**Introduction:** Qualitative organic analysis, the identification and characterization of unknown compounds, is an important part of organic chemistry. Every chemist must learn the appropriate methods (physical, chemical, spectroscopic) for establishing the identity of a compound. In this experiment, you will investigate chemical methods for the identification of various functional groups in organic compounds.

1. **Tests for Halides: Silver Nitrate in Ethanol**
A reagent composed of silver nitrate dissolved in ethanol is useful in classifying alkyl halides according to their reactivity in an SN1 reaction. Nitrate ion is a poor nucleophile, and ethanol is a moderately powerful ionizing solvent. The silver ion, because of its ability to coordinate the leaving halide ion to form a silver halide precipitate, greatly assists the ionization of the alkyl halide.

The most reactive compounds are those able to form stable carbocations in solution and those equipped with good leaving groups. Benzyl, allyl, and tertiary halides react immediately with silver nitrate. Secondary and primary halides do not react at room temperature but react readily when heated. Aryl and vinyl halides do not react at all.

\[
RX + AgNO_3 \rightarrow AgX \text{ (precipitate)} + RNO_3
\]

**Procedure:** In each test tube, add 2 mL of a 2% ethanolic silver nitrate solution. Add 1-2 drops of each of the test halide solutions. If no reaction is observed after 5 minutes at room temperature, heat the solutions in a hot water bath and note whether a precipitate forms.

2. **Tests for Unsaturation: Potassium permanganate (Baeyer Test)**
This test is positive for double and triple bonds but not for aromatic rings. It depends on the conversion of the purple ion MnO₄⁻ to a brown precipitate of MnO₂ following the oxidation of an unsaturated compound.

\[
\text{C=C} + \text{MnO}_4^- \rightarrow \text{C=O} + \text{MnO}_2
\]

**Procedure:** Dissolve 2 drops of a liquid unknown in 2 mL of 1,2-dimethoxyethane (or 95% ethanol). Slowly add a 1% aqueous solution of potassium permanganate, drop by drop while shaking, to the unknown. In a positive test, the purple color of the reagent will disappear and a brown precipitate of MnO₂ forms, usually within 1 minute.

3. **Test for Unsaturation: Bromine in Carbon Tetrachloride**
A successful test depends on the addition of bromine, a red liquid, to a double bond or triple bond to give a colorless dibromide. Aromatic compounds do not react with bromine-carbon tetrachloride reagent.

***Carbon Tetrachloride posed certain health hazards so the instructor or lab assistant***
will demonstrate this test.

4a. Test for Aldehydes and Ketones: Chromic Acid Test

This test has as its basis the fact that aldehydes are easily oxidized to the corresponding carboxylic acid by chromic acid. The green precipitate is due to chromous sulfate.

$$3 \text{RC} = \text{H} + \text{H}_2\text{Cr}_2\text{O}_7 + 3 \text{H}_2\text{SO}_4 \rightarrow \text{RC} = \text{OH} + \text{Cr}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O}$$

**Procedure:** Dissolve one drop of a liquid in 1 mL of acetone. Add several drops of the chromic acid reagent, a drop at a time while shaking the mixture. A positive test is indicated by a green precipitate and a loss of the orange color in the reagent. With aliphatic aldehydes, the solution turns cloudy within 5 seconds and a precipitate appears within 30 seconds. With aromatic aldehydes, it generally takes 30-120 seconds for a precipitate to form, but with some it may take even longer. In a negative test, there is usually no precipitate.

4b. Test for Alcohols: Chromic Acid Test

This test is based on the reduction of chromium(VI), which is orange, to chromium(III) which is green, when an alcohol is oxidized by the reagent. Primary alcohols are oxidized by the reagent to carboxylic acids; secondary alcohols are oxidized to ketones. Tertiary alcohols are not oxidized at all by the reagent.

