6-1984

The Microstructure Determination of Poly(B-Pinene)

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THE MICROSTRUCTURE DETERMINATION OF POLY(B-PINENE)

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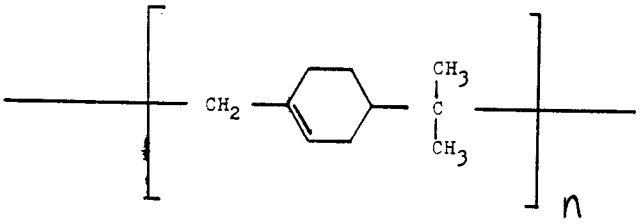
Submitted in partial fulfillment
of the requirements for the degree of
Bachelor of Science

UNION COLLEGE

March, 1984

ABSTRACT

The microstructure of poly(B-pinene) was determined through analysis of pyrolysis products. Terpinolene and 2,4(8)-p-menthadiene were prepared via the base catalyzed isomerization of limonene. The base catalyzed isomerizations of limonene, γ-terpinene, and α-terpinene were thoroughly studied and mechanisms proposed. The oxidation of γ and α-terpinene to p-cymene was studied with DMSO, DMSO and dimethyl sulfone, DMSO and dimethyl sulfide, DMSO and air, and air. B-phellandrene was prepared from Cryptone and from the fractional distillation of Canada Balsam Oil. The following repeat unit was determined as the microstructure of poly(B-pinene):



This Thesis submitted by

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to the Department of Chemistry of Union College
in partial fulfillment of the requirements
for the degree of Bachelor of Science
with a major in Chemistry.

This Thesis is approved by

Howard E. Shaffer

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Dr. Howard E. Sheffer for the countless hours of help, guidance, and inspiration which made this work possible. His assistance in the Laboratory and analytical work were invaluable. In particular, I would like to acknowledge his gifted insights and overall dedication to the Project.

Thanks to Andrew Elkowitz for the preparation of the Menthenes and his companionship in the Laboratory.

I would also like to express my gratitude to Dr. Donald Foust, Dr. Leslie Hull, and Dr. Lawrence McGahey for their guidance and insights throughout the Project.

Special thanks to Dr. William Martin for his invaluable aid in the operation of the Gas Chromatograph/ Mass Spectrometer.

Thanks to Union College Librarian Eileen Kilrain for her assistance in conducting a thorough literature search.

Finally, thanks to Glenn Ledder for his help in the Stockroom and knowledge of Chemicals.

Most importantly I would like to thank my parents whose continued support has made possible my entire education.

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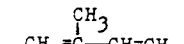
THE MICROSTRUCTURE DETERMINATION OF POLY(B-PINENE)

BACKGROUND

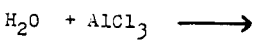
B-Pinene is one of the naturally occuring compounds known as terpenes. Found in the essential oils of many plants, terpenes are made up of units of isoprene, one of nature's favorite building blocks.[1]

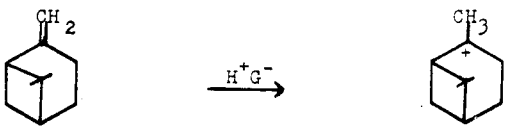


Isoprene

We are interested in determining the microstructure of poly(B-pinene). An earlier work has discussed the cationic polymerization of B-pinene in detail.[2] It was found that the B-pinene monomers are activated by a cationogen derived from a Lewis Acid catalyst/co-catalyst system. The propagating species of B-pinene was found to rearrange to an energetically preferred structure before propagation so that the repeat unit of the polymer is different in structure from that of the original monomer. Termination appears to occur by rearrangement of the active end to a non-propagating bicyclic camphenic type moiety. Another work suggests a fenchenic type moiety.[3] B-pinene cationically polymerizes according to the following scheme:

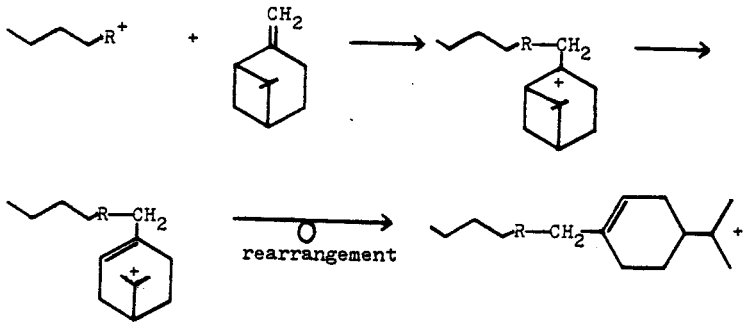
Initiation:



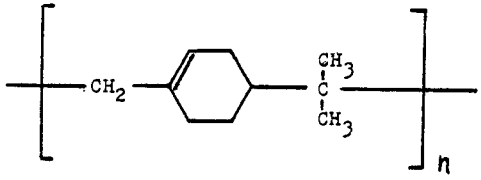


B-Pinene

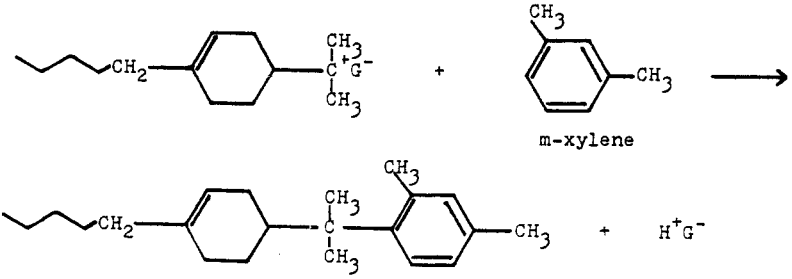
Propagation:



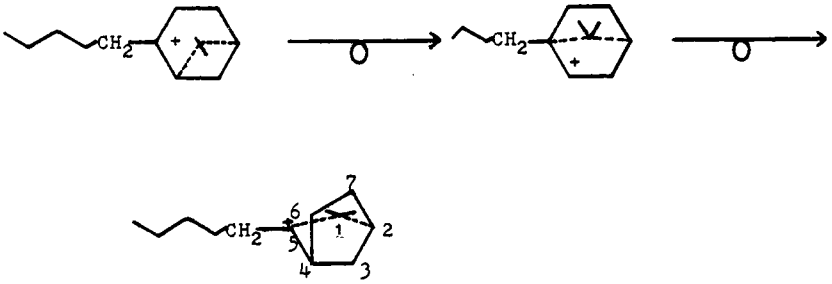
Repeat Unit: (At least 50%)



Chain Transfer to Solvent:



Rearrangement to non-propagating Camphenic End Group:



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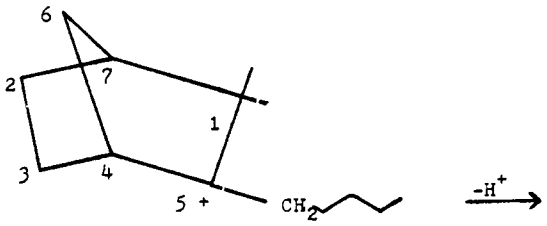
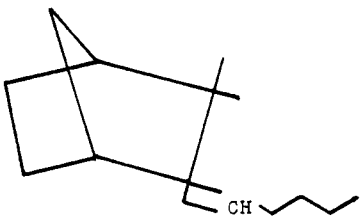
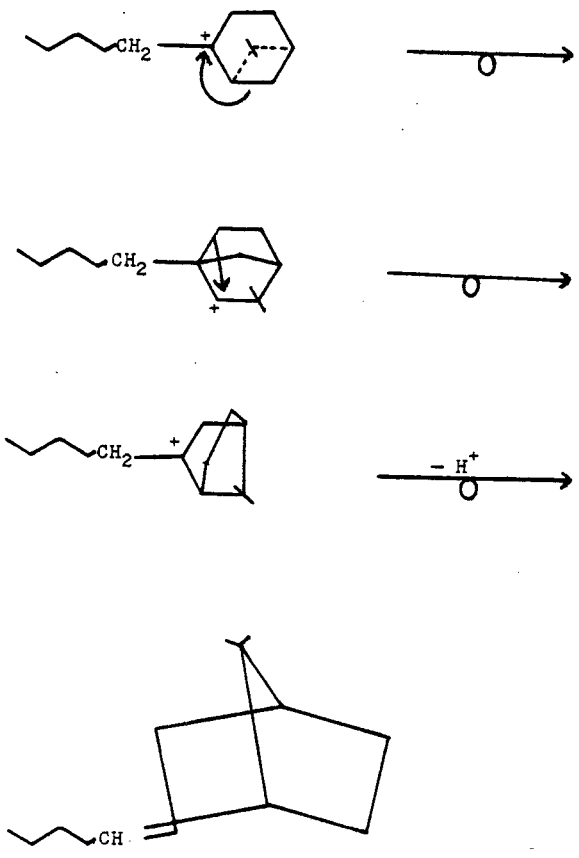




Camphenic End Group

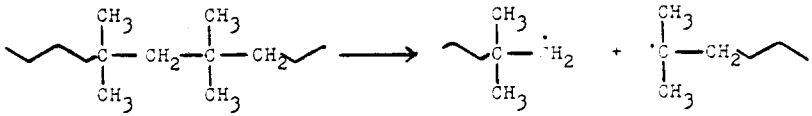
Rearrangement to non-propagating Fenchenic End Group:



Fenchenic End Group

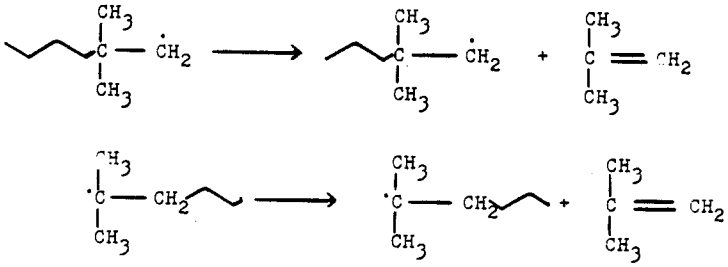
We will be using pyrolysis to determine the microstructure of poly(B-pinene). The extent of degradation of poly(B-pinene) will be followed by monitering the formation of the decomposition products. By knowing the amounts of pyrolysis products, mechanisms for the degradation of poly(B-pinene) can be written. The microstructure of the polymer can then, in turn, be determined either proving or disproving the previously proposed repeat unit.

Much work has been done on the pyrolysis of polymers. One group found pyrolytic reaction mechanisms limited to three types: depolymerization to monomer, random chain scission, and loss of volatile products without much main chain scission.[4] Another group used pyrolysis-gas chromatography to characterize samples of styrene-acrylonitrile copolymers.[5] The pyrolysis of the pinene monomers has already been determined.[6] B-pinene on pyrolysis is shown to give mainly myrcene and limonene. Crowley and Traynor[7] show the mechanism of formation for the allo-ocimenes from pyrolysis of α-pinene. The same authors also state that limonene similarily yields the allo-ocimenes by pyrolysis.[8] Kiran, et. al.,[9] give detailed mechanisms for the thermal decomposition of the polyolefins polyethylene, polypropylene, and polyisobutylene. In the case of polyisobutylene, they found that initiation by chain scission results in primary and tertiary radicals:

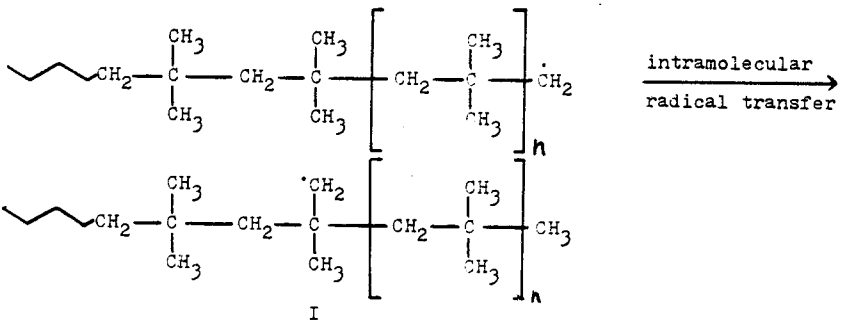


polyisobutylene primary tertiary

Either of these radicals can depolymerize to monomer.

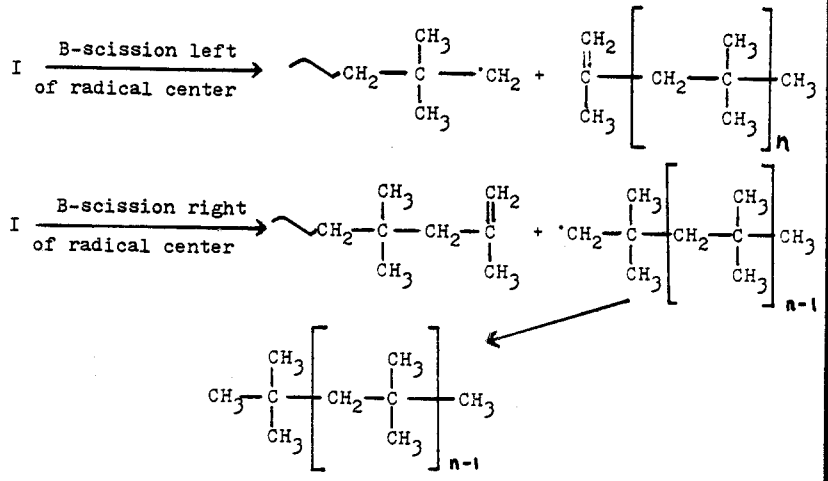


These processes are expected to dominate in part for the reason that the methyl groups on the alternate quaternary carbon atoms sterically hinder intramolecular transfer processes. Therefore, the principal product is formed by B-scission to monomer. Other processes include:

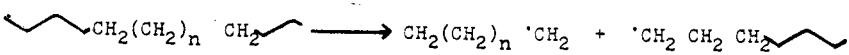


I

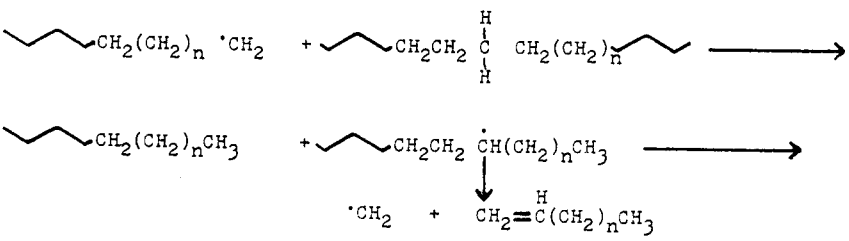
Radical I can dissociate in two ways:



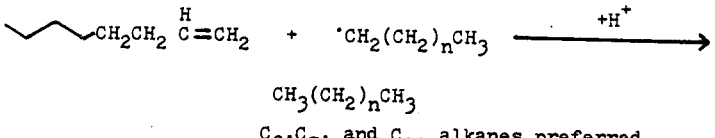
In the case of polyethylene, the dominant processes are intramolecular radical transfer. Main chain scission by thermal energy results in two primary radicals:



Intramolecular radical transfers yield:



C_6, C_{10}, C_{14}, C_{18}, and C_{22} alkenes preferred



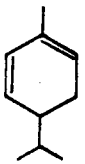
The previous work on mechanisms of pyrolysis will aid us greatly in writing the mechanisms of degradation of poly(B-pinene).

Before any mechanisms of degradation can be written, all of the pyrolysis products must be identified. Professor Sheffer, in previous work involving co-polymerization of styrene and B-pinene,[10-14] has identified many of the pyrolysis products by comparing the pyrolysis-gas chromatographic retention times he obtained with literature values and with known retention times for available terpene standards.

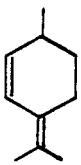
One research group did a thorough study of terpenes on efficient gas chromatographic packed columns.[15] They found the optimum conditions of separation to consist of two columns; one with the non-polar liquid hydrocarbon phase of Apiezon L and the other a polar liquid phase of Reoplex 400 (poly(propyleneglycoladipate)). These two columns facilitate the separation of rather complex mixtures of terpene hydrocarbons. They investigated many terpene hydrocarbons and published the retention times on both columns relative to the retention time of limonene.

Although a retention time check on two columns is generally acceptable evidence for identifying a compound, we intend to couple pyrolysis-gas chromatography with mass spectroscopy to give more substantial results. By obtaining samples of each of the pyrolysis products and storing their retention times and mass spectra in the library of the gas chromatograph-mass spectra instrument, poly(B-pinene) can be pyrolyzed in the instrument and the pyrolysis products can be compared with the standards by the computer. This combination of pyrolysis, Gas Chromatography, and Mass Spectroscopy provides a very powerful method for the identification of the pyrolysis products, much better than retention times alone. Obtaining some of the samples of the pyrolysis products will be difficult since some terpenes are not commercially available. A list of the proposed pyrolysis products is given below.

Toluene

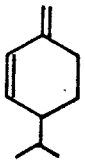


α -phellandrene

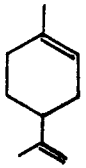


isoterpinolene
or
2,4(8)-p-menthadiene

B-pinene

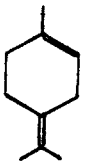


B-phellandrene

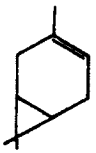


Limonene

α -pinene

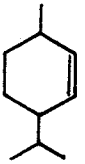


Terpinolene

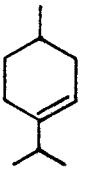


Δ^3carene

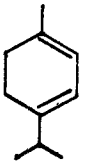
1-p-menthene



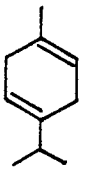
2-p-menthene



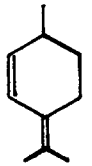
3-p-menthene



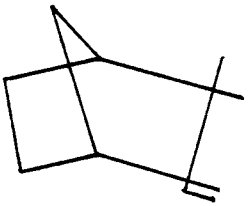
α -terpinene



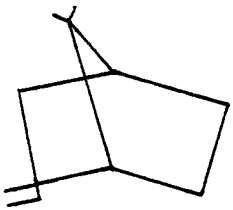
γ -terpinene



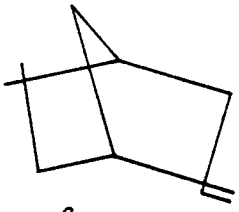
2,4(8)-p-menthadiene



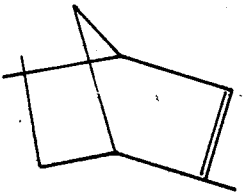
Camphene



α -fenchene



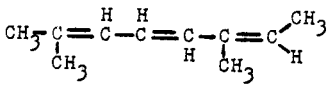
β -fenchene



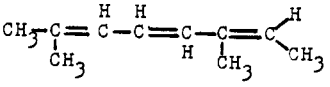
γ -fenchene

Allo-ocimene

trans-cis

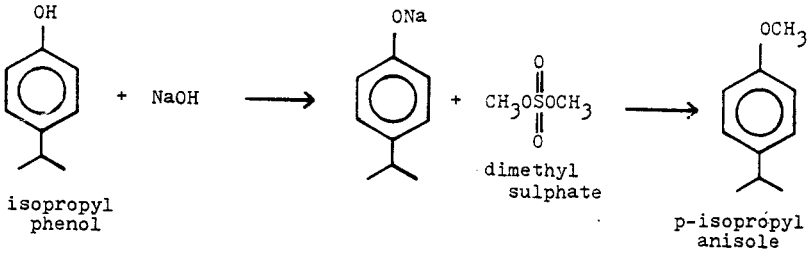


trans-trans

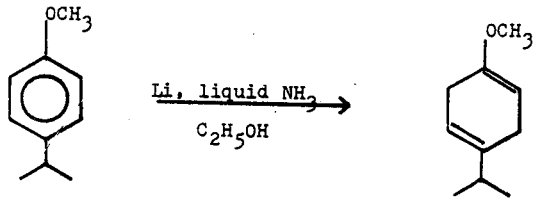


Of these possible pyrolysis products, the following are not commercially available: 2-p-menthene, 3-p-menthene, 1-p-menthene, the fenchenes, 2,4(8)-p-menthadiene, and B-phellandrene, the major proposed pyrolysis product. It is my objective to prepare samples of B-phellandrene and 2,4(8)-p-menthadiene to use as standards for the pyrolysis-gas chromatography-mass spectra work.

