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CHEM 346 AB

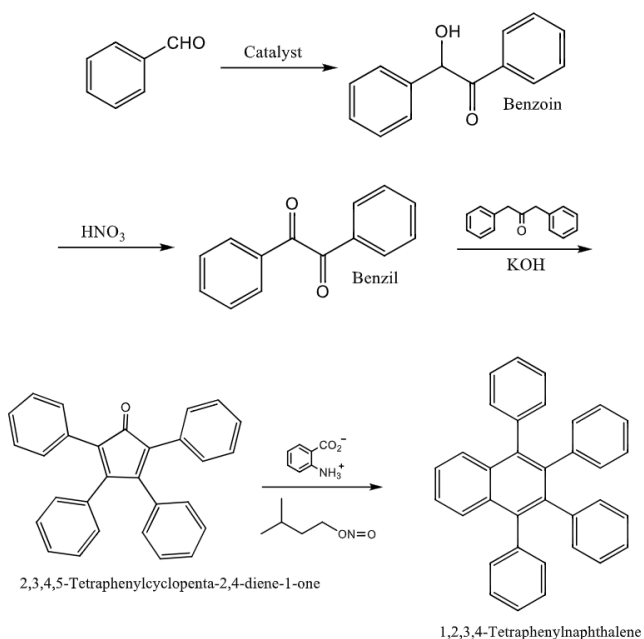
6 March 2021

Multistep Synthesis Lab Report

I. Purpose

The purpose of this lab was to use many of the techniques and reactions that we have learned this quarter to prepare at least a few milligrams of 1,2,3,4-tetraphenylnaphthalene through a 4-step synthesis.

General Reaction



(Multistep Synthesis Lab Manual, pg.1)

II. Experimental Approach

1,2,3,4-tetraphenylnaphthalene was synthesized through four steps. First, benzoin was synthesized from benzaldehyde with a thiamine catalyst (Lab Manual, pg. 2). Second, nitric acid oxidation of benzoin produced benzil, and TLC was used to monitor the reaction for completion. In the third and fourth steps, benzil, dibenzyl ketone, and potassium hydroxide were reacted to

form tetraphenylcyclopentadienone, which was reacted with benzyne (produced from the reaction of isopentyl nitrite and anthranilic acid) to form the final product. To confirm the correct compounds were synthesized, nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), and melting point data were used.

III. Summary of Findings

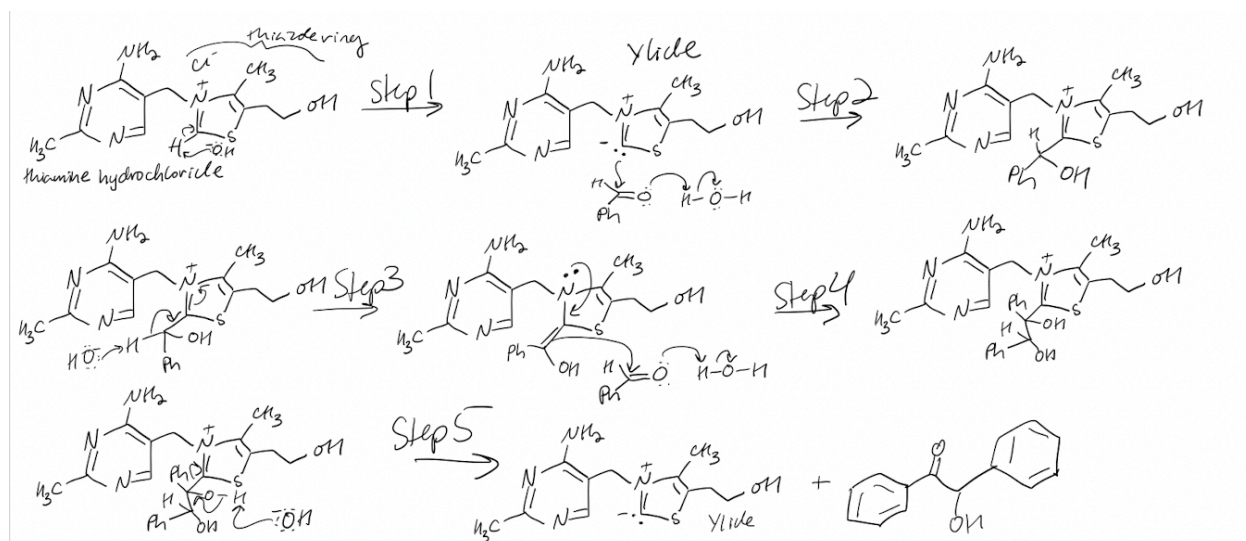
The experiment was successful in its purpose of preparing at least a few milligrams of 1,2,3,4-tetraphenylnaphthalene, as it yielded 3.652g of it with an overall percent yield of 34.49%. In the first step, the correct compound of benzoin was synthesized, which was indicated by the melting point of 132.4-135.7°C, the NMR peak at about 5.9ppm, and the MS peaks at m/z 107 and 79 (which indicate a hydroxy group in the benzylic position). The second step also produced the correct compound (benzil), indicated by the boiling point of 86.4-89.6°C, the NMR peaks at around 7.9, 7.4-7.5, and 7.6 ppm, and the MS peak at m/z 105. The third step produced tetraphenylcyclopentadienone, as the product had a melting point of 216.5-219.8°C, two NMR peaks at about 6.9 ppm and 7.2 ppm, and a base peak representing the molecular ion at m/z 384. Lastly, the final product of 1,2,3,4-tetraphenylnaphthalene was successfully formed, indicated by the melting point of 185-189°C and the MS parent peak representing the molecular ion at m/z 432.

