Name

Lab 173-20#

01-20-05

Identification of a Conjugated Diene from Eucalyptus Oil (Standard Scale)

PURPOSE:

The purpose of this experiment was to prepare the Diels-Alder adduct of the unknown conjugated diene in “eucalyptus oil”, separate the adduct, and identify the unknown diene from the melting point of its adduct.

INTRODUCTION:

This experiment was performed in order to introduce the technique of infrared (IR) spectrometry, though the techniques of heating under reflux, vacuum filtration, recrystallization, melting point measurements and gas chromatography were also emphasized. These techniques were used to separate the Diels-Alder adduct of the unknown conjugated diene in “eucalyptus oil” and identify the diene and product. Dienes contribute to the characteristic flavors and aromas that are found in the essential oils of many plants. Some of these dienes are conjugated and have the ability to make Diels-Alder adducts with maleic anhydride. “The Diels-Alder reaction is the conjugate addition of an alkene to a diene” (Carey, 409).

In order for a Diels-Alder reaction (also known as a cycloaddition reaction) to occur the diene must exist as an s-cis conformation and must be conjugated. “One reactant (the diene) contributes four carbons and the other reactant (the dienophile) contributes two carbons to the six-membered ring of the resulting cyclic compound (the

adduct)" (Lehman, 244). This reaction proceeds in one step with no intermediates. This reaction is also stereoselective and yields either two adducts, exo and endo in order to give the more stable adduct. This reaction is important because it provides the ability to separate dienes from plant oils as well as identify them.

Gas chromatography was used in this experiment to determine the percentage of diene in the eucalyptus oils in order to estimate the amount of maleic anhydride (the dienophile) needed to react with the unknown diene. This technique is important because it allows the separation of volatile components of mixtures. The Diels-Alder reaction was carried out by heating the reactants under reflux in ethyl ether. This technique is important because it heats the reaction mixture, therefore, increases its reaction rate and brings the reaction as close as possible to completion.

The technique of vacuum filtration was used in this experiment in order to separate the adduct from the reaction mixture. Vacuum filtration is important because it offers a speedy and convenient way of separating a solid from a solid-liquid mixture. The technique of recrystallization was used in this experiment in order to purify the adduct and prepare it for analysis. This method is important because it helps purify crystals.

An IR spectrum consists of a series of characteristic peaks, each corresponding to a different kind of bond vibration. An IR spectrometer analyzed the amount of IR radiation the adduct absorbed over a broad frequency range. This technique is important because it "detects the presence or absence of specific functional groups and other structural features from band positions and intensities" (Lehman, 746).

MATERIALS AND METHODS:

This experiment was performed according to the methods of Lehman (2002, 243-249). After the adduct was collected by vacuum filtration, the melting point of the crude sample was taken. After recrystallization with methanol was complete the sample was dried and separated by vacuum filtration.

RESULTS:

The recrystallized adduct appeared as white, thin, long crystals weighing 2.47g (49% recovery) and with melting point ranges of 123.1-126.4ºC (Trial 1) and 121.2-124.6ºC (Trial 2). The crude sample of the adduct appeared as yellow-white crystals with melting point ranges of 47.6-123.4ºC (Trial 1) and 52.3-124.1ºC (Trial 2). Based on the gas chromatogram, peak four was the highest peak which represented the unknown diene. The mass of maleic anhydride needed to react with the diene was 2.34g. According to the IR spectrum of the adduct, sp^2 and sp^3 C-H bonds were present at 3052.63cm^{-1}, 2970.70cm^{-1}, 2945.48cm^{-1} and at 2868.28 cm^{-1}. An acid anhydride stretching band appeared at 1835.58 cm^{-1}; a C=O bond appeared at 1775.47 cm^{-1}; sp^3 C-O stretching bands appeared at 1088.91 cm^{-1} and 1231.63 cm^{-1}; alkene ($RCH=CH_2$) bands appeared 907.85 cm^{-1} and 955.74 cm^{-1}.

DISCUSSION:

Based on the melting point ranges (refer to Table 3) of the pure adduct sample, it was concluded that the unknown diene was _-phellandrene whose adduct has a literature melting point range of 126-127ºC (Lehman, 246). The experimental melting point ranges were similar to the expected value. Broad melting point ranges were caused by impurities remaining in the sample and by not allowing the adduct to dry long enough after

recrystallizing with methanol. The recrystallized adduct had a 49% recovery. Low recovery was due to loss of sample when the reaction mixture was transferred from a round-bottom flask to an Erlenmeyer flask. Low recovery was also caused by losing some sample during vacuum filtration.

According to the IR spectrum and the bands it showed it was concluded that the structure of the product was:

Clues such as a stretching C=O band (1775.47cm^{-1}) confirmed the presence of maleic anhydride in the product. Evidence of the structure drawn above also included C-H (3052.63 cm^{-1}, 2970.70 cm^{-1}, 2945.48 cm^{-1}, and 2868.28 cm^{-1}) and C-O stretching bands (1231.63 cm^{-1} and 1088.91 cm^{-1}) present in the IR spectrum as well as the rest of the bands mentioned in the results.

REFERENCE/LITERATURE CITED:

1. Lehman, John W. *Multiscale Operational Organic Chemistry*; Prentice Hall: Upper Saddle River, 2002; (Part II, 243-249).
2. Carey, F. A, *Organic Chemistry* 5th Ed., McGraw-Hill, 2003, (409).

FIGURES, TABLES, DATA, SPECTRA:

Table 1: MSDS Data on Various Reactants and Products

Reactant/Product	Molecular Weight (g/mol)	Melting Point (ºC)	Boiling Point (ºC)	Density (g/ml)
Diene from Eucalyptus Oil	136.2	N/A	172	0.841
Maleic Anhydride	98.1	53	202	N/A
Ethyl Ether	74.1	-116	34.5	0.714
Petroleum Ether	87-114	-73	20-75	0.60-0.75
Methanol	32.04	-98	64.5	0.8

Table 2: Melting Points of Maleic Anhydride Adducts of the Dienes

Diene	Melting Point of Adduct (ºC)
_-mycrene	33-34
Allo-ocimene	83-84
_-phellandrene	126-127
_-terpinene	60-61

Table 3: Melting Point Ranges of the Crude and Pure Sample of Adduct

	Melting Point Range of Adduct (ºC)
Crude Sample Trial 1	47.6-123.4
Crude Sample Trial 2	52.3-124.1
Pure Sample Trial 1	123.1-126.4
Pure Sample Trial 2	121.2-124.6

Table4: Weight of Eucalyptus Oil and Percent Recovery of Adduct

Weight of Eucalyptus Oil	5.00g
Weight of 10mL beaker	9.23g
Weight of 1omL beaker + pure adduct	11.70g
Weight of pure adduct	2.47g
Percent Recovery	49%

Table 5: Absorption bands and regions from IR Spectrum data

Stretching Band	Region
C-H stretching band	3052.63, 2970.70, 2945.48, 2868.28 cm^{-1}
Acid anhydride stretching band	1835.58 cm^{-1}
C=O stretching band	1775.47 cm^{-1}
C—O stretching band	1231.63, 1088.91 cm^{-1}
Alkene ($RCH=CH_2$) stretching band	955.74, 907.85 cm^{-1}

Figures 1 and 2 are on following page