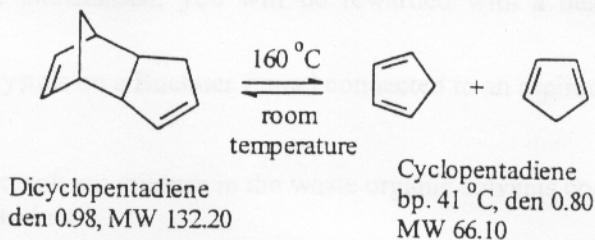


Experiment 5 cis-Norbornene-5,6-endo-dicarboxylic acid by Diels-Alder Reaction

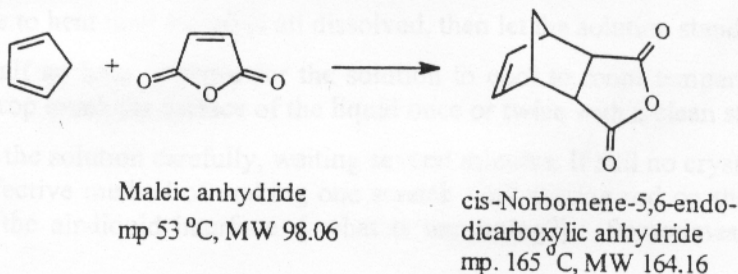
Part A: Cracking of Dicyclopentadiene (performed by your instructor, see figure 1)



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



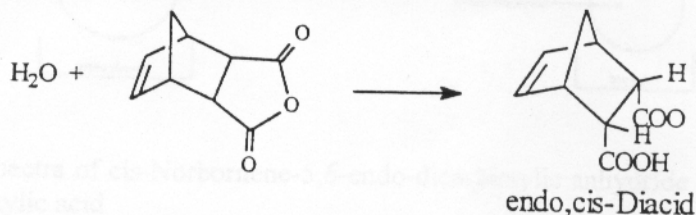
1. Place 6g of maleic anhydride in a 125 ml Erlenmeyer flask and dissolve the anhydride in 20 ml of ethyl acetate. (You may gradually heat the solution in order to dissolve thoroughly, **Caution.** Do not leave your hot plate unattended!) [What did these materials look like before they were mixed? What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

- 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?]
- 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.
- 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.

Part C. Synthesis of cis-Norbornene-5,6-endo-dicarboxylic acid



- For preparation of the endo,cis-diacid, place 4.0g of bicyclic anhydride product (from part B) and 50 ml of distilled water in a 125 ml Erlenmeyer flask. [Is there any evidence of a reaction?]
- Grasp the flask with a clamp and swirl it over a hot plate. When flask contents start to boil, the solid partly dissolves and partly melts.
- Continue to heat until the oil is all dissolved, then let the solution stand undisturbed.
- Allow half an hour or more for the solution to cool to room temperature. If no crystal forms, drop touch the surface of the liquid once or twice with a clean stirring rod.
- Observe the solution carefully, waiting several minutes. If still no crystal forms, apply the more effective method of making one scratch with stirring rod on the inner wall of the flask at the air-liquid interface. [what is happening?] Sometimes, more scratch are needed.
- Let crystallization proceed spontaneously to give large needles.
- Then collect the product on a Buchner funnel connected to an aspirator. Do not attempt to determine the melting point of your product. It does not melt; it decomposes to form an anhydride at 180-185 °C. [what do these diacid crystals look like? color? shapes? Size? Do they appear any difference from the anhydride crystals your isolated in part B?]

Clean Up.

The aqueous filtrate from the crystallization contains a very small quantity of the diacid. It can be flushed down the drain.

Figure 1 Experimental setup for cracking of dicyclopentadiene

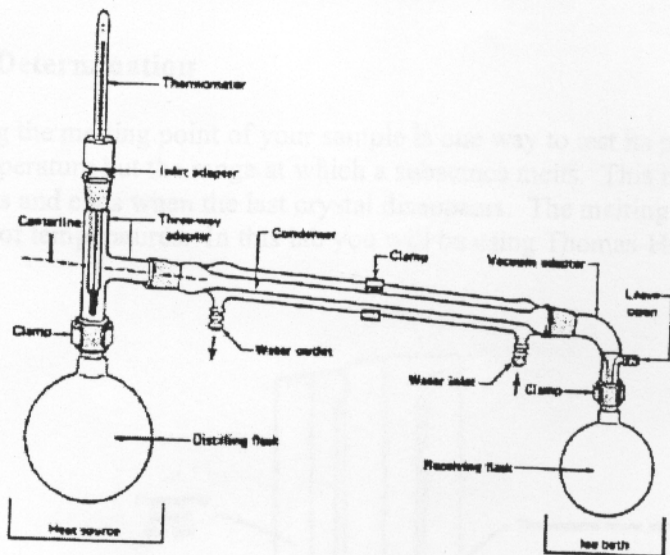


Figure 2. NMR spectra of cis-Norbornene-5,6-endo-dicarboxylic anhydride and cis-Norbornene-5,6-endo-dicarboxylic acid

