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THE SYNTHESIS OF SOME ISOMERIC
POLYALKYLOCYCLOPARAFFINS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Bruce Michael Otto, B.S.
The Ohio State University
1963

Approved by

[Signature]
Adviser
Department of Chemistry
ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Melvin S. Newman and to Dr. Kenneth W. Greenlee, under whose guidance this investigation was carried out.

Acknowledgment is also made to Mr. Vincent G. Wiley for his technical assistance and determination of some of the chromatographic and physical property data.

The financial support of this work by the American Petroleum Institute is gratefully acknowledged.
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>11</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF PLATES</td>
<td>x</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. STATEMENT OF THE PROBLEM</td>
<td>3</td>
</tr>
<tr>
<td>III. HISTORICAL</td>
<td>4</td>
</tr>
<tr>
<td>IV. DISCUSSION AND RESULTS</td>
<td>22</td>
</tr>
<tr>
<td>V. EXPERIMENTARY</td>
<td>49</td>
</tr>
<tr>
<td>A. Determination of Physical Constants</td>
<td>49</td>
</tr>
<tr>
<td>1. Cryoscopic Constants</td>
<td></td>
</tr>
<tr>
<td>2. Cottrell Boiling Points</td>
<td></td>
</tr>
<tr>
<td>3. Refractive Indices</td>
<td></td>
</tr>
<tr>
<td>4. Densities</td>
<td></td>
</tr>
<tr>
<td>5. Gas-Liquid Partition Chromatography</td>
<td></td>
</tr>
<tr>
<td>6. Infrared Spectrograms</td>
<td></td>
</tr>
<tr>
<td>B. Synthesis of 1,1,4-Trimethylocyclohexane</td>
<td>52</td>
</tr>
<tr>
<td>1,3-Dibromo-3-methylbutane (I)</td>
<td></td>
</tr>
<tr>
<td>1,5-Dibromo-3,3-dimethylpentane (II)</td>
<td>111</td>
</tr>
<tr>
<td>Chapter</td>
<td>Diethyl-4,4-dimethyleclohexane-1,1-dicarboxylate (III)</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------------</td>
</tr>
<tr>
<td></td>
<td>4,4-Dimethyleclohexylmethanol (III)</td>
</tr>
<tr>
<td></td>
<td>4,4-Dimethyleclohexylcarboxylate (IV)</td>
</tr>
<tr>
<td></td>
<td>4,4-Dimethyleclohexyl-1,1-dicarboxylic acid (V)</td>
</tr>
</tbody>
</table>

| Table of Contents (contd.) |
|---------------------------|---------------|
| 1-Methyl-3-ethylbene (V)  |
| trans-1-Methyl-3-ethylclohexane (VII) |
| 3-Methyl-5-ethyl-4,6-dicarbethoxy-2-cyclohexene-1-one (VIII) |
| Synthesis of 1-Methyl-3-ethylclohexanes (IX) |
| 1,1,4-Trimethylclohexane (X) |
| 4,4-Dimethyleclohexylmethanol (XI) |
| 4,4-Dimethyleclohexylcarboxylate (XII) |
| 4,4-Dimethyleclohexyl-1,1-dicarboxylic acid (XIII) |
TABLE OF CONTENTS (contd.)

Chapter                                                                 Page

D. Synthesis of 1,cis-2,cis-4-Tri-methylcyclopentane . . . . . . . . . . 67

5-Norbornene-2-carboxaldehyde (I)

1,2,3-ENDO and EXO-5-Methyl-2-norbornene (II)

cis and trans-4-Methyl-1,cis-3-cyclopentanedicarboxylic acid (III)

Dimethyl-cis and trans-4-methyl-1,cis-3-cyclopentanedicarboxylate (IV)

cis and trans-4-Methyl-1,cis-3-cyclopentanedicarboxylmate (V)

cis and trans-4-Methyl-1,cis-3-cyclopentanedicarboxylmethanol (V)

cis and trans-4-Methyl-1,cis-3-cyclopentanedicarboxylmethanoldi-p-toluene-sulfonate (VI)

1,cis-2,cis-4-Trimethylcyclopentane (VII)

E. Synthesis of 1,trans-2,cis-3,trans-4-Tetramethylcyclopentane . . . . . . . . . . 74

trans-3-Methyl-5-norbornene-2-carboxaldehyde (I)

trans-5,6-Dimethyl-2-norbornene (II)

cis-4,trans-5-Dimethyl-1,cis-3-cyclopentanedicarboxylic Acid (III)

Dimethyl-cis-4,trans-5-dimethyl-1,cis-3-cyclopentanedicarboxylate (IV)

Dimethyl-cis-4,trans-5-Dimethyl-1,trans-3-cyclopentanedicarboxylate (V)

v
TABLE OF CONTENTS (contd.)

Chapter                                                                                       Page

- \textit{cis-4, trans-5-Dimethyl-1, trans-3-cyclopentanediethanol (VI)}

- \textit{cis-4, trans-5-Dimethyl-1, trans-3-cyclopentanediethanol-di-p-toluene sulfonate (VII)}

\textit{1, trans-2, cis-3, trans-4-Tetramethylocyclopentane (VIII)}

\textbf{F. Synthesis of 1, cis-2, cis-3, trans-4-Tetramethylocyclopentane} ........ 81

- \textit{endo-cis-5-Norbornene-2,3-dimethanol (I)}

- \textit{endo-cis-5-Norbornene-2,3-dimethanol-di-p-toluene sulfonate (II)}

- \textit{endo-cis-5,6-Dimethyl-2-norbornene (III)}

- \textit{cis-4, cis-5-Dimethyl-1, cis-3-cyclopentanedicarboxylic acid (IV)}

- \textit{cis-4, cis-5-Dimethyl-1, cis-3-cyclopentanedicarboxylic acid anhydride (V)}

- \textit{cis-4, cis-5-Dimethyl-1, trans-3-cyclopentanedicarboxylic acid (VI)}

- \textit{Dimethyl-cis-4, cis-5-dimethyl-1, trans-3-cyclopentanedicarboxylate (VII)}

- \textit{cis-4, cis-5-Dimethyl-1, trans-3-cyclopentanediethanol (VIII)}

- \textit{cis-4, cis-5-Dimethyl-1, trans-3-cyclopentanediethanol-di-p-toluene sulfonate (IX)}

vi
TABLE OF CONTENTS (contd.)

Chapter | Page
--- | ---
1, cis-2, cis-3, trans-4-Tetra-methylcyclopentane (I) | 87
G. Synthesis of 1, cis-2, trans-3, trans-4-Tetra-methylcyclopentane | 87
cis-4, trans-5-Dimethyl-1, cis-3-cyclopentanedicarboxyl chloride (I) | 87
cis-4, trans-5-Dimethyl-1, cis-3-cyclopentane-N,N-dimethylidicarboxamide (II) | 87
cis-4, trans-5-Dimethyl-bis (1, cis-3-dimethylaminomethyl) cyclopentane (III) | 87
 cis-4, trans-5-Dimethyl-bis (1, cis-3-dimethylaminomethyl) cyclopentane-di-N-oxide (IV) | 87
 cis-4, trans-5-Dimethyl-1,3-dimethyl-encyclopentane (V) | 87
1, cis-2, trans-3, trans-4-Tetramethylcyclopentane (VIa) | 95
VI. CONCLUSION | 95
VII. INFRARED SPECTROGRAMS | 97
BIBLIOGRAPHY | 101
AUTOBIOGRAPHY | 105
<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Physical Properties of 1,1,2; 1,1,3; and 1,1,4-Trimethylcyclohexanes</td>
<td>7</td>
</tr>
<tr>
<td>II. Physical Properties of the Methylethylcyclohexanes</td>
<td>11</td>
</tr>
<tr>
<td>III. Physical Properties of the Methylethylbenzenes</td>
<td>13</td>
</tr>
<tr>
<td>IV. Physical Properties of the 1,2,4-Trimethylcyclopentanes</td>
<td>17</td>
</tr>
<tr>
<td>V. Physical Properties of the six 1,2,3,4-Tetramethylcyclopentanes</td>
<td>19</td>
</tr>
<tr>
<td>VI. Computed Physical Properties of the six 1,2,3,4-Tetramethylcyclopentanes</td>
<td>20</td>
</tr>
<tr>
<td>VII. Conversion of trans-4,5-Dimethyl-1,3-dimethylene cyclopentane to the Corresponding Cycloparaffins</td>
<td>46</td>
</tr>
</tbody>
</table>
# LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Schematic outline of the synthesis of</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,1,4-Trimethylcyclohexane</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>1-Methyl-3-ethylcyclohexanes</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>1,cis-2,cis-4-Trimethylcyclopentane</td>
<td>31</td>
</tr>
<tr>
<td>4</td>
<td>1,trans-2,cis-3,trans-4-Tetramethyl-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cyclopentane</td>
<td>37</td>
</tr>
<tr>
<td>5</td>
<td>1,cis-2,cis-3,trans-4-Tetramethyl-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cyclopentane</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td>1,cis-2,trans-3,trans-4-Tetramethyl-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>cyclopentane</td>
<td>43</td>
</tr>
</tbody>
</table>
LIST OF PLATES

<table>
<thead>
<tr>
<th>Plate</th>
<th>Fig. 1</th>
<th>Fig. 2</th>
<th>Fig. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>4,4-Dimethylmethylene cyclohexane</td>
<td>1,1,4-Trimethylcyclohexane</td>
<td>1-Methyl-3-ethylcyclohexane</td>
</tr>
<tr>
<td>II.</td>
<td>cis-1-Methyl-3-ethylcyclohexane</td>
<td>ccc-1,2,4-Trimethylcyclopentane</td>
<td>ctct-1,2,3,4-Tetramethylcyclopentane</td>
</tr>
<tr>
<td>III.</td>
<td>trans-4,5-Dimethyl-1,3-dimethylene cyclopentane</td>
<td>ctt-1,2,3,4-Tetramethylcyclopentane</td>
<td>cctt-1,2,3,4-Tetramethylcyclopentane</td>
</tr>
</tbody>
</table>

Page 98
Page 99
Page 100
I. INTRODUCTION

The synthesis, purification and determination of physical properties of pure hydrocarbons has long been in progress at The Ohio State University. Since 1938, most of this work has been under the sponsorship of the American Petroleum Institute whose program originally called for an extended series of engine tests on each hydrocarbon included in gasoline.

More recently, however, emphasis has been shifted to the preparation of very pure hydrocarbons on which physical and thermodynamic property determinations are made. These pure hydrocarbons, as standard samples, are also made available for the calibration of analytical instruments such as ultra-violet, infrared and mass spectrometers, and more recently gas chromatographs and nuclear magnetic resonance spectrometers.

Polyalkyl cyclopentanes and cyclohexanes have long been known to occur in petroleum and have been recognized as important constituents of light napthas. The need for their identification and characterization has prompted the work on the synthesis of the geometrical isomers of some of these derivatives. In most cases stereospecific
syntheses seemed desirable, since separation of a mixture of structural and geometric isomers on the basis of their physical properties seemed likely to be virtually impossible.
II. STATEMENT OF THE PROBLEM

The purpose of this research was the synthesis and characterization of the following alkyl cycloparaffins:

a. 1,1,4-trimethylcyclohexane; b. cis and trans-1-methyl-3-ethylcyclohexanes; c. 1,cis-2,cis-4-trimethylcyclopentane; and d. 1,trans-2,cis-3-trans-4-tetramethylcyclopentane, 1,cis-2,cis-3,trans-4-tetramethylcyclopentane, 1,cis-2,trans-3,trans-4-tetramethylcyclopentane.

Methods were sought which would allow their subsequent preparation in large scale by the American Petroleum Institute.
III. HISTORICAL

This section will consist of a literature survey concerning previous attempts to synthesize the seven hydrocarbons listed in the Statement of the Problem. It will also include the syntheses of position or geometrical isomers which can be expected as impurities.

Emphasis will be placed on methods which have been shown to give a product of highest purity.

1. 1,1,4-Trimethylcyclohexane

Of the twelve isomeric trimethylcyclohexanes, three have geminal pairs of methyl groups and will be discussed in this section.

The first reported synthesis of any of these was that of the 1,1,2-isomer by Craig (1). The hydrocarbon was obtained by hydrogenation of 4-methylspiro-(2.5)-octane. Its identity was further established by Evans (2) and API

(1) R. Craig, Master's thesis, The Ohio State University, 1944.

(2) G. L. Evans, doctoral dissertation, The Ohio State University, 1947.
Research Proj. 45 (3) by two different syntheses. Evans


made his specimen from 4,5,5-trimethyl-1,3-cyclohexanedicione by a series of hydrogenations, dehydrations and rehydrogenations. The API synthesis was based on the Diels-Alder condensation of piperylene and methacrolein, the adduct of which was reduced by the method of Wolff-Kishner and then hydrogenated.

The synthesis of the 1,1,3-isomer has also been reported. Isophorone was used as the starting material and was treated in the following manner: hydrogenation to the alcohol, dehydration to the diene and hydrogenation to the cycloparaffin (4). Purification and characterization of this compound was later reported by API (5).


Only one report has appeared concerning the isolation of the 1,1,4-isomer. Chiurdoglu (6) synthesized the compound starting with the condensation product of diethyl malonate and mesityle oxide (4-methyl-3-pentene-2-one). The diketone obtained (5,5-dimethyl-1,3-cyclohexanedione) was alkylated with methyl iodide giving a mixture of tri and tetramethylcyclohexanediones. Hydrogenation, dehydration, and rehydrogenation gave a mixture of tri and tetramethylcyclohexanes. The desired 1,1,4-trimethylcyclohexane (b.p. 134.2-134.9°C; nD 1.4253; d4 0.7722) was not completely free of impurities and a melting point could not be obtained.

The physical properties of the three isomers are listed in Table I (5). It can be seen that the 1,1,4-isomer must be free of any of the 1,1,3-isomer to be readily purified. In the present research, an unequivocal route to the compound, free of isomeric impurities, has been carried out and the product's identity proven.

2. cis and trans-1-Methyl-3-ethylcyclohexanes

There are seven isomeric methylethylcyclohexanes, six of which exist as stereo isomers and these will be discussed here.
Table I

<table>
<thead>
<tr>
<th>Property</th>
<th>1,1,2&lt;sup&gt;a&lt;/sup&gt;</th>
<th>1,1,3&lt;sup&gt;a&lt;/sup&gt;</th>
<th>1,1,4&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.p.°C./760mm</td>
<td>145.99</td>
<td>136.626</td>
<td>136.53</td>
</tr>
<tr>
<td>n&lt;sub&gt;D&lt;/sub&gt;&lt;sup&gt;20&lt;/sup&gt;</td>
<td>1.4381</td>
<td>1.42955</td>
<td>1.4262</td>
</tr>
<tr>
<td>d&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;20&lt;/sup&gt;</td>
<td>0.7986</td>
<td>0.77883</td>
<td>0.7737</td>
</tr>
<tr>
<td>M.p.°C.</td>
<td>-25.99</td>
<td>-65.750</td>
<td>-86.47</td>
</tr>
<tr>
<td>Purity %</td>
<td>99.98</td>
<td>99.78</td>
<td>99.40</td>
</tr>
</tbody>
</table>

<sup>a</sup>See ref. 5.

<sup>b</sup>This work.
The cis and trans-1-methyl-2-ethylcyclohexanes have been synthesized (6) and characterized (7).


