CHEM 2425. Review for Test 4 (chapter 22, 23, 24). TR. Stafford

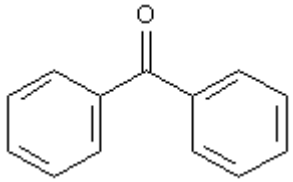
True/False
Indicate whether the statement is true or false.

____ 1. Tautomerization is catalyzed by both acids and bases.

____ 2. The alkyl halide that should be used to produce octanoic acid via the malonic ester synthesis is 1-bromooctane.

____ 3. Using the acetoacetic ester synthesis, to produce 5-methyl-2-heptanone, the alkyl halide that should be used is 1-bromo-2-methylbutane.

____ 4. The following molecule will not undergo an aldol condensation with another like molecule.

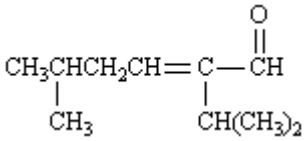


____ 5. In carbonyl condensation reactions new carbon-to-carbon bonds are formed and enolate anions can act as a nucleophiles.

____ 6. A 1,6-diester will produce a five-membered ring via a Dieckmann cyclization.

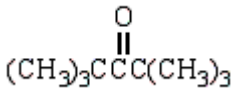
____ 7. Claisen and aldol condensations can result in cyclization but the Robinson annulation cannot.

____ 8. An aldol condensation using 3-methylbutanal could produce the following compound.

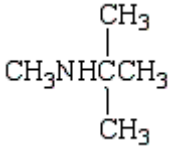


____ 9. A Claisen condensation could be considered to the an ester analog of an aldol condensation.

____ 10. The following compound can act as a nucleophile in an aldol reaction.



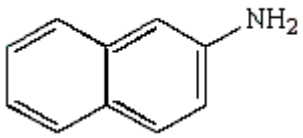
____ 11. The following structure is classified as a 3° amine.



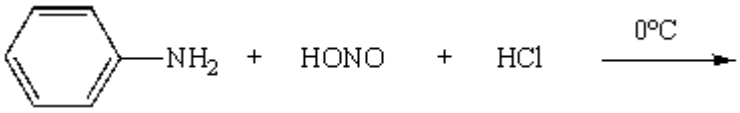
____ 12. To separate a mixture of *p*-toluidine and *p*-nitrotoluene dissolved in ether,extract the ether solution with aqueous HCl and treat the water layer with aqueous NaOH.

____ 13. Aliphatic 3º amines with three different groups on nitrogen can be resolved.

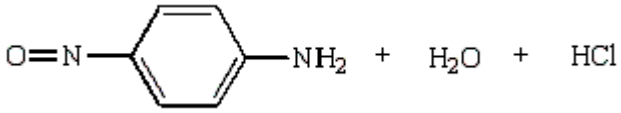
____ 14. The following amine can be converted to an aryl diazonium salt.



____ 15. Consider the following reaction.

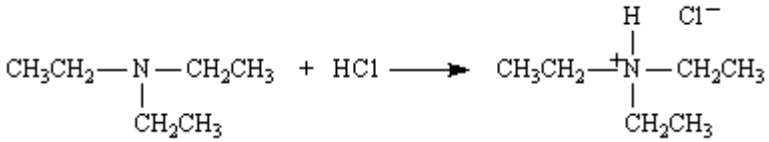


The products of this reaction are shown below.

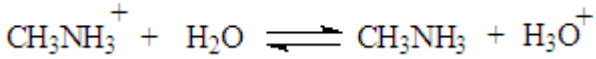


____ 16. The reaction of a 2º amine with nitrous acid gives a nitrosamine.

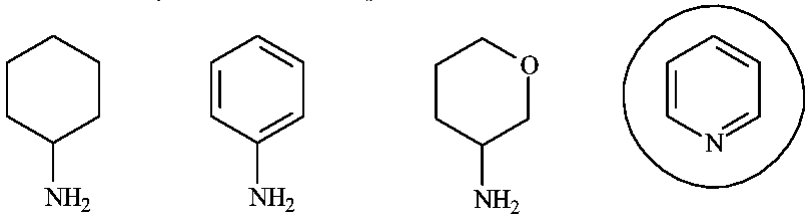
____ 17. The following represents an acid-base reaction between the given amine and HCl.



____ 18. The pK_a of methyl amine is represented by the following reaction.

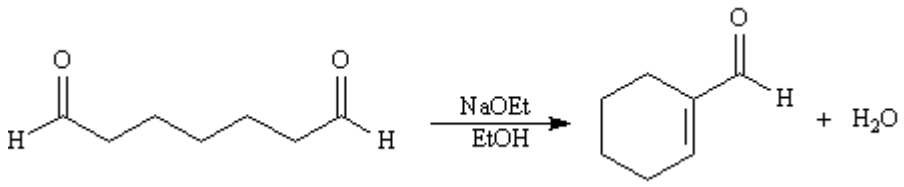


____ 19. The compound circled below represents a heterocyclic amine.



Completion
Complete each statement.

