

Name: _____ Last four numbers of the ID: _____

Part A

1. The IR spectrum of which type of compound will not show evidence of hydrogen bonding?

- A) Aldehyde
- B) Alcohol
- C) Carboxylic acid
- D) Phenol
- E) Primary amine

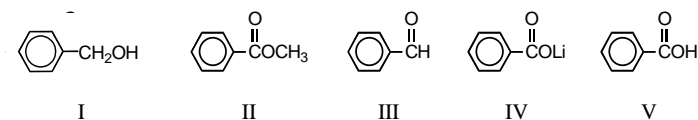
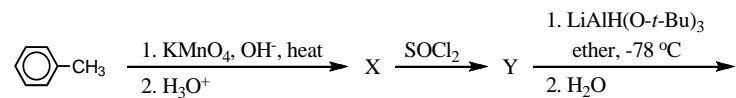
2. LiAlH_4 (LAH) cannot be used to convert carboxylic acids to the corresponding aldehydes because:

- A) LAH is not sufficiently reactive.
- B) RCOOH is converted into RCOOLi .
- C) LAH is too reactive and RCOOH is reduced to RCH_2OH .
- D) RCOOH is reduced to RCH_3 .
- E) RCOOH is converted into $\text{R}_2\text{C}=\text{O}$.

3. A compound with formula $\text{C}_5\text{H}_{10}\text{O}$ gives two signals only, both singlets, in the ^1H NMR spectrum. Which of these structures is a possible one for this compound?

- A) $\text{CH}_3\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{CH}_3$
- B) $(\text{CH}_3)_2\text{CHC}(=\text{O})\text{CH}_3$
- C) $(\text{CH}_3)_3\text{CC}(\text{H})=\text{O}$
- D) $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{H})=\text{O}$
- E) $(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{H})=\text{O}$

4. What is the final product, Z, of the following synthesis?

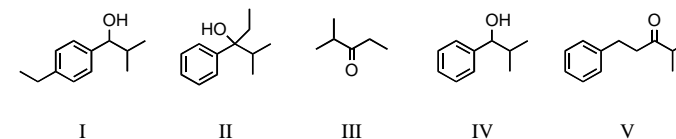
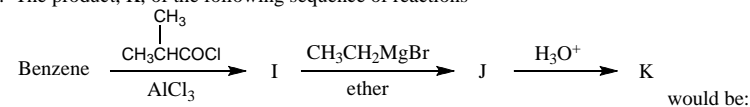


- A) I
- B) II
- C) III
- D) IV
- E) V

5. An aldehyde results from the reaction of which of these compounds with aqueous base?

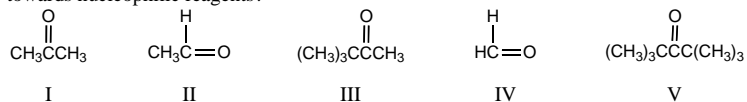
- A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
- B) $\text{CH}_3\text{CHClCH}_2\text{Cl}$
- C) $\text{CH}_3\text{CH}=\text{CCl}_2$
- D) $\text{CH}_3\text{CH}_2\text{CHCl}_2$
- E) $\text{CH}_3\text{CCl}_2\text{CH}_3$

6. The product, K, of the following sequence of reactions



- A) I
- B) II
- C) III
- D) IV
- E) V

7. What, in general, is the order of decreasing reactivity of these carbonyl compounds towards nucleophilic reagents?

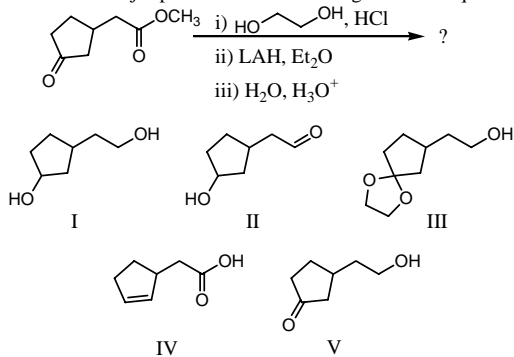


- A) I > III > V > II > IV
 B) IV > II > I > III > V
 C) V > III > I > II > IV
 D) II > I > V > III > IV
 E) III > V > IV > II > I