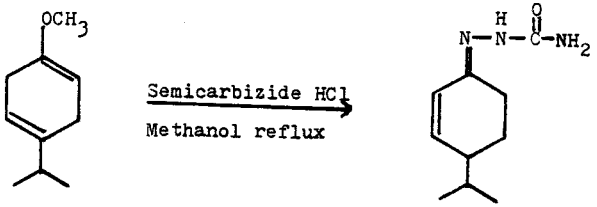
An early effort to prepare B-phellandrene was the fractional distillation of Canada Balsam Oil.[16] A much later effort was the separation of B-phellandrene from Limonene by extractive crystallization with thiourea.[17] A synthetic route to B-phellandrene is given by the synthesis of Cryptone and then converting to B-phellandrene. This multi-step process proceeds as follows. The first step involves the reaction of isopropyl phenol to p-isopropyl anisole.[18]



The next step involves the Birch Reduction of p-isopropyl anisole.[19]

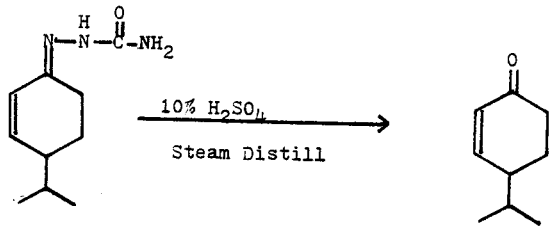


Next the enol ether is converted to 4-isopropyl-2-cyclohexanone Semicarbizone.[20]



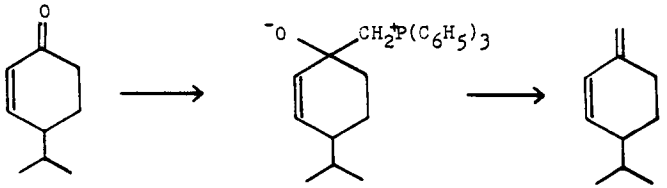
4-isopropyl-2-cyclohexanone Semicarbizone

The next step involves the generation of Cryptone from 4-isopropyl-2-cyclohexanone Semicarbizone.[21]



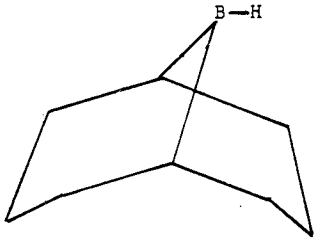
Cryptone

The final step employs the Wittig reaction in the conversion of Cryptone to B-phellandrene.[22]

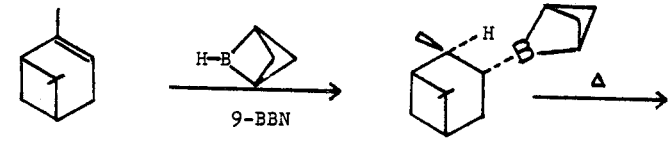


B-phellandrene

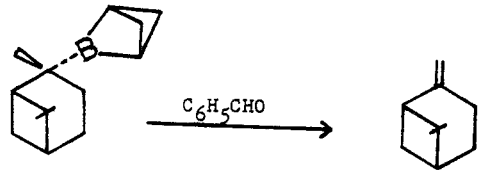
Further examination of the literature revealed another possible route to B-phellandrene. This involved the isomerization of alkenes using hydroboration.[23] Of particular interest was the study which showed that under the influence of heat organoboranes undergo a relatively rapid isomerization which moves the boron atom from an internal position in the chain to the terminal position.[24] The study indicated that the conversion of endocyclic to exocyclic double bonds was possible. The reagent for hydroboration in this and other works was 9-Boracyclo(3.3.1.) nonane or more simply, 9-BBN.[25,26] This hydroborating agent has the following structure:



The most significant application of 9-BBN in the literature was the conversion of ∝-pinene to B-pinene.[27] It was found that the endocyclic double bond of ∝-pinene was easily moved to the exocyclic position forming B-pinene according to the following:



∝-pinene

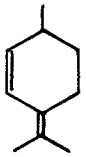


B-pinene

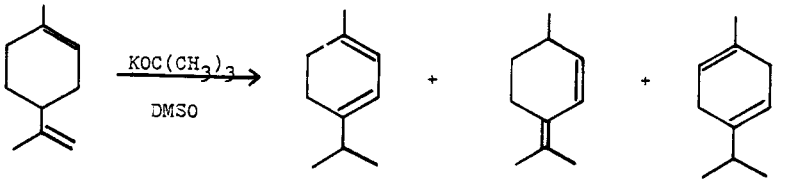
It was believed from the evidence of the ∝-pinene to the B-pinene system and the generalization that the boron migrates to the terminal position of a ring and that hydroboration proceeds by way of a cis addition, preferentially from the less hindered side of the double bond that 9-BBN chemistry might be applied to the synthesis of B-phellandrene. It was proposed that it may be possible to prepare B-phellandrene from ∝-phellandrene in a manner similar to the ∝-pinene to B-pinene system, the only difference being the presence

of the additional double bond in the phellandrenes. Experimental work is now needed to determine whether the isomerization of α-phellandrene to B-phellandrene is feasible or if the additional double bond will have any effect on the reaction.

The next compound which was synthesized was 2,4(8)-p-menthadiene. This terpene has the following structure:



An examination of the literature revealed only one route in obtaining 2,4(8)-p-menthadiene. This involves the base-catalyzed isomerization of dipentene, or limonene.[28] The researchers found that after four days at 100°C a mixture of isomers was obtained according to the following:



Limonene — α-terpinene : 2,4(8)-p-menthadiene : γ-terpinene

5 : 3 : 1

The products obtained appeared in a 5 : 3 : 1 mole ratio with the conjugated dienes being present in greater quantities than the unconjugated diene, γ-terpinene.

Much work has been done in the area of base-catalized isomerizations. One group studied extensively the base-catalyzed disproportionation of cyclohexadiene.[29] They reported that intermolecular hydride transfer resulted in cyclohexadiene disproportionating to benzene and cyclohexene in dimethyl sulfoxide with the base being potassium tert-butoxide. Another group showed that proton migration was intramolecular in the system dimethyl sulfoxide and potassium tert-butoxide for the isomerization of 2-methyl-1-pentene.[30] The same group employed the same solvent-base system in the investigation of the isomerization of three bicyclic olefins with exocyclic double bonds.[31] They found the importance of angle strain contributions to be minor when compared to those involved in the isomerization of endocyclic olefins. The group had earlier reported the presence of a carbanion intermediate which followed the order of carbanion stability, vis., primary > secondary > tertiary.[32] They also determined that the addition of tert-butyl alcohol slowed the reaction considerably. They concluded, using tritium analysis, that the carbanion intermediate exchanges protons with the solvent. Another group found evidence for the carbanion intermediate in the base-catalyzed

isomerization of medium ring dienes and trienes.[33]

Some work also has been done involving the choice of solvents for the base-catalyzed isomerizations of olefins. One work showed that the use of dimethyl sulfoxide allowed double bond isomerization to take place with ease and high selectivity.[34] Another work showed dimethyl sulfoxide to yield faster reaction times than 1,2-dimethoxyethane and tert-butyl alcohol.[35]

Based on the previous work, we will also employ the dimethyl sulfoxide-potassium tert-butoxide system in the isomerization of limonene to prepare 2,4(8)-p-menthadiene.

EXPERIMENTAL

All isomerizations were carried out in a two liter three-necked round bottomed flask fitted with a mechanical stirrer, condensor, and nitrogen inlet unless otherwise stated. The round bottomed flask was submerged in a constant temperature bath of diethylene glycol and glycerine. The specific conditions for each run are as follows:

Isomerization of Limonene, Run 1

The round bottomed flask was charged with 92.9g limonene(0.682 moles), 31.4g $KOC(CH_3)_3$(0.280 moles), and 400ml of DMSO. The reaction mixture was stirred at 100°C for 4 days.

Isomerization of Limonene, Run 2

The round bottomed flask was charged with 92.9g limonene(0.682 moles), 31.4g $KOC(CH_3)_3$(0.280 moles), and 400ml of DMSO. The reaction mixture was stirred under nitrogen atmosphere at 100°C for 4 days. 50ml samples were taken for GC analysis at 4, 18, 28, and 96 hours.

Isomerization of Limonene, Run 3

The round bottomed flask was charged with 18.8g limonene(0.138 moles), 6.30g $KOC(CH_3)_3$(0.056 moles), and 80ml of DMSO. The reaction mixture was stirred under nitrogen atmosphere at 100°C for 8 days. 10ml samples were taken for GC analysis at 10, 20, and 30 minutes, 1, 2, and 4 hours, and 4 and 8 days.

Isomerization of Limonene, Run 4

The round bottomed flask was charged with 37.6g limonene(0.276 moles), 12.6g $KOC(CH_3)_3$(0.112 moles), and 160ml of DMSO. The reaction mixture was tirred under nitrogen atmosphere for 8 days at 100°C. 5ml samples were taken for GC analysis at 0, 1, 2, 3, and 4 hours, and 1, 2, 3, 4, 6, and 8 days.

Isomerization of γ-terpinene, Run 1

The round bottomed flask was charged with 9.4g γ-terpinene(0.069 moles), 3.15g $KOC(CH_3)_3$(0.028 moles), and 40ml of DMSO. The reaction mixture was stirred under nitrogen atmosphere at 100°C for 4 days.

Isomerization of γ-terpinene, Run 2

The round bottomed flask was charged with 18.8g γ-terpinene(0.138 moles), 6.30g $KOC(CH_3)_3$(0.056 moles), and 80ml of DMSO. The reaction was stirred under nitrogen atmosphere at 100°C for 4 days. 10ml samples were taken for GC analysis at 4, 18, 28, and 96 hours.

Isomerization of γ-terpinene, Run 3

The round bottomed flask was charged with 18.8g γ-terpinene(0.138 moles), 6.30g $KOC(CH_3)_3$(0.056 moles), and 80ml of DMSO. The reaction mixture was stirred under nitrogen atmosphere at 100°C for 4 days. 10ml samples were taken for GC analysis at 10, 20, and 30 minutes, 1,2, and 4 hours, and at 2 and 4 days.

Isomerization of γ-terpinene, Run 4

The round bottomed flask was charged with 37.6g γ-terpinene(0.276 moles), 12.6g $KOC(CH_3)_3$(0.112 moles), and 160ml of DMSO. The reaction was stirred under nitrogen atmosphere at room temperature (19°C) for one day. 5ml samples were taken for GC analysis at 0, 1, 2, 4, 8, and 24 hours. After 44 hours at room temperature, the temperature was raised to 50°C and held for one hour. A 5ml sample for GC analysis was taken at this time. After 1 hour at 50°C, the temperature was raised to 75°C, held for an hour and a sample taken for GC analysis. The temperature was then raised to 100°C and samples taken at 0 and 1 hour, and 1, 2, 4, and 8 days.

Isomerization of γ-terpinene, Run 5

A 250 ml round bottomed flask was charged with 5.8g γ-terpinene(0.0426 moles), 1.96g $KOC(CH_3)_3$(0.0175 moles), and 25ml of DMSO. The reaction mixture was stirred under oxygen free nitrogen atmosphere for 14 days.* 1ml samples were taken for GC analysis at 1, 2, 6, and 14 days.

Isomerization of α-terpinene, Run 1

The round bottom flask was charged with 23.2g α-terpinene(0.170 moles), 7.84g $KOC(CH_3)_3$(0.070 moles), and 100ml of DMSO. The reaction mixture was stirred under nitrogen atmosphere at room temperature (19°C) for 1 hour. 5ml samples were taken for GC analysis at 0 and 1 hour. The temperature was then raised to 50°C, held

* at 100°C.

for one hour, and a 5ml sample taken for GC analysis. The temperature was then raised to 75°C, held for one hour and a 5ml sample taken for GC analysis. The temperature was then raised to 100°C with 5ml samples for GC analysis taken at 0,1,2, and 4 hours, and 1, 2, 3, 4, 7, and 8 days.

The following isomerizations were run with no catalyst. They were each run in a 100ml round bottomed flask fitted with an air condensor and a nitrogen inlet. The round bottomed flask was submerged in a constant temperature bath of glycerine. The specific conditions for each run are as follows:

Isomerization of γ-terpinene with DMSO, Run 1

The round bottomed flask was charged with 3.76g γ-terpinene(0.0276 moles) and 16ml of DMSO lot number 221578. The reaction mixture was maintained at 100°C under nitrogen atmosphere for 15 days. 1ml samples were taken for GC analysis at 1, 6, 13, and 15 days.

Isomerization of γ-terpinene with DMSO, Run 2

The round bottomed flask was charged with 3.76g γ-terpinene(0.0276 moles) and 16ml of DMSO lot number 221578. The reaction mixture was maintained at 100°C under nitrogen atmosphere for 13 days. 1ml samples were taken for GC analysis at 1, 5, 9, and 13 days.

Isomerization of γ-terpinene with distilled DMSO, Run 1

The round bottomed flask was charged with 3.76g

γ-terpinene(0.0276 moles) and 16ml of distilled DMSO lot number 221578. The reaction mixture was maintained at 100°C under nitrogen atmosphere for 14 days. 1ml samples for GC analysis were taken at 1, 5, 12, and 14 days.

Isomerization of γ-terpinene with distilled DMSO, Run 2

The round bottomed flask was charged with 3.76g γ-terpinene and 16ml of distilled DMSO lot number 221578. The reaction mixture was maintained at 100°C under nitrogen atmosphere for 13 days. 1ml samples were taken for GC analysis at 1, 5, 12, and 13 days.

Isomerization of γ-terpinene with DMSO and 2% $(CH_3)_2SO_2$, Run 1

The round bottomed flask was charged with 3.76g γ-terpinene(0.0276 moles), 16ml DMSO, and 0.32g $(CH_3)_2SO_2$ (0.0034 moles). The reaction mixture was maintained at 100°C under nitrogen atmosphere for 12 days. 1ml samples were taken at 1, 5, 9, and 12 days for GC analysis.

Isomerization of γ-terpinene with DMSO and 2% $(CH_3)_2SO_2$, Run 2

The round bottomed flask was charged with 3.76g γ-terpinene(0.0276 moles), 16ml DMSO, and 0.32g $(CH_3)_2SO_2$ (0.0034 moles). The reaction mixture was maintained at 100°C under nitrogen atmosphere for 14 days. 1ml samples were taken for GC analysis at 1, 2, 6, and 14 days.

Isomerization of γ-terpinene with DMSO and 2% $(CH_3)_2S$, Run 1

The round bottomed flask was charged with 3.76g γ-terpinene(0.0276 moles), 16ml DMSO, and 2g $(CH_3)_2S$

(0.0322 moles). The reaction mixture was maintained at 100°C under nitrogen atmosphere for 15 days. 1ml samples for GC analysis were taken at 1, 3, 7, 12, and 15 days.

Isomerization of γ-terpinene with DMSO and 50% $(CH_3)_2S$, Run 1

The round bottomed flask was charged with 3.76g γ-terpinene(0.0276 moles), 16ml DMSO, and 8g $(CH_3)_2S$ (0.129 moles). The reaction mixture was maintained at 100°C under nitrogen atmosphere for 7 days. 1ml samples for GC analysis were taken at 1, 2, 4, and 7 days.

Isomerization of γ-terpinene with DMSO and 50% $(CH_3)_2S$, Run 2

The round bottomed flask was charged with 3.76g γ-terpinene(0.0276 moles), 16ml DMSO, and 8g $(CH_3)_2S$ (0.129 moles). The reaction mixture was maintained at 100°C under nitrogen atmosphere for 14 days. 1ml samples for GC analysis were taken at 1, 2, 6, and 14 days.

Isomerization of γ-terpinene with DMSO and air, Run 1

The round bottomed flask was charged with 3.76g γ-terpinene(0.0276 moles) and 16ml DMSO. The reaction mixture was maintained at 100°C for 2 days. 1ml samples for GC analysis were taken at 1 and 2 days.

Isomerization of γ-terpinene and air, Run 1

The round bottomed flask was charged with 3.76g γ-terpinene(0.0276 moles). The γ-terpinene was maintained at 100°C for 6 days. 1ml samples for GC analysis were

taken at 1, 2, and 6 days.

Isomerization of α-terpinene with DMSO, Run 1

The round bottomed flask was charged with 3.76g α-terpinene(0.0276 moles) and 16ml of DMSO. The reaction mixture was maintained at 100°C for 15 days under nitrogen atmosphere. 1ml samples for GC analysis were taken at 1, 2, 7, 9, and 15 days.

Isomerization of α-terpinene with distilled DMSO, Run 1

The round bottomed flask was charged with 3.76g α-terpinene(0.0276 moles) and 16ml of distilled DMSO. The reaction mixture was maintained at 100°C under nitrogen atmosphere for 15 days. 1ml samples were taken for GC analysis at 1, 2, 5, and 9 days.

All samples were worked up in the following manner. The reaction was quenched with water and extracted three times with pentane. The pentane extracts were combined, washed with water and dried over magnesium sulfate and filtered.

Gas Chromatographic analyses were performed on a GOW-MAC model 550 equipped with a hot wire detector and both Apiezon L and Reoplex 400 columns.

The limonene used in the isomerizations was provided by Schenectady Chemicals, Inc. and was 96% pure. The impurities were α, β, and γ- fenchene and α-pinene. The γ-terpinene was from Aldrich and was 92.5% pure, the primary impurity being p-cymene. The α-terpinene,

DMSO, $KOC(CH_3)_3$, $CH_3SO_2CH_3$, and CH_3SCH_3 were also from the Aldrich Chemical Company.

Preparation of B-phellandrene:

Distillation of Canada Balsam Oil, Run 1

Approximatly 50g of Canada Balsam Oil were fractionally distilled at reduced pressure in a short-path distillation apparatus equipped with a Vigreux column. A silicone oil bath was employed to control the temperature of the distillation pot. Fraction 3, taken at 90mm Hg and 140-150°C, was believed to contain B-phellandrene but after GC analysis was shown to consist of a mixture of limonene, α and γ-terpinene, and B-phellandrene. Fraction 3 was redistilled to yield a fraction at 110mm Hg and 63°C which contained limonene, γ-terpinene, and B-phellandrene. A UV-VIS spectrum of this fraction proved the existence of a conjugated diene and is reproduced in Appendix 1. Another fraction at 100mm Hg and 160°C proved to be primarily polymers obtained from the high temperature distillation.

Synthesis of B-phellandrene from Cryptone. Step 1

Synthesis of p-isopropyl anisole from p-isopropyl phenol[18]

Isopropyl phenol, 119g(0.875 moles), 35g NaOH(0.875 moles), and 350ml of water were charged to a 5l three necked round bottomed flask. The mixture was cooled in an ice-salt bath to less than 10°C. 110.4g of dimethyl sulfate (0.875 moles) were then added over the period of one hour.

The reaction mixture was then heated over a water bath for ½hour. At the end of this time, another 119g of isopropyl phenol(0.875 moles), 35g NaOH(0.875 moles), and 350ml of water were added over a period of 15 minutes. The reaction mixture was then refluxed vigorously for 15 hours. The p-isopropyl anisole was recovered by extraction with 200ml of benzene. The benzene extract was washed with water, dried over calcium chloride, and filtered under suction. The product was distilled under vacuum yielding 250ml of distillate at 104mm Hg and 122°C.

Synthesis of B-phellandrene from Cryptone. Step 2

Birch Reduction of p-isopropyl anisole[19]

12.2g of p-isopropyl anisole(0.081 moles), 800ml dry ether, and 1000ml of liquid ammonia were added to a 4l unsilvered dewar flask fitted with a mechanical stirrer, dropping funnel, and soda lime drying tube. 16.8g of lithium wire(2.42 moles) were added to the homogenius solution over a period of 10 minutes. After stirring for 10 minutes, absolute alcohol was added dropwise over a period of 10 minutes. When the blue color had disappeared, the ammonia was evaporated, ether and water added, separated, and the aqueous layer re-extracted with ether. After washing the combined extracts with a saturated salt solution and drying over K_2CO_3, the ether was removed and 7.3g of 2,5-dihydro-4-isopropylanisole (59% yield) were recovered.

Birch Reduction of p-isopropyl anisole, Run 2

12.2g of p-isopropyl anisole(0.081 moles), 800ml of dry ether, 16.8g of lithium wire(2.42 moles), and 800ml of liquid ammonia were reacted in a 4l unsilvered dewar flask under the same conditions as Run 1. 7.0g of 2,5-dihydro-4-isopropylanisole(56% yield) were recovered.

Synthesis of B-phellandrene from Cryptone, Step 3[20]

Preparation of 4-isopropyl-2-cyclohexanone Semicarbizone, Run 1

0.152g of the enol ether(0.0011 moles) from the lithium reduction was refluxed for twenty minutes with 1.1g semicarbizide hydrochloride(0.0099 moles) in 10ml of methanol. Water was added until the solution became turbid and the mixture was refluxed ten minutes longer. The semicarbizone was precipitated in fine white needles by further dilution with water. 0.02g of 4-isopropyl-2-cyclohexanone semicarbizone (melting point 183-185°C) were recovered.

Preparation of 4-isopropyl-2-cyclohexanone Semicarbizone, Run 2

0.304g of 2,5-dihydro-4-isopropylanisole(0.0022 moles), 2.2g of semicarbizide hydrochloride(0.0198 moles), and 20ml of methanol were reacted under the same conditions as Run 1. The reaction contents were refrigerated overnight and 0.76g of the semicarbizone melting at 192-194°C were recovered.

