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Walter Maurey Henley

Louisiana State University and Agricultural & Mechanical College

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PART I
ACETIC-OXALIC ANHYDRIDE

PART II
A STUDY OF SOME n-ALKYL-CYCLOHEXYLCARBINOLS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Walter Maurey Henley
B.S., Southeastern Louisiana College, 1947
M.S., Louisiana State University, 1949
August, 1952
MANUSCRIPT THESIS

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PART I

ACETIC-OXALIC ANHYDRIDE
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ABSTRACT

The synthesis of acetic-oxalic anhydride was attempted in four ways: (1) by the reaction of acetic anhydride with anhydrous oxalic acid; (2) by the reaction of acetyl chloride with sodium oxalate; (3) by the reaction of acetyl chloride with silver oxalate; and (4) by the reaction of ketene with anhydrous oxalic acid. Synthesis by method (1) was not successful and only slight success was obtained with method (2). The most favorable results were given by method (3). A thorough examination of the potentialities of process (4) was not made, though a certain amount of compound was obtained by this method.

An approximate determination of the temperature at which the compound decomposes was made. The anhydride is quite thermo-labile, decomposes at $-3.5^\circ$ to give acetic anhydride, carbon dioxide, and carbon monoxide. It reacts vigorously with aniline to form oxanilide; hydrolyzes readily forming oxalic and acetic acids; and to a slight degree is susceptible to alcoholysis.

An explanation of the results obtained upon the interaction of one equivalent weight of the anhydride with 2 equivalent weights of aniline is offered.
An explanation of the mode of decomposition of anhydrous oxalic acid by acetic anhydride has been offered.
INTRODUCTION AND SELECTED LITERATURE SURVEY

The synthesis and study of mixed anhydrides (R-C-O-C-R'), occasionally referred to as double or unsymmetrical anhydrides, have attracted attention since shortly after the middle of the past century, at which time Gerhardt (1) first prepared this type of compound. Interest in this phase of organic chemistry increased steadily for a number of years whereupon the study gradually declined until in 1932 Hurd's work (2) utilizing ketene and a carboxylic acid as a mode of preparation initiated new investigations along this line. The utilization of ketene in this type of preparation has since become the object of a number of patents (3,4).

Until Hurd introduced ketene into this field, mixed acid anhydrides were generally prepared (a) by the method of Autenrieth (5) which involved refluxing an organic acid with acetic anhydride; or (b) by the interaction of an acyl chloride and the sodium salt of an acid (6,7,8); or (c) by the reaction of the acid with acetyl chloride and pyridine (9).

Due to their thermal instability, these anhydrides exhibit a marked tendency to disproportionate in the following manner;

\[ 2 \text{R-C-O-C-R'} \rightarrow (\text{R-C-O})_2 \text{O} \neq (\text{R'-C-O})_2 \text{O} \]
This property is further enhanced by great differences between the length of \( R \) and \( R' \), though this latter magnification is of a secondary nature. Thus, through the avoidance of prolonged elevated reaction temperatures, Hurd's method simplifies the purification process. The method is somewhat limited, however, since acetic acid is necessarily one of the acid constituents of the anhydride.

The thermo-labile nature of double anhydrides becomes an advantage in the preparation of simple anhydrides of certain fatty acids which would otherwise be difficult to obtain (10,11,12). The preparation of simple anhydrides of aromatic acids by means of this disproportionation has been reported (2,13,14) and is illustrated by the equation below.

\[
\begin{align*}
\text{NO}_2 & \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{O} \\
\text{NO}_2 & \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{O} 
\end{align*}
\]

Similar compounds of heterocyclic acids such as the one shown in the equation below have been reported (2).

\[
\begin{align*}
2 \quad & \quad \text{HC-CH} \\
& \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{CH}_3 \rightarrow \quad \text{HC-CH} \\
& \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{CH} \end{align*}
\]

To a large extent the development of double anhydrides in which one of the acid moieties is dicarboxylic (12,13,14) has lagged far behind that type of anhydride which consists exclusively of monocarboxylic components. The most complete study of this type anhydride has been that of Adams (12,13)
who prepared nitro-substituted benzoic-oxalic anhydrides in excellent yields by refluxing the aromatic acid with oxalyl chloride. It was further demonstrated that the presence of a nitro group in the aromatic nucleus was not a prerequisite to the formation of a reasonably stable anhydride. Contrary to what might have been expected, the interaction of the sodium salt of the acid and oxalyl chloride yielded the simple aromatic anhydride and not the mixed anhydride.

The decomposition of oxalic acid anhydrides occurs in a manner somewhat analogous to the scission of monocarboxylic double anhydrides; the disproportionation being as follows:

\[
\begin{align*}
R\-\overset{O}{C}\-O\-C &= 0 \\
R\-O\-C &= 0 \\
\overset{O}{C}\-C &= O
\end{align*}
\]

As early as 1887 it was noted by Behal (15) that formic-acetic anhydride when treated with pyridine evolved carbon monoxide and formed acetic acid. Whitford (16) showed that pyridine possessed a marked positive catalytic effect on the decomposition of oxalic acid by acetic anhydride. This may be interpreted as a catalytic action of pyridine on the decomposition of the mixed oxalic anhydrides, as well as those of other types.
In addition to being useful for the preparation of simple anhydrides, a study of the utility of the double anhydrides for the purposes of ketone synthesis by means of the Friedel-Crafts reaction has been carried out. An examination of the reactions of some unsymmetrical aromatic anhydrides with benzene in the presence of aluminum chloride has been made by Zeavin and Fisher (14). They found that the ketone of lower molecular weight was generally obtained in the greater quantity or as the sole product. When unsymmetrical aliphatic anhydrides were employed, Williams and coworkers (17) showed that the yield of the higher ketone was larger.

Studies of the above nature, as well as investigations of the course of esterification with mixed anhydrides, have attracted further attention because of the theoretical aspects. It was proposed by Baroni and coworkers (18) that decomposition of mixed anhydrides by alcohols depends upon the strength of the acids composing the anhydride, i.e., the ester of the stronger acid is obtained in greater quantity or exclusively. Their experimental results were in partial agreement with those of Kahn (19) and Behal (15). The latter, however, had proposed that the acid with the lower number of carbon atoms was the only one esterified. Serevin (20) later pointed out that a generalization such as Behal's does not apply to all mixed anhydrides. Data
from the esterification study of Baroni et. al. and Behal are given in Table I.

Table I

Esterification Studies of Some Mixed Anhydrides

<table>
<thead>
<tr>
<th>Anhydride</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic-acetic</td>
<td>Acetate</td>
</tr>
<tr>
<td>Propionic-acetic</td>
<td>Acetate</td>
</tr>
<tr>
<td>Chloro-acetic--acetic</td>
<td>Chloro-acetate</td>
</tr>
<tr>
<td></td>
<td>Acetate (trace)</td>
</tr>
<tr>
<td>Aceto-trichlorobutyric</td>
<td>Trichlorobutyrate</td>
</tr>
<tr>
<td></td>
<td>Acetate (trace)</td>
</tr>
<tr>
<td>Acetic-formic</td>
<td>Formate</td>
</tr>
</tbody>
</table>

As an esterifying agent the mixed anhydrides have found limited use in cases where stronger agents would result in modification or decomposition of the alcohols. An example of this is the preparation of 2-furfuryl-formate by Edwards and Reeves (21). Strong acids produced resins on reacting with furfuryl alcohol; and lack of a suitable anhydride or acyl halide of formic acid made the usual methods of ester formation inapplicable. The reaction attempted between the alkyl halide and the sodium salt of the acid was unsuccessful. Traces of the sought-for ester were obtained by alcoholysis involving the n-heptyl formate and by the
reaction of formamide and 2-furfuryl alcohol. By contrast, yields up to 30% of the theoretical amount of ester were obtained by the action of the mixed formic-acetic anhydride on sodium formate and 2-furfuryl alcohol. In addition, these mixed anhydrides have been shown to be quite adaptable for the synthesis of mixed esters of polyhydroxy compounds (10), and cellulose (3).

The reaction of unsymmetrical anhydrides with amines and ammonia has been the object of several investigations. Selected results from these papers are given in Table II.

Table II

The Reactions of Some Mixed Anhydrides with Ammonia and Aniline

<table>
<thead>
<tr>
<th>Anhydride</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amide</td>
</tr>
<tr>
<td>Benzoic-acetic</td>
<td>Acetamide</td>
</tr>
<tr>
<td>Formic-acetic</td>
<td>Formamide</td>
</tr>
<tr>
<td>Furoic-acetic</td>
<td>Acetanilide</td>
</tr>
<tr>
<td>Butyric-acetic</td>
<td>Butytranilide</td>
</tr>
<tr>
<td></td>
<td>Acetanilide (traces)</td>
</tr>
</tbody>
</table>

Examination of these data and those of Table I indicates that the acid moiety of the mixed anhydride which is esterified is also the acid which forms the amide.

Hurd pointed out that the results obtained in the case
of benzoic-acetic and propionic-acetic anhydrides is predictable on the basis of the generally recognized greater electron attraction of aryl over alkyl radicals and the slightly greater attraction of methyl over \( \text{\textit{n}} \)-propyl inasmuch as the molecule of the anhydride is entirely symmetrical except for the terminal groups. The electronic configuration for benzoic-acetic anhydride which expresses these factors is:

\[
\begin{align*}
\text{C}_6\text{H}_5: \text{O} &: \text{C} & \text{CH}_3 & \text{O} \\
& \text{O} & \text{O}
\end{align*}
\]

It might be expected that a slight resemblance would exist between formic-acetic and acetic-oxalic anhydrides since removal of the formyl hydrogen of the former would leave exactly half of the latter molecule. Behal (15) described the formic-acetic anhydride as a liquid with an odor similar to that of acetic anhydride, boiling at 29\(^\circ\) at a pressure of 18 mm. On being treated with sodium acetate, quinoline, pyridine, and dimethylaniline the compound was degraded to carbon monoxide and acetic acid. With primary, secondary, and tertiary alcohols, formic acid esters of the alcohol and acetic acid were formed without a trace of acetic acid esters.

One may summarize as follows:

1. Mixed anhydrides can be synthesized, in at least some instances, by (a) the interaction of an acid anhydride with
an acid, (b) the action of an acid halide on the sodium salt of an acid, (c) the reaction of an acid halide with an acid in either the presence or absence of pyridine, (d) the addition of ketene to an acid.

2. The last method (d) is advantageous because of the absence of by-products, but it is limited to the preparation of mixed acetic anhydrides.

3. The compounds are more or less thermally unstable, this quality varying widely in different instances. The disproportionation is catalysed by pyridine. The anhydrides are quite susceptible to hydrolysis and in general react with alcohols and amines to give predominantly the esters or amides of the stronger acid.

4. Double anhydrides have been employed in the synthesis of simple anhydrides and ketones.

With these factors in mind, the synthesis of the mixed anhydride of oxalic and acetic acids was undertaken. The principal objects were:

(1) To prepare, purify, and characterize this compound.

(2) To determine its thermal stability, and to observe its behavior upon thermal decomposition.

(3) To determine the relative proportions of such theoretically-possible derivatives as oxanilide and acetonilide, etc.
In the event that it proved sufficiently stable, to study its usefulness as a reagent for the preparation of such derivatives as esters of oxalic acid, particularly, ones which could not be prepared in satisfactory fashions by other methods.

Of these objects, (1) was partly achieved. The oxalic-acetic anhydride was prepared but proved too unstable for purification or for any characterization. Objects (2) and (3) were more nearly achieved. The thermal instability of the compound prevented any real progress toward object (4).
EXPERIMENTAL METHODS

Preparation of Anhydrous Oxalic Acid (22).

The method consists essentially of refluxing pure crystalline hydrated oxalic acid (1362 g.) with carbon tetrachloride (2 l.) in such a manner that the volatilized liquids, water and carbon tetrachloride, are condensed and separated gravitationally. The latter liquid is returned to the original flask. Analysis of the acid showed it to be 99.5 pure. The solid appeared to change slightly at 185-195° and decomposed instantaneously at 195°.

Reaction of Anhydrous Oxalic Acid with Acetic Anhydride at Various Temperatures.

To a dry two-neck flask of 100-ml. capacity, equipped with a mechanical stirrer and drying tubes, was introduced 22.5 g. (0.25 mole) of anhydrous oxalic acid and 59.5 ml. (0.875 mole) of acetic anhydride. Carbon dioxide and carbon monoxide were liberated immediately at 25°. The reactants were stirred for 30 minutes at this temperature and then quickly cooled to 0°. The liquid layer was siphoned off, divided into two portions, hereafter designated as A and B, and treated as follows:

Portion A was extracted with four 50-ml. portions of petroleum ether "A" (commercial grade) and the combined
extracts distilled at 30-32° at 38.5 mm. The fraction obtained in this manner was identified as petroleum ether. The residue consisted of acetic anhydride.

Portion B was subdivided into four portions which were treated at 5° with (a) excess methyl alcohol, (b) excess ethyl alcohol, (c) excess aniline and (d) water. No trace of a derivative of oxalic acid was obtained.

The above experiment was repeated at reaction temperatures of 70°, 50°, 40°, 30°, and 10°. The results in each case were similar to those above except that at the lower temperatures the reaction appeared to be extremely slow.

**Action of Acetyl Chloride on Sodium Oxalate.**

A dry three-neck flask of 100-ml. capacity was equipped with a mechanical stirrer, dropping funnel, drying tubes, and surrounded with an iced water-bath maintained at /5 to / 10° C. Into the flask was introduced 28 g. (0.21 mole) of sodium oxalate which had been dried previously for 6 hours at 110°. By means of a dropping funnel, 53.5 ml. (0.75 moles) of acetyl chloride was added rapidly. The mixture, which very slowly evolved a gas, was stirred 3 hours and then allowed to stand 24 hours at 0 to 5°. The liquid layer was removed by siphoning. Distillation of this phase yielded one fraction which boiled at 23 to 24° at 58.5 mm. and a liquid residue of 10-15 ml. which evolved a gas.
vigorously at room temperature. On treatment with aniline the distillate yielded a white crystalline product which after one crystallization from hot water melted at 112 to 114°. The residue reacted with aniline to produce (I) an ether-soluble product which, after crystallization from hot water, melted at 112 to 114°; and (II) an ether-insoluble portion which after being washed with hot water and dried, melted at 246 to 248°.

