This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is “Missing Page(s)”. If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in “sectioning” the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from “photographs” if essential to the understanding of the dissertation. Silver prints of “photographs” may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

University Microfilms International
300 North Zeeb Road
Ann Arbor, Michigan 48106 USA
St. John's Road, Tyler's Green
High Wycombe, Bucks, England HP10 8HR
GECKLE, John Michael, 1948-
THE SYNTHESIS AND STUDY OF CONJUGATION EFFECTS ON THE BARRIER TO ROTATION OF UNSYMMETRICAL TERTIARY BENZYLIC LITHIUM COMPOUNDS.

The Ohio State University, Ph.D., 1977
Chemistry, organic

University Microfilms International, Ann Arbor, Michigan 48106
THE SYNTHESIS AND STUDY OF CONJUGATION EFFECTS ON THE BARRIER TO
ROTATION OF UNSYMMETRICAL TERTIARY BENZYLIC LITHIUM COMPOUNDS

DISSERTATION

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

By
John Michael Geckle, B.S.

* * * * *

The Ohio State University
1977

Reading Committee:
Cideon Fraenkel
John Swenton
Robert Ouellette

Approved By

Gideon Fraenkel
Advisor
Department of Chemistry
ACKNOWLEDGEMENTS

I wish to thank Professor Gideon Fraenkel for his patience and encouragement and Susan Sheatzley for typing the paper.
VITA

April 5, 1948 . . . . . . Born - Baltimore, Maryland

1970 . . . . . . . . . . . . B.S., Chemistry, Merrimack College, North Andover, Massachusetts

1970-1972 . . . . . . . . Teaching Assistant, Department of Chemistry, The Ohio State University, Columbus, Ohio

1972-1974 . . . . . . . . Departmental NMR Operator, Department of Chemistry, The Ohio State University, Columbus, Ohio

1974-1976 . . . . . . . . Research Assistant, Department of Chemistry, The Ohio State University, Columbus, Ohio

FIELDS OF STUDY

Major Field: Organo-Metallic Chemistry

Studies in Nuclear Magnetic Resonance. Professor Gideon Fraenkel
# TABLE OF CONTENTS

ACKNOWLEDGMENTS .................................................. ii
VITA ........................................................................... iii
LIST OF TABLES .......................................................... v
LIST OF FIGURES ..................................................... vii
LIST OF ABBREVIATIONS ........................................... iii
INTRODUCTION ......................................................... 1
HISTORICAL ............................................................... 3

RESULTS AND DISCUSSION

Part I - Synthesis and Chemistry of Benzylid Lithium Compounds ................. 8
Part II - Nuclear Magnetic Resonance Analysis of Benzylid Lithium Compounds .... 63
Part III - Dynamic nmr Results ........................................ 98