8. The compound $\text{C}_6\text{H}_5\text{-CH=N-NH}_2$ is produced by the reaction of benzaldehyde with which compound?

- A) Ammonia
 B) Hydrazine
 C) Nitrogen
 D) Phenylhydrazine
 E) Hydroxylamine

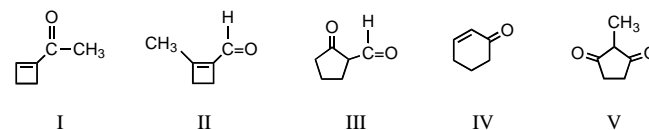
9. What is the major product of the following reaction sequence?



- A) I
 B) II
 C) III
 D) IV
 E) V

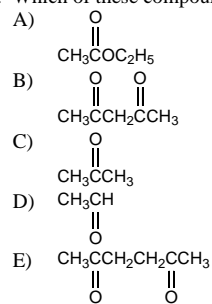
10.

The aldol cyclization of $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{H}$ produces which of these?



- A) I
 B) II
 C) III
 D) IV
 E) V

11. Which of these compounds would have the lowest pKa?



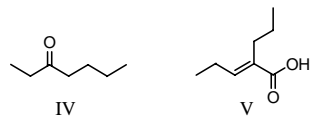
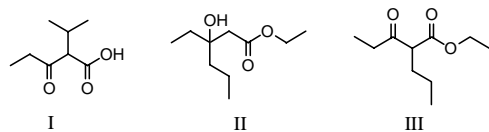
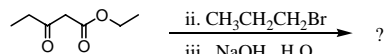
12. Predict the product of the following reaction sequence.

i. NaOC_2H_5

ii. $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

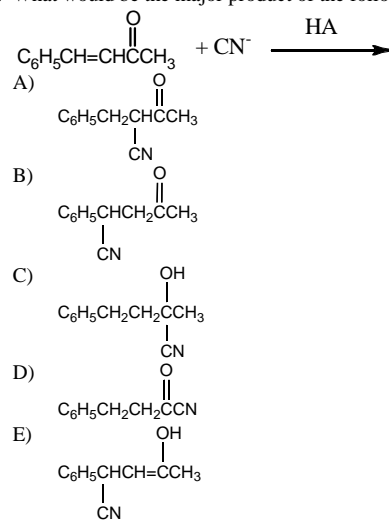
iii. NaOH , H_2O

iv. H_3O^+ , heat



- A) I
B) II
C) III
D) IV
E) V

13. What would be the major product of the following reaction?



14. What final product is expected when toluene ($\text{C}_6\text{H}_5\text{CH}_3$) is subjected to the following reaction sequence?

i) KMnO_4 , NaOH ;

ii) H_3O^+ (product = $\text{C}_7\text{H}_6\text{O}_2$);

iii) SOCl_2 ;

iv) NH_3 (product = $\text{C}_7\text{H}_7\text{NO}$);

v) Br_2 , NaOH

A) $\text{C}_6\text{H}_5\text{CONH}_2$

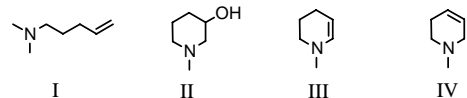
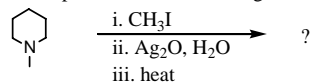
B) $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

C) *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$

D) *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$

E) $\text{C}_6\text{H}_5\text{NH}_2$

15. What would be the product of the following reaction sequence?

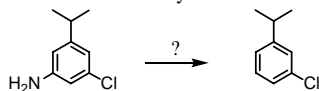


- A) I
 B) II
 C) III
 D) IV
 E) I and II only

16. When an equimolar mixture of ammonia and butyl bromide reacts, which of these products will form?

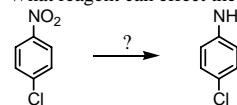
- A) Butylamine
 B) Dibutylamine
 C) Tributylamine
 D) Tetrabutylammonium bromide
 E) All of these

