

**Review #2: Chap 4 Aromatic Reactions**

Complete the following table. Write the equations using benzene as the starting organic molecule.

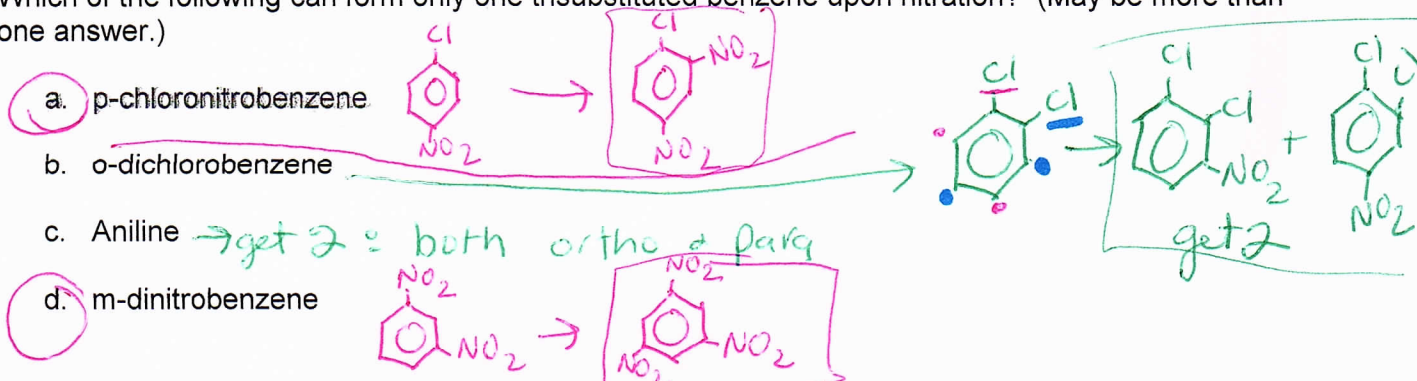
	Type Reaction	Equation	Explain or diagram how the catalyst interacts with the reagent to create the electrophile
1.	Bromination (Would be similar for any halogen)	<chem>c1ccccc1.BrBr&gt;&gt;[AlBr3][FeBr3]c1ccccc1Br.Br</chem>	$Br-Br + \overset{\text{vacant side}}{\rightarrow} AlBr_3 \rightarrow Br-Br-AlCl_3$ * Similar to #4 below δ+ electrophile
2.	Nitration	<chem>c1ccccc1.O=[N+]([O-])O&gt;&gt;[H+][H2SO4]c1ccccc1[N+](=O)[O-].O</chem>	Catalyst H <sup>+</sup> combines w/ the OH of HO-NO <sub>2</sub> to form H <sub>2</sub> O leaving +NO <sub>2</sub> as electrophile
3.	Sulfonation	<chem>c1ccccc1.O=S(=O)(O)O&gt;&gt;[SO3]c1ccccc1S(=O)(=O)O.O</chem>	XXX SKIP THIS ONE XXX
4.	Alkylation (Add an ethyl group)	<chem>c1ccccc1.CC&gt;&gt;[AlCl3][FeCl3]c1ccccc1CC.Cl</chem>	Catalysts AlCl <sub>3</sub> or FeCl <sub>3</sub> have an empty spot in valence shell that pulls 1 Cl off Cl <sub>2</sub> leaving Cl <sup>+</sup> as electrophile
5.	Alkylation again! (2 <sup>nd</sup> way to add ethyl)	<chem>c1ccccc1.C=C&gt;&gt;[H+][H2SO4]c1ccccc1CC</chem>	no inorganic product H <sup>+</sup> adds to 1 of the carbons of double bond, following Markovnikov's rule, resulting in + charge on other carbon
6.	Acylation (create acetophenone as a product)	<chem>c1ccccc1.CC(=O)Cl&gt;&gt;[AlCl3][FeCl3]c1ccccc1C(=O)C.Cl</chem>	Empty side on AlCl <sub>3</sub> pulls Cl off reagent, leaving + charge on the carbon double bond to the O
7.	Hydrogenation	<chem>c1ccccc1.3H2&gt;&gt;[Ni][Pd][Pt]C1CCCC1</chem>	no inorganic product X Not needed

Complete the following table on Ortho, Para vs. Meta Directors, Activating vs. Deactivating

