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The Ohio State University, Ph.D., 1968
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1969
STUDIES OF THE BEHAVIOR AND GENERATION OF CARBANIONS

PART I. INVERSION OF SECONDARY CYCLIC GRIGNARD REAGENTS

PART II. FRAGMENTATION OF AZOFORMATE SALTS AND ACYLAZO COMPOUNDS WITH BASES

DISSERTATION

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

By

Engelbert Pechhold

The Ohio State University

1968

Approved by

S Fraenkel
Adviser

Department of Chemistry
DEDICATION

To my wife, Ingrid, and my parents,
whose love, understanding, and encouragement
have made this venture possible.
ACKNOWLEDGEMENTS

I wish to express my deepest appreciation to Professor Gideon Fraenkel for suggesting this problem, and for his guidance and encouragement throughout the course of this research. His assistance in the preparation of this dissertation is gratefully acknowledged. It is an understatement to say that without his unusual courage of conviction and high standards for academic performance, this work could not have come into being. I owe special debt of gratitude to my colleagues for many stimulating discussions of chemical matters and otherwise. In particular, I wish to express my gratitude to Dr. Don Dix, Dr. Dave Adams, and James Morton, who gave me much insight in my research.

I wish also to thank Dr. Ralph Dougherty for his advice and help in interpreting the mass spectra. Furthermore, I wish to thank Dr. C. J. Pedersen of Du Pont Company who provided us with dicyclohexyl-18-crown-6, and Dr. K. Greenlee of Chemical Samples Company who supplied us with a few alicyclic hydrocarbons.

The National Institutes of Health and the United States Air Force are thanked for research assistantships which provided financial support during the course of this work.
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Chemistry of Carbanions Professor Gideon Fraenkel
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEDICATION</td>
<td>i</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>ii</td>
</tr>
<tr>
<td>VITA</td>
<td>iv</td>
</tr>
<tr>
<td>TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>ILLUSTRATIONS</td>
<td>viii</td>
</tr>
<tr>
<td>PART I</td>
<td></td>
</tr>
<tr>
<td>CHAPTER I</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION AND HISTORICAL REVIEW</td>
<td></td>
</tr>
<tr>
<td>Historical Background</td>
<td>3</td>
</tr>
<tr>
<td>Previous Research</td>
<td>4</td>
</tr>
<tr>
<td>II. PURPOSE AND METHOD OF RESEARCH</td>
<td>6</td>
</tr>
<tr>
<td>CHAPTER II EXPERIMENTAL</td>
<td></td>
</tr>
<tr>
<td>I. CHEMICALS</td>
<td>8</td>
</tr>
<tr>
<td>II. IDENTIFICATION OF SYNTHESIZED COMPOUNDS</td>
<td>9</td>
</tr>
<tr>
<td>III. SYNTHESES</td>
<td></td>
</tr>
</tbody>
</table>

- 1-Bromo-3,3-dimethylcyclobutane: 10
- 1-Phenyl-3,3-dimethylcyclobutanecarboxylic acid: 14
- 1-Bromo-2,2-dimethylcyclopentane: 16
- 1-Bromo-2,2-dimethylcyclohexane: 19
- 1-Bromo-3,3-dimethylcyclohexane: 24
- 1-Bromo-4,4-dimethylcyclohexane: 25
IV. PREPARATION OF THE ORGANOMETALLIC COMPOUNDS

Solvents, Metals .................................. 29
NMR Sample Tubes ................................. 30
Instrumentation ................................... 30
Procedure for the Preparation of Organometallic Compounds ................. 32
Grignard Reagents ................................. 32
3,3-Dimethylcyclohexyllithium .................. 35

CHAPTER III RESULTS AND DISCUSSION

Syntheses of Cyclic Bromides ....................... 36
Grignard Reagents .................................. 41
General Considerations ............................. 42

BIBLIOGRAPHY ....................................... 53

PART II

CHAPTER I

I. INTRODUCTION AND HISTORICAL REVIEW

Historical Background ............................. 55
Preparative Methods of Organometallic Compounds of Group IA-IIIA .......... 56

II. PURPOSE AND METHOD OF RESEARCH ................

I. CHEMICALS ...................................... 71

II. IDENTIFICATION OF SYNTHESIZED COMPOUNDS ............ 73

III. SYNTHESSES

Potassium Phenylazoformate ....................... 74
Benzoylphenylidimide ............................. 76
Phenyl-p-toluylidimide ............................ 77
(Dimethoxyphosphinyll)phenylidimide ............. 77
Benzoyl-t-butyldiimide ............................ 78
Carbomethoxy-t-butyldiimide ...................... 82
Dicyclohexyl-18-crown-6 .......................... 83
IV. FRAGMENTATION REACTIONS

Decarboxylation of Potassium Phenyl-azoformate .................. 86
General Procedure for the Base-catalyzed
Fragmentation of Acylazo Compounds .................. 88
Fragmentations of Benzoylphenyldiimide ........... 89
Fragmentation of Phenyl-p-toluoyldiimide .......... 91
Fragmentations of Benzoyl-t-butyldiimide .......... 92

V. REACTION OF t-BUTYLLITHIUM WITH METHYL BENZOATE

Products .......... 97

VI. METHYL BENZOATE(2,4,6-d3)

Preparation .......... 103
Reaction with t-Butyllithium .......... 105

VII. REACTIONS OF COMPOUND XXXVII ........ 106

CHAPTER III RESULTS AND DISCUSSION

Syntheses of Azoformate Salts .......... 109
Decarboxylation of Azoformate Salts .......... 110
Syntheses of Acylazo Compounds .......... 114
Base-catalyzed Fragmentations of Acylazo Compounds .......... 116
Reaction of t-Butyllithium with Methyl Benzoate .......... 130

BIBLIOGRAPHY .......... 159

TABLES

Table No. Page

1. Chemical Reagents, Part I .................. 8
2. Chemical Reagents, Part II .................. 71
3. Fragmentation of Acylazo Compounds .......... 117
4. Fragmentation of Benzoyl- and p-Toluoylphenyl-
diimide with Potassium Methoxide .......... 121
5. Fragmentation of Benzoyl-t-butyldiimide with Sodium and Potassium Methoxide .......... 122
6. Products from the Reaction of Methyl Benzoate with t-Butyllithium .......... 129
### ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Apparatus for Grignard and Organolithium Preparations</td>
<td>31</td>
</tr>
<tr>
<td>2.</td>
<td>Nmr Spectrum(60 MHz) of 3,3-Dimethylcyclobutylmagnesium Bromide, 1.5 M in Diglyme</td>
<td>44</td>
</tr>
<tr>
<td>3.</td>
<td>Nmr Spectrum of 3,3-Dimethylcyclobutylmagnesium Bromide, Methyl Region, Expanded Scale</td>
<td>45</td>
</tr>
<tr>
<td>4.</td>
<td>Nmr Spectrum(60 MHz) of 2,2-Dimethylcyclopentylmagnesium Bromide, Methyl Region</td>
<td>46</td>
</tr>
<tr>
<td>5.</td>
<td>Nmr Spectrum(60 MHz) of 2,2-Dimethylcyclohexylmagnesium Bromide, Methyl Region, a) at 60°, and b) at 170°</td>
<td>47</td>
</tr>
<tr>
<td>6.</td>
<td>Nmr Spectrum(60 MHz) of 3,3-Dimethylcyclohexylmagnesium Bromide, Methyl Region</td>
<td>48</td>
</tr>
<tr>
<td>7.</td>
<td>Nmr Spectrum(60 MHz) of 3,3-Dimethylcyclohexylmagnesium Bromide, 1.4 M in Diglyme</td>
<td>49</td>
</tr>
<tr>
<td>8.</td>
<td>Nmr Spectrum(60 MHz) of 4,4-Dimethylcyclohexylmagnesium Bromide, Methyl Region</td>
<td>50</td>
</tr>
<tr>
<td>9.</td>
<td>Nmr Spectrum(60 MHz) of 4,4-Dimethylcyclohexylmagnesium Bromide as a Function of Temperature, Methyl Region, a) at 75° b) at 175° c) at 200°</td>
<td>51</td>
</tr>
<tr>
<td>10.</td>
<td>Nmr Spectrum(60 MHz) of 3,3-Dimethylcyclobutylmagnesium Bromide, Methyl Region</td>
<td>52</td>
</tr>
<tr>
<td>11.</td>
<td>Apparatus for the Fragmentation of Acylazo Compounds</td>
<td>85</td>
</tr>
<tr>
<td>12.</td>
<td>Nmr Spectrum(60 MHz) of α-4-t-butylbenzylalcohol(XXXII)</td>
<td>145</td>
</tr>
<tr>
<td>13.</td>
<td>Nmr Spectrum(60 MHz) of l-Pivaloyl-4-t-butylcyclohexadiene-1,5(XXXIII)</td>
<td>146</td>
</tr>
<tr>
<td>14.</td>
<td>Nmr Spectrum(60 MHz) of l-Pivaloyl-4-t-butylcyclohexadiene-2,5(XL), Vinyl Region</td>
<td>147</td>
</tr>
<tr>
<td>15.</td>
<td>Nmr Spectrum(60 MHz) of α,α-Dimethyl-p-t-butylpropiophenone(XXXIV)</td>
<td>148</td>
</tr>
<tr>
<td>16.</td>
<td>Nmr Spectrum(60 MHz) of α,α-Di-t-butylbenzylalcohol(XXXV)</td>
<td>149</td>
</tr>
<tr>
<td>17.</td>
<td>Nmr Spectrum(60 MHz) of α,α-Di-t-butylbenzylalcohol-2,4,6-d3(XXXV-d3)</td>
<td>150</td>
</tr>
<tr>
<td>18.</td>
<td>Nmr Spectrum(60 MHz) of α-p-Di-t-butylbenzylalcohol(XXXVI)</td>
<td>151</td>
</tr>
<tr>
<td>19.</td>
<td>Nmr Spectrum(60 MHz) of Compound XXXVII</td>
<td>152</td>
</tr>
<tr>
<td>20.</td>
<td>Nmr Spectrum(100 MHz) of Compound XXXVII after Decoupling of the Vinyl Protons</td>
<td>153</td>
</tr>
</tbody>
</table>
21. Nmr Spectrum (60 MHz) of Compound XXXVII-d2 ........................................ 154
22. Nmr Spectrum (60 MHz) of Compound XXXVII-d8 ........................................ 155
23. Nmr Spectrum (60 MHz) of Compound XLII ...................................................... 156
24. Nmr Spectrum (60 MHz) of Compound XXXVIII ............................................... 157
25. Nmr Spectrum (60 MHz) of Compound XXXVIII-d8 ......................................... 158
PART I
CHAPTER I
I. INTRODUCTION AND HISTORICAL REVIEW

During the last decade the chemistry of organometallic compounds has undergone considerable progress and has become of great interest in the field of synthetic organic chemistry. Indeed, fundamental organometallic chemistry now represents one of the most fruitful sources of useful synthetic methods and mechanistic studies in the discipline of organic chemistry.

The first preparation of an organometallic compound was reported in 1849 when Frankland (1) accidently isolated dialkylzinc compounds by the reaction of alkyl iodides with metallic zinc. Shortly afterwards alkyl compounds of mercury, tin, and germanium were isolated. But probably the most far-reaching discovery came with the first preparation of organomagnesium halides by Grignard (2) in 1900 and the research on organoalkali compounds by Schlenk (3) in the 1910's. The discovery of these types of organometallic compounds had considerable impact on synthetic organic chemistry. Since then efforts were made to characterise the nature of the carbon metal bond in organometallic compounds of group IA and IIA. These organometallic reagents are usually described as having ionic or partially ionic carbon metal bonds since the products of their
reactions can easily be rationalized in this way. A pyramidal configuration is assumed for carbanions as the methide ion is isoelectronic with ammonia. Ammonia is known to have a rapidly inverting pyramidal structure (4). Such a configuration places the unshared pair of electrons and the negative charge of carbanions in an sp³ orbital.

Saunders and Yamada (5) were the first investigators to study the inversion of amines by the use of nuclear magnetic resonance technique. For the inversion of dibenzylmethylamine they found a rate constant of $2 \pm 1 \times 10^5 \text{ sec}^{-1}$ at 25°.

Chemical studies of organometallic reagents of lithium and magnesium revealed evidence for the inversion of carbanions at carbon bonded to metal. Since an asymmetric carbanion has a tetrahedral geometry one would expect that optically active precursors should result in organometallic reagents having retention of configuration. The first stereochemical evidence concerning carbanions was reported by Letsinger (6). He prepared 2-octyllithium at -70° from optical active 2-octyl iodide and sec-butyllithium. The product was carbonated, still at -70°, to give 2-methyloctanoic acid with 20% retention of configuration. However, carbonation of the 2-octyllithium at 0° gave inactive acid. This clearly indicated that the rate of
inversion is a function of temperature. A much more extensive study of the stereochemistry of carbanions was undertaken by Curtin and Koehl (7,8). They started with optically active di-sec-butylmercury and prepared the corresponding lithium compound by reaction with octyllithium. By carrying out the reaction in pentane below -80°C, they obtained upon carbonation 2-methylbutanoic acid with up to 85% net retention. At temperatures above 0°C or by using a pentane-ether(6%) solvent mixture, the acid obtained was completely racemic.

Others have used nmr spectroscopy as a tool to investigate the inversion phenomenon. In the nmr spectra of organometallic reagents, the hydrogen atoms adjacent to the carbon metal bond are shifted to high field, 10 to 12 τ, well above the protons in the corresponding hydrocarbons. These shifts have been attributed in part to the ionic character of the carbon metal bond (9). An upfield shift occurs as the electronegativity of the metal decreases. The ionic character of the carbon metal bonds and the inversion parameters obtained from nmr data are closely related (10), downfield shifts can usually be correlated with a decrease in the inversion rate. This takes place in the order Li>Mg>Al>Hg.

Independently, Fraenkel and Roberts studied the rate of inversion of some organometallic compounds. Roberts and co-workers used 3,3-dimethylbutylmetallic reagents as model compounds (11). They
found considerable temperature dependence for the $\alpha$- and
$\beta$-methylene proton resonance of 3,3-dimethylbutylmagnesium chloride.
The nmr spectrum changed from an $A_2X_2$ at $35^\circ$ to an $AA'XX'$ pattern
at $-50^\circ$.

The observation of two distinct vicinal coupling constants at low
temperature indicated that inversion of configuration at the
$\text{CH}_2\text{MgX}$ center is slow on the nmr time scale. The authors believed
that changes in conformational population are not responsible for
the thermal changes among the spectra and attributed it to inversion
at the methylene center. At the same time Fraenkel and Dix (12)
reported the kinetics of inversion of 2-methylbutylmagnesium bromide.
At $-30^\circ$ the methylene protons at the carbon-magnesium center of this
compound gave rise to the $\text{AB}$ portion of an $\text{ABX}$ spectrum. With
increasing temperature, this pattern progressively collapsed to
$A_2$ of an $A_2X$ spectrum. Analysis of the results revealed that changes
among the nmr spectra were due to different rates of inversion at
the $\text{CH}_2\text{Mg}$ carbon atom.

In 1965 Roberts (13) reported that secondary Grignard reagents
invert much more slowly than primary reagents. As reasonable models
for secondary Grignard reagents he used 3,3-dimethylcyclobutylmagnesium
bromide and 2,4-dimethyl-pentyl-3-magnesium chloride. Neither of
these two compounds showed a significant temperature dependence in its spectrum. The doublet for the methyl protons in the cyclic Grignard reagent and the two symmetrical doublets for the isopropyl methyl protons in the 2,4-dimethylpentyl-3-magnesium chloride did not change between 30 and 120°, indicating inversion to be slow. No attempts have been made to study more flexible five- and six-membered rings.
II. PURPOSE AND METHOD OF RESEARCH

At the time this research was undertaken there was, and still is, considerable interest in the nature of organometallic reagents and their degree of carbanionic character. The favored method for the study of these has been nmr spectroscopy. So far, only primary Grignard reagents and lithium compounds have been examined by different researchers (9, 10, 11, 12, 13). A comparison of the rate of inversion of primary and secondary Grignard reagents might be useful for determination of the inversion mechanism.

The method we have chosen consisted of synthesizing several cyclic geminally methylated organomagnesium compounds, and monitoring their nmr spectra as a function of temperature.

\[
\begin{align*}
\text{CH}_3 & \quad (\text{CH}_2)_n \quad \text{H} \\
\text{CH}_3 & \quad (\text{CH}_2)_n \quad \text{MgX}
\end{align*}
\]

It has been known that ring inversion of four- and six-membered cyclic compounds is usually fast on the nmr time scale at room temperature (14, 15, 16). Therefore if inversion at the CH-Mg center is slow one should see a doublet for the methyl protons. In the event of fast inversion one would expect collapse of the two methyl peaks to one sharp line halfway between the two original peaks. This
applies also to the five-membered ring compound, since it has been
found by Brutcher(16a) that the circulating puckering motion of these
rings is extremely fast.
Thus from the nmr lineshapes of the methyl resonance, it should be
possible to obtain the rate of inversion from the nmr spectrum.

Below we describe the synthesis of a number of cyclic halides.
Because some of these reactions involved interesting carbonium ion
ring expansions, we have investigated these systems in some detail.
The conversion of these halides to organometallic reagents is
discussed. The nmr spectra of the reagents is compared to what would
be expected for various relative rates of carbanion inversion. This
will lead to some qualitative conclusions concerning carbanion
inversion in cyclic organomagnesium reagents.
CHAPTER II
EXPERIMENTAL

I. CHEMICALS.
Chemical reagents used in this work which were obtained from commercial sources are listed in the following table:

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Manufacturer</th>
<th>Grade, Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis(2-methoxyethyl) ether</td>
<td>Matheson Coleman</td>
<td></td>
</tr>
<tr>
<td>Cyclobutanecarboxylic acid</td>
<td>Columbia Org. Chem.</td>
<td></td>
</tr>
<tr>
<td>Cyclopentanecarboxylic &quot;</td>
<td>Columbia Org. Chem.</td>
<td></td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>Eastman Org. Chem.</td>
<td>East. Grade</td>
</tr>
<tr>
<td>Diethyl malonate</td>
<td>Eastman Org. Chem.</td>
<td>East. Grade</td>
</tr>
<tr>
<td>1,2-Dimethylcyclopentene-1</td>
<td>Chemical Samples Co</td>
<td></td>
</tr>
<tr>
<td>3,3-Dimethylcyclohexanol</td>
<td>Chemical Samples Co</td>
<td>Practical</td>
</tr>
<tr>
<td>3,3-Dimethylglutaric acid</td>
<td>Eastman Org. Chem.</td>
<td>East. Grade</td>
</tr>
<tr>
<td>Lithium dispersion + 1% Na</td>
<td>Lithium Corporation</td>
<td>30% in Wax</td>
</tr>
<tr>
<td>Magnesium metal</td>
<td>Dow Chemical Co</td>
<td>Triply Subl.</td>
</tr>
<tr>
<td>Methanesulfonyl chloride</td>
<td>Matheson Coleman</td>
<td>Practical</td>
</tr>
<tr>
<td>Methylmagnesium iodide</td>
<td>Arapahoe Chemicals</td>
<td>3 M in Ether</td>
</tr>
<tr>
<td>Neopentyl chloride</td>
<td>K &amp; K Laboratories</td>
<td></td>
</tr>
<tr>
<td>Neopentyl glycol</td>
<td>Eastman Org. Chem.</td>
<td>East. Grade</td>
</tr>
<tr>
<td>Phenylacetonitrile</td>
<td>Eastman Org. Chem.</td>
<td>East. Grade</td>
</tr>
<tr>
<td>p-Toluenesulfonyl chloride</td>
<td>Eastman Org. Chem.</td>
<td></td>
</tr>
</tbody>
</table>
II. IDENTIFICATION OF SYNTHESIZED COMPOUNDS.

Physical Constants:

All boiling points were those obtained during distillation and are uncorrected. All melting points were determined using a capillary apparatus or a Fisher-Johns apparatus and are uncorrected.

Analyses:

Elemental microanalyses of synthesized compounds were carried out by the microanalytical laboratories of Dr. A. Bernhardt, Mühlheim (Germany), or Galbraith Analytical Laboratories.

Spectrometric Methods:

Nuclear magnetic resonance spectra were obtained on a Varian Model A-60 spectrometer. Infrared absorption spectra were obtained with a Perkin-Elmer Model 137 sodium chloride spectrometer.

Vapor phase chromatographic work was undertaken with an Aerograph Hy-FI Model 600 and an Aerograph 'Autoprep' Model A-700. All analyses determined by v.p.c. have been corrected for the weight:area factor utilizing an internal standard, except where otherwise designated. All v.p.c. analyses were done on a 30% Silicon gum rubber SE-30 on 45/60 chromosorb W or 20% FFAP on 60/80 chromosorb W.
III. SYNTHESSES.

Preparation of 1-Bromo-3,3-dimethylcyclobutane(I)

1,3-Dibromo-2,2-dimethylpropane.

The bromide was prepared following the procedure of Franke (17).

In a 1-l three-necked flask fitted with a mechanical stirrer, a reflux condenser with a dropping funnel, and a thermometer was placed 104 g (1 mole) of neopentyl glycol (recrystallized from benzene).

Neopentyl glycol was heated above its melting point and 270 g (1 mole) of phosphorus tribromide was slowly added through the dropping funnel over a period of two hours. Evolution of hydrobromic acid occurred. After all the phosphorus tribromide had been added, the yellow solution was gently refluxed with stirring for fourteen hours. After that the same amount of water was added to the highly viscous, orange solution, and the bromide was separated by steam distillation. The bromide was then extracted with ether, washed with distilled water, dried over magnesium sulfate, and finally distilled under reduced pressure to give 84 g (36.6%) of 1,3-dibromo-2,2-dimethylpropane, b.p. 66-67.5° (14 mm). (Lit. b.p. 67°, 13 mm).

1,3-Diiodo-2,2-dimethylpropane.

In a 3-l three-necked flask equipped with a mechanical stirrer, thermometer, and dropping funnel, were placed 137.2 g (1.32 moles) of neopentyl glycol, 1060 ml of chloroform and 343 g (3 moles) of methanesulfonyl chloride. After stirring was started the flask was
cooled by an ice bath, and 850 ml (10.55 moles) of pyridine was added dropwise at a temperature below 5°. Stirring was continued at this temperature for five hours and for an additional three hours at room temperature. The reaction mixture was acidified with a 10% solution of hydrochloric acid to remove the pyridine and washed three times with distilled water. The solution was dried over magnesium sulfate and the chloroform removed by distillation at reduced pressure. The solid residue was recrystallized from absolute ethanol to give 315g (92%) of neopentyl glycol dimesylate, m.p. 61-61.5°.

A 5-l three-necked flask was equipped with a reflux condenser, mechanical stirrer, and dropping funnel. In the flask were placed 312g (1.2 moles) of dimesylate, 720g (4.8 moles) of sodium iodide, and 2100 ml of ethylene glycol monoethyl ether. The iodide dissolved completely in the cellosolve. Stirring was started and the reaction mixture was heated under reflux for one day. A mixture of 1000 ml of ether: benzene/1:1 and 1000 ml of water was added next. The ether-benzene layer was washed once with sodium bisulfite solution and then several times with distilled water and dried over magnesium sulfate. The solvent was evaporated and the residue distilled under reduced pressure to yield 332g (85.4%) as colorless 1,3-diiodo-2,2-dimethylpropane, b.p. 77° (1.5 mm). (Lit.19 b.p. 70-71°, 1 mm).
3,3-Dimethylcyclobutane-1,1-dicarboxylic acid.

The acid was prepared following the procedure of Campbell (19).