**Procedure:** Dissolve 1-2 drops of the test solution in 1 mL of acetone. Add one drop of chromic acid reagent and not the result that occurs in 2 seconds. A positive test for a 10 alcohol or a 2' alcohol is the appearance of a blue-green color. Tertiary alcohols do not produce the test result in 2 seconds, and the solution remains orange.

5. Test for Alcohols: Lucas Test

This test depends on the appearance of an alkyl chloride as an insoluble second layer when an alcohol is treated with a mixture of hydrochloric acid and zinc chloride. Primary alcohols do not react at room temperature; therefore, the alcohol is seen simply to dissolve. Secondary alcohols react slowly, whereas tertiary, benzylic, and allylic alcohols react instantly.

**Procedure:** In each test tube, place 2 mL of Lucas reagent in a small test tube and add 3-4 drops of the test alcohol. Stopper the test tube and shake it vigorously. Tertiary, benzylic, and allylic alcohols give an immediate cloudiness in the solution as the insoluble alkyl halide separates from the aqueous solution. After a short time, the immiscible alkyl halide will form a separate layer. Secondary alcohols produce a cloudiness after 2-5 minutes. Primary alcohols dissolve in the reagent to give a clear solution. Some secondary alcohols may have to be heated slightly to encourage reaction with the reagent.
Experiment cis-Norbronene-5,6-endo-dicarboxylic acid by Diels-Alder Reaction

Part A: Cracking of Dicyclopentadiene (performed by your instructor, see figure 1)

\[
\begin{align*}
\text{Dicyclopentadiene} & \quad \text{bp. 41°C, den 0.80} \\
& \quad \text{MW 66.10} \\
\text{Cyclopentadiene} & \quad \text{den 0.98, MW 132.20}
\end{align*}
\]

1. Measure 20 ml of dicyclopentadiene into a 100 ml flask and arrange for fractional distillation.

2. Heat the dimer with an electric flask heating mantle until it refluxes briskly at such a rate that the monomeric diene begins to distill in about 5 min and soon reaches a steady boiling point in the range 40-42°C.

3. Apply heat continuously to promote rapid distillation without exceeding the boiling point of 42°C.

Your instructor will have a vial of freshly cracked cyclopentadiene stored on ice ready for your use at the beginning of the lab period. Observe and record how it was made in your lab notebook. Please keep in mind that chromatographic analysis (McMurry p. 466-7) has revealed that cyclopentadiene is 8% dimerized in 4 hours and 50% dimerized in 24 hours at room temperature. Therefore, it should be kept on ice and used as soon as possible.

Part B: Synthesis of cis-Norbornene-5,6-endo-dicarboxylic anhydride

\[
\begin{align*}
\text{Maleic anhydride} & \quad \text{mp 53°C, MW 98.06} \\
\text{cis-Norbornene-5,6-endo-dicarboxylic anhydride} & \quad \text{mp. 165°C, MW 164.16}
\end{align*}
\]

1. Place 6g of maleic anhydride in a 125 ml Erlenmeyer flask and dissolve the anhydride in 20 ml of ethyl acetate. (You may gradually heat the solution in order to dissolve thoroughly. Caution. Do not leave your hot plate unattended!) [What did these materials look like before they were mixed? What does the mixture look like?]

2. Add 20 ml of ligroin (b.p. range 60-90°C), cool the solution thoroughly in an ice/water bath. Leave in the bath (some anhydride may crystallize). [Did any maleic anhydride crystals form?]

3. Measure 6 ml of dry cyclopentadiene, and add it to the ice-cold solution of maleic anhydride. [Caution; do not try smelling the cyclopentadiene.] [Is there any evidence of a chemical reaction? Are the two solutions miscible or immiscible?]
4. Swirl the solution in the ice bath for a few minutes until the exothermic reaction is over and the product separates as a white solid. [Did you observe the heat release and the white solid formation?]

5. Then heat the mixture on a hot plate until the solid is all dissolved. Now, if you let the solution stand undisturbed, you will be rewarded with a beautiful display of crystal formation.

