Delta-3-carene : a raw material for saturated monocyclic monoterpene alcohols
by Mark Andrew Hannah

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering
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Abstract:
Delta-3-carene, a constituent of the by-product turpentine from Kraft pulp mills in the Rocky Mountain region, was used as a raw material for the production of monoterpene alcohols. A four-step process, including hydrogenation, hydrobromination, esterification, and hydrolysis was used.

The final alcohol products were identified as cis- and trans-8-p-menthanol and cis- and trans-8-m-menthanol.

The liquid phase hydrogenation of (+) Δ-3-carene was investigated in a continuous fixed-bed catalytic reactor using a reduced nickel catalyst containing 58% nickel on a kieselguhr support (Harshaw Ni-OlO4-T).

The operating conditions were as follows: 25-115°C, 0-1500 psig, LHSV .05-.50, and H2 rate 38-376 SCF/gal. Δ-3. The production of (-) cis-carane was favored by high pressure, lower temperatures, and low space velocity while 1,1,4-trimethylcycloheptane (the major by-product) was favored by low pressures, high temperature, and high space velocity. Carane yields of 90-95% with 100% conversion of Δ-3-carene were obtained at 60-70°C, 750-1000 psig, and LHSV .10-.20. The catalyst activity was decreased by a poison suspected to be water. The selectivity was unaffected.

The hydrobromination of carane, was carried out in a semi-batch reactor using gaseous HBr. Organic peroxides were used to try to reverse Markovnikov's rule of addition so that secondary bromides could be obtained. This failed completely with carane, with about equal amounts of the tertiary meta and para derivatives being the only products obtained.

The operating conditions were as follows: 5-100°C and initial carane concentration .30-1.60 g-moles/l. The high temperature favored the meta derivatives slightly while the lower carane concentrations decreased the reaction rate. Conversions of over 95% were obtained in most of the experiments with the reaction proceeding very rapidly generating exothermic heat. The acetate esters were produced from the terpinyl bromides because elimination predominated when direct hydrolysis of bromides was tried. The batch esterification went instantaneously in an acetic acid medium using silver acetate. The operating conditions were as follows: 2-112°C, initial bromide concentration .12-1.30 g-moles/l. and reaction time 2-60 min. Temperature up to about 70°C had no effect on the yield of ester but at 112°C the yield dropped. At higher bromide concentrations the yield was decreased slightly, also. The maximum amount of ester obtained was 60% at 17°C using .25 g-moles bromide/l.

The batch hydrolysis reaction was investigated with menthyl acetate in a Parr bomb using aqueous NaOH. The operating conditions were as follows: 95-245°C, .25-2.92 g-moles Na0H/l. H2O, .23-1.08 g-moles ester/l. H2O, and reaction time 15 min. to 13 hours. At temperatures over 120°C the reaction went easily with 80-100% conversions and 90-100% alcohol yields. Reaction times over one hour provided nearly complete conversion while reactant concentration had no effect on the reaction. Hydrolysis of crude tertiary esters yielded approximately 50% alcohols at 170°C after 10-12 hours.

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ABSTRACT

Delta-3-carene, a constituent of the by-product turpentine from Kraft pulp mills in the Rocky Mountain region, was used as a raw material for the production of monoterpene alcohols. A four-step process, including hydrogenation, hydrobromination, esterification, and hydrolysis was used. The final alcohol products were identified as cis- and trans-8-p-menthanol and cis- and trans-8-m-menthanol.

The liquid phase hydrogenation of (+) Δ-3-carene was investigated in a continuous fixed-bed catalytic reactor using a reduced nickel catalyst containing 58% nickel on a kieselguhr support (Harshaw Ni-0104T). The operating conditions were as follows: 25-115°C, 0-1500 psig, LHSV .05-.50, and H_2 rate 38-376 SCF/gal. Δ-3. The production of (-) cis-carane was favored by high pressure, lower temperatures, and low space velocity while 1,1,4-trimethylcycloheptane (the major by-product) was favored by low pressures, high temperature, and high space velocity. Carane yields of 90-95% with 100% conversion of Δ-3-carene were obtained at 60-70°C, 750-1000 psig, and LHSV .10-.20. The catalyst activity was decreased by a poison suspected to be water. The selectivity was unaffected.

The hydrobromination of carane was carried out in a semi-batch reactor using gaseous HBr. Organic peroxides were used to try to reverse Markovnikov's rule of addition so that secondary bromides could be obtained. This failed completely with carane, with about equal amounts of the tertiary meta and para derivatives being the only products obtained. The operating conditions were as follows: 5-100°C and initial carane concentration .30-1.60 g-moles/l. The high temperature favored the meta derivatives slightly while the lower carane concentrations decreased the reaction rate. Conversions of over 95% were obtained in most of the experiments with the reaction proceeding very rapidly generating exothermic heat.

The acetate esters were produced from the terpinyl bromides because elimination predominated when direct hydrolysis of bromides was tried. The batch esterification went instantaneously in an acetic acid medium using silver acetate. The operating conditions were as follows: 2-112°C, initial bromide concentration .12-1.30 g-moles/l. and reaction time 2-60 min. Temperature up to about 70°C had no effect on the yield of ester but at 112°C the yield dropped. At higher bromide concentrations the yield was decreased slightly, also. The maximum amount of ester obtained was 60% at 17°C using .25 g-moles bromide/l.

The batch hydrolysis reaction was investigated with menthyl acetate in a Parr bomb using aqueous NaOH. The operating conditions were as follows: 95-245°C, .25-2.92 g-moles NaOH/l. H_2O, .23-1.08 g-moles ester/l. H_2O, and reaction time 15 min. to 13 hours. At temperatures over 120°C the reaction went easily with 80-100% conversions and 90-100% alcohol yields. Reaction times over one hour provided nearly complete conversion while reactant concentration had no effect on the reaction. Hydrolysis of crude tertiary esters yielded approximately 50% alcohols at 170°C after 10-12 hours.

I. INTRODUCTION

A. Oil of Turpentine

Oil of turpentine is believed to have been the first essential oil ever isolated, being mentioned by the Greek historian Herodotus[1] (484 to 425 B.C.). It has been commercially produced both as a by-product from pulp mills[2] and as a direct product from pine tree resins[3] for at least 100 years and perhaps even before that.

Turpentine production in the United States had been static at about 30 million gallons annually from 1900 to 1960 but has started to increase and about 40 million gallons is predicted for 1970[4]. Its sources, however, have changed from being produced exclusively from pine gum (oleoresin) in 1900 to about 50% produced now as by-product from Kraft pulp mills, with 25% still coming from pine gum and another 25% coming from steam distilling pine stump resins. The United States leads in world production of turpentine today, with about 40-50% of the total.

B. Delta-3-Carene

The turpentines from India and Scandinavia were noticed early to be quite different from the American and French turpentines[3]. Distillation of these turpentines indicated a much smaller fraction of the Indian and Scandinavian turpentine boiling at 167°C or less (the alpha- and beta-pinene fractions). Simonsen et al[5] carefully fractionated the Indian turpentine in 1920 and found it contained alpha-pinene, beta-pinene, a new bicyclic terpene for which the name Δ-3-carene was proposed, and a sesquiterpene called longifolene. The properties of the new terpene

hydrocarbon were b.p. 168-169°/705 mm Hg, d_{30}^{30} .8586, n_D^{30} 1.469, and $[\alpha]_D^{30}$ + 7.69°. The following structure was eventually assigned.

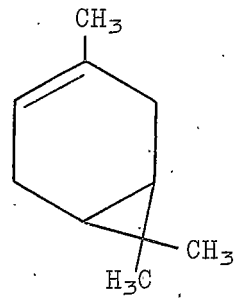


Figure 1. The Chemical Structure of Δ -3-Carene.

Delta-3-carene has been found [6,7,8] in the turpentines from many species of coniferous trees of the United States and Canada. It ranges in amounts in different species from only a trace to nearly 100%. Table I gives a summary of the trees containing substantial amount of Δ -3-carene and their locations. In addition to North American sources for Δ -3-carene, it is also found in other areas of the world, as previously mentioned. The Pinus longifolia found in various parts of Asia and Europe is reported [10,11] to have 45-70% Δ -3-carene in its turpentine; the Pinus silvestria in Poland is reported [12] to have about 35% Δ -3-carene; and undesignated pines of Sweden are reported [13] to have 25-33% Δ -3-carene. Undoubtedly, it occurs in many other countries which have not been mentioned.

All of the above information indicates the potential availability of Δ -3-carene in various parts of the world. In the United States at the present time, Δ -3-carene is available only in the by-product turpentine recovered from three western Kraft pulp mills*, and will be available from two other mills** if and when they start recovering their turpentine.[14] There is no commercial facility in the U.S. now for the sole purpose of separating pure Δ -3-carene from turpentine mainly because there is no ready market for it in this country either as a chemical raw material or as an end product in its pure state. However, there has been a considerable amount of research done on the chemistry of Δ -3-carene[4,15-27] some of which may open the door for commercial utilization in the near future.

* Waldorf-Hoerner Paper Products Co., Missoula, Montana.
Southwest Forest Industries, Snowflake, Arizona.
Boise-Cascade Corp., Wallula, Washington.

** Potlatch Forests, Inc., Lewiston, Idaho.
Northwestern Pulp & Power, Ltd., Hinton, Alberta.

TABLE I. Approximate Percentage of Δ -3-Carene in the Turpentine of Various Coniferous Trees of the United States and Canada.

Tree Common Name	Botanical Name	Major Locations	% Δ -3-Carene in Turpentine	Reference
Mason & Stockwell Pine	Pinus Washoensis	Western Nevada	Chiefly Δ -3	8
Western Larch	Larix Occidental	Mont., Wash., Ida., Ore., & B.C. in Canada	49%	6
Ponderosa Pine	Pinus Ponderosa	Western U.S.	36%	6
Whitebark Pine	Pinus Albicaulis	Alb., B.C., Mont., Wyo., Nev., & Cal.	35%	7
Lodgepole Pine	Pinus Contorta	Western U.S. & Canada	21%	6
Engleman Spruce	Picea Engle Manii	Rocky Mt. Region of U.S. and Canada	21%	6
Tamarack	Larix Laricina	Canada & Great Lakes Region of U. S.	9%	6
Sugar Pine	Pinus Lambertiana	California & Oregon	7%	6

C. Saturated Monocyclic Alcohols

The primary objective of this research, therefore, was to try to utilize Δ -3-carene as a raw material for the production of other terpene chemicals which have a ready market now or to develop new or unique terpene derivatives which might have desirable properties for which new

outlets could be established. Most terpenes today are utilized in the fragrance, flavor, and cosmetic industries with some of them having lucrative prices. Many of these terpenes are alcohols isolated from various naturally occurring essential oils or produced synthetically; thus, the research on Δ-3-carene was directed toward the general area of the terpene alcohols. Eight alcohols, among the many which could possibly be attained from Δ-3-carene, are given in Figure 2.

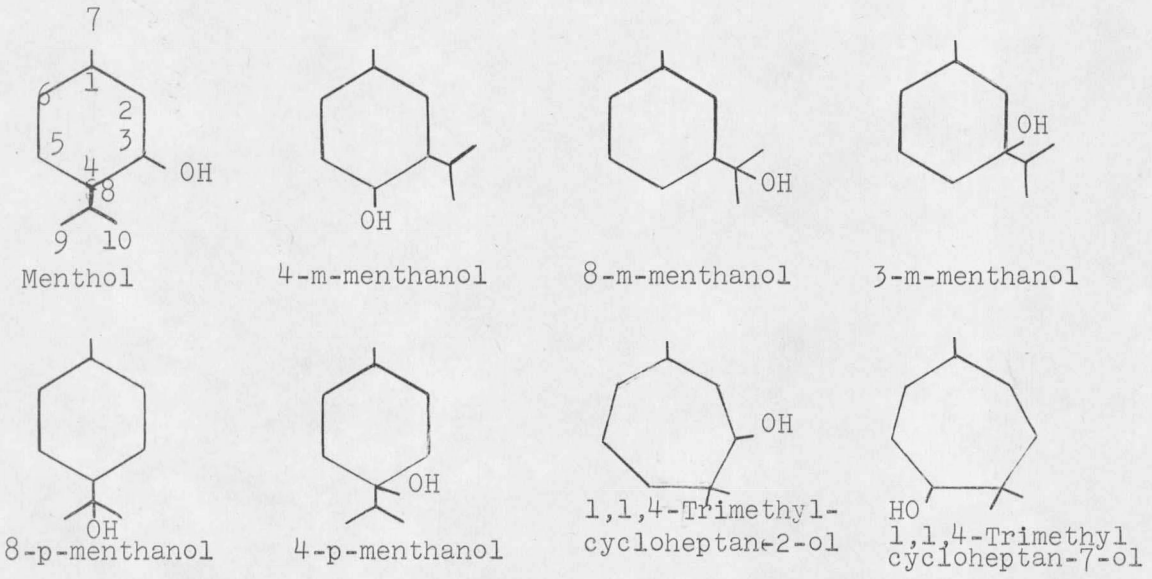


Figure 2. Some Saturated Monocyclic Monoterpene Alcohols.

These saturated alcohols which could be obtained by substitution at the reactive cyclopropane ring were chosen as the general type of monoterpene alcohols to try to obtain primarily because menthol is among them and is probably the most valuable of all the terpene alcohols. It has a domestic market of about two million pounds annually,[28] and a value which fluctuates from about $3.50/lb. to $6.50/lb.[29] depending on the

supply and demand situation prevailing at the time. It is widely used in cigarette filters, cosmetics, toiletries, flavoring agents and various ointments. However, the menthol situation is complicated because four different geometric isomers each having optical pairs exist. These isomers are d & l-menthol, d & l-neomenthol, d & l-isomenthol and d & l-neoisomenthol. Of the eight possible isomers of menthol, only levomenthol has the desired cooling properties*. Some of the other isomers do have some cooling powers and similar fragrances and therefore have a value which has been estimated at about $1/lb. [30]. They occur naturally along with menthol in the mint oils, although in smaller amounts. Most of the l-menthol used in the United States is extracted from naturally occurring Brazilian peppermint oil [31]. In addition, there have been many ways reported [28,32-41] for synthesizing the menthol isomers. Of the other seven terpene alcohols shown which might be obtained from Δ-3-carene, only the 8-p-menthanol (dihydro-α-terpineol) has commercial outlets. It occurs in pine oil which is widely used as a floatation agent in the mineral industries [42]. Pine oil contains 60-70% tertiary alcohols, which include 8-p-menthanol, 15-20% secondary alcohols (borneol and fenchol), with the remainder being hydrocarbons. The tertiary alcohols have been found to give the pine oil its floatation activity. Eight-p-menthanol is also used to make heat setting printing inks.

*Racemic dl-menthol has about half of the cooling powers of l-menthol so it is used also.

The meta-isomeric terpene alcohols and 4-p-menthanol are only mentioned briefly in the literature [44,45] and apparently there is no present commercial outlet for these alcohols, possibly because they are not readily available. These materials may have certain desirable properties which could give them commercial value either as chemical intermediates or as end products in their pure state. Nothing could be found on the cycloheptyl alcohols in the literature.

In addition to the final alcohol products which will be obtained there will be various other terpenes produced as intermediates in the process for synthesizing the alcohols since it will require four reaction steps. Some of these intermediate products may have interesting properties, also.

D. General Objectives

There are two important reasons for doing research on chemicals from the sulfate turpentine of Montana and other western pulp mills. First, it is desired to try to develop commercial outlets for the by-product sulfate turpentine and its constituent terpenes in order to give pulp mills an incentive to condense their turpentine, which, in many mills, enters the atmosphere containing foul smelling sulfur contaminents. This would help abate a serious air pollution problem. Second, it is desired to develop chemical processes which could lead to the establishment of a highly attractive and sorely needed new industry in Montana.

II. RESEARCH OBJECTIVES

The objectives of this research were as follows: 1) determine from theoretical considerations a series of reactions to convert Δ-3-carene into monocyclic terpene alcohols with a hydroxyl group located at the 3,4, or 8 carbon atom; 2) investigate each of the reaction steps experimentally to determine the effects of the major operating variables on the product distribution and yield; and 3) identify the major products formed in each of the reactions.

Since the research was basically exploratory in nature, no attempt was made to pinpoint the most optimum operating conditions for each reaction. Emphasis was placed instead on the establishment of basic trends whenever possible for the effects of the major operating variables.

Since menthol was the most interesting terpene alcohol from an economic point of view, the research efforts were directed toward obtaining this material as a major product but considerable interest was still retained in the other alcohols which could also be formed.

III. THEORETICAL CONSIDERATIONS FOR THE REACTIONS INVESTIGATED

As a starting point for this research project, a series of chemical reactions which were theoretically sound had to be determined such that the hydrocarbon raw material, Δ-3-carene, could be converted into some terpene alcohol, preferably menthol, with reasonably high yields. The number of reaction steps had to be kept at a minimum because of time limitations on the project and also because the yield of the final product would be a function of the yields of the various intermediates formed and each step of the process would increase the cost of producing the final product.

The process devised originally was the following:

$$\Delta\text{-3-carene} \xrightarrow{H_2} \text{carane} \xrightarrow{HBr} \text{terpinyl bromides} \xrightarrow{OH^-} \text{terpinyl alcohols}$$

In this process the Δ-3-carene would be hydrogenated to carane first, followed by the formation of a bromide intermediate from which the alcohol could be obtained by direct hydrolysis. However, because of the inherent difficulty of hydrolyzing secondary and tertiary cyclic bromides directly, the process was modified to include one additional step. This was to form the acetate ester from the bromide first and then to convert this ester into the corresponding alcohol. Therefore, the process investigated experimentally was the following:

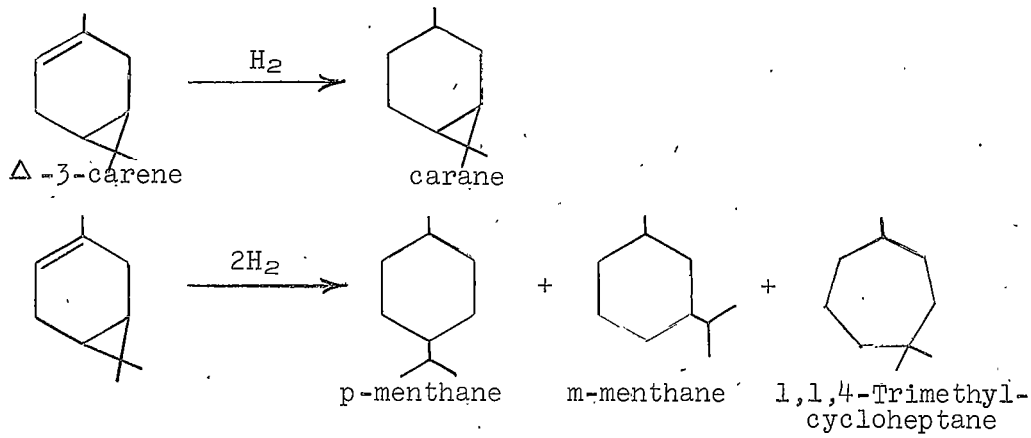
$$\Delta\text{-3-carene} \xrightarrow{H_2} \text{carane} \xrightarrow{HBr} \text{terpinyl bromides}$$

$$\text{terpinyl bromides} \xrightarrow[O^-]{CH_3(=O)} \text{terpinyl esters} \xrightarrow{\text{hydrolyze}} \text{terpinyl alcohols}$$

The basic reasoning and theoretical considerations behind the choice of these particular reactions follows.

A. Hydrogenation of Δ-3-carene

Since the desired alcohols were to have the hydroxyl group located on the 3,4, or 8 carbon atom, the double bond in Δ-3-carene would have to be hydrogenated to eliminate any possibility of intermediate formation at that point on the molecule. It was desired also to try to keep the strained cyclopropane ring from fissioning during hydrogenation to preserve the reactivity of that portion of the molecule. This would require hydrogenation under fairly mild conditions utilizing a very active but selective hydrogenation catalyst. The three carbon molecule, cyclopropane, hydrogenates with ring cleavage to propane at 80°C using a nickel catalyst [46]; therefore, it was felt that the reaction temperature would probably have to be less than 80°C depending, of course, on the catalyst activity. The effect that pressure would have on the reaction was not known although it was felt that perhaps low pressure would also be required. This turned out to be wrong but the pressure effects will be discussed later. The hydrogenation reactions with the four possible saturated products are as follows:



All of the last three hydrogenation by-products shown above would occur if there was ring fission at the three different points of the cyclopropane ring followed by hydrogenation. If the hydrogenation was not complete and the ring fission occurred, then a variety of terpene olefins could be formed also. However, since carane was the desired product, conditions were sought which would completely hydrogenate the double bond of the cyclohexene ring and therefore suppress the amounts of any olefins formed.

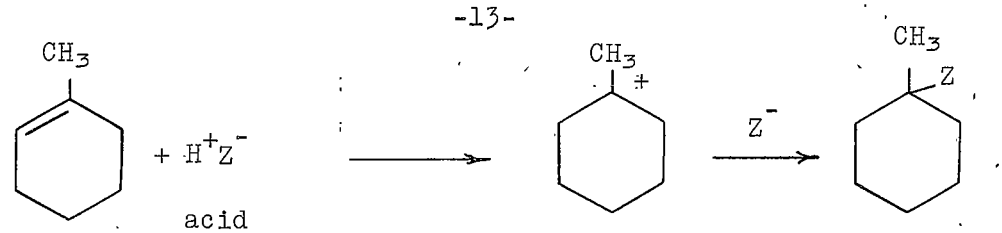
It was felt that the hydrogenation of the double bond would produce both the cis and trans geometric isomers of carane. It was difficult to predict which of the isomers would predominate. The trans isomer is usually the more stable of the two geometric isomers but in this case its formations could be hindered somewhat because of the position of the cyclopropane ring on the Δ-3-carene molecule, resulting in considerable cis isomer formation. In order to form menthol or neomenthol, trans-carane would be required. Cis-carane would lead to isomenthol

and neoisomenthol unless some isomerization occurred in one of the following steps of the process.

B. Hydrobromination of Carane

As mentioned in the introduction, there was the possibility of forming both tertiary and secondary alcohols from Δ-3-carene. It was assumed that reactions occurring at the cyclopropane ring of carane would be analogous to the reactions of an olefinic bond. Therefore, it is expedient to discuss briefly some of the addition reactions to olefins and then apply the same reasoning to carane.

Alcohols can be obtained by the hydrolysis of alkyl halides (chlorides, bromides, or iodides) and alkyl sulfates ($ROSO_3H$) and directly by hydration of an olefinic bond with water. There are other means, of course, but they will not be discussed here. The alkyl halides and sulfates can be obtained by the reaction of the appropriate acid with an olefin. The reactions of these acids and water, all of which have an ionizable hydrogen, normally follow ionic addition to an olefinic bond under Markovnikov's rule which states in essence that the hydrogen of the acid will attach itself to the carbon atom of the olefinic bond which holds the greater number of hydrogen atoms. Using 1-methylcyclohexene which has a double bond between tertiary and secondary carbons as an example, the reaction can be illustrated as follows:



1-methylcyclohexene — Tertiary Carbonium Ion — Addition Derivative

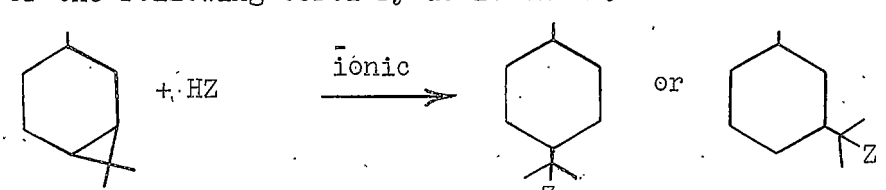
(where Z^- can be Cl^-, Br^-, I^-, $^-OSO_3H$, or ^-OH)

The addition reaction with 1-methylcyclohexene follows Markovnikov's rule with the intermediate formation of the tertiary carbonium ion which is more stable than the secondary carbonium ion. According to carbonium ion theory [46] the greater the number of alkyl groups on a carbonium ion, the more dispersed will be the positive charge resulting in greater stability. Therefore, the stability of carbonium ions decreases in order from the tertiary ion to the methyl ion:

Stability of $R-\overset{R}{\underset{R}{\overset{|}{\underset{|}{C}}}}{}^{+} > R-\overset{+}{C}H-R > R-CH_2^{+} > H-CH_2^{+}$

Tertiary — Secondary — Primary — Methyl

In any addition reaction proceeding by an ionic mechanism in which there is the possibility of forming two different carbonium ions, the more stable ion will form faster and thus predominate. Applying this well established theory to carane, ionic addition should result in one or more of the following tertiary derivatives:



carane

From these considerations it would appear impossible to form secondary intermediates from carane with any of the reactants mentioned above, from which menthol might subsequently be obtained. Fortunately, however, hydrogen bromide can add to an olefinic bond abnormally in violation of Markovnikov's rule. In this type of reaction, secondary bromide formation should predominate over tertiary bromide formation. This peculiar phenomenon has been investigated (47) and the abnormal addition found to be caused by the presence of organic peroxides in trace amounts which initiate a free radical reaction rather than an ionic reaction. Hydrogen bromide is apparently the only acidic reagent among those mentioned above which will undergo this abnormal addition in the presence of peroxide (46).

There is strong evidence that the free radical addition of hydrogen bromide to an olefinic bond follows a chain reaction mechanism because of the very small amounts of peroxide required to make the reaction go. The peroxide apparently initiates the reaction by breaking down to form a free radical which abstracts hydrogen from the hydrogen bromide molecule creating a bromine atom. The bromine atom then attacks the olefin in such a manner that the most stable organic free radical is formed*. The organic free radical sustains the reaction by abstracting hydrogen from another hydrogen bromide molecule, releasing a bromine atom which reacts

*The stability of free radicals is identical to that of carbonium ions in that tertiary free radicals are more stable than secondary free radicals, etc.

with another olefin molecule. The reaction is propagated in a repetitive manner until terminated by the collision of two free radicals or the exhaustion of one of the reactants. Using carane, the reaction is illustrated below, assuming ring fission to produce only the para-intermediate:

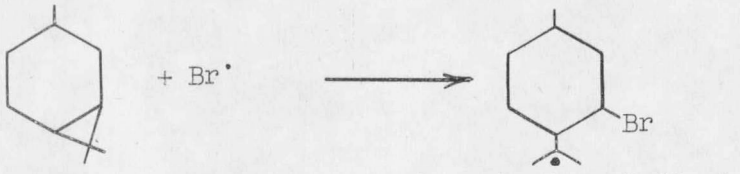
Free Radical Formation



Peroxide — Peroxide Free Radical

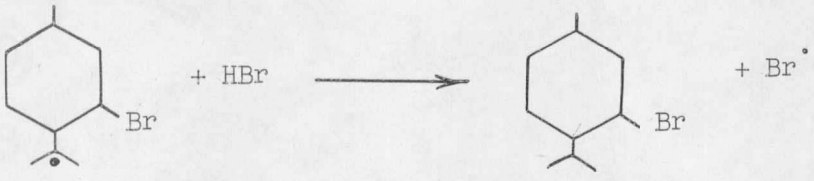
Initiation





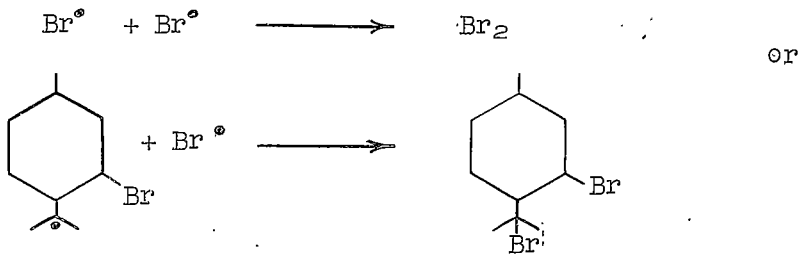
Organic Free Radical

Propagation



Secondary Bromide

Termination



The basic difference between the ionic and free radical mechanisms is that during an ionic reaction the hydrogen ion reacts first with the organic compound and during the free radical reaction the bromine atom reacts first with the organic compound, thus reversing the orientation of the bromide. The free radical addition of hydrogen bromide to carane appears, therefore, to be a feasible means of producing an intermediate from which the secondary alcohol might be obtained.

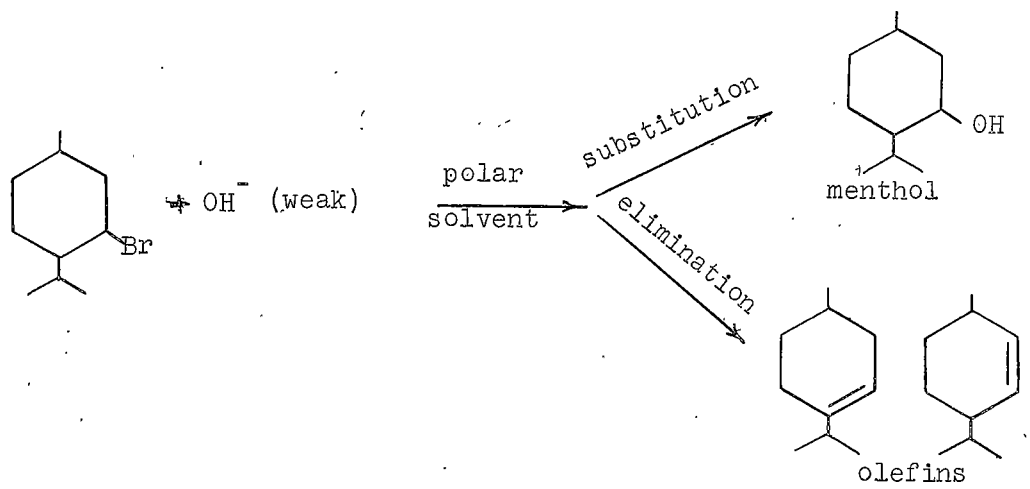
C. Hydrolysis of Terpinyl Bromides

The direct hydrolysis of bromide intermediates to their corresponding alcohols was considered originally as the third and last step of the process. The literature describes various methods of directly hydrolyzing alkyl bromides. Some of these methods in brief are as follows: hydrolysis of the halide in a solution of potassium formate in absolute methanol [48], hydrolysis with aqueous sodium carbonate [49], hydrolysis with aqueous alkalies [46,50], hydrolysis with an aqueous slurry of silver hydroxide [51], hydrolysis with aqueous silver nitrate [52], hydrolysis with an aqueous slurry of calcium hydroxide [53], hydrolysis with water using a surface active agent [54], and hydrolysis with aqueous alkali using an emulsifier to reduce mass transfer problems. All of

these methods are based on a reaction involving nucleophilic* substitution of the hydroxyl ion for the bromine. Unfortunately, an interfering side reaction, during which hydrogen is eliminated from the molecule to form an olefin, usually accompanies the hydrolysis substitution reaction. The relative rates of the two competing reactions can be influenced by the type of base, solvent, and the reaction conditions used. The choice of a weak base and a hydrogen bonded solvent usually favors the substitution reaction (51). In addition to the above conditions, orientation of the bromine itself influences the predominance of one reaction over another, i.e., the tendency to eliminate rather than substitute increases in order from primary to secondary to tertiary orientation. Many tertiary bromides undergo elimination by merely refluxing them with water at 95-100°C. The secondary bromide is also prone to eliminate but not so much as the tertiary bromide, even in aqueous base. On top of these problems the cyclic alkyl halides show a greater tendency to eliminate than do the acyclic halides (55).

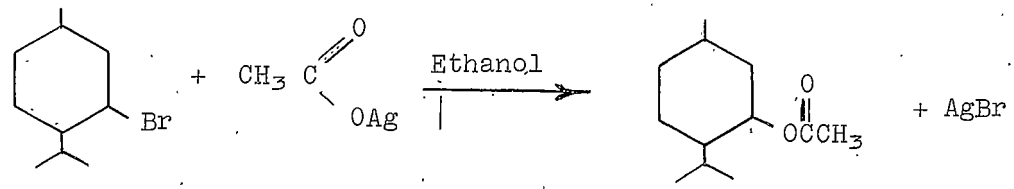
With full awareness of the elimination problem, however, investigation of the direct hydrolysis of the alkyl bromides was undertaken. The two reaction possibilities are illustrated below with 3-bromo-p-menthane:

*A nucleophile is an electron-rich ion.



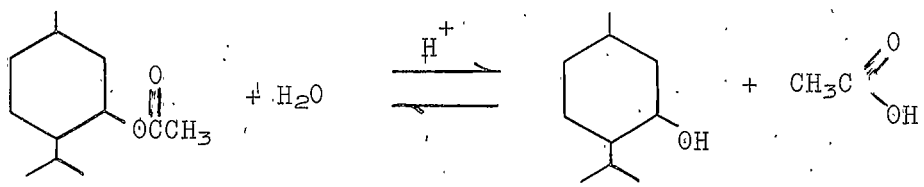
D. Esterification of Terpinyl Bromides

This step of the process was added after considerable experimentation revealed the difficulty of directly hydrolyzing the terpinyl bromides because of the ease with which elimination occurs with the cyclic bromides. A comprehensive literature survey of some advanced organic texts disclosed that alkyl bromides can often be converted to the corresponding alcohols more easily and in higher yields if the acetate ester is first formed and then hydrolyzed or reduced to the alcohol. The esterification reaction is favorable for substitution because the acetate ion is actually a very weak base (50). Silver acetate is recommended for best results because the silver acts as an electrophilic catalyst (55) pulling the bromine from the organic molecule. However, there is the possibility that sodium or potassium acetate might react also under more severe conditions. The reaction with silver acetate apparently goes well in an ethanol carrier at refluxing temperature. An example of this reaction with 3-bromo-p-menthane is shown:



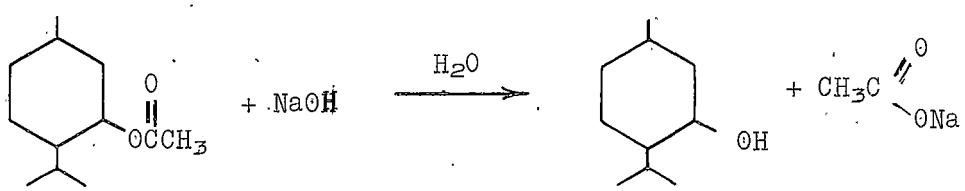
E. Hydrolysis of Terpinyl Acetates

The hydrolysis of esters to form alcohols has been thoroughly investigated and is usually accomplished by one of two methods. The first method is acid catalyzed hydrolysis. This reaction is shown below with menthyl acetate.



The reaction is reversible with esterification occurring in the opposite direction.

The other method of hydrolyzing esters is saponification with aqueous sodium hydroxide. This reaction is illustrated as follows:



The saponification reaction is much faster than the acid catalyzed hydrolysis [50] and is essentially an irreversible reaction because the acetate ion is tied up with the sodium. A mutual solvent for the aqueous base and the organic ester may be desired also to eliminate mass transfer problems which could reduce the overall reaction rate.

IV. EXPERIMENTAL

A. Materials and Equipment
Hydrogenation of Δ-3-Carene

Delta-3-Carene Feedstock: The Δ-3-carene raw material for the hydrogenation reaction was obtained as a product from graduate research on crude turpentine in the chemical engineering laboratories at Montana State University. It can be isolated from the crude sulfate turpentine at about 95% purity by a precision steam distillation with 45-50 theoretical trays and 20 to 30:1 reflux ratios. The gallon quantities required for continuous operation of the hydrogenation unit were produced in an eight-inch packed column, 52 feet in height, being operated as a pilot plant for Waldorf-Hoerner Paper Products Company, Missoula, Montana. The purity of the Δ-3-carene used throughout the project ranged from about 70-98%. Impurities in the Δ-3 included other monoterpenes such as beta-pinene, dipentene, and myrcene; small quantities of the epoxides or peroxides of Δ-3 (less than 0.5%); and a few parts per million sulfur contaminants. Other contaminants may have been present also but analyses were not made for anything but the above. Routine analyses were made for the terpenes present in the Δ-3 by gas chromatography but only a few analyses were carried out to determine the amount of peroxide and sulfur contaminants present. The 98% Δ-3-carene has the following properties: b.p. 163-164/623 mm Hg, $d_{25}^{25} = .856$, $n_D^{20} = 1.4718$ and $(\alpha)_D^{25^\circ} = +14.9^\circ$.

Hydrogen Gas: The hydrogen gas was purchased from the H & R Oxygen and Supply Company of Billings, Montana, in high pressure cylinders at 2000 psig. The hydrogen is produced electrolytically by the National Cylinder Gas Division of Chemetron Corporation, Chicago, Illinois.

Catalysts: The catalysts investigated included the following:

Harshaw Ni-0104T -- a reduced and stabilized active nickel catalyst containing about 58% Ni on a kieselguhr support. (Manufactured by the Harshaw Chemical Company, Cleveland, Ohio.)

Girdler G-G9RS -- a reduced and stabilized, promoted nickel catalyst containing about 50% Ni on a kieselguhr support. (Manufactured by the Girdler Catalyst Division, Chemetron Chemicals, Louisville, Kentucky.)

Raney Nickel #28 -- an extremely active and pyrophoric nickel catalyst. (Manufactured by W. R. Grace and Co., Chatanooga, Tennessee.)

In addition to these four very active hydrogenation catalysts, the other catalyst materials investigated were cobalt-molybdate, nickel-molybdate, and nickel oxide. Of these seven catalysts the Harshaw Ni-0104T was found to be the most favorable from technical and economic standpoints (discussed later), so it was chosen as the catalyst to use for the bulk of the hydrogenation experimental work. The properties of this catalyst are given below:

TABLE II. Properties of the Harshaw Ni-0104T Catalyst

Chemical Make-up	58% nickel on a kieselguhr support Reduced and stabilized against pyrophoricity
Packed Density	85 lbs/cu ft (1/8 in. pellet)
Surface Area	150 m^2/gm
Pore Volume	0.5 cc/gm

The support material for the catalyst bed was 1/8-inch and 1/4-inch Alundum pellets (Norton Company).

Batch Reactor: The preliminary catalyst evaluations were carried out batchwise in a Parr #4001, high pressure, rocking type bomb (The Parr Instrument Co.). Figure 3 is a schematic diagram of the Parr bomb. The bomb cylinder and gage head are constructed of Type 316 stainless steel. The apparatus is heated by two 750 watt sheathed wire elements. One heater operates directly on 115 volts, AC, the other through a 115 volt "Powerstat" variable transformer. The heater with the Powerstat is used for maintaining the temperature at the desired value. The bomb has a capacity of 480 cc and can be operated up to 350°C at a maximum pressure of 6000 psi. The bomb has thermowells for a thermocouple and stem thermometer. The pressure is indicated by a gage on the bomb head.

The temperature in the bomb was regulated for some experiments by a Capacitrol controller (Wheelco Instrument Co.), which operated in an off-on mode. The temperature was continuously recorded by a Micromax potentiometric recorder (Leeds & Northrup Co.).

Fixed-Bed Reaction System: A flow diagram of the final continuous hydrogenation reaction system used is given in Figure 4. The reaction was carried out in a 31 inch flow tube reactor utilizing a fixed bed catalyst. A more detailed description of the reactor is given in the next section. The reactor is jacketed allowing hot water to circulate around the outside of the reaction zone to supply heat to sustain the reaction and also to remove excess exothermic heat from the reactor. The water jacket is insulated with one-inch layer of fiberglass. The hot water circulates in a closed system with the aid of a small centrifugal pump at a maximum rate of about 40 gallons per hour. The water temperature is maintained at the desired value by a 1000 watt, 118 volt electrical immersion type heater in a five-gallon holding tank. A temperature-sensitive switch (Fenwal, Inc.) is utilized as an off-on controller.

The Δ-3-carene feedstock is pumped to the top of the reactor with a chemical proportioning pump (Hills & McCanna). The feed rate of Δ-3 is determined by using a burette and measuring the time to pump a certain volume of the Δ-3. The feedstock is stored in a graduated 1000 ml cylindrical glass vessel adjacent to the burette. The hydrogen gas is metered to the reactor out of a high pressure cylinder through a back pressure regulator (Matheson). A high pressure rotometer (Brooks) is used to determine the flow rate of the hydrogen. The hydrogen enters at the top of the reactor and flows in a co-current manner with the Δ-3-carene through the catalyst bed. The pressure in the

reactor is controlled by a "Mitey-Mite" back pressure regulator (Grove). The products from the reaction exit through a cooler before entering the "Mitey-Mite" and are discharged from the reactor at atmospheric pressure. The excess hydrogen is vented to the atmosphere and the liquid products are collected in an Erlenmeyer flask. The hydrogen rotometer was used in conjunction with a "Precision" wet test meter.

Temperatures at four points in the reaction zone and at the inlet and outlet of the water jacket are monitored continuously by thermocouples and recorded by a Micromax six point potentiometric recorder. The pressure in the reactor is indicated by a pressure gauge. The temperature in the water holding tank is indicated by a thermometer.

Fixed-Bed Reactor: A detailed schematic diagram of the fixed-bed reactor for the hydrogenation reaction is shown in Figure 5. The reactor was constructed from a one-inch schedule 80 stainless steel pipe. The reactor is 31 inches long with a high pressure cross welded to the top and a flanged union welded to the bottom. The water jacket is 27.5 inches long and was made from a three-inch schedule 40 steel pipe.

The hydrogen and Δ-3-carene enter the reactor together through one side of the cross. The other side of the cross is connected to a hydrogen safety vent line containing a 2050 psi monel rupture disk. A 1/4-inch stainless steel thermowell is situated in the center of the reactor extending from the opening at the bottom up through the cross at the top. It is held in the center of the bed by the catalyst and the

catalyst support. A stainless steel coil is fitted in the reactor at the bottom to hold the catalyst and the alundum supports in place when the reactor is in an upright position. Thermowells are located at the top and bottom of the water jacket, also. The thermocouples in the catalyst bed were placed at distances of 14 inches, 19 inches, 23 inches, and 26 inches from the top of the cross. The thermocouples in the reactor are soldered to a detachable four-prong electrical plug which plugs in at the top of the reactor supporting rack to the thermocouple leads of the recorder. The two thermocouples in the water jacket were connected directly to the recorder.

Before the final heating system for the reactor as described above was constructed, three other systems were used for the first 18 runs with the continuous unit. The first heating system was electrical and consisted of nichrome heating elements wrapped about the reactor in three sections and controlled individually with powerstats. The reactor and heating elements were covered with about a two-inch layer of insulating cement (Denver Fire Clay Co.). The second heating system used was partly electrical and partly hot water. The pre-heat and exit sections of the reactor were heated with nichrome elements. However, to obtain better temperature control, the reaction zone was wrapped with 1/4-inch copper tubing so hot water could be circulated. The whole thing was then covered with the insulating cement. Hot and cold water streams from the tap were blended together to obtain the correct temperature before the water circulated through the copper coil around the reactor.

This system did not provide a steady temperature either, so a third system was designed. This system included the water jacket used in the final design. Cold water from the tap, with the flow controlled by a water pressure regulator, was passed through a steam heat exchanger to obtain the desired temperature. The temperature was manually controlled by adjusting the water flow rate through the heat exchanger. A constant flow through the reactor was maintained by using a by-pass set up. This system proved unsatisfactory also because the steam pressure varied and was too low to put a controller or regulator on it. Therefore, to enable 24-hour operation of the reactor, the final design with the closed heating system was installed.

Distillation Column: Some of the hydrogenated product was steam distilled to determine the feasibility of separating the two products (carane and 1,1,4-trimethylcycloheptane) and the feasibility of separating the products from unreacted Δ-3-carene. Steam distillation was used to keep the temperature down (94-95°C) to prevent decomposition of the terpenes. The distillation column was made up of three 4 foot x 1 inch sections stacked vertically to obtain a 12-foot column. Each section was packed with 1/8-inch stainless steel helices (Fenske rings). The sections had been calibrated previously and found to have approximately 25 theoretical plates each so that the column had a total of about 75 theoretical plates. A Corad condensing head was used which provided various reflux ratios up to 30:1, the ratio used. A three-liter stillpot was used which was heated by a Powerstat controlled Glas-Col

heating mantle. Each of the sections of the column was electrically heated (controlled individually with Powerstats) to provide nearly isothermal operation. The product was collected in a graduated cylindrical separatory funnel so that the water in the distillate could be separated.

Hydrobromination

Hydrocarbon Reactants: The only carane which was available for experimentation was that produced as a product in the hydrogenation step. There are no commercial sources available even from such rare chemical suppliers as K & K Laboratories. The carane used in the hydrobromination studies usually contained two other reaction products from the hydrogenation step: 1,1,4-trimethylcycloheptane and 2,6-dimethyloctane. In some of the preliminary runs a small amount of Δ-3 was present, also. The purity of carane ranged from 64% to about 88%. Some of the carane reactant was distilled to remove Δ-3-carane but most was used directly out of the reactor, especially when Δ-3 conversions were 99-100% complete. The 1,1,4-trimethylcycloheptane was the major by-product from the hydrogenation of Δ-3-carene while 2,6-dimethyloctane came from myrcene present in the Δ-3-carene feedstock for the hydrogenation step. In addition to carane, 1-methylcyclohexene (K & K Labs) and 2,4,4-trimethylpentene-2 (Phillips Petroleum Co.) were also investigated. Both of these olefins could yield secondary or tertiary derivatives depending on how the HBr added across the double bond. These hydrocarbons were purchased in technical grade purities.

Hydrogen Bromide Gas: The HBr gas used for this investigation was purchased from the Matheson Company in 10-pound cylinders as a liquid under its own vapor pressure (320 psig.). The purity is listed as 99.8% min.

Miscellaneous Materials: Reagent grade quantities of the following peroxides were obtained from K & K Laboratories: benzoyl peroxide, lauroyl peroxide, and cumene hydroperoxide. Diphenylamine was used as a free radical inhibitor. Technical grade pentane was used as a diluent for most of the experimental studies to control the temperature. Other diluents used, mainly to obtain different temperatures, were n-hexane, cyclohexane, n-heptane, and glacial acetic acid. Pentane and 1,1,4-trimethylcycloheptane were used in various proportions in the final runs to control both the initial carane concentration and the temperature.

Reaction System: The reaction system for the hydrobromination studies is shown schematically in Figure 6. The reactor used most often was a 500 cc, round bottom pyrex flask having three ground joint necks. The same type of flask, modified by placing a one-inch diameter optical quartz glass window in the side, was used when the effect of ultraviolet radiation was investigated. Preliminary runs were carried out in a Vycor quartz test tube, 22mm x 200mm, but this proved to be too small.

The hydrogen bromide gas is fed to the reactor through a gas rotometer (Fisher-Porter). The pressure of the gas is reduced from cylinder

pressure with a pressure regulator (Matheson) constructed of monel. The gas is dispersed into the hydrocarbon reactant from a fritted glass, gas bubbler tube while the reactants are kept in constant agitation with a magnetic stirrer. When desired, heat can be supplied from a Glas-Col heating mantle regulated by a Powerstat. Temperatures down to 5°C were obtained by using an ice bath. The HBr not reacting passes out of the reactor through a cooler, provided to condense any entrained vapors, and into a gas absorber which discharges into the sewer. The absorber is packed with 1/2-inch ceramic Berl saddles and is 24 inches long x 1-1/2 inches in diameter. The temperature in the reactor is indicated by a thermometer or continuously recorded with a Micromax potentiometric recorder. The ultraviolet radiation is generated with a Sylvania germacidal lamp. The reactor and germacidal lamp are enclosed in a plate glass case to screen out ultraviolet radiation. The entire reaction system is enclosed in a hood to remove HBr fumes and ozone generated from the ultraviolet radiation.

Vacuum Distillation Column: The terpinyl bromide products were distilled under vacuum to remove unreacted carane and any olefins formed from decomposition of the bromides. No attempt was made to separate the various bromide components, however. An 18-inch x 1-inch Vigreaux distillation column was used for this purpose because of its very low holdup of distillate and low pressure drop. The distillation was carried out at about 5 mm Hg and vacuum was supplied by a Cenco-Megavac pump

(Central Scientific Co.). The vacuum is indicated by a mercury manometer with an accuracy of one millimeter.

Esterification

Bromides: The terpinyl bromides used in the investigation of this reaction were produced in the hydrobromination step. The product mixture contained mainly cis- and trans-8-bromo-p-menthane and cis- and trans-8-bromo-m-menthane. No commercial sources for these materials could be found. No attempt was made to separate the bromides into the individual components contained in the product mixture. However, the hydrobromination product was vacuum distilled to remove unreacted carane, the inert 1,1,4-trimethylcycloheptane and any terpene olefins formed by decomposition of the bromides. The bromide reactant mixtures which were esterified probably contained 95-99% bromides. The purity was estimated by boiling point and density. The bromide mixtures, after vacuum distillation to remove terpene hydrocarbons, were found to have a boiling point of about 72°C/5 mm Hg and a density of about 1.18 gms/cc. The identity of the terpinyl bromides was not known when the esterification reaction was studied.

In addition to the terpinyl bromides, cyclohexyl bromide was also studied. It was assumed that its reactions would be somewhat similar to those of any seconday terpinyl bromides in the reactant mixture and it could be analyzed directly in the chromatograph. The cyclohexyl bromide was obtained from K & K Laboratories.

Acetate Salts: The silver, sodium, and potassium salts of acetic acid were investigated in the esterification of the bromides. All three were used with cyclohexyl bromide but only the silver acetate was used with the terpinyl bromides. Reagent grade, anhydrous forms of the salts were purchased for use in the experiments with cyclohexyl bromide. However, because of the high cost of silver acetate ($4.50/oz.), it was synthesized in the laboratory from sodium acetate and silver nitrate for use in esterification of the terpinyl bromides. The reaction was very simple, with the silver acetate being precipitated when aqueous solutions of the two reagents were mixed. The silver acetate was then filtered, washed with deionized water and dried in an oven at about 200°F. The purity of the silver acetate synthesized in the laboratory would probably be equivalent to a technical grade because some surface oxidation occurred when the material was dried and trace quantities of silver nitrate and sodium acetate were probably also present. No analysis of the silver acetate was done, though.

Diluents: The diluents used in the esterification studies were absolute ethanol, reagent grade glacial acetic acid, and propionic acid assaying 99%.

Reaction System: The reaction system is shown in Figure 7. The reactor used for the esterification was a 500 ml round bottom pyrex flask with three ground joint necks. The reactants were mixed with a motor driven agitator consisting of a glass shaft with a Teflon impeller. A glass tube was used as a bearing for the shaft with a piece of rubber

tubing forming a seal. Glycerin was used as the lubricant on the rubber. A condenser was used on the reactor when it was operated at refluxing temperatures. The reactor was heated with a Glas-Col heating mantle regulated through a Powerstat. For runs at lower temperatures a cold water bath or ice bath was used. The temperature was indicated with a thermometer for some experiments and recorded on a Micromax recorder for others.

Hydrolysis

Ester Reactants: The esters which were investigated in the hydrolysis step included menthyl acetate and mixtures of the terpinyl acetates produced from Δ-3-carene. The terpinyl acetate product mixture was found to contain cis- and trans-8-p-menthyl acetate and cis- and trans-8-m-menthyl acetate. The menthyl acetate (menthol ester) was purchased from K & K Laboratories. The terpinyl acetates were vacuum distilled to remove olefins before saponifying them. However, there were still some terpinyl bromides present which could not be separated from the esters by distillation.

The terpinyl acetates were not used in the hydrolysis investigations to establish the basic trends of the reaction because the ester components and their corresponding alcohol derivatives could not all be resolved in the chromatograph, making the analysis for individual components impossible. Therefore, menthyl acetate was used to obtain some of the trends and the terpinyl acetates were used only for checking some

of the reaction conditions used with the menthyl acetate.

Cyclohexyl Bromide: In addition to the investigations of the hydrolysis of esters, considerable effort was spent in trying to hydrolyze the bromide directly to the alcohol. Cyclohexyl bromide was used in this investigation because it was one of the few bromides available which is similar in structure to the secondary terpinyl bromides, which were not available. No tertiary cyclic bromides could be obtained.

Hydrolyzing Agents: The hydrolyzing agents which were tried with cyclohexyl bromide are as follows: aqueous solutions of sodium hydroxide; a methanolic solution of potassium formate; an aqueous solution of sodium carbonate; water with an olefin present to take up hydrogen bromide (patented method); an aqueous solution of sodium hydroxide with a hydrocarbon solvent for the bromide and a sodium oleate emulsifier (patented); an aqueous solution of sodium hydroxide with a sodium oleate emulsifier; and an aqueous slurry of silver oxide.* All of the above hydrolyzing agents were tried with the cyclohexyl bromide. With the esters, only the aqueous solutions of sodium hydroxide were investigated, except for one experiment trying an acid (H_2SO_4) catalyzed water hydrolysis of menthyl acetate.

* The silver oxide was prepared from silver nitrate and an excess of sodium hydroxide. For some runs the precipitate was filtered, washed and dried before use, while in others it was prepared in the reactor.

Reaction Systems: Two different systems were used in the hydrolysis investigations. For the reactions which were carried out at refluxing temperatures, a 250 ml or 500 ml round bottom pyrex flask was used having a refluxing condenser and a thermowell for a thermometer. This type reactor was agitated with a magnetic stirrer and heated by a heating mantle regulated with a Powerstat. For the reactions with the silver oxide slurry, a mechanical agitator had to be used. The esterification reaction system was employed in this case.

For the reactions which were conducted at temperatures above the boiling point of the reactant mixture, the Parr bomb was used. The temperature of the hydrolysis reactions was recorded periodically from a thermometer or recorded continuously by a Micromax recorder.

Steam Distillation: The final alcohol products were steam distilled in the same column used for the distillation of the hydrogenation product described previously.

B. Experimental Procedure

Batch Hydrogenation: The Parr bomb assembly was used for all of the batch hydrogenation experiments. A known weight of catalyst (15-40 gms.) was charged to the clean bomb with 40-100 ml of Δ -3-carene reactant, the bomb sealed, placed in the heater-rocker assembly and pressurized with hydrogen to a predetermined value at 25°C which would give the desired pressure at the operating temperature used. Both heaters were then turned on at 110 volts until the bomb heated to within

about 20°C of the desired temperature at which time the heaters were turned off and the temperature allowed to drift (because of the lag) to the desired value. When the desired temperature was reached, the rocking was started, the hydrogen valve opened (at operating pressure), and the heater with the Powerstat (preset at a value to maintain the temperature through the controller) turned on. The temperature could also be maintained reasonably well by adding just enough heat to the bomb at the operating temperature to off-set the heat loss to the surroundings. At the end of the desired reaction time the bomb was removed from the heater-rocker assembly and quenched in cold water. When the bomb was cool, the excess H_2 was vented off and the hydrogenation product and spent catalyst removed. The product was filtered and then analyzed in the chromatograph.

The Raney nickel catalyst had to be dried before it was used since it was received in an activated state but under water. The catalyst is extremely pyrophoric so it had to be dried under an inert atmosphere. This was accomplished by heating the wet catalyst in a flask and purging nitrogen over it. The nitrogen provided the inert atmosphere after the catalyst dried and also swept out the moisture during the drying process. When the catalyst was to be used, it was placed under Δ-3-carene in the flask and then transferred to the bomb.

The four hydrogenation catalysts were evaluated in the bomb using the following conditions:

Charge	25 gms catalyst 50 ml 93% Δ-3-carene
Temperature	70°C
Pressure	600 psig
Reaction Time	2 hours

Duplicate runs were made for each catalyst. For the catalyst durability test, two runs were made with the same catalyst used over again in the second run to observe if there was any degradation. The conditions used were not the same for the three catalysts tested, however. After the first run was made the hydrogenation product was drained from the bomb and a fresh charge of Δ-3-carene added to the used catalyst for the second run.

Continuous Hydrogenation:* The fixed-bed reactor was prepared for a run in the following manner. The reactor was removed from the rack and the spent catalyst and supports emptied out. Periodically the reactor was flushed out with acetone before adding the new catalyst. The reactor was filled from the bottom. The upper support of alundum pellets was added first, followed by the catalyst and then the lower support of alundum pellets. To obtain a catalyst bed consistent each time in length and uniformity, the supports and catalyst were packed in the

* Procedure described is only for the reactor in its final design.

reactor to the same depths for each run using the same volume of catalyst. For a different volume of catalyst the depths were changed accordingly. The catalyst bed was placed approximately in the middle of the reactor. For example, for a catalyst bed containing 224 cc of 1/8-inch Harshaw Ni-0104T, the following specifications were followed:

Upper support ---------	115 gms of 1/8-inch alundum packed to a depth of 26 inches from the bottom of the reactor.
Catalyst ----------	300 gms, packed to a depth of seven inches from the bottom of the reactor.
Lower support ---------	97 gms of 1/4-inch alundum packed to a depth of 3/4 of an inch from the bottom of the reactor.

Runs were made with amounts of catalyst varying from 100 cc to 224 cc for 1/8-inch pellets.

When the catalyst and supports were in place a stainless steel coil was put in the bottom of the reactor to hold the bed in place when the reactor was inverted. The flanged union was cleaned thoroughly and covered with a thin layer of silicone grease to obtain a good seal when the reactor was mounted on the rack.

After the reactor was mounted in place, the heating water was started circulating and the reactor brought to the desired temperature. The reactor was then pressurized with hydrogen and tested for leaks. After purging with hydrogen for about an hour, the rotometer settings

were checked with the wet test meter. The reactor was then ready to operate. The Δ-3-carene was started into the reactor at the desired feed rate and the unit was considered on stream.

Sampling of reaction products was done usually after the reactor had lined out, which required two to six hours, depending upon the feed rate of Δ-3-carene. When extended runs were made at a fixed set of operating conditions, the products were sampled about every two to four hours over about a sixteen hour period during the day. The reactor ran unattended for about eight hours during the night. Point samples of about one ml in volume were most frequently obtained. During some runs, however, accumulative samples up to eight hours were taken.

When a sample was taken the time was noted and the pressure, H_2 flow rate, Δ-3-carene feed rate, and temperature recorded. The time and sample number were recorded on the temperature recorder paper, also. In addition to the above operating data, information on the changes of hydrogen cylinders, changes in Δ-3-carene feedstock, etc., and observations on the reaction were recorded.

Distillation of the Hydrogenation Product: As mentioned previously, the hydrogenation product was distilled to see if the products could be separated and also to see if the unreacted Δ-3-carene could be recovered. The vapor pressures of the water and the monoterpene hydrocarbons (b.p. 170°C) were such that approximately one volume of water was required to distil one volume of the hydrocarbon. The stillpot was

charged, therefore, with about 1000 ml of water and 750 ml of the terpenes, which gave a small excess of water. The column sections were heated to about 90°C and then the stillpot heater turned on. The column was run at total reflux and flooded to wet the packing. The boil-up rate was then lowered to a little below flooding, the Corad condenser set at a 30:1 reflux ratio, and the run started. Samples were taken of the overhead at intervals of five percent of the charge. The distillate was collected during the day and the column put on total reflux during the night. The distillation was carried out until Δ-3-carene started to show up in the overhead since it was the highest boiler in the product mixture.

Hydrobromination: The pyrex glass reactor (500 cc) was charged with a volume of the hydrocarbon reactant (usually 10-50 ml) along with the diluent. The amount of diluent used varied depending upon the concentration of reactant that was desired. If a peroxide or inhibitor was to be used it was added next. Three moles of these materials were used per 100 moles of the hydrocarbon reactant. The reactor was then placed in the hood with the refluxing condenser and the reactants stirred until the solid material (peroxides) was dissolved; the reactor was brought to the operating temperature at the same time. The HBr was then introduced through the bubbler at a predetermined rate (25 psig at the tank outlet) and the reaction carried out, usually for a length of time in slight excess of that required to feed in a stoichiometric quantity of the HBr (the reaction was instantaneous in nearly all runs). Some runs were

carried out longer than the theoretical time required, however. When an experiment was completed the HBr was shut off and the reactor purged with nitrogen to flush out excess HBr. The reactor was then removed, cooled (if necessary) in a water bath and the product mixed with a small amount of solid Na_2CO_3 to remove any dissolved HBr. The mixture was then filtered and the diluent removed by evaporation in a vacuum (water aspirator) flask.

When the 1-methylcyclohexene or 2,4,4-trimethylpentene-2 was used, no further treatment of the product was necessary since the bromide derivatives of these olefins could be analyzed directly in the chromatograph without any elimination of HBr occurring. However, because of the thermal instability of the bromide derivatives of carane, direct chromatographic analysis could not be used.

The terpinyl bromide product mixture was subjected to a vacuum distillation to remove unreacted carane, the inert terpene hydrocarbons, and any olefins formed from elimination of the bromides. The distillation was carried out using, in some cases, only a distillation flask and in other cases, for more precise work, the 18-inch Vigreaux column. After the hydrocarbons had been removed the bromide product mixture could be characterized by density, boiling point, and refractive index. The conversion of carane could be determined from the amount of unreacted carane in the distillate relative to the inert hydrocarbons: 1,1,4-trimethylcycloheptane and 2,6-dimethyloctane. To analyze for

the distribution of bromide derivatives in the product it was necessary first to convert them to their corresponding esters which could be analyzed in the chromatograph. This was done in accordance with the experimental procedure for esterification (discussed next).

Esterification: The reactor was charged with a known amount (normally a 10% excess) of the acetate salt and a volume of diluent, the amount used being dependent upon the desired reactant concentration. The agitator was placed in the reactor, the condenser put in place and the contents mixed and brought to the desired operating temperature. The correct amount of bromide was then added and the reaction carried out. When the reaction had occurred for the desired length of time, the reactor was removed, cooled in a water bath if necessary, and the contents filtered with the aid of an aspirator. The bromide salt was extracted several times with acetone and the total filtrate then mixed with water to separate the organic ester phase. The ester product was washed with water several times and analyzed in the chromatograph.

Hydrolysis of Cyclohexyl Bromide: When refluxing conditions were used the pyrex reactor (500 cc) was charged with a known amount of cyclohexyl bromide (5-25 ml) and the hydrolyzing agent in the desired concentration. Usually a 10% excess of the hydrolyzing agent was used. The reactants were mixed, brought to the operating temperature, and the reaction carried out for the desired length of time. When the experiment was finished the reactor was cooled in a water bath, the contents removed and filtered, and the products washed free of the hydrolyzing

agent with water. The product was then analyzed in the chromatograph. For those experiments in which silver oxide was used the procedure was identical to that for the esterification. For those experiments in which the sodium oleate emulsifier was used, a few drops of de-emulsifying agent, Tret-O-Lite #F-46, were required to separate the organic and aqueous phases. The product was then processed in the same manner as described above. Several experiments were carried out in the Parr bomb, also. The procedure was about the same as for the batch hydrogenations except, of course, no hydrogen was used. This procedure is described in the next section.

Hydrolysis of Esters: The hydrolysis of menthyl acetate was studied briefly in the refluxing reactor, trying acid catalyzed hydrolysis once and saponification with aqueous sodium hydroxide once. For the acid catalyzed hydrolysis the reactor was charged with 10 ml of menthyl acetate, 350 ml of water, and two to three drops of concentrated sulfuric acid. The same procedure as for the hydrolysis of cyclohexyl bromide was then followed. The saponification in the refluxing reactor of the menthyl acetate was done following the same procedure also, with a charge of 10 ml acetate, 100 ml of water, and 10 gms of sodium hydroxide.

The majority of the experiments on the hydrolysis of menthyl acetate was carried out in the Parr bomb since the saponification required temperatures greater than the normal boiling point of water. The bomb was charged with menthyl acetate (5-20 ml), deionized water (85-100 ml) and

solid sodium hydroxide (1-10 gms), sealed and placed in the heater-rocker assembly. The amounts of each reactant used varied between the limits given above depending upon the concentrations desired. In all cases, however, the total volume of the mixture was kept at 105 ml so that the mixing efficiency in the bomb would be constant for all runs. The bomb was heated to within 20°C of the desired operating temperature (120-190°C) with the two heaters both operating with 110 volts; then the heat was shut off while the temperature increased the 20°C lag because of the large heat capacity of the bomb. When the desired temperature was reached, the rocking was turned on and the heater regulated through the Powerstat set at a predetermined voltage to maintain the desired temperature. The reaction was carried out for the desired length of time and then the bomb was removed and quenched. The products were removed, the aqueous phase separated, the organic phase dissolved in acetone and the solution filtered. The filtrate was then mixed with water and the product separated and collected.

The hydrolysis of the terpinyl esters produced in the process was carried out only to obtain a quantity of the final alcohol for identification purposes. The Parr bomb was used and the reaction carried out repeatedly with a maximum of 20 ml of ester and a maximum total volume of 140 ml. The efficiency of mixing and resulting conversion decreased considerably when greater volumes of this heterogeneous mixture were tried. The procedure was the same as for menthyl acetate.

