

REPORT
of
Committee on Thesis

The undersigned, acting as a Committee of
the Graduate School, have read the accompanying
thesis submitted by Allen T. Newman
for the degree of Master of Science.

They approve it as a thesis meeting the require-
ments of the Graduate School of the University of
Minnesota, and recommend that it be accepted in
partial fulfillment of the requirements for the
degree of Master of Science.

Geo B Frankforter
Chairman

Welf Krutchevsky

B. J. Pasoy

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T H E S I S

ON

MENTHONE; ITS CONDENSATION AND ADDITION
PRODUCTS IN THE PRESENCE OF
ALUMINUM CHLORIDE.

BY

A . T . . N E W M A N .

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MENTHONE; ITS CONDENSATION AND ADDITION
PRODUCTS IN THE PRESENCE OF
ALUMINUM CHLORIDE.

Historical.

Menthone, the ketone of menthol, is now made commercially from menthol by the oxidation of the carbinol to the ketone group. These two compounds are not only closely related chemically but are also very closely associated in nature as for example in the oil of peppermint. Owing to these facts it was thought advisable to study menthol in as much as its physical and chemical properties have not been exhaustively studied; but more especially as it was used in preparing the menthone for the experiments which follow.

Menthol, $C_{10}H_{18}OH$, formerly known as "Mentha Camphor" or "Peppermint Camphor" is a naturally occurring product found together with terpenes, menthene and menthone in peppermint oil. It is prepared

from peppermint oil by first distilling off the menthene and terpenes; on cooling the remaining oil menthol crystallizes out from the menthone present. It can also be obtained directly from peppermint oil by cooling when the menthol separates out. Menthol can also be prepared by the reduction of the ketone, $C_{10}H_{18}O$, in the presence of an excess of nascent hydrogen as with sodium and water¹.

Menthol crystallizes in colorless prisms. It has a strong peppermint odor and a burning taste. It melts at $43^{\circ} C.$ and boils at $212^{\circ} C.$ It has a specific gravity of 0.890 at 15° and a molecular refractive power of 47.52 μ .

Menthone, $C_{10}H_{18}O$, as stated above is found as a naturally occurring product in small quantities in the oil of peppermint. Power and Kleber³ state

¹ Beckmann, Jour. pr. Chem. 55 (II) 14.

² Brühl, Ber. 21, 457.

³ Schimmel and Co. Semi-annual report, April, 1895, 56.

that the amount of menthone in American oil of peppermint reaches 12.38 o/o. It cannot be separated from menthol by fractional distillation as it boils only 5° or 6° below the latter compound. It is more generally prepared by the oxidation of menthol. This was first done by Moriya ¹ by the action of $K_2Cr_2O_7$ and H_2SO_4 on menthol heated in a sealed tube for ten hours. He also obtained the same oil by the action of $K_2Cr_2O_7$ and glacial $HC_2H_3O_2$ on menthol and describes it as boiling at 204-5°, with a specific gravity of 0.9032 at 15°, of an agreeable odor and optically inactive.

Later Atkinson and Yoshida ² prepared strongly dextro-rotatory menthone by repeated treatments of menthol with a chromic acid mixture at 135°. This would tend to show that the optical inactivity of Moriya's compound was due to the presence of laevo-rotatory menthone as an impurity. Atkinson ³ suggests

¹ London Chem. Jour. Vol. 39, p. 77.

² Jour. Chem. Soc. 1881, 77; Jahresb. Chem. 1881, 629.

³ Chem. Jour. London, vol. 40, p. 83.

that menthol is a secondary alcohol derived from a saturated closed chain hydrocarbon formed by the addition of six hydrogen atoms to ordinary cymene, $C_{10}H_{14}$, which is a p-isopropylmethylbenzene and that the oxidation product, menthone, $C_{10}H_{18}O$, obtained by Mr. Moriya, is the corresponding ketone.

In 1907 N. A. Speransky ¹ made thiomenthone by the action of phosphorous trisulphide on menthone, while in the same year A. Schaeffer and A. Muria ² in working with ketones added a solution of Zn p-nitrobenzylmercaptide to menthone and obtained menthone-p-nitrobenzylmercaptol. During the following year A. Kötze and A. Schwarz ³ made optically active menthone in two ways from B-methyl- α -isopropyl-pinelic acid.

In 1909 Ernest Beckmann ⁴ prepared dextromenthone by the inversion of laevo-menthone and found

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- ¹ J. Russ. Phys. Chem. Soc. 38, 1288 and 1346-50.
 - ² Ber. 40, 2007-8.
 - ³ Ann. 357, 209-13.
 - ⁴ Ber. 42, 846-50.

it to be a mixture of laevo menthone and dextro-iso-menthone. He also prepared dextro-menthone-oxime, laevo-menthone-oxime, d-menthone-semicarbazone, d-iso-menthone-semicarbazone and l-menthone-semicarbazone, all of which were optically active.

