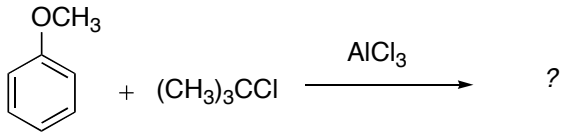
Chem 2062 Spring 2006
Ch 17 group work

1. The Friedel-Crafts Alkylation is a method for attaching alkyl groups to aromatic rings using a strong Lewis acid like $AlCl_3$ and an alkyl halide. The halogen atom of the alkyl halide attacks the electrophilic alumium atom, and at the same time, the carbon-halogen bond weakens and breaks. This forms an alkyl carbocation, with a negative aluminum species as the counterion. The alkyl carbocation is attacked by the aromatic system forming a sigma complex, which is deprotonated and rearomatized by the negative aluminum species. This regenerates the catalyst.

   Since the electrophile is usually large, ortho substitution is unfavorable. Also, since a carbocation is involved, it is prone to rearrangements, severely limiting the types of alkyl groups which can be attached. Also, deactivated systems will not react (*e.g.* nitrobenzene, etc.).

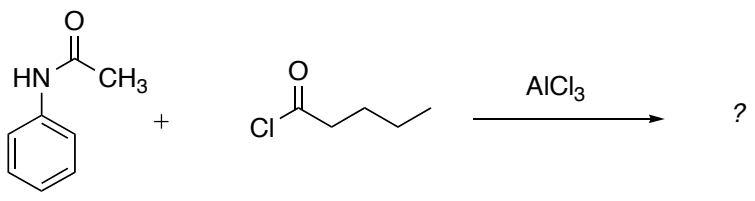
   Draw a mechanism and predict the major product for the following reaction:



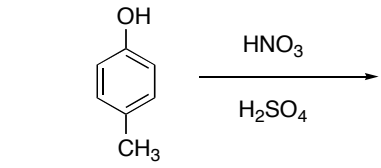
2. The Friedel-Crafs Acylation is more versatile than the alkylation above, mainly because there is no chance for carbocation rearrangement. In this reaction, an acyl group (–COR) can be attached to an aromatic ring. Like the alkylation above, we use a strong Lewis acid like $AlCl_3$ but instead of an alkyl halide, we use an acyl chloride (RCOCl). The Cl of the acyl chloride attacks Al, and the C-Cl bond weakens and breaks, leaving an acylium ion, with resonance structures delocalizing the positive charge between the C and the O. A negative aluminum species is the counterion. This strong electrophile is attacked by the aromatic system, forming a C–C bond in the sigma complex, which is deprotonated and rearomaticzed by the negative aluminum species. This regenerates the catalyst.

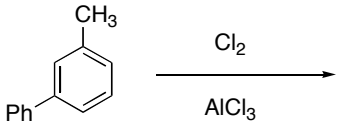
   Like the alkylation, ortho substitution is unfavorable due to the size of the electrophile, but we no longer have to worry about any carbocation rearrangements, since the positively charged carbon in the acylium ion is stabilized by the adjacent oxygen. Deactivated systems such as nitrobenzene will not react.

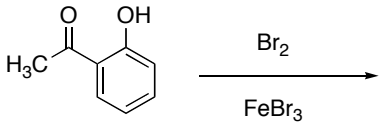
   Draw a mechanism and predict the major product for the following reaction:

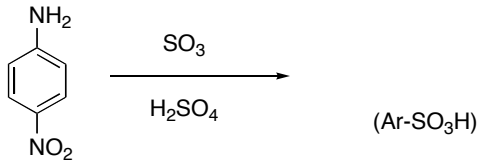


3. Predict the major product for the following reactions, keeping in mind that regioselectivity will most significantly be determined by strongly activating ortho, para-directing groups, and will only be directed by meta-directing groups if it does not conflict with the directing effects of other groups.









4. Predict the best conditions to make the following compounds from the given starting materials. Some may take more than one step.