Pure 1-Methyl-3-ethylbenzene isolated from a commercial grade was prepared by azeotropic distillation with ethyleneglycol monobutyl ether. The purified aromatic was hydrogenated and the mixture of cis and trans isomers was separated by fractional distillation.

Several reports have appeared concerning the identification of cis and trans 1,4-isomer (8, 9). The physical properties and spectra indicated in all cases that isomeric impurities were present, namely, the 1,3-isomer. Recently however, the two compounds have been prepared in demonstrably high purity (10). The syntheses were accomplished by the hydrogenation of 1-methyl-4-ethylbenzene (95-98%) which had been prepared from 4-bromotoluene (of the same purity) by reaction of the corresponding Grignard reagent.
with diethylsulfate. The geometric isomers were separated by fractional distillation.

The isomeric 1-Methyl-3-ethylcyclohexanes have been reported by many workers. Mahle (11) first synthesized a concentrate of the two 1,3-isomers (b.p. 145-146°C, \( n_D^{20} 1.460, d_A^{20} 0.8213 \)) from 3-methylcyclohexanone and ethylmagnesium bromide. The ketone, however, had been made from m-cresol which admittedly contained some p-cresol. Dehydration and hydrogenation of the Grignard product afforded his material. Granger (12) and Mousseron (13)

(11) A. Mahle, Bull. soc. chim. 1, 1083 (1911).


used the same synthetic scheme and, in addition, attempted the separation of the cis and trans isomers, which had the following properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>cis</th>
<th>trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>b.p. °C</td>
<td>147.5</td>
<td>148.5</td>
</tr>
<tr>
<td>( n_D^{20} )</td>
<td>1.4311</td>
<td>1.4295</td>
</tr>
<tr>
<td>( d_A^{20} )</td>
<td>0.783</td>
<td>0.786</td>
</tr>
</tbody>
</table>

Shinkin (9) found that when 1,3-pentadiene was pyrolyzed over quartz at 500°C, a fair amount of 1-methyl-3-ethylbenzene was formed. Hydrogenation afforded the two
corresponding cis and trans cyclopentaaffins. There was, in addition, a small amount of the 1,4-isomer (identified by Raman spectra) which could not be removed.

These examples will serve to indicate the many difficulties connected with the syntheses and separations of the desired stereo-isomers free of geometrically isomeric impurities. The present work has shown that a simple synthetic scheme has made it possible to prepare both cis and trans-1-methyl-3-ethylcyclohexane free of either the 1,2 or 1,4 isomers. Table II lists the physical properties of the three isomers.

3. 1-Methyl-3-ethylbenzene

Several methods of synthesis have been devised to prepare pure 1-methyl-3-ethylbenzene. The obvious routes offer laborious purifications at one or more stages due to the close physical properties of the isomers. Lamberti (14)


synthesized this compound in 98% purity based on m-cresol as starting material. This method is hampered by the difficulty to obtain m-cresol free of p-cresol. It is no more advantageous to effect the purification at a later stage since the same problem exists throughout the synthesis.
### Table II

**Methylethylcyclohexanes**

<table>
<thead>
<tr>
<th>Property</th>
<th>( \text{I}^5 )</th>
<th>( \text{II}^5 )</th>
<th>( \text{III}^a )</th>
<th>( \text{IVA} )</th>
<th>( \text{v}^b )</th>
<th>( \text{VI}^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.p. ( \text{C.} / \text{760mm} )</td>
<td>155.98</td>
<td>151.70</td>
<td>148.35</td>
<td>151.06</td>
<td>152.28</td>
<td>148.78</td>
</tr>
<tr>
<td>( \eta^{20} )_D</td>
<td>1.4436</td>
<td>1.4381</td>
<td>1.4327</td>
<td>1.4374</td>
<td>1.4370</td>
<td>1.4301</td>
</tr>
<tr>
<td>( d^{20}_4 )</td>
<td>0.8097</td>
<td>0.794</td>
<td>0.7837</td>
<td>0.8012</td>
<td>0.7965</td>
<td>0.7794</td>
</tr>
<tr>
<td>M.p. °C.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-80.1</td>
</tr>
<tr>
<td>Purity %</td>
<td>99.5</td>
<td>99.5</td>
<td>99.5(est.)</td>
<td>99.5(est.)</td>
<td>98.5(est.)</td>
<td>99.5</td>
</tr>
</tbody>
</table>

*a* This work.

*b* See ref. 5.
API (15) used m-toluidine with somewhat better results, in


that the purity of the product was at least 98.5%. In the
synthesis, m-bromotoluene was made by decomposing the
diazonium salt of m-toluidine in the presence of hydro-
bromic acid. The bromide was converted to the correspond-
ing Grignard reagent and reacted with diethyl sulfate.
The final aromatic did however, contain a small amount of
1-methyl-4-ethylbenzene.

A third method is based on the effective separation
of a mixture of all three methylethylbenzenes (15, 16).

(16) R. J. Thomas, Ind. and Eng. Chem., 32, 408
(1940).

The ortho can be removed by distillation at atmospheric
pressure. Most of the para-isomer is easily removed by
crystallization. The resultant liquor, consisting of only
meta and para, is then sulfonated selectively to remove
the meta isomer. Repeated sulfonation and desulfonation
afford the meta-isomer with only a trace of the para.
However, some difficulty is usually encountered in the
desulfonation step. Table III lists physical properties
of the compound.
### Table III

**Methylethylbenzenes**

I. 1-Methyl-2-ethylbenzene  
II. 1-Methyl-3-ethylbenzene  
III. 1-Methyl-4-ethylbenzene

<table>
<thead>
<tr>
<th>Property</th>
<th>I&lt;sup&gt;a&lt;/sup&gt;</th>
<th>II&lt;sup&gt;a&lt;/sup&gt;</th>
<th>II&lt;sup&gt;b&lt;/sup&gt;</th>
<th>III&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.p.°C./760 mm</td>
<td>165.153</td>
<td>161.30</td>
<td>161.33</td>
<td>161.989</td>
</tr>
<tr>
<td>n&lt;sub&gt;D&lt;/sub&gt;&lt;sup&gt;20&lt;/sup&gt;</td>
<td>1.50456</td>
<td>1.49660</td>
<td>1.4966</td>
<td>1.49500</td>
</tr>
<tr>
<td>d&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;20&lt;/sup&gt;</td>
<td>0.88069</td>
<td>0.86452</td>
<td>0.8647</td>
<td>0.86118</td>
</tr>
<tr>
<td>M.p.°C.</td>
<td>-80.833</td>
<td>-96.96</td>
<td>-97.201</td>
<td>-62.350</td>
</tr>
<tr>
<td>Purity %</td>
<td>99.92</td>
<td>99.8</td>
<td>99.51</td>
<td>99.90</td>
</tr>
</tbody>
</table>

<sup>a</sup> See ref. 50.  
<sup>b</sup> This work.
The present research offers a method of synthesis applicable to both small and large scale involving no difficult separations. It has been shown that the product is not contaminated by any isomeric impurities.

4. 1,cis-2,cis-4-Trimethylcyclopentane

The first record of a 1,2,4-trimethylcyclopentane appeared in 1904 by Zelinsky (17). He prepared the compound from the Dieckmann condensation product of 3-methyladipic ester. The sodium derivative of the cyclic keto-ester (2-carboethoxy-4-methylcyclopentanone) was reacted with methyl iodide to produce the corresponding 2,4-dimethylcyclopentanone (after hydrolysis and decarboxylation of the ester).

Reaction of methyl Grignard reagent with the ketone yielded 1,2,4-trimethylcyclopentanol. Dehydration and hydrogenation resulted in the cycloparaffin; b.p. 112.5 - 113.0°C., n^20_D 1.4156, d^20_4 0.7565. No mention was made of the stereochemistry of the product which was most likely a mixture of all three isomers (oto, oct, and occ).
Of the three stereoisomers, two have been reported to have been isolated (18) and characterized (19). The syn-


thesis started with 3,5-xylenol, purified by crystallization, which was hydrogenated to the corresponding cyclo-

hexanol derivative. Oxidation with nitric acid gave 2,4-
dimethyladipic acid, which was ketonized via the barium salt to cis and trans-2,4-dimethylcyclopentanone. Reaction with methyl Grignard reagent followed by dehydration and hydrogenation afforded presumably a mixture of the three isomers. Straight distillation at high efficiency afforded the lowest boiling oct isomer in high purity. This same distillation failed to effect the separation of the two higher boiling isomers (cot and coc). Recourse was had to a series of azeotrope distillations with ethyleneglycol monobutyl ether. Repeated redistillation of the lower boiling azeotrope afforded one of the isomers in high (99.8%) purity. On the basis of the lower boiling point, it was designated as the cot isomer. The discarded residues, therefore, was made up primarily of the coc
isomer, which could not be purified. Table IV lists the physical properties of the compounds.

The aim of the present work was to synthesize this missing cto isomer by a stereospecific route. Numerous reports have claimed its existence although none have isolated and characterized it (20, 21, 22). A synthetic scheme has been proposed and completed by a route known to be stereospecific on analogous compounds (23). The only possible impurity must be the ctc isomer which is easily removed by distillation.

5. 1,2,3,4-Tetramethylcyclopentanes

There are six stereoisomers of the 1,2,3,4-tetramethylcyclopentanes, cccc, otto, ctc, ctt, cctt, ctct. Three of these (cccc, otto, and ctc) have been recently synthesized (23) by stereospecific methods. The all cis isomer (cccc) was obtained in the following manner: cyclopentadiene and maleic anhydride were reacted to give
Table IV

Physical Properties of the 1,2,4-trimethylcyclopentanes

<table>
<thead>
<tr>
<th>Property</th>
<th>ctc&lt;sup&gt;a&lt;/sup&gt;</th>
<th>cct&lt;sup&gt;a,b&lt;/sup&gt;</th>
<th>ccc&lt;sup&gt;c&lt;/sup&gt;</th>
<th>cct&lt;sup&gt;a&lt;/sup&gt; (predicted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.p.&lt;sup&gt;0&lt;/sup&gt;°C./760mm</td>
<td>109.290</td>
<td>116.731</td>
<td>116.75</td>
<td>116.76</td>
</tr>
<tr>
<td>n&lt;sub&gt;D&lt;/sub&gt;&lt;sup&gt;20&lt;/sup&gt;</td>
<td>1.41060</td>
<td>1.41855</td>
<td>1.4186</td>
<td>1.4186</td>
</tr>
<tr>
<td>d&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;20&lt;/sup&gt;</td>
<td>0.74727</td>
<td>0.76345</td>
<td>0.762</td>
<td>-</td>
</tr>
<tr>
<td>M.p.&lt;sup&gt;0&lt;/sup&gt;°C.</td>
<td>-130.78</td>
<td>-132.26</td>
<td>-132.32</td>
<td>-138.9</td>
</tr>
<tr>
<td>Purity %</td>
<td>99.80</td>
<td>99.83</td>
<td>99.77</td>
<td>100</td>
</tr>
</tbody>
</table>

<sup>a</sup>See ref. 19.

<sup>b</sup>Designated such on the basis of boiling point.

<sup>c</sup>This work.
the endo-5-norbornene-2,3-dicarboxylic anhydride, esterification and reduction gave the corresponding diol; the diol and p-toluenesulfonfyl chloride yielded the corresponding ditosylate; hydrogenolysis afforded endo-cis-5,6-dimethyl-2-norbornene. The pure norbornene was oxidized to the all cis cyclopentane diacid, and converted to the tetramethylcyclopentane by reactions similar to the above (see Part 4 of this section).

In a like manner, the other two isomers (cctc and otto) were prepared from trans-5,6-dimethyl-2-norbornene and exo-cis-5,6-dimethyl-2-norbornene respectively. Table V lists the properties of these isomers along with the remaining three.

Of the original six isomers, therefore, the remaining three are the otot, cott, and the octt varieties.

A compound tentatively assigned the otot isomer has been isolated from a representative petroleum fraction (24).


Synthesis and confirmation remained for more positive designation of this isomer. The other two (cott, cctt) have never been mentioned in the literature.

From the computed values of the six isomers (see Table VI), one most envisage a synthetic route which will
Table V
Physical Properties of the Six 1,2,3,4-Tetramethylcyclopentanes

<table>
<thead>
<tr>
<th>Property</th>
<th>I&lt;sup&gt;a&lt;/sup&gt;</th>
<th>II&lt;sup&gt;a&lt;/sup&gt;</th>
<th>III&lt;sup&gt;a&lt;/sup&gt;</th>
<th>IV&lt;sup&gt;b&lt;/sup&gt;</th>
<th>V&lt;sup&gt;b&lt;/sup&gt;</th>
<th>VI&lt;sup&gt;b&lt;/sup&gt;</th>
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</thead>
<tbody>
<tr>
<td>B.p. °C./760mm</td>
<td>147.30</td>
<td>133.86</td>
<td>134.53</td>
<td>140.71</td>
<td>142.94</td>
<td>127.23</td>
</tr>
<tr>
<td>n&lt;sub&gt;D&lt;/sub&gt;&lt;sup&gt;20&lt;/sup&gt;</td>
<td>1.4332</td>
<td>1.4208</td>
<td>1.4219</td>
<td>1.4248</td>
<td>1.4297</td>
<td>1.4155</td>
</tr>
<tr>
<td>d&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;20&lt;/sup&gt;</td>
<td>0.7924</td>
<td>0.7669</td>
<td>0.7687</td>
<td>0.7763</td>
<td>0.7733</td>
<td>0.7562</td>
</tr>
<tr>
<td>T&lt;sub&gt;f&lt;/sub&gt;</td>
<td>-100.32</td>
<td>-110.71</td>
<td>-109.63</td>
<td>glassy</td>
<td>-112.02</td>
<td>glassy</td>
</tr>
<tr>
<td>T&lt;sub&gt;f0&lt;/sub&gt;</td>
<td>-100.22</td>
<td>-110.52</td>
<td>-113.12(est)</td>
<td>--</td>
<td>-111.34(min)</td>
<td>--</td>
</tr>
<tr>
<td>A</td>
<td>0.040</td>
<td>0.044</td>
<td>0.04</td>
<td>--</td>
<td>0.059(max)</td>
<td>--</td>
</tr>
<tr>
<td>Purity %</td>
<td>99.6</td>
<td>99.14</td>
<td>96+(est)</td>
<td>98+(est)</td>
<td>96.5(min)</td>
<td>98+(est)</td>
</tr>
</tbody>
</table>

<sup>a</sup>See ref. 23.

<sup>b</sup>This work.
<table>
<thead>
<tr>
<th>Property</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.p.°C/760mm</td>
<td>145</td>
<td>135</td>
<td>135</td>
<td>140</td>
<td>143</td>
<td>127.4</td>
</tr>
<tr>
<td>n°D</td>
<td>1.433</td>
<td>1.417</td>
<td>1.416</td>
<td>1.421</td>
<td>1.420</td>
<td>1.415</td>
</tr>
<tr>
<td>d°4</td>
<td>0.792</td>
<td>0.764</td>
<td>0.759</td>
<td>0.769</td>
<td>0.770</td>
<td>0.748</td>
</tr>
</tbody>
</table>

*See ref. 19.*
net result in a mixture containing a pair of isomers inseparable on the basis of their boiling points.

The present research has accomplished the synthesis of the three unknown stereoisomers (actct, octt, ctcct) and has shown them to be free of isomeric impurities.
IV. DISCUSSION AND RESULTS

The synthetic route to each of the previously named hydrocarbons will be discussed in detail in this section. The identity of each intermediate and product will be indicated by comparison to known compounds if possible and by both physical and chemical evidence in the case of new compounds.