During the year 1912 Ivan Vanin ¹ by the action of Et-I and Mg or Zn on menthone obtained a hydrocarbon C₁₂H₂₂. At about the same time M. Murat ² obtained corresponding tertiary alcohols by the condensation of natural l-menthone or synthetic, optically inactive menthone with Ph-Mg-Br and cyclohexyl Mg Br respectively.

During the following year Hans Stobbe and Arthur Rosenberg ³ found that in the presence of Et-O-Na, menthone condenses with Bz-CH : CH-Ph giving a single addition product. They state further that this is not a 1, 5-semicyclic diketone as would be ex-

¹ J. Russ. Phys. Chem. Soc. 43, 355.

² J. Pharm. Chin. 4, 294-9; through J. Soc. Chem. Ind. 30, 1332.

³ J. prakt. Chem. 86, 226-232.

pected but is a dicyclic ketoalcohol.

While Beckmann, Mehrländer ¹, Werner ², and Wallach ³ made various compounds from menthone and Stobbe and Rosenberg, above mentioned, made some condensation products no one, so far as we have been able to learn from the literature at our disposal, has ever made any condensation products of menthone by the use of $AlCl_3$.

Experimental.

All of the experimental work following was done with menthone made from pure Japanese menthol which melted at $41-43^\circ C.$ with a specific gravity of 0.8705 at $60^\circ C.$ referred to H_2O at 4° and a laevo-rotatory power of $(\alpha)_D^{20} = -49.50$ and $(\alpha)_D^{25} = -49.55$. The menthone was made by the oxidation of menthol with $K_2Cr_2O_7$ and conc. H_2SO_4 according to the process used by Beckmann with the exception of the purification by

¹ A. 289, 386; A. 289, 382.

² B. 27, 1657.

³ A. 277, 156; 278, 304; A. 278, 305.

steam distillation ¹. The product was a colorless, mobil oil of soft peppermint-like odor. It boiled at 206-7° C., had a specific gravity of 0.8968 at 20° and a specific rotatory power of $(\alpha)_D^{20} = -3.53$ and of $(\alpha)_D^{25} = -3.67$. The probable reaction for the above oxidation is more complex than would at first appear. The $K_2Cr_2O_7$ and conc. H_2SO_4 are dissolved in water and heated to 30° when the menthol is added. The liquid immediately turns dark colored, the menthol gets soft and is converted into a chromium compound. The menthone is not formed at once but separates out when the reaction mixture gets above 53°. This temperature is usually reached without heating in about thirty minutes. At 53° the chromium compound suddenly decomposes and the menthone separates out.

F powdered $AlCl_3$ was added very slowly to a solution of menthone in carbon disulphide. The reaction was immediate and vigorous, the $AlCl_3$ going into solu-

¹ Ann. Chem. 250, 322; 289, 362.

tion with the evolution of considerable heat and fumes of HCl. The solution became thicker and assumed a deep reddish-brown color. The speed of the reaction depends upon the amount of the solvent (CS₂) present and the temperature at which the reaction is allowed to proceed. After repeated experiments it was found that the maximum yield of the condensed product was obtained from a mixture of two gram molecules of AlCl₃ to one of menthone with only a small amount of the solvent present. After the first vigorous reaction had passed the mixture was set aside and allowed to stand for several hours with an occasional shaking. It was then boiled slowly under a reflux condenser for about four hours. Considerable care is required at this point to keep from overheating the mixture. If overheated the entire mass will puff up and turn black charring the organic matter present and reducing the yield of the condensed product. When it had been boiled enough the flask was removed from the condenser and while it was held in a

stream of tap water to keep it cool water was added to remove the excess of aluminum chloride and also to break up any aluminum organic compounds that might have been formed. A heavy, dark colored oil separated out and came to the surface. This was dissolved in CS_2 , then poured off and distilled. Part of this oil distilled off at $198-201^\circ \text{C}$., was quite mobil, of a decided red color and slightly fluorescent. The remainder of the oil distilled over at $225-230^\circ \text{C}$. and 37 m. m. pressure. It was lemon yellow in color without any trace of the red coloration found in the preceding distillate.

Several other methods were tried in an attempt to obtain a larger yield of the condensed oil but with indifferent success. The reaction of AlCl_3 on a solution of menthone in CS_2 in the cold was tried. For the first six hours it was kept in an ice-water bath and was not allowed to get above 20°C . for five weeks. Water was then added to dissolve the excess AlCl_3

and to break up any aluminum organic compounds formed. It was then treated as above outlined. The condensed product was carefully examined and found to correspond with the oils obtained by the other method. Hence it is assumed that the reaction in the cold is the same as when heated except that it requires considerably more time.

