

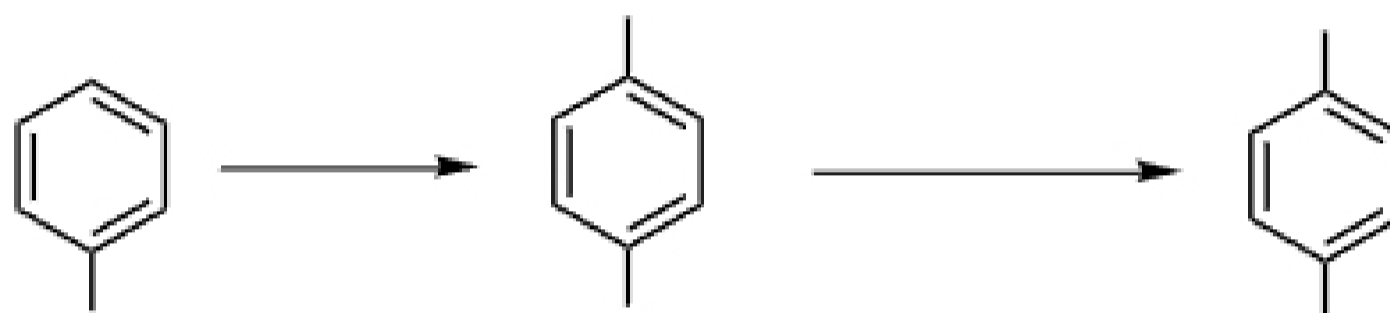
## Chapter 25a: Aromatic amines

**Suggested Problems:** 3, 4, 5, 6, 7, 8, 21, 27, 28 (Problems in bold face are HIGHLY recommended).

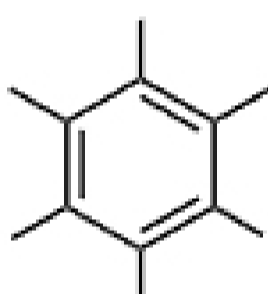
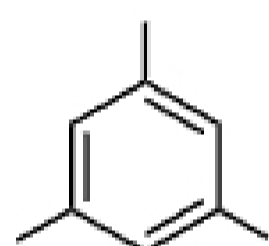
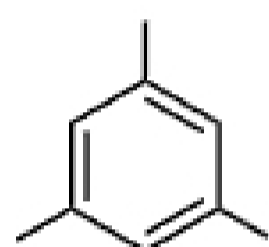
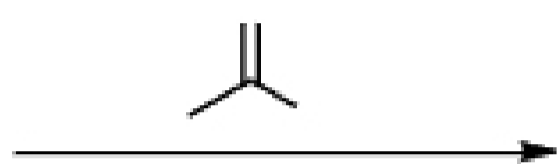
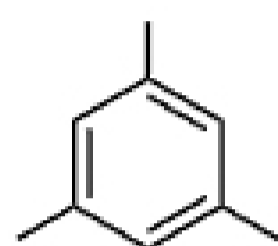
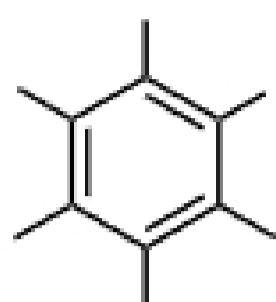
Aromatic amines are certainly related in their behavior to the aliphatic amines we have just discussed. However, because of the highly conjugated benzene rings attached to them, the lone pair on aromatic amines is far less “active” than the lone pair on aliphatic amines (you should be able to draw resonance structures showing the delocalization of the nitrogen lone pair over the ring). This means that they are less basic, and less nucleophilic. However, they are fantastic synthetic “handles” on a benzene ring, and thus quite useful synthetically.

### Preparation

There is basically one method commonly used to prepare aromatic amines, and you have already seen it. The reduction of aromatic nitro compounds (WHICH YOU SHOULD KNOW HOW TO PREPARE) leads to the aromatic amine under quite mild conditions. While there are a number of methods that *can* be used, the one I would remember is  $\text{SnCl}_2 / \text{HCl}$  followed by  $\text{NaOH}$  in water:



next section...



The next cool reaction you can do with aromatic amines is the **Sandmeyer**. This reaction is probably the neatest thing about aromatic compounds in general. The Sandmeyer proceeds in two stages. First, reaction with sodium nitrite to give the **diazo** compound. Basically, you're now looking at a benzene ring with nitrogen gas stuck onto it. Who could ask for a better leaving group? Next, you add your favorite nucleophile as a copper salt (for example, if you wanted to add bromide, you'd dump in some CuBr. If you wanted to add cyanide, dump in CuCN, etc). Warm that puppy up for a few minutes, and *voilà!* Instant substitution! First, a simpler example:

