

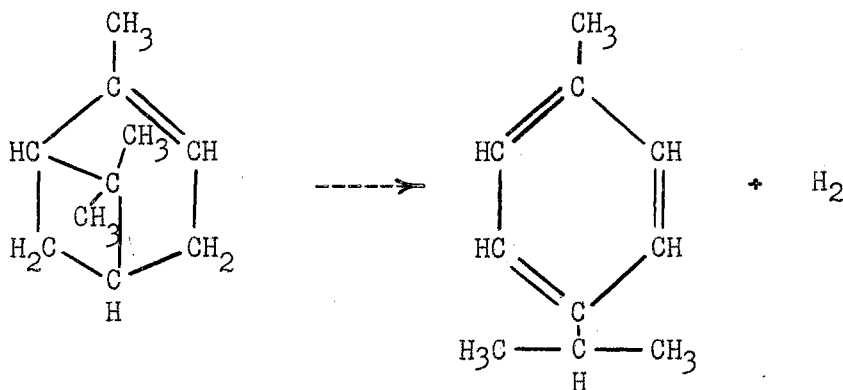
HISTORICAL

When most terpenes are brought in contact with dehydrogenation catalysts, para-cymene is formed (1). The yields are usually low, but the conversions are of value in establishing the molecular configuration of the terpenes.

The main source of para-cymene has been as a by-product of the sulfite process of manufacturing paper. It is extracted from the liquid mixture obtained when wood is subjected to calcium bisulfite cooking in the presence of steam.

The sulfite process is expensive, both in the amount of wood lost in the treatment, and in the cost of the reactants. For this reason the sulfate process, utilizing sodium hydroxide and sodium sulfide, has largely replaced the more expensive sulfite process. The sulfate process produces alpha and beta pinene rather than para-cymene.

Since the two processes are quite similar it has been suggested that para-cymene might be produced by dehydrogenation of the pinenes:



CONVERSION OF ALPHA AND
BETA PINENE TO PARA-CYMENE

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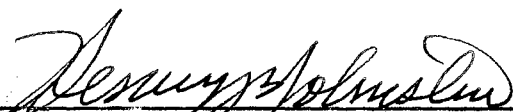
1951

Submitted to the Faculty of the Graduate School of
the Oklahoma Agricultural and Mechanical College
in Partial Fulfillment of the Requirements
for the Degree of
MASTER OF SCIENCE
May, 1953

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CONVERSION OF ALPHA AND
BETA PINENE TO PARA-CYMENE

Thesis Approved:



Thesis Adviser





Dean of the Graduate School

Acknowledgment

The author wishes to express his sincere gratitude to Dr. H. P. Johnston whose suggestions and guidance made the pursuance of this study possible and more enjoyable and to other members of the staff for their suggestions.

He also wishes to express his appreciation to Oklahoma A. and M. College for financial aid in the form of a graduate fellowship in the Chemistry Department.

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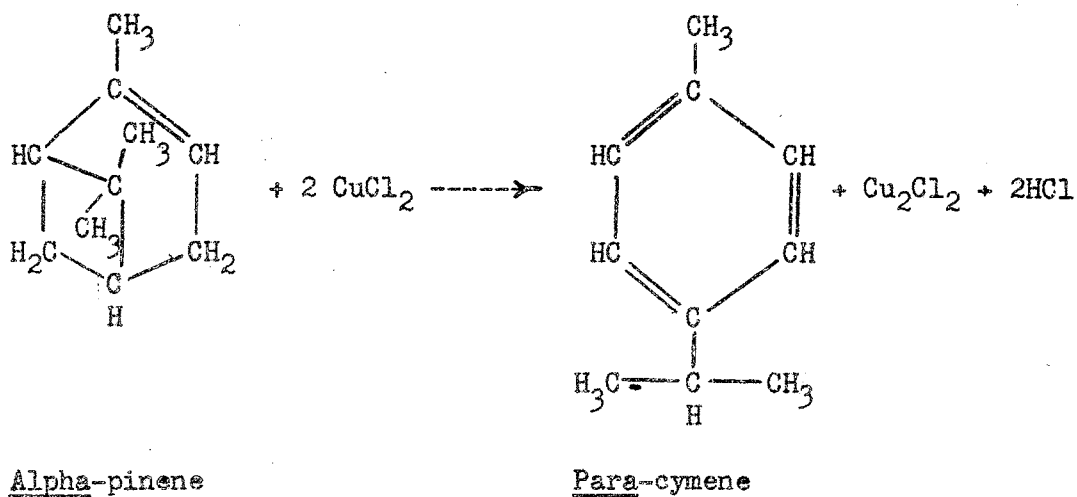
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INTRODUCTION

The principal purpose of this research was to determine the feasibility of converting alpha and beta pinene to para-cymene.

It had been hoped that metal-metal oxides or one metal in two different oxidation states would act as catalytic couples for this conversion.

When these couples failed to give the desired results, cupric chloride in cellosolve was investigated as a dehydrogenation agent:



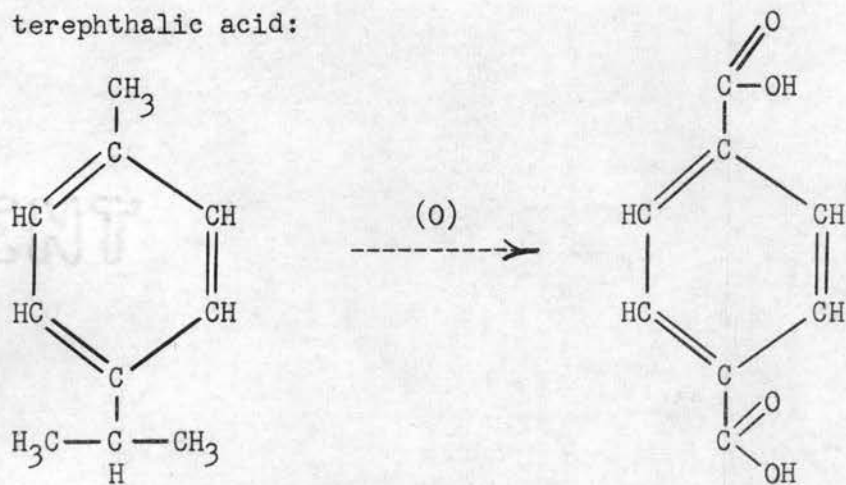
This is similar to the copper sweetening process of gasolines, and uses a homogeneous reaction mixture. The process would be commercially useful since the cuprous chloride formed by the reaction could be converted back to the cupric chloride by passing air through the solution.

The products were identified by means of boiling points and refractive indices. No attempt was made to identify any of the

by-products of the reaction except dipentene. It was assumed that products in the higher-boiling fractions were polymerization products of either pinene or dipentene.

Technical, pure alpha-pinene and pure beta-pinene were used in this work. The technical-grade pinene was the 154-160° fraction obtained from the distillation of natural turpentine. The pure alpha and beta pinenes were obtained from the Hercules Chemical Company.

The demand for para-cymene is dependent upon its conversion to terephthalic acid:



Para-cymene

Terephthalic Acid

Terephthalic acid is a valuable monomer in the production of some of the nylon-type synthetic fibers.

