

Part One: Mirrors

Part Two: Synthesis of Camphor

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1908

A senior thesis project of the University of Kansas

SENIOR THESIS

ROBERT C. KENT

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CHEMICAL ENGINEERING .

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PART ONE .

MIRRORS .

PART TWO .

THE SYNTHESIS OF CAMPHOR .

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P A R T O N E .

M I R R O R S .

Mirrors made by polishing metals and hard stones, and glass with a reflecting surface of gold leaf, tin and lead have been known from a very early time.

Looking glasses made by coating glass with a tin amalgam came into use about the middle of the fifteenth century, but its origin is unknown.

For a long time the actual details of the process were carefully guarded as a trade secret, and the first explicit directions for carrying out the process were given by Johannes Porta, an Italian, about the middle of the sixteenth century. He directs that a thin sheet of tin be spread on a flat table, a little mercury poured upon it and rubbed with a hare foot until the whole surface is coated and has a silvery appearance. On this a clean sheet of white paper is placed and on the paper a clean piece of glass. The paper is drawn out and the glass pressed down with weights until the excess of mercury is removed.

The manufacture of tin amalgam mirrors was begun in Venice in 1507, but it was not well established in

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Northern Europe until the middle of the eighteenth century, and reached its most extensive development during the latter half of the last century.

The process used ~~was~~^{was} much the same as that given by Porta, except that ^{more} mercury was used and the sheet of paper was discarded.

The process has many draw-backs; it takes a long time to complete, and is often subject to failure; plates frequently break; mercury is apt to streak the mirror; the amalgam may crystallize; and lastly the process is very unhealthy for the working people.

At the present time, owing to the discovery of methods of depositing silver on glass, tin amalgam mirrors are not manufactured extensively except in France where the yellow tint of the silver mirrors is regarded as objectionable.

Liebig first noted that silver could be deposited on glass as a mirror in 1835. He reduced the silver from the solution of ^{silver} nitrate in ammonia with formaldehyde.

The first attempt to make use of the reduction of silver in the manufacture of mirrors, was made by Thomas Drayton in 1843. He reduced the silver from a

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solution of silver nitrate in ammonia with various essential oils. His process was not successful because the mirrors in time developed spots.

No satisfactory method of depositing silver was devised until Liebig took up the study of the process with the object of finding a liquid able to deposit silver in a firm film at ordinary temperature, that would not develop spots. The following is the solution he found satisfactory:- One gram of silver nitrate dissolved in 20 $\frac{cc}{cc}$ of water, ammonia added until the silver oxide at first formed is dissolved. This is mixed with 45 $\frac{cc}{cc}$ of a solution of caustic soda, Sp.- G. 1.035, and the precipitate dissolved with ammonia. dilute silver nitrate is added until ~~at~~ a slight^{3h} permanent precipitate is formed. The solution is made up to 150 $\frac{cc}{cc}$. For using, this solution is mixed with a ten per cent solution of milk sugar. It may be here noted that Liebig was first to recognize^g the effect of caustic alkali in accelerating the reduction of the metal.

The following is the method of silvering given by Kayser, which I find gives very satisfactory results. To prepare the silver solution, dissolve ten grams of silver nitrate in 50 $\frac{cc}{cc}$ of water, add ammonia until the

precipitate first ~~formed~~ formed just dissolves. Then add a dilute solution of silver nitrate till a slight opalescence appears. Dilute to liter. To make the reducing liquid dissolve twenty grams of Rochelle salts and twenty grams of cane sugar in 200 cc of water. To this add a solution of four grams of silver nitrate in 20 cc of water and boil gently for half an hour, dilute to a liter.

On silvering equal volumes of the two liquids are poured on the plates to the depth of 1.5 to 2 cm for from fifteen to twenty minutes.

Copper, which in the cuprous state is quite like silver in its properties has been deposited on glass in various ways. Faraday in 1857, when silver mirrors were attracting wide attention, observed that a deposit of copper in the form of a mirror is obtained by heating olive oil in which is dissolved a little copper oxide to the decomposing temperature of the oil.

This ¹method gives a very beautiful copper mirror, and may quite easily be formed on a small beaker or test tube. But for making a copper mirror of comparatively large size, it is difficult to get a perfect

mirror owing to the dark spots formed from the decomposition products of the oils.