The following mixed melting point data was obtained:

**Table III**

**Melting Point Data for Several Amides**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetanilide</td>
<td>112.5-114°</td>
</tr>
<tr>
<td>Compound I</td>
<td>112 -114°</td>
</tr>
<tr>
<td>Mixture of acetanilide and Compound I</td>
<td>112 - 114°</td>
</tr>
<tr>
<td>Oxanilide</td>
<td>248 - 249°</td>
</tr>
<tr>
<td>Compound II</td>
<td>246 - 248°</td>
</tr>
<tr>
<td>Mixture of oxanilide and Compound II</td>
<td>247 - 250°</td>
</tr>
</tbody>
</table>

Several attempts were made to duplicate the results given above. In two such instances the conditions under which the reaction was attempted were as described before,
however, there were no indications of mixed anhydride formation. A lowering of the reaction temperature to $0^\circ$ followed by removal of the volatile components at this same temperature and a pressure of 8 mm. was no more successful in obtaining the desired product.

The evolved gaseous products of the reaction first described, upon being passed through an alkaline BaCl$_2$ solution, were partially absorbed, resulting in the formation of a white precipitate. That gas which was not removed by this solution burned with a blue flame characteristic of carbon monoxide.

**Action of Acetyl Chloride on Silver Oxalate.**

The reaction was carried out in the system previously described. The reaction flask was surrounded with an ice-salt mixture contained in a Dewar flask and the temperature maintained at $-7$ to $-3^\circ$ throughout the experiment. The reaction flask was protected from light and into the flask was introduced 39 g. (0.13 mole) of powdered silver oxalate and 200 ml. anhydrous ether. The system was stirred for 5 minutes before adding, by means of a dropping funnel, 19 ml. (0.26 moles) acetyl chloride dissolved in 50 ml. anhydrous ether. This latter addition was extended over a period of 2 hours. The reaction mixture was then allowed to stand overnight at a temperature of $-5^\circ$.

Though the reaction appeared to involve no
exceptional danger when carried out in the above manner, it was quite explosive in nature when carried out at room temperature in the absence of a solvent. This explosion occurred upon the addition of approximately 2 ml. of acetyl chloride to approximately 5 g. of powdered silver oxalate, the latter contained in a 100 ml. round-bottom flask which had been painted black to exclude light.

The ethereal layer was siphoned directly into a dry flask equipped for a vacuum distillation. The flask was surrounded by a cooling bath maintained at -5 to -10° and the volatile matter removed by distillation. Toward the end of the distillation a white crystalline solid separated. The solid product was redissolved in 50 ml. of cold ether which was subsequently removed as before and the product allowed to remain under a pressure of 3 to 5 mm. for 1 hour. The compound (III), presumably acetic-oxalic anhydride, was stored at a temperature of -19° or below when not used immediately. Assuming the product to be acetic-oxalic anhydride the yield was 8.9%.

The above preparation was performed five times in essentially the same manner. In each preparation, the quantity of silver oxalate was either in excess of or equivalent to the quantity of acetyl chloride. The temperatures at which the reactions occurred were -5°, -10°, -15° to -25°, and -20°.
The only alterations in the purification process were a reduction of the temperature and pressure at which the volatile material was removed and an increase in the length of time the product was maintained under reduced pressure.

(a) Hydrolysis of Acetic Oxalyl-Anhydride.

An 11 ml. ether solution of III was hydrolyzed at -10° by adding 10 ml. of water dropwise with stirring. The temperature of the mixture was maintained at this level for 2 hours and then allowed to rise slowly to that of the room. The white crystalline solid (IV) (M.p. 100-101°) which separated upon cooling the solution, was removed by filtration, washed with 15 ml. dry ether, and dried. After removal of the ether, the filtrate was separated by distillation into two fractions, b.p. 99-110° and 110-114°. The higher boiling fraction (V) possessed an odor of acetic acid and upon being heated with aniline yielded a product (VI) which melted at 112.5-114° after recrystallization from water. There was no depression of the melting points when IV was mixed with pure oxalic acid or when VI was mixed with pure acetalanilide.

(b) Determination of the Acetyl-Oxalyl Ratio.

Since it is theoretically possible for this mixed anhydride to contain either 1 or 2 acetyl groups per oxalyl group, the actual ratio was determined as follows:
Ethereal samples of the compound assumed to be acetic-oxalic anhydride were hydrolyzed and analyzed for total acidity and apparent oxalic acid by titrating with standard sodium hydroxide and potassium permanganate. An analysis was performed on two 10-ml. portions taken from the same preparation (which for the sake of clarity has been designated preparation "A"). After the hydrolysis as described above, the ether was removed by heating the solutions on the steam bath for a short interval. The samples were then titrated with standard sodium hydroxide to the phenolphthalein end point, the sample made acid with 2 ml. concentrated sulfuric acid, and the permanganate titration accomplished as indicated by Kolthoff and Furman (23).

A second preparation of anhydride (A') was dissolved in 65 ml. of ether which had been precooled to -19°. Two samples of 5 ml. each were pipetted into 250 ml. Erlenmeyer flasks. By means of a dropping funnel, 25 ml. of a 1:1 ethyl alcohol-water solution (t = -19°) of normality 0.1701 with respect to potassium hydroxide was added at the rate of 1 drop/4-5 sec. The funnel was then rinsed with 2 small portions of alcohol, the rinse being added to the flask. After standing for 18 hours at -19° the samples were allowed to stand 2 hours at 3°, 15 ml. potassium hydroxide-ethyl alcohol were added to completely neutralize the acid present, and the solutions evaporated
Assay of total acidity was accomplished by titrating the excess base with standard sulfuric acid. Apparent oxalic acid was determined as before. Corrections for foreign acidic and oxidizable materials were made by means of appropriate blanks.

Table IV

<table>
<thead>
<tr>
<th>Preparation</th>
<th>Sample Number</th>
<th>Molar ratio x 10⁻¹</th>
<th>Ratio Acetyl/Oxalyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1</td>
<td>10.9/5.95</td>
<td>1.86</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>11.33/5.90</td>
<td>1.90</td>
</tr>
<tr>
<td>A'</td>
<td>1</td>
<td>34.0/14.8</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>34.2/14.8</td>
<td>2.31</td>
</tr>
</tbody>
</table>

(b) Thermal Decomposition of Acetic-Oxalic Anhydride.

Three 13 x 100 mm. test tubes were arranged in series and equipped with delivery tubes such that with the exception of the last test tube, the delivery tube of one extended to within 4-5 mm. of the bottom of the next test tube. The delivery tube of the last vessel was so arranged as to be within 2 or 3 mm. of the flame of a microburner. The first vessel was surrounded with an ice-salt bath at a temperature of -8°.

To the first tube was added an ethereal sample (5 ml.) of preparation "A"; to the second, 2 ml. of 5 N sodium
hydroxide followed by careful addition of 8 ml. of 5% barium chloride so as not to mix these two solutions; to the last 10 ml. of water. The tubes were tightly stoppered and the temperature of the ice bath was allowed to rise gradually. At a temperature of -3.5°C small bubblelets of gas were detectable in the ether solution. A portion of the evolved gases was absorbed by the alkaline barium chloride solution resulting in the formation of a white precipitate. That gas which was not removed by the solutions in tubes 2 and 3 ignited and burned with a blue flame characteristic of carbon monoxide.

A solid sample of product "A" was protected from moisture and allowed to decompose by warming to room temperature. The decomposition residue (8.3 ml.) was separated into the following fractions by distillation.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>B.P.</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>126-134°C</td>
<td>0.9 ml.</td>
</tr>
<tr>
<td>2</td>
<td>134-136.5°C</td>
<td>6.0 ml.</td>
</tr>
<tr>
<td>Residue</td>
<td>134-136.5°C</td>
<td>1.0 ml.</td>
</tr>
</tbody>
</table>

Fraction 2 reacted quite readily with aniline to give, after purification, a white crystalline solid which melted at 112.6-114°C.

To quantitatively determine the end products of such a thermal decomposition, a weighed quantity of preparation "A" was allowed to decompose in a manner such that any carbon
dioxide which might be evolved would be absorbed in a weighed tube containing ascarite. The residue remaining after decomposition was then weighed. The residue (0.5081 g.) was lower than that expected (0.5251 g.) whereas the apparent carbon dioxide evolved (0.1756 g.) was lower than the expected loss due to carbon dioxide (0.2264 g.). These theoretical values were based upon the assumption that the compound was acetic-oxalic anhydride and decomposed as follows:

\[
\begin{align*}
\text{CH}_3\text{C} &= 0 \\
\text{CH}_3\text{O} &= 0 \\
\end{align*}
\]

(c) Reaction of Acetic-Oxalic Anhydride with Aniline.

Into each of two dry 125-ml. Erlenmeyer flasks equipped with drying tubes and dry separatory funnels which were also protected from moisture was pipetted at -19° a 20-ml. portion of preparation A'. On the basis of the analytical data of Table IV there should be present the equivalent of 0.005916 moles of oxalic acid in 20 ml. solution which would be equivalent of 0.01183 moles (1.10 g.) of aniline. This quantity of aniline (b.p. 184.4°) was dissolved in 15 ml. dry ether, cooled to -19° and by means of the dropping funnel, added to the ethereal solution of product A' at the rate of 1 drop per 10-15 seconds. Upon completion of the addition the reactants were allowed to
stand for 12 hours at -19° and for 6 hours at 27°, after which the product was filtered, washed with 10 ml. of cold ether, two 10 ml. portions of warm water, and dried under reduced pressure. The combined filtrate and ether and water washes from one of the reactions yielded an oil which could not be crystallized; the wash solutions and filtrate from the other contained an oily material in trace quantities only. Table V summarizes these results.

Table V

Reaction of Oxalic-Acetic Anhydride with Aniline

| Reaction No. | Wt. of Product (g.) | Calc. as | M₈P. Kjeldahl N% | Amount of oil
<table>
<thead>
<tr>
<th></th>
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If, in the above process, an excess of aniline was used (2/₇ equivalents) a lower melting product (112-114°) was obtained in addition to the higher melting product (247.5-249). When the lower melting compound was mixed with an authentic sample of acetalanilide, no depression of the melting point occurred.
(d) Reaction of Acetic-Oxalic Anhydride with Selected Alcohols.

Ether solutions of the presumed acetic-oxalic anhydride were treated with (a) methyl alcohol, (b) ethyl alcohol, (c) sec-butyl alcohol, (d) tert-butyl alcohol, (e) phenol, and (f) furfuryl alcohol. The anhydride preparation, obtained from the interaction of ketene and anhydrous oxalic acid, was known to be impure due to observed decomposition. The anhydride and alcohol in each case were placed in separate 250 ml. Erlenmeyer flasks so arranged that by increasing the pressure above the alcohol solution, this reactant could be forced through a delivery tube into the flask containing the anhydride. Moisture was excluded from the system by means of drying tubes. Previous to the addition the reactants were cooled to -30°. The reactants were then mixed and allowed to remain at -30° for 12-24 hours before warming slowly to room temperature. At 0° a slow evolution of gases was discernable. No clearly defined products were isolated from the reaction mixtures. Indications were that some oxalates and possibly a larger quantity of acetates were formed. The quantity of these products was so small as to make purification and identification impractical. The reaction appeared to occur very slowly at temperatures below which the anhydride is known to decompose. Though the quantities of materials obtained were such as to make purification and analysis impractical, some
oxalates and possibly a larger quantity of acetates appeared to have been products of the reaction.

The product obtained from the attempted esterification of furfuryl alcohol exploded when subjected to a vacuum distillation.

Calibration of Ketene Generator and Action of Ketene on Anhydrous Oxalic Acid.

The ketene used in this work was prepared by the method of Hurd (2). By this method vaporized acetone is pyrolyzed by a chromel filament heated to a dull red glow or a temperature of 700-750°. Unreacted acetone, acetic acid, and other by-products are removed by means of two traps placed in series. The ketene generator was calibrated by adsorbing the product in a known volume of cold standard potassium hydroxide; the unreacted base being determined by titrating with standard acid. The results of the calibration indicated the production of 0.62 moles ketene/hour with the consumption of 0.89 mole of acetone or a yield of 69.5% of the theoretical.

Powdered anhydrous oxalic acid (0.5 mole, 45 g.) and 150 ml. of dry ether were placed in a 500-ml. 3-neck flask equipped with a ground glass inlet tube, the tip of which was below the surface of the solvent; a mechanical stirrer; and an outlet tube which led to a potassium hydroxide trap. The flask was surrounded with a dry ice-alcohol bath at -17° and connected to the ketene lamp by means of the ground glass
inlet tube. One of the traps on the ketene generator was kept at -10° while the other was maintained at -20°. With stirring ketene was passed through the reaction mixture for three and a quarter hours. The product was purified as described in the previous section. During this process the substance (estimated to be 15-20 g.) slowly evolved a gas. The product was treated with an excess of aniline. The reaction which was quite vigorous, yielded an ether insoluble substance m.p. 249-250° and an ether soluble fraction, m.p. 113-114°.

Nitrogen Determinations.

Percentage nitrogen in the various compounds was determined by the modified Kjeldahl method of Kolthoff and Stenger (24).
DISCUSSION

A review of the literature revealed no record of an attempt to synthesize acetic-oxalic anhydride. In this work the anhydride has been prepared by the action of acetyl chloride on silver oxalate and by the action of ketene on anhydrous oxalic acid. A typical preparation by means of the former method gave a yield of 8.9%, and the crude material obtained utilizing the latter method was estimated to be approximately 10% of the theoretical. The action of acetyl chloride on sodium oxalate and the action of acetic anhydride on anhydrous oxalic acid will be discussed later.