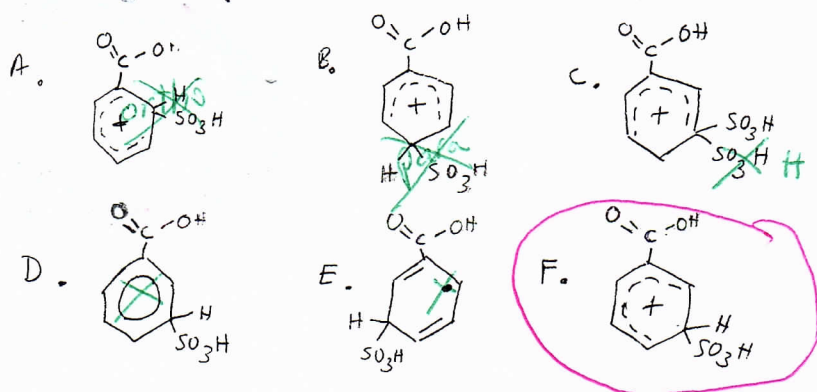
	Substituent	Is it an o,p-director or m-director?	Explain why it is that type of director. (Example: If you drew out the intermediate resonance structures, what would you circle as evidence?)	Is it Activating or Deactivating?
8.	-CN	m	oN more electronegative than C δ+ on C too close to + in resonance	de
9.	<chem>-C(=O)OH</chem>	o,p	• 3 <sup>o</sup> carbocation in o,p resonance	act
10.	-CO <sub>2</sub> H	m	• δ+ on C because O is more electronegative • + charge too close in o,p	de
11.	<chem>-NHC(=O)CH3</chem>	o,p	4 <sup>th</sup> resonance structure in o,p b/c of unshared e- pair on N	act

12.	-NO <sub>2</sub>	m	δ+ on N b/c O more electroneg + charge too close in of resonance	de
13.	-SO <sub>3</sub> H	m	δ+ on S b/c O more electroneg + charge too close in of resonance	de
14.	-OH	o,p	4th resonance in o,p resonance due to unshared e- pair on Oxygen	act
15.	-OCH <sub>3</sub>	o,p	Same	act
16.	-F	o,p	4th resonance in o,p due to unshared e- pair on F	de

17. Which of the following can form only one trisubstituted benzene upon nitration? (May be more than one answer.)



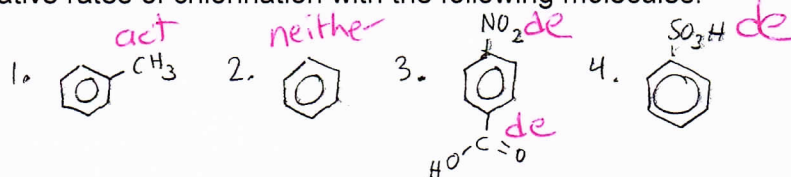
18. Which of the following is the predominate intermediate in the sulfonation of benzoic acid?



19. Name the product of the following reaction:

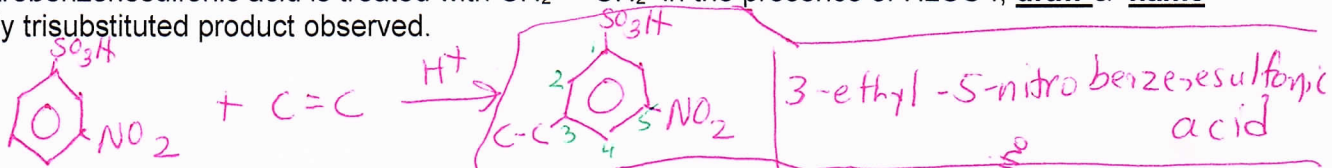


20. Rank the relative rates of chlorination with the following molecules:



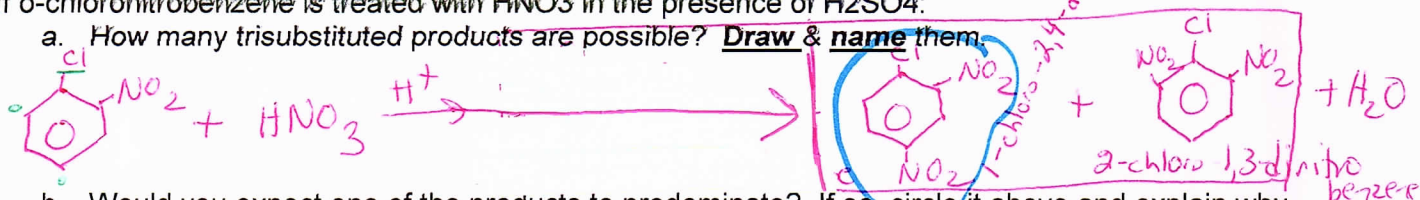
- A. 4 > 2 > 1 > 3    B. 3 > 2 > 1 > 4    C. 2 > 1 > 4 > 3    D. 1 > 2 > 3 > 4    E. 1 > 2 > 4 > 3

21. If m-nitrobenzenesulfonic acid is treated with  $\text{CH}_2 = \text{CH}_2$  in the presence of  $\text{H}_2\text{SO}_4$ , **draw & name** the only trisubstituted product observed.



