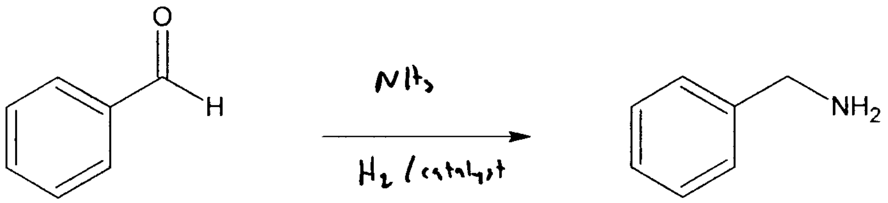
START 5:50pm

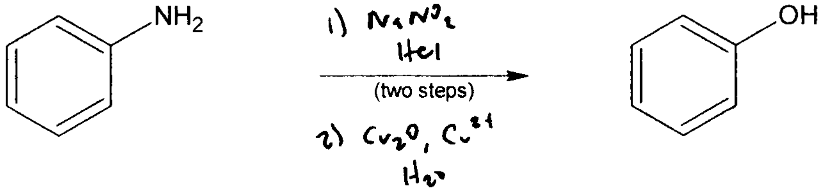
CHT 212
Exam II

1. Provide reagents to accomplish the following transformations.

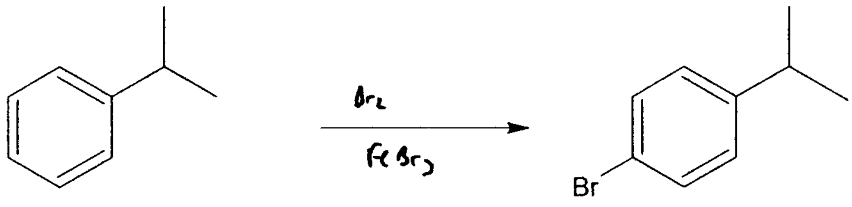
a)



b)

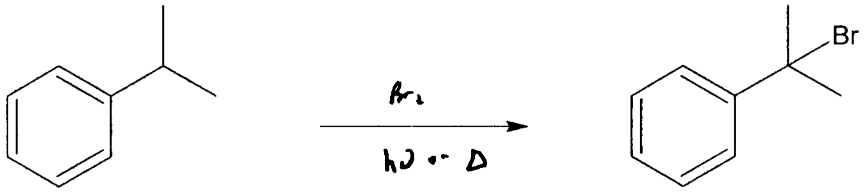


c)

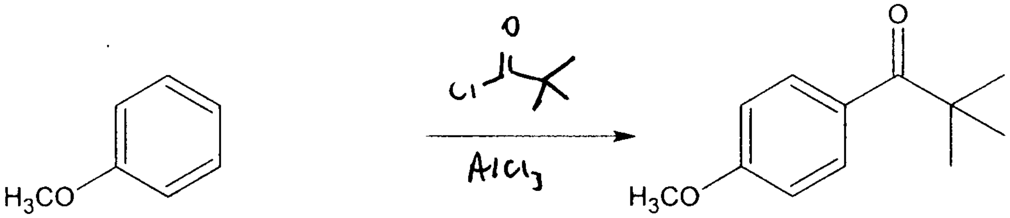


3es.

d)



e)



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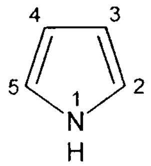
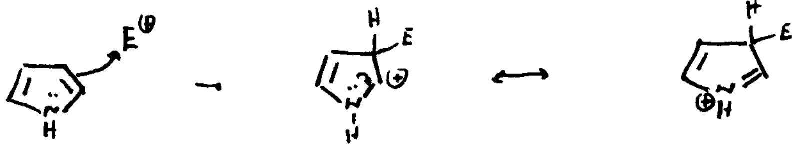
2. Electrophilic aromatic substitution occurs on heterocyclic substrates as well as benzene rings. For this problem, we will consider the electrophilic aromatic substitution of pyrrole, shown and numbered to the right.



a) Pyrrole has three distinct positions at which an incoming electrophile can attack: nitrogen 1, carbon 2 (or 5), and carbon 3 (or 4). Draw the arenium ion resulting from the attack of the generic electrophile E$^+$ on each of these three positions, and draw reasonable resonance structures as appropriate to show how the positive charge in each arenium ion is stabilized.