Distillation of Terpinyl Alcohols: The mixture of terpinyl alcohols containing cis- and trans-8-p-menthanol and cis- and trans-8-m-menthanol was distilled in the hope of separating the various components. The 75 theoretical tray distillation column was used and operated as a steam distillation again to prevent decomposition of the alcohols. The charge to the column was 184 ml of the alcohol product which contained about 50 mole percent terpene olefins, 1500 ml of water (about five volumes of water were required to distil one volume of alcohol, b.p. about 210°C), and 40 ml of Dowtherm A (b.p. = 250°C) which was used as a chaser. The distillation was carried out at reflux ratios varying from 2.5:1 up to 30:1 since the terpene hydrocarbons were cut out first at the lower reflux ratios. Otherwise, the procedure was the same as that used for the distillation of the hydrogenation product.

C. Compound Identification and Analysis
Chromatographic Analysis of Materials

Gas Chromatographs Used: The organic nature of the terpene hydrocarbons and their derivatives involved in this research, and the possibility of isomers occurring in the products of each reaction, necessitated the use of the gas chromatograph as an analytical tool for both qualitative and quantitative use. A Wilkens Aerograph "Moduline" model 202 dual column gas chromatograph with a dual thermal conductivity detector was used for the majority of the analytical work. The chromatograph also had a linear temperature programmer which made possible the analysis of compounds with a wide range of boiling points. A Sargent Model SR recorder was used in conjunction with the chromatograph.

Other chromatographs used at various times during the project included the following: an Aerograph "Moduline" model 661 with a flame detector; an F & M Biomedical Gas Chromatograph model 400 with a flame detector (Chem. Dept.); and an Aerograph Autoprep model A-700 preparative gas chromatograph (Chem. Dept.). The Aerograph model 661 was used during the first part of the project for hydrogenation product analysis. The F & M model 400 chromatograph was used for analysis of the complex ester product mixture because it had a recorder with a disk integrator which afforded more precise quantitative analysis. The Aerograph Autoprep was used for the isolation of pure samples of terpene olefins from the elimination products and also for the isolation of some of the alcohol components. Samples were injected and collected manually, however. The Aerograph model 202 was used for manual isolation of the terpinyl ester components, also.

Chromatograph Liquid Stationary Phases: A considerable number of liquid stationary phases were tried in order to find those which would give a satisfactory resolution of the products and reactants for each reaction. The stationary phases, column dimensions, and operating conditions found to be the best for each type of compound are listed below along with some other phases tried which separated some of the materials but not as well. Sample chromatograms for the product mixtures obtained from the reactions in the process are given in the appendix.

Monoterpene Hydrocarbons -- carane, Δ-3-carene, 1,1,4-trimethylcycloheptane, 2,6-dimethyloctane, myrcene, alpha- and beta-pinene, and dipentene.

Stationary Phase ---- 20% β,β'-oxydipropylnitrile
Support ---------- 60/80 acid washed Chromosorb P
Column ---------- 20' x 1/4" ss
Conditions ---------- 75-80°C, carrier gas 50-60 cc/min
Sample Size ---------- 1-2 microliters

Other phases used, but which gave poorer separations, were 20% Carbowax 4000 on 35/80 Chromosorb P in a 6' x 1/4" ss column and 20% Ucon Polar 50 HB5100 on 35/80 Chromosorb P in a 7' x 1/4" ss column.

Monoterpine Olefins -- 3-p-menthene, 8-p-menthene, 4(8)-p-menthene, 4(8)-m-menthene, 3-m-menthene and 8-m-menthene.

Stationary Phase ---- 20% Carbowax 20 M
Support ---------- 60/80 KOH washed Chromosorb W
Column ---------- 10' x 3/8" aluminum
Temperature ---------- 75°C
Sample Size ---------- 2-4 microliters

The β,β'-oxydipropylnitrile column gave nearly as good a separation as the Carbowax 20 M, also, as did the PDEAS column described below. However, none of these columns would separate all of these isomers.

Terpinyl Bromides -- cis- and trans-8-bromo-p-menthane, and cis- and trans-8-bromo-m-methane. No stationary phase was satisfactory for these materials because they are thermally unstable at the temperatures required to analyze them.

Terpinyl Esters -- Menthyl acetate; cis- and trans-8-p-menthyl acetate; and cis- and trans-8-m-menthyl acetate.

Stationary Phase	10% Phenyl diethanolamine succinate (PDEAS)
Support	60/80 acid washed Chromosorb P
Column	10' x 1/4" copper
Temperature	170°C
Carrier Gas Rate	60 cc/min
Sample Size	2 microliters

Other columns used were 10% Hyprose SP-80 on 60/80 Chromosorb P in a 13' x 1/4" ss column, 20% Carbowax 20 M on 60/80 Chromosorb W in a 10' x 1/4" copper column, 10% 1,2,3 tris (2 cyano ethoxy) ethane (TCEP) on 60/80 acid washed Chromosorb P in a 10' x 1/4" copper column and 20% Carbowax 4000 on 60/80 Chromosorb P in a 20' x 1/8" ss column.

Terpene Alcohols -- Menthol, isomenthol, neomenthol, cis- and trans-8-p-menthanol, 4-terpinenol, 4-p-menthanol, and cis- and trans-8-m-menthanol. No one column was found which would separate completely all of the above alcohols. The Hyprose SP-80 and the TCEP were found to be the best of all the columns tried for general terpene alcohol separations.

Stationary Phase	10% Hyprose SP-80
Support	60/80 acid washed Chromosorb P
Column	13' x 1/4" ss
Temperature	160°C
Carrier Gas Rate	60-70 cc/min
Sample Size	2 microliters

The other columns which could be used are those mentioned under the terpinyl esters although separations were somewhat poorer for the alcohols than for the esters.

Miscellaneous Materials -- The following chromatograph columns were used for the separation of the materials listed below: 1-methylcyclohexene, 1-bromo-methylcyclohexane, and 2-bromo-1-methylcyclohexane.

Stationary Phase	15% Apiezon N
Support	60/80 Chromosorb W
Column	6' x 1/4" ss
Temperature	125°C
Carrier Gas Rate	40-50 cc/min
Sample Size	2 microliters

2,4,4-trimethylpentene-2, 2-bromo-2,4,4-trimethylpentane and 3-bromo-2,4,4-trimethylpentane.

Column	β,β'- oxydipropylnitrile, the same as for hydrogenation products
Temperature	90°C
Carrier Gas Rate	50-60 cc/min

cyclohexene, cyclohexyl bromide, and cyclohexanol.

Column	Apiezon N same as for the 1-methylcyclohexene derivatives with same conditions

cyclohexene, cyclohexyl bromide, and cyclohexyl acetate

Stationary Phase	20% Carbowax 4000
Support	35/80 Chromosorb P
Column	6' x 1/4" ss
Temperature	100°C
Carrier Gas Rate	60-70 cc/min
Sample Size	2 microliters

cyclohexene, cyclohexyl acetate, and cyclohexanol.

Column	Apiezon N at the same conditions as described above

The Apiezon N column was used for the analysis of the hydrolysis product of menthyl acetate because the Hyprose SP-80 resolved the menthol product into its various geometric isomers from which the unreacted menthyl acetate could not be clearly resolved. This made the product too compli-

cated to analyze. The conditions used with the Apiezon N column were 150°C with a carrier gas rate of about 40-50 cc/min. The oxygenated derivatives produced as by-products from the esterification of crude hydrobromination product (assumed to be epoxides and a lactone) were easily resolved in the PDEAS column when used at the same conditions for analyzing the terpinyl esters.

Compound Identification

Retention Time in the Chromatograph: Whenever it was possible, samples of the expected materials were obtained so that tentative identifications could be made by comparing the retention times of the known and unknown samples in the chromatograph. Unfortunately, only a few materials could be obtained. Carane was obtained from the Hercules Powder Company and also from W. Cocker and his associates at the University of Dublin. 1,1,4-trimethylcycloheptane was also obtained from the University of Dublin. None of the terpinyl bromides were available and among the terpinyl esters only menthyl acetate was available. Menthol, isomenthol, neomenthol, and cis- and trans-8-p-menthanol were obtained from various fragrance and flavor companies while 4-p-menthanol was synthesized in this laboratory by hydrogenating 4-terpinenol. None of the cyclohepty alcohol derivatives were available nor were any of the meta isomers.

Infrared Spectra: For those products for which known samples were available, positive identifications could be made by a comparison of infrared spectra. A Beckman IR-4 infrared spectrophotometer was available for this purpose in the Department of Chemistry. The spectrums for some of the products and known materials are given in the appendix. For some of the terpene olefins for which samples could not be obtained, the literature [56] provided infrared spectrums from which positive identifications could be made.

Preparative Chromatography: In order to obtain infrared spectra for the unknown products and also to obtain nuclear magnetic resonance (NMR) spectra, samples of the materials of 95% or greater purity were required. The preparative chromatograph provided a very efficient means of isolating high purity samples of material from product mixtures which could not be easily separated with ordinary operations such as distillation. Samples of the olefins produced from the dehydrobromination of the terpinyl bromide products, samples of the terpinyl esters and samples of the terpinyl alcohols were obtained in this manner. The column used for the olefins and alcohols was described previously (10' x 3/8" Carbowax 20 M). The column used for the ester isolations was a 20' x 3/8" PDEAS with the same composition and support as was used in the 1/4" PDEAS column. The greater diameter of the preparative columns allows much larger sample injections to be used without a significant decrease in component resolution. Usually, samples up to 25-50 microliters can be injected in a 3/8" column and good separation can still be obtained.

The terpinyl esters contained unreacted bromides which could not be readily separated. This caused a problem in the isolation of the various components in the chromatograph because of the decomposition of the bromides at the temperatures used, contaminating the samples with an olefin bleed. After repeated injections of the isolated samples, the bromides were destroyed and most of the olefin contamination removed. However, the esters were also found to be somewhat prone to decomposition so purities greater than about 90-95% were impossible to achieve.

Since a microcell (.025 mm in thickness) was available for use with the infrared spectrophotometer, only five to ten microliters of a sample were required to obtain a good spectrum. For the NMR, however, a minimum of about ten microliters was required.

Nuclear Magnetic Resonance: A Varian model A-60 nuclear magnetic resonance spectrometer was used to obtain information to aid in the identification of the unknown products from the reactions. The spectra are produced by energy transformations in the protons of an organic molecule induced by an external magnetic field. The locations of various peaks in the spectrum and the area under these peaks are correlatable to the effect the structure of the molecule has on its various protons, to the influence of various functional groups, and to the number of protons (relative area).

The NMR spectra for the terpinyl alcohols, terpinyl acetates, the epoxides, and the lactone, and also for the monocyclic monoterpene ole-

fins are given in the appendix. Typical operating conditions used with the A-60 are as follows:

Solvent	CCl_4
Temperature	Ambient
Filter Bandwidth	4.0 cps
R.F. Field	0.2 mg
Sweep Time	250 sec
Sweep Width	500 cps
Sweep Offset	0 cps
Spectrum Amp.	5-8
Integral Comp.	5-8

V. Results and Discussion

A. Hydrogenation of Δ-3-Carene

Products of the Hydrogenation of Δ-3-Carene; (-) Cis-carane and 1,1,4-trimethylcycloheptane were found to be the major products from the hydrogenation of (+) Δ-3-carene for the operating conditions used in this research. The structures of these saturated terpene hydrocarbons are given in Table IV along with the other terpene hydrocarbons which were associated with the hydrogenation of Δ-3-carene. The structural differences between cis- and trans-carane are given in Figure 8. Carane was tentatively identified at first by a comparison of retention times in the chromatograph with known samples. 1,1,4-trimethylcycloheptane was mistakenly identified as p-menthane at first by this same method. When pure samples of these products had been produced later, the infra-red spectra verified the carane product and showed that the product which has been thought to be p-menthane was actually 1,1,4-trimethylcyclo-heptane. The relative composition of carane and 1,1,4-trimethylcyclo-heptane in the product from the hydrogenation reaction was found to be strongly dependent upon the reaction conditions used (discussed later).

There were also a few minor products produced in the reaction but no identification of these materials was attempted, except for 2,6-di-methyloctane which was produced from the hydrogenation of myrcene present in the Δ-3-carene feedstock. The other minor products are suspected to be p-menthane and m-menthane and possibly two olefins, produced when the hydrogenation was incomplete.

The carane produced in this research had identical retention times to the cis-carane obtained by Cocker et al [16] in a chromatograph column which readily separated the cis and trans isomers of p-menthane (β,β' -oxydipropylnitrile). The IR spectra of the carane product and the cis-carane sample matched very closely, also (Figure 56). The infrared spectra of cis and trans isomers usually show small but discernible differences, also, which were not evident. The cis structure of carane was assigned by Cocker by analogy to the characteristics and properties of cis-pinane and cis-p-menthane since no trans-carane was available.

The properties of a sample of carane 95% pure were as follows: b.p. 160-161°/623 mm Hg, $d_{25}^{29^\circ}$ = .810, $n_D^{20^\circ}$ = 1.4541 and $(\alpha)_D^{25^\circ}$ = -13.6°. The carane is by no means optically pure since levo-carane is reported to have $(\alpha)_D$ = -34°. Other investigators [57] have reported the following properties of carane: b.p. 162°/684 mm, 169.5°/759 mm, and 165-166°/750 mm; $d_D^{20^\circ}$ = .8411, $d_{26^\circ}^{26^\circ}$ = .836 and $d_{20^\circ}^{20^\circ}$ = .8381; and $n_D^{20^\circ}$ = 1.455-1.4582.

The properties 1,1,4-trimethylcycloheptane (about 95% pure) were found to be b.p. 160-161°/623 mm Hg, $d_{25^\circ}^{25^\circ}$ = .796, $n_D^{20^\circ}$ = 1.4408 and $(\alpha)_0^{25^\circ}$ 0°*. Cocker reports the refractive index to be $n_D^{20^\circ}$ = 1.4414. The infrared spectra of 1,1,4-trimethylcycloheptane for a known sample and for a sample produced in this laboratory are shown in Figure 57.

*The hydrocarbon was apparently a racemic mixture.

Probably the most interesting result of this reaction was the selectivity in the fissioning of the cyclopropane ring of Δ^{4}-3-carene. Rather than fissioning externally to produce p-menthane after hydrogenation, which was the expected by-product, or m-menthane, the cyclopropane ring was found to fission internally on the six-membered ring to produce 1,1,4-trimethylcycloheptane. The most probable explanation for this occurrence would be that the bulky cyclopropane ring with its gem dimethyl groups made it difficult for the external bonds of the cyclopropane ring to get close to the active sites of the catalyst while the internal bond with no steric problems could be situated very close to the catalyst sites when the molecule was adsorbed. Thus the internal bond was probably excited more than the other two carbon-carbon bonds in the cyclopropane ring resulting in the selective fissioning.

The Δ -3-carene also hydrogenated very selectively to form cis-carane. This was more than likely a result of steric hindrance from the cyclopropane ring, also. A model of the Δ -3-carene molecule shows that the double bond is partially shielded by one of the methyl groups on the cyclopropane ring which would hinder catalytic adsorption and hydrogen addition on that side of the molecule. Apparently the hindrance was strong enough so that addition took place predominantly on the back side of the molecule, forcing the methyl group on the number one carbon into a cis position with the cyclopropane ring. The steric problem had been considered at the start of the project but it did not appear to be too bad, especially since the trans-carane isomer would probably

be the more stable of the two geometric isomers. It was felt at that time that a mixture of the two would probably be obtained. The trans-carane isomer had been desired because it has the methyl group on the top of the molecule in the correct position to give the right isomer of menthol.

Preliminary Batch Hydrogenation Investigations: The preliminary experiments on the hydrogenation of Δ-3-carene were carried out in a semi-batch manner in the Parr high pressure bomb. The objectives of these first investigations were to test several hydrogenation catalysts briefly and to gain some insight into the temperature and pressure which would favor the synthesis of carane. The reaction was carried out with the Δ-3-carene in the liquid state and hydrogen gas constantly fed to the bomb to replenish that which reacted.

The results of these investigations with six catalysts are given in Table V. The first experiments were carried out with the three hydro-desulfurization catalysts: cobalt-molybdate, nickel-molybdate, and nickel oxide. The temperature was varied over a range from 100-250°C, the pressure varied from 200-1000 psig and reaction time varied from 15-170 minutes. The results show that these catalysts were relatively ineffective for producing carane. The maximum amount of carane that was obtained was 27% when the nickel-molybdate catalyst was used at 200°C and 500 psig for 90 minutes. No reaction could be made to go with these catalysts until the temperature was up around 200°C. The major products

were menthadienes produced from the isomerization of the Δ-3-carene. When no catalyst was used, the Δ-3-carene was found to be unaffected by a hydrogen atmosphere at 200°C and 850 psig after 50 minutes.

Six experiments were made with the powdered Girdler G-69RS nickel catalyst with the temperature varied from 25-100°C, the pressure varied from 100-175 psig and reaction time varied from 84-204 minutes. At 25°C very little reaction occurred while at 100°C the predominant product was 1,1,4-trimethylcycloheptane with complete conversion of the Δ-3. At 50°C and 125 psig, however, a product containing 56% carane was obtained after 204 minutes with complete conversion of the Δ-3-carene.

The Harshaw nickel and rhodium catalysts were looked at only briefly in these preliminary experiments. A product containing 25% carane was obtained with 40% conversion of the Δ-3 using the Harshaw catalyst at 50°C and 125 psig after 210 minutes. Forty-three percent carane was obtained using the rhodium catalyst at 50°C and 200 psig after 120 minutes with about 70% conversion of the Δ-3.

The preliminary tests on three of the active hydrogenation catalysts (Girdler nickel G-69RS, Harshaw Ni-0104T, and Englehard rhodium) showed that carane could be produced with all of them. It was decided to make some more detailed tests on all four catalysts (including the Raney nickel) to determine which of the four would be better to use in the continuous fixed-bed hydrogenation reactor.

Catalyst Evaluation: The active hydrogenation catalysts were investigated in the Parr bomb and were compared economically to determine which of the four would be better for use in the investigation of the hydrogenation of Δ-3-carene in the continuous fixed-bed reactor. These catalysts were the Girdler G-69RS nickel, the Harshaw Ni-0104T nickel, the Englehard .5% rhodium, and the Raney nickel #28. The catalysts were evaluated first in the bomb at a fixed set of operating conditions. The results are given in Table VI. Fifty ml of Δ-3-carene (88% pure) and 25 gms of catalyst were placed in the bomb and the hydrogenation carried out at 70°C and 600 psig for two hours. Duplicate runs were made for each catalyst and the results averaged. The results show that 83% carane was obtained with the rhodium catalyst, 70% with the Harshaw catalyst, 31% with the Girdler catalyst, and only 9% with the Raney nickel. Complete conversion of the Δ-3 was obtained with all the catalysts except the Girdler G-69RS. The Raney nickel was obviously much more active than the other catalysts at this temperature because ring fission had occurred appreciably producing 86% 1,1,4-trimethylcycloheptane.

The next test was made to determine if the reaction had any degrading effects on the catalysts. In this test, one run was made and the product separated from the catalyst. The catalyst was then used over again for another run with fresh Δ-3 reactant. The operating conditions for the different catalysts were not the same in these tests, however. The results are given in Table VII. It can be seen that the Harshaw nickel appeared to lose some of its activity after the first

run, the rhodium appeared unaffected and the Raney nickel appeared to be enhanced in selectivity. When the Harshaw nickel was used twice, the conversion of Δ-3 decreased from about 80% to 71%. The amount of carane in the product decreased from 50% to 42%. With the rhodium catalyst the conversion was 100% for both runs while the amount of carane decreased only from 86% to 83%. The Raney nickel was tested at 25°C (compared to 73-78°C for the other two catalysts) and the conversion was 100% in both runs. The amount of carane in the product increased from 74% in the first run to 82% in the second run.

With these brief results on hand, the cost of the catalysts was then investigated. Table III gives the prices for commercial lots of three of the catalysts. It can be seen that the nickel catalysts were comparable in price, while the initial cost of the rhodium was much higher.

TABLE III. Catalyst Prices* for Commercial Lots

Harshaw Ni-0104T ----------	$ 2.47/pound	
Raney Nickel #28 ----------	2.46/pound	
Englehard .5% Rhodium --------	16.60/pound	(initial cost)
	6.60/pound	(min. regeneration cost)

*Prices were quoted f.o.b. by the manufacturer about Sept., 1964.

Even the minimum regeneration cost of the rhodium was over 2-1/2 times the initial cost of the nickel catalysts.

One other factor was taken into consideration in the catalyst evaluation. This was the ease of handling of the catalysts. The Harshaw and Girdler nickel catalysts were stabilized against oxidation so they could be handled in the atmosphere with no problems. Likewise, there was no problem in handling the rhodium catalyst. However, the Raney nickel was received in an activated state under water which required that the catalyst be dried and then handled under an inert atmosphere since it is very pyrophoric when dry.

From the technical and economic considerations given above, the choice was made to use the Harshaw Ni-0104T in the continuous unit since it seemed to be the better of these four catalysts when all the factors were taken into account.

Actually, even though less carane had been obtained with the Harshaw Ni-0104T in the tests conducted in the bomb, there was no reason to believe that operating conditions could not be found which would give equivalent or perhaps even better results with the Harshaw nickel. Obviously, the same reasoning could have been applied to the Girdler nickel but since the Harshaw catalyst had a little higher activity it was selected. Carane has also been produced from the hydrogenation of Δ-3-carene with catalysts such as platinum black [23], Adams catalyst (platinum oxide) [59], and platinized charcoal [16], so undoubtedly there are many which would be satisfactory from a technical point of view.

Hydrogenation of Δ-3-Carene in the Fixed-Bed Reactor: The experimental data and results for all of the runs made in the continuous fixed-bed reactor are given in Table VIII. Only a part of these data was used for the final results but all of it contributed in some manner or another to the knowledge gained about the reaction, so it is all included on that basis.

Preliminary Runs in the Continuous Unit: Even though the experiments on the hydrogenation of carane, carried out in the bomb in a semi-batch manner, indicated that high conversions of the Δ-3-carene and high yields of carane could be obtained, it was desirable to investigate the reaction in a continuous unit for the usual reasons. These are, of course, the ease of operation of a continuous unit, better control of the operating conditions providing better quality control on the product and usually the lower labor costs (which would apply more to a commercial facility). The reactants were well suited for a continuous unit, being fluids and essentially non-corrosive. The reaction was of heterogeneous nature having liquid and gaseous reactants and a solid catalyst. This required the use of a fixed catalyst bed in the reactor. The reactants were fed to the unit in a co-current manner since the hydrogen was used in excess and also because it simplified the fabrication of the unit.

The first runs in the continuous unit were actually made at the same time the batch hydrogenation experiments were being carried out. The hydrodesulfurization catalyst, cobalt-molybdate, was investigated

very briefly (Runs CH-1 and -2) in an electrically heated reactor. The results were about the same as found when the batch reactor was used. Isomerization predominated and very little hydrogenation took place. The temperature used was about 200°C with pressures up to 700 psig. The maximum amount of carane obtained in the product when the Co-Mo catalyst was used was about 12% at 200°C and 500 psig with a hydrogen rate of 2.2 SCF/hr and a Δ-3 feed rate of .90 cc/min. The reactor was operated only during the day, being shut down each night. The first 18 runs were made in this manner.

Ten of the next twelve runs were made using the Harshaw Ni-0104T catalyst and two of the runs were made with the Girdler G-69RS nickel catalyst. These twelve runs were carried out over a range of operating conditions as follows:

Temperature	18-114°C
Pressure	0-1000 psig
H_2 Rate	38-407 SCF/gal. Δ-3)
LHSV*	.10-.86 hr^{-1}

The results obtained were generally quite inconsistent and no satisfactory correlations were obtained on the effects these operating variables had on the conversion of Δ-3-carene and the yield of carane. Runs CH-6 and CH-7 contain the results obtained when the Girdler catalyst was used.

*The liquid hourly space velocity is abbreviated as LHSV or referred to as just the space velocity. The units are cc of Δ-3 feedstock /hr/cc of catalyst, or just hr^{-1}.

A comparison of these two runs with Run CH-8 verifies that the Harshaw catalyst is much more active than the Girdler catalyst at about the same operating conditions.

The preliminary runs with the Harshaw catalyst definitely indicated that the total conversion* of Δ-3-carene was favored by higher temperatures (which was expected) while the carane yield was favored by lower temperatures. Pressure appeared to strongly favor the yield of carane but the effect on conversion could not be established. The lower space velocities were found to favor higher conversions of the Δ-3-carene. The effects of the hydrogen rate on conversion and yield and the effect of space velocity on the yield could not be well established because of the scattering of the data. However, the results of these runs did narrow down the operating conditions to a set of values which seemed to favor carane production with the Harshaw catalyst. These conditions were as follows:

Temperature	70°C
Pressure	800-1000 psig
LHSV	.20 hr^{-1}
H_2 Rate	38 SCF/gal. -3

During brief tests at about these conditions, yields of carane in the neighborhood of 85-95% with 90-100% conversions of Δ-3 had been obtained.

* The conversion is defined as the fraction of the total Δ-3-carene in the feedstock which reacts. The yield is the fraction of the Δ-3-carene which reacts going to a particular product.

In addition to the general data obtained, data were obtained in one run (CH-12A) on the time required for the reactor product composition to line out after a step-change had been made in temperature for a feed rate of Δ-3 of .47 cc/min. (LHSV = .20 hr^{-1}). The reactor was started* at a temperature of about 44-45°C and 300 psig with a hydrogen rate of .38 SCF/gal. Δ-3 and a space velocity of .20 hr^{-1} and allowed to run for seven hours. At this time the temperature was increased to about 75°C with the other conditions held constant. The reactor product was sampled every half hour for two hours and then on the hour for an additional four hours. The results can be seen in Figure 9. The amount of unreacted Δ-3-carene in the product was 28% after one-half hour, declined to about eight per cent after three hours and then leveled out at about this value. The line-out time for the product composition at this feed rate (.47 cc/min.) was about three hours.

Other information that had been obtained when these preliminary runs were completed was that the catalyst was deactivating during a run, causing a drop in conversion, and that shutting the reactor down overnight affected the first results obtained after start-up the next day.

* This was not an initial start-up with dry catalyst since the reactor had been operated for ten hours the previous day.

Catalyst Deactivation Investigations: The next runs were made to obtain information on the catalyst deactivation during a run when a constant set of operating conditions was used. The runs were made in the unit which had been previously modified to include a water jacket, replacing the copper heating coil, but the water was still heated with the steam heat exchanger, so temperature control was not the best. Also, the reactor could not be left unattended at night, so it was operated during the day only. The results of the first two of these runs are given in Table VIII (Runs CH-15 and CH-17) and the catalyst deactivation is indicated in Figure 10 by the decline in the conversion of the Δ-3-carene. It can be seen that the conversion was low right after start-up when the bed was being wetted, but reached 100% after about 8-10 hours on stream. As the run was continued, the conversion of the Δ-3-carene declined at a gradual rate to about 95% after nearly 60 hours of operation. On the other hand, the selectivity of the catalyst for carane production was apparently being enhanced as shown by the increase in the yield of carane during the run. The yield started rather low at about 55% after five hours on stream, increased fairly rapidly to about 72% after 20 hours, and then started to increase at a less rapid rate reaching about 78% after 60 hours. This run was made at 69-76°C and 1025 psig with a space velocity of .20 hr^{-1} and a hydrogen rate of 94 SCF/gal. Δ-3.

More data were obtained on the catalyst deactivation after the reactor water heating system had been changed to the closed system des-

cribed in the experimental section. With the reactor temperature now under good control (about a 2° difference from the top of the bed to the bottom), the reactor could be operated continuously 24 hours/day. Figure 11 shows the results of two runs made at different temperatures (66°C and 76°C) continuously over a time period of about 170 hours. The effect of temperature on the conversion of Δ-3-carene is apparent. The graph shows also that temperature had no apparent effect on the rate of catalyst deactivation. At 76°C the conversion dropped from 97% to about 80% over about a 160-hour period, while at 66°C the conversion dropped from 82% to about 63% over the same period. Figure 12 shows that the deactivation of the catalyst has no effect on the selectivity. At 76°C, the yield of carane lined out at about 87% after only 15 hours on stream while at 66°C the yield went through a maximum of 96% after about 20 hours on stream and then leveled out at 90% after 40 hours. The higher yield at the lower temperature verified what was expected. The fixed operating conditions for these runs were 1050 psig, LHSV = .20 hr^{-1} and 100 SCF of H_2 per gallon of Δ-3 used.

These results suggested very strongly that the chemical nature of the catalyst was not being changed after the first 10-20 hours on stream, which would most likely effect the selectivity, but that a portion of the catalyst was being rendered ineffective by the presence of some material which had no effect on the reaction other than to slow it down.

Although the catalyst manufacturer had stated that no significant oxidation of the nickel catalyst should occur under normal ambient conditions, the results in Figure 13 indicate that this may not be true. Two runs are compared which were made eight months apart with catalyst from the same container which had been closed after removing catalyst but not purged with nitrogen. It can be seen that the catalyst in the earlier run appears to be more active, with the conversion being 100% after 10 hours on stream and declining to only 94% over a 48-hour period. The run made eight months later started at a conversion of 97% after 13 hours and declined to 80% over a 50-hour period. The yield of carane appeared to be greatly improved, however, from the apparent partial oxidation as can be seen in Figure 14. In the early run, the yield increased gradually to 77% after 58 hours while the later run showed a constant yield of 87% lining out at after 15 hours on stream. The results are not conclusive, however, since some of the runs made later in the research indicated that the catalyst poison could affect both the initial catalyst activity and the rate of deactivation (discussed later). After this suspected change in the catalyst was noticed, the storage container was purged with nitrogen each time some catalyst was removed. This was done to prevent further oxidation from occurring.

Since the feedstock had not been pre-treated in any manner as it came from the distillation unit, an attempt was made to determine what effect a caustic wash and moisture removal would have. Figure 15 shows the results of one such attempt. The Δ-3-carene feedstock was pre-

treated by shaking it with a five percent solution of caustic water, washing it with deionized water and then drying it with a $CaSO_4$ desiccant, Drierite. The results of the run with the pre-treated feed were then compared with a run which had been made at the same operating conditions but with untreated feedstock. It can be seen that the pre-treatment seemed to have an adverse effect on the initial catalyst activity although the rate of deactivation appeared unaffected. The run with the treated feed showed a conversion about 15 percentage points lower than the run with the untreated feed. The selectivity of the catalyst appeared to be decreased also when the treated feedstock was used, being about three percent less (Figure 16). Apparently pre-treating the feed in this manner removed something which was necessary in promoting the initial catalyst activity and selectivity but did not remove the poison causing the gradual deactivation. The spent caustic wash did turn an orange color after scrubbing the Δ-3-carene, however, which indicates that it did pick up some contaminant. Also, after repeated washings with fresh caustic solutions the color changes became much lighter. This indicates that some material had been removed from the Δ-3-carene but no analyses were made at that time to determine what had caused the color change. The orange color of sodium sulfide in caustic solutions suggests that the unknown material could have been sulfurous in nature, especially since ASTM analyses of the Δ-3-carene for sulfur had shown amounts up to 40 parts per million. However, since the deactivation still occurred after this pre-treatment, either sulfur was not the contaminant or not enough had been removed to help. At any

rate, additional research (discussed later) has shown that the catalyst can be temporarily regenerated by hydrogen purges and by merely allowing the catalyst to stand overnight with no reactants entering. This pretty much eliminates a permanent poison such as sulfur as the cause of the rapid deactivation of the catalyst. Nevertheless, a slower permanent type of poisoning could also be taking place at the same time.

Another run was made with feedstock treated only with a caustic wash and a water wash. This run was made at 86°C, however, so no comparison could be made with a similar run having untreated feedstock. Figure 17 shows the results. It can be seen that the catalyst deactivation is still present which eliminates the $CaSO_4$ dessicant as a possible additional contaminant since it was not used in this run. The initial conversion was 100% at the high temperature but started to decline after about 20 hours on stream, dropping to about 80% after 150 hours. The carane yield in this run increased gradually from about 75% to 83% and never did level out.

Water had been noticed in the product from some of the runs which made it a strong suspect for the catalyst poison. To determine if the poisoning was permanent or temporary, a run was made in which a hydrogen purge was used and also the reactor allowed to stand overnight with no reactants entering. The effect of these tests are shown in Figure 18. The run was started with untreated feedstock at 75°C and 1050 psig with a space velocity of .20 hr^{-1} and a hydrogen rate of 100 SCF/gal. Δ-3.

The conversion was about 91% after 10 hours and decreased to about 77% after 48 hours on stream. At this time the Δ-3-carene feed was shut off and the reactor purged with hydrogen at the same rate and conditions for about 14 hours. The reactor was restarted and the first sample of product (two hours later) showed that the conversion had increased to 92%. It rapidly declined to about 79% over an eight-hour period, though. Despite the more rapid drop in the conversion, the results after the purge showed that part of whatever had been rendering the catalyst ineffective was at least temporarily removed.

At this time (after 72 hours from start-up) both the Δ-3 and H_2 feed streams were shut off and the reactor allowed to sit overnight for eight hours at the operating temperature and pressure. When the reactor was started the conversion again showed an increase to 91% but it decreased to 85% after six hours. The reactor was then flooded with 300 ml of Δ-3-carene and allowed to drain for about 12 hours with no H_2 or Δ-3 entering. This time when the reaction was started the conversion had decreased to 60%. It rapidly increased to 75% after only two hours but then started to decrease again. After this test the Δ-3-carene feed rate was decreased by one-half and the run continued for another 26 hours. At the new space velocity of .10 hr^{-1}, the conversion increased to 91% and then started a slow decline, being 89% when the run was stopped.

The carane yield during these tests showed sharp drops after each of the first three tests but increased each time after the reaction was

underway. When the space velocity was reduced the yield came back to about 90%, the value it had had when the tests were started.

The results of this run give evidence for the poison being a material like water which could be removed by evaporation. Krylov et al [59] have reported water to be a poison for nickel catalyst, also, and that the activity can be restored by treatment with hydrogen.

All of the information that had been obtained to this point indicated very much that the poison was physically coating the catalyst surface gradually during a run, causing, in effect, a part of the catalyst to be rendered inactive. Since traces of water had been picked up in the product, it was strongly suspected to be the poison. However, runs had been made showing catalyst deactivation when the initial water content of the Δ-3-carene feedstock had been removed by a desiccant. Therefore, it seemed likely that if the poison was water, it was being generated during the reaction. The hydrogen feed was eliminated as a possible source of water because of the effects of the H_2 purge.

Delta-3-carene had been found [57] to oxidize rapidly in the presence of air, probably forming some kind of peroxide and/or epoxide. If the Δ-3-carene feedstock contained peroxides, they could conceivably hydrogenate [60] during the reaction to give water as a by-product, thus providing a continual source of the contaminant. A quick test of the Δ-3-carene feedstock had shown that it contained some peroxides. The test [46] that was used consists of shaking the Δ-3-carene with a solu-

tion of ferrous ammonium sulfate containing potassium thiocyanate as an indicator. If peroxides are present they oxidize the ferrous ion to ferric ion which in turn reacts with the thiocyanate ion to give a deep red color.

To obtain some additional information on the catalyst deactivation problem, a run was made in which various Δ-3-carene feedstocks were used which had been treated in different ways. The results of this run are shown in Figure 19. The run was started at 55°C and 1000 psig with a space velocity of .20 hr^{-1} and a hydrogen rate of 112 SCF/gal. Δ-3. The starting feedstock was untreated. The conversion was initially at about 66% but decreased very rapidly to about 33% after 20 hours on stream and then leveled out at this value for another 22 hours. The yield of carane had increased from about 75% to 90% over this same period. After 42 hours on stream, a feedstock which had been caustic (5%) washed, water washed, and dried with silica gel was started into the reactor. With this treated feedstock in the reactor the conversion increased from 32% to a maximum of 55% over a ten-hour period and then decreased again to about 40% over the next seventeen hours. The yield of carane reacted in just the opposite manner. When the treated feed was added the yield dropped from about 89% to a low of 80% and then increased back to 90%.

After 75 hours on stream the Δ-3-carene feed was shut off and the reactor purged with hydrogen at 90°C and 1000 psig for 25 hours. The reactor was started up at the end of this period using another feedstock treated this time with a two percent aqueous solution of ferrous ammonium

sulfate (to remove peroxides) followed by a five percent caustic wash, a water wash and finally moisture removal with silica gel. The first product after the purge indicated a conversion of 70% which, in the next three hours, dropped to 45% before starting to decrease at a slower rate over the next 23 hours to 32%. The yield, after the hydrogen purge, dropped rapidly also from 75% to 55% but then increased gradually up to 75%.

After 125 hours from start-up, the feedstock was changed to one which had been dried with silica gel only. With this feedstock conversion increased to 43% but then dropped to 37% where it leveled off for about 10 hours. The yield was decreased from 76% to 67% after the new feed was added, but then increased back to 74%. After 150 hours from start-up, a feedstock of which 20% had been air-blown at 85°C for 10 hours, was tried. The Δ-3-carene was air-blown to increase its peroxide content, if possible. The feedstock was dried but was given no other treatment. With the high peroxide feed reacting the conversion immediately dropped from 37% to 31% and remained there for the next 18 hours. The yield, on the other hand, increased from 74% to 84%.

At this time (170 hours after start-up) another hydrogen purge was made at 55°C and 1000 psig for 27.5 hours. The reactor was restarted using a feedstock pre-treated with an aqueous solution containing five percent sodium hydrosulfite and five percent sodium bisulfite (for peroxide removal) for 15 minutes at 25°C, followed by a water wash and moisture removal with silica gel. The first sample of product showed a con-

version of 29% which decreased further to 25% over the next 18 hours. The yield decreased from 82% to 77% over this same period.

Another hydrogen purge was used at 216 hours after start-up at 70°C and 1000 psig for eight hours. The reactor was restarted at 70°C with a feedstock treated the same as the previous feed had been except that it was washed with the solution for two hours. The conversion showed a sharp increase from 25% to 45% but then decreased again back to 30% by the end of the run. The yield decreased rapidly from 78% to 69% and then leveled out at this value to the end.

The results of this run showed that temporary increases in the conversion could be obtained whenever delta-3-carene feedstock was used which had been treated in a manner to reduce peroxide or initial water content. The usual increases in conversion were observed after hydrogen purges had been carried out.

Quantitative tests for the peroxide in the untreated Δ-3-carene feedstock and in some of the treated feedstocks had been tried using a chemical analytical method (Sodium Iodide Titrative Method)[61]. This method was tested with cumene hydroperoxide and was found to give results which were fairly consistent but which deviated considerably from the actual peroxide content. Therefore, no absolute quantitative values for peroxide content in the Δ-3-carene were reported based on this method. The peroxide analysis of the Δ-3 treated with ferrous ammonium sulfate showed no significant decrease in the peroxide content when compared to

untreated feed. However, after treatment of the Δ -3 with the $Na_2S_2O_4$ -- $NaHSO_3$ solution, the peroxide content appeared to be appreciably reduced. The latter method is a patented technique [62] for removing peroxides from petroleum olefins. The feedstock which was blended with Δ -3-carene that had been air blown (which should have appreciably increased the peroxide content) showed a definite increase in peroxide content when compared to the untreated feedstock.

Overall, the results seem to indicate that an equilibrium relationship was reached for the amount of poison (water, peroxides, or both) adsorbed on the catalyst surface when untreated feedstock was used. When a feedstock was tried that had no moisture in it or that had a low peroxide content, the equilibrium was apparently disturbed resulting in a temporary increase in the conversion and at the same time a temporary decrease in the carane yield. When the feedstock that had a higher peroxide content was tried, the conversion dropped to a lower level while the yield increased.

All of the information obtained on the catalyst deactivation indicates strongly that the poison is coming from the autoxidized materials in the Δ -3-carene. Whether the poison is water, peroxides, or both could not be determined. The poison reduces the activity of the catalyst probably because it is more strongly adsorbed on the nickel surface than the hydrocarbon and tends to gradually cover the surface of the catalyst during a run. This decreases the amount of surface which can adsorb the Δ -3-carene

and hydrogen molecules and therefore reduces the reaction rate. The results from the previous runs also showed that the selectivity of the catalyst for producing carane was increased during the first 20 hours or so in a run and then lined out at a constant level even though the activity of the catalyst continued to decrease throughout a run.

Comparison of the Rhodium and Nickel Catalysts: In order to be satisfied that the correct choice of catalysts had been made, a run was made in the fixed-bed reactor using the Englehard .5% rhodium on alumina catalyst. The run was made at 75°C and 1000 psig with a space velocity of .15 hr^{-1} and a hydrogen rate of 94 SCF/gal. Δ-3. The Δ-3-carene feedstock was untreated. The results of this run are compared to the results obtained with the Harshaw Ni-0104T nickel catalyst at about the same conditions in Figures 20 and 21. It can be seen in Figure 20 that for the first half of the run the rhodium catalyst appeared to be less active than the nickel catalyst; but after 93 hours on stream and for no apparent reason the activity of the rhodium catalyst suddenly increased. The conversion had started at about 97% with both catalysts but it had decreased more rapidly with the rhodium catalyst, being about 66% after 93 hours compared to 79% with the nickel catalyst. At this time, however, the conversion in the run with the rhodium catalyst increased suddenly to 83%. After this quirk, the catalyst deactivated at a normal rate to give a conversion of about 70% after 160 hours on stream compared to the final conversion of 73% obtained with nickel catalyst.

The only change that was made in the run with the rhodium catalyst at about the time of the sudden increase in activity was that additional Δ -3-carene had been placed in the feed reservoir. The research notes indicated that the additional Δ -3-carene was taken from the same storage container of feedstock that had been used throughout the run so it should not have been different, but, of course, it is always possible that some contaminant had been picked up which enhanced the rhodium.

The selectivity of the catalysts are compared in Figure 21 which shows the carane yields obtained. It can be seen that the nickel catalyst gave a higher yield of carane throughout the run, lining out at about 87%. The yield with the rhodium catalyst was about 75% before the sudden change which increased it to about 80%.

Procedure for Obtaining the Effects of Operating Variables: One of the primary objectives of the research was to obtain the basic trends of the important operating variables for each reaction. For the hydrogenation reaction the operating variables which had been studied were temperature, pressure, liquid hourly space velocity and hydrogen rate. To obtain the trends for the effects of these variables on the conversion of the Δ -3-carene and the yield of carane, the catalyst activity had to be accounted for. Two different methods for taking account of the catalyst deactivation during a run were tried.

The first method was based on obtaining the data at certain fixed times in the life of the catalyst after a run had been started. Two variables were to be investigated during a run, one in the first half and the other in the second half, obtaining one data point for a certain value of each variable during the run. If five data points were desired for each of the two variables, five runs would be required. A set of base conditions was chosen so that when one variable was being investigated the other three could be kept constant at the base conditions. The variables to be studied together were chosen arbitrarily; pressure and space velocity data would be obtained together in the same run and temperature and hydrogen rate data would be obtained in the same run. Thus the pressure and temperature effects would be obtained at one point in the catalyst life while the space velocity and hydrogen rate effects would be obtained at another. This method, then, would give only data relative to the catalyst activity at the time it was obtained. In other words, one would not be able to take these effects and determine for a certain set of operating conditions what the absolute conversion of Δ-3-carene and the yield of carane would be. The Δ-3-carene for all of the runs carried out using this method was not pre-treated in any manner.

In the first try at using this method each run was designed so that the data for the first variable would be obtained over the period of 36-44 hours after start-up (from an accumulative product sample) while data for the second variable would be obtained over the period 64-72 hours. A run was started at the value of the variable desired and carried out until the

eight-hour accumulative sample had been obtained for the data point. At this time the reactor was shut down for four hours, new hydrogen flow rate settings obtained, and the run re-started at the base conditions. The operating conditions were changed for the second variable 60 hours after start-up and four hours allowed for lineout before the accumulative sample for the second variable was started. The results of the runs carried out in this first attempt at obtaining the effects of the operating variables are given in Table VIII for runs 24 through 34. The initial catalyst activity was so inconsistent in these runs that no satisfactory correlations could be obtained. Only the pressure and space velocity data were investigated in this first attempt. The effects on the yield of carane were fairly consistent but the conversion data was very bad.

It was felt that the problem of the inconsistent effects on conversion may have resulted from a variation in the degree of oxidation of the catalyst in the storage container from top to bottom. The catalyst had been stored under nitrogen just prior to and during these runs but it had not been mixed up thoroughly before starting the runs. The activity of the catalyst taken from the lower parts of the container appeared to be appreciably greater. Therefore, the remaining catalyst was mixed up very thoroughly and another series of runs were started. Each time catalyst was removed for a run the container was repurged with nitrogen.

The runs made in this second attempt at obtaining the data using the first method were carried out in the same manner as in the first try except

that each run was shortened. Data for the first variable was obtained 16-20 hours after start-up and the data for the second variable was obtained 40-44 hours after start-up. Again no satisfactory correlations for the effects of the operating variables could be obtained because of apparent differences in initial catalyst activity again and because of inconsistent deactivation rates for various runs. The results for this series of runs (CH-35 through CH-44) are given in Table VIII. The problem of the inconsistencies in the reactions is illustrated in Figure 22 for the effect of pressure on the conversion of Δ-3-carene. Since the catalyst for each of these runs should have been the same, it was felt that the catalyst poison, presumably in the Δ-3-carene, was affecting both the initial catalyst activity and the rate of deactivation. Delta-3-carene feedstock from different distillation batches was used for these runs and the amount of poison in the Δ-3 may have varied from batch to batch.

In the second method that was used (which was successful) the effects of the operating variables on the conversion of Δ-3-carene and the yield of carane were established in two runs. The second of these runs was made only to verify the results of the first. These runs were carried out continuously over a 200-hour period varying the operating conditions during the course of the run. Data on the effect of pressure was obtained first, followed by the effect of temperature, then the effect of the hydrogen rate and lastly, the effect of the liquid hourly space velocity. Only one variable was changed at a time with the others being held constant at a set of base conditions. These base conditions were as follows:

Temperature	-----	70°C
Pressure	-----	1000 psig
LHSV	-----	.20 hr^{-1}
H_2	-----	94 SCF/gal. Δ-3

The data were obtained over a 12-16 hour period during the day and the reactor returned to the base conditions for the night. When the value of a variable was changed to get a data point, four hours were allowed for lineout* and then a two-hour accumulative sample of product was obtained at the desired conditions. Point samples were taken every two hours during the day, also.

Enough Δ-3-carene for the two runs was obtained and was treated for peroxides. The Δ-3 was mixed for three hours at 25°C with an aqueous solution of five percent sodium hydrosulfite and five percent sodium bisulfite. Eleven volumes of Δ-3 were treated with one volume of the aqueous solution. Approximate analysis showed the peroxide content to be significantly decreased. A chromatogram of the Δ-3-carene feedstock is given in Figure 47.

Enough catalyst for the two runs had been mixed thoroughly together. When the catalyst for the first run was taken out of the container, the remainder was stored under a nitrogen atmosphere until it was used in the second run.

*Six hours lineout were allowed for space velocity data at .05 hr^{-1}.

A run was started at the base conditions and the reactor operated for 24 hours. The first accumulative sample was then obtained. The pressure was changed to 750 psig, the reactor run for four hours at the new pressure, and then another two-hour accumulative sample obtained. The pressure was changed again to 500 psig, four hours lineout allowed, and another accumulative sample obtained. In this manner data on the pressure were obtained and in turn, data on the other variables were obtained as the run progressed. The range of operating conditions investigated for each variable was as follows:

Temperature	-----	50-80°C
Pressure	-----	0-1000 psig
LHSV	-----	.05 - .50 hr^{-1}
H_2 Rate	-----	38-376 SCF/gal. Δ -3

The experimental data for these two runs (CH-46 and CH-47) are given in Table VIII. The changes in the conversion and the yield during each run are given in Figures 23 to 26. These graphs each show four things. First, the actual path of the reaction is shown by the solid black curve. The solid data points indicate the conversion or yield obtained at the base conditions. The open data points indicate the conversion or yield obtained with one variable at some value other than the base conditions. Second, the dashed curve follows the data points obtained at the base conditions and shows the decline in catalyst activity throughout a run (Figures 23 and 25) and the changes in the selectivity of the catalyst (Figures 24 and 26). Thus, the dashed curve provided a means of evaluating the change in the catalyst over the time period data for a variable

was obtained so that corrections could be made accordingly. This allowed all the data for one variable to be placed on the same level of catalyst activity. Third, the graphs show horizontal lines extending out over the time period for which each variable was investigated. These horizontal lines provided the basis for making the corrections in the results obtained for a variable caused by changes in the catalyst over the time period it was studied. This was done by determining the difference in conversion or yield between the dashed curve and the horizontal line at the time an accumulated sample for one of the variables was obtained. If the horizontal line was above the dashed curve the correction was added and if it was below the dashed curve the correction was subtracted. This technique for accounting for the changes in the catalyst during a run put each of the four variables on a different basis and made the values of the conversion and yields obtained relative to the activity and selectivity of the catalyst at a particular time in the run. Fourth, the graphs show the particular value of the variable being investigated at the time each accumulative sample was taken.

The results for the effects of the operating variables on the conversion of Δ-3-carene and the yield of carane are given in Tables IX and X along with the corrections for changes in the catalyst during each run. The basic trends for these variables are given in Figures 27 to 35.

Effect of Pressure: The effect of pressure on the conversion of Δ-3 is shown in Figure 27. It can be seen that as the pressure was increased from atmospheric to about 500 psig there was a fairly rapid increase in the conversion. After a pressure of 500 psig was reached the conversion appeared to level off and perhaps even declined a little as the pressure approached 1000 psig, although there was no conclusive evidence for this effect. The difference in the absolute values of conversion is evident between the two runs even though operating conditions, catalyst and feedstock were the same for the two runs. The difference is attributed to changes occurring in the Δ-3-carene feedstock in its storage container over the time period between the first and second runs. Figure 28 shows the effect of pressure on the carane yield. As the pressure was increased from atmospheric to 1000 psig, the yield of carane increased steadily. In these two runs, though the activity of the catalyst was different, the selectivity was about the same. The yield increased from about 10% at atmospheric pressure (0 psig) to about 60% at 1000 psig.

The conversion of Δ-3-carene is directly related to the reaction rate. Since pressure affects the hydrogen concentration in the reactor it is also tied to the reaction rate, assuming, of course, that the rate is dependent upon the hydrogen concentration, which is logical. Therefore, when the pressure is increased causing an increase in the hydrogen concentration (in moles/volume, for example) the reaction rate should be expected to speed up.

The yield of carane was also found to increase when the pressure was increased up to 1000 psig. A chromatogram of hydrogenation product obtained at 1000 psig is given in Figure 48. This same effect was observed by Cocker et al [16] in their investigations of the catalytic hydrogenation of Δ -3-carene. Using a platinised charcoal catalyst at 20°C and 100 atmospheres pressure the hydrogenation of (+) Δ -3-carene in ethanol gave (-) cis-carane as the principal product. On the other hand, when the hydrogenation was carried out at 20°C and 1 atmosphere pressure using a pallidized charcoal catalyst, the product contained about equal amounts of (-) cis-carane and 1,1,4-trimethylcyloheptane. A chromatogram of reactor product obtained at 0 psig is given in Figure 49.

Unlike the conversion, the yield was found to increase continually as the pressure was increased to 1000 psig. However, pressures from 1000 to 1500 psig were found earlier (Run CH-18) not to have any appreciable effect on the reaction, so the yield probably starts to level off at pressures over 1000. This difference in the effects of pressure on the conversion and yield can be explained in terms of a possible mechanism for the hydrogenation reaction given in Figure 29. The mechanism is shown as a series-parallel type. The Δ -3-carene can either hydrogenate to form a relatively stable, saturated molecule (carane) or it can undergo ring fission and then hydrogenate to form 1,1,4-trimethylcyloheptane. Now, when the pressure is increased giving a higher concentration of hydrogen, the first reaction should speed up, resulting in a higher yield of carane. The total conversion of Δ -3-carene is a function of the rates of both of

the competing reactions. One possible reason why the total reaction rate levels off after a pressure of 500 psig is reached would be that while the first reaction is speeding up, the second reaction is being retarded so that the net effect is to keep the total rate of conversion at about the same level.

Effect of Temperature: The effect of temperature on the conversion is shown in Figure 30. The figure shows that the conversion increased as the temperature was increased, which was to be expected. As the temperature was raised from 50 to 81°C the conversion was increased from about 70% to 85-90%. Again the difference in catalyst activity between runs is apparent. Also, as expected, increasing the temperature had an adverse effect on the yield of carane, as shown in Figure 31. For these two runs as the temperature was changed from 50 to 80°C the yield declined from about 60% to 45%. Keep in mind, now, that these conversions and yields are not necessarily what would be obtained in any run at these conditions but that the absolute values are very dependent upon the catalyst activity which is influenced by exposure to air and by some contaminant in the Δ^3-carene feedstock, which is strongly suspected to be peroxides.

The temperature effects are exactly what was expected. The higher temperature should increase the reaction rate of both competing reactions but it should, at the same time, favor the second reaction because of the relative thermal sensitivity of the strained cyclopropane ring. Cocker and his associates found essentially the same effect, also. When they

hydrogenated Δ-3-carene in propionic acid at 96°C using palladized charcoal, 1,1,4-trimethylcycloheptane was the exclusive product. The reaction did not go in the propionic acid at this temperature, however, when the catalyst was not present.

Effect of Hydrogen Rate: As can be seen in Figures 32 and 33, the flow rate of hydrogen through the reactor had very little influence on the reaction. The hydrogen rate was varied over a range from about 40 SCF/gal. Δ-3 feed to nearly 400 SCF/gal. Δ-3. There was some indication of a slight decrease in the yield of carane at the lower flow rates, however.

The hydrogen rate gives primarily a measure of the velocity of the gas through the reactor and really has very little effect on the relative concentration of hydrogen to Δ-3-carene within the reactor. It probably affects to a small degree, also, the retention time of the Δ-3-carene in the reactor, tending to sweep part of the liquid out faster or vaporize more at the high hydrogen rates.

Effect of Space Velocity: The effect of space velocity on the conversion is shown in Figure 34. It can be seen that as the space velocity was increased, the conversion dropped off considerably, which was expected. For Run CH-46 the conversion dropped from 94% at a LHSV of 0.5 hr^{-1} to about 40% at .50 hr^{-1}. For Run CH-47 the conversion was a little lower, being 80% at .05 hr^{-1}, but it declined to 40% at .50 hr^{-1}, also. Figure 35 shows that the yield of carane decreased as the space velocity was increased. These results also indicated that lowering the space

velocity below about .10 hr^{-1} did not produce any appreciable increase in the yield. This effect was also noticed in the results of prior runs, specifically in Runs CH-35 through -39. In Figure 35 the yield can be seen to be a little over 60% when the space velocity was at .10 hr^{-1} or less but decreased to about 40-45% as the space velocity was increased up to .50 hr^{-1}.

The space velocity is usually just a measure of the retention time in the reactor but for this case the amount of liquid reactant passing through the reactor also affects the liquid loading on the surface of the catalyst. This assumes, of course, that the liquid trickles over the surface of the catalyst in a thin layer and that the bed void volume is filled for the most part with the gas phase. Thus, the drop in conversion when the space velocity was increased can probably be attributed to two factors -- the decrease in retention time of the liquid reactant and the extra liquid loading on the catalyst, slowing down both the hydrogen and Δ-3-carene diffusion rates to the catalyst surface. The second factor could also account for the drop in the yield of carane which would occur with a decrease in hydrogen concentration at the catalyst surface.

Runs Giving High Carane Production: The results of the research on the continuous hydrogenation of Δ-3-carene in the fixed-bed reactor using the Harshaw Ni-0104T catalyst have shown that the production of carane is very dependent upon an intricate balance among the operating conditions, the catalyst activity, and the nature of the Δ-3-carene with respect to

trace amounts of certain materials contained in it. On many occasions when the reaction was being investigated, the correct balance was achieved by chance and high percentages of carane were obtained in the product. Figures 36 and 37 show the results of two such occasions. These results were actually obtained during the first attempts at gathering data on the effects of the operating conditions on the conversion and yield. The runs were actually detrimental to those attempts because of the high conversions and yields which were obtained. In Run CH-31 (Figure 36) the reactor was operated at 1000 psig and 75°C with a LHSV of .14-.16 hr^{-1} and a H_2 rate of 94 SCF/gal. Δ -3 for the first 60 hours; for the remainder of the run the space velocity was changed to .07 hr^{-1} and the H_2 rate to 376. The results show 100% conversion of Δ -3 throughout the run with yield of about 90%. The yield dropped slightly after the reactor had been shut down from 44-48 hours but it came back up after restarting. Run CH-32, shown in Figure 37, gave even better results. This run was started at 750 psig, 75°C, a LHSV = .16 hr^{-1} and an H_2 rate of 94 SCF/gal. Δ -3. After 48 hours the pressure was increased to 1000 psig and after 60 hours the space velocity was increased to .19 hr^{-1} and the H_2 rate increased to 376 SCF/gal. Δ -3. The conversion in this run was 100% throughout; the yield was about 92% at the start and increased to 95% when the pressure was increased. No deactivation of the catalyst with its resulting decrease in conversion occurred.

The proof is available here that the reaction can be carried out in a continuous manner in a fixed-bed catalytic reactor to obtain a carane

product of at least 90% purity. This still leaves room for improvement, however, especially in view of the difficulty there is in trying to purify the product further by an operation such as distillation, which is discussed next.

Distillation of the Carane Product: The distillation of some of the hydrogenated products was attempted mainly to determine the feasibility of separating unreacted Δ-3-carene from the product for recycle purposes. If this could have been done easily the reaction could have been carried out at conditions which favored the carane yield but did not give a complete reaction of the Δ-3-carene. The boiling points of carane and 1,1,4-trimethylcycloheptane were found to be nearly the same (160°--161°/623 mm Hg) while Δ-3-carene was found to boil a little higher 163°--164°/623 mm Hg). The relative boiling points of similar type materials can usually be estimated also from their retention times in the chromatograph. On this basis it appeared that the 1,1,4-trimethylcycloheptane would have a slightly lower boiling point than carane. Figure 38 shows the distillation curves for a typical experiment using a batch steam distillation with a column having about 75 theoretical plates at a reflux ratio of 30:1. A steam distillation was used to keep the temperature down ($\approx$ 94°C) to prevent decomposition. It can be seen that the 1,1,4-trimethylcycloheptane did have a slightly higher volatility at this temperature than the carane but that the separation between these two components was very poor at these conditions. However, the separation between carane and Δ-3-carene appeared to be fairly good. A better separation

of the Δ-3-carene could probably be achieved with more theoretical plates and higher reflux ratios. However, it appears that the two products could not be feasibly separated by a steam distillation. Other methods of separating close boiling isomers such as azeotropic distillation or crystallization might be applied successfully to carane and 1,1,4-trimethylcycloheptane.

B. Hydrobromination Investigations

Hydrobromination of 1-methylcyclohexene: The hydrobromination of 1-methylcyclohexene was briefly investigated as an analogous reaction to the hydrobromination of carane since both can, in theory at least, give secondary and tertiary bromides. The analogy is not exact, however, because carane is not an olefin. Four experiments were made in various diluents with temperatures varying from 12-100°C and with free radical initiators and a free radical inhibitor. The results of these four experiments are given in Table XI. The hydrogen bromide feed rate was too low during Runs HB-13 and HB-14, so the conversions in these two runs are probably low.

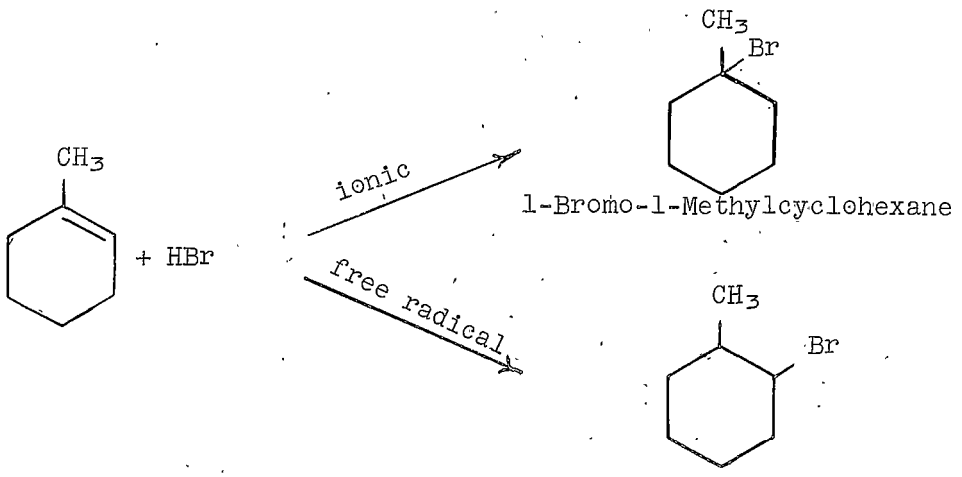
A maximum yield* of 77% of the secondary bromide, 1-bromo-2-methylcyclohexane, was obtained in these experiments using n-hexane as a diluent and benzoyl peroxide as a free radical initiator. The reaction was carried out at 55-60°C for five hours. The conversion obtained was

*The olefin could form two bromides. The yield of a particular bromide is the fraction of the total olefin that reacts which formed that bromide. Conversion is the total fraction of olefin reacting.

only 15%. When the free radical mechanism was retarded by using diphenylamine in an acetic acid medium, the yield of secondary bromide was decreased to 11%. At a temperature of 100°C with an acetic acid medium, no secondary bromide was obtained at all, even with benzoyl peroxide present. When cyclohexane was used as the diluent at 65-72°C with benzoyl peroxide present, the yield of secondary bromide was 45% with a conversion of 31%, the highest conversion obtained in these four experiments. In a preliminary run, however, a conversion of about 80% was achieved but no resolution of tertiary and secondary bromides could be obtained with the chromatograph column (Ucon Polar) being used at that time, so yields were not determined. This run was made with no diluent present, at 35°C for three hours.

In addition to 1-methylcyclohexene, 2,4,4-trimethylpentene-2 was also investigated. No resolution of the tertiary and secondary bromide products from this olefin could be obtained so the results were inconclusive. Several chromatograph columns were tried including the Apiezon N column which easily separated the secondary and tertiary bromides from 1-methylcyclohexene, but no separation could be made. The maximum olefin conversion obtained was 80% after seven hours at 34°C. The total yield of bromide product was 50%. Pentane was used as a diluent in this reaction.

The hydrobromination reactions with 1-methylcyclohexene are shown below:



About the same results were found by Goering et al [63] in their investigations with 1-methylcyclohexene. The secondary bromide was formed when organic peroxides were used while mainly the tertiary bromide was formed when diphenylamine was used. Apparently the diphenylamine inhibits free radical production arising from trace amounts of oxygen present in the system so that the ionic mechanism predominates. Goering also found that temperatures over about 35°C tend to favor the yield of the secondary bromide.

The results with both the 1-methylcyclohexene and the 2,4,4-trimethylpentene-2 indicated that the reaction does not proceed at a very fast rate. Goering and his co-workers also found that the reaction rate was relatively slow, obtaining a maximum conversion of 89% after four hours at 35°C. They attributed the slow rate to the low concentration of HBr gas in the liquid system.

The investigation of the reaction with 1-methylcyclohexene verified that Markovnikov's rule of HBr addition could be reversed by the use of organic peroxides which are believed to induce a free radical mechanism. However, the question of how the reaction would proceed when carane was used could not be exactly answered since it was not known how closely the cyclopropane ring would parallel the olefin reaction.

Products from the Hydrobromination of Carane: The individual components in the product mixture of terpinyl bromides obtained from cis-carane were not isolated for separate identification. The products were identified only in an indirect manner from the alcohols which were obtained from them. From these considerations the bromide product was felt to be composed mainly of cis- and trans-8-bromo-p-menthane and cis- and trans-8-bromo-m-menthane, which are tertiary bromides. If any secondary bromides were formed, they only occurred in minor amounts.

The mixture of bromides was found to be a colorless liquid with very little characteristic odor. The bromides degraded to a dark reddish brown color upon exposure to light or heat. The properties of the mixture were found to be as follows: b.p. 64-65°/3 mm Hg, d_{25}^{25} = 1.165-1.179, and n_D^{25} = 1.4884. The bromides were found to be quite unstable decomposing to olefins nearly completely at temperatures of about 150-175°C. Borowiecki et al [58] reports the properties of 8-bromo-p-menthane to be as follows: b.p. 65-66°/3 mm Hg, d_4^{20} = 1.1617, n_D^{20} = 1.4887 and $[\alpha]_D^{20}$ = 0°.

It is doubtful, however, that their 8-bromo-p-menthane was geometrically pure or free of the meta isomer.

