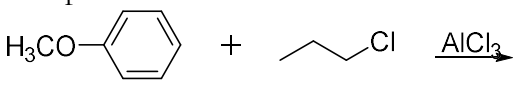
Experiment 16

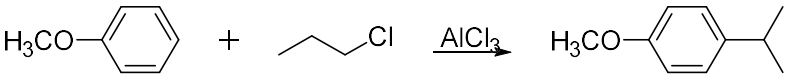
Electrophilic Aromatic Substitution: Friedel-Crafts Acylation

Study Questions

1) A carbocation produced during a Friedel-Crafts alkylation may undergo rearrangement. What rearranged product might you expect from the reaction below?

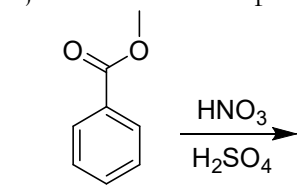


Answer:

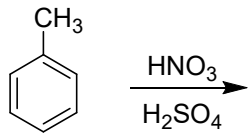


+ some minor ortho and disubstituted products

2) Predict the major mononitration products of methyl benzoate and of toluene.

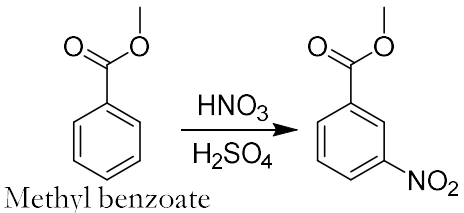


Methyl benzoate

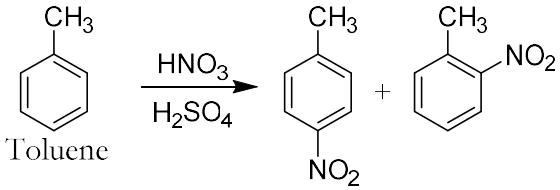


Toluene

Answer:

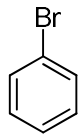


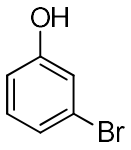
Methyl benzoate

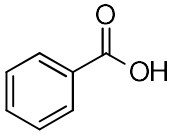


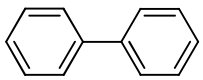
Toluene

3) Predict the major monoalkylation products you would expect to obtain from the reaction of the following compounds with iodomethane (CH_3I) and $AlCl_3$. (Note: Iodomethane is one of the most common methylating agents. You are probably more accustomed to seeing alkyl halides that contain bromine and chlorine; in this case they are not used because both chloromethane and bromomethane are gases at room temperature).

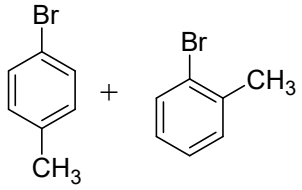
a. 

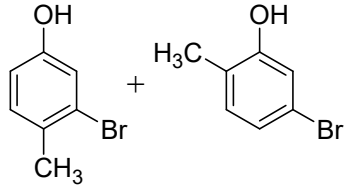
b. 

c. 

d. 

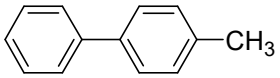
Answer:

a. 

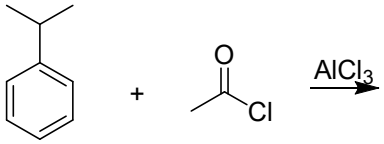
b. 

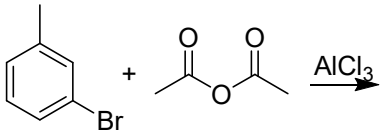
The site between OH and Br is too hindered to allow addition

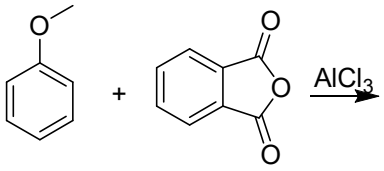
c. No reaction (this group is too deactivating to permit Friedel-Crafts)

d. 

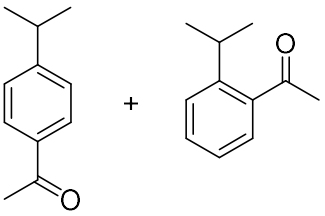
4) What product(s) would you expect to obtain from the following reactions?

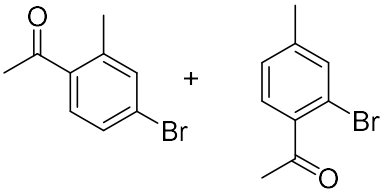
a. 