Because of the marked disproportionation tendencies of the anhydride as well as its great susceptibility to hydrolysis, the purification and analytical techniques which could be applied feasibly were rather limited. Thus, any method of synthesis which formed easily removable by-products was relatively advantageous. The ultimate degree of purity achieved depended primarily on the success with which a synthesis possessing these characteristics could be performed. The synthesis involving the interaction of silver oxalate and acetyl chloride was expected to yield a product of very high purity; however, the analytical data indicated that at best the degree of purity approached 95%.

Samples weighed with significant accuracy were
practically impossible to obtain even when weighings were performed in a room maintained at -19°.

An ethereal solution of acetic-oxalic anhydride was observed to decompose at -3.5°. This temperature does not necessarily represent the precise decomposition temperature of the compound since its thermal stability might conceivably be altered by such factors as the nature of the solvent or the presence of impurities. Qualitative observations showed that the anhydride decomposed in the following manner:

\[
\begin{align*}
\text{CH}_3\text{C}=\text{O} & \rightarrow \text{CH}_3\text{C}=\text{O} \quad \text{+ CO}_2 \quad \text{+ CO} \\
\text{CH}_3\text{C}=\text{O} & \rightarrow \text{CH}_3\text{C}=\text{O} \\
\end{align*}
\]

The mixed nitrobenzoic-oxalic anhydrides prepared by Adams (12,13) decomposed in the same manner, i.e., upon disproportionation the simple anhydride, carbon monoxide, and carbon dioxide were formed. A quantitative determination of the decomposition products of the acetic-oxalic anhydride indicated that the amount of acetic anhydride formed was of the same order of magnitude as would be expected from the above equation. The determination was complicated by the ease with which the compound underwent decomposition or hydrolysis or both.

The acetyl-oxalyl ratio determined on samples of anhydride from two different preparations had an average
value of 1.88 in one case and 2.27 in the other. Since it is theoretically possible to introduce either one or two acetyl groups into oxalic acid, then the expected acetyl/oxalyl ratio would be 1.0 or 2.0. The lower value of 1.88 might be due to the presence, or apparent presence, of an unexpectedly high concentration of oxalic acid. This condition might arise through one or a combination of the following factors:

(a) occurrence of hydrolysis and subsequent removal of the acetic acid during the purification process;
(b) presence of impurities in the form of materials oxidizable by permanganate, chloride being one such possibility;
(c) presence of a second anhydride which had an acetyl-oxalyl ratio of 1.0.

The higher value of 2.27 would be expected if the anhydride had partially decomposed as indicated by the equation above.

The interpretation of the results of esterification studies involving mixed anhydrides and alcohols, and results obtained from studies of the interaction of such anhydrides with ammonia or amines, and the generalizations based upon such studies have followed two lines of thought in the publications of workers in this field. The explanation offered by Behal (15) was that the acid with the smaller
number of carbon atoms was esterified or formed the amide.

Kahn (19) and Baroni (13) proposed that esters or amides of the stronger acid were obtained upon treatment of the anhydride with alcohols or amines. An examination of Tables I and II clearly indicates that neither of these generalizations is applicable in every case. The second postulation is further complicated by the polemics surrounding the interpretation of acid strength.

Consideration of the electronic factors involved, as advanced by Hurd (2), appears to offer a much more satisfactory interpretation. Hurd argued that the behavior of aniline toward the mixed anhydrides acetic-benzoic and acetic-butyric (which yield exclusively acetanilide in the former case and a greater quantity of butyranilide than acetanilide in the latter case) was predictable on the basis of the generally recognized greater electron attraction of the phenyl radical over the alkyl and the slightly greater attraction of methyl over n-propyl, inasmuch as the molecule of the mixed anhydride is entirely symmetrical except for the terminal groups. The electronic configuration for benzoic-acetic anhydride which expresses these factors is:

\[
\begin{align*}
C_6H_5 & : O : C_6H_5 \\
& : S : CH_3
\end{align*}
\]

The inference of Hurd's explanation apparently was, that in the above formula, the phenyl group causes an electronic displacement away from the acetyl group such that the
carbonyl carbon of the acetyl group is more electron-deficient than the carbonyl carbon of the benzoyl group. Under such circumstances a nucleophilic attack by an agent such as aniline or ammonia would be expected to occur at the more positive carbon. An interpretation of a similar nature might be applied to the results obtained from esterification studies.

In the present work it was noted that the treatment of one equivalent of acetic-oxalic anhydride with 2 equivalents of aniline produced oxanilide exclusively. An interpretation of these results through consideration of the possible electronic configuration can be made in a manner similar to that offered in the preceding paragraph. In this case, however, the mixed anhydride molecule is perfectly symmetrical and there would be no general electronic displacement within the molecule due to the relative differences in electron affinity of the terminal groups. The terminal methyl groups, however, would tend to function in a donor capacity such that the carbonyl carbons of the oxalyl group would be positive relative to the carbonyl carbons of the acetyl groups. The following diagram illustrates these factors:

\[
\text{CH}_3\xrightarrow{\text{C}}-\text{O}-\text{C}^+\text{O}\xrightarrow{\text{C}}-\text{O}-\text{C}^+\xrightarrow{\text{C}}\text{CH}_3
\]

Thus a nucleophilic attack would be expected at the carbonyl carbons of the oxalyl group.
Reactions of alcohols with the anhydride would be expected to yield exclusively or principally oxalates. The explanation in this case would be much the same as that offered for anilide formation. Unfortunately the results obtained from the esterification studies of this work were quite inconclusive. This was due in large part to the fact that at or below a temperature at which the anhydride would be expected to be stable, esterification apparently occurs at a very slow rate. Disproportionation of the anhydride becomes more pronounced at higher temperatures and under prolonged reaction time at sufficiently elevated temperatures the ultimate esterifying reagent would be acetic anhydride. Thus, it is quite possible that the relative quantities of acetate and oxalate obtained could be altered considerably by varying the conditions of temperature and time under which the esterification occurs; the former tending to predominate at the higher temperature and longer time due to decomposition of the anhydride. The conditions under which oxalic acid esters might be expected to be formed appear to be quite critical and the yields of such esters would be quite small.

Attempts to prepare the anhydride by other methods, i.e., (a) by the reaction of acetic anhydride with anhydrous oxalic acid, (b) by the reaction of acetyl chloride with sodium oxalate, and (c) by the reaction of ketene with
anhydrous oxalic acid, met with varying degrees of success. A complete study of the potentialities of process (c) was not made though a certain amount of impure compound was obtained by this method. Method (b) was only partially successful whereas method (a) resulted in the decomposition of the oxalic acid by acetic anhydride.

The decomposition of anhydrous oxalic acid by acetic anhydride is well known, having been the object of a thorough kinetics study by Whitford (16). Whitford proposed the formation of the intermediate \((\text{COOH})_2 \cdot (\text{CH}_3\text{CO})_2\text{O}\) which decomposed very readily to produce the final products. The complete reaction being as follows:

\[
\text{(COOH)}_2 \cdot (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{(COOH)}_2 \cdot (\text{CH}_3\text{CO})_2\text{O} + 2\text{CH}_3\text{-C-OH} + \text{CO}_2 + \text{CO}
\]

In fact, by using pyridine to catalyze the reaction, acetic anhydride can be determined quantitatively by measuring the volume of gases evolved. This method, as applied by Hurd (2) to the analysis of the mixed acetic-benzoic and acetic-furoic anhydrides yielded excellent results.

In a somewhat analogous manner acetic anhydride acts upon formic acid to produce acetic acid and carbon monoxide (25). Use has been made of this reaction to prepare formic-acetic anhydride (15). Schierz (24), however, was unable to isolate the anhydride from such a preparation as did Behal.
In view of the facts presented immediately above and the unstable nature of acetic-oxalic anhydride as noted in this work, it appears probable that the interaction of acetic anhydride and oxalic acid results in the formation of acetic-oxalic anhydride rather than the complex (COOH)₂(CH₃CO)₂O as proposed by Whitford. On the basis of qualitative observations, i.e., the apparent rate at which gases are evolved from an acetic anhydride-oxalic acid mixture at room temperature as compared to the apparent rate of decomposition of acetic-oxalic anhydride at this same temperature, the decomposition of the anhydride appears to occur at a rate much greater than that by which it is formed. At temperatures below which the mixed anhydride might be expected to be stable the interaction of acetic anhydride with oxalic acid appears to occur at a very slow rate. Under such circumstances the isolation of acetic-oxalic anhydride from such a reaction would appear to be quite difficult. Furthermore, it also appears possible that in the presence of anhydrous oxalic acid, mixed acetic anhydrides such as acetic-benzoic and acetic-furolic are converted to acetic-oxalic anhydride, as an unstable intermediate which decomposes almost immediately.

Acetyl chloride acts upon sodium oxalate to evolve carbon monoxide and carbon dioxide. In one case the interaction of these two compounds produced a small amount of crude material which when treated with aniline, yielded
oxanilide. Formation of acetic-oxalic anhydride by this process would explain these facts. The apparent isolation of such a small quantity of acetic-oxalic anhydride by this method and the inability to reproduce the results might have been due to several factors: (a) the slowness with which acetyl chloride and sodium oxalate interact at low temperatures, (b) the fact that sodium acetate catalyzes the disproportionation of mixed anhydrides (15,16), or (c) the polar nature of the solvent (7).
SUMMARY

1. Two methods of synthesis have been given for the preparation of the new compound acetic-oxalic anhydride. The compound has been partially characterized.

2. The reaction between the anhydride and aniline and to a smaller extent the reactions between the anhydride and selected alcohols have been studied. Certain theoretical aspects of the results of these reactions have been discussed.

3. Two other reactions which conceivably might have yielded the anhydride were found to be unsatisfactory.
BIBLIOGRAPHY

1. Gerhardt, Ch.
Recherches sur les acides organiques anhydrides.
Ann. (3)t, 37, 285 (1853).

2. Hurd, G. G. and Dull, M.F.
The use of ketene in the preparation of simple and mixed anhydrides.
J. Am. Chem. Soc. 54, 3427 (1932).


4. Gleason, A.H. (Standard Oil Development Company)

5. Autenrieth, W.
Ueber gemische saureanhydride. Ber. 20, 3187 (1887).
Ueber einfache und gemische saureanhydride. Ber. 34, 168 (1901).
and Thomsen, G.,

6. Polya, J.B. and Spotswood, T.B.

7. Ralston, A.W. and Reck, R.A.
The preparation and properties of several isomeric unsymmetrical anhydrides of the saturated aliphatic monocarboxylic acids.

8. Knoll and Company, German patent 117, 267 (Frdl. 6, 146, 1900-1902).

9. Einhorn, A. and Seuffert, R.

10. Dunbar, R.E. and Garvin, F.C.
Anhydrides of the normal saturated monocarboxylic acids.


13. Adams, R., Wirth, W.V., and French, H.E.
Oxalyl chloride as a reagent in organic chemistry. II. Preparation of aromatic acid anhydrides; Reactions with alcohols. J. Am. Chem. Soc. 40, 424 (1918).


15. Behal, A.

16. Whitford, E.L.

17. Williams, J.W., Deckert, Y.J., and Kryntsky, J.A.


19. Kahn, R.
Ueber die Einwirkung von Alkoholen auf gemischte anhydride. Ber. 36, 2535 (1903).

20. Serevin, M.E.

Furfuryl formate. J. Am. Chem. Soc. 64, 1583 (1942).

22. Clarke, H.T. and Davis, A.W.


PART II

A STUDY OF SOME n-ALKYL-CYCLOHEXYLCARBINOLS
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This investigation was concerned with the study of eight members of the \( n \)-alkyl-cyclohexylcarbinol series. These members were the methyl-, ethyl-, \( n \)-propyl-, \( n \)-pentyl-, \( n \)-hexyl-, \( n \)-heptyl-, \( n \)-octyl-, and \( n \)-nonyl-cyclohexyl-carbinols. Crystalline 3,5-dinitrobenzoates, \( N \)-phenylcarbamates, and 1-naphthalene-carbamates of several of the alcohols were prepared and their melting points determined. Density determinations at 25° were made on all members of the series. In some instances this physical property was measured at 0° and at 15°. Refractive index measurements were made. From the density and refractive index data the molar refraction was calculated for each carbinol. Four of the alcohols (\( n \)-pentyl-, \( n \)-heptyl-, \( n \)-octyl-, and \( n \)-nonyl-cyclohexylcarbinols) had not been prepared previously. Only partial characterization of the other four was reported in the literature.

The methyl- and ethyl-cyclohexylcarbinols were dehydrated with sulfuric acid. An attempt was made to determine the positions of the double bonds in the dehydrated products.

The 2,4-dinitrophenylhydrazones of cyclohexyl-aldehyde and two compounds presumed to be methyl- and ethyl-
cyclohexyl ketone were prepared and their melting points recorded. These derivatives had not been previously prepared. The wave length of maximum light absorption and the R value of the 2,4-dinitrophenylhydrazone of cyclohexylaldehyde was determined.

A plot of the densities and refractive indices against the number of carbon atoms in the alkyl group was made. A break occurs in the density curve at n-heptyl-cyclohexylcarbinol. The refractive index curve was rather irregular. The density curve of this series and that of the 1,n-alkyl-cyclohexanols were compared by means of a suitable graph. Factors concerning the break in the density curve were discussed.
INTRODUCTION

On purely geometrical considerations it has been shown that theoretically there are possible an infinite number of strainless cyclohexyl rings (1). Ergo, the number of cyclohexyl derivatives would also be infinite. In reality, the number of cyclohexyl derivatives or the number of compounds for which cyclohexane acts as a precursor have, indeed, been large. This research study has been concerned with eight of the m-alkyl-cyclohexylcarbinols. A survey of the literature indicated that only four members of this series had been synthesized and that these four had not been completely characterized.