6. Isolate your crystals on a Buchner funnel connected to an aspirator.

**Clean Up**

Place the crystallization solvent mixture in the waste organic solvents container. It contains a very small quantity of the product.

Figure 1 Experimental setup for cracking of dicyclopentadiene

![Experimental setup for cracking of dicyclopentadiene](image1)

Figure 2. NMR spectra of cis-Norbornene-5,6-endo-dicarboxylic anhydride and cis-Norbornene-5,6-endo-dicarboxylic acid

![NMR spectra](image2)
General Reaction

\[
\text{Ph} - \text{C} - \text{C} - \text{Ph} + \text{HNO}_3 \rightarrow \text{Ph} - \text{C} - \text{C} - \text{Ph} + \text{NO}_2 + \text{H}_2\text{O}
\]

B. The Balanced Oxidation Reaction

1. \textit{Balancing by The Half-Reaction Method}

a. Oxidation Half Reaction (increase in oxidation number)

\[
\begin{align*}
\text{Ph} - \text{C} - \text{CH} - \text{Ph} & \quad \text{ox. nos.: } C=+1; \text{CH}=0 \\
\rightarrow & \quad \text{Ph} - \text{C} - \text{C} - \text{Ph} + 2e^- + 2H^+ \\
& \quad C=+2; H=+1 \quad \text{[change} = (+3) - (+1) = +2]\end{align*}
\]

b. Reduction Half Reaction (decrease in oxidation number)

\[
\begin{align*}
2 \text{ HNO}_3 + 2e^- + 2H^+ & \rightarrow 2 \text{ NO}_2 + 2 \text{ H}_2\text{O} \\
\text{ox. nos.: } 2N=+10 & \quad 2N=+8 \quad \text{[change} = (+8) - (+10) = -2]\end{align*}
\]

\[
\text{Ph-CO-CH(OH)Ph} + 2 \text{ HNO}_3 \rightarrow \text{Ph-CO-CO-Ph} + 2 \text{ NO}_2 + 2 \text{ H}_2\text{O}
\]

2. Note: Benzoin has been oxidized to benzil, nitric acid has been reduced to nitrogen dioxide, a red-brown gas (with an odd electron) which rapidly dimerizes to an equilibrium mixture of NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{4} (nitrogen dioxide and dinitrogen tetroxide).

C. Mechanism for The Oxidation Reaction (two-step sequence)

1. \textit{Step one:} formation of a nitrate ester intermediate

\[
\begin{align*}
\text{Ph} - \text{C} - \text{CH} - \text{Ph} + \text{HONO}_2 & \rightarrow \text{Ph} - \text{C} - \text{C} - \text{Ph} + \text{H}_2\text{O}
\end{align*}
\]

2. \textit{Step two:} a 1,2-elimination of the elements of nitrous acid

\[
\begin{align*}
\text{Ph} - \text{C} - \text{C} - \text{Ph} + \text{NO}_2^- + \text{H}_3\text{O}^+ & \rightarrow \text{Ph} - \text{C} - \text{C} - \text{Ph} + \text{H}_2\text{O} + \text{NO}_2
\end{align*}
\]

3. \textbf{NOTE:} the nitrate ester intermediate undergoes a very common E2 type elimination where water (or nitrate ion) functions as the base, and nitrite ion functions as the leaving group. The overall result is the introduction of a new C-O double bond, which provides the driving force for the elimination reaction.
**Synthetic Route of Benzylic Acid**

