Homework Four

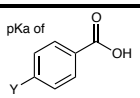
Organic Chemistry II (224) • Prof. Chad Landrie

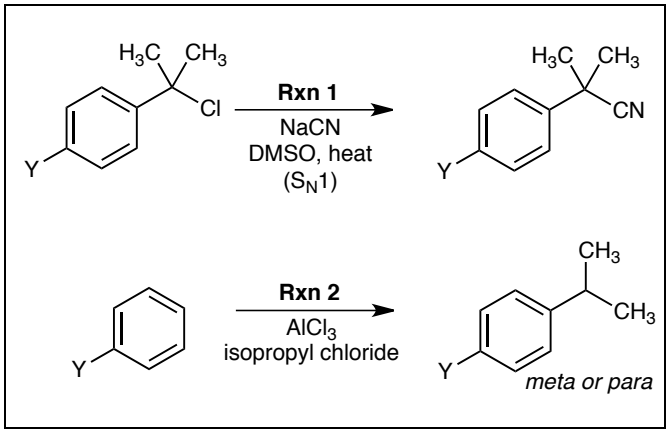
Spring 2013

Completion (6 pts)		**Name**	
Random Sample(s) (4 pts)		**BID**	
Total (10 pts)		**Section-CRN**	

Additional Recommended Problems from McMurray (8th Ed.)	

1. Using the pKa table of benzoic acid derivatives, rank each reaction in order of increasing rate (1 = slowest; 5 = fastest). In both cases, consider when the aromatic compound is acting as a nucleophile or an electrophile. Then, using the table of pKas, determine whether each group with increase or decreases the nucleophlicity or electrophilicity of the aromatic reactant.

Y	pKa of 	Rank **Rxn 1** (5 = fastest)	Rank **Rxn 2** (5 = fastest)
$-Si(CH_3)_3$	4.27		
$-CH{=}CHCN$	4.03		
$-HgCH_3$	4.10		
$-OSO_2CH_3$	3.84		
$-PCl_2$	3.59		



2. What was your reasoning for ranking **Rxn 1**? Be specific.

3. What was your reasoning for ranking **Rxn 1**? Be specific.

4. **First**, draw the complete structure of the benzoic acid derivative with Y = $-OSO_2CH_3$. **Second**, explain why this is an electron withdrawing group even though the oxygen bonded to the ring contains electron lone-pairs.

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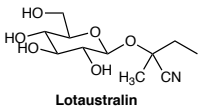
5. Naturally occurring compounds called cyanogenic glycosides, such as lotaustralin, release hydrogen cyanide when treated with aqueous acid. The reaction occurs by hydrolysis of the acetal to form glucose and a cyanohydrin. The cyanohydrin then hydrolyzes to HCN and a carbonyl compound.

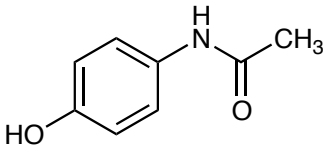


Lotaustralin

   a. Draw the mechanism for acetal hydrolysis of lotaustralin.

   b. Propose a mechanism for the loss of HCN and show the structure of the carbonyl compound that is formed.

6. A chemist was attempting to make the compound below. They dissolved p-aminophenol in anhydrous diethyl ether and then added acetyl chloride slowly. After workup, only 50% of the desired product was obtained. **First**, explain what mistake the chemist made and why the yield will never rise above 50% under these conditions. Draw a chemical reaction to support your explanation. **Second**, list two modifications that could be made to increase the yield of the acylation.



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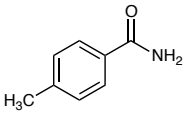
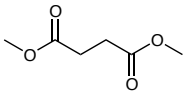
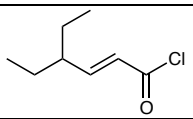
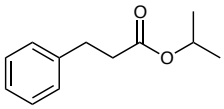
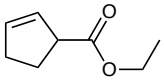
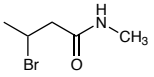
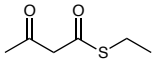
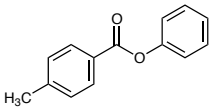
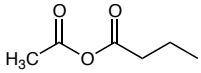
7. Write the IUPAC name for each molecule.

8. Draw the Lewis structure for:

a. *p*-bromophenylacetamide	b. *p*-bromophenylacetamide	c. 2,2-dimethylhexanamide
d. ethyl 2-cyclobutenecarboxylate	e. *m*-benzoylbenzamide	f. cyclohexyl cyclohexanecarboxylate

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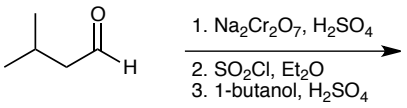
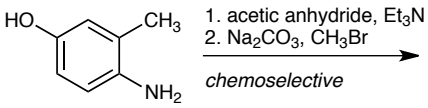
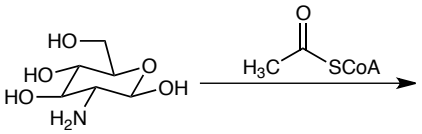
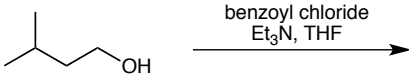
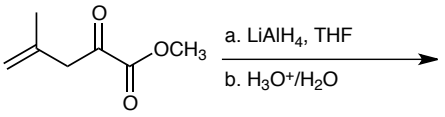
9. Draw the *major* product for each transformation. Be sure to consider whether the reaction is regio-, chemo- or stereoselective.

