Ref: Organic Experiments
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Kenneth L. Williamson
D C Heath & Company p 289

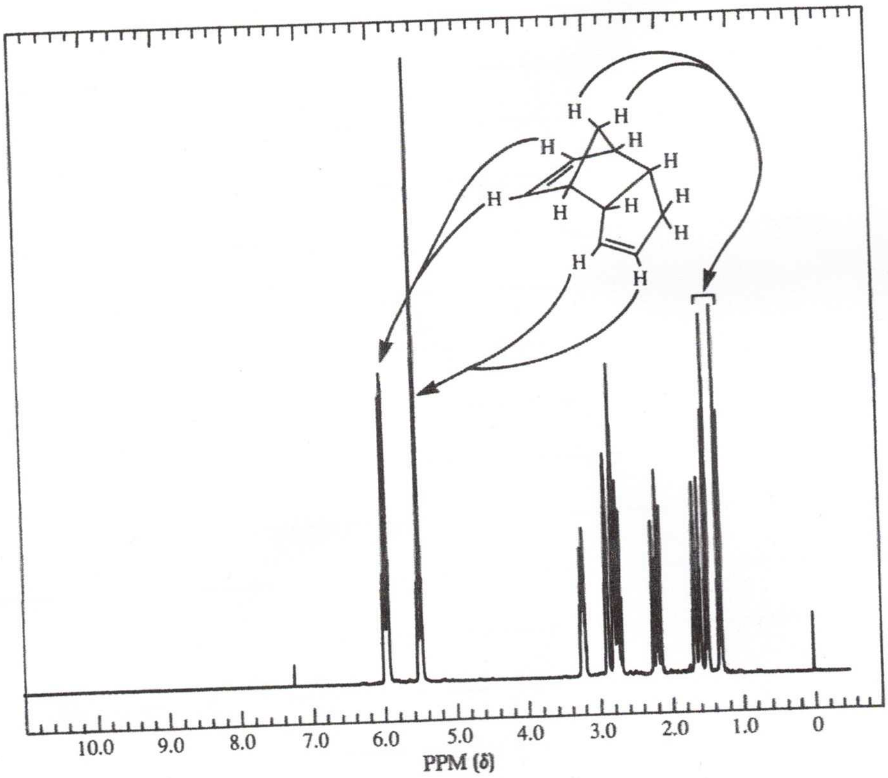


FIG. 1 ^{1}H nmr spectrum of dicyclopentadiene (250 MHz).

Experiments

Gas chromatography reveals that cyclopentadiene is 8% dimerized in 4 h and 50% dimerized in 24 h at room temperature. It should be kept on ice and used as soon as possible after being prepared.

1. Cracking of Dicyclopentadiene

Reverse Diels-Alder

Measure 20 mL of dicyclopentadiene into a 100 mL flask and arrange for fractional distillation into an ice-cooled receiver (Fig. 1 in Chapter 11). Heat the dimer with a Bunsen burner until it refluxes briskly and 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. Apply heat continuously to promote rapid distillation without exceeding the boiling point of 42°C. Distillation for 45 min should provide the 12 mL of cyclopentadiene required for two preparations of the adduct; continued distillation for another half hour gives a total of about 20 mL of monomer.

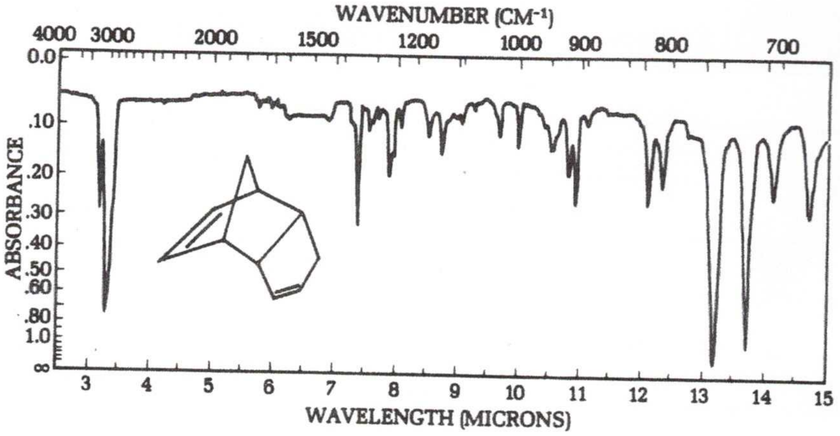


FIG. 2 Infrared spectrum of dicyclopentadiene.