EXPERIMENTAL ........................................................ 123
REFERENCES ............................................................. 164
APPENDIX A ............................................................... 170
APPENDIX B ............................................................... 188
<table>
<thead>
<tr>
<th>Table No.</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Effect of ligand on yield, stability and solubility of 2</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>Effect of ligand on yield, solubility and stability of 5</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>Nmr parameters-I</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>Nmr parameters-II</td>
<td>46</td>
</tr>
<tr>
<td>5</td>
<td>Nmr parameters-III</td>
<td>48</td>
</tr>
<tr>
<td>6</td>
<td>Nmr parameters-IV</td>
<td>51</td>
</tr>
<tr>
<td>7</td>
<td>Reaction of α-methyl-α-neopentylbenzyltrimethyltin and t-butyllithium in the presence of co-ligands</td>
<td>57</td>
</tr>
<tr>
<td>8</td>
<td>Nmr parameters-V</td>
<td>61</td>
</tr>
<tr>
<td>9</td>
<td>Nmr parameters-VI</td>
<td>64</td>
</tr>
<tr>
<td>10</td>
<td>Nmr parameters-VII</td>
<td>65</td>
</tr>
<tr>
<td>11</td>
<td>Variation in ortho proton resonances with para substituent in TMEDA-isoctane at 31°C</td>
<td>66</td>
</tr>
<tr>
<td>12</td>
<td>Variation in aromatic proton shifts of 2 and 5 with ligand</td>
<td>68</td>
</tr>
<tr>
<td>13</td>
<td>Chemical shift assignment of spectrum depicted in Figure 20</td>
<td>76</td>
</tr>
<tr>
<td>Table No.</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>14.</td>
<td>Integration values for the benzylic and aromatic carbons of 2 and 5</td>
<td>77</td>
</tr>
<tr>
<td>15.</td>
<td>Nmr parameters-VIII</td>
<td>80</td>
</tr>
<tr>
<td>16.</td>
<td>Nmr parameters-IX</td>
<td>82</td>
</tr>
<tr>
<td>17.</td>
<td>Para carbon-13 shifts of hydrolysates and benzylic lithiums (δ(ppm)/TMS)</td>
<td>85</td>
</tr>
<tr>
<td>18.</td>
<td>SIS values for hydrolysates and benzylic lithiums</td>
<td>85</td>
</tr>
<tr>
<td>19.</td>
<td>Deviations (SIS) for para substituents</td>
<td>86</td>
</tr>
<tr>
<td>20.</td>
<td>Ortho carbon-13 shifts of para substituted benzylic lithiums</td>
<td>87</td>
</tr>
<tr>
<td>21.</td>
<td>Carbon-13 shifts (back ring) of benzylic lithiums and hydrolysates</td>
<td>92</td>
</tr>
<tr>
<td>22.</td>
<td>Nmr parameters-X</td>
<td>95</td>
</tr>
<tr>
<td>23.</td>
<td>Thermodynamic activation parameters for rotation in benzylic lithiums</td>
<td>106</td>
</tr>
<tr>
<td>24.</td>
<td>Effect of ligand on rate of rotation of 5 at 380º K</td>
<td>121</td>
</tr>
<tr>
<td>25.</td>
<td>Nmr parameters-XI</td>
<td>146</td>
</tr>
<tr>
<td>26.</td>
<td>Nmr parameters-XII</td>
<td>148</td>
</tr>
<tr>
<td>27.</td>
<td>Nmr parameters-XIII</td>
<td>150</td>
</tr>
<tr>
<td>28.</td>
<td>Nmr parameters-XIV</td>
<td>151</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Average proton shifts for benzylic lithiums (ppm from TMS)</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>Nmr spectrum, 90 MHz, 27°C, for aromatic protons of 2, ca. 1.0 M in TMEDA-isoctane</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Nmr spectrum, 90 MHz, 27°C for aromatic protons of 2H, ca. 1.0 M in THF-pentane</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>Nmr spectrum, 90 MHz, 27°C, for aromatic protons of 25, 20% v/v in CDCl3</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>Nmr spectrum, 90 MHz, 27°C, for aromatic protons of 9, 20% v/v in CDCl3</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>Structure of benzylic lithium-TMEDA complex</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>Possible polymeric-like structure for RLi-tertiary amine complexes. Alkyl groups around N atoms are omitted for clarity</td>
<td>16</td>
</tr>
<tr>
<td>8</td>
<td>Nmr spectrum, 100 MHz, 33°C, for aromatic protons of 5, ca. 0.75 M in TMEDA-isoctane</td>
<td>18</td>
</tr>
<tr>
<td>9</td>
<td>Nmr spectrum, 100 MHz, 33°C, for aromatic protons of 12, ca. 0.75 M in TMEDA-isoctane</td>
<td>23</td>
</tr>
<tr>
<td>10</td>
<td>Nmr spectrum, 100 MHz, 33°C, for aromatic and vinylic protons of 13 and 14, total concentration ca. 1.0 M in TMEDA-isoctane</td>
<td>24</td>
</tr>
<tr>