Consider the following reaction.

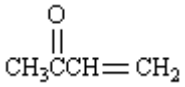


Use this reaction to answer the following questions.

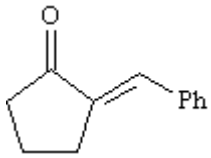
1. This reaction is an example of _____.
   a. an intramolecular Claisen condensation
   b. an intramolecular aldol condensation
   c. a Robinson annulation
   d. a Michael reaction

2. The product of this reaction is _____.
   a. a β, γ-unsaturated aldehyde
   b. an α, β-unsaturated ketone
   c. an α, β-unsaturated aldehyde
   d. an enol

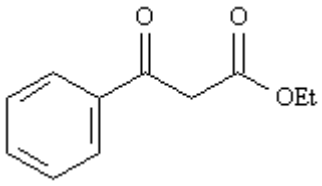
3. In an aldol reaction the following substance could be produced by the reaction of acetone (propanone) and _____. Enter the name of the substance.



4. In an aldol reaction the following substance could be produced by the reaction of benzaldehyde and _____. Enter the name of the substance.

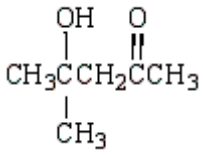


5. In a Claisen condensation the following substance could be produced by the reaction of ethylbenzoate and _____. Enter the name of the substance.

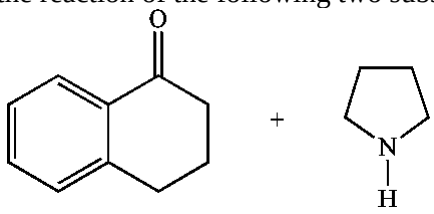


6. Consider the steps in the mechanism for a base catalyzed aldol condensation. The _____ step in the base catalyzed aldol condensation is addition of an enolate to a carbonyl group.

7. The structure of the aldol shown below can be produced by reacting _____ with NaOH. Enter the name of the compound.



8. The class of compound formed in the reaction of the following two substance is a(n)_____.

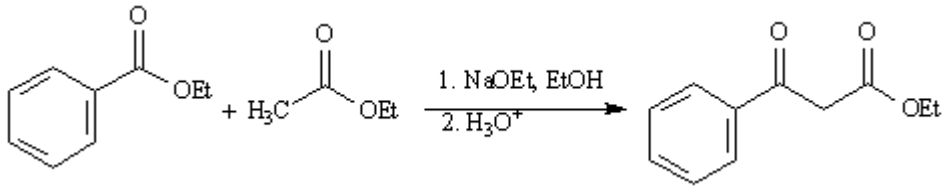


Consider the following types of reactions:

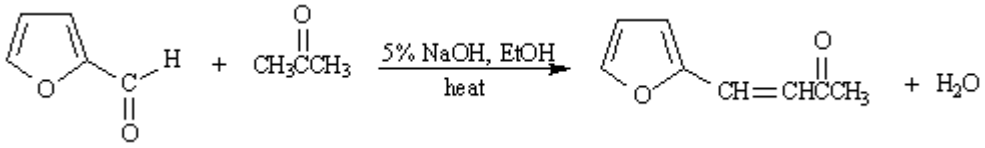
1. aldol condensation
2. Claisen condensation
3. Robinson annulation
4. Dieckmann condensation
5. Michael reaction

Classify the following reactions by placing the appropriate number in the blank.

