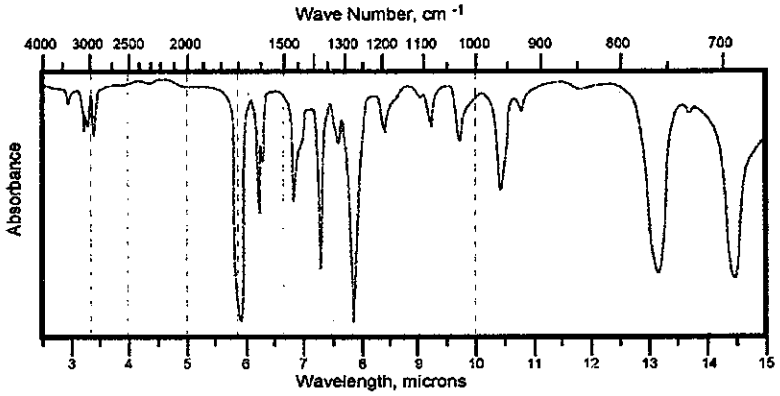
Data for the ^{1}H NMR and IR spectrum of **Compound A**, and for the ^{13}C NMR of **Compound F** are given below. Draw the structures of these compound in the spaces provided on the preceding page. Also, in the spaces provided here, clearly indicate the information which you obtained from each spectral source.(25 **points for each spectrum)**

Compound A:

^{1}H NMR:



IR Spectrum:



Compound F:

^{13}C Spectral Data: singlet, 197.6 ppm; singlet, 172.0 ppm; singlet, 137.4 ppm; doublet, 132.9 ppm; doublet, 128.6 ppm; doublet, 128.4 ppm; triplet, 59.2 ppm; triplet, 46.6 ppm; quartet, 13.6 ppm

Analysis:

