

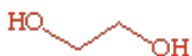
**CHEM 163 MIDTERM**  
**February 13, 1997**  
**Dr. John C. Vederas**

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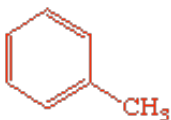
**I. Structure and Nomenclature - 43 Points -**

**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 (\*\*). (2 points each - 20 points total)

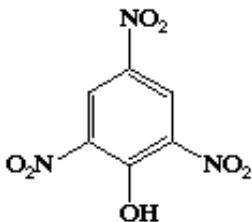
1. ethylene glycol (antifreeze constituent)



2. toluene (used as solvent in glue)

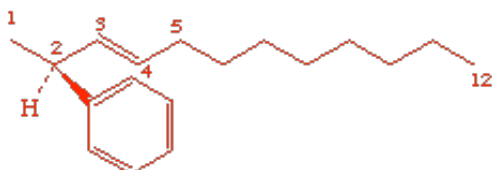


3. (explosive in match heads)

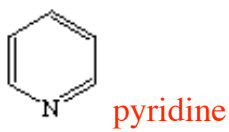


2,4,6-trinitrophenol or picric acid (or name as a hydroxybenzene)

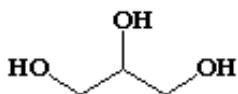
4. (S)-trans-2-phenyl-3-dodecene



5. commonly used as a base or solvent

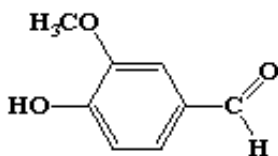


6. (common lubricant, also occurs in cells)



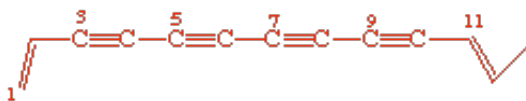
glycerol or 1,2,3-propanetriol or will accept 1,2,3-trihydroxypropane

7. Available in Safeway as a food additive

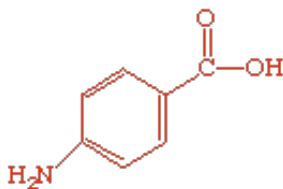


vanillin or 4-hydroxy-3-methoxybenzaldehyde

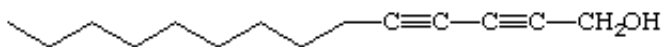
8. trans-1,11-tridecadiene-3,5,7,9-tetrayne (flower colour in dahlias)



9. para-aminobenzoic acid (a key bacterial product necessary for folic acid synthesis - sulfa drugs mimic this compound)



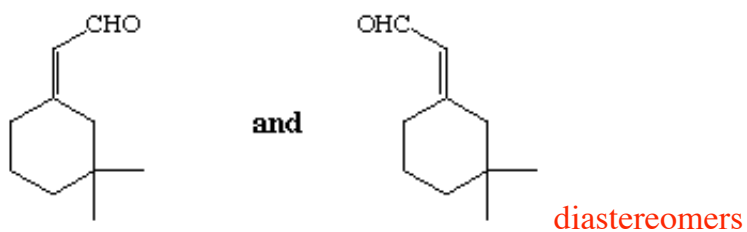
10. sperm attractant for coral polyps



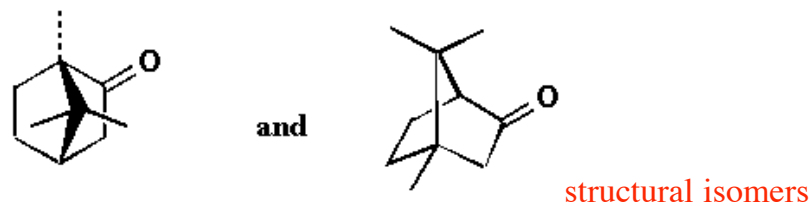
2,4-tetradecadiyne-1-ol

B. Determine whether the following pairs of structures are identical (i.e. different pictures of the same molecule), structural isomers, diastereomers, or enantiomers. (2 points each - 8 pts total).

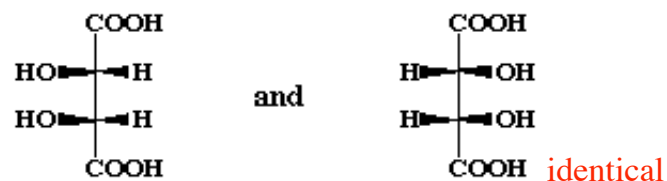
1.