In the Chemical News of January 10, 1908, F.D. Chattaway gives a new method for making copper mirrors. He reduces copper from a solution of copper hydroxide in ammonia with an aqueous solution of phenylhydrazine by heating the two solutions together. The following is the method he gives:- A mixture of one part of freshly distilled phenylhydrazine and two parts of water ^{heated} until a clear solution is obtained. To this add about half its bulk of a warm saturated solution of cupric hydroxide in strong ammonia, nitrogen is evolved during the addition and the cupric is reduced to cuprous. Next add a hot solution of ten per cent caustic potash until a ^{gh}slight permanent precipitate is formed. If this colorless or pale yellow liquid is heated in contact with a clean glass surface, metallic copper is deposited upon it in the form of a coherent perfectly reflecting mirror.

This process gives quite satisfactory results. I obtained three or four copper mirrors on crystallizing dishes and beakers that were quite perfect, accompanied

by about twice as many failures.

The mirrors obtained by this process are lighter and somewhat more brilliant than those obtained by the Faraday process.

In making the mirrors, too much stress can not be laid on the cleaning of the glass, as the presence of a slight amount of dust or grease is apt to make a flaw in the mirror. The glass should be washed with a hot solution of soap, nitric acid and caustic soda, and rubbed with a cotton wool pad saturated with the cleaning reagents and ~~is~~ rinsed with an abundance of distilled water.

Although this method of depositing copper on glass is not as nearly ideal as some of the methods of depositing silver, owing to the imperfections that are some times caused by the oily decomposition product of the phenylhydrazine, the copper is deposited in a much firmer film than the silver. Silver deposited on glass can be readily removed by rubbing with a soft cloth, whereas the copper film is not affected.

The cause of the deposition of metals such as copper and silver on glass in the form of a coherent mirror is not known. It seems essential that the compound

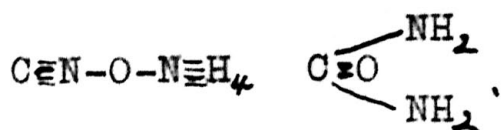
being reduced shall be in solution and that the concentration of the compound be small, that the liquid in which the reduction takes place shall be alkaline; it has been shown that alkalies eccelerate while ammonia retards the reaction; and it seems necessary that the action be more rapid at the surface of the glass than elsewhere. It seems probable that the glass its self act as a catalyzer locally accelerating the reaction.

P A R T T W O .

S Y N T H E S I S O F C A M P H O R .

Organic Chemistry originally treated of those compounds found in plant and animal life, and it was believed that life was essential to the formation of such compound; but gradually this idea has been abandoned, for one by one compounds that are found in plants and animals have been made in the laboratory without the aid of life. The term, organic chemistry is now applied to the study of the compound of carbon.

Urea ~~was~~^{was} the first organic compound made artificially. Wöhler in 1828 prepared urea by allowing a solution of ammonium cyanate to evaporate, the urea crystallizing out. Reaction being.



Later other organic compounds were prepared artificially, potassium cyanide, cyanate and formate, acetylene, etc. Still later many more organic compounds

were made artificially. Vanillin and indigo are two important compounds that are produced artificially on a commercial scale, and to day the synthetic indigo is driving the natural indigo of the Madder plant out of the market.