IV. Data and Analysis

Step	Product	Melting Point (°C)	Mass (g)	% yield
1	benzoin	132.4-135.7	5.351	103%
2	benzil	86.4-89.6	2.887	54.45%
3	tetraphenylcyclopentadienone	216.5-219.8	4.410	83.54%
4	1,2,3,4-tetraphenylnaphthalene	185-189	3.652	73.61%

Step One: Coenzyme synthesis of benzoin from benzaldehyde

Mechanism:



(Pavia et. al)

The NMR and MS spectra of the product both indicate that benzoin was indeed formed from this synthesis step. On the NMR spectrum, the peak at around 7.9 ppm with a relative integration of 2.001 corresponds to the two benzene ring hydrogen atoms closest to the ketone group and is the most downshifted peak due to the proximity to the electronegative oxygen atom. The peaks around 7.2-7.5 ppm correspond to the other 8 hydrogen atoms on the two benzene rings (since benzene ring hydrogens usually have peaks around 6.0-9.5 ppm). The peak at 4.5 ppm with a relative integration of 1.039 corresponds to the hydrogen in the -OH group, and the peak at 5.95 ppm with a relative integration of 1.171 corresponds to the hydrogen bonded to the carbon bearing the -OH group. Although hydrogens on carbon atoms bearing -OH groups usually absorb in the region between 3-4 ppm, this peak is downshifted due to the electron-withdrawing ketone oxygen on the adjacent carbon.

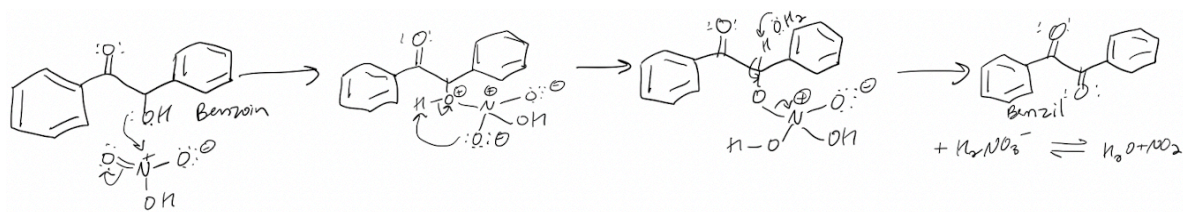
There was also an extra peak at 2.165 ppm (relative integration of 7.531). This peak comes from acetone, which is a common solvent used for cleaning glassware. It is possible that the glassware was not dried properly, leading to the extra peak.

The mass spectra contained 5 prominent peaks. Cleavage of the bond between the carbonyl carbon and the carbon bearing the hydroxy group produced two of those peaks. The base peak at m/z 105 represents a resulting resonance-stabilized acylium ion and the peak at m/z 107 corresponds to the other possible resonance-stabilized cation fragment from this cleavage. The peak at m/z 77 corresponds to the phenyl cation that is formed when monosubstituted benzenes (like those in benzoin) lose a pi electron and then their substituent. The peak at m/z 51 is also common with monosubstituted benzenes, and the fragment at m/z 79 can be formed through the fragmentation of a benzylic alcohol (the hydroxy group is in the benzylic position in benzoin).

The melting point of the product at 132.4-135.7°C also supports that benzoin was formed, as the literature value of the melting point of benzoin is 134-138°C (PubChem). The melting point was slightly depressed, indicating impurities in the product. This could have been from several different sources: some catalyst from the reaction could have been present in the product, or it is possible that not all of the ethanol was filtered off. These impurities also led to a percent yield of 103%. The impurities could have added extra mass to the product, leading to a percent yield over 100%.

Step Two: Nitric acid oxidation of benzoin to benzil

Mechanism:



(Graham et. al)

The NMR spectrum for the product indicates that the second step did in fact produce benzil. The peak around 7.9 ppm corresponds to the benzene hydrogens closest to the ketone oxygen atoms (which are electron-withdrawing and therefore deshield the protons). The peak at 7.6 ppm corresponds to the benzene hydrogens that are farthest from the substituent on the ring, and the peak around 7.4-7.5 ppm corresponds to the remaining benzene hydrogens. This is supported by the relative integrations as well. The peak at 7.6 ppm has a relative integration of 1.000, indicating that it represents two hydrogens on the molecule while the peaks at 7.4-7.5 ppm and 7.9 ppm both have relative integrations of around 2, indicating 4 hydrogens for each peak. The NMR spectrum only gave three distinct peaks for the 10 hydrogens because of the molecule's symmetry and the identical chemical environments of certain protons on the molecule. There was also a small extra peak at 7.260 ppm, which could correspond to a small amount of unreacted benzoin in the product, since the benzoin NMR spectrum had a peak around 7.2ppm and largely overlaps with the peaks on this spectrum.