Two series of tertiary alcohols, in some degree related to these, have been comprehensively studied. McLellan and Edwards (2) observed a peculiar phenomenon in a study of the 1,m-alkyl-cyclopentamols. When the densities were plotted against the number of carbon atoms in the alkyl group, an abrupt change of slope occurred at the seventh carbon atom. A similar, but less striking change appeared when the refractive indices were plotted against the number of carbon atoms in the alkyl group. They also noted that data collected from the literature would indicate an analogous break occurring in the density curve for the corresponding
An extension of the former study was made by Williams and Edwards (3) using the 1,2-alkyl-cyclohexanols. They found a parallel situation for both density data and refractive indices. Published values for densities of the members of the corresponding cyclohexane series were shown to follow the pattern of the other three groups. The break in these latter two cases appeared to occur at the sixth carbon atom. Tatum (4) working with the same series, reported similar breaks in the curves representing density and viscosity. In this case the break occurred at the seventh carbon atom.

The n-alkyl-cyclohexylcarbinols, then, became of interest, not only because these compounds had been so little studied, but also because they offered a means of further examining this phenomenon. If it were found to extend to the secondary as well as the tertiary type alcohols, some further basis for an explanation might be available. It also seemed likely that some helpful information might be obtained by dehydrating those members of the series which were in the region of unusual behavior, determining the position of the double bonds in the resultant hydrocarbons, and comparing the results obtained from the dehydration study of these and other members of the series.

Alcohols of this general group were first prepared by the Grignard method. Bouveault’s procedure for making a secondary alcohol (5) was later extended to include the
primary (6) and tertiary (7) types. Certain of the tertiary alcohols were earlier prepared by the diazo reaction (8).

Five members of the \( n \)-alkyl-cyclopentylcarbinol series were synthesized by Edwards and Reid (9). The preparation involved the reaction between cyclopentyl-magnesium-bromide and various aldehydes. Zelinsky (6) had previously obtained several of these alcohols by means of the Grignard reaction. \( n \)-Methyl-cyclopentylcarbinol had also been obtained by Bedes (10).

The first member of the \( n \)-alkyl-cyclohexylcarbinol series was, historically, the first to be prepared. Bouveault (5) in 1903 produced the methyl-cyclohexylcarbinol by the reaction of acetaldehyde on cyclohexyl-magnesium-chloride. The boiling point was listed as 87° at 11 mm. pressure, and the yield described as "excellent". The alcohol \( d_4^0 = 0.942 \), was reported to be readily oxidized with chromic acid to a ketone which formed a solid bisulfite addition product.

One year later the same alcohol was prepared in the same manner by Sabatier and Mailhe (11). They noted that this colorless liquid boiled without decomposition at 189° at 755 mm. The alcohol, \( d_4^0 = 0.9456 \) was dehydrated with zinc chloride to give an ethylic hydrocarbon which boiled at 135°. These authors at the same time prepared several other alcohols: isobutyl-cyclohexylcarbinol,
cyclohexyl-phenylcarbinol, and dicyclohexylcarbinol. Employing the method of Sabatier and Mailhe (11) for the preparation of methyl-cyclohexylcarbinol, but utilizing cyclohexyl-magnesium-iodide rather than cyclohexyl-magnesium-chloride, DomLee and Kenyon (12) reported that even under the most favorable conditions a yield of only 35% was obtained. The boiling point was given as 85-95° at 10 to 12 mm.

The preparation of ethyl-cyclohexylcarbinol using an analogous method was reported by Hell and Schaal (13). These investigators recorded a boiling point of 199-201° for the compound. It was found to undergo chromic acid oxidation readily forming the corresponding ketone. Both n-hexyl-cyclohexylcarbinol (14) and n-propyl-cyclohexylcarbinol (14) have been reported in Russian journals. The originals of the publications were not available, however, and only boiling points and yields were quoted in the abstracts. The n-propyl-cyclohexyl variant exhibited a boiling point of 98-103°/10 mm. and was obtained in 72% yield. The n-hexyl-cyclohexylcarbinol was obtained in 55% yield, boiling at 135-137°/10 mm.

As previously noted the 1,n-alkyl-cyclohexanols (3,4) and the 1,2-alkyl cyclopentanols (2) have been rather thoroughly studied. More recently a study of the mode of dehydration of the latter series has been made by Woodward (15). He concluded that these alcohols containing eleven
or fewer carbon atoms in the alkyl groups lost water by removal of the hydroxyl group and extraction of a ring hydrogen atom. Vail (16) studied the dehydration of three members of the \( \alpha \)-alkyl-cyclopentanol series: the methyl, the ethyl, and the isopropyl. The methyl variant dehydrated exclusively by extracting a hydrogen from the cyclopentyl ring, whereas the ethyl and the isopropyl dehydrated by removal of the ring hydrogen to the extent of 64% in the former case and 55% in the latter. Leach (17) investigated the dehydration of 1-isopropyl-, 1-benzyl-, 1-allyl-2-methyl-, and 1-vinyl-cyclopentanols. The first two dehydrated predominantly by removing a hydrogen atom from the side chain, whereas removal of a hydrogen atom from the ring predominated in the other two.

Many olefins, such as those that could occur in the above dehydration studies, can be converted easily to the corresponding glycols. Thus after Criegee's (18) notation that lead tetracetate was capable of cleaving a carbon chain between two hydroxyl-bearing carbon atoms, it became possible to determine the location of carbon to carbon double bonds within a molecule. Scanlan and Swern (19) determined the position of the carbon to carbon double bond in a series of unsaturated fatty acids by this method. Their results were very good. The dehydration study of Vail, noted above, also employed this method of locating the position of carbon to carbon double bonds.
The cleavage of alpha-glycols by lead tetracetate proceeds under very mild conditions to yield aldehydes and ketones. Quantitative and qualitative studies of mixtures of carbonyl compounds utilizing chromatographic techniques have been studied quite extensively in recent years. Most of these studies have been confined, however, to the corresponding 2,4-dinitrophenylhydrazones \(20,21,22,23\). By such a procedure, data of considerable accuracy can be obtained even on relatively small samples of a mixture.

In summary: Several series of compounds have been synthesized and characterized with a fair degree of completeness; these include: 1,\(n\)-alkyl-cyclohexanols, the 1,\(n\)-alkyl-cyclopentanols, and the \(n\)-alkyl-cyclopentylcarbinols. Dehydration studies have been made on selected members of the latter two groups. Since the series of \(n\)-alkyl-cyclohexylcarbinols has not been thoroughly studied, it was selected for development along the following lines:

1. Augment the series by the synthesis of additional members. Characterize these by the determination of appropriate physical properties. Determine the melting points on several crystalline derivatives. Prepare samples of those members of the series which have already been partially described in order to characterize them on a comparative basis with the new members.

2. Compare densities and refractive indices of the
members of this series to ascertain whether the phenomenon observed by McClellan and Edwards, by Williams and Edwards, and by Tatum in studies of the related tertiary alcohols extends to this type of secondary alcohol. This peculiarity is a distinct break in the curve obtained by plotting the appropriate physical property against the number of carbon atoms in the alkyl group.

3. Dehydrate several selected members of this series; and determine the positions of the double bonds in the resultant olefins.
EXPERIMENTAL METHODS

A. Organic Preparations.

1. General Methods.

a. n-Alkyl Cyclohexylcarbinols.

Approximately equimolar quantities of magnesium, cyclohexyl bromide, and the appropriate aldehydes were used in these Grignard preparations which were based on the method of Sabatier (11).

The Grignard reagent was prepared in each case by the reaction of magnesium with cyclohexyl bromide in the presence of ether. The aldehyde in a cold ether solution was then added very slowly to the reaction flask while stirring. After additional stirring the mixture was hydrolyzed with dilute sulfuric acid and ice. The aqueous layer was extracted with ether, the ether solution washed free of acid, dried over calcium oxide, and the ether evaporated on a steam bath. The alcohol so obtained was then distilled at reduced pressure.

b. Esters of 3,5-dinitrobenzoic acid.

These compounds were prepared as derivatives by the method of Cheronis and Entikin (24). The 3,5-dinitrobenzoyl chloride, dissolved in anhydrous ether
containing a few drops of pyridine was added to an equivalent amount of alcohol. After standing for several days at room temperature the ether suspension was treated with sufficient sulfuric acid to remove the excess pyridine, and washed with water and sodium bicarbonate to neutralize. The ether was evaporated and the remaining material recrystallized from petroleum ether "B".

c. **N-Phenylcarbamates** (25)

Equimolar quantities of phenyl isocyanate and the alcohol were placed in tightly stoppered flasks and allowed to stand for several days at room temperature. The product required several recrystallizations from petroleum ether before a sharp melting point was obtained. Crystals generally appeared at quite low temperatures.

d. **1-Naphthalenecarbamates** (26).

Equimolar quantities of alpha-naphthyl isocyanate and the alcohol were placed in a tightly stoppered flask and allowed to stand several days until the contents of the flask had solidified. The product was recrystallized from petroleum ether several times. Recrystallization generally required rather low temperatures.

e. **Methods of analysis**.

The percentage of nitrogen was determined by a modification of the Kjeldahl method according to Kolthoff and
Stenger (27). The carbon and hydrogen analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

f. Dehydration of n-alkyl-cyclohexylcarbinols.

The alcohol was in each case converted to the corresponding olefin by heating 2.5 hours at 140° with sulfuric acid. The product was poured into crushed ice, washed free of acid, dried over anhydrous sodium sulfate, and distilled.

g. Oxidation and Cleavage of dehydration products of n-alkyl-cyclohexylcarbinols (19, 28).

To convert the olefin to the corresponding glycol, it was suspended in formic acid and treated with hydrogen peroxide. After several hours of mechanical agitation at 40°, the glycol layer was separated and the formic acid layer extracted with ether. The glycol and ether extracts were combined and washed with sodium carbonate and water to remove acid.

The glycol was dissolved in glacial acetic acid, treated with lead acetate and stirred for an hour at 60-65°. After completion of the reaction, water was added and the product steam distilled into a solution of 2,4-dinitrophenylhydrazine. After standing for 36 hours the precipitate was filtered, washed with the original reagent, with HCl, and with water until free of acid, and dried in a desiccator.
Separation and identification of the 2,4-dinitrophenylhydrazone mixture.

The mixture of 2,4-dinitrophenylhydrazones obtained as indicated above were separated by chromatographic techniques. A representative sample of the mixture was dissolved in a small amount of warm benzene and separated on a number 5 column using silicic acid as an adsorbent and a developer of either 96% benzene, 3% ethyl alcohol, and 1% nitromethane or 94% petroleum ether "B", 5% diethyl ether, and 1% nitromethane. The zones were cut from the column, eluted, the eluate evaporated almost to dryness on the steam bath, and the residue desiccated over calcium chloride under reduced pressure. Those zones which did not appear to be distinctly separated from adjacent zones and which did not melt sharply were rechromatographed and treated as described above.

The identification of the components of the mixture was attempted as follows:

(a) by comparison of melting points of the unknowns with those of known compounds.

(b) by melting points of mixtures of known and unknown compounds.

(c) by comparison of $R$ values of known and unknown compounds.

(d) by comparison of chromatograms of the unknown mixture to chromatograms of a mixture of authentic samples of
the expected 2,4-dinitrophenylhydrazones.

**Determination of R values of the 2,4-dinitrophenylhydrazones.**

The R value was defined by LeRosen (29) as the velocity (mm./min.) of movement of adsorptive zone divided by the velocity of flow of the developing solvent. These values were determined on a number 1 chromatographic column using Merck Reagent silicic acid as an adsorbent.

Approximately 0.001 molar solutions of the compounds to be studied were used for the determination, benzene being utilized as the solvent. On a number 1 column of tightly packed silicic acid was placed 2 or 3 drops of the 2,4-dinitrophenylhydrazone solution and the column was treated with 7 to 8 ml. of developer. As the developer neared the bottom of the column the development was discontinued. The distances which the zone and the developer had moved down the column were measured and used to calculate the R value.

3. **Preliminary or Incidental Preparations.**

a. Cyclohexyl bromide (30).

Two hundred and forty ml. of cyclohexanol were added to a solution of 1 liter of 41% hydrogen bromide combined with 3.6 moles of sulfuric acid. The mixture was permitted to stand overnight and then heated on the steam bath.
for 30 minutes. The bromide layer was separated and washed first with cold 85% sulfuric acid (5 volumes of concentrated acid to 1 volume of water), then with sodium carbonate, and finally with water. The product was dried over calcium chloride and distilled under vacuum. The yield of product boiling at 64-65.5°/25 mm. pressure was 239 g., equivalent to 61.6% of the theoretical.

b. **Lead tetracetate** (31).

Three hundred sixty grams of acetic acid were mixed in a two liter flask. With stirring, 600 g. of red lead oxide were gradually added to the reaction mixture. The temperature was not permitted to rise above 65° during the addition. The product was filtered and washed with glacial acetic acid containing 1% acetic anhydride. The yield was 300 g. (75.3%).

c. **Ethyl orthoformate** (32).

Three hundred ml. of absolute alcohol were placed in a liter flask equipped with a stirrer, a condenser, and a short corked tube for the addition of sodium and chloroform. Fifty-one g. of sodium (2.2 moles) and 64 ml. (0.7 mole) of chloroform were added alternately by sixths. The sodium was allowed to dissolve before slowly adding the chloroform. The mixture was maintained at its boiling point by suitable additions of sodium. The flask was allowed to cool slightly
before each new addition of the reactants. When the reaction was complete, the sodium chloride residue was filtered off, washed with ethyl alcohol and the combined filtrate fractionally distilled. Thirty-one grams of product were collected at 144 - 146°. Calculated on the basis of the sodium used, the yield was 30%.

d. *Cyclohexylaldehyde* (32).

In a 3-neck flask were placed 4.8 g. of magnesium (0.20 mole), 50 ml. of anhydrous ether, and 3 g. of cyclohexyl bromide. A crystal of iodine was used to spark the reaction. When the reaction had begun an additional 29.6 g. (0.20 mole, total) of cyclohexyl bromide in 100 ml. of ether were added. After the Grignard reagent had been formed, 30 g. (0.20 mole) of ethyl orthoformate were added gradually and the mixture heated under reflux for 5 hours. The bulk of the ether was removed and the remaining material decomposed by the addition of a minimal quantity of dilute hydrochloric acid. A small portion of the acetal was placed in direct contact with 2,4-dinitrophenylhydrazone in 2 N hydrochloric acid. Within minutes the dinitrophenylhydrazine had flocculated. The remainder of the acetal was hydrolyzed with three times its volume of 5 N hydrochloric acid. The product was separated, was washed free of acid, and converted to the bisulfite derivative.
e. Methyl-cyclohexyl ketone (33) and its 2,4-dinitrophenylhydrazone.