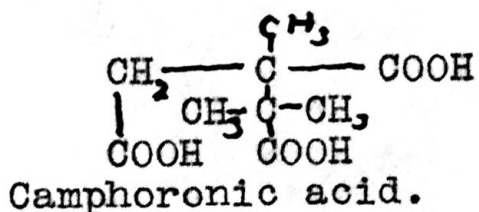
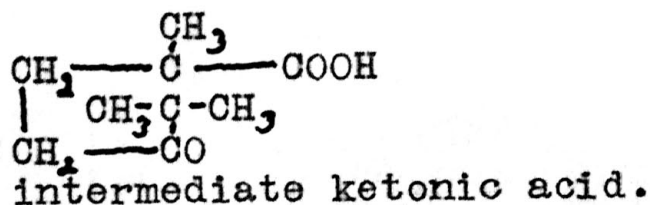
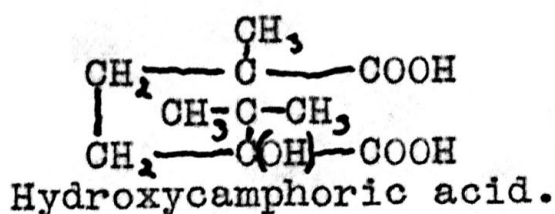
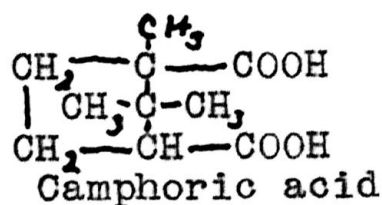
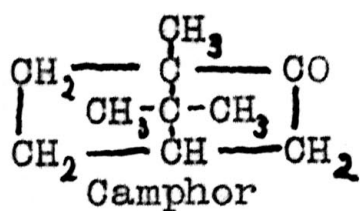
One of the latest and most important synthesis of an organic compound is that of camphor. Camphor is obtained in Japan and China from different species of the genus *Camphora* of the *Laurus* family, by distillation of the chips with steam. Camphor is one of the oldest known organic compound, and by reason of its crystalline character, its ^{easy} purification, its extraordinary reactivity, and comparative abundance, it has attracted much attention among chemists. It was analysed by Dumas and found to have the formula $C_{10}H_{16}O$, in 1785. Kosegarten, obtained an acid now known as camphoric acid, by the oxidation of camphor with nitric acid.

During the last twentyfive or thirty years many, skilled chemists have concentrated their efforts in ~~an~~ attempts to determine the structure of camphor. As a result as many as thirty formulae have at times been

proposed. Early formulae were based on the behaviour of camphor with dehydrating and other agents. Phosphorous pentoxide, zinc chloride, hydriodic acid and iodine all yielded more or less of aromatic compound, which fact pointed to a benzene skeliton for camphor.

In 1893 new light was thrown upon the structure of camphor by Bredt's discovery of the composition of camphoronic acid, which Kachler had found with camphoric acid among the oxidation products of camphor. Later the structure of champhoronic acid was established by Perkins and Thorpe.

According to Bredt the degradation of camphor was as follows:-



At first Bredt's formula was accepted with reserve. But since the discovery of Komppa's synthesis of camphoric acid, and the relation between camphoric acid and camphor has been established by Haller, Bredt's formula for camphor is generally accepted.

The following are the facts proving the correctness of Bredt's formula.

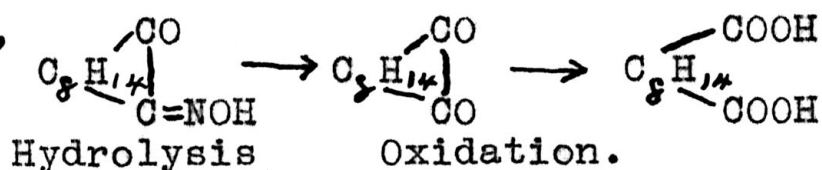
1. The empirical formula for camphor is $C_{10}H_{16}O$.
2. Camphor is a ketone, for it forms an oxime $C_{10}H_{15}NOH$ and on reduction forms a secondary alcohol, borneol $C_{10}H_{18}OH$.
3. Camphor has the carboxyl group attached to a methylene group. Claissen and Manasse showed that when camphor is treated with nitrous acid it forms isonitrosocamphor $C_8H_{14}CO$ + N^O_{OH} = $C_8H_{14}C=NOH$.

And treated with formic ethylate forms hydroxymethylene camphor, $C_8H_{14}CO$ + $HCOOC_2H_5$ = $C_8H_{14}C-CHOH$ + C_2H_5OH .

Both of the above reactions are associated with the group $\overset{\cdot}{CH_2}\overset{\cdot}{C}=O$.