<td>Figure No.</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>------------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>11.</td>
<td>Nmr spectrum, 100 MHz, 95° C, for aromatic protons of 28, ca. 0.9 M in THF-pentane</td>
<td>30</td>
</tr>
<tr>
<td>12.</td>
<td>Nmr spectrum, 90 MHz, 27° C, for aromatic protons of 35, ca. 1.0 M in TMEDA-isooctane</td>
<td>34</td>
</tr>
<tr>
<td>13.</td>
<td>Nmr spectrum, 22.63 MHz, 33° C, for aromatic and vinylic carbons of 34, 20% v/v in CDCl₃</td>
<td>35</td>
</tr>
<tr>
<td>14.</td>
<td>Nmr spectrum, 22.63 MHz, 33° C, for aromatic and vinylic carbons of 36, 20% v/v in CDCl₃</td>
<td>35</td>
</tr>
<tr>
<td>15.</td>
<td>Nmr spectrum, 90 MHz, 27° C, for aromatic protons of 38 and 39, ca. 1.0 M in THF-pentane</td>
<td>37</td>
</tr>
<tr>
<td>16.</td>
<td>Nmr spectrum, 90 MHz, 0° C, for aromatic protons of 38, ca. 1.0 M in THF-cyclopentane</td>
<td>38</td>
</tr>
<tr>
<td>17.</td>
<td>Carbon-13 shifts of isooctane (δ(ppm/TMS))</td>
<td>47</td>
</tr>
<tr>
<td>18.</td>
<td>Newman projections of 2 and 57</td>
<td>53</td>
</tr>
<tr>
<td>19.</td>
<td>Arrangement for stereospecific protonation of 38</td>
<td>56</td>
</tr>
<tr>
<td>20.</td>
<td>Nmr spectrum, 22.64 MHz, 33° C, for 2, ca. 1.0 M in TMEDA-pentane</td>
<td>74</td>
</tr>
<tr>
<td>21.</td>
<td>Nmr spectrum, 22.63 MHz, 33° C, for 5, ca. 1.0 M in THF-pentane</td>
<td>75</td>
</tr>
<tr>
<td>22.</td>
<td>Preferred axis or reorientation in tertiary benzylic lithiams</td>
<td>78</td>
</tr>
<tr>
<td>23.</td>
<td>Nmr spectrum, 22.63 MHz, 33° C, for 12, ca. 1.0 M in THF-pentane</td>
<td>89</td>
</tr>
<tr>
<td>24.</td>
<td>Nmr spectrum, 22.63 MHz, 33° C, for 28, ca. 1.0 M in THF-pentane</td>
<td>90</td>
</tr>
<tr>
<td>Figure No.</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>25. Nmr spectrum, 22.63 MHz, 33° C, for 2b, ca. 1.0 M in THF-pentane</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>26. Huckel charges in odd alternate anions</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>27. Nmr spectra, 100 MHz, variable temperature, for ortho protons of 26, ca. 1.0 M in TMEDA-isoctane</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td>28. Calculated line shapes for ortho protons of 26 at different rates of rotation</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>29. Eyring plot of rate versus temperature data for 26</td>
<td>109</td>
<td></td>
</tr>
<tr>
<td>30. Arrhenius plot of rate versus temperature data for 26</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>31. Mechanism for rotation in benzylic lithiums</td>
<td>111</td>
<td></td>
</tr>
<tr>
<td>32. Simplified reaction profile for rotation in benzylic lithiums</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>33. Molecular orbital diagram I</td>
<td>117</td>
<td></td>
</tr>
<tr>
<td>34. Molecular orbital diagram II</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>35. Synthetic scheme for para substituted α-methyl-styrenes I</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>36. Synthetic scheme for para substituted α-methyl-styrenes</td>
<td>144</td>
<td></td>
</tr>
<tr>
<td>37. Synthetic scheme for the preparation of 1-phenyl-cyclobutene</td>
<td>145</td>
<td></td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Name</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>TMEDA</td>
<td>N,N,N',N'-tetramethyl ethylenediamine</td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
<td></td>
</tr>
<tr>
<td>TMS</td>
<td>tetramethylsilane</td>
<td></td>
</tr>
<tr>
<td>TMMDA</td>
<td>N,N,N',N'-tetramethylthiadiaminomethane</td>
<td></td>
</tr>
<tr>
<td>TMPDA</td>
<td>N,N,N,N'-tetramethylpropylenediamine</td>
<td></td>
</tr>
<tr>
<td>nmr</td>
<td>nuclear magnetic resonance</td>
<td></td>
</tr>
<tr>
<td>TMA</td>
<td>trimethylamine</td>
<td></td>
</tr>
<tr>
<td>TEA</td>
<td>triethylamine</td>
<td></td>
</tr>
<tr>
<td>MCPBA</td>
<td>meta-chloroperbenzoic acid</td>
<td></td>
</tr>
<tr>
<td>NBS</td>
<td>N-bromosuccinimide</td>
<td></td>
</tr>
<tr>
<td>DMM</td>
<td>dimethoxymethane</td>
<td></td>
</tr>
<tr>
<td>DME</td>
<td>dimethoxyethane</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td></td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
<td></td>
</tr>
<tr>
<td>eq</td>
<td>equivalents</td>
<td></td>
</tr>
</tbody>
</table>
INTRODUCTION

