3. Diels-Alder Reactions: Formation of Dimethyl Tetraphenylphthalate, Tetraphenylnaphthalene, and Hexaphenylbenzene

M. Jones: Diels-Alder, 12.12, pgs 587-598, Problems 12.45, 12.49, 12.51, 12.52, pgs 611-613.
Benzyne, 14.14, pgs 733-735, Problem 14.65 p 745

This procedure has been adapted from the microscale procedure described in *Macroscale and Microscale Organic Chemistry Experiments* by Kenneth L. Williamson. The general information is from the book listed above and M. Jones's *Organic Chemistry* textbook.

Introduction

In this experiment, you will perform three reactions, each include a Diels-Alder reaction.

Background

First, let's review the Diels-Alder reaction. It is a one-step reaction of a diene (in the *s-cis* form) and a dienophile, which is reversible. The general reaction and mechanism is depicted in Figure 1.

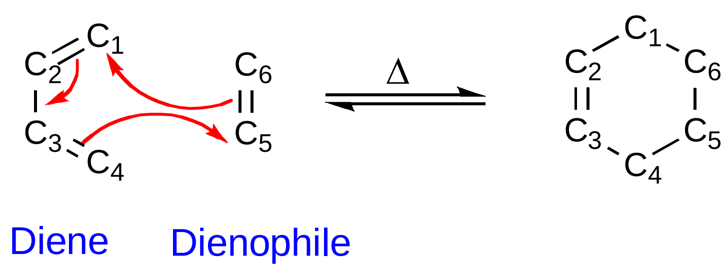


Figure 1. A general Diels-Alder reaction.

If the diene cannot convert from its *s-trans* (more stable form) to its *s-cis* form, the reaction will not occur. The three π bonds (two from the diene and one form the dienophile) are used to form a six-membered ring with at least one π and two σ bonds. The reaction is usually exothermic.

The reaction is even more favorable when the diene is fixed in the *s-cis* form as in the case of cyclopentadiene (see Figure 2).

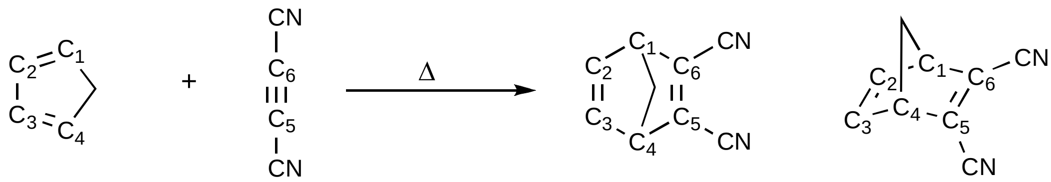
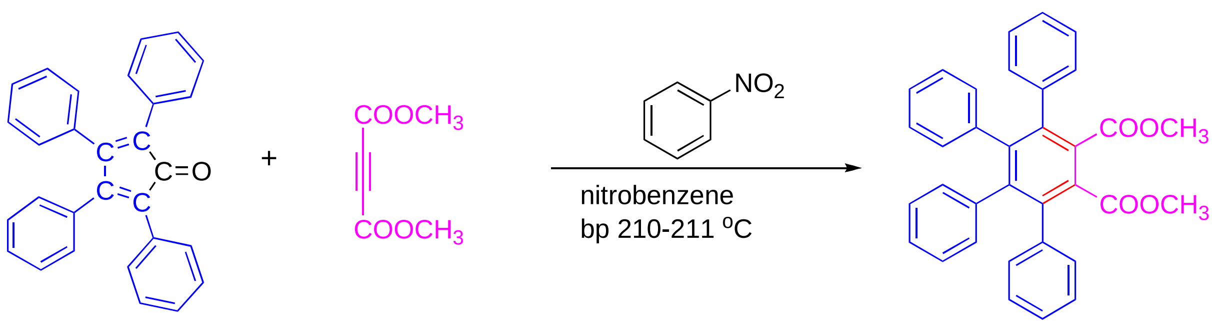


Figure 2. Another example of a Diels-Alder reaction.