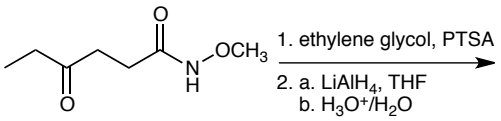


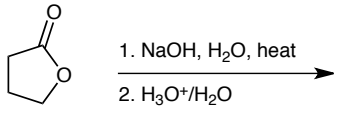


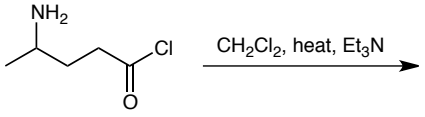












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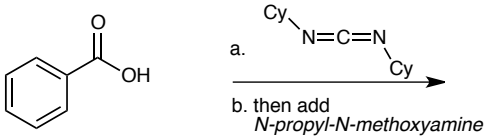

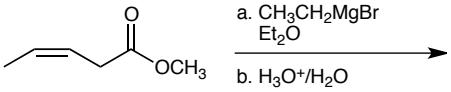

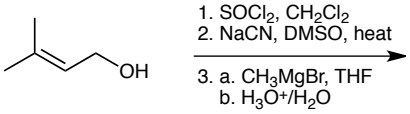

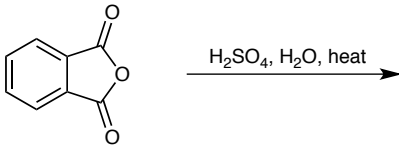

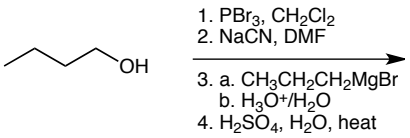

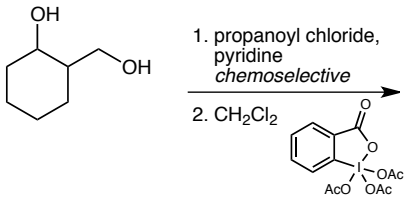

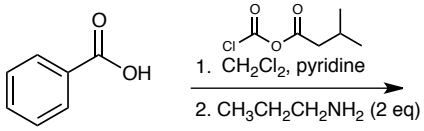

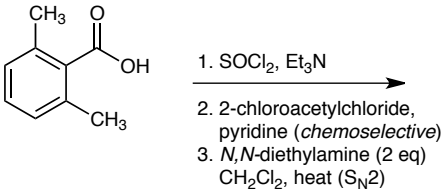

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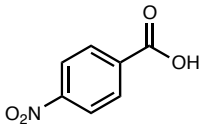
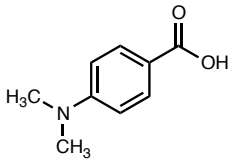
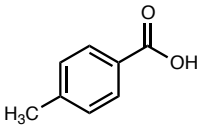
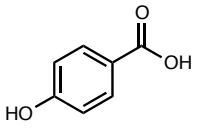
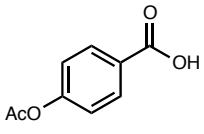
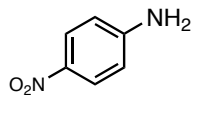
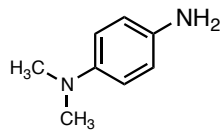
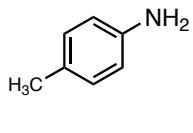
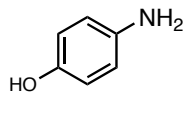
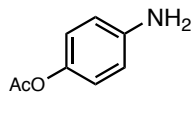
10. Rank in order of increasing acidity (1 = weakest acid, largest pKa; 5 = strongest acid, smallest pKa).

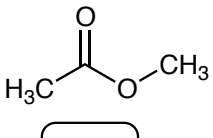
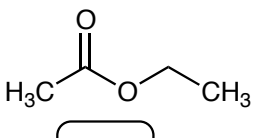
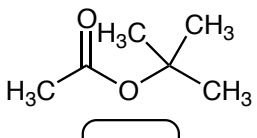
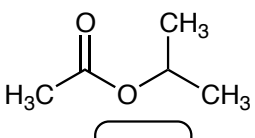
What was your reasoning?:

11. Each of the anilines (benzene with $-NH_2$) below undergoes SN2 with CH3Br. Rank in order of increasing rate of nucleophilic addition. (1 = slowest reaction; 5 = fastest reaction).

What was your reasoning?:

12. Rank in order of increasing rate of saponification with aqueous NaOH (1 = slowest rate; 4 = fastest rate).

What was your reasoning?:

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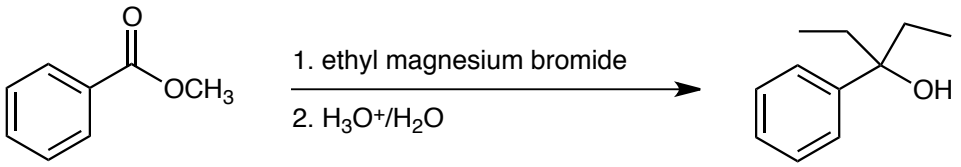
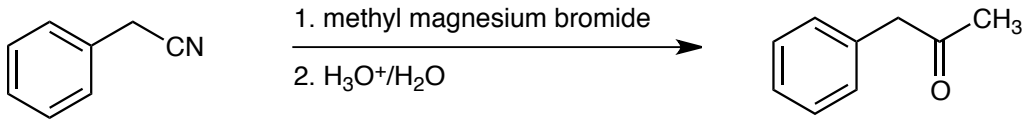
13. Draw the complete mechanism for each transformation.





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14. Design a synthesis for each of the following molecules. Where stereochemistry is shown, your synthesis must be stereoselective.