In a 25 ml. erlenmeyer flask were placed 0.02 mole of sulfuric acid and 2 - 4 ml. of water. After cooling, 0.01 mole of methyl-cyclohexylcarbinol was added. An amount of sodium dichromate five per cent in excess of that required to react with the alcohol was dissolved in 1 ml. of water. This solution was added dropwise to the original mixture. The temperature was maintained at 20-40°. After all the sodium dichromate had been added the upper layer of the mixture was pipetted off and treated with 2,4-dinitrophenylhydrazone. After one crystallization from alcohol, crystals of the 2,4-dinitrophenylhydrazone melted sharply at 137-137.5°.

f. Ethyl-cyclohexyl ketone and its 2,4-dinitrophenylhydrazone.

A procedure similar to that above was used to prepare ethyl cyclohexyl ketone from ethyl cyclohexylcarbinol. The melting point of the crystalline 2,4-dinitrophenylhydrazone obtained was 138.5-140°.

3. Preparation of the n-Alkyl-Cyclohexylcarbinols.

a. Methyl-cyclohexylcarbinol.

One hundred ml. of dry ethyl ether, 30 g. of magnesium turnings, and 10 ml. of cyclohexyl bromide were
placed in a 3-neck flask equipped with reflux condenser, mechanical stirrer, and separatory funnel. A crystal of iodine was added to spark the reaction. One-hundred-thirteen-and-a-half milliliters of cyclohexyl bromide dissolved in 200 ml. of diethyl ether were added over a period of 2 hours. The system was stirred an additional 45 minutes, the reaction flask surrounded with an ice bath, and the depolymerized acetaldehyde dissolved in 50 ml. of ether added during 45 minutes. The mixture was stirred for an additional half hour and then hydrolyzed with 50 ml. of concentrated sulfuric acid and 500 g. ice. The aqueous layer was separated and extracted with four 50-ml. portions of ether. The combined ether fractions were washed with water until free of acid, dried over calcium oxide, the solvent evaporated on a steam bath, and the remaining alcohol distilled under reduced pressure. When two successive distillations effected no appreciable alteration of the refractive index of the major fraction the compound was assumed to be pure. The major fraction was collected between 76-76.5°/9.5 mm. pressure:

\[
d_H^25 = 0.9200 \text{ g.}/\text{ml.}, \quad d_D^0 = 0.9388, \quad n_D^{25} = 1.4649, \quad \text{yield} = 67\%.
\]

3,5-Dinitrobenzoate of methyl-cyclohexylcarbinol.

Two-hundredths of a mole of the alcohol was dissolved in 5 ml. of dry pyridine in a test tube and 0.02 mole of 3,5-dinitrobenzoyl chloride dissolved in anhydrous
ether was added slowly with shaking. The mixture was allowed to stand in a stoppered test tube for several days. It was then treated with enough 6 N sulfuric acid to remove excess pyridine, and washed with 10% sodium carbonate and water to remove all free 3,5-dinitrobenzoic acid. The ether was evaporated and the crystals were recrystallized five times from petroleum ether "B". These white needles showed a melting point of 90.8-91.6°. The yield was 28.3%.

N-Phenylcarbamate of methyl-cyclohexylcarbinol.

Methyl-cyclohexylcarbinol (0.02 mole) and phenyl isocyanate (0.02 mole) were mixed and allowed to stand two days in a tightly stoppered flask at room temperature. At the end of this period the contents of the flask had solidified. The reaction product was dissolved in petroleum ether "B" and filtered while hot. The filtrate was cooled and the crystalline product removed by filtration. Several recrystallizations were necessary to obtain a sharply melting product. Crystals generally appeared only after cooling the petroleum ether solution of the product for some time by means of an ice-salt mixture. The melting point of these crystals was 80.0-80.4°; the yield, 18.2%.
Analysis:
Calculated for \( \text{C}_{15}\text{H}_{21}\text{NO}_2 \)
Nitrogen: . . . . . . 5.66%

Found
Nitrogen: . . . . . . 5.52%

1-Naphthalenecarbamate of methyl-cyclohexylcarbinol.

The alcohol (0.02 mole) and 0.02 mole of \( \text{alpha-} \)
napthyl isocyanate were placed in a tightly stoppered
flask and allowed to stand until the contents of the flask
had solidified (2-4 days). The solid was dissolved in
petroleum ether "B" and the solution filtered. The
filtrate was cooled and the product removed by filtration.
The product was then recrystallized from petroleum ether
until it exhibited no alteration of the melting point
after two successive crystallizations. Recrystallization
generally required rather low temperatures. The yield
was 74.3%. M.P. 117.2-118°.

Analysis:
Calculated for \( \text{C}_{19}\text{H}_{23}\text{NO}_2 \)
Nitrogen: . . . . . . 4.71%

Found
Nitrogen: . . . . . . 4.63%

Dehydration of methyl-cyclohexyl carbinol.

A mixture of 25.6 g. (0.2 mole) alcohol and 1.12
ml. of 50% sulfuric acid (volume ratio of acid to alco-
hol = 0.04/1) was heated at 110° for 1 hour. The acid
content was trebled after the first hour, i.e., 2.24 ml. of 50% sulfuric acid was added. The temperature was then elevated to 140° and the system allowed to reflux for 1 hour. At the end of the heating period the mixture was poured into crushed ice and the product washed free of acid. The product was dried over anhydrous sodium sulfate and distilled. A 58.5% yield of product boiling at 130-134° was obtained. On a second dehydration the yield was increased to 83.3% by increasing the acid to alcohol ratio to 0.2/1.

**Oxidation and cleavage of dehydration products of methyl-cyclohexylcarbinol.**

Thirteen and nine-tenths grams of the unsaturated compound obtained above were dissolved in 41.7 ml. of formic acid and treated with 0.12 moles of hydrogen peroxide. The mixture was heated at 40° with stirring for 2 hours, and then stirred 4 hours at room temperature. The glycol layer was separated and the formic acid layer was extracted with ether. The glycol and combined ether extracts were washed with sodium bicarbonate and water to remove acid. A product of 10.73 g. was obtained.

The entire yield of glycol was dissolved in glacial acetic acid and treated with 32 g. of lead tetracetate dissolved in 250 ml. of glacial acetic acid. The mixture was stirred for three hours while the temperature was
maintained at 60-65°. The above reactions were carried out in a one liter 3-neck flask. One neck served as an inlet for steam, another was equipped with a mechanical stirrer, and the third was adapted for the addition of lead tetracetate through a dropping funnel, as well as serving as an outlet for a water condenser.

After completion of the reaction, water was added and the product was steam distilled directly into the 2,4-dinitrophenylhydrazine (a saturated solution of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid). The steam distillation was carried out until the distillate caused only a very faint turbidity when a small sample of the distillate was added to 2,4-dinitrophenylhydrazine solution. The product was allowed to stand in the above solution for 36 hours. It was then filtered, washed with 200 ml. of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid, and then with water until free of acid. The product was placed in a desiccator to dry. Thirteen and six-tenths grams of the mixed 2,4-dinitrophenylhydrazones were obtained. The yield (24.6%) was calculated on the assumption that the mixture consisted exclusively of equal molar quantities of the 2,4-dinitrophenylhydrazones of cyclohexanone and acetaldehyde.
b. Ethyl-cyclohexylcarbinol.

Ninety-one hundredths mole of cyclohexyl bromide was converted to the Grignard reagent. To this was added an equimolar quantity of propionaldehyde. A crude product of 119 grams was obtained which upon redistillation yielded 75 g. (52.7%). The fraction collected boiled at 83.3-84.5° under 8.8 mm. pressure:

\[ d_{25} = 0.9134, \quad d_{4}^0 = 0.9261, \quad n_{25}^D = 1.4650. \]

3,5-Dinitrobenzoate of ethyl-cyclohexylcarbinol.

Two hundredths of a mole of alcohol was treated with 0.02 mole of the aryl chloride. The procedure was the same as described previously except that 16 ml. of dry benzene were used as solvent and the amount of pyridine was decreased to 15 drops. The mixture was heated for four hours on a water bath at 60°. The yield of crystals was 2.1 g. (28.4%) of melting point 102.8-104.5°.

N-Phenylcarbamate of ethyl-cyclohexylcarbinol.

Eighteen thousandths of a mole of alcohol and 0.02 mole of phenyl isocyanate were brought together and treated in the manner previously described. A yield of 1.78 g. (38%) of crystals with a melting point of 52.5-53.9° were obtained.
Analysis:
Calculated for C_{16}H_{23}NO_{2}
Nitrogen — — — — 5.37%

Found
Nitrogen — — — — 5.31%

1-Naphthalenecarbamate of ethyl-cyclohexylcarbinol.

Two-hundredths of a mole of alcohol and 0.02 mole of alpha-naphthyl isocyanate were combined and treated in the manner previously described. Three and two tenths grams of crystals (51.5% yield) melting at 121.2-122.2° were obtained.

Analysis:
Calculated for C_{20}H_{25}NO_{2}
Nitrogen — — — — 4.51%

Found
Nitrogen — — — — 4.44%

Dehydration of ethyl-cyclohexylcarbinol.

Twenty-eight and four tenths grams of alcohol were refluxed at 165° with 10 ml. of 70% sulfuric acid for 2 hours and then treated as previously described in the directions for the dehydration of methyl-cyclohexyl carbinol. A product of 17.3 g. (0.14 mole) boiling at 156.5-169° was obtained. This represented a yield of 69.8%.

Oxidation and cleavage of dehydration products of ethyleyclohexyl carbinol.

One-tenth mole of this olefin was suspended in
37.2 ml. of formic acid. To this was added 11.1 g. of 30% hydrogen peroxide. The glycol was obtained and treated as described before. A yield of 12.21 g. was obtained.

Eleven grams of the glycol were dissolved in glacial acetic acid and treated with lead tetracetate (32.46 g.) dissolved in glacial acetic acid. The procedure was similar to that used for the methyl variant. The yield was 2.2 g. or 5.9% based on the theoretical yield of the 2,4-dinitrophenylhydrazones of cyclohexanone and propionaldehyde.

c. n-Propyl-cyclohexylcarbinol.

One and twenty-five hundredths mole of cyclohexyl bromide was converted to the Grignard reagent and then treated with an equimolar quantity of n-butyraldehyde. A crude product of 140 g. was obtained. After distillation to constant refractive index a 55-57% yield was obtained. Fractions were collected at 74-77.5° under 2.5 mm. pressure or at 86-87.2° at 3.5 mm. pressure:

\[ d_{25}^0 = 0.9044, \quad d_4^0 = 0.9162, \quad \eta_P^25 = 1.4635. \]

3,5-Dinitrobenzoates of n-propyl-cyclohexylcarbinol.

Equimolar quantities of the alcohol and 3,5-dinitrobenzoyl chloride were placed in a 100 ml. flask equipped with a reflux condenser. To this was added 40 ml. of dry benzene and 1 ml. of pyridine. The reactants were
refluxed on the steam bath for 24 hours. The unreacted acid chloride was removed in the usual manner. After four recrystallizations from petroleum ether, 2.0 g. (52.3% yield) were obtained, melting at 81.5°.

N-Phenylcarbamate of \textit{n}-propyl-cyclohexylcarbinol.

Equimolar quantities of the two compounds were mixed and treated as before. An 18.2% yield of crystals melting at 80.0-80.4° was obtained.

Analysis:

Calculated on the basis of \(\text{C}_{17}\text{H}_{25}\text{NO}_{2}\)

Nitrogen: \(-\quad-\quad-\quad-\quad5.10\%\)

Found

Nitrogen: \(-\quad-\quad-\quad-\quad5.10\%\)

\(1\)-Naphthalenecarbamate of \textit{n}-propyl-cyclohexylcarbinol.

Equimolar quantities of \textit{alpha}-naphthyl isocyanate and the alcohol upon reaction yielded 2.55 g. (39.4%) of crystals melting at 121.4-123°.

Analysis:

Calculated on the basis of \(\text{C}_{21}\text{H}_{27}\text{NO}_{2}\)

Nitrogen: \(-\quad-\quad-\quad-\quad4.32\%\)

Found

Nitrogen: \(-\quad-\quad-\quad-\quad4.19\%\)

d. \textit{m}-Pentyl-cyclohexylcarbinol.

One and two-tenths mole of cyclohexyl bromide was converted to the Grignard reagent and then treated with 1.1
moles of n-hexaldehyde in the usual fashion. A crude product of 178.5 g. was obtained. At the end of the purification process the fraction collected as the sought-for alcohol boiled at 99° under 1.8 mm. pressure or at 106° under 4.8 mm. pressure. The yield of pure product was 67%, $d_4^{25} = 0.8937$, $n_D^{25} = 1.4641$.

Analysis:

Calculated on the basis of $C_{12}H_{24}O$.

Carbon: 12.24 78.12%
Hydrogen: 2.4 13.13%

Found

Carbon: 12.24 78.03%
Hydrogen: 2.4 13.01%

3,5-Dinitrobenzoate of n-pentyl-cyclohexylcarbinol.

The aryl chloride and the alcohol were refluxed in benzene as described before. A 57.6% yield of crystals melting at 62-63.5° was obtained.

N-Phenylcarbamate of n-pentyl-cyclohexylcarbinol.

Equimolar quantities of the phenyl isocyanate and n-pentyl-cyclohexylcarbinol were mixed and treated as before. A yield of 93.2% was obtained, the crystals melting at 94-95.5°.