1. **Benzaldehyde**
   
   $\text{C}_{8}\text{H}_{8}\text{COH}$
   
   **Vitamin B$_1$**
   
   aq MeOH
   
   $\text{C}_{8}\text{H}_{7}\text{COCH}_{2}\text{C}_{8}\text{H}_{6}\text{OH}$
   
   **Benzoin**

2. **Benzoin**
   
   $\text{C}_{8}\text{H}_{7}\text{COCH}_{2}\text{C}_{8}\text{H}_{6}\text{OH}$
   
   **HNO$_3$**
   
   $\text{C}_{8}\text{H}_{7}\text{CONC}_{8}\text{H}_{6}$
   
   **Benzil**

3. **Benzil**
   
   $\text{C}_{8}\text{H}_{7}\text{CONC}_{8}\text{H}_{6}$
   
   **$\text{KOH/H}_2\text{O}$**
   
   MeOH
   
   $\text{C}_{8}\text{H}_{6}\text{COOH}$
   
   **Benzylic Acid**

---

**Experiment 2-6**

---
Experiment 2 The Benzoin Condensation: Thiamine Catalyzed

\[
\begin{align*}
2 \quad \text{Benzaldehyde} & \quad \text{CN}^- \\
\text{MW 106.12} & \quad \text{or thiamine} \\
\text{bp 178°C} & \quad \text{Benzoin} \\
\text{MW 212.24} & \quad \text{mp 135°C}
\end{align*}
\]

1. Dissolve 2.6 g of thiamine hydrochloride in 8 ml of water contained in a 250-ml round bottom flask equipped with a magnetic stir bar and a condenser for reflux. Add 20 ml of 95% ethanol and cool the solution in an ice bath. Turn on the magnetic stirrer.

2. Over a period of 10 about min, add 5 ml of 3M sodium hydroxide dropwise with swirling such that the temperature of the solution does not rise above 20°C.

3. Add 7 ml of pure benzaldehyde to the yellow mixture and heat it gently at reflux temperature for 1-1.5 hours (gentle reflux means at a slow drip rate; i.e., just a few drops per minute).

4. Cool the reaction mixture to room temperature and then in an ice bath.

5. If recrystallization does not occur, withdraw a drop of the solution with the stirring rod and rub it against the inside surface of the flask to induce recrystallization.

6. Collect the product with a Buchner funnel. Wash the product twice with 50 ml portions of cold water.

7. Recrystallize the crude product from 95% aq methanol. (Note: the solubility of benzoin in hot 95% aq methanol is about 1g/ml; if you have about 1g of crude product, use 10ml of aq MeOH; about 2g, use 20 ml of aq MeOH, and so forth.)

8. Collect the product with a Buchner funnel. Transfer the product to dry paper and allow it is air dry for 10 to 15 min.

9. Determine the melting point of the product. Calculate the percent yield of the product.

Answer the following questions in your notebook. (The reaction mechanism is shown in the next three pages)

1. What is the structure of the thiazole ring?
2. How many steps are there in the reaction mechanism?
3. What is the name of each reaction mechanism step?
4. What is the structure of the Enamine (Deprotonated “Catalyst” Adduct)
INTRODUCTION

1. The reaction of two moles of benzaldehyde to form a new carbon-carbon bond is known as the benzoin condensation. It is usually catalyzed by cyanide ion, which has just the right balance of nucleophilicity, ability to stabilize the intermediate ion, and good leaving group qualities.

2. A number of biochemical reactions bear a close resemblance to the benzoin condensation but are not, obviously, catalyzed by the highly toxic cyanide ion. Some 35 years ago Breslow proposed that vitamin B1, thiamine hydrochloride, in the form of the coenzyme thiamine pyrophosphate, can function in a manner completely analogous to the cyanide ion in promoting the benzoin condensation. The resonance-stabilized conjugate base of the thiazolium ion (thiamine-ylide), and the resonance-stabilized carbanion (the enamine/betaine) are the keys to the reaction.

