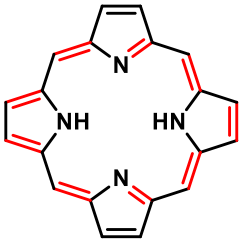
Homework 6 – 2017/05/08

1) a) Compound **I** (= a porphyrin) is an aromatic compound. Explain why.

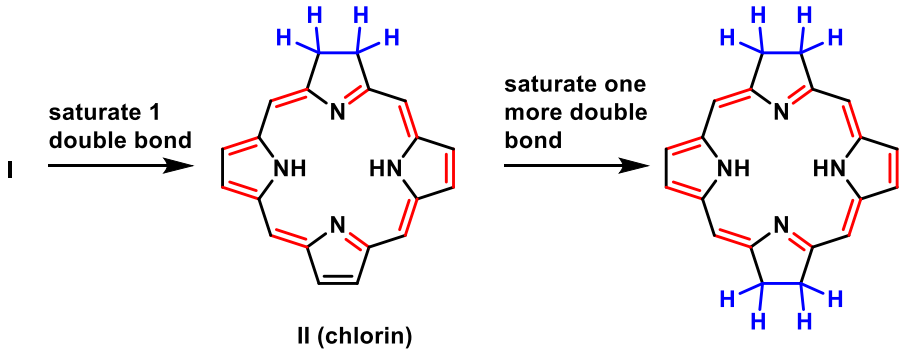
b) Take away first one (**II**), then a second (**II**) double bond (i.e. replace a CH=CH unit with CH_2-CH_2) while retaining the aromaticity! Explain why **II** and **III** are aromatic!



1) all the carbon atoms are sp^2 - full conjugation
2) cyclic
3) 18 π-electrons, which is 4n + 2 (n = 4)

The figure also tells you that the double bonds left in black are not needed for the aromaticity. These you can saturate to get II and III, which still retain the cyclic, conjugated 18 π-electron system.

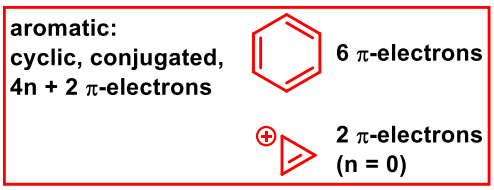
I (porphyrin)
its metal complexes are found in a lot of enzymes. it is also the core of heme

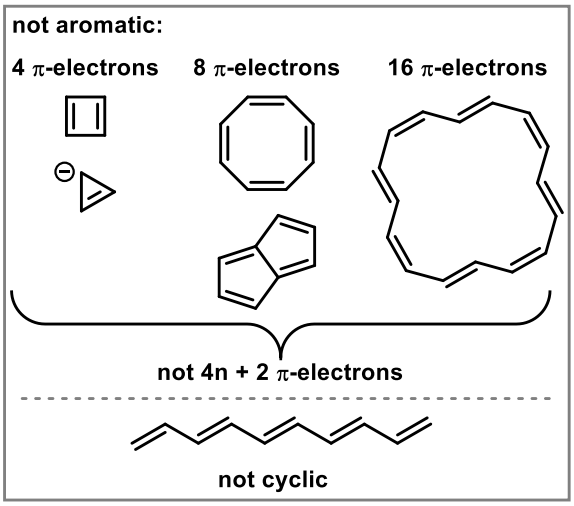


II (chlorin)
the core structure of the chlorophylls, which are responsible for most photosynthetic light harvesting on Earth

III (bacteriochlorin)