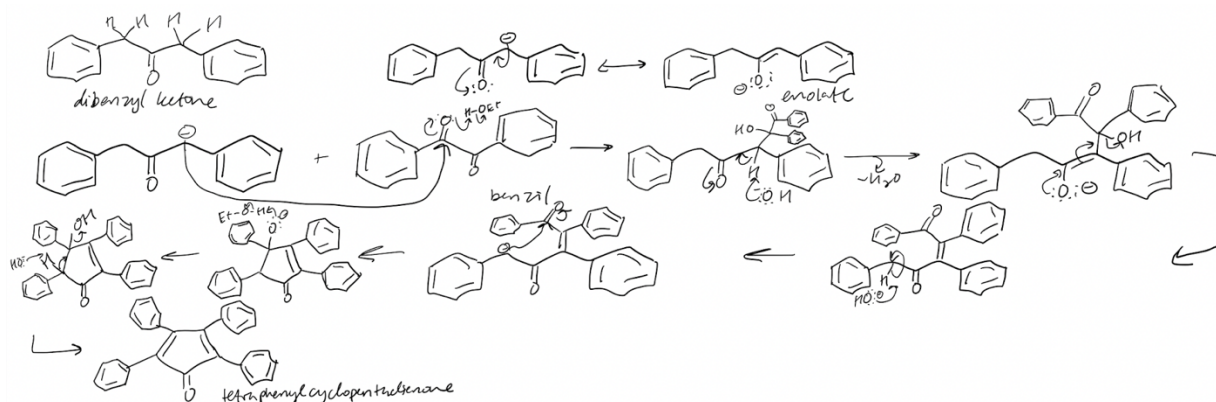
The mass spectrum has three distinct peaks, all of which are indicative of benzil. The base peak at m/z 105 corresponds to a resonance-stabilized acylium ion that can be formed by the cleavage between the two carbonyl carbons. The peaks at m/z 51 and 77 are both common for monosubstituted benzene rings, with the peak at m/z 77 formed by the cleavage of the benzene ring from the substituent (in this case the carbonyl groups with the other benzene ring in benzil).

The melting point of the product, 86.4-89.6°C, also indicates that the product is benzil (lit. value of 94.8°C) (PubChem). This significant melting point depression also supports the presence of the benzoin impurity shown in the NMR spectrum.

The percent yield of the reaction was 54.45%. This could be due to the recrystallization step and could possibly be improved by ensuring that too much ethanol is not added, since too much solvent can decrease the amount of crystal formation that takes place.

Step Three: Synthesis of tetraphenylcyclopentadienone

Mechanism:



(CHEM 346 lectures with Dr. Dustin Maly, University of Washington)

The NMR spectrum indicates that tetraphenylcyclopentadienone was formed in the third step. The peak at about 6.9 ppm corresponds to the four benzene hydrogens closest to the ketone oxygen, and the peaks from 7.136-7.228 ppm correspond to the other benzene hydrogens. On the spectrum, the relative integrations are 18.387 (7.136-7.228 ppm) and 4.606 (6.9 ppm). If these values are divided by 1.15, they give relative integrations of around 16 and 4, which fit the number of hydrogen atoms that correspond to the respective peaks. These peaks all fit in the range of chemical shifts for benzene hydrogens of 6.5-8ppm.

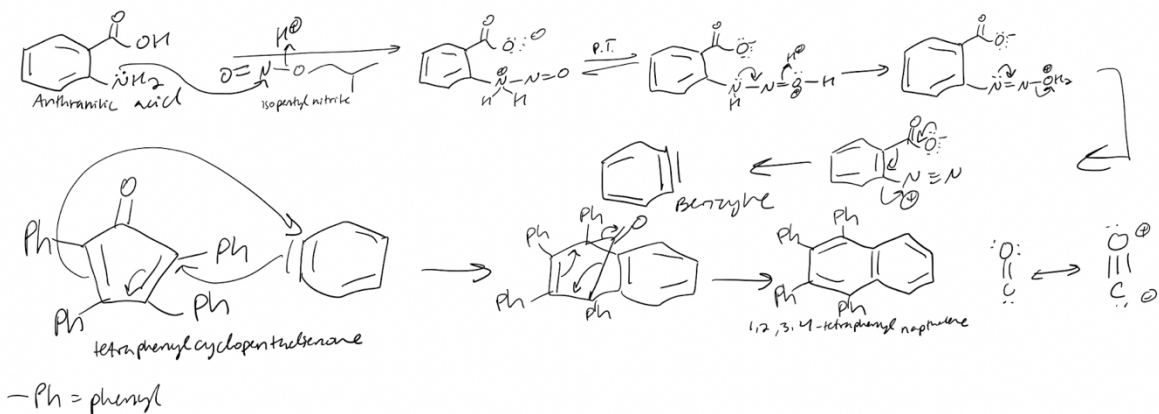
On the MS spectrum, the greatest peak is at m/z 384, which corresponds to the molecular ion of tetraphenylcyclopentadienone. The peak at m/z 356 results from the loss of carbon

monoxide from the molecule, leading to a four-membered radical cation ring with a double bond and four phenyl substituents. The peak at m/z 178 could result from further cleavage, effectively splitting that radical cation in half.