SOME GENERAL CONSIDERATIONS CONCERNING THE REACTION

1. First of all, we will look at the structure of vitamin B1 (thiamine hydrochloride)

![Thiamine structure]

2. Next, we will look at the acidity of the thiazolium cation. Basically, it is understandable in terms of the activating (electron-withdrawing) effect of the adjacent positive charge on nitrogen and the resonance interaction with the neighboring sulfur atom

![Thiazolium and conjugate base]

3. Lastly, we will define some terms whose understanding is basic to understanding the reaction mechanism of the vitamin B1 catalyzed benzoin-condensation.

a. **Catalyst**: A catalyst is a substance that speeds up a reaction; that is, it increases the rate at which the product is formed. It does so by allowing reactants and products to be interconverted by a new pathway in which the rate-determining step has an activation energy lower than the reaction would have in the absence of the catalyst. In other words, the catalyst lowers the **activation energy barrier**. Also during the course of the reaction, the **concentration of the catalyst remains essentially unchanged**.
b. Vitamin B1 is a good catalyst for the benzoin condensation reaction because: (i) it is a good nucleophile; that is, in the presence of strong base, it forms a high concentration of its ylide; and (ii) it is a good leaving group; that is its ylide is stable.

c. The ylide of vitamin B1 is especially stable because: the carbanion carbon (the C2 carbon of the thiazole ring) is stabilized by the adjacent positive charge on nitrogen and a strong resonance interaction with the neighboring sulfur atom.

d. An Ylide is a dipolar compound with adjacent plus and minus charges.

e. A Betaine is a dipolar compound with non-adjacent plus and minus charges.

REACTION MECHANISM FOR THE VITAMIN B$_1$-CATALYZED BENZOIN CONденСATION

Step one: generation of the thiamine-ylide. Because its pKa value is relatively high (ca 10), a strongly basic solution is required to generate an adequate concentration - once formed, however, it can function as a good nucleophile.

Step two: generation of the enamine/betaine. The ylide, functioning as a strong nucleophile, attacks the weakly electrophilic carbonyl-carbon of a benzaldehyde molecule - the resultant adduct is sufficiently acidic to be transformed into its conjugate base: the enamine/betaine intermediate (NOTE: the enamine is a resonance-stabilized carbanion, so it can function as a strong carbon-nucleophile, much like the enolate ion in an aldol condensation reaction).

Step three: coupling reaction of two benzaldehyde molecules. The enamine, functioning as a strong carbon nucleophile, attacks the weakly electrophilic carbonyl-carbon of another benzaldehyde molecule (NOTE: the adduct contains a new carbon-carbon bond coupling two benzaldehyde molecules together).

Step four: liberation of the $\alpha$-hydroxy ketone, benzoin. This is accomplished by the expulsion of the ylide catalyst functioning as a good leaving group, and is assisted by the formation of the double bond in the reformed carbonyl group.

Overall, then, vitamin B1 is an effective catalyst for the benzoin condensation: because its conjugate base - thiamine ylide - has just the right balance of nucleophilicity, ability to stabilize the intermediate enamine/betaine, and good leaving group qualities.
Mechanism, step one: generation of "YLIDE" catalyst from vitamin B1

Vitamin B1

\[ \text{NH}_2 \]
\[ \begin{array}{c}
\text{N} \\
\text{3} \\
\text{2} \\
\text{1}
\end{array} \]

\[ \text{OH}^- \]
\[ \begin{array}{c}
\text{S} \\
\text{4} \\
\text{5}
\end{array} \]

\[ \text{H}_2\text{O} \]

\[ \text{Ylide} \]

**NOTE:** in the resonance-stabilized conjugate base of the thiazolium ion, the thiamine ylide, the carbanion carbon at C2 is conjugated with the neighboring sulfur atom.

