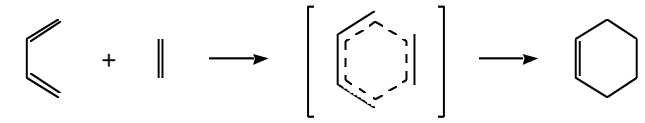
The Diels-Alder Reaction

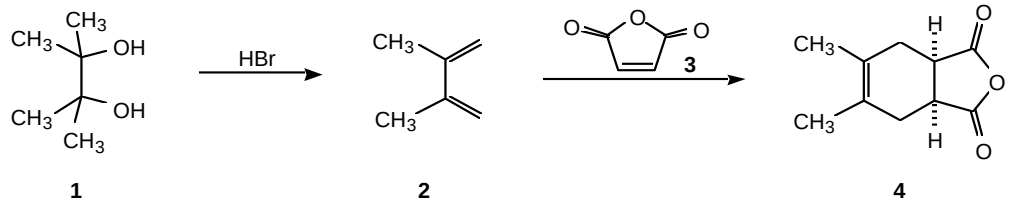
Background

The Diels-Alder reaction is one of the most useful reactions in Organic Chemistry. It involves the addition of an olefin or alkyne (the dienophile) to a diene, and results in the formation of a cyclohexene ring. The reaction takes place in a concerted fashion via the intermediacy of a six-membered cyclic transition state as shown in the simple example below.



"diene" "dienophile"

In this experiment, you will first prepare a diene by dehydration of 2,3-dimethylbutane-2,3-diol (**1**) with HBr. The product of this reaction, 2,3-dimethyl-1,3-butadiene (**2**), will then be utilized in a Diels-Alder reaction using maleic anhydride (**3**) as the dienophile. The reaction takes place stereoselectively, resulting in formation of the bicyclic Diels-Alder adduct, 4,5-dimethyl-*cis*-cyclohex-4-ene-1,2-dicarboxylic anhydride (**4**).



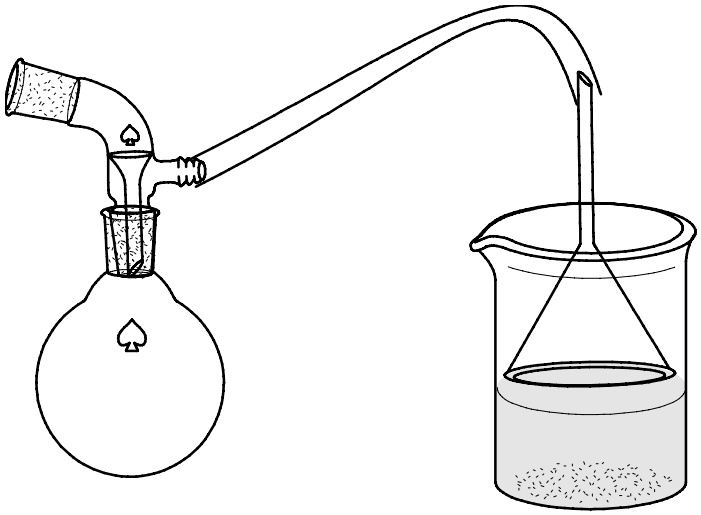
1 **2** **4**

mp = 73-74 °C□
(CAS Registry 5438-24-4)

Procedure

A. Synthesis of 2,3-Dimethyl-1,3-butadiene

With a clean mortar and pestle, grind 6 g of 2,3-dimethylbutane-2,3-diol (pinacol) to a coarse powder. Transfer the crushed pinacol to a 50-mL round-bottomed flask and then add 2.0 mL 48% HBr (CAUTION! HBr fumes are hazardous, and HBr is corrosive!) Stir the resulting mixture for 15 min, then isolate the product by simple distillation. (NOTE: Include a fume trap (Figure 1) in your distillation setup. This practice helps to trap fumes from the distillation.) Distill the mixture slowly, and collect the product that comes over up to 100°C. Transfer the distillate (it should consist of two phases) to a separatory funnel. Drain off the lower, aqueous layer, and wash the organics twice with 3-mL portions of water. Dry the organics with $MgSO_4$. Gravity filter into a 125-mL Erlenmeyer flask. If necessary, the diene may be stored in tightly closed vials in a refrigerater until a subsequent lab period, however, we will use it immediately.



There should be a small gap between the bottom of the funnel and the surface of the water.

Figure 1

B. The Diels-Alder Reaction

Add 1.0 g of maleic anhydride to the 2,3-dimethyl-1,3-butadiene (from part A) in a 125 mL Erlenmeyer flask. Heat the reaction mixture with the warmth of your hands. After a short period of time, an exothermic reaction should begin, and the temperature will rise rapidly to *ca*. 100°C. To avoid boiling off the diene, remove your hands as soon as the reaction begins. If white solid remains, stir occasionally (and carefully!) with a 250°C thermometer. While waiting for the mixture to cool, prepare a gravity filtration with glass stem funnel and fluted filter paper (your TA will demonstrate how to fold a fluted filter paper). Once the reaction mixture cools, add 15 mL hexanes, warm the mixture in a hot water bath, and stir until no more solid dissolves. Remove the thermometer and allow the test tube to stand undisturbed for 1 min. Then, using gravity filtration, transfer the warm filtrate to a 25-mL Erlenmeyer flask. The insoluble residue left behind is unreacted butenedioic anhydride. Allow the solution to cool for 15 min in an ice-bath, then isolate the resulting crystals by vacuum filtration, washing them with a small quantity (*ca*. 2 mL) of ice-cold hexanes. When the crystals are dry, obtain a melting point of your product, an IR, and an NMR. Calculate the percent yield of your product based on the amount of maleic anhydride you used.

Results and Discussion

Discuss your results for each step of this procedure. Indicate why you believe each step of your reaction sequence was (or was not!) successful. Be sure to clearly explain how and why you reached your conclusions. Use your experimental data to prove proposed structures. Remember, spectral data must include functional group/proton assignments, and be clearly interpreted. Be sure to include your spectra (IR, NMR) in Appendix B. An NMR spectrum of 2,3-dimethyl-1,3-butadiene will be provided on ICON. Print this spectrum off and interpret it as part of your report. Does NMR confirm that the reaction was successful?

When analyzing the NMR spectrum, take note of the symmetry in the structure. If there are extra peaks in your spectrum (aside from peaks from water and the NMR solvent), consider these in your analysis of the purity of the product.

References

Harwood, L.M.; Moody, C.J. "Experimental Organic Chemistry: Principles and Practice"; Blackwell Scientific Publications: Oxford, England, 1989, pp. 627-629.

Loudon, G.M. "Organic Chemistry", 2nd ed.; Benjamin/Cummings: Menlo Park, CA, 1988, pp. 592-600.

Name: _____ Section: _____

ID #: _____ Date: _____

2,3-Dimethyl-1,3-butadiene

Distillate volume: _____

Distillate mass _____

Distillate bp range: _____

4,5-Dimethyl-*cis*-cyclohex-4-ene-1,2-dicarboxylic anhydride

Mass Maleic Anhydride Used (g): _____

Mass of Diels Alder product (g): _____

% Yield (based on maleic anhydride): _____

(**Note**: % Yield overall will be same as % Yield (based on maleic anhydride) since it is assumed that the fraction used for the Diels-Alder reaction is 100% diene)

mp: _____