A. 1,1,4-Trimethylcyclohexane

The synthesis of this hydrocarbon was effected by the scheme as depicted in Figure 1.

Isoprene was reacted with dry hydrogen bromide to yield 1,3-dibromo-3-methylbutane (I) (25). Ethylene alkylation afforded 3,3-dimethyl-1,5-dibromopentane (II) (25). In this step, it was found desirable to introduce fresh portions of aluminum chloride throughout the reaction rather than add it all at the start as done by Schmerling. It was also found that the reaction was very much affected by temperature changes. The rate of ethylene absorption was greatest at -12° to -10° and dropped off markedly at both higher and lower temperatures.

Figure 1
Synthesis of 1,1,3-trimethylcyclohexane

\[
\begin{align*}
\text{H}_3\text{C} & \overset{\text{C}}{\text{CH}_2} + 2\text{HBr} \rightarrow \text{BrCH}_2\text{CH}_2\text{Br} \\
\text{CH}_3 & \overset{\text{CH}_2\text{CH}_2\text{Br}}{\text{BrCH}_2\text{CH}_2\text{Br}} \\
\text{H}_2\text{C} & = \text{CH}_2 \rightarrow \text{BrCH}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{Br} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \overset{\text{CH}_2\text{CH}_2\text{Br}}{\text{BrCH}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{Br}} \\
\text{CH}_3 & \overset{\text{CH}_2\text{CCH}_2\text{CO}_2\text{C}_2\text{H}_5}{\text{BrCH}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{Br}} \\
\text{CH}_3 & \overset{\text{CH}_2\text{CCH}_2\text{CO}_2\text{C}_2\text{H}_5}{\text{BrCH}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{Br}} \\
\text{H}_3\text{C} & \overset{\text{CO}_2\text{C}_2\text{H}_5}{\text{CO}_2\text{C}_2\text{H}_5} \\
\text{H}_3\text{C} & \overset{\text{CH}_2\text{OH}}{\text{CH}_2\text{OH}} \\
\text{H}_3\text{C} & \overset{\text{CH}_2\text{OAc}}{\text{CH}_2\text{OAc}} \\
\text{H}_3\text{C} & \overset{\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}}{\text{BrCH}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{Br}} \\
\text{H}_3\text{C} & \overset{\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}}{\text{BrCH}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{Br}} \\
\end{align*}
\]
The cyclo-alkylation of dibromide II with diethylmalonate with sodium ethoxide as the base was essentially the same as reported by Perkin (26) on 1,5-dibromopentane. In this work, as in Perkin's case, a 100% excess of malonic ester was employed. Heisig (27) used a stoichiometric amount in the synthesis of cyclobutane derivatives. Both methods were tried here and a 20% increase in yield was realized by means of a 100% excess of malonate. Only a small amount of non-cyclic tetraester (by reaction of two molecules of malonic ester with one molecule of dibromide) could have been formed since no high boiling residue was encountered in the distillation of the desired product (III). As can be easily seen, this type of ring formation avoids the formation of any 1,3-disubstituted isomer, the removal of which would probably be impossible. Table I (Page 7) illustrates this by comparing the boiling points of the final hydrocarbons.

Saponification of the diester (III) was effected in good yield with aqueous potassium hydroxide. A small amount of detergent was used as a phase-jointer and increased the reaction rate considerably. In liberating the diacid...
(IV), it was necessary to add the solution of dipotassium salt to a rapidly stirred excess of hydrochloric acid. Inverse addition resulted in incomplete acidification with trapping of the mono and dipotassium salts in the free acid particles. Decarboxylation to mono-acid V was carried out by heating to boiling (26). The use of powdered Pyrex glass was found to facilitate the reaction. Esterification with methanol gave good yields following a known procedure (28). Reduction by means of lithium aluminum hydride was carried out in tetrahydrofuran according to Miller and Greenlee (23). The corresponding alcohol (VII) was obtained in good yield by this method. Acetylation to the acetate (VIII) with acetic anhydride at reflux gave good yields. The acetate was not further purified, but the absence of unchanged alcohol was indicated by G.L.C. analysis. The crude acetate was pyrolyzed at 550° through a tube packed with glass helices. The reaction rate was controlled so that the retention time in the furnace was short, minimizing chances for isomerization. Bailey (29) has shown that no skeletal rearrangement


occurs under these conditions. Conversion per pass was held to less than 50% to insure the mildest possible conditions. The olefin product (IX) was shown to be of high purity by G.L.C. analysis. Catalytic hydrogenation was effected at a maximum temperature of 125°, a condition known not to promote alkyl group migration. The cycloparaffin (X) was distilled at about 25 plate efficiency. The purity of the product, according to G.L.C. analysis and the cryoscopic data, was very high. G.L.C. analysis was able to show the presence of as little as 2-3% of added 1,1,3-trimethylcyclohexane (obtained from A.P.I.). The physical properties of the two make it imperative for the 1,1,3-isomer to be absent (see Table I, Page 7) in order to obtain the 1,1,4-isomer in high purity.

B. 1-Methyl-3-ethylcyclohexanes

The synthetic route used for the cis and trans isomers of this hydrocarbon is depicted in Figure 2. The main object was to employ reactions which would exclude even trace amounts of the corresponding 1,4-derivatives (see Table II, Page 11) which could not be easily removed.

The key intermediate in this synthesis was a cyclohexenone with methyl or ethyl groups in the 3-position or both the 3 and 5-positions. Horning (30) has outlined a

Figure 2
Synthesis of 1-methyl-5-ethylcyclhexenes

\[
\begin{align*}
2\text{CH}_3\text{CCH}_2\text{COC}_2\text{H}_5 & \quad \xrightarrow{\text{dehydration}} \quad \text{CH}_3\text{COC}_2\text{C}_2\text{H}_5 \quad \xrightarrow{\text{Ketenation}} \quad \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{C}=\text{CH}_2 & \quad \xrightarrow{\text{Ketenation}} \quad \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\end{align*}
\]

\( \text{V} \text{a} \) cis
\( \text{V} \text{b} \) trans
general procedure (modified considerably here in view of the large scale-up) in which ethylacetooacetate is condensed with aldehydes to yield cyclohexanone derivatives with alkyl groups in exclusively the 3 or the 3,5-positions. Thus, with formaldehyde, 3-methyl-2-cyclohexenone results, and the use of propionaldehyde yields 3-methyl-5-ethyl-2-cyclohexenone.

In the present work both of the above methods were used. The bulk, however, employed the use of propionaldehyde. In the case of formaldehyde, 3-methyl-2-cyclohexenone, the decarboxylation product, was reacted with ethyl Grignard reagent to give the corresponding methyl-ethylcyclohexenol. Dehydration and hydrogenation gave the desired cis and trans-1-methyl-3-ethylcyclohexanes. As depicted on Figure 2, the use of propionaldehyde gave diester I. In Horning's (30) case, the reaction was carried out at low temperatures over a long period of time, producing the non-cyclic precursor. Here, however, it was found that cyclization occurred readily without changing the catalyst (piperidine) used for the initial condensation. Decarboxylation to II proceeded in modest (30-50%) yield, probably due to self-condensation during the necessary long heating period in acetic acid and sulfuric acid. The starting materials were commercially
available at low cost, however, and large runs were easily made.

Hydrogenation of the ketone afforded high yields of the corresponding alcohol (III) which was homogeneous by G.L.C. analysis. Nearly complete conversion of the alcohol to the olefin (IV) was realized in one pass over alumina at 350°. Catalytic hydrogenation over a nickel-kieselguhr catalyst yielded a 60:40 mixture of cis and trans-1-methyl-3-ethylcyclohexane (Va and Vb). The crude cycloparaffin mixture showed a small amount of unsaturation (bromine test) which could not be removed by hydrogenation, and hence was scrubbed with aqueous permanganate prior to distillation at 120 plate efficiency on an 18 foot still. This product ratio (cis over trans) is reasonable since the more stable cis isomer can be in a conformation such that both alkyl groups are in the more stable equatorial position. This also explains the fact that the cis isomer is the lower boiling.

Table II (Page 11) lists the physical properties of the pure samples obtained here along with those of the two comparable isomeric pairs.

C. 1-Methyl-3-ethylbenzene

The general utility of the previous method (section B) is further exemplified in its application to the synthesis of metadisubstituted alkylbenzenes free from ortho and
para impurities. Thus, 1-methyl-3-ethylbenzene was obtained from the vapor phase dehydrogenation of olefin IV over a chromia-alumina catalyst. Conversion per pass was held to 30-40% to minimise any possible rearrangement. The aromatic product (80-90% yield) was distilled at only moderate (20 plate) efficiency. The purity of the product must imply that the synthetic route was responsible and not an elaborate purification. Table III (Page 13) records the physical properties of the product obtained here and of the ortho and para-isomers. It can be seen that the para isomer can only be removed by painstaking chemical means. The above method, therefore, offers a simple, new route to meta-dialkylbenzenes of high purity.

D. 1,cis-2,cis-4-Trimethylcyclopentane

As stated in the historical section, the synthesis of this stereoisomer requires that it be free of the close boiling cxt isomer. Figure 3 depicts the proposed scheme (listing only the pertinent isomer), which is similar to that used by Miller and Greenlee (23) for the synthesis of stereoisomeric 1,2,3,4-tetramethylcyclopentanes.

Diels-Alder condensation of cyclopentadiene and acrolein afforded a mixture of endo and exo-5-norbornene
Figure 3

Synthesis of 1,6-cis-2,5-cis-6,6-trimethylcyclohexene

\[ \text{acyclic ketone} + \text{enamine} \rightarrow \text{cyclohexene} \]

\[ \text{IV} \rightarrow \text{III} \rightarrow \text{II} \rightarrow \text{I} \]

\[ \text{V} \rightarrow \text{VI} \rightarrow \text{VII} \]
-2-carboxaldehyde (presumably 75-80% endo) (31). The crude product was used as is for the next step since the small amount of residual dicyclopentadiene was more easily removed there. Wolff-Kishner reduction of the aldehyde afforded fair yields of endo and exo-5-methyl-2-norbornene. The hydrocarbon product was distilled at 20 plate efficiency. It appeared from the physical properties of the distilled fractions that there was little chance for separation of the two isomers. In fact, G.L.C. analysis was also ineffective in splitting the two. It was not valid to assume that a single isomer was present since epimerization during the Wolff-Kishner reduction could be expected. However, one can see that regardless of the presence of the unwanted exo-isomer, it could be carried through to the end and its product (exo-1,2,3-trimethylcyclopentane) would be easily removed by distillation.

Oxidation of the norbornene mixture by an adaptation of a procedure already reported (23) afforded diacid III along with the gto isomer. Yields of 60-70% were consistently obtained using aqueous potassium permanganate (containing a small amount of potassium nitrate) as oxidant, t-butyl alcohol as a phase joiner, and gaseous carbon dioxide to prevent a strongly basic solution. Diacid III
has been reported in the literature (m.p. 90°0.) as the nitric acid oxidation product of endo-5-methyl-2-norbornene (32). The diacid in the present work had, after repeated crystallisation, a melting point of 101.0-102.5°, possibly indicating a purer product. Esterification to the dimethyl-ester (IV) was carried out following the method of Clinton and Laskowski (28). Lithium aluminum hydride reduction of the diester afforded excellent yields of the corresponding diol. The stereospecificity of this reduction has been emphasised many times in the literature (33-36).


Reaction of the diol with p-toluenesulfonyl chloride in pyridine, known to be stereospecific with respect to carbinol configuration, yielded the corresponding ditosylate (VI). Excellent yields were obtained by a procedure essentially the same as described in Organic
Synthesis (37) except that a lower temperature (-10-0°C)


was employed here. Reductive hydrogenolysis was accomplished in refluxing tetrahydrofuran using lithium hydride with lithium aluminum hydride as carrier (23). This method has been previously described and used with confidence for stereospecificity (38-40).


The resulting hydrocarbon product, a mixture of oct (70%) and acc (30%) was distilled at about 25 plate efficiency to afford the pure low boiling isomer (oct), identical to an authentic sample (22), and pure acc (VII). Physical properties were determined for this higher boiling isomer and were found to compare almost identically to the values reported for the previously designated oct isomer. When 5% of the material prepared here (99.77% pure) was added to an authentic sample (98.15% pure) designated as oct in the literature (5), the melting point of the mixture was raised from that of the 98.15% pure material. One
concludes, therefore, that the compounds are identical and must explain this apparent anomaly.

There are only two possibilities: a. the original designation was incorrect, i.e., oct is actually ooc or, b. rearrangement occurred during the present synthesis resulting in the oct isomer.

The original designation was made merely on the basis of boiling point, i.e., the oct was assumed to boil lower than the ooc. It must be remembered that the purification of the ooc isomer from a mixture (which could not be separated by G.L.C.) of the two (oct and ooc) was accomplished by azeotropic distillation and the corresponding azeotropes may have inverted boiling points. Also, recently it was proven that cis-1,3-dimethylcyclopentane boils lower than the trans variety (41), due to a semi-chair form of the cyclopentane ring. One would predict that the addition of a third methyl group in a like manner to each isomer would change the physical properties in the same direction, i.e., ooc boiling lower than the oct.

Considering the possibility of rearrangement during the synthesis, it has already been shown that the exact same sequence has been found to be stereoselective on three compounds having one more methyl group. If, however,

rearrangement has occurred, it must have been due to epimerization of the unhindered substituent (the 3-position of compounds III-VI). This does not seem likely since epimerization of the group adjacent to the methyl, i.e., cis to it would be more expected, which would give a (ciss configuration.

A mixture of the two high boiling isomers (42) (cot


and cocc) was obtained which, by cryoscopy proved to be largely (84%) cot. From this data and from its other properties, estimates for the pure compound, along with the properties of the other isomers, are in Table IV, Page 17.

It is, therefore, the proposal of this work that the cocc isomer has been prepared here as it was previously, but given an erroneous designation.

E. 1,trans-2,cis-3,trans-4-Tetramethylcyclopentane

Figure 4 depicts the method of synthesis of this hydrocarbon. Diels-Alder condensation of crotonaldehyde and cyclopentadiene (as dicyclopentadiene) was carried out by an adaptation of a procedure by Alder and Stein (43).

Figure 4

Synthesis of 1,4-cyclopentadiene-3,4-dione - 4-toluene-1,4-diol.
The aldehyde adduct consisted of a mixture of all four possible isomers (four semi-carbazides could be isolated) though the two trans isomers made up about 80% of the total. The crude mixture was distilled and reduced by the Wolff-Kishner method to the dimethylnorbornene. The lower boiling trans isomer (II) was isolated in high purity after distillation. It was necessary to first vacuum distil the crude hydrocarbon to remove it from a small amount of dicyclopentadiene which could not be easily removed in the distillation of the aldehyde. The pure norbornene was oxidized with aqueous potassium permanganate and the diacid (III) was obtained in 50-60% yield. Esterification with methanol yielded diester IV. Compounds II-IV prepared here had physical properties identical with those already reported (23).