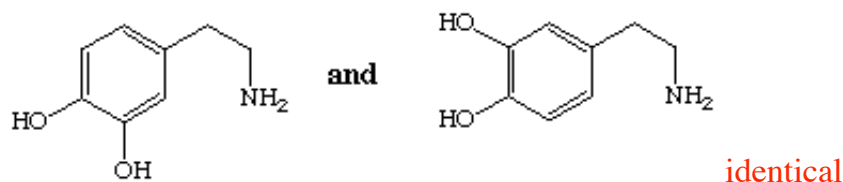
2.



3.

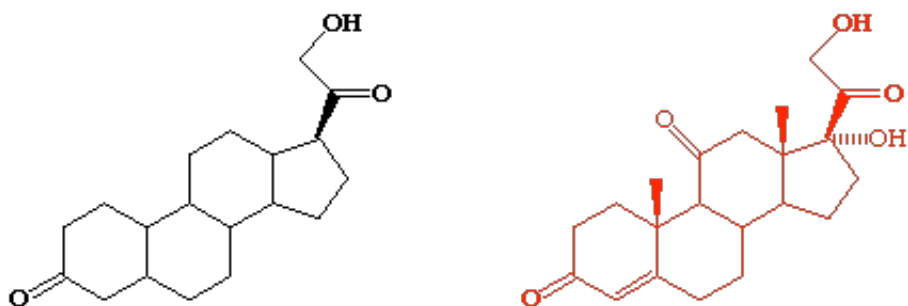


4.



**C. 1.** Cortisone is a natural adrenocorticoid hormone that has anti-inflammatory properties. Complete its structure using the partial drawing given below by adding the following groups with correct stereochemistry: (5 pts total)

- a. beta-methyl group at C-10
- b. beta-methyl group at C-13
- c. doubly bonded oxygen at C-11 (i.e. there is a ketone at C-11)
- d. double bond at C-4 to C-5
- e. alpha-hydroxy group at C-17



**2.** Answer the following questions by giving the correct numbers (1 point each): (3 pts total)

- a. The number of carbons in the cortisone molecule is: **21**
- b. The number of stereogenic (i.e. chiral) centres in cortisone is: **6**
- c. The number of hydrogens in the cortisone molecule is: **28**

**3.** Indicate whether the following statements are true (**T**) or false (**F**). No penalty for guessing. (1 pt each - 7 pts total)

- a. To draw an enantiomer of cortisone it is necessary to change all of the stereocenters to the

opposite stereochemistry **True**

b. Changing the 17-alpha hydroxy group in cortisone to beta will generate a structural isomer.

**False**

c. Cortisone has the same number of carbons as the pregnancy hormone, progesterone. **True**

d. A human produces about 1 milligram of male or female sex hormone per day. **True**

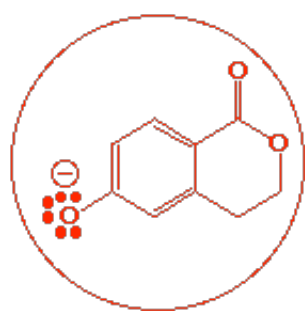
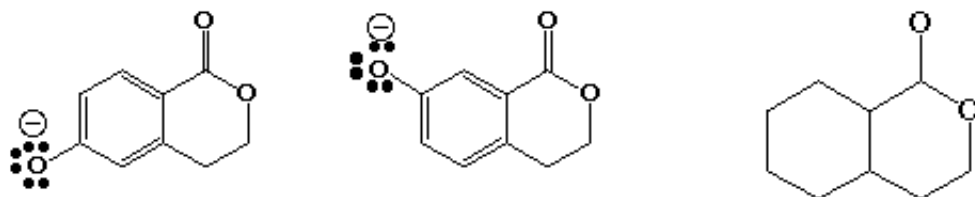
e. Cholesterol is made in the body by humans. **True**

f. The difference between androgen and estrogen skeletons is one methyl group. **True**

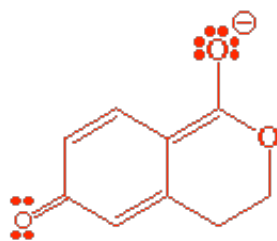
g. Cortisone has an estrogen skeleton. **False**

## II. Physical Properties and Reactivity - 13 Points

A. It would be predicted that one of the two phenolate anions shown below would form more readily and be more stable. Circle the more stable structure (1 pt) and draw the extra resonance form which accounts for this behaviour by completing the partially drawn structure on the right. (3 points total)