For this series of three experiments, a diene, tetraphenylcyclopentadienone, is reacted with different alkyne dienophiles to form products of greater aromatic stabilization. In the first reaction (Figure 3), the tetraphenylcyclopentadienone is reacted with the dienophile, acetylene dicarboxylate, to form a reactive intermediate, which upon losing carbon monoxide produces dimethyl tetraphenylphthalate.



tetraphenylcyclo-
pentadienone
mp 219 ^oC

dimethyl acetylene-
dicarboxylate d 1.156 g/mL
bp ~300 ^oC

dimethyl tetraphenyl-
phthalate
mp 258 ^oC

Figure 3. The Diels-Alder reaction for the formation of dimethyl tetraphenylphthalate.

Even though, a strained intermediate is formed (see Figure 4). The overall reaction is favored because a resonance-stabilized aromatic ring is formed. The reaction is irreversible because carbon monoxide is lost.

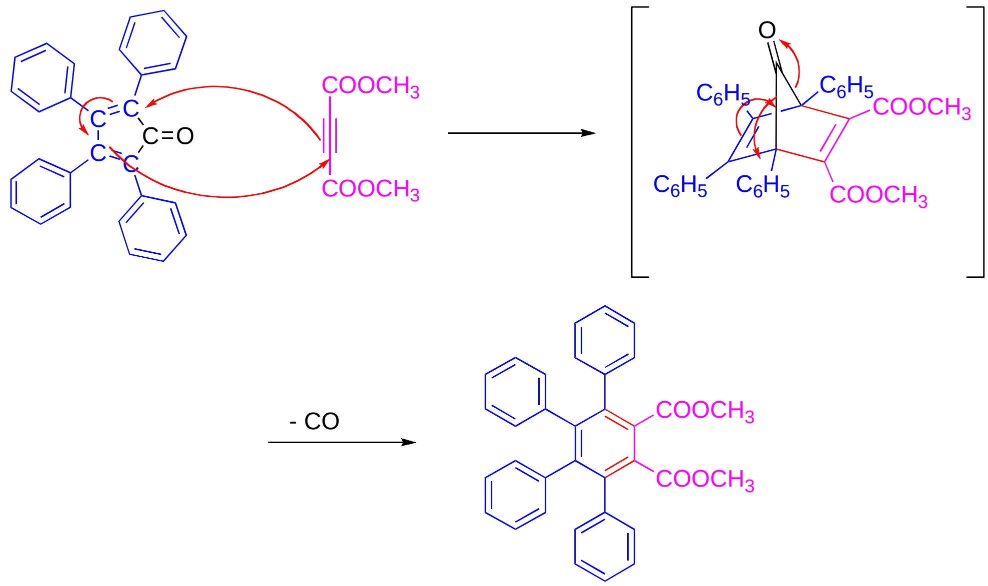
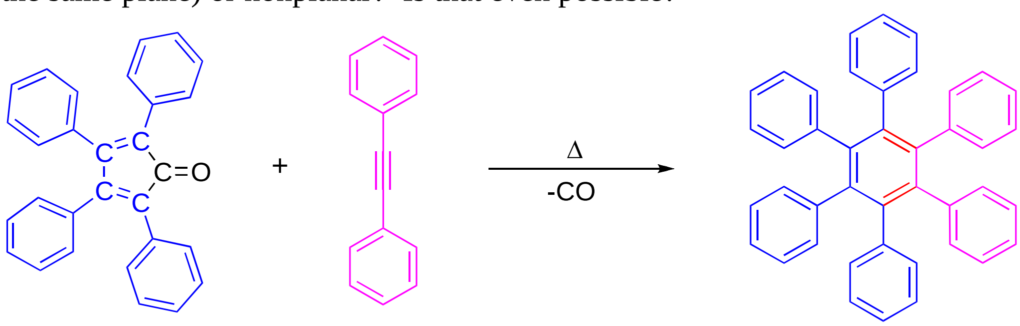


Figure 4. The mechanism for the formation of dimethyl tetraphenylphthalate.

In the second reaction, the dienophile is diphenyl acetylene and the reaction is performed neat (i.e., without solvent). However, the mechanism is the same and yields an aromatic product (Figure 5). Do you think that this product is more or less stable than the first product? Is it planar (i.e., all of the benzene rings are in the same plane) or nonplanar? Is that even possible?



tetraphenylcyclo-pentadienone
mp 219 °C

diphenyl acetylene
mp 59-61 °C

hexaphenylbenzene
mp 465 °C

Figure 5. The Diels-Alder reaction for the formation of hexaphenylbenzene.