17. How would one carry out the following transformation: ?



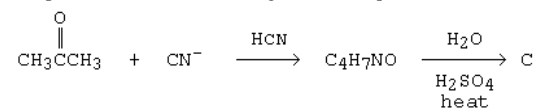
- A) $\text{NaNO}_2, \text{HCl}, 0-5^\circ\text{C}$; then HNO_3
 B) $\text{NaNO}_2, \text{HCl}, 0-5^\circ\text{C}$; then H_3PO_2
 C) $\text{NaNO}_2, \text{HCl}, 0-5^\circ\text{C}$; then H_2, Ni
 D) $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}, \text{OH}^-$; then HCl
 E) NaH, DMSO

18. What reagent can effect the following transformation?



- A) $\text{Sn} + \text{HCl}$; then OH^-
 B) NH_2Cl
 C) H_3PO_2
 D) CuCN
 E) HONO , then NH_3

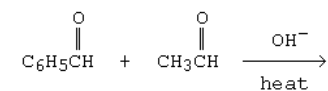
19. The product, C, of the following reaction sequence,



would be:

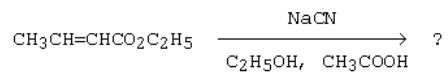
- A) $\text{CH}_3\text{CH}=\text{C}(\text{OH})\text{CH}_3$
 B) $\text{CH}_3\text{CH}_2\text{COOCH}_3$
 C) $\text{CH}_3\text{CH}(\text{CN})\text{CH}_3$
 D) $\text{CH}_3\text{CH}=\text{CHCOOH}$
 E) None of these

20. What would be the major product of the following reaction?



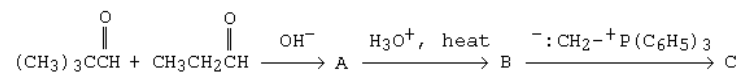
- A) $\text{C}_6\text{H}_5\text{CH}_2\overset{\text{O}}{\parallel}\text{CCH}_3$
- B) $\text{C}_6\text{H}_5\overset{\text{O}}{\parallel}\text{CCH}_2\overset{\text{O}}{\parallel}\text{CH}$
- C) $\text{C}_6\text{H}_5\underset{\text{OH}}{\text{CH}}\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}_2$
- D) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{CH}$
- E) $\text{C}_6\text{H}_5\text{CH}=\overset{\text{O}}{\parallel}\text{CH}$

21. What would be the product of the following reaction?



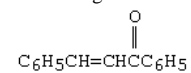
- A) $\text{CH}_3\text{CH}_2\underset{\text{CN}}{\text{CH}}\text{CO}_2\text{C}_2\text{H}_5$
- B) $\text{CH}_3\text{CH}=\text{CHCO}_2\text{CN}$
- C) $\text{CH}_3\text{CH}=\text{CHCN}$
- D) $\text{CH}_3\underset{\text{CN}}{\text{CH}}\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$
- E) $\text{CH}_3\text{CH}=\underset{\text{OH}}{\underset{\text{CN}}{\text{C}}}\text{CO}_2\text{C}_2\text{H}_5$

22. What would be the product, C, of the following reaction sequence?



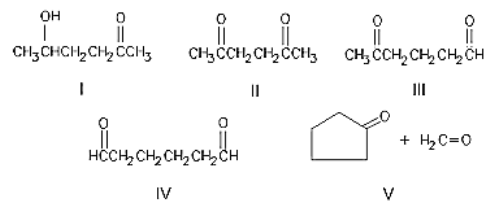
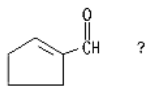
- A) $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{OH}$
- B) $(\text{CH}_3)_3\underset{\text{OH}}{\text{C}}\text{CHCH}_2\text{CH}=\text{CH}_2$
- C) $(\text{CH}_3)_3\text{CCH}_2\underset{\text{CH}_3}{\text{C}}=\text{CH}_2$
- D) $(\text{CH}_3)_3\text{CCH}=\underset{\text{CH}_3}{\text{C}}\text{CH}=\text{CH}_2$
- E) $(\text{CH}_3)_3\underset{\text{CH}_3}{\text{C}}\text{CHCH}=\text{CH}_2$