The next step in the synthesis consisted of a base catalyzed epimerization of the octc diester (IV). The sole product at equilibrium was the desired octe isomer (V). It has been shown that dimethyl-1, cis-3-cyclopentane-dicarboxylate is converted to the trans isomer when treated under the same conditions (41). In the present case, the stereochemistry of the two additional methyl groups would be expected to drive the equilibrium in favor of the more stable all trans isomer. A short (3-4 hours) reflux period in sodium methoxide-methanol effected complete conversion.
Reduction of the diester with lithium aluminum hydride in tetrahydrofuran gave the desired diol (VI) in good yield. The use of diethyl ether resulted in gummy precipitates and poor (50%) yields. Ditosylation by a procedure already reported (see Page 34) gave excellent yields. Reductive hydrogenolysis of ditosylate VII afforded the desired 1,trans-2,cis-3,trans-4-tetramethylcyclopentane (VIII). The hydrocarbon was distilled at 10 plate efficiency and its physical properties were determined (see Table V, Page 19). The properties compared almost exactly to those reported for the compound tentatively identified as this isomer. As can be seen, no absolute value of the purity could be obtained cryoscopically, an experience not too uncommon for low melting hydrocarbons. Highly efficient G.I.C. analysis indicated a product of very high purity.

F. 1,cis-2,cis-3,trans-4-Tetramethylcyclopentane

The synthesis of this hydrocarbon was accomplished by following the scheme depicted on Figure 5.

In this sequence the first five compounds (I-V) were prepared by methods already reported (23, 54). The identities of all compounds were confirmed by agreement of their physical properties. The next step (V-VI) actually involves two non-isolated intermediates. Reaction of the anhydride (V) with an equimolar amount of sodium methoxide
Figure 5

Synthesis of 1,3-cis-2,4-cis-tetra-1,3,4,5-tetramethylcyclopentene
presumably afforded the corresponding ester–acid salt, a well known type of conversion. All four substituents would be expected to be in a cis configuration. However, if an excess of base is used, epimerization of the ester group could be expected if the removal of the tertiary hydrogen (by the base) is not prohibited by the proximity of the carboxylate ion (as the sodium salt). This proved to be the case since the product isolated after saponification was a diacid different from the starting material, i.e., diacid IV (melting point and mixed melting point). It was also shown that the carboxyl groups in diacid VI were trans to each other since no anhydride could be obtained by admixture with acetyl chloride under conditions that formed anhydride V from diacid IV. Esterification gave diester VII which was shown by G.L.O. analysis and physical properties to be different from the corresponding diester of Diacid IV. The final three steps resemble those of the previous section. The final product, 1, cis-2, cis-3, trans-4-tetramethylocyclopentane was distilled at 20 plate efficiency and its physical properties determined (Table V, Page 19). The product failed to form a crystalline compound and hence the purity by cryoscopic could not be determined. However, G.L.O. analysis indicated a purity of at least 98%. Stereoisomeric impurities could not have
been present in more than trace amounts since these isomers were shown to be easily separable by this method (G.L.C.).

G. 1, cis-2, trans-3, trans-4-Tetramethylocyclopentane

Figure 6 depicts the synthetic route used in the synthesis of this compound.

The starting material used was the diacid (I) already described in a previous section on Page 36. Conversion of the diacid to the corresponding diacid chloride (IV) was effected in two ways: a. treatment with oxalyl chloride; and b. with phosphorus pentachloride. The use of oxalyl chloride has been successful under very mild reaction conditions (44). Phosphorus pentachloride, more readily available, gave slightly lower yields but the product was of comparable purity. The bulk of the material was prepared using this last method. The identity and stereochemistry of the diacid was indicated by its hydrolysis back to the original diacid (I). Elemental analysis and infrared spectroscopy substantiated the presumed structure. Thionyl chloride was also tried but the product was a mixture of diacid chloride and the corresponding anhydride.

The next step in the synthesis consisted in the reaction of the diacid chloride with an excess of dimethyl
Figure 6.
Synthesis of 1,3,4-trimethyleicyclopanone.
amine, an adaptation of a procedure already reported (44). The desired diamide (III) was formed in high yield. It was necessary to employ large volumes of ethyl ether in the reaction since the insoluble dimethylamine hydrochloride formed caused stirring problems. The yields in concentrated solutions were lower, presumably due to trapping of unreacted diacid chloride by the amine hydrochloride. The diamide was found to be extremely hygroscopic, hence the workup was performed as much as possible under nitrogen.

Lithium aluminum hydride reduction of the diamide to the diamine was carried out essentially like that of a similar case already reported (44). The diamine (IV) was obtained in modest (65-75%) yield along with a very high boiling residue which was not characterized.

Oxidation of the diamine with 25% hydrogen peroxide at low (5-10°) temperatures afforded the di-N-oxide (V) in good yield. The excess peroxide was decomposed smoothly with the enzyme catalase. Pyrolysis of the di-N-oxide was carried out at 135°/50 mm. by the well known procedure of Cope (45). The elimination, shown to be a highly specific (45) A. C. Cope, J. Am. Chem. Soc. 79, 4729 (1957).

cis-elimination, afforded the desired dicolefin (VI) of very high purity.
However, before recourse to the Cope elimination, a seemingly simpler attack was carried out. This consisted in esterifying the diacid (I), reducing the resulting diester to the diol, followed by acetylation to the corresponding diacetate. The pyrolysis of this diacetate at temperatures ranging from 475° to 575° was studied. In each case an unbelievably large number (up to 32) of components were detected by G.L.C. analysis, none in more than 35% of the total. No attempt was made to identify these products although an ultra-violet spectrogram revealed that a conjugated diene was present (max. 235 μ). Therefore, another case showing the greater selectivity of the pyrolysis of amino-oxides over that of acetates has been established.

The last step in the synthesis required a method of hydrogenation of the two double bonds while avoiding rearrangements and polymerization. It can be seen that (barring rearrangement) three isomeric cycloparaffins can result, the ctcot (Page 36), cctc (23), and the desired cttc. It must be necessary to be able to separate the three, preferably by distillation. This requirement was met, as seen by the boiling points (see Tables V and VI).

The different methods used and the results are seen in the following table:
Table VII

Conversion of Dimethyldimethylenecyclopentane (VI) to the Corresponding Cycloparaffin

<table>
<thead>
<tr>
<th>Method</th>
<th>ctct, %</th>
<th>cota, %</th>
<th>cotti, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;/Ni, 125°C.</td>
<td>60</td>
<td>37</td>
<td>3</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;/Pt, 25°C.</td>
<td>20</td>
<td>60</td>
<td>20</td>
</tr>
<tr>
<td>B&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;/0°C.</td>
<td>20</td>
<td>45</td>
<td>35</td>
</tr>
<tr>
<td>R&lt;sub&gt;2&lt;/sub&gt;bBH/0°C</td>
<td>2</td>
<td>31</td>
<td>67</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by G.L.C. by admixture with authentic samples.

<sup>b</sup>R = sec-iscamyl (3-methyl-2-butyl-).
As can be seen in Table VII, catalytic hydrogenation offered little hope in obtaining more than G.L.C. samples of the desired isomer. However, the use of the hydroboration technique originated by Brown (46) showed considerable promise. The more selective di-sec-isoamylborane proved to give the highest percentage of the desiredcott isomer. In theory, the incoming borane, presumed to react via a four-centered intermediate, will attack from the least hindered side. This has been shown to be the case in other hydroboration (46). In the present case, then, the steric effect would favor the cott isomer which was borne out by the product ratio. Protonation of the resulting alkyl borane produced the hydrocarbon product.

The product mixture was distilled at about 20 plate efficiency enabling a clean separation of the three stereoisomers. Physical properties of the cott isomer were determined and are listed in Table V (Page 19).

Considerable difficulty was encountered in obtaining an accurate purity by cryoscopic means. The compound obviously had a very high A (mole fraction/degree lowering
of the M.p.) value causing poor equilibrium in the freezing point determination. The extrapolated freezing point at 100% purity ($T_{fo}$) was therefore only a minimum value which would project a minimum purity value. G.L.C. analysis indicated a purity of at least 98%. 
V. EXPERIMENTAL

A. Determination of physical constants

1. Cryoscopic constants

Cryoscopic data was taken on all hydrocarbons which would crystallize. Purities were calculated from the freezing and melting points obtained. The apparatus used was similar to that of the National Bureau of Standards (47). Freezing and melting temperatures were measured with a platinum resistance thermometer (calibrated by the National Bureau of Standards) in conjunction with a Muller resistance bridge (Leeds and Northrup, Type G-2). Temperature differences of less than 0.01° could be accurately determined. Since cryoscopic constants were known for only a few of the hydrocarbons synthesized, the method of Mair, Glasgow and Rossini (48) was used to determine the necessary constants for the new hydrocarbons. By this method, the theoretical freezing point of 100% material \( T_{FO} \) was determined from the actual freezing point.
(T_f) and the midpoint temperature (T Δ/2) on a time-
temperature freezing curve. The assumptions are made
that at the midpoint, exactly one-half of the liquid phase
has been crystallized and that this midpoint temperature
(T Δ/2) represents the melting point of the liquid phase
when it contains exactly twice the impurity that it does
at the actual freezing point. These assumptions are rea-
sonably valid if the solution is sufficiently dilute, if
the impurities from an ideal solution with the solvent,
and if the impurities are insoluble in the solid phase.
The true freezing point (T_{f0}) can then be calculated by
adding the temperature differences between the freezing
point (T_f) and the midpoint (T Δ/2) to the freezing point
(T_f). This can be expressed by the following equation,
\[ T_{f0} = T_f + (T_f - T Δ/2). \]
A value for the cryoscopic constant (K_f) in terms of de-
grees lowering per mole percent impurity is then deter-
mined experimentally by adding to a known weight of the
material under study, having a known freezing point (T_f),
a weighed amount of a suitable impurity and measuring the
freezing point (T_{fm}) of the mixture. Another useful form
of the cryoscopic constant is represented by A, in terms
of mole fraction per degree of freezing point lowering.
Both may be expressed by the following:
\[ K_f = \frac{T_f - T_{fm}}{\text{Mole } \% \text{ impurity}} \quad A = \frac{1}{K_f \times 100} \]

Then, the purity (P) of the compound can be calculated from the following equation:

\[ \log_{10} P = 2.00000 - \left( \frac{A}{2.30259} \right) (T_{fo} - T_f) \]

2. Cottrell boiling points

The boiling points reported in this dissertation as "Cottrell b.p.'s" were those determined in a modified Cottrell ebulliometer, described by Quiggle, Tonberg and Fenske (49), which was attached to an electronically controlled barostat that maintained a constant pressure of 760mm. of nitrogen in the ebulliometer. The actual temperatures were measured with the same platinum resistance thermometer and Mueller bridge used for the cryoscopic determinations and are accurate to about ± 0.01°.

3. Refractive indices

Refractive indices were determined with a Valentine Precision Refractometer, manufactured by the Industro-Scientific Company, connected to an electronically controlled constant temperature bath. The refractive indices are accurate to about ± 0.0001.

4. Densities

The densities were determined using a 20 ml. pycnometer which was accurately calibrated using pure benzene.
and certified iso-octane. The water bath used for these measurements was electronically controlled to maintain a temperature of 20.00 ± 0.02°. The densities obtained are believed accurate to ± 0.0001 g./ml.

5. Gas-Liquid chromatography (G.L.C.)

The G.L.C. studies were all done on a Barber-Colman IDS Model 20 gas chromatograph with capillary columns. A variety of substrates was used with either a hydrogen flame or an argon ionization detection system. Strict linearity of concentration was not realized with the argon ionization detector, but is believed to be 98.5-99.0% linear.

6. Infrared spectrograms

The infrared absorption spectrograms reported herein were determined by means of either of two instruments; a Perkin Elmer Model 21 or Perkin Elmer Infracord, both double beam spectrometers.

B. Synthesis of 1,1,4-Trimethylcyclohexane

1,3-Dibromo-3-methylbutane (I)

Into a 2-liter wide mouth bottle was charged 483 g. (7.2 moles) freshly distilled isoprene. The reaction bottle was immersed in an ice-water bath and the contents cooled to 0°. Gaseous hydrogen bromide from a cylinder was bubbled in through a tube extending below the surface
of the isoprene. The addition rate was such that the tempera-
ture did not rise above 10° and little outgassing was
noted on a bubbler connected to an outlet tube. The ad-
dition was continued for three hours at which time the
gross weight of the bottle and fittings indicated 1184 g.
(14.6 moles) of hydrogen bromide (103% of theory) had been
added. The mixture was then transferred to a glass lined
autoclave and subjected to the full pressure of the hydro-
gen bromide cylinder for three hours at room temperature.
Vacuum distillation of the crude material afforded 1,3-
dibromo-3-methylbutane (I) (1510 g., 6.6 moles) in 92.5% 
based on isoprene; b.p. 57-58°/5mm., nD^20 1.5063, (lit. b.p.
54-55°/4mm., nD^20 1.5065) (25, 51).

(51) U. N. Ipatieff, J. prakt. Chem., (2) 55, 4
(1897).

1,2-Dibromo-3,3-dimethylpentane (II)

The ethylene alkylation of dibromide (I) was carried
out by a somewhat revised procedure outlined by Schmer-
ling (25). To a 3-liter, 3-necked round bottom flask
equipped with a motor driven glass stirrer and a thermom-
eter well was charged dibromide I (1510 g., 6.6 moles)
and aluminum chloride (5 g.). The flask was partially im-
mersed in a dry-ice-isopropanol bath maintained at -20°.
The mixture was cooled to -15° and ethylene from a cylinder
was bubbled into the rapidly stirred mixture through a glass tube extending below the surface of the liquid. The rate of addition was adjusted such that the temperature remained between -15° and -10°. At appropriate intervals, 5 g. quantities (two) of fresh aluminum chloride were added to the mixture. After three and one-half hours the ethylene absorption was very slow as noted by bubblers on either side of the reaction flask. The amount of ethylene absorbed was 183 g. (6.55 moles) or 99% of theory. The crude mixture was stored in an ice chest for twelve hours and hydrolyzed while cold with ice-water.

The organic layer was separated, washed successively with water, dilute sodium bicarbonate solution, and again with water, and dried through a column of anhydrous sodium sulfate. Vacuum distillation of the dried material afforded 1,5-dibromo-3,3-dimethylpentane (II) (1328 g., 5.25 moles) in 78% based on dibromide I with the following properties; b.p. 82-84°/1mm., n_20^D 1.5088-1.5091, (lit. b.p. 98-99°/3mm., n_20^D 1.5091) (25).

Diethyl-4,4-dimethylcyclohexane-1,1-dicarboxylate (III)

In a typical reaction, a 5-liter, 3-necked reaction flask fitted with a motor driven Hershberg stirrer, multi-bulb reflux condenser, and an electric heating mantle was charged with dibromide II (272 g., 1.06 moles), diethylmalonate (339 g., 2.12 moles), and sodium (48.8 g., 2.12 g. atoms) pre-reacted with 3 liters of absolute ethanol. The
homogeneous solution was refluxed with stirring for four hours. After cooling to room temperature, the sodium bromide which had precipitated was filtered off and the bulk of the ethanol was distilled at atmospheric pressure. The residue was mixed with an equal volume of diethyl ether and washed twice with cold water. The ether solution was dried through anhydrous magnesium sulfate and stripped of ether. Vacuum distillation of the residue afforded diethyl-4,4-dimethylcyclohexane-2,2-dicarboxylate (III) (228 g., 0.89 moles) in 84% yield based on dibromide II with the following properties; b.p. 102-103°/20 mm., n_D^20 1.4470. G.L.C. analysis showed the material to be completely free of any close boiling impurities.