Preparation of 4-isopropyl-2-cyclohexanone Semicarbizone, Run 3

6.27g of 2,5-dihydro-4-isopropylanisole(0.0464 moles) and 46.6g of semicarbizide hydrochloride(0.418 moles) were refluxed in 250ml of methanol under the same conditions as Run 1. 2.18g of semicarbizone(melting point 180°C) were recovered.

Preparation of 4-isopropyl-2-cyclohexanone Semicarbizone, Run 4

1.0g of 2,5-dihydro-4-isopropylanisole(0.0074 moles) and 7.44g of semicarbizide hydrochloride(0.0667 moles) were refluxed in 150ml of methanol under the same conditions as Run 1. 0.87g of semicarbizone(melting point 182-186°C) were recovered.

Preparation of 4-isopropyl-2-cyclohexanone Semicarbizone, Run 5

6.0g of 2,5-dihydro-4-isopropylanisole(0.0444 moles) and 44.6g of semicarbizide hydrochloride(0.40 moles) were refluxed in 300ml of methanol under the same conditions as Run 1. 3.77g of semicarbizone(melting point 182-184°C) were recovered.

Synthesis of B-phellandrene from Cryptone, Step 4

Generation of Cryptone from Semicarbizone[21]

4.0g of the purified semicarbizone(0.022 moles) were added to 50ml of 10% sulphuric acid and steam distilled under nitrogen atmosphere. The distillate was extracted with ether three times. The ether extracts were combined, dried, and the ether removed under vacuum yielding 0.25g of Cryptone.

Generation of Cryptone from Semicarbizone, Run 2

4.64g of the purified semicarbizone(0.025 moles) were added to 250ml of 10% sulphuric acid and steam distilled under nitrogen atmosphere. After following the procedure of Run 1, 2.8g of Cryptone were recovered.

Synthesis of B-phellandrene from Cryptone, Step 5

B-phellandrene from Cryptone[22]

1.4g of lithium(0.2 moles) were gradually added to 10g of bromobenzene(0.064 moles) in 100ml of dry ether under nitrogen atmosphere. The phenyl lithium solution was filtered into a stirred suspension of 25.5g of methyl triphenyl phosphonium iodide(0.063 moles) in 200ml of dry ether and the whole mixture stirred for 2.5 hours under nitrogen atmosphere at room temperature. 3g of Cryptone(0.022 moles) were then added during a period of 15 minutes. The entire mixture was heated and ligroin added as the ether distilled to give a refluxing temperature of 40-60°C. The mixture was refluxed for 5 hours when the solution was cooled and filtered. The ligroin was evaporated and run through an aluminum oxide column two feet in length. The column was eluted with ligroin and 4 fractions of 25-30ml in volume were collected. The ligroin was evaporated and white crystals of triphenyl phosphonium iodide(melting point 80-92°C) and a yellow oil were left behind. The yellow oil was taken up in pentane and shown to be B-phellandrene by GC analysis. (Yield: 0.8g)

The Canada Balsam Oil used in the fractional distillation was obtained from Fluka. The isopropyl phenol used in the synthesis of B-phellandrene was lot number 17,540-4 from the Aldrich Chemical Company. The dimethyl sulfate was obtained from Eastman Chemical and was from lot number B398. The semicarbizide HCl was from MCB and the Aluminum Oxide for the column was lot number 71307 from Merck & Company. The bromobenzene and triphenyl phosphonium iodide were both obtained from the Aldrich Chemical Company.

Reaction of ∝-phellandrene with 9-BBN, Run 1

A 250ml three necked round bottomed flask fitted with reflux condensor, thermometer, and magnetic stirrer was charged with 1.00g ∝-phellandrene(0.00735 moles) and 29.6ml of 0.5M 9-BBN in THF(0.0148 moles). The reaction mixture was stirred at reflux for 7 days. At the end of this time, 1.6ml of benzaldehyde(0.0144 moles) was added and the reaction mixture stirred at reflux for another 7 days. At the end of this time, 9.5ml of 3N NaOH and 7ml of 30% H_2O_2 were added and the whole stirred for two hours at 50-60°C. The products were taken up in pentane and dried over anhydrous magnesium sulfate. The products were identified using gas chromatographic analysis.

The ∝-phellandrene was obtained from Fluka and the 9-BBN from Aldrich Chemical Company.

Pyrolysis/Mass Spectroscopy

Mass spectra were obtained from a Hewlett-Packard 5992 GC/MS system equipped with our Apiezon L column. The following terpene standards were put into the library of the instrument: 2,4(8)-p-menthadiene and terpinolene from the isomerization of γ-terpinene, Run 2, B-phellandrene via the Wittig reaction of Cryptone, trans 2-p-menthene and 3-p-menthene from Andy Elkowitz's dehydration of menthol, α and Δ fenchene from Professor Sheffer's reaction of fenchyl amine with nitric acid, and 1-p-menthene, α-phellandrene, and allo ocimene, trans - cis from Fluka Chemical Company. The mass spectra of these compounds are provided in Appendix IV along with the spectra of other terpenes already stored in the Pollution Library of the Instrument.

Poly(B-pinene)(Professor Sheffer's Run 207), 6.2mg, was pyrolyzed for 30 seconds at 500°C on a Hewlett Packard 80 Pyrolysis Unit. The pyrolysis unit was coupled directly to the GC/ Mass Spectrometer with the following conditions: Column Temperature 120°C, Injection Port Temperature 150°C, and Helium flow rate 30 psi. The mass spectra of the pyrolysis products are given in Appendix IV.

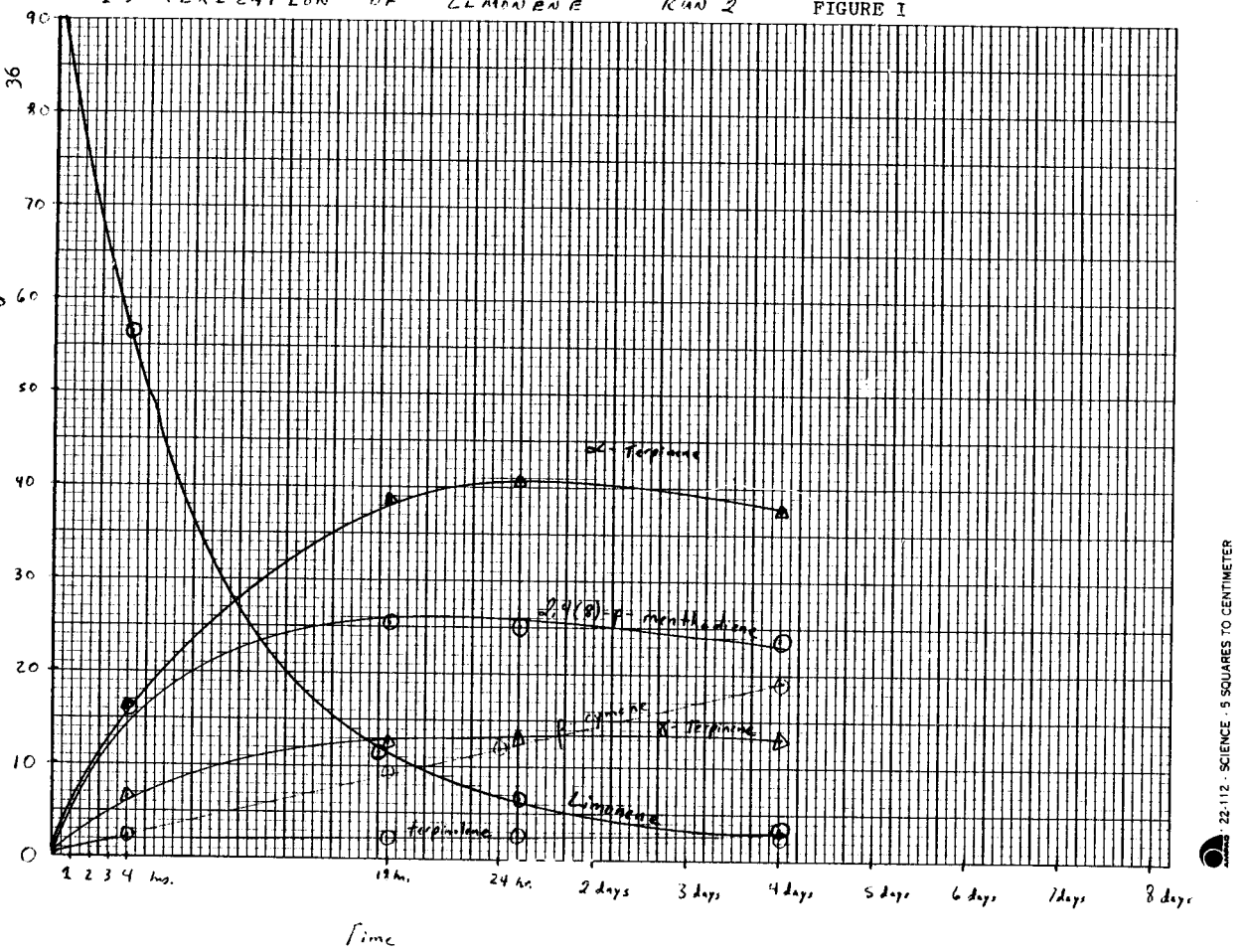
RESULTS AND DISCUSSION

The gas chromatographic analysis of the isomerization of Limonene, Run 1, led us to an extensive study of the reaction. Expecting α-terpinene, 2,4(8)-p-menthadiene, and γ-terpinene in a 5 : 3 : 1 mole ratio,[28] we were quite suprised to find five products as well as some unreacted limonene. P-cymene and terpinolene were identified in the reaction mixture after four days as well as the expected α and γ-terpinene and 2,4(8)-p-menthadiene. Spiking with pure samples of α and γ-terpinene, p-cymene, and limonene on both the Reoplex 400 and Apiezon L columns was employed to prove their existence. These results prompted the isomerization of limonene, Run 2 for verification. Run 2 was monitered to follow the percent composition of products with time. The results of Run 2 are as follows.

Table I: Isomerization of Limonene, Run 2*

	4hrs.	18hrs.	28hrs.	96hrs.
α-terpinene	16.2%	38.7%	40.7%	37.6%
p-cymene	2.3	9.6	12.0	19.1
limonene	56.7	11.5	6.5	3.4
γ-terpinene	6.6	12.4	13.1	13.3
terpinolene	2.1	2.3	2.7	2.8
2,4(8)-p-menthadiene	16.0	25.5	25.0	23.9

*A plot of these results is provided in Figure I.


ISOMERIZATION OF LIMONENE RUN 2
FIGURE I
Percent of Product
Time
α-Terpinene
Δ(8)-P-menthadiene
γ-terpinene
α-Terpineol
Limonene
terpinolene
1 2 3 4 hrs.
12 hr.
24 hr.
2 days
3 days
4 days
5 days
6 days
7 days
8 days
36
22-112 · SCIENCE · 5 SQUARES TO CENTIMETER

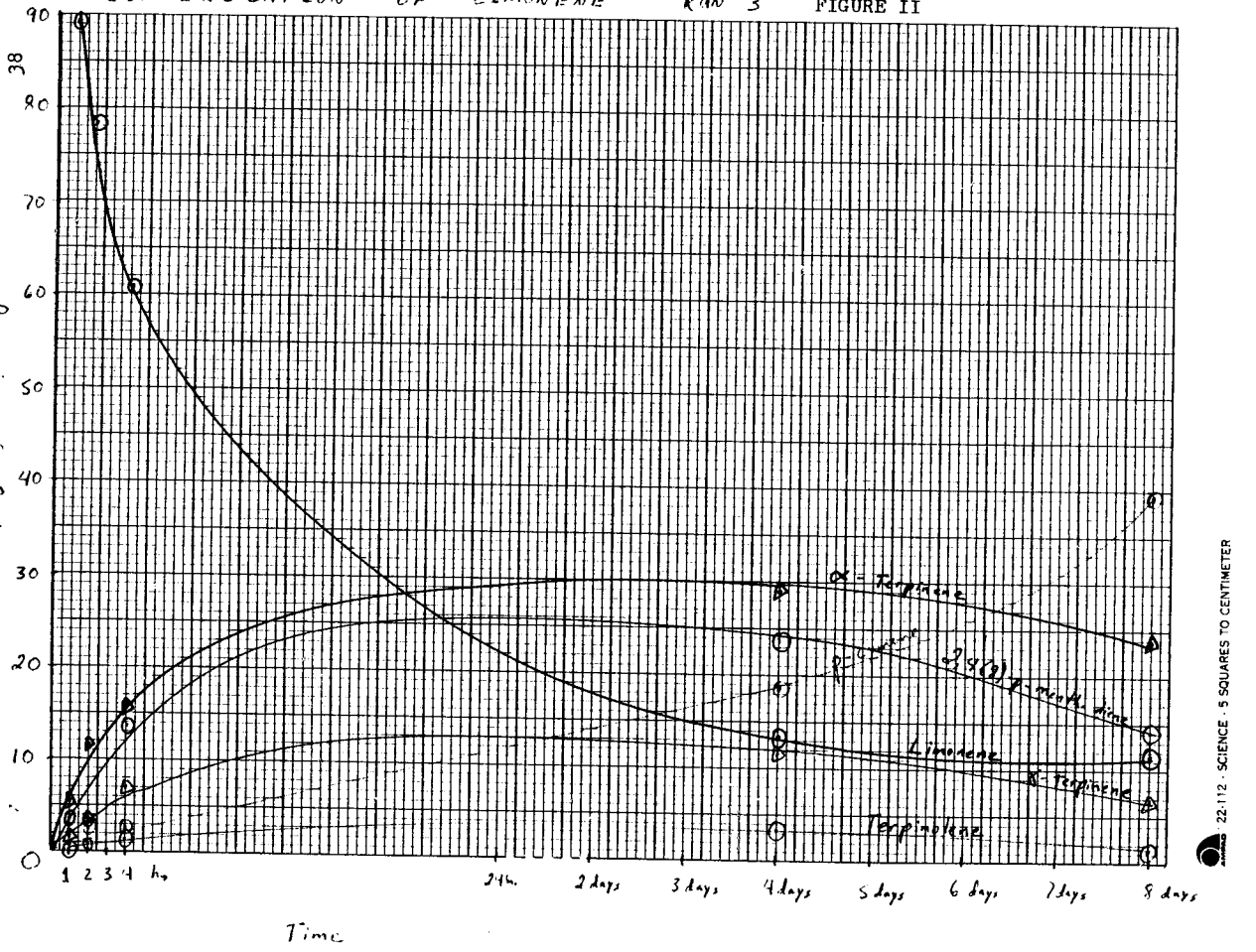
These results allowed us to follow the disappearance of limonene and formation of products. However, four days seemed to be insufficient as an end point of the reaction as it seemed that ∝-terpinene and 2,4(8)-p-menthadiene were disappearing and p-cymene still forming. Run 3 was allowed to react for 8 days to get a better idea of what was happening. The results of Run 3 follow.

Table II: Isomerization of Limonene, Run 3*

	1hr.	2hrs.	4hrs.	4days	8days
∝-terpinene	5.4%	11.5%	15.6%	29.0%	23.8%
p-cymene	0.0	2.9	2.4	18.5	39.6
Limonene	89.3	78.1	60.8	13.6	11.7
ɣ-terpinene	1.6	3.7	6.0	11.9	6.8
terpinolene	0.0	0.7	1.3	3.3	1.6
2,4(8)-p-menthadiene	3.7	3.1	13.7	23.7	14.0

*A plot of these results is provided in Figure II.

The results would indicate that all species are disappearing to form p-cymene. However, the limonene is not disappearing at the same rate as it did in Run 2. It was then decided to start a new run using oxygen free nitrogen in order to curtail the oxidation of reaction products to p-cymene. Run 4 was also monitered more closely than the previous runs in order to obtain a clearer picture of what was happening. The


ISOMERIZATION OF LIMONENE RUN 3
FIGURE II
Percent of Product
Time
α - Terpinene
γ - Terpinene
Limonene
Terpinolene
1 2 3 4 hr.
24 hr.
2 days
3 days
4 days
5 days
6 days
7 days
8 days
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results of Run 4 follow.

Table III: Isomerization of Limonene, Run 4*

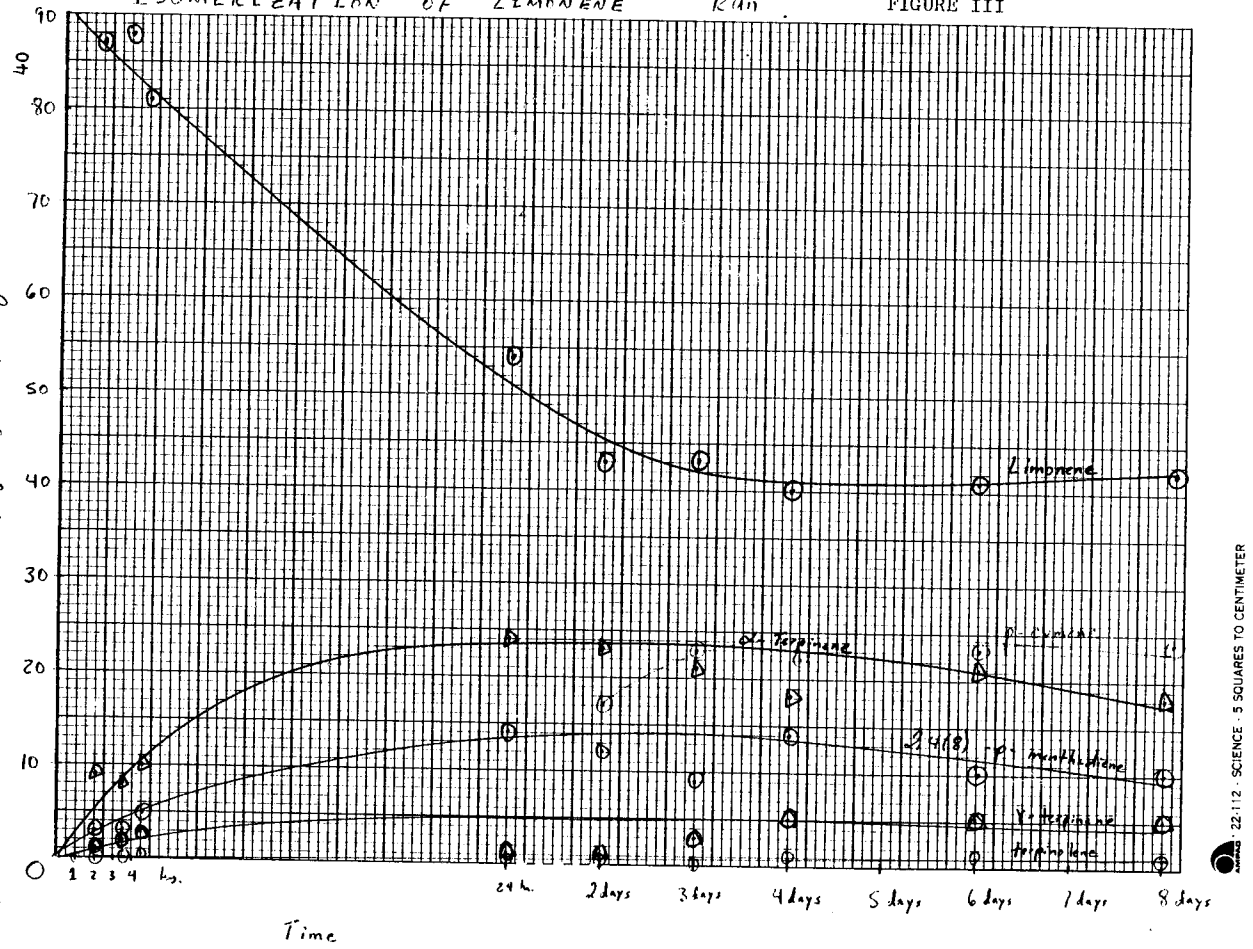
	2hrs.	3.5hrs.	4.5hrs.	1day	2days
∝-terpinene	9%	7%	10%	24%	23%
p-cymene	0	0	0	0	17
limonene	87	88	81	54	43
ɣ-terpinene	1	2	3	1	3
terpinolene	0	0	0.4	0	0.5
2,4(8)-p-menthadiene	3	3	5	14	12

Table III continued

	3days	4days	6days	8days
∝-terpinene	21%	18%	21%	18%
p-cymene	23	22	23	24
limonene	43	40	41	42
ɣ-terpinene	4	5	5	5
terpinolene	0	1	0	1
2,4(8)-p-menthadiene	9	14	10	10

*A plot of the percent of product vs. time is provided in Figure III.

