Isomerization of Cycloalkanes
Under
Carbonium Ion Conditions

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A Thesis

submitted to the College of Natural
Science of Michigan State University
in partial fulfillment for the degree
of Master of Science in Chemistry

by

Edward J. Apple

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ABSTRACT

The liquid phase isomerizations of methylcyclopentane, cyclohexane, ethylcyclopentane, methylcyclohexane and cycloheptane under carbonium ion conditions were studied. The catalysts used were aluminum chloride and the corresponding alkyl chloride of the cycloalkane, i.e. 1-chloro-1-methylcyclopentane in the isomerization of methylcyclopentane. The effect of time, temperature and aluminum chloride concentration on the above hydrocarbons was studied.

The question of whether primary carbonium ions are formed as reaction intermediates from the more stable secondary and tertiary carbonium ions was examined. In all cases where they have been postulated, the data are also in accord with a bimolecular process which does not involve primary carbonium ions. No evidence was found in this work supporting bimolecular reactions, although the results do not exclude their occurrence.

Five, six and seven-membered rings interconvert under the experimental conditions. In all cases the predominant product is a six-membered ring.

INTRODUCTION

The isomerization of hydrocarbons and related compounds in liquid phase reactions has been studied for many years. These studies have included different types of catalysts and reaction conditions. Relative to this work are those carried out with Friedel-Crafts catalysts such as aluminum chloride and aluminum bromide.

The proposed mechanisms for these reactions involve carbonium ions as intermediates.

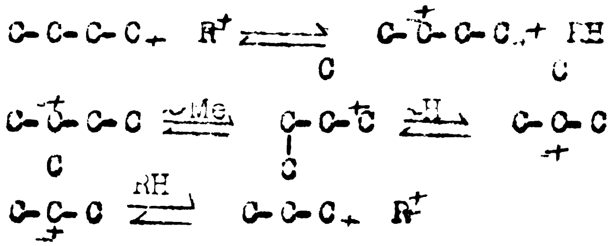
The general concept of the intermediate formation of carbonium ions was first stated by Whitmore[1] to explain the 1,2 shifts so common in organic chemistry. Then, followed several discoveries of importance relating to aluminum halide induced rearrangements. Heldman[2] reported that in addition to aluminum halide, hydrogen halide and water, or an alkyl halide must be present to induce isomerization. Pines and Wacker[3] also observed that an olefin or alkyl halide was needed in catalytic amounts to initiate the reaction. These findings coupled with the discovery by Bartlett, Condon and Schneider[4] of the rapid hydrogen-halogen exchange between isoparaffins and alkyl halides under the influence of Lewis Acids firmly established the intermediacy of carbonium ions. The

concepts developed therein[4] form the basis of much of the modern mechanistic interpretations of liquid phase isomerizations occurring under these conditions.

By consideration of the above observations and concepts, one is able to rationalize the formation of any product under liquid phase carbonium ion conditions. However, the number of mechanistic paths able to rationalize a given product is usually large. This makes the problem of singling out one specific mechanistic path as the correct or even dominant one very difficult.

Mechanisms suggested for some of the more common liquid phase isomerizations involve the intermediate formation of primary carbonium ions from the more stable secondary and tertiary carbonium ions. The following are typical examples:

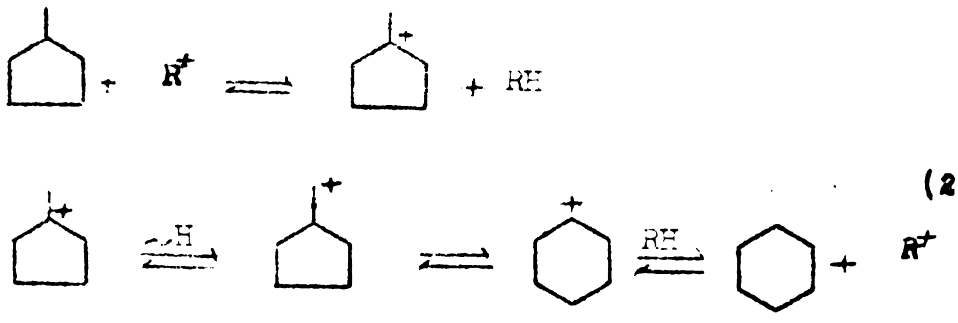
The isomerization of n-butane to isobutane.[5]



$$C{-}C{-}C{-}C + R^+ \rightleftharpoons C{-}\overset{+}{C}{-}C{-}C + RH$$
$$\underset{C}{C{-}\overset{+}{C}}{-}C{-}C \xrightleftharpoons{\sim Me} \underset{C}{C}{-}C{-}\overset{+}{C} \xrightleftharpoons{\sim H} \overset{C}{C{-}\underset{+}{C}{-}C}$$
$$C{-}\underset{+}{C}{-}C \xrightleftharpoons{RH} C{-}C{-}C + R^+$$

(1)

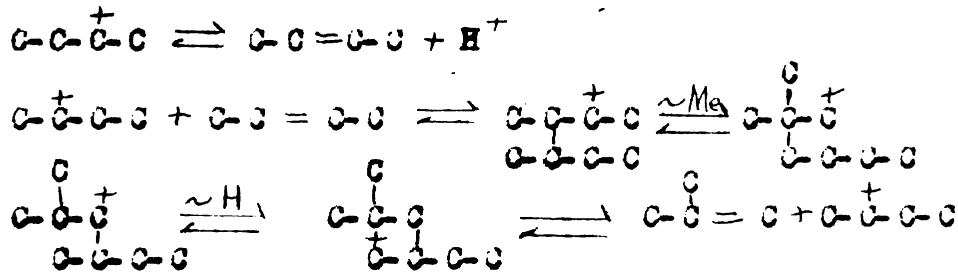
The isomerization of methylcyclopentane to cyclohexane.[6]



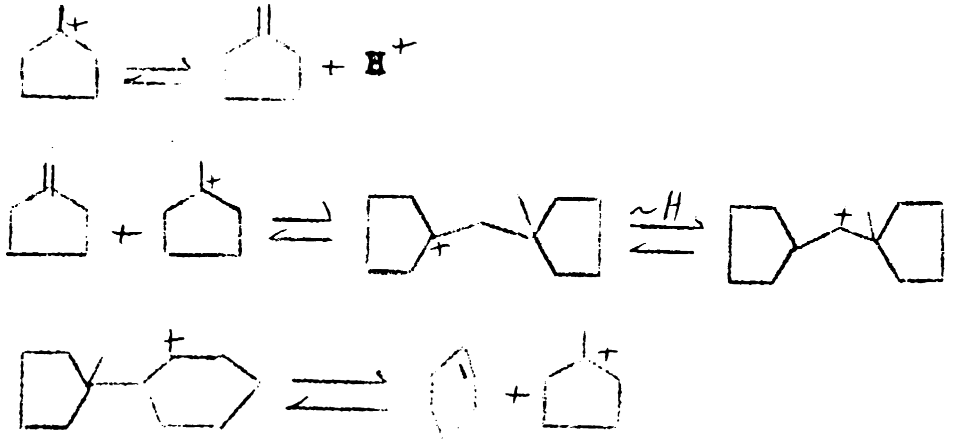
(2)

The above mechanisms are consistent with the observed results; however, calculations[7] show that at least 33 kcal/mole of activation energy is required to convert a tertiary carbonium ion to a primary carbonium ion and 22 kcal/mole of activation energy is required to convert a secondary carbonium ion to a primary carbonium ion. These energy requirements justify the examination of alternate mechanistic routes.