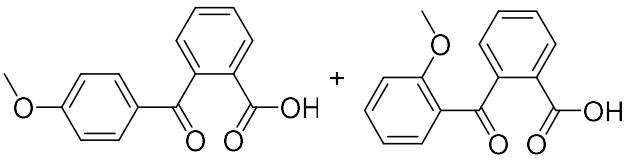
b. 

c. 

Answer:

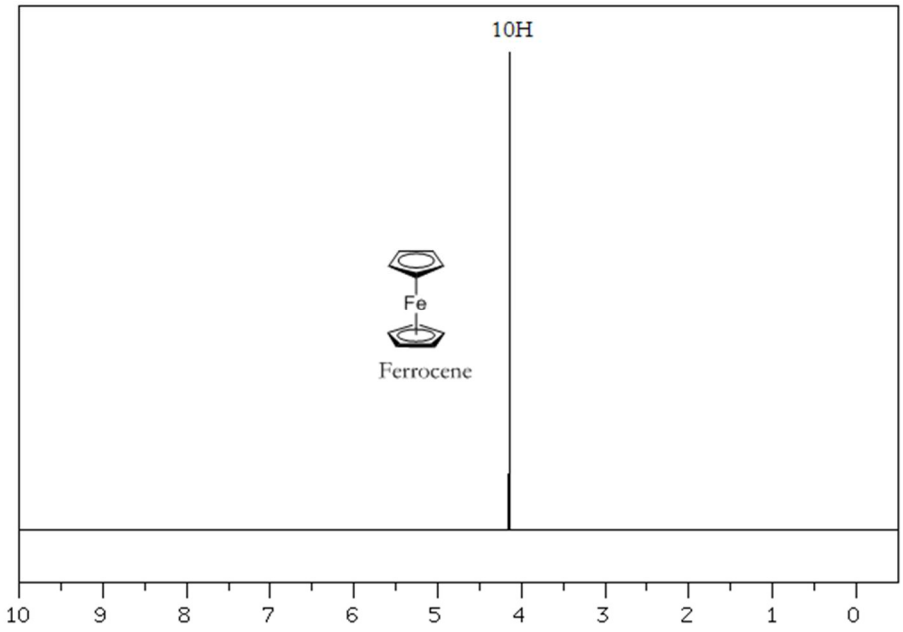
a. 

b. 

c. 

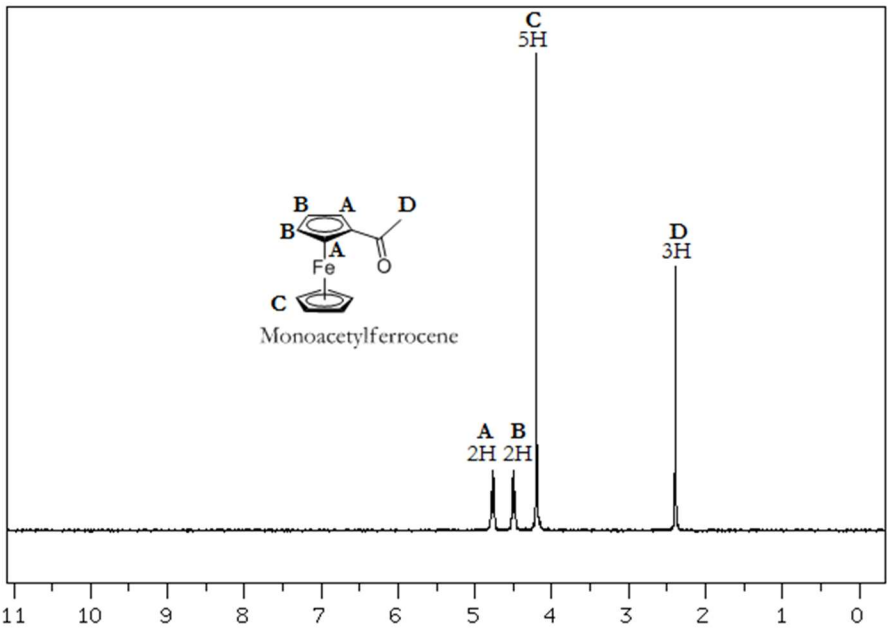
5) The NMR spectrum of ferrocene is shown below (taken from SDBS). Explain why the aromatic

protons show a single band at 4.2 ppm.