The bromide product was considered to have major amounts of trans-8-bromo-m-menthane and cis-8-bromo-p-menthane and lesser amounts of cis-8-bromo-m-menthane and trans-8-bromo-p-menthane. The cis-trans isomerization undoubtedly was promoted by the presence of the acidic hydrogen bromide [50].

Dehydrobromination of the Terpinyl Bromides: The formation of olefins from the terpinyl bromides by elimination of hydrogen bromide was investigated as a possible means of analysis. No direct gas chromatographic analysis of the bromides could be made because of their thermal unstability.

Each terpinyl bromide should theoretically eliminate hydrogen bromide to form olefins in accordance with 1) Saytzeff's rule [50] and 2) the cis-trans orientation between the bromine atom and the hydrogen atoms on adjacent carbon atoms. The theoretical elimination reactions of several terpinyl bromides are given in Figure 39. Isomenthyl bromide with only one hydrogen atom in a trans-position to the bromine should follow the trans-orientation rule to form predominantly 2-p-menthene [64]. On the other hand, neoisomenthyl bromide, with two hydrogen atoms trans-oriented with respect to the bromine should follow Saytzeff's rule to give mostly 3-p-menthene. Cis-8-bromo-p-menthane would be expected to eliminate HBr to give mostly 4(8)-p-menthene with lesser amounts of cis-

8-p-menthene. However, the reaction is complicated because the 4(8)-p-menthene has a strained olefinic bond [65] making it less stable than the 8-p-menthene. Because of the unstability factor more 8-p-menthene might be produced than would be predicted by normal rules of elimination.

The results of three experiments on the dehydrobromination of the terpinyl bromides are given in Table XII. It can be seen that the product composition was strongly dependent upon the type of reaction used. Gas chromatographic analysis in three columns (20' $\beta\beta$'-oxydipropylnitrile, 10' Carbowax 20M and 10' PDEAS) indicated only four major components as shown in Figure 50. However, the infrared spectra of each of the components in the mix showed the presence of impurities in all except the 4(8)-p-menthene (Figures 58 to 61). The olefins obtained as by-products from the saponification of individual esters (discussed later) also indicated that the meta and para isomers could not be resolved except for 4(8)-m-menthene and 4(8)-p-menthene. Therefore, the results of the elimination reactions are reported in terms of mixtures of the meta and para isomers. The results show only small differences between the reactions in KOH at 75°C and NaOH at 150°C. However, at 125°C in NaOH, isomerization appeared to occur much more, with the amount of the 3-p-menthene and 3-m-menthene increasing from 34-40% to about 60%. The isomerization occurred in the expected direction [64] but it seems odd that it happened more so at 125°C in the caustic and not at 150°C. However, it is obvious that isomerization was occurring during all three reactions since 3-p-menthene and 3-m-menthene would not be produced directly

from the elimination of 8-bromo-p-menthane and 8-bromo-m-menthane, respectively.

Since the composition of the bromide mixture could not be determined with any accuracy from the olefins produced by elimination, the dehydrobromination investigations were discontinued.

Hydrobromination Reaction with Carane: The hydrobromination of carane was carried out as a semi-batch reaction. The carane, in a liquid state, was contacted with the gaseous hydrogen bromide by dispersing the HBr into the liquid through a fritted glass gas bubbler tube. The reaction was found to proceed nearly as fast as the HBr could be fed to the reactor. The reaction was also found to be highly exothermic, most likely a result of the energy released as the cyclopropane ring of the carane molecule was fissioned. The reaction was investigated using organic peroxides to promote the free radical mechanism and a free radical inhibitor to promote the ionic mechanism. The distribution of bromides in the product was determined indirectly from the corresponding esters which were obtained by reaction with silver acetate in glacial acetic acid. It would be well to keep in mind when examining the results that the relative amounts of cis and trans isomers reported could have been influenced when the bromides were esterified.

The conversion of carane was determined from the amount of unreacted carane in the reaction mixture. The unreacted carane was separated from the bromides along with the inert hydrocarbons by vacuum distillation.

In some cases the conversion had to be estimated because of the presence of olefins. Carane could not be resolved from 3-p-menthene in the gas chromatograph.

Effect of Temperature: The effect of temperature on the reaction was investigated over a range from about 5°C to 100°C. The results are given in Table XIII. The temperature was found to have essentially no effect on the reaction rate with conversions of 95% or greater being obtained in the four experiments. This effect is not particularly surprising since Goering et al [63] in their investigations with 1-methylcyclohexene found that the reaction went as well at 0°C as it did at 65°C. The lower temperature probably increases the solubility of the HBr in the reaction mixture providing a slightly greater concentration which might tend to offset any decline in reaction rate at the lower temperature.

The results seem to indicate also that the higher temperatures favored the formation of the meta isomer. The amount of trans-8-bromo-m-menthane in the product increased from 44% to about 58% as the temperature was increased from 35°C to 100°C. There did not seem to be any appreciable effect on the product distribution between 5°C and 35°C. The effect of temperature on meta isomer formation is shown in Figure 40.

The isomerization of the cis and trans isomers appeared not to be affected by temperature.

These four experiments were carried out with a constant initial carane concentration, a constant HBr feed rate and a constant reaction time. Benzoyl peroxide was used in the experiments to try to induce the free radical mechanism. The temperature apparently had no influence on the reaction mechanism, i.e., ionic or free radical, since no secondary bromides were obtained.

Effect of Initial Carane Concentration: The results for the investigation of the effect of initial carane concentration on the conversion of carane and the distribution of the bromides in the product are given in Table XIV. The carane concentration was varied over a range from .30 g-moles/liter to 1.60 g-moles/liter. The reaction time and HBr feed rate were held constant and the temperature was kept at about 28-37°C for the four experiments. Benzoyl peroxide was used as a free radical initiator. The conversion (a measure of reaction rate) was found to increase from about 60% when the concentration was .30 g-moles/liter to about 95% when the concentration was 1.60 g-moles/liter. The reaction rate is dependent upon reactant concentration so a decrease in the rate would be expected at the lower carane concentrations. The HBr concentration was presumably lowered also at the lower carane concentrations since additional diluent was used to decrease the concentration rather than decreasing the amount of carane charged initially. Figure 41 illustrates the effect of concentration on the conversion. The reactant concentration apparently had no effect on the distribution of the meta and para isomers.

Effect of Various Additives: Various additives were investigated to determine if a free radical mechanism could be induced to reverse Markovnikov's rule of addition. Benzoyl peroxide, lauroyl peroxide, and cumene hydroperoxide were investigated for this effect. In addition, the effects of ultra-violet radiation and diphenylamine were investigated. One run was made using no additive, also. The reaction was carried out with the HBr feed rate, the initial carane concentration, and the temperature essentially held constant. The results of these experiments are given in Table XV. It is apparent that neither the presence nor the nature of the additives had an effect on the conversion of carane which was 95% or greater in all the experiments.

There were no secondary bromides obtained when the peroxides were used, so it appears very likely that the cyclopropane ring of carane, when under a free radical attack by $Br^{\cdot}$ (if it occurred), does not react like an olefin to allow the abnormal addition violating Markovnikov's rule. This is discussed in more detail in the next section.

Hydrobromination Reaction Mechanism: The results of the hydrobromination investigation have shown that the free radical mechanism failed to work with the carane molecule. No good reason can be given for why the cyclopropane ring would not react in an analogous manner to an olefin. Apparently, the ionic mechanism was favored regardless of the presence of the free radicals. The question could be raised that possibly the organic peroxides did not function properly to form the

free radicals necessary for secondary addition. The answer to this, of course, is that the reaction with carane was carried out in an identical manner to the reaction with 1-methylcyclohexene for which secondary addition occurred. There is always the possibility, however, that the carane reactant contained some contaminant which may have inhibited free radical formation. It is difficult for the author to understand why secondary bromides were not obtained since the theoretical considerations on the reaction seemed very sound.

The reaction as it most likely occurred is shown in Figure 42. The fissioning of the cyclopropane ring to form the meta and para isomers obviously must proceed as a parallel reaction. An ionic reaction mechanism must have predominated with carane in order to get almost exclusive tertiary addition. This is the mechanism shown. The cyclopropane ring fissions to cis-orientation under attack by a hydrogen ion to form the most stable tertiary carbonium ion which is on the #8 carbon atom. The bromine ion then rapidly reacts to form the tertiary bromide. The isomerization of the cis to the trans isomers probably started with the cis-carane before it had reacted with HBr and continued after ring fissioning and addition had taken place.

C. Esterification Investigations

Esterification of Cyclohexyl Bromide: The esterification of cyclohexyl bromide was studied as an analogous reaction to the esterification of the terpinyl bromides. The cyclohexyl bromide and reaction products were all easily analyzed in the gas chromatograph with good

separations of cyclohexyl bromide and cyclohexyl acetate achieved in a six-foot Carbowax 4000 column. The reaction was investigated using sodium acetate, potassium acetate and silver acetate in ethanol and acetic acid mediums. The results are given in Table XVI.

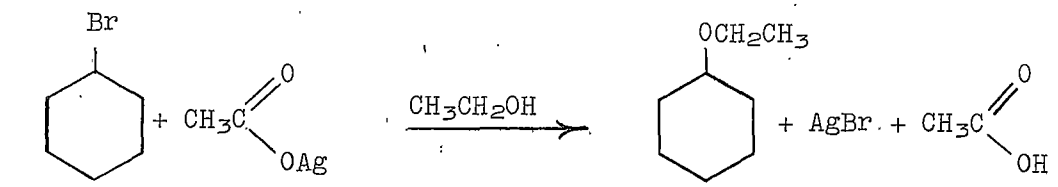
The sodium and potassium salts were found in general to be rather unreactive. A maximum bromide conversion of 48% was obtained with potassium acetate in a 10% aqueous acetic acid medium after 10 hours with the temperature ranging from 30 to 90°C; however, the ester yield* was only five percent. The maximum ester yield obtained with potassium acetate was 25% at 110°C after five hours in a glacial acetic acid medium while the bromide conversion was 15%.

When the silver acetate was used, conversions of 100% were obtained in several of the experiments. A maximum ester yield of 55% was obtained at 95°C after about two hours using a glacial acetic acid medium. The corresponding bromide conversion was 100%. Commercial silver acetate (Baker) was used in this experiment. When silver acetate which had been synthesized in the chemical engineering laboratory was used, the yields

*The bromide could react to form both an ester and an olefin. The ester yield is defined as the fraction of the total amount of bromide which reacted and formed ester. The conversion is the fraction of the bromide which reacted forming both ester and olefin.

were considerably lower, perhaps because of the assumed lower purity of the acetate salt. Lower yields also occurred when an absolute ethanol medium was used, the maximum being 25% after one hour at 74°C.

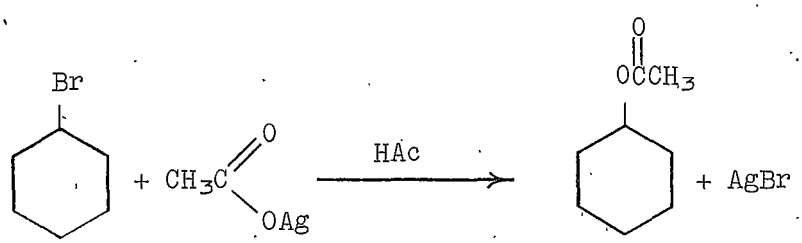
It is believed that an ether product was formed when ethanol was used. The probable reaction is shown below:



Cyclohexyl Bromide

Cyclohexyl-ethyl ether

The reaction in acetic acid occurred in the desired manner as follows:



Cyclohexyl acetate

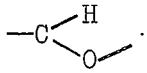
Ethanol is the medium suggested by Finar [50] but no mention is made of ether formation. The suspected ether product was never verified, however.

Products from the Esterification of the Terpinyl Bromides: The four esters obtained from the esterification of the terpinyl bromides were identified from the corresponding alcohols. These esters were cis- and trans-8-m-menthyl acetate and cis- and trans-8-p-menthyl acetate. Small quantities of the esters were isolated from the chromatograph in order to obtain their infrared spectra and NMR spectra. However, no positive identifications of these esters could be made directly because no spectral information was available on the known esters. Two of the esters were isolated in a fairly pure state. These two are trans-8-m-menthyl acetate and cis-8-p-menthyl acetate. The cis-8-m-menthyl acetate and trans-8-p-menthyl acetate could not be resolved in the chromatograph so they were isolated together as a mixture. The infrared spectra and NMR spectra of these esters are given in Figures 62 and 68, respectively.

The pure esters were found to be colorless liquids with a very characteristic odor. Not enough of the pure esters was obtained to determine any physical properties, however. No physical properties were obtained for the ester product mixture either, since the product contained unreacted bromides.

The esters could be produced only when an acetic acid medium was used. When absolute ethanol was used as the medium, other products were obtained. These materials were never identified but are suspected to be ethers, as mentioned previously.

In addition to the suspected ethers which were obtained in the ethanol medium, three other unidentified by-products occurred, mainly during the esterification of the products from the hydrobromination reaction. These materials were isolated from the ester product mixtures and infrared and NMR spectra obtained for them. The spectra are shown in Figures 63 and 69, respectively.

A chromatogram of an esterified hydrobromination product containing these materials is given in Figure 51. The infrared spectra indicated that two of these products were not esters since they did not have the characteristic strong ester carbonyl band at 1730-1750 cm^{-1}. These were the two major by-products. The minor by-product which occurred between the two major by-products in the GLC showed a -C=O group in its infrared spectrum at 1730-1750 cm^{-1} so there was still the possibility of it being an ester. The NMR spectra of the two major products showed resonance for single hydrogens attached to carbons which were attached to oxygen, like . This occurred at δ = 3.32 - 3.5 (2 doublets, 1 proton each). This indicated that perhaps these materials were epoxides of some sort. A carbon-hydrogen analysis* of these unknowns showed 55.42 wt.% carbon and 8.64 wt.% hydrogen. If the molecule contained only carbon, hydrogen, and oxygen, then the oxygen content would be 35.95 wt.%. The empirical formula works out to be $C_{4.62}H_{8.64}O_{2.25}$. In terms of whole numbers this could be $C_{10}H_{19}O_5$ or perhaps $C_{12}H_{22}O_6$. The oxygen content seems very high and the imagination is defied when one tries to piece together some kind of chemical

*Elek Microanalytical Laboratories, Torrance, California.

structure from $C_{10}H_{18}$ olefins and acetic acid having even multiple epoxide or ether type linkages and one of these empirical formulas. Apparently there was an error in the analysis, the sample was contaminated, or there are other elements present in the structure, perhaps bromine. At any rate, no further attempt was made at identifying these materials. The minor by-product showed no ester methyl protons on the NMR so a lactone structure is suggested for it. No elemental analyses were done on this material.

These by-products occurred in major amounts when olefins and unreacted carane were in the hydrobromination product produced with an organic peroxide present. Very little of these materials occurred when terpinyl bromides which were free of olefins were esterified or when hydrobromination product made with diphenylamine present was esterified (Figure 52). It was also discovered that the esterified hydrobromination products would undergo a reaction to form the unknown materials in the gas chromatograph when the phenyl diethanolamine succinate preparatory column was used. The reaction occurred only when the materials were recycled back through the chromatograph several times with large sample injection volumes (200-300 μl). The temperature of the detector was about 215°C, the column at 170°C and the injector at about 210°C. In these reactions, approximately equivalent amounts of the three by-products were produced.

Esterification Reaction with the Terpinyl Bromides: The terpinyl bromides were esterified in a batchwise manner in a stirred reactor. The reaction appeared to go extremely fast in acetic acid with considerable

exothermic heat liberated. This required that the bromides be added to the slurry of acetic acid and silver acetate rather than mixing everything together at the start. Only small amounts of bromide were used (5-10 ml) so that the reaction temperature could be controlled. Silver acetate was the only salt used (synthesized in this laboratory).

The analysis of the products from the esterification reactions was done in the gas chromatograph. The unreacted bromides decomposed to olefins in the chromatograph so conversion data was impossible to obtain in this manner since olefins were also a by-product in the reaction. The results are, therefore, reported in terms of the amounts of olefin and total ester (including the unknown by-products when they occurred) in the product and the distribution of individual components in the ester.

A chemical method of analysis for total unreacted bromide in the product was investigated but it was found to be unsatisfactory. The method involved a conversion of the organic bromide into sodium bromide by a reaction with sodium ethoxide (sodium metal in absolute ethanol) followed by a volumetric analysis for the bromide using Fajans Method (66,67). The analysis with standard NaBr worked beautifully, but when the organic bromides were used the final end point in the volumetric analysis was impossible to see. Complete conversion of the organic bromides to NaBr could not be achieved and the unreacted bromides degraded to a dark brown color which obscured the salmon colored end point.

The effects of the solvent medium used, temperature, bromide concentration and reaction time were investigated. All of the experimental data and results for the esterification reactions are given in Table XVII.

Effect of the Solvent Medium: As mentioned previously, very little ester could be obtained when absolute ethanol was used. This was attributed to the reaction forming ethers as being predominant. The probable products were terpinyl-ethyl ethers. No attempt was made to verify the structure of these materials, however.

When acetic acid or propionic acid was used none of the suspected ethers occurred.

Effect of Temperature: The temperature was investigated over a range from about 2°C (in propionic acid) to a 112°C, the boiling point of acetic acid at 640 mm Hg. The effect of temperature on the total amount of ester that was obtained was not very clear-cut except that at 112°C the amount was rather low, being only 21%. At the other temperatures, 2°C -70°C, the amount of ester in the product varied from 45-59% with no definite trend apparent. The maximum amount of ester (59%) was obtained at 16-19°C in an acetic acid medium, which was about as low a temperature as could be used with acetic acid since the freezing point is 16-17°C.

The temperature appeared to have no appreciable effect on the distribution of esters. The composition of product from Run E-56 was somewhat different, mainly because of the considerable amount of by-products

present. Runs E-56 and E-55 were the last runs made, so perhaps the bromide reactant had decomposed somewhat so that enough olefins were present to form the unknown by-products.

The bromide concentration was .24-.25 g-moles/liter and the reaction time 15 minutes for these runs except for Run E-28 which was carried out for 60 minutes.

Effect of Initial Bromide Concentration: The initial bromide concentration was investigated over a range from .12 to 1.30 g-moles/liter. In these runs the temperature was kept between 20-30°C with reaction times of 15 or 30 minutes used. Increasing the bromide concentration seemed to have a detrimental effect on the amount of ester in the product as can be seen in Figure 43. The amount of ester in the product decreased from a little less than 60% to about 43% when the initial bromide concentration was increased from about .16 g-moles/liter to 1.3 g-moles/liter. There was no noticeable effect on the ester product distribution.

The high concentrations of bromide were obtained by decreasing the amount of acetic acid used while keeping the initial amount of bromide used constant. At the high concentrations the slurry of silver acetate and acetic acid became rather thick, so perhaps the mixing efficiency was poorer and localized hot spots occurred causing more HBr elimination to take place. It had been found in previous tests that very poor yields of ester were obtained whenever the silver acetate and terpinyl bromides were placed in direct contact without any acetic acid present. The re-

action was found to be instantaneous with considerable heat evolved.

Effect of Reaction Time: The esterification reaction was carried out from two minutes up to 60 minutes with the other variables held constant. The amount of ester in the product after two minutes reaction time was found to be as high as 57% with no appreciable increases for reaction times up to 60 minutes. Undoubtedly the reaction was essentially complete well before two minutes. The observations on the reaction in many experiments indicated that the reaction was instantaneous probably going nearly to completion a few seconds after the bromide had been added to the silver acetate-acetic acid slurry. This was apparent from the immediate increase in temperature as the reactants were mixed. It was mechanically impossible to try to stop the reaction after only a few seconds with the reaction system that was used. However, the reaction could probably have been slowed down by using very cold temperatures, (e.g., that of liquid N_2) if kinetic data had been desired.

Miscellaneous Experiments: In addition to the above effects, the reaction was also investigated with the individual reagents added slowly. The results of these experiments are given in Runs E-34 and E-35, Table XVII. In Run E-34, the bromide was added gradually to the slurry while in Run E-35 the silver acetate was added gradually to a solution of the bromide in acetic acid. In both experiments about 50% ester was obtained with the similar product distributions. In another experiment a 2:1 ratio of silver acetate to bromide was used rather than the usual 10%

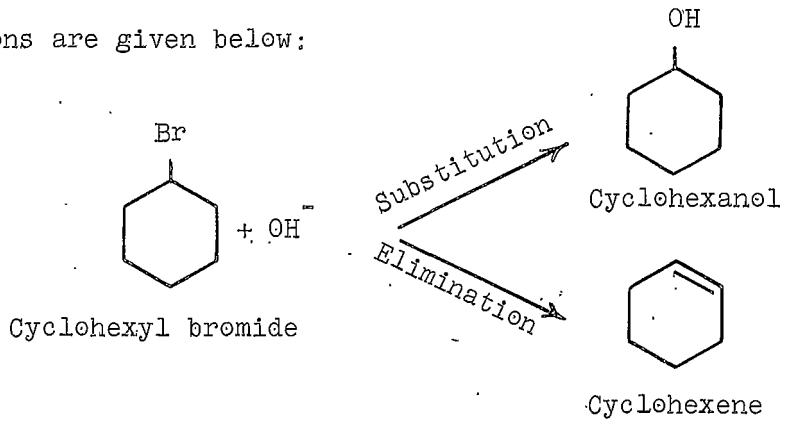
excess. The results of this experiment are given in Run E-37 and can be compared to the results of an equivalent run (E-30) in which only a 10% excess of silver acetate was used. The results in both cases showed about 55% ester with about the same product distributions indicating that a 10% excess of silver acetate was adequate.

Esterification Reaction Mechanism: The esterification of the terpinyl bromides with silver acetate was found to be a very rapid reaction which was accompanied by HBr elimination. These two reactions most likely occur in parallel. The ester yields were reasonably good (up to about 60% ester in the product) when acetic acid or propionic acid was used as the reaction medium. However, an undesirable reaction predominated when absolute ethanol was used as the medium, resulting in the formation of suspected ether products with very little ester produced. The reactions in acetic acid are shown in Figure 44. The substitution reaction most likely takes plane with an S_n^1 mechanism. In this mechanism the bromine actually leaves the molecule forming an intermediate carbonium ion. This carbonium ion then reacts very rapidly with the acetate ion (which is a weak nucleophile) to form the ester. The silver acts as an electrophilic catalyst pulling the bromine off the molecule and speeding up the reaction. If, however, the bromine ion tends to pull a trans-oriented hydrogen ion off the molecule when it leaves, then elimination will occur with the resulting olefin formation. For the reaction with 8-bromo-p-menthane, the two possible olefins would be 4(8)-p-menthene and 8-p-menthene as shown in Figure 44.

D. Hydrolysis Investigations

Hydrolysis of Cyclohexyl Bromide: The direct hydrolysis of the bromides to their corresponding alcohols was originally devised as the last step of the process to convert Δ-3-carene into monoterpene alcohols via the bromides. Since a supply of the terpinyl bromides was not on hand early in the research and also because of the difficulty of analyzing these bromides, cyclohexyl bromide was investigated. The results are given in Table XVIII.

It can be seen that the olefin, cyclohexene, was the major product in nearly all of the experiments rather than the desired product, cyclohexanol. Elimination nearly always accompanies the substitution reactions of secondary and tertiary bromides and in this investigation no conditions could be found to hydrolyze the cyclohexyl bromide directly without the elimination reaction predominating. The two competing parallel reactions are given below:



Six hydrolyzing agents were tried: water, aqueous sodium hydroxide, aqueous sodium carbonate, potassium formate, silver oxide, and a silver oxide-sodium nitrate mixture. No more than a trace of cyclohexanol was

obtained from any of the hydrolyzing agents except the silver oxide-sodium nitrate mixture. In Run OH-16 the cyclohexanol yield was 20% but the bromide conversion was only 20%. Silver oxide along with sodium nitrate was the hydrolyzing agent. The reaction was carried out for 2-1/2 hours at 90°C. In Run OH-25, made with the silver oxide-sodium nitrate mixture, a 34% yield of cyclohexanol was obtained with 100% conversion of the bromide. This run was carried out at 60-90°C for four hours. The sodium nitrate was present in many of the experiments because the silver oxide was produced in the reactor from sodium hydroxide and silver nitrate. When silver oxide was used (Run OH-27) which had been synthesized and water washed before placing it in the reactor, the yield of cyclohexanol was only 2%. The patented methods for hydrolyzing alkyl bromides were found to be essentially ineffective with cyclohexyl bromide.

There are two main reasons why it is difficult to hydrolyze cyclohexyl bromide without appreciable elimination occurring at the same time. First, cyclohexyl bromide is a secondary halide which is prone to eliminate although less so than a tertiary halide [46] and second, the cyclohexyl halides have a higher tendency to eliminate than do acyclic secondary halides [55]. Substitution and elimination reactions, in most cases, are favored by definite mechanisms. The S_n^1 mechanism, in which the bromide ion actually leaves the carbon atom forming an intermediate carbonium ion which, in turn, then reacts with the hydroxyl ion, would promote elimination. The S_n^2 mechanism in which the hydroxyl group attaches itself on the opposite side of the carbon atom from the bromine

group before the bromine completely leaves the carbon atom, would favor substitution. Unfortunately, the tendency to follow an S_n1 mechanism is increased from primary to secondary to tertiary halides. Also, the cyclic ring would strongly hinder the S_n2 mechanism in which the hydroxyl group must attack the carbon on the opposite side of the bromine group which would be on the inner side of the ring.

Hydrolysis of Menthyl Acetate: The hydrolysis of menthyl acetate was investigated primarily because it was the only cyclic terpinyl ester readily available. The esters produced in the laboratory could only be isolated in small quantities and only after a great deal of time. Also, any attempt at investigating the reaction with the ester mixture would have been complicated because of the difficulty in trying to analyze product mixtures containing up to seven components with the gas chromatograph.

Menthyl acetate was investigated even though no secondary esters were produced in order to gain some insight into the reaction conditions needed for the hydrolysis reaction. The reaction conditions used would probably be a little too severe for the tertiary esters which are more susceptible to elimination. The results of the investigation of the hydrolysis of menthyl acetate are given in Table XIX. A chromatogram of reaction product is given in Figure 54.

All except two experiments were carried out in the Parr bomb. These two experiments were conducted in a glass refluxing reactor. Aqueous

sodium hydroxide was the primary hydrolyzing agent used with concentrations varied from .25 to 2.50 g-moles/liter of water. The initial acetate concentration was varied from .13 to 1.08 g-moles/liter of water. The temperature was studied over a range from 95 to 245°C and the reaction time varied from 15 minutes to 28 hours.

The base temperature used for the experiments (190°C) was probably a little too high, pushing the conversion data up into the 90% range for most runs which overshadowed some of the effects of the other variables. However, the saponification of esters is a well known reaction and the effects of the variables could, if necessary, be predicted rather easily.

The reaction rate showed a remarkable increase between 95°C and 120°C. At 95°C the conversion was only 10% after 20 hours but when the temperature was increased to 120°C the conversion was 88% after 13 hours. The menthol yield in both runs was 100%. As the temperature was increased up to 190°C the conversion reached 98% while the yield dropped slightly to 97%, due to some olefin formation. The effect of reaction time was evident but distorted by the high temperature. After one hour, at 190°C, the conversion was 92%, but after two hours it was 96%, after 13 hours it was 98%. The effects of reactant concentration were not evident with conversions being 96-98% for the concentrations used and yields being 95-100%.

Acid-catalyzed hydrolysis was tried once in a glass refluxing reactor. The results are given in Run OH-35. The reaction was carried

out for 28 hours at 95°C in a large excess of water with a few drops of concentrated sulfuric acid as the catalyst. As can be seen, the conversion was only 6%. One saponification reaction was carried out at the same temperature for 20 hours and a 10% conversion was attained. In one run the reaction was stopped after 15 minutes because the temperature got too high (245°C). In this run (OH-56) a conversion of 75% was obtained with a 100% menthol yield. In another run in which the temperature got too high (up to 210°C) a conversion of 98% had been obtained when the reaction was stopped after one hour. The yield of menthol in this run was 94%.

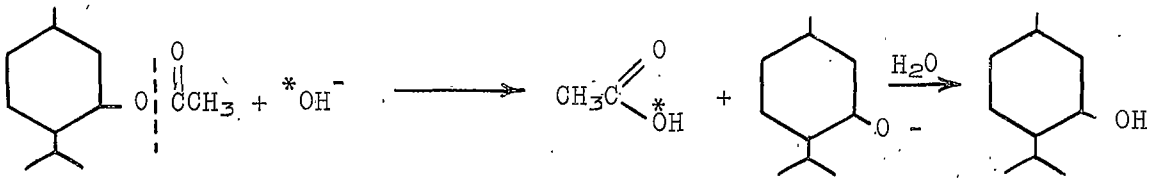
The saponification of esters is well known,* with the reaction proceeding under second order kinetics [50], i.e., the rate is proportional to the concentrations of ester and base raised to the first power (rate $\propto [\text{ester}] \times [\text{OH}]$). The effects of the menthyl acetate and sodium hydroxide concentration were not established from the experimental data but it is obvious from the general rate expression, previously determined for this type of reaction, that increasing the reactant concentrations would increase the reaction rate. The reaction rate was found to be strongly dependent on the temperature between 95°C and 120°C. If more

*Saponification in a homogeneous system is a simple second order reaction. However, in a heterogeneous system such as this, the reaction rate expression could easily be complicated because of the mass transfer effects.

conversion data had been obtained between these two temperatures, a plot of rate constant versus temperature would most likely have indicated the Arrhenius exponential relationship between reaction rate and temperature. The effect of temperatures above 120°C were less pronounced because of the depletion of menthyl acetate as the reaction approached completion.

The secondary ester, menthyl acetate, showed a very good stability toward elimination even at temperatures as high as 245°C with the very strong base used. The lack of elimination occurring with the secondary ester at conditions which would probably have caused complete elimination of the corresponding bromide, can be explained by the mechanism of ester saponification.

Recall that during the hydrolysis of cyclohexyl bromide the mechanism that was favored was the S_n1 in which the bromine actually leaves the molecule making elimination very probable because when the bromine ion leaves, it can easily take a hydrogen ion with it. In the mechanism of saponification, however, the single bonded oxygen in the ester never leaves the alkyl group. That is, the reaction proceeds with acyl-oxygen fission (50) as shown below:



Menthyl acetate Menthol

The evidence for this type of mechanism has been well established from tracer studies using ^{18}O in the water phase and also from experiments showing that the optical activity of a molecule is retained since the alkyl-oxygen bond is not broken.

The saponification of menthyl acetate was of heterogeneous nature because of the insolubility of the organic phase in the aqueous alkali. The reaction, therefore, had to take place at the interface between the two phases. The reaction time and temperature probably might have been lowered if a co-solvent for the two phases such as 2-propanol or diethylene glycol had been used to suppress the effects of the mass transfer of reactants and products to and from the interface.

Products from the Hydrolysis of Terpinyl Esters: The final terpene alcohol products, obtained from Δ-3-carene by the four-step process, were found to be cis-8-m-menthanol, trans-8-m-menthanol, cis-8-p-menthanol, and trans-8-p-menthanol, all of which are tertiary alcohols. The structures of the alcohols are given in Figure 45. Positive identifications were made for the cis- and trans-isomers of 8-p-menthanol by comparing the infrared spectra of the alcohol products with that of known samples of these alcohols. The infrared spectra are given in Figures 64 and 65. The other evidence which further strengthened the identification of the 8-p-menthanols included a comparison of retention times in three different chromatograph columns (13' Hyprose Sp-80, 10' TCEP and 10' PDEAS) and the melting points of the alcohols. Both cis- and trans-isomers are

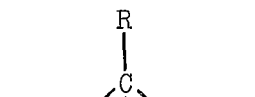
solids at room temperature, but the cis-isomer has the higher melting point. The properties of cis- and trans-8-p-menthanol given in Simonsen [44] are as follows: Trans-8-p-menthanol----m.p. 34.6-35.2°C, b.p. 209.5°/760 mm, d_{20}^{20} 0.901 and n_D^{20} 1.4630. Cis-8-p-menthanol----b.p. 210-210.5°/760 mm, d_{20}^{20} .9124 and n_D^{20} 1.4655. The cis isomer is reported by Eastman and Quinn [68] to have a melting point of 46.7-47°C. These two alcohols were synthesized from micro-quantities of the pure esters and purified in the chromatograph but not enough was obtained to make any measurements of physical properties other than the melting point of the cis isomer which was found to be about 46°C. The trans isomer apparently was not pure since it did not solidify at room temperature. The alcohols had to be made individually from the esters because they could not be separated from the alcohol mixture in the chromatograph while the esters could be separated in the chromatograph. A chromatogram of the alcohol product mixture is shown in Figure 55 which indicates the poor resolution.

The cis and trans isomers of 8-m-menthanol were identified by deduction because samples of these alcohols were not available nor was there any spectral information in the literature for them. The following is a presentation of the evidence which led to the identification of the four alcohols.

Recall that there are eight possible $C_{10}H_{19}OH$ isomers (two by simple rearrangement) which theoretically could be obtained from cis-carane, excluding all the geometric isomers. These eight alcohols are shown in

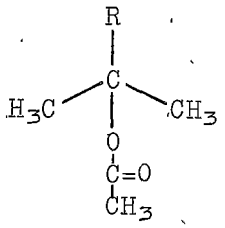
Figure 2. If all the geometric isomers are included there are twenty possible alcohols. Fortunately, only four of these alcohols were obtained in major amounts, which greatly simplified the identification.

The first step that was taken in the final product identification was to separate the three major ester components which could be resolved in the chromatograph (Figure 53). These esters (two were pure and one was a mixture of two) were isolated in a 20' x 3/8" PDEAS preparatory chromatograph column. They were purified from olefins and bromides by passing them repeatedly through the chromatograph. When the three isolated components were free of impurities infrared and NMR spectra were obtained. The infrared spectra in Figure 62 definitely showed the strong ester carbonyl bond at 1730-1750 cm^{-1} but did not provide an identification since no known ester samples were available. The NMR spectra, however, shown in Figure 68, immediately eliminated the secondary six-membered ring alcohols, 4-p-menthanol and 3-m-menthanol as possible products. All of these alcohols have a proton on the isopropyl group, as shown:



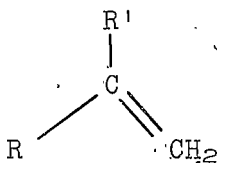
which causes the resonance of the six protons on the two methyl groups to be split into a doublet at about δ = 1.0 with a frequency of 6-7 cps. This is very clearly shown in the NMR spectrum of 4-terpinenol (Figure 71).

The esters show instead singlet resonance at δ = 1.4 (6 H) which indicated either that the acetate group was situated as shown,

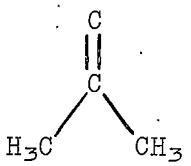


or that the seven-membered ring had been formed with its gem dimethyls which would also show up as a six-proton singlet.

One of the olefins obtained from the dehydrobromination of the terpinyl bromides (previously discussed) still had not been identified, so the NMR spectra were obtained for the four which had been previously separated in the gas chromatograph. This was done to determine if the unidentified olefin was one of the trimethylcycloheptenes. The spectra are shown in Figures 67-A and 67-B. The NMR of the spectrum of the unknown olefin indicated that it did not have the cyclic nonconjugated olefinic bond which the cycloheptene derivatives would have. This type of double bond has proton resonance at δ = 5.2 - 5.7. The spectrum of this olefin did indicate, however, impurities with a double bond of the following type



from the weak resonance at $\delta = 4.78$. It also showed singlet resonance (six protons) at $\delta = 1.69$ indicating also the presence of an olefinic bond of the following type:



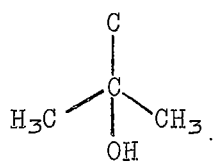
The IR spectra of the other olefins had matched reasonably close with known six-membered ring olefins so that it was reasonable to assume that no major amounts of the cycloheptyl alcohols were present.

From the evidence that had been obtained from the infrared and NMR spectra of the esters and the olefins, the number of possible alcohols which could be present was narrowed to four: cis- and trans-8-p-menthanol and cis- and trans-8-m-menthanol.

It was impossible to tell from the ester spectra which were meta derivatives and which were para derivatives so this necessitated the synthesis of the pure alcohols from the ester components. This was accomplished with 25-100 μl of the esters and 10% aqueous NaOH using sealed glass reaction tubes. The reaction tubes were placed in the Parr bomb, wrapped in cloth and surrounded by water, and the reaction carried out at a temperature of 170°C for about 10-12 hours. The yields of alcohol were about 50% with nearly complete conversion of the esters. The alcohols were purified in the gas chromatograph. It was discovered at

this time that one of the ester components isolated in the chromatograph actually was a mixture of two esters (identified later as cis-8-m-menthyl acetate and trans-8-p-menthyl acetate) as indicated in the chromatogram in Figure 52.

Three of the alcohols were obtained in sufficient quantity and purity to obtain their infrared and NMR spectra which are shown in Figures 64 to 66 and in Figure 70. The cis and trans isomers of 8-p-menthanol which had been tentatively identified by comparison of retention times in the chromatograph with the known alcohols were immediately verified from the infrared spectra. The NMR spectra for the unknown alcohol verified what had been found with the esters, i.e., that the hydroxyl was located on the isopropyl group as shown:



Since only the cis and trans meta isomers having the above structure remained as possible alcohols, the two unknown alcohols in the product were considered identified. The chromatogram of the alcohols in Figure 55 shows the cis and trans assignments given to the two geometric isomers of 8-m-menthanol. This was done purely by analogy to the relative retention times of cis- and trans-8-p-menthanol in this chromatograph column, i.e., the trans isomer has a shorter retention time than

the cis isomer. Simonsen has listed the properties of 8-m-menthanol as follows: b.p. 206-209°, d^{20} 0.9100, and n_D^{20} 1.4633. No mention was made of whether it was the cis or trans geometric isomer.

There was another minor alcohol product in the mixture but it never occurred in amounts over 5% so it was not identified. This is the first peak in the chromatogram. Trace quantities of menthol and isomenthol (identified by GLC retention time only) were observed also in the product. It is probably reasonable to assume that there were small amounts of other alcohols produced which are not evident because they could not be resolved in the chromatograph.

Hydrolysis Reaction with the Terpinyl Esters: The hydrolysis of the terpinyl esters was not investigated in detail mainly because of the complexity of analyzing a reaction mixture which would have contained as many as seven components when the reaction was incomplete. The reaction was investigated in some detail with menthyl acetate (discussed previously) because it was the only ester available. The main difference in the saponification reactions of secondary and tertiary esters would be in the degree of elimination. The effects of all the variables would be the same except that less severe conditions would probably be used with the tertiary esters.

A considerable amount of the terpinyl esters was saponified, however, in order to make enough of the alcohol product to try separating the components by steam distillation. The ester used for this purpose was syn-

thesized using a mixture of bromide product from many runs. The bromide was vacuum distilled to remove unreacted carane and olefins. The esterification was carried out in a series of runs since about 25 ml was the maximum amount of bromide that could be esterified in one run with the 500 cc reactor without getting severe heating effects from the reaction. The accumulated ester product was then vacuum distilled to remove olefins before saponifying it. The amount of unreacted bromide in the ester was not determined.

The alcohols were also synthesized in a series of runs since only about 20 ml of ester could be saponified in the Parr bomb without losing mixing efficiency.

Each run was carried out at 170°C for 13 hours using 120 ml of five percent NaOH. Approximately 180 ml of alcohol product were obtained which contained about 50% alcohols. It is apparent from this that elimination was more of a problem with the tertiary esters than it was with the secondary ester, although the amount of olefins in the product would also be dependent on the amount of unreacted bromide in the ester. Complete conversion of the ester was obtained, which was desired.

Hydrolysis Reaction Mechanism: The saponification of esters has already been discussed in some detail in the section on the hydrolysis of menthyl acetate. The reaction with 8-p-menthyl acetate is illustrated in Figure 46 showing also the elimination reaction. As mentioned previously, esters can be hydrolyzed with less elimination occurring than

with the corresponding halides because of the mechanism of the ester hydrolysis in which acyl-oxygen fission occurs leaving the oxygen attached to the alkyl part of the ester. Apparently acyl-oxygen fission does not take place predominantly in the case of tertiary esters because some elimination does occur.

Distillation of Terpinyl Alcohol Products: The distillation of the alcohol product was undertaken in the hope of separating the alcohols so that they could be identified and also so physical properties could be measured. The distillation was carried out before the alcohols had been synthesized individually from the isolated ester components.

A batch steam distillation was used with the 75 theoretical plate column. Dowtherm A was placed in the still pot to chase out the least volatile alcohols in the mixture.

The distillation was started at a reflux ratio of 2.5:1 to cut out the olefins in the product mixture. As the olefins were removed the reflux ratio was gradually raised to 30:1 so that a clean separation could be made between the olefins and the alcohols. A 30:1 reflux ratio was then used throughout the distillation of the alcohols since it was the maximum attainable on the Corad condenser. The distillation showed that no appreciable separation could be made between the meta and para alcohols. This was essentially what was expected, however, since the trans-8-m-menthanol and trans-8-p-menthanol could not be resolved completely in any of the chromatograph columns. It is not surprising since

the boiling points are probably only about 2° different at the maximum. A slight degree of separation was achieved between the cis and trans isomer mixtures, however. Better separations could probably have been made among the esters since they could at least be resolved in the chromatograph. Crystallization could perhaps be used to separate the cis and trans alcohol isomers.

E. General Discussion

Out of the twenty (two by simple rearrangement) saturated monocyclic monoterpene alcohols which could theoretically be obtained from carane, only four were produced in any major amount. These were the cis and trans isomers of 8-p-menthanol (dihydro-α-terpineol) and the cis and trans isomers of 8-m-menthanol (dihydrocarveterpineol*). Only trace amounts of the menthol isomers were detected.

This process with its two costly steps, the hydrobromination and the esterification, would probably not be economically feasible for producing these tertiary alcohols. At least one of the geometric isomers, if not both, of 8-p-menthanol could very easily be produced from α-terpineol by simple hydrogenation. Alpha-terpineol occurs naturally in several essential oils (64). Trans-8-p-menthanol also has been found

*This is the trivial name for the optically inactive alcohol. The optically active alcohol is called dihydrosylveterpineol.

in pine oil, which is a high boiling fraction of turpentine. Little is known about the 8-m-menthanol isomers. They apparently do not occur naturally. Simonsen [44] has discussed the synthesis of these alcohols by several methods, including one from sylvestrene dihydrochloride which can be made from Δ-3-carene.

The anti-Markovnikov hydrobromination of carane failed to provide any of the secondary bromides necessary for the synthesis of menthol by this process. The theoretical considerations for this reaction appeared to be very sound. Perhaps the reaction would not go because of some contaminants in the system which prevented free radical formation. On the other hand, the chemistry of the cyclopropane ring may be very much more complicated than is now known and the formation of free radicals may just not occur when the ring is fissioned. It would be interesting to see further research done on this reaction (preferably by an advanced organic chemist) to determine the mechanism of the hydrobromination at the cyclopropane ring with free radicals present.

If some way could be found to obtain the secondary bromide, more work could be done on the esterification reaction, also. This reaction went so easily with silver acetate that it would seem likely to go also with one of the cheaper acetate salts. A detailed investigation would probably be required to determine the best reaction system and operating conditions to use.

The saponification reaction was found to go very readily with the secondary ester. This reaction could probably be carried out at less severe conditions if better mixing of the heterogeneous reactants could be achieved or if a good co-solvent could be found to eliminate the mass transfer effects.

If the tertiary alcohols were desired from carane, they could probably be synthesized very easily by direct hydrolysis using dilute sulfuric acid. This is a very simple reaction with olefins and would greatly improve the economics of producing these alcohols from Δ -3-carene. However, the problem of separating the meta and para derivatives in the final product would still be present.

*Their value is about 80¢/lb.

VI. Conclusions

1. The hydrogenation of (+) Δ-3-carene was found to yield (-)cis-carane and 1,1,4-trimethylcycloheptane. The reaction was found to proceed well with reduced nickel and rhodium catalysts generating some exothermic heat.

2. In a continuous fixed-bed catalytic reactor using an active reduced and stabilized nickel catalyst (Harshaw Ni-0104T), the yield of carane was found to be favored by pressure up to at least 1000 psig, by temperatures somewhat less than about 80°C and by liquid hourly space velocities of .10 or less. The yield of 1,1,4-trimethylcycloheptane was found to be favored by atmospheric pressure, by temperatures greater than about 80°C and by liquid hourly space velocities greater than .10 hr^{-1}. In some experiments carane yields of 95% were obtained with nearly complete conversion of Δ-3-carene. The operating conditions for these high yields were as follows: T = 60-70°C, P = 750-1000 psig, and LHSV = .10-.20. The hydrogen rate was found to have little effect on the reaction as long as the hydrogen was in excess.

3. The nickel and rhodium catalysts were both found to be badly poisoned during a run causing a drop in activity but not in selectivity. The poison is suspected to be water, assumed to be generated in the reaction from peroxide contaminants in the Δ-3-carene feedstock.

4. The boiling points of (-)cis-carane and 1,1,4-trimethylcycloheptane were found to be less than a degree apart making separation of

these products by normal distillation extremely difficult. The Δ -3-carene, however, had a boiling point about 3° higher than the hydrogenation products so it could be separated from a product mixture by distillation using 75-100 theoretical plates and reflux ratios of 30:1 to 40:1 and with considerable mid-fraction recycle.

5. The anti-Markovnikov hydrobromination of cis-carane was found to yield meta and para tertiary derivatives only. No secondary bromides of any amount were formed nor were any seven-membered ring bromides formed. The product was considered to contain the cis- and trans- isomers of 8-bromo-p-menthane and 8-bromo-m-menthane. These bromides were found to be very unstable, decomposing to olefins upon mild heating.

6. During the hydrobromination, the cyclopropane ring was found to react much faster with HBr than olefins did, producing considerable exothermic heat when the ring was fissioned. Nearly complete conversion was obtained at most of the reaction conditions tried. Higher temperatures (up to 100°C) were found to favor slightly the formation of the meta derivatives. Low carane concentrations (down to .30 g-moles/liter) were found to decrease the reaction rate at a fixed hydrogen bromide feed rate. Organic peroxides were found to have no appreciable effect on the product content other than to suppress slightly the cis-trans isomerization occurring.

7. For the esterification of cyclohexyl bromide, silver acetate was found to be the best acetate salt for the reaction.

8. The esterification of the terpinyl ester product with silver acetate was strongly influenced by the solvent medium used. An absolute ethanol medium was found to suppress ester formation, favoring instead the formation of products which were suspected to be ethers. Glacial acetic acid or propionic acid mediums were found to favor ester formation with the reaction proceeding instantaneously, generating considerable exothermic heat. Temperature over a range from about 2°C to 70°C was found to have no appreciable effect on the ester yield but the yield was found to be considerably decreased at the refluxing temperature of acetic acid (112°C). The maximum amount of ester in the product was found to be about 60% at a temperature of about 20°C and an initial bromide concentration of about .25 g-moles/liter. Higher concentrations of bromide were found to decrease the ester yield. The major by-products of this reaction were olefins produced by elimination of hydrogen bromide.

9. When crude hydrobromination products (containing bromides, olefins, and unreacted carane) which had been obtained with free radicals present were esterified, additional products were formed along with the esters. These products could not be positively identified but from infrared and NMR spectral considerations were considered to contain oxygen and are believed to be of epoxide and lactone nature.

10. The final alcohol products were found to be cis- and trans-8-p-menthanol and cis- and trans-8-m-menthanol. The identification of these alcohols was accomplished from infrared and NMR spectral evidence,

retention times in the gas chromatograph, and from the melting points of the alcohols.

11. The hydrolysis of the terpinyl ester products was not investigated in detail. However, a detailed investigation of the reaction with the secondary ester, menthyl acetate, indicated that high yields and conversions could be obtained using sodium hydroxide saponification at temperatures greater than about 120°C. The reaction rate was found to be strongly dependent upon the temperature. Nearly complete conversion could be obtained after one hour when the temperature was around 200°C but the reaction was found to be very slow at a temperature of 95°C. Elimination was found to be no problem with the secondary ester but it occurred considerably more with the tertiary esters. Approximately 50% yields of the tertiary alcohols could be obtained at 170°C after 10-12 hours.

12. The direct hydrolysis of the cyclohexyl bromide was found to be very difficult to achieve with elimination predominating with nearly all the hydrolyzing agents tried. A mixture of silver oxide and sodium nitrate was found to be partially effective, however. The reaction was never tried with the tertiary bromides, which more than likely would have been even more difficult to hydrolyze.

VII. Recommendations

The exploratory nature of this research problem opened the door to many areas of new research which could not be followed up in detail because of the time limitations. Some of the more interesting of these research areas are listed below. It is recommended that they be investigated in the future.

1. Research on the hydrogenation of Δ-3-carene to carane and also to 1,1,4-trimethylcycloheptane is by no means complete. These materials are not unknown but they are unavailable at the present time. The distribution of samples of them would help in the market development of Δ-3-carene. Before any attempt is made to produce quantities of carane and 1,1,4-trimethylcycloheptane for sample distribution, however, the following research should be undertaken:

   (a) The problem of deactivation of the hydrogenation catalyst should be solved. It is recommended to determine the nature and amount of contaminants in the Δ-3-carene. An elemental analysis of the Δ-3-carene would be most helpful in this area. When the poisons are found (peroxides are a good lead) efforts should be made to eliminate them or render them harmless.

   (b) A more detailed investigation of other hydrogenation catalysts would be helpful. The Girdler nickel and rare metal catalysts are recommended.

(c) To learn more about the reactions taking place, it is recommended that an investigation of the kinetics of the reactions be made to establish the exact mechanism.

(d) An optimization of the reactor operating variables is recommended with strong emphasis placed on a statistical analysis.

2. The separation of unreacted Δ-3-carene from the hydrogenation product would probably facilitate maximum production of carane in high purity. It is recommended that various means (distillation, extraction, crystallization, etc.) of separating Δ-3-carene and carane be investigated.

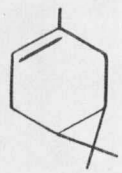
3. The olefins produced from the dehydrobromination of the mixture of 8-bromo-p-menthane and 8-bromo-m-menthane isomers showed strong inclinations to isomerize forming 3-p-menthene and 3-m-menthene. The anti-Markovnikov hydrobromination would probably go reasonably well with these olefins to produce the secondary bromides. Therefore, it is recommended to investigate possible ways of obtaining 3-p-menthene from carane in high yield.

VIII APPENDIX

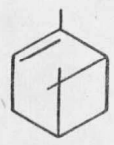
TABLE IV. Structures of Some Terpene Hydrocarbons Associated with the Hydrogenation Reaction.

Terpenes in Δ-3-Carene Feedstock

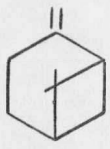
Δ-3-Carene



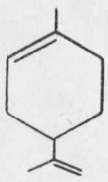
α-Pinene



β-Pinene



Dipentene



Myrcene

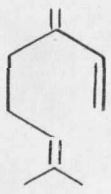
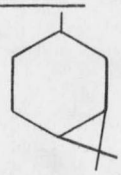


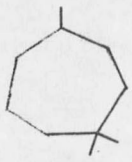
TABLE IV (continued)

Possible Saturated Products of the Hydrogenation Reaction

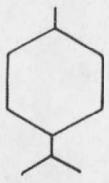
Carane



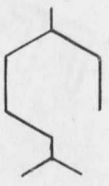
1,1,4-Trimethylcycloheptane



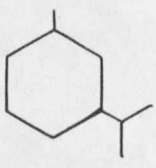
p-Menthane



2,6-Dimethyloctane



m-Methane



Pinane



TABLE V. Experimental Data and Results for the Preliminary Batch Hydrogenation Experiments in the Parr Bomb.

Run No.	(1) Catalyst	Weight Catalyst (gms)	Volume Δ-3 (2) (ml)	Temp. (°C)	Press. (psig)	Reaction Time (min)	Product Analysis, % Carane	(3) TMCH	Δ-3-Carene	Other
1	None	----	100	200	850	50	No Reaction			(4)
2	Co-Mo	18	62	200	500	30	17	6	11	66
3	Co-Mo	18	50	100	200	30	No Reaction			
4	Ni-Mo	15	40	100	500	15	No Reaction			
5	Ni-Mo	15	40	200	500	90	27	10	12	51
6	NiO	15	56	145	1000	60	No Reaction			
7	NiO	15	56	200	200	60	No Reaction			
8	Ni-Mo	20	50	100	500	90	No Reaction			
9	Ni-Mo	20	50	250	550	15	25	6	13	46
10	Ni-Mo	20	80	180	1000	170	12	8	8	72

Notes:

1. The Girdler G-69RS nickel catalyst used in the bomb was in powdered form. The other catalysts were in 1/8" pelletized form. Ni-0104T was the Harshaw catalyst and .5% Rh was the Englehard rhodium catalyst.

2. The Δ-3 purity for various runs was as follows:

1-10	----	99%
14-18	----	70%
20	----	88%
22-23	----	86%
24	----	80%
25	----	70%

3. TMCH refers to 1,1,4-trimethylcycloheptane.

4. The other products obtained in the hydrogenation with the desulfurization catalysts consisted mainly of menthenes and menthadienes (isomerization products). The other products from the hydrogenation with the Girdler, Harshaw and Englehard catalysts consisted of pinane, 2,6-dimethyloctane from myrcene in the Δ-3 feed, and some unknown materials.

TABLE V (continued)

Run No.	(1) Catalyst	Weight Catalyst (gms)	Volume Δ-3 (2) (ml)	Temp. (°C)	Press. (psig)	Reaction Time (min)	Product Analysis, % Carane	(3) TMCH	Δ-3-Carene	Other
14	G-69RS Ni	12	90	100	175	84	4	72	0	24
15	G-69RS Ni	12	100	50	100	140	10	0	42	48
17	G-69RS Ni	12	75	25	135	167	Very Little Reaction			
18	G-69RS Ni	12	60	50	125	204	56	22	0	22
19	G-69RS Ni	12	75	70	125	180	40	49	0	11
20	G-69RS Ni	12	100	50	125	180	32	20	7	41
23	Ni-0104T	40	100	50	125	210	25	2	52	21
24	.5% Rh	20	50	25	125	150	1	8	80	11
25	.5% Rh	20	50	50	200	120	43	6	22	29

TABLE VI. Comparison of Active Hydrogenation Catalysts in Parr Bomb.

Catalyst	Average Product Analysis, %			
	Carane	TMCH*	Δ-3	Other
Harshaw Nickel Ni-0104T	70	23	0	7
Englehard .5% Rh	83	11	0	6
Girdler Nickel G-69RS	31	7	41	21
Raney Nickel #28	9	86	0	5

Notes: These runs were carried out in duplicate at about 70°C and 600 psig for two hours using 50 ml of Δ-3-carene and 25 gms of catalyst. The "other" products not specified above were 2,6-dimethyloctane, pinane, and one unknown.

The Δ-3-carene used had the following analysis:

88.4%	----	Δ-3
5.0%	----	myrcene
4.2%	----	dipentene
2.3%	----	beta-pinene

*TMCH = 1,1,4-trimethylcycloheptane.

TABLE VII. Results of the Durability Tests for the Catalysts.

Catalyst		Product Analysis 1st Run	2nd Run
Harshaw Nickel	Carane	50%	42%
73-78°C	TMCH	14%	12%
590 psig	Δ-3	18%	26%
60 min	other	18%	20%
Englehard Rhodium	Carane	86%	83%
73°C	TMCH	9%	12%
590 psig	Δ-3	0%	0%
60 min	other	5%	5%
Raney Nickel	Carane	74%	82%
25°C	TMCH	22%	13%
600 psig	Δ-3	0%	0%
60 min	other	4%	5%

Notes: 15 gms of the Harshaw and Englehard catalysts were used while approximately 20 gms of the powdered Raney nickel catalyst were used. 25 ml of Δ-3 were used. The Δ-3 had the following analysis:

91.0% ---- Δ-3
4.2% ---- myrcene
3.4% ---- dipentene
1.4% ---- beta-pinene

TABLE VIII. Experimental Data for the Continuous Hydrogenation of Δ-3-Carene in the Fixed-Bed Reactor.

Runs CH-1 and CH-2

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/hr)	Δ-3-Carene Feed Rate (cc/min)	% Carane in Prod.
1	4:40 PM	start					
	7:45 PM	1	160	500	2.20	.90	6.6
	8:45 PM	2	200	500	2.20	.90	11.7
2	12:30 AM	3	200	500	2.30	2.00	7.5
		shut down					
	7:45 PM	restart					
	9:30 PM	4	210	700	3.20	3.00	6.0
	11:25 PM	5	190	500	1.70	2.00	6.0
		shut down					

Catalyst: 200 cc of 1/8" cobalt-molybdate.
Δ-3-Carene Feedstock -- 85% pure.
Minimum line-out time for a sample was two hours.
Reactor -- 31" x 1", heated electrically.

TABLE VIII (continued)

Run CH-3

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv.* Δ-3	% Carane in Prod.
1	2:00 PM	start						
	4:00 PM	1	63	100	75	.86	43	25
	7:10 PM	2	60	100	193	.30	63	37
	9:40 PM	3	61	100	407	.23	69	36
		shut down						
2	2:08 PM	restart						
	6:40 PM	4	54	100	117	.26	69	32
	9:05 PM	5	60	100	121	.46	54	34
		shut down						
3	10:35 PM	restart						
	2:10 PM	6	62	100	121	.78	34	20
	4:40 PM	7	73	100	117	.65	51	27
		shut down						

Catalyst: 137.5 gms (100 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 61% pure for 1-5, 81% pure for 6-7.
Reactor: 31" x 1", heated electrically.

*The percent conversion of the Δ-3-carene is total conversion based on the amount of Δ-3 present in the feedstock.

TABLE VIII (continued)

Run CH-4

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Carane in Prod.
1	1:00 PM	start						
	5:00 PM	1	53	100	119	.14	73	40
	7:30 PM	2	69	100	119	.46	68	34
		shut down						
2	10:30 AM	restart						
	12:30 PM	3	45	100	119	.45	53	27
	3:30 PM	4	90	100	119	.45	100	27
	5:10 PM	5	114	100	119	.45	100	7
	10:20 PM	6	61	300	119	.45	60	24
3	12:05 AM	7	68	200	119	.45	72	29
		shut down						
	10:20 AM	restart						
	12:50 PM	8	44	0	119	.45	38	9
		shut down						
4	2:30 PM	restart						
	6:00 PM	9	52	100	119	.45	47	24
	10:15	10	56	100	119	.45	53	25
		shut down						

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ -3-Carene Feedstock: 78% pure.
Reactor: 31" x 1", heated electrically.

TABLE VIII (continued)

Run CH-5

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Carane in Prod.
1	11:00 AM	start						
	1:00 PM	1	54	100	37.6	.20	81	34
		shut down						
	7:50 PM	restart						
	10:15 PM	2	28	100	37.6	.20	57	34
		shut down						
2	12:00 PM	restart						
	3:15 PM	3	69	100	37.6	.20	96	37
		shut down						
	4:25 PM	restart						
	6:25 PM	4	50	100	37.6	.40	66	24
		shut down						
3	1:40 PM	restart						
	4:30 PM	5	56	100	37.6	.10	94	41

Catalyst: 170 cc of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 98% pure.
Reactor: 31" x 1" with copper heating coil.

TABLE VIII (continued)

Run CH-6

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Carane in Prod.
1	3:50 PM	start						
	8:00 PM	1	49	0	37.6	.45	21	10
	10:10 PM	2	47	50	37.6	.45	18	9
2	12:00 AM	3	49	100	37.6	.45	18	10
		shut down						
	9:00 AM	restart						
	11:00 AM	4	51	200	37.6	.45	16	10
	1:10 PM	5	56	100	37.6	.45	18	10
	3:00 PM	6	26	100	37.6	.45	10	5
	5:30 PM	7	51	100	75.3	.45	17	19
		shut down						
	7:40 PM	restart						
	8:40 PM	8	53	100	112.9	.45	19	13
	10:40 PM	9	51	100	150.6	.45	14	8
		shut down						
3	10:45 AM	restart						
	12:20 PM	10	63	100	37.6	.45	26	13
	4:10 PM	11	50	100	37.6	.20	36	18
	6:30 PM	12	56	100	37.6	.60	13	7
		shut down						
4	10:00 AM	restart						
	1:00 PM	13	49	100	37.6	.80	7	5
	3:50 PM	14	51	100	37.6	.45	13	8

Catalyst: 100 cc of 1/8" Girdler nickel G-69RS.
Δ-3-Carene Feedstock: 87% pure for 1-8, 97% pure for 9-14.
Reactor: 31" x 1" with copper heating coil.

TABLE VIII (continued)

Run CH-7

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Carane in Prod.
1	10:30 AM	start						
	1:30 PM	1	22	100	37.6	.45	17	8
	3:30 PM	2	54	100	37.6	.45	25	13
	11:05 PM	3	79	100	37.6	.45	52	29
		shut down						
2	10:15 AM	restart						
	12:10 PM	4	51	100	75.3	.45	31	13
	2:25 PM	5	54	100	112.9	.45	22	11
	4:20 PM	6	52	100	150.6	.45	22	12
		shut down						
3	11:00 AM	restart						
	2:00 PM	7	50	0	37.6	.45	12	5
	4:30 PM	8	53	50	37.6	.45	27	13
		shut down						
4	12:30 PM	restart						
	2:30 PM	9	53	200	37.6	.45	26	15
		shut down						
5	2:30 PM	restart						
	4:30 PM	10	51	100	37.6	.20	24	11
	7:15 PM	11	56	100	37.6	.60	23	11
	9:30 PM	12	54	100	37.6	.80	16	7
		shut down						
6	11:30 AM	restart						
	3:00 PM	13	56	100	37.6	.45	21	10

Catalyst: 100 cc of 1/8" Girdler nickel G-69RS.
Δ-3-Carene Feedstock: 97% pure for 1-9, 94% pure for 10-13.
Reactor: 31" x 1" with copper heating coil.

TABLE VIII (continued)

Run CH-8

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield* Carane	% Carane in Prod.
1	2:00 PM	start					-		
	6:00 PM	1	20	100	37.6	.45	33	53	16
2	12:00 PM	2	53	100	37.6	.45	59	53	30
		shut down							
	11:00 AM	restart							
	12:50 PM	3	75	100	37.6	.45	67	57	36
		shut down							
3	10:30 AM	restart							
	1:00 PM	4	48	0	37.6	.45	31	44	13
		shut down							
	1:20 PM	restart							
	3:45 PM	5	55	200	37.6	.45	54	44	39
	5:00 PM	6	53	100	37.6	.45	54	80	31
	9:00 PM	7	54	100	37.6	.20	61	62	38
	11:20 PM	8	51	100	37.6	.60	44	69	26
		shut down							

(continued)

TABLE VIII (continued)

Run CH-8 (continued)

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield* Carane	% Carane in Prod.
4	11:00 AM	restart							
	1:30 PM	9	55	100	37.6	.80	26	64	17
	3:45 PM	10	50	100	75.3	.45	40	71	23
	6:00 PM	11	52	100	112.9	.45	41	62	24
	9:10 PM	12	52	100	150.6	.45	45	64	25
	11:00 PM	13	54	200	37.6	.20	44	64	26
		shut down							
5	9:15 AM	restart							
	11:00 AM	14	49	200	37.6	.20	71	64	42
	12:00 PM	15	51	200	37.6	.20	76	63	44
	1:00 PM	16	51	200	37.6	.20	76	63	44

Catalyst: 131.9 gms (100 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 94% pure for 1-3, 92% pure for 4-16.
Reactor: 31" x 1" with copper heating coil.

*The yield of carane is the fraction of carane obtained from the Δ-3-carene which reacted.

TABLE VIII (continued)

Run CH-10

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
1	4:20 PM	start							
	10:00 PM	1	65	300	37.6	.20	100	71	67
		shut down							
2	11:20 AM	restart							
	2:40 PM	2	65	300	37.6	.20	98	71	65
	4:50 PM	3	65	400	37.6	.20	98	74	68
	7:30 PM	4	65	400	37.6	.20	99	81	75
	11:15 PM	5	65	600	37.6	.20	99	85	79
		shut down							
3	10:35 AM	restart							
	1:15 PM	6	65	575	37.6	.20	99	86	79
	4:30 PM	7	65	490	37.6	.20	99	85	79
		shut down							
4	11:30 AM	restart							
	2:15 PM	8	70	820	37.6	.20	100	84	79
	4:45 PM	9	70	830	37.6	.20	100	89	84
		shut down							
5	11:45 PM	restart							
	2:30 PM	10	70	1130	37.6	.20	100	88	83

Catalyst: 170 cc of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 94% pure.
Reactor: 31" x 1" with copper heating coil.