Mechanism, step two: generation of ENAMINE nucleophile

**Ylide**

\[ \text{OH}^- \]
\[ \begin{array}{c}
\text{N} \\
\text{3} \\
\text{2} \\
\text{1}
\end{array} \]

\[ \text{Ph} \]

\[ \text{H}_2\text{O} \]

**ENAMINE-BETAINE FORM**

**BETAIN form**

\[ \begin{array}{c}
\text{N} \\
\text{3} \\
\text{2} \\
\text{1}
\end{array} \]

\[ \text{Ph} \]

\[ \text{OH}^- \]

**ENAMINE form**

\[ \begin{array}{c}
\text{N} \\
\text{3} \\
\text{2} \\
\text{1}
\end{array} \]

\[ \text{Ph} \]

\[ \text{OH} \]

**TE:** an enamine is a resonance-stabilized carbanion so it can function much like the enolate-ion

Mechanism, step three: coupling reaction of two benzaldehyde molecules

**Carbon nucleophile**

\[ \text{Ph} \]

**Carbon electrophile**

\[ \text{Ph} \]

\[ \text{H}_2\text{O} \]

**Benzaldehyde adduct**

Mechanism, step four: expulsion of the THIAMINE-YLIDE catalyst from the benzaldehyde adduct

**Benzaldehyde adduct**

\[ \text{OH}^- \]

\[ \begin{array}{c}
\text{N} \\
\text{3} \\
\text{2} \\
\text{1}
\end{array} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{ylide catalyst} \]

**Benzoin product**

**NOTE:** expulsion of the thiamine-ylide catalyst is assisted by the formation of the stable carbonyl group as well as by the stability of the thiamine-ylide
Experiment 3: Characterization of Benzoin by FT-IR

The introduction and representative infrared spectra of various organic compounds are given in McMurry's Organic Chemistry, 5th ed. Chapter 12. Some characteristic stretching frequencies are shown in table 1.

<table>
<thead>
<tr>
<th>Characteristic Stretching Frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond</td>
</tr>
<tr>
<td>-------------------------------------</td>
</tr>
<tr>
<td>C-H</td>
</tr>
<tr>
<td>(a) C-H\text{sp}^3-H</td>
</tr>
<tr>
<td>(b) C-H\text{sp}^2-H</td>
</tr>
<tr>
<td>(c) C-H\text{sp}-H</td>
</tr>
<tr>
<td>C-C</td>
</tr>
<tr>
<td>(c) C-C</td>
</tr>
<tr>
<td>(b) C=CC</td>
</tr>
<tr>
<td>(c) C≡CC</td>
</tr>
<tr>
<td>O-H</td>
</tr>
<tr>
<td>(a) ROH</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>(b) RCO_2H</td>
</tr>
<tr>
<td>Aldehydes</td>
</tr>
<tr>
<td>(a) RCCHO</td>
</tr>
<tr>
<td>(b) C=CCCHO</td>
</tr>
<tr>
<td>(c) ArCHO</td>
</tr>
<tr>
<td>Ketones</td>
</tr>
<tr>
<td>(a) R_2C\text{sp}=-O</td>
</tr>
<tr>
<td>(b) C=CC=O</td>
</tr>
<tr>
<td>(c) Ar-C=O</td>
</tr>
<tr>
<td>(d) four-membered cyclic</td>
</tr>
<tr>
<td>(e) five-membered cyclic</td>
</tr>
<tr>
<td>(f) six-membered cyclic</td>
</tr>
<tr>
<td>Carboxylic acids</td>
</tr>
<tr>
<td>(a) RCOOH</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>(b) C\equivC-C=COH</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>(c) RCO_2^-</td>
</tr>
<tr>
<td>Aromatic</td>
</tr>
<tr>
<td>(a) mono-</td>
</tr>
<tr>
<td>(b) o-</td>
</tr>
<tr>
<td>(c) m-</td>
</tr>
<tr>
<td>(d) p-</td>
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### Report: Peak Pick – Benzaldehyde Infrared Spectrum

<table>
<thead>
<tr>
<th>Peak Pick (cm⁻¹)</th>
<th>Functional Group</th>
</tr>
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<tbody>
<tr>
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### Report: Peak Pick – Benzoin Infrared Spectrum

<table>
<thead>
<tr>
<th>Peak Pick (cm⁻¹)</th>
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<tbody>
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</tbody>
</table>
Part 1- Nitric Acid Oxidation of Benzoin

1. Heat a mixture of 4 g of benzoin and 14 ml of concentrated nitric acid on a steam bath for 11 minutes. Carry out the reaction under the hood.

