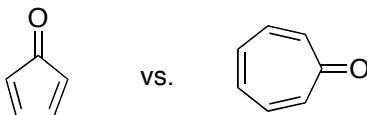


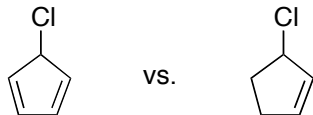
CHEM 252 – Honors Organic Chemistry II
Friday Afternoon Problem Session, 2:00 to 2:50 pm
Dr. W. Edward Billups, Dr. David Lapinsky, and Joel Stevens

1/28/05: Material Derived from Chapter 15 of Vollhardt and Schore (Benzene and Aromaticity: Electrophilic Aromatic Substitution)

1a.) One of the ketones pictured below is very stable while the other is quite unstable and rapidly undergoes a Diels-Alder reaction with itself. (a) Propose an explanation for the different stabilities of these two compounds. (b) Write the structure of the Diels-Alder adduct.



1b.) Which of the following chlorides would you expect to undergo S_N1 solvolysis with H_2O faster? Explain your answer.

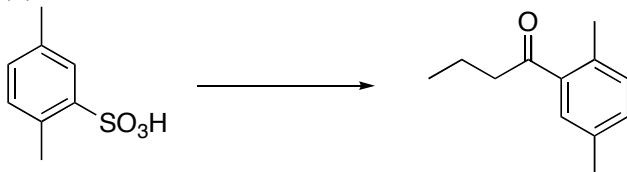


1c.) Suggest reagents suitable for carrying out each of the following conversions.

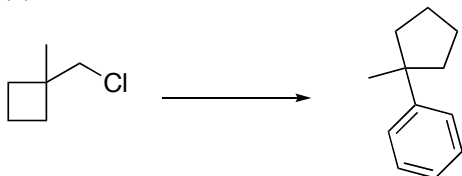
(a)



(b)



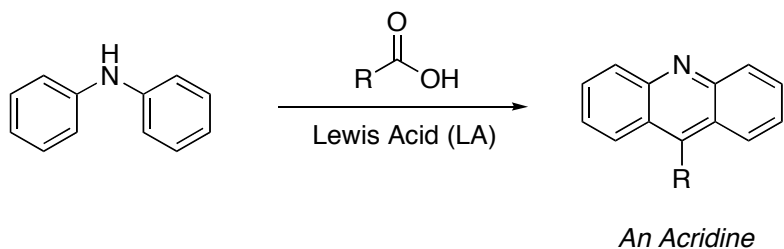
(c)



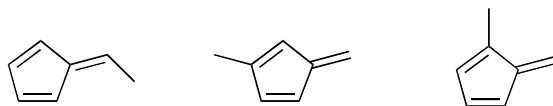
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2a.) Recently in CHEM 443 (Principles of Medicinal Chemistry II), we discussed the synthesis of acridine ring systems that could potentially be used as DNA intercalators in the treatment of cancer. As a student of CHEM 252, you should be able propose a suitable mechanism for the following transformation.



2b.) Which of the following hydrocarbons is expected to be the most acidic? Please explain.

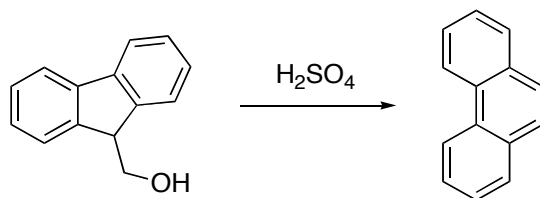


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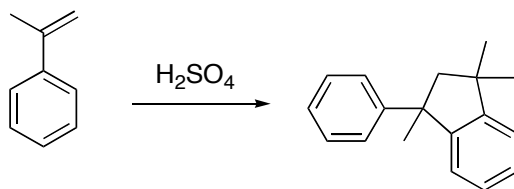
1/28/05: Material Derived from Chapter 15 of Vollhardt and Schore (Benzene and Aromaticity:
Electrophilic Aromatic Substitution)

3.) Provide a mechanism for each of the following transformations:

3a.)



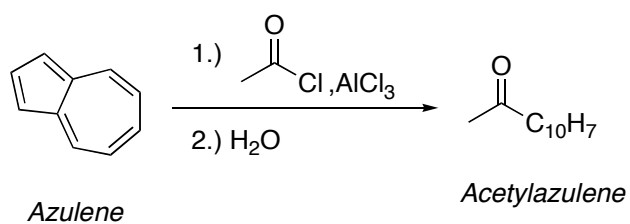
3b.)



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4a.) The following reaction gives mainly one isomer. Propose a suitable mechanism in order to predict the structure of the acetylazulene product that forms.