22. If o-chloronitrobenzene is treated with  $\text{HNO}_3$  in the presence of  $\text{H}_2\text{SO}_4$ :

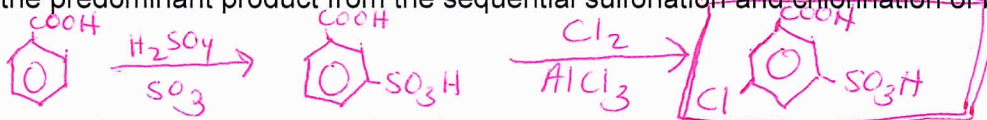
a. How many trisubstituted products are possible? **Draw & name them.**



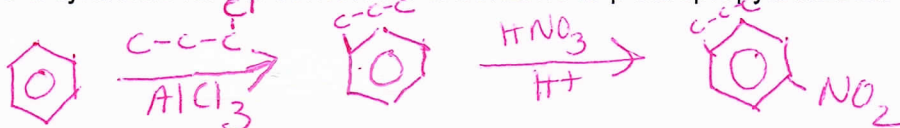
b. Would you expect one of the products to predominate? If so, circle it above and explain why it would predominate.

predom b/c substituents further apart

23. Draw the predominant product from the sequential sulfonation and chlorination of benzoic acid.



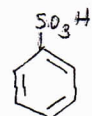
24. Devise a synthesis for the conversion of benzene to p-nitropropylbenzene.



25. Write an equation for the synthesis of chlorobenzene from benzene



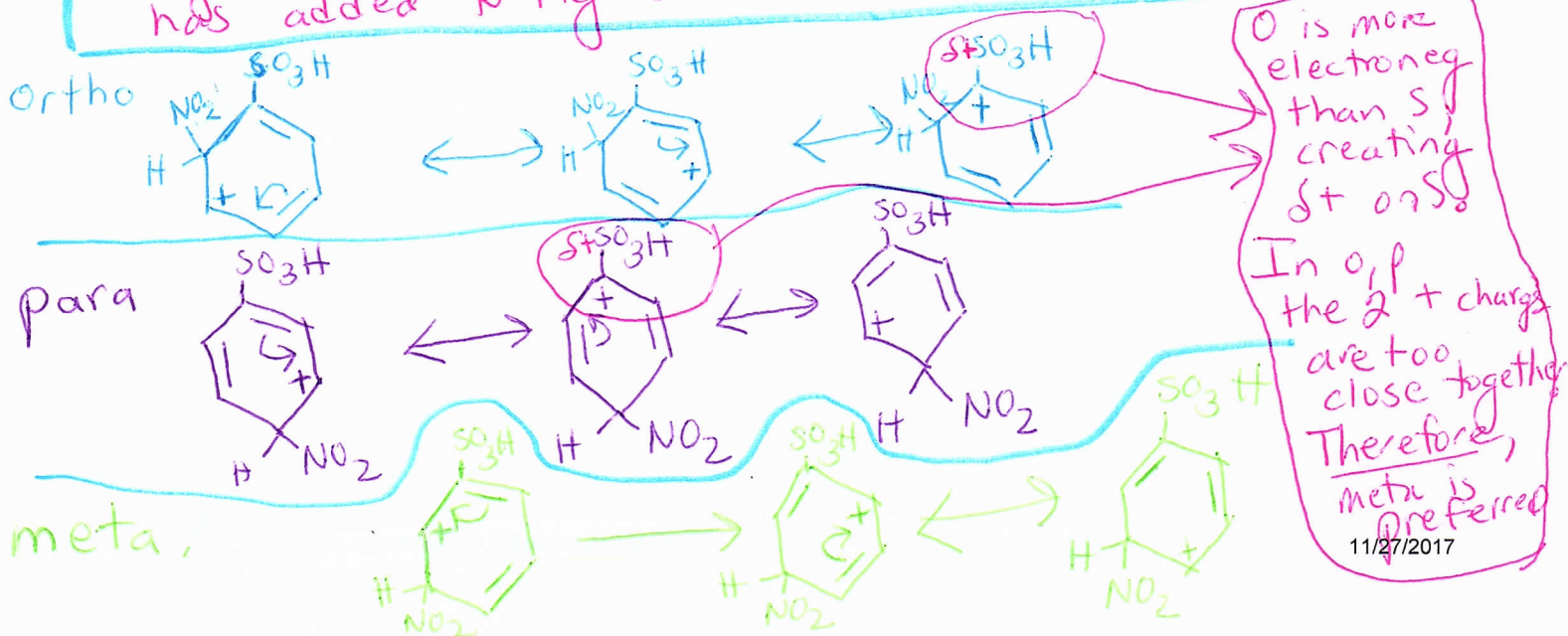
26. Draw the resonance structures for the carbocations formed during the nitration of the following molecule.