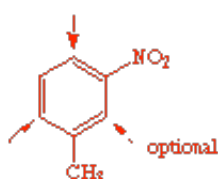
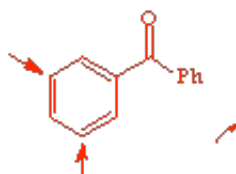
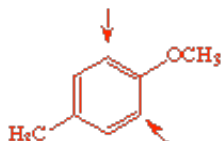
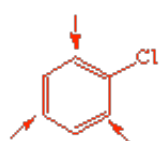
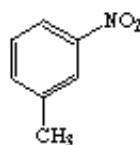
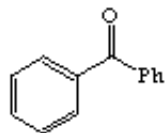
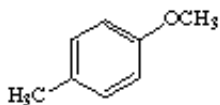
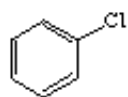
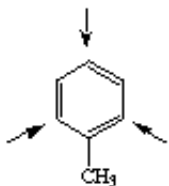
1 pt



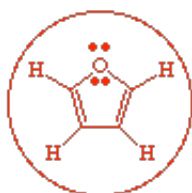
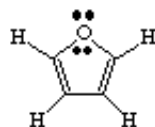
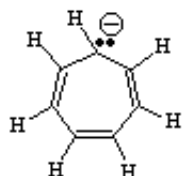
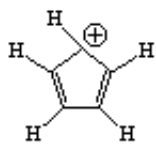
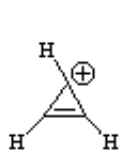
2 pts

B. In the group below use an arrow to indicate the position(s) on the aromatic ring which would be most likely to be attacked by chlorine in the presence of  $\text{FeCl}_3$ . (4 pts - 1 pt each)

Example:



C. In the group below Circle all aromatic compounds or ions. (4 pts)



D. List the key features which a molecule or ion must have to be aromatic. In other words, define aromatic compound in ten words or less. (2 pts).

cyclic

conjugated around ring

planar

$4n+2$  pi electrons where  $n = 0, 1, 2, \dots$

### III. Definitions and Applications - 15 Points

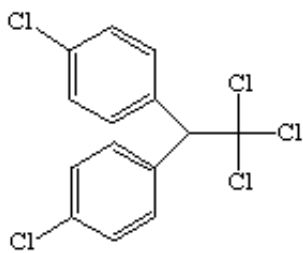
A. A number of terms are given below with a preceding identifying letter. Make the best match of these terms with the short statements which follow by putting the correct letter on the line provided after the statement. Use each letter no more than once. (12 Points total - 1 pt each)

(A) SN2 Reactions	(B) Meso Compounds	(C) Electrocyclic Reactions
(D) Dyes	(E) Racemates	(F) SN1 Reactions
(G) E2 Reactions	(H) Atomic Numbers	(I) Addition Reactions
(J) Nucleophiles	(K) Resonance Forms	(L) Tautomers
(M) Hydrations	(N) Androgens	(P) Estrogens
(Q) Oxidations	(R) Enol Forms	(S) Optical Purities
(T) Pregnanes	(U) Radicals	

1. Male Sex Hormones.....**N**
2. Diels Alder Reactions.....**C**
3. Enantiomeric Mix (1:1).....**E**
4. Achiral Molecules.....**B**
5. Carbocation Intermediates.....**F**
6. Structural Isomers.....**L**
7. Azo Compounds.....**D**
8. Identical Compounds.....**K**
9. Markovnikov Rule.....**I**
10. Birth control pills.....**T**
11. Walden Inversions.....**A**
12. Negative Species.....**J**

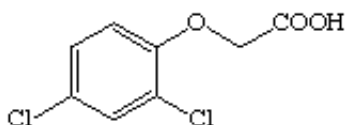
B. The compounds shown below were discussed in class. Identify them by common name and briefly (10 words or less) describe their importance or use. (3 pts total - 1 pt each)

- 1.



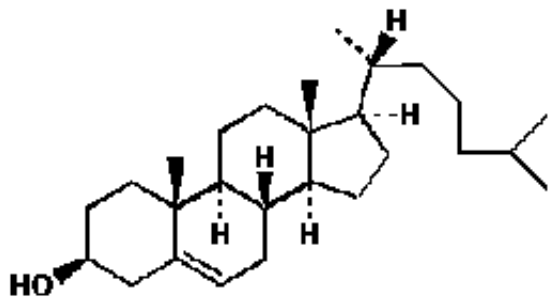
DDT - an insecticide and environmental contaminant

2.