The product had a melting point of 216.5-219.8°C, which is significantly overlapping the literature value of 217-219°C for tetraphenylcyclopentadienone, indicating few impurities (ChemSpider). The NMR spectrum also indicates few impurities due to the lack of extra peaks. The percent yield of this reaction was fairly good at 83.54%.

Step Four: Preparation of 1,2,3,4-tetraphenylnaphthalene

Mechanism:



(from CHEM 346 lectures with Dr. Dustin Maly, University of Washington)

The NMR spectrum of the product indicates that the final product is 1,2,3,4-tetraphenylnaphthalene. The two peaks at around 7.0 ppm and 7.4 ppm, both with relative integrations around 10, correspond to the twenty hydrogen atoms on the phenyl substituents, and the peaks around 7.6 ppm and 7.8 ppm correspond to the hydrogens on the naphthalene portion of the molecule (each with a relative integration around 2). The spectrum contains extra peaks around 1.2ppm, 1.7ppm, and 4.3 ppm. These chemical shift values are consistent with literature spectra of 2-propanol, which usually has peaks around these areas (“SDBS-1H 2-propanol”).

The MS spectrum of the molecule contains two prominent peaks, the largest of which at m/z 432 corresponds to the molecular ion of the compound. The other, which is around m/z 77 corresponds to the fragment that is formed from the cleavage of the bond between the phenyl substituents and the naphthalene portion of the molecule.

The final product had a melting point of 185-189°C, compared to the literature value of 199-201°C (Sigma Aldrich). This significant melting point depression could be due to the 2-propanol impurities found in the NMR spectrum for the product and likely arose from the recrystallization from 2-propanol and insufficient drying. The percent yield of the fourth step was a reasonable 73.61%. The overall percent yield of the experiment was 34.49%.

Percent Yield Calculations

Step 1

$$\text{mol benzoil} = 5.351 \text{ g} \cdot \frac{1 \text{ mol}}{212.24 \text{ g}} = 0.02521 \text{ mol}$$

$$\% \text{ yield} = \frac{0.02521 \text{ mol}}{0.049 \text{ mol}} \cdot \frac{2 \text{ eq}}{1 \text{ eq}} \cdot 100\% = 103\%$$

Step 2

$$\text{mol benzil} = 2.887 \text{ g} \cdot \frac{1 \text{ mol}}{210.23 \text{ g}} = 0.01373 \text{ mol}$$

$$\% \text{ yield} = \frac{0.01373 \text{ mol}}{0.02521 \text{ mol}} \cdot \frac{1 \text{ eq}}{1 \text{ eq}} \cdot 100\% = 54.45\%$$

Step 3

$$\text{mol tetraphenylcyclopentadiene} = 4.410 \text{ g} \cdot \frac{1 \text{ mol}}{384.5 \text{ g}} = 0.01147 \text{ mol}$$

$$\% \text{ yield} = \frac{0.01147 \text{ mol}}{0.01373 \text{ mol}} \cdot \frac{1 \text{ eq}}{1 \text{ eq}} \cdot 100\% = 83.54\%$$

Step 4

$$\text{mol 1,2,3,4-tetraphenyl-naphthalene} = 3.652 \text{ g} \cdot \frac{1 \text{ mol}}{432.55 \text{ g}} = 0.008443 \text{ mol}$$

$$\% \text{ yield} = \frac{0.008443 \text{ mol}}{0.01147 \text{ mol}} \cdot \frac{1 \text{ eq}}{1 \text{ eq}} \cdot 100\% = 73.61\%$$