The properties of benzylic lithium compounds have been the subject of extensive studies.\textsuperscript{1-6,24,25} These investigations have been prompted by both the synthetic utility of these compounds, most notably as anionic catalysts in styrene polymerization,\textsuperscript{2} and the fact that the basic structure of these $\pi$-conjugated carbanions is yet to be unambiguously determined. Problems which concern the structure and behavior of these species include the charge distribution,\textsuperscript{6} degree of covalency of the carbon lithium bonds\textsuperscript{1,3} and various types of ion-pairing involved.\textsuperscript{4,5} Furthermore, benzylic lithium compounds may possess a non-rigid structure. For our purposes the term "non-rigid structure" may be defined as the ability of groups bonded to the benzylic carbon to change their relative orientation towards each other either through rotation around individual bonds or inversion at the benzyl carbon. It seems reasonable to assume that the three interactions listed above are to some degree interdependent on each other. Also, each should exert some influence on the overall rigidity of the benzylic lithium. For instance, the charge distribution between the aromatic ring and benzylic carbon must depend on the lithium-carbon covalency, since electron density utilized in a lithium-carbon bond is not available for conjugative transfer into the aromatic ring. Since this conjugative transfer of charge into the aromatic ring predicates
some additional bond order between the benzylic carbon and the aromatic ring, the rigidity of the benzylic lithium or more specifically the barrier to rotation about the benzylic carbon-aromatic ring bond should be affected. By undertaking a quantitative study of this barrier some insight into the conjugative interactions in benzylic lithiums and the basic nature of these species, the charge distribution, degree of covalency and type of ion-pairing, may be gained. Further, any perturbation which affects the conjugative interaction between the benzylic carbon and the aromatic ring should also affect the barrier to rotation.