From the plot of the percent of product vs. time, it can be seen that p-cymene is not formed until two days into the reaction using oxygen free nitrogen. The formation of p-cymene with time levels off as the limonene is consumed more slowly than in Runs 2 and 3. However, the other reaction products still follow the


ISOMERIZATION OF LIMONENE Run
FIGURE III
Percent of Product
Time
Limonene
α-Terpinene
γ-Terpinene
Terpinolene
1 hr.
2 hrs.
3 hrs.
4 hrs.
24 hr.
2 days
3 days
4 days
5 days
6 days
7 days
8 days
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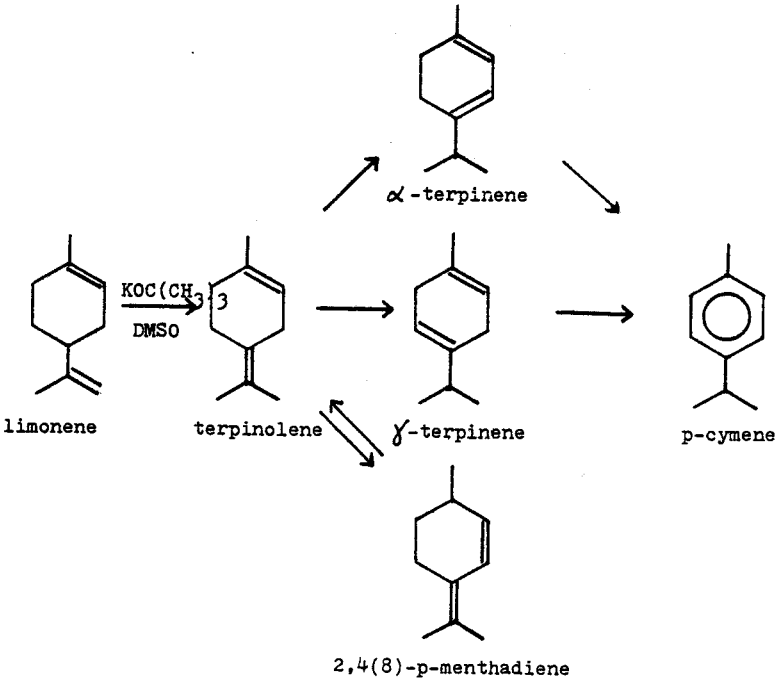
earlier trends. It still seems as though p-cymene is formed from the products α and γ-terpinene and 2,4(8)-p-menthadiene. A summary of the base-catalyzed isomerization of limonene, based on our experimental evidence, follows:



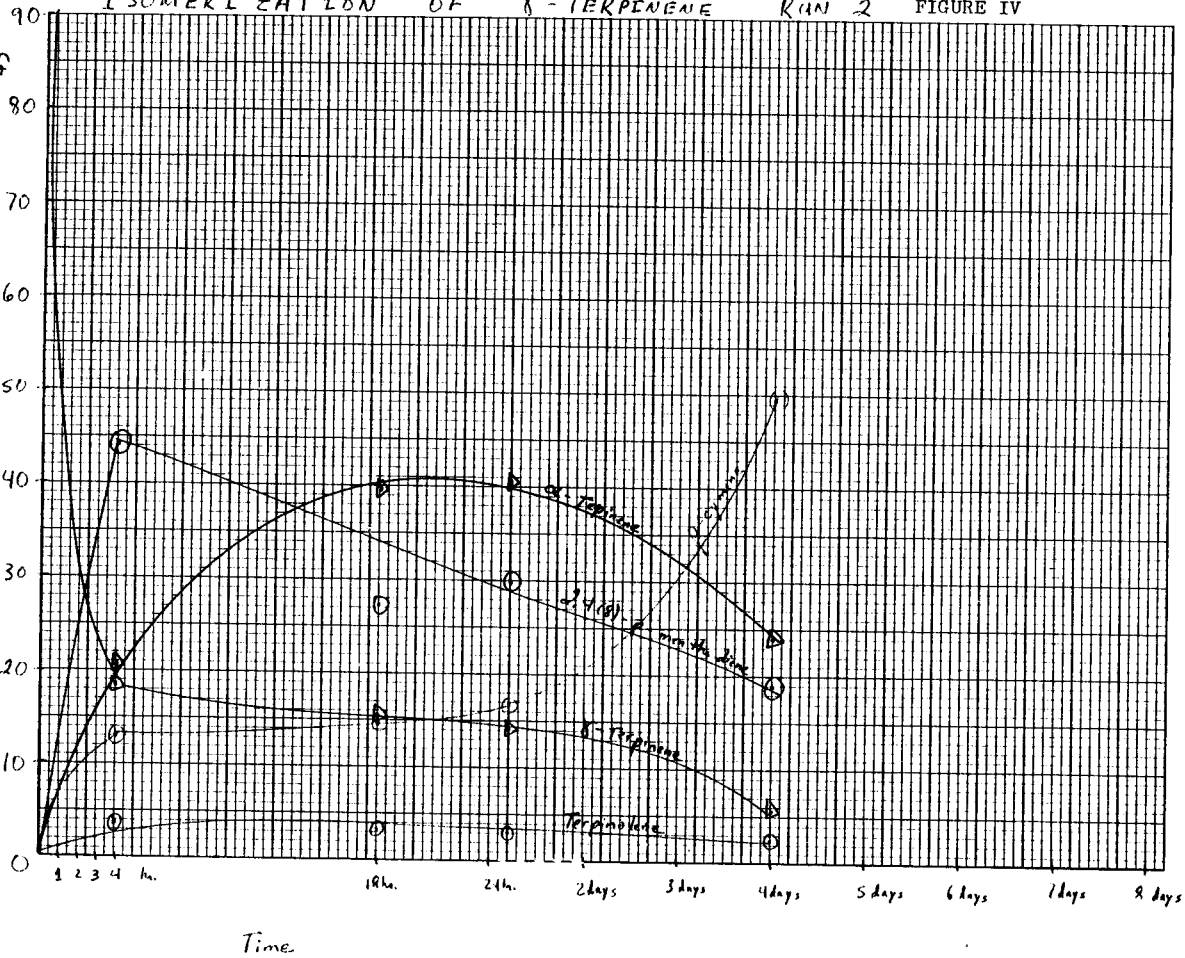
The results of the base-catalyzed isomerization of limonene sparked interest in the reaction. It was decided that other terpenes be isomerized and their reactions followed. Since both α and γ-terpinene were readily available and involved in the limonene isomerization, they too were isomerized under the same conditions as limonene. The isomerization of γ-terpinene, Run 1, yielded five terpenes after reacting for four days at 100°C. α-terpinene, γ-terpinene, p-cymene, terpinolene, and 2,4(8)-p-menthadiene were identified. A second run was made and followed gas chromatographically. The results of the isomerization of γ-terpinene, Run 2 follow:

Table IV: Isomerization of γ-terpinene, Run 2

	4hrs.	18hrs.	28hrs.	4days
α-terpinene	20.5%	39.9%	40.1%	24%
p-cymene	13.0	14.6	16.8	49.6
γ-terpinene	18.5	15.1	14.2	5.3
terpinolene	3.8	3.2	3.1	2.5
2,4(8)-p-menthadiene	44.2	27.2	29.8	18.7

A plot of the percent of product vs. time is provided in Figure 4. The reaction of γ-terpinene is much faster than the isomerization of limonene. Major differences include the much faster disappearance of γ-terpinene and the immediate formation of p-cymene.

ISOMERIZATION OF γ-TERPINENE RUN 2 FIGURE IV



The formation of terpinolene, which may be an intermediate in both reactions, remains the same. Another run was needed to determine the extent of reaction at much earlier times than in Run 2. The results of Run 3 follow:

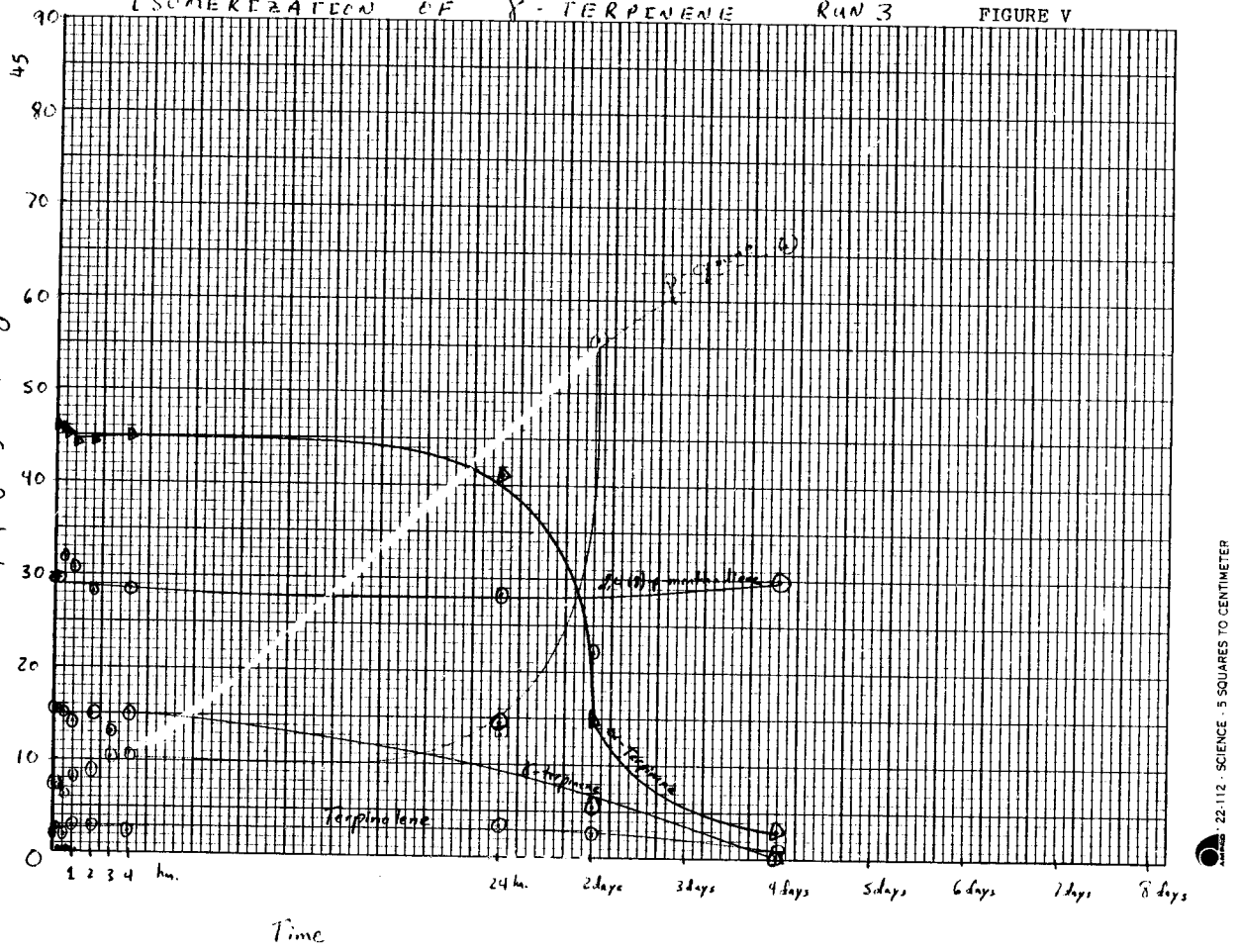
Table V: Isomerization of γ-terpinene, Run 3

	10min.	20min.	30min.	1hr.	2hrs.
α-terpinene	46.4%	45.0%	45.1%	44.2%	44.7%
p-cymene	2.3	7.0	6.2	8.3	8.7
γ-terpinene	15.3	15.4	15.0	14.4	15.4
terpinolene	2.0	2.9	1.7	2.7	2.8
2,4(8)-p-menthadiene	29.0	29.7	32.0	30.4	28.4

Table V continued

	4hrs.	25hrs.	2days	4days
α-terpinene	45.7%	41.1%	14.6%	2.9%
p-cymene	10.2	13.1	55.4	66.3
γ-terpinene	13.3	14.5	5.5	---
terpinolene	2.4	3.2	2.5	0.8
2,4(8)-p-menthadiene	28.4	28.1	22.0	30.0

A plot of the percent of product vs. time is provided in Figure V. It can be seen from this plot that the reaction is 85% complete after the first ten minutes. The plot also provides evidence for the formation of p-cymene from both α and γ-terpinene. The amount of terpinolene still remains constant as does the amount of 2,4(8)-p-menthadiene. The reaction was occuring so fast,


ISOMERIZATION OF γ - TERPINENE RUN 3
FIGURE V
Percent of Product
Time
Terpinolene
α-Terpinene
γ-Terpinene
1 2 3 4 hr.
24 hr.
2 days
3 days
4 days
5 days
6 days
7 days
8 days
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however, that we needed to lower the temperature and then moniter the reaction while raising the temperature. Run 4 was run at room temperature for two days before bringing the temperature gradually up to 100°C. The results of Run 4 are as follows:

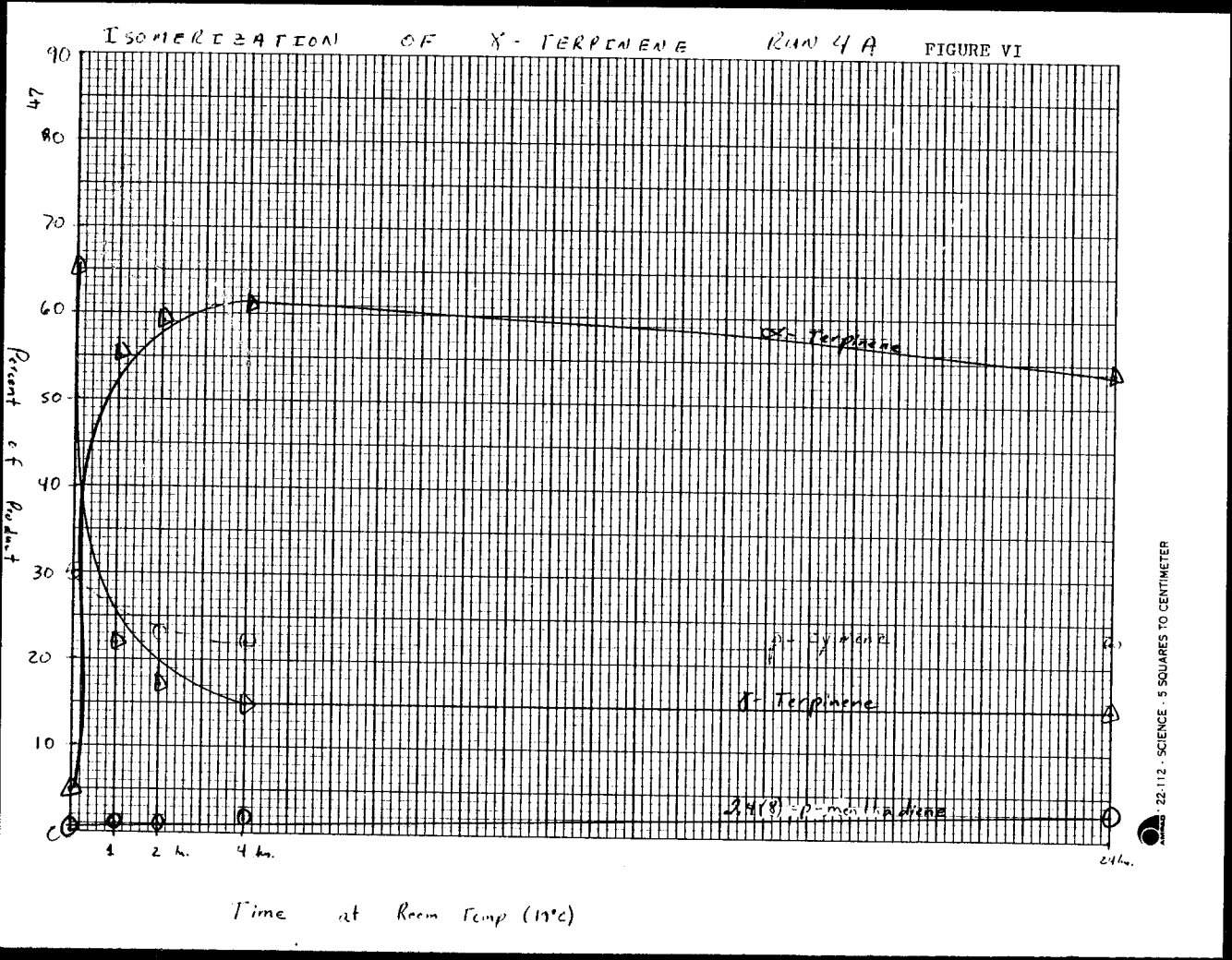
Table VI: Isomerization of γ-terpinene, Run 4

	Room Temperature(19°C)				
	0hr.	1hr.	2hrs.	4hrs.	24hrs.
α-terpinene	5%	55%	59%	61.5%	54%
p-cymene	30	22	23	22	23
γ-terpinene	65	22	17	15	15
terpinolene	0	0	0	0	0.5
2,4(8)-p-menthadiene	0	1	1	1.5	3

Table VI continued

	50°C	75°C		100°C		
	1hr.	1hr.	2hrs.	1day	2days	5days
α-terpinene	51%	49%	34%	37%	39%	35%
p-cymene	26	18	21	30	28	37
γ-terpinene	14	13	12	12	12	9
terpinolene	0.5	2	2	2	2	2
2,4(8)-p-menthadiene	8.5	18	21	19	19	17

The percent of product vs. time at room temperature is plotted in Figure VI and the percent of product vs. time for the remaining temperatures is plotted in Figure VII. At 0hr. at room temperature, the reaction is 35% complete. α-terpinene is the major product at room


ISOMERIZATION OF X-TERPINENE RUN 4A
FIGURE VI
Percent of Product
Time at Room Temp (19°C)
X-Terpinene
γ-Terpinene
2,4(8)-p-menthadiene
1
2 h.
4 h.
24 h.
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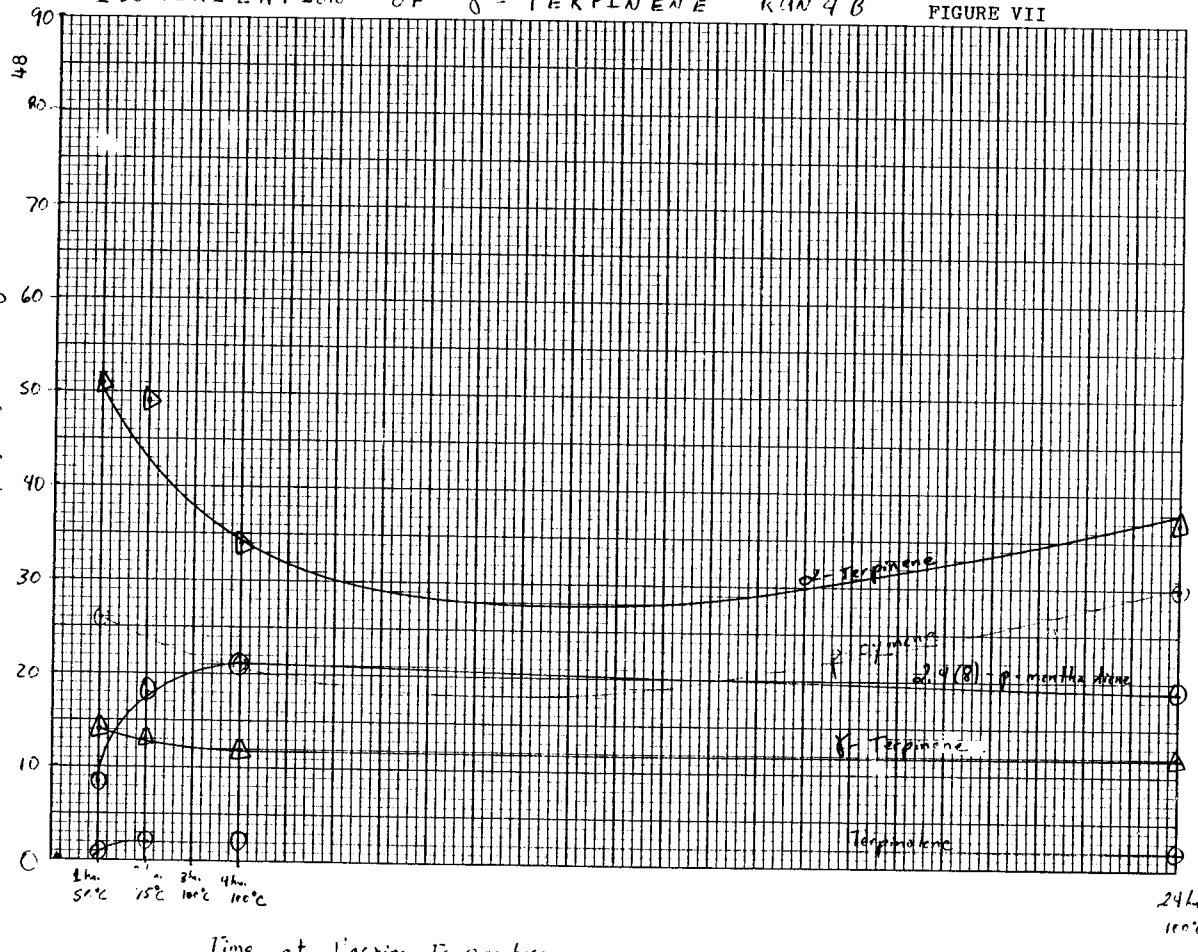
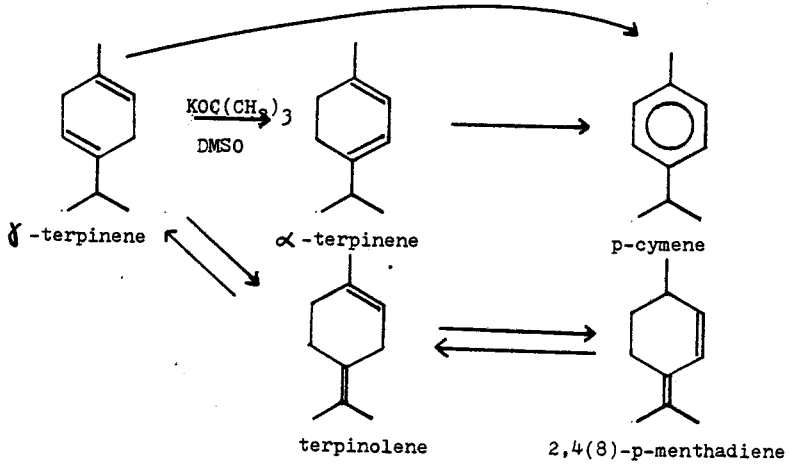
ISOMERIZATION OF γ-TERPINENE RUN 4B