23. Which reagents would you use to synthesize this compound by an aldol condensation?



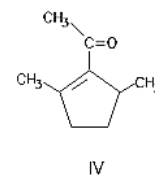
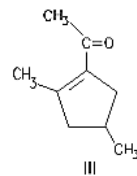
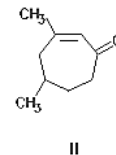
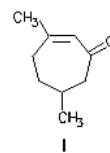
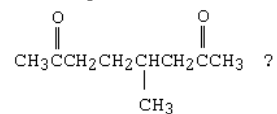
- A) $\text{C}_6\text{H}_5\overset{\text{O}}{\parallel}\text{CH}$ and $\text{C}_6\text{H}_5\text{CH}_2\overset{\text{O}}{\parallel}\text{CH}$
- B) $\text{C}_6\text{H}_5\text{CH}_2\overset{\text{O}}{\parallel}\text{CH}$ and $\text{C}_6\text{H}_5\overset{\text{O}}{\parallel}\text{CCH}_3$
- C) $\text{C}_6\text{H}_5\text{CH}=\text{CH}\overset{\text{O}}{\parallel}\text{H}$ and $\text{C}_6\text{H}_5\text{OH}$
- D) $\text{C}_6\text{H}_5\overset{\text{O}}{\parallel}\text{CCH}_3$ and $\text{C}_6\text{H}_5\overset{\text{O}}{\parallel}\text{CH}$
- E) $(\text{C}_6\text{H}_5)_2\text{CuLi}$ and $\text{CH}_2=\text{CH}\overset{\text{O}}{\parallel}\text{C}_6\text{H}_5$

24. What starting compound(s) would you use in an aldol reaction to prepare



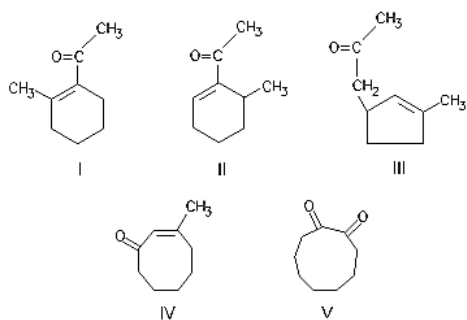
- A) I
B) II
C) III
D) IV
E) V

25. What compound results from the aldol cyclization of



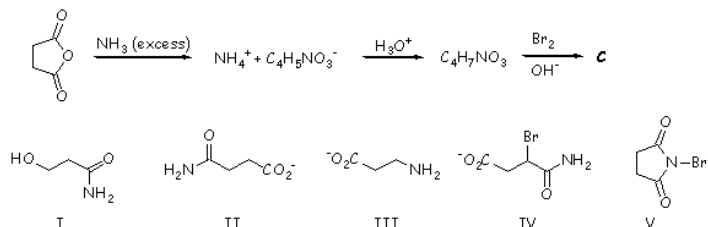
- A) I
B) II
C) III
D) IV
E) Both III and IV

26. When $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{CH}_3$ cyclizes in basic solution, which of these compounds will be formed?



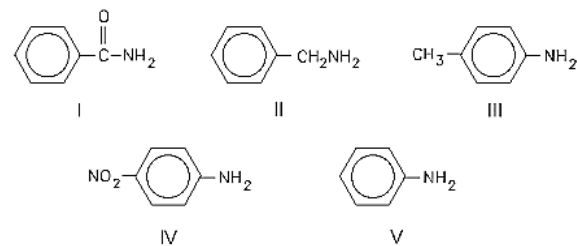
- A) I
B) II
C) III
D) IV
E) V

27. What is the final product, C?



- A) I
B) II
C) III
D) IV
E) V

28. Which of the following compounds would be the strongest base?



- A) I
B) II
C) III
D) IV
E) V

29. Which would be the weakest base?

- A) p-Methylaniline
B) p-Methoxyaniline
C) Hexylamine
D) p-Nitroaniline
E) Dipropylamine