TABLE VIII (continued)

Run CH-11

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
1	3:30 PM	start							
	9:15 PM	1	57	800	37.6	.20	94	67	60
		shut down							
2	8:30 AM	restart							
	11:45 AM	2	18	800	37.6	.20	94	74	66
		shut down							
3	4:00 PM	restart							
	7:00 PM	3	69	300	37.6	.20	97	71	66
	10:30 PM	4	21	300	37.6	.20	72	72	49
		shut down							
4	10:30 AM	restart							
	1:15 PM	5	40	300	37.6	.20	78	77	57
		shut down							
	8:00 PM	restart							
	11:00 PM	6	42	800	37.6	.20	86	81	66
		shut down							
5	7:45 PM	restart							
	10:35 PM	7	22	1000	37.6	.20	75	90	64
		shut down							

(continued)

TABLE VIII (continued)

Run CH-11 (continued)

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
6	11:30 AM	restart							
	3:00 PM	8	71	500	37.6	.20	96	87	79
	7:30 PM	9	20	500	37.6	.20	47	86	38
		shut down							
7	3:00 PM	restart							
	5:00 PM	10	45	500	37.6	.20	75	85	61
		shut down							
8	8:00 AM	restart							
	11:00 AM	11	73	1000	37.6	.20	94	90	81
		shut down							
9	9:45 AM	restart							
	2:00 PM	12	42	1000	37.6	.20	83	95	75

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 95% pure.
Reactor: 31" x 1" with copper heating coil.

TABLE VIII (continued)

Run CH-12A

Time Elapsed from Start (hours)	Sample	Temp. (°C)	% Δ-3 in Product	% Carane in Product
1.0	1	42	23	51
2.0	2	45	18	53
3.0	3	44	23	46
4.0	4	44	25	44
5.0	5	45	28	43
6.0	6	45	24	49
7.0	step change in temperature to 73°C			
7.5	7	73	28	44
8.0	8	78	27	46
8.5	9	77	22	48
9.0	10	75	13	53
10.0	11	72	8	56
11.0	12	77	9	56
12.0	13	76	9	56
13.0	14	75	6	58

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 93% pure.
Reactor: 31" x 1" with copper heating coil.
Fixed Operating Conditions -- P = 300 psig
H_2 Feed Rate = 37.6 SCF/gal Δ-3
LHSV = .20 hr^{-1}

The reactor was operated for 10 hours the day before the line-out tests were run at 40°C and 500 psig with a H_2/Δ-3 mole ratio of 2:1 and a LHSV of .20.

TABLE VIII (continued)

Run CH-12B

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
1	11:30 AM	start							
	3:30 PM	1	19	300	37.6	.20	60	71	43
	10:30 PM	2	81	300	37.6	.20	98	70	68
		shut down							
2	9:30 AM	restart							
	3:00 PM	3	17	500	37.6	.20	59	78	46
	10:00 PM	4	79	500	37.6	.20	97	82	79
		shut down							
3	1:15 PM	restart							
	5:00 PM	5	58	500	37.6	.20	93	83	77
		shut down							
4	11:00 AM	restart							
	3:00 PM	6	58	1000	37.6	.20	94	88	82
		shut down							
5	9:00 AM	restart							
	1:00 PM	7	18	1000	37.6	.20	61	88	53
	8:00 PM	8	40	1000	37.6	.20	74	89	66
		shut down							
6	4:00 PM	restart							
	8:40 PM	9	85	1000	37.6	.20	99	88	86
		shut down							

(continued)

TABLE VIII (continued)

Run CH-12B (continued)

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
7	11:40 AM	restart							
	3:00 PM	10	18	800	37.6	.20	61	88	53
		shut down							
8	5:00 PM	restart							
	9:00 PM	11	80	800	37.6	.20	95	88	83
		shut down							
9	9:30 AM	restart							
	2:00 PM	12	60	800	37.6	.20	83	87	72
	12:40 PM	13	41	800	37.6	.20	67	91	61

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 93% pure.
Reactor: 31" x 1" with copper heating coil.

This run was made with the same catalyst used in CH-12A.

TABLE VIII (continued)

Run CH-13

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
1	11:00 AM	start							
	3:00 PM	1	67	800	37.6	.20	99	79	78
		shut down							
2	9:50 AM	restart							
	2:00 PM	2	76	800	37.6	.40	100	72	72
		shut down							
3	1:50 PM	restart							
	6:00 PM	3	60	800	37.6	.10	100	72	72
		shut down							
4	10:50 AM	restart							
	3:00 PM	4	66	800	37.6	.30	100	76	75
		shut down							
5	9:45 AM	restart							
	4:00 PM	5	70	500	37.6	.30	100	71	71
		shut down							
	7:45 PM	restart							
	11:35 PM	6	75	500	37.6	.40	99	70	69
		shut down							
6	9:15 AM	restart							
	1:00 PM	7	68	500	37.6	.20	100	74	74
		shut down							
	2:00 PM	restart							
	6:00 PM	8	61	500	37.6	.10	100	76	75
		shut down							

TABLE VIII (continued)

Run CH-13 (continued)

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
7	10:20 AM	restart							
	3:30 PM	9	67	300	37.6	.10	100	72	71
		shut down							
	7:30 PM	restart							
	11:40 PM	10	68	300	37.6	.20	95	63	60
		shut down							
8	9:30 AM	restart							
	1:00 PM	11	72	300	37.6	.30	94	62	57
		shut down							
9	8:00 PM	restart							
	11:40 PM	12	71	300	37.6	.40	89	59	52
		shut down							
10	11:10 AM	restart							
	3:00 PM	13	64	1000	37.6	.10	99	73	72
		shut down							
	3:15 PM	restart							
	11:40 PM	14	65	1000	37.6	.20	94	88	82
		shut down							
11	9:35 AM	restart							
	1:45 PM	15	66	1000	37.6	.30	87	88	76
	5:30 PM	16	66	1000	37.6	.40	83	81	66
		shut down							

Catalyst: 170 cc of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 95% pure. Reactor: 31" x 1" with copper heating coil.

TABLE VIII (continued)

Run CH-14

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
1	11:00 AM	start							
	4:15 PM	1	77	990	94.1	.20	100	67	66
	8:30 PM	2	78	1000	94.1	.20	100	61	66
	11:00 PM	3	76	1000	94.1	.20	100	59	58
		shut down							
2	10:00 AM	restart							
	11:30 AM	4	70	990	94.1	.20	100	59	58
	3:10 PM	5	74	970	94.1	.20	100	64	63
	4:15 PM	6	74	990	94.1	.20	100	65	64
	7:40 PM	7	70	990	--*	.20	100	70	69
	10:30 PM	8	69	990	94.1	.20	100	72	71
		shut down							
3	10:00 AM	restart							
	2:30 PM	9	76	1000	94.1	.20	100	70	69

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T (upper support was 1/8" Nalco alumina).
Δ-3-Carene Feedstock: 94% pure.
Reactor: 31" x 1" with copper heating coil.

*H_2 flow dropped off for a short time.

TABLE VIII (continued)

Run CH-15

Time on Stream* (hours)	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
1.0	70	1020	56.5	.20	100	68	67
1.8	72	1020	56.5	.20	100	75	74
3.3	73	1020	56.5	.20	100	75	74
5.0	66	1020	56.5	.20	100	79	78
6.8	62	1020	56.5	.20	100	73	72
9.0	66	1020	56.5	.20	100	75	75
10.3	65	1020	56.5	.20	100	76	75
12.0	70	1030	56.5	.20	100	77	76
15.0	67	1000	56.5	.20	100	76	75
19.0	64	1000	56.5	.20	95	79	75
22.5	64	1000	56.5	.20	99	81	79
25.0	64	1000	56.5	.20	99	82	80
26.5	64	1020	75.3	.20	100	81	81
28.3	66	1020	75.3	.20	96	85	81
31.1	70	1020	75.3	.20	97	84	81
34.3	66	1020	75.3	.20	91	85	77

Catalyst: 263.4 gms (200 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 95% pure.
Reactor: 31" x 1" with heating water jacket. All remaining runs with this reactor.

*The reactor was not operated continuously 24 hours/day but was shut down at night. The time on stream refers to accumulated operating time from initial startup. The reactor was operated over a five-day period.

TABLE VIII (continued)

Run CH-17

Time on* Stream (hours)	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane
4.5	76	1030	94.1	.20	95	55
6.5	72	1030	94.1	.20	100	61
9.0	69	1030	94.1	.20	100	53
17.7	70	1020	94.1	.20	98	73
24.0	69	1030	94.1	.20	97	72
30.8	73	1030	94.1	.20	98	73
42.5	71	1030	94.1	.20	97	75
48.5	70	1025	94.1	.20	93	73
53.8	69	1030	94.1	.20	94	77
58.3	73	1030	94.1	.20	94	78

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 87% pure.

*Reactor was not operated continuously 24 hours/day but was shut down at night. The time on stream refers to the accumulated operating time from initial startup. The reactor was operated over a three-day period.

TABLE VIII (continued)

Run CH-18

Day	Operating Time	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane
1	8:40 AM	start						
	5:00 PM	1	66	1050	113	.20	96	75
		shut down						
2	4:00 PM	restart						
	9:50 PM	2	66	1500	113	.20	95	78
	10:50 PM	3	67	1500	113	.20	94	80
		shut down						
3	8:00 AM	restart						
	3:15 PM	4	66	1060	113	.20	90	78
	4:00 PM	5	66	1060	113	.20	90	78

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 98% pure.

TABLE VIII (continued)

Run CH-19

Time on Stream (hours)	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
7.1	66	1050	102	.20	83	88	72
8.8	66	1050	102	.20	78	86	66
17.3	66	1050	102	.20	79	97	76
19.4	66	1050	102	.20	79	96	74
21.3	66	1050	102	.20	80	90	71
25.6	66	1050	102	.20	79	93	72
29.3	66	1050	102	.20	79	94	73
33.3	66	1050	102	.20	78	91	70
42.5	66	1050	102	.20	75	91	67
45.3	66	1050	102	.20	72	90	64
50.5	66	1050	102	.20	71	91	65
56.3	66	1050	102	.20	70	91	63
65.7	66	1050	102	.20	74	90	66
71.3	66	1050	102	.20	76	92	69
72.3	66	1050	102	.20	73	91	66
80.3	66	1050	102	.20	73	90	66
90.4	66	1050	102	.20	70	89	62
92.3	66	1050	102	.20	72	88	63
93.3	66	1050	102	.20	71	91	64
94.6	66	1050	102	.20	69	91	63
99.0	66	1050	102	.20	69	86	59

(continued)

TABLE VIII (continued)

Run CH-19 (continued)

Time on Stream (hours)	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
104.0	66	1050	102	.20	69	90	62
115.0	66	1050	102	.20	72	90	65
117.0	66	1050	102	.20	70	90	63
123.3	66	1050	102	.20	68	87	59
128.3	66	1050	102	.20	71	89	63
139.3	66	1050	102	.20	66	88	58
144.0	66	1050	102	.20	67	90	60
147.5	66	1050	102	.20	65	87	58
153.5	66	1050	102	.20	64	92	59
161.5	66	1050	102	.20	66	92	61
167.0	66	1050	102	.20	65	91	59
170.0	66	1050	102	.20	57	89	51
175.3	66	1050	102	.20	62	92	56

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 98.5% pure.

TABLE VIII (continued)

Run CH-20

Time on Stream (hours)	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
4.5	76	1050	100	.20	87	72	63
7.0	76	1050	100	.20	82	78	74
11.0	76	1050	100	.20	81	81	66
25.0	76	1050	100	.20	77	85	65
30.5	76	1050	100	.20	82	83	68
37.8	76	1050	100	.20	76	84	63
49.3	76	1050	100	.20	71	83	59
56.3	76	1050	100	.20	69	81	56
62.3	76	1050	100	.20	68	82	56
75.5	76	1050	100	.20	64	83	53
80.8	76	1050	100	.20	68	83	56
85.0	76	1050	100	.20	69	84	58
95.3	76	1050	100	.20	68	83	56
100.7	76	1050	100	.20	67	85	57
105.0	76	1050	100	.20	65	85	55
109.3	76	1050	100	.20	61	82	50
122.5	76	1050	100	.20	61	85	52

(continued)

TABLE VIII (continued).

Run CH-20 (continued)

Time on Stream (hours)	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
127.0	76	1050	100	.20	59	85	50
131.5	76	1050	100	.20	59	84	49
133.8	76	1050	100	.20	57	86	49
143.5	76	1050	100	.20	59	83	49
148.8	76	1050	100	.20	61	82	50
155.5	76	1050	100	.20	56	81	45
159.0	76	1050	100	.20	58	83	48
168.8	76	1050	100	.20	56	84	47
173.5	76	1050	100	.20	52	85	44
174.7	76	1050	100	.20	52	86	45

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ -3-Carene Feedstock: 99% Δ -3, 1% β-pinene, pretreated with a 5% NaOH wash, water washed, filtered and dried with $CaSO_4$.

TABLE VIII (continued)

Run CH-21

Time on Stream (hours)	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
3.3	86	1050	94	.20	76	75	56
6.5	86	1050	94	.20	100	74	74
11.5	86	1050	94	.20	100	79	77
21.6	86	1050	94	.20	100	78	78
28.3	86	1050	94	.20	99	78	77
34.3	86	1050	94	.20	98	78	76
44.3	86	1050	94	.20	97	82	78
49.3	86	1050	94	.20	96	79	76
52.2	86	1050	94	.20	94	79	75
56.6	86	1050	94	.20	90	79	71
69.0	86	1050	94	.20	91	80	73
74.0	86	1050	94	.20	91	82	74
77.4	86	1050	94	.20	90	81	73
81.7	86	1050	94	.20	89	82	73
91.6	86	1050	94	.20	86	82	71
95.5	86	1050	94	.20	85	84	71
101.5	86	1050	94	.20	86	84	72
104.3	86	1050	94	.20	85	84	71
116.4	86	1050	94	.20	82	82	67
121.3	86	1050	94	.20	85	84	71
125.6	86	1050	94	.20	83	83	69
127.9	86	1050	94	.20	83	82	68
138.3	86	1050	94	.20	83	83	68
147.5	86	1050	94	.20	80	83	67
148.3	86	1050	94	.20	81	84	68

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 99% Δ-3, pretreated with a 5% wash, water washed and filtered.

TABLE VIII (continued)

Run CH-22

Time on Stream (hours)	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3.	% Yield Carane	% Carane in Prod.
0.8	76	1055	100	.20	6	67	4
2.8	76	1055	100	.20	93	76	70
13.2	76	1055	100	.20	97	88	85
19.5	76	1055	100	.20	95	87	83
24.0	76	1055	100	.20	93	85	79
27.3	76	1055	100	.20	87	87	76
36.5	76	1055	100	.20	88	87	76
44.0	76	1055	100	.20	86	89	76
49.6	76	1055	100	.20	86	86	74
62.8	76	1055	100	.20	80	87	69
70.0	76	1055	100	.20	79	88	69
86.1	76	1055	100	.20	80	86	68
91.1	76	1055	100	.20	80	87	70
96.1	76	1055	100	.20	79	86	69
99.6	76	1055	100	.20	79	86	68
109.5	76	1055	100	.20	78	88	69
118.8	76	1055	100	.20	78	88	68
123.3	76	1055	100	.20	74	88	66
135.8	76	1055	100	.20	77	86	67
140.8	76	1055	100	.20	79	89	70
146.1	76	1055	100	.20	77	88	68
156.5	76	1055	100	.20	74	88	65
162.7	76	1055	100	.20	72	88	63
167.7	76	1055	100	.20	69	87	60
170.3	76	1055	100	.20	67	88	59

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 99% Δ-3, no pretreatment. Catalyst bed was flushed with 200 ml of Δ-3-carene before starting.

TABLE VIII (continued)

Run CH-23

Time from Startup (hours)	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
10.5	75	1050	100	.20	93	85	79
15.2	75	1050	100	.20	86	87	75
18.2	75	1050	100	.20	86	87	75
22.8	75	1050	100	.20	88	88	78
35.9	75	1050	100	.20	78	89	69
39.7	75	1050	100	.20	78	90	71
45.0	75	1050	100	.20	80	87	70
47.0	75	1050	100	.20	79	88	70
Stopped Δ-3 Feed. Purged the bed with H_2 at 75°C and 1050 psig for 17 hours. Restarted at 64 hours.							
65.3	75	1050	100	.20	92	83	76
69.7	75	1050	100	.20	83	78	65
71.5	75	1050	100	.20	79	84	66
Shut off the Δ-3-carene feed and H_2 overnight. Off for 10 hours. Restarted at 81.5 hours.							
85.4	75	1050	100	.20	91	78	71
90.5	75	1050	100	.20	85	84	71
92.9	75	1050	100	.20	85	84	71
Flooded the bed with about 300 ml of Δ-3 and then shut down for the night. Restarted at 106.4 hours.							

(continued)

TABLE VIII (continued)

Run CH-23 (continued)

Time from Startup (hours)	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
107.8	75	1050	100	.20	65	60	39
109.9	75	1050	100	.20	75	76	57
113.4	75	1050	100	.20	72	83	60
Decreased the -3 carene feed rate to 1/2 initial value to reduce the space velocity to .10 hr^{-1}.							
121.0	75	1050	113	.10	91	90	81
130.5	75	1050	113	.10	91	91	82
133.8	75	1050	113	.10	90	91	83
136.9	75	1050	113	.10	89	91	81

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ -3-Carene Feedstock: 99% Δ -3 for first 113 hours, 97% Δ -3 for remainder, untreated.

TABLE VIII (continued)

Run CH-24

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
13	1	71	1000	94	.16	89	87	78
16	2	71	1000	94	.16	86	90	78
21	3	71	1000	94	.16	78	91	71
24	4	71	1000	94	.16	77	92	73
27	5	71	1000	94	.16	77	93	73
36	P-1	71	1000	94	.18	75	93	66
39	P-2	71	1000	94	.18	74	93	65
41	P-3	71	1000	94	.18	73	93	64
44	P-4	71	1000	94	.18	73	91	63
	P-Acc.* (8 hr)							
Shut down for four hours. Restart at 48 hours.**								
60	6	74	1000	94	.18	77	92	75
66	SV-1	74	1000	376	.072	97	92	89
68	SV-2	74	1000	376	.072	99	92	91
71	SV-3	74	1000	376	.072	99	90	89
74	SV-4	74	1000	376	.072	98	87	86
	SV-Acc. (8 hr.)							

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 96% Δ-3, untreated.

*The accumulative samples were obtained over the time period that the point samples were taken to obtain the data on the variable.

**The reactor was restarted at 75°C, 1000 psig with a LHSV of .18 and H_2 rate of 94 SCF/gal. Δ-3 and run until 60 hours, at which time the conditions were changed for space velocity data.

TABLE VIII (continued)

Run CH-25

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
13	1	75	750	94	.16	89	87	76
17	2	75	750	94	.16	86	87	74
20	3	75	750	94	.16	87	89	76
25	4	75	750	94	.16	81	89	71
36	P-1	75	750	94	.16	74	89	65
39	P-2	75	750	94	.16	74	90	66
41	P-3	75	750	94	.16	73	90	65
44	P-4	75	750	94	.16	77	90	68
	P-Acc.					77	88	65
Shut down for four hours.*								
60	5	75	1000	94	.18	76	90	66
64	SV-1	75	1000	376	.15	78	93	70
66	SV-2	75	1000	376	.15	78	92	70
68	SV-3	75	1000	376	.15	84	93	76
70	SV-4	75	1000	376	.15	85	93	76
72	SV-5	75	1000	376	.15	86	89	74
	SV-Acc.					83	94	75

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 97% Δ-3, untreated.

*See Run Ch-24 for explanation.

TABLE VIII (continued)

Run CH-26

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
12	1	75	500	94	.17	96	78	72
17	2	75	500	94	.17	87	77	64
20	3	75	500	94	.17	91	75	71
25	4	75	500	94	.17	87	77	64
36	P-1	75	500	94	.17	84	87	70
39	P-2	75	500	94	.17	86	86	71
41	P-3	75	500	94	.17	84	86	69
44	P-4	75	500	94	.17	84	87	70
	P-Acc.					84	86	69
Shut down for four hours.*								
60	5	75	1000	94	.16	79	89	67
64	SV-1	75	1000	376	.35	62	88	51
67	SV-2	75	1000	376	.35	60	84	47
70	SV-3	75	1000	376	.35	61	88	49
72	SV-4	75	1000	376	.35	57	87	46
	SV-Acc.					57	88	47

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 93% Δ-3, untreated.

*See Run CH-24 for explanation.

TABLE VIII (continued)

Run CH-27

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
12	1	76	250	94	.16	90	58	49
16	2	76	250	94	.16	86	59	49
20	3	76	250	94	.16	88	59	50
23	4	76	250	94	.16	88	63	52
26	5	76	250	94	.16	89	63	53
36	P-1	76	250	94	.16	88	67	56
39	P-2	76	250	94	.16	89	69	59
41	P-3	76	250	94	.16	89	62	53
44	P-4	76	250	94	.16	90	64	54
	P-Acc.					88	68	57
Shut down for four hours.*								
60	6	76	1000	94	.16	92	87	76
64	SV-1	76	1000	376	.20	89	88	75
66	SV-2	76	1000	376	.20	84	88	70
70	SV-3	76	1000	376	.20	86	89	74
72	SV-4	76	1000	376	.20	85	90	72
	SV-Acc.					86	87	71

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 95% Δ-3, untreated.

*See Run CH-24 for explanation.

TABLE VIII (continued)

Run CH-28

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
12	1	76	0	94	.15	99	3	3
15	2	76	0	94	.15	94	6	5
20	3	76	0	94	.15	97	5	5
27	4	76	0	94	.15	94	8	7
36	P-1	76	0	94	.15	90	14	12
39	P-2	76	0	94	.15	85	14	11
42	P-3	76	0	94	.15	86	12	10
44	P-4	76	0	94	.15	89	11	10
	P-Acc.					87	10	9
Shut down for four hours.*								
59	5	76	1000	94	.16	98	84	80
64	SV-1	76	1000	376	.35	91	87	76
67	SV-2	76	1000	376	.35	91	87	77
70	SV-3	76	1000	376	.35	90	87	76
72	SV-4	76	1000	376	.35	92	89	79
	SV-Acc.					91	88	78

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 97% Δ-3, untreated.

*See Run CH-24 for explanation.

TABLE VIII (continued)

Run CH-29

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
12	1	75	875	94	.16	99	87	81
17	2	75	875	94	.16	99	91	85
20	3	75	875	94	.16	99	91	85
24	4	75	875	94	.16	99	89	83
36	P-1	75	875	94	.16	98	91	84
39	P-2	75	875	94	.16	98	91	84
42	P-3	75	875	94	.16	98	92	85
44	P-4	75	875	94	.16	97	90	83
	P-Acc.					98	90	83
Shut down for four hours.*								
50	5	75	1000	94	.16	98	90	83
60	6	75	1000	94	.16	99	89	83
64	SV-1	75	1000	376	.36	98	86	79
66	SV-2	75	1000	376	.36	98	89	82
69	SV-3	75	1000	376	.36	98	88	81
72	SV-4	75	1000	376	.36	97	87	80
	SV-Acc.					98	88	81

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 94% Δ-3, untreated.

*See Run CH-24 for explanation.

TABLE VIII (continued)

Run CH-30

Time on Stream (hours)	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
13	75	1000	94	.15	97	69	64
17	75	1000	94	.15	95	70	63
21	75	1000	94	.15	83	72	57
24	75	1000	94	.15	83	73	58
27	75	1000	94	.15	81	74	57
38	75	1000	94	.15	78	76	56
43	75	1000	94	.15	77	76	55
48	75	1000	94	.15	74	76	54
51	75	1000	94	.15	74	70	50
61	75	1000	94	.15	69	74	49
64	75	1000	94	.15	69	73	49
69	75	1000	94	.15	71	68	46
72	75	1000	94	.15	71	75	51
75	75	1000	94	.15	72	74	51
85	75	1000	94	.15	67	73	47
89	75	1000	94	.15	62	74	44
93	75	1000	94	.15	67	74	47
99	75	1000	94	.15	84*	70	56

(continued)

*No readily apparent reason for the sudden increase in the conversion and yield.

TABLE VIII (continued)

Run CH-30 (continued)

Time on Stream (hours)	Temp. (°C.)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
110	75	1000	94	.15	82	79	63
114	75	1000	94	.15	80	80	60
118	75	1000	94	.15	81	80	61
126	75	1000	94	.15	84	81	65
134	75	1000	94	.15	78	80	60
137	75	1000	94	.15	81	78	60
141	75	1000	94	.15	80	80	61
147	75	1000	94	.15	76	78	57
157	75	1000	94	.15	69	76	50
160	75	1000	94	.15	71	77	53

Catalyst: 141.3 gms (140 cc) of 1/8" Englehard .5% Rhodium.
Δ-3-Carene Feedstock: 95% Δ-3, untreated.

TABLE VIII (continued)

Run CH-31

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
12	1	75	1000	94	.14	100	88	85
15	2	75	1000	94	.14	100	89	86
21	3	75	1000	94	.14	100	90	87
26	4	75	1000	94	.14	100	91	87
35	5	75	1000	94	.14	99	91	87
36	P-1	75	1000	94	.14	99	91	87
39	P-2	75	1000	94	.14	100	91	87
42	P-3	75	1000	94	.14	100	91	88
44	P-4	75	1000	94	.14	100	92	88
	P-Acc.					100	91	88
Shut down for four hours.*								
51	6	75	1000	94	.16	99	86	83
59	7	75	1000	94	.16	99	91	87
64	SV-1	75	1000	376	.07	100	90	87
66	SV-2	75	1000	376	.07	100	91	87
70	SV-3	75	1000	376	.07	100	91	88
72	SV-4	75	1000	376	.07	100	91	88
	SV-Acc.					100	91	88

Catalyst: 300 gms (224 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 96% Δ-3, untreated.

*See Run CH-24 for explanation.

TABLE VIII (continued)

Run CH-32

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	$LHSV_1$ (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
12	1	75	750	94	.16	100	88	83
17	2	75	750	94	.16	100	90	84
21	3	75	750	94	.16	100	89	85
28	4	75	750	94	.16	100	92	87
36	P-1	75	750	94	.16	100	92	87
39	P-2	75	750	94	.16	100	92	87
42	P-3	75	750	94	.16	100	91	87
44	P-4	75	750	94	.16	100	93	89
	P-Acc.					100	92	87
Shut down for four hours.*								
49	5	75	1000	94	.16	100	91	87
60	6	75	1000	94	.16	100	96	91
64	SV-1	75	1000	376	.19	100	95	90
66	SV-2	75	1000	376	.19	100	94	89
68	SV-3	75	1000	376	.19	100	94	89
70	SV-4	75	1000	376	.19	100	94	89
72	SV-5	75	1000	376	.19	100	95	90
	SV-Acc.					100	94	89

Catalyst: 300 gms (224 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 95% Δ-3, untreated.

*See Run CH-24 for explanation.

TABLE VIII (continued)

Run CH-33

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
13	1	75	370	94	.15	97	78	72
16	2	75	370	94	.15	100	79	75
20	3	75	370	94	.15	99	82	77
28	4	75	370	94	.15	99	79	76
36	P-1	75	370	94	.15	96	76	70
39	P-2	75	370	94	.15	97	79	74
41	P-3	75	370	94	.15	97	79	74
44	P-4	75	370	94	.15	96	78	71
	P-Acc.					97	77	72
Shut down for four hours.*								
49	5	75	1000	94	.16	99	77	73
60	6	75	1000	94	.16	97	89	83
64	SV-1	75	1000	376	.09	99	89	85
67	SV-2	75	1000	376	.09	99	88	85
71	SV-3	75	1000	376	.09	99	87	84
72	SV-4	75	1000	376	.09	98	89	84
	SV-Acc.					99	89	86

Catalyst: 300 gms (224 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 95% Δ-3 for first 16 hours, 96% Δ-3 for next 33 hours, and 97% Δ-3 for last 23 hours.

*See Run CH-24 for explanation.

TABLE VIII (continued)

Run CH-34

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
13	1	75	0	94	.16	100	0	0
15	2	75	0	94	.16	100	0	0
20	3	75	0	94	.16	100	3	2
23	4	75	0	94	.16	100	2	2
27	5	75	0	94	.16	98	2	2
36	P-1	75	0	94	.16	100	6	5
39	P-2	75	0	94	.16	100	6	6
41	P-3	75	0	94	.16	100	8	7
44	P-4	75	0	94	.16	98	7	7
	P-Acc.	75	0	94	.16	99	7	6
Shut down for four hours.*								
50	6	75	1000	94	.16	100	48	45
60	7	75	1000	94	.16	100	84	80
62	8	75	1000	94	.16	86	85	66
64	SV-1	75	1000	376	.42	79	88	63
66	SV-2	75	1000	376	.42	75	87	60
68	SV-3	75	1000	376	.42	69	88	55
70	SV-4	75	1000	376	.42	71	90	58
72	SV-5	75	1000	376	.42	69	90	57
	SV-Acc.					72	88	58

Catalyst: 300 gms (224 cc) of 1/8" Harshaw Ni-0104T.
Δ -3-Carene Feedstock: 95% Δ -3 for the first 60 hours and 91% Δ -3 for the remainder.

*See Run CH-24 for explanation.

TABLE VIII (continued)

Run CH-35

Time on Stream (hours)	Sample	Temp., (°C)	Press., (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv., Δ-3	% Yield Carane	% Carane in Prod.
12	1	60	1000	94	.19	80	81	63
14	P-1	60	1000	94	.19	82	82	66
16	P-2	60	1000	94	.19	84	83	67
18	P-3	60	1000	94	.19	79	83	64
20	P-4	60	1000	94	.19	78	84	64
	P-Acc. (6 hr.)					80	82	65
25	2	60	1000	94	.20	73	82	58
35	3	60	1000	94	.20	74	84	61
36	4	60	1000	376	.05	74	83	60
38	5	60	1000	376	.05	76	85	63
39	6	60	1000	376	.05	79	85	65
40	SV-1	60	1000	376	.05	84	87	71
41	SV-2	60	1000	376	.05	86	87	73
42	SV-3	60	1000	376	.05	89	87	75
43	SV-4	60	1000	376	.05	91	88	78
44	SV-5	60	1000	376	.05	91	88	78
	SV-Acc. (4 hr.)					88	87	74

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 97% Δ-3, untreated.

TABLE VIII (continued)

Run CH-36

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
12	1	60	750	94	.20	81	73	58
14	P-1	60	750	94	.20	78	74	56
16	P-2	60	750	94	.20	74	74	54
18	P-3	60	750	94	.20	76	77	57
20	P-4	60	750	94	.20	73	75	53
	P-Acc.	60	750	94	.20	76	77	57
23	2	60	1000	94	.20	76	82	60
27	3	60	1000	94	.20	73	85	61
35	4	60	1000	94	.20	69	87	58
36.5	5	60	1000	376	.09	65	88	55
37.5	6	60	1000	376	.09	72	87	61
38	7	60	1000	376	.09	74	86	62
39	8	60	1000	376	.09	81	87	69
40	SV-1	60	1000	376	.09	83	88	71
42	SV-2	60	1000	376	.09	81	88	70
44	SV-3	60	1000	376	.09	81	87	69
	SV-Acc.					81	88	70

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 97% Δ-3, untreated.

TABLE VIII (continued)

Run CH-37A

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
12	1	60	500	94	.20	56	58	32
14	P-1	60	500	94	.20	51	58	29
16	P-2	60	500	94	.20	47	60	28
18	P-3	60	500	94	.20	44	59	26
20	P-4	60	500	94	.20	43	59	25
	P-Acc.					47	59	27
25	2	60	1000	94	.20	61	58	41
35	3	60	1000	94	.20	47	76	35
37	4	60	1000	376	.12	47	75	35
38	5	60	1000	376	.12	56	80	43
39	6	60	1000	376	.12	59	79	45
40	SV-1	60	1000	376	.12	57	81	45
42	SV-2	60	1000	376	.12	57	82	46
44	SV-3	60	1000	376	.12	59	85	48
	SV-Acc.					59	83	47

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 97% Δ-3, untreated.

TABLE VIII (continued)

Run CH-37B

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
12	1	60	500	94	.19	53	63	33
14	P-1	60	500	94	.19	47	66	30
16	P-2	60	500	94	.19	50	68	33
18	P-3	60	500	94	.19	56	65	35
20	P-4	60	500	94	.19	58	62	35
	P-Acc.					55	65	35
25	2	60	1000	94	.19	73	67	48
35	3	60	1000	94	.19	55	83	45
38	4	60	1000	376	.11	68	85	57
40	SV-1	60	1000	376	.11	63	85	53
42	SV-2	60	1000	376	.11	56	85	47
44	SV-3	60	1000	376	.11	62	85	52
	SV-Acc.					59	85	50

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ -3-Carene Feedstock: 97% Δ -3, untreated.

VIII (continued)

Run CH-37C

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
11	1	60	500	94	.20	76	65	49
14	P-1	60	500	94	.20	73	67	48
16	P-2	60	500	94	.20	70	68	47
19	P-3	60	500	94	.20	67	67	44
20	P-4	60	500	94	.20	65	66	42
	P-Acc.					70	65	45
25	2	60	1000	94	.20	74	80	58
35	3	60	1000	94	.20	51	81	40
38	4	60	1000	376	.12	66	82	53
40	SV-1	60	1000	376	.12	72	85	60
42	SV-2	60	1000	376	.12	69	85	58
44	SV-3	60	1000	376	.12	63	86	53
	SV-Acc.					68	85	57

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 98% Δ-3, untreated.

TABLE VIII (continued)

Run CH-38

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
12	1	60	250	94	.20	67	52	34
14	P-1	60	250	94	.20	64	53	33
16	P-2	60	250	94	.20	63	53	33
18	P-3	60	250	94	.20	67	57	33
20	P-4	60	250	94	.20	66	53	34
	P-Acc.					67	53	35
26	2	60	1000	94	.20	71	75	53
39	4	60	1000	376	.22	70	82	57
40	SV-1	60	1000	376	.22	68	79	53
42	SV-2	60	1000	376	.22	70	81	56
44	SV-3	60	1000	376	.22	62	79	48
	SV-Acc.					71	81	56

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 98% Δ-3, untreated.

TABLE VIII (continued)

Run CH-39

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
12	1	60	0	94	.21	52	7	3
14	P-1	60	0	94	.21	48	7	3
16	P-2	60	0	94	.21	48	8	4
18	P-3	60	0	94	.21	47	9	4
20	P-4	60	0	94	.21	42	10	4
	P-Acc.					46	9	4
25	2	60	1000	94	.20	87	61	59
35	3	60	1000	94	.20	82	84	67
36	4	60	1000	376	.52	63	77	47
37	5	60	1000	376	.52	61	74	44
39	6	60	1000	376	.52	56	75	41
40	SV-1	60	1000	376	.52	55	75	40
42	SV-2	60	1000	376	.52	52	75	38
44	SV-3	60	1000	376	.52	50	76	38
	SV-Acc.					51	76	38

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 97% Δ-3, untreated.

TABLE VIII (continued)

Run CH-40

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
5	1	60	0	94	.20	92	2	2
13	2	60	0	94	.20	68	5	4
14	P-1	60	0	94	.20	65	6	4
16	P-2	60	0	94	.20	58	7	4
19	P-3	60	0	94	.20	48	9	4
20	P-4	60	0	94	.20	46	9	4
	P-Acc.					54	8	4
25	3	60	1000	94	.20	79	63	29
36	4	60	1000	94	.20	59	64	21
38	5	60	1000	376	.53	45	57	25
40	SV-1	60	1000	376	.53	40	58	23
42	SV-2	60	1000	376	.53	42	59	24
44	SV-3	60	1000	376	.53	40	60	23
	SV-Acc.					42	58	24

Catalyst: 300 gms (224 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 97% Δ-3, untreated.

TABLE VIII (continued)

Run CH-41

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
12	1	60	250	94	.20	68	56	37
14	P-1	60	250	94	.20	64	56	35
16	P-2	60	250	94	.20	64	58	36
18	P-3	60	250	94	.20	66	57	36
20	P-4	60	250	94	.20	62	57	34
	P-Acc.					64	57	36
26	2	60	1000	94	.20	66	80	51
36	3	60	1000	94	.20	59	86	50
40	SV-1	60	1000	376	.20	55	88	47
42	SV-2	60	1000	376	.20	55	88	47
44	SV-3	60	1000	376	.20	55	88	47
	SV-Acc.					55	89	47

Catalyst: 300 gms (224 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 97% Δ-3, untreated.

TABLE VIII (continued)

Run CH-42

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
12	1	60	500	94	.20	61	66	39
14	P-1	60	500	94	.20	57	66	37
16	P-2	60	500	94	.20	51	67	33
18	P-3	60	500	94	.20	48	67	32
20	P-4	60	500	94	.20	48	69	32
	P-Acc.					50	67	33
26	2	60	1000	94	.20	62	82	49
36	3	60	1000	94	.20	46	87	39
38	4	60	1000	376	.12	51	87	44
40	SV-1	60	1000	376	.12	51	88	44
42	SV-2	60	1000	376	.12	49	88	42
44	SV-3	60	1000	376	.12	50	89	43
	SV-Acc.					51	89	44

Catalyst: 300 gms (224 cc) of 1/8" Harshaw Ni-0104T.
Δ -3-Carene Feedstock: 97% Δ -3, untreated.

TABLE VIII (continued)

Run CH-43

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
12	1	60	750	94	.19	88	80	69
14	P-1	60	750	94	.19	89	76	66
16	P-2	60	750	94	.19	83	78	63
18	P-3	60	750	94	.19	80	77	60
20	P-4	60	750	94	.19	77	79	60
	P-Acc.					82	77	62
25	2	60	1000	94	.20	74	82	59
35	3	60	1000	94	.20	67	88	57
38	4	60	1000	376	.10	79	89	69
40	SV-1	60	1000	376	.10	78	90	68
42	SV-2	60	1000	376	.10	82	91	73
44	SV-3	60	1000	376	.10	77	89	67
	SV-Acc.					78	91	69

Catalyst: 300 gms (224 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 97% Δ-3, untreated.

TABLE VIII (continued)

Run CH-44

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
12	1	60	1000	94	.20	72	83	58
14	P-1	60	1000	94	.20	67	84	55
16	P-2	60	1000	94	.20	65	87	55
18	P-3	60	1000	94	.20	60	86	50
20	P-4	60	1000	94	.20	58	87	49
	P-Acc.					61	86	51
26	2	60	1000	94	.20	52	88	45
35	3	60	1000	94	.20	47	93	43
37	4	60	1000	376	.08	66	91	59
39	5	60	1000	376	.08	76	98	72
40	SV-1	60	1000	376	.08	79	90	70
42	SV-2	60	1000	376	.08	75	90	66
44	SV-3	60	1000	376	.08	76	91	68
	SV-Acc.					76	91	67

Catalyst: 300 gms (224 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 97% Δ -3, untreated.

TABLE VIII (continued)

Run CH-45

Time Elapsed From Startup (hours)[1]	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
4	55	1000	112	.20	66	75	48
8	55	1000	112	.20	57	77	43
12	55	1000	112	.20	45	81	36
22	55	1000	112	.20	33	87	28
25	55	1000	112	.20	33	87	28
30	55	1000	112	.20	32	91	28
34	55	1000	112	.20	32	92	29
45[2]	55	1000	112	.20	34	88	29
48	55	1000	112	.20	46	86	39
51	55	1000	112	.20	54	81	43
53	55	1000	112	.20	55	83	44
57	55	1000	112	.20	50	85	42
60	55	1000	112	.20	47	85	39
70	55	1000	112	.20	40	89	34
72	55	1000	112	.20	40	94	91
74[3]	55	1000	112	.20	41	91	36
100	55	1000	112	.20	70	75	51
103	55	1000	112	.20	45	55	24
107	55	1000	112	.20	44	60	26
117	55	1000	112	.20	39	68	26
120	55	1000	112	.20	36	71	25
123	55	1000	112	.20	33	77	24
124[4]	55	1000	112	.20	32	76	24
128	55	1000	112	.20	43	72	30

(continued)

TABLE VIII (continued)

Run CH-45 (continued)

Time Elapsed From Startup (hours)[1]	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
132	55	1000	112	.20	41	67	26
140	55	1000	112	.20	36	70	25
144	55	1000	112	.20	38	74	26
147	55	1000	112	.20	37	75	27
149[5]	55	1000	112	.20	38	74	27
153	55	1000	112	.20	31	77	23
156	55	1000	112	.20	31	81	24
165	55	1000	112	.20	32	85	27
168[6]	55	1000	112	.20	32	84	26
198	55	1000	112	.20	29	81	23
203	55	1000	112	.20	26	82	21
213	55	1000	112	.20	25	79	19
216[7]	55	1000	112	.20	26	77	19
225	70	1000	112	.20	39	78	30
226	70	1000	112	.20	45	73	32
227	70	1000	112	.20	37	72	26
237	70	1000	112	.20	32	67	21
240	70	1000	112	.20	29	71	20
243	70	1000	112	.20	31	71	22
244	70	1000	112	.20	32	67	21

Catalyst: 187.4 gms (140 cc) of 1/8" Harshaw Ni-0104T.
(Notes on following page).

TABLE VIII (continued)

Run CH-45 (continued)

Notes:
1. Started the run with a Δ-3-carene feedstock, 97% pure and untreated.
2. Shut down for about one hour. Restarted with a Δ-3 feedstock washed with 5% NaOH, water washed, dried with silica gel and filtered.
3. Shut off the Δ-3 feed. Purge with H_2 at 90°C and 1000 psig for 25 hours. Restart at 98 hours with Δ-3 treated with a 2% solution of ferrous ammonium sulfate to try to remove peroxides, then caustic washed, water washed, dried with silica gel and filtered.
4. Changed to a Δ-3 feedstock just dried with silica gel and filtered.
5. Changed to a Δ-3 feedstock of which 20% had been air blown for about 10 hours at 85°C to try to increase peroxide content.
6. Shut off Δ-3 feed and purge with H_2 at 55°C and 1000 psig for 27.5 hours. Restart at 195.5 hours with a Δ-3 feed mixed for 15 minutes at room temperature with one volume of an aqueous solution containing 5% $Na_2S_2O_4$ and 5% $NaHSO_3$ per 11 volumes of Δ-3. (For peroxide removal).
7. Shut Δ-3 feed off and purge with H_2 at 70°C and 1000 psig for eight hours. Restart at 70°C with a new Δ-3-carene feedstock, 98% pure, treated two hours with the $Na_2S_2O_4$ - $NaHSO_3$ solution.

TABLE VIII (continued)

Run CH-46

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
3	1	73	1000	94	.19	98	60	57
4	2	71	1005	94	.19	99	59	57
6	3	71	1002	94	.20	98	60	57
9	4	71	1003	94	.20	95	61	58
13	5	71	1002	94	.19	92	60	55
15	6	71	1000	94	.20	89	63	55
24	7	71	1009	94	.18	84	65	54
26	8	71	1000	94	.20	81	61	48
	9(Acc.)*					81	62	50
28	10	71	748	94	.20	89	49	43
30	11	70	747	94	.20	87	49	41
32	12	71	746	94	.19	85	48	40
	13(Acc.)					86	48	41
34	14	71	500	94	.20	88	36	31
36	15	70	500	94	.20	86	36	30
38	16	70	500	94	.20	84	37	30
	17(Acc.)					85	36	30
47	18	69	1002	94	.20	79	57	44
49	19	71	254	94	.21	81	28	22
51	20	71	255	94	.20	74	24	18
53	21	71	254	94	.20	72	25	17
	22(Acc.)					74	25	18

(continued)

*Accumulative samples were obtained over the preceding two hours. Operating conditions were changed at this time to next values shown.

TABLE VIII (continued)

Run CH-46 (continued)

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
55	23	70	0	94	.22	67	13	9
57	24	69	0	94	.20	41	2	1
59	25	69	0	94	.21	34	0	0
	26(Acc.)					36	0	0
65	27	72	1005	94	.20	82	47	37
71	28	71	1005	94	.20	77	49	37
73	29	71	1006	94	.20	76	50	37
	30(Acc.)					76	50	37
76	31	59	1008	94	.20	72	51	36
78	32	59	1010	94	.19	69	52	35
80	33	59	1009	94	.20	66	54	35
	34(Acc.)					69	54	36
84	35	51	1008	94	.20	65	56	36
85	36	49	1008	94	.20	63	59	36
87	37	48	1008	94	.20	61	59	36
	38(Acc.)					62	59	36
95	39	69	1010	94	.20	68	53	36
97	40	81	1012	94	.19	76	52	39
100	41	81	1003	94	.20	76	48	36
102	42	81	1004	94	.20	75	50	37
	43(Acc.)					76	48	36
105	44	70	1002	38	.20	67	46	30
107	45	70	1001	38	.20	67	48	32
109	46	70	1002	38	.20	65	48	31
	47(Acc.)					66	48	31

(continued)

TABLE VIII (continued)

Run CH-46 (continued)

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
119	48	70	1000	94	.20	60	51	30
121	49	70	1000	94	.20	60	51	30
	50(Acc.)					61	51	31
123	51	70	1000	188	.20	60	52	31
125	52	70	1000	188	.20	60	54	31
127	53	70	1001	188	.20	61	54	32
	54(Acc.)					59	54	31
129	55	69	1000	376	.20	59	55	32
131	56	69	1000	376	.20	58	54	31
133	57	69	1000	376	.20	58	53	30
	58(Acc.)					58	54	31
143	59	70	1000	94	.20	56	52	28
145	60	70	1000	94	.20	56	51	28
	61(Acc.)					55	52	28
148	62	69	1000	94	.10	72	55	38
150	63	69	1000	94	.10	73	60	43
152	64	69	1000	94	.10	71	62	43
	65(Acc.)					72	60	42
155	66	69	1000	94	.06	79	61	47
158	67	69	997	94	.05	76	64	48
160	68	69	997	94	.05	77	63	47
	69(Acc.)					76	63	47

(continued)

TABLE VIII (continued)

Run CH-46 (continued)

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
167	70	70	1000	94	.20	45	48	21
170	71	70	1002	94	.15	52	50	25
172	72	70	1002	94	.15	58	53	30
174	73	70	1004	94	.15	59	53	30
	74(Acc.)					58	53	30
176	75	70	1000	94	.51	30	42	12
178	76	70	1000	94	.51	27	42	11
180	77	70	1000	94	.51	28	41	11
	78(Acc.)					28	41	11
183	79	69	1000	94	.21	37	43	16
193	80	69	1005	94	.19	41	50	20
196	81	69	1006	94	.20	37	52	19

Catalyst: 300 gms (224 cc) of 1/8" Harshaw Ni-0104T.
Δ-3-Carene Feedstock: 98% Δ-3, 2% myrcene, trace dipentene.

Notes: Feedstock treated with the aqueous solution of 5% $Na_2S_2O_4$ and 5% $NaHSO_3$ for three hours at 25°C (one volume soln. per 11 volumes of Δ-3), then water-washed, dried with silica gel and filtered. Enough feedstock treated for Run CH-47 also. Reactor cleaned with acetone and the catalyst bed purged with N_2 before starting.

TABLE VIII (continued)

Run CH-47

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ-3)	LHSV (hr^{-1})	% Conv. Δ-3	% Yield Carane	% Carane in Prod.
3	1	71	1002	94	.19	100	54	53
5	2	71	1006	94	.19	100	54	53
12	3	70	1004	94	.20	100	58	56
15	4	71	1000	94	.20	99	57	56
24	5	72	998	94	.21	97	58	55
26	6	72	997	94	.20	96	58	55
	7(Acc.)					96	57	54
28	8	72	754	94	.20	98	49	47
30(2)	9	71	755	--	--	97	49	47
34	10	70	502	94	.20	96	38	36
36	11	71	502	94	.20	95	43	43
38	12	71	503	94	.21	93	42	38
	13(Acc.)					94	40	47
47	14	70	999	94	.21	90	59	52
49	15	71	258	94	.20	85	32	27
51	16	71	259	94	.20	83	30	24
53	17	71	259	94	.20	82	29	23
	18(Acc.)					83	29	24
55	19	70	0	94	.21	84	18	15
57	20	69	0	94	.21	84	9	7
59	21	68	0	94	.22	55	22	12
	22(Acc.)					70	14	10

(continued)

TABLE VIII (continued)

Run CH-47 (continued)

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
61	23	71	755	94	.20	90	37	33
63	24	71	754	94	.20	88	37	32
65	25	71	752	94	.20	86	39	33
	26(Acc.)							
71	27	71	1000	94	.20	87	51	44
73	28	71	1000	94	.20	88	54	47
	29(Acc.)					86	51	43
76	30	61	1000	94	.20	79	56	43
78	31	60	1000	94	.19	78	55	42
80	32	60	1000	94	.19	77	55	43
	33(Acc.)					79	58	45
83	34	50	1000	94	.20	70	59	41
85	35	50	998	94	.21	67	61	40
87	36	50	996	94	.20	66	63	41
	37(Acc.)					66	63	40
95	38	69	1000	94	.19	79	69	46
97	39	81	998	94	.21	81	54	43
100	40	81	996	94	.20	82	52	42
102	41	81	997	94	.20	81	53	42
	42(Acc.)					81	51	41
105	43	71	998	38	.20	75	52	38
107	44	71	999	38	.19	74	54	39
109	45	71	997	38	.21	71	54	38
	46(Acc.)					72	54	39

(continued)

TABLE VIII (continued)

Run CH-47 (continued)

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
119	47	71	998	94	.21	63	59	37
121	48	70	1002	94	.19	69	59	40
	49(Acc.)					67	55	36
123	50	71	1003	188	.20	66	57	37
125	51	70	1008	188	.19	67	61	40
127	52	71	1001	188	.19	67	60	39
	53(Acc.)					68	61	41
129(3)	54	71	1001	376	.13	65	59	37
131	55	72	1002	376	.22	64	59	37
133	56	71	1001	376	.20	66	57	37
	57(Acc.)					65	57	37
143	58	70	998	94	.20	59	58	34
145	59	70	999	94	.20	59	58	33
	60(Acc.)					59	56	33
147	61	71	1000	94	.10	72	59	42
150	62	71	1000	94	.09	75	64	47
152	63	70	1005	94	.10	73	63	45
	64(Acc.)					74	64	47
155	65	70	1000	94	.05	87	63	54
158	66	70	997	94	.05	89	63	55
160	67	70	996	94	.05	88	60	52
	68(Acc.)					89	63	55

(continued)

TABLE VIII (continued)

Run CH-47 (continued)

Time on Stream (hours)	Sample	Temp. (°C)	Press. (psig)	H_2 Rate (SCF/gal Δ -3)	LHSV (hr^{-1})	% Conv. Δ -3	% Yield Carane	% Carane in Prod.
167	69	71	993	94	.19	55	68	31
169	70	71	1001	94	.15	60	56	33
172	71	71	1003	94	.15	63	58	36
174	72	71	1000	94	.15	62	59	36
	73(Acc.)					61	60	36
176	74	70	1002	94	.50	34	50	17
178	75	70	1001	94	.50	29	48	14
180	76	70	1000	94	.50	29	48	14
	77(Acc.)					31	46	14
183	78	70	999	94	.20	49	53	26
193	79	70	1000	94	.20	48	62	29
196	80	70	1003	94	.20	46	59	27
199	81	70	1006	94	.19	47	61	28

Catalyst: 300 gms (224 cc) of 1/8" Harshaw Ni-0104T. (From same batch used for CH-46, stored under N_2 until used).
Δ -3-Carene Feedstock: Same as feed for CH-46.

Notes: 1. See Run CH-46 for explanation.
2. Ran out of H_2 and pressure dropped. Δ -3 feed rate increased temporarily.
3. Pump trouble. Δ -3 feed rate dropped off temporarily.

TABLE IX. Results for the Effects of the Operating Variables on the Δ-3-Carene Conversion and Carane Yield During Hydrogenation with Corrections for Catalyst Changes. Run CH-46.

Pressure (psig)	Actual Conv.	Correction	Corrected Conv.	Actual Yield	Correction	Corrected Yield
1000	81%	0%	81%	62%	0%	62%
750	86	+1	87	48	0	48
500	85	+2	87	36	+2	38
250	74	+3	77	25	+7	32
0	36	+4	40	0	+10	10
Temperature (°C)						
81	76	+9	85	48	0	48
71	76	0	76	50	+2	52
59	69	+2	71	54	+2	56
49	62	+4	66	59	+1	60
H_2 Rate (SCF/gal Δ-3)						
38	66	-3	63	48	0	48
94	61	0	61	51	0	51
188	59	+2	61	54	0	54
376	58	+3	61	54	0	54
94	55	+5	60	52	0	52
Space Velocity (hr^{-1})						
.05	76	+5	81	63	0	63
.10	72	+2	74	60	0	60
.15	58	+11	69	53	0	53
.20	55	0	55	52	0	52
.51	28	+13	41	41	0	41

TABLE X. Results for the Effects of the Operating Variables on the Δ-3-Carene Conversion and Carane Yield During Hydrogenation with Corrections for Catalyst Changes. Run CH-47.

Pressure (psig)	Actual Conv.	Correction	Corrected Conv.	Actual Yield	Correction	Corrected Yield
1000	96%	0%	96%	57%	0%	57%
750	86	+8	94	39	+3	42
500	94	+2	96	42	-1	41
250	83	+5	88	29	0	29
0	70	+6	76	14	+1	14
Temperature (°C)						
81	81	+10	91	51	-8	43
71	86	0	86	51	0	51
60	79	+1	80	58	-4	54
50	66	+4	70	63	-6	57
H_2 Rate (SCF/gal Δ-3)						
38	72	-5	67	54	0	54
94	67	0	67	55	0	55
188	68	+1	69	61	0	61
376	65	+3	68	57	0	57
Space Velocity (hr^{-1})						
.05	89	+4	93	63	0	63
.10	74	+2	76	64	0	64
.15	61	+7	68	60	0	60
.20	59	+1	60	56	0	56
.50	31	+9	40	46	0	46

TABLE XI. Experimental Data and Results for the Hydrobromination of 1-Methylcyclohexene.

Run No.	Reaction Time (hrs)	Temp. (°C)	Additive	Diluent	Concentration of Olefin (g-moles/liter)	% Conv. Olefin	% Yield Tert.-Bromide	% Yield Sec.-Bromide
HB-12	5.0	55-60	Benzoyl Peroxide	Hexane	0.643	15	23	77
HB-13	2.0	12-35	Diphenyl-amine	Acetic Acid	1.43	18	89	11
HB-14	2.0	100	Benzoyl Peroxide	Acetic Acid	0.877	7	100	0
HB-15	7.3	65-72	Benzoyl Peroxide	Cyclo-hexane	0.439	31	55	45

Notes: Product analyzed in a 6' x 1/4" Apiezon "N" chromatograph column at 125°C.
The HBr feed rate was about 0.001 g-moles/min.
The number of moles of olefin used in each run were as follows: 0.0834 g-moles in HB-12, 0.211 g-moles in HB-13 and -14, and 0.0928 g-moles in HB-15.

TABLE XII. Variation of Olefins in Product from the Elimination of Terpinyl Bromides.

Olefin	% Olefin in Product from Each Reaction		
	Alc. KOH at 75°C	Ag. NaOH at 150°C	Ag. NaOH at 125°C
3-p-menthene + 3-m-menthene	34.4	39.9	60.2
Trans-8-p-menthene + Trans-8-m-menthene	29.1	18.1	11.1
4(8)-m-menthene + Cis-8-m-menthene + Cis-8-p-menthene	15.7	20.5	16.8
4(8)-p-menthene	20.9	21.5	11.9

Notes: The bromide mixture for these reactions was from Run HB-28.
The NaOH concentration was 5 wt.% while the bromide concentration was about 10 wt.% for the runs with caustic. Reaction time -- 45 minutes.
The KOH concentration was about 3 wt.% and bromide about 10 wt.% for the run with KOH. Reaction time -- 120 minutes.

TABLE XIII. Experimental Data and Results for the Hydrobromination of Carane. Effect of Temperature.

Run No.	Reaction Temp. (°C)	Estimated Conv. of Carane (%)	Distribution of Bromides in Product (%)		
			Trans-8-bromo m-menthane	Mixture Trans-p- and Cis-m-isomers	Cis-8-bromo p-menthane
HB-49	5-16	95	46	21	32
HB-48	35-37	95	44	20	36
HB-47	62-68	95	53	21	26
HB-50	93-100	95	58	19	24

Notes: The carane concentration was 1.62 g-moles/liter (0.242 g-moles).
The diluent used was a solution of n-pentane, 1,1,4-trimethylcycloheptane and 2,6-dimethyloctane.
Benzoyl peroxide was used as the free radical initiator. Three moles/100 moles of carane.
The reaction time was 35 minutes with an HBr feed rate of 0.072 g-moles/min.
The product composition was determined from the corresponding esters.

TABLE XIV. Experimental Data and Results for the Hydrobromination of Carane. Effect of Initial Carane Concentration.

Run No.	Initial Carane Conc. (g-moles/l)	Estimated Conv. of Carane (%)	Distribution of Bromides in Product (%)		
			Trans-8-bromo m-menthane	Mixture Trans-p- and Cis-m-isomers	Cis-8-bromo p-menthane
HB-48	1.60	95	44	20	36
HB-51	1.16	85	43	17	40
HB-52	0.73	75	46	18	36
HB-59	0.30	60	40	17	43

Notes: The reaction was carried out at temperatures of 28-37°C.
The diluent was mainly n-pentane with lesser amounts of 1,1,4-trimethylcycloheptane and 2,6-dimethyloctane.
Benzoyl peroxide was used as a free radical generator. Three moles/100 moles of carane.
The amount of carane in each run was constant at 0.242 g-moles.
The reaction time was 35 min. with an HBr feed rate of 0.072 g-moles/min.
The product composition was determined from the corresponding esters.

TABLE XV. Experimental Data and Results for the Hydrobromination of Carane. Effect of Various Additives.

Run No.	Additive	Estimated Conv. of Carane (%)	Distribution of Bromides in Product (%)		
			Trans-8-bromo m-menthane	Mixture Trans-p & Cis-m isomers	Cis-8-bromo p-menthane
HB-48	Benzoyl Peroxide	95	44	20	36
HB-54	Lauroyl Peroxide	95	49	18	33
HB-53	Cumene Hydroperoxide	95	48	21	31
HB-57	Benz. Peroxide + UV Radiation	95	44	20	36
HB-55	UV Radiation	95	42	15	43
HB-56	None	95	43	14	43
HB-58	Diphenylamine	95	43	14	43

Notes: The reactions were carried out at temperatures of 33-36°C.
The initial carane concentration in each run was 1.62 g-moles/l. (0.242 g-moles).
The amount of each additive used was 3 moles/100 moles of carane.
The UV radiation was generated from a Sylvania germacidal lamp. The reactor with the quartz window was used.
The reaction time was 35 minutes with an HBr feed rate of 0.072 g-moles/minute.
The product composition was determined from the corresponding esters.

TABLE XVI. Experimental Data and Results for the Esterification of Cyclohexyl Bromide.

Run No.	Temp. (°C)	Reaction Time (hrs)	Acetate[1] Salt	Solvent	Initial Conc. Bromide (g-moles/l)	% Conv. of Bromide	% Yield[2] Ester
E-2	74	1.0	Silver	Abs. EtOH	0.73	12	25
E-3	74	1.5	Sodium (hydrate)	Abs. EtOH	1.62	0	--
E-4	100	3.5	Sodium (hydrate)	Glac. HAc.	1.62	6	0
E-5	74	1.5	Silver	Abs. EtOH	0.74	95	7
E-6	110	5.0	Potassium	Glac. HAc.	1.62	16	25
E-7	30-90	10.0	Potassium	10% HAc.	1.49	48	5
E-8	74	2.5	Silver	Abs. EtOH	0.90	100	7
E-9	95	2.4	Silver	Glac. HAc,	0.90	100	55
E-10	95	7.0	Silver[3]	Glac. HAc.	0.90	65	23
E-11	104	2.5	Silver	Glac. HAc.	1.06	100	11
E-12	97	3.0	Silver	Glac. HAc.	1.62	100	26

Notes: 1. The acetate salts were used in 10% excess of the theoretical requirement.
2. The other products were mainly cyclohexene and probably some cyclohexyl-ethyl ether.
3. The silver acetate for Run E-10 was synthesized from silver oxide and glacial acetic acid. The silver acetate for Runs E-11 and E-12 was synthesized from silver nitrate and sodium acetate. The reaction of Ag_2O + HAc is extremely violent.

TABLE XVII. Experimental Data and Results for the Esterification of the Terpinyl Bromide Mixtures.

	Preliminary Runs		
Run No.	E-26	E-27	E-28
Operating Conditions (1)			
Initial Bromide (2) Concentration (g-moles/l.)	0.87	0.48	0.25
Temperature (°C)	112	112	112
Reaction Time (min.)	60	60	60
Overall Product Composition, % (3)			
Olefins	69	77	79
Esters + Unknowns	31	23	21
Distribution of Esters and Unknowns			
Unidentified Ester	4	1	1
Trans-8-m-menthyl acetate	49	54	53
Cis-8-m-menthyl acetate + Trans-8-p-menthyl acetate	25	26	27
Cis-8-p-menthyl acetate	21	18	19
Unidentified Epoxide #1	--	--	--
Unidentified Lactone	--	--	--
Unidentified Epoxide #2	--	--	--

Notes are given at the end of the Table.

TABLE XVII. (continued)

	Temperature Effect						
Run No.	E-54	E-53	E-40	E-29	E-39	E-56	E-28
Operating Conditions (1)							
Initial Bromide (2) Concentration (g-moles/l.)	0.25	0.25	0.24	0.24	0.24	0.25	0.25
Temperature (°C)	2-3	11-14	16-19	25-30	37-43	65-70	112
Reaction Time (min.)	15	15	15	15	15	15	60
Overall Product Composition, % (3)							
Olefins	49	56	41	44	43	55	79
Esters + Unknowns	51	44	59	56	57	45	21
Distribution of Esters and Unknowns							
Unidentified Ester	--	1	5	4	3	2	1
Trans-8-m-menthyl acetate	38	42	48	46	47	34	53
Cis-8-m-menthyl acetate + Trans-8-p-menthyl acetate	42	36	33	33	35	30	27
Cis-8-p-menthyl acetate	20	21	12	13	13	8	19
Unidentified Epoxide #1	--	--	1	2	2	9	--
Unidentified Lactone	--	--	--	1	--	2	--
Unidentified Epoxide #2	--	--	--	1	--	15	--

Notes are given at the end of the Table.

TABLE XVII (continued)

	Concentration Effect							
Run No.	E-44	E-43	E-45	E-47	E-32	E-30	E-38	E-33
Operating Conditions[1]								
Initial Bromide[2] Concentration (g-moles/l.)	1.30	0.87	0.62	0.49	0.46	0.24	0.16	0.12
Temperature (°C)	20-25	19-28	21-29	25-30	20-27	25-30	22-26	25-28
Reaction Time (min.)	15	15	15	15	30	30	15	30
Overall Product Composition, %[3]								
Olefins	57	54	52	46	44	43	42	47
Esters + Unknowns	43	46	48	54	56	57	58	53
Distribution of Esters and Unknowns								
Unidentified Ester	2	3	3	2	5	3	3	2
Trans-8-m-menthyl acetate	50	46	48	38	49	47	48	47
Cis-8-m-menthyl acetate + Trans-8-p-menthyl acetate	30	33	30	26	32	34	34	36
Cis-8-p-menthyl acetate	13	13	13	21	13	13	12	13
Unidentified Epoxide #1	2	2	2	4	1	3	3	2
Unidentified Lactone	--	1	--	2	--	--	--	--
Unidentified Epoxide #2	2	2	2	7	--	--	--	--

Notes are given at the end of the Table.

TABLE XVII (continued)

	Reaction Time Effect					
Run No.	E-55	E-36	E-41	E-29	E-30	E-31
Operating Conditions[1]						
Initial Bromide[2] Concentration (g-moles/l.)	0.25	0.46	0.27	0.24	0.24	0.24
Temperature (°C)	24-29	25-30	22-27	25-30	25-30	25-30
Reaction Time (min.)	2	2	7	15	30	60
Overall Product Composition, %[3]						
Olefins	49	43	57	44	43	42
Esters + Unknowns	51	57	43	56	57	58
Distribution of Esters and Unknowns						
Unidentified Ester	2	6	2	4	3	4
Trans-8-m-menthyl acetate	35	49	48	46	47	47
Cis-8-m-menthyl acetate + Trans-8-p-menthyl acetate	33	31	29	33	34	34
Cis-8-p-menthyl acetate	8	11	15	13	13	13
Unidentified Epoxide #1	7	3	2	2	3	2
Unidentified Lactone	2	--	1	1	--	--
Unidentified Epoxide #2	12	--	3	1	--	--

Notes on following page.