3:



2:

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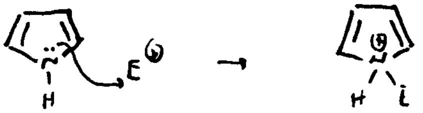
1:



b) Rank the resonance hybrids from part (a) in terms of increasing stability and explain your answer.

2 > 3 > 1

THE POSITIVE CHARGE IN INTERMEDIATE 2 IS SHARED OVER THREE ATOMS WHILE INTERMEDIATE 3 SHARES IT BETWEEN TWO ATOMS AND INTERMEDIATE 1 CANNOT DELOCALIZE THE POSITIVE CHARGE AT ALL.

4

c) In light of parts (a) and (b), at what position do incoming electrophiles tend to react with pyrrole?

INCOMING ELECTROPHILES ATTACK CARBON 2 BECAUSE THAT INTERMEDIATE IS MOST STABLE, SO THAT PATHWAY REACTS FASTEST.

3

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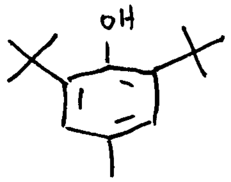
3. The compound BHT, known industrially as butylated hydroxytoluene, is frequently added to food packaging as a preservative.

a) The systematic name for BHT is 2,6-di-*tert*-butyl-4-methylphenol. Draw the structure of BHT.



b) BHT is prepared industrially from *p*-methylphenol and 2-methyl-1-propene in the presence of an acid catalyst like HCl / $AlCl_3$ in an electrophilic aromatic substitution reaction. What purpose does the acid catalyst serve?

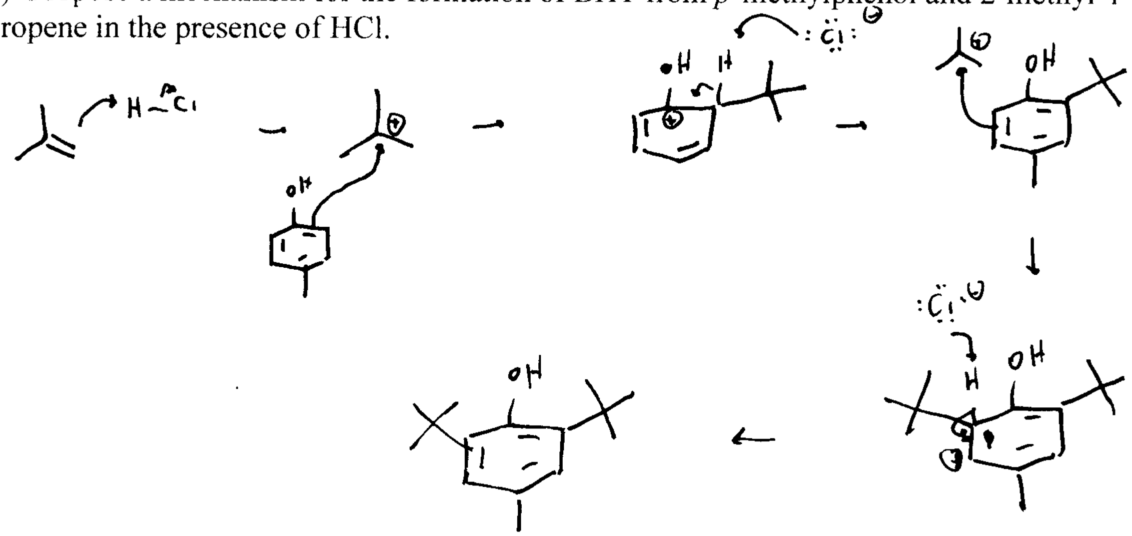
THE ACID PROTONATES THE ALKENE TO GENERATE THE ELECTROPHILE FOR ALKYLATION.

c) Why do the *tert*-butyl groups attach to the aromatic ring in these particular positions?