FIGURE VII



temperature but drops off after heating due to oxidation to p-cymene. The reaction does follow the earlier trends with both α and γ-terpinene disappearing to form the major product p-cymene. A summary of the isomerization of γ-terpinene, based on our experimental evidence, follows:



The next terpene investigated was α-terpinene. The base-catalyzed isomerization of α-terpinene was expected to be as fast as that of γ-terpinene. Therefore, the reaction was carried out in much the same manner as the isomerization of γ-terpinene, Run 4. The reaction was started at room temperature and then gradually heated. The results of the isomerization of α-terpinene, Run 1 are as follows:

Table VII: Isomerization of α-terpinene, Run 1

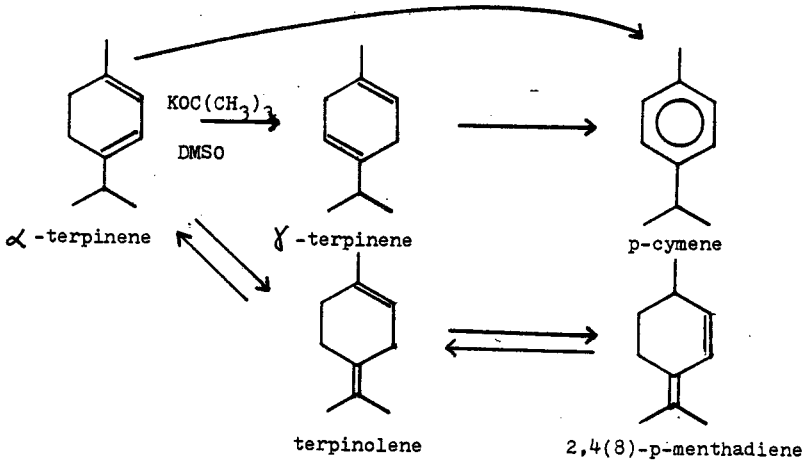
	Room Temperature (21°C)		50°C	75°C
	0hr.	1hr.	2hrs.	2hrs.
α-terpinene	71%	64%	58%	
p-cymene	20	20	17	
γ-terpinene	9	15	15	
terpinolene	0	0	1.4	
2,4(8)-p-menthadiene	0	1	10	

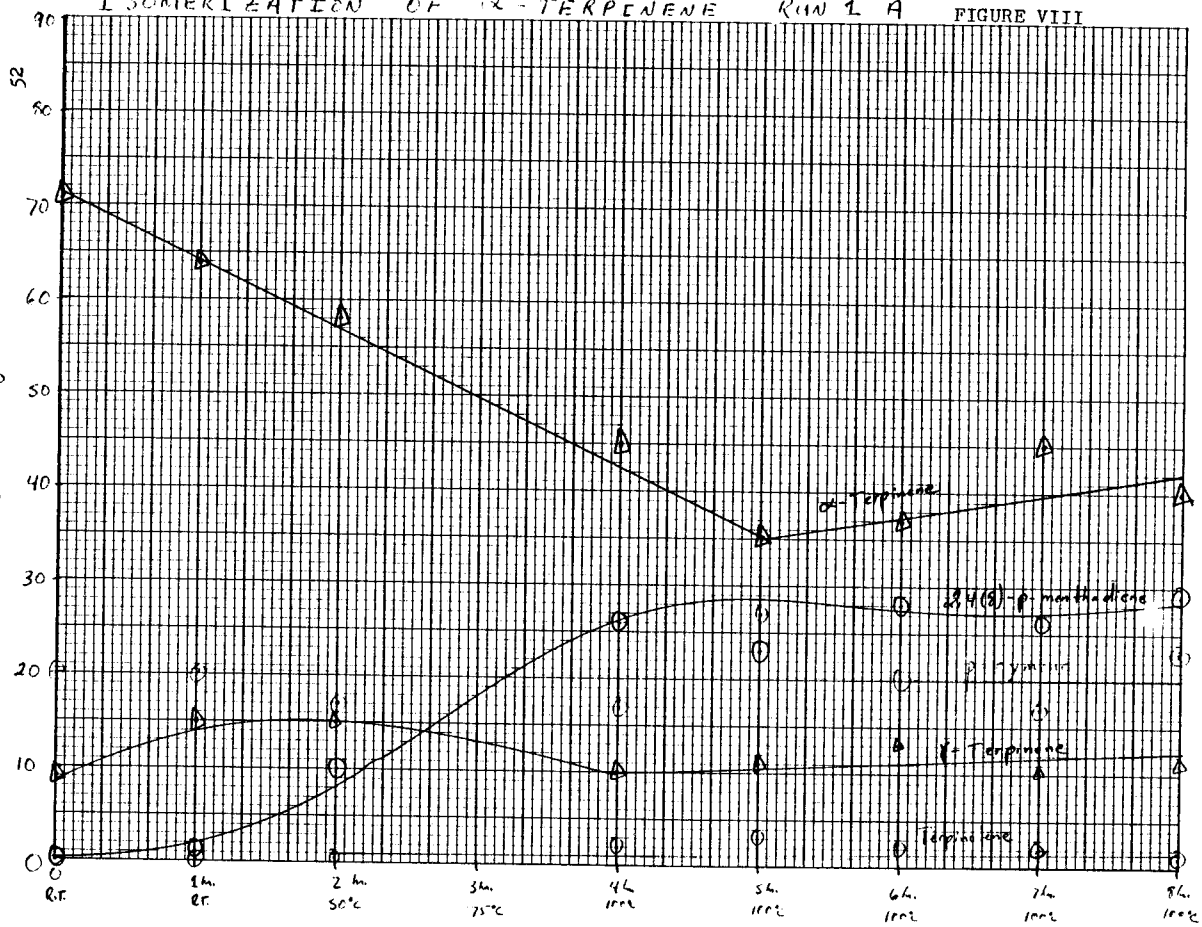
Table VII continued

	100°C						
	0hr.	1hr.	2hrs.	4hrs.	1day	4days	8days
α-terpinene	45%	35%	37%	45%	40%	32%	26%
p-cymene	17	28	20	17	23	40	48
γ-terpinene	10	11	13	10	11	9	6
terpinolene	2	3	2	2	1	1	1
2,4(8)-p-menthadiene	26	23	28	26	29	19	19

A plot of the percent of product vs. time at

varying temperatures is provided in Figure VIII and the percent of product vs. time at 100 C in Figure IX. Again, p-cymene is the major product after the slow disappearance of α-terpinene and 2,4(8)-p-menthadiene. A summary of the base-catalyzed isomerization of α-terpinene, based on our experimental evidence, follows.




ISOMERIZATION OF α-TERPINENE RUN 1 A
FIGURE VIII
52
90
80
70
60
50
40
30
20
10
0
Percent of Product
α-Terpinene
2,4(8)-p-menthadiene
γ-Terpinene
Terpinolene
R.T.
1 hr. R.T.
2 hr. 50°C
3 hr. 75°C
4 hr. 100°C
5 hr. 100°C
6 hr. 100°C
7 hr. 100°C
8 hr. 100°C
Time at Varying Temperature
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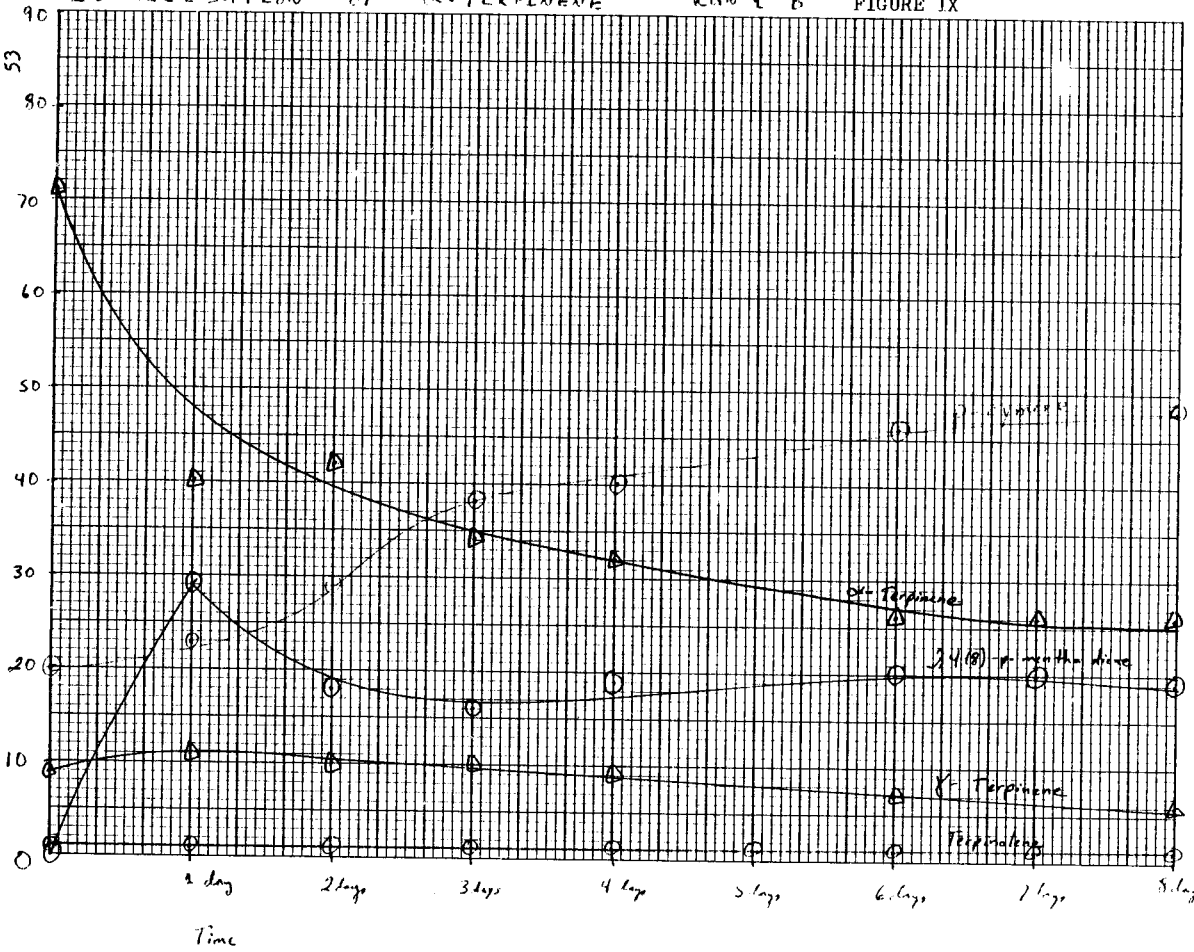
ISOMERIZATION OF α-TERPINENE RUN 1 B FIGURE IX



The products in each of the preceding isomerizations were identified as follows. The retention times of each compound on both the Apiezon L and Reoplex 400 columns were checked with literature values.[15] Limonene, p-cymene, α-terpinene, and γ-terpinene were also found by spiking with pure samples of these compounds. α-terpinene and 2,4(8)-p-menthadiene were trapped employing preparative Gas Chromatography.* Since these are both conjugated dienes, UV-VIS absorption spectroscopy was employed for identification. The results of this work follow:

Table VIII: UV-VIS Absorption Spectroscopy

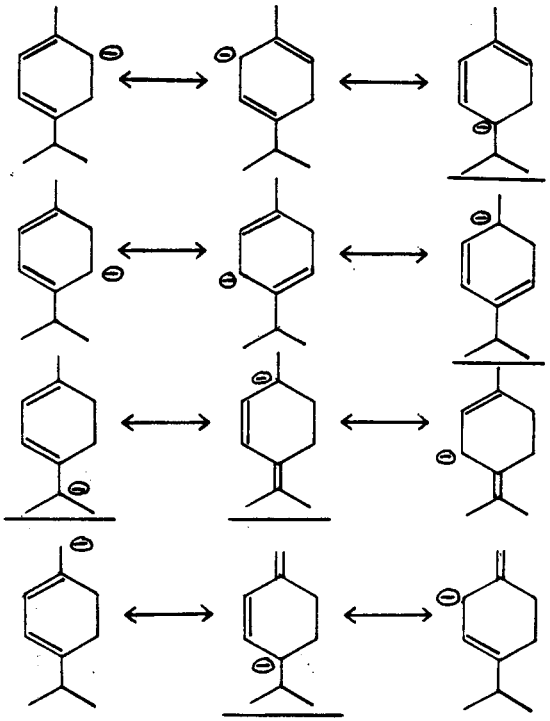
	λ max obs.(nm)	λ max calc.(nm)	λ max lit.(nm)
α-terpinene	264.8	263	265[28]
2,4(8)-p-menthadiene	243.5	239	246[28]

The UV-VIS absorption spectrum for α-terpinene is provided in Appendix II and the UV-VIS absorption spectrum for 2,4(8)-p-menthadiene is provided in Appendix III.

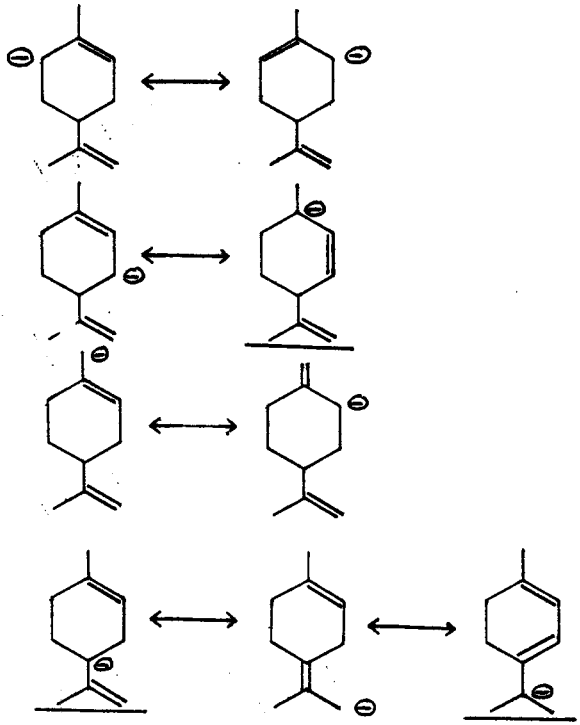
The results from the base-catalyzed isomerizations of limonene, α-terpinene, and γ-terpinene left many unanswered questions. It was not clear how the p-cymene was being formed. We were not observing any menthanes in the product which ruled out disproportionation. The reaction products must have been oxidized to p-cymene but it was unclear as to the identity of the oxidizing agent.

*The samples were trapped in a glass tube immersed in liquid Nitrogen as they came through the exit port of the GC.

It was obvious that more experimental work was needed concerning the formation of p-cymene. The other uncertainty concerning the isomerizations was the relative rates of the reactions; both α and γ-terpinene isomerized much more rapidly than limonene. An examination of the carbanions involved shows that there are less resonance structures for limonene than α and γ-terpinene.



These are the resonance structures for the carbanions of both α and γ-terpinene in the base-catalyzed isomerizations. Underlined species represent tertiary carbanions and are considered weak contributors. The resonance structures involved for the carbanions of limonene in the base-catalyzed isomerizations are given below.



The additional experimental work involving the formation of p-cymene in the preceding isomerizations yielded some interesting results. Samples of γ-terpinene were isomerized in dimethyl sulfoxide (DMSO) with no catalyst. The results of this work follow:

Table IX: Isomerization of γ-terpinene in DMSO, Runs 1 & 2

% Formation of p-cymene with time

	0days	1day	5days	6days	9days	13days	15days
Run 1	6%	18%		22%		46%	60%
Run 2	6%	15%	24%		43%	42%	

These results indicate that DMSO is acting as an oxidizing agent in the isomerizations. It is unclear, however, whether the DMSO is the sole oxidizing agent or if some impurity in the DMSO is doing the oxidizing. The next experimental steps taken were to run isomerizations in purified DMSO. Two commen impurities in DMSO capable of oxidizing, dimethyl sulfide and dimethyl sulfone, were then added to DMSO and their effects monitered in an isomerization. The results of the isomerization of γ-terpinene in distilled DMSO with no catalyst follow:

Table X: Isomerization of γ-terpinene in distilled DMSO

% Formation of p-cymene with time

	0days	1day	5days	9days	12days	13days	14days
Run 1	6%	13%	21%		88%	72%	
Run 2	6%	11%	27%	38%			33%

The distilled DMSO seems to form p-cymene at a slightly slower rate than did the non-distilled DMSO. (Note that the nitrogen was off for the last seven days of Run 1 with distilled DMSO which explains the large amounts of p-cymene at the end of the reaction.) The results for the isomerization of γ-terpinene in DMSO with 2% dimethyl sulfone, $CH_3SO_2CH_3$, follow:

Table XI: Isomerization of γ-terpinene in DMSO with 2% dimethyl sulfone, Runs 1 & 2

% Formation of p-cymene with time

	0days	1day	2days	5days	6days	12days	14days
Run 1	6%	22%		40%		84%	
Run 2	6%	12%	12%		18%		78%

The addition of dimethyl sulfone markedly increased the rate of formation of p-cymene. This would indicate that if any dimethyl sulfone were present as an impurity in the DMSO, p-cymene would be formed more rapidly than in DMSO alone. The results for the isomerization of γ-terpinene in DMSO with 50% dimethyl sulfide, CH_3SCH_3, follow:

Table XII: Isomerization of γ-terpinene in DMSO with 50% dimethyl sulfide, Runs 1 & 2

% Formation of p-cymene with time

	0days	1day	2days	4days	6days	7days	14days
Run 1	6%	15%	29%	38%		53%*	
Run 2	6%	14%	11%		18%		30%

*It is believed that this run was contaminated with air, which would explain the unexpectadly high amount of p-cymene.

These results show that dimethyl sulfoxide is not as strong an oxidizing agent as dimethyl sulfone but that both are more powerful than dimethyl sulfide.* We were also interested in how fast γ-terpinene would oxidize to p-cymene in air. Two isomerizations were run, one in DMSO and air and one in air alone. The results of this work follow:

Table XIII: Isomerization of γ-terpinene in air

% Formation of p-cymene with time

	0days	1day	2days	6days
Run 1 DMSO & air	6%	61%	86%	
Run 2 air	6%	46%	85%	100%

All of the results for the formation of p-cymene work are plotted together in Figure X. From the plot it can be concluded that DMSO and air oxidize γ-terpinene to p-cymene the fastest, air alone the next fastest followed by dimethyl sulfone, dimethyl sulfide, DMSO, and distilled DMSO. From this work we can conclude that p-cymene is least likely to be formed when distilled DMSO and oxygen free nitrogen are used.

The effects of DMSO were then investigated with α-terpinene. α-terpinene was isomerized in DMSO with no catalyst and in distilled DMSO with no catalyst. The results were analogous to γ-terpinene. The results of the isomerization of α-terpinene in DMSO and in distilled DMSO follow:

*Dimethyl sulfide should be acting as a diluent.