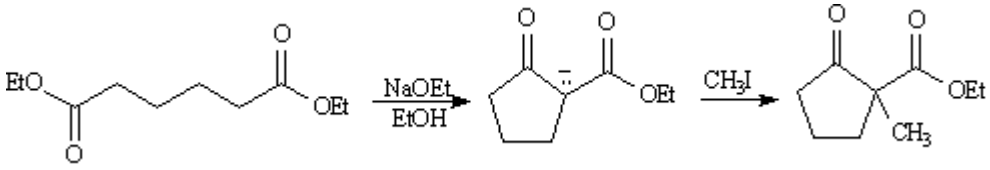
9. _____



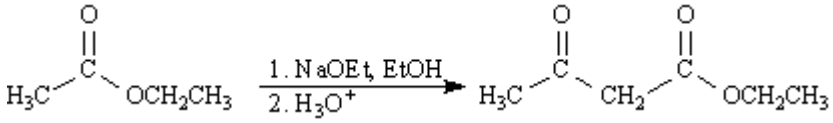
10. _____



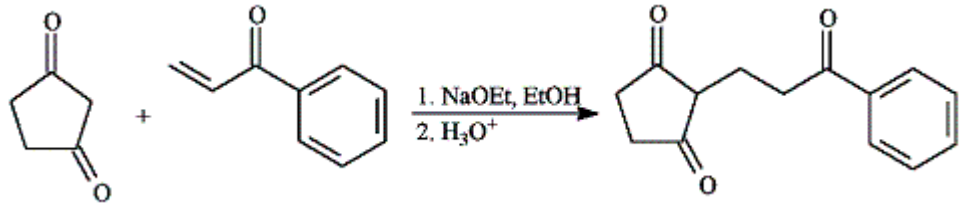
11. _____



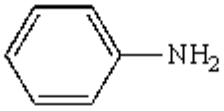
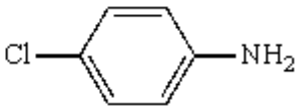
12. _____



13. _____



Consider the following compounds.

1. NH_3 2. CH_3NH_2 3.  4. 

Answer the following questions by filling in the blank with the appropriate number from the diagram or an appropriate term.

14. The ammonia ion of substance ____ will have the largest pK_a.

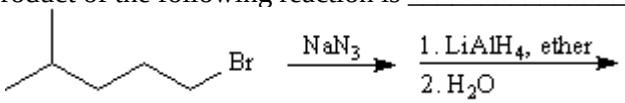
15. The ammonia ion of substance ____ will have the smallest pK_a.

16. Substance _____ is a primary alkyl amine.

17. The name of the product formed by reacting CuCl and HCl with benzenediazonium chloride is _____.

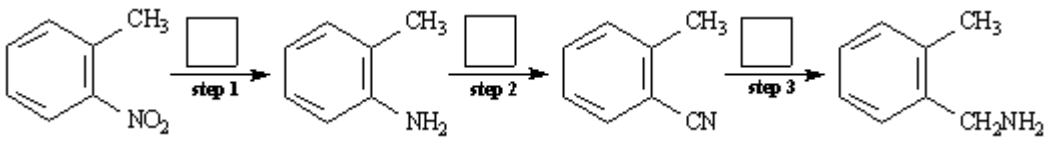
18. The name of the product formed by reacting KCN and CuCN with benzenediazonium chloride is _____.

19. The IUPAC name of the product of the following reaction is _____.



From the list provided below, choose the best reagent(s) for each step in the following synthesis. There is only one answer for each reaction. Enter the appropriate letter in the blank provided.

a. $NaBH_4$, ethanol
b. KCN, acetone
c. 1. $LiAlH_4$, THF
   2. H_2O
d. 1. $NaNO_2$, H_3O^+
   2. CuCN, KCN
e. 1. $SnCl_2$, H_3O^+
   2. NaOH, H_2O
f. HNO_3, H_2SO_4

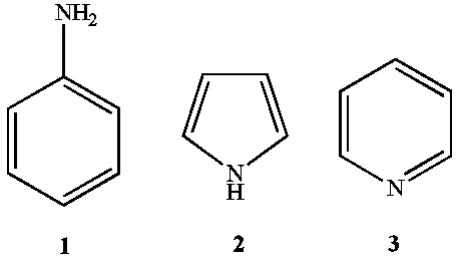


20. _____Step 1

21. _____Step 2

22. _____Step 3

Consider the following substances.



1 **2** **3**

Complete the following statements using the appropriate number.

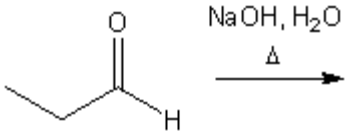
23. Substance _____ is pyrrole.

24. Substance _____ is aniline.

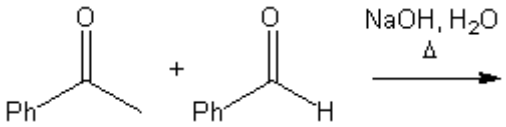
25. Substance _____ is pyridine.

Problem

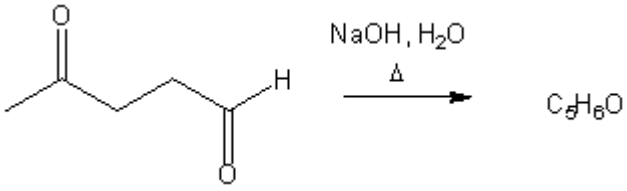
1. What is the major organic product obtained from the following reaction?



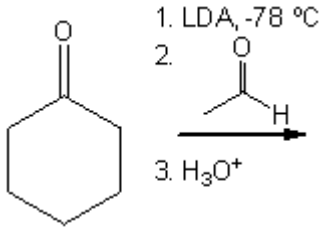
2. What is the major organic product obtained from the following reaction?