In all cases where primary carbonium ions have been postulated as reaction intermediates, the data are also in accord with bimolecular reactions not involving primary carbonium ions. The occurrence of bimolecular reactions in the isotope-position rearrangement of t-amyl chloride with aluminum chloride has been shown.[8] Bimolecular reactions may be formulated for cases (1) and (2) as follows:

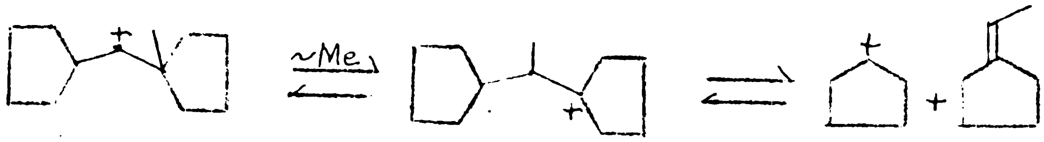


(3)

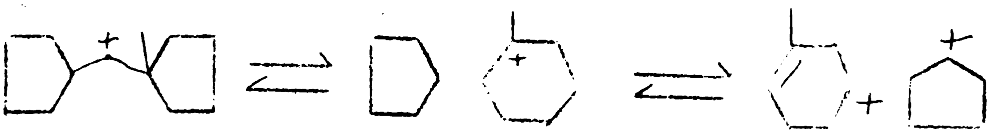


(4)

Since this work deals with cyclic hydrocarbons, the bimolecular reaction process (4) may be examined further. If the rearrangement is going by (4), then the possibility of other products being formed by rearrangement of the intermediate carbonium ion must be examined. Reactions (5) and (6) appear plausible. Identification therefore of five and seven carbon compounds in the isomerization of methylcyclopentane would constitute evidence for the occurrence of bimolecular reactions, although it would not rigorously prove the occurrence of (4).



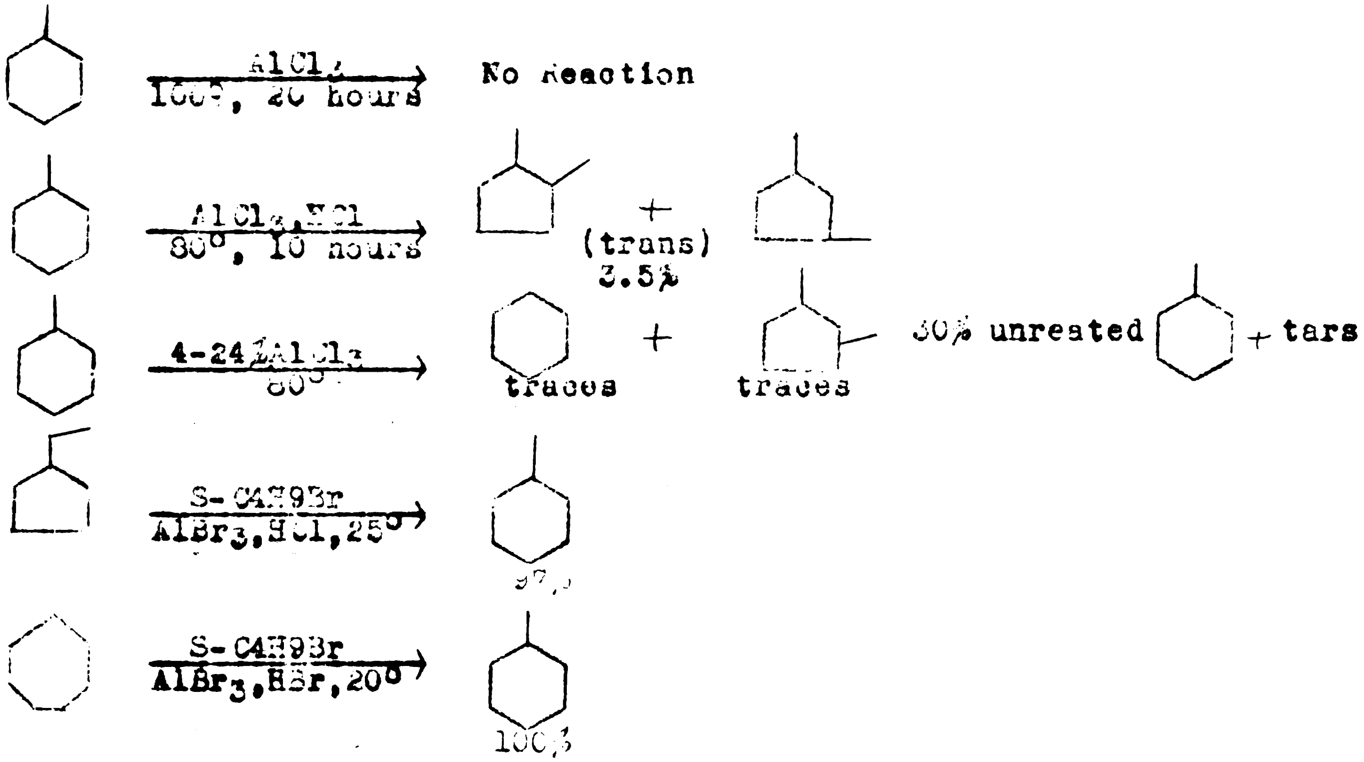
(5)



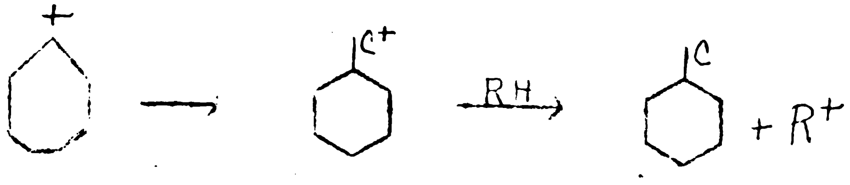
(6)

The interconversion of methylcyclopentane and cyclohexane is reported in the literature to be an equilibrium process. It appeared desirable, therefore, to study the reactions of cyclohexane and methylcyclopentane under carbonium ion conditions.