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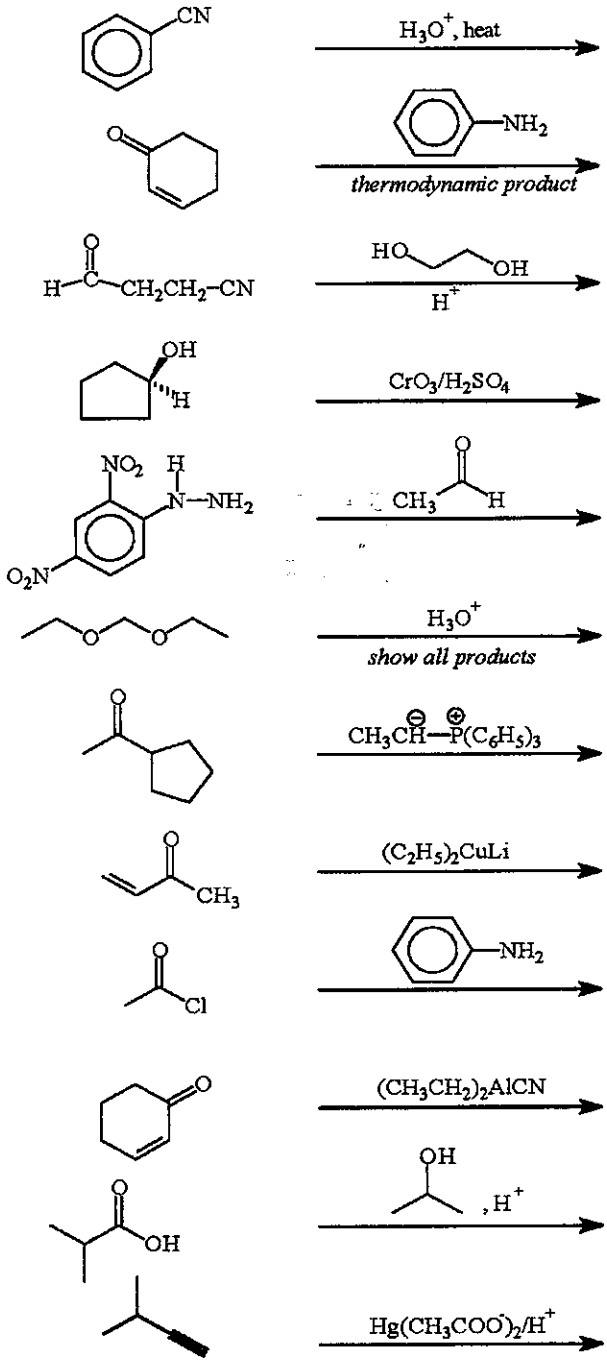
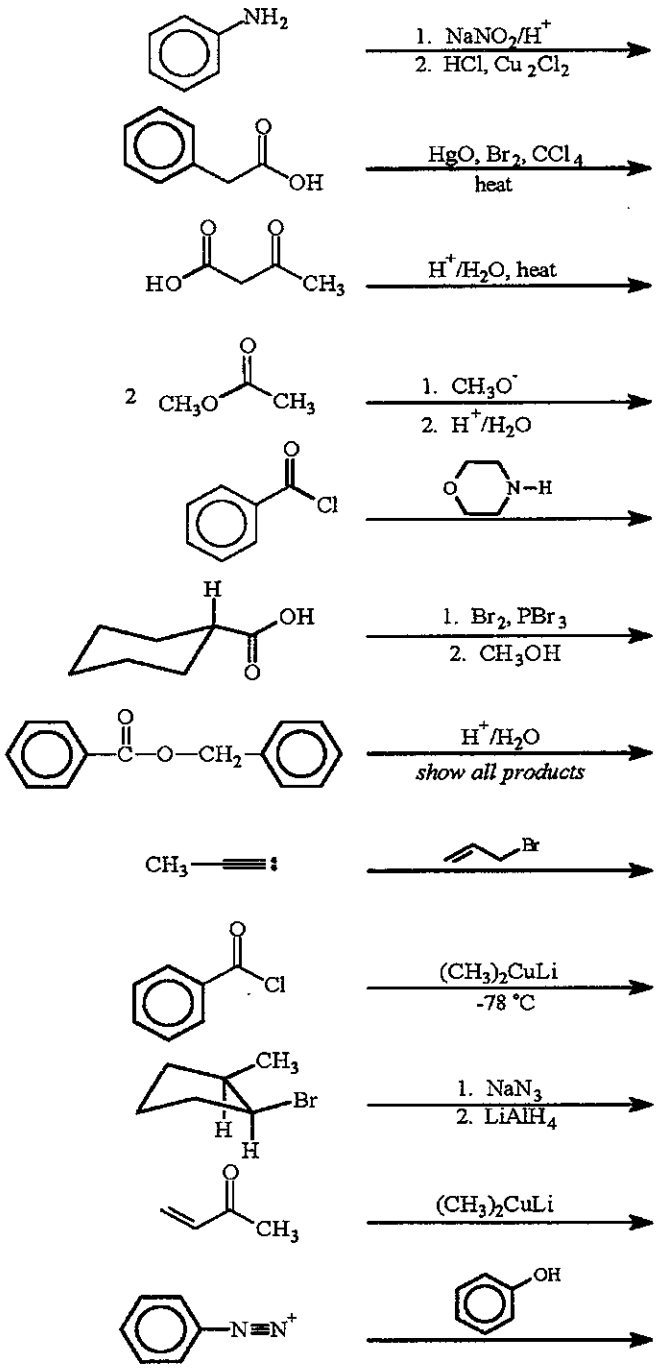
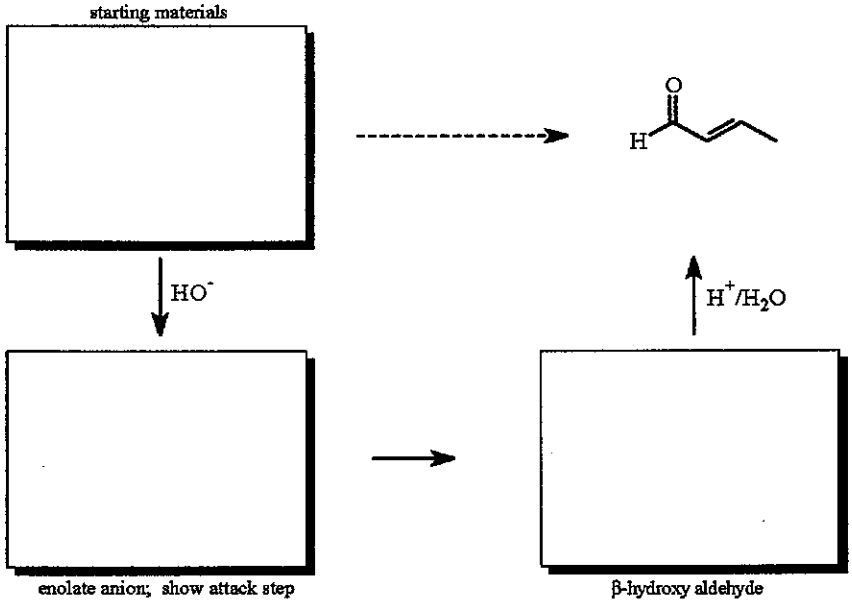
12. Draw the major product for each of the following reactions; you should assume that "excess reagents" are present, if appropriate.(15 points each)