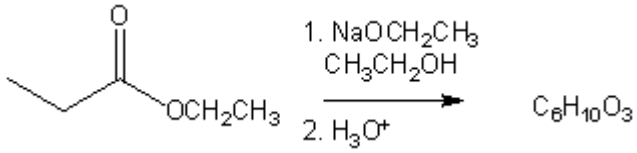
3. What is the major organic product obtained from the following reaction?



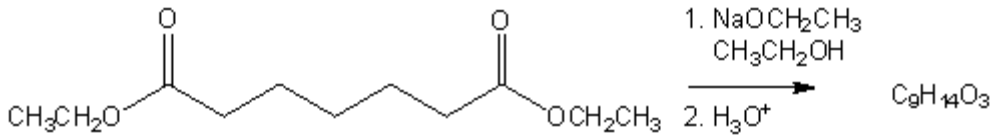
4. What is the major organic product obtained from the following reaction?



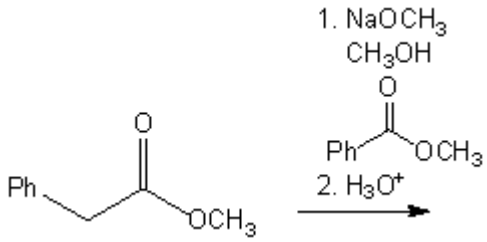
5. What is the major organic product obtained from the following reaction?



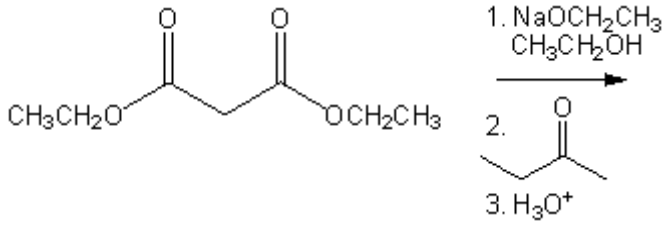
6. What is the major organic product obtained from the following reaction?



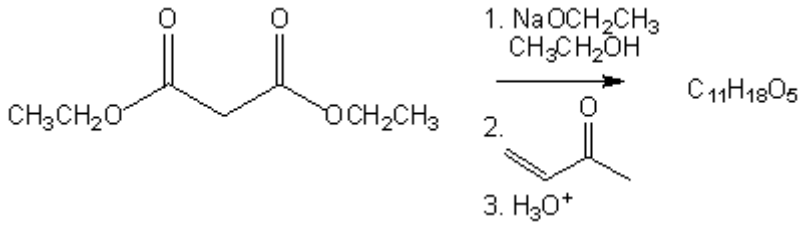
7. What is the major organic product obtained from the following reaction?



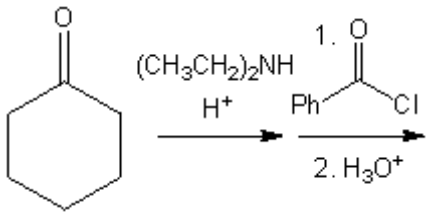
8. What is the major organic product obtained from the following reaction?



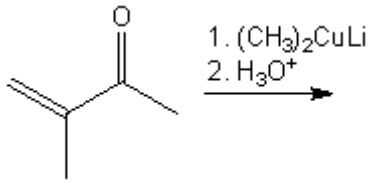
9. What is the major organic product obtained from the following reaction?



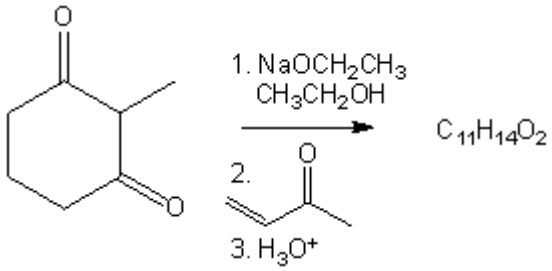
10. What is the major organic product obtained from the following sequence of reactions?



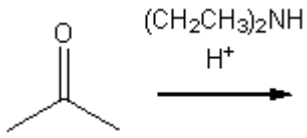
11. What is the major organic product obtained from the following reaction?



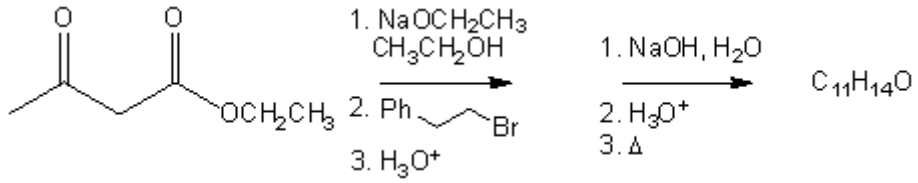
12. What is the major organic product obtained from the following reaction?