Overall percent yield

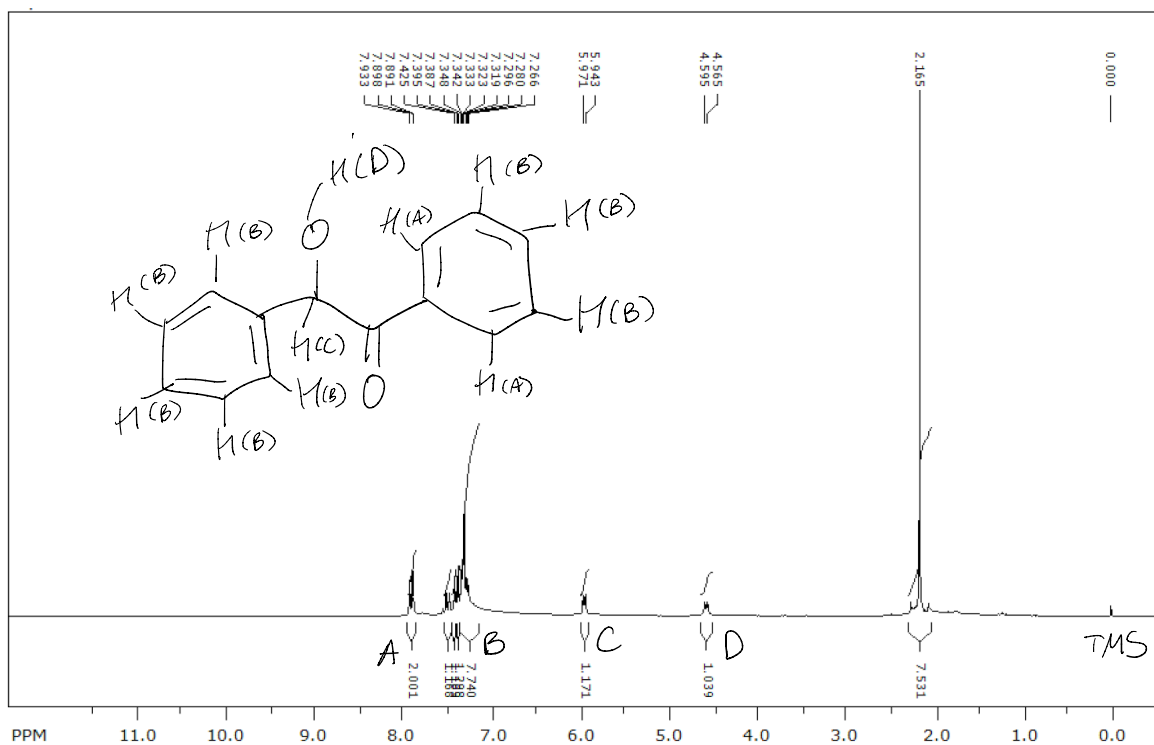
$$1.03 \times 0.5445 \times 0.8354 \times 0.7361 \times 100\% = 34.49\%$$

Part 1 – Benzoin Synthesis

Yield (g): 5.351

Melting Point (in degrees Celsius): 132.4 – 135.7

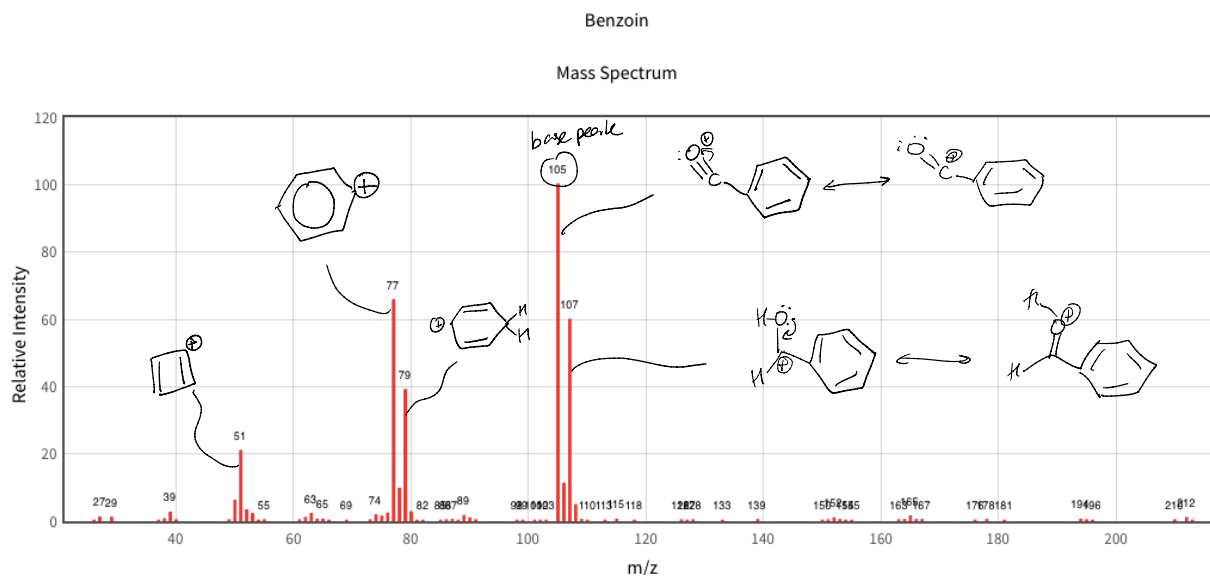
NMR:



file: ...\\Lab8_Benzoin_NicoleRoullier\1\fid exp: <zg>
transmitter freq.: 200.131201 MHz
time domain size: 32768 points
width: 2604.17 Hz = 13.0123 ppm = 0.079473 Hz/pt
number of scans: 8

freq. of 0 ppm: 200.130007 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 104.167 ppm/cm: 0.52049

Mass spectrum (from NIST database):

