Lecture 15: Electrophilic Aromatic Substitution Part 2

Discussion Section Problems Solutions

1. (a) The ester group is large enough to cause the para isomer to be formed in greater amount than the ortho isomer.

(b) To determine which reaction is faster, compare the rate-determining steps of the two reactions. For any EAS mechanism, the rds is the step in which the aromatic ring is attacked by the electrophile and aromaticity is lost. In this case, the only difference between the reactants is the presence of a hydroxyl (OH, which makes this molecule a phenol) or an ester group. How does this affect the rds? Recall that a more stable carbocation is formed more quickly. How do the hydroxyl and ester groups affect the carbocation stability? Both arenium ions have four significant resonance contributors, but the ester oxygen lone pairs are not as readily available to stabilize the carbocation as the hydroxyl oxygen lone pairs because the ester oxygen lone pairs are delocalized by resonance with the ester carbonyl:
The arenium ion of reaction (i) is more stable, and thus reaction (i) is faster.

(c) A wide variety of changes can be made. Extending the idea from part (b), any structural change that further reduces the availability of the ester oxygen lone pairs will decrease the stability of the arenium ion and hence decrease the reaction rate. Replacement of the ester methyl group (weak electron donating group) with a trifluoromethyl group (powerful electron withdrawing group) decreases the availability of the ester oxygen lone pairs due to an inductive effect.

Consider arenium ion stability plus steric effects.
(f) The answer depends upon how the benzene ring and ester are bonded. When the benzene ring is bonded to the oxygen atom of the ester, the ester is an ortho/para director (because this oxygen has two lone pairs):

When the benzene ring is bonded to the ester's carbonyl group the ester is a meta director:

3. The choice of major product is based on the assumption that a benzene ring offers more steric hindrance than a methoxy group.

4. Remember that Ph = phenyl = C₆H₅ = monosubstituted benzene ring.
The NH$_2$ and CH$_3$ (electron-donating) substituents of 4-methylaniline give its benzene ring enough nucleophilicity so that it can react with Br$_2$ in the absence of a Lewis acid catalyst such as FeBr$_3$. The reactivity is also enhanced by the increased stability imparted to the arenium ion by the NH$_2$ and CH$_3$ groups.

Potassium carbonate is a weak base that is necessary to convert all of the amine to the ammonium salt. (Work out the mechanism to see how this happens.) Other weak bases could also be used.

Bromination must be conducted before alkylation because the R$_3$N$^+$ substituent is a meta directing group. When there are multiple directing groups on the benzene ring, the strongest electron donor dominates. (In this case a methyl group is a stronger electron donor than an ammonium group, which is not an electron donor at all! For more on this concept read the EAS chapter in OCATSA.)