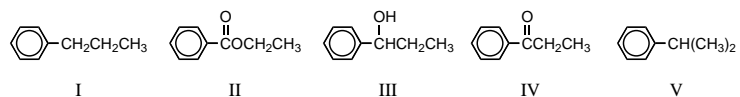
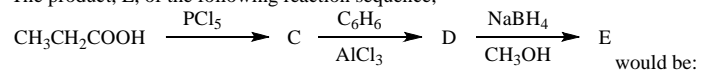
30. LSD is a common abbreviation for:

- A) lead strontium dichromate
B) least square differences method
C) lecithin sulfonium dichloride
D) lithium sulfodioxide
E) lysergic acid diethylamide

31. A correct name for $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}=\text{O}$ is?

- A) 3-Benzylpropanone
B) 3-Phenylpropanal
C) 3-Benzylpropanal
D) Nonanone
E) Nonanal

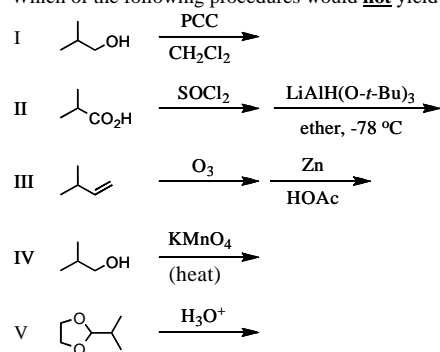
32. The product, E, of the following reaction sequence,



- A) I
B) II
C) III
D) IV
E) V

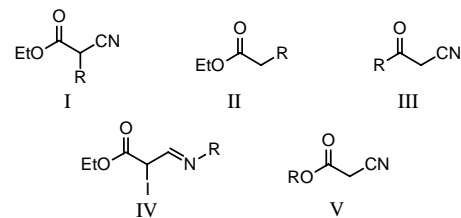
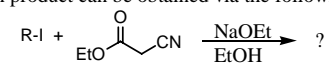
33.

Which of the following procedures would **not** yield $(\text{CH}_3)_2\text{CHCHO}$ as a product?



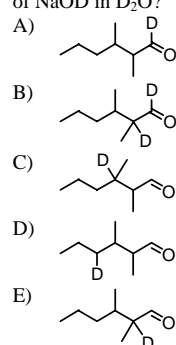
- A) I
B) II
C) III
D) IV
E) V

34. Which product can be obtained via the following generalized reaction?



- A) I
B) II
C) III
D) IV
E) V

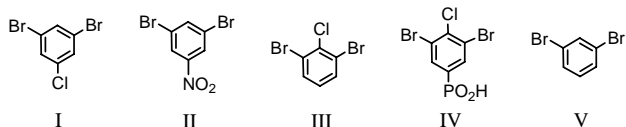
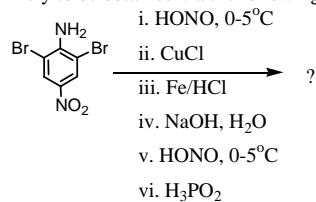
35. Which compound would be formed when 2,3-dimethylhexanal is treated with a solution of NaOD in D_2O ?



36. Which reagent could be used to separate a mixture of aniline (PhNH_2) and toluene (PhCH_3)?

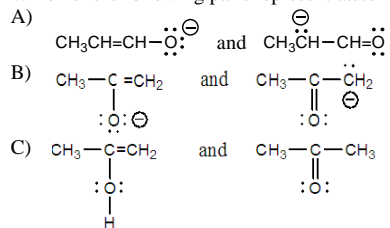
- A) KMnO_4 in H_2O
B) Dilute NaOH
C) Dilute NaHCO_3
D) $\text{Ag}(\text{NH}_3)_2\text{OH}$
E) Dilute HCl

37. What compound is likely to be obtained via the following reaction sequence?



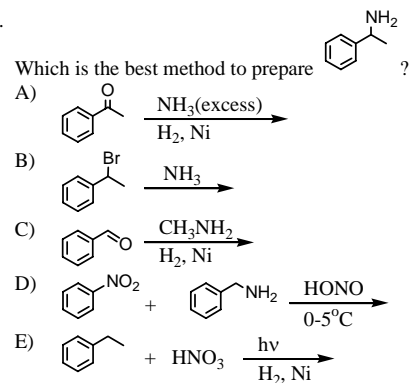
- A) I
 B) II
 C) III
 D) IV
 E) V

38. Which of the following pairs represent tautomers?



- D) All of these
 E) None of these

39.

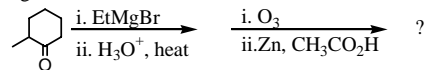


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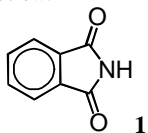
Part B

40. (10 marks) Prepare hexane-2,5-dione from acetone and acetoacetic ester (CH3C(O)CH2CO2CH3). Show a mechanism of either the first or the last step. (A tip: α -bromoacetone can be a possible intermediate).

41. (10 marks) Complete the following reaction sequence, giving structural details of all significant intermediates and the mechanism of the first step.



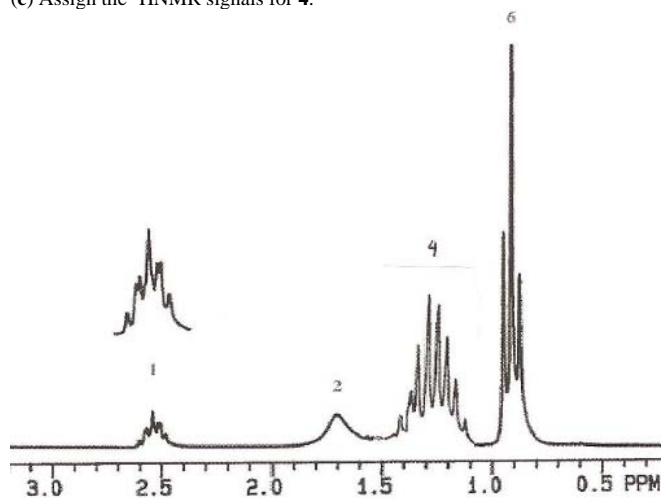
42. (10 marks) When phthalimide (**1**) is treated with a strong base and 3-bromopentane, two products (**2** and **3**) are formed. Compound **2** is a liquid with a molecular formula of C_5H_{10} that showed an infrared peak at 1620 cm^{-1} . Compound **3** has the molecular formula of $C_{13}H_{15}NO_2$. When **3** is heated with hydrazine, compound **4** is isolated ($C_5H_{13}N$) and its expected 1H NMR spectrum (with integrated peak areas) is shown below.



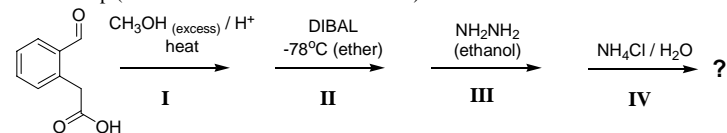
(a) Show structures for **2**, **3** and **4**.

(b) Give an arrow-pushing rationale for the formation of **2** and **3**.

(c) Assign the 1H NMR signals for **4**.



43. (10 marks) Show the final product and all intermediates of the following reaction sequence (remember that DIBAL is $AlH(i-Bu)_2$ and NH_4Cl is weakly acidic). Show the arrow pushing mechanism of step (III). What intramolecular cyclization could happen in the last step (show the structure for **1** extra mark)?



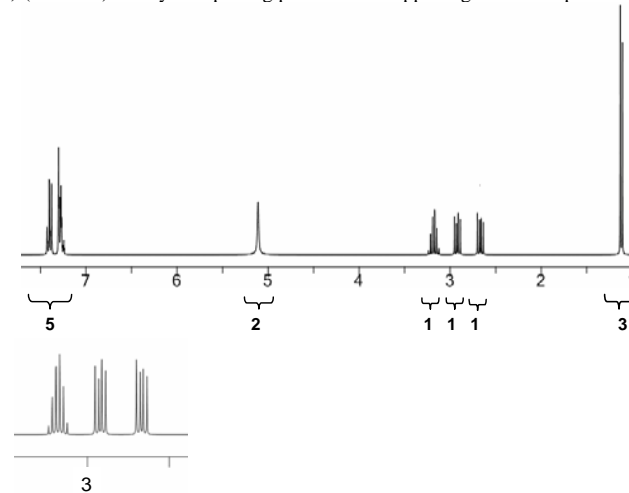
44. Benzaldehyde was treated with nitroethane and dilute base. When worked up, the product **A** ($C_9H_9NO_2$) showed 7 signals in the ^{13}C NMR spectrum.