2,4-D (2,4-dichlorophenoxyacetic acid) - a herbicide, part of Agent Orange

3.



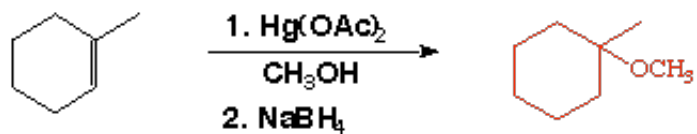
Cholesterol - occurs in all animal cell membranes and in gall stones

#### IV. Reactions - 16 Points

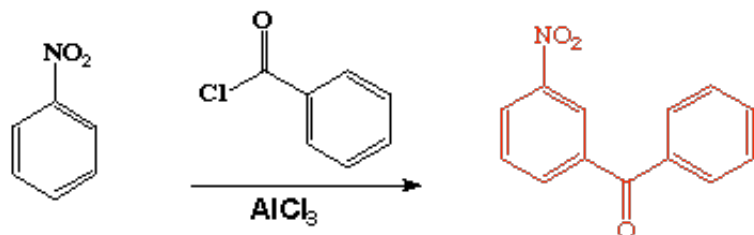
A. Show the structure of the major organic product of each of the following reactions. Show stereochemistry where indicated by asterisks (\*\*). (2 points each - 8 points total)

1.

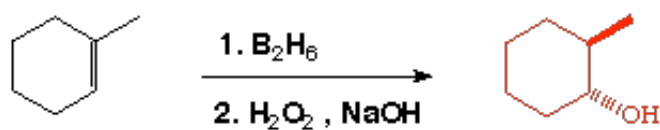




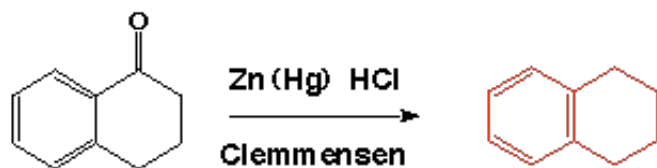
2.



3.

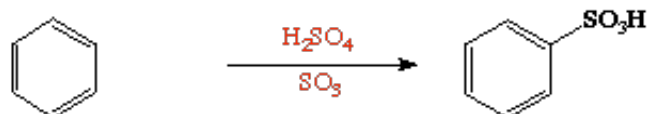


4.

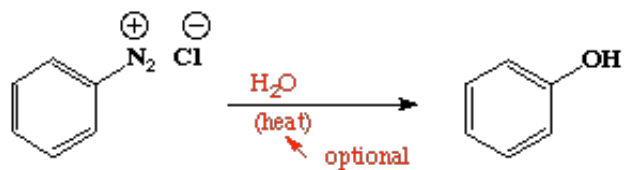


**B.** Show reagents that will do the required transformations. In some cases two or three steps may be necessary. (2 pts each - 8 pts total)

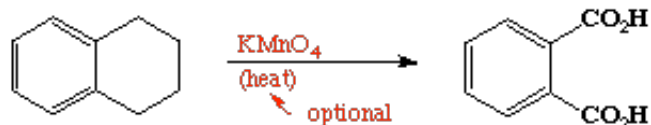
1.



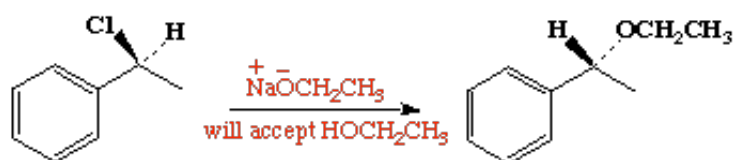
2.



3.

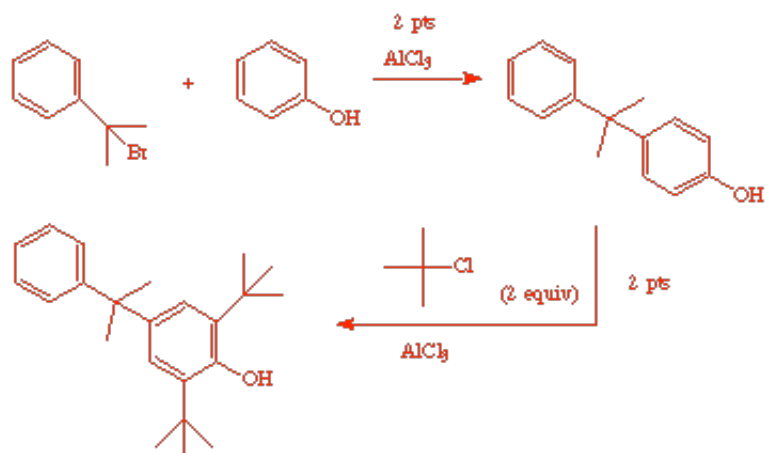
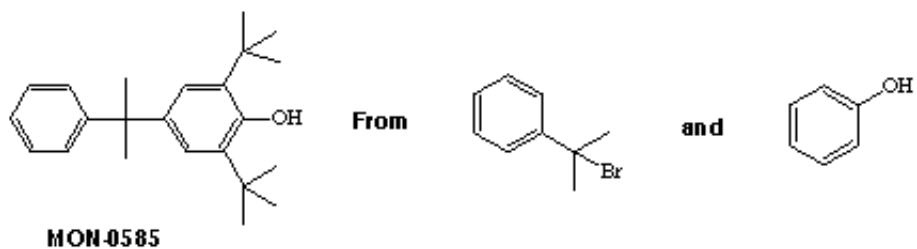


4.

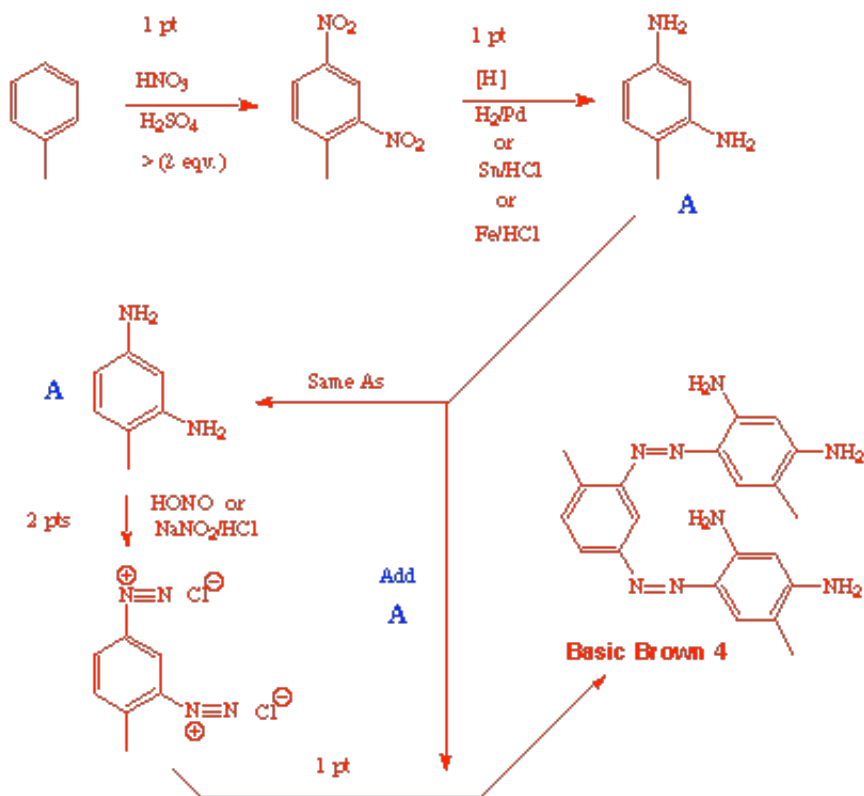
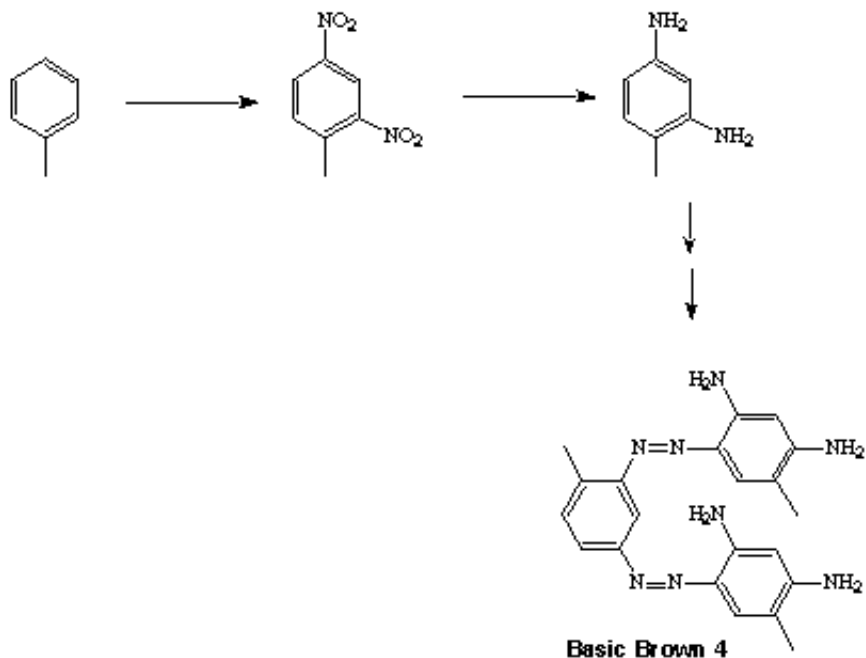