Potassium isopropoxide was prepared from 116.5g (2.96g atoms) of potassium and 3310 ml of absolute isopropanol in a 5-1 three-necked flask equipped with a mechanical stirrer, reflux condenser with drying tube and dropping funnel. Diethyl malonate (238g, 1.49 moles) were added with stirring to the potassium isopropoxide solution. A white precipitate was formed. The reaction mixture was heated at reflux temperature for four days. Next, a solution of 220g of potassium hydroxide in 1100 ml 50% aqueous ethanol was added and refluxing continued for another twelve hours. Isobutyl alcohol was then removed by steam distillation. The residual solution was acidified with hydrochloric acid and extracted with ether. Evaporation of the dried extract and crystallization from ether gave 114.6g (44%) of 3,3-dimethylcyclobutane-1,1-dicarboxylic acid (107g, 51% yield from diiodide), m.p. 171-172°.

3,3-Dimethylcyclobutancarboxylic acid.

97.6g of 3,3-dimethylcyclobutane-1,1-dicarboxylic acid was heated in 250 ml flask with a reflux condenser at 180° for three hours. The resulting yellow solution was distilled under reduced pressure, yielding 70g (97%) of colorless 3,3-dimethylcyclobutane-carboxylic acid, b.p. 106-107° (15mm). (Lit.19 b.p. 105-106°, 15mm). Decarboxylation of 3,3-dimethylcyclobutane-1,1-dicarboxylic acid-d gave the corresponding 3,3-dimethylcyclobutane-1d-carboxylic acid-d.
1-Bromo-3,3-dimethylcyclobutane (I).

The procedure used is similar to that of Cason and Wallcave (20).

A suspension of 3,3-dimethylcyclobutanecarboxylic acid (40g, 0.312 mole) in 600 ml of distilled water was neutralized with 13 ml of 30% ammonium hydroxide. A solution of silver nitrate (53.2g, 0.312 mole) in 200 ml of distilled water was added dropwise to the stirred solution of the acid. An additional 100 ml of water was added and the white precipitate was filtered, washed with water, then methanol, and dried in an oven at 50-60°. For the next step, the dried silver salt was powdered and sieved into a crystal dish. The silver salt was now dried in a vacuum oven at 80° for sixty hours. The yield consisted of 70g (90.4%) of silver 3,3-dimethylcyclobutanecarboxylate. The finely powdered silver salt (70g, 0.298 mole) was placed in a 1-l three-necked flask equipped with a dropping funnel, reflux condenser and mechanical stirrer. All this equipment had been thoroughly dried in an oven at 100°. To the salt was added 360 ml of olefin-free dry pentane. The stirrer was started and bromine (47.7g, 0.298 mole), dried over phosphorous pentoxide, was slowly added through the dropping funnel over a period of forty-five minutes. At first cooling was necessary, as the exothermic reaction was quite vigorous. When all the bromine had been added, the mixture was heated under reflux for one hour. It was then filtered and the silver bromide was washed on the filter with 100 ml of pentane. The filtrate was washed once with 200 ml of a 10% sodium
bisulfite solution, then with distilled water and dried over magnesium sulfate. Evaporation of the solvent and distillation of the residue afforded 26.5 g (54.7%) of l-bromo-3,3-dimethylcyclobutane as a colorless oil, b.p. 45.5-46.5 ° (32 mm). (Lit. 21 b.p. 132 °). The purity of the compound was confirmed by v.p.c. The infrared spectrum (NaCl, neat) showed strong bands (cm⁻¹) at 2900, 1440, 1405, 1340, 1260, 1230, 990, and 788. The nmr spectrum (benzene, TMS internal standard) showed resonance at 7.580 (quintet, methine, J=8 cps), 7.77 (doublet, methylene, J=8 cps), 8.99 (singlet, methyl), 9.19 (singlet, methyl).

Anal. Calcd for C₈H₁₁Br: C, 44.18; H, 6.80; Br, 49.02. Found : C, 44.15; H, 6.76; Br, 49.09.

The Hunsdiecker reaction of 3,3-dimethylcyclobutane-1d-carboxylic acid-d resulted in the formation of l-bromo-3,3-dimethylcyclobutane-1d.

Preparation of l-Phenyl-3,3-dimethylcyclobutanecarboxylic Acid

The procedure used was a modification of that of Weston (22).

1-Cyano-l-phenyl-3,3-dimethylcyclobutane.

In a 2-l three-necked flask fitted with a mechanical stirrer, dropping funnel, and reflux condenser with drying tube were placed sodium amide (79.5 g, 2.04 moles), and 500 ml of anhydrous ether. Phenylacetonitrile (119 g, 1.02 moles) was added slowly to the above stirred solution. The mixture was refluxed for four hours and then diluted with 500 ml of anhydrous ether. The addition of 1,3-diiodo-
2,2-dimethylpropane (330g, 1.02 moles), prepared as above, was followed by fourteen hours of refluxing. Cold water was then added cautiously, the insoluble material removed by filtration and the ether layer dried and concentrated. Distillation of the residue under reduced pressure gave 96.5g (52.2%) of 1-cyano-1-phenyl-3,3-dimethylcyclobutane, b.p. 92-94° (2mm).

Infrared (KBr, neat): cm$^{-1}$ 2250 (C=N).

l-Phenyl-3,3-dimethylcyclobutanecarboxylic acid.

A mixture of 96g (0.517 mole) of 1-cyano-1-phenyl-3,3-dimethylcyclobutane and 300 ml of 48% hydrobromic acid was refluxed with stirring for forty-eight hours. After cooling, a solid precipitated. This was filtered and dissolved in ether. The crude acid was extracted into a 10% solution of sodium hydroxide and then again liberated by acidification of the alkaline solution. The solid acid was filtered and recrystallized from Skelly B, to give 94.5g (89.8%) of l-phenyl-3,3-dimethylcyclobutanecarboxylic acid, m.p. 90-90.5°. The infrared spectrum (KBr, CCl$_4$) showed a strong, broad band (cm$^{-1}$) at 2920 (-CO$_2$H), and the nmr spectrum (CDCl$_3$) peaks at $\tau$ 2.23 (singlet, carboxyl), 2.84 (singlet, aromatic), 7.49 (center of AB quartet, methylene, J=12cps), 8.84 (singlet, methyl), and 9.02 (singlet, methyl).
Preparation of 1-Bromo-2,2-dimethylcyclopentane (II).

The procedure used was a modification of that of Kishner (23).

Methyl cyclobutanecarboxylate.

In a 500 ml three-necked flask fitted with a mechanical stirrer, dropping funnel, and reflux condenser, was placed thionyl chloride (143 g, 1.2 moles). To this was added during the course of an hour cyclobutanecarboxylic acid (100 g, 1.0 mole) by means of a dropping funnel. When all the acid had been added the mixture was heated under reflux for one hour, after which the evolution of hydrochloric acid and sulfur dioxide ceased. The solution was cooled and anhydrous methanol (38.5 g, 1.2 moles) was added slowly with stirring. The solution was then refluxed gently for two hours, cooled to room temperature, poured into a 1-l separatory funnel and extracted with ether. The organic layer was washed several times with water and dried with magnesium sulfate. After removal of the ether the methyl ester of cyclobutanecarboxylic acid was distilled under reduced pressure, b.p. 51-52° (28 mm). Yield 86 g (75.3%). (Lit. 23 b.p. 136-136.5°).

Cyclobutyldimethylcarbinol.

A dry 1-l three-necked flask was equipped with a mechanical stirrer, a dropping funnel, and an efficient reflux condenser attached to a calcium chloride tube. In the flask were placed magnesium turnings (36.5 g, 1.5 g-atoms) and 200 ml of dry ether. A slow stream
of nitrogen was passed into the flask. A solution of methyl iodide (213g, 1.5 moles) in 200 ml of dry ether was added (with stirring) at a rate which maintained rapid refluxing. The reaction began after a few ml of the iodide solution were added. The addition required two hours. The mixture was stirred and heated under reflux for one hour after all the iodide had been added. Over a period of two hours methyl cyclobutanecarboxylate (76.5g, 0.6 mole) was added very slowly to the cooled Grignard solution. The exothermic reaction caused refluxing of the solvent. The mixture was stirred and heated under reflux for one hour after completion of the addition. The reaction mixture was cooled in ice, and the addition compound decomposed with a 25% ammonium chloride solution. The ether solution became clear and the salt separated as a cake. The ether solution was decanted, combined with 150 ml of ether which had been used to rinse the salt cake, washed several times with water and dried over magnesium sulfate. After removal of the ether, the product was distilled under vacuum to give 65.5g (84.3%) of cyclobutyldimethylcarbinol, b.p. 53-54° (15mm), as a colorless oil. (Lit. 23 b.p. 167°).

The infrared spectrum (NaCl, neat) is characterized by a hydroxyl band at 3350 cm⁻¹.
1-Bromo-2,2-dimethylcyclopentane (II).

In a 250-ml two-necked flask equipped with a thermometer and a cooling tube was placed cyclobutylidimethylcarbinol (53.5g, 0.468 mole). Approximately 50 ml of fuming hydrobromic acid was slowly added with cooling by means of an ice bath. The mixture was then heated in an oil bath with stirring (magnetic) at 100° for two hours. Much hydrobromic acid was lost at this time. The resulting olive green solution was poured in a separatory funnel and washed a few times with distilled water. The lower layer of crude bromide was transferred to an Erlenmeyer flask and heated with a solution of 20g of potassium hydroxide in 50 ml of water at 100° for two hours. The bromide layer was separated, poured into a 100-ml flask, and after addition of water steam-distilled. The bromide was dissolved in ether, washed with water, and finally dried over magnesium sulfate. The ether was then removed by distillation and the residual liquid distilled under reduced pressure to give 16g of a fraction of isomeric olefins and 30.7g (36.2% of 1-bromo-2,2-dimethylcyclopentane, b.p. 55-56° (15mm), as a colorless oil. (Lit. b.p. 167°, partially dec.)

The purity of the bromide was confirmed by v.p.c.

The infrared spectrum (NaCl, neat) showed strong bands (cm⁻¹) at 2870, 1435, 1365, 1345, 1245, 1175, 858, and 804. The nmr spectrum (CCl₄, TMS internal standard) showed resonance at 7.63 (X portion of ABX, methine, J₆.13=15cps), 7.55-8.60 (multiplet, methylene), and 8.96 (singlet, methyl).
Further evidence for the correct structure of the bromide II was brought from the hydrocarbon obtained by hydrolysis of the corresponding Grignard compound. The nmr spectrum of 1,1-dimethyl-cyclopentane (diglyme) showed at $\tau$ 8.15-8.85 (multiplet, methylene), 8.98 (singlet, methyl). The peak areas were in ratio 4:3.

The isomeric olefins formed as side products from the preparation of the bromide were separated by v.p.c. Two components were obtained in the ratio of 4.5 to 95.5. The spectral properties of the lower boiling component (III) established its structure as 2-cyclobutylpropene. $\nu_{\text{max}}^{\text{NaCl}},\text{neat cm}^{-1} 2990, 2890, 2805, 1645, 1365, 1325, 1077, 1015, 915, 797$. Nmr (CCl$_4$) at $\tau$ 4.78 (center of complex multiplet, terminal vinyl protons), 7.38-8.15 (multiplet, methylene, methine), and 8.39 (singlet, methyl).

The second component (IV) was identified as 1,2-dimethyl-cyclopentane-1 by comparison of its nmr spectrum and retention time to those of an authentic sample. Nmr (CCl$_4$) at $\tau$ 7.51-8.35 (multiplet, methylene), 8.44 (singlet, methyl).

Preparation of 1-Bromo-2,2-dimethylcyclohexane (V).
The procedure used for its preparation was a modification of Nametkins$^3$, and similar to that described previously for 1-bromo-2,2-dimethyl-cyclopentane.
Methyl cyclopentanecarboxylate.

Methyl cyclopentanecarboxylate was prepared by the Favorskii rearrangement of 2-chlorocyclohexanone with sodium methoxide (26). Cyclohexanone in water was chlorinated by passing chlorine into the stirred solution at ice bath temperature. Purification of the product and fractionation under reduced pressure resulted in 2-chlorocyclohexanone (yield 59\%\textsuperscript{0}), b.p. 90-92\(^\circ\text{C}\) (15mm), (Lit.\textsuperscript{27} b.p. 90-91\(^\circ\text{C}\), 14-15mm).

To a stirred suspension of 115.5g (2.14 moles) of sodium methoxide in 660 ml of anhydrous ether was added dropwise a solution of 2-chlorocyclohexanone (247g, 2 moles) in 60 ml of dry ether. After the addition was completed, the mixture was stirred and heated under reflux for two hours and then cooled. Work-up of the ethereal solution in the usual manner gave 153g (57.5\%\textsuperscript{0}) of methyl cyclopentanecarboxylate, b.p. 74-75\(^\circ\text{C}\) (50mm). (Lit.\textsuperscript{26} b.p. 70-73\(^\circ\text{C}\), 48mm).

Cyclopentylidimethylcarbinol.

Methyl cyclopentylcarboxylate (152.4g, 1.337 moles) in 100 ml of anhydrous ether was reacted with Grignard solution prepared from magnesium turnings (73g, 3g-atoms), methyl iodide (426g, 3 moles) in 900 ml of anhydrous ether. Work-up of the product gave 128.5g (84.3\%\textsuperscript{0}) of cyclopentylidimethylcarbinol, b.p. 74-74.5\(^\circ\text{C}\) (18mm), as a colorless oil. (Lit.\textsuperscript{25} b.p. 100-101\(^\circ\text{C}\), 73mm). The infrared spectrum (NaCl, neat) was characterized by a hydroxyl band at 3360 cm\(^{-1}\).
1-Bromo-2,2-dimethylcyclohexane (V).

In a 500 ml two-necked flask equipped with a thermometer and cooling tube were placed cyclopentyldimethylcarbinol (110g, 0.858 mole) and 100 ml of fuming hydrobromic acid. The mixture was then heated in an oil bath with stirring at 100° for three hours. The heavier brown bromide layer was separated from the water. It was transferred to a 500 ml Erlenmeyer flask and heated under stirring with a solution of 40g of potassium hydroxide in 100 ml of water at 100° for two hours. The heavier crude bromide layer was separated, poured into a 1-l flask and steam-distilled. The distilled product was dissolved in ether, washed with water, and dried over magnesium sulfate. The ether was removed and the residue distilled under reduced pressure to give a fraction of isomeric olefins, b.p. 40-60° (25mm), and 99.4g (60.6%) of colorless 1-bromo-2,2-dimethylcyclohexane, b.p. 85-85.5° (25mm). (Lit.25 b.p. 85.5°, 25mm). The purity of the bromide V was confirmed by v.p.c. The infrared spectrum (NaCl, neat) showed strong bands (cm⁻¹) at 2870, 2885, 1448, 1430, 1367, 1348, 1200, 960, 854, 715, and 676. The nmr spectrum (CCl₄, TMS internal standard) showed resonance at 7.95 (ABX, methine, Jₓ+Jₓₓₓ=15cps), 7.58-8.79 (multiplet, methylene), 8.92 (singlet, methyl).

Anal. Calcd for C₇H₁₅Br:  C, 50.28; H, 7.91; Br, 41.81. Found :  C, 50.35; H, 7.87; Br, 41.78.
The structure and identity of 1-bromo-2,2-dimethylcyclohexane was further proved by its chemistry. A Grignard solution prepared in diglyme was hydrolyzed and the resulting hydrocarbon was compared in its spectral properties and retention time to a commercial sample of 1,1-dimethylcyclohexane. Their properties were the same.

\( \nu_{\text{max}} \text{NaCl, neat} 2880, 2800, 1430, 1360, 1345, 1165, 957, \text{ and } 846 \text{ cm}^{-1}. \)

\( \nu_{\text{max}} \text{CCL}_4 8.23-8.87 \) (multiplet, methylene), 9.08 (singlet, methyl).

The Grignard reagent of the above bromide in ether was oxidized with molecular oxygen and the resulting alcohol compared to an authentic sample of 1,1-dimethylcyclohexanol-2. Both compounds showed the same spectral properties and v.p.c. retention times. Treatment of the alcohol with phenylisocyanate resulted in a phenylurethane which melted at 84.5-85.0°. (Lit. m.p. 84-85°). The infrared spectrum (NaCl, neat) of the alcohol was characterized by a hydroxyl band at 3300 cm\(^{-1}\).

**Side-products from cyclopentylidimethylcarbinol-HBr reaction.**

The olefin fraction consisted of two components which were separated by v.p.c. One gram samples of these olefins were ozonized in methylene chloride at -78° for about an hour. The blue ozonide solution was poured into a flask containing 50 ml of water. The methylene chloride was removed on a steam bath. In both cases the water residue contained oils. The ozonized product of the lower boiling major olefin VI was soluble in a 5% solution of sodium bicarbonate, indicating an acid, whereas the product from olefin VII
was insoluble. The alkaline solution of olefin VI was acidified, extracted in ether and gave a very high boiling oil. With semicarbazide hydrochloride it gave a semicarbazone, m.p. 183-185°. The melting point was close to that reported for the semicarbazone of 6-methyl-5-oxy-heptanecarboxylic acid. (Lit. m.p. 182.5-183.5°). Infrared and nuclear magnetic resonance spectra further proved the identity of olefin VI as 1-isopropylcyclopentene-1.

\[ \text{NaCl, neat (cm}^{-1}\text{)} 3030, 2960, 1645, 1465, 1358, 1375, 1305, 1290, 1067, 1033, 948, 807. \]

Nmr (CCl₄) 4.75 (singlet, vinyl), 7.50-8.52 (multiplet, methine and methylene), 9.00 (center of doublet, gem-dimethyl).

The ozonized olefin VII was neutral and gave after treatment with semicarbazide hydrochloride a semicarbazone, m.p. 207-209°, was very close to the reported melting point for the semicarbazone of cyclopentanone, (Lit. m.p. 209-210°). The infrared and nuclear magnetic resonance spectra identified olefin VII as isopropylidene cyclopentane.

\[ \text{NaCl, neat (cm}^{-1}\text{)} 2910, 2820, 1645(w), 1435, 1420, 1360, 1095, 945. \]

The nmr spectrum showed no vinyl protons.

**Reaction of cyclopentylidimethylcarbinol with sulfuric acid.**

When cyclopentylidimethylcarbinol was heated with 60% sulfuric acid at 80° for four hours, it resulted in the formation of three compounds. Olefin VI (47%), b.p. 133°, (Lit. b.p. 131-133°) was
identified as 1-isopropylcyclopentene-1, olefin IX (2^) 1645 (C=C),
888 cm⁻¹ (C=CH₂), as isopropenylcyclopentane, and olefin VII (51%),
b.p. 136° (Lit.²⁵ b.p. 136-137°) as isopropylidene cyclopentane.

Preparation of 1-Bromo-3,3-dimethylcyclohexane (X).
The procedure used was a modification of that of Doering (30).

In a 100-ml three-necked flask equipped with a mechanical
stirrer, reflux condenser, and insert tube was placed 3,3-dimethyl-
cyclohexanol (32g, 0.25 mole). A stream of hydrogen bromide was
passed through the alcohol for thirty minutes at 5°, for fifteen
minutes at 100°, and for two hours at 130°. The reaction product
was first washed with concentrated sulfuric acid, with an equal
amount of 50% methanol, with ammonium hydroxide until basic, and
finally again with 50% methanol. Distillation of the dried product
gave 31g (64.8%) of colorless 1-bromo-3,3-dimethylcyclohexane,
b.p. 63-63.5° (8mm) (Lit.³⁰ b.p. 80-82°, 8mm). The purity of the
bromide was confirmed by v.p.c. The infrared spectrum (NaCl, neat)
showed strong bands (cm⁻¹) at 2880, 1445, 1375, 1350, 1330, 1312,
1285, 1250, 1235, 1205, 1170, 1150, 1042, 966, 945, 921, 840, 831,
715, and 695. The nmr spectrum (CCl₄, TMS internal standard) showed
resonance at 7.64-6.30 (complex multiplet, methine) 7.55-8.86
(complex multiplet, methylene), 9.06 (singlet, methyl), 9.09 (singlet,
methyl).

    Anal. Calcd for C₆H₁₄Br: C, 50.28; H, 7.91; Br, 41.81.
    Found : C, 50.22; H, 7.91; Br, 41.91.
Storage of this bromide X for three months caused some change in the nmr spectrum. The nmr spectrum of the bromide in benzene showed two doublets for the gem-dimethyl groups at \( \tau 9.22, 9.29 \) and \( 9.25, 9.36 \), the latter about three times the area of the former. Heating of this sample in benzene to 80-90° gave only two lines at 9.15\( \tau \) and 9.23.

Treatment of the Grignard reagent (prepared from 3.82g, 0.02 mole of 1-bromo-3,3-dimethylcyclohexane) with 1-naphthyl isocyanate (1.69g, 0.01 mole) gave after recrystallization from methanol a derivative with a melting point of 201-202.5°, very close to the reported melting point of N-1-naphthyl-3,3-cyclohexane carboxamide. (Lit.\(^{30}\) m.p. 204-204.5°).

Preparation of 1-Bromo-1,4-dimethylcyclohexane (XV).

Diethyl-\( \beta,\beta \)-dimethylglutyrate (XI).

The diester was prepared following the procedure of Perkin (31).

3,3-Dimethylglutaric acid (120g, 0.75 mole) absolute ethanol (270 ml, 3 moles), 135 ml of toluene, and 0.7 ml of concentrated sulfuric acid were placed in a 1-l Claisen flask. A mechanical stirrer was fitted into the center and the flask was connected with a downward condenser. The system was on an oil bath at 110-115°. An azeotropic mixture of alcohol, toluene, and water began to distill at 75°. Distillation was continued until the thermometer in the neck of the flask read 78°, whereupon heating was suspended. The
distillate was collected in a 1-l flask containing 450g of anhydrous potassium carbonate. It was well shaken, filtered, and returned to the reaction flask. The flask was again heated until the temperature rose to 78-80°, when distillation was continued. The residual liquid was transferred to a distilling flask. Alcohol and toluene distilled first as the temperature rose and finally diethyl-β,β-dimethylglutyrate was distilled at reduced pressure, b.p. 97-98.5° (3mm). (Lit.° b.p. 89-90°, 2mm). Yield 135g (85.3%).

3,5-Dimethyl-1,5-pentanediol (XII).
The diol was prepared following the procedure of Blomquist (33).

A solution of diethyl-β,β-dimethylglutyrate (135g, 0.625 mole) in 100 ml of anhydrous ether was added during a period of three hours to a stirred suspension of lithium aluminum hydride (34.5g, 0.9 mole) in 200 ml of anhydrous ether. The mixture was stirred for twelve additional hours. About 140 ml of water was carefully added under cooling to hydrolyse the complex. The precipitated inorganic salts were separated with a Buchner funnel. The ether solution was dried over magnesium sulfate and distilled under reduced pressure to give 71.5g (86.7%) of colorless 3,3-dimethyl-1,5-pentanediol, b.p. 110-112° (0.8mm). (Lit.° b.p. 95-98°, 0.25mm).

1,5-Dibromo-3,3-dimethylpentane (XIII)

To 3,3-dimethyl-1,5-pentanediol (71.5g, 0.542 mole) was added slowly phosphorus tribromide (149g, 0.55 mole) with stirring. The
reaction mixture was heated at 90° for twelve hours. The ether layer was washed with sodium carbonate, dried over magnesium sulfate and filtered. After evaporation of the ether, the residue was distilled under vacuum to give 116g (85.2%) of colorless 1,5-dibromo-3,3-dimethylpentane, b.p. 86-86.5° (2mm). (Lit. 34 80-81°, 1.3mm). 

4,4-Dimethylcyclohexane-1,1-dicarboxylic acid.

The acid was prepared following the procedure of Otto (34).

In a 5-l three-necked flask equipped with a mechanical stirrer, reflux condenser with a drying tube, and a dropping funnel, was placed 2000 ml of absolute ethanol. The ethanol was slowly reacted with sodium (20.7g, 0.9g-atom) added over a period of two hours. Diethyl malonate (71g, 0.45 mole) was added to the alkoxide solution followed by 1,5-dibromo-3,3-dimethylpentane (116g, 0.448 mole). The reaction mixture was refluxed with stirring for four days. A solution of 100g of sodium hydroxide in 500 ml of aqueous ethanol (50%) was then added and refluxing continued for ten hours. Ethanol was removed by steam distillation and the residual solution acidified with hydrochloric acid, extracted with ether, and washed with distilled water. After the ethereal extract was dried over magnesium sulfate, the ether was evaporated and white crystals of 4,4-dimethylcyclohexane-1,1-dicarboxylic acid, m.p. 190-190.5°, (Lit. 34 m.p. 190-192°), were obtained. Yield 71g (79.2%).
4,4-Dimethylcyclohexanecarboxylic acid (XIV).

4,4-Dimethylcyclohexane-1,1-dicarboxylic acid (70.7g, 0.353 mole) was heated with 0.3g of powdered pyrex glass in a 1-l flask equipped with a reflux condenser carrying a thermometer. Evolution of carbon dioxide commenced soon after all the diacid had melted. The temperature was held for about two hours at 220°. Upon cooling, the residue solidified to shiny white needles. Recrystallization from ethanol - water gave 53.4g (95.8%) of 4,4-dimethylcyclohexanecarboxylic acid, m.p. 45-46° (Lit.34 m.p. 45-47°).

1-Bromo-4,4-dimethylcyclohexane (XV).

The acid was converted to the bromide by the Hunsdiecker reaction of the silver salt in a procedure similar to that described above. Thus 53.4g of 4,4-dimethylcyclohexanecarboxylic acid (0.342 mole) gave together with 58.3g of silver nitrate (0.343 mole) 82g (91.2%) of dry silver salt. The dry silver 4,4-dimethylcyclohexanecarboxylate (81.5g, 0.31 mole) was reacted with bromine (49.5g, 0.31 mole) in 500 ml of dry pentane. Work-up of the product in the usual manner resulted in 26.5g (40.5%) of colorless 1-bromo-4,4-dimethylcyclohexane, b.p. 57-58° (5mm). The purity of the bromide was confirmed by v.p.c. The infrared spectrum (NaCl, neat) showed strong bands (cm⁻¹) at 2850, 1455, 1440, 1325, 1305, 1285, 1250, 1205, 1172, 1135, 928, 973, 935, 842, 714, 699, and 686. The nmr spectrum (CCl₄, TMS internal
standard) showed resonance at $\tau 5.87$ (center of symmetrical multiplet, methine), 7.72-8.89 (multiplet, methylene), 9.04 (singlet, methyl), and 9.10 (singlet, methyl).

**Anal.** Calcd for $C_6H_{15}Br$: C, 50.28; H, 7.91; Br, 41.81.

**Found:** C, 50.04; H, 7.84; Br, 42.05.

**IV. Preparation of the Organometallic Compounds.**

**Solvents:** The solvents used for the preparation of organometallic compounds were distilled directly into the reaction vessel from a flask containing drying reagent. Diethyl ether was distilled from commercial methylmagnesium bromide. Dimethoxymethane, n-pentane, and benzene were distilled from lithium aluminum hydride. Diglyme was distilled twice from lithium aluminum hydride and then from methylmagnesium iodide under reduced pressure (50mm).

**Metals:** Lithium metal dispersed in wax and containing 1% of sodium was used for the preparation of the lithium compounds. The wax was removed just before reaction by washing the dispersion several times with dry solvent. Triply sublimed magnesium milled into fine shavings was used for the preparation of the Grignard compounds. The shavings were washed with dry ether, dried in a stream of helium, and stored in a desiccator.

**Apparatus:** All micro-preparations were carried out in an apparatus shown in Figure 1.

Hypodermic syringes were used for the addition of the bromides and the transfer of the organometallic compounds. The syringes were equipped with a stopcock, and 6 or 8 inch, 18 gauge needles.
Vacuum vials fitted with a 1mm straight bore stopcock and a 12/30 male joint were used sometimes for storing or purification of organometallic reagents.

All the above mentioned equipment was cleaned and dried prior to its use.

**Nmr sample tubes:** These were made by cutting 5mm (0.197-0.199 inch) O.D. Pyrex tubing into 7 to 9 inch lengths. Each was individually machine ground to 0.195 ± 0.001 inches by the Yorde Machine Company, Nelsonville, Ohio. The tubes were first cleaned by heating in aqueous trisodium phosphate for one hour and rinsing with distilled water. They were then heated for one hour in aqua regia, rinsed with distilled water, 10% ammonium hydroxide, and again with distilled water. Finally, they were dried in an oven at 90°. Before use, the tubes were closed at one end by slowly rotating the end of the tube near the bottom of a small oxygen gas flame. In this way the end sealed hemispherically.

**Instrumentation:** All nmr spectra of organometallic compounds were obtained with an Varian A-60 high resolution nmr spectrometer equipped with a variable temperature probe.
Figure 1. Apparatus for Grignard and Organolithium Preparations.
Procedure for the Preparation of Organometallic Compounds.

Grignard reagents (general): A 500-ml flask containing solvent and drying agent was connected to the apparatus shown in Figure 1, together with the reaction vessel containing the required amount of magnesium metal and a Teflon stirring bar. The apparatus was dried in a stream of helium as a flame was applied to the glass parts. The remaining opening of the apparatus was connected to a drying tube. The solvent was then distilled over in two 20 ml portions. Each was removed with a hypodermic syringe. Finally, a 10-ml portion was distilled over, stirring was begun, and a few drops of bromide were added to the reaction vessel through the Teflon stopcock. Sometimes reaction set in within a few minutes, but in some instances, heating or addition of 1-3 drops of 1,2-dibromoethane was necessary. The remaining bromide was then added at the rate of about 1 mmole/minute, and the mixture heated afterwards for two hours to complete reaction. Stirring was then discontinued and the magnesium was allowed to settle. Aliquots were taken for nmr and base analysis.

Organolithium compounds (general): With the exception of the reaction vessel, the same apparatus was used as described for Grignard reagents and shown in Figure 1. A specially designed reaction vessel, containing the desired amount of lithium dispersion in wax and a Teflon stirring bar was used. Solvent was distilled into the reaction vessel. The wax solution was filtered through the frit and then removed by means
of a hypodermic syringe through stopcock(B). The washing was repeated until the solvent decante showed no paraffin on evaporation (usually about three times). Next fresh solvent was distilled in and the bromide slowly added through stopcock(A). After completion of the reaction, the apparatus was tilted and the organolithium compound filtered through the frit under slight helium pressure.

3,3-Dimethylcyclobutylmagnesium bromide.

Into the helium flushed reaction vial, containing magnesium (0.865g, 0.036g-atom) was distilled 10 ml of dry diglyme. Stirring was started after the flask was immersed in an oil bath and heated to 50°. 1-Bromo-3,3-dimethylcyclobutane (2.93g, 0.018 mole) was added slowly by means of a hypodermic syringe through the Teflon stopcock. The reaction mixture became cloudy after the first few drops, indicating initiation of the reaction. The rest of the bromide was added and stirring continued for two hours at 50°. A considerable amount of white solid precipitated after the solution had come to room temperature. One sample of the clear solution was withdrawn from the reaction vessel and injected through a syringe cap into a dry nmr tube. The latter was cooled with liquid nitrogen and sealed off with a hot flame. Another sample was titrated with 0.1 N hydrochloric acid (methyl orange as indicator), indicating a 1.5 M solution (95%). The nmr spectrum is shown in Fig. 2 and 3. The nmr spectrum of the hydrolysate showed absorption only for 1,1-dimethylcyclobutane (7.890 for methyl).
2,2-Dimethylcyclopentylmagnesium bromide.

Magnesium (0.865g, 0.036g-atom) was reacted with 1-bromo-2,2-dimethylcyclopentane (3.18g, 0.018 mole) in 10 ml of dry diglyme at 50°C. The solution had a concentration of 1.4 M (94.5%). The nmr spectrum is shown in Fig. 4. The hydrolysate showed a single peak for the methyl protons at 8.98τ.

2,2-Dimethylcyclohexylmagnesium bromide.

Magnesium (0.58g, 0.024g-atom) was reacted with 1-bromo-2,2-dimethylcyclohexane (2.29g, 0.012 mole) in 10 ml of dry diglyme at 70°C. The solution had a concentration of 0.9 M (86.8%). The nmr spectrum is shown in Fig. 5. The hydrolysate showed a single peak for the methyl protons at 9.12τ.

3,3-Dimethylcyclohexylmagnesium bromide.

Magnesium (0.97g, 0.04g-atom) was reacted with 1-bromo-3,3-dimethylcyclohexane (3.82g, 0.02 mole) in 10 ml of dry diglyme at 50°C. The solution had a concentration of 1.5 M (94.8%). The nmr spectrum is shown in Fig. 6 and 7. The hydrolysate showed a single methyl peak at 9.12τ.

Magnesium (0.865g, 0.036g-atom) was reacted with 1-bromo-3,3-dimethylcyclohexane (3.44g, 0.018 mole) in 5 ml of dry dimethoxymethane at 40°C. The solution had a concentration of 2.2 M (90.2%).

4,4-Dimethylcyclohexylmagnesium bromide.

Magnesium (0.58g, 0.024g-atom) was reacted with 1-bromo-4,4-
dimethylcyclohexane (2.29 g, 0.024 mole) in 10 ml of dry dimethoxy-
methane at 40°. The solution had a concentration of 0.95 M (91.7%).
Nmr spectrum Fig. 8 and 9. The hydrolysate showed a single methyl
peak at 9.11 τ.

3,3-Dimethylcyclobutyllithium.

Lithium (0.55 g, 0.056 atom) from 1.83 g of 30% lithium dispersion
in wax was reacted with 1-bromo-3,3-dimethylbutane (4.07 g, 0.025 mole)
in 10 ml of dry benzene in the same manner as described in the
general procedure. The solution had a concentration of 1.7 M (87%).
Nmr spectrum Fig. 10. The hydrolysate showed a single methyl peak
at 8.95 τ.

 Attempted preparation of 2,2-dimethylcyclopentyl-.

2,2-dimethyl--.,3,3-dimethyl--., and 4,4-dimethylcyclohexyllithium
in benzene.

Reaction of lithium with those bromides did not occur at room
or slightly elevated temperature (30-35°). At higher temperature,
an exothermic reaction took place, but only coupling products were
found. The reaction in benzene or pentane could be initiated by
c. 5-10% of diethyl ether or trimethylamine.
CHAPTER III

RESULTS AND DISCUSSION

The synthetic route to each of the cyclic halides previously named is described briefly in this section.

1-Bromo-3,3-dimethylcyclobutane (I) was prepared in 54.7% yield by a Hunsdiecker reaction from 3,3-dimethylcyclobutanecarboxylic acid; this in turn was the result of a decarboxylation of the corresponding dicarboxylic acid. 3,3-Dimethylcyclobutane-1,1-dicarboxylic acid itself was obtained from 1,3-dibromo-2,2-dimethylpropane or 1,3-diodo-2,2-dimethylpropane in a typical diethyl malonate cyclization reaction. Starting from neopentyl glycol, the overall yield of the diacid was by large greater via the diiodide (39.7%) than the dibromide (16.1%). The diiodide was obtained by a iodide displacement reaction of neopentyl dimesylate, whereas the synthesis of the dibromide was accomplished by treating neopentyl glycol with phosphorus tribromide according to the procedure of Franke (17).

1-Bromo-2,2-dimethylcyclopentane (II) was obtained in 36% yield in addition to olefin III and IV by the action of fuming hydrobromic acid on cyclobutyldimethylcarbinol followed by work-up with base by a modified procedure of Kishner (23). Evidence for the correct structure of bromide II was obtained from the hydrocarbon produced by hydrolysis of the corresponding Grignard compound. The spectral and
physical properties were identical with those of an authentic sample of 1,1-dimethylcyclopentane. The isomeric olefins III and IV formed as side products from the preparation of bromide II were identified through their spectral properties and by comparison to authentic samples. Olefin III was found to be 2-cyclobutylpropene and IV 1,2-dimethylcyclopentene-1.

The following mechanism for the formation of the above products through a carbonium ion mechanism seems to be the most reasonable one (Eq. 1).
Similar ring expansions were observed by treatment of cyclobutyldimethylcarbinol with formic acid (35) and oxalic acid (36). In the first case the products were 1,2-dimethylcyclopentene-1 (IV), 1,1-dimethylcyclopentene-2, and 1,5-dimethylcyclopentene-1, whereas the latter gave mainly 1,2-cyclopentene-1 (IV).

1-Bromo-2,2-dimethylcyclohexane (V) was prepared in an analogous way to that of bromide II. According to the procedure of Nametkin, (25) cyclopentyldimethylcarbinol was reacted with fuming hydrobromic acid and the crude bromide treated with a 29% aqueous solution of sodium hydroxide at 100° for two hours. The bromide V was obtained in 60.6% yield together with two isomeric olefins VI and VII. The structure and identity of 1-bromo-2,2-dimethylcyclohexane (V) was proved by comparison of the hydrocarbon obtained by hydrolysis of its Grignard reagent with an authentic sample of 1,1-dimethylcyclohexane and by oxidation of this reagent to the known 2,2-dimethylcyclohexanol. Ozonization of olefin VI gave a keto acid whose semicarbazone was identical to that from 6-methyl-5-oxy-heptanecarboxylic acid. These results together with the spectral properties were consistent with 1-isopropylcyclopentene-1 for VI. Ozonization of olefin VII gave a ketone whose semicarbazone had a similar melting point to that of cyclopentanone. Spectral properties and chemical behavior identified olefin VII as isopropylidene cyclopentane. As in the case of cyclobutyldimethylcarbinol the products from the reaction of cyclopentyldimethylcarbinol with hydrobromic acid can be explained by
means of a carbonium ion mechanism (Eq. 2).

Treatment of cyclopentyldimethylcarbinol with 60% sulfuric acid at 80° produced 47% of 1-isopropylcyclopentene-1 (VI), 51% of isopropylidine cyclopentane (VII), traces of isopropenylcyclopentane (IX) but no ring expanded products. These results indicate formation of the ring enlarged dimethylcyclohexyl cation (VIII) is a reversible process as already mentioned by Johnson (57). In the formolysis of 2,2-dimethylcyclohexanol he obtained besides starting material smaller amounts of isopropylidine cyclopentane (VII), 1-isopropylcyclopentene-1 (VI) and cyclopentyldimethylcarbinol.
1-Bromo-3,3-dimethylcyclohexane (X) was prepared by reacting 3,3-dimethylcyclohexanol with hydrogen bromide according to a modified procedure of Doering (30). Treatment of the Grignard reagent of bromide X with 1-naphthyl isocyanate gave a carboxamide which had the same physical properties as those reported for 3,3-dimethylcyclohexanoic α-naphthalide.

1-Bromo-4,4-dimethylcyclohexane (XV) was obtained in 40.5% yield by means of a Hunsdiecker reaction from 4,4-dimethylcyclohexanecarboxylic acid (XIV). The complete synthesis of XV is illustrated by Eq. 3.

(Eq. 3)

The hydrocarbon obtained from the hydrolysis of the Grignard reagent of bromide (XV) confirmed its structure to be 1-bromo-4,4-dimethylcyclohexane (XV).
The preparation of the Grignard reagents of the bromides I, II, V, X, and XV was best accomplished by use of diglyme as solvent at slightly elevated temperatures (40-70°). The use of tetrahydrofuran and dimethoxymethane as reaction media was abandoned since the reactions in those solvents resulted in the formation of large amounts of coupling products. The nmr spectra of the hydrolysates of the above Grignard reagents showed only absorption belonging to the corresponding hydrocarbon. Attempts to prepare the corresponding lithium compounds in benzene by using lithium dispersion (1% sodium) failed. Only bromide I gave a fairly pure sample of the corresponding lithium compound in benzene.

The nmr spectra of the Grignard reagents prepared from the cyclic bromides I, II, V, X, and XV are illustrated in Figures 2, 3, 4, 5, 6, 7, 8, and of the lithium compound (I) in Figure 10. With the exception of 3,3-dimethylcyclobutylmagnesium bromide the methylene protons of the above Grignard reagents exhibited complex multiplets due to extensive coupling. The methine protons at the carbon bearing the magnesium were difficult to detect because of their relatively small concentration and coupling with neighboring protons. Two well separated lines for the methyl protons were observed in all spectra.

The nmr spectra of the Grignard reagents were studied at temperatures between 40° and the boiling point of diglyme. None of these compounds showed a significant temperature dependence in their spectra as illustrated by the example of 2,2-dimethylcyclohexyl-
magnesium bromide (V) and 4,4'-dimethylcyclohexylmagnesium bromide (XV) in Figures 5 and 9. At approximately 170° each sample became cloudy and the spectrum changed to that of the corresponding hydrocarbon, indicating proton abstraction from the solvent had occurred.

As already pointed out in the introduction, one can assume rapid ring inversion for all the four- and six-numbered rings above room temperature. The fact that the chemical shift between the methyl protons of these reagents did not change over the temperature range of 35 to 170° suggests that inversion of configuration at the CH-Mg center is slow on the nmr time scale. This conclusion applies also to the five-numbered ring reagent.

The absence of significant temperature dependencies in the spectra of the cyclic organomagnesium compounds indicates that the barrier to inversion of configuration is higher in secondary than in primary Grignard reagents. The reason for such behavior might be found in steric requirements and/or bonding. It was found (10) that the inversion in primary Grignard reagents probably takes place via polarized dimeric transition states involving bridged species. Such transition states for the cyclic systems might be prohibited energetically from steric considerations. Further, one might consider the bonding in secondary Grignard reagents as compared to primary reagents. There are indications that the carbon-metal bond in primary compounds is more ionic than in secondary compounds (38).
The findings in this work have proved it impossible to measure the rate of inversion of cyclic secondary organomagnesium compounds by the nmr lineshape method, since these compounds invert slowly on the nmr time scale.
Fig. 2. NMR Spectrum (60 MHz) of 3,3-Dimethylcyclobutylmagnesium Bromide in Diglyme.
Fig. 3. NMR Spectrum (60 MHz) of 3,3-Dimethylcyclobutylmagnesium Bromide in Diglyme, Methyl Region.
Fig. 4. NMR Spectrum (60 MHz) of 2,2-Dimethylcyclopentylmagnesium Bromide, Methyl Region.
Fig. 5. NMR Spectrum (60 MHz) of 2,2-Dimethylcyclohexylmagnesium Bromide, Methyl Region, at 60° and 170°.
Fig. 6. NMR Spectrum (60 MHz) of 3,3-Dimethylcyclohexylmagnesium Bromide in Diglyme, Methyl Region.
Fig. 7. NMR Spectrum (60 MHz) of 3,3-Dimethylcyclohexylmagnesium Bromide in Diglyme.
Fig. 8. NMR Spectrum (60 MHz) of 4,4-Dimethylcyclohexylmagnesium Bromide in Diglyme, Methyl Region.
Fig. 9. NMR Spectrum (60 MHz) of 4,4-Dimethylcyclohexylmagnesium Bromide in Diglyme, a) at 75°, b) at 175°, c) at 200°.
Fig. 10. NMR Spectrum (60 MHz) of 3,3-Dimethylcyclobutyl-lithium in Benzene.
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I. INTRODUCTION AND HISTORICAL REVIEW

The organic derivatives of the alkali and the lighter elements of group II and III are usually described as having ionic metal-carbon bonds. Due to their carbanionic character, these compounds play a major role in modern organic synthesis. Despite their sensitivity to hydrolysis and oxidation, their flammable and sometimes poisonous character, such organometallic compounds are now made on a fairly large scale and find widespread use as catalysts in industrial chemistry.

The first preparation of an organometallic compound of this type goes back to 1900, when Grignard and Barbier (1) reported the successful isolation of methylmagnesium iodide as an etherate. It took 17 more years before the first organoalkali compounds were prepared and isolated by Schlenk and Holtz (2). My treating various dialkylmercury compounds with alkali metals, they succeeded in preparing potassium, sodium and lithium alkyls. Thanks to their effort, chemists became more interested in the field of organometallic compounds of group IA-IIIA. In the following years, a large number of publications appeared concerning the preparation, isolation and characterization of these compounds. Especially, the pioneering work...
by Morton and co-workers (3,4,5) should be mentioned. Their method for the preparation of alkali alkyls from alkyl halides and alkali metals is still today the most widely one used. Also dating back to these years is the description of the first preparation of aluminum alkyl etherates from the reaction of aluminum chloride with Grignard reagents (6).

Many different reactions have been used to effect the formation of carbon-metal bonds. Some of the reactions are highly specialized, whereas others are very general and are applicable to the preparation of most organometallic compounds of group IA-IIIA. These preparative methods can be classified into the following groups:

A. Substitution Reactions:

Three types of substitution reactions have been used.

1. Metal-metal exchange also known as transmetalation.

\[ R M + R' M' \rightleftharpoons R M' + R' M \]

Reactions of this type are, as indicated, reversible. The position of the equilibrium is such as to favor the formation of the less reactive and more ionic metal alkyl. Often, however, the course of a reaction is influenced by the insolubility of one of the products in the solvent used. The scope of this reaction and its preparative applications were investigated rather recently by Seyferth (7,8). It now provides the most convenient route to vinyl-, allyl-, methallyl- and isopropenyllithium (Eq. 4).
\[ 4 \text{C}_{6}\text{H}_{5}\text{Li} + (\text{CH}_2=\text{CH})_4\text{Sn} \rightarrow 4 \text{CH}_2=\text{CHLi} + (\text{C}_{6}\text{H}_{5})_4\text{Sn} \]  

(Eq. 4)

2. **Metal-hydrogen exchange commonly known as metalation.**

\[ \text{RM} + \text{R}'-\text{H} \leftrightarrow \text{R'}\text{M} + \text{R-H} \]

This reaction is of prime importance in the synthesis of many organoalkali compounds. From the thermodynamic viewpoint, the equilibrium lies on the side of the weaker acid, \( \text{R-H} \), and the more stable carbanion \( \text{R'}\Theta \) (Eq. 5). From the kinetic standpoint, the most efficient metalating agents are alkyls of alkali and alkaline earth metals.

\[ \text{H} \]
\[ \text{H} \]
\[ + \text{C}_2\text{H}_5\text{MgBr} \rightarrow \text{H} \]
\[ \text{MgBr}^{\Theta} \]
\[ \text{(Li)} \]

(Eq. 5)

The choice of the proper solvent is important. The reactivity of the attacking metal alkyl is increased by basic solvents, due to increased ionic character of the carbon-metal bond. The most remarkable and reactive of the lithium alkyl complexes are those formed by tetramethylethylenediamine XVI (9).

\[ \text{CH}_2\text{N} \]
\[ \text{CH}_3 \]
\[ \text{CH}_3 \]
\[ \text{Li-R} \]
\[ \text{CH}_3 \]
\[ \text{CH}_3 \]

XVI
The metal-carbon bond is so strongly polarized that the complex represents one of the most reactive carbanionic reagents known. For example, benzene is metalated completely within one hour with n-butyl-lithium-TMED at 50°C. It has been reported that alkoxides have a similar activating effect upon the metal alkyls (10).

3. Metal-halogen exchange. \( \text{RM} + \text{R'}X \rightleftharpoons \text{R'M} + \text{RX} \)

This interconversion is closely related to metal-metal exchange and is uniquely important. The equilibrium favors the attachment of the more electropositive metal with the more electronegative organic group. The interaction between metal alkyl and aryl halides is particularly favored to completion because of the formation of the more stable carbanion (Eq. 6).

\[
\text{n-C}_4\text{H}_9\text{Li} + \begin{array}{c} \text{Br} \\
\end{array} \begin{array}{c} \text{Li} \\
\end{array} \rightarrow \begin{array}{c} \text{Li} \\
\end{array} \begin{array}{c} \text{Br} \\
\end{array} + \text{n-C}_4\text{H}_9\text{Br}
\]

(Eq. 6)

B. Displacement Reactions:

1. Metal-halogen displacement. \( \text{RX} + 2\text{M} \rightarrow \text{RM} + \text{MX} \)

The reaction of metals with organic halides is the most fundamental one in organometallic chemistry. The metal alkyls are probably formed by homolysis of the C-X bond and pairing with single electrons of the metal surface (11).
The reaction between organic halides and sodium or potassium normally leads to coupling products, the usual products of Wurtz-Fittig reactions. Also, some organic halides like benzyl- or allylchloride react with lithium metal giving rise only to coupling products.

2. Metal-metal displacement

The interaction of a metal with an organometallic compound can lead to metal displacement. Reactions of this type are usually reversible.

\[ RM + M' \rightleftharpoons R M' + M \]

Usually, a more reactive organometallic compound is formed in the reaction of a metal with a less reactive organometallic compound. Organomercury compounds are especially suitable for this kind of reaction. Amalgamation of the displaced metal contributes to the completion of the reaction. This type of reaction has great preparative utility for the synthesis of solvate-free metal alkyls of group IA- IIIA.
C. Addition Reactions:

The following two types of addition reactions to olefins or acetylenes are the most common such reactions used for the preparation of organometallic compounds.

1. Addition of metal hydrides also known as hydrometalation.

\[
M - H + \overset{\sigma}\text{C} \rightarrow CH_{\text{\overset{\sigma}{\sigma}}} \quad \text{M}
\]

Especially, the addition of alkalimetal hydrides is reversible. Smoother addiction occurs with group IIA or IIIA metal hydrides. Eq. 7(12).

\[
(CH_3)_2C=CH_2 + AlH_3 \rightarrow [(CH_3)_2CH-CH_2]_2Al \quad (\text{Eq. 7})
\]

2. Addition of metal alkyls to olefins, carbometalation.

The addition of metal alkyls to unsaturated linkages is limited to alkyls of group IA to IIIA. The process is reversible but can be driven to completion through formation of more stable carbanions. Such reactions are associated with the mechanism for the anionic polymerization of conjugated dienes, styrenes (Eq. 8), and certain types of nonconjugated olefins.

\[
\begin{align*}
&\text{C}_6\text{H}_5-\overset{\sigma}{\text{CH}}=\text{CH}_2 + \text{R}Li^+ \rightarrow \text{R}-\overset{\sigma}{\text{CH}}=\text{CH}_2 \quad \overset{\sigma}{\text{CH}}=\text{CH}_2-\overset{\sigma}{\text{CH}}=\text{CH}_2 \quad \overset{\sigma}{\text{CH}}=\text{CH}_2-\overset{\sigma}{\text{CH}}=\text{CH}_2 \quad \overset{\sigma}{\text{CH}}=\text{CH}_2 \\
\text{R}=\overset{\sigma}{\text{CH}}=\text{CH}_2, \text{CH}2, \text{CH}_2-\overset{\sigma}{\text{CH}}=\text{CH}_2, \text{C}_6\text{H}_5-\overset{\sigma}{\text{CH}}=\text{CH}_2 \quad \text{(Eq. 8)}
\end{align*}
\]
D. Cleavage Reactions:

1. Cleavage of ethers with alkali metals. \( R-OR' + 2M \rightarrow RM + R'OH \)

Few reactions are known in which alkoxy serves as a leaving group. Certain monomethyl or monophenyl ethers having phenyl or allyl substituents in \( \alpha \)-positions, undergo cleavage with sodium or potassium metal at room temperature. Enhanced stabilization of the carbanion \( R^- \) promotes the \( R-OR' \) bond rupture. Very little is known about the mechanism of the reaction. However, the cleavage must involve electron transfer from the alkali metal. In the case of benzyl ether, one might speculate that the electron enters the aromatic ring, giving rise to a radical ion and that this species in turn reacts with a second electron at the benzyl position (Eq. 9).

\[ \begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{M}^+ & \quad \text{M}^+ \\
\text{M}^- & \quad \text{M}^- \\
\text{CH}_2 & \quad \text{CH}_2
\end{align*} \]  

\( + \text{CH}_2\text{OM} \)  

(Eq. 9)
2. Cleavage of carbon-carbon bonds.

Substituted ethanes having at least two aryl substituents on each carbon are cleaved by alkali metals (Eq. 10). The mechanism might be similar to that described for the ether cleavage and must involve electron transfer from the metal (13).

\[(\text{C}_6\text{H}_5)_2\text{CH-CH(C}_6\text{H}_5)_2 + 2 \text{K} \rightarrow 2 (\text{C}_6\text{H}_5)_2\text{CH}^-\text{K}^+\]  

(Eq. 10)

E. Electrochemical Reactions:

Organometallic compounds of group IA to IIIA can be indirectly prepared from ketones by electrochemical means via dialkylmercury compounds. Amazingly not much research has been done since the first reports by Tafel (14, 15), although the method seems a very attractive one (Eq. 11-12).

\[\text{CH}_3-\text{C-CH}_3 \xrightarrow{\text{Hg-cathode}} (\text{CH}_3^-\text{CH})_2\text{Hg} \text{ 20%} \]  

(Eq. 11-12)

The decarboxylation of calcium and barium salts of collidine-3,5-dicarboxylic acid, di(o-chlorophenyl) acetic acid and 2-methylpyrole-3-carboxylic acid proceeds readily
between 150-180°. Only a few examples are known where
decarboxylation occurs at reasonable temperature. R must
be a strongly electron-withdrawing group (Eq. 13-14).

\[
\text{Cl}_3\text{C-CO}_2\text{Na} \xrightarrow{70°} \text{THF} \xrightarrow{\text{CO}_2 + \text{Cl}_3\text{C}^- + \text{H}_2\text{O}} \xrightarrow{\text{HCl}} \text{CHCl}_3
\]

(Eq. 13-14)

\[
\text{(C}_6\text{H}_5)_3\text{C-CO}_2\text{K} \xrightarrow{>300°} (\text{C}_6\text{H}_5)_3\text{C}^- + \text{CO}_2
\]

G. Carbanions Generated with Nitrogen as the Leaving Group.

Carbanions have been postulated as intermediates in
the Wolff-Kishner reduction and in the base-catalyzed
oxidation of hydrazine (20). In both reactions the inter­
mediates may be alkylidiimides (Eq. 15). These have been
recently detected by Kosower (16,17,18) in other systems
(Eq. 15)

The fragmentation of the diimide could proceed through two
different path ways:
A homolytic cleavage would involve free radicals in a solvent cage which recombine after the loss of nitrogen (Eq. 16).

\[
\begin{align*}
R'CH-N=N-H & \xrightarrow{solvent cage} \left[ R'CH\cdot \cdot N_2H \right] \xrightarrow{solvent cage} R'CH_2 + N_2 \\
\text{(Eq. 16)}
\end{align*}
\]

The presence of base may favor a diimide anion intermediate, subsequent loss of nitrogen and formation of a carbanion. The Wolff-Kishner reaction may proceed through such a conjugate base of the diimide (Eq. 17).

\[
\begin{align*}
R\text{-C=N-NH}_2 & \rightarrow R\text{-C=N-NH}^- \rightarrow R\text{-CH-N=N}^- \rightarrow R\text{-CH}^- + N_2 \\
\text{(Eq. 17)}
\end{align*}
\]

Cram (19) studied the base-catalyzed cleavage of optically active 2-phenylbutylhydrazine with potassium periodate in different solvents (Eq. 18).

\[
\begin{align*}
\text{C}_6\text{H}_5\text{-C}^\prime \text{-NH-NH}_2 & \xrightarrow{\text{KIO}_4, \text{B}} \text{C}_6\text{H}_5\text{-C}^\prime \text{-H} + N_2 \\
\text{C}_2\text{H}_5 & \xrightarrow{\text{C}_6\text{H}_5\text{-C}^\prime \text{-H} + N_2}
\end{align*}
\]

\[
\text{Eq. 18}
\]
The resulting 2-phenylbutane showed 42% (methanol) to 80% (t-butanol) retention. The presence of optically active hydrocarbon was interpreted by Cram(20) as involving an anionic intermediate; base suppressed the homolytic cleavage to a large degree. Further study of the mechanism seems necessary since no direct proof for the presence of carbanions has been obtained until now.
II. PURPOSE AND METHOD OF RESEARCH

It was of interest to develop new ways to generate carbanions. We considered the decomposition of carboxylic acid salts and certain azo compounds.

The decomposition of carboxylic acid salts did not seem to be a promising lead. In general, fragmentation of carboxylic acid salts occurs only at extremely high temperature under circumstances when compounds derived from free radicals are the predominant products. In the past most decompositions were carried out in heterogeneous systems or by pyrolyzing solid salts. Because of insolubility of the salts in aprotic solvents no experiments have been undertaken in decarboxylating the salts in a homogeneous system. Crown ether(XXIV) which is a good ligand for potassium ion (30), might allow decomposition of potassium salts under milder, homogeneous conditions.

The base-catalyzed fragmentation of compounds having an azo linkage seems more promising than the pyrolysis of carboxylic acid salts. The azo compounds in question must possess certain structural features as to allow the loss of one substituent with subsequent formation of an alkyl- or aryldiimide anion.

Two types of compounds seem most suitable for this fragmentation process: Salts of alkyl- or arylazoformic acid and alkyl- or arylbenzoyldiimides. These are now considered separately.
Theoretically, the loss of carbon dioxide and nitrogen during pyrolysis of azoformate salts could lead to the formation of carbanions (Eq. 19)

\[
\text{R-N=N-C}_6\text{H}_5^- M^+ \xrightarrow{\Delta} R^- M^+ + N_2 + CO_2 \quad \text{(Eq. 19)}
\]

The preparation and pyrolysis of some potassium arylazoformates was first discussed by Hantzsch and Schultze (21), however no decomposition products were mentioned. Recently, Hoffmann reported the decomposition of (2-bromo-phenyl)-benzoyldiimide in refluxing phenol containing potassium phenoxide (Eq. 21) and in ethanol containing potassium ethoxide (Eq. 20). (22)

\[
\text{N=N-C}_6\text{H}_5^- \xrightarrow{\text{reflux}} \text{N=N-C}_6\text{H}_5^- + \text{C}_6\text{H}_5\text{O}^+ + \text{C}_2\text{H}_5\text{O}^-
\]

\[
\text{N=N-O-C}_6\text{H}_5^- \xrightarrow{\text{reflux}} \text{N=N-O-C}_6\text{H}_5^- + \text{C}_6\text{H}_5\text{O}^+ + \text{C}_2\text{H}_5\text{O}^-
\]

The formation of the products was interpreted as involving an initially formed 2-bromophenyl anion which either loses bromide ion to give benzyne or acquires a proton to give bromobenzene (Eq. 22).
With the exception of the work above, no attempts had been made to decompose alkyl- or arylazoformate salts. Therefore, we undertook the problem of preparing arylazoformates and decomposing them in heterogeneous or homogeneous systems in the absence of protonic solvents. The purpose of the study was to isolate or prove the intermediacy of carbanions in these systems.

The second possibility for generating carbanions from compounds having azo linkages in the fragmentation of alkyl- or arylbenzoyl-diimides with bases. This process might be envisaged as occurring by attack of the base at the benzoyl carbon with subsequent loss of nitrogen and formation of the corresponding carbanion (Eq. 23).

\[
R-N=N-C_6H_5 \xrightarrow{RO^\cdash} R^- + C_6H_5-C-O-R' + N_2 \quad \text{(Eq. 23)}
\]

The fragmentation of this type of compound was first studied by Cohen(23). From the products he obtained in the acid- and base-catalyzed methanolysis of benzoylphenyldiimide he concluded that the process under these conditions proceeds through a phenyl radical. No products or conclusions concerning an anionic mechanism were made.
Shortly afterwards, Hoffmann reported the fragmentation of some alkyl- and arylbenzoyldiimides with ethanolic sodium ethoxide (24,25). In contrast to Cohen he found striking evidence for the existence of an anionic mechanism by using ethanol-OD. The ideas behind their experiments were based upon the work by Urry and co-workers (26). They found that hydrogen abstraction of a radical always takes place on the \( \alpha \)-position of an alcohol, whereas the hydroxyl proton is abstracted by a base. Thus, Hoffmann was able to study the mechanism of the fragmentation process. By decomposing \( \alpha \)-bromophenylbenzoyldiimide with sodium ethoxide in ethanol-OD he found that the amount of deuterium incorporated in bromobenzene largely depended upon the concentration of base. The yields of deuterobromobenzene varied from 29 up to 94% at the highest concentration of base. From this, Hoffman concluded that there are two different pathways involved in the base-catalyzed fragmentation of alkyl- and arylbenzoyldiimides. He concluded that an increase in the base concentration suppresses the decomposition by the radical path. This is in good agreement with the results of Cram (19) on the base-catalyzed oxidation of alkylhydrazines.

There are no reports of fragmentation reactions of alkyl- or arylbenzoyldiimides carried out in aprotic solvents. We therefore felt that the decomposition of alkyl- and arylbenzoyldiimides with alkali alkoxides in heterogeneous and homogeneous systems might provide
interesting evidence on the intermediacy of carbanions. During the course of this work we came upon the reaction of t-butyllithium with methyl benzoate. Some unexpected results motivated further investigation of this reaction, and they are reported here also.
CHAPTER II
EXPERIMENTAL

1. CHEMICALS.

Chemical reagents used in this work which were obtained from commercial sources are listed in the following table:

TABLE 2

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Manufacturer</th>
<th>Grade, Purity</th>
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</thead>
<tbody>
<tr>
<td>Acetophenone</td>
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<td>East. Grade</td>
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<td>Mallinckrodt</td>
<td>Purified</td>
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<td>Supplier</td>
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<tr>
<td>p-Toluic acid</td>
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</table>
II. IDENTIFICATION OF SYNTHESIZED COMPOUNDS.

Physical Constants:

All boiling points were those obtained during distillation and are uncorrected. All melting points were determined using a capillary apparatus or a Fisher-Johns apparatus and are uncorrected.

Analyses and Molecular Weights:

Elemental microanalyses of synthesized compounds were carried out by the microanalytical laboratories of Dr. A. Bernhardt, Mühlheim (Germany), or Galbraith Analytical Labs.

The molecular weights of some compounds were determined by using the Mechrolab osmometer.

Spectrometric Methods:

Mass spectral analyses were performed on an Associated Electrical Industrial Model MS-9 mass spectrometer. Nuclear magnetic resonance spectra were obtained on a Varian Model A-60 or HA-100 spectrometer. Infrared absorption spectra were determined with a Perkin-Elmer Model 137 sodium chloride spectrometer.

Vapor phase chromatographic work was undertaken with an Aerograph Hy-FI Model 600 and an Aerograph 'Autoprep' Model A-700. All analyses determined by v.p.c. have been corrected for the weight: area factor by utilizing an internal standard, except where otherwise designated. All v.p.c. analyses were done on 30% Silicon gum rubber SE-30 on 45/60 chromosorb W or 20% FFAP on 60/80 chromosorb W.
III. SYNTHESIS.

Preparation of Potassium Phenylazoformate (XVII)

Ethyl Phenylhydrazoneformate.

Freshly distilled phenylhydrazine (170 g, 1.575 moles) in 1500 ml of dry ether was placed in a 3 l three-necked flask fitted with a condenser, dropping funnel, and mechanical stirrer. Ethyl chloroformate (85 g, 0.787 mole) was added slowly to the solution with stirring at 30°. During the addition, a white solid was formed. Stirring was continued for another hour after completing the addition. The solid was separated and the filtrate concentrated. Crystals precipitated out of the solution which were filtered and recrystallized (pet. ether—benzene) giving 103.5 g (73.2%) of ethyl phenylhydrazoformate, m.p. 80-81.5° (Lit. 23 m.p. 81-82°).

Ethyl Phenylazoformate. According to the procedure of Cohen (23).

Ethyl phenylhydrazoformate (103.5 g, 0.575 mole) was dissolved with stirring in 1600 ml of glacial acetic acid. To the cooled solution was added dropwise 1000 ml of a 0.2 M solution of potassium permanganate and at the end, 5 ml of 30% hydrogen peroxide. Stirring was continued for one hour after which 500 ml of chloroform was added. The chloroform extract was washed once with a 5% solution of sodium
bicarbonate and distilled water. After drying over magnesium sulfate, the chloroform was removed, using a rotary evaporator, to give a red oil. Distillation gave 87.5g (85.6%) of dark-red ethyl phenylazoformate, b.p. 107-108.5° (0.5mm) (Lit. b.p. 108°, 0.5mm).

The infrared spectrum (NaCl, neat) was characterized by a strong band at 1760 cm⁻¹ (C=O) and a weak band at 1675 cm⁻¹ (-N=O). 

**Potassium Phenylazoformate (XVIII)**

Finally powdered potassium hydroxide (3.36g, 0.06 mole), powdered in a drybox, was dissolved in a 500-ml flask equipped with a Teflon stirring bar and a dropping funnel with attached drying tube. After the solution had been cooled in an ice bath, ethyl phenylazoformate (10.68g, 0.06 mole) was added under high speed stirring. During the addition, an orange precipitate was formed. The mixture was allowed to stir for an additional thirty minutes at room temperature after which the precipitate was filtered through a Buchner funnel, washed with cold absolute ethanol and lastly with anhydrous ether. The salt was then dried in a vacuum oven at 50° and stored in a desiccator. A yield of 10.2g (90.5%) of potassium phenylazoformate, yellow leaflets, was obtained.

The infrared spectrum (KBr) had bands (cm⁻¹) at 3070, 1665, 1627(w), 1452, 1358, 962, 918, 878, 795, 757, 619, and 682. The salt is insoluble in most organic solvents with the exception of alcohols and dicyclohexyl-18-crown-6.
Sodium phenylazoformate (XVIII), was prepared in the same manner as described above. The saponification with sodium hydroxide was considerably slower.

All attempts to oxidize potassium phenylhydrazoformate (prepared by the procedure of Stern) with mercuric oxide were fruitless.

Preparation of Benzoylphenyldiimide (XIX)
The acylazo compound was prepared following the procedure by Cohen. (23)

N-Phenyl-N'-benzoylhydrazine.
To an ice-cold solution of freshly distilled phenylhydrazine (21.6g, 0.2 mole) in 100 ml of dry pyridine was slowly added benzoyl chloride (28.1g, 0.2 mole). The mixture was stirred overnight and treated with an excess of sulfuric acid. The white precipitate was filtered and recrystallized from absolute ethanol, giving 52.4g (76.5%) of N-phenyl-N'-benzoylhydrazine, m.p. 167-168° (Lit. 23 m.p. 168°).

Benzoylphenyldiimide.

N-Phenyl-N'-benzoylhydrazine (31.6g, 0.15 mole), yellow mercuric oxide (32.5g, 0.15 mole), anhydrous sodium sulfate (50.5g, 0.225 mole), and 1000 ml of dry petroleum ether (30-60°) were placed in a 2-l flask equipped with a drying tube and magnetic stirrer. The reaction mixture was stirred at room temperature for four hours, after which the color changed to red brown. The mixture was filtered; the filtrate was concentrated to about 400 ml. Cooling of the solution in a mixture of carbon tetrachloride and Dry Ice caused precipitation of a red solid which was filtered and dried in a vacuum desiccator, giving 24.3g
(77.2%) of benzoylphenyldiimide, m.p. 27-28° (Lit.23 m.p. 28-29°).

The infrared spectrum (CCl₄) was characterized by a strong band at 1712 (ν=0) and weak bands at 1685, 1650 cm⁻¹ (-N=N-⁻).

Preparation of Phenyl-p-toluoyldiimide (XX).

N-Phenyl-N'-p-toluoylhydrazine.

The same procedure was used as described above. Freshly distilled phenylhydrazine (37.8g, 0.35 mole) in 170 ml of dry pyridine was reacted with p-toluoyl chloride (54.1g, 0.35 mole). Recrystallization of the precipitate from absolute ethanol gave 57.5g (72.7%) of N-phenyl-N'-p-toluoylhydrazine, m.p. 167.5-169°, as white needles.

Phenyl-p-toluoyldiimide (XX)

Reaction of N-phenyl-N'-p-toluoylhydrazine (57.5g, 0.254 mole) with yellow mercuric oxide (55g, 0.254 mole) in the presence of 50g of anhydrous sodium sulfate and 700 ml of petroleum ether (30-60°) gave after cooling 47.5g (83.4%) of orange phenyl-p-toluoyldiimide, m.p. 41-42.5°. The infrared spectrum (CCl₄) had a strong band at 1708 (ν=0) and a medium band at 1693 cm⁻¹ (-N=N-⁻).

Preparation of (Dimethoxyphosphinyl)phenyldiimide (XXI).

The diimide was prepared by the method of Ribka (28). Freshly distilled aniline (46.5g, 0.5 mole) was dissolved in 150 ml of distilled water and 168 ml of hydrochloric acid (d 1.19). The hot solution was poured on 300g of ice. Sodium nitrite (42g, 0.608 mole) in 120 ml of
water was added slowly to the stirred solution at 0-5°. The ice-cold mixture was neutralized with a solution of 20% sodium acetate. Dimethyl phosphite (72.6g, 0.66 mole) in 150 ml of distilled water was then added, followed by 82g of sodium bicarbonate. The mixture was stirred for two hours at 10°C during which time the color changed to a deep red. The solution was extracted with ether, washed with distilled water, and dried over magnesium sulfate. The ether was removed with a rotary evaporator, resulting in a red undistillable oil.

Preparation of Benzoyl-\(t\)-butylidimide (XXII)

\(t\)-Butylhydrazine.

\(t\)-Butylhydrazine was prepared according to the procedure of Smith and co-workers. Benzophenone hydrazone (980g, 5 moles), yellow mercuric oxide (1100g, 5 moles) and 5000 ml of petroleum ether (30-60°C) were placed in a pressure bottle and shaken for ten hours. The mixture was then filtered and the red filtrate was concentrated to dryness, giving 878g (90.7%) of diphenyldiazomethane.

A solution of diphenyldiazomethane (873g, 4.5 moles) in 2000 ml of dry ether was slowly added with stirring to 2500 ml of 1.8M ethereal solution of \(t\)-butylmagnesium chloride. Upon completing the addition, the mixture was stirred for twelve hours and then slowly hydrolyzed with a solution of 5% ammonium chloride. The ether extract was dried and the solvent removed, leaving 985g (86.3%) of benzophenone \(t\)-butylhydrazone, m.p. 68-70°C (Lit. m.p. 68-72°C).
A mixture of 963g (3.8 moles) of benzophenone t-butylhydrazone, 1300 ml of conc. hydrochloric acid, and 2000 ml of ethanol was stirred at room temperature for one day. The solution was then evaporated at reduced pressure to remove all the ethanol and water. The solid residue was washed with ether and filtered, giving 270g (57.2\%) of t-butylhydrazine hydrochloride, m.p. 187-189°, (lit.\(^2\) m.p. 189°).

t-Butylhydrazine hydrochloride (261g, 2.1 moles) was treated with a solution of 500 ml of 30% sodium hydroxide. The mixture was warmed and most of the liquid distilled out. The distillate was treated with sodium hydroxide pellets until a water layer no longer appeared and distilled from barium oxide to give 136g (73.5\%) of colorless t-butylhydrazine, b.p. 109°, (lit.\(^2\) b.p. 109°).

N-Benzoyl-N′-t-butylhydrazine.

\(^{-}\)-Butylhydrazine (8.8g, 0.1 mole) was refluxed with methyl benzoate (27.7g, 0.2 mole) under stirring for three days. The excess methyl benzoate and the unreacted t-butylhydrazine were distilled off under vacuum at 10mm. The oily residue was dissolved in petroleum ether and a very small amount of chloroform. Cooling of the solution caused precipitation of a solid material. The solid was dispersed in 5% hydrochloric acid, slightly warmed and shaken. The water insoluble material was dissolved in ether and gave after evaporation 1.2g of benzoic acid. The acidic aqueous solution was concentrated to dryness giving a white solid which was recrystallized from absolute ethanol, m.p. 218-220° C. The salt was dissolved in a small amount of
water, treated with a 20% solution of sodium hydroxide and extracted with chloroform. After drying over magnesium sulfate, the solution was concentrated. Cooling and addition of a small amount of petroleum ether resulted in the precipitation of 10.3g (53.7%) of N-benzoyl-N'-t-butylhydrazine, m.p. 94-95.5°.

Nmr (CCl₄) τ 2.07-2.82 (multiplet, aromatic protons), and 8.93 (singlet, t-butyl protons).

**Benzoyl-t-butylidimide (XXII)**

N-Benzoyl-N'-t-butylhydrazine (13.2g, 0.0688 mole), yellow mercuric oxide (14.95g, 0.0688 mole), anhydrous sodium sulfate (14.4g), and 110 ml of dry petroleum ether (30-60°C) were stirred for four hours under anhydrous conditions. The color of the suspension changed from colorless to orange-red. The solution was filtered and concentrated. The dark-red oil was distilled under reduced pressure, giving 11.8g (90.05%) of benzoyl-t-butylidimide, b.p. 78-79° (0.7mm), 83.5-85° (1mm). The infrared spectrum (CCl₄) showed a strong carbonyl band at 1720 and a medium band at 1655 cm⁻¹ (-N=N-?). The nmr spectrum (CCl₄, TMS internal standard) showed resonance at τ 2.13-2.81 (multiplet, aromatic) and 8.68 (singlet, t-butyl).

**Anal. Calcd. for C₁₁H₁₄N₂O: C, 69.44; H, 7.42; N, 14.73; O, 8.41.  Found : C, 69.35; H, 7.51; N, 14.64; O, 8.50.**
Benzoyl-t-butyldiimide is fairly stable. White crystals appeared and gas was formed after the diimide had been stored for ca. one month in the refrigerator. Vapor phase chromatography of the clear liquid indicated the presence of benzil. Recrystallization of the solid from chloroform gave white needles, m.p. 73-74.5°. The compound was identified from its physical and spectral properties as \( N,N'\text{-di-t-butyldiimide} \) (XXV).

Molecular weight found: 248 (calcd 248).

The infrared spectrum (CCl₄) was characterized by a weak band at 3310 (H-N=) and strong at 1654 cm⁻¹ (\( \gamma(C=O) \)).

The nmr spectrum (CCl₄) showed resonance at \( \tau \) 2.21-2.73 (multiplet, aromatic protons), 5.20 (broad singlet, \( \gamma(N-H) \)), and 8.89, 8.95 (two singlets, t-butyl protons). The peak areas were in the ratio 5:1:18.

Mass spectrum, m/e (relative intensity) 57(52), 77(30), 87(36), 103(15), 105(100), 106(10), 136(20), 143(14), 177(44), 178(7), 192(25), 193(6), 148(3, \( M^+ \)).

**Anal.** Calcd. for \( C_{15}H_{24}N_2O \): C, 72.54; H, 9.74; N, 11.28; O, 6.44.

Found: C, 72.41; H, 10.08; N, 10.99; O, 6.52.

The same compound, m.p. 73-74.5°, was formed by photolysis of a solution of benzoyl-t-butyldiimide in pentane or by heating benzoyl-t-butyldiimide in a sealed tube for two days at 130-150°.
Preparation of Carbimethoxy-t-butylidiimide (XXIII)

N-t-Butyl-N'-carbimethoxyhydrazine.

t-Butylhydrazine (4.4 g, 0.05 mole) and dimethyl carbonate (9.01 g, 0.1 mole) were refluxed for four days with stirring. The volatile materials were removed under reduced pressure leaving a yellow oil which crystallized after the addition of a small amount of chloroform. Filtration of the solid gave 3.8 g (52.1%) of crude N-t-butyl-N'-carbimethoxyhydrazine as impure crystals. Sublimation gave colorless needles, m.p. 73-74°.

The infrared spectrum (CDCl₃) showed characteristic bands at 3380, 3260 (-NH-) and a strong band at 1722 cm⁻¹ (=O).

Nmr (CDCl₃) 6.40 (singlet, methoxyl), 8.94 (singlet, t-butyl). The peak areas were in ratio 1:3.

Methyl t-Butylazoformate.

A mixture of N-t-butyl-N'-carbimethoxyhydrazine (1.4 g, 0.01 mole), yellow mercuric oxide (2.17 g, 0.01 mole), anhydrous sodium sulfate (2 g), and 15 ml of dry petroleum ether (30-60°) was stirred at room temperature for two hours. The yellow solution was filtered and the solvent removed on a rotary evaporator. The residue was distilled under reduced pressure, giving 1.1 g (76.4%) of methyl t-butylazoformate, b.p. 53-54° (10 mm), as a yellow oil. The IR spectrum (neat) showed a strong carbonyl band at 1765 cm⁻¹ and the nmr (CDCl₃) 6.07 (singlet, methoxyl), 8.70 (singlet, t-butyl). The peak areas were in ratio 1:3.
Attempts to saponify the azo ester with potassium hydroxide in absolute ethanol failed.

\[
2,5,8,15,18,21-\text{Hexaoxatricyclo}[20.4.0.0^{9,14}]\text{Hexacosane.}
\]

\[(\text{Dicyclohexyl-18-crown-6})(XXIV).\]

The cyclic polyether was prepared according to the procedure of Pedersen. A mixture of pyrocatechol (220g, 2 moles), sodium hydroxide (80g, 2 moles), and 1500 ml of n-butanol was condensed with bis(2-chloroethyl)ether (143g, 1 mole) for three hours at reflux temperature. After the temperature had been lowered to 90°, the mixture was reacted with an additional 80g of sodium hydroxide and 143g of bis(2-chloroethyl)ether. Refluxing was continued for one day. Eleven ml of concentrated hydrochloric acid then was slowly added and the major part of the n-butanol removed by steam distillation. The remaining solid material was filtered and recrystallized from hot benzene, giving 167.5g (46.6%) of 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene.

A 1-1 stainless steel bomb was charged with dibenzo-18-crown-6 (157g, 0.437 mole), 850 ml of dry dioxane, and 15.7g of ruthenium catalyst (5% ruthenium on alumina). The mixture was hydrogenated at 100° and 1600 psi with good agitation until the theoretical amount of hydrogen (2.62 moles) had been absorbed. The catalyst was removed by filtration and the solvent was removed under vacuum with a rotary evaporator. The crude dicyclohexyl-18-crown-6 was dissolved in 300 ml
of dry n-pentane and the solution allowed to drain through an acid-washed alumina column. The elution was continued (500 ml of n-pentane) until the infrared spectrum of the eluate showed no hydroxyl band. The OH-free cycloether was further purified by distilling it from powdered calcium hydride at 194-197° (0.6mm).
Figure 11. Apparatus for the Fragmentation of Acylazo Compounds.
IV. FRAGMENTATION REACTIONS.

Decarboxylation of Sodium Phenylazoformate (XVIII)

When sodium phenylazoformate was heated under vacuum to 180°, it decomposed instantly. The products were collected in a Dry Ice trap. They consisted mainly of biphenyl and a number of nitrogen containing compounds. There was no evidence to indicate the presence of phenylsodium.

Decarboxylation of Potassium Phenylazoformate (XVII) in Dicyclohexyl-18-crown-6—Tetrahydrofuran (open system).

Potassium phenylazoformate (1g, 5.3 mmoles) dissolved in 3 ml of dry dicyclohexyl-18-crown-6 and 8 ml of dry tetrahydrofuran was refluxed with stirring for three hours. During this time, the color changed from yellow to brown. Evaporation of the volatile material (180-200°C, 1mm) into a Dry Ice trap resulted in a solid, which after acidification and purification, gave 0.052g (8.05%) of benzoic acid, m.p. 121°. Vapor phase chromatography of the volatile material indicated presence of benzene and traces of aniline, but no biphenyl.

Decarboxylation of Potassium Phenylazoformate in Dicyclohexyl-18-crown-6—Tetrahydrofuran (closed system).

A solution of potassium phenylazoformate (1g, 5.3 mmoles) in 3 ml of dry dicyclohexyl-18-crown-6 and 8 ml of dry tetrahydrofuran was placed in a 25-ml flask together with a Teflon stirring bar. The flask was attached to a condenser and connected to the gas burette.
shown in Figure 11. The system was evacuated, filled with helium to normal pressure and closed. The solution was stirred and refluxed for three hours. The collected gas was a mixture of nitrogen and carbon dioxide, 116.5 ml (corrected). Distillation of all the volatile material into a Dry Ice trap left a solid, which after acidification and purification, gave 0.108 g (16.7%) of benzoic acid, m.p. 120-122°. The volatile material was analyzed by v.p.c. It contained 0.195 g (47%) of benzene, 5 mg (1.0%) of aniline, and some high molecular nitrogen compounds, but no biphenyl.

Decarboxylation of Potassium Phenylazoformate in Cycloether—Tetrahydrofuran in the Presence of Amyl acetate (closed system).

A solution of potassium phenylazoformate (1g, 5.32 mmoles) in 3 ml of dry cycloether and 8 ml of dry tetrahydrofuran was decarboxylated in the presence of 1 ml of dry amyl acetate under the same conditions as described above. 117.5 ml (corrected) of gas was collected. This consisted of nitrogen and carbon dioxide. The residue from the distillation gave 0.092 g (14.2%) of benzoic acid. Besides benzene (0.235 g, 56.7%), aniline (14 mg, 2.8%), the vapor phase chromatography of the volatile material showed about 1 mg (0.16%) of acetophenone (comparison of the retention time with an authentic sample).

Reaction of Potassium Phenylazoformate with Bromine.

Potassium phenylazoformate (0.47 g, 2.5 mmoles) and 10 ml of dry benzene were placed in a 25-ml flask. The flask was attached to a
dropping funnel containing bromine (0.4 g, 2.5 mmole) in 6 ml of dry benzene. This system was connected to the gas collection apparatus described in Figure 11. After the air had been displaced by helium, the system was closed and the bromine solution added slowly to the suspended salt under high speed stirring. Addition was completed within one hour and stirring was continued for twelve hours. 96 ml (corrected) of nitrogen was collected (85.7%). Analysis of the solution by vapor phase chromatography indicated the presence of 0.154 g of bromobenzene (0.98 mmole, 39.2%), and 0.077 g of biphenyl (0.5 mmole, 40%).

General Procedure for the Base-Catalyzed Fragmentation of Acylazo Compounds.

The fragmentations were carried out in the apparatus shown in Figure 11. The base and the solvent were placed in a 100-ml flask equipped with a dropping funnel. The dropping funnel, containing the required amount of diimide, was connected to the apparatus. The system was evacuated, refilled with helium to normal pressure and closed. The solution of azo compound was slowly added to the stirred base. Volume readings were made periodically for the first two hours and corrected to standard conditions. After completion of the addition, the mixture was stirred for twelve hours. The liberated gas was analyzed at room temperature by vapor phase chromatography using a 9-ft. x 1/4-inch column containing silica gel and a 20-ft. x 1/4 inch column with 50% Dowtherm on firebrick. The reaction
mixture was filtered and analyzed by vapor phase chromatography. The retention times of the products were compared with those of authentic samples. When these were found to be identical, the samples were added to small portions of the product mixture and the chromatogram was examined for symmetry of the peak in question. When possible, products were isolated and characterized. The mixtures were analyzed quantitatively by comparing the ratios of peak areas with those from mixtures of known composition.

Fragmentation of Benzoylphenyldiimide with CH₃OK in Pentane.

Benzoylphenyldiimide (1.05 g, 5 mmoles) in 50 ml of dry pentane was reacted with a suspension of potassium methoxide (0.35 g, 5 mmoles) in 10 ml of dry pentane. 76.5 ml (3.41 mmoles yield 68.3%) of nitrogen gas was liberated. The precipitate was separated from the solution and hydrolyzed giving after acidification and extraction with ether, 0.13 g (1.07 mmoles yield 21.3%) of benzoic acid, m.p. 118-120°. Vapor phase chromatography of the organic material indicated 0.365 g (2.68 mmoles yield 53.7%) of methyl benzoate, 0.025 g (0.32 mmmole, yield 6.4%) of benzene, 0.03 g (0.195 mmmole, yield 7.8%) of biphenyl, 0.051 g (0.28 mmmole, yield 5.62%) of benzophenone, 0.0041 g (0.016 mmmole, yield 0.67%) of triphenylmethanol, and other unidentified products such as benzoyl-diphenylhydrazines.
Fragmentation of Benzoylphenyldiimide with CH₃OK in Benzene.

Benzoylphenyldiimide (1.05 g, 5 mmoles) in 10 ml of dry benzene was reacted with a suspension of potassium methoxide (0.35 g, 5 mmoles) in 40 ml of dry benzene. 52.5 ml (2.34 mmoles, yield 46.8%) of nitrogen gas was liberated. Isolation and work-up of the precipitate gave 0.168 g (1.378 mmoles, yield 27.5%) of benzoic acid, (m.p. 118-121°) and 20-30% of a brown solid, consisting of a number of nitrogen containing compounds. Only one compound was isolated in fairly pure form with a melting point of 201-205°, aromatic absorption in the nmr spectrum, and carbonyl stretching in the IR spectrum.

Mass spectrum, m/e (relative intensity), 51(26), 77(69), 105(100), 121(39), 167(7), 180(7), 181(7), 183(7), 184(7), 270(16), 271(16), 288(3), 303(6), 346(2), 347(2), 422(1,M⁺).

The compound (XXVII) is believed to be a dimer (C₆H₅-N₂H-C₆H₅)₂.

Distillation of the organic material left a solid consisting of 0.0274 g (0.095 mmole, yield 3.8%) of N,N-diphenyl-N'-benzoylhydrazine XXVIII, m.p. 191-193° (Lit. 189-191°), and 0.0151 g (0.052 mmole, yield 2.1%) of N,N'-diphenyl-N-benzoylhydrazine XXVIII, m.p. 138-140° (Lit. 136-138°). Vapor phase chromatography indicated 0.212 g (1.56 mmoles, yield 31.2%) of methyl benzoate, 0.094 g (0.61 mmole, yield 24.4%) of biphenyl, and 0.0334 g (0.184 mmole, 3.67%) of benzophenone. There were traces of toluene present but no benzil. Repetition of the experiment in the presence of cyclohexene failed to give any norcarane.
Fragmentation of Benzoylphenyldiimide with Potassium Methoxide in Cycloether—Benzene.

Benzoylphenyldiimide (0.635g, 3.02 mmoles) in 10 ml of dry benzene was added slowly to 55 ml of a 0.055 M solution of potassium methoxide (0.212g, 3.02 mmoles) in cycloether—benzene 1:1. 62 ml (2.77 mmoles, yield 91.7%) of nitrogen gas was collected. Vapor phase chromatography of the organic material indicated, besides some minor products, 0.242g (1.78 mmoles, yield 58.8%) of methyl benzoate, 0.011g (0.076 m mole, yield 5.1%) of biphenyl, and 0.045g (0.247 m mole, yield 8.2%) of benzophenone. There were also traces of triphenylmethanol present. Distillation of all the volatile material left a solid. Work-up of the residue gave 0.105g (0.86 m mole, yield 28.5%) of benzoic acid, m.p. 119-121°.

Fragmentation of Phenyl-\(p\)-toluoyldiimide with Potassium Methoxide in Benzene.

Phenyl-\(p\)-toluoyldiimide (1.12g, 5 m moles) in 10 ml of dry benzene was reacted with a suspension of potassium methoxide (0.35g, 5 m moles) in 40 ml of dry benzene. 55 ml (2.46 m moles, yield 49.2%) of nitrogen gas was liberated. Work-up of the blue-gray precipitate gave 0.195g (1.435 m moles, yield 28.7%) of \(p\)-toluic acid (m.p. 179-181°), and other unidentified products. Analysis of the organic material by vapor phase chromatography indicated 0.17g (1.35 m moles, yield 22.7%) of methyl \(p\)-toluate, 0.095g (0.617 m mole, yield 24.7%) of biphenyl, and 0.0139g (0.071 mole, yield 1.42%) of 4-methylbenzophenone.
Fragmentation of Benzoyl-\(t\)-butyldiimide with Sodium Methoxide in Benzene.

Benzoyl-\(t\)-butyldiimide (0.76g, 4 mmoles) in 10 ml of dry benzene was reacted with a suspension of sodium methoxide (0.22g, 4 mmoles) in 20 ml of dry benzene. The gas liberated consisted of 53 ml (2.39 mmoles, yield 59.7%) of nitrogen, 17.5 ml (0.78 mmole, yield 19.5%) of isobutane, and 1.2 ml (0.054 mmole, yield 1.3%) of isobutylene. Filtration of the precipitate gave a white solid whose infrared spectrum (KBr) was identical to that of an authentic sample of sodium benzoate. Acidification of an aqueous solution of the solid and extraction with ether gave 0.161g (1.32 mmoles, yield 32.9%) of benzoic acid, m.p. 119-121°. Vapor phase chromatography indicated besides other products, the presence of 0.15g (1.1 mmoles, yield 20.2%) of methyl benzoate, 0.121g (0.75 mmole, yield 18.7%) of 2,2-dimethylpropiophenone, 0.008g (0.042 mmole, yield 1%) of \(N\)-benzoyl-\(N\'-\(t\)-butylhydrazine, and 0.053g (0.214 mmole) of a white solid which was separated by thin-layer chromatography into white needles, m.p. 73-74.5°, and a white crystalline material, m.p. 154-156°. The first compound was identical with \(N,N\'-di-\(t\)-butyl-\(N\)-benzoylhydrazine XXV described above. The second compound was identified from its spectral properties as \(N,N\'-di-\(t\)-butyl-\(N\'-benzoylhydrazine (XXVI). The infrared spectrum (\(CCl_4\)) was characterized by a weak band at 3350 (\(\text{H-N}\)) and a strong one at 1687 cm\(^{-1}\) (\(\nu=0\)).
The nmr spectrum (CCl₄) showed resonance at 72.12-2.73 (multiplet, aromatic) and 8.71 (singlet, t-butyl protons). The peak areas were in the ratio 5:18.

Mass spectrum: m/e (relative intensity) 57(40), 77(18), 87(16), 103(6), 105(100), 106(8), 136(43), 177(45), 178(5), 192(39), 248(2, M⁺).

The yields of products reported above represented the average values from six runs. The compound designated as 2,2-dimethylpropiophenone was isolated by v.p.c. and compared to a sample of 2,2-dimethylpropiophenone prepared from pivaloyl chloride and phenylmagnesium bromide in 82% yield, b.p. 102-103° (12 mm). (Lit. b.p. 102°, 12 mm). Spectral properties were the same for both compounds.

The infrared spectrum (CCl₄) was characterized by a strong band at 1676 cm⁻¹ (C=O).

The nmr spectrum (CCl₄) showed resonance at 72.39-2.91 (multiplet, aromatic protons) and 8.70 (singlet, t-butyl protons).

**Fragmentation of Benzoyl-t-butylidimide with Methanolic Sodium Methoxide in Benzene.**

Benzoyl-t-butylidimide (0.76g, 4 mmoles) in 10 ml of dry benzene was reacted with a solution of sodium methoxide (0.22g, 4 mmoles) in 2 ml of absolute methanol and 20 ml of dry benzene. The gas liberated consisted of 65 ml (2.9 mmoles, yield 72.5%) of nitrogen, 29 ml (1.295 mmoles, yield 32.4%) of isobutylene. Filtration and work-up of the precipitate gave 0.155g (1.27 mmoles, yield 31.7%) of benzoic acid, m.p. 118-121°. Vapor phase chromatography indicated the presence
of 0.157g (1.55 mmoles, yield 29.9%) of methyl benzoate, 0.006g
(0.037 mmole, yield 0.92%) of 2,2-dimethylpropiophenone, and other
minor products. (Average values of two runs).

Fragmentation of Benzoyl-t-butyldiimide with Sodium Methoxide in
Benzene in the Presence of Ethyl Acetate (Benzophenone).

When a solution of benzoyl-t-butyldiimide (0.76g, 4 mmoles) in
10 ml of dry benzene was reacted with a suspension of sodium methoxide
(0.22g, 4 mmoles) in dry ethyl acetate (0.88g, 10 mmoles) and 20 ml
of dry benzene, the reaction ceased after about 20 ml of gas had been
collected. Deactivation of sodium methoxide was observed also in
the fragmentation of benzoyl-t-butyldiimide in the presence of benzo­
phenone. The reaction proceeded only after a large excess of methoxide
was added. In both cases, no carbonyl addition products were observed.

Fragmentation of Benzoyl-t-butyldiimide with Potassium Methoxide in
Benzene in the Presence of Bromine.

A solution of benzoyl-t-butyldiimide (0.76g, 4 mmoles) in 10 ml
of dry benzene was slowly added to a suspension of potassium methoxide
(0.28g, 4 mmoles) in 20 ml of dry benzene containing bromine (0.64g,
4 mmoles). The collected gas consisted of 62 ml (2.77 mmoles, yield
69.2%) of nitrogen, 1.6 ml (0.07 mmole, yield 1.78%) of isobutylene,
0.7ml (0.31 mmole, yield 0.78%) of isobutane, and 10.2 ml (0.455 mmole)
of ethylene. In separate experiments it was shown that ethylene comes
from the reaction of potassium methoxide with bromine. No benzoic acid
was present. Vapor phase analysis of the organic layer indicated a number of compounds with 2-bromo-2-methylpropane and methyl benzoate as major products, with 2,2-dimethylpropiophenone as a minor product (1% of the ester).

**Fragmentation of Benzoyl-t-butyldiimide with Sodium Methoxide in Benzene in the Presence of Carbon Tetrachloride.**

The reaction product contained besides methyl benzoate, 2,2-dimethylpropiophenone, a small amount of 2-chloro-2-methylpropane.

**Fragmentation of Benzoyl-t-butyldiimide with Potassium Methoxide in Cycloether — Benzene.**

Benzoyl-t-butyldiimide (0.346g, 1.82 mmoles) in 10 ml of dry benzene was slowly added to 28 ml of a 0.065 M solution of potassium methoxide (0.127g, 1.82 mmoles) in cycloether — benzene 1:1. The gas collected consisted of 37 ml (1.65 mmoles, yield 90.75%) of nitrogen, 3.6 ml (0.161 mmole, yield 8.82%) of isobutane, and 0.5 ml (0.022 mmole, yield 1.22%) of isobutylene. Distillation of the volatile material under reduced pressure (<1mm) left a residue, which after acidification and extraction with ether, gave 0.045g (0.369 mmole, yield 20.3%) of benzoic acid, m.p. 117-119°.

Vapor phase chromatography of the volatile material indicated 0.5-4.0% of methyl benzoate, 30-45% of 2,2-dimethylpropiophenone, 17-20% of products derived from 2,2-dimethylpropiophenone and t-butyllithium (see reaction of methyl benzoate with t-butyllithium), and 15-25% of other unidentified products (average values of three runs).
Fragmentation of Benzoyl-t-butyldiimide with CH₃OK in Cycloether — Benzene in the Presence of Ethyl Acetate.

Benzoyl-t-butyldiimide (0.19g, 1 mmole) in 5ml of dry benzene was slowly added to 20 ml of a 0.05 M solution of potassium methoxide (0.07g, 1 mmole) in cycloether — benzene 1:1 containing dry ethyl acetate (0.044g, 0.5 mmole). Besides the compounds described in the previous fragmentation process, there was a very small amount of pinacolone (about 10% of 2,2-dimethylpropiophenone).

Fragmentation of Benzoyl-t-butyldiimide with Sodium Oxide in Tetrahydrofuran.

Benzoyl-t-butyldiimide (0.76g, 4 mmoles) in 10 ml of dry tetrahydrofuran was slowly added to a suspension of sodium oxide (0.37g, 6mmoles) in 20 ml of dry tetrahydrofuran. Work-up of the products gave 0.17g (1.4 mmoles, 34.8% yield) of benzoic acid. Vapor phase chromatography indicated that 64.7% of the organic material consisted of 2,2-dimethylpropiophenone.
V. REACTION OF t-BUTYLLITHIUM WITH METHYL BENZOATE.

85 ml of a 1.8M solution of t-butyllithium in pentane was added to 10g of methyl benzoate in 50 ml of n-pentane by means of a hypodermic syringe inside a drybox. The reaction mixture was shaken during the addition. Stirring was continued for one hour, after which the reaction mixture was hydrolyzed with water at reflux temperature. The organic layer was separated, washed with distilled water, and then dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator. All the volatile material was distilled under reduced pressure (30-200°, <1mm) into a receiver cooled with Dry Ice. Addition of pentane to the oily residue gave a solid which upon recrystallization from pentane — chloroform resulted in ca. 0.1 g of colorless needles, m.p. 243-245°, later described as compound XXXVII. The distillate was fractionated by using gas chromatography. Separation of some compounds was very difficult, therefore, a second fractionation was often necessary.

All six compounds present in the reaction product were isolated.

Compound XXXI 4-10% yield.

Colorless liquid, b.p. 102-103° (12mm), was identified as 2,2-dimethyl-propiophenone (Lit.31 b.p. 102°, 12 mm). An authentic sample showed the same retention time and spectral properties.

The infrared spectrum (CCl₄) exhibited a band at 1676 cm⁻¹ (>C=O)

The nmr spectrum (CCl₄) showed resonance at 2.39-2.91 (multiplet, aromatic protons) and 8.70 (singlet, t-butyl protons).
Mass spectrum, m/e (relative intensity), 57(15), 77(9), 99(3), 105(100), 106(17), 119(5), 162(20), 162(5, M⁺).

**Compound XXXII**: 37-39% yield as colorless needles, m.p. 42-43°C.

The compound was identified as α-t-butylbenzyl alcohol (Lit.32,33 m.p. 45°C, m.p. 40°C). Molecular weight found: 166 (calcd. 164.24).

The infrared spectrum (neat) showed strong hydroxyl bands at 3700 (free) and 3570 cm⁻¹ (bonded). The nmr spectrum (CCl₄) showed resonance at τ2.83 (singlet, aromatic protons), 5.82, 7.77 (two singlets, hydroxyl and methine proton) and 9.16 (singlet, t-butyl protons). The peak areas were in the ratio 5:1:1:9. Cooling of the nmr sample to -40°C did not change the spectrum. Mass spectrum, m/e (relative intensity), 57(85), 79(85), 91(20), 105(60), 107(100), 108(80), 131(10), 149(30), 164(50, M⁺).

**Anal.** Calcd for C₁₁H₁₅O: C, 80.44; H, 9.82; O, 9.74.

Found: C, 80.36; H, 9.83; O, 9.81.

**Compound XXXIII**: 12-21% yield as colorless oil.

The compound was identified as 1-pivaloyl-4-t-butylocyclohexadiene-1,5.

The infrared spectrum (CCl₄) was characterized by strong bands at (cm⁻¹) 1655 ( >C=O) and 862, 755 (vinyl). The ultraviolet spectrum (isooctane) showed absorption at μ₂ 230 as a slight shoulder and 285 (e2,000). The nmr spectrum (CCl₄) showed resonance at τ3.54 (one vinyl proton, part of unsubstituted double bond), 3.78 (unsymmetrical triplet, vinyl proton of substituted double bond), 4.20 (one vinyl proton, part
of unsubstituted double bond), 7.41-8.08 (one methine proton, multiplet), 7.75, 7.81 (unsymmetrical doublet, two methylene protons), 8.77, 9.07 (two singlets, t-butyl protons).

Mass spectrum, m/e (relative intensity), 57(100), 77(18), 78(10), 79(17), 85(10), 91(18), 93(10), 105(22), 107(20), 118(8), 121(8), 135(6), 161(82), 162(10), 163(44), 164(24), 220(5, M⁺).

**Compound XXXIV**: 6-13% yield as colorless crystals, m.p. 44-46°.

The compound was identified as α,α-dimethyl-2-t-butylpropiophenone. Molecular weight found: 218 (calcd 218.34). The infrared spectrum (neat) exhibited strong bands at cm⁻¹ 1668 (carbonyl) and 858 (para disubstituted benzene). The nmr spectrum (CCl₄) showed resonance at 2.53, 2.68 (AB, aromatic protons) and 8.66 (singlet, t-butyl protons). The peak areas were in the ratio 2:9.

Mass spectrum, m/e (relative intensity), 57, 85(12), 118(15), 133(6), 146(15), 161(100), 162(45), 163(10), 203(5), 218(5, M⁺).

**Anal. Calcd for C₁₅H₂₂O**: C, 82.51; H, 10.16; O, 7.33.

**Found**: C, 82.39; H, 10.57; O, 7.04.

**Compound XXXV**: 20-25% yield as colorless oil.

The compound was identified as α,α-di-t-butylbenzylalcohol. Molecular weight found: 224 (calcd 220.36). The infrared spectrum (CCl₄) was characterized by strong bands at cm⁻¹ 3730 (hydroxyl) and 743, 707 (monosubstituted benzene).
The nmr spectrum (CCl₄) showed resonance at τ2.18-2.98 (multiplet, aromatic protons), 8.20 (singlet, hydroxyl proton), and 8.91 (singlet, t-butyl protons). The peak areas were in the ratio 5:1:18. Heating of a nmr sample of α,α-di-t-butylbenzylalcohol in diglyme to 150°, gave little or no change in the spectrum. The nmr spectrum (CCl₄) of α,α-di-t-butylbenzylalcohol-2,4,6-d₃ showed resonance at τ2.78, 2.86 (two singlets, m-protons), 8.28 (singlet, hydroxyl proton), and 8.92 (singlet, t-butyl protons). Mass spectrum, m/e (relative intensity), 57(100), 77(27), 79(6), 85(46), 91(10), 105(60), 106(5), 119(10), 163(100), 164(15), 220(1, M⁺).


Found: C, 82.04; H, 11.24; O, 6.72.

Compound XXXVI: 7-10% yield as colorless crystals, m.p. 77-80°.
The compound was identified as α-p-di-t-butylbenzylalcohol. The infrared spectrum (CCl₄) showed strong bands at cm⁻¹ 3668, 3550 (free and bonded hydroxyl) and 832 (para disubstituted benzene).
The nmr spectrum (CCl₄) showed resonance at τ2.87 (singlet, aromatic protons), 5.75, 8.75 (two singlets, hydroxyl and methine proton), 8.69 and 9.11 (two singlets, t-butyl protons). Mass spectrum, m/e (relative intensity), 57(100), 77(17), 79(17), 91(35), 133(30), 147(25), 148(27), 149(20), 161(50), 163(100), 164(45), 165(25), 187(35), 221(40), 222(17, M⁺).


Found: C, 81.70; H, 11.39; O, 6.91.
**Compound XXXVII**: ca. 1% as colorless needles, m.p. 243-244.5°

From the data available we believe that compound XXXVII is a tricyclo \([6.2.2.0^{2,7}]\) dodeca-4,9-diene.

![Chemical Structure](image)

Until now we have not been able to assign the positions for the two t-butyl and the two pivaloyl groups. Molecular weight found: 428 (calcd 440.714). The infrared spectrum (KBr) had bands at cm\(^{-1}\) 2980(s), 1650(s), 1640(s), 1608(w), 1470(s), 1457(m), 1423(w), 1384(s), 1355(s), 1315(w), 1283(m), 1272(m), 1244(w), 1223(w), 1212(w), 1175(m), 1160(s), 1142(s), 978(w), 935(m), 913(w), 886(m), 764(s).

The nmr spectrum (CDCl\(_3\)) was characterized by resonance at \(\tau 3.22, 3.53\) (two sets of doublets, each part of separate AX systems; two vinyl protons), and four sharp singlets at \(\tau 8.78, 8.83, 9.20, 9.26\) (t-butyl protons). The ultraviolet spectrum (isooctane) showed absorption at \(\lambda = 234\) m\(\mu\) (e=1,400).

Mass spectrum, m/e (relative intensity), 57(100), 58(6), 69(8), 77(6), 79(8), 83(5), 85(9), 87(7), 91(5), 105(38), 107(9), 135(4), 151(6), 161(4), 163(15), 164(6), 165(10), 221(10), 222(4), 299(2), 327(24), 328(6), 355(2), 383(59), 384(18), 425(3), 440(3, \(M^+\)).

Compound XXXVII decolorized bromine and formed an oxime with hydroxyl-amine, m.p. 169-171°.
Compound XXXVII was obtained in ca. 4.5% yield when the hydrolysis was carried out at higher temperature (60-90°) by using hexane or heptane as solvent. Hydrolysis of the reaction mixture with deuterium oxide afforded a compound containing two deuteriums. The nmr spectrum (CDCl₃) of compound XXXVII-d₂ was similar to that of XXXVII; the only difference was the disappearance of a relative sharp singlet at 78.32.

An additional compound was isolated once from the reaction of methyl benzoate with t-butyllithium. This compound (IXL) was not detected in later runs. Compound IXL was identified as 1-pivaloyl-4-t-butyldicyclohexadiene-1,3. The infrared spectrum (neat) was characterized by bands at (cm⁻¹) 1665(s), 1613(m), 1373(m), and 843(s). The nmr spectrum (CCI₄) showed resonance at 3.26, 4.19 (two doublets, AB vinyl protons), 7.77 (multiplet), and 8.75, 8.89 (sharp singlets, t-butyld protons). Mass spectrum, m/e (relative intensity), 57(100), 77(12), 85(8), 91(15), 93(10), 115(5), 135(5), 135(8), 161(100), 162(30), 163(85), 218(3), 220(6, M⁺).

When the solid material formed by the addition of t-butyllithium to methyl benzoate was separated, extracted with tetrahydrofuran and the solution hydrolyzed, an additional diene was detected. It was not isolated, since it seems thermally unstable (100°). The nmr spectrum
(CCl₄) was characterized by resonance at 4.23, 4.73 (center of symmetrical A₂B₂ system). It seems that this compound (XI) is 1-pivaloyl-4-t-butylcyclohexadiene-2,5.

**Preparation of Methyl Benzoate (2,4,6-d₃).**

The procedure employed was a modification of that of Schmid. Aniline hydrochloride (22.5 g, 0.1735 mole) was heated with 22 ml of deuterium oxide for one day at an oil bath temperature of 105°. All the H₂O - D₂O was removed under reduced pressure and the remaining solid dried in vacuo for another six hours at 105° (1mm). This process was repeated four times. The aniline was liberated by the addition of an aqueous solution of 28.2 g of sodium carbonate and extracted into ether. The ethereal solution was dried over magnesium sulfate, concentrated on a rotary evaporator, and the residue distilled, giving 15.5 g (93.1%) of aniline-2,4,6-d₃, b.p. 182-184°. The nmr spectrum (CCl₄) showed a single peak for the m-protons at 73.03, indicating total exchange of the 2,4,6-hydrogens by deuteriums.

Aniline was converted to the nitrile by the Sandmayer reaction. A solution of aniline-2,4,6-d₃ (14.5 g, 0.15 mole) in 40 g of concentrated hydrochloric acid and 250 ml of water was cooled to 0-5°. To the stirred mixture was added slowly a solution of 13.3 g of sodium nitrite in 65 ml of water until KI-starch paper indicated nitrous acid. The diazonium chloride, prepared as such, was added to a solution of 41.7 g of cupric sulfate and 46 g of potassium cyanide in 170 ml of water at 60-70°. Because of the liberation of hydrogen cyanide, the
reaction had to be carried out in a well ventilated hood. The cooled solution was extracted with ether and washed with aqueous sodium hydroxide, water, and finally dried over magnesium sulfate. Concentration and distillation of the latter extract afforded 8.4 g (52.8%) of benzonitrile-2,4,6-d₃, b.p. 189-191°C. The nmr spectrum (CCL₄) showed a single peak for the m-protons at δ 2.53.

Benzonitrile-2,4,6-d₃ (8.26 g, 0.073 mole) was refluxed with a solution of 6.7 g of sodium hydroxide in 50 ml of 80% ethanol for five hours. The ethanol was removed and the aqueous solution was acidified with dilute sulfuric acid, and extracted with ether. The solution was dried over magnesium sulfate and the ether evaporated, leaving 9.3 g (95.5%) of benzoic-2,4,6-d₃ acid, m.p. 120-122°C. The nmr spectrum (CCL₄) showed a sharp peak at δ-2.30 for the carboxyl hydrogen and at 2.61 for the m-hydrogens.

To prevent the exchange of deuterium by hydrogen, it was necessary to use a low temperature and a mild acidic medium. A combination of the procedures by Adams (35) and Hesse (36) seemed to fit these conditions. In a 100 ml two-necked flask attached to a reflux condenser were placed oxalyl chloride (9.53 g, 0.075 mole) and 20 ml of dry benzene. Sodium benzoate-2,4,6-d₃ (10.6 g, 0.0722 mole) was then added in small portions through a side arm. With each addition gas was evolved. After all the sodium salt had been added, the mixture was refluxed for two hours with stirring. The solution
was diluted with 60 ml of dry benzene and filtered. The filtered, clear solution of benzoyl-2,4,6-d₃ chloride was slowly dropped into an ice-cold solution of absolute methanol (3.5g, 0.109 mole) and 7.7 g of pyridine in 25 ml of petroleum ether (60-90°). The addition was completed after two hours and the pyridine hydrochloride was filtered. The filtrate was washed with dilute sulfuric acid to remove the pyridine. Drying over magnesium sulfate and subsequent evaporation of the solvent gave a yellow oil. Distillation of the residual oil afforded 7.65g(76.4%) of methyl benzoate-2,4,6-d₃, b.p. 192-195°.

The nmr spectrum (CDCl₃) showed resonance at 7.26 (m-protons) and 6.13 (methoxyl protons).

**Reaction of Methyl Benzoate-2,4,6-d₃ with t-Butyllithium.**

Addition of 35 ml of 2.2M solution of t-butyllithium in pentane to 5g of methyl benzoate-2,4,6-d₃ in 50 ml of pentane gave a yellow oil after hydrolysis with deuterium oxide. The product was worked up and chromatographed as described for ordinary methyl benzoate. 0.05 g of compound XXXVII-d₃ was isolated as colorless needles, m.p. 242-244°. The nmr spectrum of compound XXXVII-d₃(CDCl₃) showed resonance at 7.39, 7.69, 8.05, 9.13 (four singlets, each corresponding to one proton), and 8.77, 8.83, 9.20, 9.26 (four sharp singlets, corresponding to thirty-six protons).
Structural Change of Compound XXXVII.

Compound XXXVII was recovered unchanged when a solution in diglyme or o-dibromobenzene was heated in the absence of light for three months at 150°. Compound XXXVII underwent a complete structural change when a solution in CDCl₃ or crystals were stored in a Pyrex container in sunlight for three to four weeks. The melting point of the white crystalline solid changed to 146-147.5°.

Ultraviolet irradiation with a medium pressure 450 watt Hanovia lamp of a solution of compound XXXVII in isooctane caused rapid and quantitative conversion into the saturated isomer (XXXVIII), within less than five minutes. Compound XXXVIII is believed to be a pentacyclo[6.4.0.0^3,8,0^4,12,0^5,9] dodecane.

Until now we have not been able to assign the positions for the two t-butyl and the two pivaloyl groups.

The infrared spectrum (KBr) had bands at cm⁻¹ 2980(s), 1665(s), 1470(s), 1387(s), 1357(s), 1282(w), 1237(w), 1192(w), 1160(m), 1126(m), 118(m), 1108(m), 1060(w), 1037(w), 1003(w), 984(s), 958(m), 937(w), 895(m), 888(w), 875(w), 865(m), 851(w), 795(w), and 764(w).

The ultraviolet spectrum of compound XXXVIII (isooctane) showed a very slight shoulder at μ 234 with tailing to ca. 270. The nmr
spectrum (CDCl₃) showed in contrast to compound XXXVII no resonance in the vinyl region. Four sharp singlets at 7.80, 8.85, 8.95, and 9.22 marked the t-butyl protons.

Mass spectrum, m/e (relative intensity), 57(100), 58(8), 69(9), 77(8), 79(10), 85(5), 85(11), 87(11), 91(8), 105(17), 107(10), 135(7), 151(7), 161(7), 163(22), 165(9), 165(10), 221(6), 222(3), 299(5), 327(24), 328(6), 355(7), 383(60), 384(15), 425(3), 440(3, M⁺).

The only change of the nmr spectrum of XXXVIII-d₂ was the disappearance of the singlet at 7.89.

The nmr spectrum of compound XXXVIII-d₂ (CDCl₃) showed resonance at 7.74 (singlet, one methine proton), 8.49 (singlet, one methine proton), 9.14 (broad singlet, one or two methine protons), and 8.80, 8.85, 8.95, 9.22 (four sharp singlets, t-butyl protons).

Reduction of Compound XXXVII with Sodium Borohydride.

Compound XXXVII was recovered unchanged after treatment with sodium borohydride in methanol - tetrahydrofuran at room temperature. By heating compound XXXVII with sodium borohydride at 70° in a mixture of isopropanol-tetrahydrofuran a colorless solid (XLI) was isolated melting at 186-188°.

The infrared spectrum (KBr) of XLI showed a hydroxyl (3530 cm⁻¹) and carbonyl band (1650 cm⁻¹).

The nmr spectrum (CDCl₃) exhibited characteristic absorption in the vinyl region (two protons centered at 7.32 and 4.27), and four sharp singlets at 7.82, 9.11, 9.20, 9.23 (t-butyl).
Reduction of Compound XXXVII with Lithium Aluminum Hydride.

Compound XXXVII was dissolved in tetrahydrofuran-ether and refluxed with an excess of lithium aluminum hydride. The product was hydrolyzed with water after a day of refluxing. Work-up of the organic layer resulted in a white solid (XLII), m.p. 135-140°. The infrared spectrum (CCl₄) showed a hydroxyl band at 3650 cm⁻¹, but no carbonyl band. The nmr spectrum (CDCl₃) showed resonance at τ 4.06, 4.18 (two doublets, two vinyl protons), 6.08 (singlet, two protons), 7.41 (doublet, one proton), 7.91 (broad singlet, four protons), 8.14 (sharp singlet, two protons), 8.41 (broad singlet, two protons) 8.97, 9.05, 9.07, 9.21 (four single peaks, t-butyl protons). Mass spectrum, m/e (relative intensity), 57(100), 58(10), 67(8), 69(22), 70(5), 71(14), 73(12), 75(6), 77(10), 79(20), 81(8), 83(10), 85(8), 87(38), 91(26), 92(12), 93(8), 95(7), 105(23), 106(5), 107(37), 108(7), 109(15), 117(5), 119(6), 121(5), 129(6), 131(6), 133(5), 135(14), 137(5), 147(18), 148(12), 149(16), 151(6), 163(8), 165(8), 166(5), 205(13), 222(6), 313(17), 369(13), 370(5), 426(2), 427(0.5).
CHAPTER III

RESULTS AND DISCUSSION

In this section are described experiments which establish the intermediacy of carbanions to certain fragmentation reactions. Also it is shown that certain azobenzoyl compounds decompose by an alkoxide induced radical path.

Azoformate salts.
The potassium (XVII) and sodium (XVIII) salts of phenylazoformic acid were prepared by hydrolysis of ethyl phenylazoformate with a solution of the corresponding hydroxide in absolute ethanol. The ester in turn was obtained by condensation of phenylhydrazine with ethyl chloroformate followed by oxidation with potassium permanganate according to the procedure of Cohen (23).
Attemps to prepare the corresponding lithium salt, using lithium hydroxide in absolute ethanol failed. We were not able to isolate salts of t-butylazoformic acid by basic hydrolysis of methyl t-butylazoformate (XXIII). The ester XXIII was prepared by the reaction of t-butylhydrazine with dimethyl carbonate followed by oxidation with mercuric oxide.
The potassium XVII and sodium XVIII phenylazoformates are yellow crystalline solids which show a remarkable stability. Even after storage in a desiccator for two years they remain unchanged. Accompanied by evolution of nitrogen and carbon dioxide the salts immediately decompose at room temperature in water, acid or base, giving rise to benzene, azobenzene, and hydrazobenzene (37). In preliminary experiments it was found that free phenylazoformic acid generated from the salts at -76° seems to be quite stable at this low temperature.

Our interest in the salts of phenylazoformic acid originated from the idea that their decomposition may produce carbanions according to Eq. 24.

\[
C_6H_5-N=\equiv-CO_2M \xrightarrow{\Delta} C_6H_5M + N_2 + CO_2 \quad (\text{Eq. 24})
\]

At first we tried to decompose the pure salts by vacuum pyrolysis. They decompose instantly at about 180°. The products consisted mainly of biphenyl and benzamide, but there was no evidence for the intermediacy of phenylanion. It seems that under these conditions the decomposition follows a radical path.

The idea to run the decomposition in a homogeneous system seemed most appealing. Unfortunately the salts were not soluble in all aprotic media tried. At this time, it was communicated to us by C.J. Pedersen (38,30), Du Pont, that a cyclic ether he had developed, 2,5,8,15,18,21-, hexaoxatricyclo [20.4.0.0^9,14] hexacosane (XXIV),
was found to be an excellent ligand for potassium ion and rendered many potassium salts soluble in nonpolar media.

Indeed it was found that potassium phenylazoformate XVIII was soluble in a mixture of crown ether XXIV and tetrahydrofuran. A solution of potassium phenylazoformate in this mixture was heated in an open and a closed system. At the reflux temperature of tetrahydrofuran the degassed solution of potassium phenylazoformate began to change color from yellow to brown and liberation of gas was observed. From the amount of gas liberated it was concluded that about 50-60% of the salt had undergone decomposition. The products consisted of two major components, benzene and benzoic acid, together with small amounts of aniline. The benzene formed varied between 47 and 57%, whereas the yield of benzoic acid mainly depended upon the way how the experiments were carried out. Only 8% of benzoic acid was formed by decomposing the salt in an open system with helium ebullition, however, decomposition in a closed system yielded about twice as much benzoic acid. When the decarboxylation was carried out in the presence of amyl acetate a small amount of acetophenone (0.16%) was detected.
Since phenylpotassium seems a likely intermediate in the decomposition reaction we were curious to see what stability phenylpotassium in crown ether XXIV - benzene might have. In spite of distilling the cycloether XXIV from calcium hydride and the use of dry benzene the wine red solution of phenylpotassium (approximately 0.01 M) became cloudy after 1-2 minutes and changed color. After that time the reaction mixture gave no benzoic acid by carbonation.

The above experiment shows that under our reaction conditions where the azoformate salt fragments in the presence of crown ether XXIV, the generated phenylpotassium will rapidly deprotonate the solvent. Further it is understandable that more benzoic acid would be obtained in systems containing a higher concentration of carbon dioxide. The reaction of amyl acetate with phenylpotassium is probably a much slower process compared to carboxylation or deprotonation.

