CHEMISTRY 263 - Section A2

Final Exam - December 11, 2013 - Dr. John C. Vederas

300 Points - 3 Hours

Part	Points		PRINT LAST NAME:
I	110		
II	30		TURN IN THIS BOOKLET WITH ANSWER SHEET
III	20		
IV	104		PUT ALL ANSWERS ON COLOUR ANSWER SHEET
V	36		
Total	300		

Before you begin be sure that your exam has **17** consecutively numbered pages including this cover sheet. **Do not begin until told to do so**. When you begin, please **print** your name **on each page** of this exam question sheet in the upper right hand corner. **Also** please **print** your name **on the colour answer sheet** in the correct slot. Illegible answers will be marked as incorrect. No books, notes, or unauthorized communications are permitted. If you have any questions or problems, please raise your hand. Do not leave your seat without permission. **Models are permitted but may not be handed to another and NO calculators, phones or other electronic devices are to be used. Turn in BOTH the exam booklet and the coloured answer sheet when you are finished.** Please place your **ID Card** on your desk.

Good Luck ! - Have an Enjoyable Holiday !

Place all answers on coloured Answer Sheet **NAME**_____

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I. Structure and Nomenclature - 110 Points

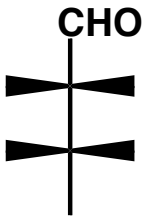
A. Draw structures for which names are given, or name the given structures by any correct (systematic or common) nomenclature. Be sure to give cis or trans (or if appropriate Z or E) or R or S assignment to the isomer where indicated by asterisks (***). **(4 points each - 60 points total)**

This is NOT your answer sheet : the space here is for preliminary work / scratch paper only- not graded
However, you will need to turn in this question sheet to receive credit for your answers

1. ethylene glycol

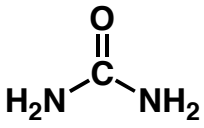
2. polystyrene (use bracket notation)

*** **3.** D-Glucose - open chain form - (use part structure in your drawing to assist grading)

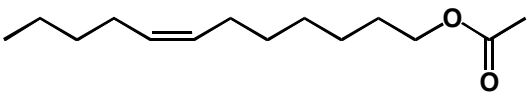


4. Calcium oxalate

5. (a common metabolite)



*** **6.**



(a moth pheromone)

Place all answers on coloured Answer Sheet **NAME**_____

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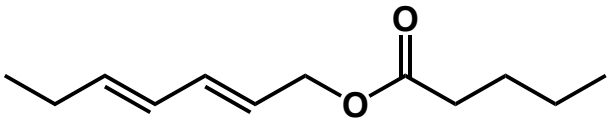
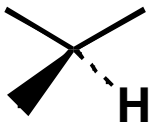
This is NOT your answer sheet : the space here is for preliminary work / scratch paper only- not graded
However, you will need to turn in this question sheet to receive credit for your answers

*** **7.**



*** **8.** (S)-4,4-diphenyl-6-(N,N-dimethylamino)-3-heptanone (methadone, a heroin substitute)

(use part structure to assist grading)



9. Succinyl chloride

10. Benzyl vinyl ether

Place all answers on coloured Answer Sheet **NAME**_____

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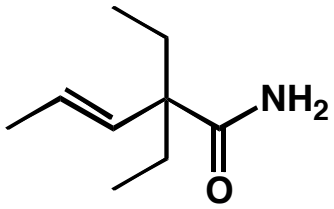
11. (a sedative)



*** **12.** (responsible for odor of cucumbers)

13. phosgene (toxic war gas)

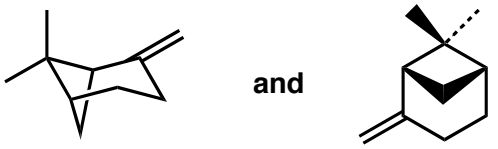
14. 3-phenoxytoluene

15. pyridine

Place all answers on coloured Answer Sheet **NAME**_____

B. Determine whether the following pairs of structures are identical (i.e. different pictures of the same molecule), structural isomers, diastereomers, or enantiomers. **(4 pts each - 20 pts total)**

16.



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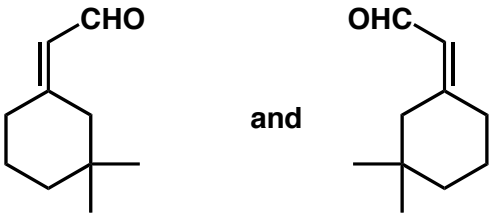
α-pinene (major constituent of turpentine)

17.



