The Diels-Alder Reaction of a Conjugated Diene in Eucalyptus Oil

BACKGROUND
The Diels-Alder reaction is one of the most powerful tools used in the preparation of important organic molecules. When two carbon-carbon double bonds are positioned next to one another, a conjugated diene is formed. A non-conjugated diene is a molecule that has two olefins that are not next to each other. Conjugated dienes undergo a cycloaddition reaction with certain double bonds to afford cyclohexenes and related compounds. This reaction is named for Otto Diels and Kurt Alder who received the 1950 Nobel Prize for discovering this useful transformation. The simplest Diels-Alder reaction is between 1,3-butadiene and ethylene to produce cyclohexene.

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\text{diene} + \text{dienophile} \rightarrow \text{cyclohexene}
\]

This example illustrates what is known as the \textit{Endo Rule}. The addition of maleic anhydride to a diene yields entirely the \textit{endo} product in which the bulkier parts of the dienophile are closer to the carbon-carbon double bond.

Dienes and trienes occur in the essential oils of a number of plants and contribute to their flavors and aromas. You will separate the conjugated diene that is present in eucalyptus oil by allowing it to react with maleic anhydride. The unknown diene will be one of the four following conjugated dienes shown below:

In order to determine the stoichiometric amount of maleic anhydride to react with all of the conjugated diene present, you will estimate the percentage of diene found in eucalyptus oil using the gas chromatogram. Since both maleic anhydride and the product of the Diels-Alder reaction can be hydrolyzed by water, it is important to use dry glassware and to exclude moisture during the reaction and the work-up.

The melting point of the product will reveal the identity of the conjugated diene in the oil. In addition, you will characterize the product by obtaining an infrared spectrum. You will obtain a spectrum of the solid product in a Nujol mull or a KBr pellet. Compare your spectrum to that of maleic anhydride itself.
INTRODUCTION
Since you do not know which diene you have, you will not be able to write a balanced equation until you write your analysis. Include all four dienes in your physical data table.

We will do the following together in class, but it belongs in your introduction section:
Estimate the mass of the unknown diene present in 0.5 g of eucalyptus oil using the GC trace. Assume that the unknown conjugated diene corresponds to the largest peak on the chromatogram and that the peak areas are proportional to the component masses. Calculate the mass of maleic anhydride needed to react with that much diene. Notice that all the unknown dienes have the same molecular weight.

PROCEDURE
In a 5 mL round bottom flask, dissolve 0.5 g (weigh to 0.001 g) of the eucalyptus oil in 1 mL of anhydrous diethyl ether and add the amount of maleic anhydride that you calculated above.

Diethyl ether is highly flammable! Maleic anhydride is corrosive and toxic.

Set up a reflux apparatus and gently reflux the for 45 minutes. While it is warm, transfer the reaction mixture to a small beaker, cover with a watch glass, and let cool to room temperature. Cool it further on ice before collecting the crystals by vacuum filtration. Wash the crystals with 1 mL of cold petroleum ether. Recrystallize the Diels-Alder product from methanol. Heat the methanol gently.

Important! Methanol can cause the product to undergo solvolysis, so it is important that you avoid prolonged boiling during recrystallization.

Measure the melting point of the product so that you can identify which of the four possible dienes is present in eucalyptus oil. Leave the solid in your drawer until next week and re-measure the melting point when it is dry. Weigh the dry product next week. Grind a small amount (spatula-tip full, 20+ mg) of the product on a watch glass with the end of a stirring rod until it has a glassy appearance. Add 2-3 drops of Nujol to the watch glass and grind the mixture until it has the consistency of Vaseline. Using a rubber policeman, transfer some of the mixture to a salt plate. Spread the mull evenly over the surface of the plate using the second plate. Be especially careful to exclude air bubbles. Run the spectrum. A spectrum of pure Nujol is taped to the IR spectrometer. Wash your salt plates with a little acetone!

ANALYSIS
Calculate the percent yield of the Diels-Alder product based on the mass of maleic anhydride used. Attach your IR spectrum or include a table of peaks. Identify which peaks in your spectrum arise from Nujol and which arise from your product. You should be able to identify the two bands which arise from the carbonyl stretching modes. Identify the diene found in eucalyptus oil. Write the correct structure of the Diels-Alder product you believe was formed in the reaction. Draw the mechanism for the formation of the Diels-Alder product.

DISCUSSION
Briefly restate the product, your yield, and any other major points. Remember to include a discussion of how well your experiment went, and what you’d do differently next time.