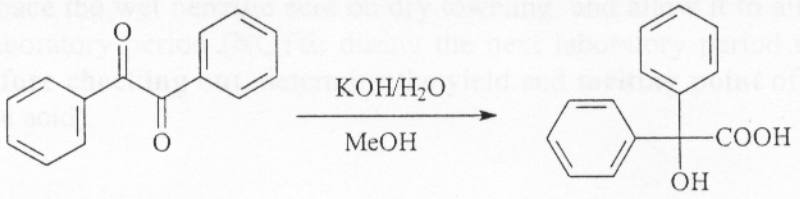
Experiment 5. Benzilic Acid Preparation and Purification



Benzil

Benzylic Acid

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 Erlenymer 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.

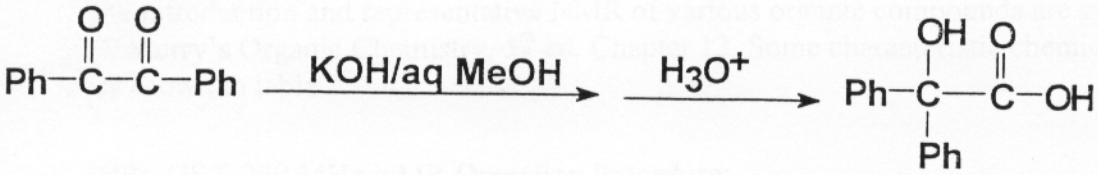
12. Collect the precipitated benzilic acid upon your Buchner funnel, and wash it **thoroughly** with water to remove any trace of salt present.
13. Then, pace the wet benzilic acid on dry toweling, and allow it to air dry until the next laboratory period (NOTE: during the next laboratory period **after 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?

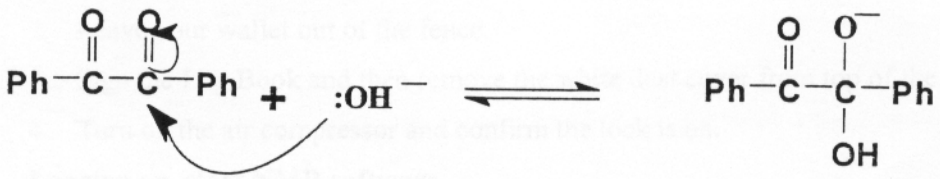
LECTURE#5B.254 EXPERIMENT #5 - PREPARATION AND PURIFICATION OF BENZILIC ACID

A. OVERALL REACTION

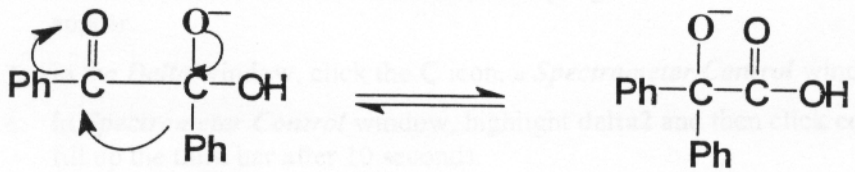


B. MECHANISM OF THE BENZIL-BENZILIC ACID REARRANGEMENT

1. *Step one: adduct formation*

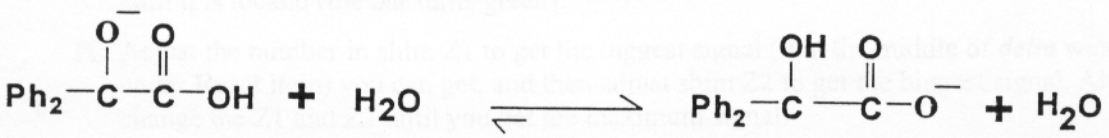


2. *Step two: rearrangement* (**rate determining step**)



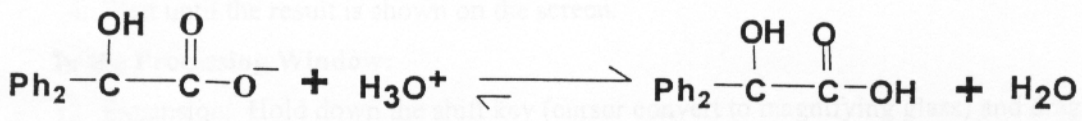
(**NOTE:** formation of the **C=O group** provides the driving force for the rearrangement)

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



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

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



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

TABLE A

Approximate proton chemical shifts

TYPE OF PROTON	CHEMICAL SHIFT (δ, ppm)
1° Alkyl, RCH_3	0.8–1.0
2° Alkyl, RCH_2R	1.2–1.4
3° Alkyl, R_3CH	1.4–1.7
Allylic, $R_2C{=}C(R){-}CH_3$	1.6–1.9
Benzylic, $ArCH_3$	2.2–2.5
Alkyl chloride, RCH_2Cl	3.6–3.8
Alkyl bromide, RCH_2Br	3.4–3.6
Alkyl iodide, RCH_2I	3.1–3.3
Ether, $ROCH_2R$	3.3–3.9
Alcohol, $HOCH_2R$	3.3–4.0
Ketone, $RC(=O)CH_3$	2.1–2.6
Aldehyde, $RC(=O)H$	9.5–9.6
Vinylic, $R_2C{=}CH_2$	4.6–5.0
Vinylic, $R_2C{=}CH(R)$	5.2–5.7
Aromatic, ArH	6.0–9.5
Acetylenic, $RC{\equiv}CH$	2.5–3.1
Alcohol hydroxyl, ROH	0.5–6.0[a]
Carboxylic, $RC(=O)OH$	10–13[a]
Phenolic, ArOH	4.5–7.7[a]
Amino, $R{-}NH_2$	1.0–5.0[a]

[a]The chemical shifts of these protons vary in different solvents and with temperature and concentration.

TABLE B

Approximate carbon-13 chemical shifts

TYPE OF CARBON ATOM	CHEMICAL SHIFT (δ, ppm)
1° Alkyl, RCH_3	0–40
2° Alkyl, RCH_2R	10–50
3° Alkyl, $RCHR_2$	15–50
Alkyl halide or amine, $-\overset{|}{C}-X$ (X = Cl, Br, or $-\overset{|}{N}-$)	10–65
Alcohol or ether, $-\overset{|}{C}-O$	50–90
Alkyne, $-C{\equiv}$	60–90
Alkene, $>C{=}$	100–170
Aryl, 	100–170
Nitriles, $-C{\equiv}N$	120–130
Amides, $-C(=O)-N-$	150–180
Carboxylic acids, esters, $-C(=O)-O$	160–185
Aldehydes, ketones, $-C(=O)-$	182–215