2. Once the reaction is complete add 75 ml of water to the reaction mixture, cool to room temperature, and swirl for a minute or two to coagulate the precipitated product.

3. Collect the product on a Buchner funnel. Press the product well to remove the moisture.

4. Recrystallize the product from 10 ml of ethanol. Once the product is dissolved add water dropwise to reach the cloud point. Allow the product to recrystallize.

5. Once the product has recrystallized collect it on a Buchner funnel and dry it. What is the appearance of the purified benzil?

6. Determine the melting point and theoretical yield of the product.

Part 2- Testing for the Presence of Unoxidized Benzoin

7. Dissolve about 5 mg of the purified benzil in 0.5 ml of 95% ethanol and add 1 drop of 10% sodium hydroxide. If benzoin is present the solution will acquire a purplish color.

8. If no color appears in 2-3 minutes, an indication that the sample is free of benzoin, add a small amount of benzoin and observe the color that develops.

9. Did your product contain unoxidized benzoin?

10. Dispose of the waste in the organic waste container.
An orbital examination of the π-bonding network of benzil reveals that each carbon atom possesses a p orbital that can overlap with the p orbitals of the neighboring carbon atoms on both sides. This orbital arrangement leads to an extended conjugation system involving all 14 carbon atoms, and makes it possible for a wavelength of visible light to effect a π-π* electronic transition in the conjugated molecule. Such molecular interaction with electromagnetic radiation remove one or more wavelength components from the light reflected to our eye. We interpret this wavelength absence as color.

The structure of Benzil and its conjugation system

Observed Physical Properties
Melting point: 94-95 °C. Yellow Color power.

Answer the following questions on your notebook.

1. The balanced equation for the oxidation of benzoin with nitric acid requires how many moles of nitric acid per mole of benzoin?
2. In the balanced equation for the oxidation of benzoin with nitric acid, what compound is the oxidizing agent?
3. How many steps are involved in the mechanism?
4. Step two involves what types of reaction?
5. What is an extended conjugation system?
6. The extended conjugation system in benzil involves how many carbons?
1. In your 100 ml round bottom flask containing 12 ml of methanol, dissolve 2.3g of benzil, heating the mixture slightly (by means of a heating mantle) if necessary to dissolve the benzil.

2. Add 8 ml of the prepared KOH solution to the reaction flask, while stirring the contents with your magnetic stir bar.

3. After attaching your condenser to the reaction flask, reflux the stirred mixture for at least 30 minutes (use a Variac setting of about 40; During this time, the initial blue-black coloration will change to a brown coloration).

4. Allow the reaction mixture to cool (remove the heating mantle!), and when the flask is cool enough to handle, transfer its contents to your evaporating dish.

5. Place the dish on your stirred/hot plate, and, with low heat, evaporate most of the solvent (this means that when a layer of solid has formed on the surface of the liquid, STOP THE EVAPORATION PROCESS).

6. Then, by means of an ice/water bath, cool the dish until the residue solidifies (if this does not happen in a few minutes, reheat the dish to evaporate more solvent, and repeat the cooling process).

7. Collect the precipitated solid (crystallized potassium benzilate) upon your Buchner funnel, and wash it with 2 ml of ice-cold 95% of aq methanol.

8. Next, by means of your hot plate, dissolve the crude potassium benilate in a minimum amount of hot water contained in a 250 ml Erlenmeyer flask (NOTE: more than 50 ml of hot water may be needed to dissolve the solid).

9. Add a small amount of decolorizing carbon to the flask and stir the hot mixture for a few minutes, then immediately filter the hot solution by gravity, using two fluted filter papers (one paper inside the other), and collecting the filtrate in a 250 ml Erlenmeyer flask.