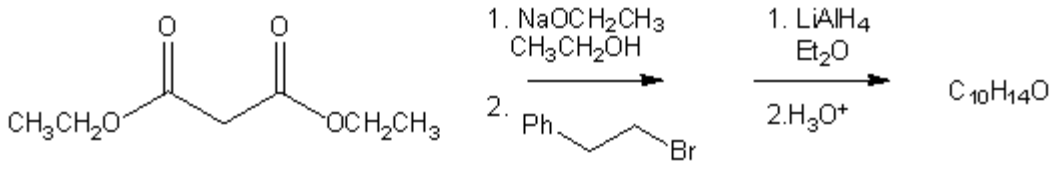
13. What is the major organic product obtained from the following reaction?



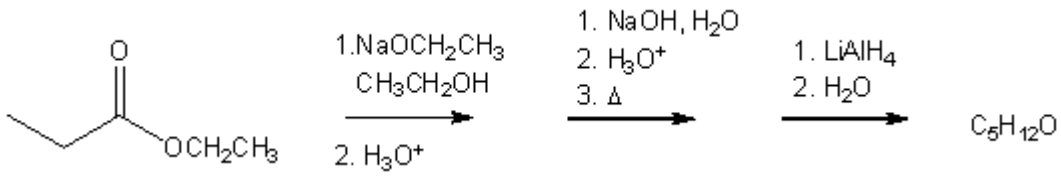
14. What is the major organic product obtained from the following sequence of reactions?



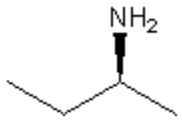
15. What is the major organic product obtained from the following sequence of reactions?



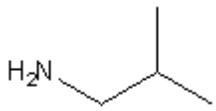
16. What is the major organic product obtained from the following sequence of reactions?



17. What is the IUPAC name of the following compound?



18. What is the IUPAC name of the following compound?



19. Provide a line-bond structure of *N*,*N*-dimethylcyclopentanamine.

20. Provide a line-bond structure of *N*-methylaniline.

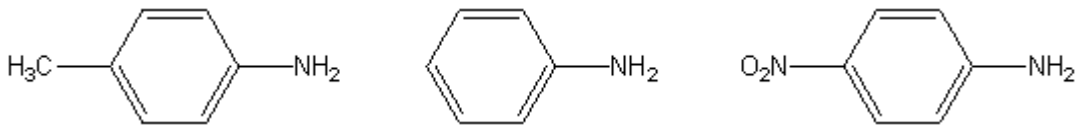
21. Provide a brief explanation, based on features of the molecules, for the following difference in pK_a values?

CH_3NH_2 > NH_3
10.64 9.26

22. Provide a brief explanation, based on features of the molecules, for the following difference in pK_a values?

CH_3NH_2 > $PhNH_2$
10.64 4.63

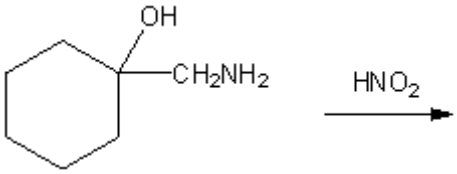
23. Provide a brief explanation, based on features of the molecules, for the following trend in pK_a values?



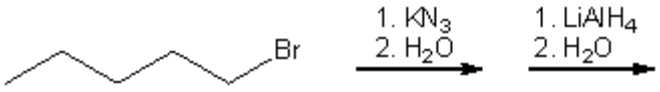
4.15 4.63

1.0

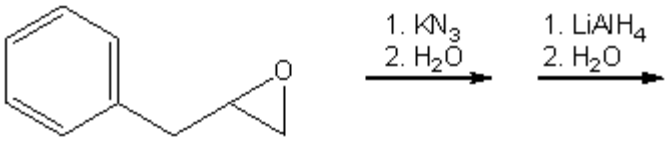
24. What is the major organic product obtained from the following reaction?



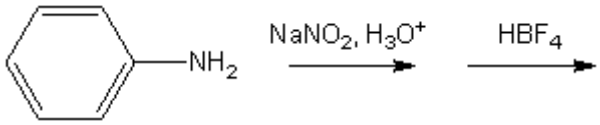
25. What is the major organic product obtained from the following sequence of reactions?



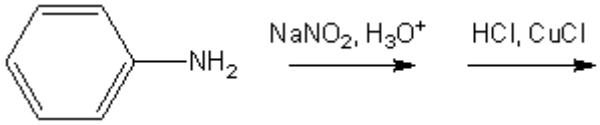
26. What is the major organic product obtained from the following sequence of reactions?



