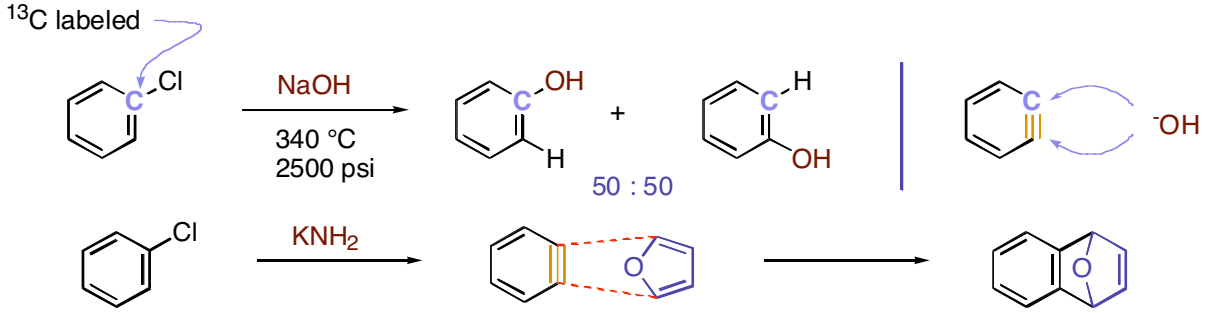
These notes can be obtained at: http://www.ndsu.nodak.edu/instruct/grcook/chem342/notes.shtml

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

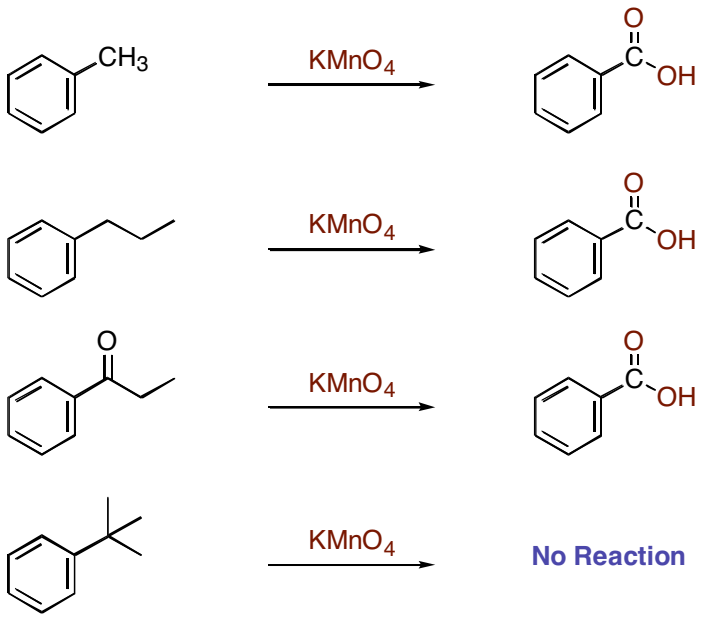
### Benzynes

The evidence for the presence of benzynes comes from the formation of two product in equal amount when the starting material is labeled. This suggests a symmetrical intermediate. Also, products of a Diels-Alder reaction indicate that there is a pi-bond in the intermediate.

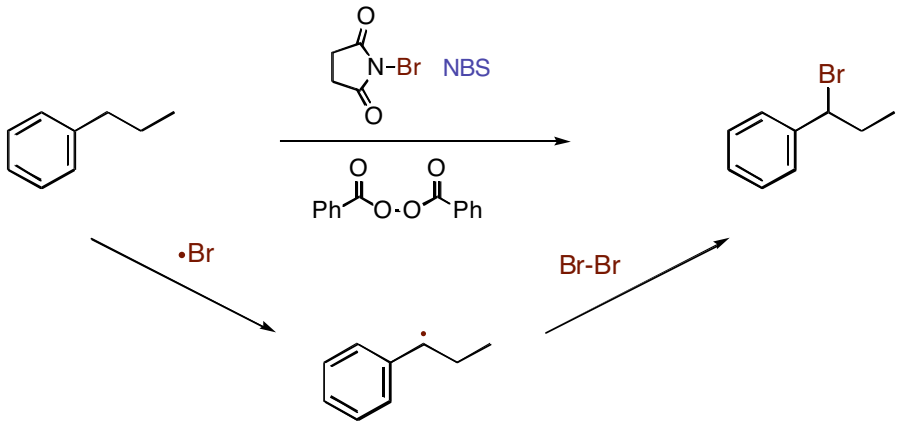



### Oxidation

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).

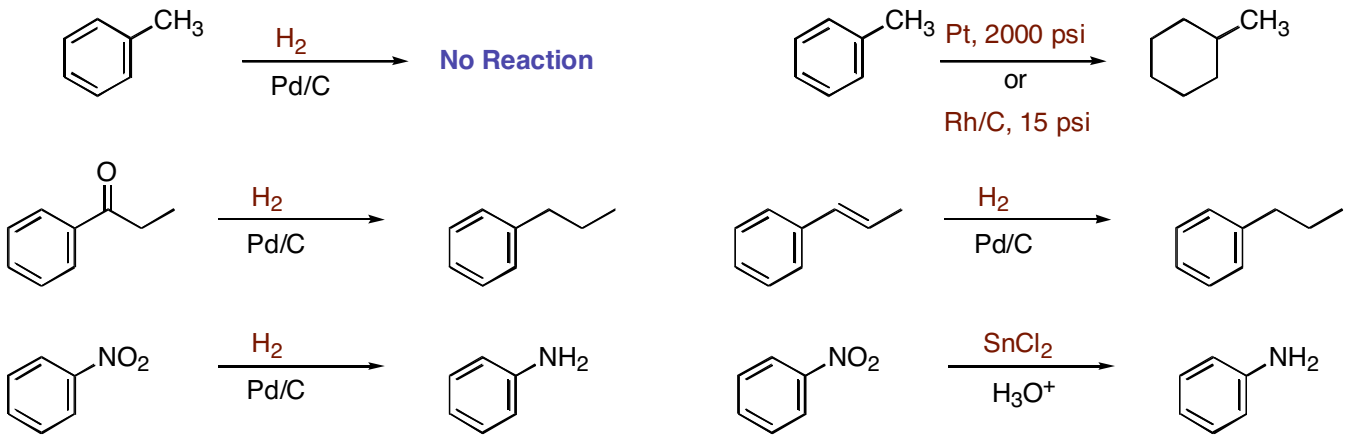


Benzylic bromination occurs just like allylic bromination of alkenes. Bromination under these radical conditions occurs in the benzylic position because this is the most stable radical.




## Reduction

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).




## Synthesis Strategies

When trying to think about multistep synthesis there are some strategies to keep in mind:

Work Backwards from the product to the starting materials.

Think about what reactions are reasonable and which are not.

Friedel-Crafts Acylation is usually better than Alkylation (carbocation rearrangement).

Benzoic acids can be made by oxidation of alkyl benzenes

Remember which groups are activators/deactivators, and which are o,p-directors and m-directors.