TABLE XVII (continued)

	Miscellaneous		
Run No.	E-34[4]	E-35[5]	E-37[6]
Operating Conditions[1]			
Initial Bromide[2] Concentration (g-moles/l.)	--	0.24	0.24
Temperature (°C)	25-28	25-29	21-27
Reaction Time (min.)	50	35	15
Overall Product Composition, %[3]			
Olefins	50	53	45
Esters + Unknowns	50	47	55
Distribution of Esters and Unknowns			
Unidentified Ester	6	4	5
Trans-8-m-menthyl acetate	50	49	46
Cis-8-m-menthyl acetate + Trans-8-p-menthyl acetate	27	28	31
Cis-8-p-menthyl acetate	15	14	15
Unidentified Epoxide #1	2	3	2
Unidentified Lactone	--	--	--
Unidentified Epoxide #2	--	2	1

Notes are given at the end of the Table.

TABLE XVII (continued)

Notes: 1. The amount of silver acetate used was 10% in excess of the theoretical requirement.

2. The bromide for E-26 to E-29 came from Run HB-34; the bromide for Runs E-30 to E-45 came from Run HB-60; the bromide for Run E-47 came from HB-62; the bromide for remainder of runs came from a mixture of many bromide products.

3. Product composition based on area percent in a 10' x 1/4" PDEAS gas chromatograph column using flame detector.

4. The bromides were added to the reactor gradually.

5. The silver acetate was added to the reactor gradually.

6. A 2:1 mole ratio of silver acetate to bromide was used.

7. The medium in Runs E-53 and E-54 was propionic acid.

TABLE XVIII. Experimental Data and Results for the Hydrolysis of Cyclohexyl Bromide.

Run No.	Hydrolysis Agent	Initial Bromide[1] Conc. g-moles/l.	Temp. (°C)	Reaction Time (hrs)	% Conv. Bromide	% Yield Alcohol	% Yield Olefin
HCHB-1	1.2 wt. % NaOH	0.27	90	3.2	77	0	100
HCHB-2	Potassium Formate[2]	0.81	58	2.3	7	Trace	99
OH-9	Water[3] (with olefin)	1.38	205	7.8	100	0	100
OH-10	5% NaOH[4] (with HC)	1.14	180	2.0	90	Trace	99
OH-11	5% NaOH[5] (HC + emulsifier)	1.14	125	3.0	100	0	100
OH-12	5% NaOH (HC + emulsifier)	1.14	70	2.0	Very little reaction		
OH-13	5% NaOH (HC + emulsifier)	1.14	90	21.0	30	0	100
OH-14	5% NaOH (emulsifier)	1.14	100	8.8	Very little reaction		
OH-15	2.5% NaOH[6]	0.46	58	2.5	20	Trace	99
OH-16	15% Ag_2O (+ $NaNO_3$)[7]	2.02	90	2.5	20	20	80
OH-17	5% Ag_2O (+ $NaNO_3$)	0.67	85	7.0	56	0	100

TABLE XVIII (continued)

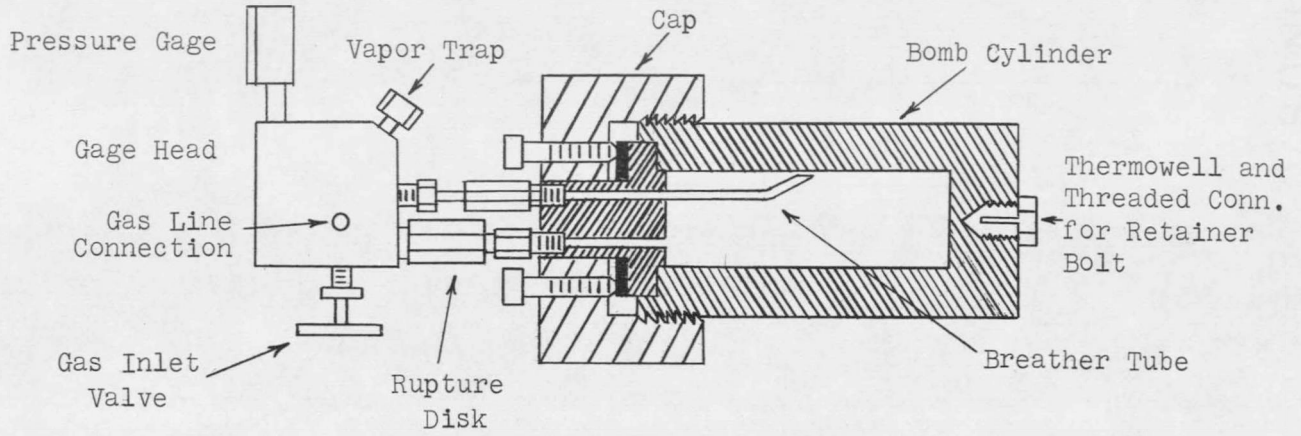
Run No.	Hydrolysis Agent	Initial Bromide[1] Conc. g-moles/l.	Temp. (°C)	Reaction Time (hrs)	% Conv. Bromide	% Yield Alcohol	% Yield Olefin
OH-18	6% Na_2CO_3	2.02	90	23.0	40	0	100
OH-20	2.5% NaOH	0.59	160	5 min.	10	0	100
OH-21	5% NaOH	1.16	160	15 min.	94	1	99
OH-22	10% NaOH	2.54	160	25 min.	95	0	100
OH-25	10% Ag_2O (+ $NaNO_3$)	0.75	60-90	4	100	34	66
OH-27	12% Ag_2O	1.00	65-70	10.5	90	2	98

Notes:
1. The initial cyclohexyl bromide concentration is based on the aqueous phase.
2. Potassium formate was made in the reactor from KOH + $HCOOCH_3$ in MeOH solvent. Bromide concentration based on MeOH.
3. Method patented by Benedictis et al. (53). Olefin used was 2,4,4-trimethyl-pentene-2, same number of moles as bromide.
4. HC stands for hydrocarbon diluent for bromide. Volume equivalent to bromide.
5. Method patented by Barnes et al. (54). Emulsifier used was sodium oleate. Volume of cyclohexane diluent equivalent to volume of bromide.
6. Acetone-water solution (1.5:1 acetone to water).
7. Equivalent amount of $NaNO_3$ present because Ag_2O was made in reactor from $AgNO_3$ + NaOH.

TABLE XIX. Experimental Data and Results for the Hydrolysis of Menthyl Acetate

Run No.	Initial Conc.[1] NaOH	Initial Conc. Acetate	Temp. (°C)	Reaction Time (hrs)	% Conv.[2] Acetate	% Yield Menthol
OH-42	2.50	0.23	120	13	88	100
OH-37	2.50	0.23	150	13	79	94
OH-39	2.50	0.23	190	13	98	97
OH-53	2.50	0.23	190	1	92	98
OH-55	2.50	0.23	190	2	96	98
OH-43	2.50	0.23	190	4	95	90
OH-45	2.50	0.23	190	8	96	94
OH-39	2.50	0.23	190	13	98	97
OH-44	0.25	0.23	190	13	97	98
OH-46	1.26	0.23	190	13	96	95
OH-39	2.50	0.23	190	13	98	97
OH-54	2.50	0.23	190-210	1	98	94
OH-56	2.64	0.48	200-245	0.25	75	100
OH-57	2.64	0.48	190	13	95	100
OH-58	2.92	1.08	190	13	98	100
OH-35[3]	----	0.13	95	28	1	100
OH-46[4]	2.50	0.46	95	20	10	100

Notes:
1. The initial concentrations of NaOH and menthyl acetate are based on the volume of water only, in g-moles/liter. The total volume of water + acetate was kept at 105 ml so mixing efficiency in the bomb would be constant.
2. The analysis of the product was done with a 6' x 1/4" Apiezon N GLC column which did not resolve the menthol product into its geometric isomers, simplifying the analysis.
3. Run OH-35 was an acid catalyzed (H_2SO_4) hydrolysis with water only.
4. Run OH-36 was carried out in a glass refluxing reactor, as was OH-35. All the other runs were carried out in the Parr bomb.



Parr Bomb and Gage Head

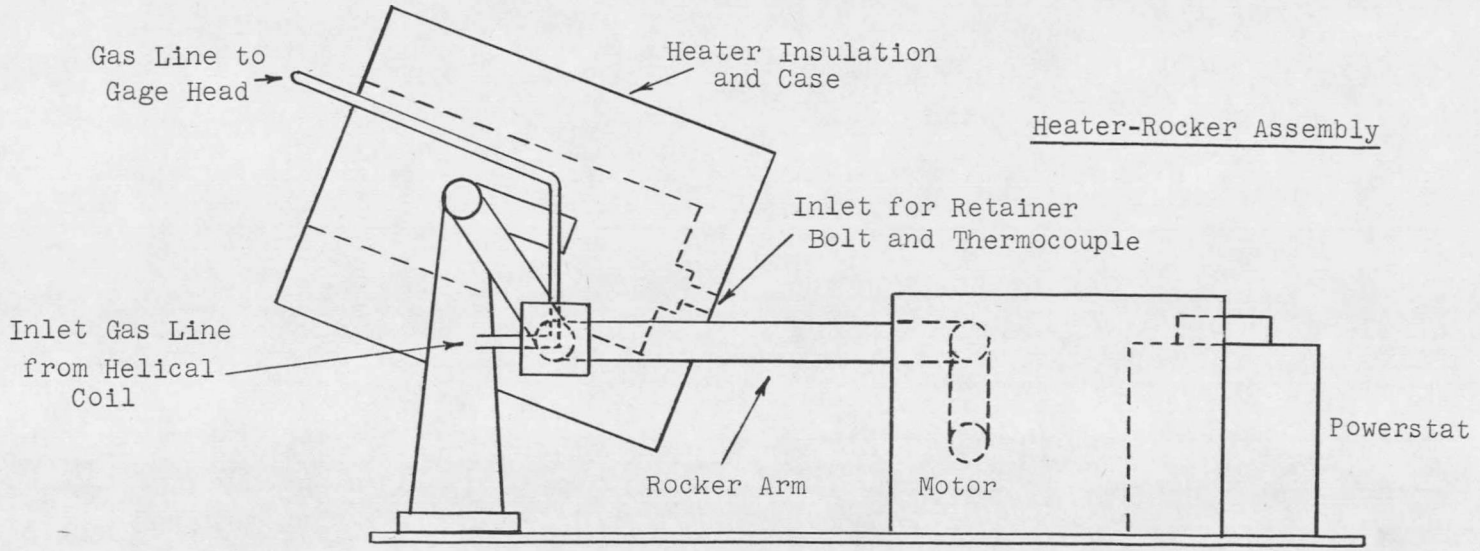


Figure 3. Parr Bomb Reaction Apparatus

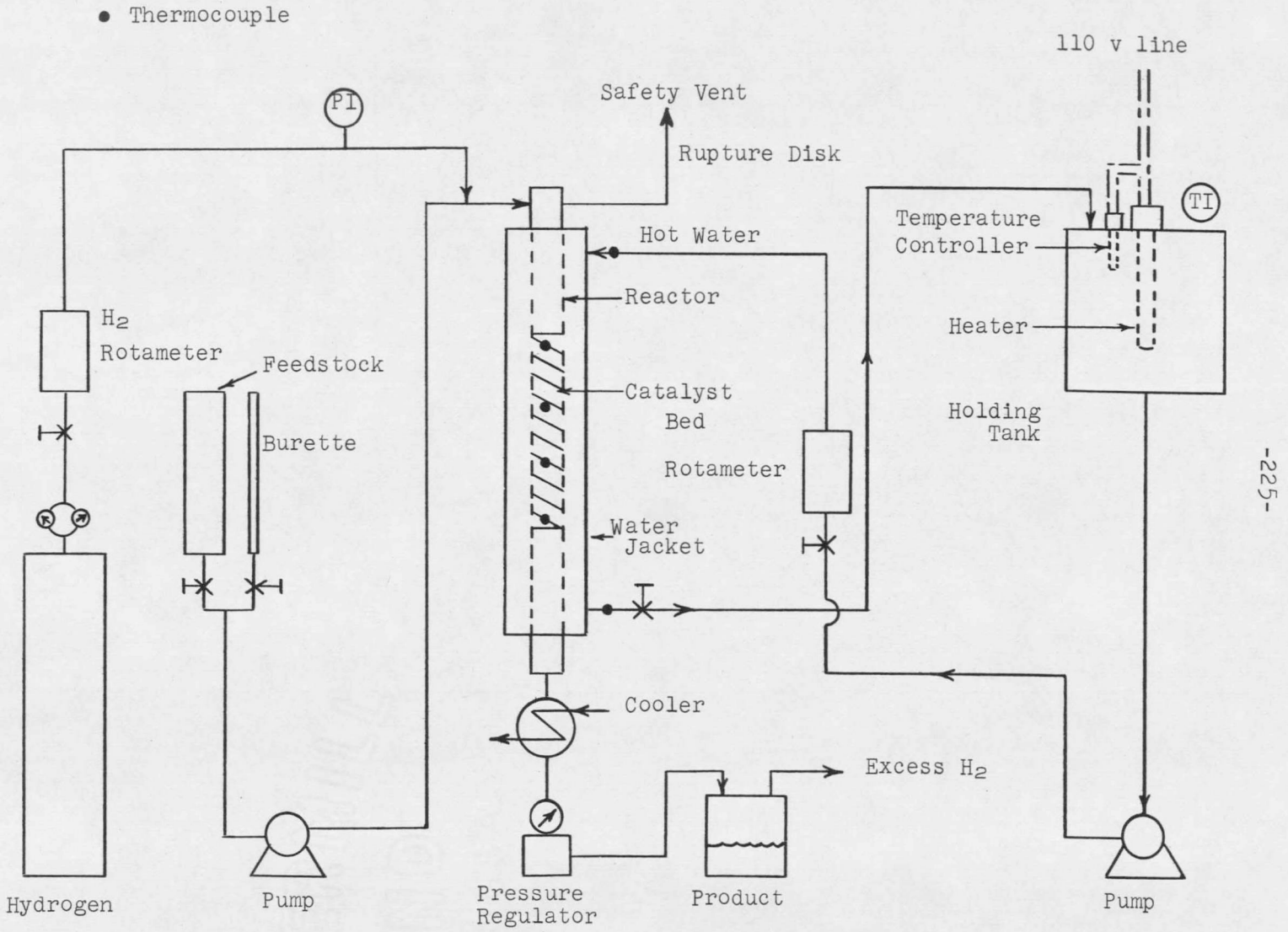


Figure 4. Schematic Diagram of the Hydrogenation Unit

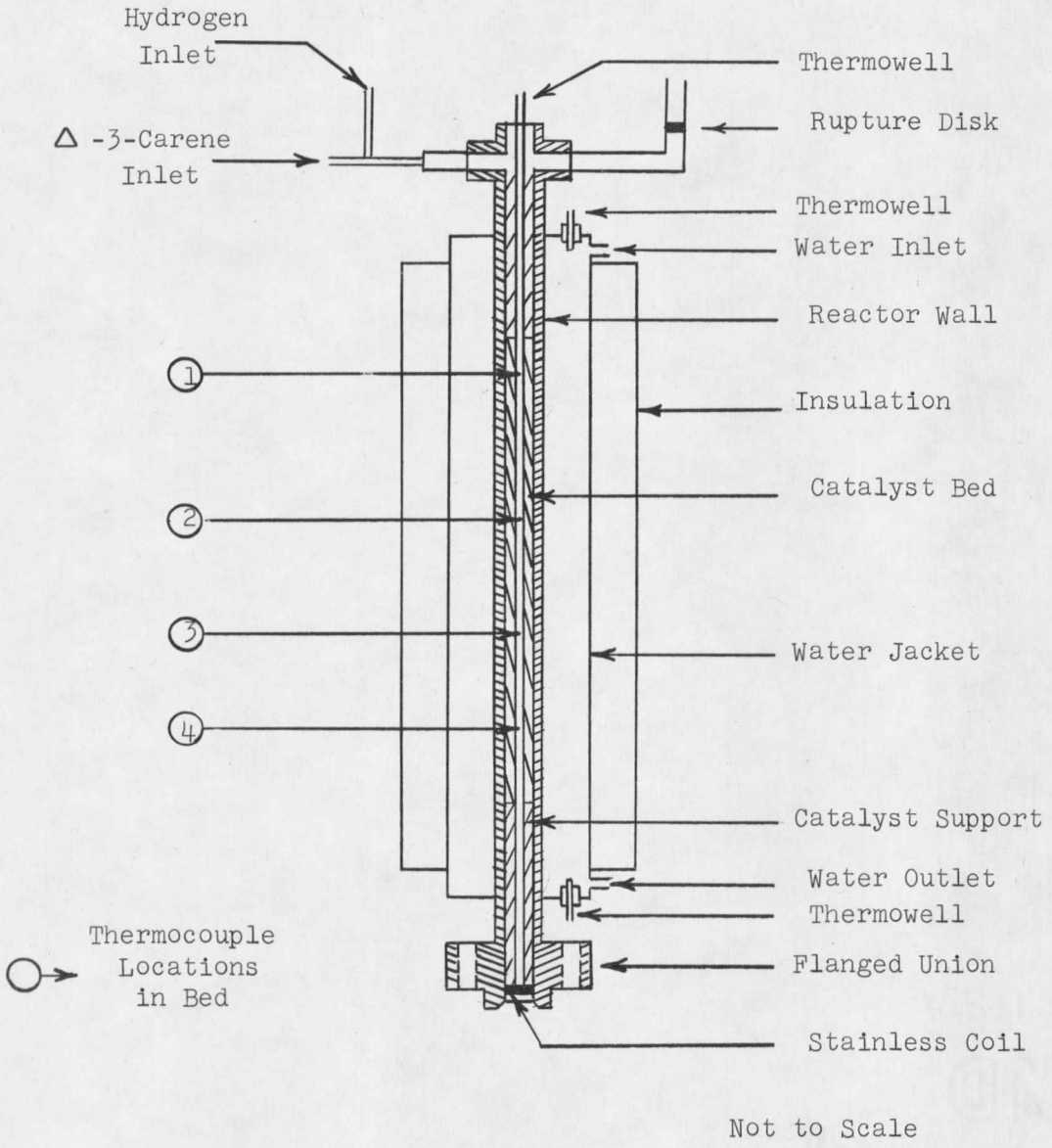


Figure 5. Detailed Diagram of the Fixed-Bed Reactor.

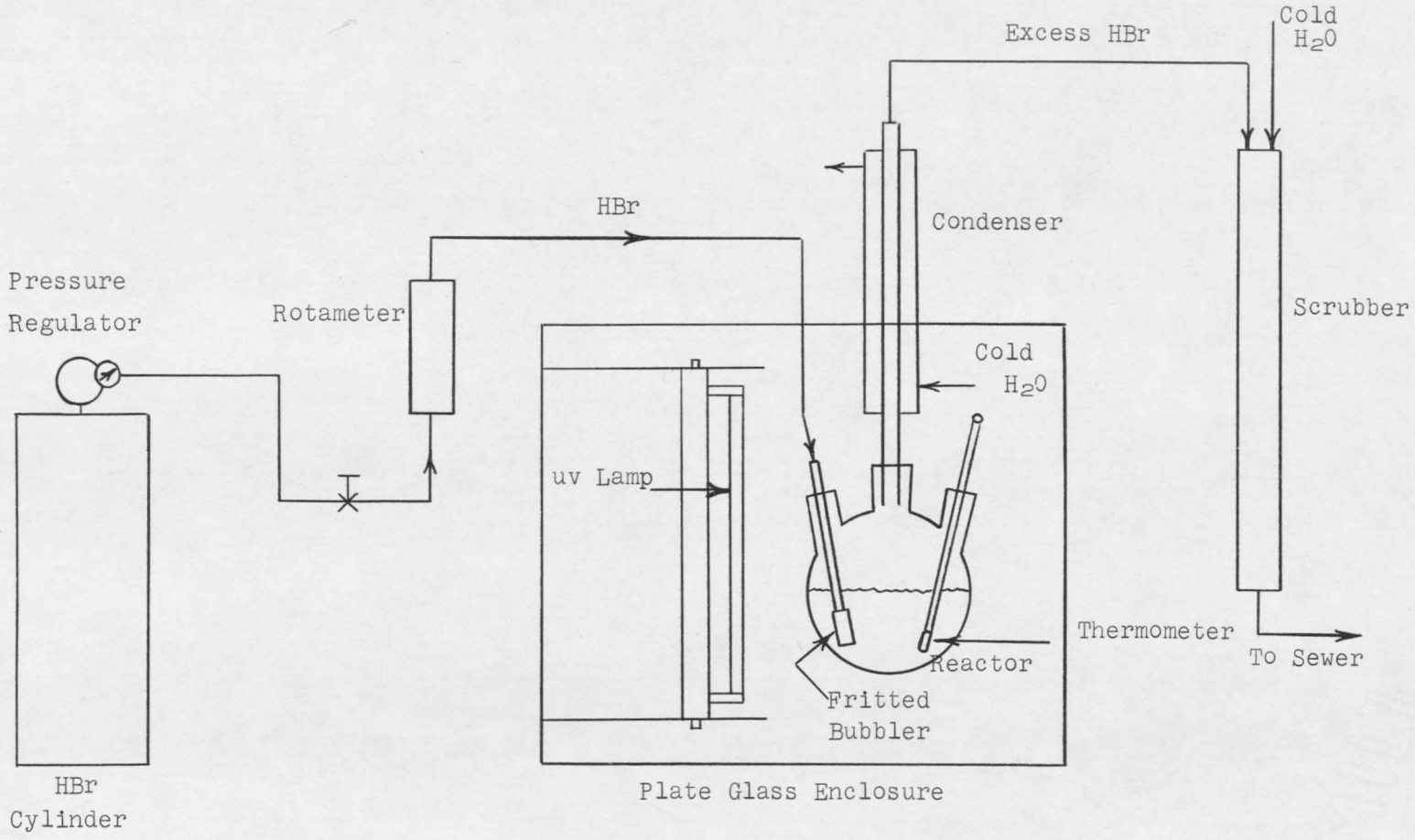


Figure 6. Flow Diagram of the Hydrobromination Reaction System.

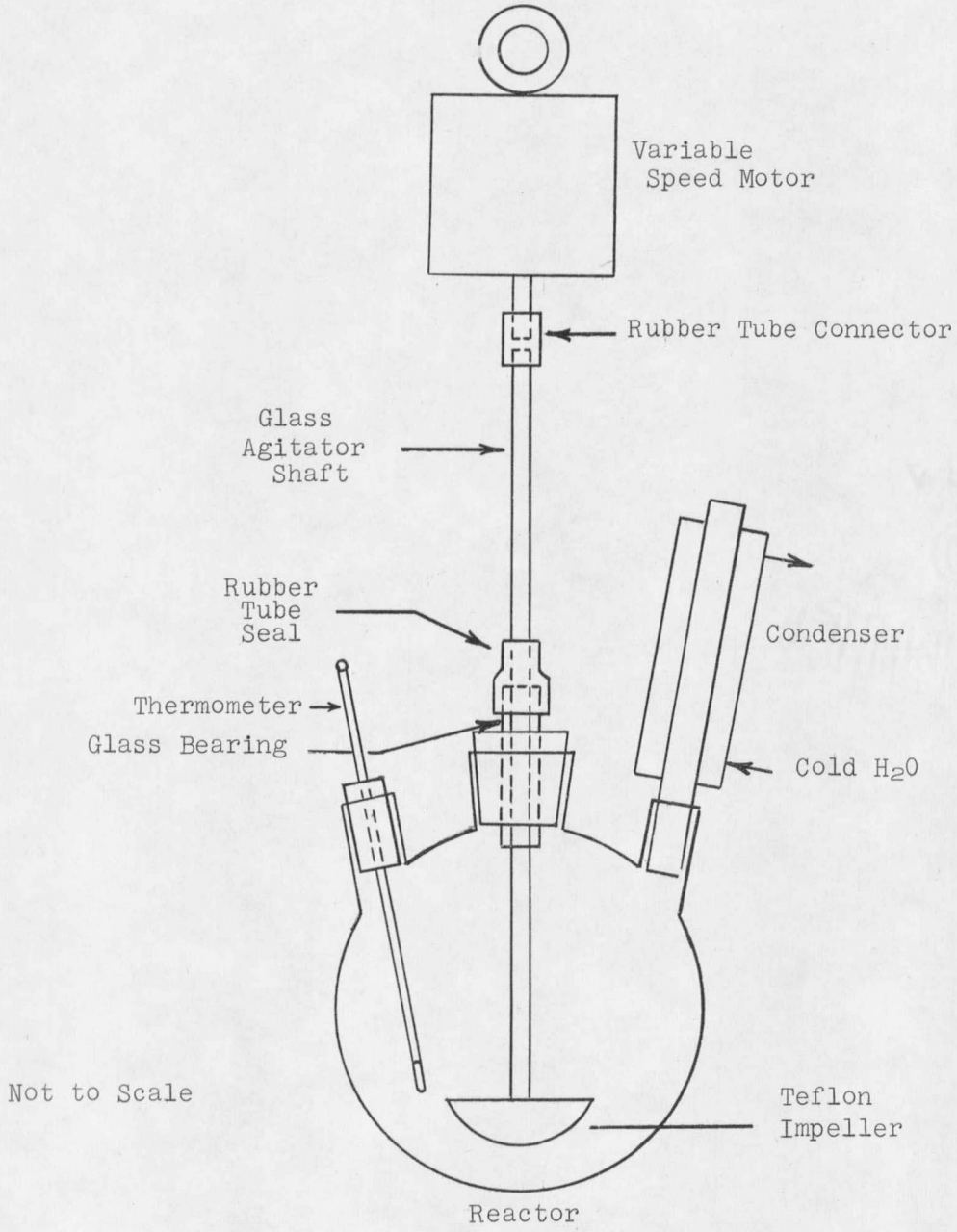
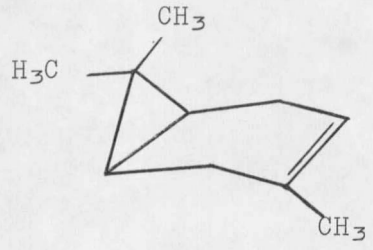
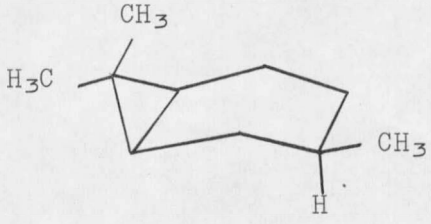


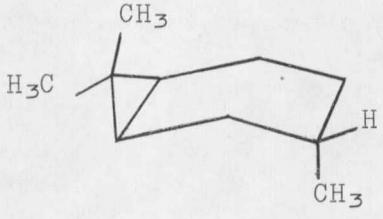
Figure 7. Schematic Diagram of the Esterification Reactor



Δ -3-Carene



Cis-Carane



Trans-Carane

Figure 8. Structural Comparison of Δ -3-Carene, Cis-Carane and Trans-Carane

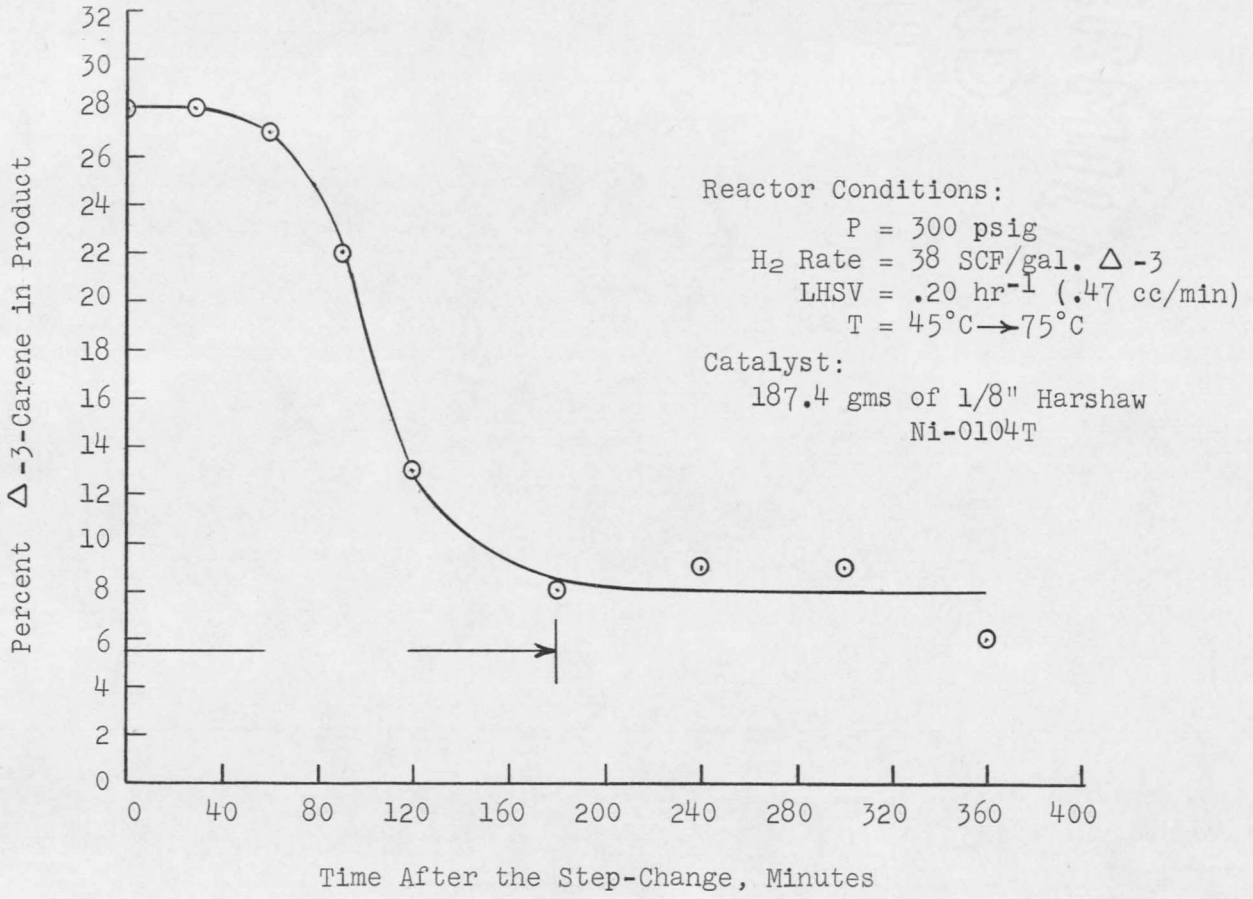


Figure 9. Response of Product Composition for a Step-Change in Temperature in the Hydrogenation Unit

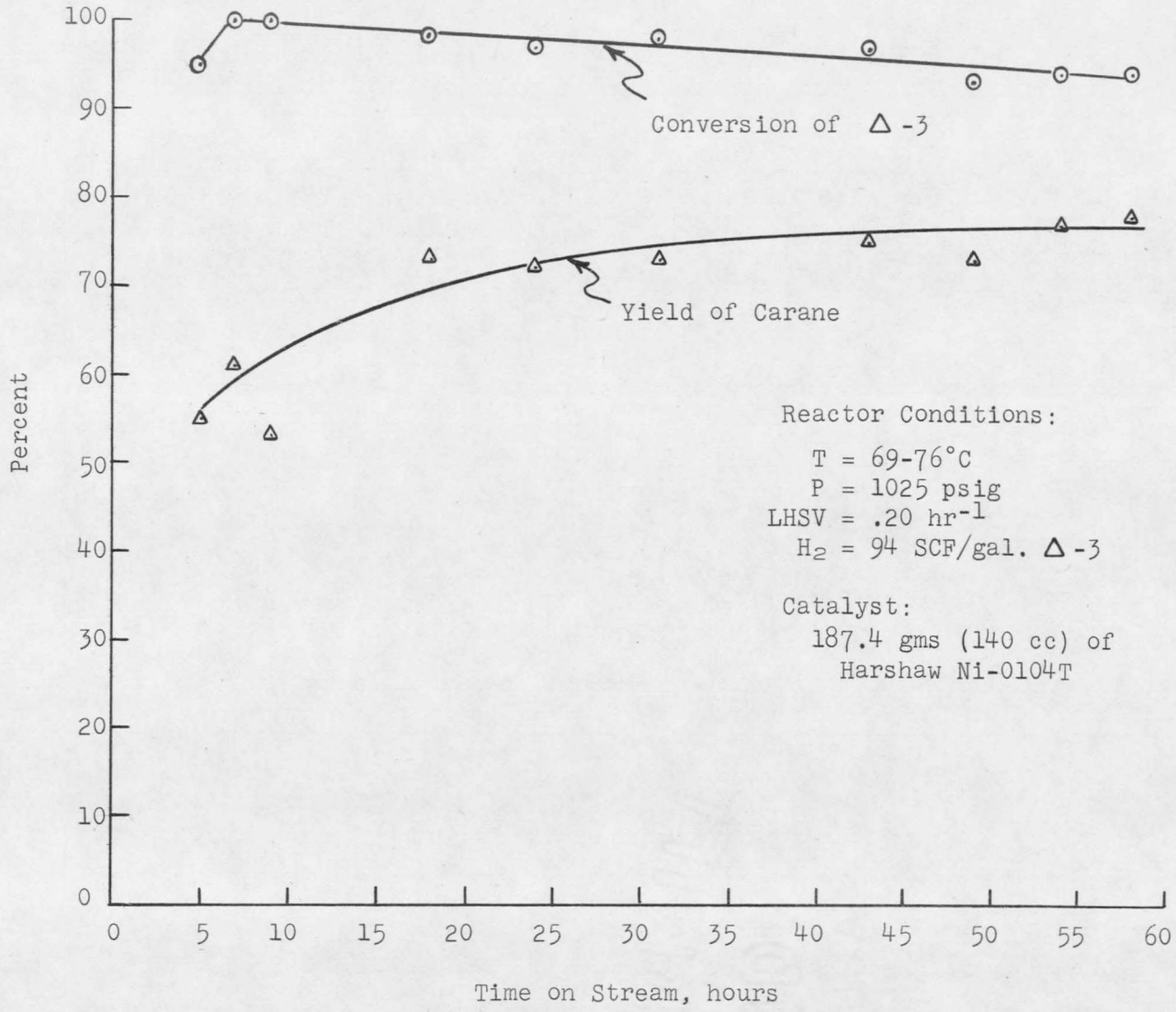


Figure 10. Effect of Catalyst Deactivation on the Conversion of Δ-3-Carene and the Yield of Carane During Hydrogenation in the Fixed-Bed Reactor

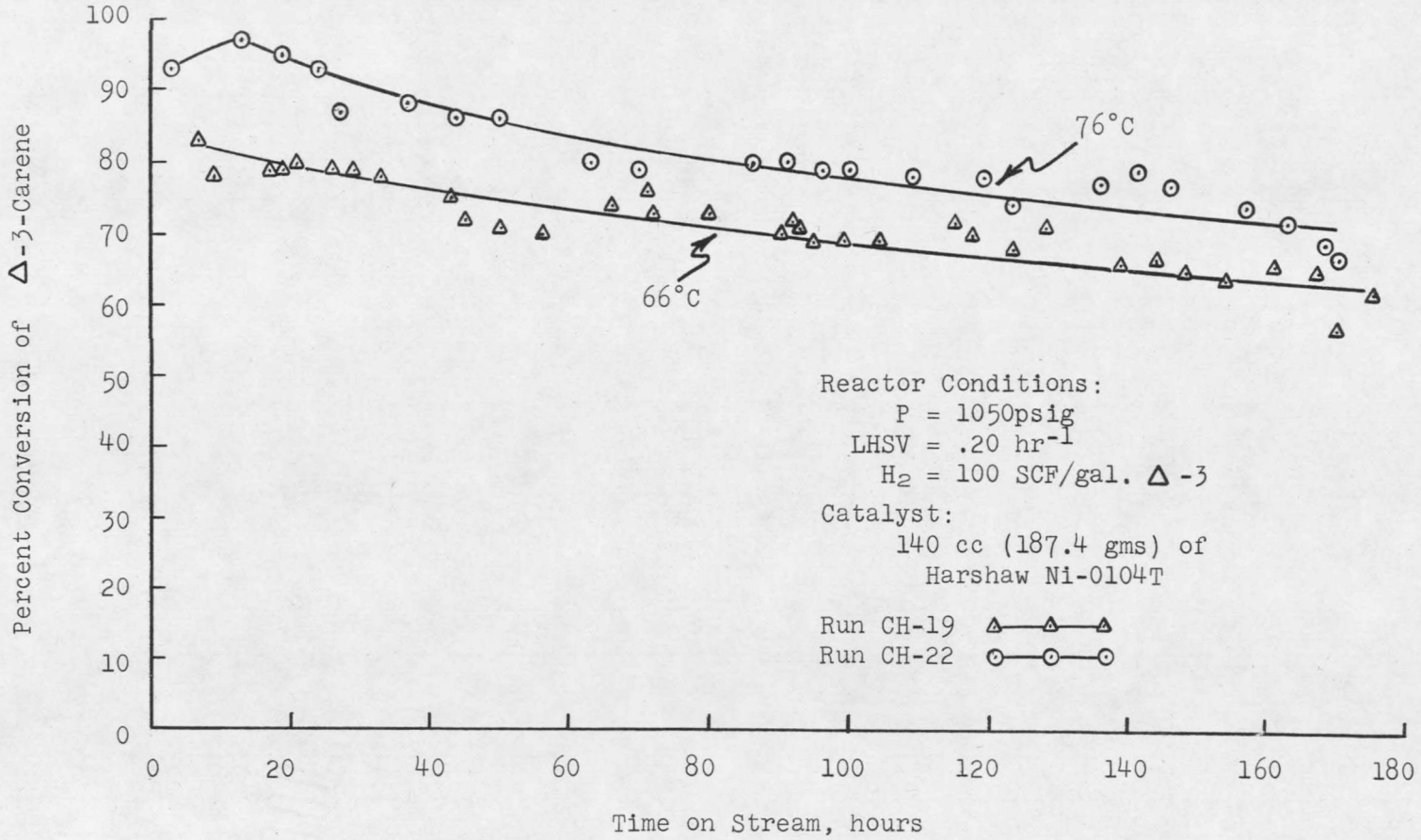


Figure 11. Effect of Catalyst Deactivation on the Conversion of Δ -3-Carene During Hydrogenation at 66°C and 76°C in the Fixed-Bed Reactor

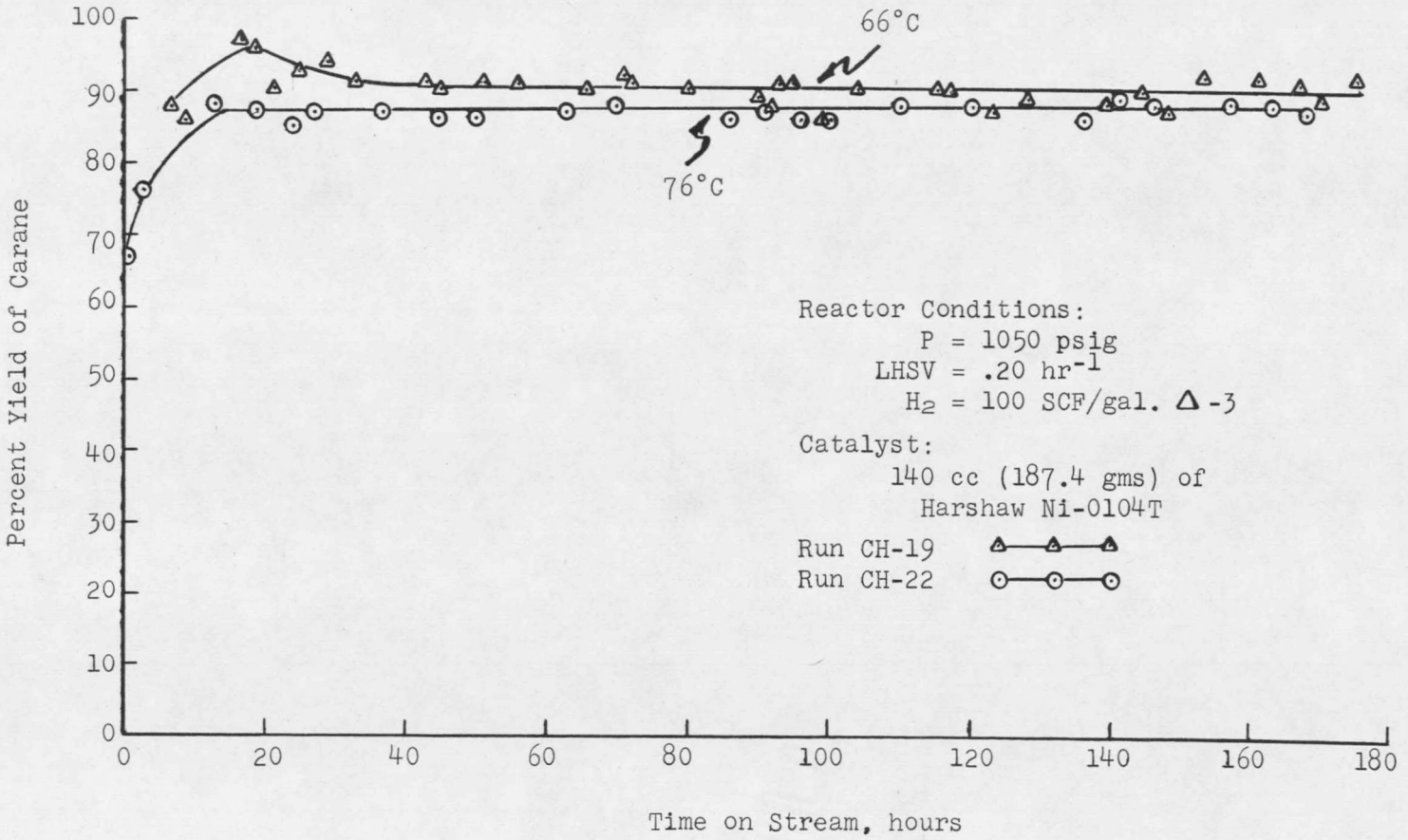


Figure 12. Effect of Catalyst Deactivation on the Yield of Carane During the Hydrogenation of Δ-3-Carene at 66°C and 76°C in the Fixed-Bed Reactor

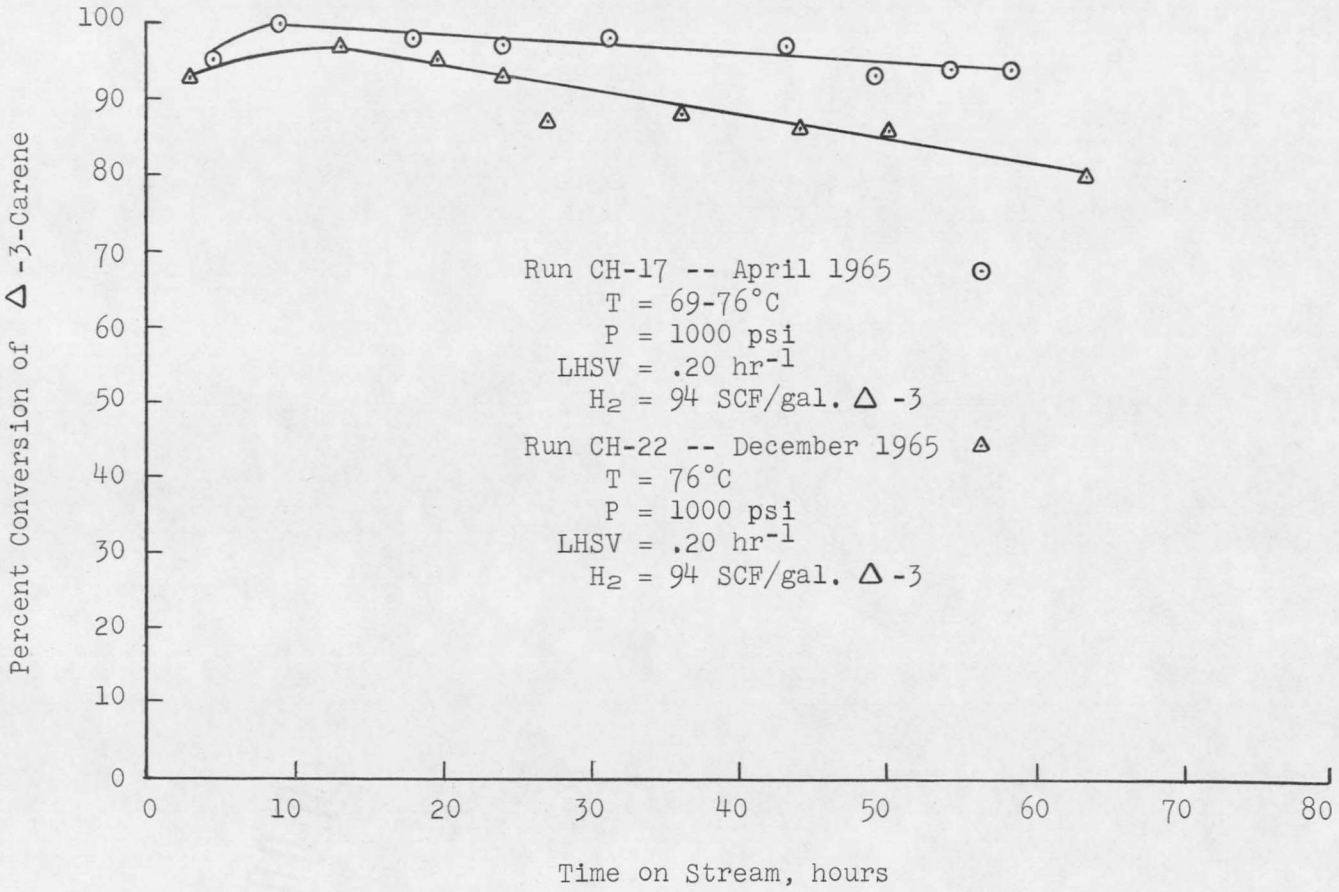


Figure 13. Effect of Partial Air Oxidation of the Harshaw Ni-0104T Catalyst Under Normal Ambient Conditions on the Conversion of Δ-3-Carene During Hydrogenation in the Fixed-Bed Reactor.

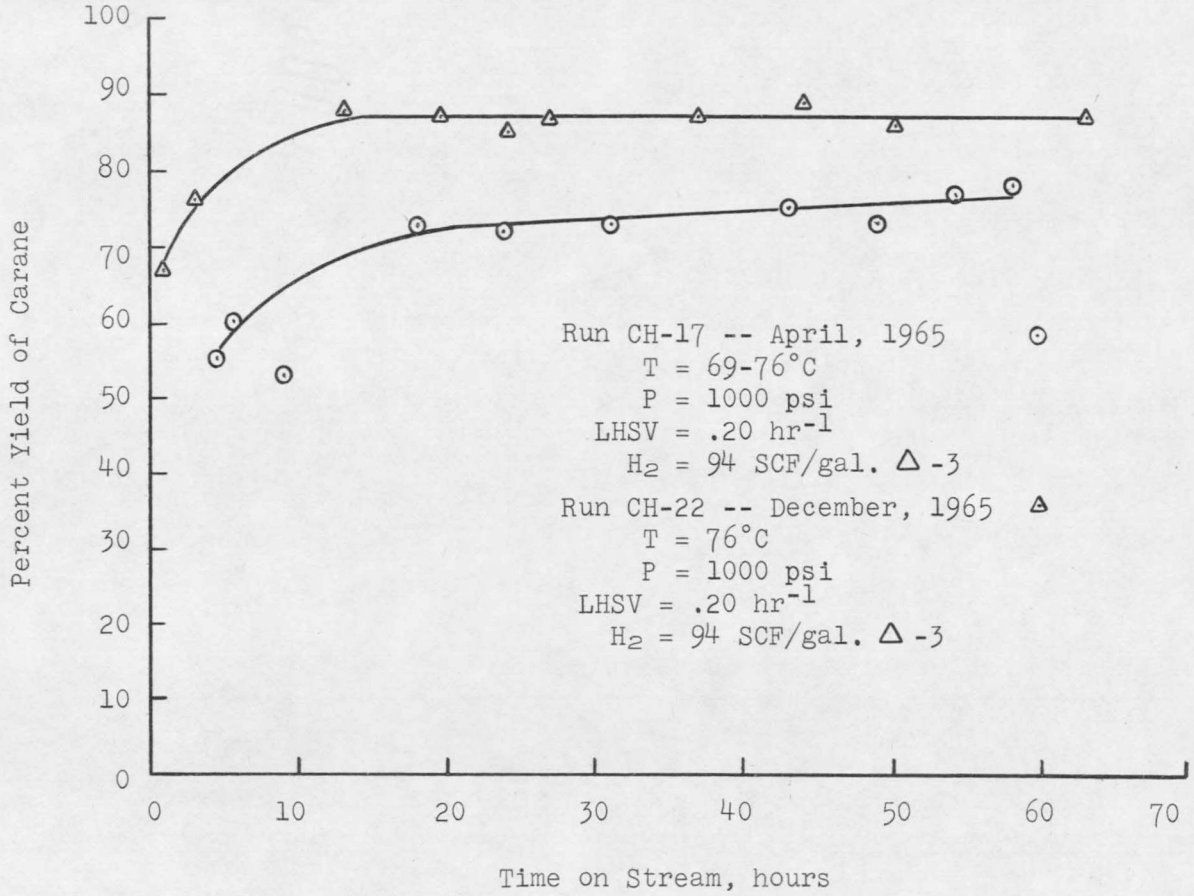


Figure 14. Effect of Partial Air Oxidation of the Harshaw Ni-0104T Catalyst Under Normal Ambient Conditions on the Yield of Carane During the Hydrogenation of Δ-3-Carene in the Fixed-Bed Reactor

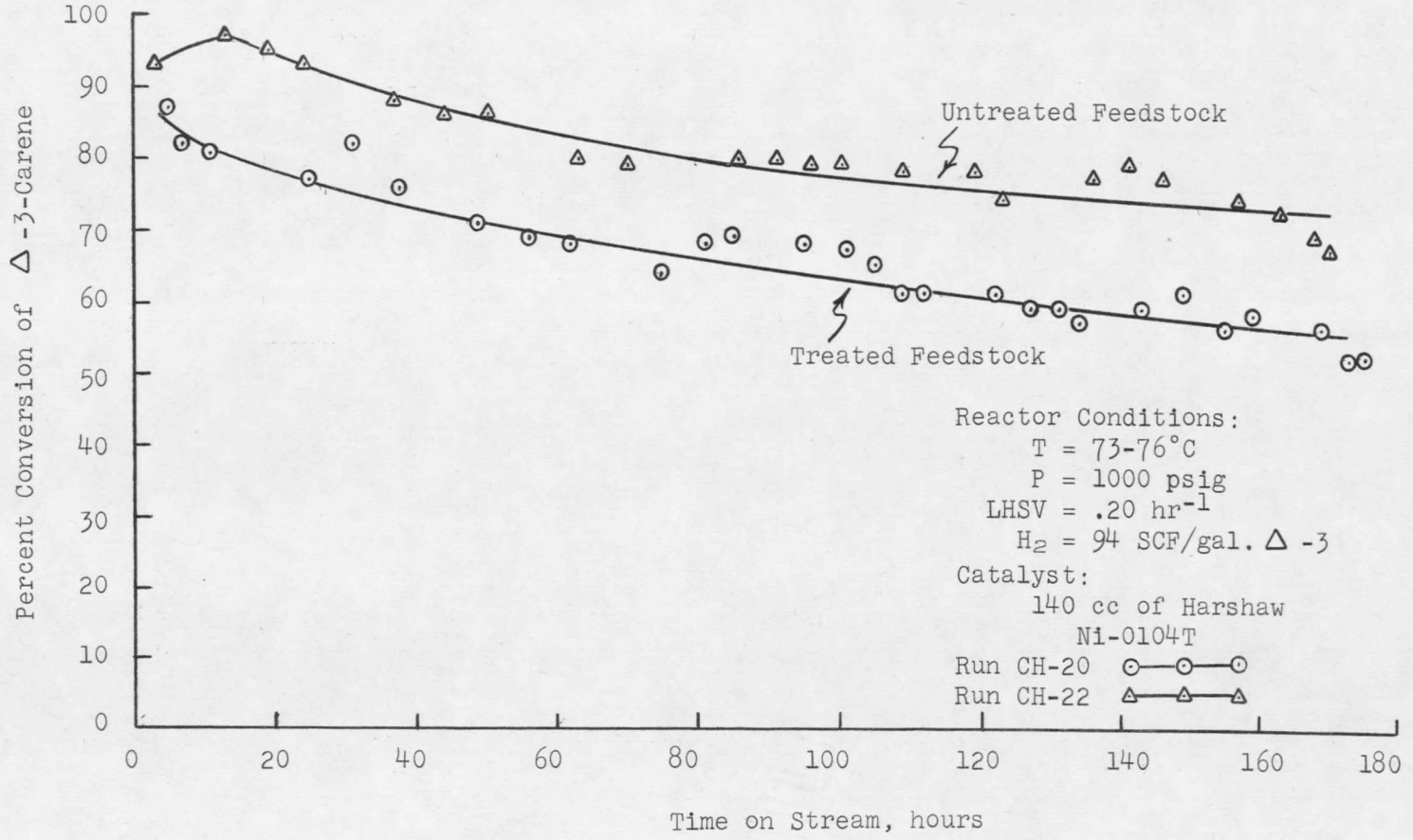


Figure 15. Effect of Pre-Treating the Reactor Feedstock with a Caustic Wash and for Moisture Removal with $CaSO_4$ on the Conversion of Δ-3-Carene During Hydrogenation in the Fixed-Bed Reactor

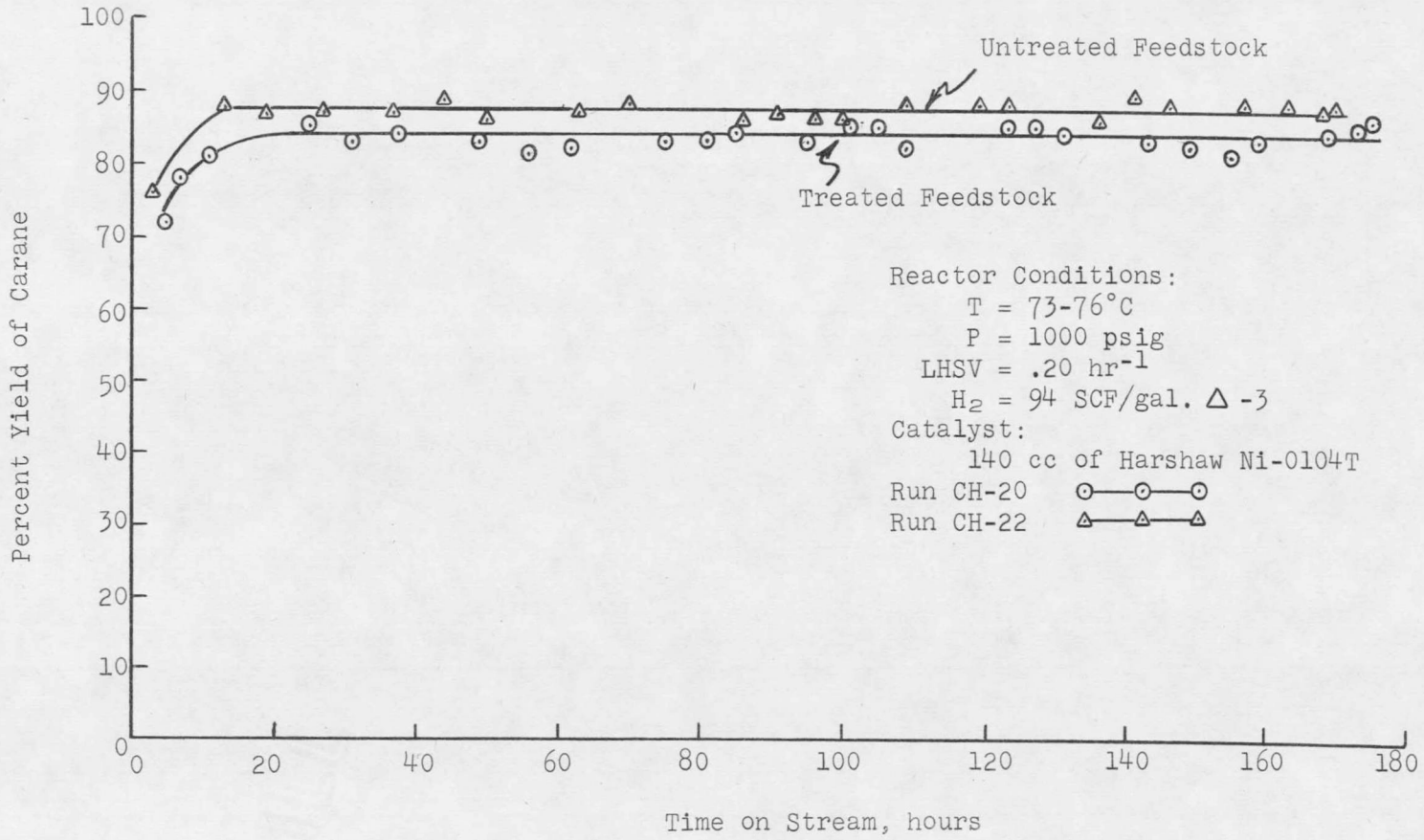


Figure 16. Effect of Pre-Treating the Reactor Feedstock with a Caustic Wash and for Moisture Removal with $CaSO_4$ on the Yield of Carane During the Hydrogenation of Δ-3-Carene in the Fixed-Bed Reactor

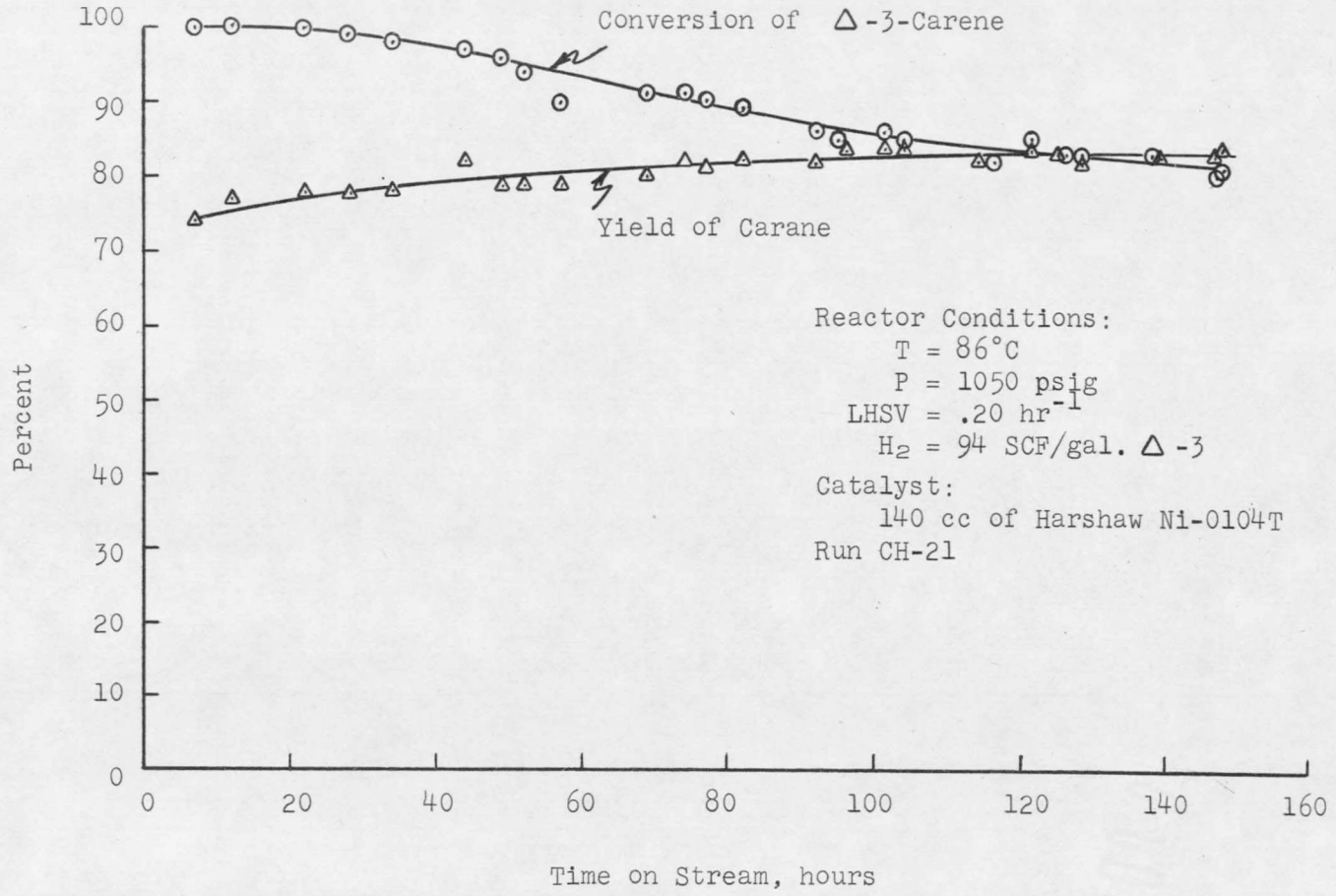


Figure 17. Effect of Catalyst Deactivation on the Conversion of Δ-3-Carene and the Yield of Carane During Hydrogenation at 86°C with Caustic Washed Feedstock

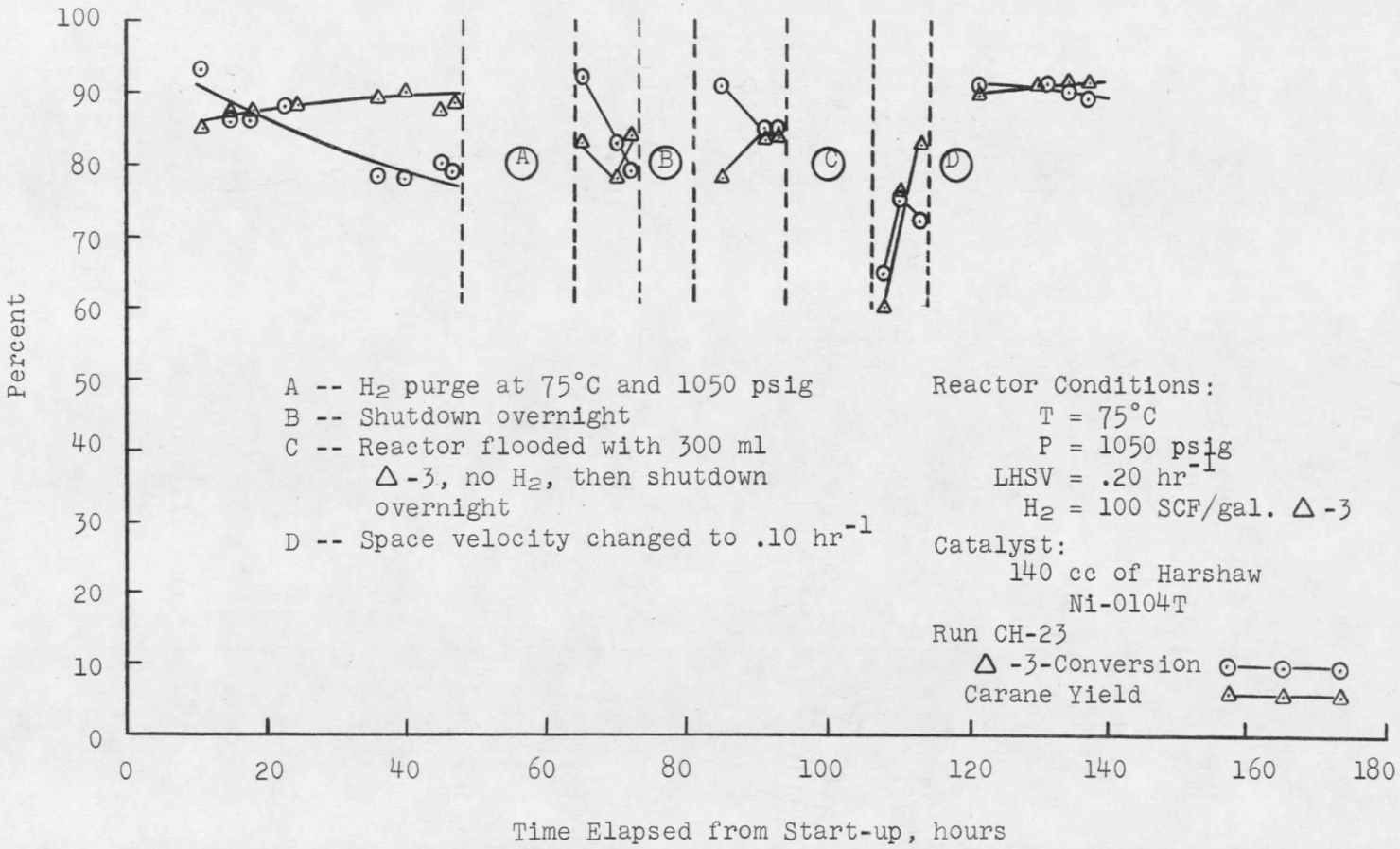


Figure 18. Effect of a Hydrogen Purge, a Δ-3-Carene Saturation of the Bed, and an Overnight Shutdown on the Hydrogenation Catalyst Activity and Selectivity

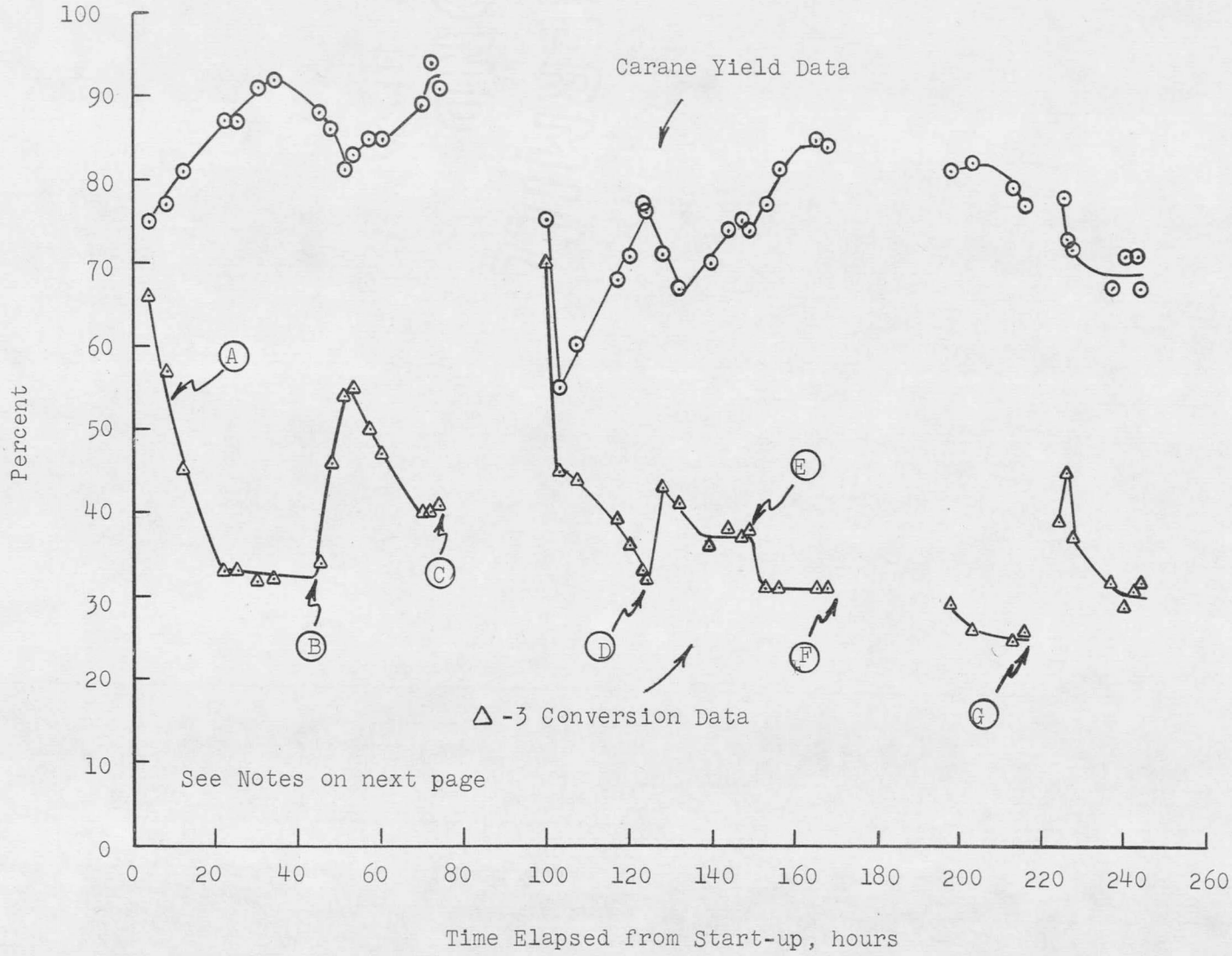


Figure 19. Effect of Hydrogen Purges and Various Types of Feedstock Pre-Treatments on the Activity and Selectivity of the Hydrogenation Catalyst

Notes for Figure 19.