Check old dicyclopentadiene for peroxides

Cleaning Up Pour the pot residue of dicyclopentadiene and unused cyclopentadiene into the recovered dicyclopentadiene container. This recovered material can, despite its appearance, be cracked in the future to give cyclopentadiene. If the pot residue is not to be recycled, place it in the organic solvents container. If calcium chloride is used to dry the cyclopentadiene allow the organic material to evaporate from the drying agent and then place it in the nonhazardous solid waste container.

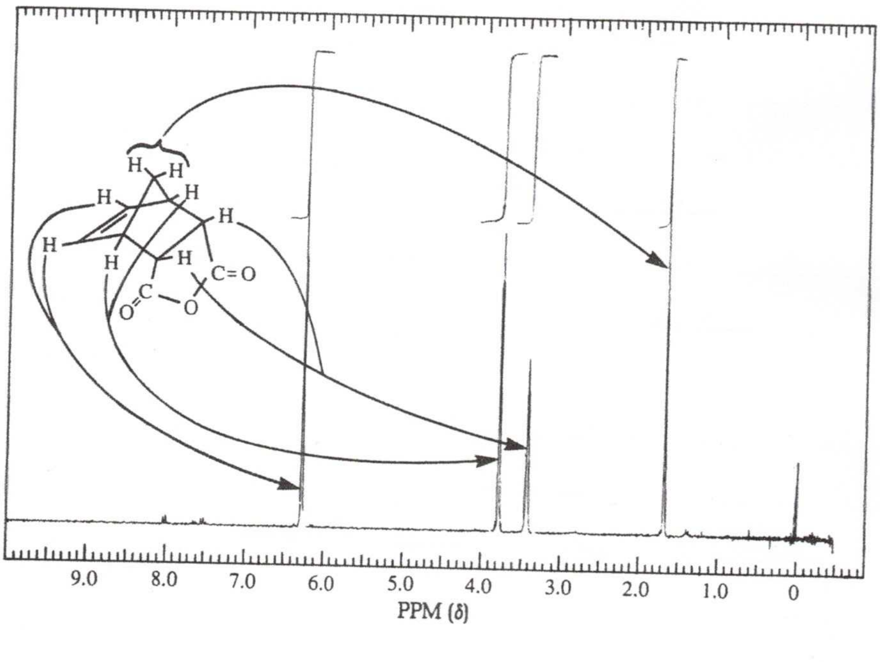
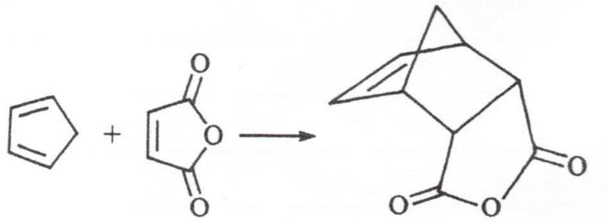


FIG. 3 ¹H nmr spectrum of *cis*-norbornene-5,6-*endo*-dicarboxylic anhydride (250 MHz).

2. *cis*-Norbornene-5,6-*endo*-dicarboxylic Anhydride



Maleic anhydride
mp 53°C, MW 98.06

***cis*-Norbornene-5,6-*endo*-dicarboxylic anhydride**
mp 165°C, MW 164.16

Place 6 g of maleic anhydride in a 125-mL Erlenmeyer flask and dissolve the anhydride in 20 mL of ethyl acetate by heating on a hot plate or steam bath. Add 20 mL of ligroin, bp 60–90°C, cool the solution thoroughly in an ice-water bath, and leave it in the bath (some anhydride may crystallize).

Cyclopentadiene is flammable

Rapid addition at 0°C

The distilled cyclopentadiene may be slightly cloudy, because of the condensation of moisture in the cooled receiver and water in the starting material. Add about 1 g of calcium chloride to remove the moisture. It will redimerize; use it immediately. Measure 6 mL of dry cyclopentadiene, and add it to the ice-cold solution of maleic anhydride. Swirl the solution in the ice bath for a few minutes until the exothermic reaction is over and the