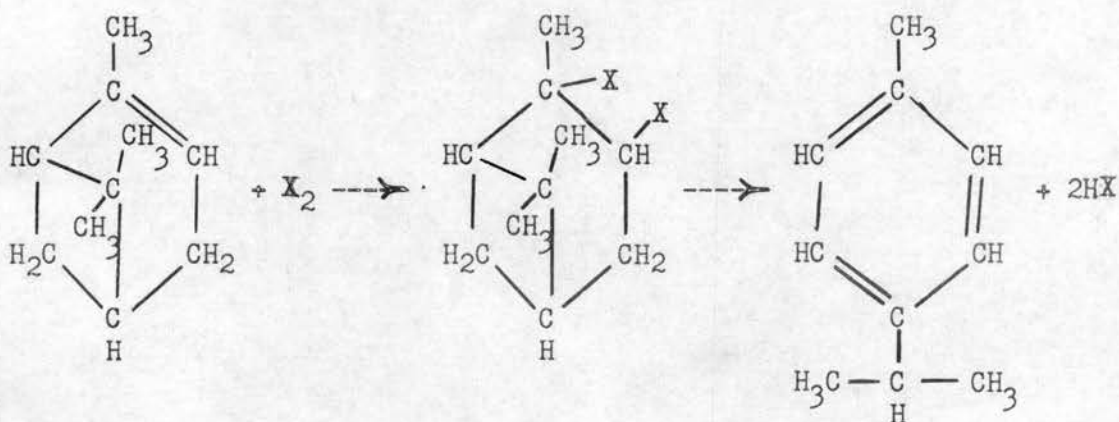
Much work has been done on the conversion of pinene to para-cymene, and a number of patents have been issued, but no manufacturing plants have been placed in operation on the basis of these patents.

A number of reagents have been credited with conversion of pinene to para-cymene. Acids, carbon, dehydrated gypsum, finely divided metals, clays, and oxides are the more common. In addition, concentrated alcoholic solutions of sulfuric, phosphoric, and acetic acids have been reported to produce para-cymene from pinene (20,21, 22,25). The reactions give many by-products and the yields of para-cymene are very low. Some of the by-products formed are camphene, dipentene, terpinolene, and terpene hydrate. Concentrated alcoholic hydrochloric acid fails to produce any para-cymene but produces most of the same by-products as alcoholic sulfuric acid.

When bicyclic terpenes were passed over activated carbon at a suitable temperature, para-cymene was formed (2,3,4,10,19). Pinene was converted to para-cymene by passing it into a mixture of very concentrated sulfuric acid, carbon and some silicon dioxide at 150-250° and at atmospheric pressure. It was claimed that in this way all the pinene was converted to para-cymene (30).

Activated coke and dehydrated gypsum have been reported to give almost the theoretical yield of para-cymene in both the vapor and the liquid phase (10). Other workers have repeated this experiment and reported very little or no para-cymene (19,41).

The halogens have been reported to react with pinene to give a product which decomposed readily to form para-cymene and the hydrogen halide (2,4,13,16,17,26,27,28,36,42):



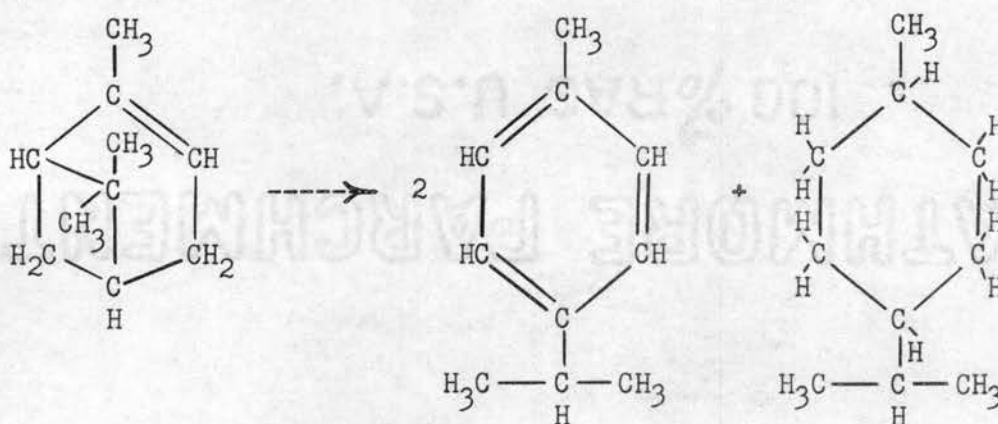
Alpha-pinene

As would be expected, the intermediate formed by the iodine was the least stable. The yields were poor in all cases.

Para-cymene

It has been noted that chromic oxide and aluminum oxide, separately or together, act as dehydrogenation catalysts and convert pinene to para-cymene (18,38,40). When pinene was passed over a catalyst composed of hydrated chromic oxide on an aluminum oxide

support at 200-500°, it was shown that simultaneous hydrogenation and dehydrogenation occurred:



Alpha-pinene

Para-cymene

Para-menthane

The best yield of para-cymene was obtained at 350°. A 52% yield was reported with a 1° boiling range (38,40). Other oxides such as silicon dioxide, ferric oxide, calcium oxide, magnesium oxide, and titanium oxide have been found to act similarly. Fuller's earth has also been used to convert pinene to para-cymene (24,25).

When pinene was passed over finely divided copper and nickel in the vapor phase and at 600-630°, para-cymene as well as many other products was formed (42). When pinene was passed over palladinized or platinized asbestos in a slow current of carbon dioxide at 190-200°, para-cymene and dihydropinene were produced.

Even though many catalysts have been used and high yields reported in patent literature, apparently it is still unprofitable to prepare para-cymene from pinene on a commercial scale. Since the conversion of pinene to para-cymene would certainly be used by industry if feasible, it is felt that many claims are of doubtful value.

EXPERIMENTAL

Iron-Ferric Couple:

Five grams of ferric oxide, 2.5 grams of iron powder, and 200 ml. of technical grade pinene were placed in a flask equipped with a stirrer, water condenser, and thermometer. The flask was then placed over a steam bath and the contents were kept at $94-95^{\circ}$ for six hours. The stirrer was used to keep the iron powder and the ferric oxide in suspension.

The mixture was filtered while hot. The precipitate was found to contain both ferric oxide and iron powder. The filtrate was distilled. The entire volume distilled between $158-160^{\circ}$. The refractive index was 1.4615. These physical properties checked with those of the technical grade pinene.

Duplicate results were obtained when 3 grams of ferric oxide and 2 grams of iron powder in 150 ml. of pinene were placed in the apparatus described above and heated to 158° for six hours.

When 5 grams of ferric oxide and 5 grams of iron powder in 150 ml. of pinene were heated for $21\frac{1}{2}$ hours at 158° , no para-cymene was formed. It was concluded that the ferric oxide-iron couple would not act as a catalyst in the pinene-to-para-cymene conversion.

Sulfur-Sulfide Couple:

One hundred milliliters of pinene and 50 ml. of ammonium polysulfide were placed in a three-neck flask equipped with a stirrer, reflux condenser, and a thermometer. The mixture was kept at 71° for five hours by the use of a steam bath. The mixture was allowed to cool and the top layer was separated from the rest of the mixture by using a separatory funnel. This layer was washed twice with 200 ml. portions of water, once with 200 ml. of 1% hydrochloric acid solution, twice with a 1% sodium bicarbonate solution, and finally with 200 ml. of water. The liquid was dried over anhydrous calcium chloride. When the dry material was fractionated, it was found to be unchanged pinene. The boiling point was $157-163^{\circ}$, and the refractive index was 1.4620.

The residue (about 6 ml.) left in the distillation flask had a mercaptan odor and a very high boiling point.

Cuprous-Cupric Couple:

Five grams of cuprous hydroxide and 5 grams of cupric hydroxide, previously prepared by treating aqueous solutions of cuprous chloride and cupric chloride with sodium hydroxide, and 150 ml. of pinene were placed in the reaction apparatus as previously described. Ten milliliters of Aerosol OT solution was added, as the cuprous hydroxide was still wet and would not emulsify with the pinene. This reaction mixture was kept at reflux (100°) for seven hours. After about two hours the reaction mixture became quite thick. This was probably owing to an emulsion.