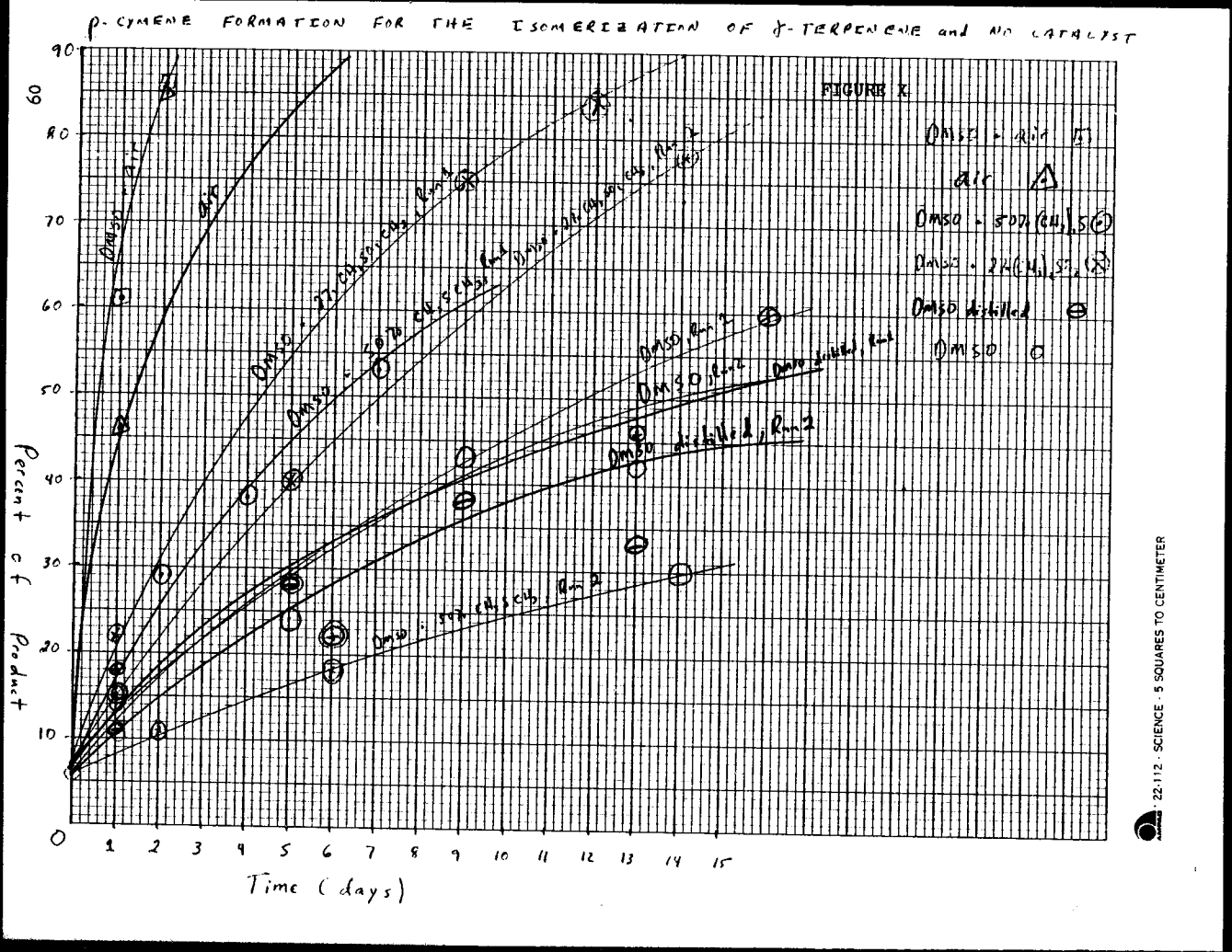

p-CYMENE FORMATION FOR THE ISOMERIZATION OF δ-TERPENENE and NO CATALYST
FIGURE X
Dmso + Air
Air
Dmso + $SnCl_2(CH_3)_2SO$
Dmso + $ZnCl_2(CH_3)_2SO$
Dmso distilled
Dmso
Dmso, Rm 2
Dmso distilled, Rm 2
Dmso + $ZnCl_2(CH_3)_2SO$, Rm 2
Dmso + $SnCl_2(CH_3)_2SO$, Rm 2
Dmso + Air, Rm 2
Dmso + $ZnCl_2(CH_3)_2SO$, Rm 1
Dmso + $SnCl_2(CH_3)_2SO$, Rm 1
Dmso distilled, Rm 1
Percent of Product
Time (days)
0
10
20
30
40
50
60
70
80
90
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
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Table XIV: Isomerization of ∝-terpinene in DMSO

% Formation of p-cymene with time

	0days	1day	7days	11days	15days
Run 1	6%	34%	53%	35%	61%

Table XV: Isomerization of ∝-terpinene in distilled DMSO

% Formation of p-cymene with time

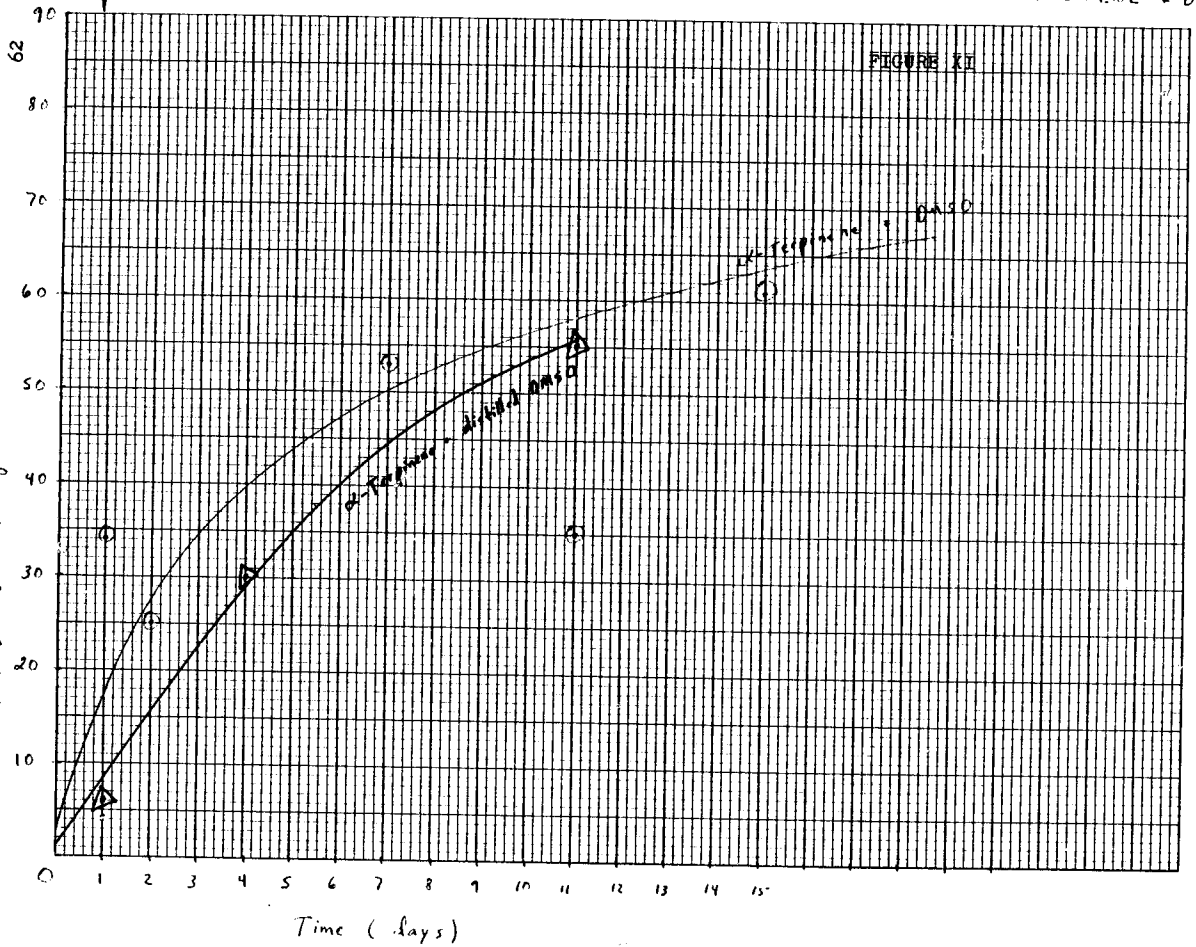
	0days	4days	11days
Run 1	6%	30%	55%

The results of this work are plotted in Figure XI. The distilled DMSO seems to form p-cymene more slowly than the non-distilled DMSO.

It is interesting to note that some of the runs with no catalyst yielded other terpenes beside p-cymene and the starting material. The isomerization of γ-terpinene in DMSO, Run 1 with no catalyst resulted in the formation of 0.6% ∝-terpinene and 0.6% 2,4(8)-p-menthadiene. Run 1 of the isomerization of γ-terpinene with distilled DMSO yielded 19% ∝-terpinene and 1.2% 2,4(8)-p-menthadiene after 14 days. The isomerization of γ-terpinene with 50% CH_3SCH_3, Run 2 yielded 10% ∝-terpinene and 1% 2,4(8)-p-menthadiene after 14 days.

p-CYMENE FORMATION FOR ISOMERIZATION OF α-TERPINENE + DMSO

FIGURE XI



We next turned our attention to the preparation of a sample of B-phellandrene. We first attempted to isolate the material from Canada Balsam Oil via fractional distillation. We did isolate B-phellandrene in this manner, but only as a mixture along with limonene and γ-terpinene. B-phellandrene was identified by a retention time check on both the Apiezon L and Reoplex 400 columns with the literature values.[15] Since B-phellandrene was the only conjugated diene in the mixture, a UV-VIS absorption spectrum was run for more positive identification. The results of this work follow:

Table XVI: UV-VIS absorption Spectroscopy of B-phellandrene*

λ max observed	λ max calculated	λ max literature[28]
230nm	229nm	231.2

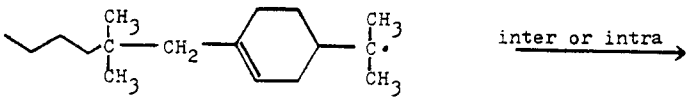
We then prepared B-phellandrene via the synthetic route from Cryptone. After all the steps were completed, approximately 0.8g of B-phellandrene were isolated. GC analysis revealed B-phellandrene(87%), p-cymene(6%), B-terpinene(6%), and 3-p-menthene(1%). This sample of B-phellandrene would be adequate for our pyrolysis-gas chromatography-mass spectral work.

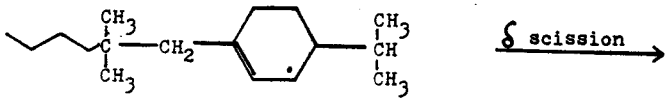
We also attempted to prepare B-phellandrene from α-phellandrene using 9-BBN. After several batches at various conditions it was obvious that we were not getting B-phellandrene as we had hoped. The major product was 4(8)-p-menthene along with other menthenes and few dienes.

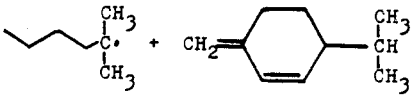
*The UV-VIS absorption spectrum of B-phellandrene is given in Appendix I.

Finally, we turned our attention to the determination of the microstructure of poly(B-pinene). The following terpenes, possible pyrolysis products of poly(B-pinene), were put into the library of the Gas Chromatograph/Mass Spectrometer: p-cymene, Δ-3-carene, α-terpinene, γ-terpinene, camphene, α-pinene, α-phellandrene, B-pinene, limonene, toluene, allo-ocimene trans-cis, β-phellandrene, 1-p-menthene, terpinolene, trans 2-p-menthene, 3-p-menthene, and 2,4(8)-p-menthadiene. The mass spectra of these standards are provided in Appendix IV. A sample of poly(B-pinene) was pyrolyzed in the instrument and a library search performed on the pyrolysis products. Using the information provided by the library search, knowledge of the retention times of the pyrolysis products, and visual analysis of the mass spectra with comparison to literature values[36], we determined the major pyrolysis products to be α-phellandrene, α-terpinene, trans 2-p-menthene, and B-phellandrene. The major pyrolysis product was B-phellandrene. Mechanisms of degradation can now be written and the microstructure of the polymer determined.

Formation of B-phellandrene:

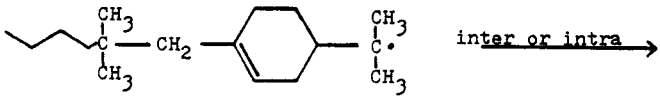


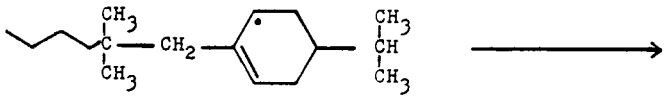


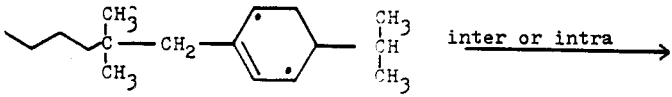


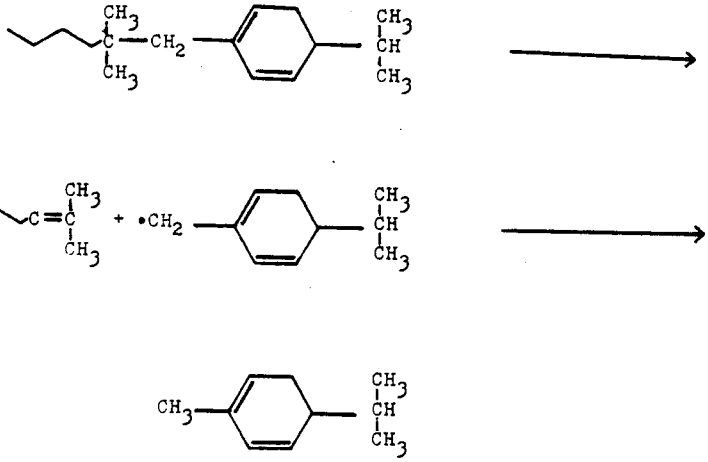
B-phellandrene

Formation of ∝-phellandrene



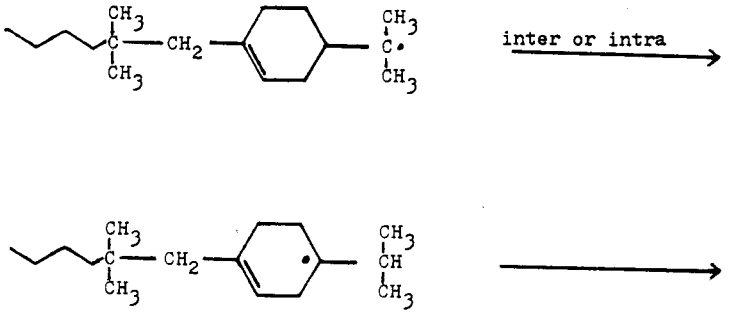


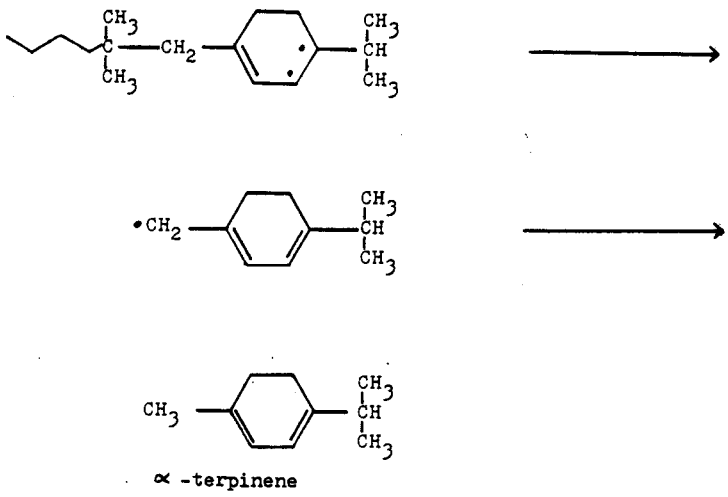




∝ -phellandrene

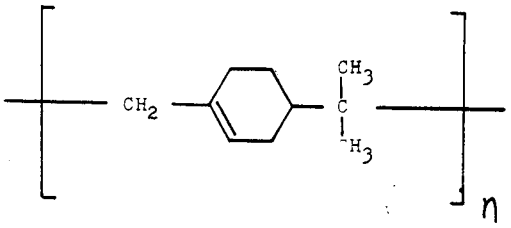
Formation of ∝ -terpinene





∝ -terpinene

All of these mechanisms of degradation seem to indicate the previously proposed repeat unit.[2] We can therefore conclude that this repeat unit is present in amounts greater than the 50% previously reported. When greater amounts of polymer are pyrolyzed, there are traces of both ∝-fenchene and camphene indicating that both are possible end groups. The microstructure of poly(B-pinene) is therefore:



THE NEXT STEP

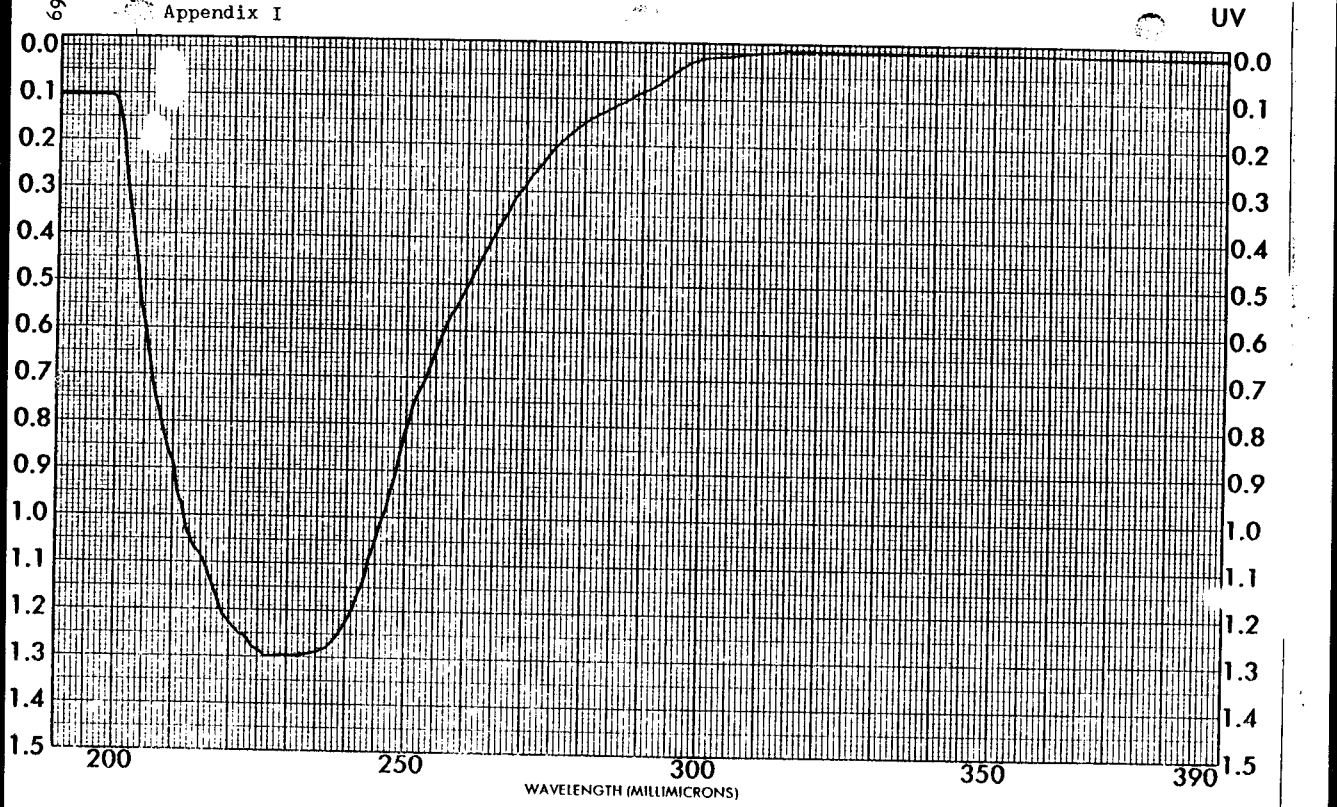
Further research should be conducted in the following areas:

The reaction of 9BBN and various terpenes should be thoroughly studied. One should react both dienes and enes to determine the rate and extent of reaction. The reaction should be monitered using NMR analysis to determine the intermediates involved.

DMSO should be carefully analyzed to determine the nature and amounts of any impurities capable of oxidation. Also the isomerization of terpenes with no catalyst in DMSO should be investigated.