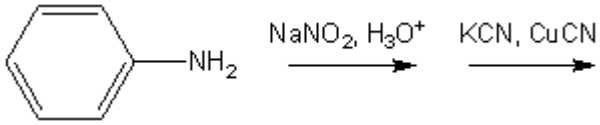
27. What is the major organic product obtained from the following sequence of reactions?



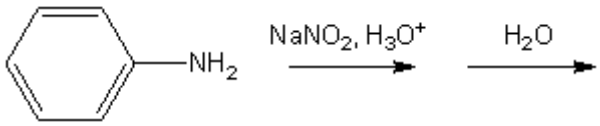
28. What is the major organic product obtained from the following sequence of reactions?



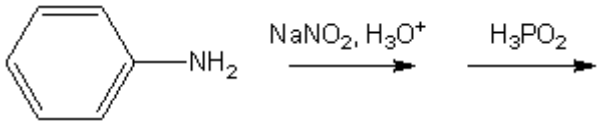
29. What is the major organic product obtained from the following sequence of reactions?



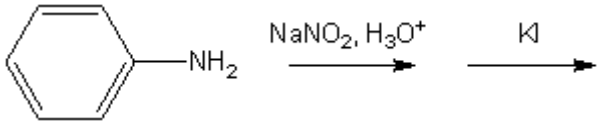
30. What is the major organic product obtained from the following sequence of reactions?



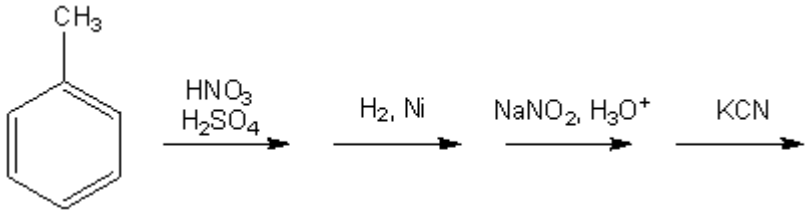
31. What is the major organic product obtained form the following sequence of reactions?



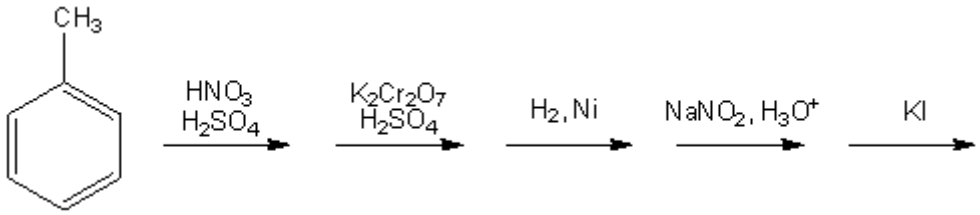
32. What is the major organic product obtained form the following sequence of reactions?



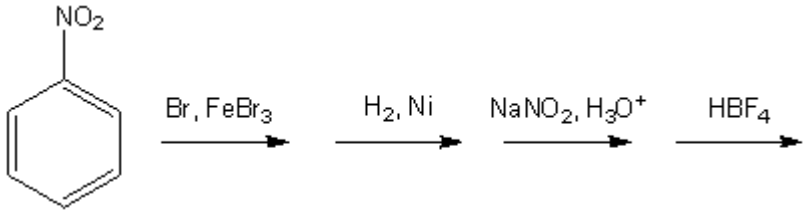
33. What is the major organic product obtained from the following sequence of reactions (assume that mixtures of *ortho* and *para* disubstituted compounds can be separated; continue the synthesis with *either one)*?



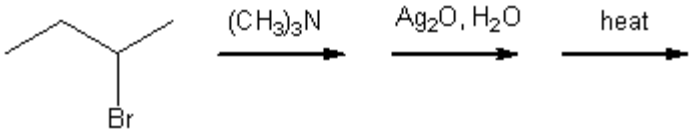
34. What is the major organic product obtained from the following sequence of reactions (assume that mixtures of *ortho* and *para* disubstituted compounds can be separated; continue the synthesis with *either one)*?



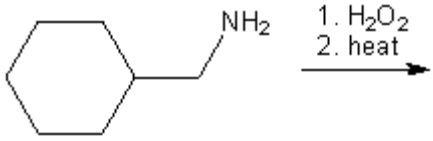
35. What is the major organic product obtained form the following sequence of reactions (assume that mixtures of *ortho* and *para* disubstituted compounds can be separated; continue the synthesis with *either one)*?



