Experiment #49: The Diels-Alder Reaction: The Reaction of Furan with Maleic Anhydride

I. Prelab.
Read the introduction section in your book for experiment #49. This section provides important information on the history, utility, and function of the Diels-Alder reaction.

Important Information: Melting point of the pure endo product = 80°C. Melting point of the pure exo product = 114°C.


![Chemical Structures]

**Furan**
- b.p. = 31°C, d = 0.94 g/mL
- MW = 68.07 g/mol

**Maleic Anhydride**
- m.p. = 53°C
- MW = 98.06 g/mol

**3,6-Epoxy-1,2,3,6-Tetrahydrophthalic Anhydride**
- m.p. = 80°C (endo), 114°C (exo)
- MW = 166.13 g/mol

Caution: Maleic anhydride, and the Diels-Alder adducts are intense skin irritants - WEAR GLOVES! Furan is a very low boiling liquid, so be careful when using heat.

**Synthesis:** Prepare 10 mL of a 4 M solution of maleic anhydride in CH₂Cl₂. (Show your calculations in your lab notebook). Filter off the insoluble maleic acid using a Hirsch funnel and suction filtration.

Place 1.0 mL of furan into a 50 mL round bottomed flask. Add to the reaction tube the appropriate equimolar amount of maleic anhydride solution (show your calculations!). Seal the flask with a stopper (glass or rubber will do), and wrap the stopper with Parafilm. Set the reaction tube in a safe place in your drawer until the next laboratory period because the reaction takes 24-48 hours to complete.

**Isolation:** If crystals haven’t formed yet, insert a clean stirring rod or boiling stick into the reaction tube, remove the wet rod or stick, and allow it to dry, forming seed crystals. When reinserted, crystallization should be instantaneous. Isolate the solids using a Hirsch funnel, and wash with a small amount of ice-cold CH₂Cl₂. Let the crystals dry, and determine the yield and melting point.

**Recrystallization:** Take the melting point of the furan adduct BEFORE recrystallization. The furan adduct requires much more “fineness” to recrystallize because it undergoes a “reverse” or “retro” Diels-Alder reaction at the melting point to produce furan and maleic anhydride. Use a hot water bath adjusted to a temperature just below the melting point, which you should have obtained prior to the recrystallization, and dissolve your adduct in 3.8 mL of a 5:2 mixture of hexane:ethyl acetate using your prewarmed water bath as the heating source. NOTE: USE ONLY HALF OF YOUR CRUDE PRODUCT IN THE RECRYSTALLIZATION!!! Otherwise, you might lose all
of your product due to the retro Diels-Alder reaction mentioned previously. As an alternative recrystallization, you can try dissolving your crude adduct in acetone and induce crystallization by dripping hexane into the acetone solution. Obtain the melting point of the recrystallized product.

Compare the melting point you obtained for your recrystallized material to the melting point of the exo and endo isomers given in the prelab section of this handout. Which isomer have you obtained?

III. Clean-Up:
Dispose of leftover maleic anhydride/CH₂Cl₂ solution in the Halogenated Organics container and the solids and leftover recrystallizing solvents in Nonhalogenated Organics container