Analysis: C_{14}H_{24}O_4

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>68.3%</td>
<td>68.2%</td>
</tr>
<tr>
<td>H</td>
<td>5.8%</td>
<td>5.8%</td>
</tr>
</tbody>
</table>

4,4-Dimethylcyclohexane-1,1-dicarboxylic acid (IV)

A 5-liter, single-necked, round bottomed flask equipped with a multi-bulb reflux condenser and an electric heating mantle was charged with diester III (556 g., 2.11 moles), potassium hydroxide (268 g., 4.78 moles) pre-dissolved in 3 liters of water, and 0.5 g. commercial detergent. The two phase mixture became homogeneous after two hours at reflux. After cooling to 0°, the solution was added slowly to a rapidly stirred excess of 20%
hydrochloric acid at 0°. The fluffy, white precipitate of the desired diacid (IV) was filtered on a Buchner funnel, washed 3 times with cold water and air dried. The yield of 4,4-dimethylcyclohexane-1,1-dicarboxylic acid (IV) (400 g., 2.0 moles) was 92% based on diester III. A small sample was recrystallized three times from 1:1 water:ethanol, and dried in a desiccator. Analytical sample: m.p. 190.0-192.0°.

Analysis: C_{10}H_{16}O_{4}

\[
calcd. \quad C \quad 60.0\% \quad H \quad 8.1\%
found \quad C \quad 59.7\% \quad H \quad 8.0\%
\]

4,4-Dimethylcyclohexanecarboxylic acid (V)

Decarboxylation of the diacid (IV) was effected by heating the diacid (136 g., 0.72 moles) with 0.5 g. of powdered pyrex glass in a 1-liter, round bottom flask equipped with a multi-bulb reflux condenser. Evolution of carbon dioxide commenced soon after all the diacid had melted, as noted with the aid of a bubbler connected to the top of the condenser. The reaction usually required 1/2 hour to complete. Upon cooling, the residue solidified with the formation of shiny, white needles. Crystallization from ethanol-water mixture (1:1) afforded 4,4-dimethylcyclohexanecarboxylic acid (V) (94 g., 0.63 moles) (m.p. 45-47°) in 87% yield based on diacid (IV). A small amount was recrystallized from ethanol-water giving as an
analytical sample, material which had a m.p. of 47.0-48.2°.

Analysis: \( \text{C}_9\text{H}_{16}\text{O}_2 \)

- calcd. C 69.2% H 10.3%
- found C 69.4% H 10.4%

Methyl-4,4-dimethylcyclohexanecarboxylate (VI)

The esterification of acid V was carried out following the method of Clinton and Laskowski (28).

To a three liter, single-necked round bottomed flask equipped with a multi-bulb reflux condenser and an electric heating mantle was charged acid V (312 g., 2.0 moles), absolute methanol (192 g., 6.0 moles), ethylene dichloride (1-liter), and concentrated sulfuric acid (3 ml.). The homogeneous solution was refluxed for twelve hours, cooled, and washed successively with water, dilute sodium bicarbonate solution, and again with water, and dried by percolation through anhydrous magnesium sulfate. The dried material was stripped of ethylene dichloride and distilled at atmospheric pressure. There was obtained methyl-4,4-dimethylcyclohexanecarboxylate (VI) (306 g., 1.8 moles) (b.p. 201-202°, \( n^D_{20} 1.4438 \)) in 90% yield based on acid V.

Analysis: \( \text{C}_{10}\text{H}_{18}\text{O}_2 \)

- calcd. C 70.5% H 10.7%
- found C 70.0% H 10.7%

4,4-dimethylmethanolicyclohexane (VII)

To a 3-necked, 3-liter flask equipped with an aluminum coil reflux condenser, Hershberg stirrer, addition
funnel, and an electric heating mantle was charged powdered lithium aluminum hydride (72.2 g, 1.9 moles) and dry ether (1.5 liters). The stirred suspension was brought to reflux and ester VI (305 g, 1.8 moles) was added at such a rate that vigorous reflux was maintained without external heating. After the addition was completed (about one hour), the solution was refluxed an additional hour, cooled to room temperature, and partially hydrolyzed with ice water (until hydrogen evolution ceased). Complete hydrolysis was then effected with cold, dilute sulfuric acid. The organic layer was separated, washed with water, and dried by percolation through magnesium sulfate. The ether was moved on a rotary vacuum stripper to afford 4,4-dimethylmethanolcyclohexane (VII) (181 g, 1.4 moles) in 78% yield based on ester VI. The alcohol was not further purified. G.L.C. and I.R. analyses confirmed the absence of unchanged ester and also the homogeneity of the material.

4,4-Dimethylacetoxymethylcyclohexane (VIII)

To a 1-liter, single-necked flask equipped with a multi-bulb reflux condenser was charged acetic anhydride (132.5 g, 1.3 moles) and methanesulfonic acid (1 ml.). The solution was heated to reflux with an electric heating mantle and alcohol VII (181 g, 1.4 moles) was added through the condenser at such a rate so as to maintain a vigorous reflux without external heating. Reflux was continued an
additional 1/2 hour. After cooling, an equal volume of ether was added and the organic residue washed successively with water, dilute sodium bicarbonate solution, and again with water. The ether-acetate solution was dried through magnesium sulfate and stripped of ether. The crude acetate (194 g., 1.19 moles, an 85% yield based on alcohol VII) was not further purified. G.L.C. analysis indicated that but one compound was present.

4,4-Dimethylmethylenecyclohexane (IX)

The pyrolysis of the above acetate was carried out by passing the crude acetate through a vertical glass tube packed with glass helices and heated with an electric furnace. The temperature of the tube was electronically controlled at 570 ± 5° and acetate VIII (194 g., 1.19 moles) was added at a rate of 5 ml./minute. The crude pyrolysate was taken up in an equal volume of ether and washed successively with water, dilute sodium bicarbonate solution, and again with water. The organic solution was dried through magnesium sulfate, stripped of ether and distilled at about 5 plate efficiency affording 4,4-dimethylmethylenecyclohexane (IX) (102 g., .83 moles) in 70% yield (b.p. 136-137°/750mm.). It was redistilled at about 25 plate efficiency to yield IX (90 g., 0.725 moles) with b.p. 138.84°/760mm., nD 1.4484-1.4486.
Analysis: C₉H₁₆

  calcd.  C  87.1%  H  12.9%
  found   C  86.9%  H  13.1%

Infrared spectrograms: Plate I, Fig. 1, page 98.

1,1,4-Trimethylcyclohexane (X)

Hydrogenation of the olefin (IX) was carried out in a 300 ml. stainless steel autoclave which was electronically heated and thermostated. To the bomb was charged olefin (IX) (89 g., 0.72 moles) and 1 g. 20% nickel-on-Kieselguhr catalyst ground in 5 ml. of 99% grade n-hexane. The bomb was flushed with nitrogen and pressured to 1500 psig. with hydrogen and heated at 100° for 3/4 hours. After cooling and filtration of the catalyst, the hydrocarbon mixture showed no unsaturation by a bromine test. Distillation of the mixture at about 25 plate efficiency yielded 2,2,4-Trimethylcyclohexane (X) (88 g., 0.70 moles) in 98% based on olefin IX having the following physical properties (see Table I, page ?);

<table>
<thead>
<tr>
<th>Property</th>
<th>This work</th>
<th>Lit. (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.p. °C/760mm.</td>
<td>136.53</td>
<td>135.</td>
</tr>
<tr>
<td>n²⁰</td>
<td>1.4262</td>
<td>1.4251</td>
</tr>
<tr>
<td>d²⁰</td>
<td>0.7737</td>
<td>0.7722</td>
</tr>
<tr>
<td>M.p. °C</td>
<td>-86.47</td>
<td>--</td>
</tr>
<tr>
<td>Tfo</td>
<td>-86.33</td>
<td>--</td>
</tr>
<tr>
<td>Α</td>
<td>0.029</td>
<td>--</td>
</tr>
<tr>
<td>Purity</td>
<td>99.40</td>
<td>--</td>
</tr>
</tbody>
</table>
Infrared spectrogram: Plate I, Fig. 2, page 98.

Analysis: \( C_9H_{18} \)

Calcd. C 85.6%  H 14.4%

Found  C 85.5%  H 14.5%

C. Synthesis of cis and trans-1-Methyl-3-ethylcyclohexanes

3-Methyl-5-ethyl-4,6-dicarboethoxy-2-cyclohexene-1-one (I)

The condensation of ethyl acetoacetate and propionaldehyde was carried out according to the procedure of Horning et al. (30) extensively modified to fit the large scale-up used in this work. To a 15-gallon, monel metal, reaction vessel equipped with a motor-driven stirrer and multi-channel reflux condenser, and jacketed for use with refrigerated water or steam, was charged ethyl acetoacetate (19.39 kg., 149.2 moles) and piperidine (350 ml.). The mixture was cooled to 15° and propionaldehyde (4.315 kg., 74.45 moles) was added with stirring. The temperature of the reaction mixture was not allowed to exceed 25° over the period of addition (about two hours). The mixture was stirred over night (twelve hours) at 15-20°. The cooling was halted and the cold water replaced with hot water (55°). Stirring was continued at this temperature for twenty-four hours. The hot water was then replaced with steam. The temperature of the reaction mixture reached 90°, which produced a vigorous reflux. Steam was continued for twenty-four hours, maintaining a temperature of 90°. After cooling, the crude mixture of
3-methyl-5-ethyl-4,6-dicarboethoxy-2-cyclohexene-1-one (I) and water, formed by spontaneous dehydration, was used without further purification for the next step.

3-Methyl-5-ethyl-2-cyclohexene-1-one (II)

The crude diester (I) was divided into two equal portions and each was charged to a 22-liter, round bottomed flask equipped with a teflon paddle, motor-driven stirrer and a multi-bulb reflux condenser to which was attached a tube leading to a bubbler. To each flask was added glacial acetic acid (8.0 liters) and concentrated sulfuric acid (1.0 liter). The addition of acids caused an immediate exothermic reaction which produced a gentle reflux and slow evolution of carbon dioxide, as noted on the bubbler. After the initial reaction had subsided (1 hour), external heat was applied with an electric heating mantle and stirring was started. Vigorous reflux and evolution of carbon dioxide was produced. Heating was continued for three days, at which time the carbon dioxide evolution had become negligible. After cooling, sodium hydroxide (2.0 kg.) dissolved in 4 liters of water, was added (with care to prevent violent reflux). Addition of the alkali produced a two phase mixture accompanied by precipitate of sodium sulfate in the lower, aqueous layer. The organic layer was separated and washed four times with 1/3 the volume of a hot (50°) saturated sodium sulfate solution. The washed organic residue (17.8 kg.) was very quickly
vacuum distilled to remove it from any high boiling mate-
rial. The distillate was then redistilled to yield 3-
methyl-5-ethyl-2-cyclohexene-1-one (II) (6.42 kg., 46.6
moles), in 31.4% yield based on ethyl acetoacetate. The
ketone had; b.p. 103-105°/10mm., n^20 \text{D} 1.4855-1.4859, (lit.
98-102°/9mm.) (30). Along with the desired ketone (II),
there was obtained the mono-decarboxylated compound 3-
methyl-5-ethyl-4-carboethoxy-2-cyclohexene-1-one (1.0
kg.) which was recycled through the decarboxylation step.
Analysis: \( C_{9}H_{14}O \)

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>78.2%</td>
<td>78.1%</td>
</tr>
<tr>
<td>H</td>
<td>10.2%</td>
<td>10.1%</td>
</tr>
</tbody>
</table>

3-Methyl-5-ethylcyclohexanol (III)

Hydrogenation of ketone II was carried out in a 1-
gallon, stainless steel, mechanically stirred autoclave.
In a typical experiment ketone II (2530 g., 18.33 moles)
and nickel on Kieselguhr catalyst (5 g.) (activated by
passing hydrogen over it at 400°) was charged to the auto-
clave. The autoclave was flushed with nitrogen and then
pressured to 2000 psig. with hydrogen. The autoclave
was heated slowly, the absorption of hydrogen beginning
at 50°. Heating was continued to 220°, at which tempera-
ture absorption ceased after one-half hour. The contents
were cooled and the catalyst was removed by filtration on
a Buchner funnel affording crude 3-methyl-5-ethylcyclo-
hexanol (III) (2570 g., 18.08 moles) in 98.7% yield which
was not further purified. Infrared and G.L.C. analyses indicated the absence of unchanged ketone. The crude alcohol was presumed to be a complex mixture of stereoisomers (indicated by the G.L.C. analysis).

**Methylethylcyclohexenes (IV)**

The thermal dehydration of alcohol III was carried out in the following manner. In a typical experiment, alcohol III (5115 g., 36.0 moles) was mechanically pumped through a $2.2 \times 100$ cm. column of alumina (2-4 mesh) at a rate of 5 ml./minute. The temperature of the pyrolysis tube was electronically controlled at $375 \pm 5^\circ$ throughout the addition of the alcohol. The effluent gases were condensed with a spiral type glass condenser yielding a two phase mixture. The lower, aqueous layer was siphoned out and the upper, hydrocarbon layer was dried by passing it through a column of 40-200 mesh silica gel. The crude hydrocarbon was then distilled quickly to remove any unchanged alcohol and other high boiling material. The fraction boiling at $147-148^\circ$ was taken as material for the next step. The dehydration step was expected to produce a complex mixture of olefin isomers. However, G.L.C. analysis was unable to resolve more than one component, which was present in at least 97% of the total. The yield of methylethylcyclohexenes (IV) was 4320 g. (34.9 moles), or 97% based on alcohol III.
cis and trans 1-Methyl-3-ethylcyclohexane (Va and Vb)

Hydrogenation of the olefinic mixture (IV) was carried out in a manner similar to that previously used. The 1-gal. top stirring autoclave was charged with the mixture of olefins (IV) (2407 g., 19.45 moles), nickel catalyst (5 g.), flushed with nitrogen, and pressured to 2000 psig. with hydrogen. The stirred mixture was heated to 150° and appeared to be saturated after one hour. Removal of the catalyst afforded crude cis and trans-1-methyl-3-ethylcyclohexane (Va and Vb) (2379 g., 18.87 moles) in 97.4% based on olefin IV. G.L.C. analysis indicated the mixture to be comprised of 65.8% of the lower boiling cis isomer and 34.2% of the higher boiling trans isomer, having $n_D^{20}$ 1.4374. A bromine test for unsaturation indicated some unsaturation. Rehydrogenation following the above procedure afforded material having the same ratio of isomers with $n_D^{20}$ 1.4370. An unsaturation test was still positive. The crude mixture was then subjected to aqueous, basic potassium permanganate solution for twenty four hours. Only a trace of unsaturation appeared in a third bromine test. The hydrocarbon mixture was then distilled at about 120 plate efficiency to yield cis and trans 1-methyl-3-ethylcyclohexane. G.L.C. analysis indicated virtually no trace of impurities, however, the high boiling trans-isomer showed unsaturation by a bromine test as did the last few
fractions of the distillation. A small fraction of the trans isomer was treated successively with aqueous potassium permanganate, molten sodium, and finally aqueous sodium permanganate. After washing with water and drying through a column of silica gel, the hydrocarbon showed no sign of unsaturation. The two isomers had the following physical properties (see Table II, page 11):

<table>
<thead>
<tr>
<th></th>
<th>cis-1-methyl-3-ethylcyclohexane (Va)</th>
<th>trans-1-methyl-3-ethylcyclohexane (Vb)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>B.P. °C/760mm.</strong></td>
<td>Va 148.35</td>
<td>Vb 151.06</td>
</tr>
<tr>
<td></td>
<td>Lit. (19) 148. 151.</td>
<td></td>
</tr>
<tr>
<td><strong>n D</strong></td>
<td>Va 1.4327</td>
<td>Vb 1.4374</td>
</tr>
<tr>
<td></td>
<td>Lit. (19) 1.433 1.439</td>
<td></td>
</tr>
<tr>
<td><strong>d 4</strong></td>
<td>Va 0.7837</td>
<td>Vb 0.8012</td>
</tr>
<tr>
<td></td>
<td>Lit. (19) 0.785 0.795</td>
<td></td>
</tr>
<tr>
<td><strong>M.P. °C</strong></td>
<td>Va (glassy)</td>
<td>Vb (glassy)</td>
</tr>
<tr>
<td></td>
<td>Lit. (19) --</td>
<td></td>
</tr>
<tr>
<td><strong>Purity %</strong></td>
<td>Va 99.5+(est)</td>
<td>Vb 99.5+(est)</td>
</tr>
<tr>
<td></td>
<td>Lit. (19) --</td>
<td></td>
</tr>
</tbody>
</table>

Analysis: \( C_9H_{18} \)

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>Vb found</th>
<th>Vb found</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C</strong></td>
<td>C 85.6%</td>
<td>C 85.6%</td>
<td>C 85.6%</td>
</tr>
<tr>
<td><strong>H</strong></td>
<td>H 14.4%</td>
<td>H 14.5%</td>
<td>H 14.6%</td>
</tr>
</tbody>
</table>

Irradiated spectrogram: Va Plate II, Fig. 1, page 99
Vb Plate I, Fig. 3, page 98.

1-Methyl-3-ethyl benzene (VI)

Aromatization of methylethylcyclohexene (IV) was effected by dehydrogenation over pelletized chromia-alumina catalyst. The catalyst tube (2.2 x 35 cm.) was heated to 450° and the olefin mixture IV (343 g., 2.80 moles) was added at a rate of 6 ml./minute. The effluent vapors were
condensed (except hydrogen, which was routed to the outside) through a spiral, glass condenser. G.L.C. analysis of the crude condensate indicated a 75% conversion to the aromatic product. Distillation at 25 plate efficiency afforded 1-methyl-3-ethyl benzene (VI) having the following properties (See Table III, page 13):

<table>
<thead>
<tr>
<th>Property</th>
<th>This work</th>
<th>Lit. (50)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P. °C/760mm.</td>
<td>161.33</td>
<td>161.305</td>
</tr>
<tr>
<td>n°D</td>
<td>1.4966</td>
<td>1.49660</td>
</tr>
<tr>
<td>d°D</td>
<td>0.8647</td>
<td>0.86452</td>
</tr>
<tr>
<td>M.P. °C</td>
<td>-97.201</td>
<td>(I) -95.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(II) -96.96</td>
</tr>
<tr>
<td>Purity</td>
<td>99.51</td>
<td>99.87</td>
</tr>
</tbody>
</table>


Analysis: C$_9$H$_{12}$

calcd. C 89.9%  H 10.1%
found C 89.9%  H 10.1%

D. Synthesis of 1,cis-2,cis-4-Trimethylcyclopentane exo and endo-5-Norbornene-2-carboxaldehyde (I)

To a 5-liter, three-necked, round-bottomed flask equipped with a motor driven, teflon paddle stirrer, multi-bulb reflux condenser, dropping funnel and an electric heating mantle was charged freshly dedimerized cyclopentadiene (475 g., 7.2 moles) and ether (1 liter). The homogeneous mixture was stirred rapidly and acrolein (403 g.,
7.2 moles) was added from a dropping funnel. The addition was continued at a rate such that mild reflux was maintained. After the addition of acrolein was completed, (two and one-half hours) the mixture was heated to reflux and was stirred for an additional twelve hours. The homogeneous solution was stripped of ether on a steam bath and the nearly colorless residue was distilled under reduced pressure at about 5 plate efficiency. There was obtained a mixture of \textit{exo} and \textit{endo}-5-norbornene-2-carboxaldehyde (I) (700 g., 6.47 moles) in 90\% yield based on acrolein. The adduct had the following physical properties; b.p. 63-65\(^\circ\)/17\text{mm.}, \(n_D^{20}\) 1.4878-1.4899 (lit. b.p. 70-72\(^\circ\)/20\text{mm}, \(n_D^{19}\) 1.4886) (31).

\textit{exo} and \textit{endo}-5-Methyl-2-norbornene (II)

The conversion of the aldehyde (I) to the hydrocarbon was effected by the method of Wolff-Kishner. To a 5-liter, three-necked, round-bottomed flask equipped with a motor driven Hershberg stirrer, multi-bulb reflux condenser, dropping funnel, thermometer well, and electric heating mantle, was charged commercial grade sodium hydroxide (400 g., 10.0 moles), dihydrazine sulfate (810 g., 10.0 moles), and diethylene glycol (1400 ml.). The mixture was stirred rapidly and heated to 95\(^\circ\) and aldehyde I (620 g., 5.0 moles) was added without external heating. Heating and stirring were continued for two hours at a maximum pot temperature of 120\(^\circ\). Heating was halted
momentarily and more sodium hydroxide (200 g., 5.0 moles) was added. The reaction flask was fitted with a large bore glass tube leading to a water-cooled 5-liter receiving flask. The mixture was heated moderately and the hydrocarbon product distilled out into the receiver, accompanied by vigorous nitrogen evolution. When the distillation approached completion (slow nitrogen evolution), water (200 ml.) was added to drive out any remaining hydrocarbon. The condensed hydrocarbon was separated from the water layer and dried through a column of silica gel. The dried residue was distilled at atmospheric pressure at about 20 plate efficiency. There was obtained exo and endo-2-methyl-5-norbornene (445 g., 3.7 moles) in 74% based on aldehyde (I). An analytical sample had the following properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>This work</th>
<th>Lit. (31)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P. °C/760mm.</td>
<td>116.24</td>
<td>115.5-117°/750mm.</td>
</tr>
<tr>
<td>( n_D^{20} )</td>
<td>1.4596</td>
<td>( n_D^{18} ) 1.4606</td>
</tr>
<tr>
<td>( d_4^{20} )</td>
<td>0.8665</td>
<td>( d_4^{18} ) 0.8668</td>
</tr>
<tr>
<td>M.P. °C</td>
<td>-67.35</td>
<td>--</td>
</tr>
</tbody>
</table>

Analysis: \( C_8H_{12} \)

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>88.8%</td>
<td>88.6%</td>
</tr>
<tr>
<td>H</td>
<td>11.2%</td>
<td>11.1%</td>
</tr>
</tbody>
</table>

exo and trans-4-Methyl-1,cis-3-cyclopentanedicarboxylic acid (III)

In a typical experiment, an 8 gal., glass lined steel reactor equipped with a motor driven stirrer, ther-
momometer well, and cooling jacket was charged with methyl-norbornene II (216 g., 2.0 moles), t-butyl alcohol (600 ml.), water (9.0 l.), and potassium nitrate (40 g.). The mixture was cooled to 5° and saturated with gaseous carbon dioxide. To the rapidly stirred mixture was added finely crystalline potassium permanganate (632 g., 4.0 moles). During addition, the mixture was continually suffused with gaseous carbon dioxide and not allowed to exceed a temperature of 10°. The addition usually required two and one-half to three hours. The reaction mixture was stirred at 5-10° an additional twelve hours after the addition of the permanganate. The reaction products were filtered from the manganese dioxide on a Buchner funnel and the filter cake was washed three times with water. The clear, light-yellow filtrate was concentrated to a small volume on a steam bath and acidified with 37% hydrochloric acid. The diacid did not precipitate, hence was extracted with ether. The ether extracts were combined, dried through magnesium sulfate and stripped of ether, affording cis and trans-4-methyl-1,cis-3-cyclopentanedicarboxylic acid (III) (190 g., 1.1 moles) in 55% yield from norbornene II, which crystallized on standing. Properties of an analytical sample (recrystallized three times from water) were: m.p. 101.0-102.5° (lit. m.p. 94°) (32).
Analysis: $C_8H_{12}O_4$

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>55.8%</td>
<td>55.6%</td>
</tr>
<tr>
<td>H</td>
<td>7.0%</td>
<td>6.9%</td>
</tr>
</tbody>
</table>

Dimethyl-cis and trans-4-methyl-1,cis-3-cyclopentanedicarboxylate (IV)

The esterification of diacid III was carried out according to the method of page 57. In a typical experiment, a 3-liter single-necked, round-bottomed flask equipped with a reflux condenser and electric heating mantle was charged with diacid III (360 g., 2.09 moles), absolute methanol (768 g., 12.4 moles), ethylene dichloride (1300 ml.), and conc. sulfuric acid (5.0 ml.). The mixture was refluxed for twelve hours, cooled, and washed successively with water, dilute sodium bicarbonate solution, and finally again with water, and dried through anhydrous magnesium sulfate. The ethylene dichloride was removed on a rotary evaporator and the residue vacuum distilled affording dimethyl-cis and trans-4-methyl-1,cis-3-cyclopentanedicarboxylate (IV) (393 g., 1.97 moles) in 94% yield having the following physical properties:

b.p. 119-120°C/15mm., $n^20_D$ 1.4515

Analysis: $C_{10}H_{16}O_4$

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>60.0%</td>
<td>60.4%</td>
</tr>
<tr>
<td>H</td>
<td>8.1%</td>
<td>8.0%</td>
</tr>
</tbody>
</table>
cis and trans-4-methyl-1,cis-3-cyclopentanediolmethanol (V)

The hydride reduction of diester IV was carried out essentially by the method of Miller and Greenlee (23). In a typical experiment, diester (IV) (156 g, 0.78 moles) was reacted with lithium aluminum hydride (38.0 g, 1.0 moles) in tetrahydrofuran (700 ml, freshly distilled and dried over lithium aluminum hydride). There was obtained cis and trans-2-methyl-1,cis-3-cyclopentanediolmethanol (V) (100 g, 6.95 moles) in 89% yield based on diester IV.

The vacuum distilled material had the following physical properties: b.p. 101-102°C/1mm., n_D^20 1.4803.

Analysis: C_9H_18O_2

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>66.6%</td>
<td>66.5%</td>
</tr>
<tr>
<td>H</td>
<td>11.2%</td>
<td>11.3%</td>
</tr>
</tbody>
</table>

Ditosylation of diol (V) was effected by a method already reported (37) except that the temperature was held between -20 and -15°C. The diol (V) (288 g, 2.0 moles) was dissolved in anhydrous pyridine (900 ml.) and cooled in an isopropanol:dry-ice bath. Powdered p-toluenesulfonyl chloride (838 g, 4.4 moles) was added with the aid of a powder funnel at a rate such that the temperature remained below -15°C. After stirring an additional hour, the bath was changed to ice-water and stirring was continued overnight. While cool, the thick mixture was poured over
dilute sulfuric acid and ice. The acidified mixture was filtered on a Buchner funnel, washed several times with cold water and air dried. Recrystallization from methanol afforded the desired cis and trans-4-methyl-1, cis-3-cyclopentanedicarboxylate (VI) with m.p. 52°C. An analytical sample had the following property; m.p. 56-57.8°C.

Analysis: C_{22}H_{28}O_{6}S_{2}

<table>
<thead>
<tr>
<th></th>
<th>calcd</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>58.4%</td>
<td>58.3%</td>
</tr>
<tr>
<td>H</td>
<td>6.2%</td>
<td>6.2%</td>
</tr>
<tr>
<td>S</td>
<td>21.2%</td>
<td>21.3%</td>
</tr>
</tbody>
</table>

1, cis-2, cis-4-Trimethylcyclopentane (VII)

In a typical reaction lithium aluminum hydride (8 g., 0.21 moles) and lithium hydride (24 g., 3.0 moles) were suspended in dry tetrahydrofuran (3.0 liters). The mixture was heated to reflux and finely powdered ditosylate VI (452 g., 1.0 moles) was added from a powder funnel. The reaction was very mildly exothermic but external heating was maintained throughout addition and for 12 hours following. The tetrahydrofuran solvent was then removed by distillation under reduced pressure and condensed in dry-ice-cooled traps. Very little hydrocarbon distilled over during this process (fractionation of condensate yielded only a trace of high boiling material). Ether (3.0 l.) was added and hydrolysis was effected partially with water then with completely with cold dilute sulfuric acid. The ether hydrocarbon layer was separated and the
aqueous layer was extracted with ether, combining the extracts with the original ether layer. The combined ether solution was washed with dilute sodium bicarbonate solution and then with glycerin-water (1:1) and dried through anhydrous magnesium sulfate. The ether was removed on a steam bath and the hydrocarbon residue was fractionated at about 20 plate efficiency affording a 70:30 mixture of ctc and ccc-1,2,4-trimethylcyclopentanes. The physical properties of the desired ccc isomer were as follows:
(see also Table IV, page 17).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P.°C/760mm</td>
<td>116.75</td>
</tr>
<tr>
<td>nD20</td>
<td>1.4185</td>
</tr>
<tr>
<td>d420</td>
<td>0.762</td>
</tr>
<tr>
<td>M.P.°C</td>
<td>-132.32</td>
</tr>
<tr>
<td>Purity %</td>
<td>99.77</td>
</tr>
</tbody>
</table>

Analysis: C8H16

calcd. C 85.7% H 14.3%
found  C 85.7% H 14.3%

Infrared spectrogram: Plate II, Fig. 2, page 99.

E. Synthesis of 1,trans-2,cis-3-trans-4-Tetramethylcyclopentane

trans-3-Methyl-5-norbornene-2-carboxaldehyde (I)

In a typical experiment, crotonaldehyde (970 g., 13.0 moles) and dicyclopentadiene (924 g., 7.0 moles) was charged to a glass lined 3.5 l. autoclave. The homogeneous mixture was heated slowly, without shaking, to 150°. External heating was halted, after which the temperature
rose spontaneously to 200° in a period of thirty-five minutes. The temperature was allowed to drop on its own to 170°, at which point it was held with external heating an additional hour. G.L.C. analysis of the crude reaction product indicated a 65-70% conversion to the mixture of **trans** aldehydes, along with smaller amounts of the two **cis**-aldehydes. Vacuum distillation of the crude product afforded the aldehyde mixture (1060 g., 7.8 moles) having the following physical properties: b.p. 84-88°C/30mm. (lit. b.p. 80°C/15mm.) (52).