THE -OH GROUP IS MUCH MORE STRONGLY ACTIVATING THAN THE ALKYL GROUPS, SO INCOMING ELECTROPHILES ORIENT ORTHO- TO IT.

d) Propose a mechanism for the formation of BHT from *p*-methylphenol and 2-methyl-1-propene in the presence of HCl.

2x



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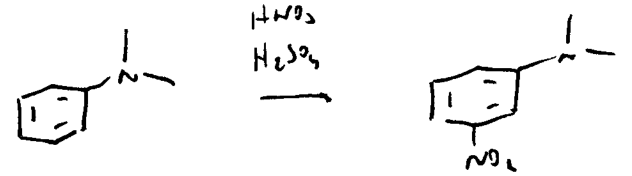
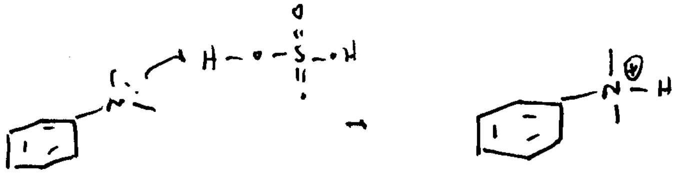
4. Provide reasonable explanations for the following phenomena:

a) The compound N,N-dimethylaniline reacts with a mixture of nitric and sulfuric acids to produce primarily 3-nitro-N,N-dimethylaniline, despite the fact that the dimethylamino group is strongly activating.





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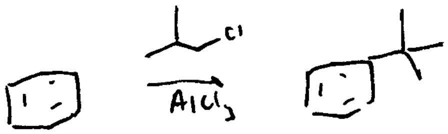
THE DIMETHYL AMINO GROUP IS ALSO BASIC, SO IT IS PROTONATED UNDER THESE CONDITIONS. THE $\overset{\oplus}{N}R_2H$ GROUP IS ELECTRON WITHDRAWING AND THUS DIRECTS META.

b) Friedel-Crafts alkylation of benzene with 1-chloro-2-methylpropane yields only *tert*-butylbenene.



THE 1° ISOBUTYL CARBOCATION REARRANGES TO THE MORE STABLE 3° t-BUTYL CARBOCATION.

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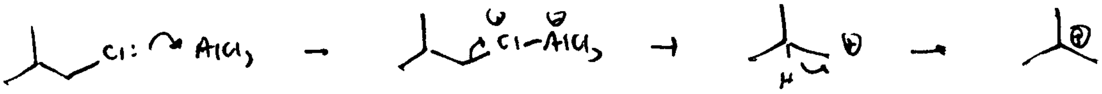
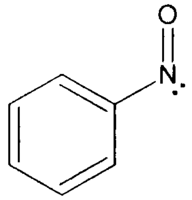


c) Nitrosobenzene, shown to the right, reacts slower than benzene in electrophilic aromatic substitution reactions to give primarily *ortho-* and *para-*substituted products.



THE NITROSO GROUP IS ELECTRON WITHDRAWING BY VIRTUE OF THE DOUBLE BOND TO OXYGEN, SO IT DEACTIVATES THE RING AND NITROSOBENZENE REACTS SLOWER THAN BENZENE.

