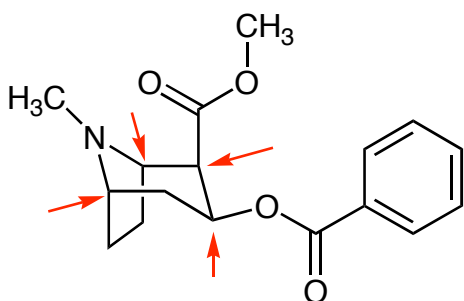


Name:

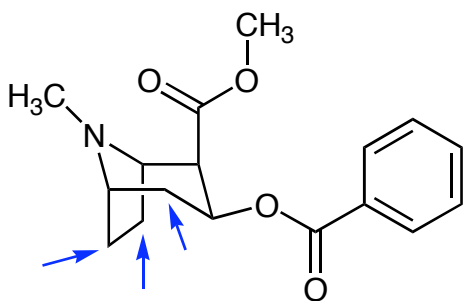
CHEMISTRY 249S  
Examination 1: Answer Guide  
February 13th 2006

1. (15 Points)

(a) How many chiral centres are there in this molecule? **4**



(b) How many methylene group signals would you expect to see in the DEPT NMR? **3**



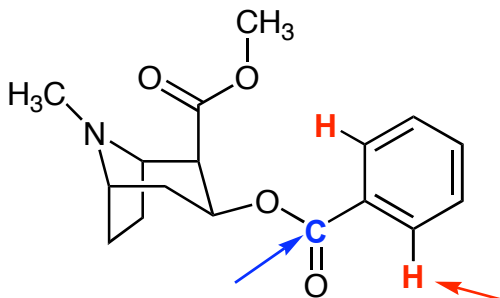
(c) How many aromatic carbon signals (peaks) would you see in the <sup>13</sup>C NMR? **4**

**there are only 4 signals because the aromatic ring is monosubstituted. There is therefore a symmetry plane/axis in this ring.**

Name:

(d) What is the most downfield signal you would expect to see in the  $^1\text{H}$  NMR? Indicate this on the structure above by drawing an **arrow to the hydrogen**.

See structure below:



(e) What is the most downfield signal you would expect to see in the  $^{13}\text{C}$  NMR? Indicate this on the structure above by **circling the carbon**.

See structure above:

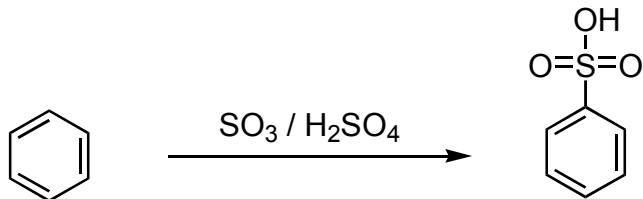
**The carbonyl indicated is more downfield than the other ester carbonyl, due to the ring-current effect of the neighbouring phenyl ring.**

(f) What splitting pattern (multiplicity) would the N-methyl group (the methyl group attached to the nitrogen atom) show in the  $^1\text{H}$  NMR?

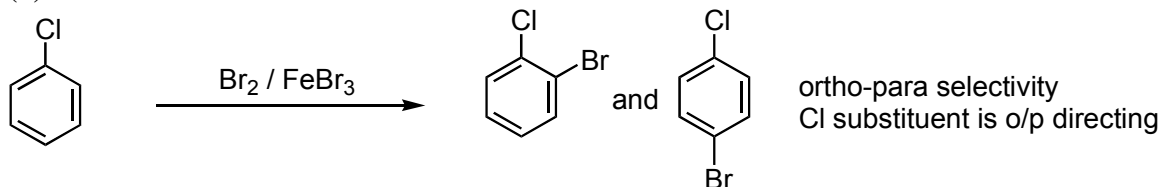
**A singlet**

2. (25 Points) What are the final products of the following reactions? You should clearly indicate the selectivity of the reactions?

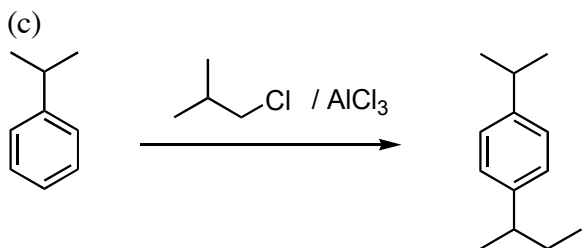
(a)



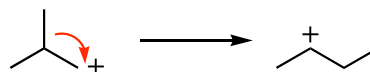
(b)



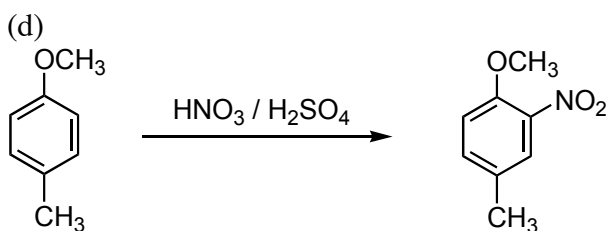
Name:



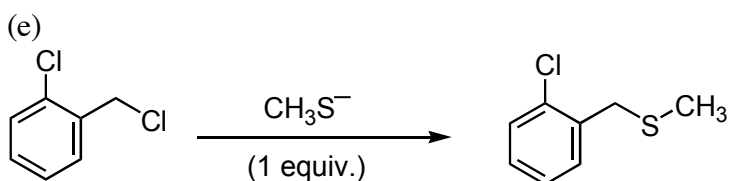
in this case the initial carbocation rearranges through a 1,2-methyl shift to give the more stable secondary carbocation.



substitution then occurs at the para position. The ortho position is disfavoured in this case by steric effects.



