1. Complete 5 out of the 6 following reactions, showing the main organic products. Cross one out or graded in order.

(a) Friedel-Crafts Acylation, CH₃ is o,p director

(b) benzylic substitution

(c) reaction thru benzyne intermediate

(d) Nucleophilic Aromatic Substitution

(e) o,p directed electrophilic aromatic substitution.

(f) meta directed, EAS
2. Fill in the proper reagents A- F

\[
\begin{align*}
&\text{A} \quad \text{Br}_2, \text{FeBr}_3 \\
&\text{B} \quad \text{HNO}_3/\text{H}_2\text{SO}_4 \\
&\text{C} \quad \text{Na}^+\text{CH}_3\text{O}^- \\
&\text{D} \quad \text{Cl}^-\text{CH}_3\text{O}^-\text{AlCl}_3 \\
&\text{E} \quad \text{H}_2\text{Pt} \\
&\text{F} \quad \text{KMnO}_4
\end{align*}
\]

3. In the following reaction of chlorobenzene with nitric/sulfuric acid, complete the resonance structures below with the correct bonds. Then answer the questions underneath.

(a) Why is the sulfuric acid necessary? Nitric acid is already acidic, isn’t it? (Note: pKa (Nitric Acid) = -1.5, pKa (Sulfuric Acid) = -10).

(b) What is the reactive electrophile in the above reaction? NO$_2^+$, nitronium ion.

(c) If we used only pure (fuming) sulfuric acid, what would be the product(s)? mostly sulfonation of Cl benzene, both o and p, because SO$_3$H$^+$ becomes the superelectrophile and there is not as much protons for the dehydration of nitric acid.

(d) Chlorine is o,p directing group but chlorobenzene is slower to react with nitric/sulfuric acid than benzene is. Why? Chlorine is o,p directing because of resonance. Note the bonus structure above. 4 resonance structures vs 3 for meta subst. Chlorine is EWG through sigma bonds because of its high electronegativity. Chloro-substituted benzene has less electron density to donate towards the NO$_2^+$ group.
4. Starting with toluene, design syntheses, providing the correct reagents for the following transformations. Both processes can be accomplished with 2 steps, but there is more than one correct answer for each. Assume that ortho and para isomers can be separated.

\[
\text{Toluene is reacted with } \text{KMnO}_4 \text{ to make benzoic acid. Benzoic acid is then brominated, Br}_2, \text{FeBr}_3 \text{ to give meta-bromobenzoic acid. Carboxylic acids are EWG.}
\]

\[
\text{Toluene is first brominated with Br}_2, \text{FeBr}_3. \text{ Then KMnO}_4 \text{ turns the methyl group into a carboxylic acid. This is the only way to make para substitution, because Br is o,p director.}
\]

5. Assign the NMR spectrum below to the molecule with the formula C₈H₈O₂ that reacts with nitric/sulfuric acid to make the meta product. Draw arrows to peaks. This is the reactant not the product. IR peak near 1700 cm⁻¹, 1620 cm⁻¹ and C-H sp²

Molecule is single substituted benzene (5H) with a C=O (1700 cm⁻¹ IR peak) and EWG-meta director.
6. Draw the following alcohols:

(S)-2-butanol  allyl alcohol  isobutyl alcohol

7. Rank the order of acidity from 1 most acidic → 3 least acidic.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol</td>
<td>methyl alcohol</td>
<td>isopropyl alcohol</td>
<td></td>
</tr>
<tr>
<td>phenol</td>
<td>p-methylphenol</td>
<td>p-chlorophenol</td>
<td></td>
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</tbody>
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8. Write the reagent that you would use to reduce the following carbonyl compounds over the arrow. Predict the product.

9. Write reagents over the arrows for these transformations:

10. What would be the product of

(a) 1-propanol + PBr₃ →
(b) cyclohexanol + POCl₃ →
(c) (S)-2-butanol + TosCl/pyridine followed by NaBr in DMF?
(d) 1-propanol + Jones Reagent (CrO₃-H₂SO₄) →
(e) 1-propanol + PCC →

11. Predict the products of the reaction of Phenyl MgBr with the carbonyl compounds below (assume acid workup):

12. The alcohol in 11.c would cause trouble. Why?
How could we get around this problem?
12. The problem is the alcohol will react with Grignard to make benzene and alkoxide.

\[
R\text{-OH} + R\text{-MgBr} \rightleftharpoons R\text{-O}^- + R\text{-H}
\]

\[
p\text{Ka} \quad 16 \quad 45 \quad \text{Keq} = 10^{30}
\]

The solution is to protect the alcohol, perform the Grignard and then deprotect.