36. What is the major organic product obtained form the following sequence of reactions?



37. What is the major organic product obtained form the following sequence of reactions?



CHEM 2425. Review for Test 4 (chapter 22, 23, 24). TR. Stafford
Answer Section

TRUE/FALSE

1. ANS: T PTS: 1
2. ANS: F PTS: 1
3. ANS: T PTS: 1
4. ANS: T PTS: 1
5. ANS: T PTS: 1
6. ANS: T PTS: 1
7. ANS: F PTS: 1
8. ANS: T PTS: 1
9. ANS: T PTS: 1
10. ANS: F PTS: 1
11. ANS: F PTS: 1
12. ANS: T PTS: 1
13. ANS: F PTS: 1
14. ANS: T PTS: 1
15. ANS: F PTS: 1
16. ANS: T PTS: 1
17. ANS: T PTS: 1
18. ANS: T PTS: 1
19. ANS: T PTS: 1

COMPLETION

1. ANS: b

   PTS: 1
2. ANS: c

   PTS: 1
3. ANS:
   methanal
   formaldehyde

   PTS: 1
4. ANS: cyclopentanone

   PTS: 1
5. ANS:
   ethyl acetate
   ethyl ethanoate

   PTS: 1
6. ANS:

second
2nd

PTS: 1

7. ANS:
acetone
propanone

PTS: 1

8. ANS: enamine

PTS: 1

9. ANS: 2

PTS: 1

10. ANS: 1

PTS: 1

11. ANS: 4

PTS: 1

12. ANS: 2

PTS: 1

13. ANS: 5

PTS: 1

14. ANS:
2
two

PTS: 1

15. ANS:
4
four

PTS: 1

16. ANS:
2
two

PTS: 1

17. ANS: chlorobenzene

PTS: 1

18. ANS: benzonitrile

PTS: 1

19. ANS: 4-methylpentanamine

PTS: 1

20. ANS: e

PTS: 1

21. ANS: d

PTS: 1

22. ANS: c

PTS: 1

23. ANS:
2
two

PTS: 1

24. ANS:
1
one

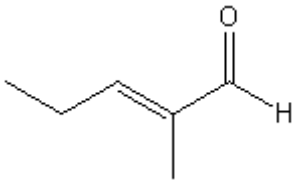
PTS: 1

25. ANS:
3
three

PTS: 1

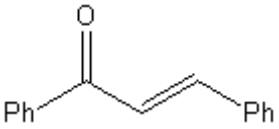
PROBLEM

1. ANS:



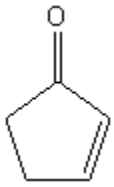
PTS: 1

2. ANS:



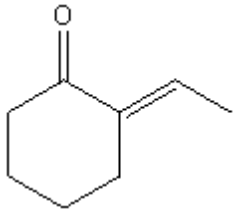
PTS: 1

3. ANS:



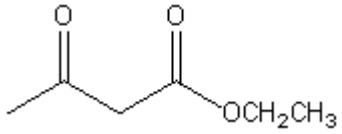
PTS: 1

4. ANS:



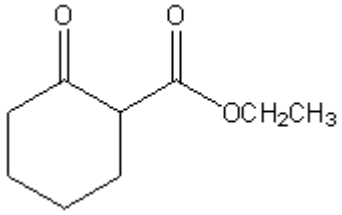
PTS: 1

5. ANS:



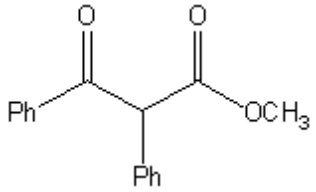
PTS: 1

6. ANS:



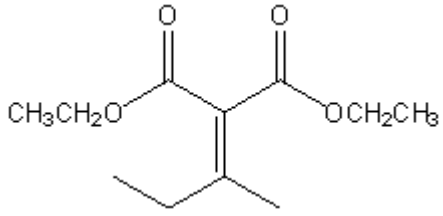
PTS: 1

7. ANS:



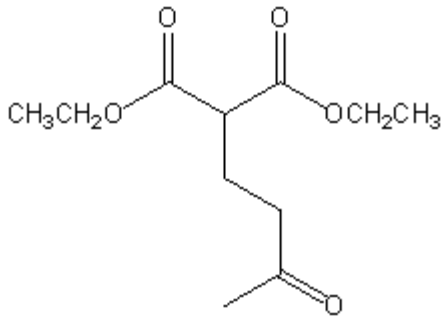
PTS: 1

8. ANS:



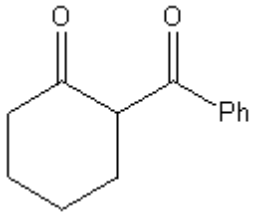
PTS: 1

9. ANS:



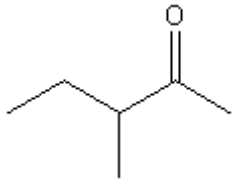
PTS: 1

10. ANS:



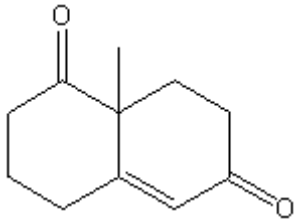
PTS: 1

11. ANS:



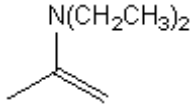
PTS: 1

12. ANS:



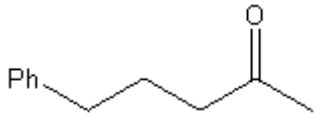