Thinking that possibly the water, added to dissolve the excess of $AlCl_3$, had a hydrolyzing effect and broke up some of the condensed oil an attempt was made to distill off the oil directly from the reaction mixture and thus get it separated from the aluminum. The attempt was a failure as the solvent distilled off first and the temperature rising the remaining oil and menthone became charred and formed a black, sticky mass.

Distillation in vacuo was then tried on the supposition that the lower temperature would not char the heavier oil. This method proved very slight-

ly better than the other. The solvent distilled off, then the unchanged menthone and finally the condensed oil which carried aluminum compounds over with it and which we were unable to separate. This last distillate solidified on standing.

A further attempt was then made to extract the oil from the aluminum chloride by means of an excess of the solvent CS_2 . This looked promising at first but later it was found that there was a considerable amount of aluminum compounds had been dissolved and carried over. The oil was obtained by this method but the yield was small and was more trouble than the first method mentioned.

A bromine derivative of the oil boiling at $225-250^\circ C.$ and 37 m. n. pressure was made by adding bromine directly drop by drop to a solution of the oil in CS_2 . The reaction was immediate and vigorous with the formation of HBr . A thick, black compound insoluble in carbon disulphide was formed. This compound became

slowly more viscous, nearly solid and when no more HBr was formed the CS₂ was poured off and the residue washed thoroughly with ethyl alcohol, in which it was insoluble, until all the free bromine was washed out. It was then dissolved in ether and precipitated by the addition of absolute alcohol. The precipitate was amorphous and of a yellow color. The precipitate was further purified by a second precipitation from ether and was then dried on a porous plate. When dry it crumbled to a fine, yellow powder which melted at about 84° C. A determination of the percent of bromine present was made by the Carius tube method which yielded results as follows:-

	Grms. of sample.	Grms. of bromine.	o/o of bromine.
No. 1, -----	0.1276	0.0718	56.26
" 2, -----	0.1249	0.0707	56.60
Calculated for the formula (C ₁₀ H ₁₂) ₂ (C ₁₀ H ₁₈) ₂ Br ₂ HBr =			57.05 o/o
Average for above experimental results			56.43 o/o

A chlorine derivative of the oil boiling

at 225-30° C. and 37 m. m. pressure was made by passing dry chlorine gas through a solution of the oil in CS₂ contained in a U tube. The reaction was immediate in the cold, the reaction mixture became thicker and changed to a distinct red color with the formation of HCl. The resulting compound was washed thoroughly with absolute alcohol, dissolved in ether and precipitated by the addition of absolute alcohol. The precipitate was yellow, slightly lighter in color than the bromine compound and when dried on a porous plate crumbled to a fine, yellow powder which melted at about 73° C. A chlorine determination by the Carius tube method yielded percentage results as follows:-

	Grms. of sample.	Grms. of chlorine.	o/o of chlorine.
No. 1,	0.1527	0.0488	31.95
" 2,	0.1891	0.0576	30.46
Calculated for the formula (C ₁₀ H ₁₃) ₂ (C ₁₀ H ₁₈) ₂ Cl ₆ HCl =			31.09 o/o
Average of above experimental results			31.20 o/o

Having determined the fact that AlCl₃,

acting as a condensing agent, formed polymers of menthone by taking out H_2O , its action on a mixture of menthone and benzene was tried.

Menthone was dissolved in an equal amount of benzene and powdered $AlCl_3$ was added. After repeated experiments it was found that two gram molecules of $AlCl_3$ to one of menthone gave the best results. As the $AlCl_3$ was slowly added the reaction mixture became hot and changed to a dark red color. The $AlCl_3$ went into solution with the formation of HCl . The reaction mixture was thoroughly shaken, allowed to stand for several hours and was then boiled under a reflux condenser for about four hours or until it became thick, syrupy and very dark red in color. It was then allowed to cool and water added to take up the excess $AlCl_3$ and to break up any aluminum organic compounds that might have been formed. As the water was added a heavy, red oil with a greenish fluorescence separated out and came to the surface. This oil was then separated from the water solution by means of a separatory funnel and distilled.

After repeated distillations a rather heavy, yellow oil boiling at 330-38° C. was obtained. It began to decompose at 338° and when heated above that point turned dark colored. After distilling off this oil there was a black residue left which, on cooling, became hard, almost brittle and very closely resembled asphalt or tar in appearance.

In making this condensation product of menthone and benzene several different methods were tried but none gave a greater yield nor worked as well as the above mentioned process. Instead of boiling under a reflux condenser for several hours the reaction mixture was allowed to stand for five weeks with the temperature never above 20° C. Water was then added as in the above mentioned processes, the oil came to the surface, was separated off and then distilled. The reaction is apparently the same in the cold as when boiled but does not progress as far in five weeks in the cold as in a few hours of boiling. The yield was very small.

Thinking that the presence of water had a tendency to break up the condensed product and thus lower the yield an attempt was made to dissolve the oil out by using an excess of benzene. Some aluminum, probably in the form of aluminum organic compounds, was dissolved by the excess of benzene and distilled over with it. Water then had to be added to break up these aluminum compounds and the result was the same as in the first mentioned process and considerably more trouble.

Direct distillation of the condensed oil from the reaction mixture was attempted but proved a failure. As the temperature rose to the boiling point of the oil the excess of benzene distilled off and the $AlCl_3$ remaining had a tendency to char the oil, thus lessening the yield and discoloring the product. With this fact in mind an attempt to distill off the oil in vacuo was made. A pressure of 58 m. m. was obtained but the boiling point of the oil even at that pressure

was too high and the mass charred as before.

A bromine derivative of the oil boiling at 350-38° and atmospheric pressure was made by adding bromine directly to a solution of the oil in CS₂. The reaction began immediately in the cold but the mixture soon became hot and HBr was formed in considerable quantities. The reaction mixture turned darker and the oil had a tendency to separate out from the carbon disulphide solution as the bromine was added. Bromine was added until there was no more HBr given off when the carbon disulphide was allowed to evaporate leaving a black and resinous residue. This residue was thoroughly washed with absolute ethyl alcohol until no more free bromine was present. It was then dissolved in ether and precipitated by adding alcohol. It was further purified by a second precipitation from ether with alcohol and a yellow, non-crystalline powder was obtained which melted at about 57° C. It gave the characteristic bromine flame with copper oxide. A determina-

tion of the percent of bromine present was made by the Carius method which yielded the following results:-

	Grms. of sample.	Grms. of bromine.	o/o of bromine.
No. 1,	0.1507	0.0731	48.50
" 2,	0.2004	0.0974	48.60
Calculated for the formula $(C_{10}H_{14})_2(C_6H_5)_2Br_4HBr$			=48.60
Average of above experimental results			=48.55

An iodine derivative of the oil boiling at 350-38° C. and atmospheric pressure was made by dissolving the oil in carbon disulphide and adding solid iodine directly. The reaction was slow, the reaction mixture changed to a dark color due to the iodine in solution and HI was formed. The vessel containing the reaction mixture was placed in a beaker of hot water for over an hour to hasten the reaction. Considerable difficulty was experienced in getting a product free of iodine. This was finally accomplished by repeated washing with alcohol, boiled in absolute alcohol and then let stand for two days in alcohol. It finally became brittle and

broke up into fine granules after which the alcohol was decanted off and the solid matter dried thoroughly on a porous plate. The iodine compound was a black powder, readily soluble in ether but not soluble in alcohol. It melted at about 147° C. A determination of the percent of iodine present was also made by the Carius tube method which resulted as follows:-

	Grms. of sample.	Grms. of iodine.	o/o of iodine.
No. 1,	0.0696	0.0139	19.97
" 2,	0.0637	0.0126	19.78

Calculated for the formula $(C_{10}H_{16})_2(C_6H_5)_2I = 20.15$

Average of the above experimental results = 19.88

The heavy, black, tar-like residue from the menthone-benzene condensation was digested with concentrated nitric acid on a water bath for one hour. Part dissolved giving the solution a deep red color. The part not soluble in HNO_3 was reddish black in color and became hard and brittle, breaking up into powder when washed with water. This powder was partially solu-

ble in absolute alcohol on boiling from which solution it precipitated yellow and flocculent. It decomposed when heated on platinum foil giving off brown fumes. In a melting point tube it decomposed at about 147°. The part not soluble in alcohol was a dark brown powder. It burned with explosive violence giving the characteristic brown fumes of a nitro compound. It showed a tendency to melt at 227° but did not wholly melt when heated up to 300° C.

The HNO_3 solution was poured off and allowed to cool. A finely divided, amorphous, brick red precipitate came down as the solution cooled. The supernatant liquid was poured off and the precipitate dried. This dry precipitate was partially soluble in absolute alcohol on boiling. The part not soluble in alcohol dried to a very fine, yellow powder. It was explosive when heated on platinum foil. It first became soft and puffed up, then burned with a flash giving off brown fumes. It partially melted at 209-10° C. and then show-

ed no further change up to 300°. The portion soluble in absolute alcohol precipitated out as a yellow, flaky, non-crystalline substance. When heated on platinum foil it puffed up and turned black, then gave off brown fumes in an explosive manner leaving a black residue which was completely burned on continued heating. It melted slightly against the walls of the melting point tube and puffed up at 164-6° but on further heating merely bubbled. The supernatant liquid that was poured off was diluted with water and immediately a light yellow, flocculent precipitate was formed. It was allowed to settle and the solution filtered off. The precipitate dissolved in alcohol from which it was precipitated to purify it. The precipitate was evidently the same compound as the last one mentioned above. a