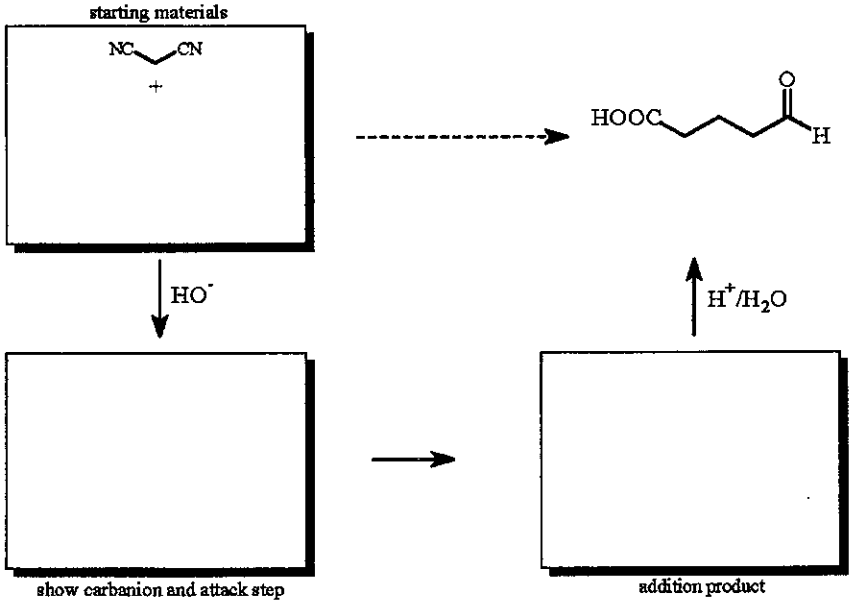
12. con't


NH2
1. NaNO2/H+
2. HCl, Cu2Cl2
OH
O
HgO, Br2, CCl4
heat
HO
CH3
H+/H2O, heat
2
CH3O
CH3
1. CH3O-
2. H+/H2O
Cl
N–H
H
OH
1. Br2, PBr3
2. CH3OH
C–O–CH2
H+/H2O
show all products
CH3
Br
(CH3)2CuLi
-78 °C
N≡N+
1. NaN3
2. LiAlH4
(CH3)2CuLi

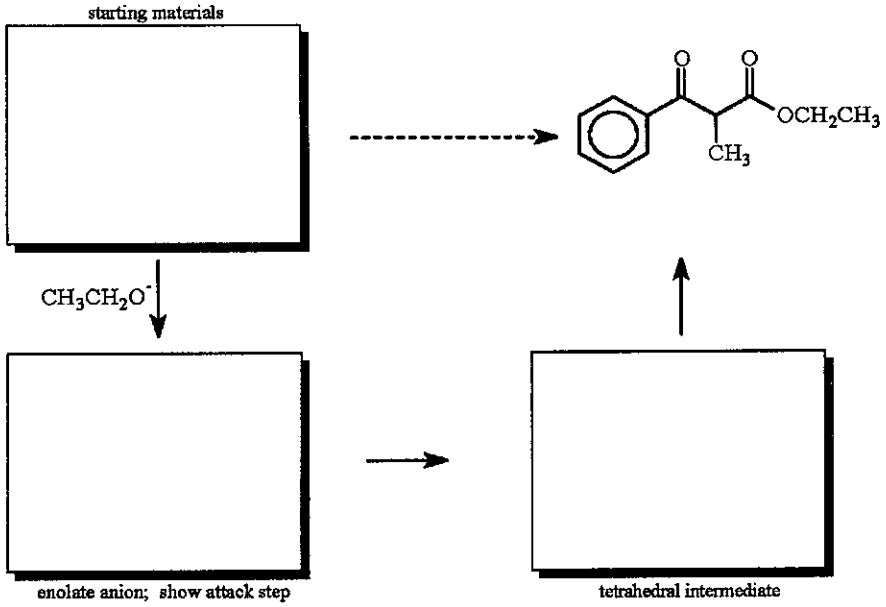
13. For the **aldol condensation** shown below, give the structures of the **starting material**, the **reactive enolate anion** (show the attack step using "curved arrows"), and the resulting **β–hydroxy ketone** (2 points for each box).