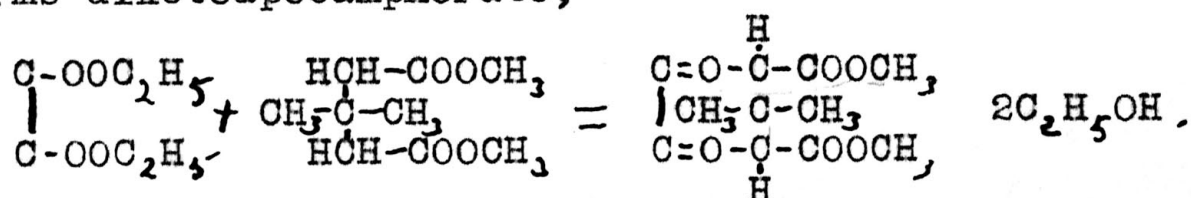
4. The group $\overset{\cdot}{CH_2}\overset{\cdot}{C}=O$ may be transformed into the two carboxyls of the camphoric acid. Claissen and Manasse

showed that isonitrosocamphor on hydrolysis forms camphor quinone, which on oxidation yields camphoric acid,

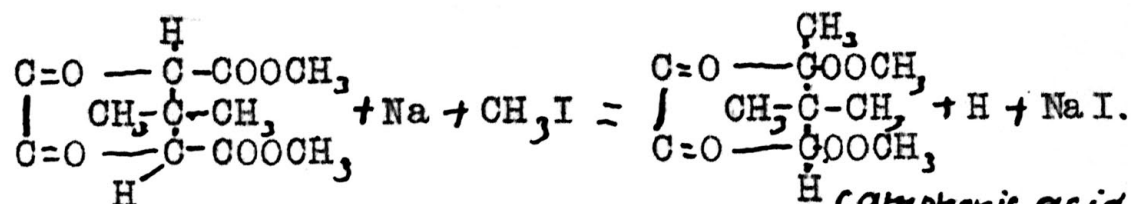


5. Komppa's synthesis of camphoric acid

β β dimethyl glutarate treated with diethyl oxalate forms diketoapocamphorate,

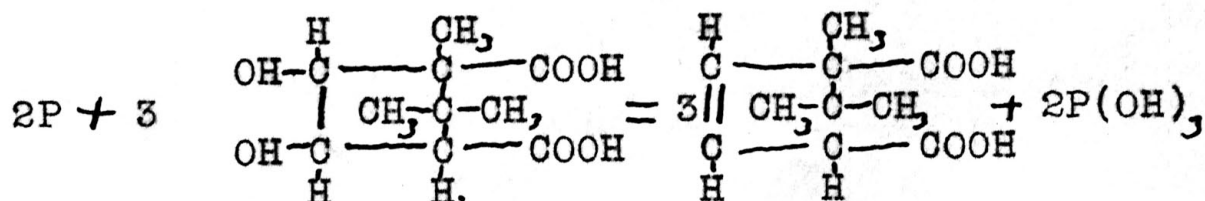


A methyl group is inserted by treating the diketoapocamphorate thus formed with sodium and methyl iodide,

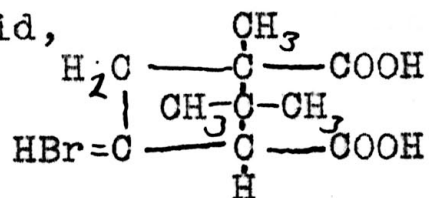


This product treated with zinc dust forms dihydroxy-1

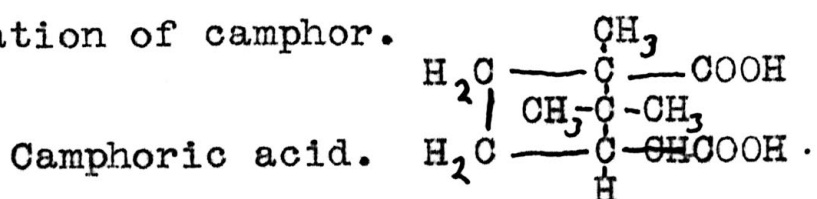
This treated with hydriodic acid and red phosphorous is converted into the ~~acid~~ unsaturated dehydrocamphoric acid



Dehydrocamphoric acid treated with hydrobromic acid forms β bromcamphoric acid,

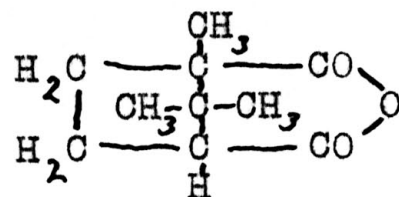


This product treated with zinc dust and acetic acid reduces to the same camphoric acid as obtained by the oxidation of camphor.