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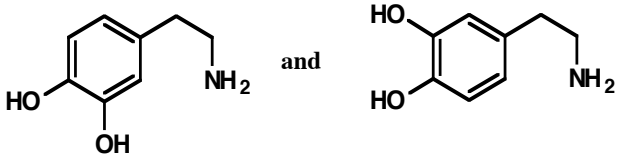
18.



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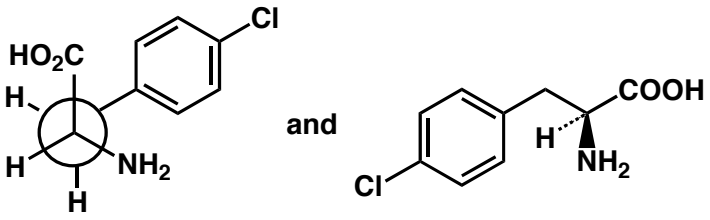
Dopamine (a neurotransmitter involved in Parkinson's disease)

19.



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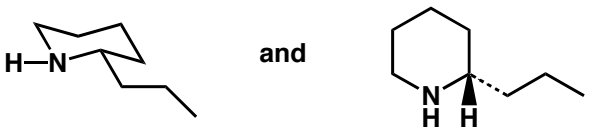
p-chlorophenylalanine - an aphrodisiac

20.



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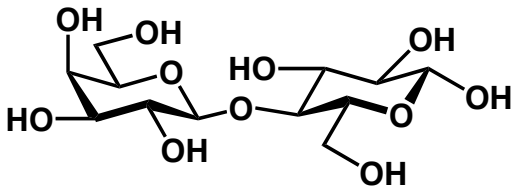
Coniine (hemlock poison which killed Socrates)

Place all answers on coloured Answer Sheet **NAME**_____

C. Lactose is a carbohydrate that occurs in milk. Examine its structure below and answer the questions that follow. **(15 points total)**



Place all answers on coloured Answer Sheet

21. The number of carbons in lactose is _____ **2 pts**

22. The number of hydrogens in lactose _____ **3 pts**

Answer the following questions as true (**T**) or false (**F**) No penalty for guessing.

(1 point each - 10 points total) **Place all answers on coloured Answer Sheet**

2**3.** lactose is more acidic than water.	**T**	**F**
24. lactose is a non-reducing sugar	**T**	**F**
25. lactose has two anomeric carbons	**T**	**F**
26. lactose could be made by coupling two <u>identical</u> monosaccharides	**T**	**F**
27. lactose is easily isomerized in water by a rapid equilibrium	**T**	**F**
28. lactose contains only D-sugar units	**T**	**F**
29. lactose should react with acetyl chloride to form an octaacetate (8 acetate esters per molecule)	**T**	**F**
30. lactose should react with acetamide to form an octaacetate (8 acetate esters per molecule)	**T**	**F**
31. the lactose structure above has only β linkages at the anomeric carbons	**T**	**F**
32. lactose contains at least three primary alcohols	**T**	**F**

Place all answers on coloured Answer Sheet **NAME**_____

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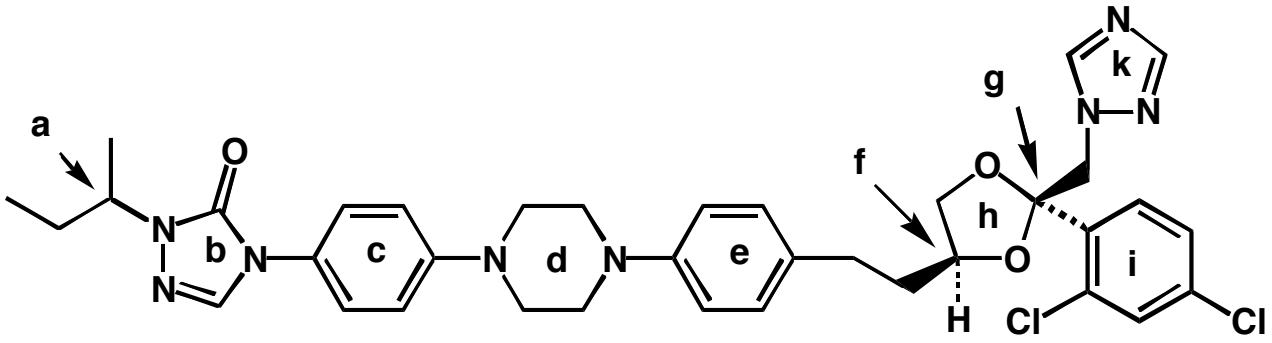
D. Itraconazole (shown below) is a widely-used antifungal agent that is made by chemical synthesis. Examine its structure and answer the questions that follow. **(10 pts total - 1 pt each)**