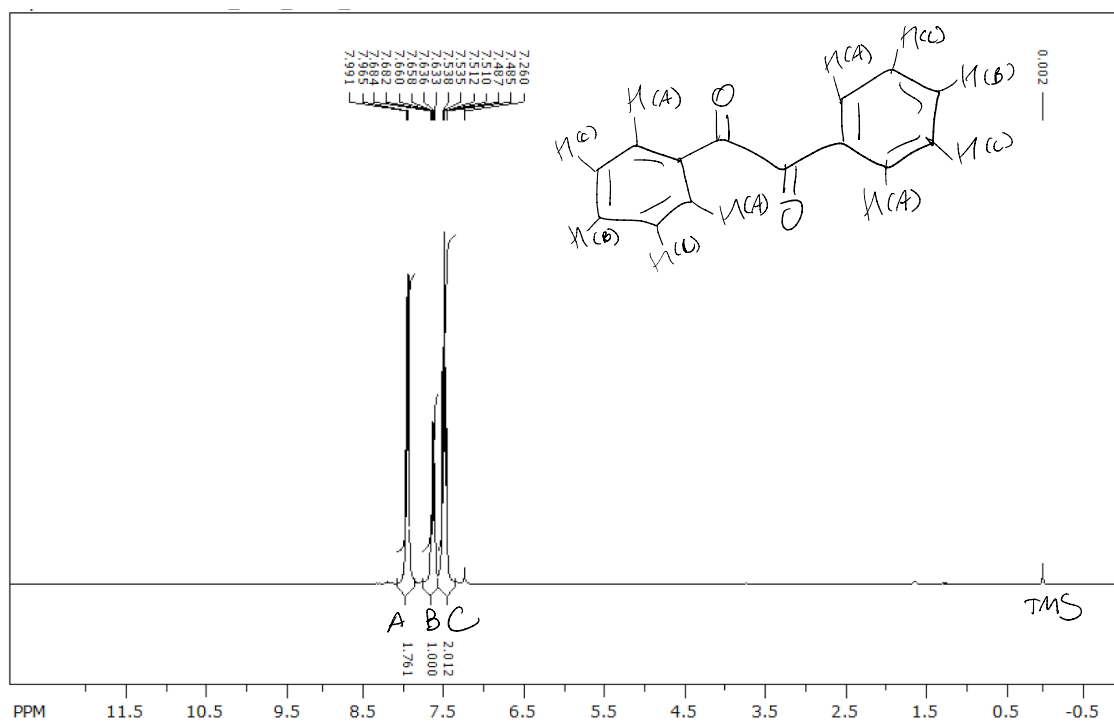


Part 2 – Benzil Synthesis

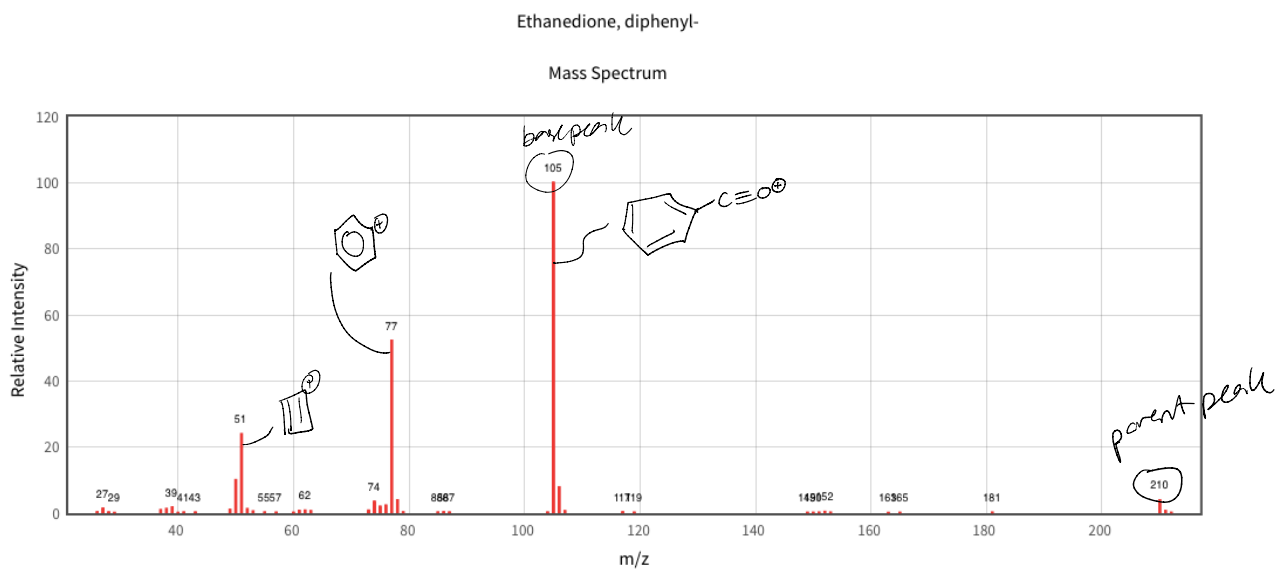
Yield (g): 2.887

Melting point (in degrees Celsius): 86.4 – 89.6

NMR:



Mass spectrum (from NIST database):