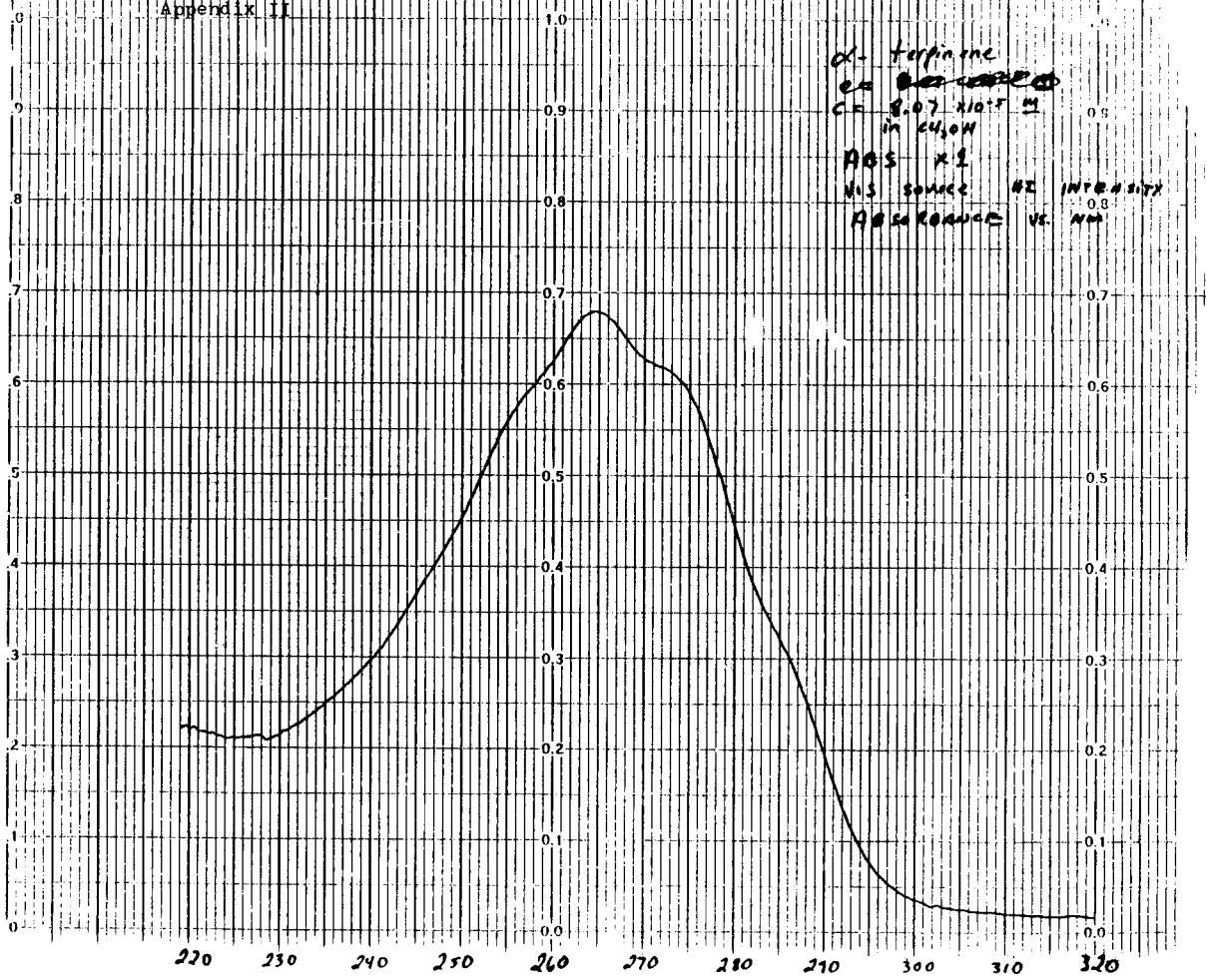
More pyrolysis work should be done using greater amounts of polymer and longer pyrolysis times in order to accurately determine all of the pyrolysis products. Samples of poly(B-pinene) with varying molecular weights should be pyrolyzed.

Appendix I

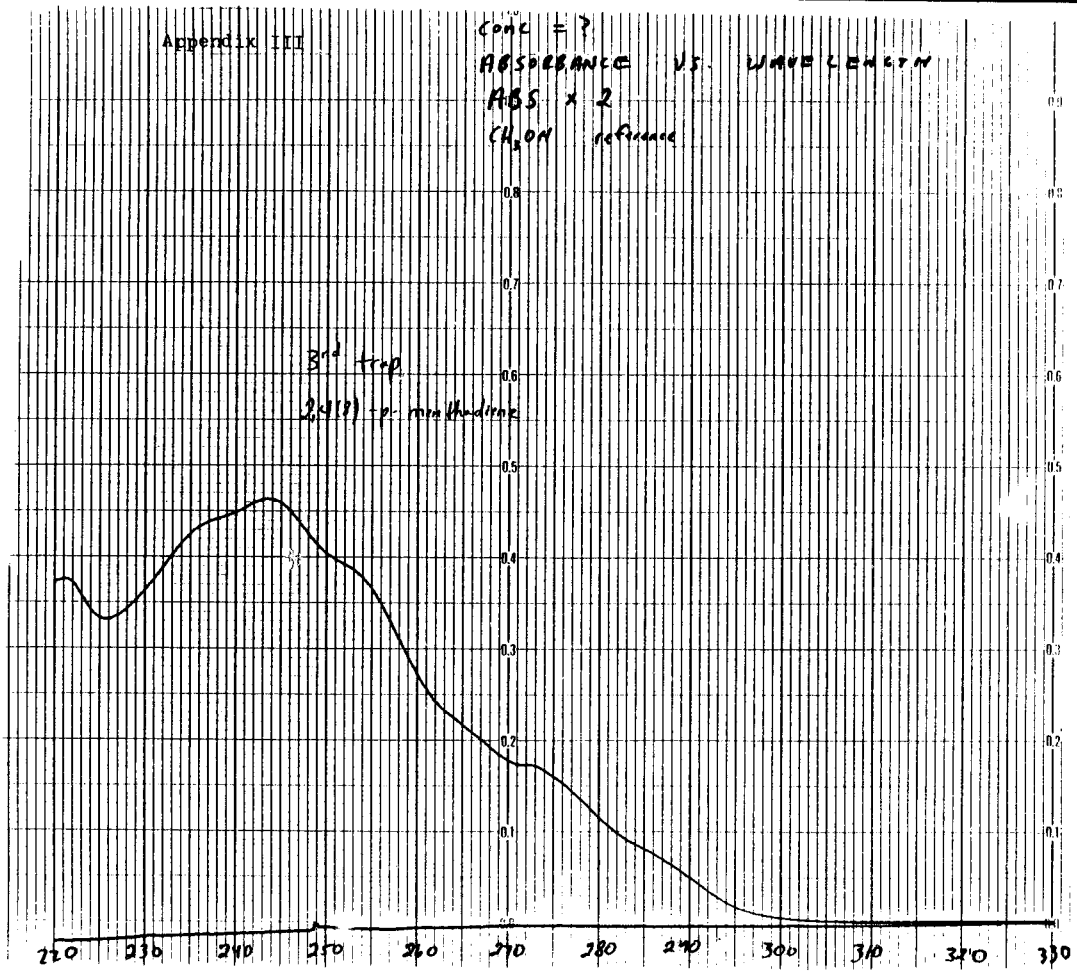


SAMPLE p17 fraction 1+2 solution of β-phellandrene from Cardbl	CURVE NO.	SCAN SPEED Fast	OPERATOR K.G.F
ORIGIN	CONC.	SLIT 25	DATE 9/19/83
SOLVENT CH_3OH	CELL PATH 1cm	REMARKS	
	REFERENCE CH_3OH		

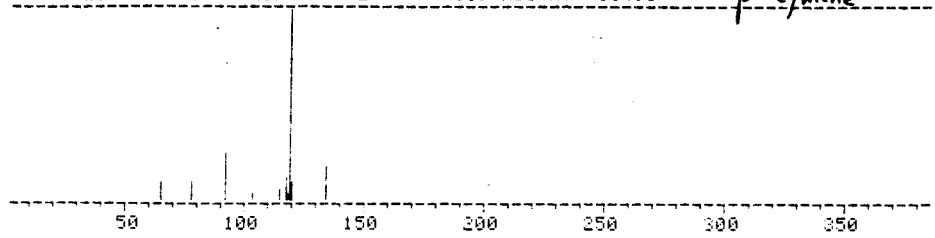
Appendix II


α- terpinene
Concentrated
C= 8.07 x10⁻⁵ M
in C₆H₁₂
ABS x1
U.V. source
Absorbance vs. nm
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
220
230
240
250
260
270
280
290
300
310
320

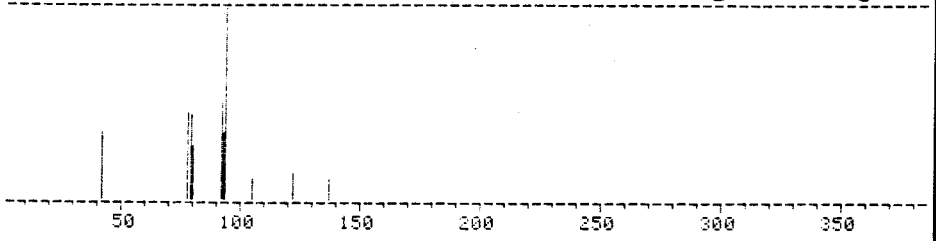
Appendix III



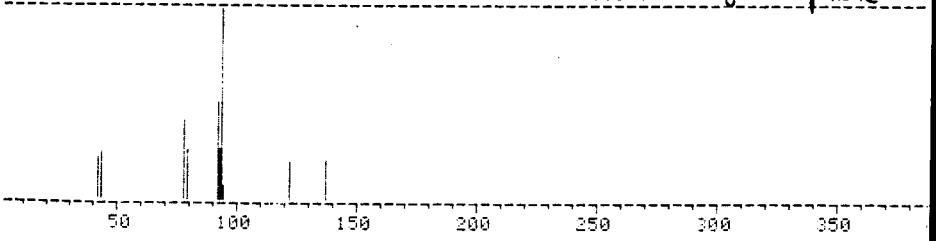
*** SPECTRUM # 261 LIBRARY 2 *** Mol. Weight= 134.0 p-cymene



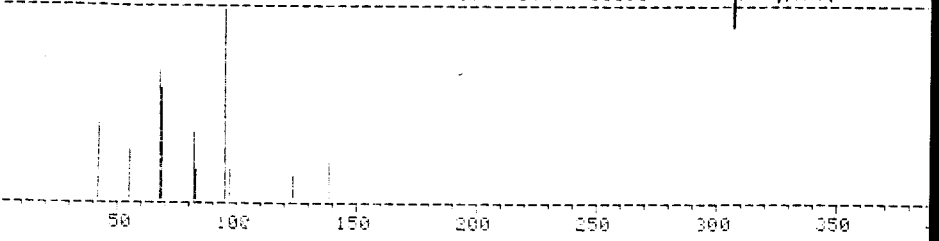
*** SPECTRUM # 263 LIBRARY 2 *** Mol. Weight= 136.0 Δ-3-carene



*** SPECTRUM # 264 LIBRARY 2 *** Mol. Weight= 136.0 γ-terpinene



*** SPECTRUM # 265 LIBRARY 2 *** Mol. Weight= 138.0 p-menthene



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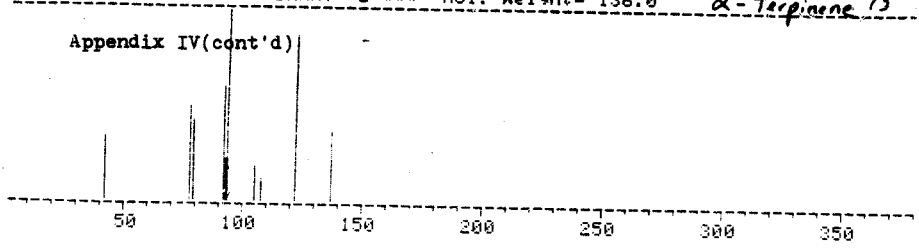
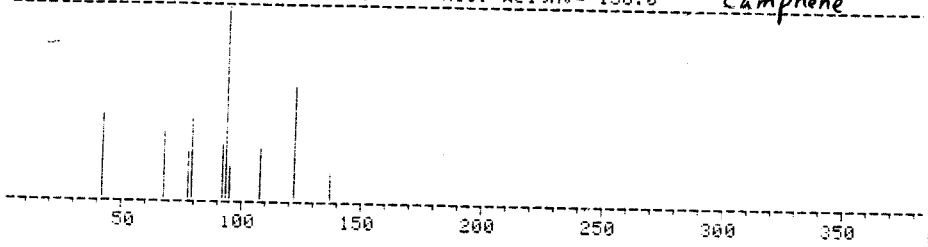
F391m/1984 SCIENCE HRS. 3/84 SHT. 2 OF 2

END

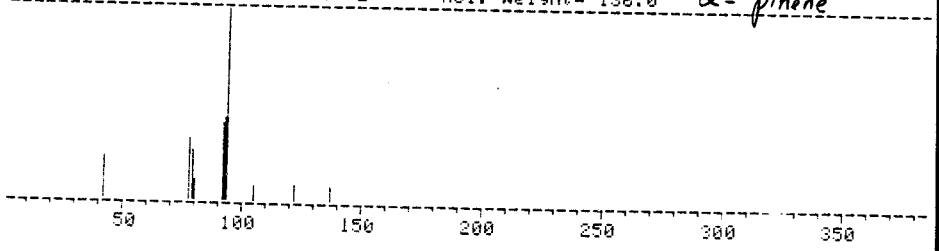
*** SPECTRUM # 257 LIBRARY 2 *** Mol. Weight= 136.0 α-Terpinene 73



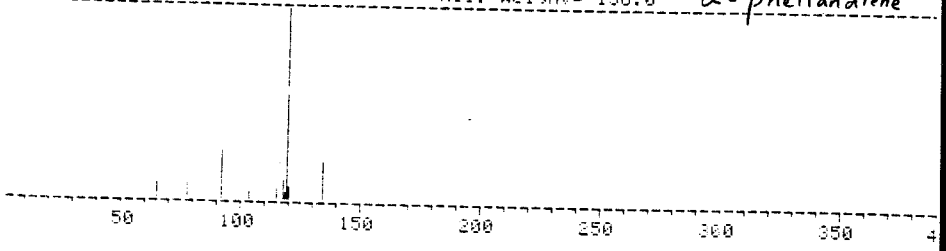
*** SPECTRUM # 253 LIBRARY 2 *** Mol. Weight= 136.0 Camphene



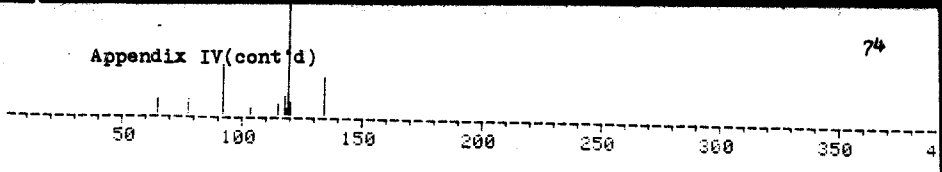
*** SPECTRUM # 255 LIBRARY 2 *** Mol. Weight= 136.0 α-pinene



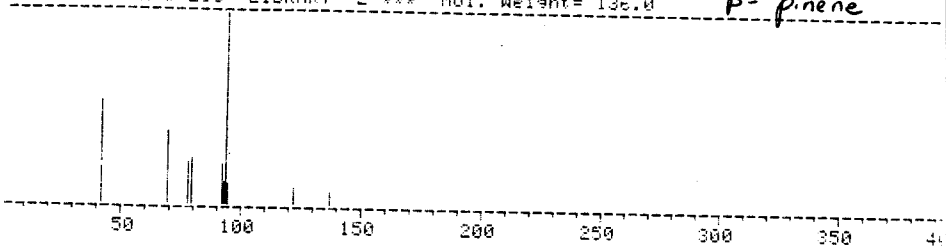
*** SPECTRUM # 256 LIBRARY 2 *** Mol. Weight= 136.0 α-phellandrene



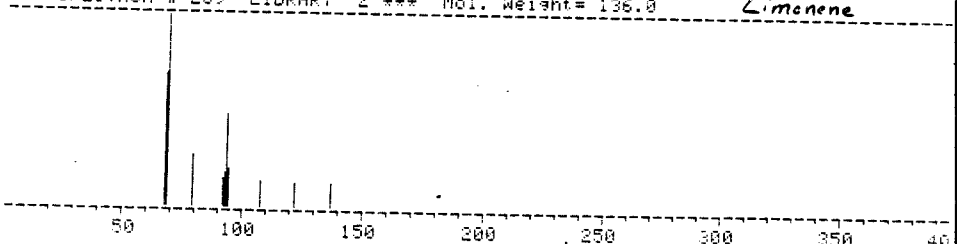
*** SPECTRUM # 258 LIBRARY 2 *** Mol. Weight= 136.0 β-pinene



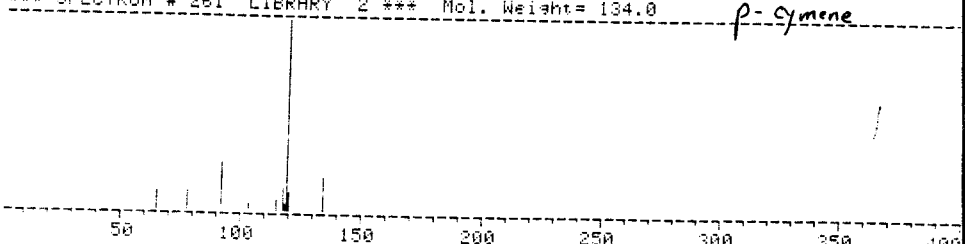
*** SPECTRUM # 258 LIBRARY 2 *** Mol. Weight= 136.0 β- pinene



*** SPECTRUM # 259 LIBRARY 2 *** Mol. Weight= 136.0 Limonene

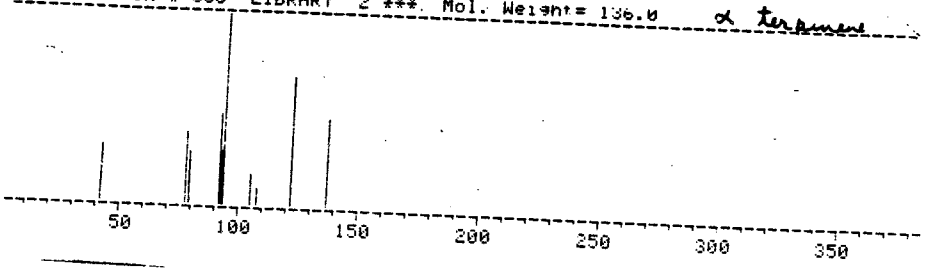


*** SPECTRUM # 261 LIBRARY 2 *** Mol. Weight= 134.0 p-cymene

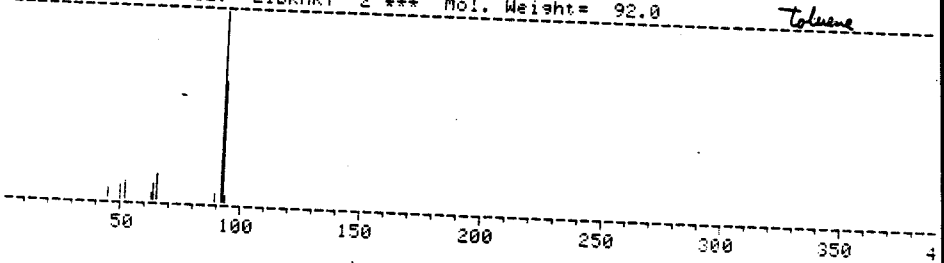


*** SPECTRUM # 263 LIBRARY 2 *** Mol. Weight= 136.0 Δ-3- carene

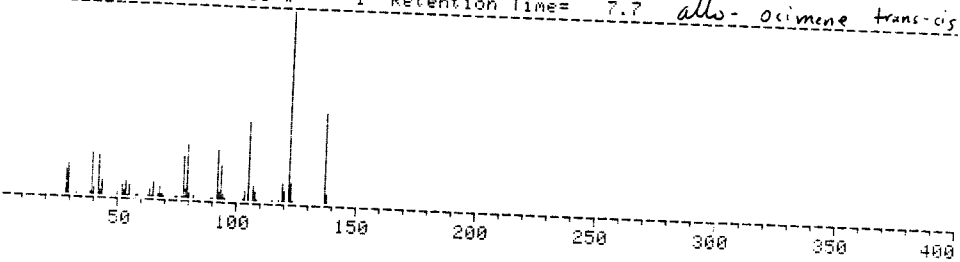
*** SPECTRUM # 536 LIBRARY 2 ***. Mol. Weight= 136.0 α terpinene



*** SPECTRUM # 529 LIBRARY 2 *** Mol. Weight= 92.0 Toluene



Spectrum # 1 Sample # 1 Retention Time= 7.7 allo-ocimene trans-cis



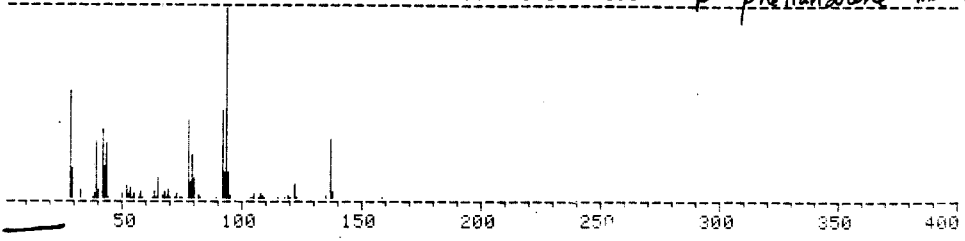
Molecular Weight = 136.0

Entry	Mass	Abundance	Mass*Abundance	Norm.Abund.
1	77	750	57750	220
2	79	942	74418	276
3	91	889	80899	261
4	93	620	57660	182
5	105	1401	147105	411
6	106	288	30528	84
7	119	343	40817	101
8	121	3409	412489	1000
9	122	346	42212	101
10	136	1612	219232	473