33. To give S stereochemistry to the hydrogen at site **a** in the structure you need a dash or a bold wedge ?

34. Heterocyclic rings in itraconazole are those labelled (give letter(s) - write **X** if none): _____

35. The functionality (functional group) at position **g** is: _____

36. Amide nitrogens are located in rings (give letter(s) - type **X** if none): _____

37. The total number of amine or imine (non-amide) nitrogens in itraconazole is: _____

38. Aromatic rings are those labelled (give letter(s) - type **X** if none): _____

39. Would itraconazole would be expected to dissolve in aqueous acid ? _____ (Yes or No)

40. If ring **i** were missing the two chlorines, is their substitution pattern such that they could both be introduced by electrophilic aromatic substitution as the last step in chemical synthesis ? _____ (Yes or No)

41. Acidic hydrolysis under forcing conditions would cleave two rings of itraconazole. Give the letters for both of these rings: _____

42. To draw an enantiomer of itraconazole, it is necessary to invert stereocentres (give letter(s)): _____

E. Indicate whether the following statements are true (**T**) or false (**F**). No penalty for guessing.

(1 point each - 5 points total) - **Place all answers on coloured Answer Sheet**

43. A cyclic amide is called a lactone	**T**	**F**
44. A Lewis acid is an electrophile	**T**	**F**
45. A Lewis acid donates a pair of electrons	**T**	**F**
46. Resonance forms are structures of rapidly interconverting molecules	**T**	**F**
47. Enolates are always negatively charged species	**T**	**F**

Place all answers on coloured Answer Sheet **NAME**_____

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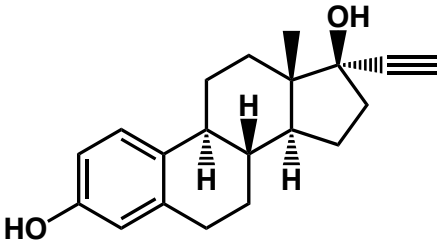
II. Physical Properties and Reactivity - 30 Points

A. Ethynylestradiol is an orally bioactive compound used in almost all modern formulations of oral contraceptive pills. Examine its structure below and answer the questions that follow.



(1 point each - 7 points total) - **Place all answers on coloured Answer Sheet**

1. The pKa of the most acidic functional group is _____

2. This group is located at carbon atom (give number) _____

3. The second most acidic functional group has a pKa of _____

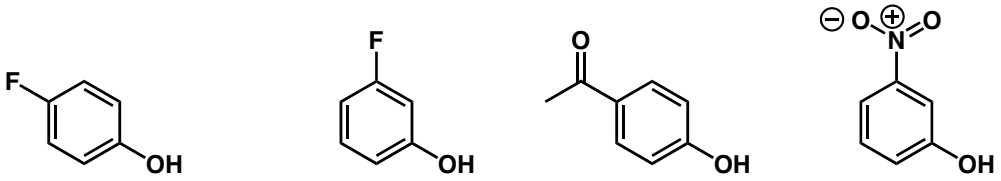
4. This group is located at carbon atom (give number) _____

5. The third most acidic functional group is called _____

6. The number of hydrogens at position 13 is _____

7. The stereochemistry (R or S) at position 9 is _____

B. **8.** In the group below, choose the most acidic compound and draw its structure in the appropriate slot on the answer sheet. **1 pt**



9. Draw a resonance structure of the corresponding anion of your choice above that illustrates what makes it especially acidic. **(4 pts)**

