

Organic Chemistry II

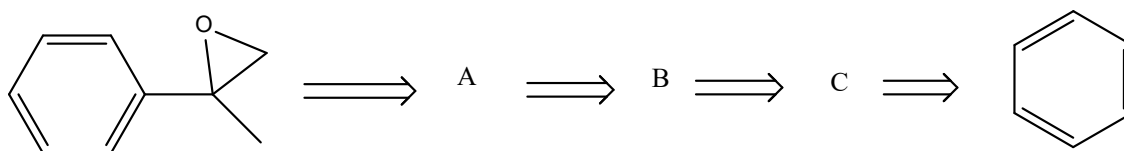
Assignment # 3

Spring 2021

Name: _____

1) Sulfonation of naphthalene is reversible at elevated temperatures. A different isomer of naphthalene sulfonic acid is the major product at 160 °C than is the case at 0 °C. Which isomer is the product of kinetic control? Which one is formed under conditions of thermodynamic control? Can you think of a reason why one isomer is more stable than the other?

2) Many syntheses can involve several functional-group transformations. Identify compounds A, B, and C in the retrosynthesis and suggest reagents for each synthetic step.



3) 4-Chloro-N-methylaniline (A) is so reactive toward electrophilic aromatic substitution that no catalyst is necessary to bring about its bromination. Write a reasonable mechanism for formation of 2-bromo-4-chloro-N-methylaniline from A based on Br_2 as the electrophile.

4) Write structural formulas for the cyclohexadienyl cations formed from aniline ($\text{C}_6\text{H}_5\text{NH}_2$) during each of the following reactions.

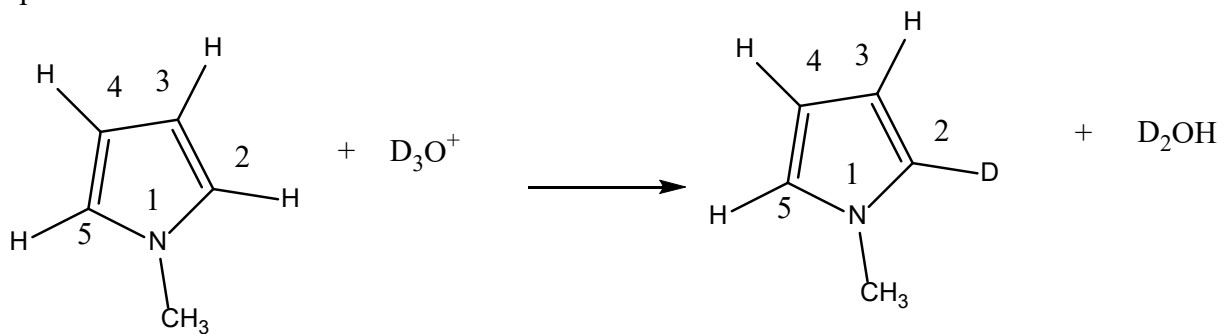
a) Ortho bromination (four resonance structures)

b) Meta bromination (three resonance structures)

c) Para bromination (4 resonance structures)

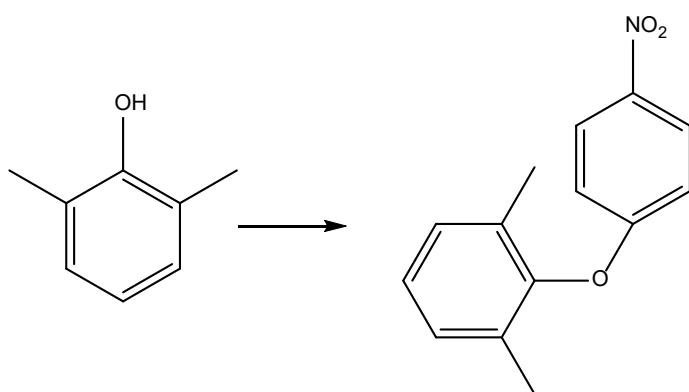
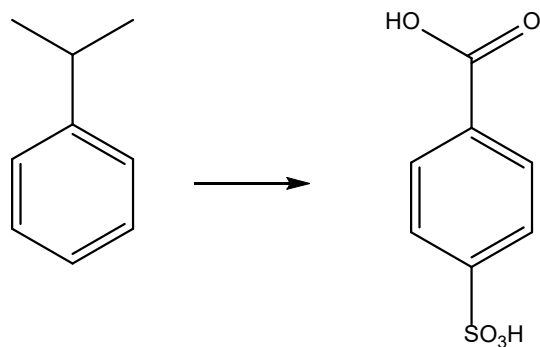
5) Using benzene and any other necessary organic or inorganic reagents, suggest an efficient synthesis of 2,2-dimethylpropylbenzene.