Above Spectrum Recorded in Library 2 as entry # 547

Appendix IV(cont'd)

Spectrum # 1 Sample # 1 Retention Time= 6.3 β-phellandrene MW = 136

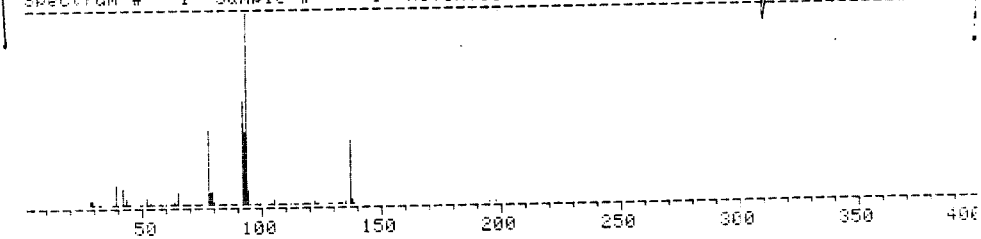


Molecular Weight = 136.0

Entry	Mass	Abundance	Mass*Abundance	Norm.Abund.
1	28	219	6132	556
2	41	140	5740	355
3	43	115	4945	292
4	77	163	12551	414
5	79	89	7031	226
6	91	183	16653	464
7	92	54	4968	137
8	93	394	36642	1000
9	94	56	5264	142
10	136	124	16864	315

Above Spectrum Recorded in Library 2 as entry # 539

Spectrum # 1 Sample # 1 Retention Time= 5.6 α-phellandrene

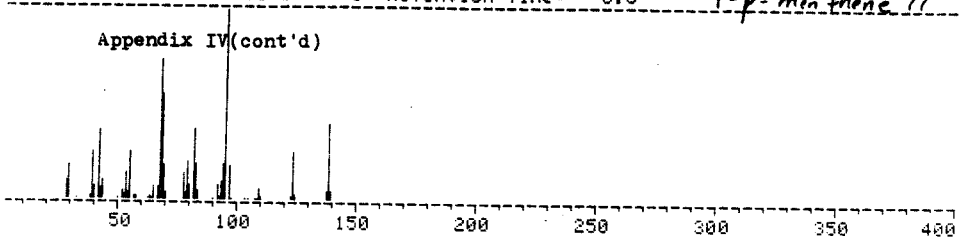


Molecular Weight = 136.0

Entry	Mass	Abundance	Mass*Abundance	Norm.Abund.
1	65	1160	75388	78
2	77	5777	444826	391
3	78	1038	80961	70
4	79	1061	83794	72
5	91	8060	733459	545
6	92	5730	527180	388
7	93	14782	1374734	1000
8	94	1321	124154	89
9	136	4978	676961	337
10	137	530	72657	36

Above Spectrum Recorded in Library 2 as entry # 519

Spectrum # 1 Sample # 1 Retention Time= 6.5 1-p-menthene ??

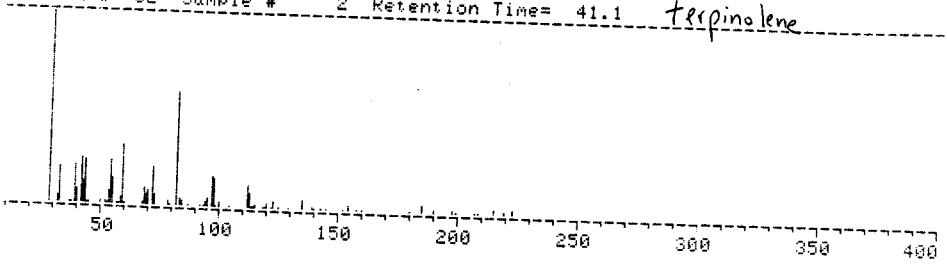


Molecular Weight = 138.0

Entry	Mass	Abundance	Mass*Abundance	Norm.Abund.
1	67	4959	332253	728
2	68	3776	256768	554
3	79	1360	107440	200
4	81	2544	206064	373
5	82	1292	105944	190
6	94	1328	124832	195
7	95	6816	647520	1000
8	96	1248	119808	183
9	123	1684	207132	247
10	138	2752	379776	404

Above Spectrum Recorded in Library 2 as entry # 548

Spectrum # 52 Sample # 2 Retention Time= 41.1 terpinolene



lecular Weight = 136.0

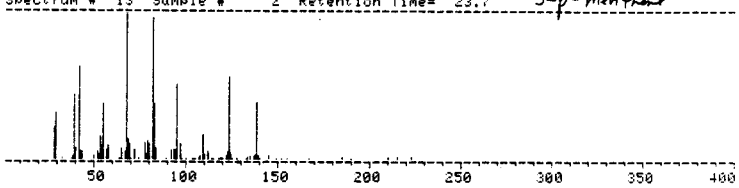
try	Mass	Abundance	Mass*Abundance	Norm.Abund.
1	28	118	3304	1000
2	41	28	1148	237
3	43	27	1161	229
4	54	27	1458	229
5	59	37	2183	314
6	71	24	1704	203
7	81	70	5670	593
8	96	19	1824	161
9	97	18	1746	153
0	111	14	1554	119

ove Spectrum Recorded in Library 2 as entry # 549

④

Library Editing Program [rev 7/26/78]

Spectrum # 13 Sample # 2 Retention Time= 23.7 3-p-menthene

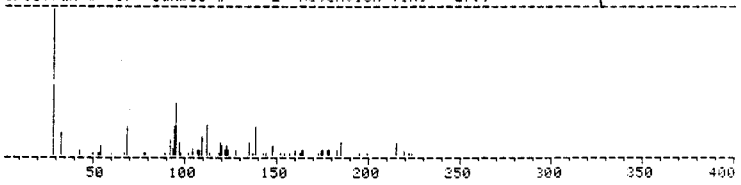


Molecular Weight = 138.0

Entry	Mass	Abundance	Mass*Abundance	Norm.Abund.
1	39	118	4602	435
2	41	171	7011	631
3	55	103	5665	380
4	67	271	18157	1000
5	81	260	21060	959
6	82	102	8364	376
7	95	139	13205	513
8	109	45	4905	166
9	123	151	18573	557
10	138	105	14490	387

Above Spectrum Recorded in Library 2 as entry # 551

Spectrum # 17 Sample # 2 Retention Time= 27.9 trans-2-p-menthene



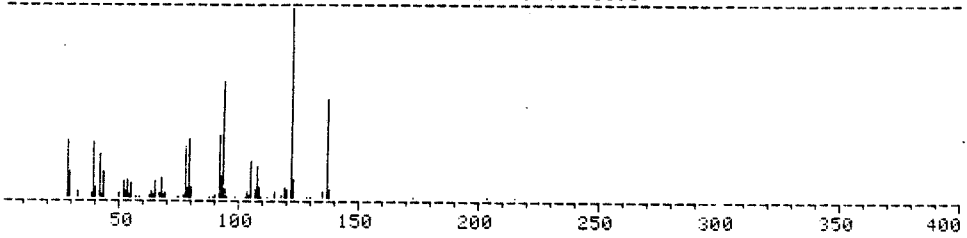
Molecular Weight = 138.0

Entry	Mass	Abundance	Mass*Abundance	Norm.Abund.
1	28	56	1568	1000
2	68	11	748	196
3	94	11	1034	196
4	95	20	1900	357
5	109	7	763	125
6	111	12	1332	214
7	135	5	675	89
8	138	11	1518	196
9	185	5	925	89
10	215	5	1075	89

Above Spectrum Recorded in Library 2 as entry # 552

2,4(18)-p-menthadiene 79

Spectrum # 37 Sample # 1 Retention Time= 53.8



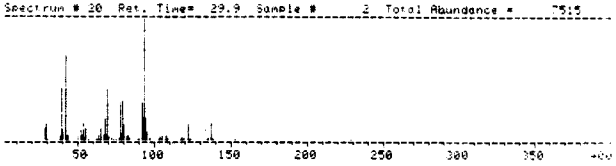
Molecular Weight = 136.0

Entry	Mass	Abundance	Mass*Abundance	Norm. Abund.
1	39	151	5889	291
2	77	139	10703	268
3	79	162	12798	312
4	91	169	15379	326
5	93	315	29295	607
6	105	102	10710	197
7	107	88	9416	170
8	121	519	62799	1000
9	122	51	6222	98
10	136	270	36720	520

Above Spectrum Recorded in Library 2 as entry # 550

trans - 2-p menthene ?

Spectrum # 20 Ret. Time= 29.9 Sample # 2 Total Abundance = 7515



10 peaks used for search:

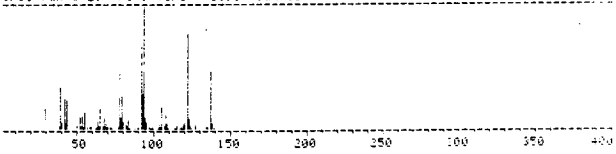
Mass	Linear Abund	% Abund	Significance
39.0	494	42.2	17.7
41.0	804	68.7	30.3
69.0	495	42.3	31.4
77.0	379	32.4	26.8
79.0	369	31.5	26.8
91.0	368	31.4	30.8
92.0	217	18.5	18.3
93.0	1171	100.0	100.0
94.0	212	18.1	18.3
136.0	167	14.3	20.9

10 BEST MATCHES: Library #2

Entry	Similarity Index	Molecular Weight
258	0.9456	136.0
266	0.8945	136.0
554	0.8755	136.0
254	0.8628	136.0
553	0.8471	136.0
263	0.8339	136.0
255	0.8254	136.0
264	0.8178	136.0
267	0.8176	136.0
221	0.7987	204.0

α-phellandrene

Spectrum # 29 Ret. Time= 35.5 Sample # 2 Total Abundance = 4061



10 peaks used for search:

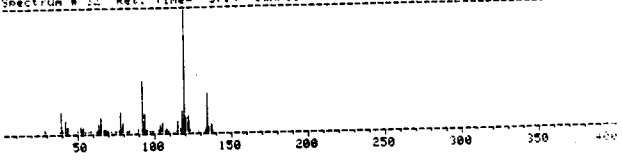
Mass	Linear Abund	% Abund	Significance
39.0	398	34.6	14.5
77.0	545	47.4	39.1
79.0	311	27.0	22.9
91.0	770	66.9	65.4
92.0	334	29.0	28.7
93.0	1151	100.0	99.8
105.0	209	18.2	20.5
107.0	136	11.8	13.6
121.0	886	77.0	100.0
136.0	560	48.7	71.0

10 BEST MATCHES: Library #2

Entry	Similarity Index	Molecular Weight
536	0.9517	136.0
257	0.9496	136.0
550	0.9151	136.0
264	0.8677	136.0
533	0.8629	136.0
519	0.8328	136.0
255	0.8180	136.0
263	0.8175	136.0
253	0.8119	136.0
266	0.8046	136.0

α-terpinene

Spectrum # 32 Ret. Time= 37.4 Sample # 2 Total Abundance = 8339



10 peaks used for search:

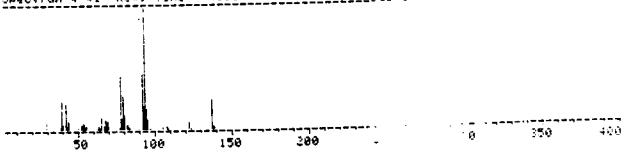
Mass	Linear Abund	% Abund	Significance
77.0	343	16.7	10.8
91.0	858	41.9	32.0
93.0	317	15.5	12.1
115.0	194	9.5	9.2
117.0	345	16.8	16.6
118.0	235	11.5	11.4
119.0	2048	100.0	100.0
120.0	237	11.6	11.7
121.0	258	12.6	12.8
134.0	633	30.9	34.8

10 BEST MATCHES: Library #2

Entry	Similarity Index	Molecular Weight
256	0.9633	136.0
161	0.9615	134.0
482	0.8636	150.0
532	0.7529	134.0
518	0.5317	316.0
379	0.4089	318.0
335	0.3568	316.0
289	0.3545	164.0
472	0.3410	106.0
334	0.3377	150.0

β-phellandrene

Spectrum # 41 Ret. Time= 40.3 Sample # 3 [illegible] dance = 19664



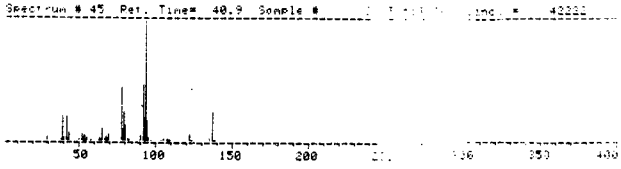
10 peaks used for search:

Mass	Linear Abund	% Abund	Significance
39.0	974	23.1	9.7
41.0	888	21.1	9.3
77.0	1820	43.1	35.7
79.0	1120	26.6	22.6
80.0	504	11.9	10.3
91.0	1882	44.6	43.7
92.0	810	19.2	19.0
93.0	4218	100.0	100.0
94.0	712	16.9	17.1
136.0	1012	24.0	35.1

10 BEST MATCHES: Library #2

Entry	Similarity Index	Molecular Weight
364	0.9454	136.0
396	0.9418	136.0
155	0.9416	136.0
163	0.9403	136.0
513	0.9337	136.0
554	0.8925	136.0
267	0.8791	136.0
539	0.8746	136.0
358	0.8610	136.0
536	0.8468	136.0

β-phellandrene



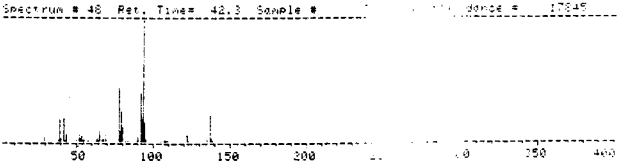
10 peaks used for search:

Mass	Linear Abund	% Abund	Significance
39.0	1946	20.8	8.7
41.0	1868	20.0	8.8
77.0	4140	44.3	36.6
79.0	2288	24.5	20.8
80.0	1190	12.7	10.9
91.0	4266	45.6	44.6
92.0	1790	19.1	18.9
93.0	9354	100.0	100.0
94.0	1566	16.7	16.9
136.0	2284	24.4	35.7

10 BEST MATCHES: Library #2

Entry	Similiarity Index	Molecular Weight
364	0.9478	136.0
255	0.9429	136.0
263	0.9410	136.0
519	0.9401	136.0
166	0.9364	136.0
554	0.8854	136.0
267	0.8780	136.0
539	0.8764	136.0
258	0.8581	136.0
536	0.8485	136.0

β-phellandrene



10 peaks used for search:

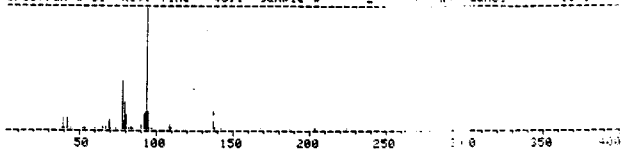
Mass	Linear Abund	% Abund	Significance
41.0	816	19.3	8.5
77.0	1916	45.3	37.5
79.0	1064	25.1	21.3
80.0	528	12.5	10.7
91.0	1682	39.7	38.9
92.0	814	19.2	19.0
93.0	4234	100.0	100.0
94.0	666	15.7	15.9
121.0	244	5.8	7.5
136.0	952	22.5	32.9

10 BEST MATCHES: Library #2

Entry	Similiarity Index	Molecular Weight
364	0.9639	136.0
255	0.9598	136.0
263	0.9576	136.0
519	0.9464	136.0
166	0.9145	136.0
267	0.8941	136.0
539	0.8843	136.0
258	0.8769	136.0
536	0.8768	136.0
554	0.8463	136.0

γ-terpinene ?

Spectrum # 51 Ret. Time= 45.1 Sample # 2 ... dance = 3040



10 peaks used for search:

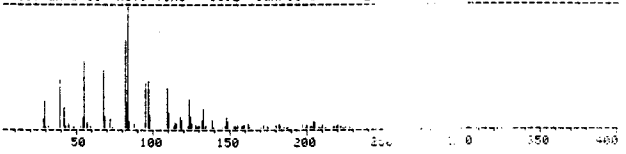
Mass	Linear Abund	% Abund	Significance
69.0	75	7.7	5.7
77.0	392	40.2	33.3
78.0	63	6.5	5.4
79.0	214	22.0	18.7
80.0	121	12.4	10.7
91.0	130	13.3	13.1
92.0	135	13.9	13.7
93.0	974	100.0	100.0
94.0	144	14.8	14.9
136.0	187	19.2	28.1

10 BEST MATCHES: Library #2

Entry	Similiarity Index	Molecular Weight
255	0.9108	136.0
519	0.9000	136.0
264	0.8986	136.0
263	0.8848	136.0
140	0.8680	248.0
266	0.8556	136.0
258	0.8489	136.0
138	0.8441	232.0
539	0.8250	136.0
267	0.8162	136.0

allo ocimene trans, cis ?

Spectrum # 58 Ret. Time= 61.2 Sample # 2 ... dance = 1468



10 peaks used for search:

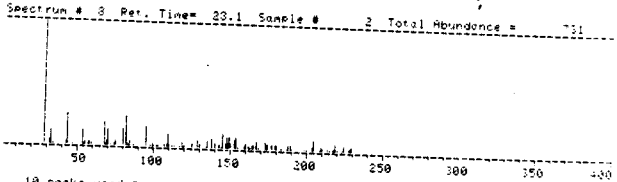
Mass	Linear Abund	% Abund	Significance
55.0	104	54.7	36.3
67.0	91	47.9	38.7
81.0	137	72.1	70.4
82.0	39	20.5	20.3
83.0	190	100.0	100.0
95.0	70	36.8	42.2
96.0	74	38.9	45.0
109.0	62	32.6	42.9
123.0	45	23.7	35.1
132.0	31	16.3	25.9

10 BEST MATCHES: Library #2

Entry	Similiarity Index	Molecular Weight
217	0.6333	152.0
506	0.6156	322.0
551	0.6067	138.0
531	0.5691	96.0
456	0.5620	294.0
245	0.5392	152.0
377	0.5204	296.0
265	0.5065	138.0
10	0.4782	378.0
548	0.4702	138.0

*** LIBRARY SEARCH [rev. 1.1 '78] ?

Spectrum # 8 Ret. Time= 23.1 Sample # 2 Total Abundance = 731



10 peaks used for search:

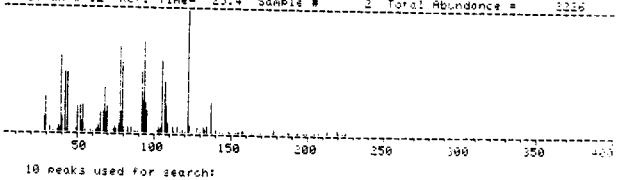
Mass	Linear Abund	% Abund	Significance
28.0	140	100.0	100.0
81.0	33	23.6	68.2
95.0	23	16.4	55.7
109.0	16	11.4	44.5
145.0	17	12.1	62.9
147.0	13	9.3	48.8
149.0	14	10.0	53.2
153.0	12	8.6	46.8
204.0	13	9.3	67.?
218.0	9	6.4	50.1

10 BEST MATCHES: Library #2

Entry	Similiarity Index	Molecular Weight
546	0.8998	28.0
544	0.3760	30.0
552	0.8682	138.0
549	0.8119	136.0
58	0.3974	179.0
539	0.3581	136.0
545	0.2889	54.0
187	0.2183	275.0
52	0.2105	358.0
51	0.2062	358.0

?

Spectrum # 12 Ret. Time= 25.4 Sample # 2 Total Abundance = 3236



10 peaks used for search:

Mass	Linear Abund	% Abund	Significance
39.0	118	60.5	19.5
57.0	71	36.4	20.2
77.0	135	69.2	44.1
79.0	109	55.9	36.5
91.0	96	49.2	37.0
93.0	143	73.3	56.4
105.0	113	57.9	50.3
106.0	79	40.5	35.5
121.0	195	100.0	100.0
136.0	49	25.1	28.2

10 BEST MATCHES: Library #2

Entry	Similiarity Index	Molecular Weight
550	0.8685	136.0
257	0.8257	136.0
547	0.8012	136.0
536	0.7789	136.0
533	0.7785	136.0
283	0.7333	136.0
286	0.6782	136.0
360	0.6660	136.0
391	0.6651	136.0
361	0.6588	136.0

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