At the end of the heating period the mixture was allowed to cool. It was filtered, washed with water, and dried over Drierite (anhydrous calcium sulfate). One hundred and forty-six milliliters of the product was recovered. When the product was fractionated in a Todd column, 139 ml. distilled at $159-161^{\circ}$ and had a refractive index of 1.4620. This identified the fraction as unchanged pinene. The residue left in the distillation flask was a reddish brown, viscous material.

Similar results were obtained when 5 grams of cupric chloride and 5 grams of cuprous chloride were heated with 200 ml. of pinene at 158° for six hours. The reaction was cooled, filtered, and washed with water. The product distilled at $157-163^{\circ}$ and had a refractive index of 1.4612.

Copper-Cupric Oxide Couple:

Ten grams of cupric oxide, 10 grams of copper powder, and 100 ml. of pinene were placed in a three-neck flask equipped with a stirrer, water condenser, and thermometer. The mixture was kept at reflux temperature (155°) for $10\frac{1}{2}$ hours. The product was filtered, washed with water, and dried over Drierite. When fractionated, the product all distilled at $154-157^{\circ}$ and had the physical properties of pinene. The refractive index was 1.4621.

Cupric Sulfate-Carbon Couple:

One hundred milliliters of pinene was heated with 10 grams of anhydrous copper sulfate and 10 grams of carbon at 115° for six hours in an apparatus as described in the copper-cupric oxide couple reaction.

The product was allowed to cool, filtered, washed with water, and dried over Drierite. The dry product distilled at 155-160° and had a refractive index of 1.4618. It was believed that no conversion had taken place and the fraction was mainly the original pinene.

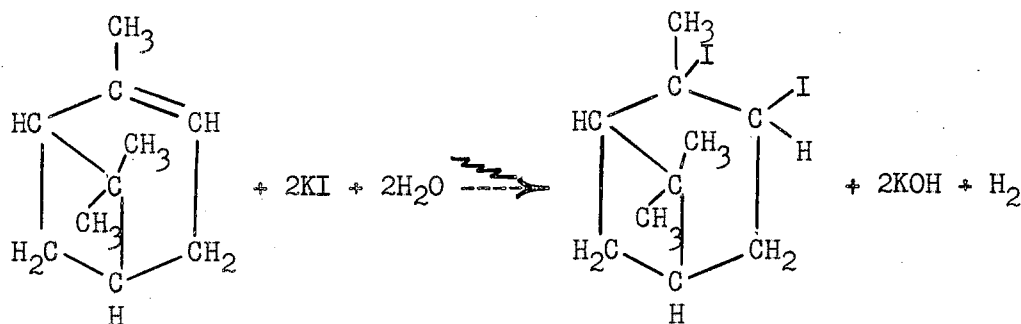
Chromic Oxide:

Ten grams of chromic oxide was placed in 100 ml. of pinene and kept at reflux (155°), for 9½ hours.

The reaction mixture was then allowed to cool, filtered to remove the oxide, and washed with water. The product was dried over Drierite. When fractionated, it was found that all the dry product distilled at 156-161° and had a refractive index of 1.4618. A small amount of residue remained in the distillation flask.

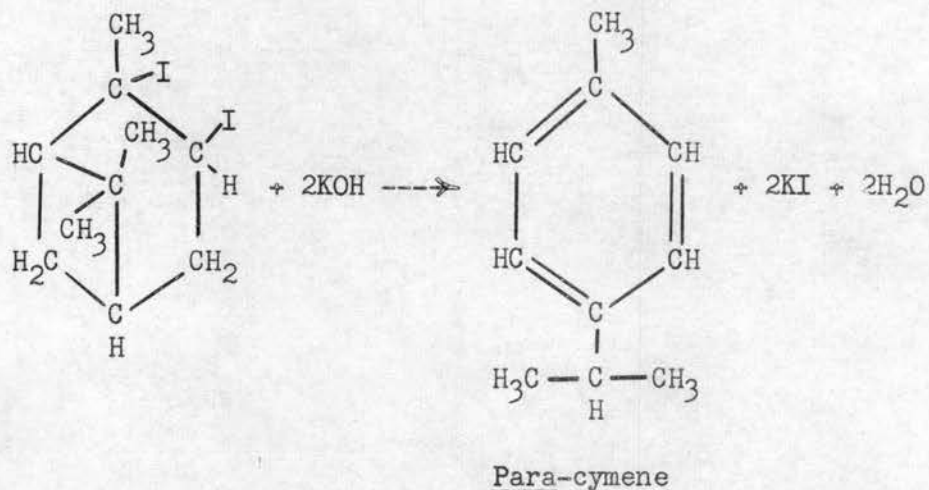
Electrolytic Oxidation with Potassium Iodide:

Since it had been reported in the literature that iodine adds to pinene with great facility and the addition product decomposes readily to form para-cymene (2,4,13,16,17,26,27,28,36,42), it was decided to attempt an electrolytic oxidation with potassium iodide:



Alpha-pinene

It was hoped that the potassium hydroxide formed in the reaction would react with the product and form para-cymene. In this fashion the potassium iodide would be constantly regenerated:



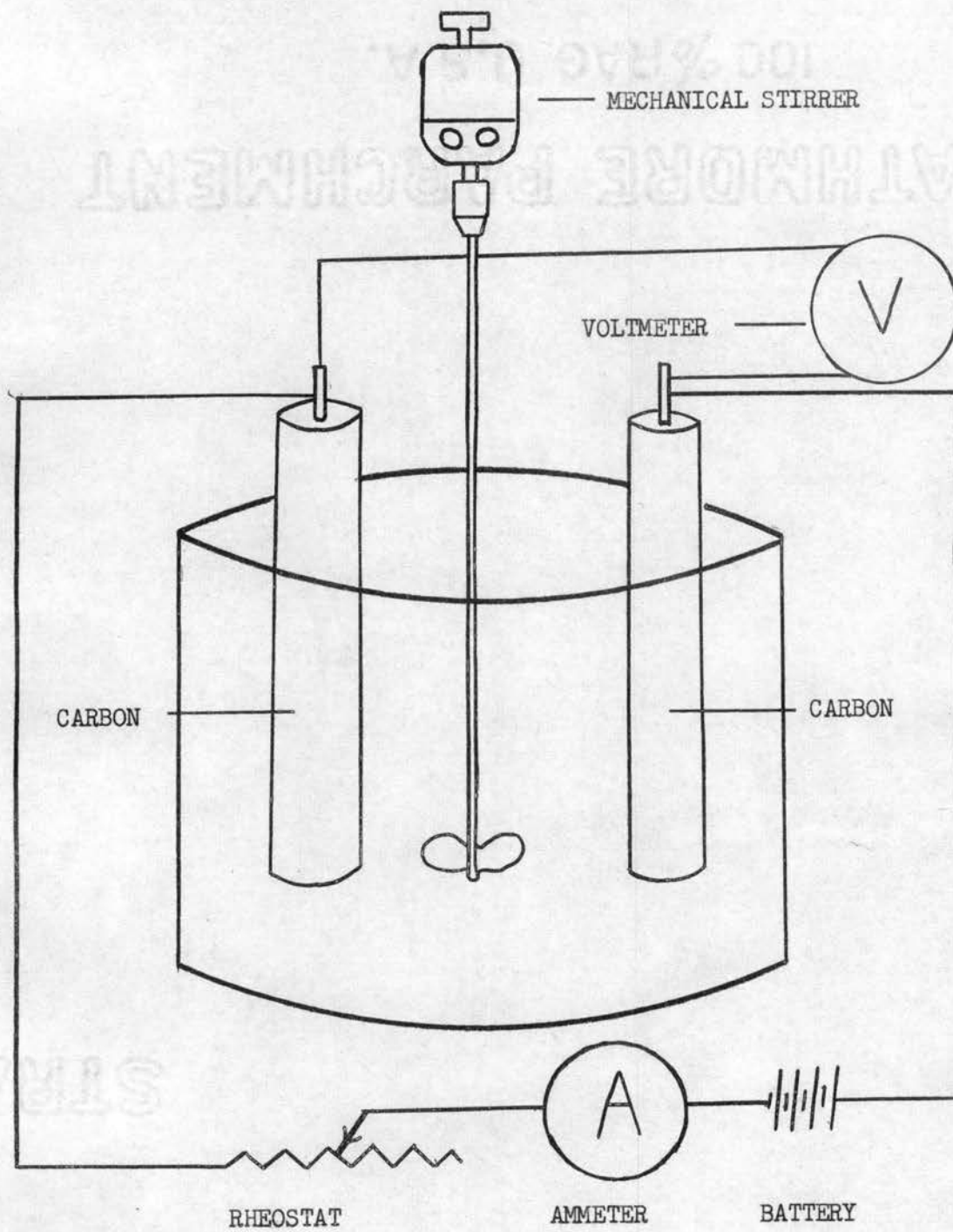
Five hundred milliliters of 1N potassium iodide was added to 150 ml. of pinene in the reaction cell as shown in Figure 1. A current of 0.25 ampere was passed through the solution with an applied potential of 2.5 volts for 144 hours. At the end of this time, a wax-like product was produced which failed to steam-distill. This proved that the material contained no para-cymene. Since the purpose of this problem was to find a conversion of pinene to para-cymene, the product was not investigated further.