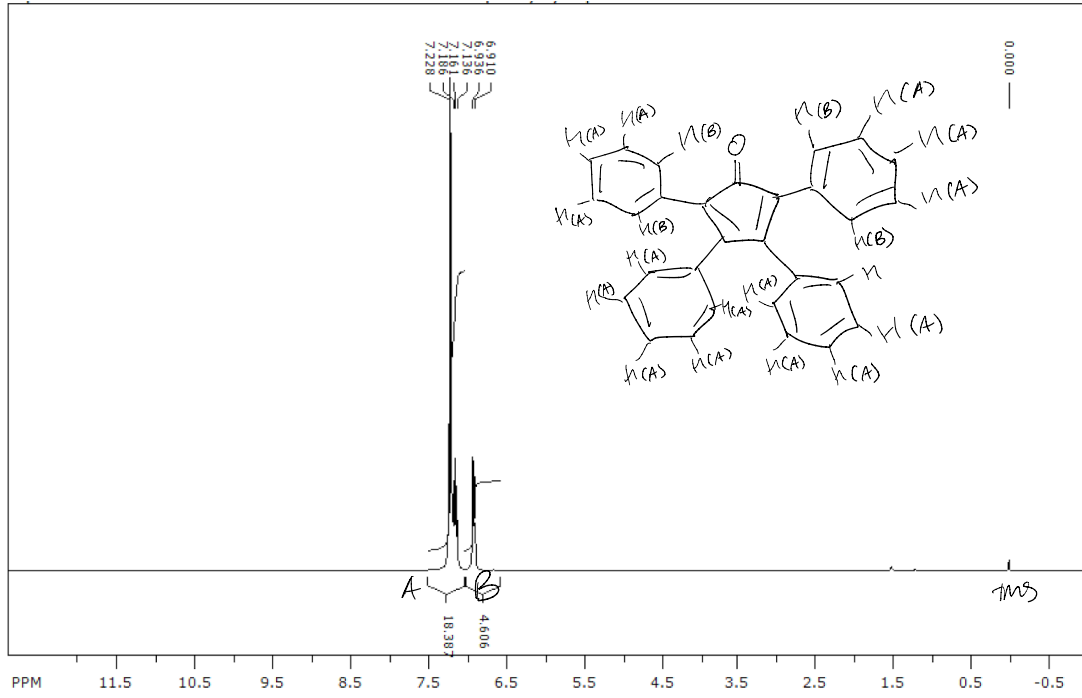


Part 3 - **Tetraphenylcyclopentadienone**

Mass (g): 4.410

Melting point (in degrees Celsius): 216.5-219.8

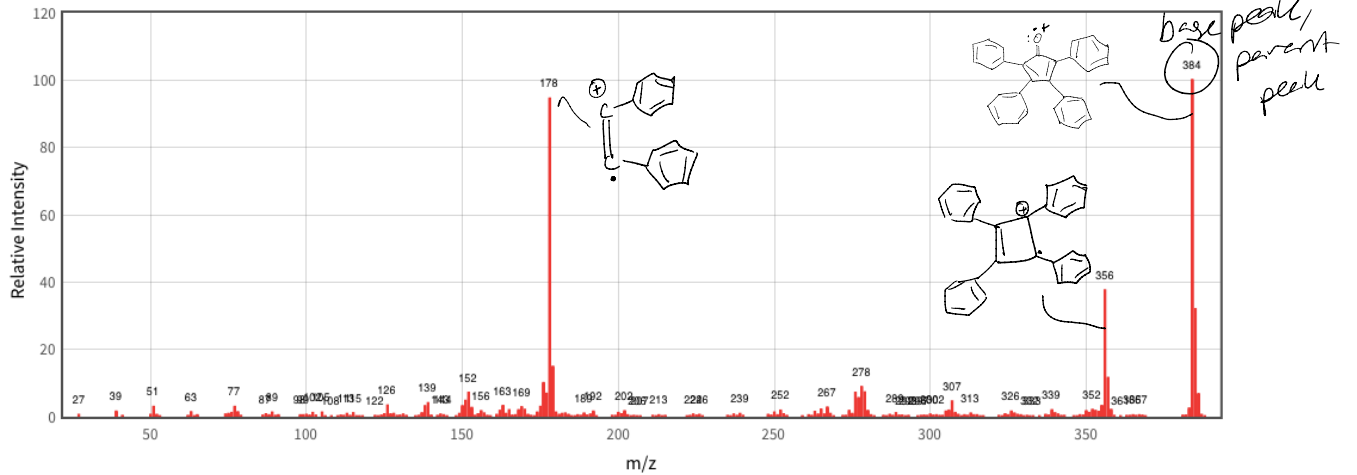
NMR:



Mass spectrum (from NIST database):