In the third reaction, benzyne is the dienophile. This reactive intermediate results from the reaction of anthranilic acid with isoamyl nitrite (Figure 6).

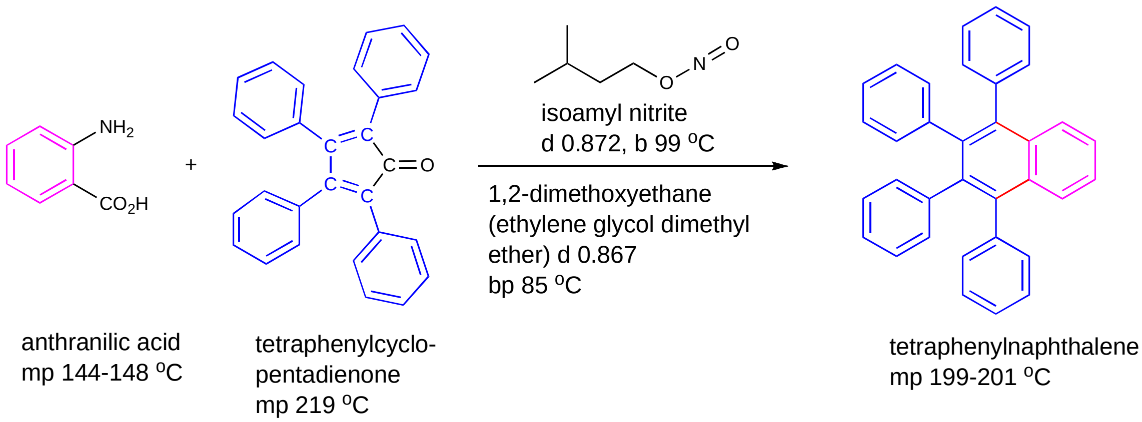


Figure 6. The Diels-Alder reaction for the formation of tetraphenylnaphthalene.

Since the benzyne is very unstable, it is prepared *in situ* and reacted immediately with the tetraphenylcyclopentadienone. Part of the mechanism is depicted in Figure 7.