Preliminary Reactions in Cellosolve:

One hundred milliliters of pinene, 100 ml. of cellosolve, 8 ml. of concentrated sulfuric acid, and 15 grams of cupric chloride were placed in a three-neck flask equipped with a reflux condenser, mechanical stirrer, and thermometer.

Before the mixture could be heated, a reaction started and the temperature rose to 115°. The color turned from the

FIGURE-1



dark green of cupric chloride in cellosolve, to a light green color. A light green precipitate was formed in the reaction flask.

After the original reaction had subsided, heat was applied and the reaction held at 115° for seven hours. During this time the reaction products turned to a dark brown and sulfur dioxide was liberated.

The reaction mixture was allowed to cool, filtered, and washed with three 100-ml. water washes, one 100-ml. wash of 1% sodium bicarbonate solution, two more water washes, and finally extracted from the water with ether. The ether was evaporated on the steam bath. Seventy milliliters of material was recovered in this fashion.

Most of the 70 ml. distilled over at 155° and was identified as pinene by its refractive index. Three milliliters distilled over at $172-180^{\circ}$ and 20 ml. remained as a dark colored, viscous liquid in the distillation flask. This residue had a strong odor similar to that of sulfur dioxide. The $172-180^{\circ}$ fraction smelled like para-cymene but failed to give any terephthalic acid when oxidized. The refractive index was 1.4742.

Similar results were obtained by the use of hydrochloric acid in place of the sulfuric acid.

Five grams of cupric chloride in 100 ml. of cellosolve was added to 50 ml. of pinene. The reaction flask was fitted with a very coarse gas dispersion tube as well as with a reflux condenser, stirrer, and thermometer. The reaction was heated to 100° without

bubbling any air through the mixture. The mixture turned to a light green color and a precipitate of cuprous chloride was formed in twenty minutes.

The reaction mixture was cooled at 50° and air was added to the reaction mixture through the gas dispersion tube. The mixture turned back to a dark green, and the precipitate disappeared in about 40 minutes. The flow of air was stopped and the reaction mixture was heated to 110° and again turned clear in 45 minutes. The air was turned on again at this temperature. The solution seemed to turn a little darker green, but the air failed to completely eliminate the precipitate. The reaction was allowed to proceed at 110° with air passing through the mixture for about seven hours.

At the end of this time the product was filtered and washed with water. Thirty milliliters of product was recovered. Twenty milliliters distilled at $155-160^{\circ}$ and was identified as pinene by its refractive index. The rest of the material was higher boiling, but did not have the physical characteristics of para-cymene.

Fifty milliliters of pinene was added, over a period of four hours, to 130 grams of cupric acetate suspended in 300 ml. of cellosolve. The reaction mixture was kept at 110° with air bubbling through it for seven hours.

The mixture was allowed to cool, filtered, and washed with water. Twenty-eight milliliters of water-insoluble material was recovered, and dried over Drierite. The dry material was fractionated and all distilled over at $155-160^{\circ}$

and had a refractive index of 1.4620. This identified the material as the original pinene.

Two hundred milliliters (176 grams or 1.3 moles) of pinene was placed with 350 grams (2.6 moles) of cupric chloride, dissolved in about 600 ml. of cellosolve. The reaction mixture was heated to 110°. The reaction started and proceeded quite rapidly. A precipitate formed and the mixture became quite light in color. However, at the end of seven hours the reaction had turned quite dark.

Ninety-five milliliters of material was recovered by washing with water. The material was less dense than water, had a dark brown color, and had a higher viscosity than did the starting materials. Fractional distillation of the isolated product produced 8 ml. of material boiling below 150° and later identified as cellosolve and 10 ml. of material boiling at 155-160°, with a refractive index of 1.4652. This fraction probably was unchanged pinene. Sixteen milliliters of the product distilled over from 173-175°. This product had an odor of lemon and had a refractive index of 1.4736. This possibly was dipentene contaminated with pinene. Nine milliliters of the material boiled at 177° and had a refractive index of 1.4763. It had the physical characteristics and odor of para-cymene. After several unsuccessful attempts, the 2,6-dinitro derivative of para-cymene was prepared from this fraction.

The rest of the product was much higher-boiling. A light yellow fraction came over at about 300°. This fraction was of interest because it had about the same apparent viscosity at its

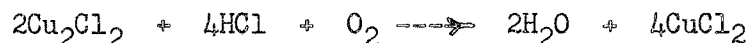
boiling point as it did at 0°. A sodium fusion was run on this fraction and it was found to contain chlorine. Since the material in the distillation flask decomposed as this fraction was distilling, it was not certain whether the chlorine was actually part of the polymer or whether it was from hydrogen chloride dissolved in the fraction.

The preceding experiment was repeated using 108 grams of cupric chloride and 75 ml. of pinene.

Four milliliters of pinene and 6 ml. of material boiling at 175-180° were recovered. The latter fraction had a refractive index of 1.4820 and gave a fair yield of the terephthalic acid derivative of para-cymene. The rest of the material was higher boiling.

Cupric Chloride in Cellosolve:

From the preceding reactions, it seemed that by keeping the hydrogen ion concentration down, polymerization of the pinene might be prevented. It was hoped that if air was continually passed through the system, it would react with any of the cuprous chloride and hydrochloric acid present,



not only reducing the hydrogen ion concentration but also regenerating the catalyst.

The apparatus used in this work consisted of a three-neck flask equipped with a burette, reflux condenser, and a gas dispersion tube that acted both as a stirrer and an inlet for air. The reflux condenser was equipped with a trap to

collect any vapors that might be swept over by the air current (See Figure 2).

The cupric chloride and cellosolve were placed in the reaction flask and air was passed through it to stir the mixture. The heat was then applied and the temperature raised to the desired value. The pinene was added from the burette at such a rate that either no, or a minimum amount of, cuprous chloride precipitated. The products from these reactions were filtered, to remove any undissolved cuprous chloride, and washed with water, dilute acid and dilute base, then with water again. The products were dried over Drierite.