Thus we found here that in a homogeneous aprotic medium potassium phenylazoformate XVIII fragments to the phenyl ion. Evidently we are observing reactions typical of the free anion, phenylazoformate, unperturbated by the proximity of cations (Eq. 25).

\[
\begin{align*}
\text{C}_6\text{H}_5\text{N} = \text{N} - \text{C}_6\text{H}_4\text{K}^+ & \xrightarrow{\Delta} \text{C}_6\text{H}_5\text{K}^+ - \text{N}_2, -\text{CO}_2 \\
\text{C}_6\text{H}_5\text{K}^+ & \xrightarrow{\text{Solvent}} \text{C}_6\text{H}_6 \\
\text{C}_6\text{H}_5\text{CO}_2\text{K} & \xrightarrow{\text{Amvl Acetate}} \text{C}_6\text{H}_5\text{C} - \text{CH}_3
\end{align*}
\]
Finally concerning the small quantity of aniline formed, it is known that extensive reduction of hydrazines and azo compounds results in amines (39). It is possible that some of the phenylpotassium caused reduction of a small amount of salt to aniline.

It was of interest to see whether anions formed in the decomposition of potassium phenylazoformate XVIII could be captured by bromine (Eq. 26) or whether an induced decomposition takes place (Eq. 27).

\[
\ce{C_6H_5^- K^+ + Br_2 -> C_6H_5Br + KBr \quad (Eq. 26)}
\]

\[
\ce{N=N \rightarrow C_6H_5Br + N_2 + CO_2 + KBr \quad (Eq. 27)}
\]

The fragmentation of potassium phenylazoformate XVIII with bromine in benzene was very rapid and resulted in the formation of 39% of bromobenzene and 40% of biphenyl. The reaction evidently proceeds through radicals. One might speculate about a reasonable mechanism for the formation of free radicals in the bromine induced decomposition of the salt, such as oxidation of the phenyl anion by bromine (Eq. 28) or a Hunsdiecker type decomposition of the potassium salt (40) through an acylhypobromide (Eq. 29). This reaction was not further investigated.

\[
\ce{C_6H_5^- K^+ + 1/2 Br_2 -> C_6H_5^* + K Br \quad (Eq. 28)}
\]

\[
\ce{C_6H_5N=NCO_2K \xrightarrow{Br_2} C_6H_5N=NCO_2Br \rightarrow C_6H_5N=NCO_2^* + Br \xrightarrow{Br} C_6H_5^* \quad (Eq. 29)}
\]
Acylazo compounds.

Decomposition of acylazo compounds with base or acid proceeds most readily with alkyl- or arylbenzoyldiimides as already indicated by Cohen (23). It is well known that azo compounds which have at least one hydrogen atom at the α-carbon tend to rearrange with base to the isomeric hydrazones (41). For our experiments we therefore selected the following three acylazo compounds: Benzoylphenyldiimide (XIX), phenyl-ɛ-toluoyldiimide (XX) and benzoyl-t-butyldiimide (XXII).

The two arylacylazo compounds were prepared following the procedure of Cohen (23). Accordingly, phenylhydrazine was treated with benzoyl chloride and ɛ-toluoyl chloride respectively and the resulting N-aryl-N′-acylhydrazines oxidized with mercuric oxide to the corresponding diimides.

The previously unknown benzoyl-t-butyldiimide XXII was synthesized successfully from t-butyldiazide and methyl benzoate followed by oxidation of the N-alkyl-N′-acylhydrazine with mercuric oxide (Eq. 31). The t-butyldiazide employed in the preparation was obtained in 36% yield by the reaction of t-butylmagnesium chloride with diphenyl-diazo methane and hydrolysis of the resulting benzophenone t-butyldiazide according to the method of Smith (29) (Eq. 30).
In general, acylation of alkylhydrazines occurs at the alkyl-bearing nitrogen. Jensen and co-workers (42) studied the thioacylation of alkylhydrazines with carboxymethyl dithioates (R-C-S-CH_2CO_2H). They found that methylhydrazine gave N,N-disubstituted hydrazines whereas N,N'-disubstitution takes place with t-butylhydrazine. The proportion of N,N'-substituted products increases with the size of the alkyl group. The product from the reaction of t-butylhydrazine with methyl benzoate supports these findings. Due to steric hindrance acylation occurs at the unsubstituted nitrogen.

The alkoxide fragmentation of (dimethoxyphosphinyl) phenyl-diimide (XXI) seemed to be a promising reaction to study. The compound was prepared according to the method of Ribka (28). Unfortunately this material could not be sufficiently purified to use in further studies.
The alkyl- and arylacylazo compounds described above are thermally quite stable and not particularly reactive to hydroxylie solvents but are readily attacked by acid and base.

Sunlight causes decomposition of the acylazo compounds with liberation of nitrogen. Benzoyl-t-butyldiimide XXII especially, showed light sensitivity since samples stored in the refrigerator, where light can only enter occasionally, underwent extensive decomposition within a month. Together with benzil a solid was isolated, identified below as N,N'-di-t-butyl-N-benzoylhydrazine (XXV). The same products were obtained by heating the diimide XXII at 130-150°C for two days.

The acylazo compounds decompose with a variety of bases such as hydroxides, amides, alkoxides, phenoxides, and sodium oxide in solvents as benzene, toluene, pentane, dioxane, tetrahydrofuran and dimethylformamide. The results of some of these fragmentation reactions are given in Table 3. Because of the simplicity of the expected fragmentation products we decided to use for the base sodium or potassium methoxide and to restrict the media to nonpolar solvents.

Our interest in alkyl- and arylacylazo compounds originated from the idea that their base-catalyzed fragmentation may generate carbanions according to Eq. 32.

\[
\text{ArN=NC}_6\text{H}_5 + \text{CH}_3\text{O}^- \rightarrow \text{C}_6\text{H}_5\text{CO}_2\text{CH}_3 + \text{N}_2 + \text{Ar}^- \quad \text{etc.}
\]

(Eq. 32)
### TABLE 3

Fragmentation of Acylazo Compounds (Preliminary Experiments).

<table>
<thead>
<tr>
<th>Acylazo Compound</th>
<th>Base</th>
<th>Solvent</th>
<th>Reactant</th>
<th>Some of the Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_6\text{H}_5-N=N-\text{C}_6\text{H}_5 )</td>
<td>( \text{CH}_3\text{ONa} )</td>
<td>toluene</td>
<td></td>
<td>no benzil</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5-N=N-\text{C}_6\text{H}_5 )</td>
<td>( \text{CH}_3\text{ONa} )</td>
<td>benzene</td>
<td>oxygen</td>
<td>61% benzoic acid</td>
</tr>
<tr>
<td>( \text{t-Bu-N=C-C}_6\text{H}_5 )</td>
<td>( \text{C}_6\text{H}_5\text{ONa} )</td>
<td>benzene</td>
<td></td>
<td>20% benzoic acid, phenyl benzoate, ketone (XXXI)</td>
</tr>
<tr>
<td>( \text{t-Bu-N}=N=\text{C}_6\text{H}_5 )</td>
<td>( \text{CH}_3\text{ONa} )</td>
<td>benzene</td>
<td>bromine</td>
<td>no benzoic acid, organic material consisted of ca. 75% t-BuBr, ester, but only 1% ketone, 0.8% isobu, some t-BuCl was isolated</td>
</tr>
<tr>
<td>( \text{t-Bu-N}=N=\text{C}_6\text{H}_5 )</td>
<td>( \text{CH}_3\text{ONa} )</td>
<td>benzene</td>
<td>( \text{CCl}_4 )</td>
<td></td>
</tr>
<tr>
<td>( \text{t-Bu-N}=N=\text{C}_6\text{H}_5 )</td>
<td>( \text{Na}_2\text{O} )</td>
<td>THF</td>
<td></td>
<td>34.8% benzoic acid, organic material consisted of 64.7% ketone (XXXI)</td>
</tr>
</tbody>
</table>
At first we carried out the fragmentation reactions in a heterogeneous system using benzene or pentane as solvent. In all cases, the diimide solution was added at room temperature slowly to a degassed suspension of the equimolar amount of methoxide suspended in solvent in an apparatus illustrated in Figure 11. The liberated gas was collected over mercury and the volume measured. The results of these experiments are summarized in Table 4 and 5.

The amount of nitrogen gas collected from the fragmentations in benzene indicated that only about 50\% of the two arylacyldiimides and 60\% of the benzoyl-\(\tau\)-butyldiimide XXII had decomposed. The products from the arylacyldiimide decompositions consisted of methyl benzoate, (methyl \(\pi\)-toluate), benzene, biphenyl, benzophenone, (\(4\)-methylbenzophenone), traces of triphenylmethanol, sodium or potassium benzoate and phenyl substituted acylhydrazines. Fragmentation of benzoyl-\(\tau\)-butyldiimide XXII in benzene resulted in the formation of isobutane, isobutylene, methyl benzoate, 2,2-dimethylpropiophenone (XXXI), alkali benzoate salts, and di-\(\tau\)-butyl substituted benzoylhydrazines.

In each of the above described reactions a fairly large amount (20-30\%) of a blue colored solid was separated which changed to brown after hydrolysis. Attempts to separate the insoluble and high melting material were unsuccessful. In the case of the fragmentation of benzoylphenyldiimide XIX, the spectral properties of one solid, isolated from
the high melting product residue suggest it to be a dimeric coupling product (XXVII), \((C_6H_5-N_2H-C-C_6H_5)_2\).

Fragmentation of benzoyl-\(t\)-butyldiimide XXII with potassium methoxide in methanol -benzene resulted in about twice as much isobutane compared to benzene alone, whereas the amount of 2,2-dimethyl-propiophenone XXXI shrank to merely 1%. No benzoic acid and only traces of 2,2-dimethylpropiophenone XXXI were obtained in the fragmentation of benzoyl-\(t\)-butyldiimide XXII with sodium methoxide in the presence of bromine. About 65% of the organic material formed in the reaction of sodium oxide with benzoyl-\(t\)-butyldiimide XXII in tetrahydrofuran consisted of 2,2-dimethylpropiophenone XXXI.

At this point it is worthwhile to formulate some general schemes to account for the fragmentation products. They may be envisaged to appear either by a carbanion path A or a radical path B (Eq. 33).

\[
\text{Ar-N=N-C}_6\text{H}_5 + \text{CH}_3\text{O}^- \xrightarrow{\text{A}} \text{Ar}^- + \text{N}_2 + \text{C}_6\text{H}_5\text{CO}_2\text{CH}_3 \quad \text{(Eq. 33)}
\]

\[
\text{Ar}^- + \text{N}_2 + \text{C}_6\text{H}_5\text{CO}_2^- + \text{CH}_3 \quad \text{(R*)}
\]

\[
\text{Ar}^- + \text{N}_2 + \text{C}_6\text{H}_5\text{CO}_2^- + \text{CH}_3 \quad \text{(R*)}
\]

Products which most likely came from carbanions include, all ketones and carbinols formed via carbonyl addition reactions (Eq. 34), benzene and isobutane formed via deprotonation of the solvent (Eq. 35) and N,N-alkylaryl or N,N-diaryl benzoylhydrazines (Eq. 36). It is well known that carbanions add exclusively 1,4 to acyldiimides (43).
Those products which might arise from radicals include biphenyl (Eq. 37), (hexamethylethane is not expected, since t-butyl radicals do not couple, \(^4\)) some benzene, isobutane and isobutylene via hydrogen abstraction or disproportion (Eq. 38-40), sodium or potassium benzoate, and some of the substituted benzoylhydrazines formed via addition to the acyldiimides.

\[
\begin{align*}
2 \text{C}_6\text{H}_5^\cdot & \rightarrow \text{C}_6\text{H}_5\text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5^\cdot + \text{RH} & \rightarrow \text{C}_6\text{H}_6 \\
(\text{CH}_3)_3\text{C}^\cdot + \text{RH} & \rightarrow (\text{CH}_3)_2\text{CH} + (\text{CH}_3)_2\text{C} = \text{CH}_2
\end{align*}
\]
### TABLE 4

Fragmentation of benzoyl- and 2-toluoylphenyldiimide with potassium methoxide.  

<table>
<thead>
<tr>
<th>Acylazo Compound</th>
<th>Solvent</th>
<th>% N₂</th>
<th>% Ø-H</th>
<th>% Ø-Ø</th>
<th>% ØCO₂CH₃ or % ØOH or %ØCO₂H</th>
<th>%ØCO₂H or %ØCO₂H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ø-N=N-Ø-Ø</td>
<td>pentane</td>
<td>68.3</td>
<td>6.4</td>
<td>7.8</td>
<td>53.7</td>
<td>5.62</td>
</tr>
<tr>
<td>Ø-N=N-C-Ø</td>
<td>benzene</td>
<td>46.8</td>
<td>24.4</td>
<td>31.2</td>
<td>3.67</td>
<td>traces</td>
</tr>
<tr>
<td>Ø-N=N-C-Ø</td>
<td>crown e.</td>
<td>91.7</td>
<td>5.1</td>
<td>58.8</td>
<td>8.2</td>
<td>traces</td>
</tr>
<tr>
<td>Ø-N=N-Ø-ØCH₃</td>
<td>benzene</td>
<td>49.2</td>
<td>24.7</td>
<td>22.7</td>
<td>1.42</td>
<td>28.7</td>
</tr>
</tbody>
</table>

a) Average of 3-6 runs each  
b) High-molecular weight nitrogen compounds were formed in all reactions (20-30%), together with some \( (C₆H₅-N₂H-Ø-C₆H₅)₂ \).  
c) 2-4% of N,N-diphenyl-N¹-benzoylhydrazine and N,N¹-diphenyl-N-benzoylhydrazine in all runs.
## TABLE 5

Fragmentation of Benzoyl-\(t\)-butyldiimide with Sodium and Potassium Methoxide.

<table>
<thead>
<tr>
<th>Base</th>
<th>Solvent</th>
<th>Component</th>
<th>% N₂</th>
<th>%(CH₃)₃CH</th>
<th>%(CH₃)₂C=CH₂</th>
<th>%CO₂CH₃</th>
<th>% (t)-BuO₂⁻</th>
<th>% other</th>
<th>%CO₂H</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃ONa</td>
<td>benzene</td>
<td></td>
<td>59.7</td>
<td>19.5</td>
<td>1.34</td>
<td>20.2</td>
<td>18.7</td>
<td></td>
<td>32.9</td>
</tr>
<tr>
<td>CH₃ONa</td>
<td>benzene</td>
<td>methanol</td>
<td>72.5</td>
<td>32.4</td>
<td>0.56</td>
<td>29.9</td>
<td>0.92</td>
<td></td>
<td>31.7</td>
</tr>
<tr>
<td>CH₃OK</td>
<td>crown e.</td>
<td>benzene</td>
<td>90.7</td>
<td>8.82</td>
<td>1.22</td>
<td>0.5-4.</td>
<td>30-45</td>
<td>17-20 b)</td>
<td>20.3</td>
</tr>
</tbody>
</table>

### Notes:

a) High-molecular weight nitrogen compounds were formed in all reactions (20-30\%), together with 4-8\% of N,N'-di-\(t\)-butyl-N-benzoylhydrazine and N,N-di-\(t\)-butyl-N'-benzoylhydrazine.

b) These compounds are also formed in the reaction of methyl benzoate with \(t\)-butyllithium. They are 1-pivaloyl-4-\(t\)-butylocyclohexadiene-1,5, \(\alpha,\alpha\)-dimethyl-p-\(t\)-butylpropiophenone, and \(\alpha,\alpha\)-di-\(t\)-butylbenzylalcohol.
We now further consider the origin of the various substituted hydrazines found among our fragmentation products. Predictions concerning the direction of the phenyl radical addition to the azo linkage in acylazo compounds are not possible. In the acid- and base-catalyzed methanolysis of benzoylphenyldiimide where cleavage to radicals is the main fragmentation path, Cohen (23) found both isomers, \( N,N' \)- and \( N,N'' \)-substitution, in about equal amounts, indicating no preference for radical addition. Surprisingly, benzoyl-\( t \)-butyldiimide XXII underwent selective addition by \( t \)-butyl radicals, probably due to steric reasons. As mentioned above the radical addition product formed by the thermal or photoinduced decomposition of benzoyl-\( t \)-butyldiimide XXII consisted of one compound, \( N,N' \)-di-\( t \)-butyl-\( N \)-benzoylhydrazine (XXV). However both isomers XXV and XXVI were isolated in the base-catalyzed fragmentation of benzoyl-\( t \)-butyldiimide XXII, indicating a \( t \)-butyl anion intermediate as well.

The structure assignments for the two isomers were based upon their spectral properties. The mass spectra were quite similar, each exhibiting a molecular ion of \( m/e \ 248 \). The major difference in the spectra was a peak of mass 143 in compound XXV not detected in XXVI, indicating the loss of mass 105, the benzoylium ion, to give \( (t-Bu)_{2}H_{2}N^+ \).

This fragmentation pattern seems most likely for a system where steric strain is released by the loss of benzoylium ion to give \( t-Bu-NH-N-Bu-t \). The nmr spectrum of the lower melting compound XXV showed magnetically
nonequivalent \textit{t}-butyl groups. Compound XXVI obtained together with XXV in the base-catalyzed fragmentation showed only a single peak for the \textit{t}-butyl protons. Inspection of a molecular model suggests XXVI to be a N,N'-disubstituted hydrazine. Such a structure would have free rotation about the nitrogen-nitrogen bond and should give a single line for the \textit{t}-butyl protons in the nmr spectrum. Therefore it seems reasonable to assign structure XXV for N,N'-di-\textit{t}-butyl-N-benzoylhydrazine and structure XXVI for N,N-di-\textit{t}-butyl-N'-benzoylhydrazine.

Now we return to the discussion of scheme B, which gives radicals. This scheme also requires cleavage of the oxygen-carbon bond in the alkoxide ion, RO\textsuperscript{−}, or methyl ester leaving the fragment R\textsuperscript{*}. All attempts to trap methyl radicals failed. Neither methane nor ethane were among the products. Minute traces of toluene were detected at the end of the reaction but not enough to account for large amounts of carbon-oxygen cleavage.

In the event that methyl radical transfers a hydrogen atom to another species carbene would be formed (Eq. 41), however no detectable amounts of norcarane were found when the fragmentation reaction was carried out in the presence of cyclohexene.
It is possible that CH$_3$ becomes oxidized to CH$_3^+$. Here the main product would be dimethyl ether or carbene, neither of which could be detected.

Therefore the fragment of formula CH$_3$ is scheme B is placed in parentheses to indicate that this is the missing portion of the mass balance and we have no evidence for what happens to it.

The formation of alkali benzoate is general to all reactions between alkoxides and azo compounds studied in this work. These alkoxides were methoxides, sec-butoxide, t-butoxide and phenoxide. Usually, alkali benzoate made up about 20-33% of the product (based on starting material). However, when the reaction was carried out in the presence of oxygen the yield of potassium benzoate rose to 61%. Note also from Cohen's work (45) that the radical path is preferred when oxidizing reagents are present. It is interesting that the fragmentation reaction with sodium oxide gave exclusively carbanionic products. From these data it is evident that 1) the radical path involves oxidation 2) it is accompanied by oxygen-carbon cleavage in the
alkoxide and therefore 3) alkoxide or alcohol are essential for radical fragmentation.

Before discussing the radical reaction further it should be pointed out that generally these cleavage reactions do not go to completion. It is not possible to account entirely for the mass balance. There are large amounts (20-30%) of higher melting solids formed which could not be purified or identified. It may be that these solids contain the above missing fragments \((R^*)\) or would give some indication from their structures, of its fate.

In the base-catalyzed methanolysis of \(p\)-chlorophenylbenzoyldiimide Hoffmann (25) obtained 40% of compound XLIII.

\[
\begin{align*}
  &\text{XLIII} \\
  &\text{CH}_2 \\
  &\text{CL-C}_6\text{H}_4-\text{N}-\text{NH}-\text{C}-\text{C}_6\text{H} \\
  &\text{CL-C}_6\text{H}_4-\text{N}-\text{NH}-\text{C}-\text{C}_6\text{H}_5
\end{align*}
\]

Analogously to Hoffmann's finding it is possible that methylene from \((R^*)\) is incorporated in so far unidentified dimeric products.

It was interesting to study the above fragmentation reactions in a homogeneous system, to see which path would be favored. Potassium methoxide is slightly soluble in benzene in the presence of crown ether (XXIV). The fragmentation reactions of benzoylphenyldiimide XIX and benzoyl-\(t\)-butyldiimide XXII with potassium methoxide in crown ether XXIV—benzene solution proceeded smoothly to about 90% completion, far more than in the heterogeneous system above. The products are all
soluble in the reaction medium. In the case of benzoylphenyldiimide, XIX, the products were similar to those obtained before, a larger proportion coming from the carbanion route. However, benzoyl-\textit{t}-butyldiimide XII gave a large yield of 2,2-dimethylpropiophenone XXXI and further products (17-20\%) which were identified to be 1-pivaloyl-\textit{t}-butylcyclohexadiene-1,5 (XXXIII), \textit{\alpha},\textit{\alpha}-dimethyl-p-\textit{t}-butylpropio­phenone (XXXIV), and \textit{\alpha},\textit{\alpha}-di-\textit{t}-butylbenzylalcohol (XXXV), plus some radical products. Most of these first products were also obtained in the reaction of \textit{t}-butyllithium and methyl benzoate and their identification is described in the last part of this discussion. The origin of these compounds can most reasonably be explained by a succession of carbonyl addition reactions to the initially formed ester (Eq. 42).

\[
\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3 + \text{t-C}_4\text{H}_9\text{K}^+ \rightarrow \text{CH}_2\text{OK} \rightarrow \text{C}_6\text{H}_5\text{O-C}_4\text{H}_9 - \text{t-C}_4\text{H}_9\text{K} \rightarrow \text{XXXI} \quad \text{(Eq. 42)}
\]

\[
\text{t-C}_4\text{H}_9\text{O-C-C}_4\text{H}_9 - \text{t} + \text{p-C}_4\text{H}_9\text{O-C-C}_4\text{H}_9 - \text{t} + \text{C}_6\text{H}_5\text{O} \rightarrow \text{XXXIII} \quad \text{XXXIV} \quad \text{XXXV}
\]

One might conclude that in a homogeneous fragmentation reaction where potassium cation is solvated by crown ether, XXIV, we are observing the reactivity of a relatively free \textit{t}-butyl anion. By relatively free is understood to mean an anion unpertubated by the proximity of the cation. The \textit{t}-butylpotassium compound may still exist as an ion pair.
The results obtained from the fragmentation of alkyl- and arylbenzoyldiimides with alkali methoxide seem most consistent with the proposal that radicals as well as anions are intermediates in the reaction. A characteristic feature of the heterogeneous fragmentations with alkoxides in benzene is the large portion of products derived from radicals whereas fragmentations in a homogeneous system of crown ether- benzene gave more products via carbanions. The data available do not give a clear picture of the radical path nor do they help formulate the reasons why each fragmentation path takes place.

The original purpose of this work was to investigate whether it was possible to generate and trap carbanions by the diimide route. In previous work where diimides or derivatives thereof were proposed to be intermediates in certain reduction reactions it was not possible to distinguish between a carbanion path or a direct collapse (Eq. 43).

\[
\begin{align*}
R-N=N-H & \xrightarrow{B;} R-N=N^- + BH \\
\text{RH} & \xrightarrow{-N_2} R^- + N_2 & \text{BH} & \rightarrow \text{RH} \\
\end{align*}
\]

(Eq. 43)

In this thesis it has been established that in two systems, alkali phenylazoformates and alkyl- or aryl- benzoyldiimides, the diimide route to $R^-$ has been observed and the $R^-$ trapped by carbonyl reagents. Furthermore phenyl and t-butyl anion have been generated in a homogeneous system as free ions and the reactions of the anions studied.
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<td>XXXII</td>
<td>m.p. 42-3</td>
<td>XXXIII</td>
<td>liquid</td>
<td>XXXIV</td>
<td>m.p. 44-6</td>
<td>XXXV</td>
<td>liquid</td>
<td>XXXVI</td>
<td>m.p. 77-9</td>
<td>XXXVII</td>
<td>mp. 243-5</td>
<td>XXXVIII</td>
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<td>a) Osmometer</td>
<td>b) 3700 cm(^{-1}) (free), 3570 cm(^{-1}) (H-bonded)</td>
<td>c) 3668 cm(^{-1}) (free), 3550 cm(^{-1}) (bonded)</td>
<td>d) Two strong bands at cm(^{-1}) 1650 and 1640</td>
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Reaction of t-Butyllithium and Methyl Benzoate.

