1) Give the major products of each of the following reactions. If a mixture is expected, identify the major product.

a) \[
\text{C}_{6}H_{5} + \text{H}_{2}
\underbrace{\text{C} = \text{C} - \text{CH}_{3}}_{\text{H}_{2}\text{SO}_{4}} \rightarrow \]

Protonation of the alkene in the normal fashion yields the more stable 2° carbocation, which is the active electrophile, and undergoes Friedel-Crafts-like chemistry to yield:

b) \[
\text{C}_{6}H_{5}^{+} + \text{HNO}_{3} \rightarrow \text{C}_{6}H_{4}^{+} + \text{NO}_{2} \]  

Here is an example of where directing effects do not work perfectly. Both alkyl groups direct ortho, para; there is a position ortho to both groups BUT it is horribly hindered sterically. We can see a position ortho to one and para to the other, and that seems to be the best option. Here’s the structure:
It might be a tougher reaction, since the chlorobenzene ring is deactivated, but chlorine is a halogen, and that is ortho, para directing, so the product is:

Here we get a mixture. The –OH group is ortho, para directing, activating, and the aryl group, despite being deactivated itself, is still ortho, para directing. Therefore, we get two isomeric acetylated products on the hydroxyphenyl ring, compounds A and B, with B edging out A as the major product for steric reasons.
2) Propose a synthesis for the preparation of the following compound from benzene and any other necessary reagents. You should be able to complete the synthesis in five steps.

I feel like “Name that Tune!” since I think I can do it in four steps! Anyway, we did something like this on the last problem set, so it might look a bit familiar. Here is the scheme:
3) Provide a reasonable mechanism to account for the formation of both \textit{p}-ethyl- and \textit{m}-ethylaniline in the following reaction:

Even though \(\text{NH}_2^+\) is a good nucleophile, this is not aromatic nucleophilic substitution, as there is no activating group on the ring. (Remember, the deactivating groups for electrophilic aromatic substitution are the activating groups for nucleophilic aromatic substitution!) We must have a benzyne intermediate. Here is the mechanism:
4) Benzene and alkyl-substituted benzenes can be hydroxylated by reaction with H₂O₂ in the presence of an acidic catalyst. What is the structure of the reactive electrophile? Propose a mechanism for the reaction.

Well, the active electrophile would have to be HO⁺, formed by the action of trifluoromethanesulfonic acid (a strong acid) on peroxide to yield HO-ÖH₂⁺, which then loses water to yield the HO⁺ ion. The full mechanism is, therefore:
5) Furan is readily acetylated on treatment with acetic anhydride and a Lewis acid, such as BF$_3$. Predict the major regioisomer produced in this reaction and justify your reasoning.

![Reaction Diagram]

The active electrophile is the CH$_3$CO$^+$ acylium ion, just like in the AlCl$_3$ catalyzed case. Addition at either the 2 or the 3 positions yields a resonance-stabilized cation, so that’s not the complete answer. Perhaps we should examine these cations more closely.

Attack at the 2 position yields a cation which has three resonance forms, as shown:

![Resonance Forms]

Attack at the 3 position yields a cation which has two resonance forms, as shown:
The cation which has three resonance forms beats the cation with only two resonance forms, so attack at the 2 position is favored.

6) Provide reasonable synthetic sequences for the preparation of the following azo compounds from aniline and any other necessary reagents:

From the hint of using aniline, and the fact that all are azo compounds, many start out with:

Call the diazonium cation formed above A.

a)
Here we are a little different.
7) An alternative method for generating benzyne involves the treatment of 1,2-dihalosubstituted benzenes with an active metal, usually magnesium:

Propose a structure for the product formed when 4-bromo-3-fluorotoluene is treated with magnesium metal in the presence of phenanthrene (shown below):
A simple Friedel-Crafts reaction with phenanthrene at the so-called 9,10 positions to yield tryptacene.

8) The Friedel-Crafts alkylation of toluene with \( \text{CH}_3\text{COCl}/\text{AlCl}_3 \) gives a high yield of the expected ketone product. However, aniline fails to react under these conditions despite the fact that the \( \text{NH}_2 \) group is a much more powerful activating group than \( \text{CH}_3 \). Explain.

The \( \text{NH}_2 \) group is also a better nucleophile than a methyl group, and the competing reaction is formation of acetanilide, shown: