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# Some reactions of chloro-cyclo-hexanone and its derivatives and the synthesis of 1 chloro-2 methyl cyclo hexene.

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UNIVERSITY OF LOUISVILLE

SOME REACTIONS OF CHLORO-CYCLO-HEXANONE AND ITS DERIVATIVES

AND

THE SYNTHESIS OF 1 CHLORO-2 METHYL CYCLO HEXENE

A DISSERTATION

SUBMITTED TO THE FACULTY

OF THE GRADUATE SCHOOL OF THE UNIVERSITY OF LOUISVILLE

IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

BY

ELLE BOLT

1948

**Name of Student**

**Elle Bolt**

**Title of Thesis**

**Some Reactions of Chloro - Cyclo -  
Hexanone and Its Derivatives,  
and The Synthesis of 1 Chloro -  
2 Methyl Cyclohexane.**

**Approved by Reading of Committee Composed of the following members:**

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**Name of Director**

**Dr. M. I. Bowman**

**Date**

**August, 1948**

3 May 1949 H R

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### Purpose

(1) In the current literature on the chlorination of cyclohexanone, no evidence could be found of the physical constants of derivatives of the chlorinated compound, chloro - cyclo - hexanone. It was thought advisable to prepare the more common derivatives of chloro - cyclo - hexanone, and to report their physical constants, both for identification and purification purposes.

(2) To synthesize chloro - methyl - cyclo - hexenes. These compounds have not yet been reported in the literature.

### Historical

The synthesis of chloro - cyclo - hexanone was reported by F. Ebel in 1929 , by direct chlorination of cyclo - hexanone in water solution in the presence of calcium carbonate. A more efficient procedure was reported by P. Bartlett in 1934(1). In this method direct chlorination was effected in glacial acetic solution, in the presence of excess of cyclo - hexanone. By this method very little high boiling residue results. This is at present the best method for preparing chloro - cyclo - hexanone.

## Experimental

### I Chlorination of Cyclohexanone (2)

A run was carried out as follows: 75 grams of cyclohexanone and 225 cc. of glacial acetic acid were placed in a 500 cc. long necked flask, and immersed in an ice bath. 50 grams of manganese dioxide were placed in a round bottom flask fitted with a dropping funnel, filled with hydrochloric acid and delivery tube. The chlorine was washed in sulfuric acid, and dried in glass wool, and introduced into the cyclo hexanone through a capillary tube. The reaction was started and the chlorine introduced in small bubbles, while the reaction mixture was shaken throughout. The chlorine was absorbed very rapidly. After all the chlorine has been introduced (14 liters), the mixture was at once vacuum distilled. All fractions boiling below the main fraction ( $82^{\circ} - 85^{\circ}$ , 14 mm.;  $105^{\circ} - 110^{\circ} - 35$  mm.) were returned to the reaction flask, and used for another run. The fraction boiling  $105^{\circ} - 110^{\circ}$ , 35 mm., was collected. The product was chloro - cyclo - hexanone.

### II. Physical Constants of Chlorocyclohexanone

- (a) B. P.  $82^{\circ} - 85^{\circ} - 14$  mm.;  $105^{\circ} - 110^{\circ} - 35$  mm.
- (b) Refractive Index  $n_D^{25} = 1.481$  g.
- (c) Density  $D_4^{25} = 1.159$

III. Quantitative Analysis of Chlorine in Chloro - Cyclo - Hexanone - Stepanoff Method

Experimental: Connect a 300 cc. Kjeldahl flask with a short condenser, whose tube is perfectly dry. Clamp over a wire gauze, covered with a thin sheet of asbestos. Introduce 0.2 grams (W) of chlorocyclohexanone into the Kjeldahl flask, and add (156 X W) cc. of isopropylalcohol. Warm with a flame until the substance is dissolved. Introduce through the condenser (19.5 X W) grams of sodium. This operation should extend over at least fifteen minutes. Keep the solution at reflux temperature for at least one hour after the last of the sodium has been introduced. Then cool, and dilute with 50 cc. of water through the condenser. Acidify the solution with nitric acid, until definitely acidic. Then add a measured amount (excess) of standardized silver nitrate ( $0.1$  N) solution. Determine the excess of silver nitrate with .1 N Potassium thio - cyanide solution, using ammonium ferric alum as indicator.

Calculated for chlorine in  $C_6H_{11}OCl = 26.5$

Found 26.3

IV. Preparation of Derivatives of Chloro - Cyclo - Hexanone (6)

(a) Preparation of the semicarbazone: 5 grams of the chloro - cyclo - hexanone was mixed with 5 grams of isopropyl alcohol, in a 250 cc. flask. A solution of 6 grams semicarbazide



hydrochloride and 8.0 grams of sodium acetate dissolved in 100 cc. of water was added. The mixture was shaken vigorously, and left to stand overnight at room temperature, and then filtered. The solid semicarbazone obtained was purified by recrystallization from alcohol.

Result: A white solid: M. P. <sup>82</sup>228°.

Calc. for Cl<sub>2</sub> in C<sub>7</sub>H<sub>12</sub>ON<sub>3</sub>Cl = 18.7%. Found Cl<sub>2</sub> = 16.8%. *anal.*

(b) Preparation of the 2,4-Dinitro-phenyl-hydrōzone:(7)

A mixture of 1.5 grams of dinitro phenyl hydrōzine, 2 cc. of chloro-cyclo hexanone and 100 cc. of isopropyl alcohol is brought to boiling. The flame is removed, and 2 cc. of concentrated hydrochloric acid is added. The color changes, and a yellow solid separates out on cooling.

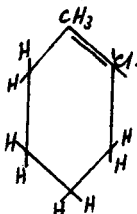
Results: A yellow solid: M. P. 150°.

Calc. for Cl in C<sub>12</sub>H<sub>15</sub>N<sub>2</sub>Cl = 15.9%.

Found = 15.6%

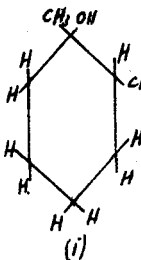
Part II

The Synthesis of 1 Chloro - 2 Methyl Cyclo Hexene:

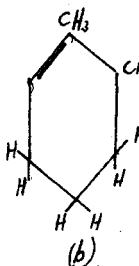
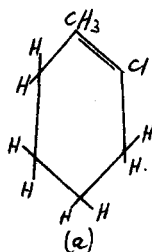


Theory and Discussion: The reaction of 2 chloro cyclo hexanone and methyl magnesium iodide (Grignard reagent) and the subsequent hydrolysis of the addition compound has already been described. <sup>6</sup>

The reaction proceeds smoothly, and yields ranging from 55 - 82% have been reported. The product was 1 methyl - 2 - chloro cyclo - hexanol,



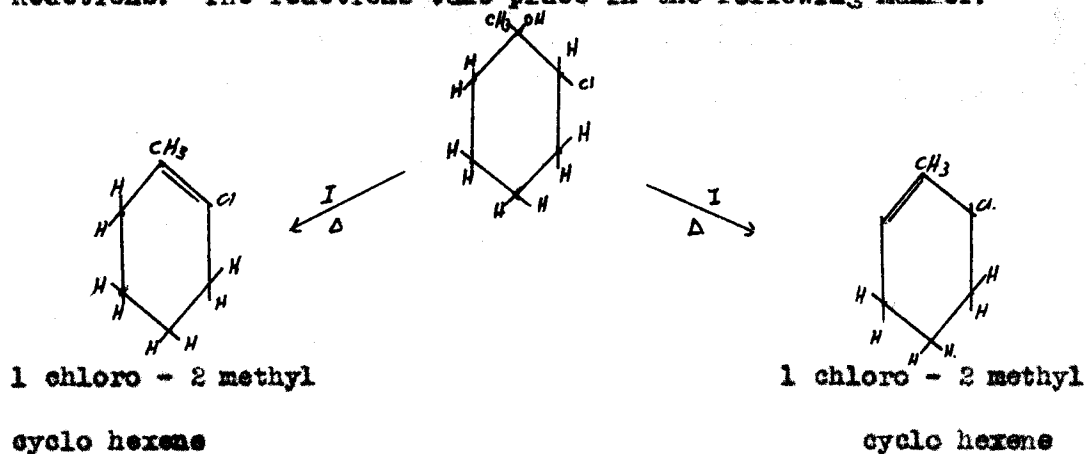
If this compound be dehydrated, it would yield the desired product, 1 Chloro - 2 methyl cyclohexene. The reaction however, could take place in two ways, yielding the isomeric compounds 1 chloro - 2 - methyl cyclohexene (a) and, or, 1 chloro 2 methyl <sup>2,3</sup> cyclohexene (b)



differing in the position of the double bonds. It was suggested to dehydrate the chlorhydrin (i) with iodine. In its compound (a) the chlorine atom will be stable, while, in the case of compound, (b),

the chlorine atom will be labile. The different reactivities of the chlorine atoms thus offered a suitable solution to this problem. If the product of the dehydration from the chlorhydrin (1) be subjected to simultaneous hydrolysis and oxidation by means of sodium dichromate and sulfuric acid(5), the chlorine in compound (a), due to its stability, will remain unchanged, while that in compound (b) will be replaced by a ketone group. After extraction of the solution with ether, the ketone, (if any) could be identified by conventional means. If no ketone be formed, the dehydration product from the chlorhydrin and iodine, will be exclusively the compound (a), 1 chloro - 2 methyl cyclohexane.

Reactions: The reactions take place in the following manner:



Experimental:

#### I Preparation of Methyl Magnesium Iodide: (Grignard Reagent)

The conventional method of preparing the Grignard Reagent was used(8) 3 grams of magnesium turnings were placed in a three necked flask, fitted with a stirrer and an efficient reflux condenser. A mixture of 30 grams of methyl iodide in 70 cc. dry ether was

introduced slowly through a dropping funnel, so as to keep the mixture boiling continually. This yields methyl magnesium iodide.

## II. Preparation of 1 Methyl 2 Chloro Cyclo Hexanol:

The flask in which the Grignard solution was prepared was surrounded by ice, and cooled to  $0^{\circ} - 5^{\circ} \text{C}$ , 5.5 grams of chloro cyclo hexanone was dissolved in 50 cc. of dry ether, and cooled to  $0^{\circ} \text{C}$ . The solution was added through the dropping funnel, and vigorous stirring was maintained. The product was then hydrolyzed with 10% sulfuric acid, which has also been cooled to between  $0^{\circ} - 5^{\circ} \text{C}$ . The solution was extracted with ether, and the ether solution washed with sodium carbonate solution, and then dried with sodium sulfate. The yield was  $\frac{1}{2}$  75% of a product B. P.  $90^{\circ}$ , 32 mm.  $n_D^{20}$  1.4810. Reported for 1 methyl 2 chloro cyclohexanol B. P.  $75 - 75^{\circ}$ , 15 mm.  $n_D^{19}$  1.4811.

## III Synthesis of 1 Chloro 2 Methyl Cyclo Hexane

The reaction was carried out in a 50 cc. three necked flask, fitted with a reflux condenser(8). The 1 methyl 2 chloro cyclohexanol (3 grams) was introduced, and heated to  $95^{\circ}$  on a water bath. A crystal of iodine was added, and the mixture held at  $95^{\circ}$  for at least thirty minutes. The solution was then vacuum distilled, and the fraction B. P.  $82 - 86^{\circ} - 40 \text{ mm.}$  was collected.

It was purified by washing with water, which removed the unchanged alcohol, and some iodine. The product had the following properties:

(1) Insoluble in water

(2) Refractive Index  $n_D^{25} = 1.4848$ .

(3) Test for unsaturation:

(a) Decolorizes Bromine water.

(b) Precipitates manganese dioxide from potassium permanganate solution.

(4) Chlorine Analysis:

Calculated for Cl in  $C_7H_{11}Cl = 27.0\%$

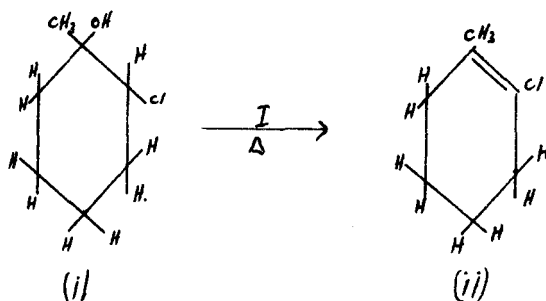
Found = 26.7%

To distinguish between isomers in the product obtained in II, the following procedure was employed: The reaction was carried out as follows(5): 1 gram of the chlorine compound was emulsified in 16 cc. water, with the aid of a mechanical stirrer. Two grams of sodium dichromate was added, and the solution heated to  $60 - 65^\circ$ . Concentrated sulfuric acid (2.5 grams) was added over a period of five minutes, the temperature being kept at  $60 - 65^\circ$ . The solution was cooled down, and extracted with ether. The ether was evaporated, and the residue treated with semicarbazide hydrochloride.

Result: No semicarbazone could be obtained. The product obtained from the ether extract in the above procedure, still gave a positive test for chlorine applying qualitative procedures. This proves that the chlorine was not removed, and therefore is bound firmly to the ring. The yield was over 80%.

Conclusion: The product of dehydration of 1 methyl 2 chloro cyclohexanol

(i) with iodine gives the product 1 chloro 2 methyl cyclohexene (ii), thus,



### Conclusions:

The chlorination of cyclo - hexanone has been carried out, and derivatives of the chlorinated compound prepared. The physical constants of these derivatives has been reported in this work.

A synthesis has been devised for the preparation of 1 methyl 2 chloro cycle hexane in high yield, which has not yet been prepared before. It has also been shown that this reaction proceeds in one way only, and that no isomeric compounds are formed.

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