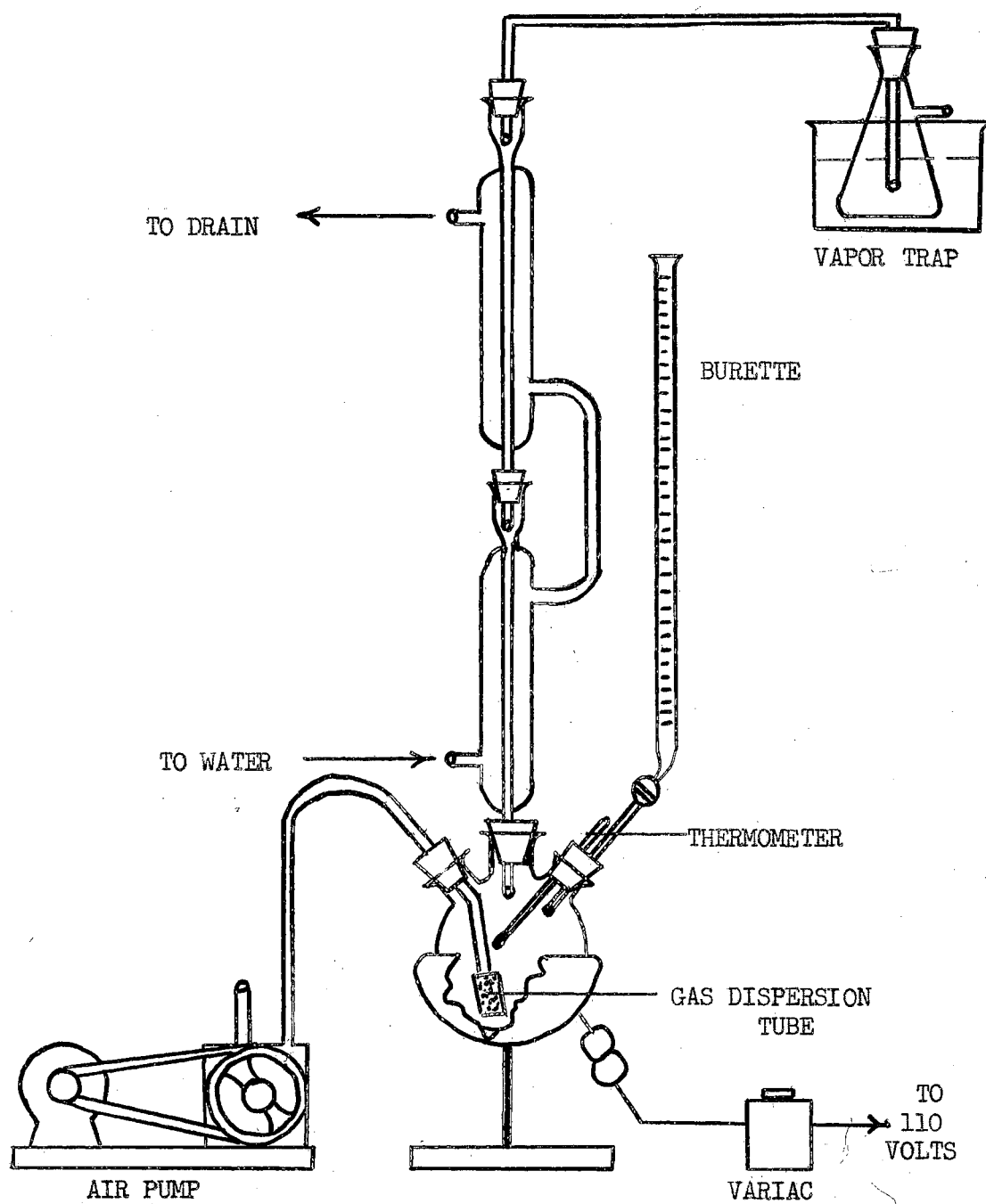
Reactions at 110°

Run 1.

One hundred milliliters of pinene was added, over a period of four hours, to 175 grams of cupric chloride (2:1 moles) dissolved in 300 ml. of cellosolve. This mixture was kept at 110° for eight hours while air was passed through it. It was very difficult to keep the cuprous chloride from precipitating during the course of the reaction.

Seventy-five milliliters of a dark brown, fairly viscous material was recovered after washing with water. Fractionation of this product gave 3 ml. of cellosolve, 9 ml. of pinene, and 15 ml. of a material boiling from 174-177°. The refractive index of this fraction was 1.4870. This fraction gave the terephthalic acid and the nitration derivatives of para-cymene. The tetra-bromo derivative of dipentene was attempted, but gave only a

FIGURE-2



trace of the derivative. The yield of para-cymene was approximately 15% based on the original pinene. Seventy-six percent of the pinene was converted to polymer.

Run 2.

Using 35 grams of cupric chloride dissolved in 200 ml. of cellosolve, and 50 ml. of pinene (2.1 moles) in a similar reaction gave a 13% yield of para-cymene, but only 1% of the pinene was recovered. The rest of the product consisted of material boiling above 200°. This was believed to be a polymer.

Run 3.

The best reaction of this work was produced when 100 ml. of pinene was added, over a period of four hours, to 10 grams of cupric chloride dissolved in 200 ml. of cellosolve. The reaction was run at 110° for eight hours, and air was bubbled through the mixture for the duration of the reaction.

During the reaction it was noticed that the material caught in the trap was in two phases. The top layer was mostly pinene, but the bottom layer proved to be water. This indicated that the reaction was taking place, as water would be the by-product of the reaction. Cuprous chloride did not precipitate out of the reaction mixture.

The reaction produced a 23% yield of para-cymene, a 5% yield of dipentene, and 14% of the pinene was recovered. The rest of the material was higher-boiling.

Run 4.

This run was to reproduce the results obtained in Run 3. Fifteen grams of cupric chloride in 250 ml. of cellosolve was heated to 110° and 100 ml. of pinene was added over a period of five hours. The reaction was run for seven hours. This run failed to product any para-cymene.

The failure of this reaction can be explained by the fact that large amounts of cuprous chloride were formed and a polymer plugged the gas dispersion tube.

Run 5.

Fifty milliliters of pinene was added, over a period of three hours, to 5 grams of cupric chloride dissolved in 150 ml. of cellosolve. This mixture was kept at 110° for 7 hours. Air was bubbled through the mixture to convert any cuprous chloride that formed back to cupric chloride and to stir the solution. Some cuprous chloride precipitated from the mixture, but the solution remained a dark green color.

Forty milliliters of a dark brown, viscous material was recovered when the product was washed with water. When fractionated, this product produced the following yields based on the original pinene: 11.2% para-cymene, 2.8% dipentene, and 68% of a material boiling above 200° . Eighteen percent of the pinene was recovered.

Reaction at 100° Run 1.

Fifty milliliters of pinene was added, over a period of

four hours, to 87.5 grams of cupric chloride (2:1 moles) dissolved in 200 ml. of cellosolve. The reaction was kept at 100° and air was bubbled through it for nine hours. It was very difficult to prevent the cuprous chloride from precipitating and the gas dispersion tube from becoming plugged. A heavy oil appeared in the reaction flask.

After washing the product with water, 35 ml. of a viscous, dark colored oil was recovered. Fractionation of this material yielded 20% unreacted pinene, 4.4% dipentene, and 5.6% para-cymene based on the original pinene. The rest of the pinene was converted to a very viscous, high-boiling material.

Reaction at 85°

Run 1.

Fifty milliliters of pinene was added, over a period of 5½ hours, to 87.5 grams of cupric chloride dissolved in 200 ml. of cellosolve. The reaction was kept at 85° and air was passed through it for twelve hours.

A dark colored, viscous liquid was again recovered when the reaction mixture was washed with water. When fractionated three cuts were obtained: three milliliters of pinene (153-155°), 11 ml. of a material boiling at 163-175°, and 5 ml. of material boiling at 175-178°.

The last fraction contained both dipentene and para-cymene. The middle fraction had a refractive index of 1.4730 and was perhaps an intermediate product such as beta-phellandrene (2,1(7) para-menthadiene). No attempt was made to analyze

this middle fraction. Since it was felt that this fraction was an intermediate, however, it was recorded in Figure 4 as recovered pinene.