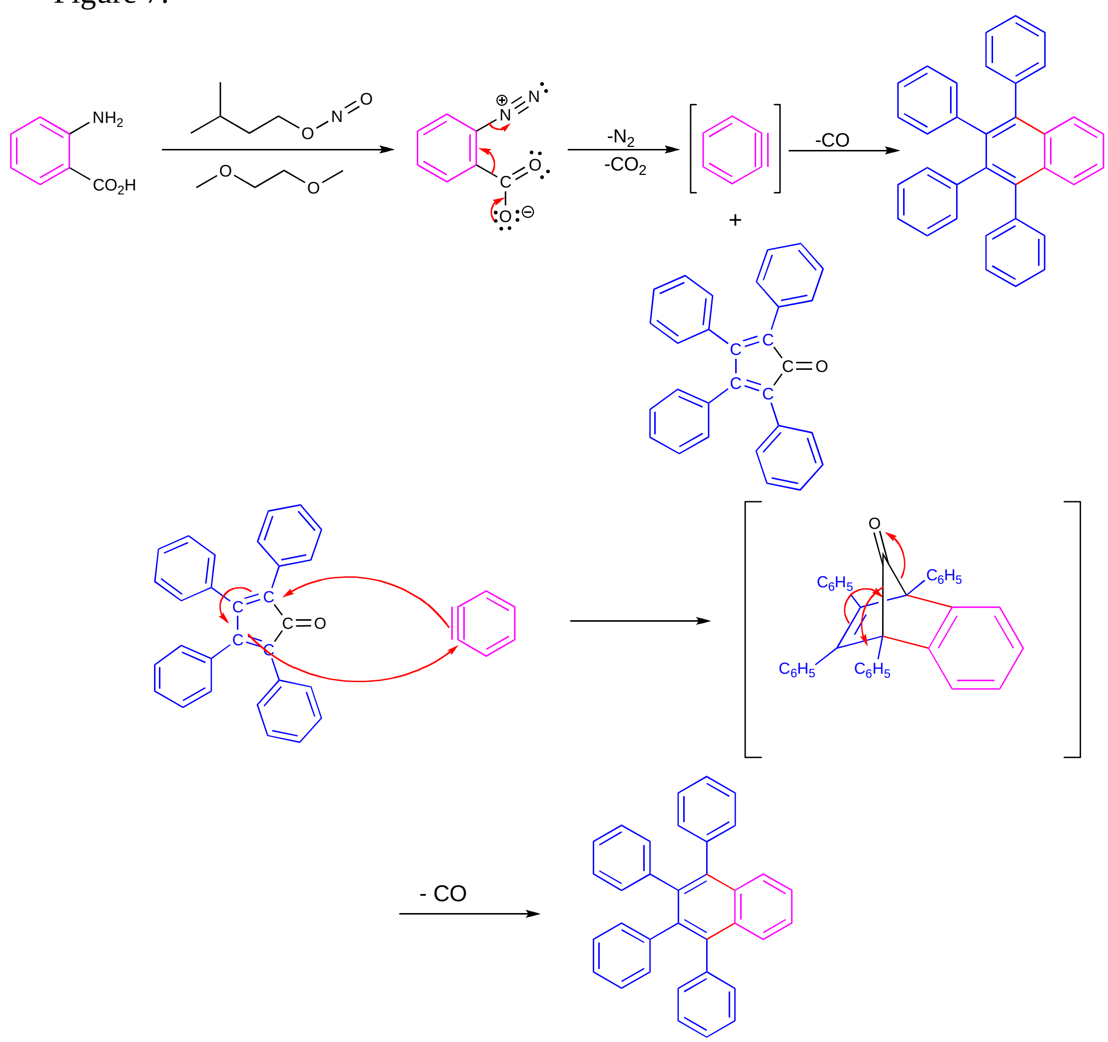


Figure 7. The mechanism for the formation of tetraphenylnaphthalene.

For these reactions, record the initial amounts used, observations made (color change, etc), amount of product recovered, IRs, and melting points if they are in a reasonable range. This data may be collected over this and the next laboratory period. Do not report any experimental data that you did not measure or take yourself.

Cautions:

Take extra care when handling these compounds.
Make sure to use a clean spatula and return the top to the bottles.
All reactions must be clean and free of water.

Experiment

Dimethyl Tetraphenylphthalate

Place 100 mg of tetraphenylcyclopentadienone, 0.1 mL of dimethyl acetylene-dicarboxylate, and 1 mL of nitrobenzene into a small reaction tube along with a boiling stick. Heat the reaction to reflux until the purple solution turns a tan color. When the solution is warm to the touch, stir in 3 mL of ethanol. Place in ice. Vacuum filter the resulting solid and wash with ethanol. Dry the solid and weigh.

Hexaphenylbenzene

Place 100 mg of tetraphenylcyclopentadienone and 500 mg of diphenylacetylene into a small reaction tube. Place a cap on the reaction tube, but do not tighten it. Using a sand bath, heat the solid mixture to reflux (no boiling aid is necessary) until the color becomes brown. While the solution is cooling to room temperature, gently shake the tube until a white solid forms at the bottom. (If the white solid does not form, reflux longer and allow to cool again.) Then, add 2 mL of diphenyl ether and heat until all of the solid is dissolved. Cool again to room temperature, add 2 mL of toluene to the product, and place it in ice. Vacuum filter the resulting solid and wash with toluene. Dry the solid and weigh.

Tetraphenylnaphthalene

Add 500 mg of tetraphenylcyclopentadienone and 3 mL of glyme (1,2-dimethoxyethane) along with a boiling chip to a large reaction tube (uncapped). Using a micropipette, slowly add 0.35 mL of isoamyl nitrite to the reaction tube and heat the mixture to a gentle reflux for about 2-5 minutes. In a separate vial, dissolve 250 mg of anthranilic acid in 2 mL of glyme. Add this anthranilic acid/glyme mixture dropwise to the refluxing solution via pipette. If you do not observe a color change from brown to yellow after 5 minutes, add an additional 0.35 mL of isoamyl nitrite. Heat the yellow solution for two minutes. Cap the large reaction tube, gently shake and allow to cool to room temperature (do not use an ice bath). After the solution has cooled, add 10 mL of ethanol and 5 mL of saturated sodium bicarbonate. Shake well and allow solid to form. Collect the resulting solid using vacuum filtration. Wash this solid twice with cold water followed by cold ethanol. Recrystallize the solid using nitrobenzene/ethanol. Filter the resulting solid, dry and weigh. Record the melting point of your product.