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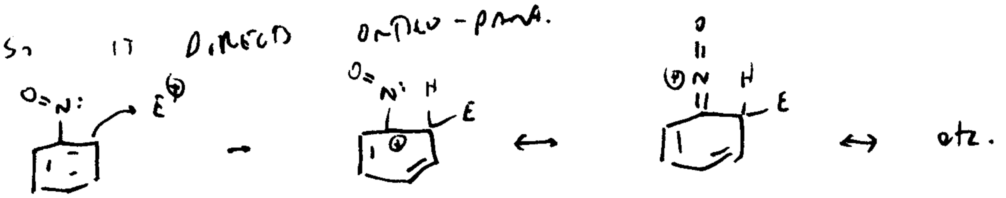
THE NITROGEN CAN DONATE ITS ELECTRON PAIR TO STABILIZE CARBOCATIONS, SO IT DIRECTS ORTHO-PARA.



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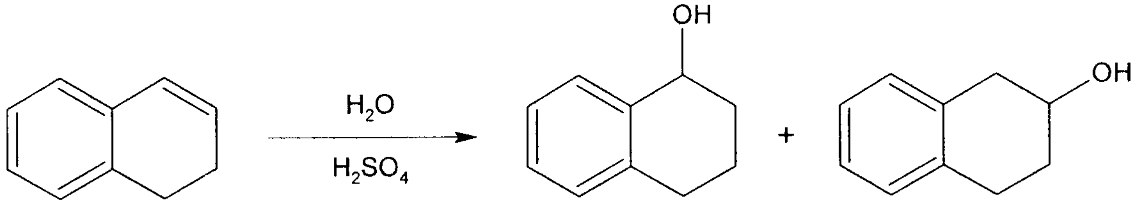
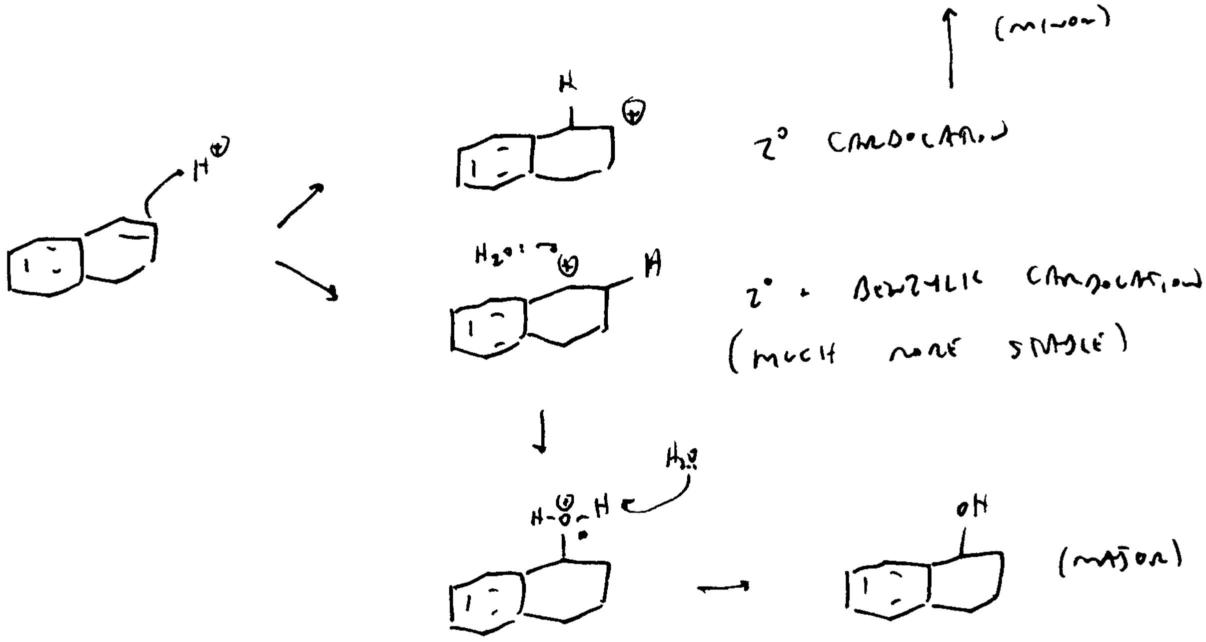
5. The compound 1,2-dihydronaphthalene undergoes acid-catalyzed hydration to form a mixture of products. Show how both products are formed, predict the major product, and explain why that product is the major product.