(trans-5,6-Dimethyl-2-norbornene (II))

To a 5-liter, three-necked, round-bottomed flask equipped with a motor driven, mercury sealed Hershberg stirrer, multi-bulb reflux condenser, and thermometer well was charged dihydrazine sulfate (810 g., 10.0 moles), sodium hydroxide (400 g., 10.0 moles), and diethylene glycol (1400 ml.). The mixture was stirred and heated with an electric heating mantle to 95° and the aldehyde mixture (I) (680 g., 5.0 moles) was added. Heating was continued for two hours at a pot temperature of 165°. The mixture was cooled to 140° and more sodium hydroxide (200 g., 5.0 moles) was added. The reaction flask was fitted with a large bore glass tube leading to a round
bottomed flask immersed in cold tap water. Heat was applied and the hydrocarbon product was distilled from the reaction flask (50 ml. n-octanol was an aid in reducing foaming due to vigorous nitrogen evolution). When the distillation neared completion (one hour), water (200 ml.) was added to drive over the remaining hydrocarbon. The hydrocarbon was separated from the water layer and steam distilled, then dried through silica-gel. Distillation at about 20 plate efficiency afforded trans-5,6-dimethyl-5-norbornene (II) (380 g., 3.12 moles), in 62.3% based on aldehyde (I) with the following physical properties:

<table>
<thead>
<tr>
<th></th>
<th>This work</th>
<th>Lit. (23)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P.°C/760mm.</td>
<td>132.50</td>
<td>132.53</td>
</tr>
<tr>
<td>n\textsuperscript{D}\textsubscript{20}</td>
<td>1.4552</td>
<td>1.4552</td>
</tr>
</tbody>
</table>

\textit{cis-4,trans-5-Dimethyl-1,cis-3-cyclopentanedicarboxylic acid (III)}

In a typical experiment dimethylnorbornene II (610 g., 5.0 moles), t-butyl alcohol (6 liters), water (20 liters), and potassium nitrate (30 g.) was charged to an 8 gal. glass lined reactor (Pfaudler Mfg. Co.) equipped with a motor driven stirrer, thermometer well and jacketed for temperature control. The mixture was cooled to 5° and finely crystalline potassium permanganate (1580 g., 10.0 moles) was added at such a rate that the temperature did not exceed 20°. The last of the permanganate was discolored immediately. The pH of the reaction mixture was
controlled by suffusing it continuously with gaseous carbon dioxide, thus maintaining a mildly basic medium. The reaction products were filtered from the manganese dioxide on a Buchner funnel. The manganese dioxide filter cake was washed three times with 1 liter portions of water and the clear, light yellow filtrate was evaporated to a small volume on a steam bath, then was acidified with 37% hydrochloric acid. The diacid which precipitated was filtered and washed with cold water on a Buchner funnel, then recrystallized from water, yielding the diacid III (650 g., 3.5 moles) in 70%; m.p. 148.0-149.2°. A small sample was recrystallized from water to give an analytical sample; m.p. 149.1-149.6°. (lit. m.p. 149.0-149.6°.) (23) Analysis: C₉H₁₄O₄

<table>
<thead>
<tr>
<th>Calcd.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 58.0%</td>
<td>C 57.8%</td>
</tr>
<tr>
<td>H 7.6%</td>
<td>H 7.7%</td>
</tr>
</tbody>
</table>

Dimethyl-cis-4,trans-5-dimethyl-1,cis-3-cyclopentanedicarboxylate (IV)

The cyclopentane diacid (III) obtained above was esterified according to a method used previously (28). To a 1-liter, single-necked, round bottomed flask equipped with a multi-bulb reflux condenser and an electric heating mantle was charged diacid (III) (158 g., 0.85 moles), absolute methanol (163 g., 5.1 moles), ethylene dichloride (510 ml.), and concentrated sulfuric acid (3 ml.). The homogeneous solution was refluxed for twelve hours, cooled and washed successively with water, dilute sodium bicar-
bonate solution and again with water, and was dried through anhydrous magnesium sulfate. The washed and dried organic residue was stripped of ethylene dichloride and distilled under vacuum. There was obtained dimethyl-cis-4, trans-5-dimethyl-1,cis-3-cyclopentanedicarboxylate (IV) (171 g., 0.80 moles) in 94% yield based on diacid III.

<table>
<thead>
<tr>
<th>This work</th>
<th>Lit. (23)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P. °C/760 mm.</td>
<td>120-121</td>
</tr>
<tr>
<td>nD</td>
<td>1.4516</td>
</tr>
<tr>
<td>M.P. °C</td>
<td>-3.85</td>
</tr>
</tbody>
</table>

Analysis: C_{11}H_{18}O_4

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>61.7%</td>
<td>61.8%</td>
</tr>
<tr>
<td>H</td>
<td>8.5%</td>
<td>8.7%</td>
</tr>
</tbody>
</table>

Dimethyl-cis-4,trans-5-dimethyl-1,trans-3-cyclopentanedicarboxylate (IV)

The isomerization of diester (IV) was accomplished by base catalyzed epimerization of the ester group in position 3. In a typical experiment the diester (IV) (254 g., 1.2 moles) was added to a solution of sodium (28 g., 1.2 g. atoms) in absolute methanol (2 liters). The homogeneous solution was refluxed overnight. G.L.C. analysis of an aliquot showed no unrearranged diester when compared to an authentic sample. The bulk of the methanol was stripped off under reduced pressure and the residue was diluted with ice water (200 ml.). Ether extraction of the aqueous solution afforded the rearranged product, dimethyl-cis-4,trans-5-dimethyl-1,trans-3-cyclopentanedi-
carboxylate (235 g., 92.5%) which crystallized from ether at dry ice temperatures. A recrystallized sample had a m.p. of 37.2-38.9°.

Analysis: $\text{C}_{11}\text{H}_{18}\text{O}_4$

- calcd. C 61.7% H 8.5%
- found C 61.8% H 8.5%

A small sample was saponified to the diacid which had the following properties; m.p. 132.4-133.4°, mixed m.p. with diacid III, 110°.

Analysis: $\text{C}_{9}\text{H}_{14}\text{O}_4$

- calcd. C 58.1% H 7.6%
- found C 58.1% H 7.7%

**cis-4,trans-5-Dimethyl-1,trans-3-cyclopentanedimethanol (VI)**

Lithium aluminum hydride reduction of diester V was effected by a procedure already described on page 72. In a typical experiment diester V (235 g., 1.1 moles) was reacted with lithium aluminum hydride (46 g., 1.2 moles) in 2 liters of dry tetrahydrofuran. There was obtained 163 g. (1.03 moles) of the desired diol (VI) in 93.7% yield. An analytical sample recrystallized from ether (at -60°) had m.p. 44.0-45.6°.

Analysis: $\text{C}_{9}\text{H}_{18}\text{O}_2$

- calcd. C 68.3% H 11.5%
- found C 68.2% H 11.3%
cis-4, trans-5-Dimethyl-1, trans-3-cyclopentanediol-ditosylate (VII)

Ditosylation of diol VI was carried out by the procedure already described on page 72. In a typical experiment diol VI (162 g., 1.02 moles) was reacted with p-toluenesulfonyl chloride (426 g., 2.24 moles) in 1200 ml. pyridine. There was obtained 490 g. (0.97 moles) of ditosylate VII in 95.6% based on diol VI. An analytical sample recrystallized from methanol had m.p. 81.6-82.4°.

Analysis: C_{23}H_{30}O_{6}S_{2}

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (%)</td>
<td>59.2%</td>
<td>59.2%</td>
</tr>
<tr>
<td>H (%)</td>
<td>6.5%</td>
<td>6.5%</td>
</tr>
<tr>
<td>S (%)</td>
<td>13.7%</td>
<td>13.7%</td>
</tr>
</tbody>
</table>

1, trans-2, cis-3, trans-4-Tetramethylcyclopentane (VIII)

Reductive hydrogenolysis of the above ditosylate (VI) was carried out according to the general procedure described on page 73. In a typical experiment ditosylate VII (489 g., 0.97 moles) was reacted with lithium aluminum hydride (7.6 g., 0.20 moles) and lithium hydride (15.3 g., 1.94 moles) in 1300 ml. tetrahydrofuran. Isolation and distillation at about 20 plate efficiency afforded 82.1 g. (0.63 moles) of the hydrocarbon (VIII) in 65% yield based on ditosylate VII. The material had the following physical properties (see Table V, page 19);
This work | Lit. (5)
---|---
B.P. °C/760mm. | 127.23 | 127.4
n\textsubscript{D}\textsuperscript{20} | 1.4155 | 1.415
\(d_4\textsuperscript{20} | 0.7562 | 0.748
M.P. °C | glassy | --
Purity % | 99+ (est) | --

Analysis: \(C_9H_{18}\)

<table>
<thead>
<tr>
<th>calcd.</th>
<th>found</th>
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</thead>
<tbody>
<tr>
<td>C 85.6%</td>
<td>C 85.4%</td>
</tr>
<tr>
<td>H 14.4%</td>
<td>H 14.4%</td>
</tr>
</tbody>
</table>

Infrared spectrogram: Plate II, Fig. 3, page 99.

F. Synthesis of 1,cis-2,cis-3-trans-4-tetramethylcyclopentane

endo-cis-5-norbornene-2,3-dimethanol (I)

Diels-Alder condensation of cyclopentadiene and cis-2-butene-1,4-diol was effected following the method of Alder and Windemuth (53). In a typical experiment di-


cyclopentadiene (512 g., 3.5 moles), cis-2-butene-1,4-diol (512 g., 5.8 moles) and dioxane (1 liter), was charged to a 3.5 liter autoclave and heated at 200° for 2 hours. Vacuum distillation afforded the desired diol (I) (539 g., 3.5 moles) in 61% yield based on the butene-1,4-diol.

The diol caused some difficulty by crystallizing in the distillation apparatus but heating tapes alleviated the problem. Recrystallization was not necessary since the
distilled material melted at nearly the same temperature as an analytical sample recrystallized from ether. The sample had m.p. 84.0-86.0° (lit. 84.5-86.2°) (23). Mixed melting point with an authentic sample (23) showed no depression.

**endo-cis-5-Norbornene-2,3-dimethanolditosylate (II)**

The tosylation of diol I was carried out according to the procedure described earlier on page 72. In a typical experiment diol I (308 g., 2.0 moles) was reacted with p-toluenesulfonyl chloride (838 g., 4.4 moles) in pyridine (900 ml.). There was obtained 838 g. (1.8 moles) of the desired totosylate II in 90% yield. An analytical sample recrystallized from methanol had m.p. 103.8-104.8° (lit. 103.6-104.6°) (23). Mixed melting point with an authentic sample showed no depression.

**endo-cis-5,6-Dimethyl-2-norbornene (III)**

Reductive hydrogenolysis of the above ditosylate was effected following the method already described on page 73. In a typical experiment ditosylate II (694 g., 1.5 moles) afforded dimethylnorbornene III (146 g., 1.2 moles) in 79% yield. The material had the following physical properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>This work</th>
<th>Lit. (23)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P. °C/760mm</td>
<td>143.28</td>
<td>143.31</td>
</tr>
<tr>
<td>n^20_D</td>
<td>1.4650</td>
<td>1.4650</td>
</tr>
</tbody>
</table>
The infrared spectrum was identical with an authentic sample.

cis-4,cis-5-Dimethyl-1,cis-3-cyclopentanedicarboxylic acid (IV)

To a 12-liter, 3-necked flask equipped with a Hershberg stirrer, thermometer well and dropping funnel and immersed in an ice-water bath was charged water (2 liters), t-butyl alcohol (500 ml.), and norbornene III (61 g., 0.5 moles). The mixture was cooled to 5° and 85% sodium permanganate (223 g., 1.3 moles) dissolved in 1.2 liters of water was added at such a rate that the temperature remained below 20°. The pH of the solution was controlled by constant suffusion with dry-ice vented in through a side neck, thus maintaining a mildly basic solution. The last of the permanganate was discolored immediately and the reaction products were filtered from the manganese dioxide on a Buchner funnel. The filter cake was washed several times with warm water and the total aqueous filtrate was evaporated to a small volume on a steam bath under a jet of dry air. The small residue was acidified with 37% hydrochloric acid. The desired diacid IV which precipitated was filtered on a Buchner funnel, washed and recrystallized from water. There was obtained 31 g. (0.38 moles) of the diacid in 33% yield with m.p. 201-202°, (lit. 201.3-202.3°) (23). Mixed melting point with authentic diacid showed no depression.
cis-4,cis-5-Dimethyl-1,cis-3-cyclopentanedicarboxylic acid anhydride (V)

In a typical experiment diacid IV (124 g., 1.52 moles) was dissolved in acetic anhydride (500 ml.) in a 1 liter flask equipped with a take-off condenser head. After refluxing for 12 hours, the bulk of the acetic anhydride-acetic acid mixture was distilled off. The residue was then distilled under reduced pressure. There was obtained 238 g. (1.41 moles) of the desired anhydride V (b.p. 102-104°/1mm) in 93% yield. The distilled material crystallized from benzene-cyclohexane for analysis: m.p. 119.6-121.3° (lit. m.p. 119°) (54).


Analysis: C₉H₁₂O₃

<table>
<thead>
<tr>
<th></th>
<th>Calcd.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>64.3%</td>
<td>64.2%</td>
</tr>
<tr>
<td>H</td>
<td>7.1%</td>
<td>7.2%</td>
</tr>
</tbody>
</table>

cis-4,cis-5-Dimethyl-1,trans-3-cyclopentanedicarboxylic acid (VI)

To a 3-liter flask was charged anhydride V (236 g., 1.4 moles) and sodium (64.4 g., 1.4 g. atoms) reacted with 1.5 liters absolute methanol. The homogeneous solution was refluxed for 12 hours, then water (300 ml.) was added and the solution refluxed for 12 more hours. The bulk of the methanol was removed by distillation and the residue was cooled to 0° and acidified with 37% hydrochloric acid. The crystalline diacid which precipitated
was filtered and recrystallized from water. There was obtained the desired trans diacid VI (242 g., 1.3 moles) in 92.5% yield. An analytical sample had the following properties: m.p. 156.5-158.0°; mixed m.p. with authentic IV, 130°.

Analysis: \( C_9H_{14}O_4 \)

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>58.1%</td>
<td>58.4%</td>
</tr>
<tr>
<td>H</td>
<td>7.6%</td>
<td>7.5%</td>
</tr>
</tbody>
</table>

Dimethyl-cis-4,cis-5-dimethyl-1,trans-3-cyclopentanedicarboxylate (VII)

Esterification of diacid (VI) was effected by the method already described earlier on page 57. In a typical experiment diacid VI (200 g., 1.16 moles) was refluxed 12 hours with absolute methanol (100 g.), ethylenedichloride (200 ml.), and concentrated sulfuric acid (1 ml.).

The crude product was purified by vacuum distillation. There was obtained 202 g. (0.95 moles) of the desired diester in 95% yield. B.p. 87-88°/0.5mm., \( n_D^{20} 1.4541 \), m.p. 31.3-31.5°.

Analysis: \( C_{11}H_{18}O_4 \)

<table>
<thead>
<tr>
<th></th>
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<th>found</th>
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</thead>
<tbody>
<tr>
<td>C</td>
<td>61.7%</td>
<td>61.6%</td>
</tr>
<tr>
<td>H</td>
<td>8.5%</td>
<td>8.6%</td>
</tr>
</tbody>
</table>

cis-4,cis-5-Dimethyl-1,trans-3-cyclopentanedicarboxylic acid methanol (VIII)

The reduction of the above diester (VII) was accomplished by the method already described on page 72. In a typical experiment 166 g. (0.78 moles) of diester was reacted with 38 g. (1.0 moles) of lithium aluminum hydride
in 1000 ml. of tetrahydrofuran to yield 120 g. (0.76 moles) of the desired diol in 97.5% yield which was vacuum desiccated and used as is for the next step. A small sample was distilled under vacuum for analytical purposes; b.p. 126-127°C/1mm., nD 1.5021.

Analysis: C9H18O2

<table>
<thead>
<tr>
<th></th>
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<th>found</th>
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</thead>
<tbody>
<tr>
<td>C</td>
<td>68.3%</td>
<td>68.5%</td>
</tr>
<tr>
<td>H</td>
<td>11.5%</td>
<td>11.4%</td>
</tr>
</tbody>
</table>

**cis-4,cis-5-Dimethyl-1,trans-3-cyclopentanedimethanolditosylate (IX)**

Tosylation of the above diol was carried out according to method described earlier on page 72. In a typical experiment diol VIII (108 g., 0.68 moles) was reacted with p-toluenesulfonyl chloride (333 g., 1.75 moles) in dry pyridine (400 ml.). There was obtained after crystallization from methanol 226 g. (0.48 moles) of the desired ditosylate (IX). A small sample was recrystallized from methanol as an analytical sample; m.p. 63.4-64.6°C.