Place all answers on coloured Answer Sheet

Place all answers on coloured Answer Sheet **NAME**_____

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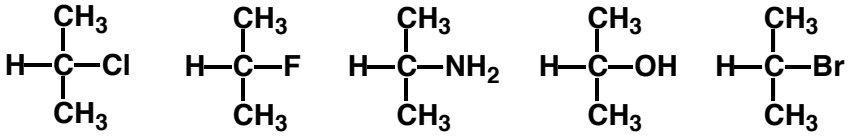
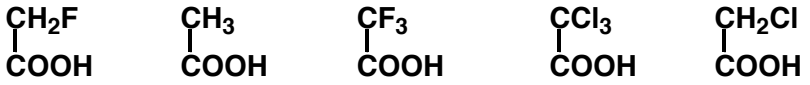
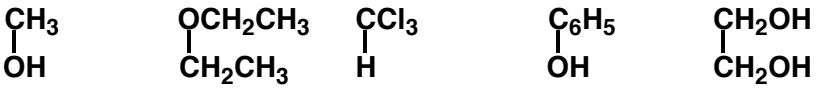
C. Examine the compounds **1-15** in the group below and answer the questions that follow. Be sure to write your answer clearly inside the boxes where provided. **(18 points total)**



1 **2** **3** **4** **5**



6 **7** **8** **9** **10**



11 **12** **13** **14** **15** **2 pts each – 8 pts total**

Place all answers on coloured Answer Sheet

10. Of all of the compounds above, the most basic and nucleophilic compound is number:

11. Of all of the compounds above, the most acidic compounds is number:

12. In the group of compounds **1-5** only, the most acidic compound is number:

13. In the group of compounds **11-15** only, the most acidic compound is number:

Indicate whether the following statements are true (**T**) or false (**F**) **(2 pts each - 10 pts total)**

Place all answers on coloured Answer Sheet

14. All compounds **1-15** are hydrogen bond acceptors

15. Compounds **3, 4, 7, 11, 12, 15** are all miscible with water

16. Compound **13** is not miscible with water

17. Compound **6** is a widely used food additive

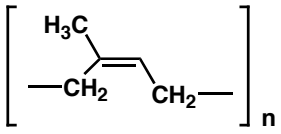
18. Compound **14** is more acidic than water

Place all answers on coloured Answer Sheet **NAME**_____

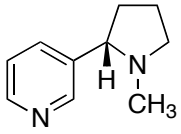
III. Applications - 20 Points

A. The compounds shown below were discussed in class. Identify them by common name.
(20 points total - 4 pts each)

1.



2.



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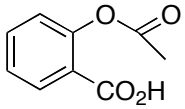

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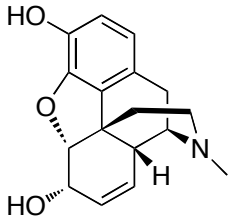
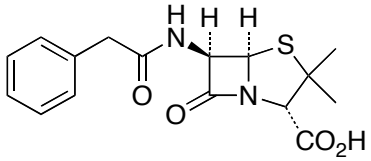


5.



Place all answers on coloured Answer Sheet

Place all answers on coloured Answer Sheet **NAME**_____

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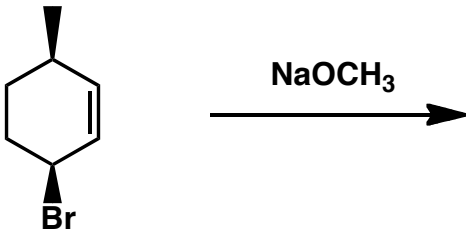
IV. Reactions - 104 Points

A. Show the structure of the major organic product of each of the following reactions. Show stereochemistry where indicated by asterisks (***). **(4 points each - 40 points total)**

*** **1**.



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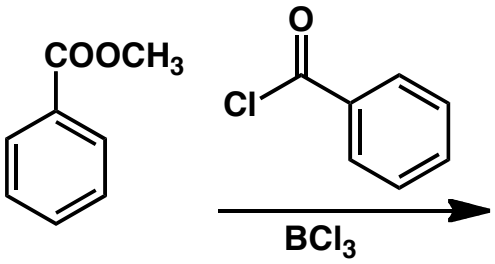

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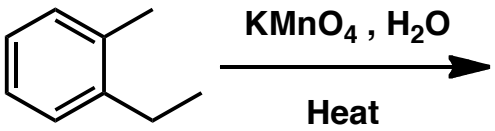

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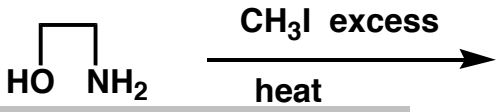

Place all answers on coloured Answer Sheet

Place all answers on coloured Answer Sheet **NAME**_____

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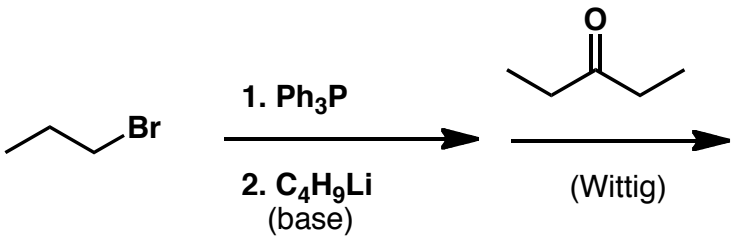
5.