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The alkene is protonated to yield the more stable benzylic carbocation intermediate, which is resonance stabilized.

Therefore, the major product will have the hydroxyl group α- to the aromatic ring.

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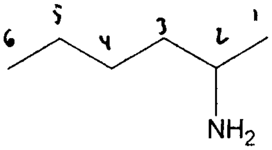
6. Provide unambiguous, systematic names for the following compounds.

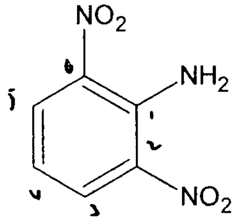
a)



2 - HEXANAMINE

2

b)



2,6 - DINITROANILINE

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7. Draw the structures of the following compounds.

a) N-ethyl-N-methyl-1-butanamine

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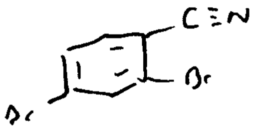
b) 2,4-dibromobenzonitrile



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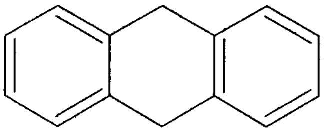
8. Starting from benzene, organic compounds of four carbons or fewer, and any inorganic reagents, propose syntheses of the following compounds.

a)



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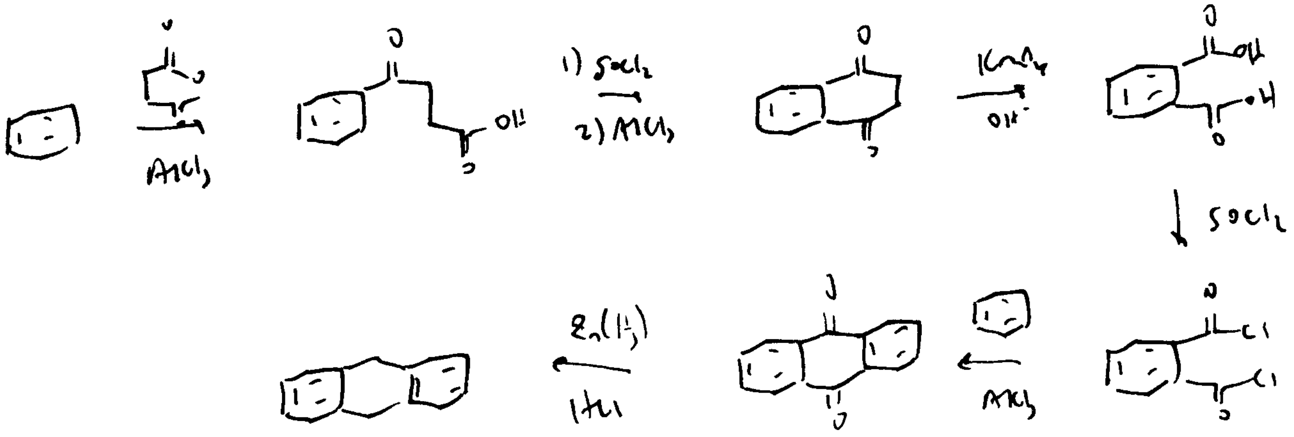

(BETTER)