PTS: 1

13. ANS:



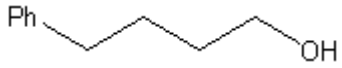
PTS: 1

14. ANS:



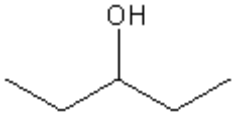
PTS: 1

15. ANS:



PTS: 1

16. ANS:



PTS: 1

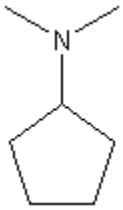
17. ANS:
(*S*)-2-butanamine

PTS: 1

18. ANS:
2-methyl-1-propanamine

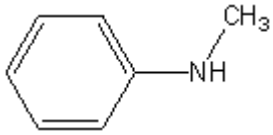
PTS: 1

19. ANS:



PTS: 1

20. ANS:



PTS: 1

21. ANS:
The methyl group of methanamine is a weak electron donating group thereby increasing the electron density of the nitrogen (relative to ammonia) and increasing the basicity. Another way of thinking abut this is that the electron donation of the methyl group stabilizes the conjugate acid of methanamine.

PTS: 1

22. ANS:
The phenyl group of aniline can serve as a resonance electron withdrawing substitutent, thereby reducing the electron density of the nitrogen (relative to methyl amine) and lowering its basicity.

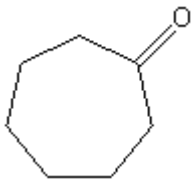
PTS: 1

23. ANS:

The para nitro group of 4-nitroaniline is a resonance electron withdrawing substitutent, thereby reducing the electron density of the nitrogen and lowering its basicity relative to aniline. The 4-methyl group of toluidine is a weak inductive electron donating group, thereby increasing the electron density of the nitrogen and increasing its basicity relative to aniline.

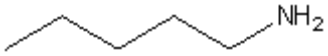
PTS: 1

24. ANS:



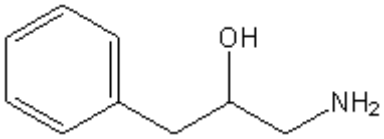
PTS: 1

25. ANS:



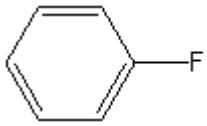
PTS: 1

26. ANS:



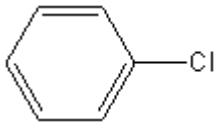
PTS: 1

27. ANS:



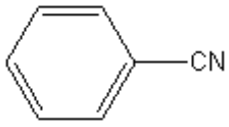
PTS: 1

28. ANS:



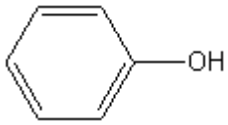
PTS: 1

29. ANS:



PTS: 1

30. ANS:

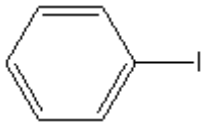


PTS: 1

31. ANS:

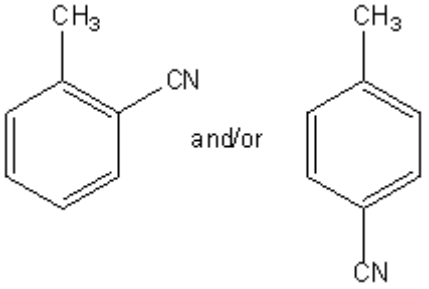
PTS: 1

32. ANS:



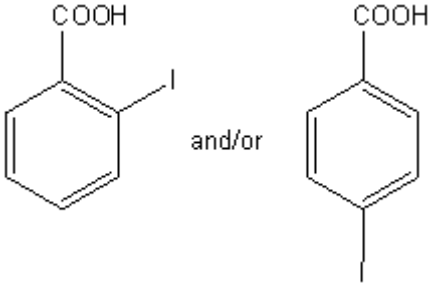
PTS: 1

33. ANS:



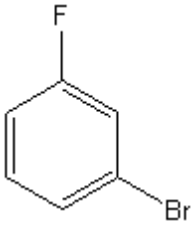
PTS: 1

34. ANS:



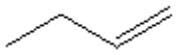
PTS: 1

35. ANS:



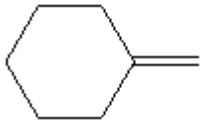
PTS: 1

36. ANS:



PTS: 1

37. ANS:



PTS: 1