Reactor Conditions:

T = 55°C
P = 1000 psig
LHSV = .20 hr^{-1}
H_2 = 112 SCF/gal. Δ-3

Catalyst:

140 cc of Harshaw Ni-0104T

Run CH-45

A. Run started with Untreated Δ-3-Carene Feedstock.
B. Changed to a feedstock treated with a 5% NaOH wash and water wash and then dried with silica gel.
C. Hydrogen purge at 90°C and 1000 psig for 25 hours. Restarted with Δ-3-carene feedstock washed with 2% solution of ferrous ammonium sulfate, caustic washed, water washed, and then dried with silica gel.
D. Changed to feedstock dried with silica gel only.
E. Added a feedstock blended (20%) with Δ-3-carene air-blown at 85°C for 10 hours. The feedstock was dried with silica gel.
F. Hydrogen purge at 55°C for 27.5 hours. Restarted with feedstock washed 15 min. at 25°C with an aqueous solution containing 5% $Na_2S_2O_4$ and 5% $NaHSO_3$, water washed and dried with silica gel.
G. Hydrogen purge at 70°C for eight hours. Feedstock treated two hours with the 5% $Na_2S_2O_4$ - $NaHSO_3$ solution, then dried.

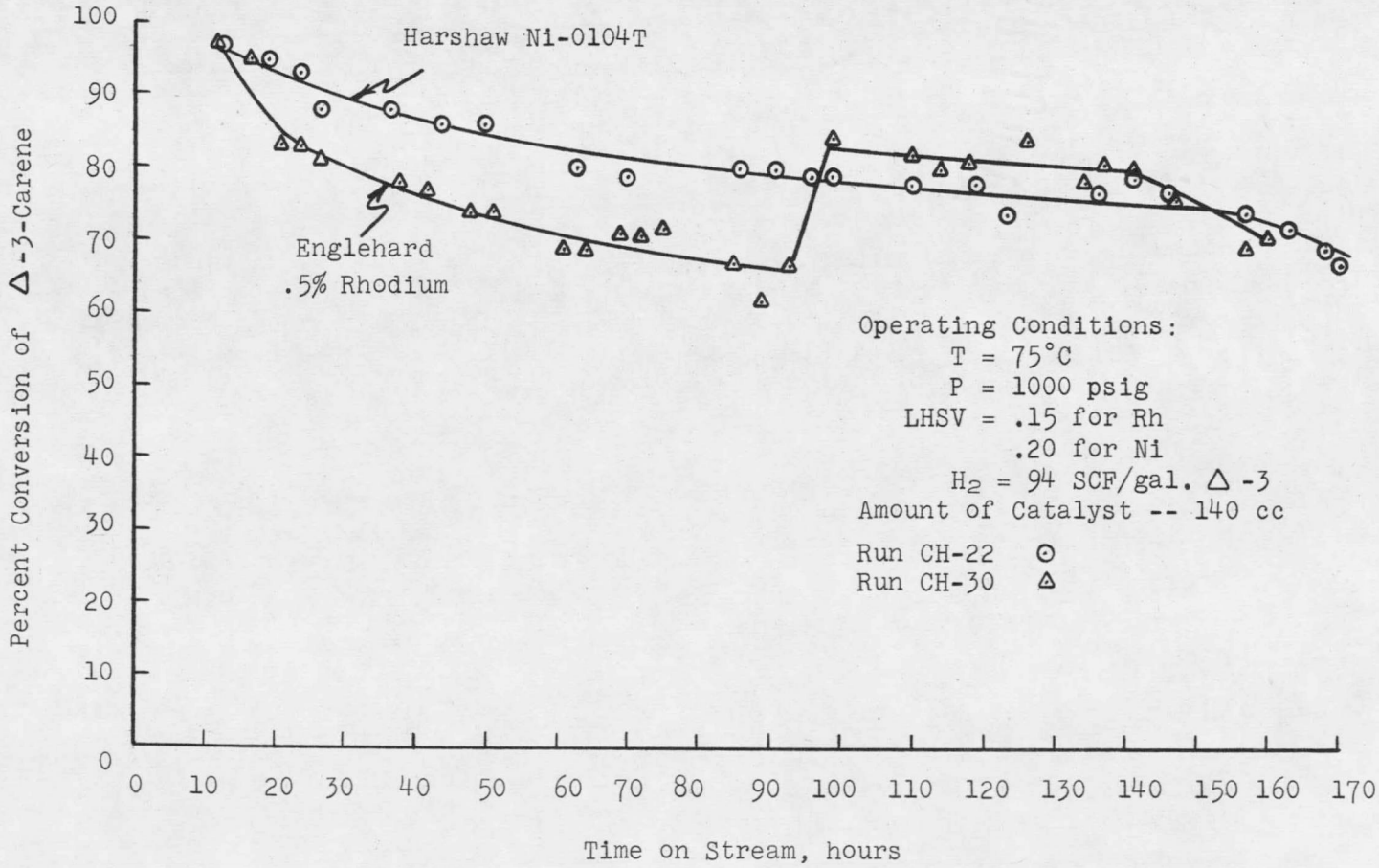


Figure 20. Comparison of the Activity of the Englehard Rhodium and Harshaw Ni-0104T Nickel in the Fixed-Bed Hydrogenation Reactor

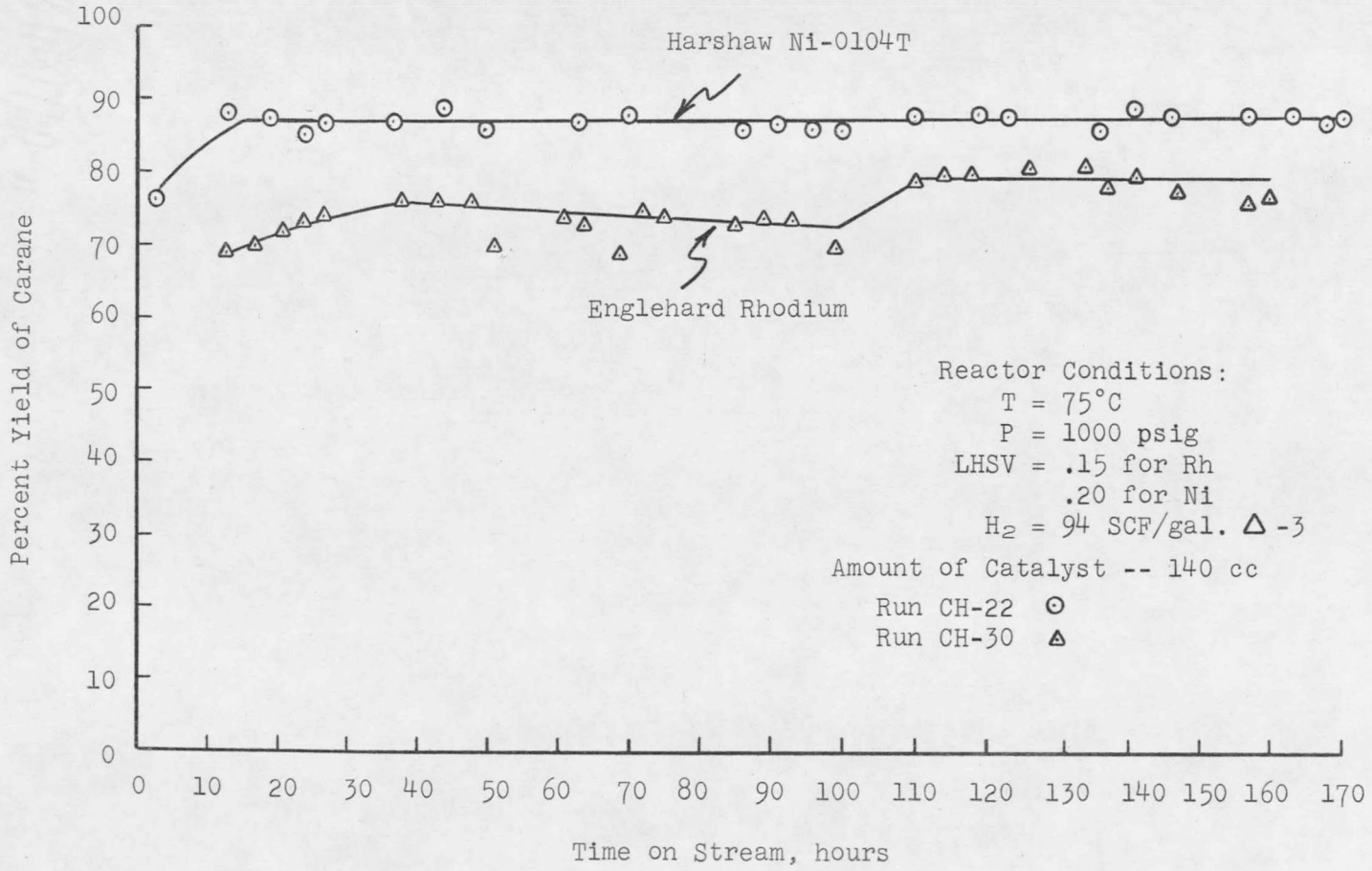


Figure 21. Comparison of the Selectivity of the Englehard Rhodium and Harshaw Ni-0104T in the Fixed-Bed Hydrogenation Reactor

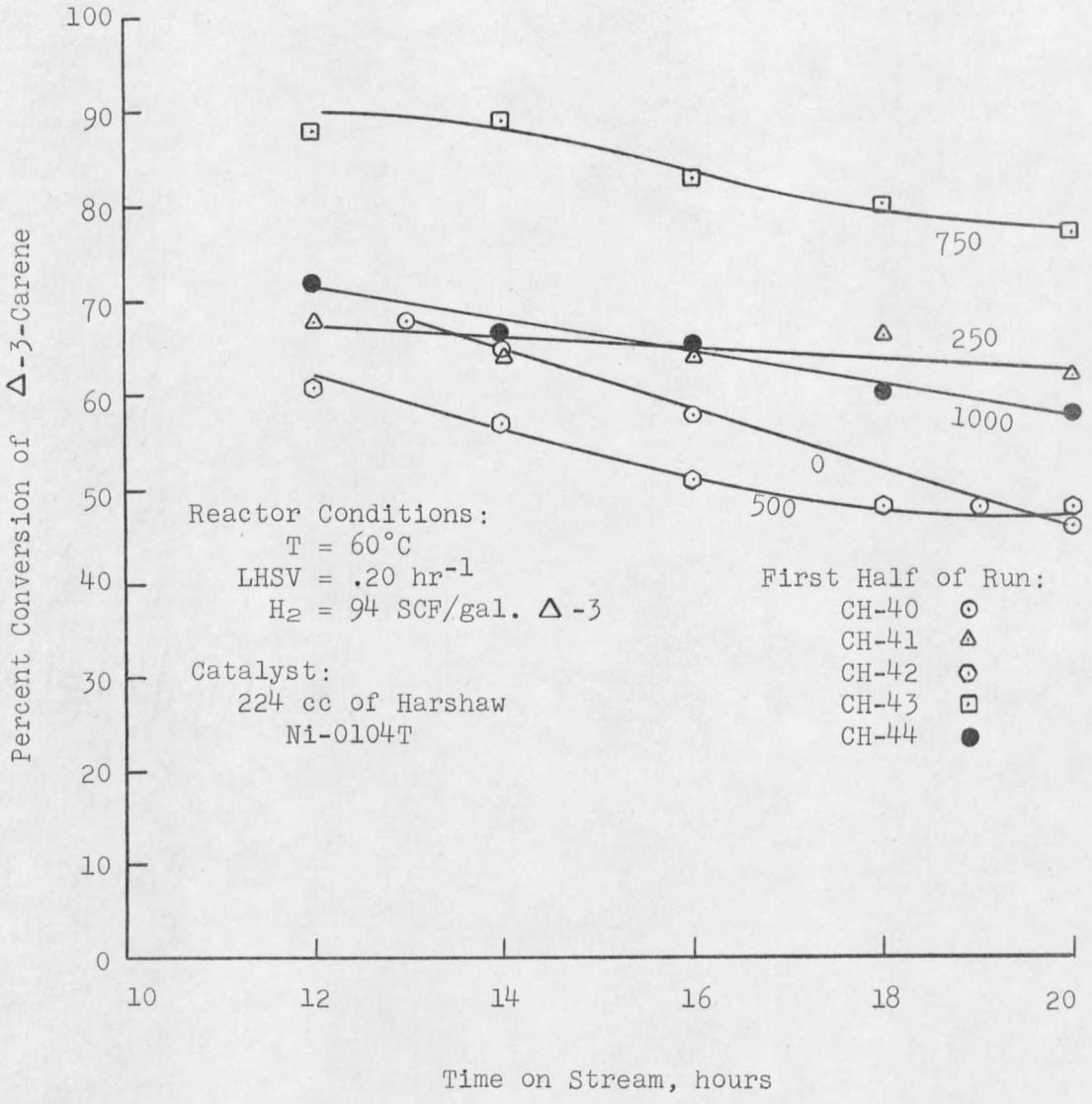


Figure 22. Effect of the Catalyst Poison on Initial Activity and Rate of Deactivation During the Hydrogenation of Δ -3-Carene in Continuous Fixed-Bed Reactor

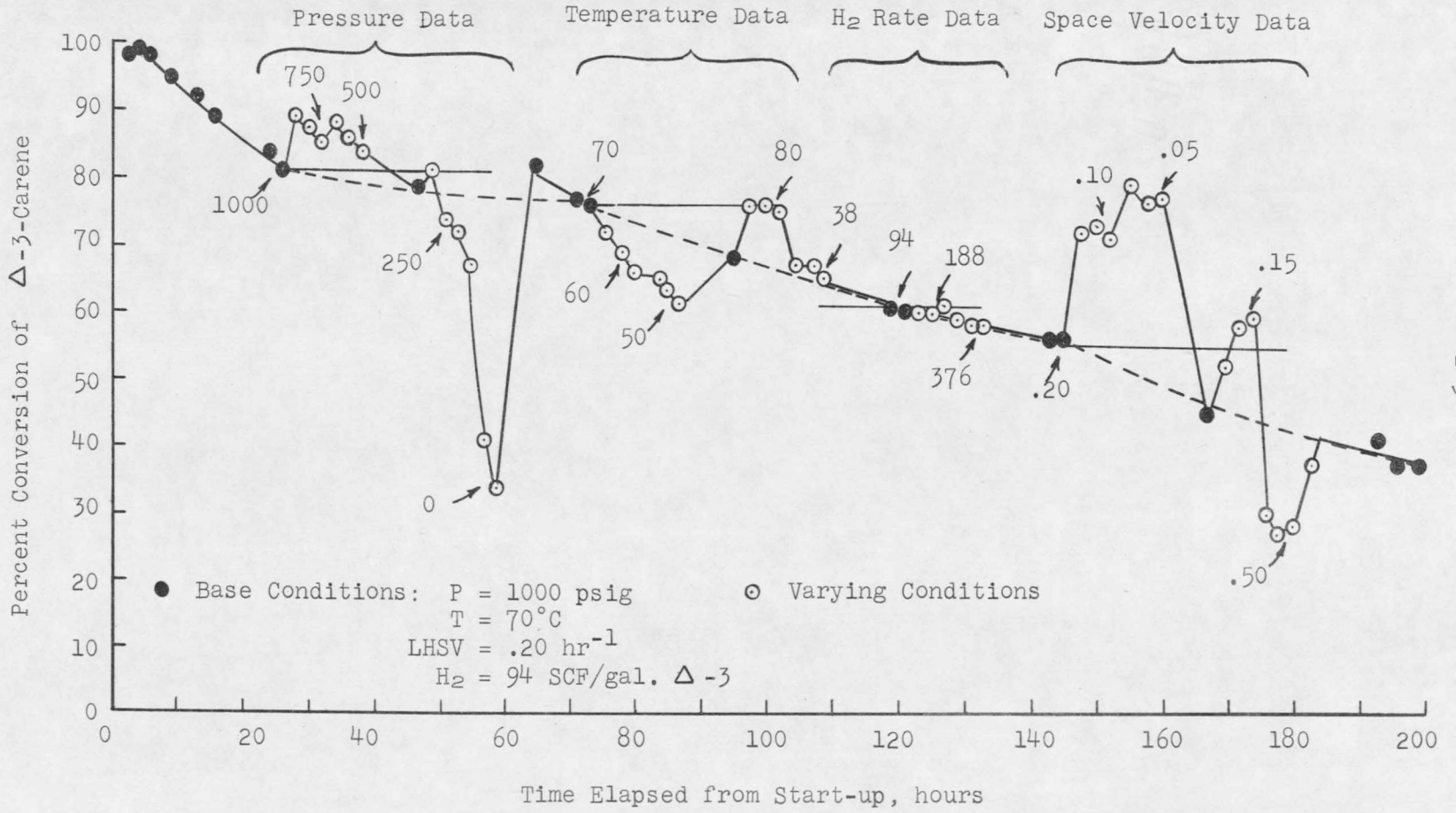


Figure 23. Changes in the Conversion of Δ-3-Carene During Run CH-46, Showing Also the Changes in the Catalyst Activity

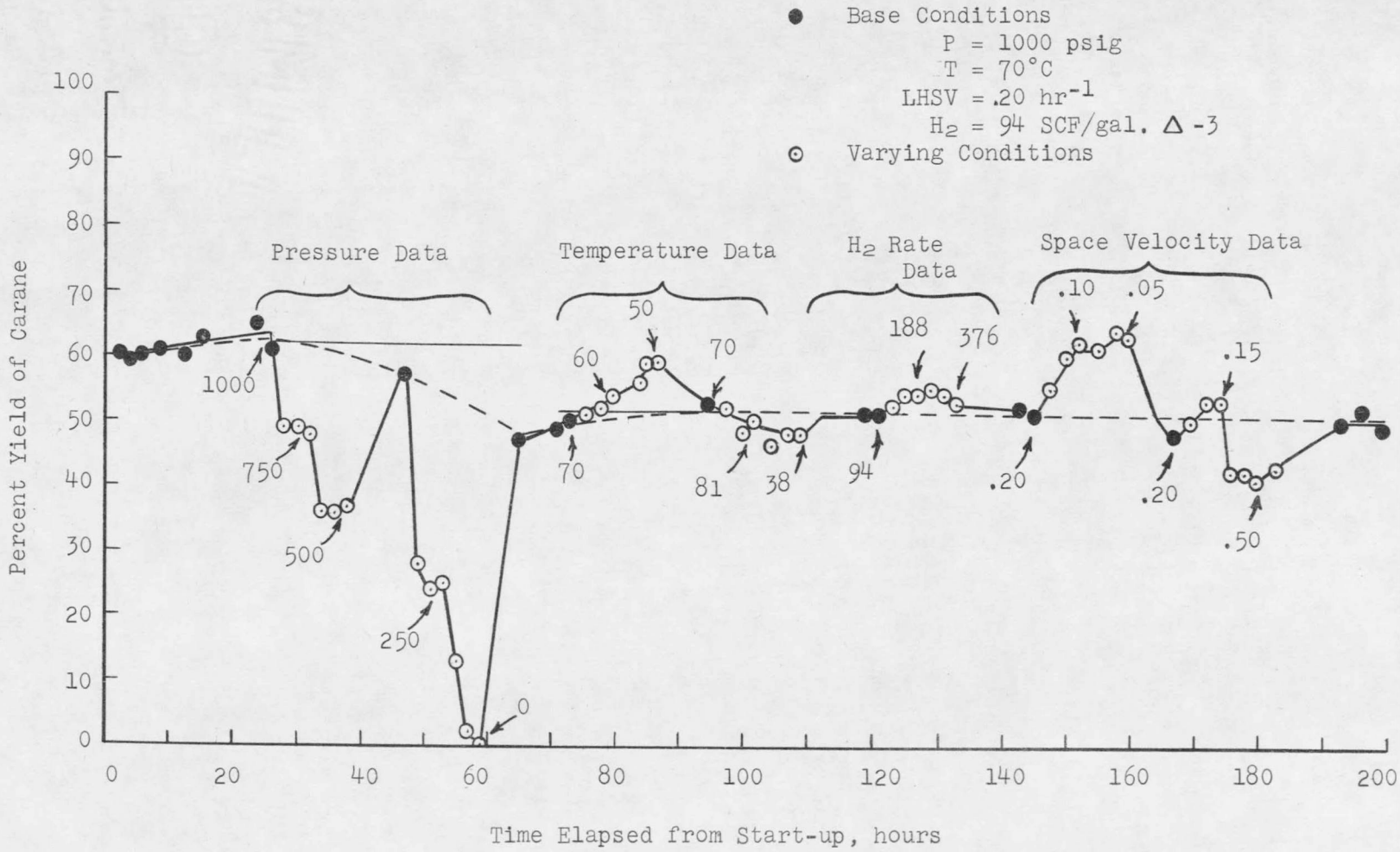


Figure 24. Changes in the Yield of Carane During Run CH-46, Showing Also the Changes in Catalyst Selectivity When They Occurred

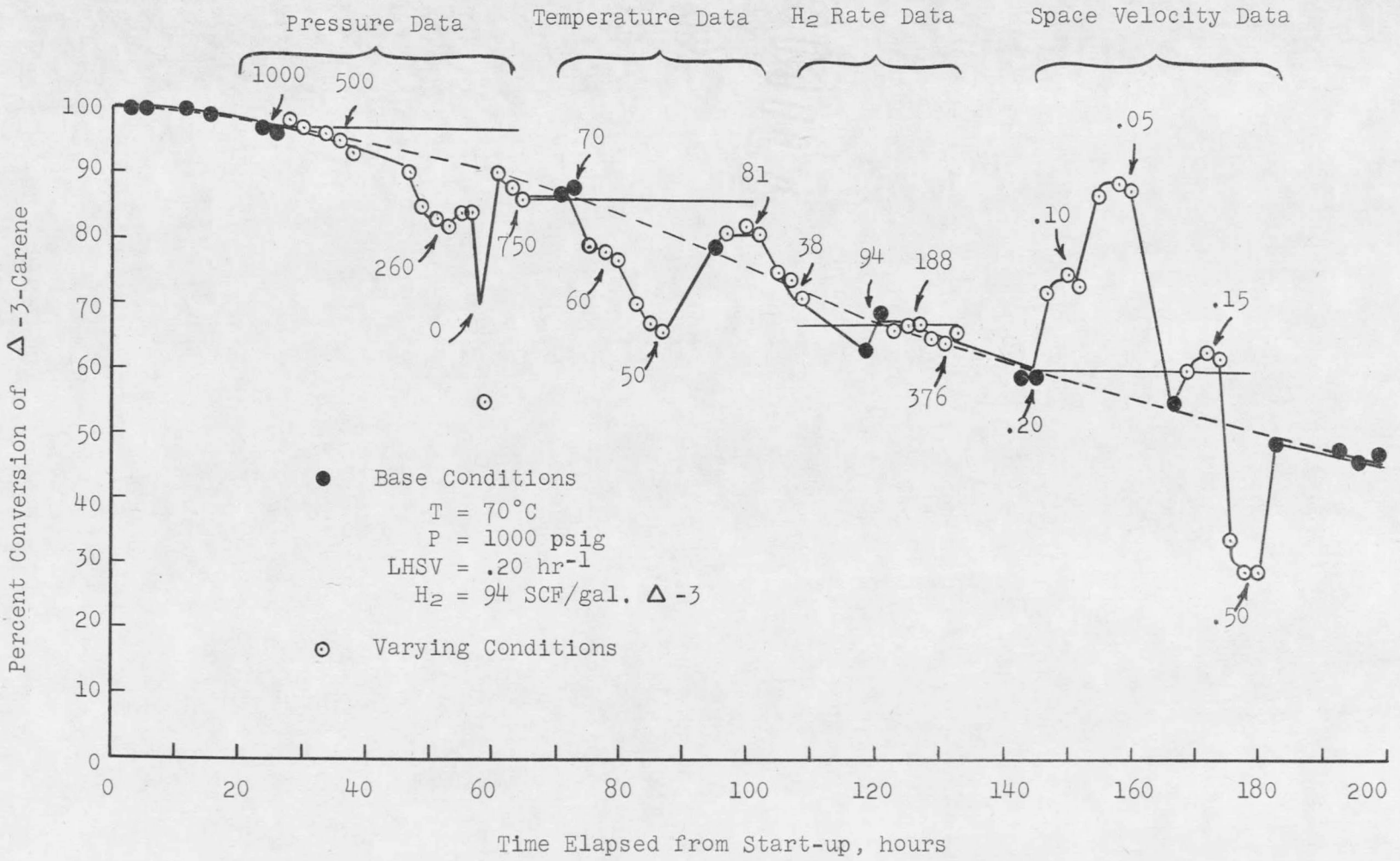


Figure 25. Changes in the Conversion of Δ -3-Carene During Run CH-47, Showing Also the Changes in the Catalyst Activity

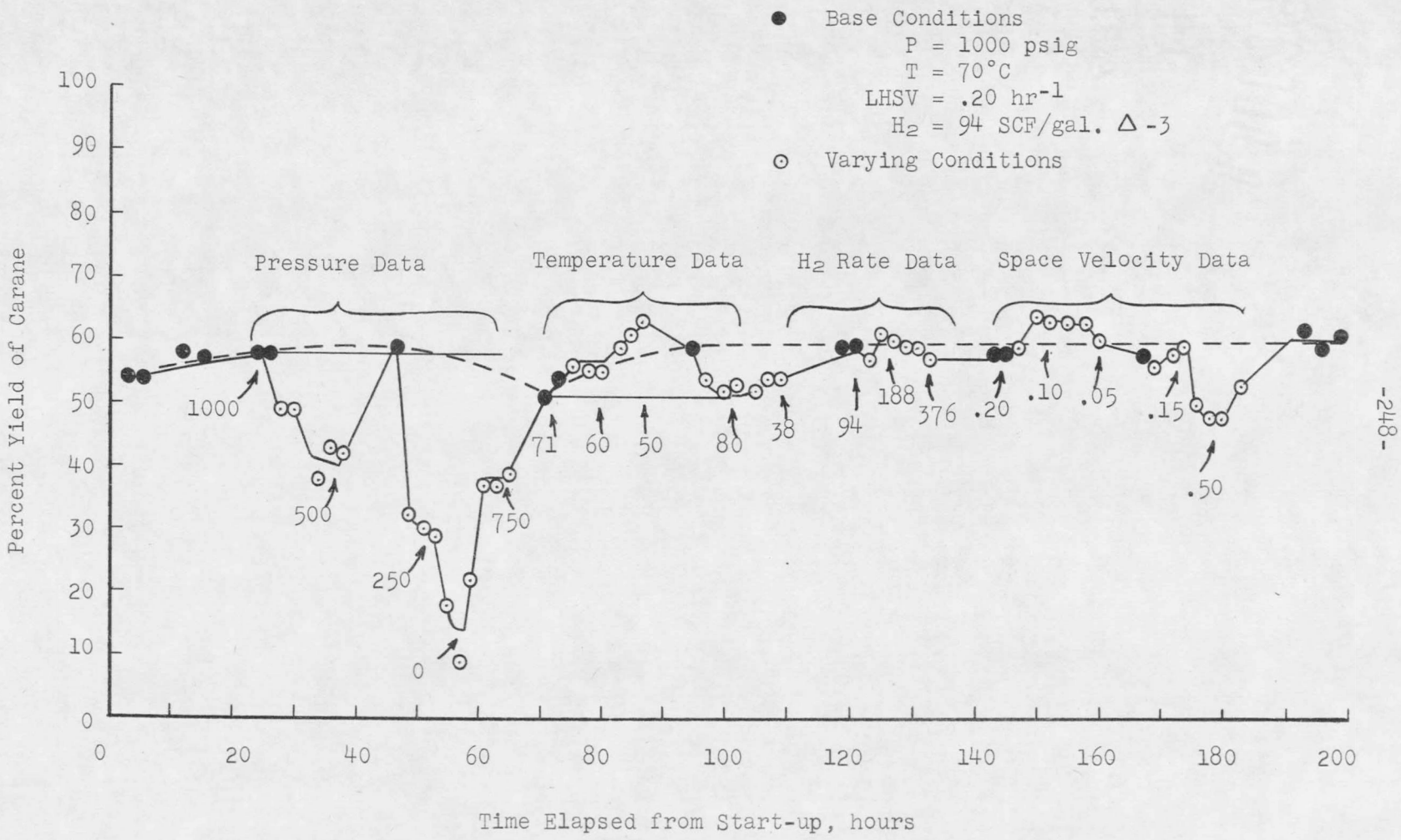


Figure 26. Changes in the Yield of Carane During Run CH-47, Showing Also the Changes in the Catalyst Selectivity When They Occurred

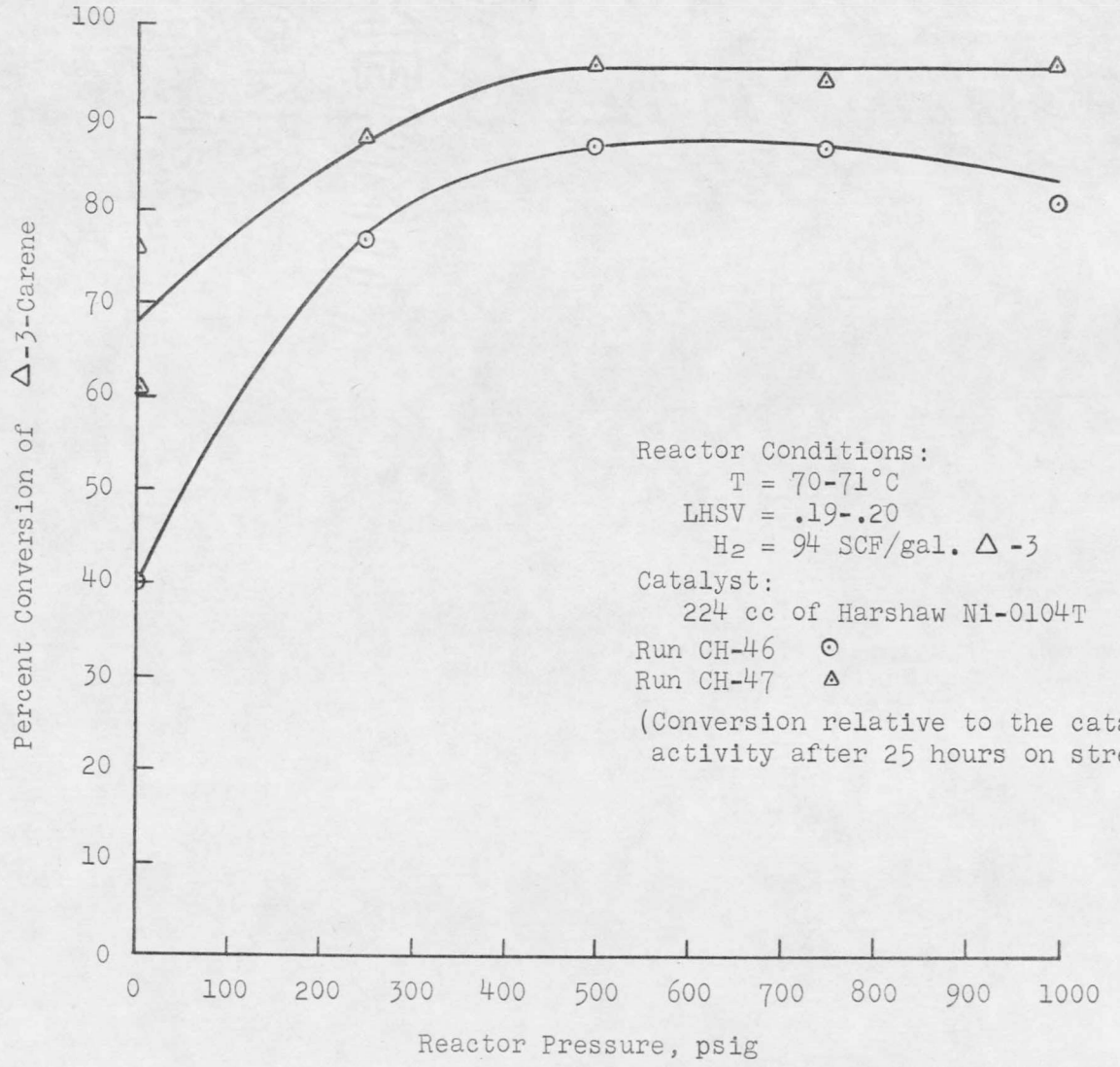


Figure 27. Effect of Pressure on the Conversion of Δ -3-Carene During Continuous Hydrogenation in Fixed-Bed Reactor

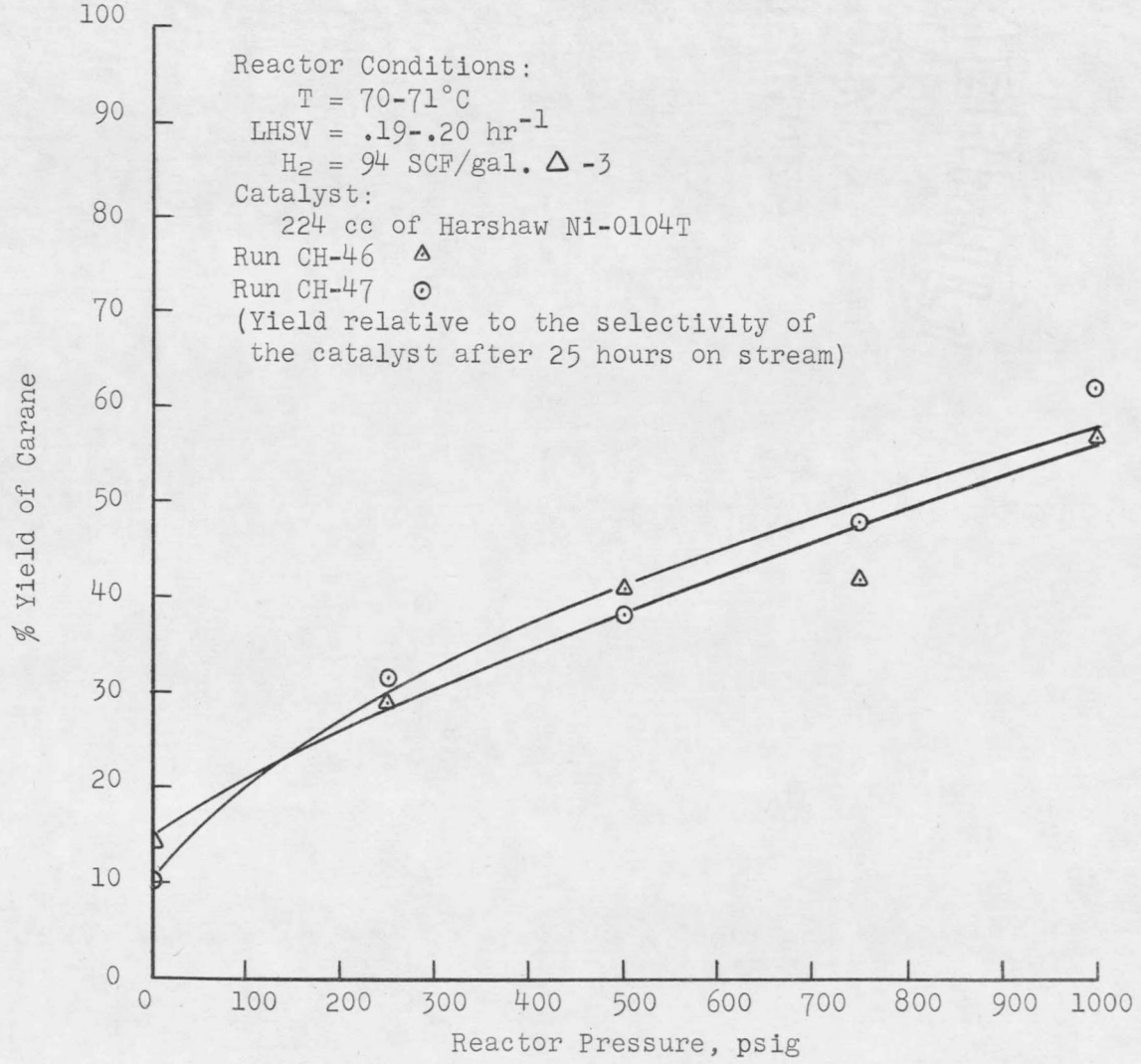


Figure 28. Effect of Pressure on the Yield of Carane During Continuous Hydrogenation of Δ -3-Carene in Fixed-Bed Reactor

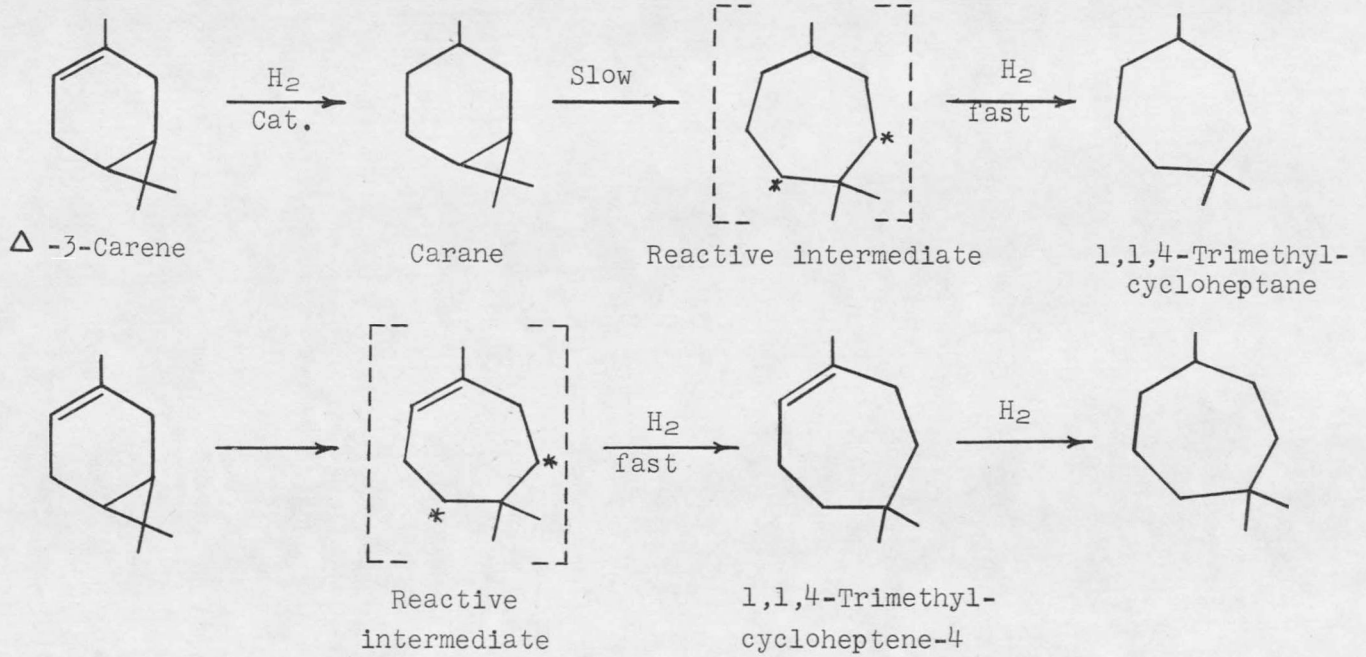


Figure 29. Proposed Reaction Mechanism for the Hydrogenation of Δ -3-Carene

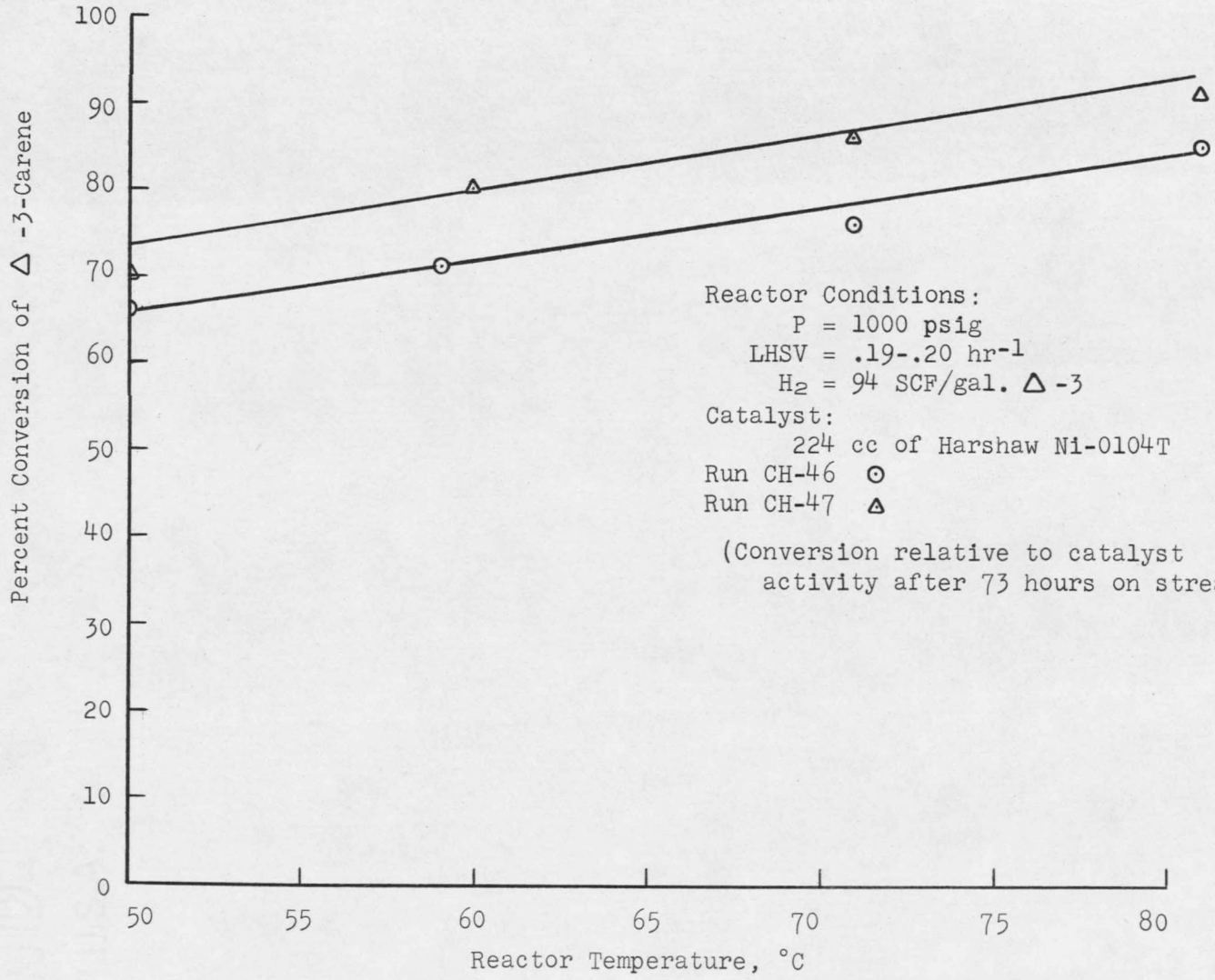


Figure 30. Effect of Temperature on the Conversion of Δ -3-Carene During Continuous Hydrogenation in Fixed-Bed Reactor

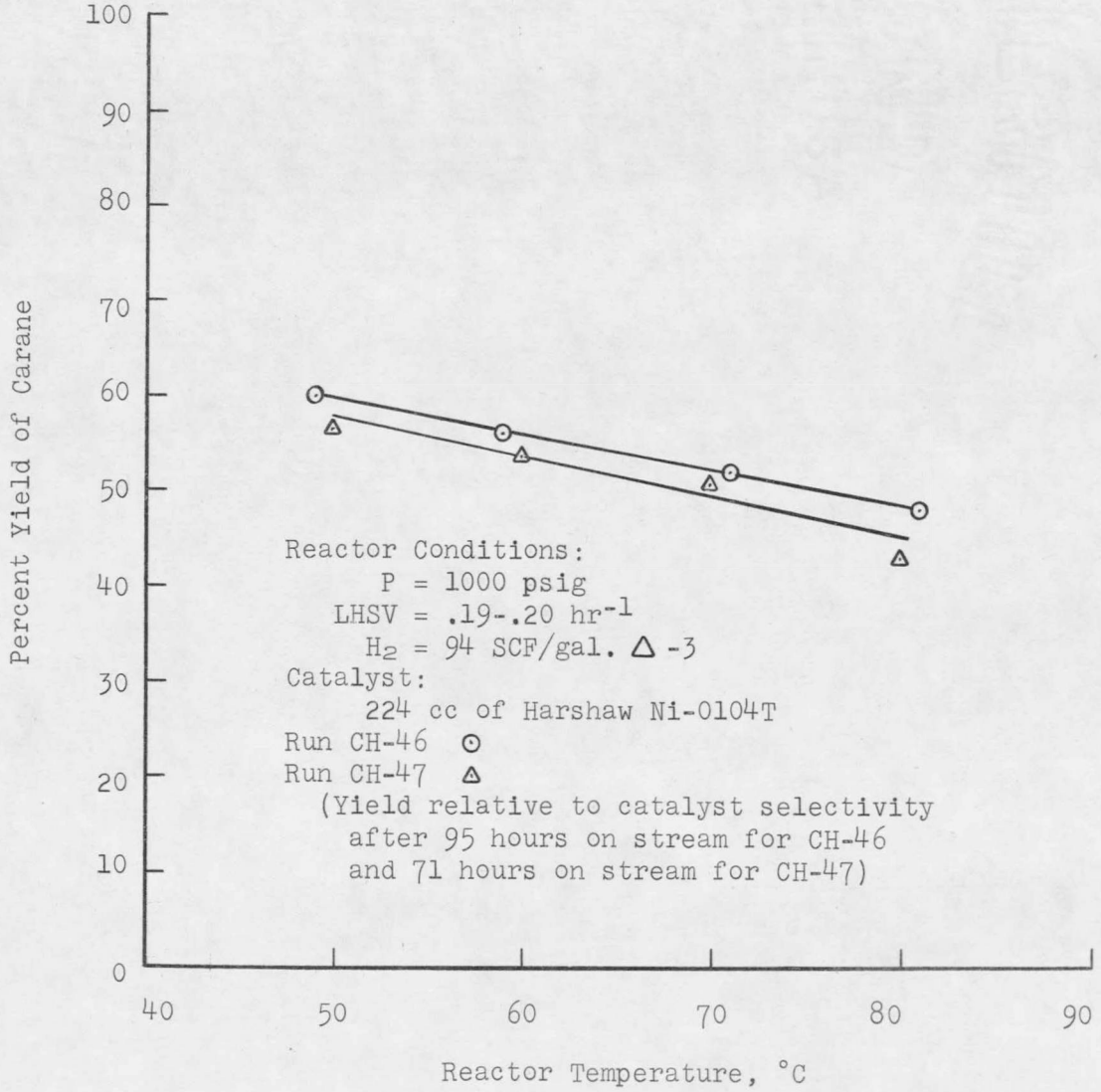


Figure 31. Effect of Temperature on the Yield of Carane During Continuous Hydrogenation of Δ-3-Carene in Fixed-Bed Reactor

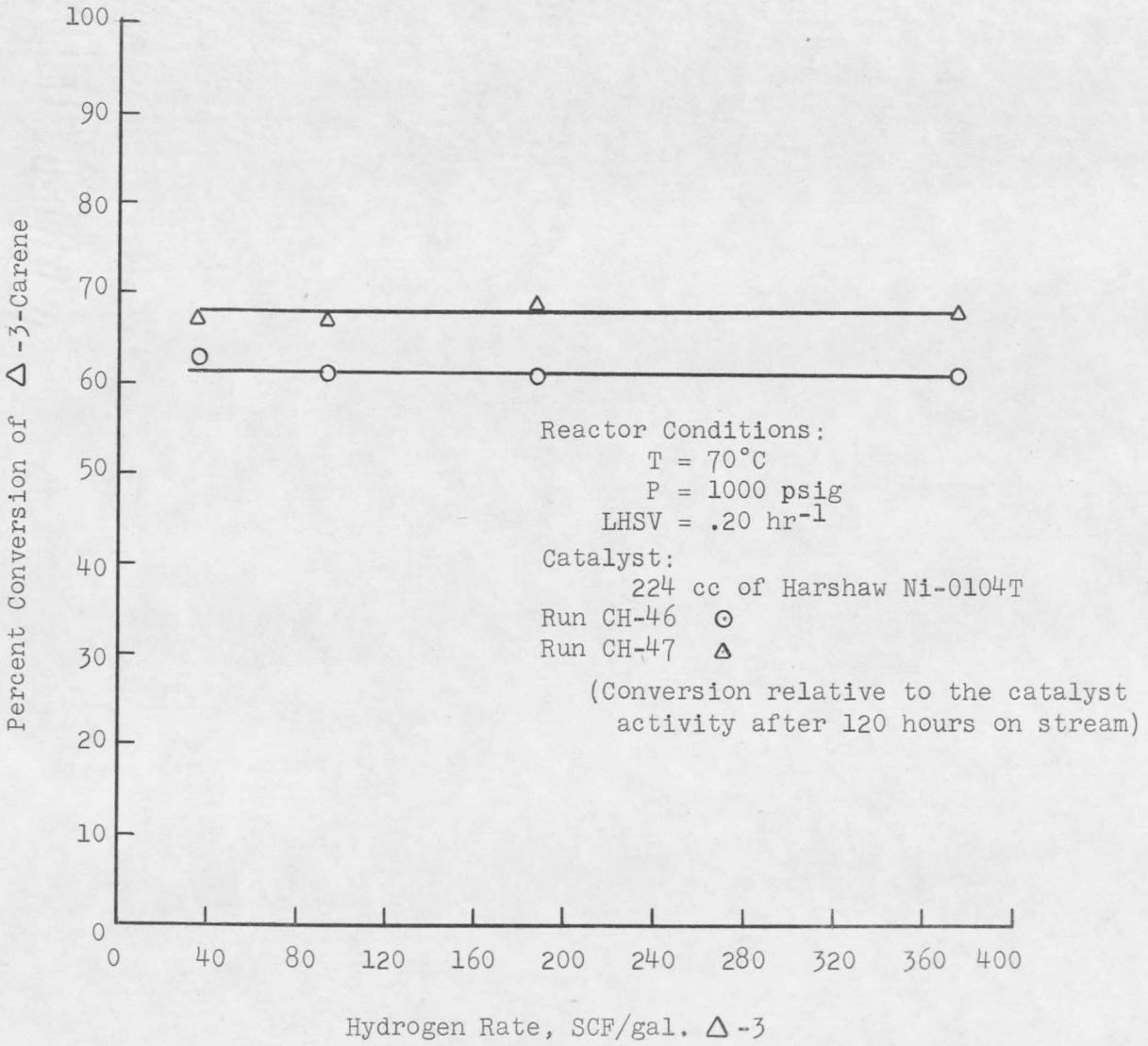


Figure 32. Effect of the Hydrogen Feed Rate on the Conversion of Δ -3-Carene During Continuous Hydrogenation in Fixed-Bed Reactor

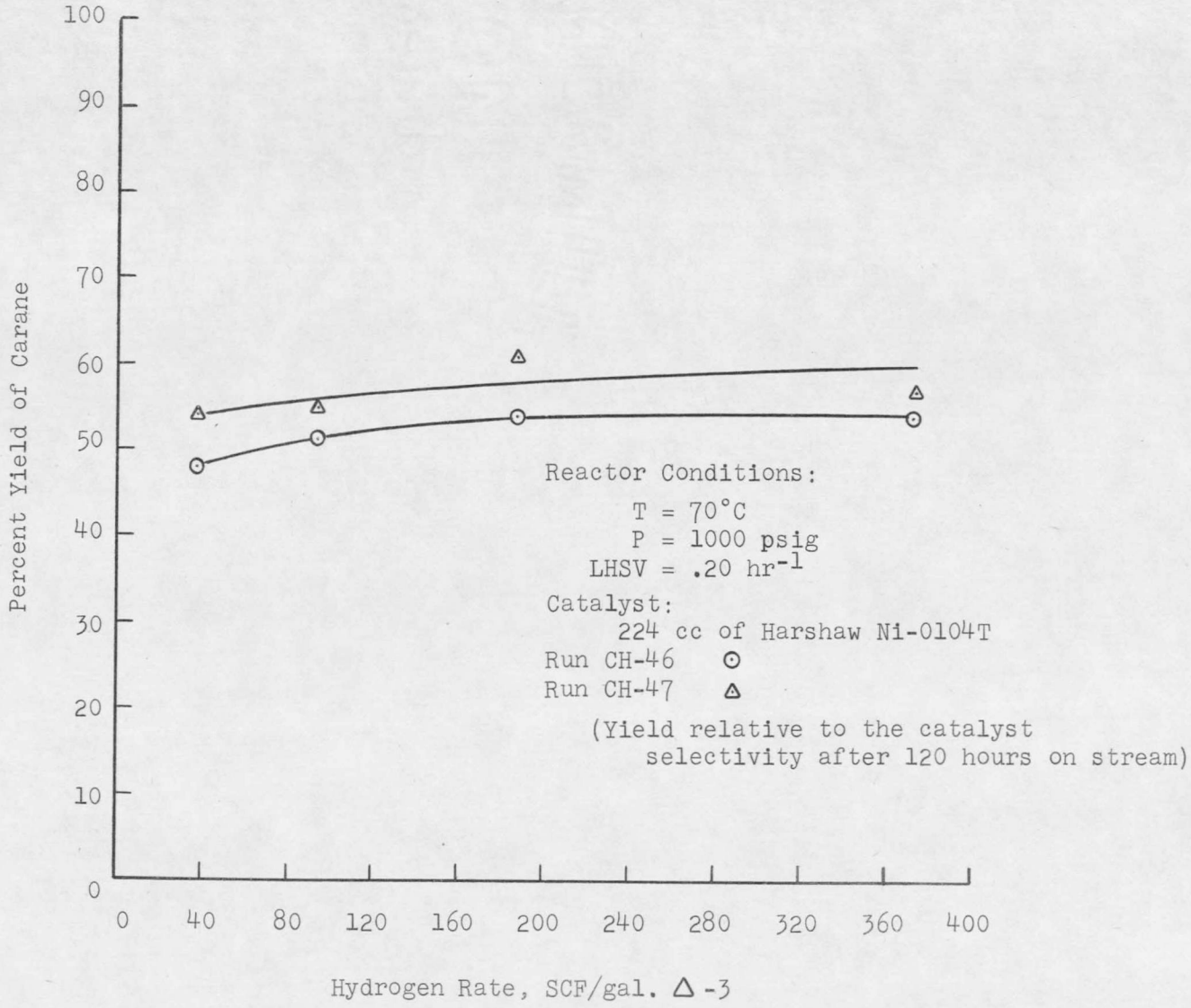


Figure 33. Effect of the Hydrogen Feed Rate on the Yield of Carane During the Continuous Hydrogenation of Δ-3-Carene in Fixed-Bed Reactor

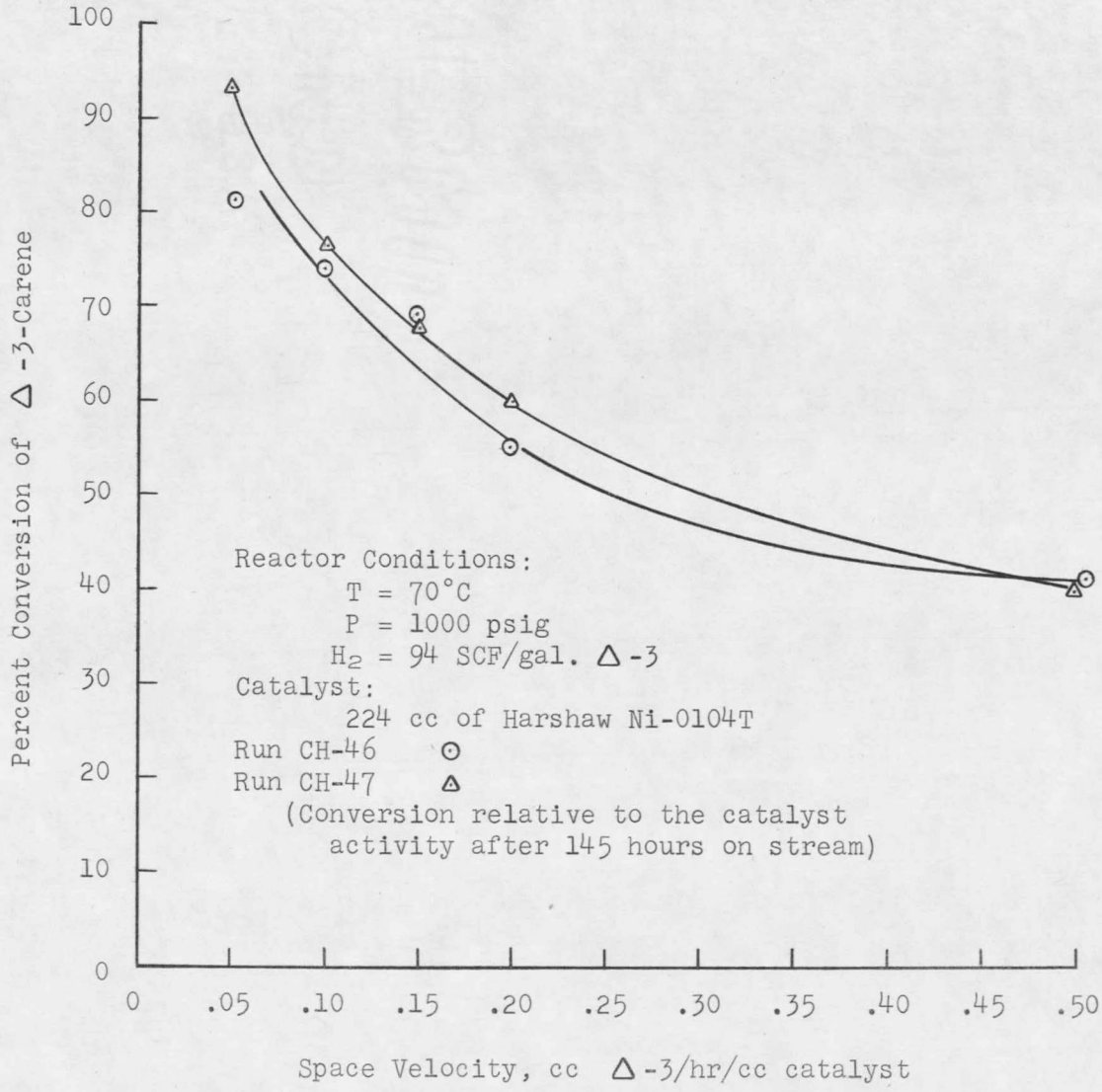


Figure 34. Effect of the Liquid Hourly Space Velocity on the Conversion of Δ-3-Carene During Continuous Hydrogenation in Fixed-Bed Reactor