Three other compounds appeared suitable for study under liquid phase carbonium ion conditions, namely ethylcyclopentane, methylcyclohexane and cycloheptane. The following reactions have been reported:[10,11,12,13,14]

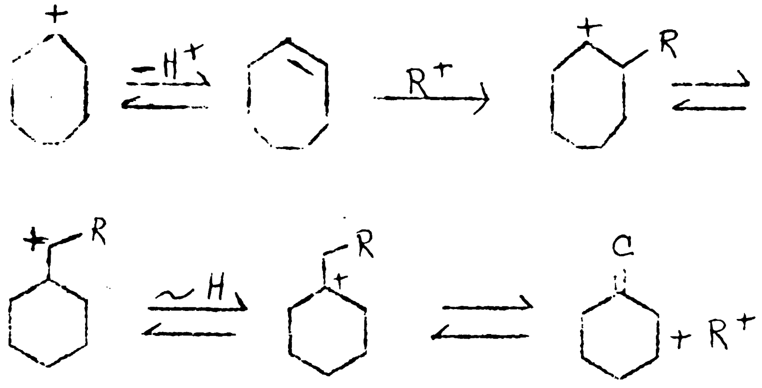


The proposed mechanisms for these reactions involve primary carbonium ions, i.e. (7). However, the results are



(7)

also explicable on the basis of bimolecular reactions, i.e. (8).



It can be seen that the predominant product in these reactions is the six-membered ring, methylcyclohexane, which is formed in preference to the five or seven-membered rings. This is undoubtedly due to the greater stability of the six-membered ring. Spitzer and Huffman[15] calculated from heats of formation that cyclohexane is 1 kcal/mole of CH_2 more stable than any other cycloalkane. Pitzer's work also leads to the same conclusions.[16]

A general study of liquid phase isomerizations of these cycloalkanes was undertaken with the following objectives: (a) to distinguish between the postulated primary carbonium ion processes and bimolecular reaction sequences, and (b) to ascertain the amount of interconversion between five, six and seven-membered rings under liquid phase carbonium ion conditions.

In order to generate the desired carbonium ions under

conditions analogous to those used for the isotope-position rearrangement of t-amyl chloride, the alkyl chlorides of the cycloalkanes were used in the presence of aluminum chloride.

A qualitative and quantitative study of time, temperature and aluminum chloride concentration upon the direction and extent of isomerization was also made.

Results and Discussion

Reactions were run on five different hydrocarbons and the results obtained, with respect to time, temperature and aluminum chloride concentration are shown in Tables I-V. The reactions consisted of a volatile fraction and a brown residue containing the aluminum chloride and polymeric material. The volatile fraction was analyzed by vapor phase chromotrography.

Several points of general interest are apparent from the results. (1) The reactions appear to stop after short periods of time. (2) Ethyl acetate was found to inhibit the reaction of methyl and ethylcyclopentane. Similar reports of inhibition by other compounds in this type of reaction may be found in the literature.[14] Therefore, deactivation of the catalyst seems to be a common phenomenon in this type of reaction. Under the liquid phase reaction conditions the deactivation of the catalyst is most likely caused by the polymer. (3) Temperature substantially affects the amount of isomerization. (4) The qualitative composition of the product is virtually unaffected by time, temperature and aluminum chloride concentration. Cycloheptane appears to be an exception.

The data given in Tables I and II summarize the results obtained in the isomerization of methylcyclopentane and cyclohexane. It can be seen that reaction of either compound leads to only one product. No product was found which would

correspond to the occurrence of reaction (5) or (6). Therefore, in the case of these two compounds, there is no evidence for the occurrence of a bimolecular reaction, but the results do not rule out this possibility, because reaction (4) may be occurring at a much faster rate than (5) or (6). Furthermore, the reaction conditions may be such that reactions (5) and (6) are highly unfavorable. These reactions involve the formation of an olefin and a secondary carbonium ion while (4) involves the formation of an olefin and a tertiary carbonium ion. It has been found[17] that fission steps leading to secondary carbonium ions do not compete favorably with those leading to tertiary carbonium ions.

Graph I shows that the amount of interconversion in the methylcyclopentane-cyclohexane system is highly temperature dependent; the ratio methylcyclopentane/cyclohexane increases with temperature. Graph II shows that reaction is complete within a short period of time.

Entries (19) and (20) of Table I when contrasted with (11) and (15) show the effect of ethyl acetate upon the amount of isomerization. From these results it must be assumed that ethyl acetate is an effective inhibitor for this type of liquid phase reaction.

Table III listed the results obtained for the isomerization of ethylcyclopentane. Entries (1),(4) and (5) were

run with ethylcyclopentane obtained from a hydrogenation reaction using ethyl acetate as solvent. It is noticeable that these reactions show relatively low percentages of rearrangement. By the use of vapor phase chromotrography, it was found that the ethylcyclopentane contained 2% ethyl acetate as impurity. Further purification of the ethylcyclopentane was carried out by use of the Beckman/Megachrome before the remaining reactions were run. Complete conversion to methylcyclohexane was obtained in all of these reactions indicating that the ethyl acetate was responsible for the inhibition of the earlier reactions. This agrees with the results obtained for the methylcyclopentane isomerization. It should be noted that the only product in this reaction is the six-membered ring system, methylcyclohexane, and that there is no further ring expansion to a seven-membered ring structure.

Table IV shows that this is also the case for methylcyclohexane. There is no ring expansion to cycloheptane, but there is a ring contraction to a dimethylcyclopentane. In the case of cycloheptane, as shown in Table V, the major product is methylcyclohexane along with small amounts of a dimethylcyclopentane. The above results, coupled with reports in the literature that dimethylcyclopentanes isomerize to methylcyclohexane,[12] leads to the following conclusions: There is an equilibrium between methyl-

cyclohexane and dimethylcyclopentane shifted highly in the direction of methylcyclohexane. The conversion of cycloheptane to methylcyclohexane is not reversible, and the methylcyclohexane formed then isomerizes to a five-membered ring structure. The stability of the various ring structures must also be considered. The conclusions agree with the previous reports;[15,16] in that the six-membered ring structure is more stable than a five or seven-membered structure. It may be further concluded that the five-membered structure, dimethylcyclopentane, is more stable than the seven-membered structure, cycloheptane.

The dimethylcyclopentane reported in the isomerization of both methylcyclohexane and cycloheptane was not definitely determined, but the following evidence points to one or both of the trans 1,2 or 1,3-dimethylcyclopentanes.

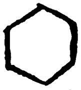
The position of the signal peak for the compound in the vapor phase chromatagraph shows it to be a seven-carbon compound with a boiling point slightly below that of methylcyclohexane. A sample of the compound was separated on the chromatagraph and analyzed by n.m.r. and infra-red spectroscopy. Figures I-IV show the spectra obtained.

The n.m.r. spectra are shown in Figures III and IV. The peak at T9.03 would correspond to the methyl groups. The presence of tertiary hydrogens is also shown in the spectra. This eliminates the presence of 1,1-dimethylcyclopentane.

The infra-red spectra are shown in Figures I and II. These show the presence of a methyl group but the absence of a gem-dimethyl compound. A comparison of the infra-red spectra obtained from the compound with spectra of the pure dimethylcyclopentanes both cis and trans shows that the compound from the isomerizations is trans 1,2 or 1,3-dimethylcyclopentane or a mixture of the two.

Table I

Isomerization of Methylcyclopentane[a]

No.	m.moles $AlCl_3$	Time (min.)	Temp. °C.	Wt. % 
1	4.34	30	-35	0
2	4.34	10	0	0.9
3	4.34	20	0	23.0
4	4.34	30	0	5.4
5	8.68	10	0	1.5
6	8.68	20	0	4.1
7	8.68	30	6	8.3
8	4.34	5	26	8.3
9	4.34	10	26	34.1
10	4.34	20	26	43.2
11	4.34	30	26	53.5
12	8.68	5	26	13.0
13	8.68	10	26	40.2
14	8.68	20	26	49.4
15	8.68	30	26	60.7
16	4.34	10	40	26.4
17	8.68	10	40	27.3
18	4.34	180	30	60.5
[b]19	4.34	30	26	0.8
[b]20	8.68	30	26	1.0

[a] 44.6 m.moles of methylcyclopentane and 1.63 m.moles of 1-chloro-1-methylcyclopentane were used in each reaction.

[b] 3.2% of ethyl acetate present.

Table II

Isomerization of Cyclohexane[a]

No.	m.moles $AlCl_3$	Time (min.)	Temp. °C.	Wt. % 
1	1.7	10	0	<1
2	1.7	20	0	<1
3	1.7	30	0	0.4
4	3.4	10	0	0.9
5	3.4	20	0	1.7
6	3.4	30	0	2.7
7	1.7	10	26	<1
8	1.7	20	26	1.9
9	1.7	30	26	6.9
10	3.4	10	26	6.3
11	3.4	20	26	11.5
12	3.4	30	26	11.6
13	1.7	180	30	8.7
14	1.7	10	40	1.3
15	3.4	10	40	5.9

[a] 46.4 m.moles of cyclohexane and 1.7 m.moles of chlorocyclohexane were used in each reaction.

Table III

Isomerization of Ethylcyclopentane[a]

No.	m.moles $AlCl_3$	% EtAc	Time (min.)	Temp. °C.	Wt. % 
1	1.16	2	30	26	14
2	1.16	0	30	26	100
3	1.16	0	5	26	100
4	.58	2	30	40	8
5	1.16	2	30	40	12
6	1.16	0	30	70	100
7	1.74	0	90	70	100

a. 15.6 m.moles of ethylcyclopentane and .58 m.moles of 1-chloro-1-ethylcyclopentane were used in each reaction

Table IV

Isomerization of Methylcyclohexane[a]

No.	m.moles $AlCl_3$	Time (min.)	Temp. °C.	Wt. % 
1	1.5	30	0	0
2	3.0	30	0	0
3	1.5	30	26	0
4	3.0	30	26	0
5	1.5	180	26	0
6	1.5	30	40	1.5
7	3.0	30	40	4.1
8	1.5	30	70	7.5
9	3.0	30	70	10.0
10	4.5	30	70	9.4
11	3.0	60	70	9.9

a. 39.3 m.moles of methylcyclohexane and 1.5 m.moles of 1-chloro-1-methylcyclohexane were used in each reaction.

Table V

Isomerization of Cycloheptane[a]

No.	m.moles $AlCl_3$	Time (min.)	Temp. °C.	Wt. % 	Wt. % 
1	1.2	30	-15	3.1	0
2	.6	30	0	3.5	0
3	1.2	30	0	5.1	0
4	.6	30	26	5.6	0
5	1.2	30	26	37.4	2.0
6	.6	30	40	14.4	0
7	1.2	30	40	52.5	2.5
8	1.2	30	70	89.7	7.2

a. 16.6 m.moles of cycloheptane and 0.6 m.moles of chlorocycloheptane were used in each reaction.

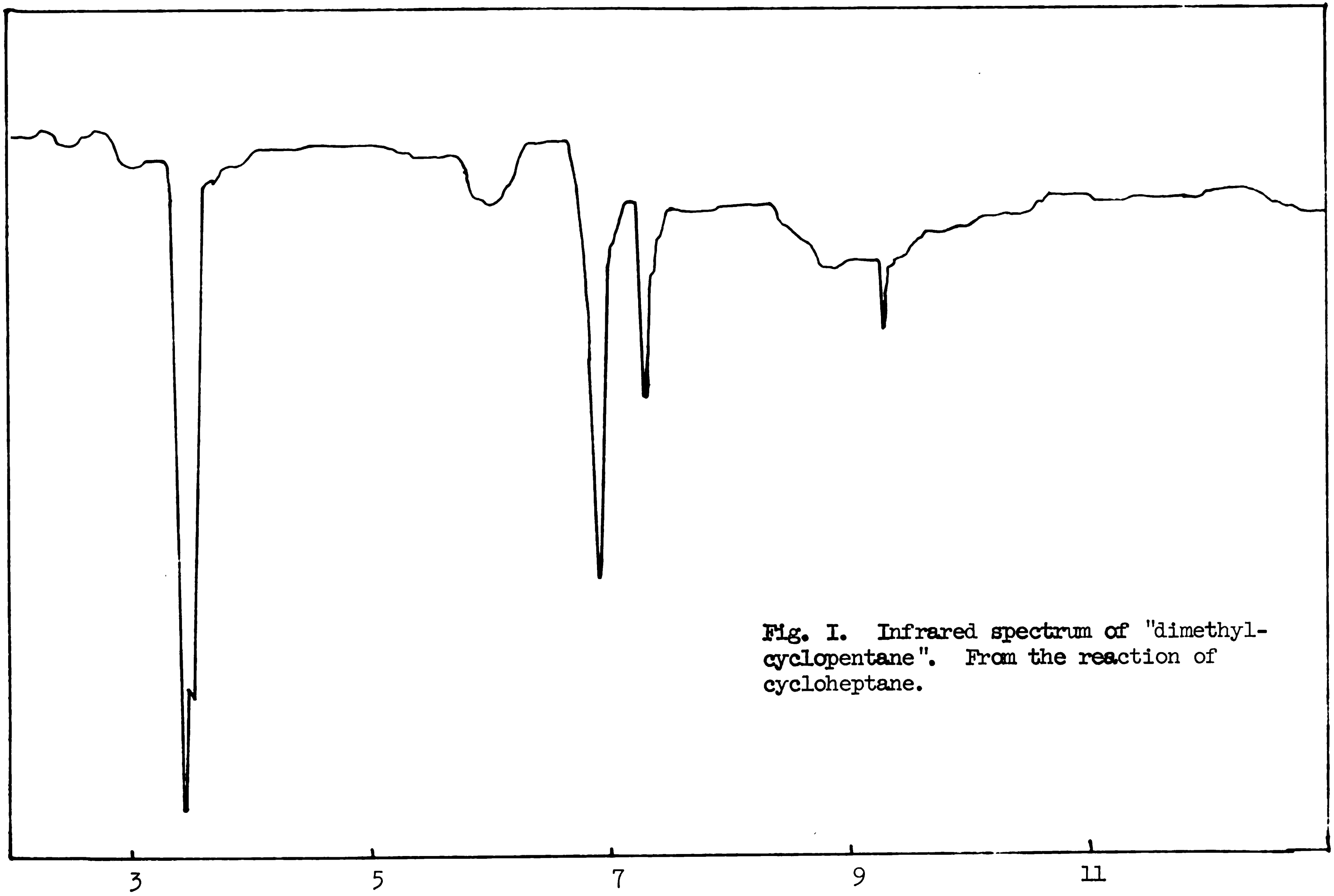


Fig. I. Infrared spectrum of "dimethylcyclopentane". From the reaction of cycloheptane.

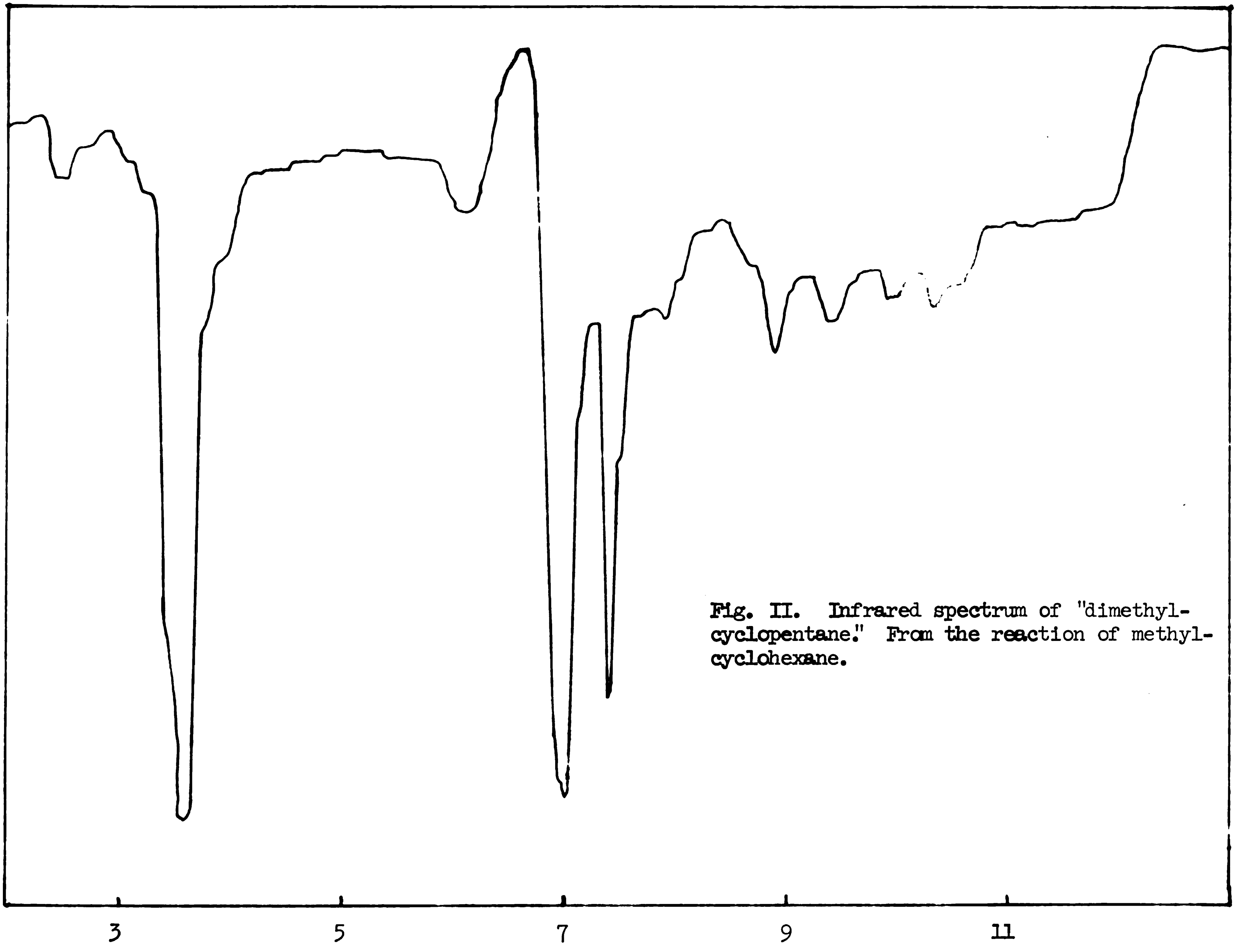


Fig. II. Infrared spectrum of "dimethylcyclopentane." From the reaction of methylcyclohexane.

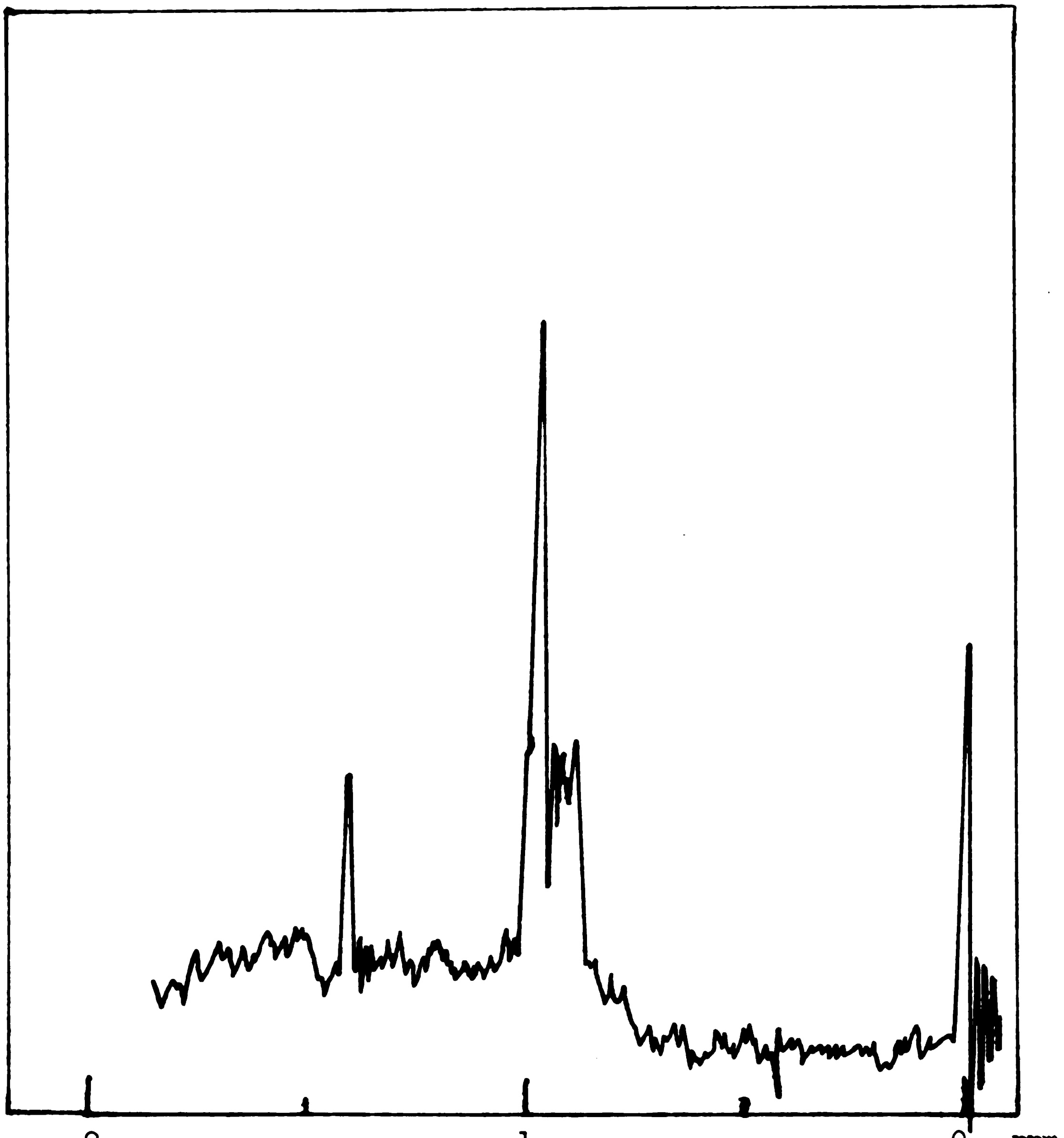


Fig. III. NMR Spectrum of "dimethylcyclopentane". From the reaction of cycloheptane.

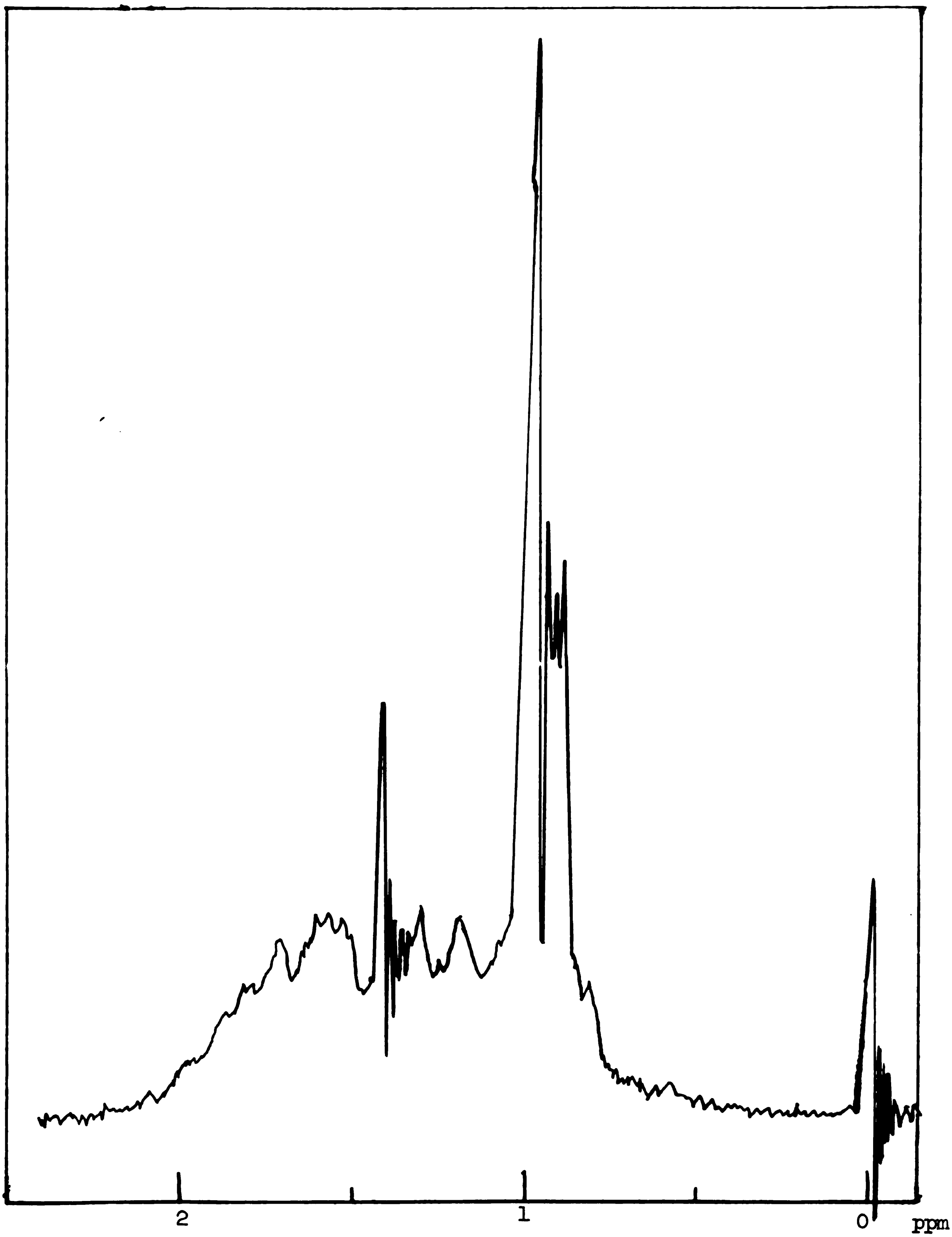
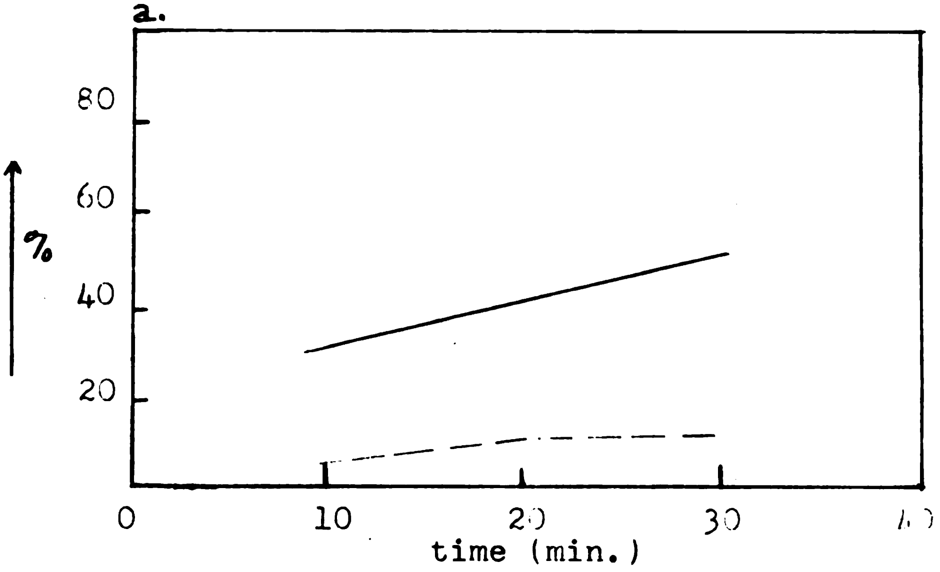


Fig. IV. NMR Spectrum of "dimethylcyclopentane". From the reaction of methylcyclohexane.