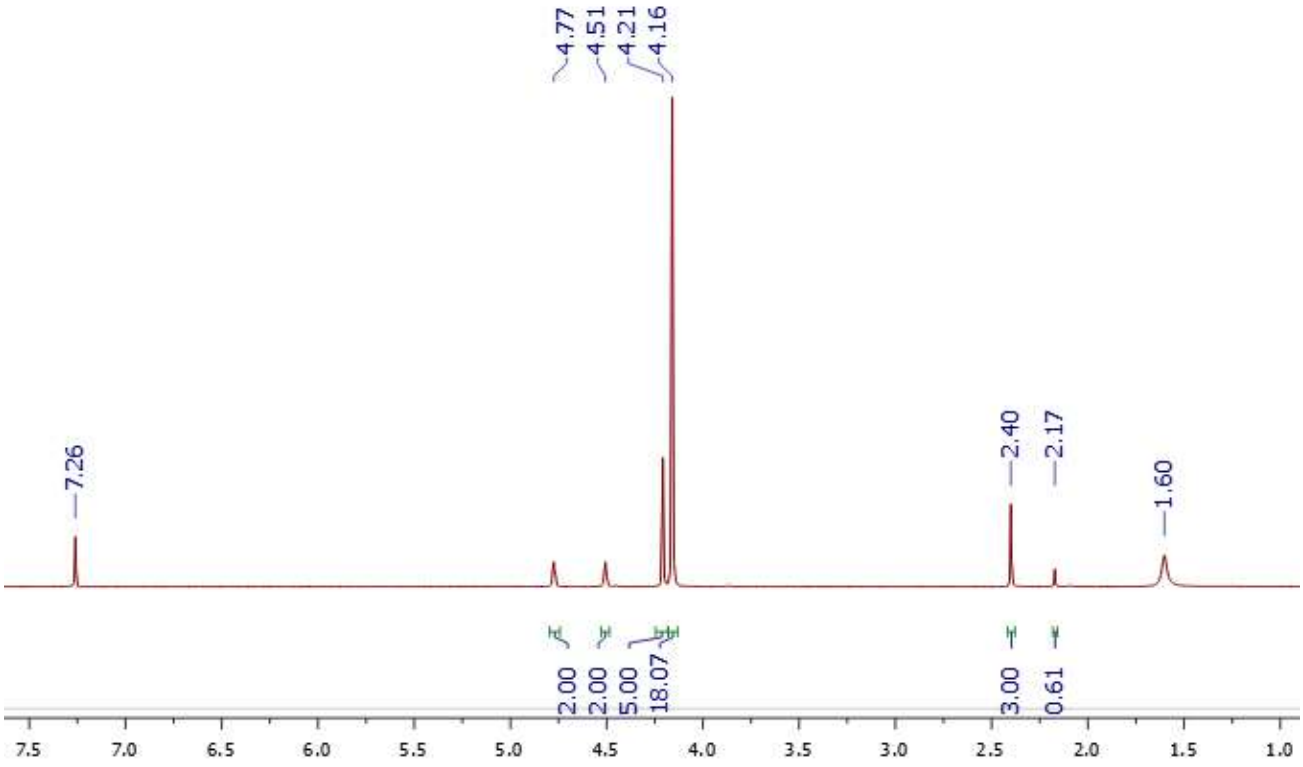
Answer: Because they are all equivalent.

6) The NMR spectrum of monoacetylferrocene is shown below (taken from SDBS). What would the NMR of diacetylferrocene look like?



Answer: The "c" peak would disappear and the others would double in intensity.

7) A student performed this experiment and obtained the NMR spectrum shown below. What other impurities are present? What is the molar ratio of ferrocene to monoacetylferrocene in the crude product? What percent of the crude product is ferrocene vs. monoacetylferrocene?



Answer: Impurities present are $CDCl_3$ (7.26 ppm), acetone (2.17 ppm), and water (1.60 ppm). For product ratios, the two easiest peaks to use are at 4.21 (5H in monoacetylferrocene) and 4.16 (10H in ferrocene).

$$\frac{\text{Moles of } \textbf{ferrocene}}{\text{Moles of } \textbf{monoacetylfer.}} = \left(\frac{18.07}{5.00}\right)\left(\frac{5\text{H}}{10\text{H}}\right) = 1.807$$

$$\text{Molar \% } \textbf{ferrocene} = \frac{1.807}{1.807 + 1} = 0.644 \text{ or } 64.4\ \%$$

$$\text{Molar \% } \textbf{monoacetylfer.} = \frac{1}{1.807 + 1} = 0.356 \text{ or } 35.6\%$$