CHEM 234: Laboratory Procedure

SYNTHESIS OF cis-NORBORNENE-5,6,-endo-DICARBOXYLIC ANHYDRIDE

Before lab: Read about Diels Alder reactions and recrystallization.

Materials: Dicyclopentadiene, 30 mL (MW 132)
Maleic anhydride, 6 g (MW 98, mp 52 to 54°C)
Toluene, 30 mL
Methylene chloride and pet ether

Precautions: Keep all glassware and solvents dry. Avoid contact with maleic anhydride dust. Conduct this procedure in a good hood.

Hazards: Maleic anhydride is a skin irritant. Cyclopentadiene and toluene fumes are toxic in high concentrations.

Helpful web site: http://www.csupomona.edu/~lsstarkey/distillation/

Experimental Procedure:

Assemble a fractional distillation apparatus consisting of a 100-mL round bottom flask, a packed distillation column, and a condenser and distillation head. Charge the round-bottom flask with 30 mL dicyclopentadiene and reflux over high heat, so that the cyclopentadiene is gradually distilled off. The head temperature during this process should be approximately 45°C. Collect the cyclopentadiene which distills over in an ice-cooled flask. Stopper the flask, set it in an ice bath, and keep it there until the remaining materials are prepared.

Charge a 125-mL Erlenmeyer flask containing 6.0 g powdered maleic anhydride with 25 mL toluene. Swirl until the maleic anhydride dissolved in the toluene. Cool the toluene mixture in an ice bath so that the internal temperature becomes approximately 10°C (check with a thermometer). Dissolve 6 mL cyclopentadiene in 5 mL toluene. Add this solution in small portions to the Erlenmeyer flask, which is immersed in the ice bath. The flask should be vigorously swirled during the addition to dissipate the heat of reaction. A paste will gradually begin to form. After the flask has been left in the ice bath approximately 20 min, warm it on a steam bath and add 35 mL petroleum ether while swirling. Cool the hot petroleum ether solution in an ice bath. The product will crystallize out and should be collected by suction filtration. Save a small amount for a melting point.

Dissolve the product in the smallest amount of hot dichloromethane necessary and dilute the resulting solution with twice its volume of warm petroleum ether or hexane. Set the flask aside. As the solution cools, colorless crystals (mp 166 to 168°C) may be collected. The total yield of pure product is generally about 5 g, mp 164-165°C.
SYNTHESIS OF cis-NORBORNENE-5,6-,endo-DICARBOXYLIC ACID

Experimental Procedure:

For preparation of the *endo-cis*-diacid, place 4.0 g of anhydride and 50 mL of distilled water in a 125-mL Erlenmeyer flask. Gently heat on a flat top heater until the solution just boils. The solid should partly dissolve. Continue to heat until the oil is all dissolved and let the solution stand undisturbed. Since 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 drop in a carborundum boiling stone. Observe the stone and its surroundings carefully and wait 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 to give large needles which will dry quickly, then cool in ice and collect. m.p. 180-185°C, dec. (anhydride formation)