Reactions at 75°

Run 1.

Fifty milliliters of pinene was added, over a period of three hours, to 87.5 grams of cupric chloride dissolved in 200 ml. of cellosolve. The reaction mixture was kept at 75° and air was passed through it for seven hours. A dark oil was formed and it was difficult to keep the gas dispersion tube from becoming plugged.

Forty milliliters of a dark brown, viscous material was obtained by washing with water. When fractionated this material yielded 20% unreacted pinene, 16% of material boiling at 175° and having a refractive index of 1.4744. This was identified as dipentene by preparing the tetra-bromo derivative. Six milliliters of the material distilled over from 175-177° and had a refractive index of 1.4764. This fraction contained a mixture of para-cymene and dipentene. The reaction gave a yield of 1.4% para-cymene and a total yield of 26.6% dipentene based on the original pinene. Fifty-two percent of the pinene was converted to polymerization products.

Run 2.

This reaction was a duplicate of Run 1 to increase the yield. The results were found to be about the same and no better yield of para-cymene was obtained. The yield was 42%

unreacted pinene, 10.6% dipentene, 45.6% high-boiling material, and 1.8% para-cymene, based on the original pinene.

Reactions at 65°

Run 1.

Fifty milliliters of pinene was added, over a period of four hours, to 87.5 grams of cupric chloride dissolved in 200 ml. of cellosolve. The temperature was kept at 65° and air was passed through the mixture to prevent the formation of cuprous chloride for seven hours. The viscous oil that developed in the higher temperature runs failed to develop at this temperature. The cuprous chloride did precipitate, but the solution remained a dark green color.

Forty-five milliliters of product was extracted by washing with water. The product in this case was a light yellow and had about the same physical properties as pinene. When fractionated this product yielded 24% recovered pinene, 9.2% dipentene, and 4.8 para-cymene, based on the original pinene. Sixty-two percent of the original pinene had been converted to a high-boiling polymer.

Run 2.

This run was to duplicate the preceding reaction.

One hundred milliliters of pinene was added over a period of four hours, to 175 grams of cupric chloride dissolved in 350 ml. of cellosolve. The mixture was heated to 65° and air was passed through the mixture for seven hours.

The product recovered when the mixture was washed with water was similar to that received in Run 1. When this product was fractionated the reaction was found to yield 20% recovered pinene, 21.8% dipentene, 5.2% para-cymene, and 54% high-boiling material. These results are very similar to the results obtained in the first run at 65°.

Reaction at 55°

Run 1.

Fifty milliliters of pinene was added, over a period of five hours, to 87.5 grams of cupric chloride dissolved in 200 ml. of cellosolve. The reaction was run at 55° and air was passed through the solution to convert any of the cuprous chloride to cupric chloride and also to stir the reaction mixture. The mixture was kept at 55° for ten hours.

A light yellow product, similar to that recovered in the 65° reactions, was extracted by washing with water. When fractionated this product gave yields of 26% recovered pinene, 9.5% dipentene, 60% high-boiling fractions, and 4.5% para-cymene, based on the starting technical grade pinene.

Reactions using Pure Alpha-pinene

Run 1.

Fifty milliliters of alpha-pinene was added, over a period of five hours, to 87.5 grams of cupric chloride dissolved in 200 ml. of cellosolve. The reaction mixture was kept at 100° and air was bubbled through the mixture for ten hours. At the end of this time, the mixture was

allowed to cool, filtered, and washed with water. Thirty milliliters of a dark, viscous material was recovered.

When fractionated this material gave yields of 22% recovered pinene, 8% para-cymene, and 70% high-boiling materials, based on the starting alpha-pinene. No dipentene was formed in this reaction.

Run 2.

Run 2 was identical with Run 1 except the temperature was kept at 80° for eleven hours.

A similar dark colored product was recovered, by washing with water, and gave yields of 20% recovered pinene, 2% dipentene, and 8% para-cymene, based on the original alpha-pinene. Seventy percent of the pinene was converted to high-boiling polymers.

Run 3.

This run was also similar to Run 1 except that the reaction was kept at 60° for eleven hours.

The extracted product, however, was a light yellow instead of the dark brown as it was in the other two runs. When fractionated this product yielded 12% recovered pinene, 10.5% dipentene, 7.5% para-cymene, and 70% high-boiling polymer, based on the original alpha-pinene.

Reactions using Pure Beta-pinene

Run 1.

Fifty milliliters of beta-pinene was added, over a period of 4½ hours, to 87.5 grams of cupric chloride dissolved in 200 ml.

of cellosolve. The mixture was held at 100° and air was bubbled into the mixture from a gas-dispersion tube for twelve hours. It was very difficult to keep the dispersion tube from becoming plugged as a dark colored viscous material was formed in the reaction flask.

The reaction mixture was filtered, washed with water, dried over Drierite and fractionated. This run gave a 4.2% yield of para-cymene, 5.8% dipentene, 18% recovered pinene, and 72% high-boiling materials, based on the original beta-pinene. The pinene recovered was a mixture of the alpha- and beta-pinene.

Run 2.

A similar reaction was run at 80° for seven hours. A product with similar physical properties was obtained when washed with water. When fractionated this product was found to yield 9.2% para-cymene, 0.8% dipentene, 18% recovered pinene, and 72% high-boiling materials, based on the original beta-pinene.

Run 3.

A similar reaction with beta-pinene was run at 60° for nine hours.

The reaction product when washed with water gave a light yellow product that was much less viscous than those produced in the higher-temperature runs. When fractionated this run was found to yield 6.4% para-cymene, 9.6% dipentene,

18% recovered pinene, and 66% high-boiling polymer, based on the original beta-pinene.

ANALYTICAL EXPERIMENTAL PROCEDURE

After each reaction had been completed the product was fractionated and each fraction, with the exception of the 173-178° fractions, was identified by refractive index, and boiling point.

The 173-178° fractions were analyzed and were found to contain mainly dipentene and para-cymene. This was shown by preparation of the tetrabromide derivative of dipentene and the terephthalic acid derivative of para-cymene.

Dipentene Tetrabromide

Approximately 2 ml. of the 173-178° fraction was dissolved in about 15 ml. of glacial acetic acid, and placed in an ice bath. This was to prevent substitutive bromination of either the dipentene or the para-cymene.

Liquid bromine was then added to the mixture until the color of the bromine persisted. The reaction mixture was then kept in the ice bath for 30 to 40 minutes with occasional stirring and scratching the sides of the test tube with a stirring rod.

The tetrabromide separated out first as a liquid, but crystallized on standing. The crystals were recrystallized from dilute methanol. The melting point was found to be 122-124°. The literature value for this derivative is 124°. The sharp melting point obtained from this derivative indicated the absence of other unsaturated terpenes in this fraction.

Terephthalic Acid (35)

About 2 grams of the 175-178° fraction was suspended in a solution of 10 grams of potassium dichromate in 20 ml. of water. The mixture was placed in a large test tube fitted with a reflux condenser. Fifteen milliliters of concentrated sulfuric acid was added dropwise to the mixture with shaking, so that the reaction would proceed at a reasonable rate. When all the sulfuric acid had been added, the reaction was placed on the steam bath and allowed to reflux for about 2½ hours.

After cooling, the mixture was diluted with an equal volume of water and the product was filtered and washed with three 10-ml. washes of 1% hydrochloric acid. It was freed of chromium salts by stirring with hot dilute sulfuric acid, cooling, filtering, and washing with five 10-ml. washes of cold water.

The crude terephthalic acid was dissolved in hot potassium carbonate solution, heated with charcoal, and filtered. The filtrate was acidified with dilute hydrochloric acid and the pure terephthalic acid was collected by filtration and washing with water.

