



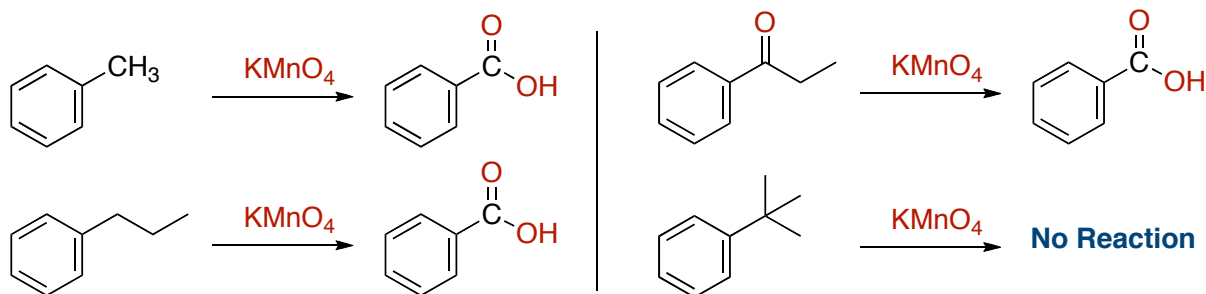
# Chem 342 • Organic Chemistry II

Lecture Summary 13 - 18 Feb 2009

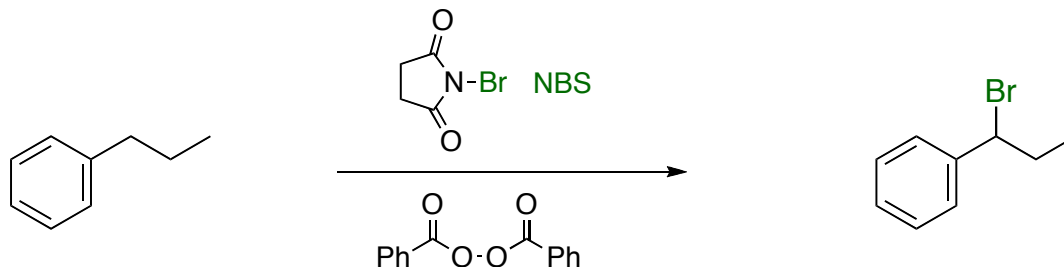
## Chapter 16 - Chemistry of Benzene: Electrophilic Aromatic Substitution

### Oxidation of Substituents

Benzene rings are inert to oxidation, but alkyl groups attached to the benzene ring can be readily oxidized to benzoic acids upon treatment with potassium permanganate. This only occurs if there are benzylic hydrogens (or oxygen, e.g. ketone).

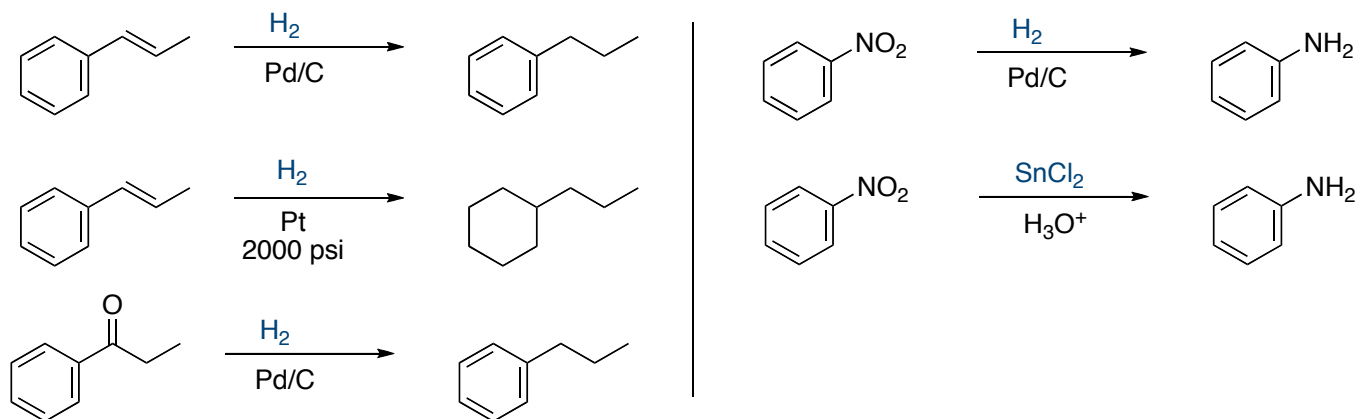


Benzylic bromination occurs just like allylic bromination of alkenes. Bromination under these radical conditions occurs in the benzylic position because this is the most stable radical.



### Reduction of Substituents

Under normal hydrogenation conditions, benzene rings are not reduced. This requires more forcing conditions and more reactive catalysts. Functional groups attached can be reduced (e.g. alkenes, nitro groups, ketones). This allows you to make products that cannot be obtained by Friedel-Crafts alkylations.



## Synthesis Strategies

In order to think about multi-step synthesis, it is useful to carry out a Retrosynthetic Analysis of the route.

Work backwards from the target molecule to the starting material  
Determine if each step is reasonable.

For synthesis dealing with Aromatic Rings, it is useful to keep in mind several things.