Analysis: C23H30O6S2

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>59.2%</td>
<td>59.2%</td>
</tr>
<tr>
<td>H</td>
<td>6.5%</td>
<td>6.6%</td>
</tr>
<tr>
<td>S</td>
<td>13.7%</td>
<td>13.6%</td>
</tr>
</tbody>
</table>

1,cis-2,cis-3,trans-4-Tetramethylcyclopentane (X)

Reductive hydrogenolysis of the ditosylate was carried out after the procedure already described on page 73. In a typical experiment ditosylate X (283 g., 0.61 moles), was reacted with lithium aluminum hydride (4.0 g., 0.11 moles), and lithium hydride (16.0 g., 2.0 moles) in tetra-
hydrofuran (800 ml.). There was obtained 68.3 g. (0.54 moles) in 89% yield. The crude material was then distilled at about 25 plate efficiency. Physical properties were as follows (see Table V, page 19);

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P. °C/760mm.</td>
<td>140.71</td>
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<tr>
<td>$n_D^{20}$</td>
<td>1.4248</td>
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<tr>
<td>$d_4^{20}$</td>
<td>0.7763</td>
</tr>
<tr>
<td>M.P. °C</td>
<td>glassy</td>
</tr>
<tr>
<td>Purity %</td>
<td>98+ (est)</td>
</tr>
</tbody>
</table>

Analysis: $C_{9}H_{18}$

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>85.6%</td>
<td>85.6%</td>
</tr>
<tr>
<td>H</td>
<td>14.4%</td>
<td>14.4%</td>
</tr>
</tbody>
</table>

Infrared spectrogram: Plate III, Fig. 2, page 100.

G. **Synthesis of 1,cis-2,trans,trans-4-Tetramethylcyclo-**

**pentane**

cis-4,trans-5-Dimethylcyclopentane-1,cis-3-dicarbonyl-

**chloride** (I)

a. using oxalyl chloride

The reaction was carried out essentially by the method of Gassman and Meinwald (44).

To a 1-liter, single necked round bottomed flask was charged the diacid prepared on page 76 (63.2 g., 0.34 moles), oxalyl chloride (100 g., 0.78 moles) and dry benzene (100 ml.). The flask was fitted with a reflux condenser and placed in a water bath maintained at 25°. The reaction commenced immediately as noted by bubbling in the flask due to the gaseous decomposition products of the mono-acid.
chloride of oxalic acid. After 3 hours, outgassing had ceased and the solution showed the absence of carboxylic acid by infrared analysis. The benzene and excess oxalyl-chloride were removed under vacuum and the residue vacuum distilled. There was obtained 67 g. (0.31 moles, 90%) of the diacid chloride (I); b.p. 110-111°/5mm., nD 1.4875.

Analysis: C9H12O2Cl2

calcd. C 48.0% H 6.3% Cl 31.5%
found C 48.5% H 5.4% Cl 30.2%

b. using phosphorous pentachloride

To a 2-liter, three necked round-bottomed flask equipped with a stirrer and reflux condenser was charged powdered phosphorous pentachloride (403 g., 1.9 moles). The flask was immersed in an ice-water bath and the dry diacid (177 g., 0.95 moles) was added from a powder addition funnel over a period of 1/2 hour. Reaction was instantaneous and the reaction mixture became liquid with the evolution of hydrogen chloride. After complete addition, the mixture was heated on a steam bath an additional hour and vacuum distilled to afford the diacid chloride (I) (200 g., 0.09 moles) in 90% yield; b.p. 108-110°/4mm., nD 1.4875. The infrared spectrum was identical to that of the material prepared in method (a) above.
cis-4, trans-5-Dimethyl-1, cis-3-cyclopentane-n,n-dimethyl-dicarboxamide (II)

In a typical experiment, a 5-liter, 3-necked round bottomed flask, equipped with an efficient stirrer, reflux condenser, and a glass inlet tube with a flared tip was charged ether (3 liters) and dicarbonyl chloride I (289 g., 1.29 moles). The flask was partially immersed in an ice-water bath and dimethylamine (234 g., 5.2 moles, 8% excess) was bubbled in below the surface of the liquid at a rate such that the reaction temperature remained below 10°. Addition usually required four hours to complete, whereupon the dimethylamine hydrochloride was filtered off on a Buchner funnel. Removal of the ether under vacuum afforded the diamide (II) (303 g., 5.19 moles, 99.5%) which solidified upon cooling. Recrystallization of a small amount from ether as an analytical sample; m.p. 69.4-71.0°.

Analysis: C₁₃H₂₄O₂Cl₂

calcd.  C 65.0%  H 10.1%  N 11.6%
found   C 64.6%  H 10.2%  N 11.4%

cis-4, trans-5-Dimethyl-bis(1, cis-3-dimethylaminomethyl) cyclopentane (III)

In a typical experiment, a 5-liter, 3-necked flask equipped with an efficient stirrer, metal coil reflux condenser and dropping funnel was charged powdered lithium aluminum hydride (95 g., 2.5 moles) and dry ethyl ether (1 liter). Diamide (II) (275 g., 1.15 moles) in 800 ml.
ether was added to the rapidly stirred suspension at a rate which maintained ether reflux. Addition usually required 2-3 hours, after which the solution was stirred an additional hour at reflux. Hydrolysis was effected with water and the inorganic salts were removed by filtration on a Buchner funnel. The filter cake was washed with ether and these washings combined with the main portion. The ether solution was dried through anhydrous magnesium sulfate and stripped of ether on a steam bath. Vacuum distillation afforded the diamine III (205 g., 0.97 moles, 81.6%); b.p. 73-74°/1mm., \( n_\text{D}^20 \) 1.4587.

Analysis: \( \text{C}_{13}\text{H}_{28}\text{N}_2 \)

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>75.6%</td>
<td>75.3%</td>
</tr>
<tr>
<td>H</td>
<td>13.3%</td>
<td>13.4%</td>
</tr>
<tr>
<td>N</td>
<td>13.2%</td>
<td>13.0%</td>
</tr>
</tbody>
</table>

\( \text{cis-4,trans-5-Dimethyl-bis(1,\text{cis-3-dimethylaminomethyl-cyclopentane-di-n-oxide}) (IV)} \)

In a typical experiment a 3-necked, 3-liter flask was immersed in an ice-water bath and charged with diamine III (102 g., 0.48 moles) and distilled water (800 ml.). The mixture was cooled to 0° and 136 ml. (1.2 moles \( \text{H}_2\text{O}_2 \)) of a 25% solution of hydrogen peroxide was added, with stirring, at such a rate that the temperature did not exceed 20°. The homogeneous mixture was stirred at 0-5° for an additional 6 hours and then overnight at room temperature, after which the solution was not basic to phenolphthalein. The solution was cooled to 10° and a small
amount of the enzyme catalase was added (as a water sus-
pension) to decompose the excess peroxide. The oxygen
produced was swept out of the flask with nitrogen. After
3 hours, the solution showed the absence of peroxide by
test with dilute aqueous potassium permanganate. The
water in the mixture was removed on a rotary vacuum strip-
per leaving a syrupy residue of crude diamine-oxide which
was used without purification for the next step. There
was obtained 119 g. (102 % based on diamine) of crude ma-
terial. A small amount was used to prepare the corre-
ponding pикrate (recrystallized from methanol); m.p.
204.0-206.2°.

*trans*-4,5-Dimethyl-1,3-dimethylenecyclopentane (V)

Pyrolysis of the above amine oxide was carried out
under conditions described by Cope (45). To a 1-liter
round bottomed flask connected to a short, wide bore glass
tube and water cooled condenser, was charged the diamine
oxide IV (119 g., 0.49 moles). A vacuum pump with large
pumping capacity was connected to the system and the amine
oxide heated to 125° at 50 mm. The pyrolysate vapors were
partially condensed in the condenser, and completely in a
dry-ice-cooled trap. The reaction was complete in 1/2
hour. The pyrolysate was washed free of dimethylhydroxyl-
amine, dried through magnesium sulfate, and distilled at
about 10 plate efficiency. G.L.C. analysis indicated a
product of very high (98+% purity, b.p. 138.30°/760 mm.,
n_D^20 1.4588.
Analysis: C_9H_{14}

calcd. C 88.4% H 11.6%
found C 88.4% H 11.5%

Infrared spectrogram: Plate III, Fig. 1, page 100.
1,cis-2,trans-3,trans-4-Tetramethylcyclopentane VIa

Method 1. To a 300 ml. stainless steel autoclave was
charged diolefin V (1.0 g.), n-hexane (30 ml.) and finely
ground nickel-kieselguhr catalyst (0.3 g.). The bomb was
flushed with nitrogen and pressured to 800 psig. with
hydrogen. The contents were heated at 125°, with shaking,
for one-half hour, after which the cooled mixture was de­
canted from the catalyst. G.L.C. analysis indicated the
product mixture to be made up of the following: 60% cctc
(VIb), 37% cctc (Vic), and 3% of the desired cctc (VIa).

Method 2. To a heavy walled glass bottle, was charged
diolefin V (1.0 g.), absolute ethanol (30 ml.), and plati­
num oxide (0.01 g.). The bottle was attached to a low
pressure hydrogenation apparatus and pressured to 50 psig.
with hydrogen. The mixture was shaken overnight at room
temperature and the catalyst removed by decantation. G.L.C.
analysis indicated a product distribution of 20% VIb, 60%
Vic, and 20% VIa.

Method 3. Hydroboration of the diene with diborane
was effected by the method of Brown (46). To a 250 ml.
round bottomed flask equipped with a teflon stirrer, reflux condenser, and dropping funnel was charged diene V (10 g., 0.008 moles), sodium borohydride (80 g., 0.20 moles), and diglyme (70 ml.). The mixture was cooled to 0° with stirring and flushed with dry nitrogen. Boron trifluoride etherate (38 g., 0.27 moles) was added over a period of 1.5 hours. The mixture was stirred an additional hour at 0° and then allowed to warm up to room temperature overnight. Propionic acid (74 g., 1.0 moles) was added and the mixture refluxed for 4 hours. Water (50 ml.) was added and the hydrocarbon-water azeotrope distilled off. There was obtained 8.2 g. (0.0067 moles) of the hydrocarbon mixture, an 84.2% yield. G.L.C. analysis of the product indicated a distribution of 20% VIb, 45% VIc, and 35% VIA.

Method 4. After a small experiment to determine the product ratio, the following procedure was used in the actual production of the desired cctt isomer (VIa).

In a typical experiment, a 2-liter, three-neck, round bottomed flask was charged with sodium borohydride (39.6 g., 1.04 moles), 2-methyl-2-butene (200 g., 2.86 moles), and diglyme (435 ml.). The mixture was cooled with stirring to 0° and boron trifluoride etherate (194 g., 1.36 moles) was added over a period of 2 hours. Stirring was continued an additional 3 hours and diene V (50 g., 0.41 moles) was added in 1/4 hour. The mixture was allowed to
warm up (with stirring) to room temperature over a 12 hour period. Propionic acid (443 g., 6.0 moles) was added and the mixture refluxed for 5 hours. The 2-methylbutane was distilled off and water (300 ml.) was added to azeotrope off the hydrocarbon product. There was obtained 40 g. of the cycloparaffin mixture, an 80% yield. Distillation of combined runs at 25 plate efficiency afforded the desired cctt isomer (VIa) having the following physical properties (see Table V, page 19);

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P. °C/760mm.</td>
<td>142.94</td>
</tr>
<tr>
<td>$n_D^{20}$</td>
<td>1.4297</td>
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<tr>
<td>$d_4^{20}$</td>
<td>0.7733</td>
</tr>
<tr>
<td>M.P. °C</td>
<td>-112.02</td>
</tr>
<tr>
<td>Purity %</td>
<td>96.5 (min.)</td>
</tr>
</tbody>
</table>

Analysis: C$_9$H$_{18}$

<table>
<thead>
<tr>
<th></th>
<th>calcd.</th>
<th>found</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>85.6%</td>
<td>85.6%</td>
</tr>
<tr>
<td>H</td>
<td>14.4%</td>
<td>14.4%</td>
</tr>
</tbody>
</table>

Infrared spectrogram: Plate III, Fig. 2, page 100.
VI. CONCLUSION

1. The synthesis and characterization of 1,1,4-trimethylocyclohexane has been accomplished. This hydrocarbon, along with the previously known 1,1,2 and 1,1,3 isomers, completes the series of geminally substituted trimethylcyclohexanes.

2. The syntheses and characterizations of cis and trans 1-methyl-3-ethylocyclohexanes have been carried out. The method has been shown to be of general utility for the preparation of related 1,3-dialkylocyclohexanes free of isomeric impurities, i.e., the corresponding 1,2 or 1,4 isomers.

3. A simple method of synthesis for meta-substituted dialkyldibenzene, free of the ortho and para isomers, has been carried out.

4. A stereospecific synthesis of 1,cis-2,cis-4-trimethylocyclopentane has been accomplished. The physical properties of this hydrocarbon were found to be identical with those of the isomeric 1,cis-2,trans-4-trimethylocyclopentane, which had been prepared previously. The original designation of this second isomer (oct) was based merely on its physical properties. The conclusion of the present research is that the isomer prepared here (coo)
bears the correct designation and the isomer previously designated as the cct was incorrect and should be changed to the cccc designation.

5. A large scale method of the oxidative cleavage of cycloolefins to the corresponding dicarboxylic acids with permanganate has been developed.

6. The synthesis and characterization of three stereoisomeric 1,2,3,4-tetramethylocyclopentanes has been accomplished. Of the six stereoisomers, the cctc, cttc, and the cccc had been previously prepared. The present research completed the series with the synthesis of the ctcct, cttct and the ccoct isomers.

7. A study of the stereospecificity of hydrogenation of trans-4,5-dimethyl-1,3-dimethylenecyclopentane has been carried out. It was found that the use of di-sec-isoamylborane followed by proton displacement of the borane was quite selective. The results indicate that the cis-1,2-dimethylcyclopentane derivative is favored over the trans isomer.
VII. INFRARED SPECTROGRAMS
Fig. 1: Trans-4,5-dimethyl-1,3-dimethylene cyclopentane

Fig. 2: 1,cis-2,trans-3,trans-4-tetramethylcyclopentane

Fig. 3: 1,cis-2,cis-3,trans-4-tetramethylcyclopentane

Plate III
BIBLIOGRAPHY


42. API RP 44, Carnegie Inst. of Tech., Pittsburgh, Pa.


AUTOBIOGRAPHY

I, Bruce Michael Otto, was born March 20, 1936 in Tomah, Wisconsin, and received my early education in the public school system of that city. I entered Carroll College in Waukesha, Wisconsin in September, 1954 and was granted the Bachelor of Science degree in January, 1958. In March, 1958, I was appointed as a Teaching Assistant in The Department of Chemistry at The Ohio State University. In June, 1958, I joined the staff of the American Petroleum Institute, Project 58, as a Research Assistant, a position I held until June, 1962. In September, 1962, I rejoined the Chemistry Department staff of The Ohio State University as a Teaching Assistant. I held this position until March, 1963, while completing the requirements for the degree of Doctor of Philosophy.

I have accepted a position as a Research Chemist with the American Oil Company, Whiting, Indiana.