2,4-Cyclopentadien-1-one, 2,3,4,5-tetraphenyl-

Mass Spectrum

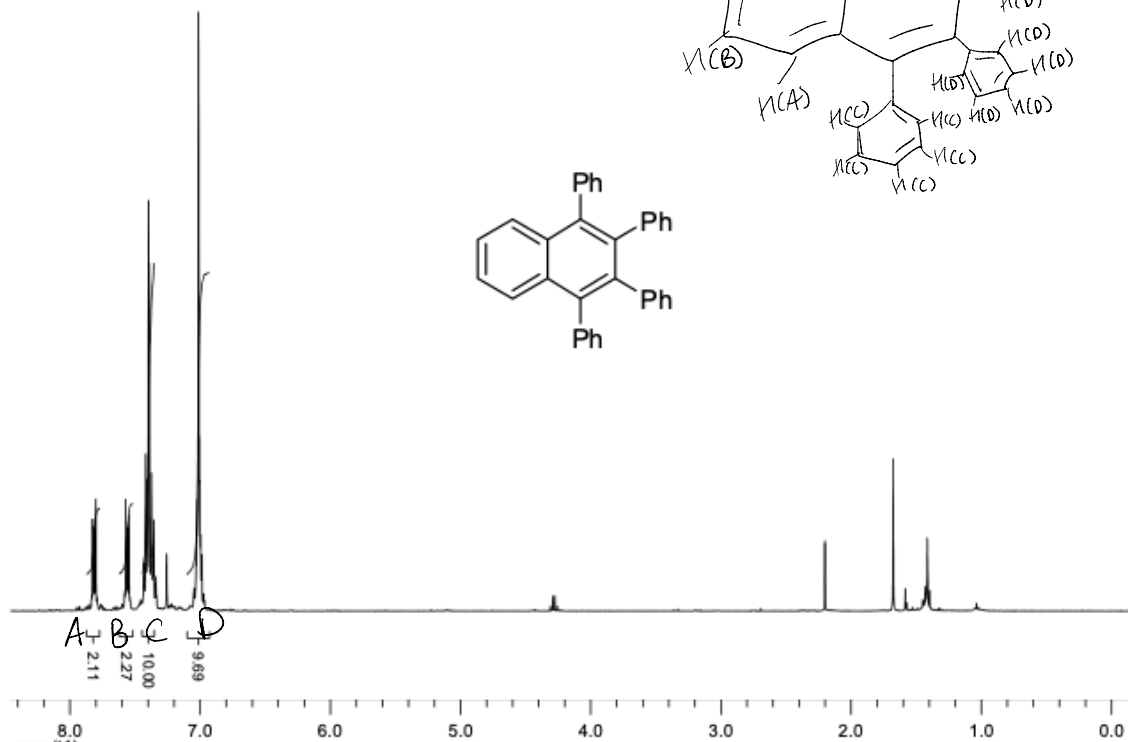


Part 4 – Tetraphenyl-naphthalene

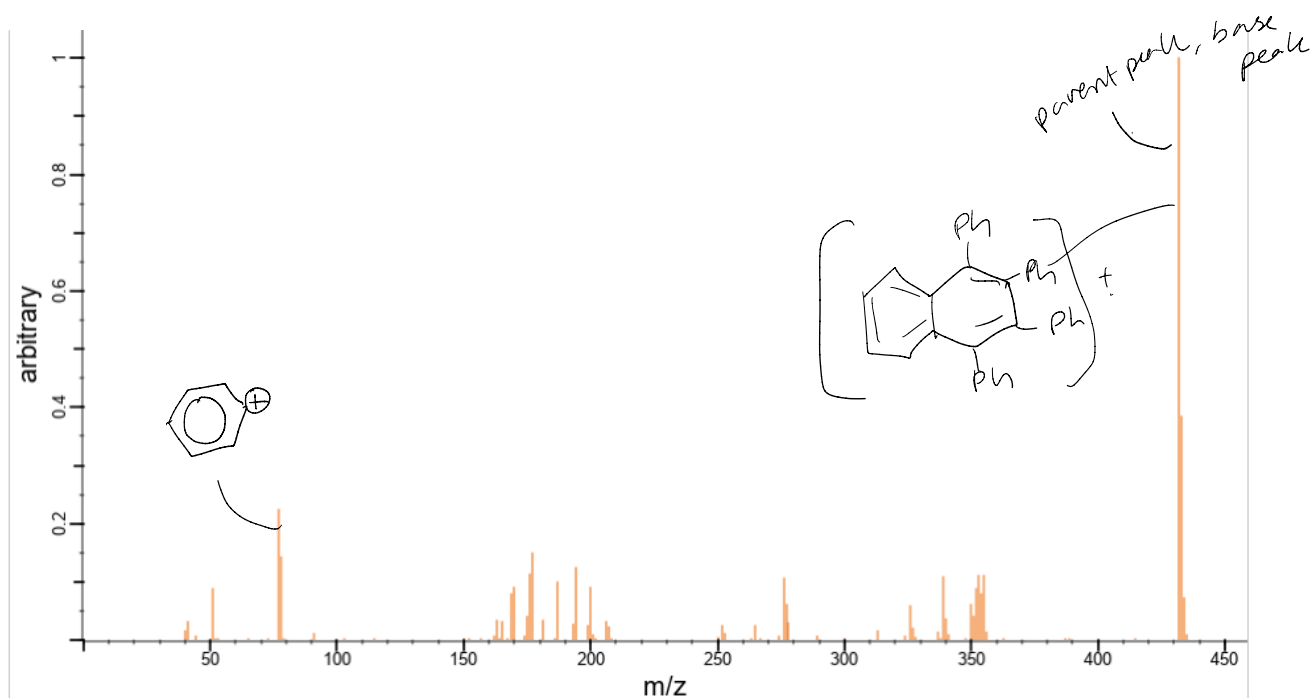
Yield (g): 3.652

Melting point (in degrees Celsius): 185-189

NMR:



Mass spectrum (from Wiley spectral database):



Works Cited

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