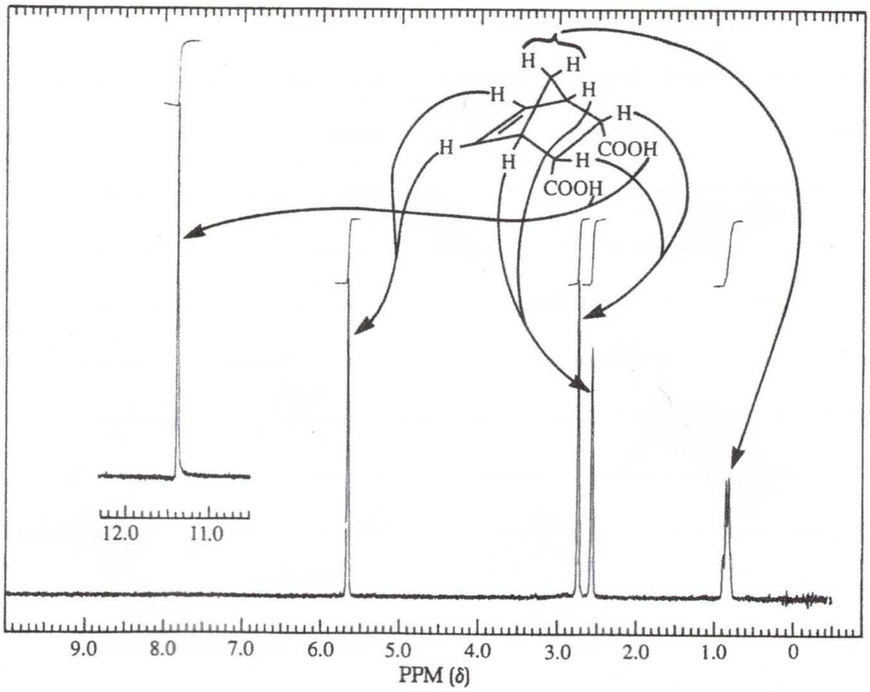
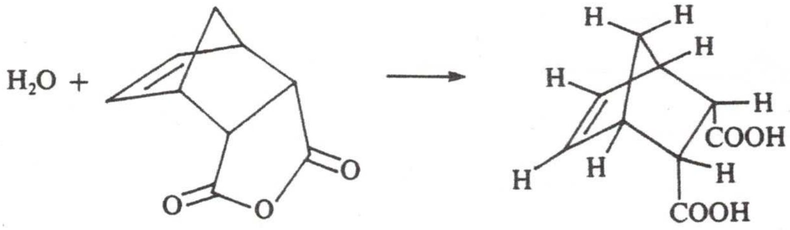


FIG. 4 ^{1}H nmr spectrum of *cis*-norbornene-5,6-*endo*-dicarboxylic acid (250 MHz).

adduct separates as a white solid. Then heat the mixture on a hot plate or steam bath until the solid is all dissolved.[2] If you let the solution stand undisturbed, you will be rewarded with a beautiful display of crystal formation. The anhydride crystallizes in long spars, mp 164–165°C; a typical yield is 8.2 g.[3]

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

3. *cis*-Norbornene-5,6-*endo*-dicarboxylic Acid



***endo,cis*-Diacid**

For preparation of the *endo,cis*-diacid, place 4.0 g of bicyclic anhydride and 50 mL of distilled water in a 125-mL Erlenmeyer flask, grasp this with a clamp, swirl the flask over a hot plate, and bring the contents to the boiling point, at which point the solid partly dissolves and partly melts. Continue to heat until the oil is all dissolved and let the solution stand undisturbed. Because the diacid has a strong tendency to remain in supersaturated solution, allow half an hour or more for the solution to cool to room temperature and then drop in a boiling stone or touch the surface of the liquid once or twice with a stirring rod. Observe the stone and its surroundings carefully, waiting several minutes before applying the more effective method of making one scratch with a stirring rod on the inner wall of the flask at the air-liquid interface. Let crystallization proceed spontaneously

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[2] In case moisture has gotten into the system, a little of the corresponding diacid may remain undissolved at this point and should be removed by filtration of the hot solution.

[3] The student need not work up the mother liquor but may be interested in learning the result. Concentration of the solution to a small volume is not satisfactory because of the presence of dicyclopentadiene, formed by dimerization of excess monomer; the dimer has high solvent power. Hence the bulk of the solvent is evaporated on the steam bath, the flask is connected to the water pump with a rubber stopper and glass tube and heated under vacuum on the steam bath until dicyclopentadiene is removed and the residue solidifies. Crystallization from 1:1 ethyl acetate-ligroin affords 1.3 g of adduct, mp 156–158°C; total yield is 95%.