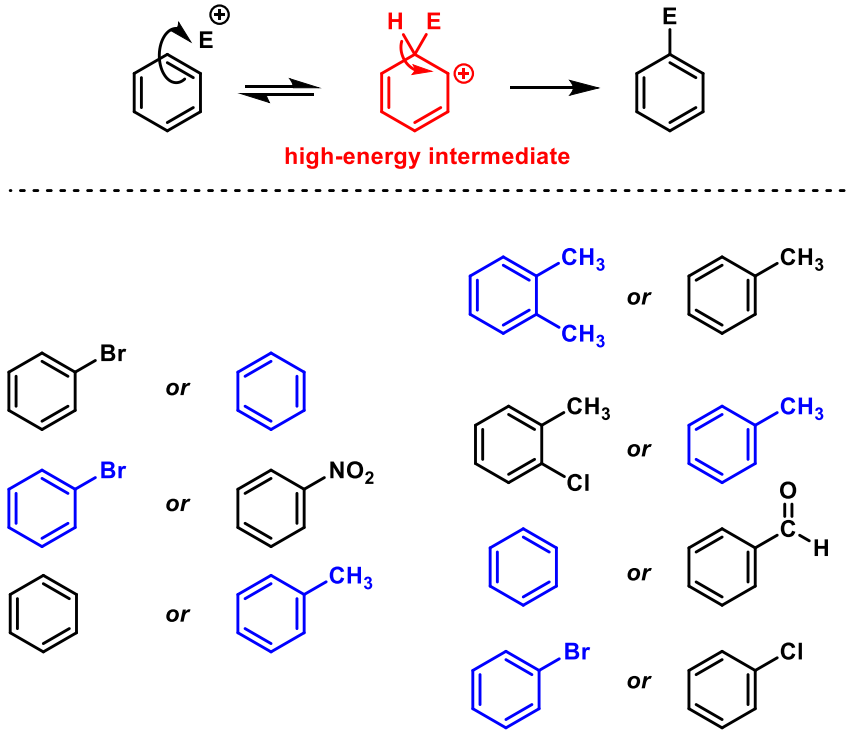
2) Which ones are aromatic, and why?



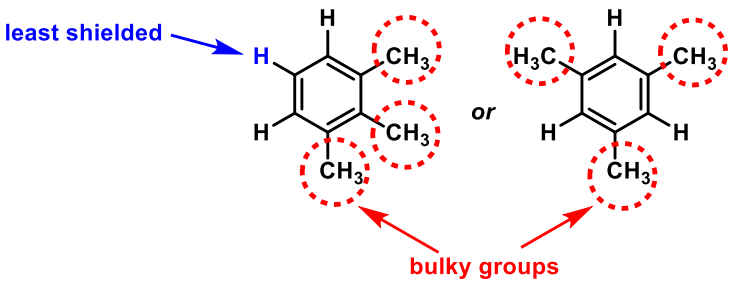


3) Which one of the pairs would you expect to react faster in an electrophilic aromatic substitution, and why?

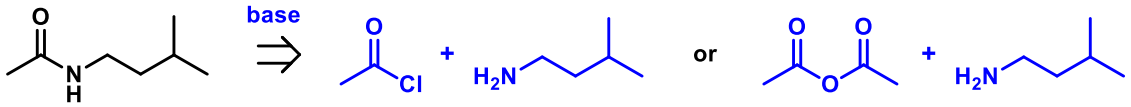
The reaction goes through a high-energy, positively charged intermediate (see below). Electron-withdrawing substituents will slow down the formation of this, while electron-donating ones will make it better. In each pair, the more electron-rich will react faster (marked in **blue**).



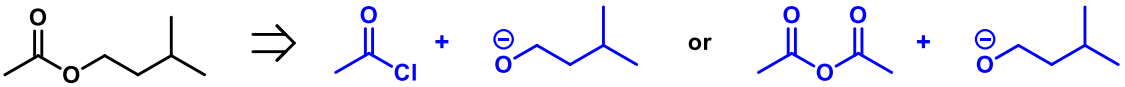
For the pair below, you have the same number of the same substituents (electron-donating alkyl groups). In this case, steric effects will decide. The compound to the right has three substitutable C-H atoms that are all flanked by two methyl groups each, all of them are quite hindered. The compound to the left has three C-H's, two of which have one H neighbor and one CH_3, while the third one (see arrow) only has two hydrogen neighbors, and is thus the least sterically shielded of them all. So the compound to the left will react faster.