## V. Synthesis and Mechanism - 13 Points

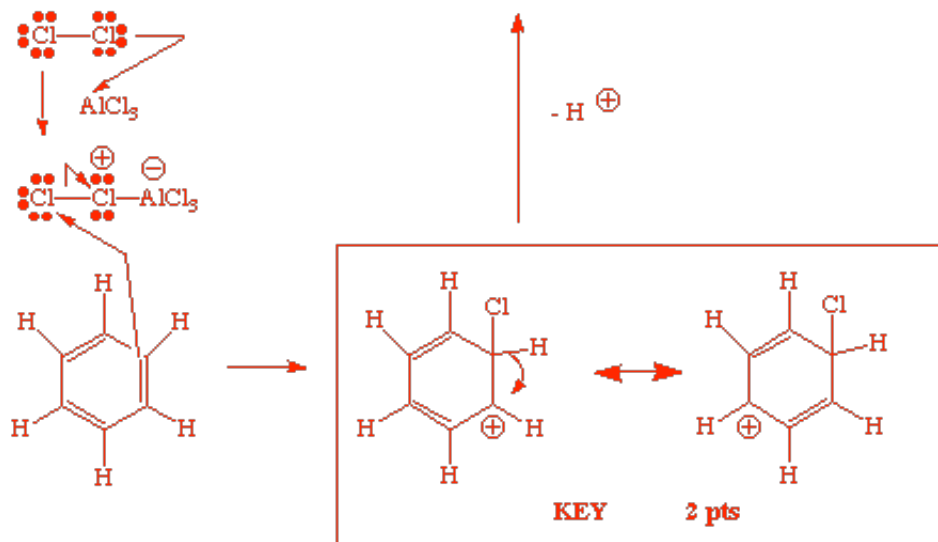
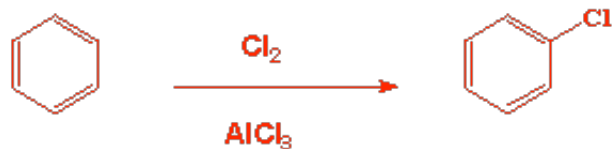
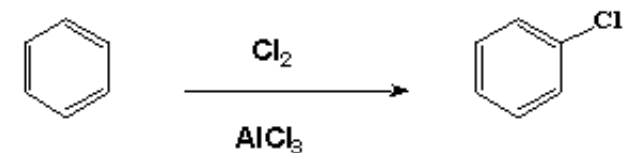
A. MON-0585 is a biodegradable substance used to kill mosquito larvae. Outline a short synthesis of MON-0585 from the bromo compound and alcohol shown below and any other necessary organic or inorganic reagents. Several steps will be required. ( 4 points this part ) (Assigned Problem 16.52)



**B.** The dye Basic Brown 4 can be synthesized from a simple substituted benzene in several steps as outlined below. The first two steps are shown, but are missing the necessary inorganic reagents. Provide the missing reagents and show how to complete the synthesis of Basic Brown 4 by giving the rest of the reagents and intermediates. (5 points)



C. Provide a detailed "step by step" mechanism for the aromatic electrophilic substitution reaction shown below. Be sure to show the structures of the key intermediate(s) and indicate the movement of electrons using the curved arrow convention. Show at least **two resonance forms** of the key intermediate which bears a charge on carbon. (4 points)



**EXTRA CREDIT (2 Points):** Provide a detailed "step by step" mechanism for reaction shown below. Be sure to show the structures of the key intermediate(s) and indicate the movement of electrons using the curved arrow convention.