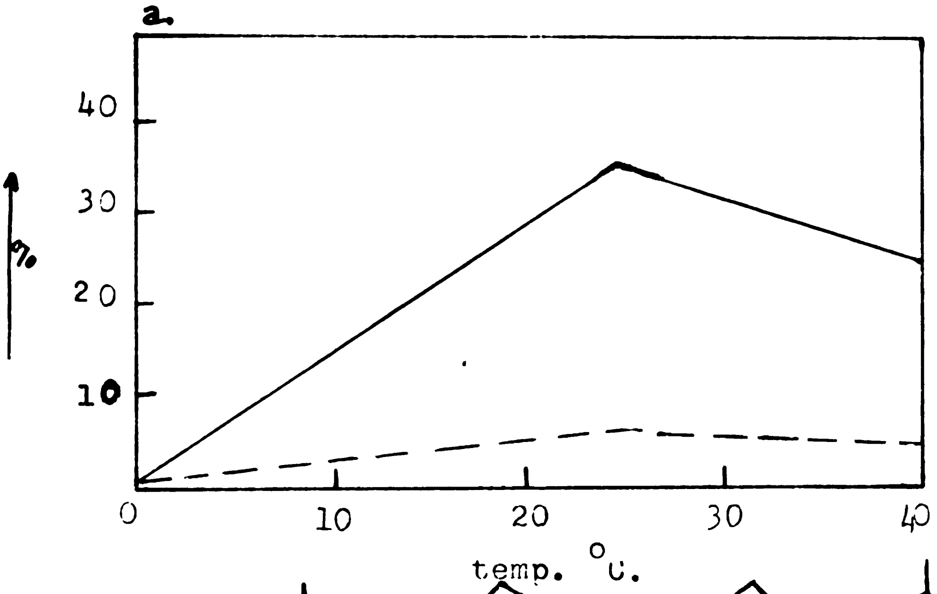
Graph I

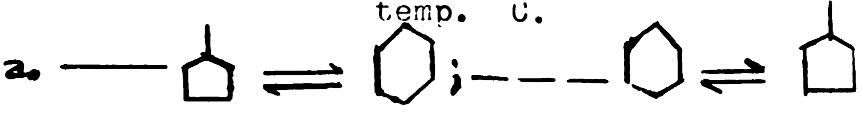
Effect of Time upon Extent of Reaction
Temperature 26° C.
Molar Ratio: $AlCl_3$/cyclic chloride 2 for 
2.66 for 



Graph II

Effect of Temperature upon Extent of Reaction
Reaction Time: 10 Minutes
Molar Ratio: $AlCl_3$/cyclic chloride 2 for 
2.66 for 





EXPERIMENTAL

Apparatus:

The reactions were carried out in a 25 ml. round bottom flask equipped with a side-arm inlet. The flask was connected to a vacuum system through a small column and distilling head.

Reaction Procedure:

Five ml. of methylcyclopentane were placed in the reaction flask and the flask was immersed in a pre-heated oil bath for ten minutes. To the magnetically stirred solution was added, through the side-arm, 0.2 ml. of 1-chloro-1-methylcyclopentane and .29 g. of aluminum chloride (Baker & Adamson, reagent grade). After thirty minutes, the liquid portion was collected under vacuum, at liquid air temperature. A brown residue remained in the reaction flask, presumably polymeric material and aluminum chloride.

The above procedure was followed for the other compounds, with variations in time, temperature and aluminum chloride concentration.

Chemicals:

Methylcyclopentane was obtained from Phillips Petroleum Company. Pure grade (99 mole % minimum purity).

Methylcyclohexane was obtained from Phillips Petroleum Company. Pure grade (99 mole % minimum purity).

Cyclohexane was freshly distilled laboratory grade. Boiling point 81-82°/751 mm. Literature values:[18] b.p. 81.4°/760 mm., n_D^{15} 1.4290.

Cycloheptane was obtained from Aldrich Chemical Company. Technical grade.

Ethylcyclopentane was prepared from cyclopentanone and ethyl bromide by a Grignard reaction, subsequent dehydration of the alcohol and hydrogenation of the resulting olefins. The Grignard reaction was run with 218 g. (2 moles) of ethyl bromide, 48 g. (2 moles) of Magnesium turnings and 84 g. (1 mole) of cyclopentanone. The reaction mixture was decomposed directly to the olefins with 10% hydrochloric acid solution. Distillation gave 39 g. (.406 moles, 40.6%) of two olefins (ethylcyclopentene and ethylidine cyclopentane) b.p. 42-48°/8 mm.

The olefins were hydrogenated in ethyl acetate, at atmospheric pressure and a temperature of 50° over platinum oxide to give a quantitative yield of ethyl-cyclopentane b.p. 101-102°/750 mm., n_D^{20} 1.4193. Literature values[19] b.p. 102-103°/760 mm., n_D^{20} 1.4194.

1-chloro-1-methylcyclopentane was prepared by the Grignard reaction of methyl iodide and cyclopentanone. Using 369.2 g. (2.6 moles) of methyl iodide, 62.4 g. (2.6 moles) of Magnesium turnings and 109.2 g. (1.3 moles) of cyclopentanone, 43.2 g. (.432 moles, 37%) of 1-methylcyclopentanol b.p. 51-54°/16 mm., n_D^{20} 1.4428 was obtained. Literature values[20], b.p. 51-53°/16 mm., $n_D^{23.5}$ 1.4429.

The 1-methylcyclopentanol was treated with a two-fold excess of cold concentrated hydrochloric acid solution and

shaken intermittently for twenty minutes. The 1-chloro-1-methylcyclopentane formed as an upper layer. This was separated, dried in an air stream for thirty minutes and distilled in quantitative yield. Boiling point 70-71°/145 mm., n_D^{20} 1.4464. Values listed in the literature,[21] b.p. 70°/145 mm., n_D^{20} 1.4463, d_4^{20} .9641.

The 1-chloro-1-methylcyclopentane was prepared immediately before use and was not stored for over six hours before use.

Chlorocyclohexane was prepared by the addition of 60 ml of concentrated hydrochloric acid solution to 20 g. (.20 moles) of cyclohexanol and refluxing for one hour. After separation, washing, drying and distillation, 13.6 g. (.14 moles 70%) of chlorocyclohexane was obtained. Boiling point 142-143°/751 mm., n_D^{20} 1.4621. Literature values,[22] b.p. 142°/760 mm., n_D^{20} 1.46264.

1-chloro-1-methylcyclohexane was prepared by the Grignard reaction of methyl iodide with cyclohexanone and treatment of the resulting alcohol with concentrated hydrochloric acid. In the reaction, 142 g. (1 mole) of methyl iodide, 24 g. (1 mole) of Magnesium turnings and 49 g. (0.5 moles) of cyclohexanol were used. Distillation yielded 36 g. (.32 moles, 63.2%) of 1-methylcyclohexanol. Boiling point 64-66°/20 mm., n_D^{20} 1.4587. Literature values,[23] b.p. 67-68°/21 mm., n_D^{20} 1.4584.

The 1-methylcyclohexanol was treated with a two-fold excess of cold concentrated hydrochloric acid and shaken for thirty minutes. The 1-chloro-1-methylcyclohexane that formed was separated, dried in an air stream for thirty minutes, and distilled in quantitative yield. Boiling point 42-43°/20 mm., n_D^{20} 1.4572. Values listed in the literature,[24] b.p. 43°/20 mm., n_D^{20} 1.4579.

