Electrophilic Aromatic Substitution
Lab Report

NAME:_____

PARTNER'S NAME:_____

LAB SECTION:_____

DATE:_____

% SCORE:

	Points possible	Points received
Lab Notebook		
Abstract		
Mechanisms		
Spectra analysis- Nitration		
Spectra analysis- alkylation		

A. ABSTRACT:

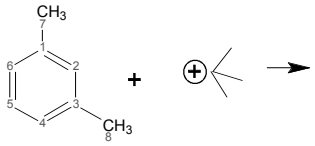
B. REACTION MECHANISM

1. Show a mechanism for the formation of the electrophile, NO_2+, from sulfuric acid and nitric acid.

2. Draw 3 resonance structures of protonated methyl benzoate, where do you predict nitration will be directed? Explain, referencing your structures

3. An excess of nitric acid and sulfuric acid is used in this reaction, why is the major product only mono-nitrated?

4. Draw all the resonance structures that would characterize the intermediate carbocation resulting from attack of the tert-butyl carbocation at C-6 of m-xylene. Do the methyl groups activate attack at C-4? Explain



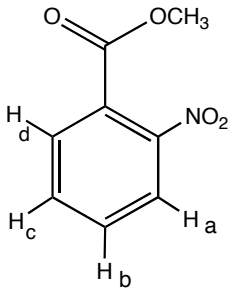
5. Which isomer of the alkylated m-xylene is thermodynamically favored? Which isomer is kinetically favored?

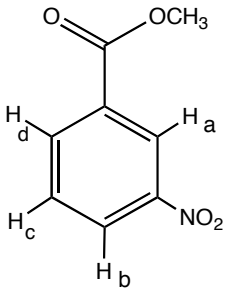
6. Which isomer of the alkylated m-xylene is produced the thermodynamic or kinetically favored isomer? Would you expect a different substitution product for alkylation of m-xylene using chloroethane instead of t-butylchloride?

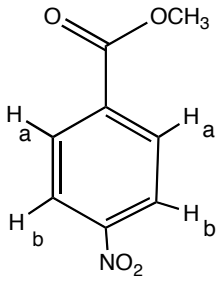
C. ^{1}H & ^{13}C NMR OF NITRATION PRODUCT

Use CNMR and HNMR to deduce the structure of the nitrated product.

The CNMR of the product is provided for you. You should be able to eliminate one isomer as a possible product using information from this spectrum.
The product HNMR is also provided. Use splitting patterns in the HNMR to determine position of the nitro group. J_{ortho}, typically about 8 Hz, is the coupling constant for aromatic hydrogens on adjacent carbons. J_{meta}, typically about 1.8 Hz, is the coupling constant between hydrogens meta to each other. Hydrogens para to each other generally do not affect each other significantly. Try and determine what proton splitting pattern would be seen in the structures below. (Hint: Will all the protons on each structure have ortho splitting?)







1. Circle the isomer above that corresponds to your nitration product.

2. Calculate peak positions for aromatic hydrogens by using the benzene substituent tables provided in the appendix. An example is shown with one isomer above in the appendix.

3. Complete the table below for aromatic protons with calculated values and values from provided HNMR.

[1]HNMR of nitration product

Peak	Peak position, ppm	Peak position, calculated, ppm	Integration	Splitting pattern (s,d,t,q etc.)	Ortho Coupling Constant (Hz) If present
a					
b					
c					
d					
-CH3		N/a			N/a

D. IR and ^{1}H NMR Spectra for Alkylation of m-Xylene

1. If you ran this experiment, attach your acquired IR with the C-H out-of-plane bending vibrations labeled. Using Table 1 below to determine the structure of your substitution product and label the spectrum with your product structure. Peaks may also appear for m-xylene if some remains in your product. Identify m-xylene on your spectrum if it is observed. Characteristic frequencies for m-xylene are given in the table below.

2. The heats of formation can be calculated in lab using HyperChem. The smaller the heat of formation the more stable the structure. In the table, record the Heat of Formation of each trisubstituted benzene and rank these structures according to relative stability based on heats of formation (1 = most stable).

Table 1 Out of plane vibrations and Stability of t-butyl substituted m-xylene

Alkyl Substituted Benzene	C-H Out-of-Plane Bending Vibrations (cm^{-1})		Heat of Formation (kcal/mol)	Relative stability
1,2,3-Trisubstituted	780-760	745-705		
1,2,4-Trisubstituted	885-870	825-805		
1,3,5-Trisubstituted	865-810	730-675		
m-Xylene	769	691	N/a	N/a

3. Report the out of plane vibrations you observed for the product of the reaction of t-butyl chloride and m-xylene: _____ _____

4. Using your IR results and Table 1 above, determine your product structure and draw it below. Label the ring hydrogens with letters using the same letter for equivalent hydrogens.

5. In the space provided below, draw the HNMR spectra you would expect for the aromatic protons in your xylene reaction product drawn in 4. Label the peaks in your drawing with the letters from your structure. Chemical shift of signals is not as crucial as signal splitting and size. Below your spectrum discuss how you predicted each proton signal.