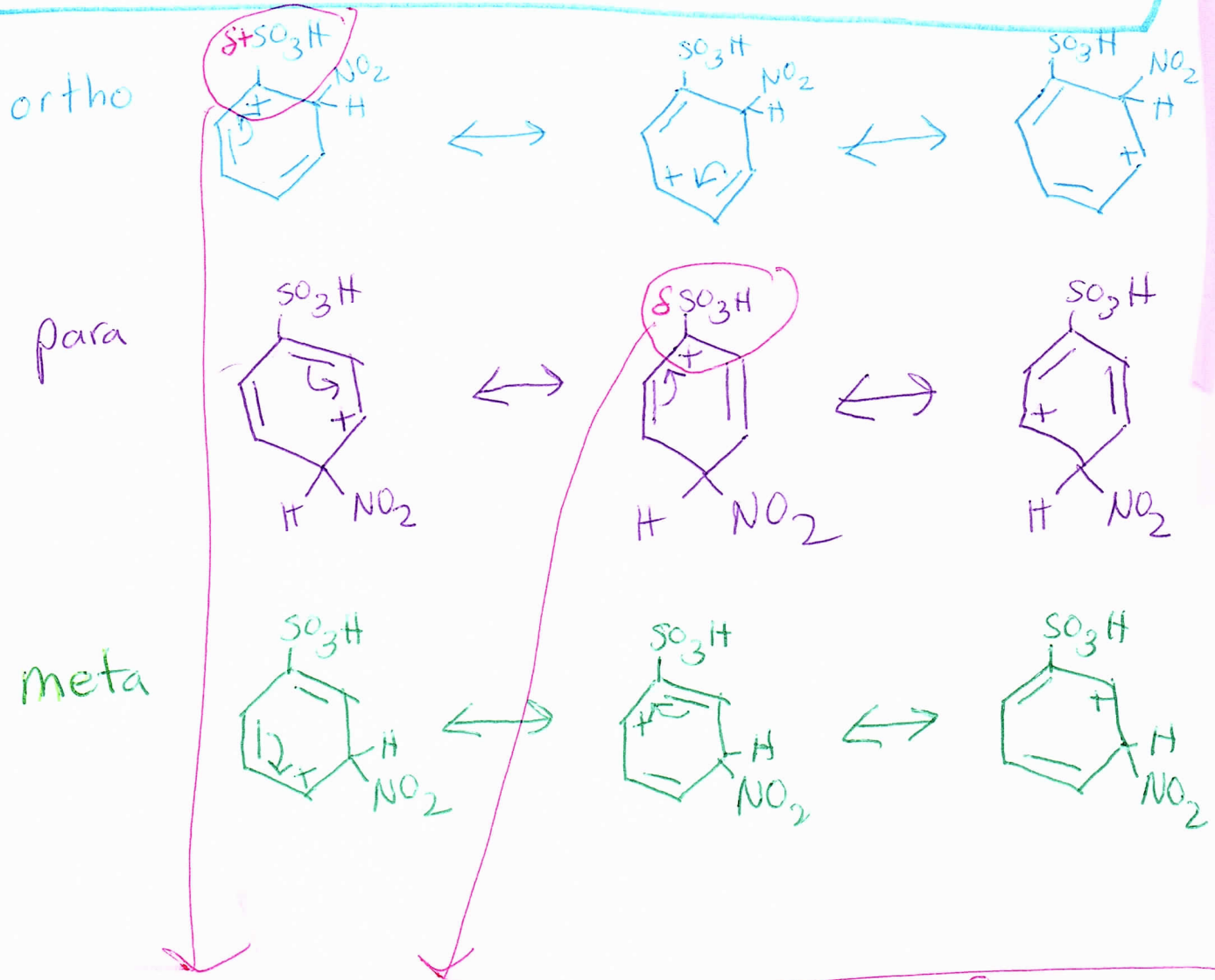
A. Include resonance drawings for ortho, para, and meta substitutions. LABEL as o, p, or m. Note: the resonance structures for each, should show proper placement of the positive charge and bonds based on the molecule drawn below.

B. Explain with words why the molecule was o,p-directing or m-directing. Then designate (circle, etc.) the portions of the drawings that support your explanation.

**Note** - Instructions forgot to specify whether to add to right or left. The 1st set adds to left. Next page has added to right.



#28 If added to right side of c1ccc(cc1)S(=O)(=O)O



O is more electronegative than S,  
 causing  $\delta^+$  on S.  
 In o/p resonance, the two positive charges  
 are too close together.  
 Therefore, meta is preferred