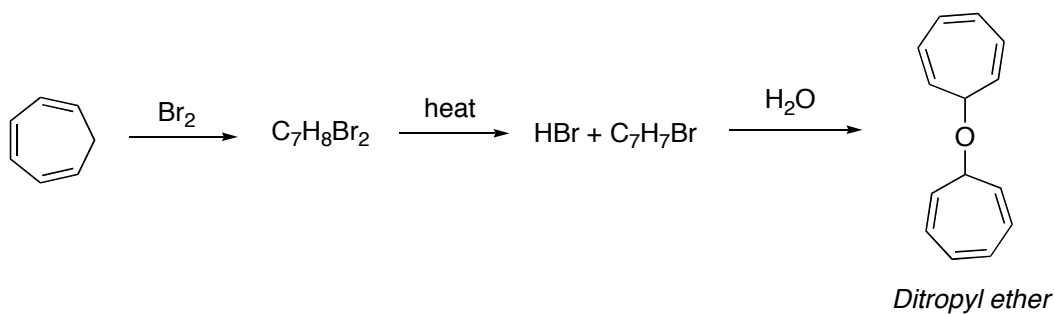


4b.) True or False: The same anion is formed by loss of the most acidic proton from 1-methyl-1,3-cyclopentadiene as from 5-methyl-1,3-cyclopentadiene. Explain.

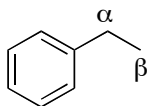
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5a.) As early as 1891 the German chemist G. Merling showed that the bromination of 1,3,5-cycloheptatriene leads to a liquid dibromide. When the dibromide is heated, HBr is evolved and a yellow solid of the formula C_7H_7Br (mp $203^\circ C$) can be isolated. This compound is soluble in water, but cannot be reisolated from water solution. Instead, ditropyl ether is obtained. Merling could not explain what was happening, but perhaps you can.



5b.) Ethylbenzene gives only the product of bromination at the α -position when treated with NBS (trace HBr) in CCl_4 . Explain why only this product is seen and the product from β -bromination is not.

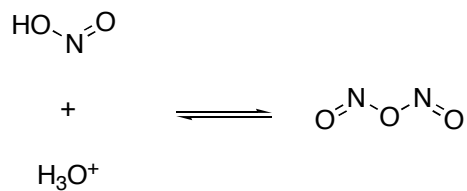


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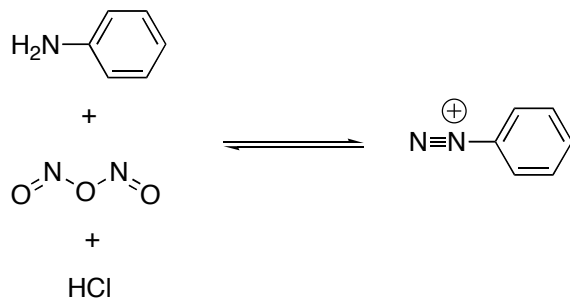
1/28/05: Material Derived from Chapter 15 of Vollhardt and Schore (Benzene and Aromaticity: Electrophilic Aromatic Substitution)

6.) Use arrow formalism to show how each of the following reactions proceeds. Account for the byproducts formed in these reactions that are not given in the problem.

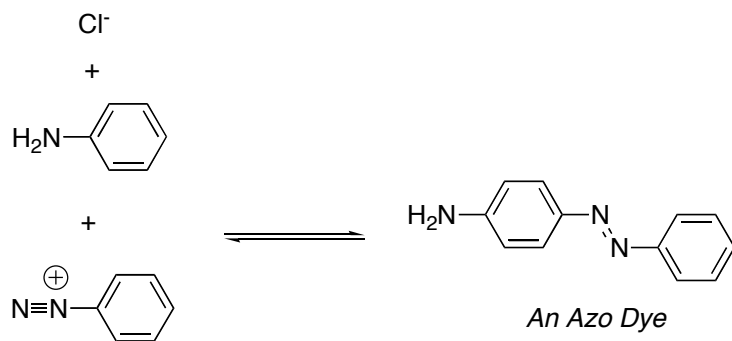
6a.)



6b.)



6c.)

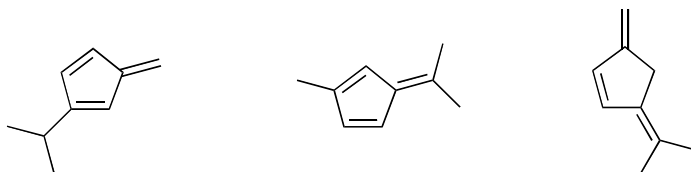


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7a.) If one attempts to methylate benzene completely with $\text{CH}_3\text{Cl} / \text{AlCl}_3$, the product contains a greenish solid of the formula $\text{C}_{13}\text{H}_{21}\text{AlCl}_4$. Propose a structure for the compound and a mechanism for its formation.

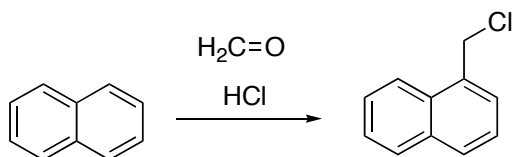
7b.) Identify the most acidic compound and provide an explanation for its exceptionally high acidity.



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8a.) Write a mechanism for the following chloromethylation reaction:



8b.) The following wonderful question appeared on a graduate cumulative exam at Princeton in January, 1993. With a little care you can do it easily. Write a mechanism for this seemingly bizarre change. *Hint.* It is not bizarre at all. Think simple! First consider what HCl might do if it reacts with the starting material.