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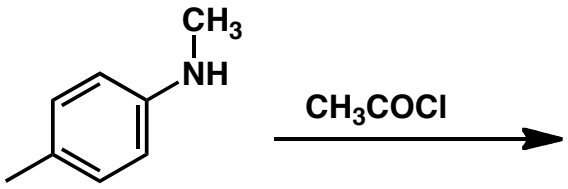

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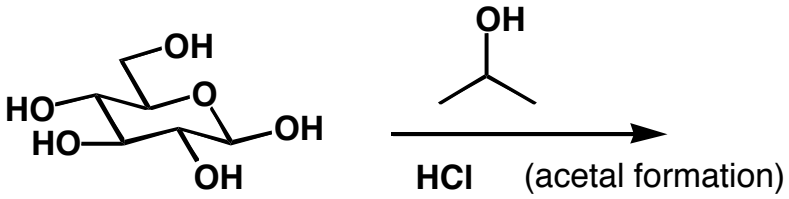
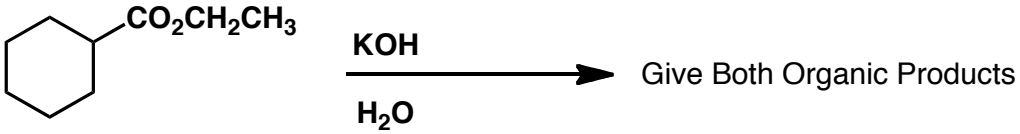


8. and 9.



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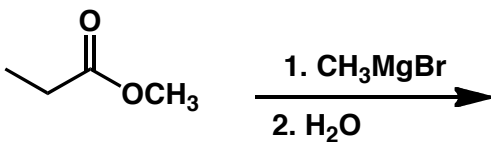
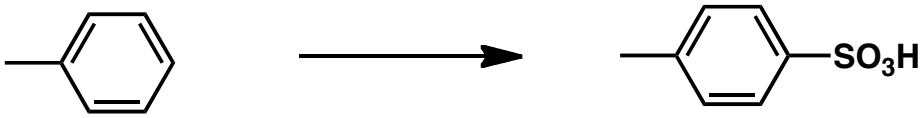


Place all answers on coloured Answer Sheet

Place all answers on coloured Answer Sheet **NAME**_____

B. Show reagents that will do the required transformations. In some cases two or three steps may be necessary. **(4 pts each - 20 pts total)**

11.



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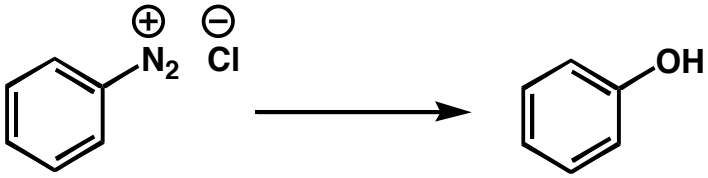

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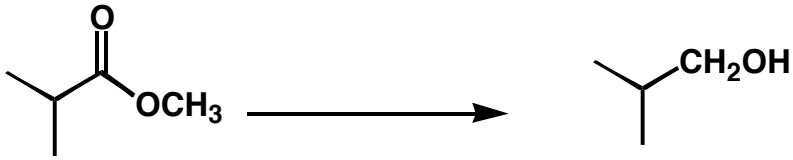
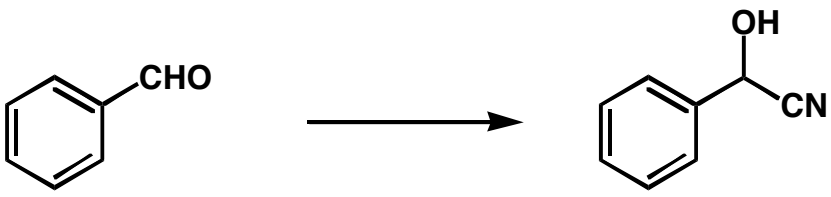


14.

15.