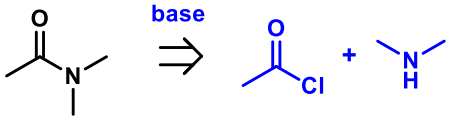
4) Suggest starting materials and reaction conditions for the synthesis of these compounds:

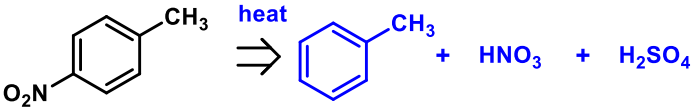


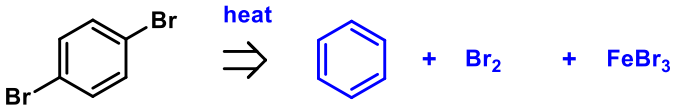
give at least two different solutions

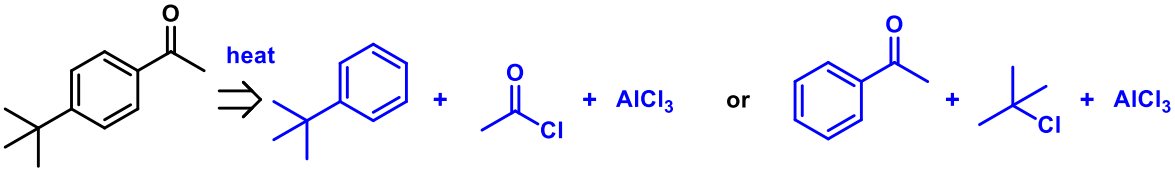


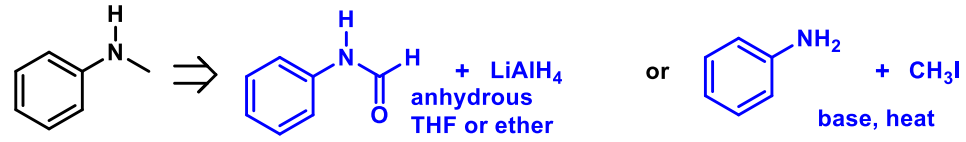
give at least two different solutions



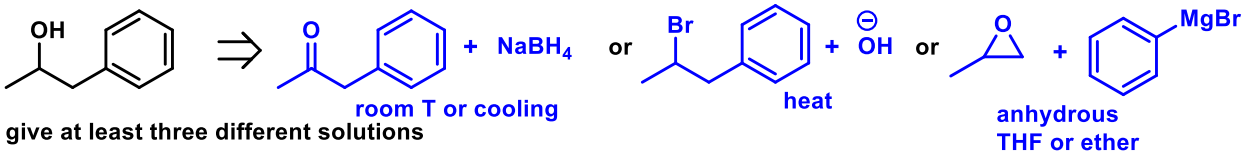




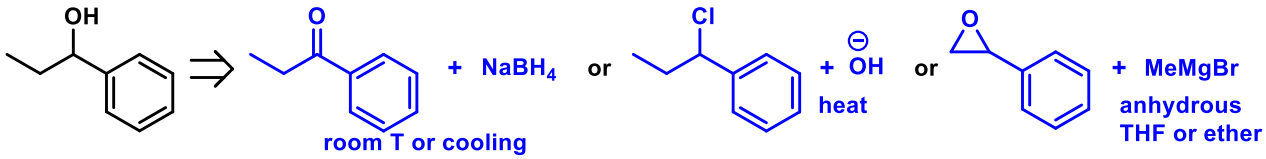




give at least two different solutions



give at least three different solutions



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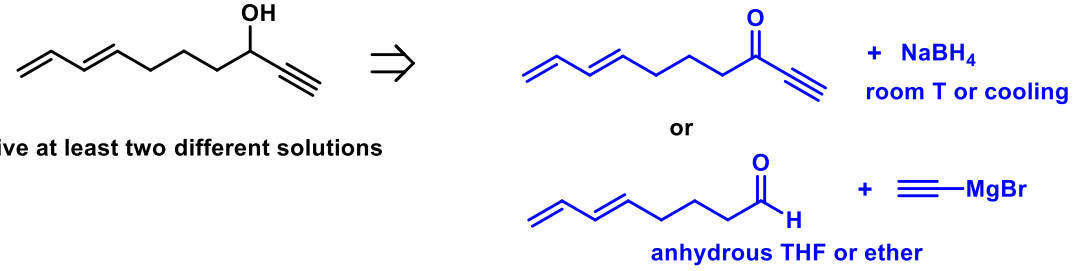

give at least two different solutions