The 1-chloro-1-methylcyclohexane was prepared immediately before use and was not stored for more than six hours before use.

<u>Chlorocycloheptane</u> was prepared by a Lithium Aluminum Hydride reduction of cycloheptanone and subsequent treatment of the alcohol with hydrochloric acid. Ten grams (.062 moles) of cycloheptanone were treated with 1.2 g. (.031 moles) of Lithium Aluminum Hydride, to yield 8.6 g. (.075 moles, 85.3%) of cycloheptanol. Boiling point 86-88°/15 mm., n_D^{20} 1.4754. Values listed in the literature,[25] b.p. 87-88°/15 mm., n_D^{20} 1.4757.

The cycloheptanol was treated with a three-fold excess of concentrated hydrochloric acid and refluxed for three hours. The chlorocycloheptane that formed was separated, washed, dried and distilled to give a quantitative yield. Boiling point 45-46°/6 mm., n_D^{20} 1.4692. Literature values,[26] b.p. 174°/760 mm., n_D^{20} not listed, D_0^0 .9957.

<u>1-chloro-1-ethylcyclopentane</u> was prepared by a Grignard reaction of ethyl bromide with cyclopentanone and treatment of the resulting alcohol with concentrated hydrochloric acid.

The 1-ethylcyclopentanol was prepared in 52% yield by the reaction of 109 g. (1 mole) of ethyl bromide and 24 g. (1 mole) of Magnesium turnings in ether with 42 g. (0.5 moles) of cyclopentanone. Obtained were 30 g. (.263 moles) of 1-ethylcyclopentanol, b.p. 43-44°/4 mm., n_D^{20} 1.4539. Literature values[27], b.p. 58.5°/8 mm., n_D^{20} 1.4540.

The 1-chloro-1-ethylcyclopentane was prepared in quantitative yield from 1-ethylcyclopentanol by treatment with a two-fold excess of cold concentrated hydrochloric acid, with shaking for thirty minutes. Physical properties found, b.p. 52-53°/35 mm., n_D^{20} 1.4523. Values listed in the literature[28], b.p. 53°/35 mm., n_D^{20} 1.4525, d_4^{20} .9548.

Analysis of Products:

Small amounts of the distilled reaction mixtures were injected into, and separated to the various components by a Perkin-Elmer Model 154 Vapor Fractometer. The columns used were 5-30% Silicon Oil on Celite and the temperatures used were 65-100°. Identification of the compounds was made by a comparison of the retention times of pure samples of known compounds with those of the reaction products, by separation, collection and infra-red and n.m.r. spectroscopy on the collected samples.

Quantitative determination of product percentages was made by integration of the areas under the signals and direct correlation of these areas to component weight.

In the case of ethylcyclopentane a different method was used. The product resulting from the isomerization of ethylcyclopentane is methylcyclohexane. A good separation of the two compounds could not be obtained by the use of vapor phase chromotrography, so quantitative determination was carried out by use of infra-red spectroscopy.

The percentage composition of the reaction mixtures were determined by comparison of several lines in the spectra with the spectra of mixtures of known composition. The following lines were used:

ethylcyclopentane- 8.04μ and 9.52μ.

methylcyclohexane- 10.80μ, 11.06μ, 11.48μ, and 11.90μ.

SUMMARY

The liquid phase isomerization of methylcyclopentane to cyclohexane in the presence of 1-chloro-1-methylcyclopentane and aluminum chloride was studied with the objective of assessing the contribution of bimolecular reactions to the rearrangement. The reverse reaction, cyclohexane to methylcyclopentane, was studied under similar conditions. No evidence was found in support of a bimolecular reaction sequence, but the data do not exclude this possibility.

Three other hydrocarbons, ethylcyclopentane, methylcyclohexane and cycloheptane were also isomerized under similar conditions. No evidence was found for the occurrence of a bimolecular process, but as above data do not rule out this possibility.

The isomerizations favor the formation of six-membered rings over the five or seven-membered rings.

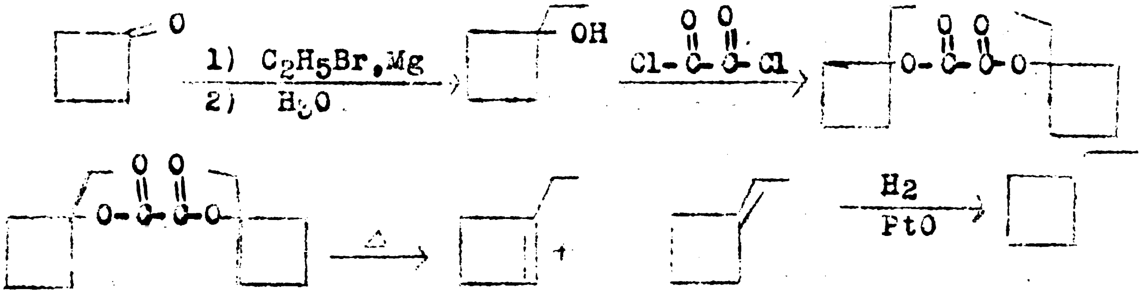
Methylcyclohexane and cycloheptane were found to yield small amounts of a mixture of trans 1,2 and/or 1,3-dimethylcyclopentane. Identification of the structures was made by infra-red and n.m.r. spectra.

Ethyl acetate was found to inhibit the isomerization of methyl and ethylcyclopentane.

APPENDIX

Attempted Preparation of Ethylcyclobutane

It has been found that dialkyl oxalates decompose in good yield to give olefins.[29] It seemed interesting to try the reaction on 1-ethylcyclobutanol. Therefore, the following reaction reaction sequence was used in an attempt to prepare ethylcyclobutane:



To 27.5 g. (1.144 moles) of Magnesium turnings in ether and 124.7 g. (1.144 moles) of ethyl bromide was added 20 g. (.286 moles) of cyclobutanone. The excess Grignard reagent was decomposed by addition of ice-cold saturated solution of ammonium chloride. The 1-ethylcyclobutanol was separated, washed, dried and distilled. The yield was 22.6 g. (.226 moles, 79.9%) with the following physical properties: b.p. 66-68°/ 40 mm., n_D^{20} 1.4410. Report of the compound in the literature could not be found so verification of the structure was made by infra-red and n.m.r. spectra.

The 1-ethylcyclobutanol was treated with oxalyl chloride to form the di-ester. This was tried in two different ways.

In the first procedure, 1-ethylcyclobutanol was dissolved

in ether and pyridine and the oxalyl chloride was added drop-wise. The mixture was refluxed for three hours and then dissolved in water. The ether layer was separated, washed and the solvent distilled off. The resulting ester was pyrolized at 130-215°.

The second procedure involved dissolving the alcohol in a six-fold excess of freshly distilled quinoline followed by drop-wise addition of the oxalyl chloride. The reaction mixture was then pyrolized directly at temperatures up to 235°.

Neither method gave satisfactory results, in that, only a small quantity of compound was recovered from the pyrolysis. The compound contained a band in the infra-red at 5.80-5.83 corresponding to a carbonyl stretch, and had a boiling point of 55°/751 mm.

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