Place all answers on coloured Answer Sheet **NAME**_____

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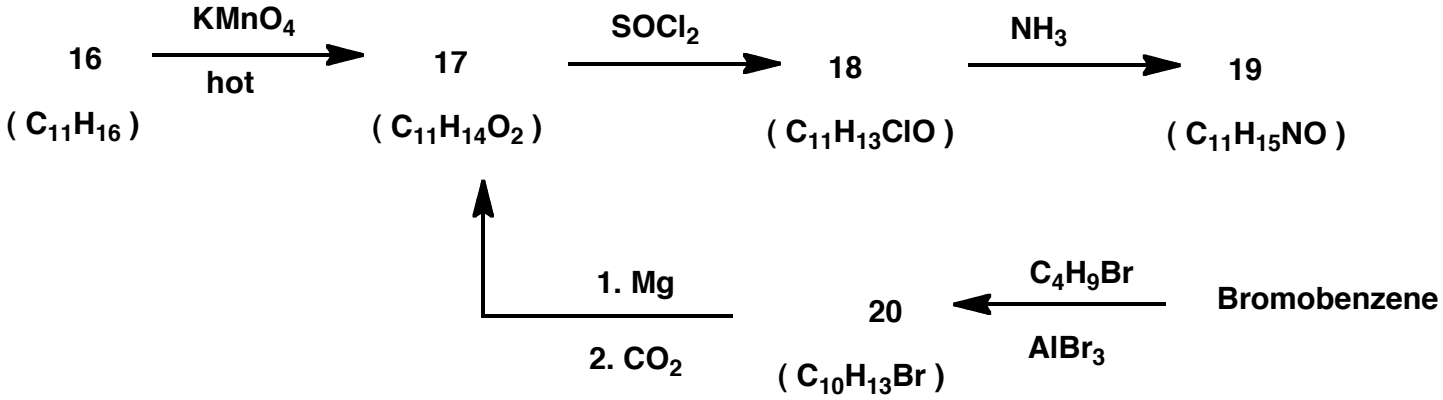
C. The transformations shown below were used to elucidate the structures of unknown compounds (molecular formulas given for each). Provide the chemical structures for **16** through **20. (20 pts - 4pts each)**



Place all answers on coloured Answer Sheet

Place all answers on coloured Answer Sheet **NAME**_____

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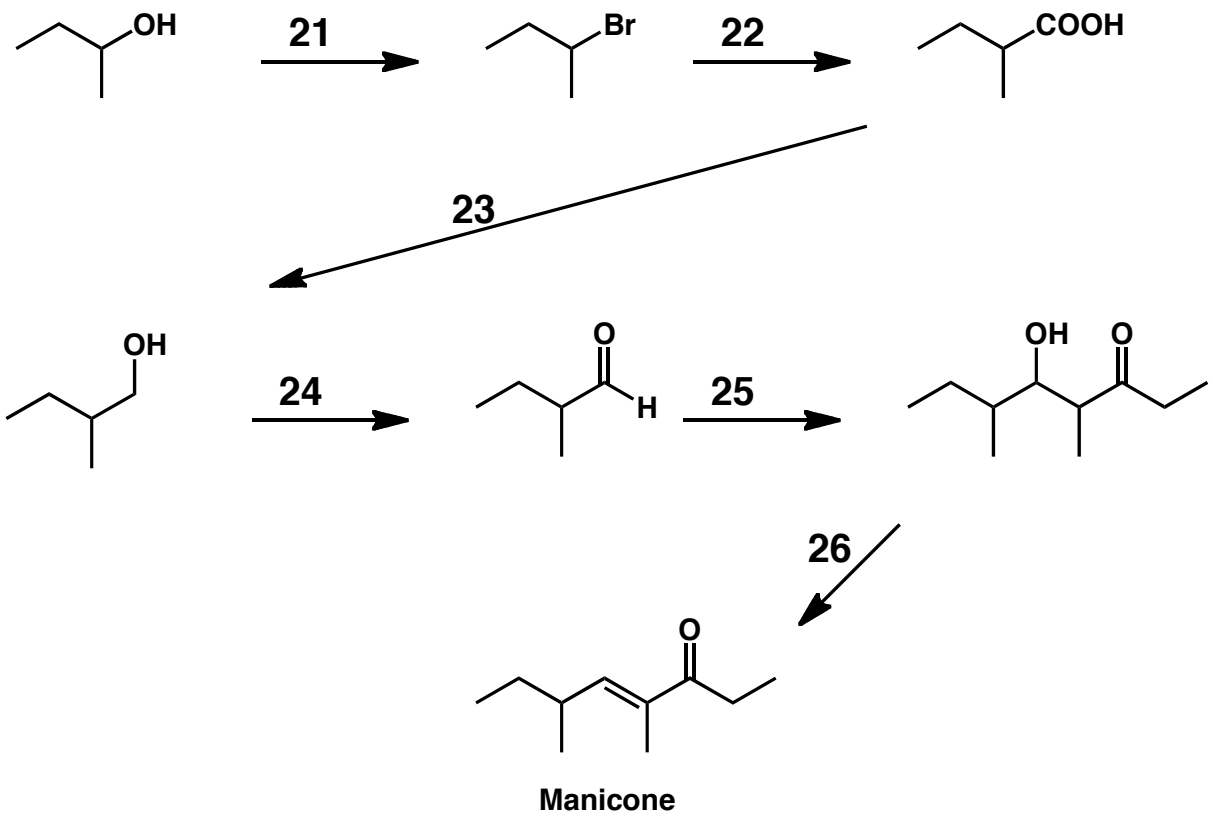
D. Manicone is an alarm pheromone for certain species of ants, and can be synthesized by the sequence shown below. Provide the missing reagents numbered **21** to **26**. More than one reagent may be necessary for a step.