Analysis:

Calculated on the basis of $C_{19}H_{27}NO_2$

Nitrogen: - 19.9 - - - - - 4.62%

Found

Nitrogen: - 19.9 - - - - - 4.69%
1-Naphthalenecarbamate of \( \text{n-pentyl-cyclohexylcarbinol} \)

1-Naphthalenecarbamate of \( \text{n-pentyl-cyclohexylcarbinol} \) was prepared as previously described. The reaction yielded 80.3% of the theoretical amount of compound. The crystals melted at 77-79°.

Analysis:

- Calculated on the basis of \( \text{C}_{23}\text{H}_{31}\text{NO}_2 \)
  - Nitrogen: \(-\) - - - - 3.96%

- Found
  - Nitrogen: \(-\) - - - - 3.85%

e. \( \text{n-Hexyl-cyclohexylcarbinol} \).

One mole of \( \text{n-heptaldehyde} \) was treated with cyclohexyl-magnesium-bromide. A crude product of 180 g. was obtained which after redistillation was cut to 59% of the theoretical yield. This purified fraction was collected at 131° under 7 mm. pressure, 120.5° under 2.7 mm. pressure, or 106° under 2.1 mm. pressure. Properties determined were: \( \text{d}_4^{25} = 0.8897 \), \( \text{d}_4^{15} = 0.8914 \), and \( \text{n}_D^{25} = 1.4641 \).

3,5-Dinitrobenzoate of \( \text{n-Hexyl-cyclohexylcarbinol} \).

Three hundredths of a mole of the acid chloride and 0.03 mole of the alcohol were converted to the ester by the previously described method. The purified product melted at 63.5-65°. Yield 34.1%. 
N-Phenylcarbamate of \textit{n}-Hexyl-cyclohexylcarbinol.

Equal molar quantities of phenyl isocyanate and the alcohol were reacted as previously described. The product melted at 68-68.8°. Yield, 27.1%.

Analysis:

Calculated on the basis of $C_{20}H_{31}NO_2$

Nitrogen: \(- - - - - 4.45\%\)

Found

Nitrogen: \(- - - - - 4.63\%\)

1-Naphthalencarbamate of \textit{n}-Hexyl-cyclohexylcarbinol.

The isocyanate and alcohol were reacted in equal molar quantities. The melting point of the product was 78.7-79.9°. Yield, 69.5%.

Analysis:

Calculated on the basis of $C_{24}H_{33}NO_2$

Nitrogen: \(- - - - - 3.82\%\)

Found

Nitrogen: \(- - - - - 3.69\%\)

f. \textit{n}-Heptyl-cyclohexylcarbinol.

Thirty-seven hundredths of a mole of \textit{n}-octyl aldehyde was treated with 0.4 mole of bromocyclohexane. The procedure was the same as that previously described, the quantity of solvent being reduced in keeping with the quantity of materials used. The fraction boiling at 124-125° at 3.2 mm. pressure was collected as pure product. The yield was 66.4% of the theoretical.
$d_{4}^{25} = 0.8881, d_{4}^{15} = 0.8948, n_{D}^{25} = 1.4650.$

Analysis:

Calculated on the basis of $C_{14}H_{28}O$

- Carbon  - - - - - 79.17%
- Hydrogen - - - - - 13.29%

Found

- Carbon - - - - - 79.07%
- Hydrogen - - - - - 13.12%

3,5-Dinitrobenzoate of $\alpha$-Heptyl-Cyclohexylcarbinol

Equal molar quantities of the acid chloride and alcohol were reacted in the manner previously described. By allowing the product to remain at a temperature of $-40^\circ$ for a period of 1 to 3 days, crystallization could be effected. The crystalline modification rapidly reverted to the liquid state upon being exposed to room temperature.

N-Phenylcarbamate of $\alpha$-Heptyl-cyclohexylcarbinol

Phenyl isocyanate (0.01 M) and $\alpha$-heptyl-cyclohexylcarbinol (0.01 M) were reacted in the manner previously described. The product melted at 49.5-52.0°. The yield was 82.8%.

Analysis:

Calculated on the basis of $C_{21}H_{33}NO_{2}$

- Nitrogen - - - - - 4.22%

Found

- Nitrogen - - - - - 4.19%
1-Naphthalenescarbamate of \( \alpha \)-Heptyl-cyclohexylcarbinol

A yield of 69.5% was obtained by reacting 0.01 mole of the isocyanate with 0.01 mole of the alcohol; m.p. 68-71°.

Analysis:
Calculated on the basis of \( C_{25}H_{35}NO_2 \)
Nitrogen -- -- -- -- 3.67%

Found
Nitrogen -- -- -- -- 3.60%

g. \( \alpha \)-Octyl-cyclohexylcarbinol.

The Grignard reagent of cyclohexyl bromide was permitted to react with \( \alpha \)-monyl aldehyde (0.54 mole). The procedure was the same as that described before. A fraction was collected which boiled between 143.5-145° at 3.2 mm. pressure. The yield was 48%, \( d^2_4 = 0.8845 \), \( d^1_4 = 0.8915 \), and \( n^2_D = 1.4654 \).

Analysis:
Calculated on the basis of \( C_{15}H_{30}O \)
Carbon -- -- -- -- 79.58%
Hydrogen -- -- -- -- 13.36%

Found
Carbon -- -- -- -- 79.55%
Hydrogen -- -- -- -- 13.30%

3,5-Dinitrobenzoate of \( \alpha \)-octyl-cyclohexylcarbinol.

The reaction of 3,5-dinitrobenzoyl chloride with \( \alpha \)-octyl cyclohexylcarbinol in the manner previously described yielded an oil.
N-Phenylcarbamate of \textit{n}-Octyl-cyclohexylcarbamate.

Phenyl isocyanate (0.01 M.) and \textit{n}-octyl-cyclohexylcarbinol (0.01 mole) were reacted by the previously described method. Crystallization was effected by maintaining the product at a temperature of -40° for 1 to 2 days. The crystalline modification rapidly melted when exposed to room temperature.

1-Naphthalene carbamate of \textit{n}-Octyl-cyclohexylcarbinol.

Equimolar quantities of the reactants were converted into the carbamate in the usual manner. The yield of product as 26.1%. The wax-like product melted at 50-52.3°.

Analysis:

Calculated on the basis of \textit{C}_{26}\textit{H}_{37}\textit{NO}_2

<table>
<thead>
<tr>
<th>Nitrogen</th>
<th>3.53%</th>
</tr>
</thead>
</table>

Found

<table>
<thead>
<tr>
<th>Nitrogen</th>
<th>3.44%</th>
</tr>
</thead>
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\textit{n}-Nonyl-cyclohexylcarbinol.

\textit{n}-Decyl aldehyde (0.81 mole) was reacted with the Grignard reagent of cyclohexyl bromide. The yield based upon the fraction boiling at 145°/2.3 mm., or 142°/1.9 mm., was 51%. Properties determined were: \(d_{4}^{25} = 0.8811\), \(d_{4}^{15} = 0.8828\), \(n_{D}^{25} = 1.4650\).
**Analysis:**

Calculated on the basis of \( \text{C}_{16} \text{H}_{32} \text{O} \)

- Carbon: 79.93%
- Hydrogen: 13.42%

**Found**

- Carbon: 79.93%
- Hydrogen: 13.40%

3,5-Dinitrobenzoate of \( \text{n-Nonyl-cyclohexylcarbinol} \).

Two and forty-two hundredths grams of the 3,5-dinitrobenzoate, melting at 59-60.5° was obtained by reacting equal molar quantities of the acid chloride and alcohol in the manner previously described. This was calculated to be 25.8% of the theoretical yield.

N-Phenylcarbamate of \( \text{n-Nonyl-cyclohexylcarbinol} \).

Phenyl isocyanate (0.01 mole) and \( \text{n-nonyl-cyclohexylcarbinol} \) (0.01 mole) were reacted in the usual manner. The resulting product was an oil at room temperature.

1-Naphthalenecarbamate of \( \text{n-Nonyl-cyclohexylcarbinol} \).

Equimolar quantities of \( \text{alpha-naphthyl isocyanate} \) and the alcohol upon reaction yielded an oil which could be crystallized at -40°.
B. Chromatographic separation and attempted identification.

1. The mixed 2,4-dinitrophenylhydrazones of methyl-cyclohexylcarbinol.

A representative sample (0.2-0.3 g.) of the 2,4-dinitrophenylhydrazone mixture of unknown composition was dissolved in 10 ml. of warm benzene. A number 5 chromatographic column was packed thoroughly with silicic acid, prewashed with 200 ml. of developer, and the dissolved mixture placed on the column. The column was developed with a solution consisting of 96% benzene, 3% ethyl alcohol, and 1% nitro-methane. In this manner seven zones were obtained; however, two of the zones were discernible only while the column was "wet" with developer. Due to the apparently minute quantity of these two zones, no attempt was made to identify them. The five major zones were cut from the column and eluted with ether, the latter being subsequently removed by heating the solution on the steam bath. The individual zones were rechromatographed in order to achieve products of a higher degree of purity. Such a process resulted in appreciable losses of material.

Identification of each zone was attempted as follows:

(a) General observations.

Theoretically, a simple dehydration of methyl-cyclohexylcarbinol could yield two olefins, as illustrated
A lead tetracetate oxidation of the glycols corresponding to (A) and (B) could form theoretically a total of four carbonyl compounds; cyclohexanone and acetaldehyde from A and cyclohexylaldehyde and formaldehyde from B. A mixture of the 2,4-dinitrophenylhydrazones of these carbonyl compounds was chromatographed using a number 1 column and the adsorbent and developer noted above. Only three of the four possible zones appeared on the column. For purposes of comparison, chromatograms of the mixtures listed below were prepared.

(a) Unknown mixture / 2,4-dinitrophenylhydrazine
(b) " " / formaldehyde DNPH*
(c) " " / acetaldehyde DNPH
(d) " " / cyclohexanone DNPH
(e) " " / cyclohexaldehyde DNPH

* Dinitrophenylhydrazone.
These latter chromatograms were compared to that of the unknown mixture. The data so obtained are summarized in Table I. The zones of the unknown mixture were assigned numbers of 1 through 5; number 1 being the top zone.

Table I
Comparative Chromatographic Data

<table>
<thead>
<tr>
<th>Component added</th>
<th>Results Noted</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of reinforced zone**</td>
</tr>
<tr>
<td>2,4-dinitrophenylhydrazine</td>
<td>1</td>
</tr>
<tr>
<td>Formaldehyde DNPH</td>
<td>4</td>
</tr>
<tr>
<td>Acetaldehyde DNPH</td>
<td>4</td>
</tr>
<tr>
<td>Cyclohexanone DNPH</td>
<td>-----</td>
</tr>
<tr>
<td>Cyclohexylaldehyde DNPH</td>
<td>5(?)</td>
</tr>
</tbody>
</table>

** Reinforced zone refers to one which is made brighter or more well-defined by the addition of another component.

(b) Data pertaining to individual zones.

Zone 1. The unknown was crystallized from 95% ethyl alcohol and desiccated over calcium chloride under reduced pressure.

M.p. of zone ----------------------------195-196.5°
M.p. of 2,4-dinitrophenylhydrazine-------197-198°
M.p. of mixture--------------------------194-197°

Zones 2 and 3. Upon elution and evaporation of the solvent, these zones did not crystallize as in the case of
the other zones. All subsequent attempts to effect crystallisation met with failure. Each of these zones was easily separated by chromatographic means from each of the theoretically possible 2,4-dinitrophenylhydrazones.

Zone 4. This zone could not be separated chromatographically from the 2,4-dinitrophenylhydrazine of either formaldehyde or acetaldehyde under the conditions used. The following physical data were accumulated in an attempt to identify these components.

a. Light absorption data:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wave length of absorption (μm)</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde DNPH</td>
<td>348</td>
<td>210.2 (calc.)</td>
</tr>
<tr>
<td>Acetaldehyde DNPH</td>
<td>358</td>
<td>224.2 (calc.)</td>
</tr>
<tr>
<td>Zone 4</td>
<td>356</td>
<td>211.4 (exptl.)</td>
</tr>
</tbody>
</table>

b. Melting point data:

- Formaldehyde DNPH: 167
- Acetaldehyde DNPH: 168.5*
- Zone 4: 140-142
- Formaldehyde DNPH and Zone 4: 124-140
- Acetaldehyde DNPH and Zone 4: 140-143

* According to Cheronis & Entrikin (34) there exists a stable isomer of acetaldehyde DNPH which melts at 168.5° and an unstable isomer which melts at 157°. A mixture of the two isomers melts about 150°.
Zone 5. This zone, which constitutes 63% of the original mixture at a minimum, was rechromatographed and small portions of the leading edge, (A), and trailing edge, (B), of the zone were removed. The lower portion (A) of zone 5 and the 2,4-dinitrophenylhydrazone of cyclohexanone were chromatographically separable. The 2,4-dinitrophenylhydrazone of cyclohexylaldehyde and (A) may have been separable although if such was the case, the zones were extremely ill-defined.

Light absorption data on the above compounds is tabulated below.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wave-length of maximum absorption (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexylaldehyde</td>
<td>358</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>363</td>
</tr>
<tr>
<td>&quot;A&quot;</td>
<td>376</td>
</tr>
<tr>
<td>&quot;B&quot;</td>
<td>363</td>
</tr>
</tbody>
</table>

After three crystallizations of zone 5 from 95% ethyl alcohol a component (C) was obtained which exhibited a melting point of 184-187° and a maximum absorption of light at a wave length of 376 μm. The bottom zone of a second chromatographic separation of the original mixture yielded a product (D) which after 3 crystallizations from ethyl alcohol melted at 186-188°. A mixture of C and D melted at 185-188°. The experimentally determined molecular weights for C and D were 457.3 and 397.7
respectively.

Analysis:

<table>
<thead>
<tr>
<th>Compound</th>
<th>%C</th>
<th>%H</th>
<th>%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>56.06</td>
<td>5.66</td>
<td>17.61</td>
</tr>
<tr>
<td>D</td>
<td>54.79</td>
<td>5.88</td>
<td>18.34</td>
</tr>
</tbody>
</table>

2. The mixed 2,4-dinitrophenylhydrazones of ethyl-cyclohexylcarbinols.

The dehydration of ethyl-cyclohexylcarbinol normally should have resulted in the formation of two olefins differing only in the position of the unsaturated linkage as indicated below.