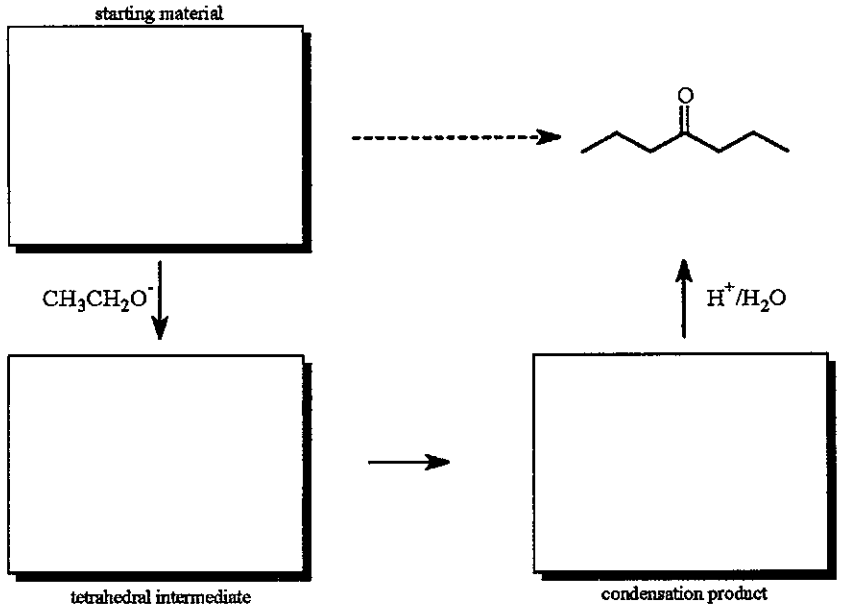
14. For the **conjugate addition** shown below, give the structures of the **starting materials**, the **reactive enolate anion** (show the attack step using "curved arrows"), and the resulting **addition product** (2 points for each box).



15. For the **mixed Claisen condensation** shown below, give the structures of the **two starting materials**, the **reactive enolate anion** (show the attack step using "curved arrows"), and the resulting **tetrahedral intermediate** (2 points for each box).



16. For the **Claisen condensation** shown below, give the structures of the **starting material**, the **tetrahedral addition intermediate**, and the resulting **condensation product** (2 points for each box).



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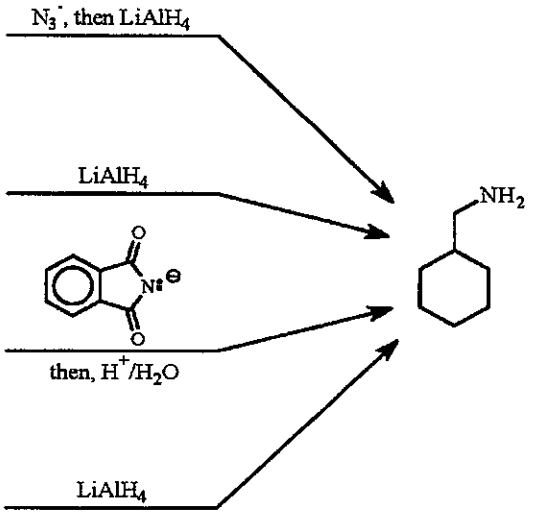
17. Aminomethylcyclohexane can be prepared from simple starting materials using the **four methods** shown below. Provide a suitable starting material for each of the reactions shown(5points each reaction).



18. Beginning with **acetophenone** (phenylethanone) suggest a synthesis of each of the following compounds. **Clearly** show all reactants and reaction conditions.(5points each)