Terephthalic acid sublimes at a temperature greater than 300°. In this work it seemed to sublime at about 312°.

Nitration of Para-cymene

Five to eight milliliters of the 175° fraction was placed in a small separatory funnel and washed three or four times with 10 ml. of cold concentrated sulfuric acid. The crude para-cymene was added to a mixture of 5 ml. of concentrated sulfuric acid and 5 ml. of concentrated nitric acid, at a rate so that the temperature would

never become higher than 50° . When all the para-cymene had been added, the test tube was placed in a water bath and kept at 40° for one hour.

When the reaction was complete, the mixture was poured from the reaction test tube into a beaker full of ice water, to crystallize the product.

The crystallized product was dissolved in hot methyl alcohol and cooled under tap water. Enough water was added to make the solution cloudy, and the solution was reheated to again clear the solution. The solution was placed in the ice bath and the 2,6-dinitro-para-cymene crystallized from the mixture. The melting point of the pure material was found to be $50-54^{\circ}$. The literature value for 2,6-dinitro-para-cymene is 54° .

This derivative was very difficult to prepare and was not used as often as the terephthalic acid derivative. The terephthalic acid derivative also required less starting material.

The presence of dipentene and para-cymene in the 173-178 $^{\circ}$ fractions having been proved, a graph was constructed with percent of para-cymene vs. refractive index. (See Figure 3). It was found that the refractive index of para-cymene-limonene mixture followed a straight line, and it was assumed that dipentene (dl-limonene)-para-cymene mixtures would follow a similar line.

The actual para-cymene present was taken from the graph.

FIGURE-3

% Para-cymene vs. Refractive Index
in a para-cymene-dipentene mixture

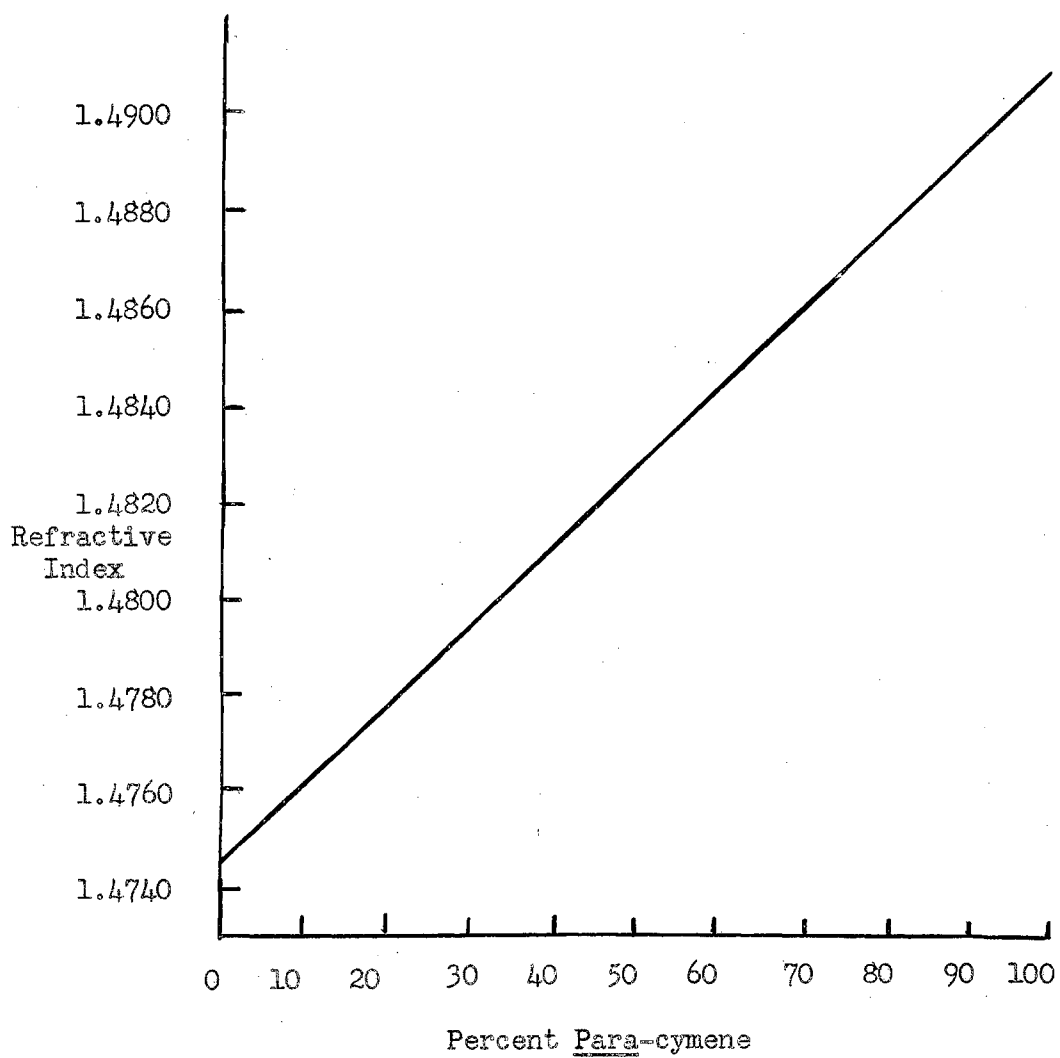


FIGURE-4

PINENE TYPE OR GRADE	TEMPER- ATURE °C	RUN	PINENE ML.	CUPRIC CHLORIDE GM/100 ml.	RECOVERED PINENE % APPROX. ¹	REFRAC- TIVE INDEX PINENE	HIGH- BOILING % APPROX. ²	DIPEN- TENE % APPROX.	p-CYMENE % APPROX.	REFRAC- TIVE INDEX CYMENE FRACTION	BOILING RANGE OF CYMENE FRACTION
Tech.	110	1	100	175	9.0	1.4631	76.0	0.0	15.0	1.4910	174-177
Tech.	110	2	50	70	1.0	1.4651	85.0	1.0	13.0	1.4894	174-177
Tech.	110	3	100	10	14.0	1.4645	58.0	5.0	23.0	1.4884	175-177
Tech.	110	4	50	30	48.0	1.4640	52.0	--	--	-----	-----
Tech.	110	5	100	10	18.0	1.4632	68.0	2.8	11.2	1.4871	175-177
Tech.	100	1	50	175	20.0	1.4628	70.0	4.4	5.6	1.4836	175-177
Tech.	85	1	50	175	28.0	1.4630	62.0	4.4	5.6	1.4835	175-178
Tech.	75	1	50	175	20.0	1.4628	52.0	26.6	1.4	1.4764	176-177
Tech.	75	2	50	40	42.0	1.4620	45.6	10.6	1.8	1.4774	175-177
Tech.	65	1	50	175	24.0	1.4613	62.0	9.2	4.8	1.4799	175
Tech.	65	2	100	175	20.0	1.4700	53.0	21.8	5.2	1.4776	175-177
Tech.	55	1	50	175	26.0	1.4623	60.0	9.5	4.5	1.4796	175-177
<u>Alpha</u>	100	1	50	175	22.0	1.4762	70.0	0.0	8.0	1.4909	175-176
<u>Alpha</u>	80	2	50	175	20.0	1.4740	70.0	2.0	8.0	1.4905	175-177

Figure-4 (Continued)

<u>Alpha.</u>	60	3	50	175	12	1.4680	70.0	10.5	7.5	1.4812	177
<u>Beta.</u>	100	1	50	175	18	1.4760	72.0	5.8	4.2	1.4814	175-178
<u>Beta.</u>	80	2	50	175	18	1.4788	72.0	0.8	9.2	1.4894	175-177
<u>Beta.</u>	60	3	50	175	18	1.4750	66.0	9.6	6.4	1.4809	175-178

¹ Contains material boiling between 155-170°.