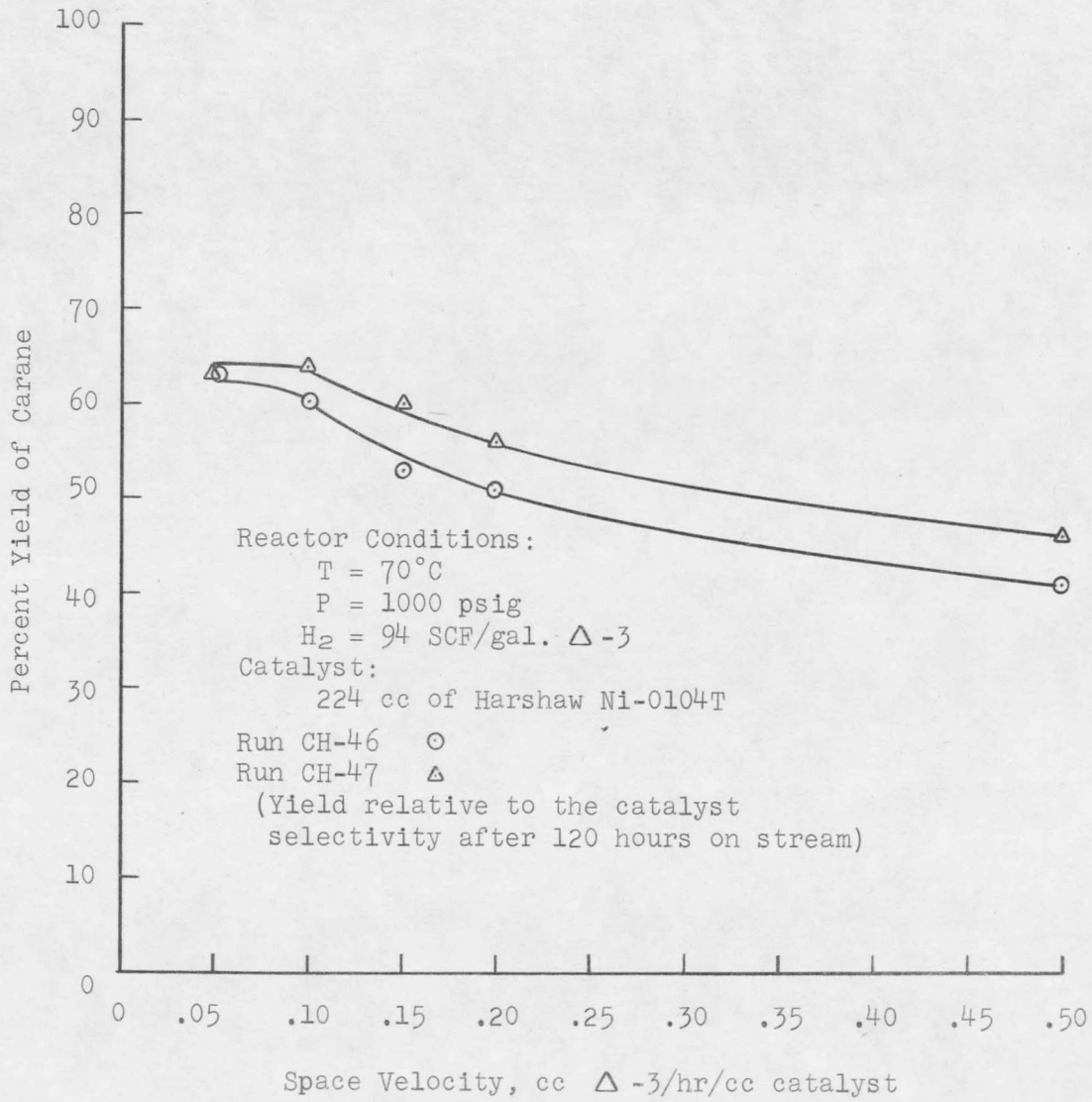


Figure 35. Effect of Liquid Hourly Space Velocity on the Yield of Carane During the Continuous Hydrogenation of Δ -3-Carene in Fixed-Bed Reactor

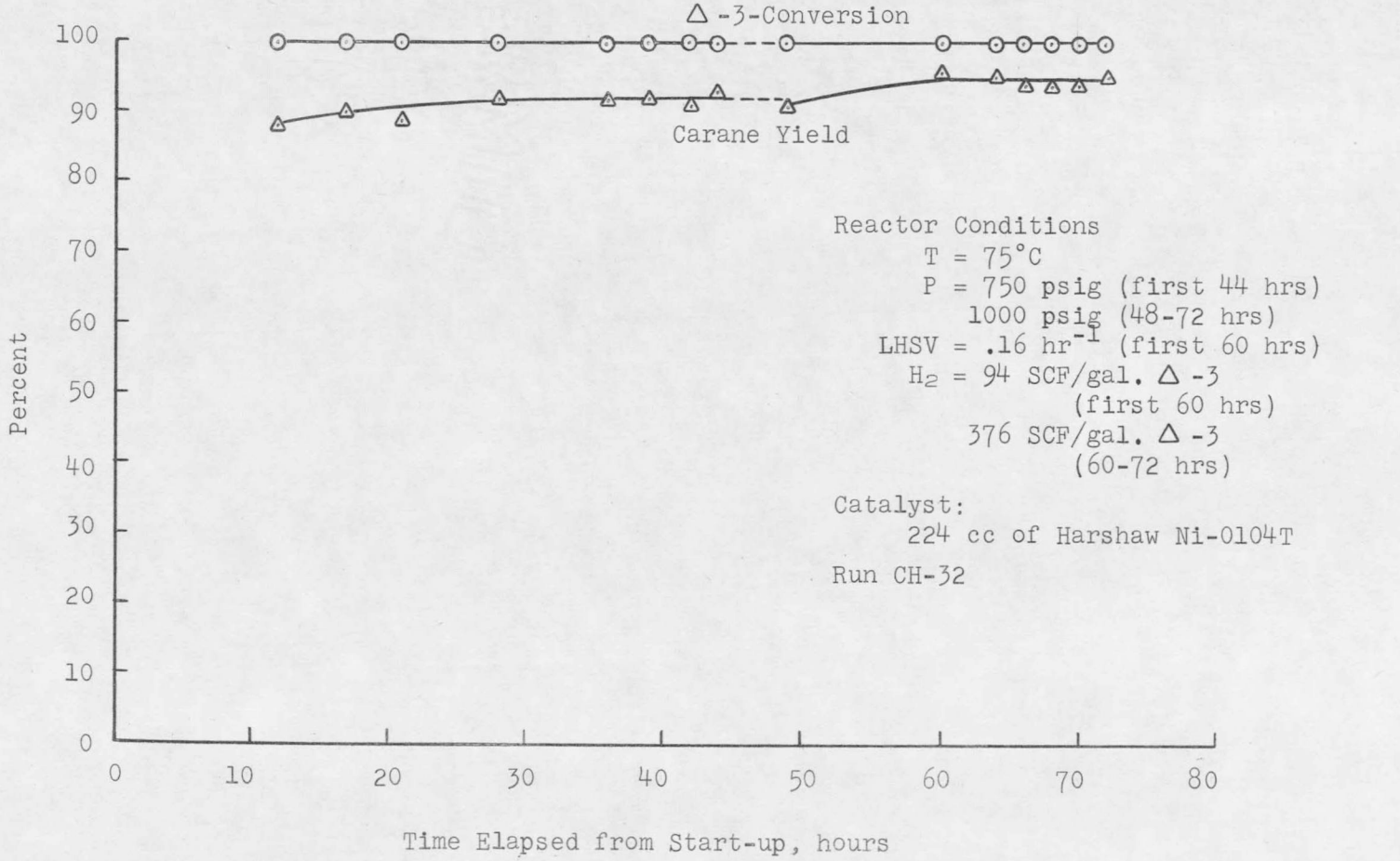


Figure 36. Example of a Run Made with Operating Conditions and Catalyst Activity in Balance for High Carane Production. Continuous Hydrogenation of Δ -3-Carene in Fixed-Bed Reactor

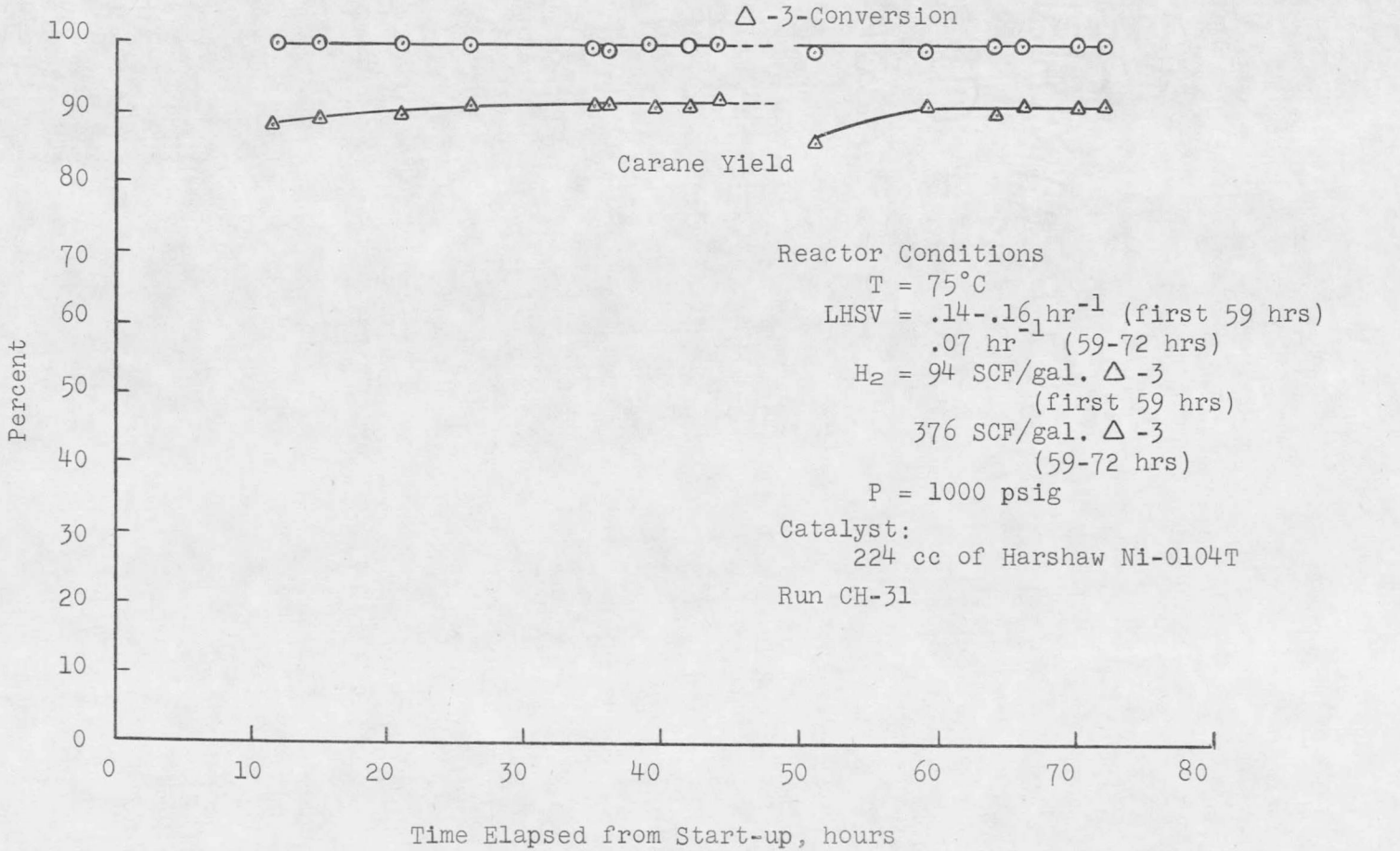


Figure 37. Example of a Run Made with Operating Conditions and Catalyst Activity in Balance for High Carane Production. Continuous Hydrogenation of Δ -3-Carene in Fixed-Bed Reactor

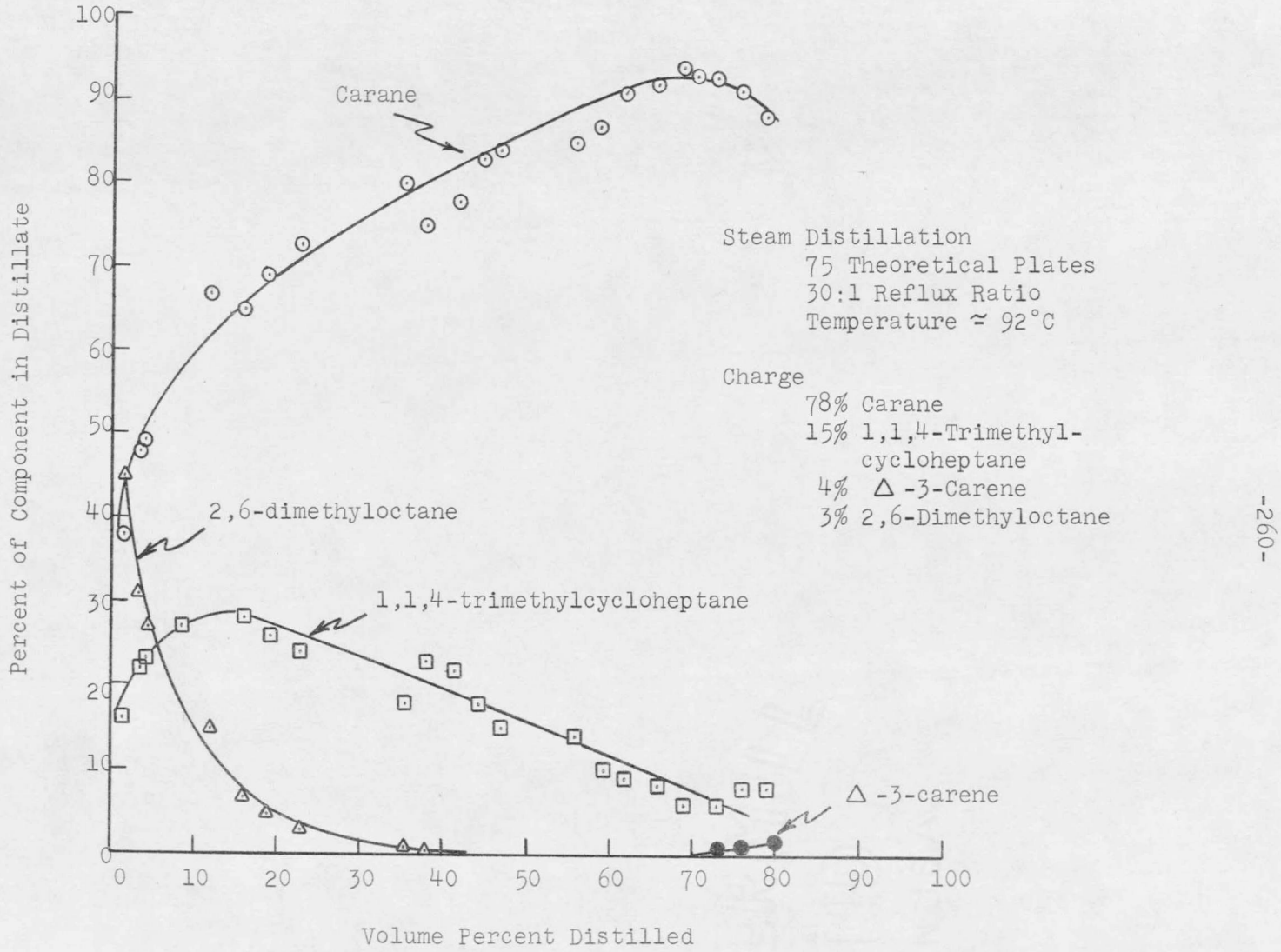


Figure 38. Distillation Curves for Hydrogenation Product. Batch Steam Distillation

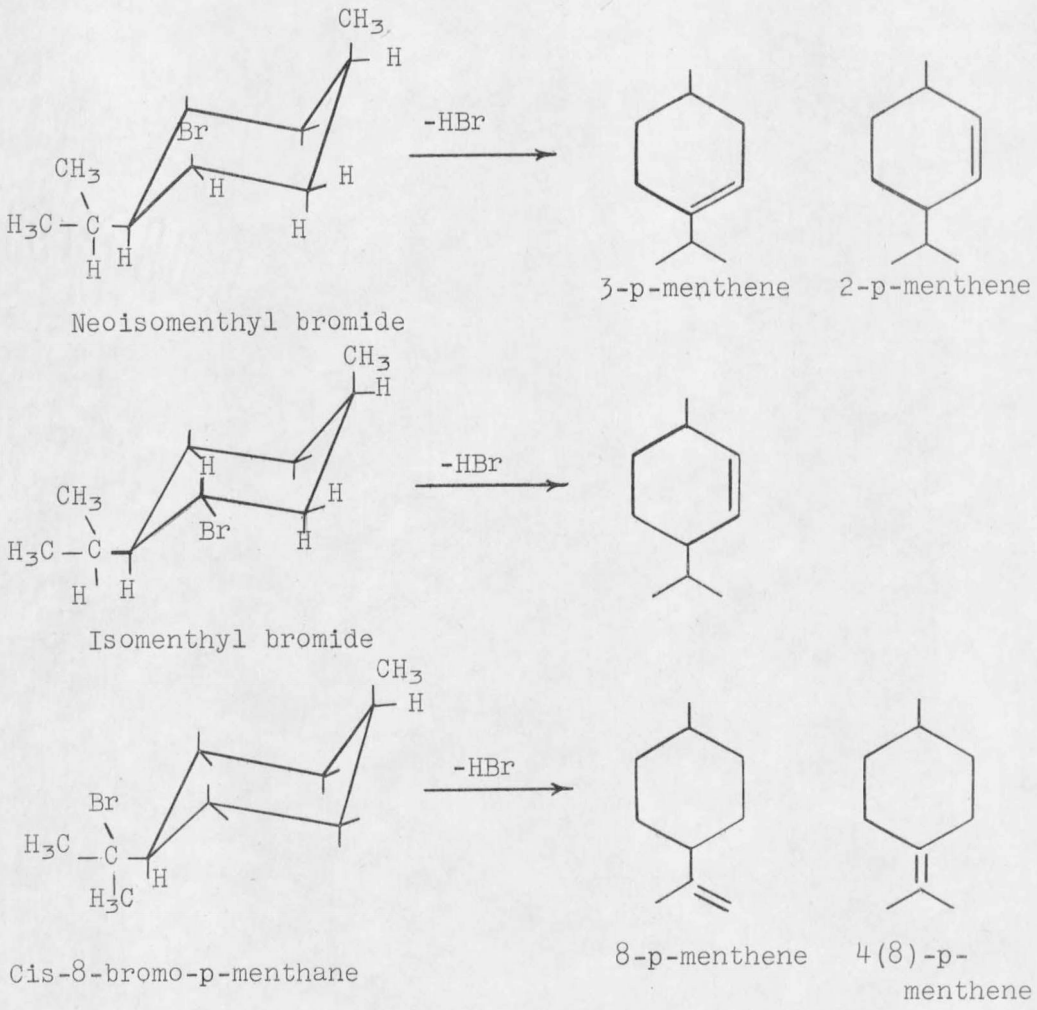


Figure 39. Elimination Products from Some Possible Bromide Derivatives of Carane

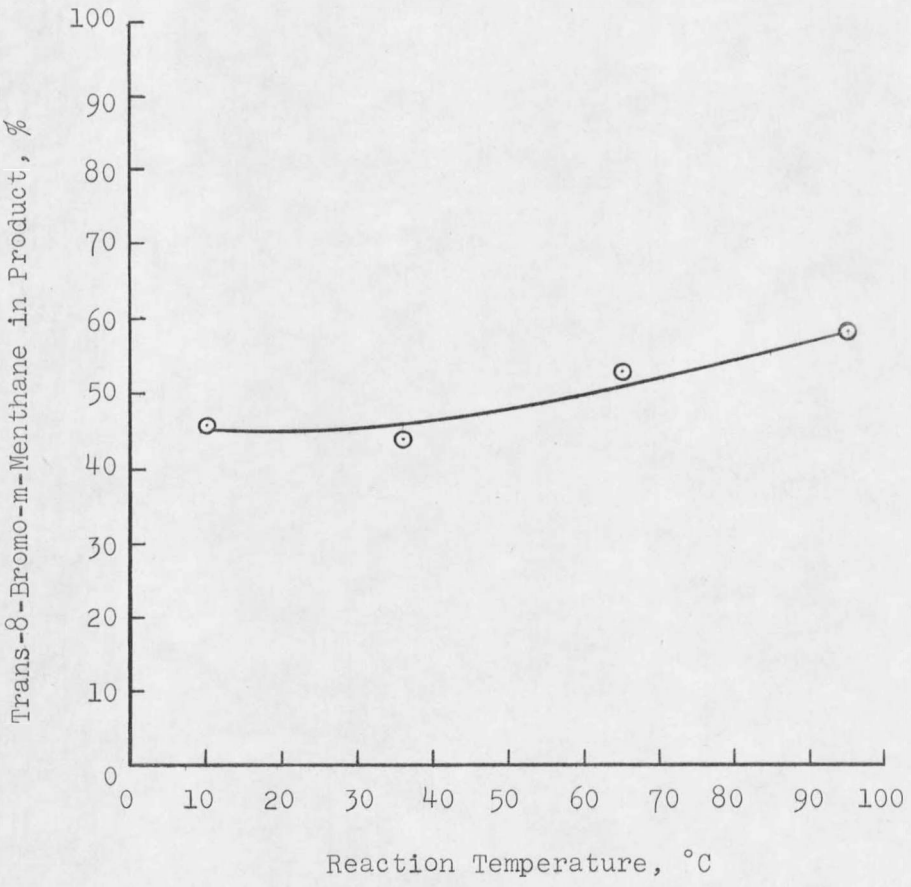


Figure 40. Effect of Temperature on Meta Isomer Formation During the Hydrobromination of Carane

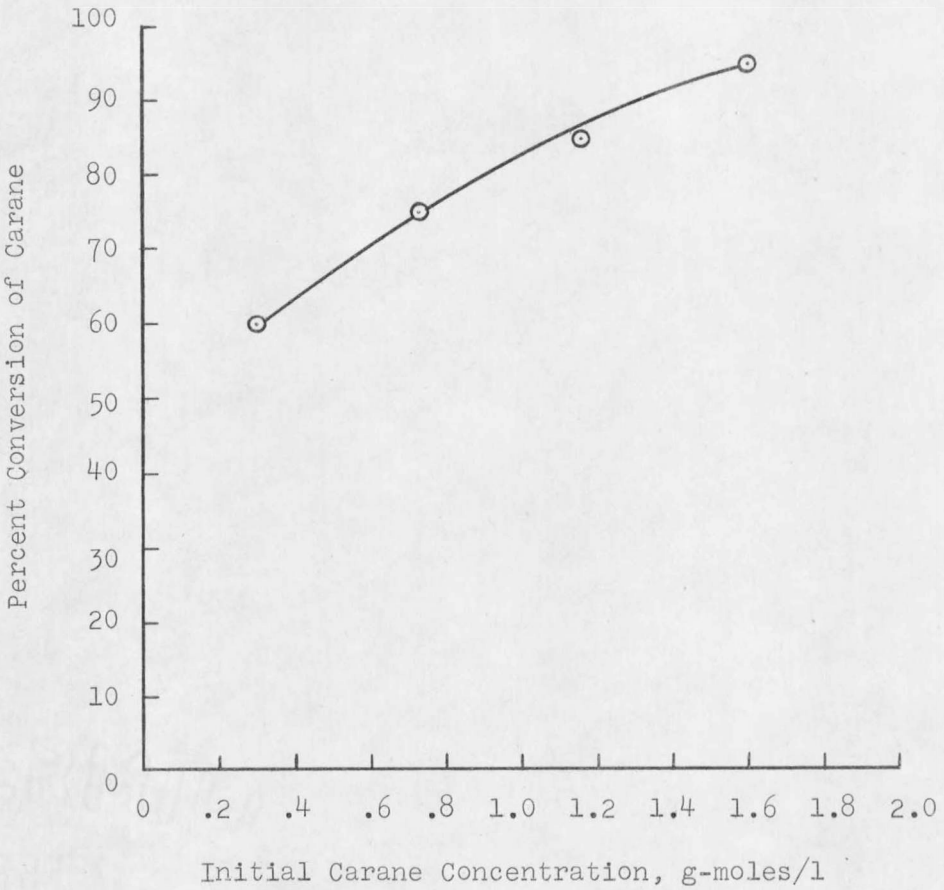


Figure 41. Effect of Initial Carane Concentration on the Conversion During Hydrobromination

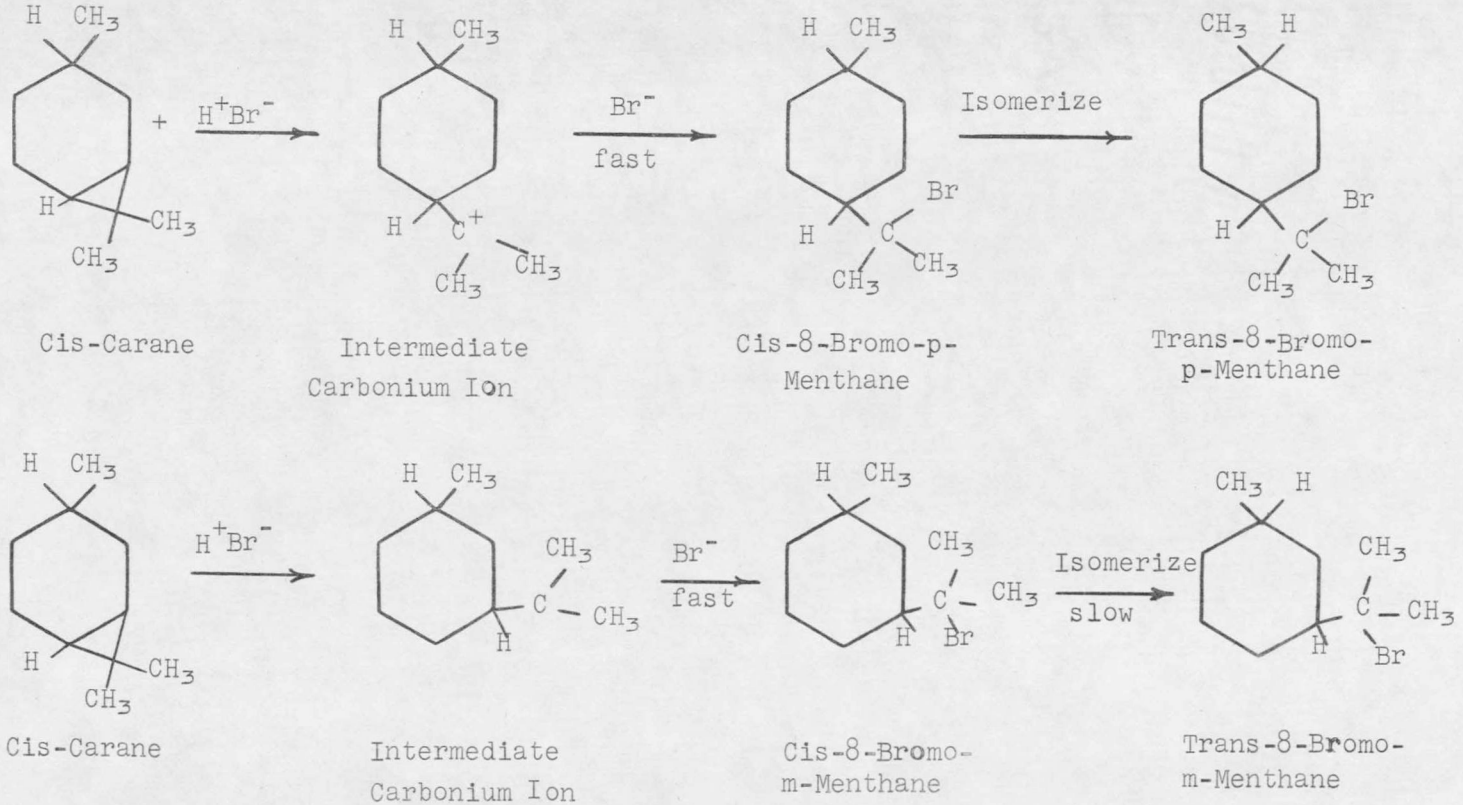


Figure 42. Probable Mechanism of the Hydrobromination of Cis-Carane.

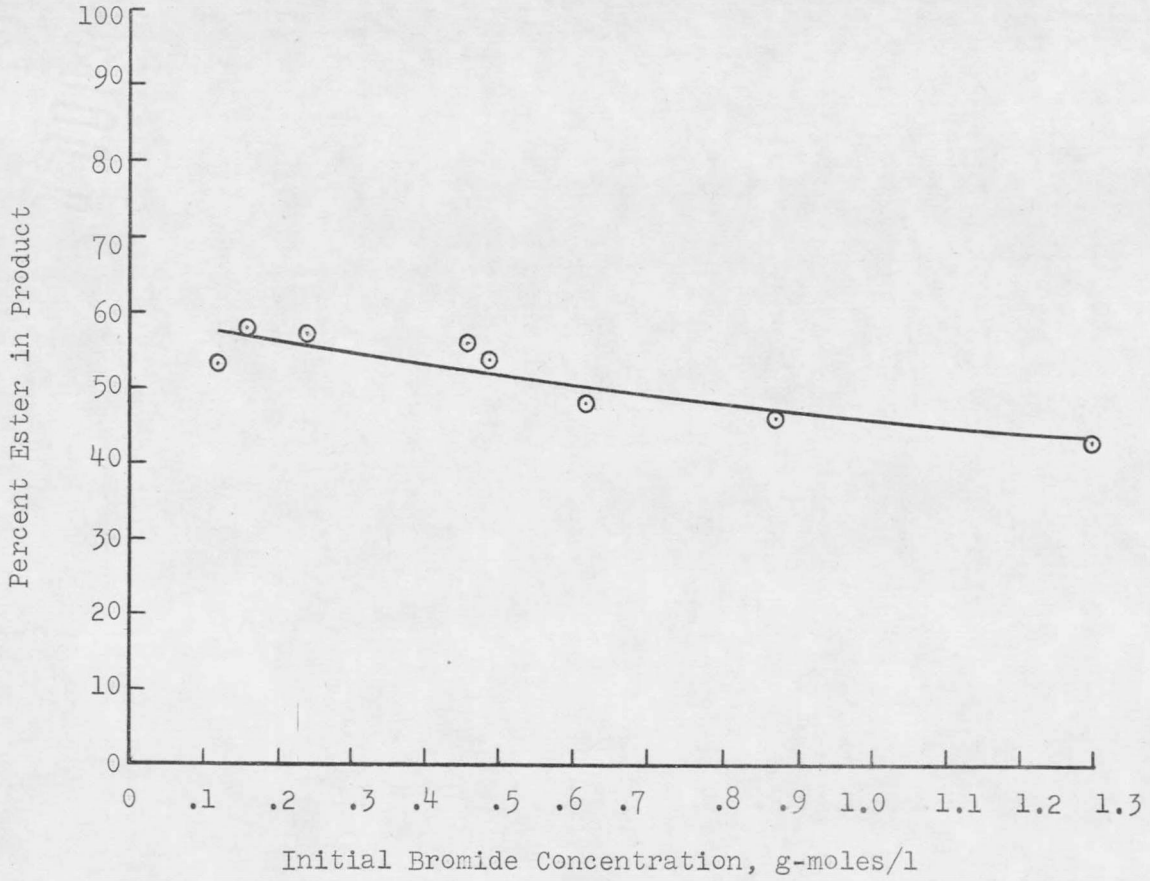


Figure 43. Effect of Initial Terpinyl Bromide Concentration on the Amount of Esters Produced

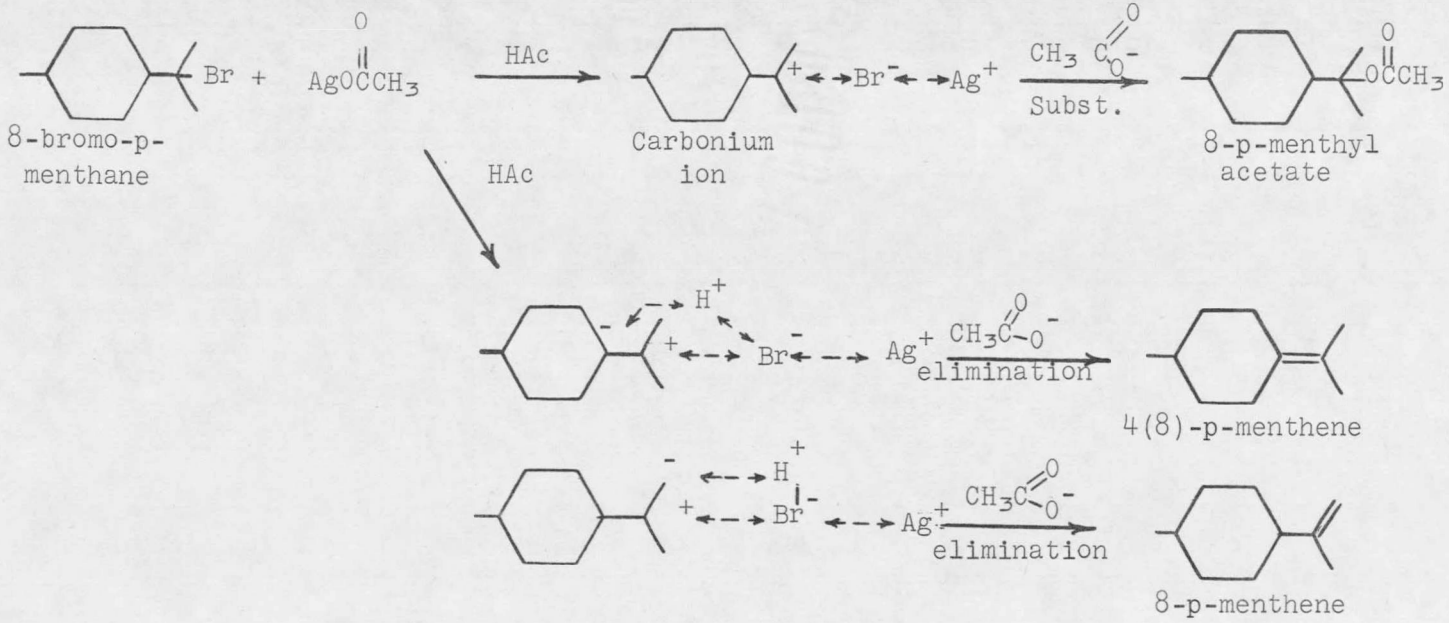
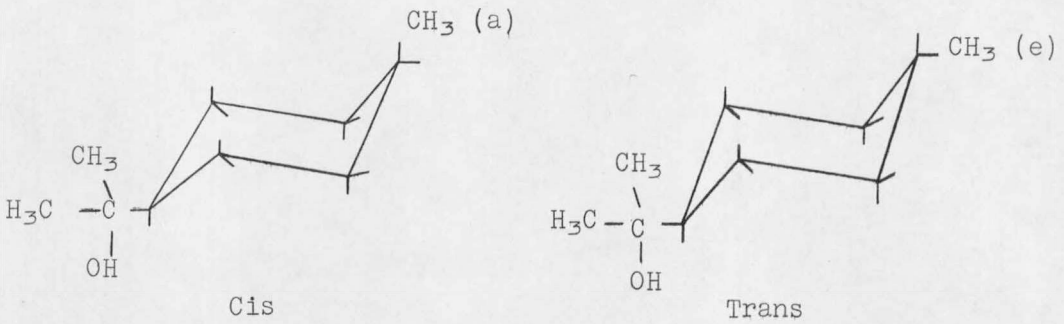
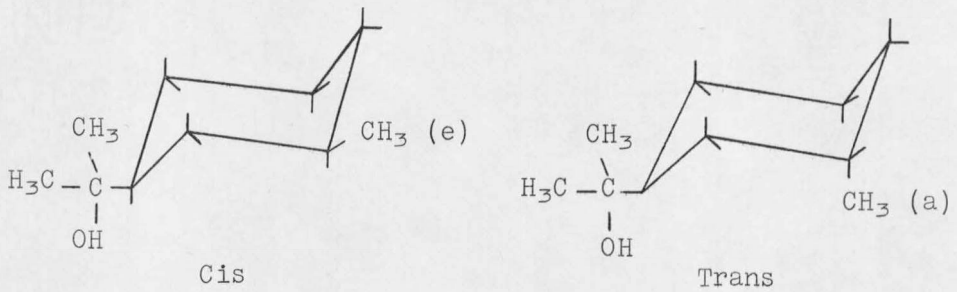


Figure 44. Reaction Mechanism for the Esterification of the Terpinyl Bromides with Silver Acetate Showing the Elimination Mechanism Also



8-p-Menthanol

(Dihydro-α-terpineol)

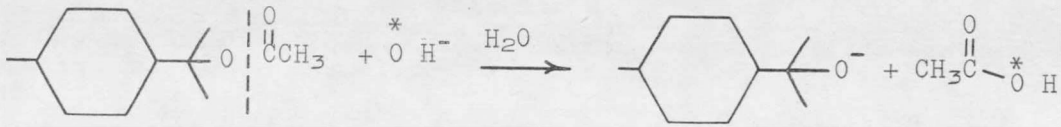


8-m-Menthanol

(Dihydrosylveterpineol)

Figure 45. Structures of the Cis and Trans Isomers of 8-p-Menthanol and 8-m-Menthanol

Substitution

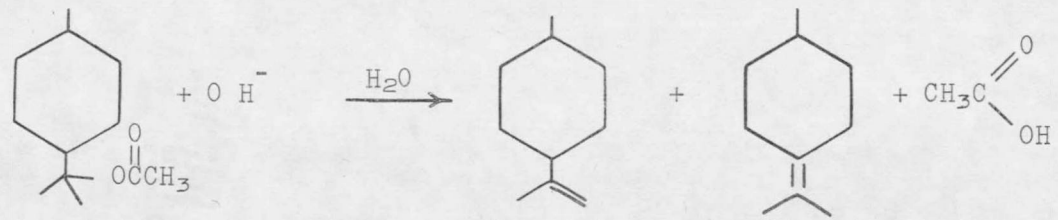


8-p-menthyl acetate



8-p-menthanol

Elimination



8-p-menthene 4(8)-p-menthene

Figure 46. Reaction Mechanism for Saponification of Esters Showing Elimination Also.

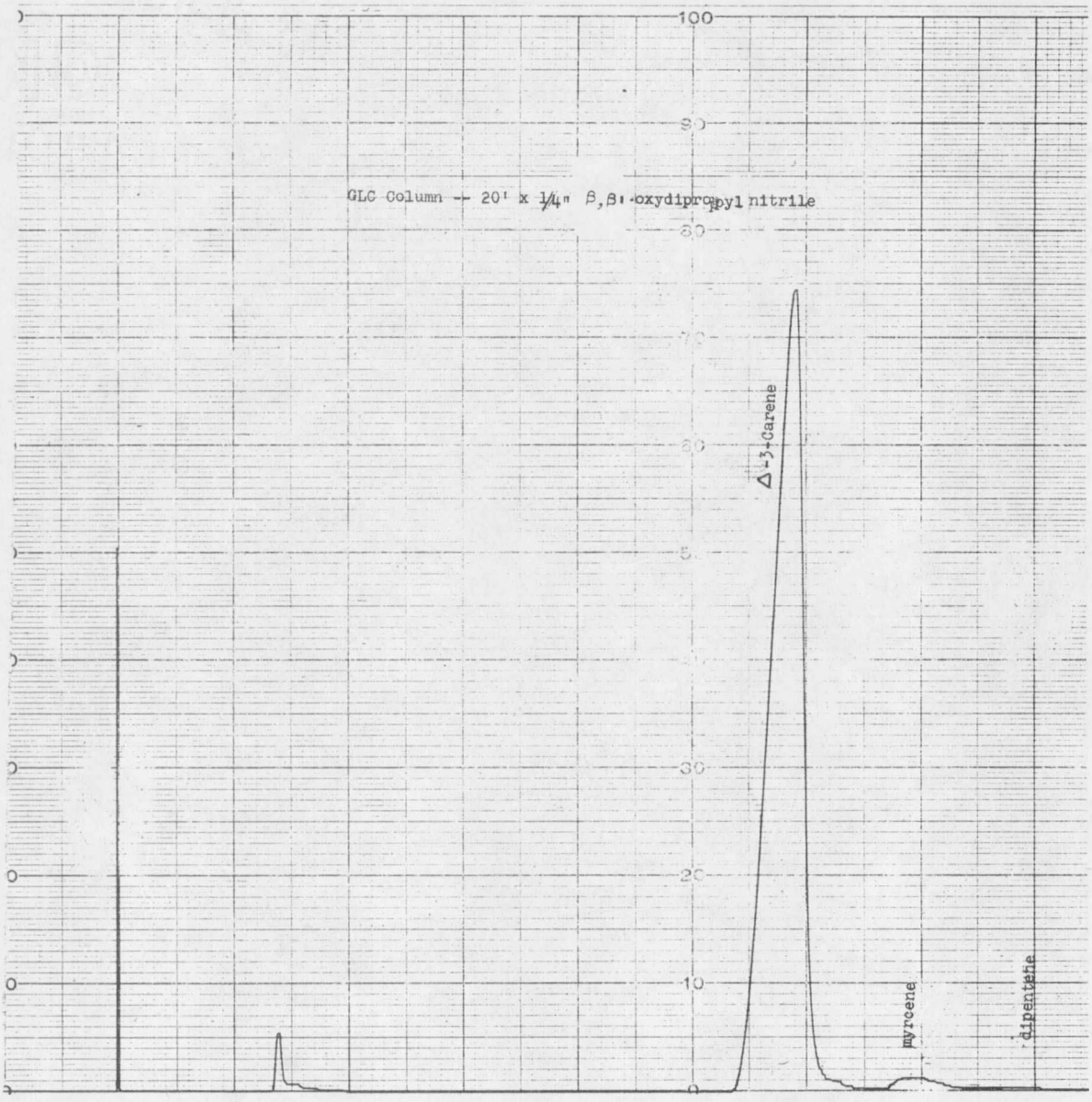


Figure 47. Chromatogram of Δ-3-Carene Feedstock for the Hydrogenation Reaction

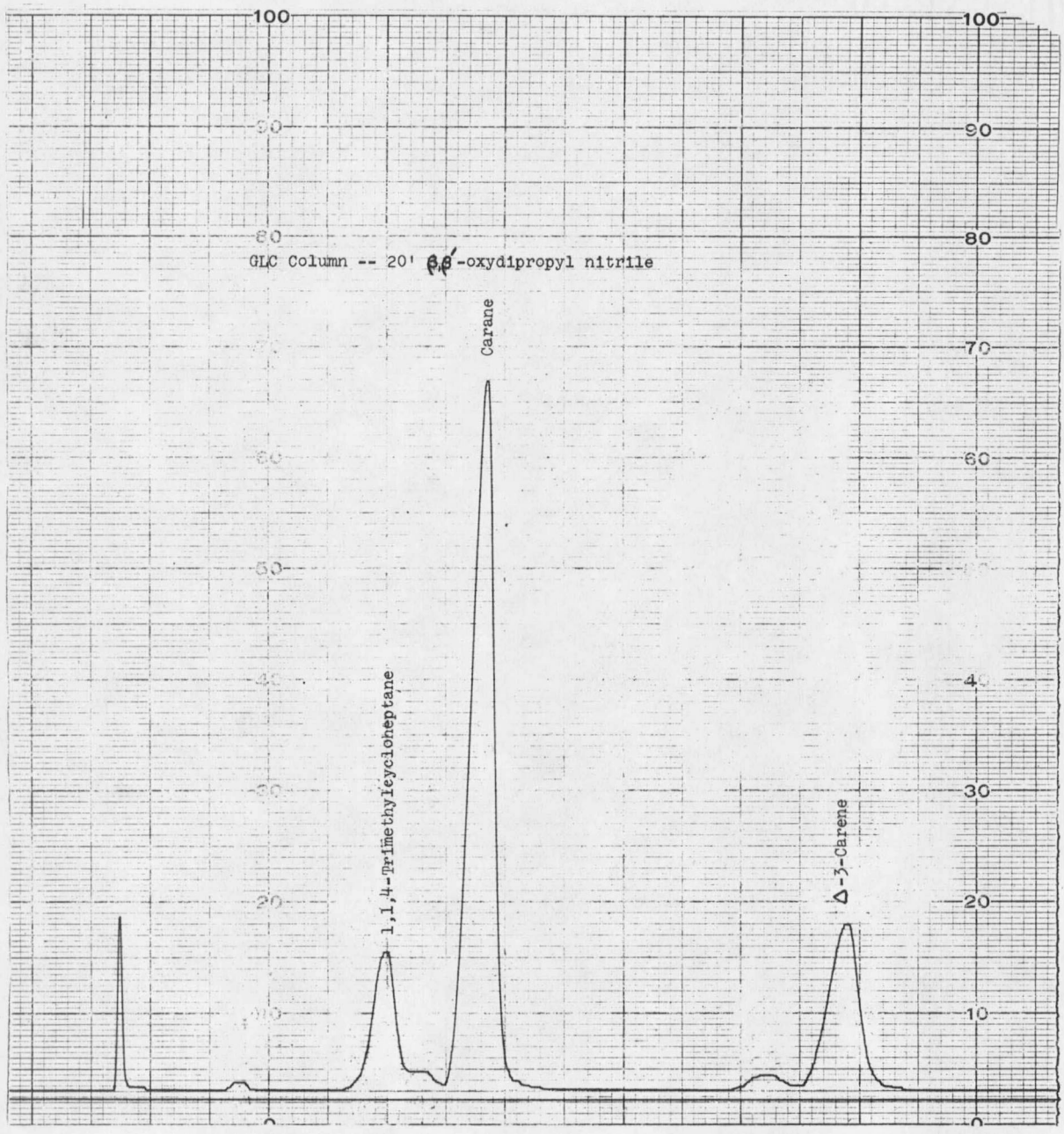


Figure 48. Chromatogram of Hydrogenation Product Produced at 60°C, 1000 psig, LHSV = .20 and H_2 Rate = 94 SCF/gal. Δ-3

GLC Column -- 20' x 1/4" β,β'-oxydipropyl nitrile

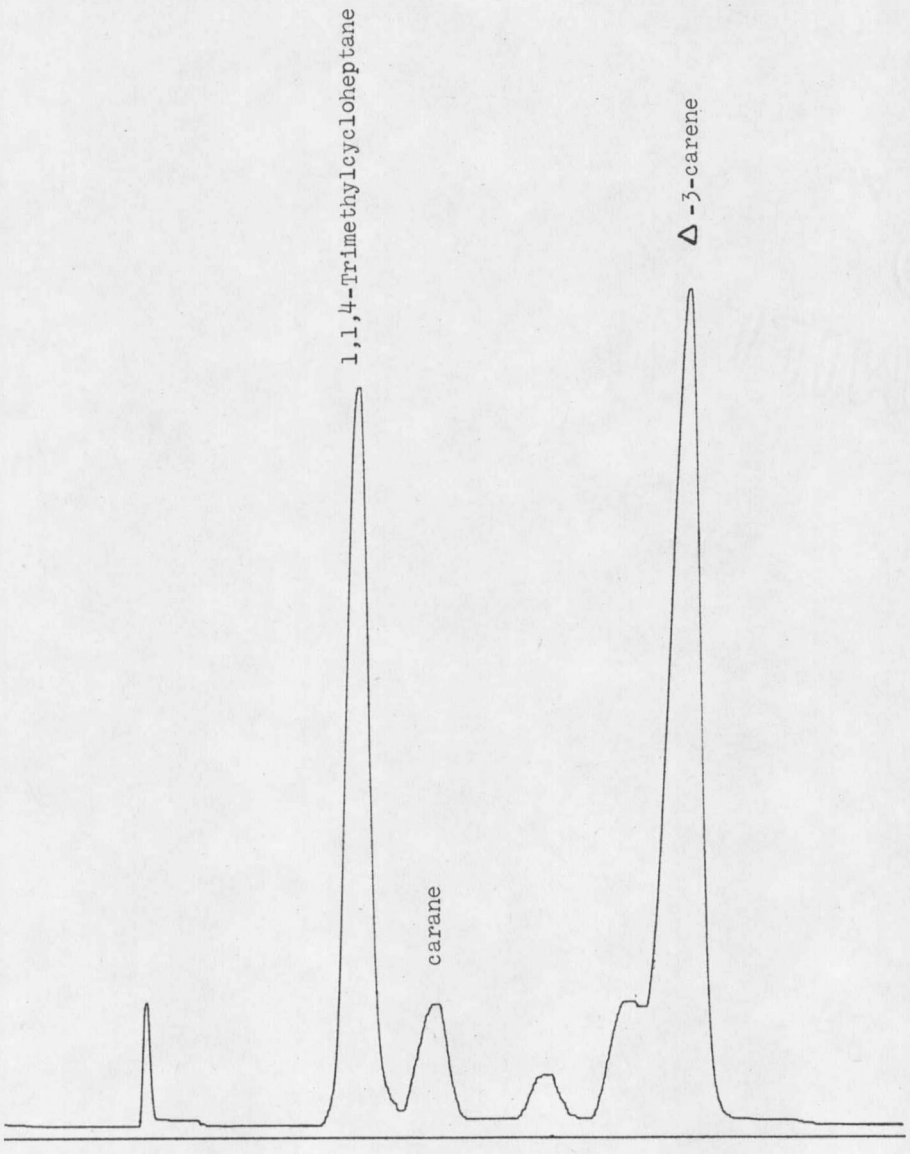


Figure 49. Chromatogram of Hydrogenation Product Produced at 60°C, 0 psig, LHSV = .20 and H_2 Rate = 94 SCF/gal. Δ-3

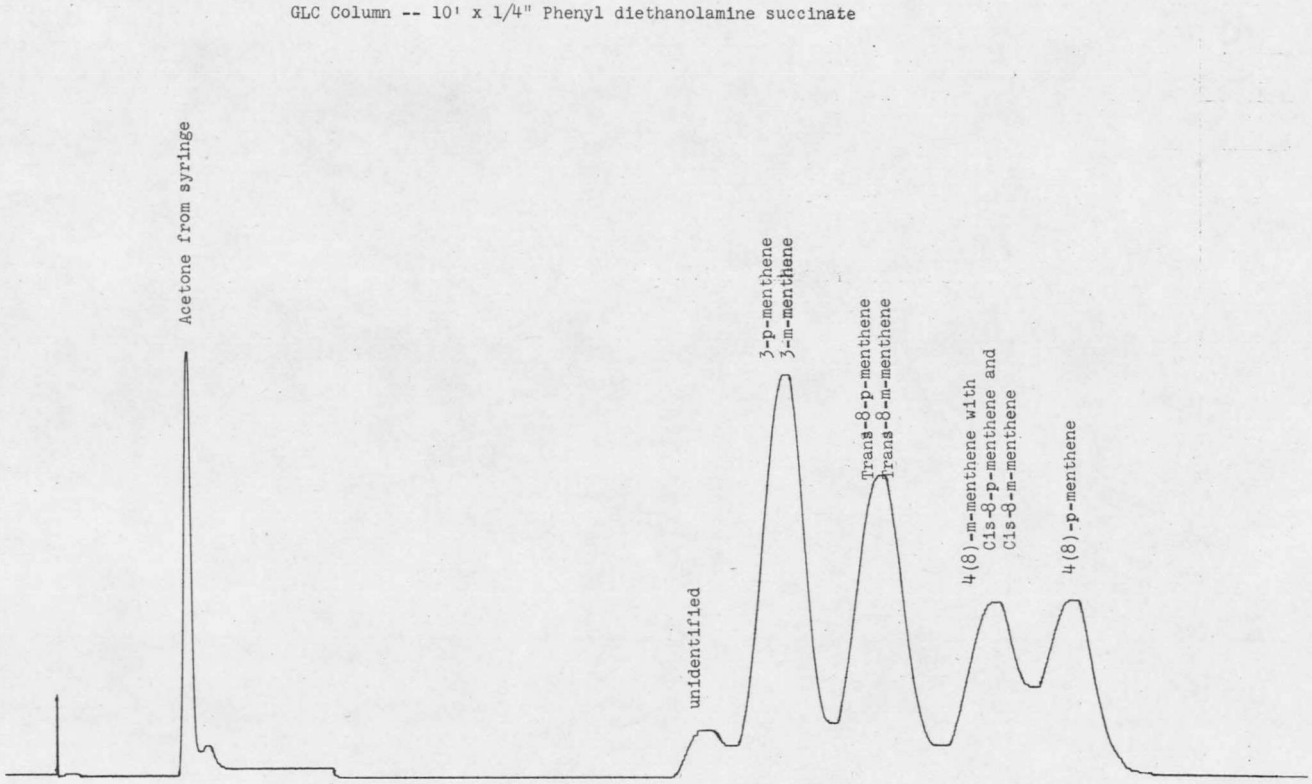


Figure 50. Chromatogram of Olefin Mixture Produced from Dehydrobromination of Terpinyl Bromides

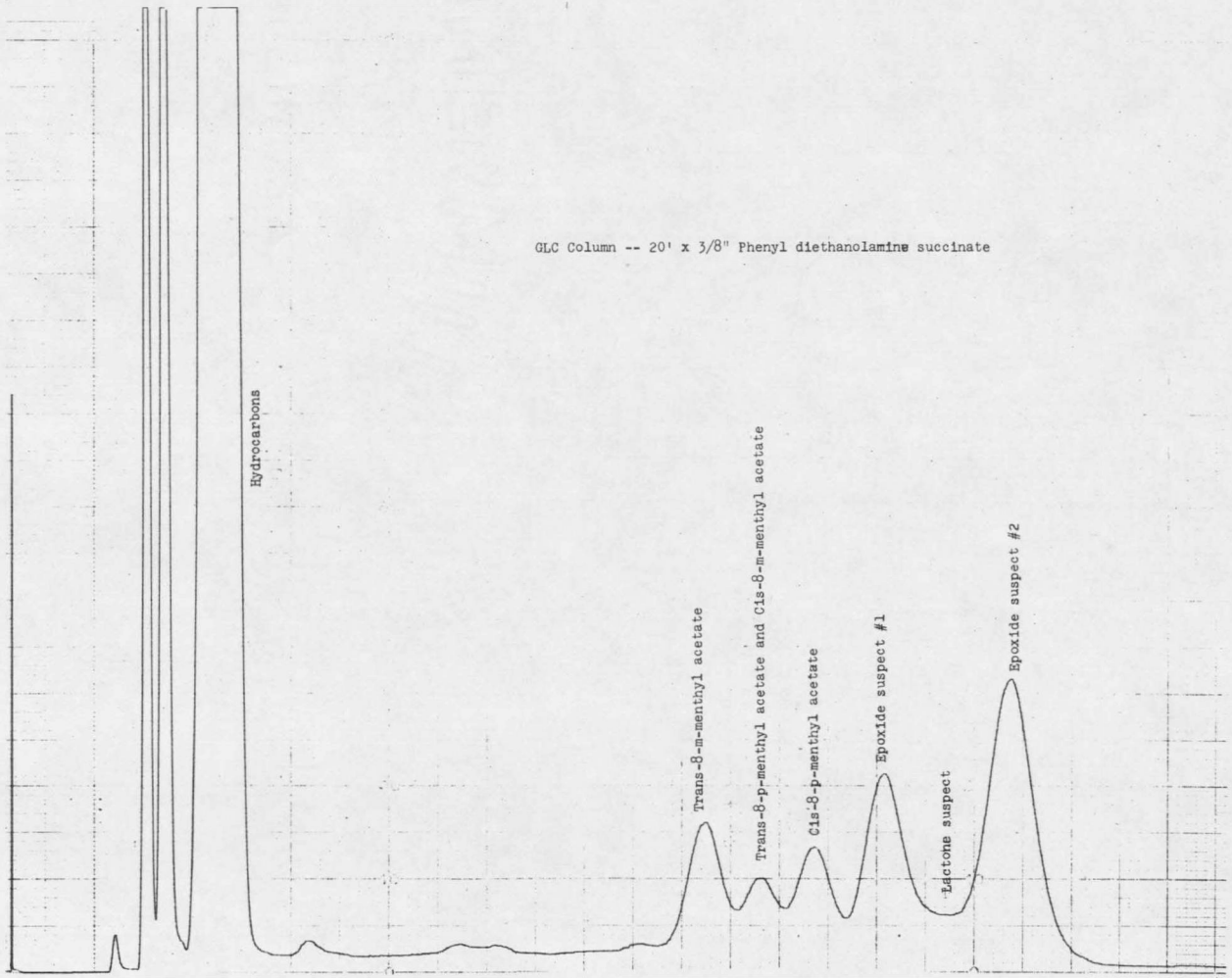


Figure 51. Chromatogram of Esters Obtained from a Hydrobromination Product Made with Benzoyl Peroxide Present

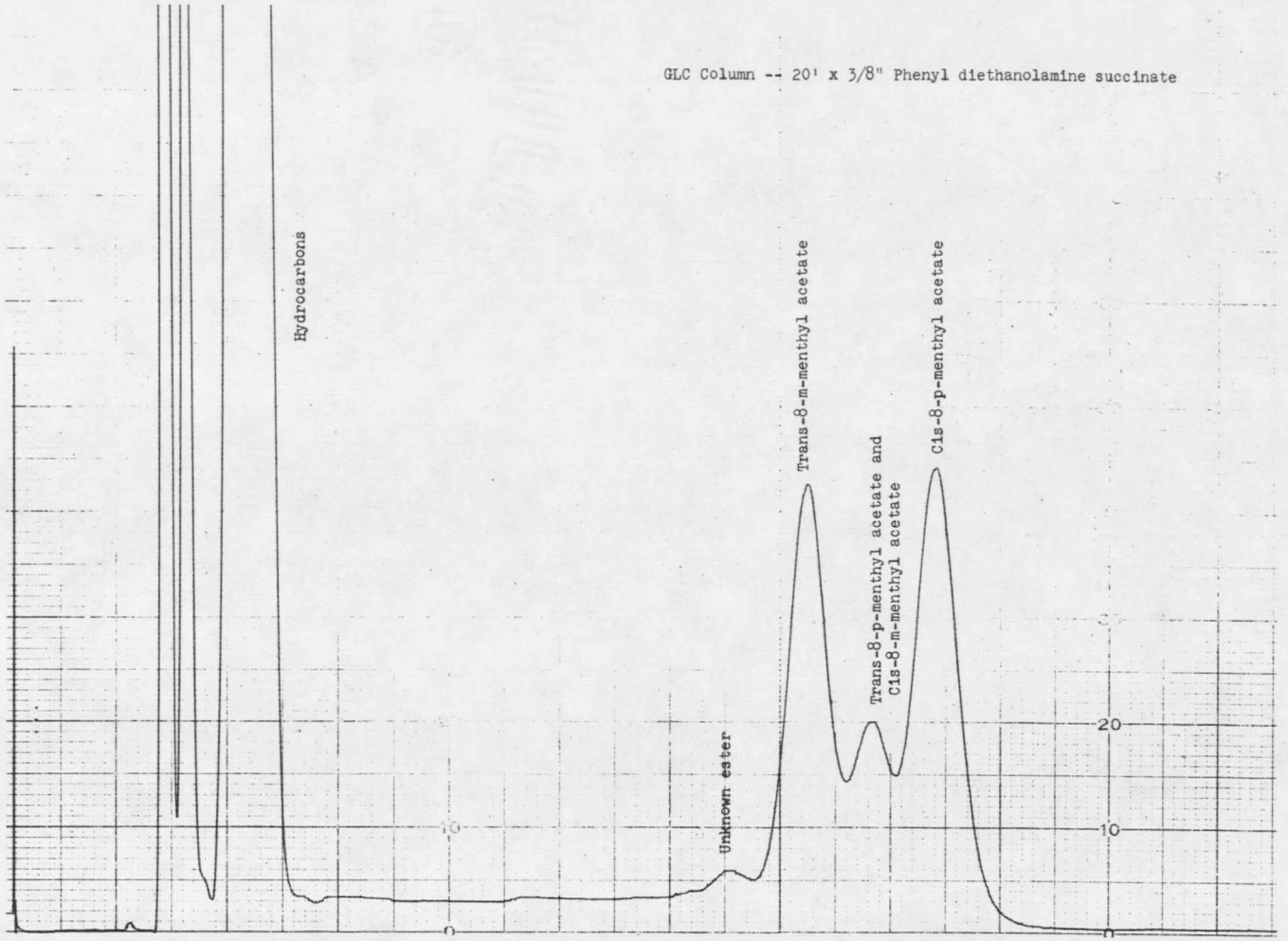


Figure 52. Chromatogram of Esters Obtained from a Hydrobromination Product Made with Diphenylamine Present

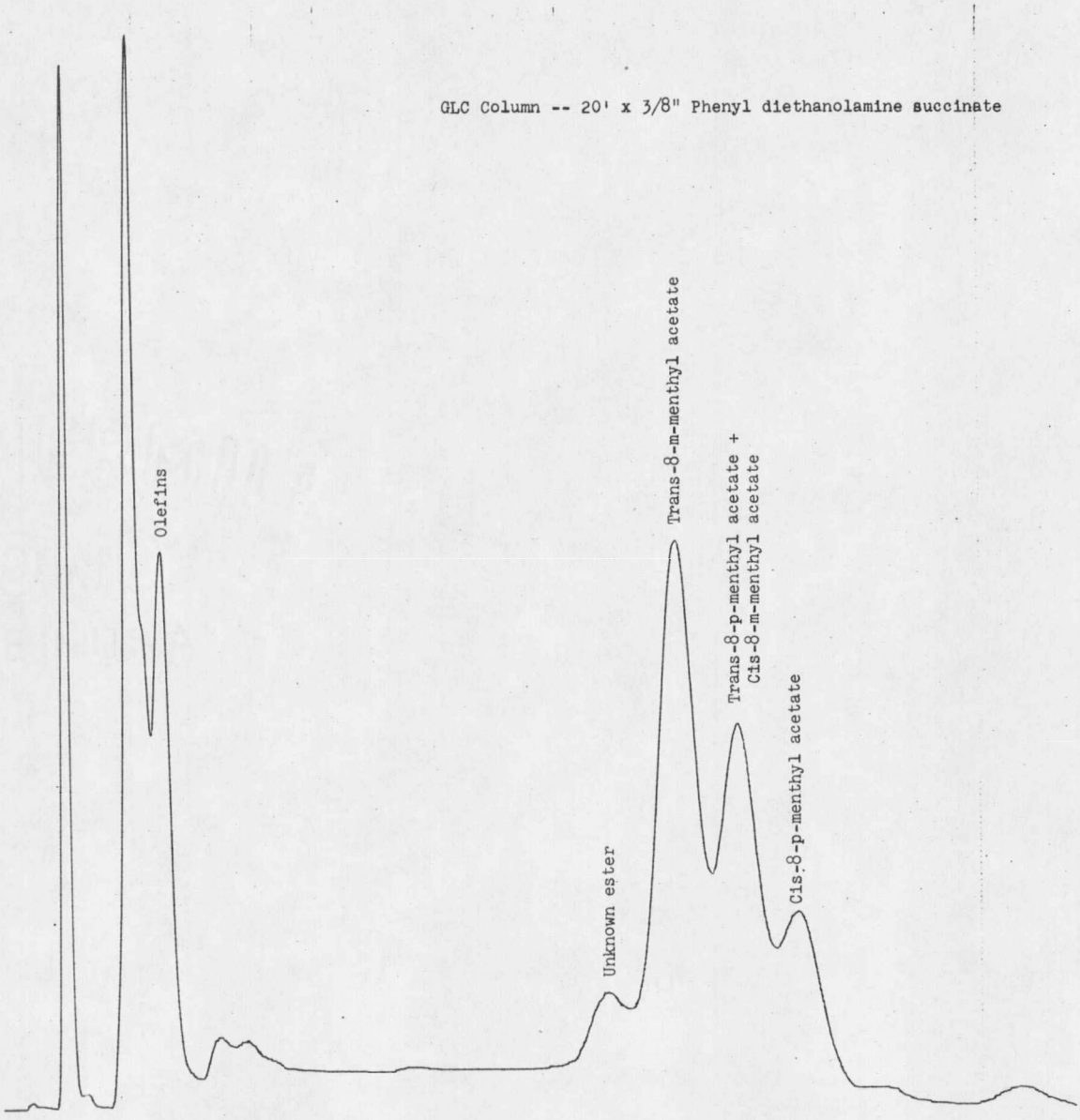


Figure 53. Chromatogram of the Terpinyl Ester Product Produced in Glacial Acetic Acid with Silver Acetate