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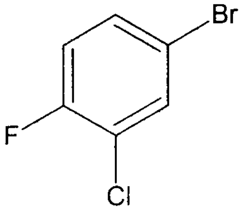
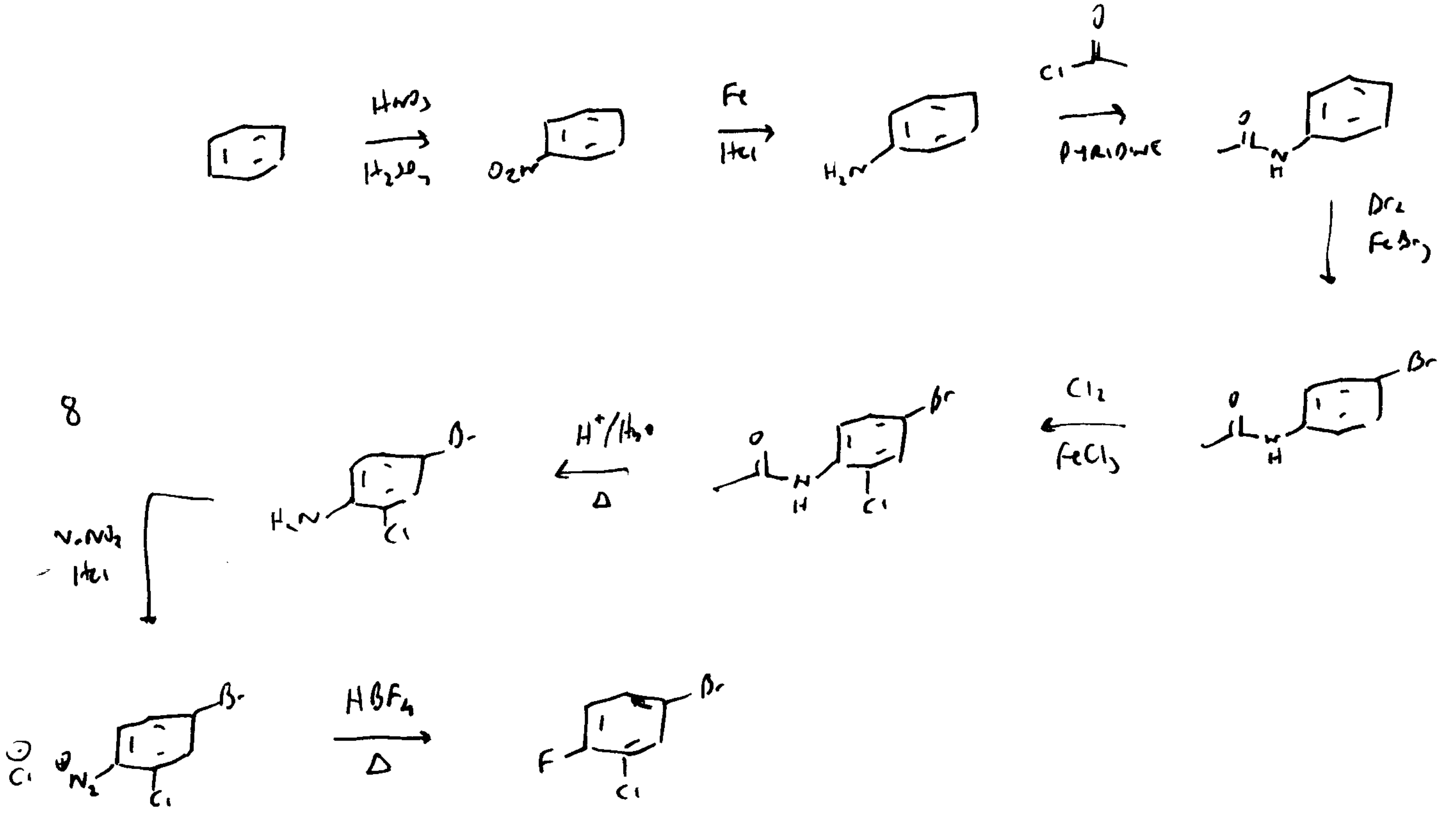
b)



Br
F
Cl



HNO₃
H₂SO₄
O₂N
Fe
HCl
H₂N
Cl
O
PYRIDINE
O
N
H
Br₂
FeBr₃
Br
Cl₂
FeCl₃
Br
Cl
H⁺/H₃O
Δ
H₂N
Br
Cl
NaNO₂
HCl
Cl
N₂
Br
Cl
HBF₄
Δ
F
Br
Cl

8