Compound **A** was then subjected to hydrogenation over a platinum catalyst to give **B** that showed an exact mass measurement of the parent ion of 135.1049 and gave the 1H NMR shown below.

C	12.0000
H	1.0078
N	14.0031
O	15.9949

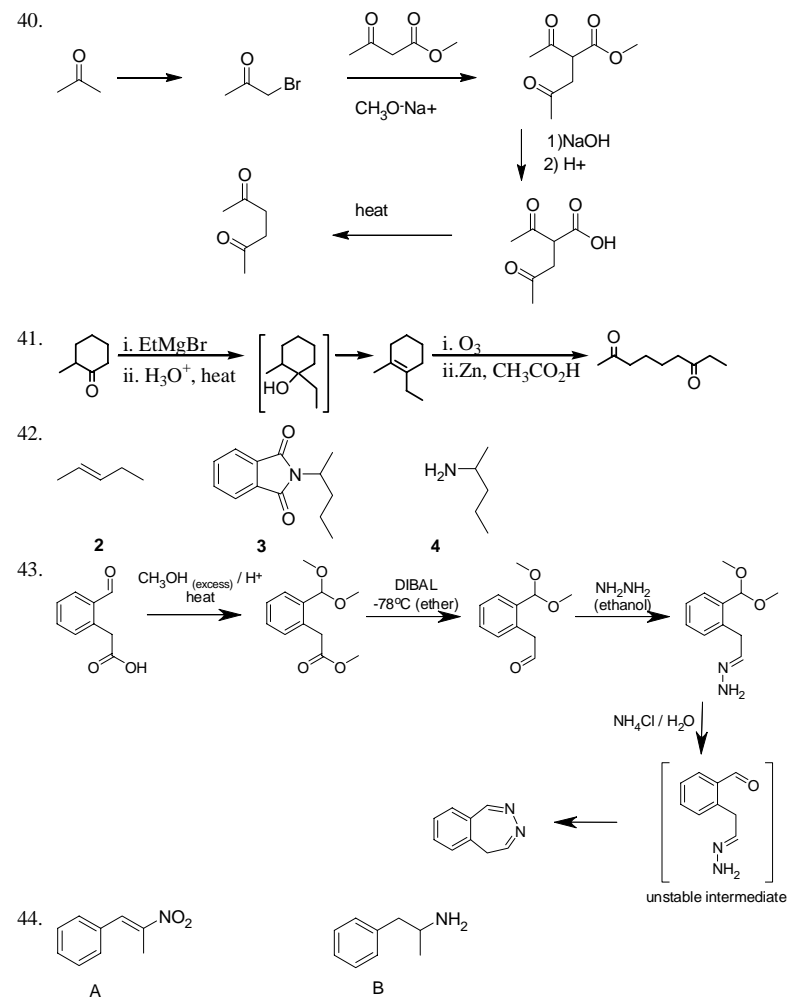
a) (7 marks) Justify the formation of **A** with curved arrows and show structures for **A** and **B**.

b) (4 marks) Justify the splitting pattern in the 3ppm region of the spectrum.



Answer Key

1. A
2. C
3. C
4. C
5. D
6. B
7. B
8. B
9. E
10. D
11. B
12. D
13. B
14. E
15. A
16. E
17. B
18. A
19. A
20. E
21. D
22. D
23. D
24. D
25. E
26. A
27. C
28. B
29. D
30. E
31. B
32. C
33. D
34. A
35. E
36. E
37. C
38. C
39. A



The splitting is due to nonequivalent protons in alpha position to Ph group (diastereotopic protons) which are next to the chiral centre (amino-substituted carbon)