Which groups can be directly added to the ring

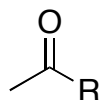
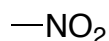
Which groups must be made by modification of other substituents

Activators, deactivators - o,p- or m- directors

For alkyl groups it is often best to do FC-Acylation followed by reduction

### Aromatic Functionalization Chart

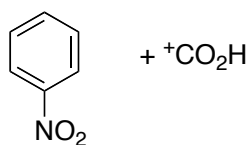
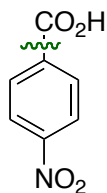
#### Substituents we can add directly



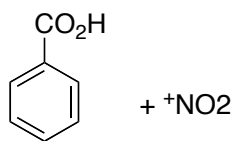
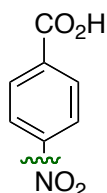
#### Substituent Modifications



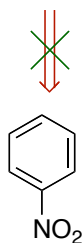
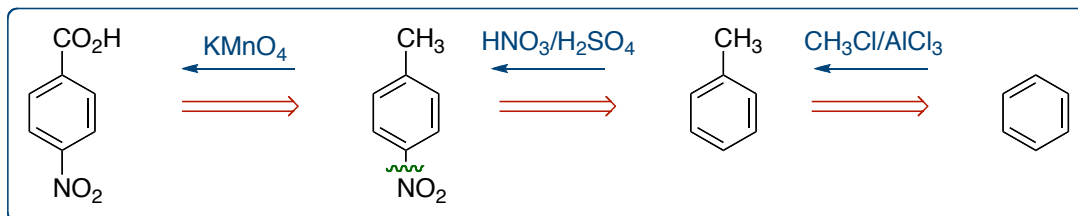
### Retrosynthetic Analysis for how to synthesize p-nitrobenzoic acid



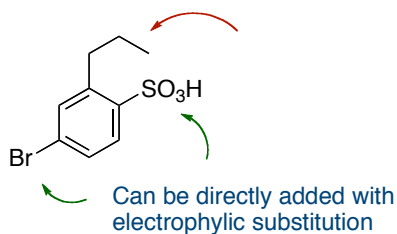
**Not Possible** - no way to add carboxylic acid directly.  
Also,  $\text{NO}_2$  is a meta-director, so anything you add would be in the wrong place.



**Not Possible** - you can add  $\text{NO}_2$  with  $\text{HNO}_3/\text{H}_2\text{SO}_4$ , but the  $\text{CO}_2\text{H}$  group would be a meta director.



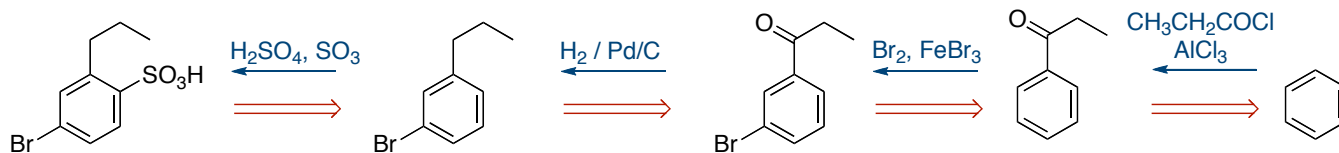
**Not Possible** -  $\text{NO}_2$  is a meta-director



**Steps needed to incorporate functional groups:**

Br<sub>2</sub>, FeBr<sub>3</sub>  
 H<sub>2</sub>SO<sub>4</sub>, SO<sub>3</sub>  
 CH<sub>3</sub>CH<sub>2</sub>COCl, AlCl<sub>3</sub>  
 H<sub>2</sub> / Pd/C (to reduce ketone to alkane)

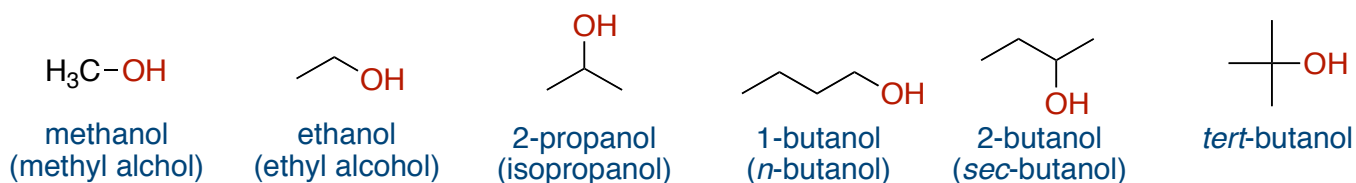
**Retrosynthesis that would work for every step**



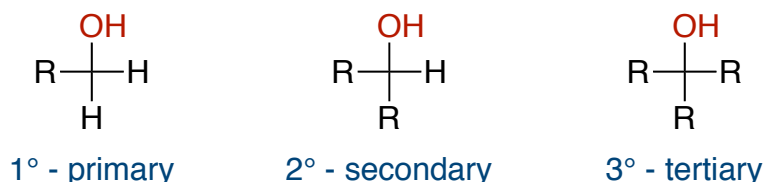
**Chapter 17 - Alcohols and Phenols**

**Naming**

Alcohols are generally named by dropping the e, and adding ol. If required, the position of the OH group is given by numbering either before the name, or in the middle of the name. There are several common names that are used for alcohols.



Alcohols are classified according to their degree of alkyl substitution.



**Properties of Alcohols**

Alcohols can be weakly acidic or weakly basic. The amount of solvent stabilization, inductive effects and resonance effects will influence the acidity of alcohols. Some pK<sub>a</sub> values for various alcohols are listed below. Notice the phenols are much more acidic than normal alcohols. This is due to resonance stabilization of the negative charged formed after deprotonation.