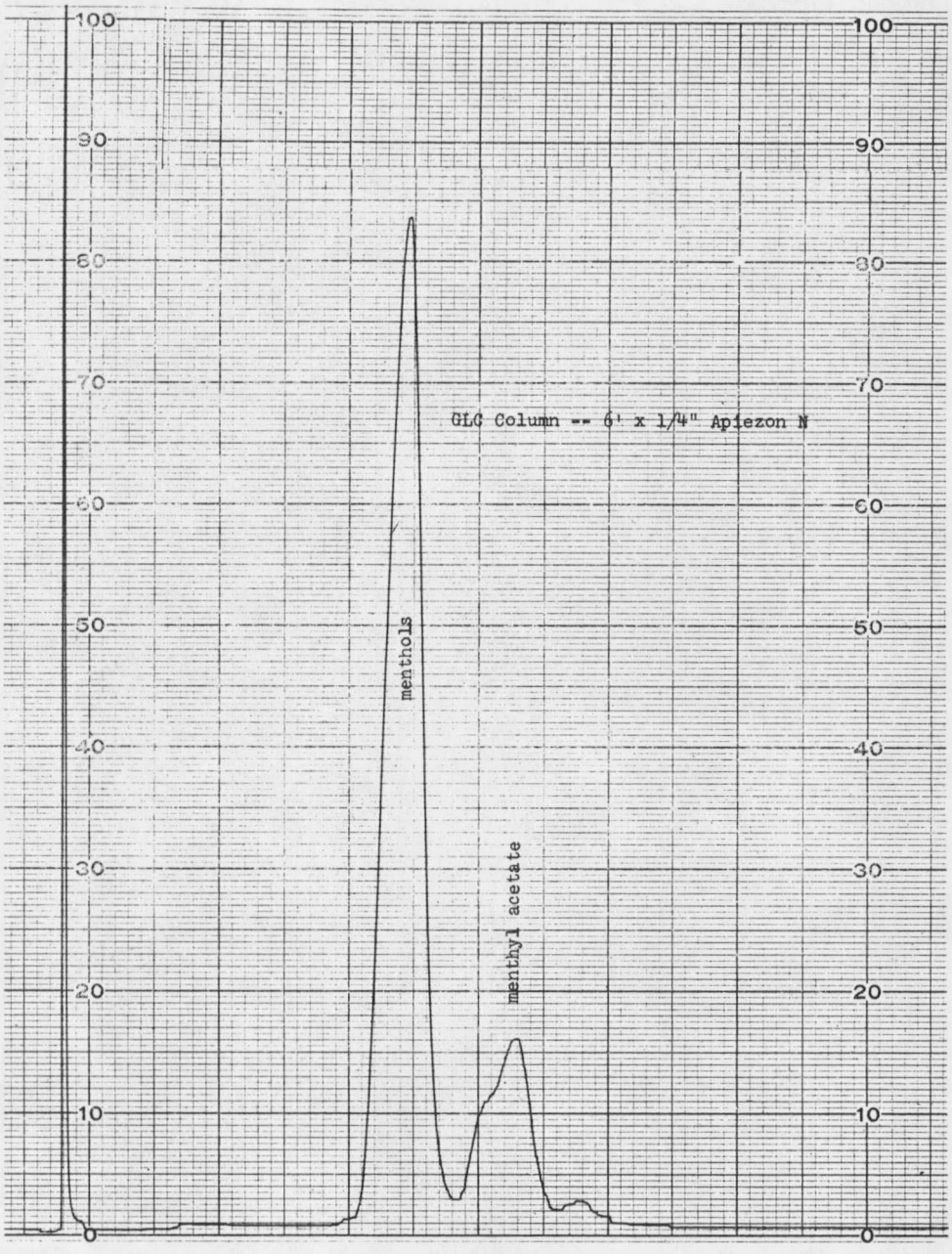


Figure 54. Chromatogram of Menthol Product from the Saponification of Menthyl Acetate

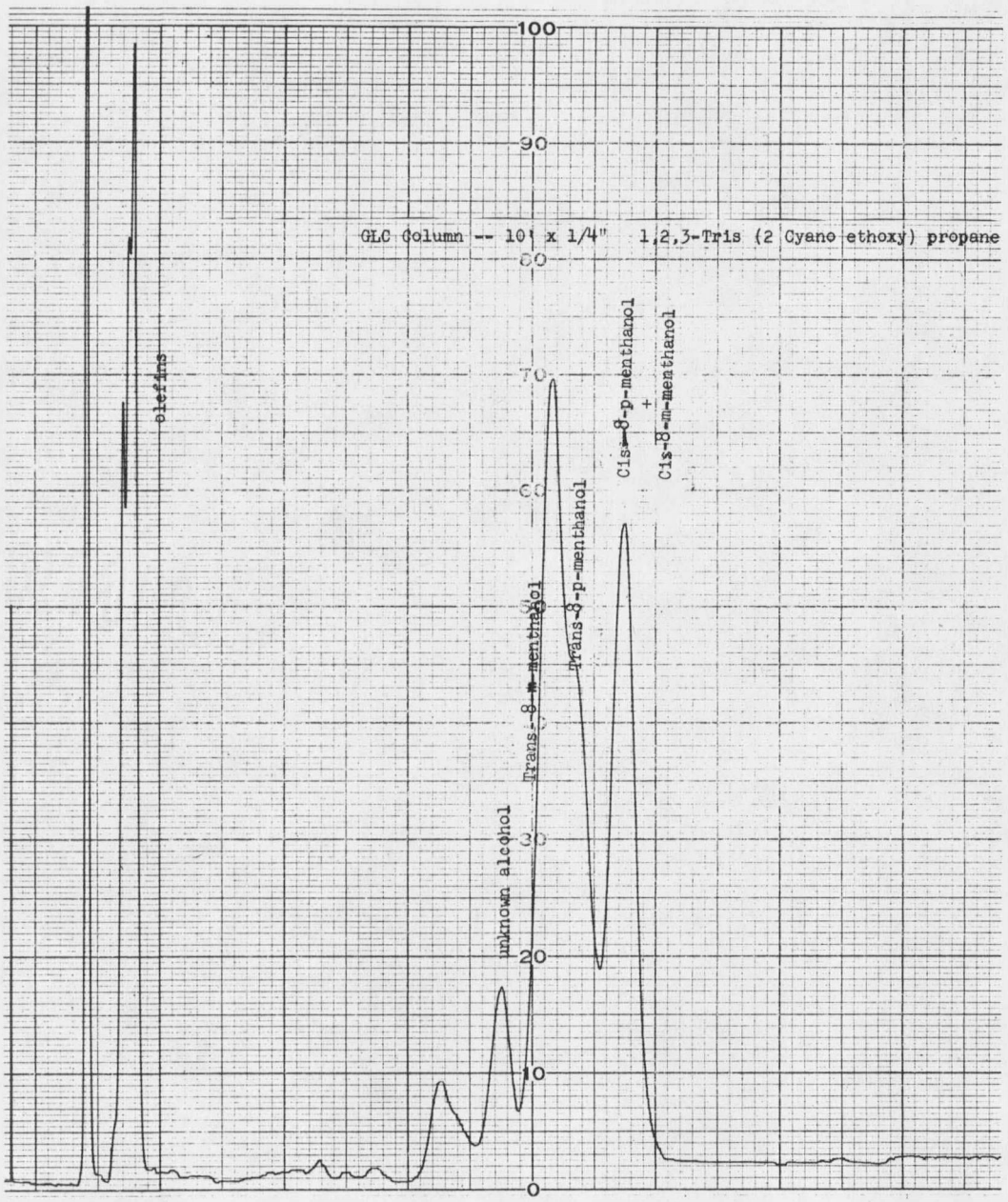
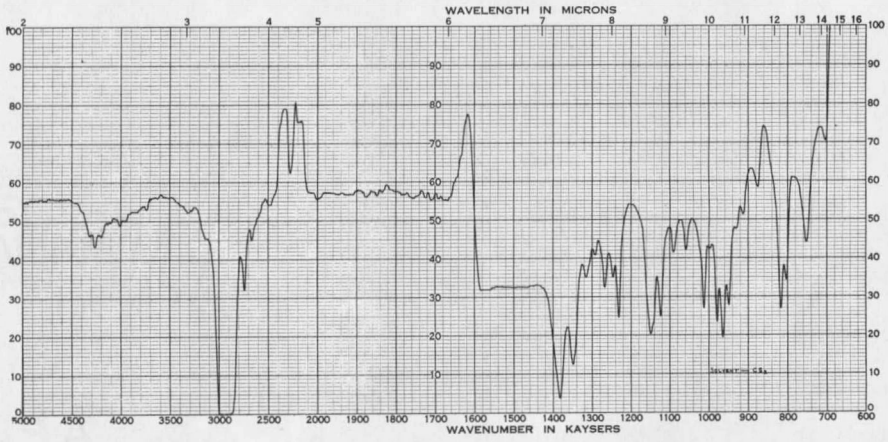
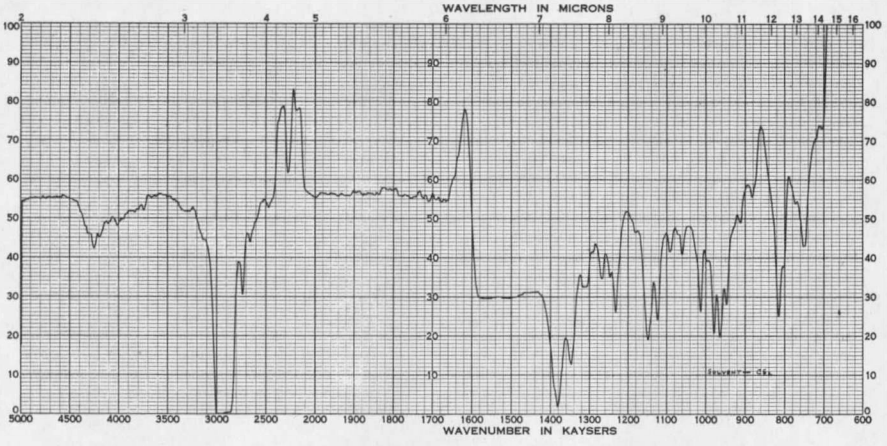


Figure 55. Chromatogram of the Alcohol Product Produced from the Terpinyl Esters by Saponification at 120°C for 13 hours

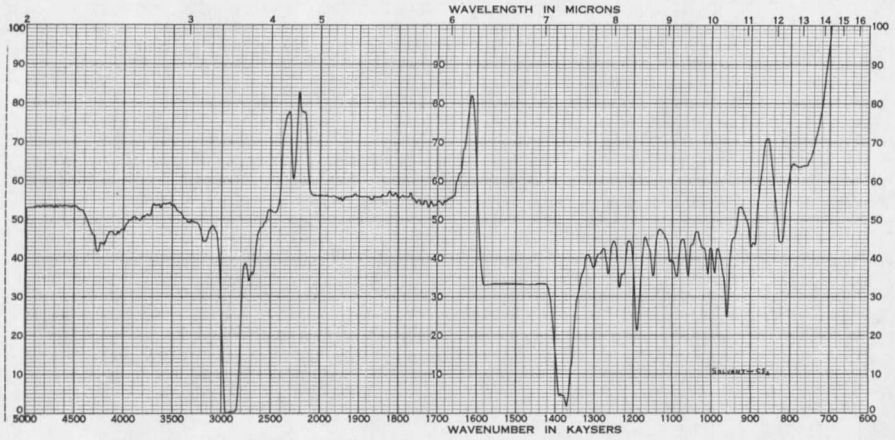


Cis-Carane from Cocker (16)

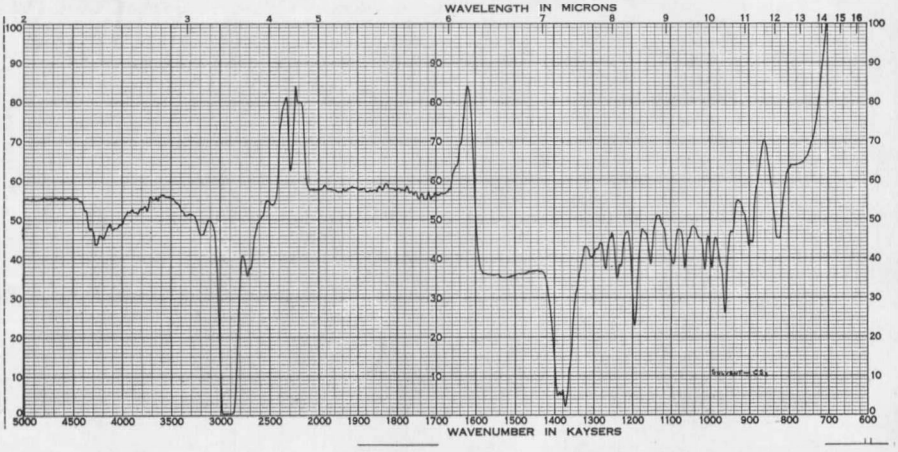


Carane from Hydrogenation Product

Figure 56. Comparison of the Infrared Spectra of Known Cis-Carane with Carane Produced in this Research

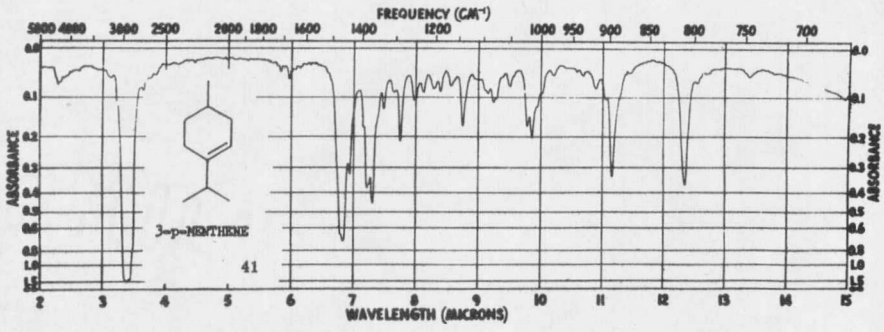


1,1,4-Trimethylcycloheptane from Cocker[16]

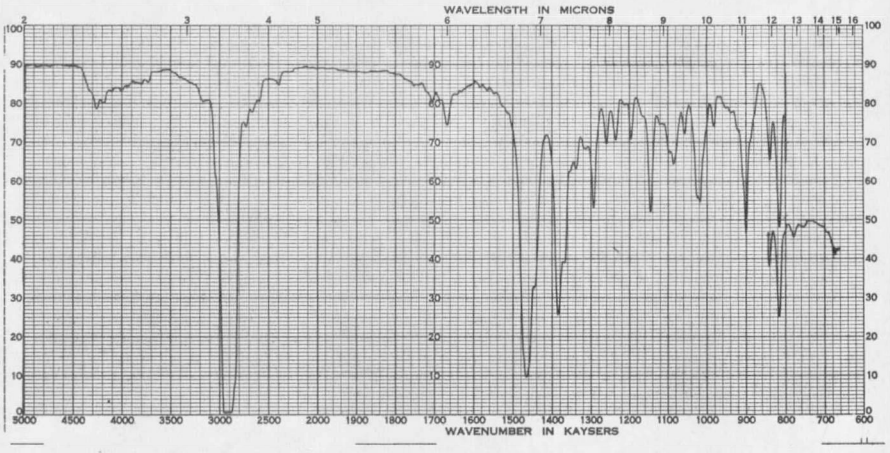


1,1,4-Trimethylcycloheptane from Hydrogenation Product

Figure 57. Comparison of the Infrared Spectra of Known 1,1,4-Trimethylcycloheptane with 1,1,4-Trimethylcycloheptane Produced in this Research

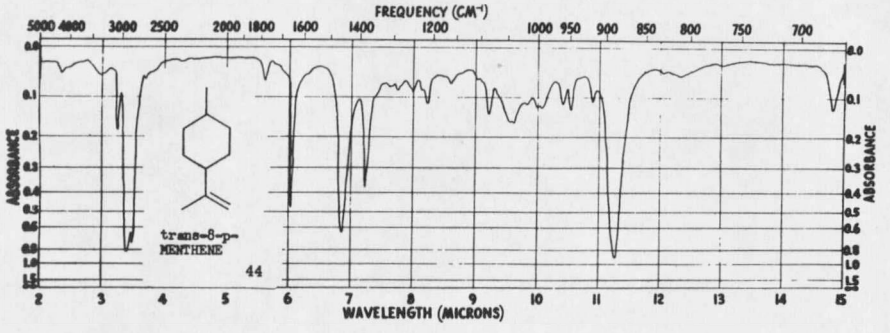


3-p-Menthene from Mitzner et al[56]

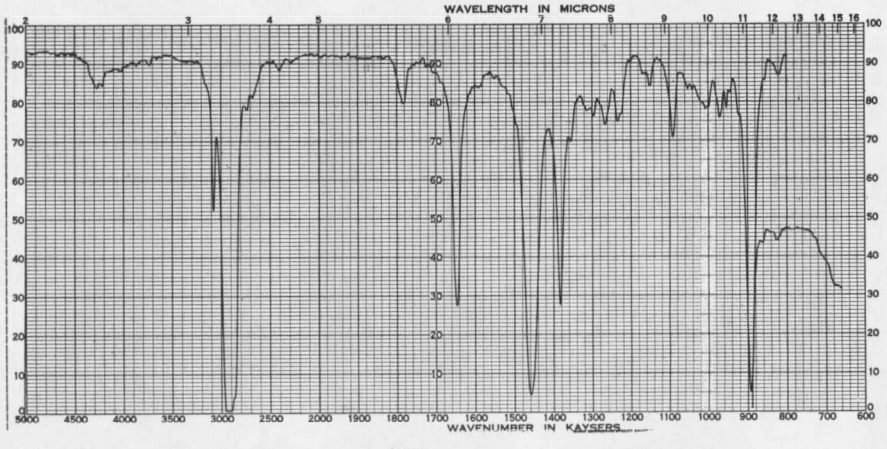


Suspected Mixture of 3-p-Menthene and 3-m-Menthene from Dehydrobromination Product

Figure 58. Comparison of the Infrared Spectra of Known 3-p-Menthene and the 3-p-Menthene and 3-m-Menthene Mixture Obtained in this Research from the Dehydrobromination of the Terpinyl Bromides

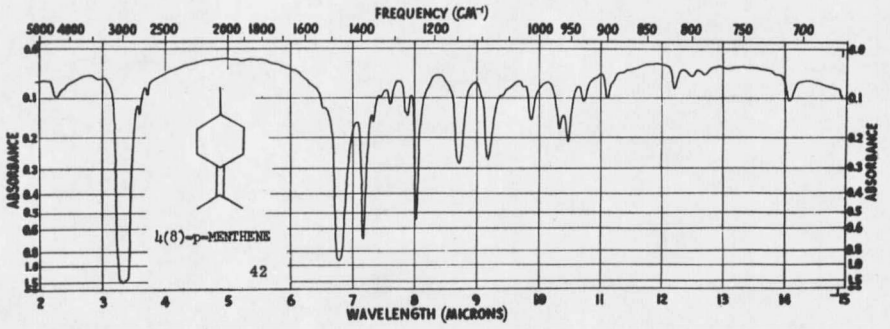


Trans-8-p-Menthene from Mitzner et al[56]

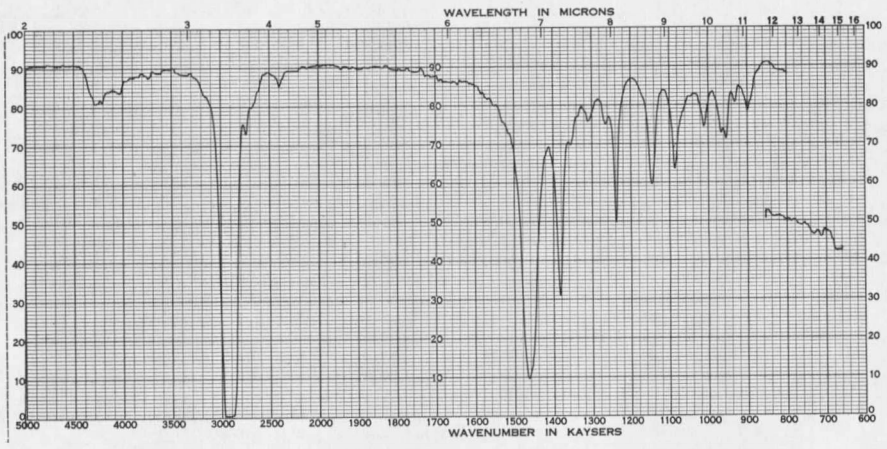


Suspected Mixture of Trans-8-p-Menthene and Trans-8-m-Menthene from Dehydrobromination Product

Figure 59. Comparison of the Infrared Spectra of Known Trans-8-p-Menthene and the Trans-8-p-Menthene and Trans-8-m-Menthene Mixture Obtained in this Research from the Dehydrobromination of the Terpinyl Bromides



4(8)-p-Menthene from Mitzner et al[56]



4(8)-p-Menthene from Dehydrobromination Product

Figure 60. Comparison of the Infrared Spectra of Known 4(8)-p-Menthene and 4(8)-p-Menthene from the Dehydrobromination of the Terpinyl Bromides

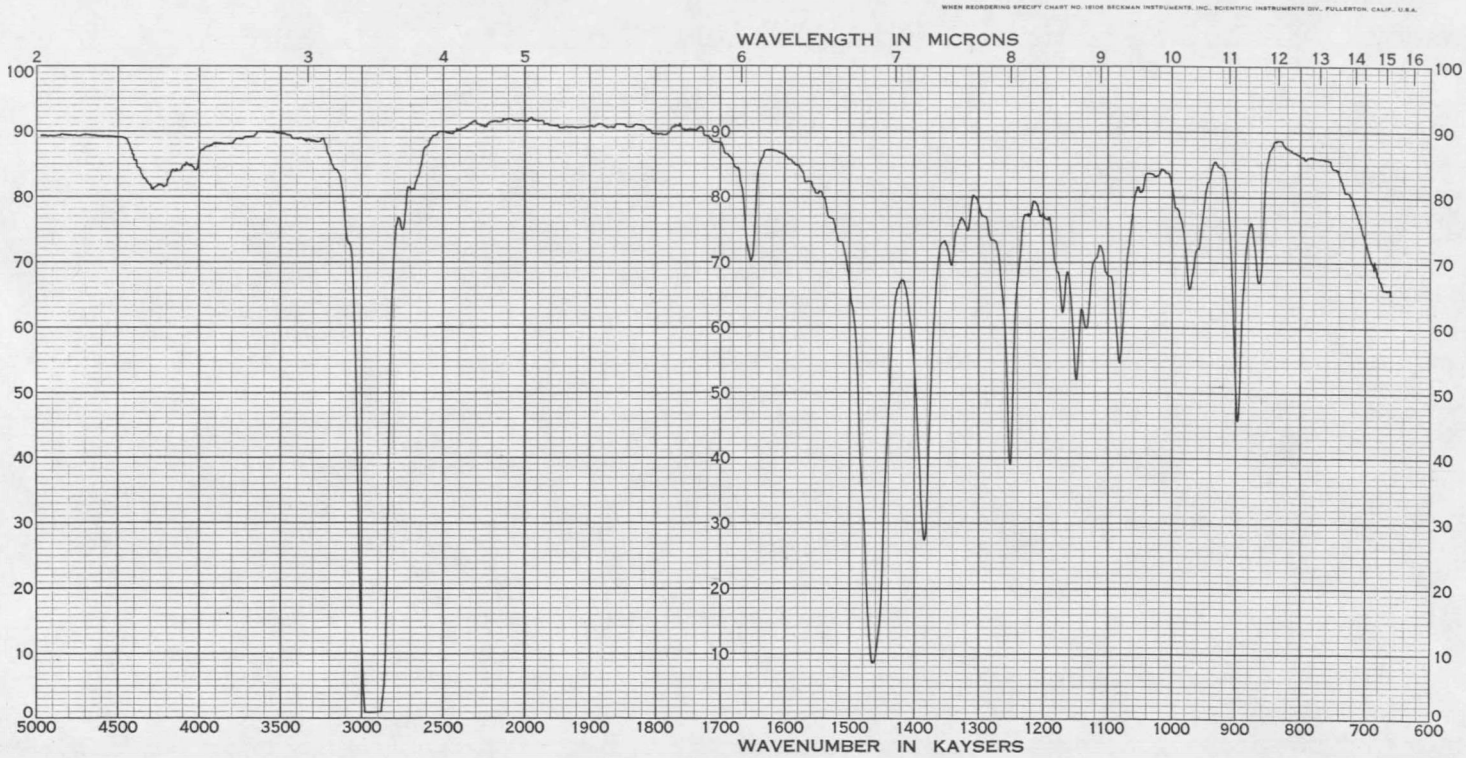
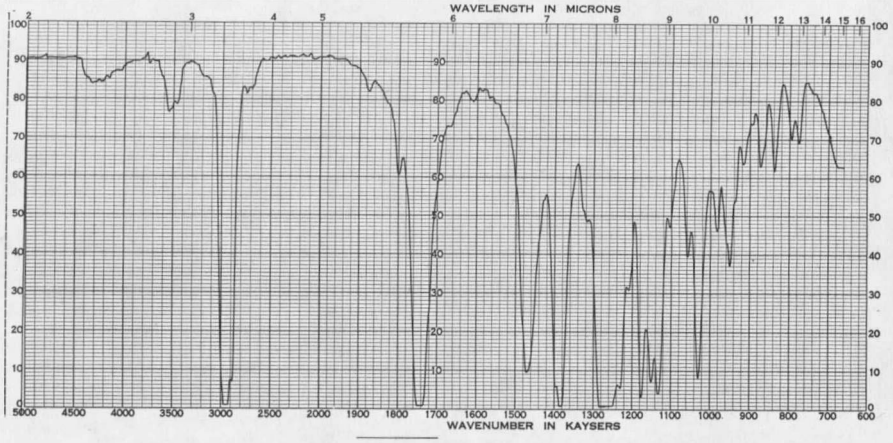
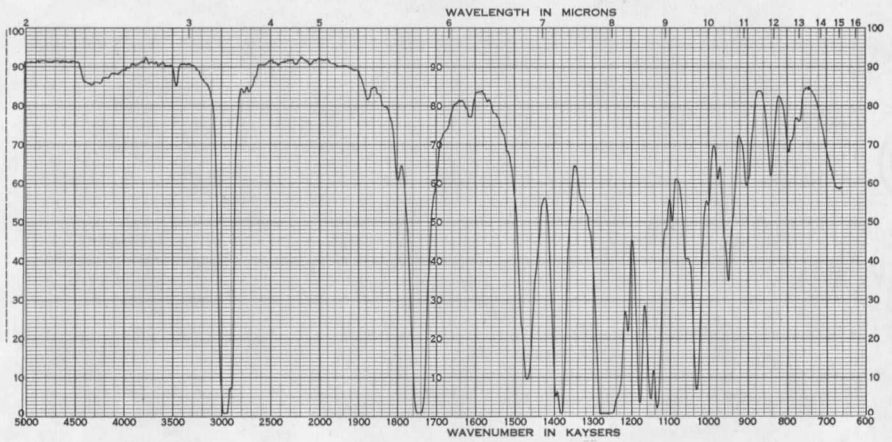


Figure 61. Infrared Spectrum of an Olefin Believed to be a Mixture of 4(8)-m-Menthene, Cis-8-m-Menthene and Cis-8-p-Menthene Obtained from the Dehydrobromination of the Terpinyl Bromides

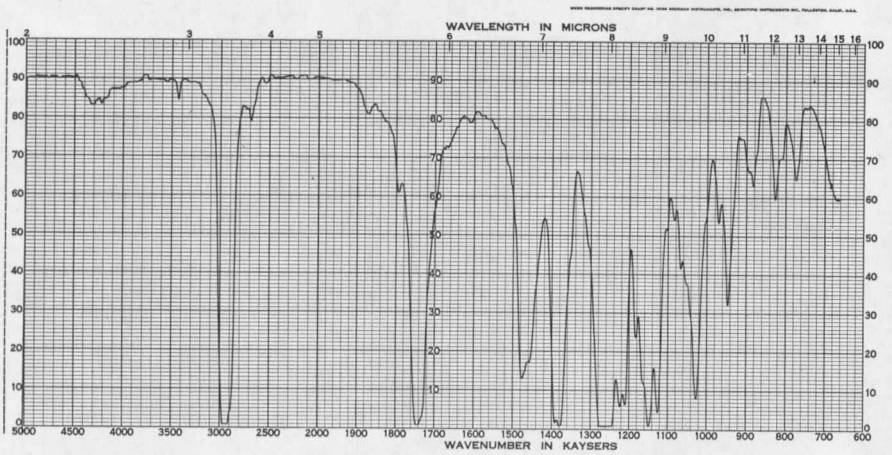


Trans-8-m-Menthyl Acetate



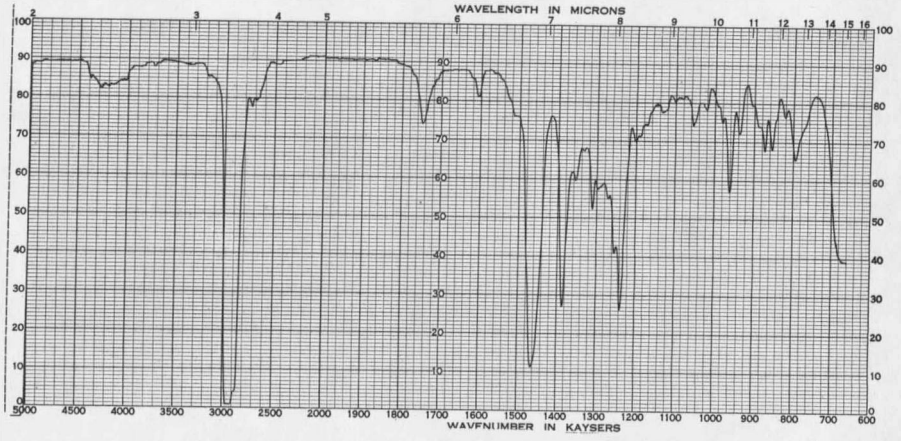
Suspected Mixture of Cis-8-m-Menthyl Acetate and Trans-8-p-Menthyl Acetate

Figure 62. Infrared Spectra of Terpinyl Esters Isolated from the Product Mixture



Cis-8-p-Menthyl Acetate

Figure 62 (continued)

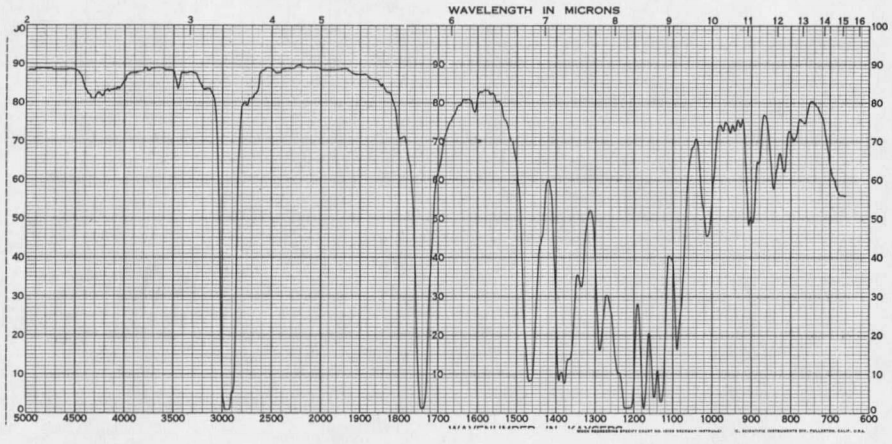


First Epoxide Suspect



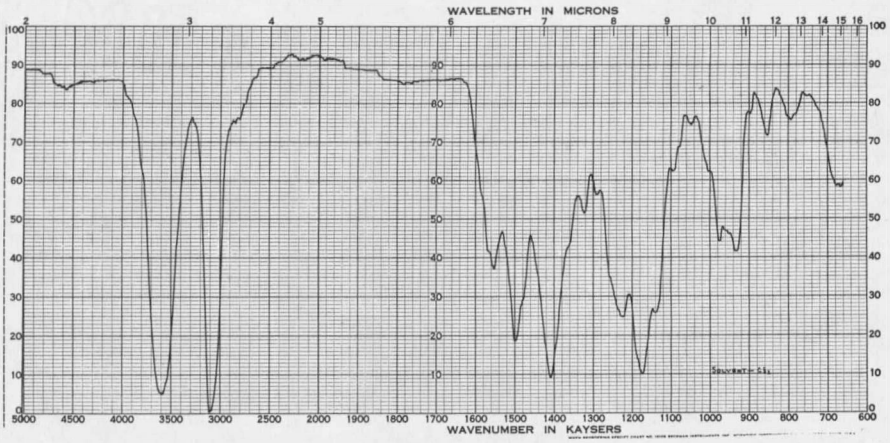
Second Epoxide Suspect

Figure 63. Infrared Spectra of the Unidentified By-Products Produced in the Esterification of the Hydrobromination Product

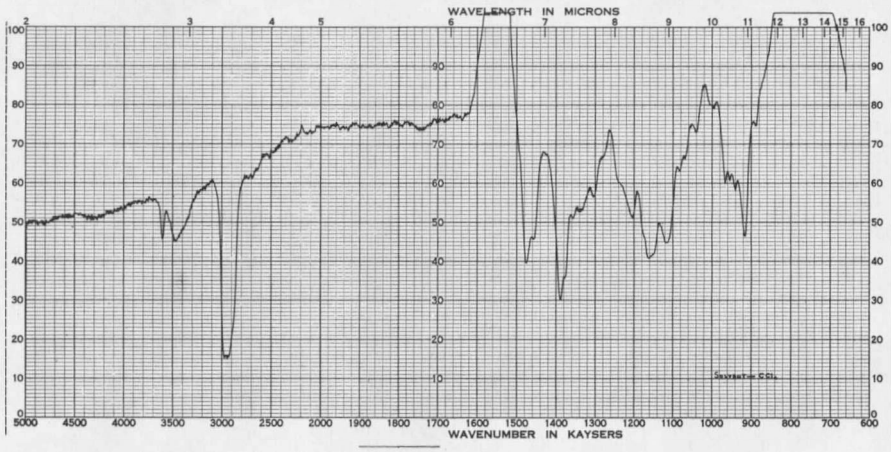


Lactone Suspect

Figure 63 (continued)

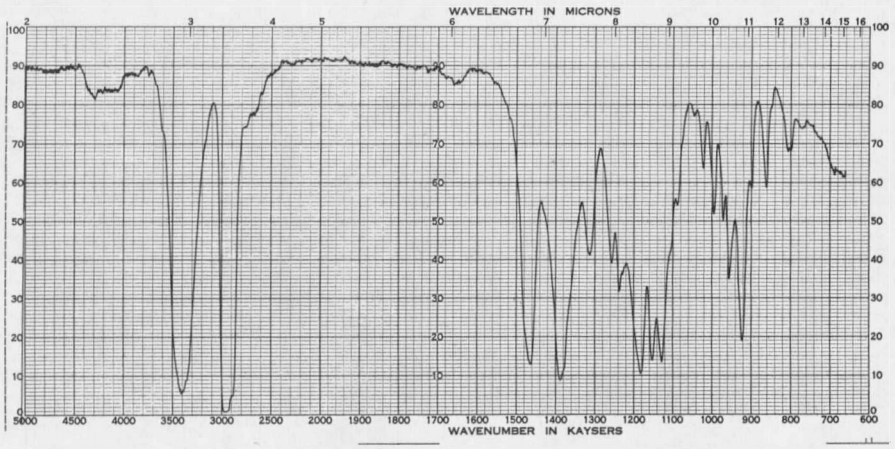


Cis-8-p-Menthanol from Heyden-Newport

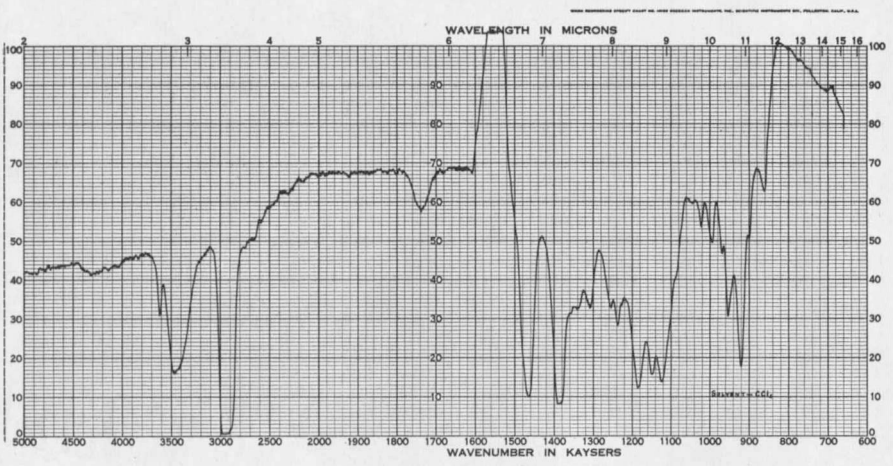


Cis-8-p-Menthanol from this Research

Figure 64. Comparison of the Infrared Spectra of Known Cis-8-p-Menthanol with the Cis-8-p-Menthanol Produced in this Research



Trans-8-p-Menthanol from Heyden-Newport



Trans-8-p-Menthanol from this Research

Figure 65. Comparison of the Infrared Spectra of Known Trans-8-p-Menthanol with the Trans-8-p-Menthanol Produced in this Research

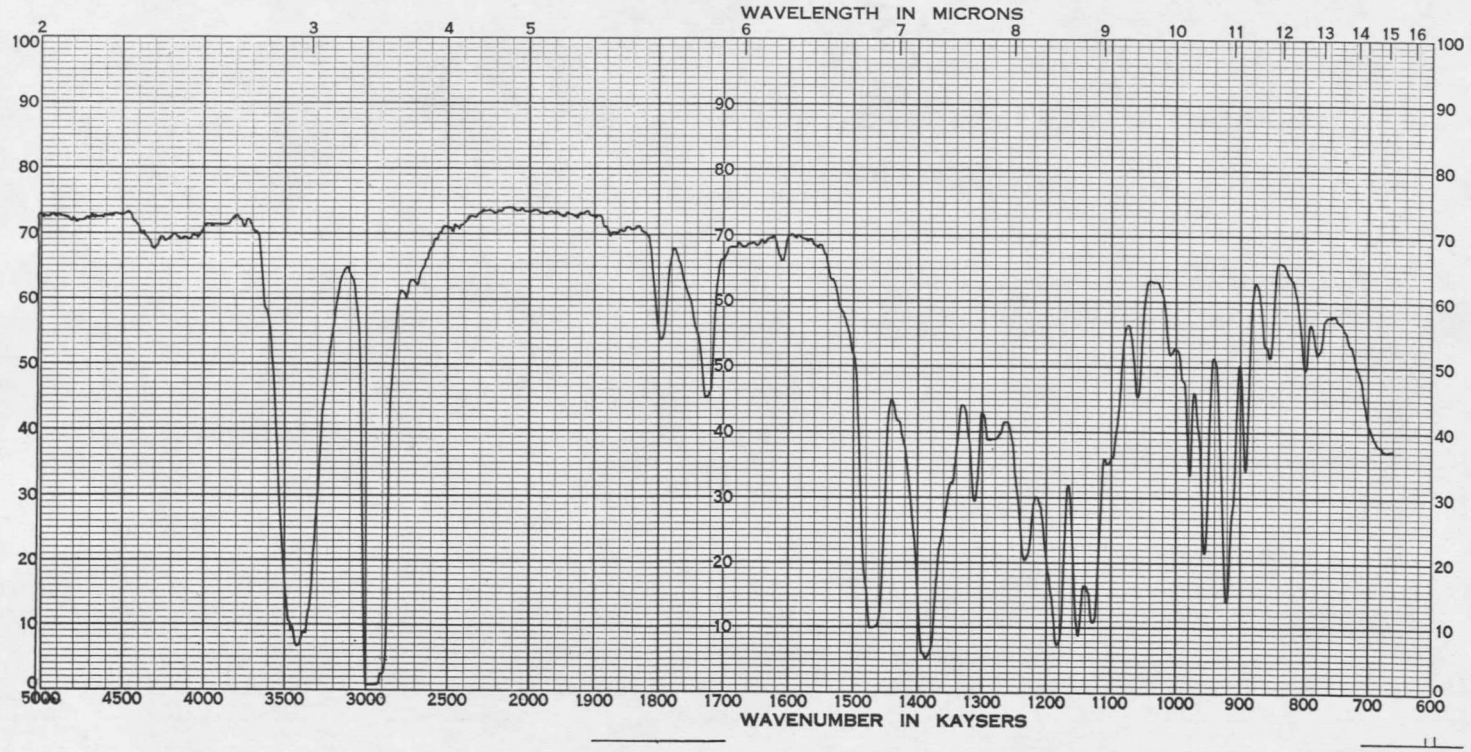
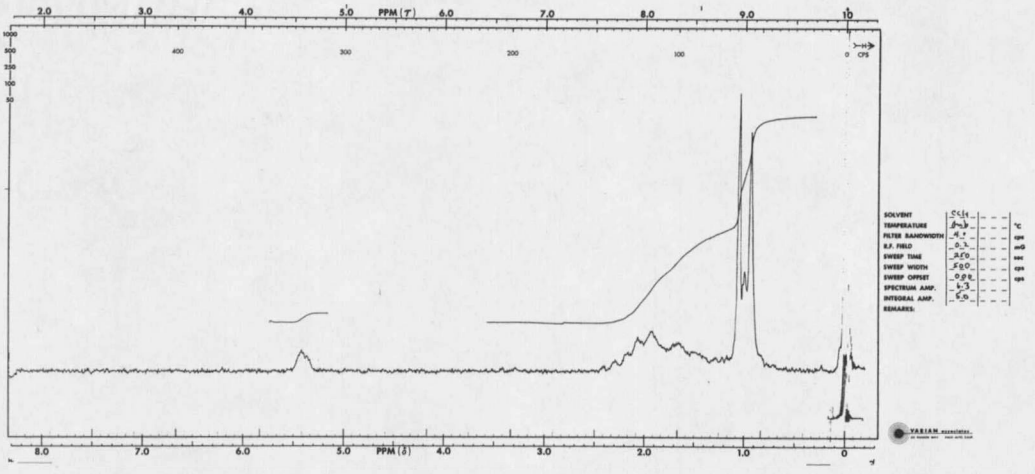
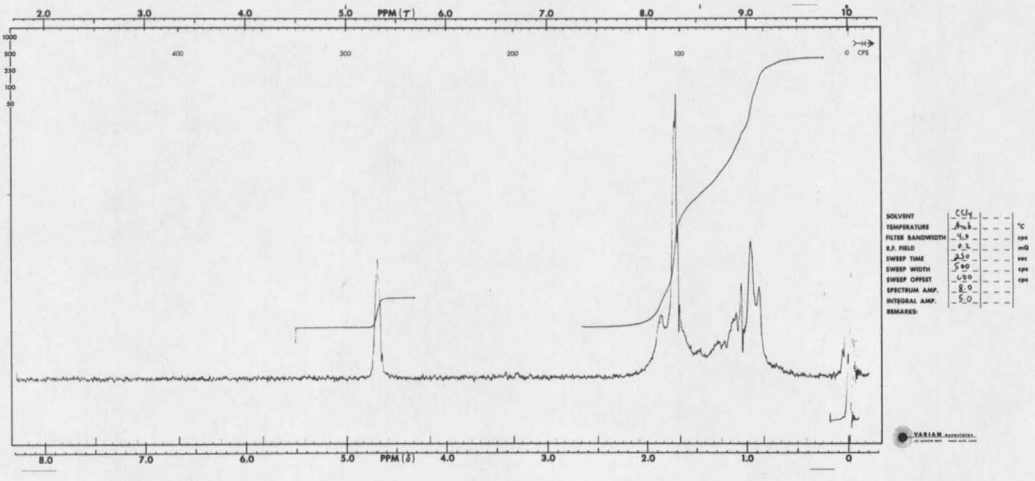


Figure 66. Infrared Spectrum of Alcohol Suspected to be Trans-8-m-Menthanol

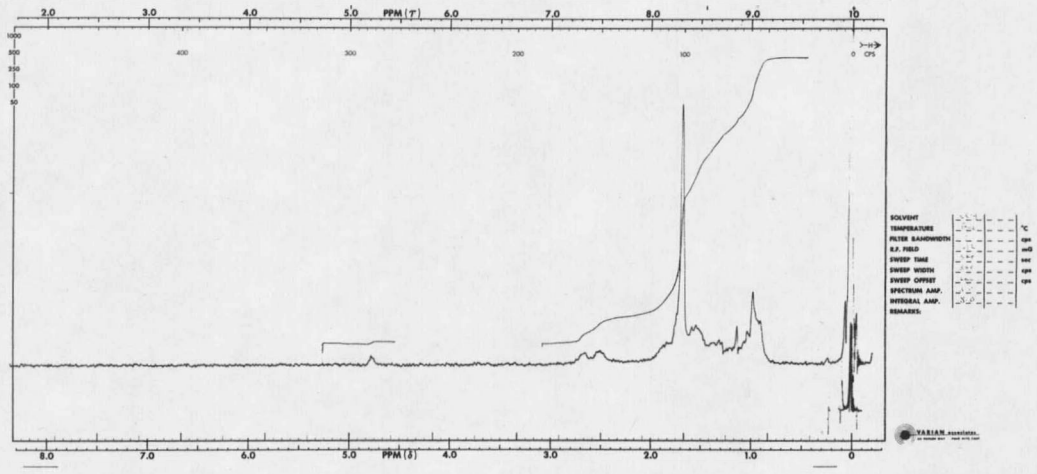


Suspected Mixture of 3-p-Menthene and 3-m-Menthene from Dehydrobromination Product

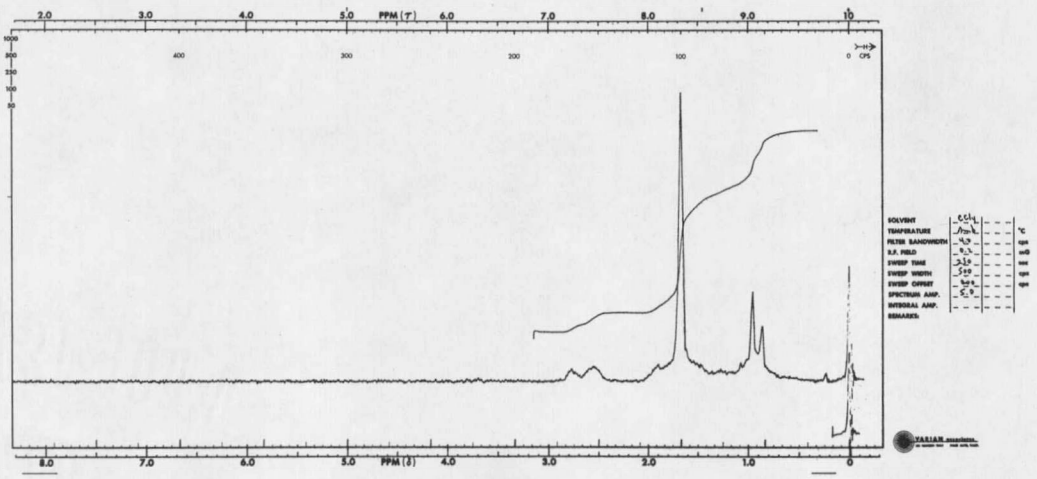


Suspected Mixture of Trans-8-p-Menthene and Trans-8-m-Menthene from Dehydrobromination Product

Figure 67-A. Nuclear Magnetic Resonance Spectra of the Olefins Obtained from the Dehydrobromination of the Terpinyl Bromides

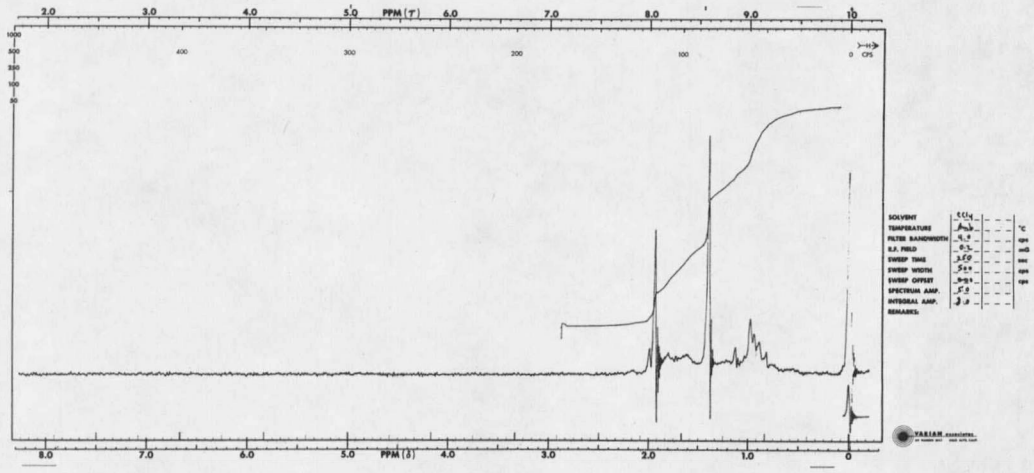


Suspected Mixture of 4(8)-m-Menthene, Cis-8-m-Menthene, and Cis-8-p-Menthene

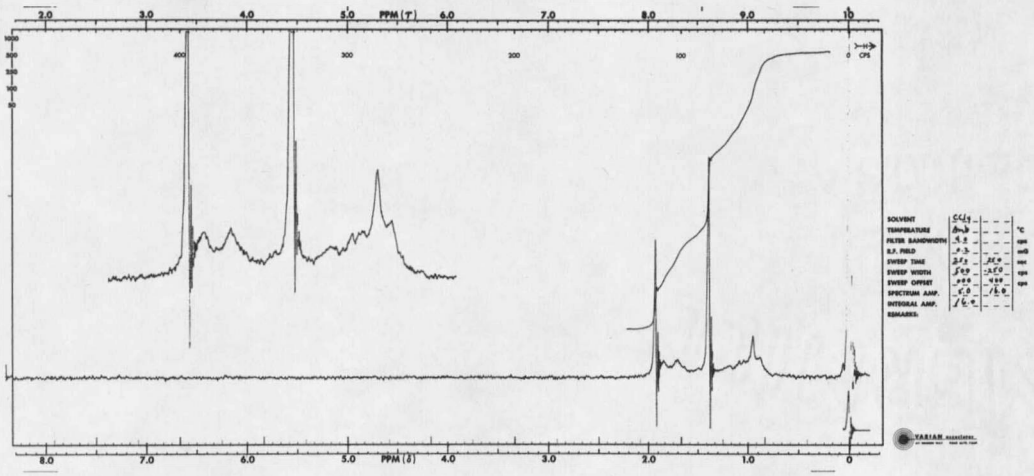


4(8)-p-Menthene from Dehydrobromination Product

Figure 67-B. Nuclear Magnetic Resonance Spectra of the Olefins Obtained from the Dehydrobromination of the Terpinyl Bromides

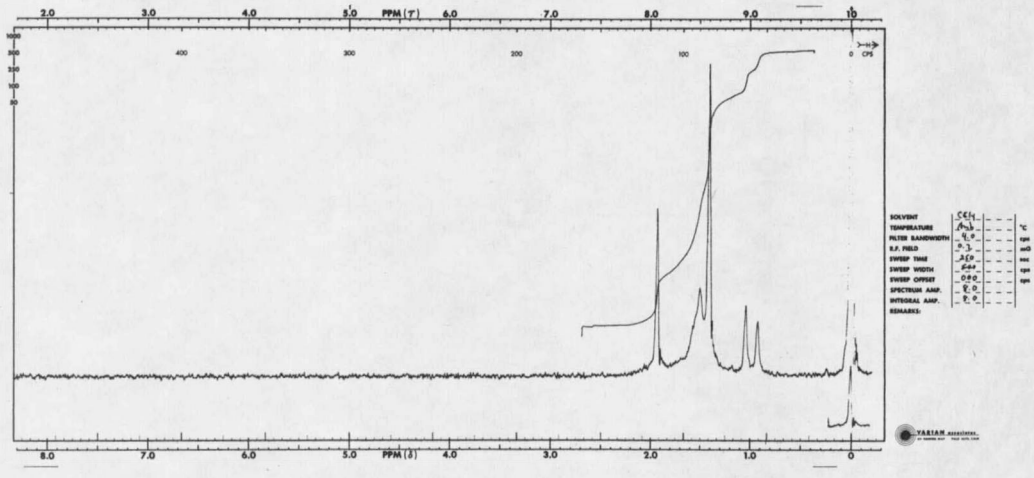


Trans-8-m-Menthyl Acetate



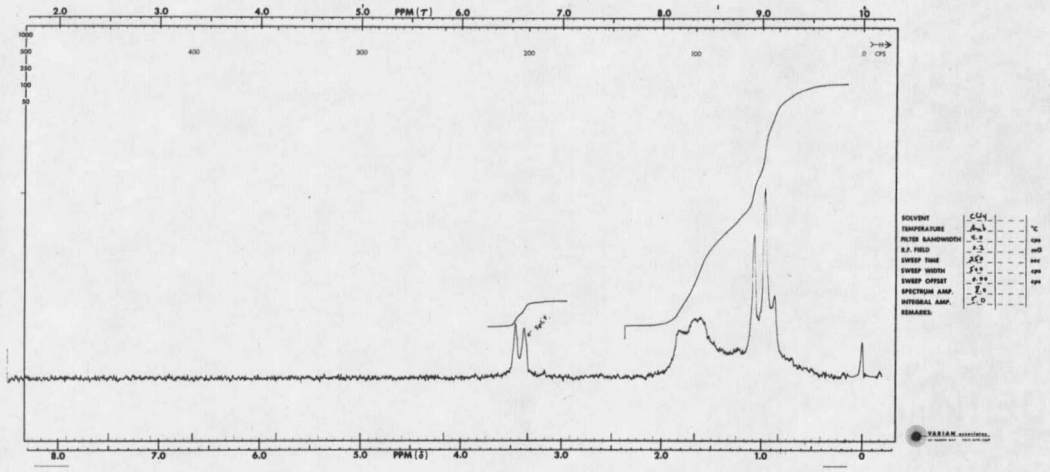
Suspected Mixture of Cis-8-m-Menthyl Acetate and Trans-8-p-Menthyl Acetate

Figure 68. Nuclear Magnetic Resonance Spectra for the Terpinyl Esters Isolated from the Product Mixture

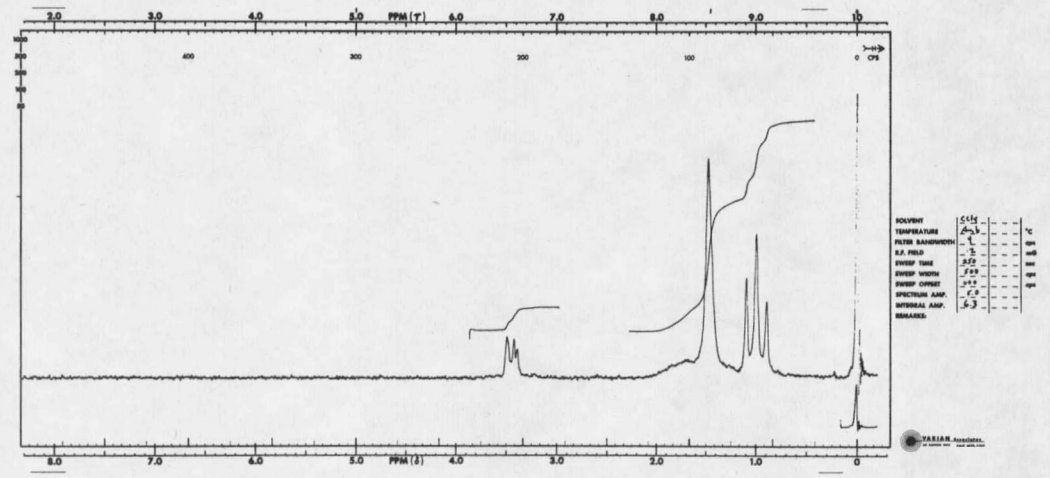


Cis-8-p-Menthyl Acetate

Figure 68 (continued)

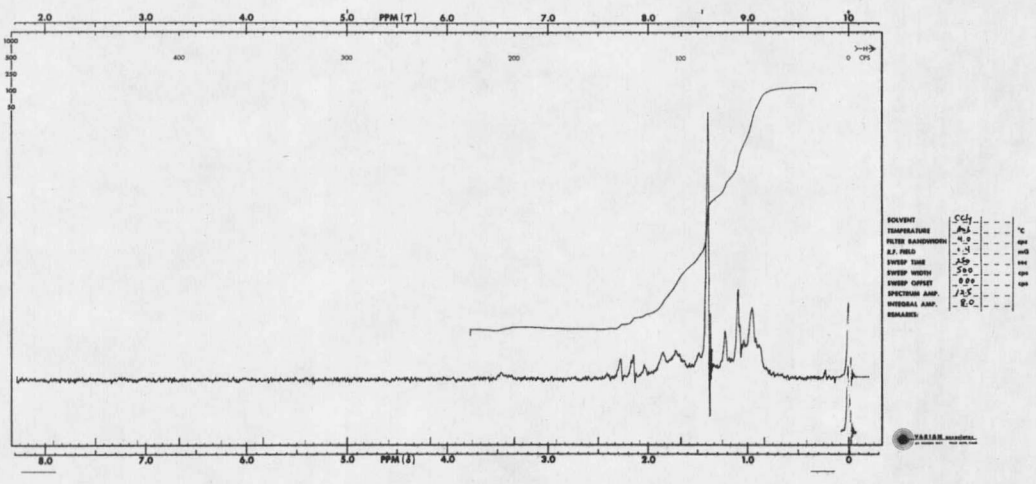


First Epoxide Suspect



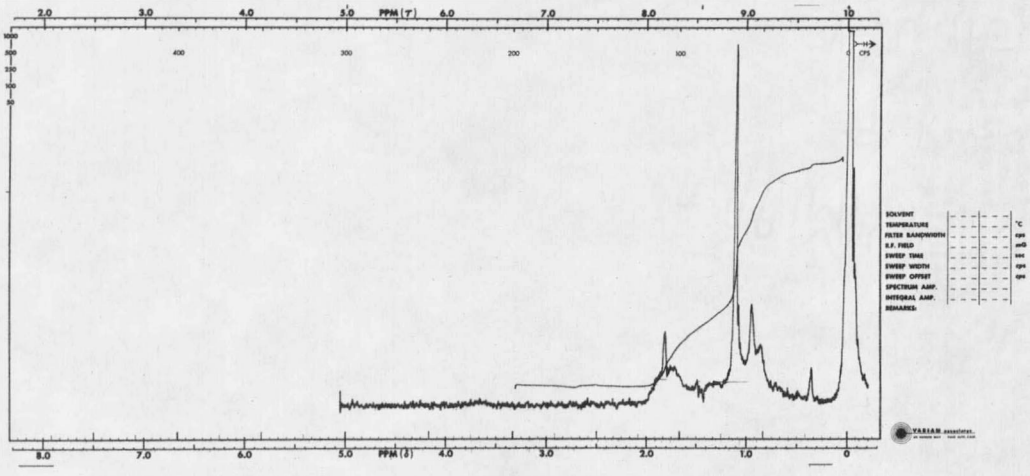
Second Epoxide Suspect

Figure 69. Nuclear Magnetic Resonance Spectra of the Unidentified By-Products in the Esterification of the Hydrobromination Product

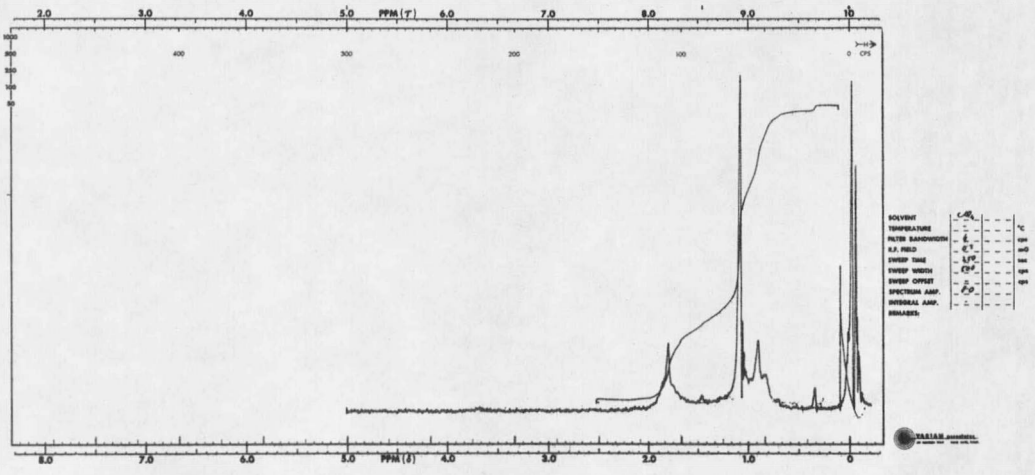


Lactone Suspect

Figure 69 (continued)

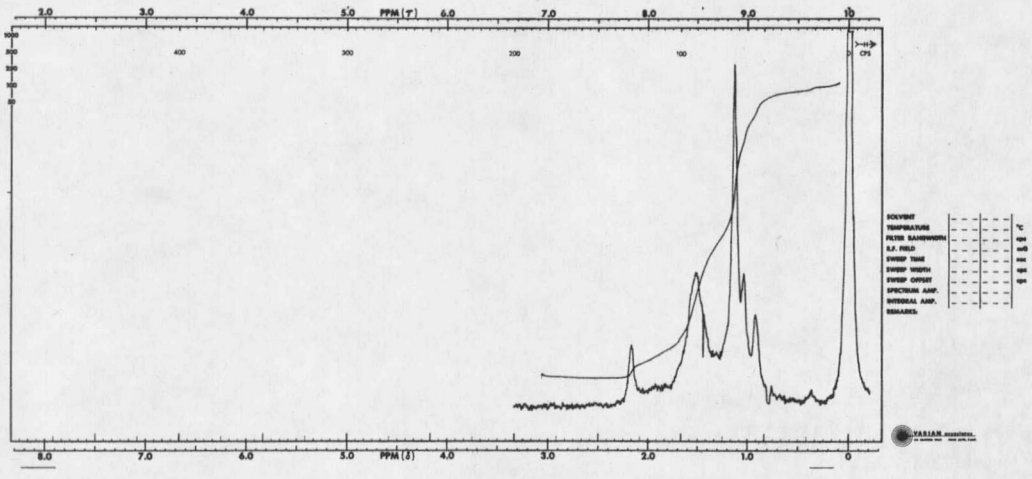


Trans-8-m-Menthanol from this Research



Trans-8-p-Menthanol from this Research

Figure 70. Nuclear Magnetic Resonance Spectra of Three of the Final Alcohol Products



Cis-8-p-Menthanol from this Research

Figure 70 (continued)

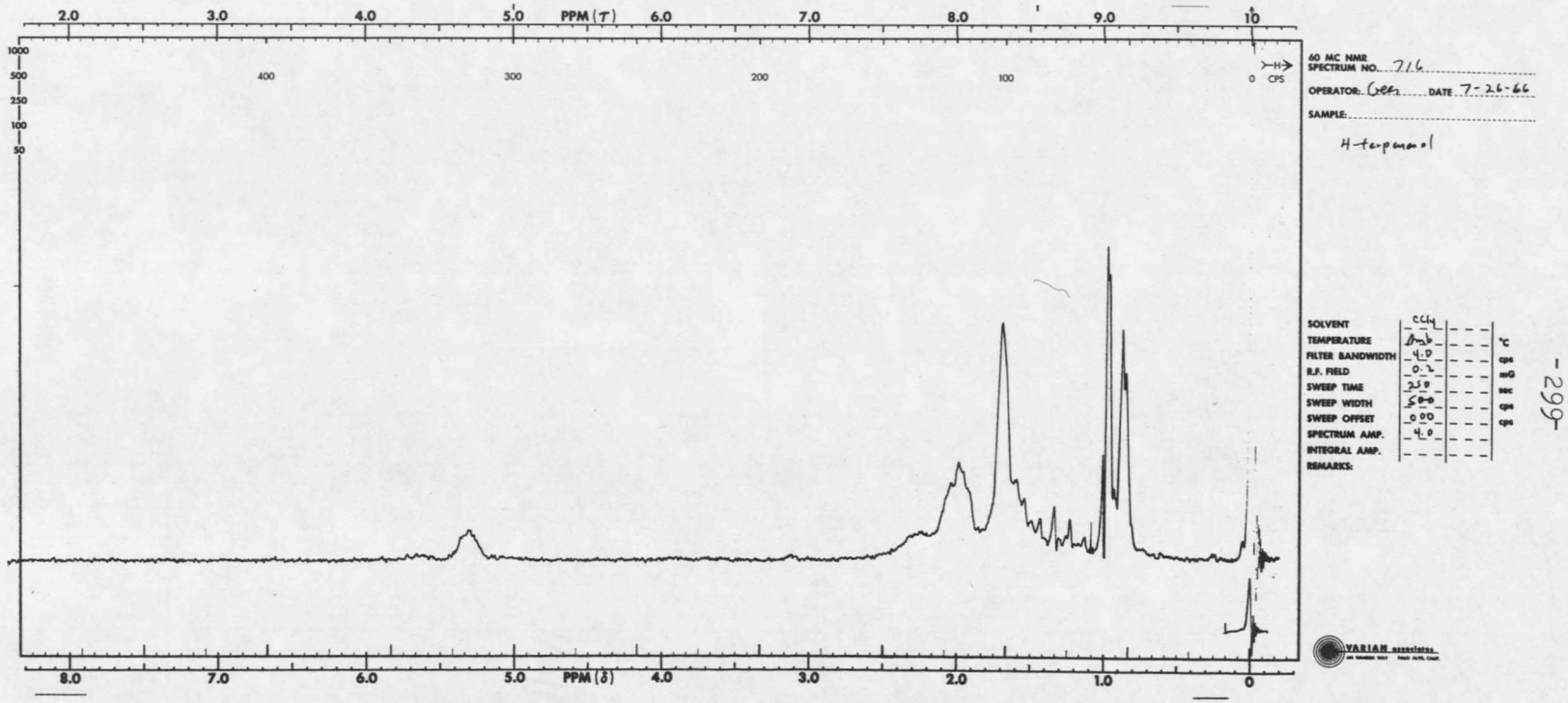


Figure 71. Nuclear Magnetic Resonance Spectra of Known 4-Terpinenol

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