![Chemical structures](attachment:image.png)

Theoretically, the cleavage of the glycols corresponding to these olefins should have resulted in the formation of cyclohexylaldehyde and acetaldehyde in the one case and cyclohexanone and propionaldehyde in the other. A mixture of the 2,4-dinitrophenylhydrazones of these compounds was chromatographed on a number 1 column using silicic acid as the adsorbent and a developer consisting of 94%
petroleum ether "B" 5% diethyl ether, and 1% nitromethane.
Four distinct zones were obtained. On the basis of the "R_L" values of these compounds the uppermost zone should have been acetaldehyde DNPH; the second, propionaldehyde DNPH; the third, cyclohexanone DNPH; and the bottom zone, cyclohexylaldehyde DNPH. The following chromatograms were prepared as described under general observations of the preceding section, but using the developer given immediately above.

<table>
<thead>
<tr>
<th></th>
<th>Unknown mixture</th>
<th>2,4-dinitrophenylhydrazine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>acetaldehyde DNPH</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>propionaldehyde DNPH</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>cyclohexanone DNPH</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>cyclohexylaldehyde DNPH</td>
</tr>
</tbody>
</table>

The unknown mixture separated into four zones. These zones were assigned numbers of 1 through 4; the top zone being designated as zone 1. Data obtained from a comparison of chromatograms 2 through 6 with chromatogram 1 are given in Table II.
Table II
Comparison of Chromatographic Data

<table>
<thead>
<tr>
<th>Component Added</th>
<th>No. of Reinforced Zone</th>
<th>Location of New Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-dinitrophenylhydrazine</td>
<td>1</td>
<td>---</td>
</tr>
<tr>
<td>Acetaldehyde DNPH</td>
<td>2</td>
<td>---</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>3</td>
<td>between zones</td>
</tr>
<tr>
<td>Cyclohexanone DNPH</td>
<td>---</td>
<td>3 and 4</td>
</tr>
<tr>
<td>Cyclohexylaldehyde DNPH</td>
<td>---</td>
<td>3 and 4</td>
</tr>
</tbody>
</table>

A representative sample (0.1178 g.) of the unknown 2,4-dinitrophenylhydrazine mixture was chromatographed on a number 4 column using silicic acid as the adsorbent and a solution consisting of 94% petroleum ether B, 5% diethyl ether, and 1% nitromethane. After the column was developed seven zones were discernible. The zones were assigned numbers of 1 through 7; the top zone being designated as zone 1. The remainder of the separation and purification procedure was as previously described.

Partial identification of these zones was made as follows:

Zone 1. Separation of this zone from an authentic sample of 2,4-dinitrophenylhydrazine could not be achieved by the chromatographic techniques employed.

Zone 2. A mixture of a portion of this zone and a small amount of acetaldehyde DNPH appeared to behave as one
component when chromatographed. After one crystallization from 95% ethyl alcohol the zone melted at 165.5-167°. A mixture of this component and acetaldehyde DNPH (m.p. 166-168°) melted at 165-168°.

Zone 3. A chromatographic separation of a mixture of this zone and propionaldehyde DNPH was attempted. Separation was not achieved. A mixture of this zone (m.p. 154-155°) and propionaldehyde (m.p. 154-156°) melted at 152-155°.

Identification of the other components of the mixture was not attempted. Estimates of the quantity of zone 7 indicated the original unknown mixture consisted of approximately 60 to 70% of this component.

C. Determination of Physical Properties.

1. Density.

Densities of the eight alcohols prepared were obtained at 25°. Density determinations were also made at 0° and 15° on selected members of the series. A modified pycnometer of approximately 15 ml. volume was used; the method is based on that of Parker and Parker (35). The essential feature of the pycnometer is the presence of the two capillary arms which make adjustment of volume more accurate and decrease the amount of surface evaporation.

Since the density is calculated from the volume and
the mass, these quantities must be known quite accurately. The capillary of the central arm was calibrated by introducing a small amount of mercury into the capillary and observing the number of scale divisions occupied. The mercury was displaced up and down the scale in order to determine the average number of scale divisions occupied. The mercury and pycnometer were then weighed and with the weight of the empty pycnometer known, the weight of mercury was obtained. From the known density of mercury at the temperature of the calibration and the number of scale divisions occupied by the mercury, the volume per scale division could be computed. Both capillaries on the pycnometer were found to have uniform bores.

To determine the volume of the pycnometer, the vessel was filled with water to some arbitrary point on the capillary arms. The pycnometer was then equilibrated at 4°C. and the liquid level noted in the capillary arms. The pycnometer was then placed in the case of an analytical balance and was weighed after having been allowed to equilibrate for one hour. Since the mass and density of water are known, the volume occupied by the water can be computed. Furthermore, since the volume of the capillaries are known, the volume of the pycnometer filled to any given level on the capillary arms can be calculated. Thus, in determining the density of a given substance by this method, any volume can be used provided the liquid level can be
read at some point on the capillary arms.

Temperature control was effected at all times through the use of constant temperature baths. The variation of these baths appeared to be less than 0.2° over a given period of time.

2. **Refractive Indices.**

The refractive indices were determined with the Abbe refractometer at a constant temperature of 25°.

3. **Molar Refractions.**

Theoretical molar refractions were calculated from the values listed for bond refractions according to Denbigh (36). These values which were said to have an average error of 0.7 to 1.5% are as follows:

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Refraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>1.69</td>
</tr>
<tr>
<td>C-C</td>
<td>1.25</td>
</tr>
<tr>
<td>O-H</td>
<td>1.73</td>
</tr>
<tr>
<td>C-O</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Experimental values were calculated according to the following equation: 

\[
R = \frac{n^2 - 1(M)}{n^2/2(d)}
\]

where \( R \) = molar refraction, \( n \) = index of refraction at a particular temperature, \( d \) = the density of the substance at the aforementioned temperature, and \( M \) = the molecular weight.

Molecular weight determinations were made by the freezing point depression method as described by Findlay (37). The molecular depression of the freezing point of the solvent, benzene, was determined using naphthalene as the solute. Using this experimental value the molecular weight of acetaldehyde-2,4-dinitrophenylhydrazone was determined and found to agree with the theoretical value to within 0.5%. Molecular weights were calculated according to the following equation:

\[
\text{M.W.} = \frac{K_f \times g \times 1000}{G \times \Delta T_f}
\]

where:
- \(K_f\) = molal freezing point constant
- \(g\) = mass of solute
- \(G\) = mass of solvent
- \(\Delta T_f\) = freezing point depression

5. Absorption Spectra.

Light absorption data were obtained for the 2,4-dinitrophenylhydrazones of those carbonyl compounds expected to be formed by the scission of the glycols corresponding to the methyl- and ethyl-cyclohexylcarbinol dehydration products. Absorption data were also determined on several individual components of the mixture. The absorption spectra were taken of solutions of appropriate concentrations (10-20 mg./liter) using the Beckman
Quartz Spectrophotometer. Commercial ethyl alcohol (95%) was used as the solvent. Using a slit width of 0.36, the wave-length range from 300 to 420 mu. was covered.
# TABLE III

Physical Properties of the \( m \)-Alkyl-Cyclohexylcarbinols

<table>
<thead>
<tr>
<th>Cyclohexyl carbinol</th>
<th>( n_D^{25} )</th>
<th>( d_4^{25} )</th>
<th>( d_4^{15} )</th>
<th>( d_4^0 )</th>
<th>3,5-Dinitro-N-Phenylbenzoate (m.p. °C.)</th>
<th>N-Phenylcarbamate (m.p. °C.)</th>
<th>1-Naphthalene-carbamate (m.p. °C.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>1.4649</td>
<td>0.9200</td>
<td>0.9388</td>
<td>90.8-91.6</td>
<td>56.0-57.8</td>
<td>117.2-117.9</td>
<td></td>
</tr>
<tr>
<td>Ethyl</td>
<td>1.4650</td>
<td>0.9134</td>
<td>0.9261</td>
<td>102.8-104.5</td>
<td>52.5-53.9</td>
<td>121.2-122.1</td>
<td></td>
</tr>
<tr>
<td>Propyl</td>
<td>1.4635</td>
<td>0.9044</td>
<td>0.9162</td>
<td>81.0-81.5</td>
<td>80.0-80.4</td>
<td>121.4-123.0</td>
<td></td>
</tr>
<tr>
<td>Pentyl</td>
<td>1.4641</td>
<td>0.8937</td>
<td></td>
<td>62-63.5</td>
<td>94-95.5</td>
<td>77-79</td>
<td></td>
</tr>
<tr>
<td>Hexyl</td>
<td>1.4641</td>
<td>0.8897</td>
<td>0.8914</td>
<td>63.5-65.0</td>
<td>68.0-68.8</td>
<td>78.7-79.9</td>
<td></td>
</tr>
<tr>
<td>Heptyl</td>
<td>1.4650</td>
<td>0.8881</td>
<td>0.8948</td>
<td></td>
<td>(oil)</td>
<td>49.5-52</td>
<td>68-71</td>
</tr>
<tr>
<td>Octyl</td>
<td>1.4654</td>
<td>0.8845</td>
<td>0.8915</td>
<td></td>
<td>(oil)</td>
<td>(oil)</td>
<td>50-52.3</td>
</tr>
<tr>
<td>Nonyl</td>
<td>1.4650</td>
<td>0.8811</td>
<td>0.8828</td>
<td></td>
<td>(oil)</td>
<td>(oil)</td>
<td>(oil)</td>
</tr>
</tbody>
</table>
### TABLE IV

Molar Refractions of the n-Alkyl Cyclohexyl Carbinols

<table>
<thead>
<tr>
<th>Cyclohexyl carbinols</th>
<th>Theoretical Value</th>
<th>Experimental Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>38.59</td>
<td>38.44</td>
</tr>
<tr>
<td>Ethyl</td>
<td>43.22</td>
<td>43.07</td>
</tr>
<tr>
<td>Propyl</td>
<td>47.85</td>
<td>47.67</td>
</tr>
<tr>
<td>Penty1</td>
<td>57.11</td>
<td>56.90</td>
</tr>
<tr>
<td>Hexyl</td>
<td>61.74</td>
<td>61.50</td>
</tr>
<tr>
<td>Heptyl</td>
<td>66.37</td>
<td>66.09</td>
</tr>
<tr>
<td>Octyl</td>
<td>71.00</td>
<td>70.80</td>
</tr>
<tr>
<td>Nonyl</td>
<td>75.63</td>
<td>75.42</td>
</tr>
</tbody>
</table>

### TABLE V

R\textsubscript{L} Values for 2,4-Dinitrophenylhydrazones of Certain Carbonyl Compounds

<table>
<thead>
<tr>
<th>2,4-Dinitrophenylhydrazone</th>
<th>R\textsuperscript{*}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>-0.155</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>-0.169</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>-0.203</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>-0.286</td>
</tr>
<tr>
<td>Cyclohexylaldehyde</td>
<td>-0.368</td>
</tr>
</tbody>
</table>

* Determinations made using silicic acid as an absorbent and a mixture consisting of 94% petroleum ether "B", 5% diethyl ether, 1% nitromethane as a developer.


**TABLE VI**

Light Absorption Data of 2,4-Dinitrophenylhydrazones

<table>
<thead>
<tr>
<th>2,4-Dinitrophenylhydrazone</th>
<th>Wave Length of Maximum Absorption μμ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>348</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>358</td>
</tr>
<tr>
<td>Cyclohexylaldehyde</td>
<td>357</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>363</td>
</tr>
</tbody>
</table>
**Figure 1**

Density curves of related substances

**Figure 2**

Refractive indices versus number of carbon atoms

- N-Alkyl-cyclohexylcarbinols
- 1,1'-N-Alkyl-cyclohexanols (2)
- 1,1'-N-Alkyl-cyclopentanols (3)
DISCUSSION

A literature survey revealed that the \( n \)-alkyl-cyclohexylcarbinols had not been developed as a series, and that those members which had been prepared were incompletely characterized. In this work the alcohols were prepared by the action of the appropriate aldehyde on the Grignard reagent of cyclohexyl bromide.

Using the procedure of Sabatier and Mailhe (7) for the preparation of methyl-cyclohexylcarbinol, but utilizing cyclohexyl-magnesium-iodide rather than cyclohexyl-magnesium chloride, DomLeo and Kenyon (12) reported that even under the most favorable conditions a yield of only 35% was obtained. In this study a preparation of this alcohol using Sabatier's method gave a crude product which represented a yield of 31.9%; however, when the acetaldehyde was depolymerized immediately before being added to the cyclohexyl-magnesium-bromide, yields calculated on the basis of the purified products obtained from two such preparations were 67.2% and 72.9%.

Yields of the other members of this series ranged from 48% in the case of \( n \)-octyl-cyclohexylcarbinol to 72% in the case of \( n \)-heptyl-cyclohexylcarbinol.

The physical properties, density and refractive
index, Table III, were determined on portions of products which on successive distillations exhibited negligible changes in boiling points and which showed no alteration of the refractive indices at 25°. Such a condition was generally achieved after the third fractionation.

Assuming that the compounds were of a pure nature, then the densities as determined by the method previously described were correct within the limitations of the method itself; these limitations being:

(a) errors in weighing.
(b) errors due to buoyancy.
(c) errors due to difference in volume of meniscus of water and the liquid whose density is to be determined.
(d) errors due to hysteresis.
(e) errors due to variation of temperature.

In the measurements reported in this work the most important of these factors was (a). As determined by this method the average variation between two successive determinations was 1 to 2 parts in 10,000.

The difference between the experimental molar refractions and the theoretical values was small, the average difference being 0.36. These values are given in Table IV.