(24 points total - 4 pts each).



Manicone

Place all answers on coloured Answer Sheet

Place all answers on coloured Answer Sheet **NAME**_____

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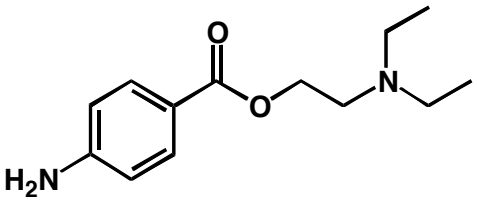
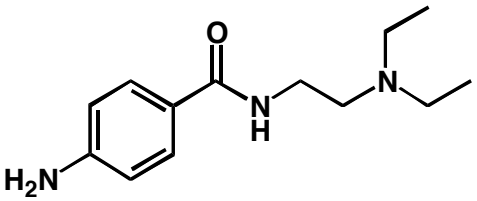
IV. Mechanism - 36 Points

A. Procaine is a local anesthetic that can also be used to control arrhytmias (disorders of heart rate and rhythm). Its intravenous use as an arrhytmic agent was limited because of central nervous system (CNS) toxicity and rapid hydrolysis of the drug. An analog, procainamide, has longer duration of action because it is more resistant to hydrolysis.

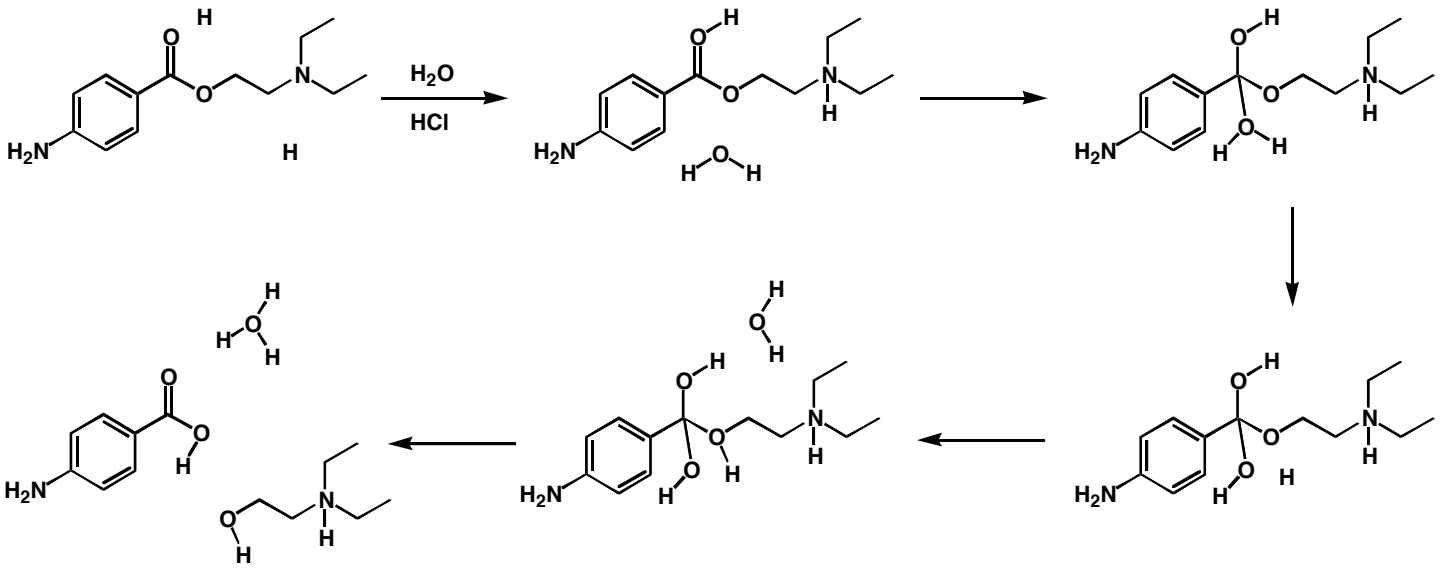


Procaine



Procainamide

1. Compete the mechanism of acid hydrolysis of procaine by putting in the missing charges and the curved arrows that show the movement of electrons. Check carefully that any necessary charges are placed on each atom. **(20 points - 4 pts each step)**