The fragmentation of benzoyl-t-butyldiimide by potassium methoxide in homogeneous media produced a number of products which were tentatively assigned to arise from various carbanion addition reactions. In the event that this was so it was decided to see if the reaction of t-butyllithium and methyl benzoate produced similar products. This process would then provide a means to prepare these products in larger amounts for purpose of identification.

No difficulties had been reported (46) for the preparation of various alkyl-di-t-butyldcarbinols by treating esters or ketones with an excess of t-butyllithium. The addition of an excess t-butyllithium to methyl benzoate in n-pentane was carried out in a drybox at room temperature. The reaction mixture was then hydrolyzed slowly at reflux temperature and separated into its components by vapor phase chromatography. We were surprised to find five more products instead of only the expected ketone and carbinol. The products and their properties are summarized in Table 6.

**Compound XXXI** (4-10\%) was a ketone having aromatic absorption; its mass spectrum showed a strong parent peak at m/e 162. Comparison with an authentic sample proved its structure as 2,2-dimethylpropiophenone. **Compound XXXII** (37-39\%) analyzed for C\textsubscript{11}H\textsubscript{16}O. It was an alcohol showing absorption for aromatic and t-butyl protons (Figure 12). The mass spectrum display a molecular ion peak at m/e 164. It was identified as the already known compound \(\alpha\)-t-butylbenzylalcohol (Lit.\textsuperscript{32,33} m.p. 45\(^\circ\), 40\(^\circ\)).
Compound XXXIII (12-21%) was an unsaturated ketone (IR at cm\(^{-1}\) 1655, 862, 755). The distinguishing feature of its nmr spectrum (Figure 13) are three vinyl protons. The vinyl hydrogen resonance consists of an ABX system weakly coupled to other hydrogens. These shifts occur at \(\tau\) 3.54 and 4.20 for AB, and 3.78 for X. Besides a multiplet for methine and methylene protons between \(\tau\) 7.41 and 8.08 the nmr spectrum further shows two sharp singlets at \(\tau\) 8.77 and 9.07 for the \(\tau\)-butyl protons. The UV spectrum (isooctane, \(\lambda_{\text{max}} = 285\) m\(\mu\), \(\varepsilon = 2,000\)) does not indicate a simple disubstituted 1,3-cyclohexadiene (usually \(\lambda_{\text{max}} = 260-265\) m\(\mu\), \(\varepsilon = 6,000\)), a cyclohexenyl ketone (ca. 242 mp), or a 1,3-dienone (\(\lambda_{\text{max}} = \text{ca.} 300-305\) m\(\mu\)) (47). Due to steric requirements in general there is less conjugation of pivaloyl groups with \(\alpha,\beta\)-double bonds. Therefore, a cross-conjugated structure is reasonable but cannot be proved. The mass spectrum displayed a molecular ion peak at m/e 220, and characteristic peaks at m/e 57(100%, \(\tau\)-butyl ion), 85 (10%, pivaloyl ion), 135 (6%, M-85), 161 (82%, M-H\(_2\)-57), 165 (44%, M-57), 164 (24%, M-56). From its spectral properties the structure of compound XXXIII was assigned to 1-pivaloyl-\(\tau\)-butylcyclohexadiene-1,5.

Compound XXXIV (6-13%) was a para disubstituted aromatic ketone (IR at cm\(^{-1}\) 1668, 858) and analyzed for C\(_{15}\)H\(_{22}\)O. The nmr spectrum (Figure 15) showed a single peak for \(\tau\)-butyl protons (\(\tau\) 8.66, 18 H) and was consistent with a para disubstituted benzene (center of A resonance at \(\tau\) 2.33, 2 H, and of B part of A\(_2\)B\(_2\) system at \(\tau\) 2.68, \(J_{A+B} = 8.5\) cps, 2 H). The mass spectrum established the molecular weight to be 218.
and gave rise to characteristic peaks at m/e 57 (100%, t-butyl ion), 85 (12%, pivaloyl ion), 133 (6%, M-85), 161 (100%, M-57), 162 (45%, M-56). The assignment of compound XXXIV as \( \alpha,\alpha' \)-dimethyl-\( p \)-t-butylpropiophenone was based upon its spectral properties. Compound XXXV (80-25%) was a monosubstituted aromatic alcohol (IR at cm\(^{-1}\) 3730, 743, 707) and analyzed for C\(_{15}\)H\(_{24}\)O. The nmr spectrum (Figure 16) showed absorption in the aromatic region (complex multiplet at \( \tau \) 2.18-2.98, 5 H), and a single peak at \( \tau \) 8.91 (t-butyl protons, 18 H). The mass spectrum displayed a molecular ion peak at m/e 220, and characteristic peaks at m/e 57 (100%, t-butyl ion), 77 (27%, phenyl cation), 85 (46%, pivaloyl ion), 91 (10%, tropylium ion), 105 (60%, benzoylium ion), 163 (100%, M-57), 164 (15%, M-57). Sternhell (48) reported the nmr spectrum of di-t-butyl-\( p \)-methoxyphenylcarbinol. The appearance of the aromatic protons as an unsymmetrical multiplet, rather than as a symmetric AA'BB' system was cited as the first example of restricted rotation about the sp\(^2\)-sp\(^3\) carbon-carbon bond in a simple aromatic derivative. Sternhell further reported the mass spectrum of this carbinol which showed significant peaks at masses derived by the loss of t-butyl ion together with isobutane (57+58=115) giving \( p \)-methoxybenzoylium ion. On the basis of the above data, consideration of molecular models and the findings by Sternhell was assigned compound XXXV to be \( \alpha,\alpha' \)-di-t-butylbenzylalcohol. The nmr spectrum of \( \alpha,\alpha' \)-di-t-butylbenzylalcohol-2,4,6-d\(_3\) (Fig. 17)
showed two singlets for the m-protons at $\tau 2.78$ and 2.86. This indicates that the molecule has no symmetry about a plane passing through C-1 and C-4 at right angles to the aromatic ring. The shift of the protons did not vary with temperature, nor did the line shape alter. We assign this shift as due to hindered rotation about the C$_1$-C-OH bond. The predominant species in solution is most likely that rotamer where the aromatic plane bisects the $\text{t-Bu-C-Bu-t}$ angle.

Compound XXXVI (7-10%) was a para disubstituted aromatic alcohol (IR cm$^{-1}$ 3668, 3550, 832) and analyzed for C$_{15}$H$_{24}$O. Its nmr spectrum (Fig. 18) exhibited a single line in the aromatic region ( $\tau 2.87$), two single lines at $\tau 5.75$, 8.75, and two sharp singlets for the t-butyl protons at $\tau 8.69$, 9.11. The mass spectrum exhibited a molecular ion peak at m/e 222, and characteristic peaks at m/e 57 (100%, t-butyl ion), 133 (30%, t-butylphenyl cation), 148 (27%, t-butyl-tropylium ion), 163 (100%, M-57), 164 (45%, M-56), 187 (35%, M-H$_2$O-CH$_3$'), 221 (40%, M-1).

The spectral properties of compound XXXVI are consistent with the structure for $\alpha$-p-di-$\text{t}$-butylbenzylalcohol.

Compound XXXVII was isolated in 1 to 4.5% yield as colorless needles, m.p. 243-244.5°. Its spectral properties and possible structure will be discussed at the end of this part.
On one occasion we accidently isolated in addition to the above described compounds a small amount of compound XXXIX. The colorless oil was a conjugated dienone (IR cm\(^{-1}\) 1663-s, 1615-m, 845-s).

The nmr spectrum was characterized by two vinyl protons (AB system centered at \(\tau\) 3.26 and 4.19, \(J=6\) cps), a multiplet (centered at \(\tau\) 7.77, methylene) and two sharp singlets at \(\tau\) 8.75, 8.89 (t-butyl).

The mass spectrum established the molecular weight to be 220 and gave rise to characteristic peaks at m/e 57 (100 %, t-butyl ion), 85 (8 %, pivaloyl ion), 135 (5 %, M-85), 161 (100 %, M-H\(_2\)-57), 162 (30 %, M-H\(_2\)-isobutylene), 163 (85 %, M-57), 218 (3 %, M-H\(_2\)).

From its spectral properties the structure of XXXIX was assigned to 1-pivaloyl-4-t-butylcyclohexadiene-1,3.

The solid material formed by the addition of t-butyllithium to methyl benzoate was separated and extracted into tetrahydrofuran. This solution had nmr absorption in the vinyl region at \(\tau\) 4.99 and 5.15.

Water was added to the tetrahydrofuran extract. The nmr spectrum of the resulting solution did not include the absorption just mentioned but showed a fairly large amount of an olefinic material as a closely coupled A\(_2\)B\(_2\) system at \(\tau\) 4.23 and 4.73 (Figure 14). No attempts were made to isolate this compound (XL) since it aromatizes by 100\(^\circ\).

From the limited information we tentatively assign XL to be 1-pivaloyl-4-t-butylcyclohexadiene-2,5.
Several examples of ring alkylation have been reported by Fuson (49,50,51), when highly hindered diaryl ketones were treated with Grignard or lithium reagents. The reaction of alkyl Grignard or lithium compounds with duryl phenyl ketone in general resulted in 20-30% of para alkylated products (Eq. 44).

\[
\text{CH}_3\text{C}_6\text{H}_5\text{C}=\text{O} \xrightarrow{\text{RMgX or RLi}} \text{CH}_3\text{C}_6\text{H}_5\text{C}=\text{O} \quad \text{(Eq. 44)}
\]

\( \text{R}=\text{isopropyl}, \text{n-butyli}, \text{t-butyli} \)

On the other hand, reaction of highly hindered aryl ketones with phenyllithium gave ortho alkylation (52,53). (Eq. 45-46).

\[
\text{CH}_3\text{C}_6\text{H}_5\text{C}=\text{O} \xrightarrow{\text{C}_6\text{H}_5\text{Li}} \text{CH}_3\text{C}_6\text{H}_5\text{C}=\text{O} \quad \text{(Eq. 45)}
\]

28%

In one case Fuson (51) isolated a para substituted 1,3-diene (Eq. 47).

\[
\text{Mes} \xrightarrow{\text{C}_6\text{H}_5\text{Li}} \text{Mes} \quad \text{(Eq. 46)}
\]

8%

\[
\text{n-C}_4\text{H}_9\text{Li} \xrightarrow{} \text{n-C}_4\text{H}_9\text{Li} \quad \text{(Eq. 47)}
\]
As indicated by the findings of Fuson some of the products isolated from the reaction of t-butyllithium with methyl benzoate are consistent with 1,6-addition of the t-butyl anion due to steric effects. The secondary alcohols arise from hydride transfer in the reaction medium (Eq. 48).

\[ \text{XXXIV} \quad \text{XXXVI} \quad \text{XXXIII} \quad \text{XXXIX} \]

The distribution of the products is very similar to that formed in the fragmentation of benzyl-t-butyldiimide with potassium methoxide in crown ether (X) where it is believed that t-buty1potassium is the reactive intermediate. Thus the relative reactivities of t-buty1potassium in crown ether and t-butyllithium in pentane to methyl benzoate and the various intermediates which are formed from it are very similar. Considering that the potassium cation in crown ether is strongly solvated we are quite likely observing the reactivity
of relatively free t-butyl anions in this case. It is interesting that t-butyllithium in pentane behaves in the same way. What this means is not clear now.

Compound XXXVII could only be isolated under specific conditions. Heating the mixture of products derived from the reaction of methyl benzoate with t-butyllithium had no effect on the yield of compound XXXVII. On the other hand the mode of hydrolysis of the original reaction mixture had a critical effect upon the yield of XXXVII. It was not formed at all when the hydrolysis was carried out at 0-10°C; the same was true for very fast hydrolysis. Medium or slow hydrolysis (10 to 30 minutes) at room or reflux temperature (ca. 35°C) resulted in various amounts of compound XXXVII (0-1%). Extended heating of the reaction mixture had no effect on the yield. The yield of compound XXXVII was increased to ca. 4.5% when the hydrolysis was carried out at higher temperature (60-90°C) by using hexane or heptane as solvent.

Compound XXXVII was isolated by distilling all volatile components from the reaction mixture (25-150°C, ca. 1mm), this left a yellow residue. Addition of pentane to the residue and cooling caused crystallization of compound XXXVII as white needles, m.p. 243-244.5°C. Varying the temperature of the distillation did not alter the yield of XXXVII. The molecular weight was found to be 428, using the osmometric method. The infrared spectrum indicated an unsaturated ketone...
(cm⁻¹ 1650-s, 1640-s, 1608-w, 1272-m, 1142-s, 764-s). The compound decolorized bromine and formed an oxime, m.p. 169-171°.

It is well known that steric effects result in the decrease of UV absorption intensities. The ultraviolet spectrum of XXXVII (isooctane, λ_max=234 μ, ε =1,400) was similar to that reported for the compound shown below (54).

The mass spectrum exhibited a molecular ion peak at m/e 440 and characteristic peaks at m/e 57 (100%, t-butyl ion), 85 (9%, pivaloyl ion), 105 (38%, benzoylium ion), 163 (15%, 1/2M-57), 165 (10%), 221 (10%, 1/2M+1), 299 (2%, M-85-5b), 327 (24%, M-57-5b), 355 (2%, M-85), 383 (59%, M-57), 384 (18%, M-56), 425 (3%, M-methyl radical).

The nmr spectrum of compound XXXVII as shown in Figure 19 was characterized by two vinyl protons, each part of a separate AX system (centered at τ 3.22 and 3.53, J=ca. 7 cps), and four sharp singlets at τ 8.78, 8.83, 9.20, 9.26 for two t-butyl and two pivaloyl groups. Decoupling experiments of compound XXXVII-d2 carried out on a Varian HA 100 spectrometer (1000 cps sweep width) indicated that irradiation of the vinyl proton at τ 3.22 caused collapse of the doublet centered at τ 7.39 to a singlet. Irradiation of the vinyl proton centered at τ 3.53 gave a relatively sharp line at τ 8.04 (Figure 20).
Compound XXXVII-d₂ prepared by the same method as described above for XXXVII by using deuterium oxide instead of water for the hydrolysis, showed a very similar nmr spectrum (Figure 21). The only observable difference to XXXVII was the absence of a relatively sharp singlet at \( \tau 8.32 \) (one proton).

Compound XXXVII-d₈ was prepared by the same method as described above for XXXVII by reacting methyl benzoate \((2,4,6-d₃)\) with t-butyl-lithium and hydrolyzing with deuterium oxide. Methyl benzoate \((2,4,6-d₃)\) was prepared by a modified procedure of Schmid \((34)\). At first aniline hydrochloride was exchanged at elevated temperature \((105^\circ)\) with deuterium oxide five times to give aniline-2,4,6-d₃. The aniline in turn was converted to the nitrile by a Sandmeyer reaction and the nitrile hydrolyzed to benzoic-2,4,6-d₃ acid. Reaction of the sodium salt of benzoic-2,4,6-d₃ acid with oxalyl chloride followed by treatment with absolute methanol in the presence of pyridine gave methyl benzoate \((2,4,6-d₃)\).

The nmr spectrum of compound XXXVII-d₈ as shown in Figure 22 exhibited resonance for four methine protons at \( \tau 7.39, 7.69, 8.05, 9.13 \) and four sharp singlets at \( \tau 8.77, 8.83, 9.20, 9.26 \) (two t-butyl and two pivaloyl groups).

Attempts to reduce compound XXXVII with sodium borohydride at room temperature in methanol-tetrahydrofuran failed, XXXVII was recovered unchanged. Reduction of XXXVII with sodium borohydride in isopropanol-tetrahydrofuran at \( 70^\circ \) gave a colorless solid (XLI).
The infrared spectrum of XLI was characterized by a hydroxyl (3530 cm\(^{-1}\)) and carbonyl band at 1650 cm\(^{-1}\). The nmr spectrum exhibited two vinyl protons centered at \(\tau\) 3.22, 4.27 and four sharp singlets for the \(t\)-butyl protons (\(\tau\) 8.72, 9.11, 9.20, 9.23). Under the above conditions sodium borohydride seems to reduce only one carbonyl group.

Reduction of compound XXXVII with lithium aluminum hydride in tetrahydrofuran-ether at reflux temperature resulted in a colorless solid (XLII). The infrared spectrum of XLII showed a hydroxyl band at 3650 cm\(^{-1}\), but no carbonyl absorption. The mass spectrum established the molecular weight to be 426 (MW of XXXVII +H\(_2\)O), and showed in addition characteristic peaks at m/e 57 (100%, \(t\)-butyl ion), 313 (17%, M-57-56), 369 (13%, M-57). The nmr spectrum of compound XLII as shown in Figure 25 exhibited resonance in the vinyl region (probably two vinyl protons closely centered at \(\tau\) 4.06 and 4.18) and four sharp singlets for the \(t\)-butyl protons (\(\tau\) 8.98, 9.05, 9.07, 9.21). The reduction of compound XXXVII with lithium aluminum hydride under the above conditions seems to reduce both carbonyl groups with subsequent loss of water. Ozonolysis of compound XXXVII using general reaction conditions left approximately 90\% of the material unchanged.

Up to this point we are not sure if compound XXXVII has two, three or four vinyl protons, in spite of only two visible in the nmr spectrum. We believe that the double bonds bear at least one substituent in the form of a pivaloyl group as shown by the infrared and ultraviolet absorption as well as by the ease of the photoaddition.
reaction mentioned below. Especially the proton centered at \( \tau \ 7.39 \) shows a similar coupling to the vinyl proton at \( \tau \ 3.22 \) and gave a sharp singlet after irradiation of the latter. One might speculate that steric effects may cause an abnormal upfield shift of one or even two vinyl protons. The interesting fact about compound XXXVII was that it underwent a complete structural change when a solution in chloroform or crystals were exposed to sunlight through pyrex glass for one to two months. This product (XXXVIII) was also obtained by irradiation of a solution of compound XXXVII in isooctane at 2550 Å with a medium pressure Hanovia lamp for less than five minutes. Compound XXXVIII was isolated as a crystalline solid, m.p. 146-147.5°. Infrared (1663 cm\(^{-1}\)) and ultraviolet spectrum (slight shoulder at 231 \( \text{m} \upmu \) ) suggest a saturated ketone. The mass spectrum displayed a molecular ion peak at m/e 440 and was in general very similar to that of XXXVII showing characteristic peaks at m/e 57 (100%, t-buty ion), 85 (11%, pivaloyl ion), 105 (17%, benzoylum ion), 163 (22%, 1/2M-57), 221 (6%, 1/2M+1), 299 (5%, M-85-56), 327 (24%, M-57-56), 355 (7%, M-85), 383 (60%, M-57), 384 (15%, M-56), 425 (3%, M-methyl radical). Some differences in intensities were detectable at m/e 71 (4%-6% XXXVII), 105 (17%-37%), 135 (7%-4%), 161 (7%-4%), 221 (6%-10%), 355 (7%-2%). The nmr spectrum as shown in Figure 24 had no resonance in the vinyl region in contrast to compound XXXVII.
Compound XXXVIII-de was prepared by ultraviolet irradiation of XXXVII-de in isooctane. The nmr spectrum (Figure 25) showed absorption at 7.47, 8.49, 9.14 (three methine protons) and 8.80, 6.85, 8.95, 9.22 (two t-butyl and two pivaloyl groups).

The structural change of compound XXXVII is believed to arise through a photoaddition reaction. The disappearance of the vinyl protons support this assumption. From molecular models it is obvious that only Diels-Alder adducts from cyclohexadiene-1,3 with cyclohexadiene-1,4 allow intramolecular cycloaddition reactions to take place. We thus expect the adduct XXXVII to have its two double bonds fairly close to each other, one presumably as bridge and the other in the boat shaped cyclohexene ring. From the data available we therefore believe that compound XXXVII is a tricyclo [6.2.2.0^{2,7}] dodeca-4,9-diene. Up to this point we are not able to assign the positions of the substituents.

Photochemical solid-state reactions of this type are reported to take place due to the proximity of the two double bonds undergoing the addition reaction proceed with a minimum of atomic and molecular motion (55). The ease with which the photoaddition occurs even in the solid-state might also be due to the sensitizing effect of the pivaloyl group on one or even both double bonds.
Based on the arguments discussed above we believe that compound XXXVIII is a pentacyclo \([6.4.0.0^3,6.0^4.12.0^5,8]\) dodecane. But up to this point we are not able to assign the positions for the two \(t\)-butyl and the two pivaloyl groups.

There are a number of examples \((56, 57)\) where similar intramolecular photoadditions occur in \(\alpha,\beta\)-unsaturated carbonyl compounds containing nonconjugated double bonds (Eq. 49-51).

(Eq. 49-50)

(Eq. 51)
Further investigations are necessary to assign the correct structures of compound XXXVII and XXXVIII. Due to steric requirements these compounds do not undergo most chemical reactions under ordinary conditions. It is for these reasons that identification of these compounds is very difficult. A number of methods are in progress which might help to solve the problem of identification. These include decoupling experiments on a 220 MHz nmr instrument, X-ray analysis, and ozonolysis. Since these compounds have interesting structures and are fairly easy to prepare further research in this field seems to be worthwhile.
Figure 12. NMR Spectrum (60 MHz) of $\alpha$-t-Butylbenzylalcohol (XXXII) in CCl$_4$. 
Figure 15. NMR Spectrum (60 MHz) of 1-Pivaloyl-4-t-butylcyclohexadiene-2,5(XXXIII) in CCl₄.
Figure 14. Nmr Spectrum (60 MHz) of 1-Pivaloyl-4-t-butylcyclohexadiene-2,5(XI), Vinyl Region.
Figure 15. NMR Spectrum (60 MHz) of $\alpha\alpha'$-Dimethyl-$p$-t-butylpropiophenone (XXXIV) in $\text{CCl}_4$. 
Figure 16. NMR Spectrum (60 MHz) of $\alpha,\alpha$-Di-$t$-butylbenzylalcohol (XXXV) in $\text{CCl}_4$. 
Figure 17. NMR Spectrum (60 MHz) of $\alpha,\alpha$-Di-t-butylbenzylalcohol-2,4,6-$d_3$ (XXXV-$d_3$) in CCl$_4$. 

$\tau$
Figure 18. NMR Spectrum (60 MHz) of $\alpha$-Di-t-butylbenzylalcohol (XXXVI) in $\text{CCl}_4$. 
Figure 19. NMR Spectrum (60 MHz) of Compound XXXVII in CDCl₃.
Figure 20. NMR Spectrum (100 MHz) of Compound XXXVII after Decoupling of the Vinyl Protons, a) before, b) Decoupling of the Vinyl proton at $\tau$ 3.22, c) Decoupling of the Vinyl Proton at $\tau$ 3.53.
Figure 21. NMR Spectrum (60 MHz) of Compound XXXVII-d$_2$ in CDCl$_3$. 
Figure 22. NMR Spectrum (60 MHz) of Compound XXXVII-d₈ in CDCl₃.
Figure 23. NMR Spectrum (60 MHz) of Compound XLII in CDCl₃.
Figure 24. NMR Spectrum (60 MHz) of Compound XXXVIII in CDCl₃.
Figure 25. NMR Spectrum (60 MHz) of Compound XXXVIII-d$_3$ in CDCl$_3$. 
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