6) Under acid-catalyzed conditions, the C-2 hydrogen of N-methylpyrrole is replaced by deuterium faster than the one at C-3 according to the equation below. Suggest a reasonable explanation for this reaction.

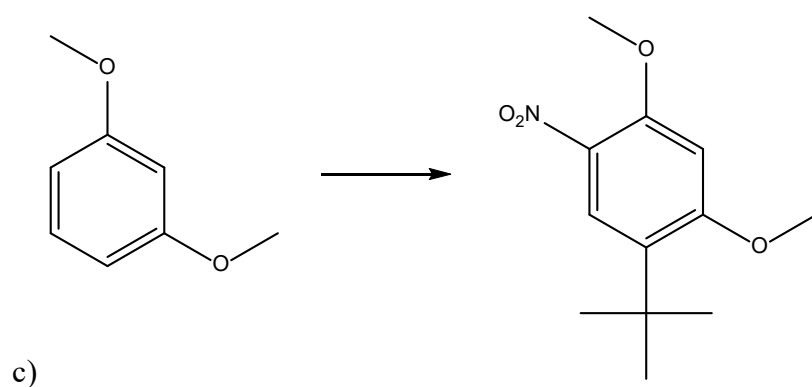


7) Suggest a suitable series of reactions for carrying out each of the following synthetic transformations:

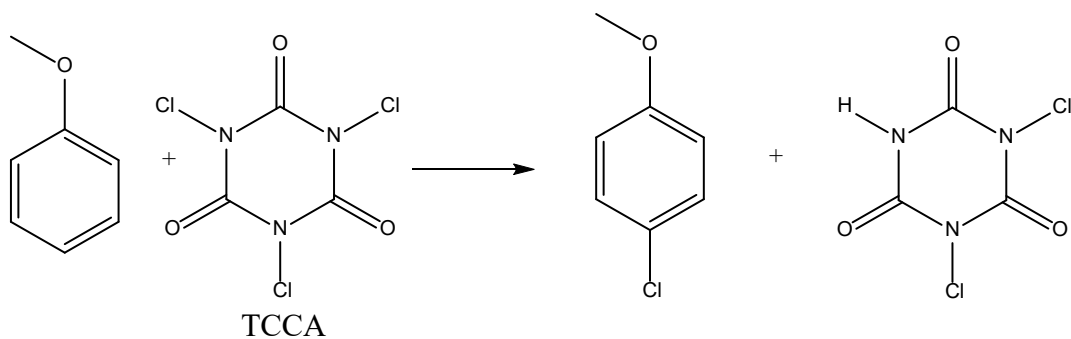
a)



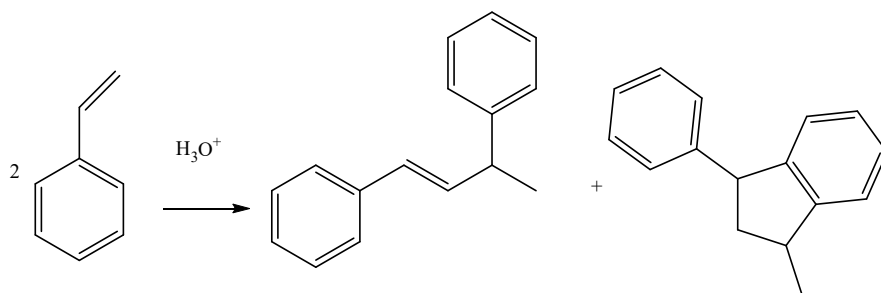
b)



8) Trichloroisocyanuric acid (TCCA) is used as a swimming pool disinfectant and also can serve as an electrophilic chlorinating agent. Write a mechanism for the chlorination of anisole with TCCA.



9) When styrene is heated with aqueous sulfuric acid, the two styrene dimers shown are the major products. Ignoring stereochemistry, suggest a reasonable mechanism for the formation of each isomer. Assume the proton donor is H_3O^+ .



10) Complete the following mechanism.