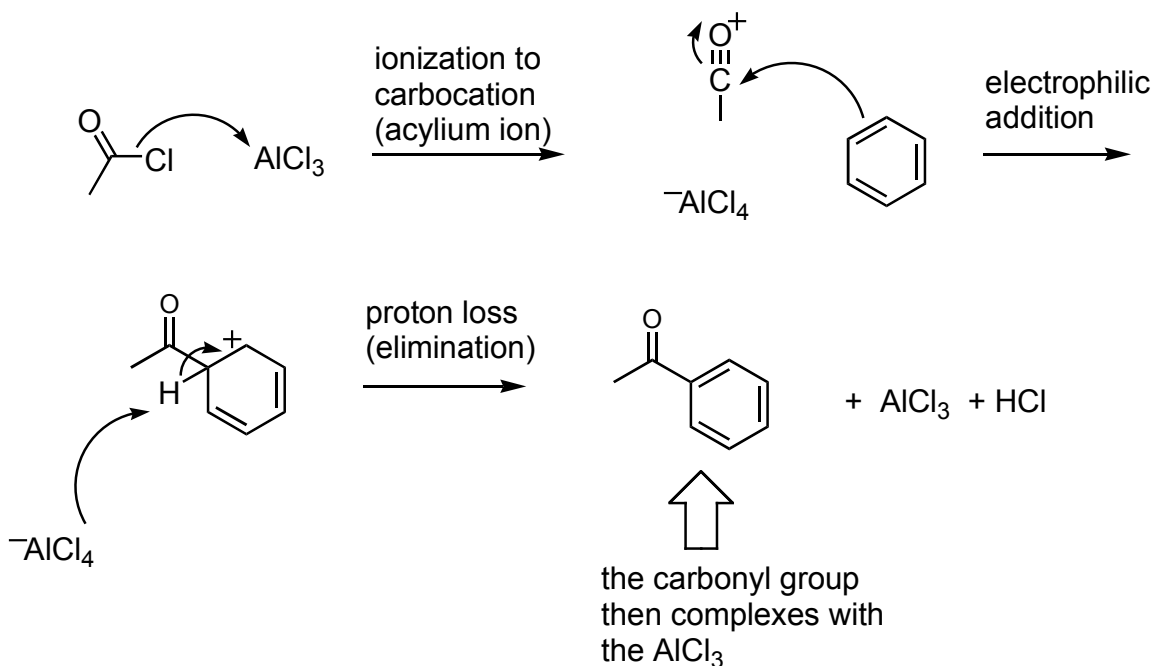
both substituents are o/p directing. However, the OMe group is a stronger directing group, leading to the observed selectivity.



this is an example of an  $\text{S}_{\text{N}}2$  substitution (review of 2nd year)

3. (25 Points)

(a) Draw a full mechanism for this transformation. Your answer should include curved arrows to show electron movement.



Name:

(b) Why are 1.1 equivalents of the catalyst needed for this reaction? What work-up step must be employed as a result?

**The carbonyl group in the product undergoes a Lewis-base-acid complexation with the catalyst. Hence, more than one equivalent is required. An aqueous work-up is required to break down this complex.**

(c) Why is this reaction more selective than the Friedel-Crafts alkylation reaction?

**The product is less reactive in this case, and therefore polyacylation is not a problem. For alkylation, the product is more reactive, and polyalkylation is a problem.**

(d) What reagents would you use to reduce the carbonyl functional group to a  $\text{CH}_2$  group?

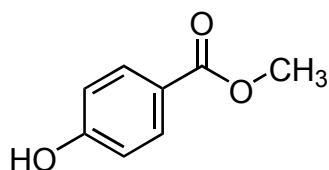
**$\text{H}_2 / \text{Pd}$**

*or*

**$\text{Zn/Hg} / \text{HCl}$**

4. (60 Points)

COMPOUND A:

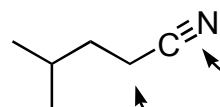


note: this is not a carboxylic acid!

A COOH group would give a much broader signal in both the  $^1\text{H}$  NMR and the IR.

The downfield signal at 10.4 ppm is from the OH group.

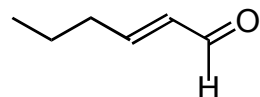
COMPOUND B:



note: CN group signals in the IR and  $^{13}\text{C}$  NMR

note: the upfield shift of this signal

COMPOUND C:



note: the trans alkene geometry