EXPERIMENT 5
SYNTHESIS OF A SUBSTITUTED AROMATIC RING BY ALDOL CONDENSATION & DIELS-ALDER REACTION

Part A adapted from: *Introduction to Organic Laboratory Techniques: A Small Scale Approach*, 2nd Ed., Pavia, D.L., Lampman, G.M., Kriz, G.S., Engel, R.G., Thompson Brooks/Cole, 2005, pp. 300-302.

Part B adapted from: *Experimental Organic Chemistry: A Balanced Approach*, Mohrig, J.R., Hammond, C.N., Morrill, T.C., Neckers, D.C., W.H. Freeman and Company, New York, 1999.

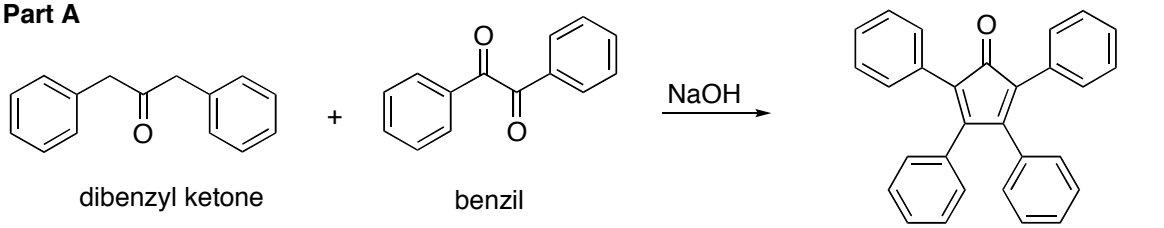
Reading Assignment: Smith Sections 16.12-16.14, 24.1-24.4

Pre-lab Questions:

1. Draw a full mechanism for the reaction of dibenzyl ketone with benzil to form tetraphenylcyclopentadienone, and the reaction of tetraphenylcyclopentadienone with dimethylacetylenedicarboxylate to form 3,4,5,6-tetraphenylphthalate.
2. Suggest several possible by-products for Part A
3. Diels-Alder reactions that are especially favorable run at room temperature. Reactions that are not as favorable require elevated temperatures. Considering the structures of the diene and dienophile in the Diels-Alder reaction in Part B, discuss some factors that favor/disfavor this reaction. Which of these factors contribute to the elevated temperature necessary for this Diels-Alder reaction *(a review of section 16.12 in Smith will be helpful)*?

In this experiments, we will use a two-part procedure to synthesize dimethyl-3,4,5,6-tetraphenylphthalate. In Part A, dibenzylketone and benzil react the presence of sodium hydroxide to form tetraphenylcyclopentadienone, *via* an aldol condensation.