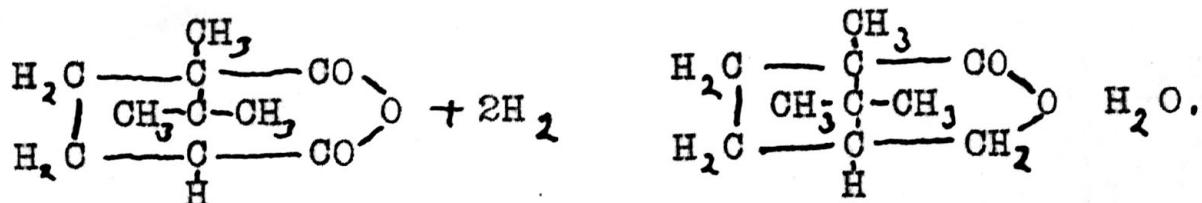


6. ~~H~~aller's camphoric acid to camphor.

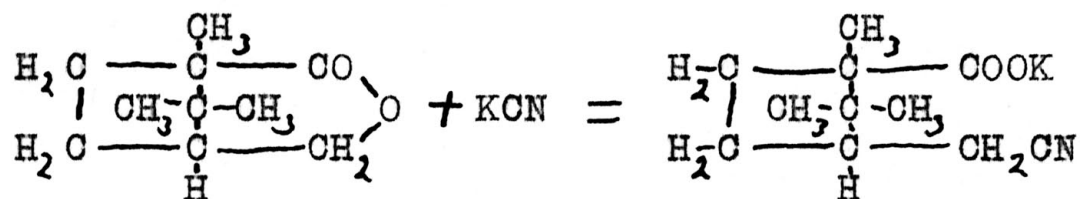
Camphoric acid dehydrated gives,



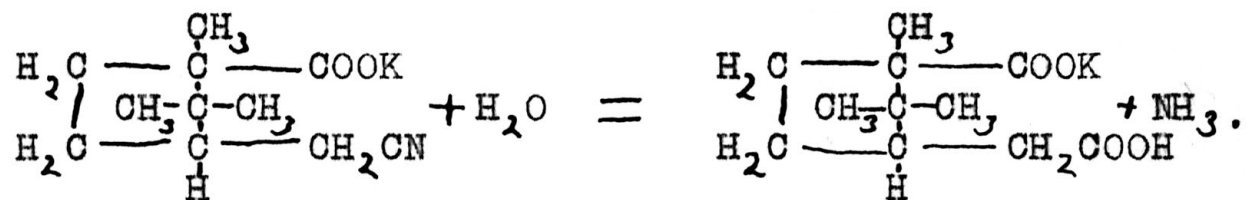
Camphoric anhydride reduced with sodium amalgam forms campholide,



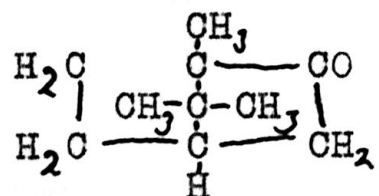
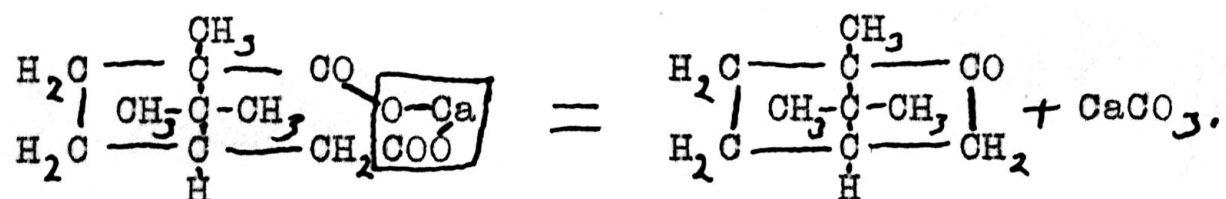
The campholide treated with potassium cyanide forms homocamphoric nitrile,



This on hydrolysis forms homocamphoric acid,



Upon heating the calcium salt of homocamphoric acid the camphor distills over,



Bredt's formula for camphor.

The discovery of the structure of camphor has been accomplished, and this fact is due not to the work of one man alone, but of many. Much credit should be given to Bredt who made the first definite headway

in determining the structure of camphor and who proposed the present formula, credit is also due to Komppa who synthesized camphoric acid, to Haller who showed the relation between camphoric acid ^{and camphor} to Claissen and Manasse, to Perkins and Thorpe.

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