² Contains also that material that might be water-soluble.

DISCUSSION

Pinene, iron powder and ferric oxide failed to produce para-cymene at 95° or at 185°. There was no appreciable amount of polymer and almost all of the pinene was recovered.

Ammonium polysulfide with pinene failed to produce any para-cymene but did produce about 10% high-boiling materials. These higher-boiling fractions had a mercaptan odor.

Cuprous hydroxide and cupric hydroxide produced no para-cymene at 100°. A small amount of high-boiling residue was formed by the reaction but most of the pinene was recovered.

Copper sulfate and carbon with pinene, at reflux temperature, failed to produce any para-cymene or polymer.

At reflux temperature chromic oxide failed to convert any pinene to para-cymene. A small amount of residue remained in the kettle after fractionation. This residue was very viscous and high-boiling.

Similar results were obtained using copper-cupric oxide and cuprous-cupric chloride couples.

Cupric acetate, suspended in cellosolve, failed to produce para-cymene from pinene when heated to 110°. There was no polymer produced by the heating.

Pinene was found to form a wax-like product when reacted in an electrolytic oxidation with potassium iodide. The product did not steam-distill. This proved the absence of para-cymene.

Cupric chloride, dissolved in cellosolve, has been found to react with pinene to produce para-cymene. Accompanying this conversion reaction, however, is an acid-catalyzed polymerization of pinene or of dipentene.

Increasing the temperature increased the yield of para-cymene, but also increased the amount of polymer formation. It has been noticed that the best yields of para-cymene and the least amount of polymer was formed when air was bubbled through the reaction mixture. When air is bubbled through the mixture, the amount of catalyst has little effect on the yield, but for larger amounts of catalyst the pinene may be added more rapidly to the reaction mixture.

Both alpha- and beta-pinene produced para-cymene when reacted with cupric chloride, in cellosolve. The presence of polymer in the reactions using chemically pure pinene proved that the polymer is derived from pinene and not other materials in the technical grade pinene.

Yields and other data on the cupric chloride in cellosolve reactions have been tabulated in Figure 4.

It would seem that materials that are insoluble in the reaction mixture fail to convert pinene to para-cymene or produce any appreciable amount of polymer. In the reactions with cupric chloride, in which both reactants were soluble in the solvent, both para-cymene and polymer were produced even at low temperatures. It is believed that a homogeneous solution is necessary to convert pinene to para-cymene.

An interesting by-product was formed from the reactions with cupric chloride. It boils at 300° and has about the same viscosity

at 300° as it has at 0°. This by-product has not been investigated in this work but might prove interesting for future research.

BIBLIOGRAPHY

1. Akiebolaget Centrallaboratorium, Norw. 31,348, Nov. 8, 1920
(C.A. 15, 2102)
2. Armstrong, Ber. 12, 1756 (1879)
3. Armstrong and Tilden, Ber. 12, 1752 (1879)
4. Barbier, Annalen 5, 99, 215 (1872)
5. Bergstrom, Cederquist, and Trobeck, Swed. 85,993 April 7, 1936
(C.A. 30, 6012)
6. Bergstrom, Cederquist, and Trobeck, U. S. 2,052,917, Sept. 1, 1934
and Ger. 625,994 (C.A. 30, 7130)
7. Bergstrom, Cederquist, and Trobeck, Svensk Papperstidn 48, 246-9
(1945) (C.A. 39, 3523)
8. Bergstrom, Cederquist, and Trobeck, Swed. 81,706, Oct. 16, 1934
(C.A. 30, 2994)
9. Bert, Bull. soc. chim. 37, 111 (1882)
10. Bhrishan, Gulati, and Joshi, J. Indian Chem. Soc. Ind. and News
Ed. 7, 93-95 (C.A. 39, 4066)
11. Bouchardat and La fond, Compt. rend. 105, 1777 (1882)
12. Bouchardat and La fond, Compt. rend. 125, 113 (1897)
13. Brit. and Foreign Chem. Producers Ltd., Brit. 156,329, Oct. 6,
1919 (C.A. 14, 2802)
14. Brit. and Foreign Chem. Producers Ltd., Brit. 142,738, Oct. 6,
1919 (C.A. 15, 1728)
15. Charlton and Day, Ind. Eng. Chem. 29, 92 (1937)
16. Denaro and Scarlato, Gazz. chim. ital. 33, 393 (1903)
17. Deville, Ann. 37, 191 (1894)
18. Dixon, U. S. 2,387,836, Oct. 30, 1945 (C.A. 40, 1174)

19. Fujita, J. Chem. Soc. (Japan) 55, 1-5 (1934) (C.A. 28, 2345)
20. Hirao and Takano, J. Chem. Soc. (Japan) 58, 213-21 (1937)
(C.A. 31, 3468)
21. Hirao and Takano, J. Chem. Soc. (Japan) 58, 1033-41 (1937)
(C.A. 32, 4158)
22. Hirao and Takano, J. Chem. Soc. (Japan) 59, 95-101 (1938)
(C.A. 32, 4970)
23. Hirao and Takano, J. Chem. Soc. (Japan) 59, 193-8 (1938)
(C.A. 32, 9072)
24. Humphrey, U. S. 1,893,802, Jan. 10, 1933
25. Imoto, J. Chem. Soc. (Japan) 42, Suppl. binding 183-5, 185-6
(1939) (C.A. 33, 7766)
26. Kekule, Ber. 6, 437 (1873)
27. Kekule and Bruylants, Ber. 6, 437 (1873)
28. Koch and Dubois, Belg. 383,373, Nov. 30, 1931
29. Kuryndin, Zhur. Priklad. Khim. (J. Applied Chem.) 21, 273-80
(1948) (C.A. 43, 6185)
30. Lege, Fr. 763,857, May 8, 1934 (C.A. 28, 5467)
31. Linstead, Michaelis, and Thomas, J. Chem. Soc. 1940, 1139-47
(C.A. 34, 7889)
32. Mosher, J. Am. Chem. Soc. 69, 2139-41 (1947)
33. Naudin, Bull. soc. chim. 33, 787 (1923)
34. Nikitin, J. Gen. Chem. (U.S.S.R.) 16, 1041-6 (1946) (C.A. 41,
2712)
35. Openshaw, H. T. "Qualitative Organic Analysis", University
Press, Cambridge, 1946, p. 26
36. Oppenheimer, Ber. 5, 94, 628 (1872)
37. Oppenheimer, Ber. 7, 625 (1874)
38. Plate and Tarasova, J. Applied Chem. (U.S.S.R.) 17, 576-80
(1944) (C.A. 43, 5656)
39. Preis and Rayman, Ber. 12, 219 (1879)

40. Rannak, Rudakova, and Titova, J. Applied Chem. (U.S.S.R.) 18, 425-9 (1945) (English Summary) (C.A. 40, 4701)
41. Rudakov, Borsova, Enel'yanova, Eroshevskit, and Komshitov, Zhur. Priklad. Khim. (J. Applied Chem.) 22, 180-98 (1949) (C.A. 43, 5656)
42. Sabatier, Mailke, and Gaudion, Compt. rend. 168, 926-30 (1919) (C.A. 13, 1838)
43. Stalman, U.S. 1,433,666 Oct. 31, 1932 (C.A. 17, 403)
44. Tishchenko and Matveev, J. Gen. Chem. (U.S.S.R.) 20, 896-904 (1950) (C.A. 44, 9381)
45. Venable, J. Am. Chem. Soc. 45, 728-34 (1923) (C.A. 17, 1454)
46. Wallach, Ann. 239, 35 (1887)
47. Zelinskie, Ber. 58B, 864-9 (1925) (C.A. 19, 2333)

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The content and form have been checked and approved by the author and thesis adviser. Changes or corrections in the thesis are not made by the Graduate School office or by any committee. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

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