The densities of this \( \text{\textit{\textit{n}}} \)-alkyl-cyclohexylcarbinol series as plotted against the number of carbon atoms in
the alkyl group (Figure 1) exhibit a slight break at the heptyl member in the resulting curve. This type phenomenon has been observed by McLellan and Edwards (2) in the 1,ₙ-alkyl-cyclopentanols and by Williams and Edwards (3) and by Tatum (4) in the 1,ₙ-alkyl-cyclo-
hexanol series. For purposes of comparison the density curves for these three series are shown in Figure 1.
It can be seen that the magnitude of the break is greater for the 1,ₙ-alkyl-cyclopentanols and the 1,ₙ-alkyl-
cyclohexanols than for the ₙ-alkyl-cyclohexylcarbinols. The curves of the cyclohexylcarbinols and cyclopentanols are quite similar to the point at which the break occurs; after this point the pathways of the curves definitely diverge. Apparently that factor which abruptly affects the general trend of the curve is more active in the 1,ₙ-
alkyl-cyclopentanols than in the ₙ-alkyl-cyclohexylcar-
binols. This might also be said of the 1,ₙ-alkyl-cyclo-
hexanols.

The tentative explanation offered by McLellan for this phenomenon was that at the break the role of dominant group was shifted from the cyclopentyl group to the alkyl group. Furthermore, it was pointed out by McLellan that this same phenomena exists in the ₙ-alkyl-
cyclopentane series. Later Williams pointed out a sim-
ilar property in the ₙ-alkyl-cyclohexanes. That this
anomaly is not due exclusively to the presence of a hydroxyl group within the molecule is clearly indicated.

Tatum, on the basis of parachor data for the 1, n-alkyl-cyclohexanols, suggested that the reason for the break in the density curve at 1, n-heptyl-cyclohexanol becomes apparent if the configuration of the heptyl group is considered as forming two quasi six-membered rings in conjunction with the cyclohexyl nucleus. Tatum further stated that a trans configuration on the part of the cyclohexyl ring would result in a break after the n-alkyl side-chain had reached a length of six carbon atoms due to the possible formation of two quasi cyclohexyl rings. In this latter case ring formation could take place when the n-alkyl group reached a length of six carbon atoms since the position which would be occupied by the seventh carbon atom in the cis form is already occupied.

The results of this study as well as that of McLellan and Edwards and of Tatum indicate quasi seven-membered ring formation by the n-alkyl group, whereas that of Williams and Edwards indicates quasi-six-membered ring formation.

The issue is further confused if the cyclohexyl group of these alcohols can be said to be of the same configuration as that which cyclohexane normally assumes at room temperature. It has been shown (38) that
cyclohexane exists in the trans configuration at room temperature. If such is the case quasi six-membered ring formation would be indicated.

It was previously pointed out that the factor which abruptly alters the course of the density curve appears to be more predominant in the 1,\textsubscript{n}-alkyl-cyclohexanols and the 1,\textsubscript{n}-alkyl-cyclopentamols than in the case of the \textsubscript{n}-alkyl-cyclohexylcarbinols. If the factor in question is a quasi ring formation phenomenon, this author can offer no explanation for its apparent relatively minor role in the \textsubscript{n}-alkyl-cyclohexylcarbinol series.

The addition of a methylene group to the alkyl side chain of a 1,\textsubscript{n}-alkyl-cyclohexylcarbinol tends to cause a decrease in density; whereas, the converse is true in the case of the \textsubscript{n}-alkyl-cyclopentanes and \textsubscript{n}-alkyl-cyclohexanes. That the alcohols tend to have greater densities than the corresponding hydrocarbons might be due in part to intermolecular association. It might be expected, therefore, that the addition of a methylene group would tend to cause a decrease in the density as a result of a diminution of the intermolecular association, through partial shielding of the hydroxyl group. The 1,\textsubscript{n}-alkyl-cyclohexanols have been shown by Williams and Nance (39) to possess intermolecular hydrogen bonding to a high degree. When these workers diluted the
compounds in question, the hydrogen bond infra-red absorption frequency was observed to vanish in approximately 2 molar solutions in hexane. It is then reasonable to assume that the addition of methylene groups will, in a manner analogous to dilution, also shield the hydroxyl group from hydrogen bonding. One might then argue that the decrease in density of analogous compounds prior to the break in the density curve can be accounted for primarily on the basis of the diminution of intermolecular hydrogen bonding. The decrease in density following the break in the density curve is then a second phenomenon, logically expected because of the spatial requirements of increased carbon-chain length. This increase in chain length produces a less symmetrical molecule and packing will be less compact.

A plot of the refractive indices versus the number of carbon atoms in the alkyl group for the n-alkyl-cyclohexylcarbinols (Figure 2) did not show a sharp change in slope at the n-heptyl variant as in the case of the density curves. McLellan and Edwards and Williams and Edwards had reported such an occurrence.

The 3,5-dinitrobenzoates, N-phenylcarbamates, and the 1-naphthalenecarbamates served satisfactorily as derivatives for methyl-, ethyl-, n-propyl-, n-pentyl-, and n-hexyl-cyclohexylcarbinol. The N-phenylcarbamate and 1-naphthalenecarbamate of n-heptyl-cyclohexylcarbinol,
the 1-naphthalene carbamate of \( n \)-octyl-cyclohexylcarbinol, and the 3,5-dinitrobenzoate of \( n \)-monyl-cyclohexylcarbinol were more difficult to crystallize and purify than the corresponding derivatives for the first five members of the series as reported in this work. The 3,5-di-nitrobenzoates of \( n \)-heptyl- and \( n \)-octyl-cyclohexylcarbinols were oils at room temperature. The same was found to be true in the case of the \( N \)-phenylcarbamates of \( n \)-octyl- and \( n \)-monyl-cyclohexylcarbinols and the 1-naphthalene carbamate of \( n \)-monyl-cyclohexylcarbinol. To obtain appreciable yields of the 3,5-dinitrobenzoates in a reasonable length of time it was necessary to esterify all except the first member of the series under conditions of reflux for 24 to 36 hours. The 1-naphthalene carbamates and the \( N \)-phenylcarbamates were generally obtained in greater yields than were the dinitrobenzoates. Generally, the derivatives were relatively easily prepared and purified and gave satisfactory melting points.

A study of the mode of dehydration of selected members of this series was undertaken with the intention of procuring information which might help clarify the relative influence which the cyclohexyl and alkyl groups exert on the mode of dehydration. By such a study, further information might be garnered concerning the anomalous density curve.
The glycols corresponding to the dehydration products of methyl- and ethyl-cyclohexylcarbinol were cleaved with lead tetracetate, a method which has seen considerable use in the structural study of unsaturated compounds. Due to the marked tendency of aldehydes to oxidize and the greater facility with which colored zones can be detected on a chromatographic column, the products obtained from such a cleavage were converted to the 2,4-dinitrophenylhydrazones. The resulting mixture was studied by chromatographic techniques.

The experimental data obtained from the dehydration study were quite inconclusive. This was due largely to the difficulty encountered in the separation processes and the presence of by-products; one of which was present in considerable quantity. The agreement between the elemental analysis data of two components (A and D) obtained from the dehydration study of methyl-cyclohexylcarbinol was rather close. Since these compounds are presumably 2,4-dinitrophenylhydrazones there must be present at least one of the following groups per molecule of the unknown compound in question: \[ \text{N-NH-C-NO}_2 \.

On the basis of the above facts, the simplest empirical formulae for A and D would be \( \text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_4 \) and \( \text{C}_{15}\text{H}_{18}\text{N}_4\text{O}_4 \) respectively. Therefore, the original carbonyl compound
apparently contained a $C_8H_{14}$ group in the case of $\mathcal{C}$ and a $C_9H_{14}$ group in the case of $\mathcal{D}$. Mixed melting point data indicated that $\mathcal{C}$ and $\mathcal{D}$ were identical. A carbonyl compound which might conceivably be formed and which could yield a 2,4-dinitrophenylhydrazone with an empirical formula in agreement with that of $\mathcal{C}$ is methyl-cyclohexyl ketone. This possibility seems somewhat doubtful, however, since oxidation of methyl-cyclohexylcarbinol yielded a product which formed a 2,4-dinitrophenylhydrazone that melted at 136-137.5°. The melting points of $\mathcal{C}$ and $\mathcal{D}$ are 184-187° and 186-188° respectively. At present the author cannot offer an explanation for the formation of these compounds nor can he offer a possible structural formula for either of the compounds.

Although the data from the dehydration study of ethyl-cyclohexylcarbinol were quite meager, indications were that considerable quantity of by-product was formed.

The $R$ values as determined in this work (Table V) were used to obtain some idea as to the possibility of separating a particular mixture by chromatographic means as well as to determine the relative positions the components of this mixture might have when separated in such a manner.

An alternate analytical technique involving spectrophotometric examination of the mixture was not
feasible due to the nature of the absorption curves of some of the pure components of the mixture. Absorption data are given in Table VI.
SUMMARY

1. Members of the n-alkyl-cyclohexylcarbinol series were prepared in which the alkyl groups were: methyl, ethyl, propyl, pentyl, hexyl, heptyl, octyl, and nonyl. Four of these carbinols (the n-pentyl, n-heptyl, n-octyl-, and n-nonyl-cyclohexylcarbinols had not been prepared previously.

2. The physical constants, density and refractive index, have been determined. These data have been represented by suitable graphs. The anomalous density curve has been discussed.

3. The 3,5-dinitrobenzoates, N-phenylcarbamates, and 1-naphthalene-carbamates of certain alcohols synthesized in this investigation were prepared and their melting points determined. None of these derivatives had been reported previously.

4. Methyl- and ethyl-cyclohexylcarbinol were dehydrated. A qualitative and quantitative study of the resulting dehydration products was attempted.

5. Two of the alcohols, methyl- and ethyl-cyclohexylcarbinol, were oxidized with chromic acid. The resulting products, presumably methyl-cyclohexyl ketone and ethyl-cyclohexyl ketone respectively, were converted to the 2,4-dinitrophenylhydrazones. The 2,4-dinitrophenylhydrazone
of cyclohexylaldehyde was prepared. None of these derivatives had been reported previously.

6. The wave length of maximum light absorption and the R values of the 2,4-dinitrophenylhydrazone of acetaldehyde were measured.
BIBLIOGRAPHY

1. Henriquez, P.C.
A mathematical analysis of the single and double six-ring.

1,3-Alkyl-cyclopentanols and their derivatives. J. Am.

3. Williams, H.B., and Edwards, W.R.
Anomalous densities of 1,3-alkyl cyclohexanols. J. Am.
Chem. Soc. 69, 336 (1947).

4. Tatum, H.W.
Viscosities, surface tensions, vapor pressures and para-
chors of 1,3-alkyl-cyclohexanols; An investigation of ab-
normalities in their physical properties. M.S. Thesis,
Louisiana State University (1948).

5. Bouveault, L.
Hexahydrobenzaldehyde, hexahydroacetophenone, and the
Corresponding secondary alcohols. Bull. Soc. Chim. (3) 29,
1049 (1903).

6. Zelinsky, M.
Hexahydrophenylethanol and cyclopentyl-carbinol. Ber.
41, 2628 (1908).

7. Sabatier, P., and Mailhe, A.
Synthese d'une serie d'alcools tertiaires issus du cyclo-

8. Markownikoff, V., and Tscherdzynzew, V.
Tertiary derivatives of methyl cyclohexane. J. Russ.
Phys. Chem. Soc. 32, 302 (1900).

Soc. 52, 3235 (1930).

10. Bedos, P.
Sur la retrogradation du cycle en C6 au cycle en C5 a l'aide
de latherate de bromure de magnesium. Compt. Rend. 189,
255 (1929).
11. Sabatier, F., and Mailhe, A.

12. DomLeo, A., and Kenyon, J.

13. Hall, C., and Schaal, O.
Ueber das Hexahydro-propionphenone, da hexahydro-benzyl-methyl keton, den cyclohexyl-acetessigester und ueber ein eigenartiges Nebenprodukt C_{10}H_{12}O_{4} bei der Herstellung des letzteren. **Ber.** 42, 2230 (1909).


15. Woodward, C.E.

16. Vail, S.L.

17. Leach, M.S.

18. Griego, R.
Eine oxydative Spaltung von Glykolen. **Ber.** 64, 260 (1939).

19. Scanlan, J.T., and Swern, D.
Action of lead tetracetate upon hydroxylated far acids and related materials.

21. Roberts, J.D., and Green, C.
Separation of 2,4-dinitrophenylhydrazones by chromatographic adsorption.


23. Kirchner, J.G., and Keller, G.J.

24. Cheronis, M.D., and Entriekin, J.B.

25. Kamm, O.

26. Bickel, V.I., and French, H.E.

27. Kelthoff, I.M., and Stenger, V.A.


29. LeRosen, A.L.

30. Reid, E.E., Ruhoff, J.R., Burnett, R.E.

31. Ballar, J.C., Jr.

32. Wood, C.E., and Comley, M.A.


VITA

Walter Maury Henley was born at Bogalusa, Louisiana on December 9, 1924. He was educated in the Bogalusa public school system, and graduated from Bogalusa High School in 1941. The following fall he enrolled at Southeastern Louisiana College. During 1943 he entered the A.S.T.P. After serving in the army from 1943 to 1945, he reentered Southeastern Louisiana College and received the Bachelor of Science Degree in chemistry in 1947. The same year he entered the Graduate School of the University of Kansas, where he served as a graduate assistant in the Department of Chemistry. In 1948 he transferred to Louisiana State University, receiving the Master of Science degree in chemistry in 1949. Since that time he has served as graduate assistant in the Department of Chemistry, has been the recipient of the honorary Coates Research Fellowship, and has been employed by the Department of Agricultural Chemistry and Biochemistry of the Louisiana Agricultural Experiment Station, Louisiana State University, as research assistant. During the latter period he has continued his studies toward the degree of Doctor of Philosophy in the field of chemistry.
EXAMINATION AND THESIS REPORT

Candidate: Walter Maurey Henley

Major Field: Organic Chemistry

Title of Thesis: Part I: Acetic-Oxalic Anhydride
Part II: A Study of Some n-Alkyl-Cyclohexylcarbinols

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

July 10, 1952