10. Acidify the filtrate by carefully adding 6 ml of phosphoric acid (NOTE: to assist smooth precipitation of the benzilic acid, occasionally swirl the Erlenmeyer flask.

11. Allow the mixture to cool to room temperature (this should take only a few minutes), then complete the crystallization process by cooling the mixture in an ice/water bath for five minutes.
12. Collect the precipitated benzilic acid upon your Buchner funnel, and wash it thoroughly with water to remove any trace of salt present.

13. Then, place the wet benzilic acid on dry toweling, and allow it to air dry until the next laboratory period (NOTE: during the next laboratory period after the test but before checking out, determine the yield and melting point of your purified benzilic acid).

Answer the following equations on your notebook.

1. How many steps are involved in the mechanism?
2. The rate determining step is what step?
3. Step one involves what types of reaction?
**A. OVERALL REACTION**

\[
\text{Ph-C-C-Ph} + \text{KOH/aq MeOH} \rightarrow \text{Ph-C-C-C-Ph} + \text{H}_3\text{O}^+ 
\]

**B. MECHANISM OF THE BENZIL-BENZILIC ACID REARRANGEMENT**

1. **Step one: adduct formation**

\[
\text{Ph-C-C-Ph} + \text{OH}^- \rightleftharpoons \text{Ph-C-C-Ph} \text{ (OH)}^-
\]

2. **Step two: rearrangement (rate determining step)**

\[
\text{Ph-C-C-Ph} \text{ (OH)}^- \rightleftharpoons \text{Ph-C-C-Ph} \text{ (OH)}^-
\]

*(NOTE: formation of the C=O group provides the driving force for the rearrangement)*

3. **Step three: protonation/deprotonation to benzilate salt**

\[
\text{Ph}_2\text{C-C-C-OH} + \text{H}_2\text{O} \rightleftharpoons \text{Ph}_2\text{C-C-C-O}^- + \text{H}_2\text{O}
\]

*(NOTE: first-formed product is a salt: potassium benzilate)*

4. **Step four: hydrolysis of benzilate salt to benzilic acid**

\[
\text{Ph}_2\text{C-C-C-O}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{Ph}_2\text{C-C-C-OH} + \text{H}_2\text{O}
\]

*(NOTE: final-product is benzilic acid, an α-hydroxy acid)*
### TABLE A

<table>
<thead>
<tr>
<th>Proton Type</th>
<th>Approximate Proton Chemical Shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>1°-5°</td>
<td>1.6-1.9</td>
</tr>
<tr>
<td>1°-1.4</td>
<td>1.4-1.7</td>
</tr>
<tr>
<td>2°</td>
<td>1.2-1.4</td>
</tr>
<tr>
<td>3°</td>
<td>1.8-1.0</td>
</tr>
</tbody>
</table>

### TABLE B

<table>
<thead>
<tr>
<th>Type of Carbon Atom</th>
<th>Approximate Carbon-13 Chemical Shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>1°-4°</td>
<td>1.6-1.9</td>
</tr>
<tr>
<td>1°-5°</td>
<td>1.4-1.7</td>
</tr>
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</tr>
<tr>
<td>3°</td>
<td>1.8-1.0</td>
</tr>
</tbody>
</table>

The chemical shifts of these protons vary in different solvents and with temperature.

- **Amino, R-NH**
- **Phenolic, ROH**
- **Carboxylic, R-COOH**
- **Alcohol, ROH**
- **Ester, R-C(=O)OR**
- **Ester, R-C(=O)OH**
- **Amine, R-NH**
- **Aldehyde, CHO**
- **Ketone, R-C=O**
- **Alcohol, HOCH₂R**
- **Ester, ROC₂H₂**
- **Ester, ROC₂H₂**
- **Aldehyde, CHO**
- **Ketone, R-C=O**
- **Alcohol, R-OH**
- **Ester, ROC₂H₂**
- **Ester, ROC₂H₂**