Part A

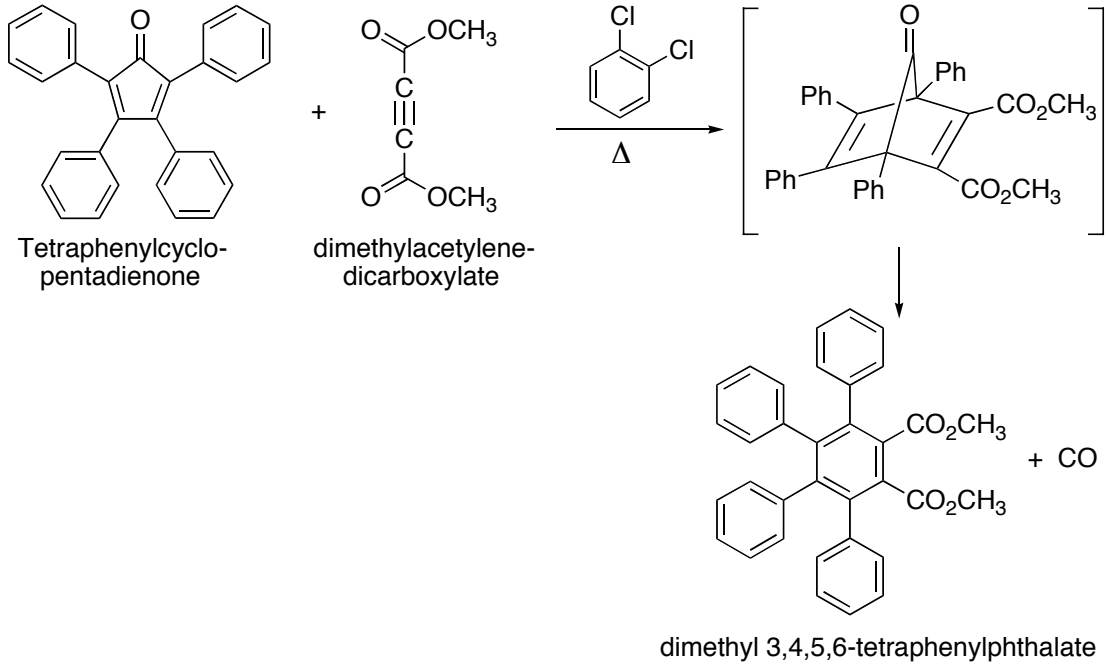


dibenzyl ketone benzil

Tetraphenylcyclopentadienone
(purple crystals)

In Part B, tetraphenylcyclopentadienone will undergo Diels-Alder reaction with dimethylacetylenedicarboxylate to form an unstable intermediate bridged bicyclic structure, which will then lose carbon monoxide to form the hexasubstituted benzene derivative dimethyl-3,4,5,6-tetraphenylphthalate, as shown below:

Part B



Tetraphenylcyclo-pentadienone

dimethylacetylene-dicarboxylate

dimethyl 3,4,5,6-tetraphenylphthalate

CAUTION

Dimethylacetylene dicarboxylate is corrosive and a lachrymator (causes tears). Do all work in the hood, wear gloves, and avoid all contact with skin, eyes, and clothing.

Dichlorobenzene is toxic and an irritant. Wear gloves, and avoid all contact with skin, eyes, and clothing.

Sodium hydroxide solutions are corrosive and cause burns. Wear gloves and avoid contact with skin, eyes, and clothing.

Ethanol is flammable.

Methanol is toxic and flammable. Pour it only in a hood.

Procedure.

Part A: Synthesis of Tetraphenylcyclopentadienone

Into a 25 ml round-bottom-flask equipped with a stir bar, place 0.75 g benzil, 0.75 g of dibenzylketone (may be labeled as 1,3-diphenyl-2-propanone or 1,3-diphenylacetone) and 6 mL absolute ethanol. Attach a water-cooled condenser, and heat the mixture in a hot water bath at 85°C until the solids dissolve. Using a Pasteur pipette, add dropwise 1.15 mL ethanolic potassium hydroxide solution through the top of the condenser into the flask. Maintaining water

bath temperature at 85°C, heat the solution for 15 minutes. After 15 minutes, allow the mixture to cool to room temperature, then place in an ice bath for 5 minutes. Isolate the product by vacuum filtration on a Büchner funnel. Wash the crystals with three 2 mL portions ice-cold 95% ethanol, then suck dry for a several minutes. Remove the product from the filter, and place in a drying oven for about 30 minutes. Obtain a crude yield.

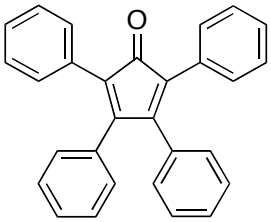
Part B: Synthesis of Dimethyl-3,4,5,6-tetraphenylphthalate

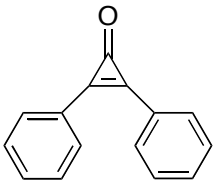
Into a dry 18×150 mm test tube, place 0.50 g the dry tetraphenylcyclopentadienone prepared in **Part A**. Add 0.25 mL dimethylacetylenedicarboxylate and 2.5 mL of 1,2-dichlorobenzene, and clamp the test tube over a sand bath. Allow the solution to gently reflux, with the reflux ring extending 2-3 cm above the boiling solution. Continue heating at reflux for 5-10 minutes. Cool the solution to 80°C, then add 3.5 mL ethanol – crystals should begin to form. Stir to mix, then allow to cool to room temperature. Cool in an ice-bath, then collect the crystals by vacuum filtration on a Büchner funnel. Rinse the crystals with several drops of ice-cold methanol to remove any remaining yellow color, then suck dry for several minutes. Crystals should be a creamy white color. Determine a crude yield.

Take an IR of the tetraphenylcyclopentadienone from Part A, and dimethyl-3,4,5,6-tetraphenylphthalate from Part B. As part of your Post-lab report, interpret both IR's, and the 'HNMR's provided for each. Report your crude yield for each step, and your overall yield.

Post-lab Questions:

1. Which of the following compounds is expected to have the largest dipole moment?





2. In the two compounds above, which would you expect to have the greatest basicity at the carbonyl oxygen?