2. Draw a resonance structure of procainamide which explains why it is more resistant to hydrolysis than procaine. **(4 points)**

Place all answers on coloured Answer Sheet **NAME**_____

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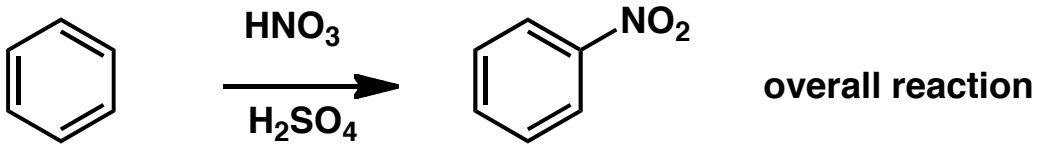
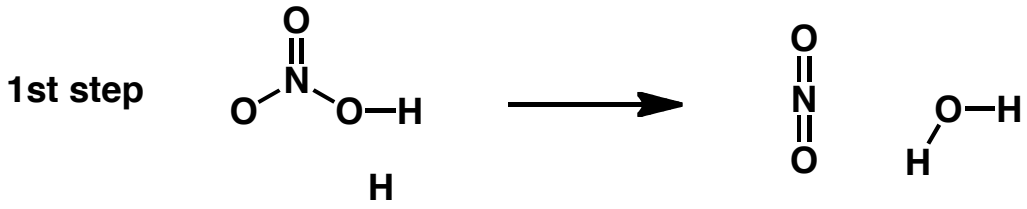
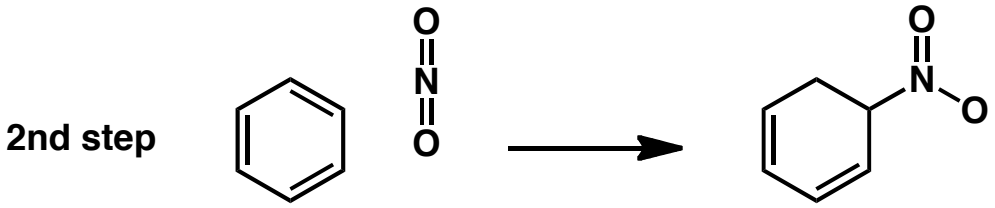
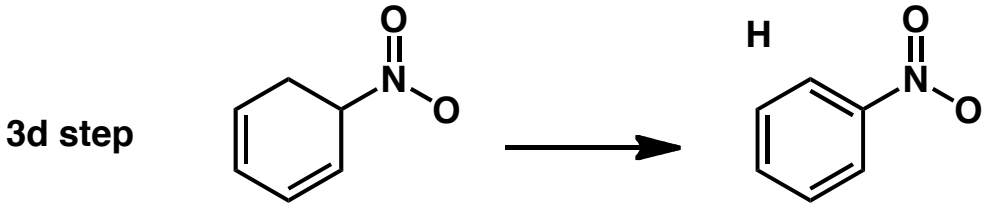
B. The mechanism for an electrophilic aromatic substitution, namely nitration of benzene, is shown below as a set of 3 steps. However, it is missing curved arrows to indicate the movement of electrons as well as all of the charges. Complete the mechanism by putting in the correct arrows and charges. It may help you to draw in all of the hydrogens on benzene and the intermediates. Check carefully – each one is worth points.

(4 points for each step - 12 Points Total)









Place all answers on coloured Answer Sheet