Obviously one can not extricate all effects by observing any or all kinds of benzylic lithium compounds. However a good model system was uncovered where it appears that the ground state consisted of solvent separated ion pairs and where it was proposed that rotation might involve some covalency developed between the carbon-lithium bond.

\[
\begin{align*}
\text{Li} \quad \text{ Benzene ring } \\
\end{align*}
\]

This provides a useful starting point to study the details of substituent conjugation on the ground state and on the barrier to rotation as well as the affect of solvent on the rotation process.

The plan was to develop a new synthesis of para substituted tertiary benzylic lithium compounds. The ground state electronic structure of the carbanionic moiety was to be studied with nmr spectroscopy. Further, the temperature dependent nmr line shapes could be used to calculate the rates of and barrier to rotation.
HISTORICAL

The preparation of benzylic lithium compounds has been accomplished by the cleavage of benzylmethyl ethers\(^7,8\) (equations 1, 2).

Surprisingly,

\[
\Phi CH_2OCH_3 \quad 2Li \quad \xrightarrow{\text{THF}} \quad \Phi CH_2-Li \quad CH_3OLi \\
-15^\circ C
\]  

(1)

\[
\Phi CHOCH_3 \quad 2Li \quad \xrightarrow{\text{THF}} \quad \Phi CH-Li \quad CH_3OLi \\
CH_3 \\
\xrightarrow{-15^\circ C} \quad \Phi CH-Li \quad CH_3OLi
\]  

(2)

1-phenylethyllithium was decomposed faster by tetrahydrofuran than methyl lithium while benzyllithium reacted more slowly than methyl lithium with tetrahydrofuran. Benzyllithium may be prepared by the reaction of toluene with \(n\)-butyllithium in the presence of TMEDA or DABCO (see below) but the product is contaminated by ring metallation products.\(^9,10\) Under these conditions ethylbenzene and cumene result in even higher yields of similar side products.\(^9,11\) Benzylolithium has

\[
\text{DABCO} \quad ---- 1,4\text{-diazabicyclo[2,2,2]octane}
\]

been generated by the alkylolithium cleavage of benzylic tin compounds and benzylic lead compounds\(^12,13\) (equations 3, 4).
The three techniques described above represent the classical methods for the preparation of benzylic lithium compounds. A fourth general method for the preparation of organolithium compounds, lithium-halogen exchange between an organic halide and either lithium metal or an alkyl lithium, fails with benzylic halides since they undergo coupling reactions under these conditions. An exception is the reaction of diphenylmethylchloride with lithium. An 80% yield of diphenylmethyl lithium can be obtained after stirring these reactants at room temperature for 18 hours. This is thought to be due to the cleavage of the coupling product itself by lithium\(^\text{14}\) (equations 5-7).

\[
(\Phi)\text{CCHCl} + 2\text{Li} \rightarrow (\Phi)\text{CCH-Li} + \text{LiCl} \tag{5}
\]

\[
(\Phi)\text{CCHCl} + (\Phi)\text{CCH-Li} \rightarrow (\Phi)\text{CCHCH}((\Phi)_2 + \text{LiCl} \tag{6}
\]

\[
(\Phi)\text{CCHCH}((\Phi)_2 + 2\text{Li} \rightarrow 2(\Phi)\text{CCH-Li} \tag{7}
\]

The formation of tertiary benzylic lithium compounds by the rearrangement of primary benzylic lithium compounds has been inferred from the quench products of the following reactions\(^\text{15},\text{16}\):

\[
((\Phi)\text{CCH}_2)_2\text{Hg} \xrightarrow{\text{n-Bu-Li}} (\Phi)\text{CCH}_2-\text{Li} \xrightarrow{<0^\circ \text{C}} (\Phi)\text{CCH}_2-\text{Li} \xrightarrow{\Delta} [(\Phi)\text{CH}_2\text{C}((\Phi)_2-\text{Li}]
\]

\[
\xrightarrow{\text{H}_2\text{O}} (\Phi)\text{CH}_2\text{CH}((\Phi)_2
\]
but in both examples the presence of neither the primary nor the tertiary species was determined by direct spectroscopic observation. All these procedures possess one major shortcoming, a side product is generated which could interfere with the nmr study or even modify the nature of the benzylic lithium compound. A method which does not possess this interference is the one to one addition of an alkyl-lithium across the double bond of a conjugated olefin such as \( \alpha \)-substituted styrenes (equation 10). This technique has received only scant attention,\(^{21,22,23,24} \) possibly because of the well known alkyl lithium catalyzed polymerization of styrenes.\(^2 \) However it is also known that the relative rates of initiation and propagation in these polymerizations vary greatly with the structure of the alkyl lithium. For example, the rate of initiation of styrene polymerization by n-butyllithium is slower than the rate of propagation in hydrocarbon solvents, while for \( s \)-butyllithium the rate of initiation is faster than propagation.\(^{17,18,19} \) In tetrahydrofuran the relative reactivities of organolithium compounds as initiators in the polymerization of styrene is alkyl > benzyl > allyl > phenyl > vinyl > triphenylmethyl.\(^{20} \)
Thus it seems that with the proper choice of alkyl lithium and solvent, the formation of a one to one adduct, an unsymmetrical benzylic lithium, by the reaction outlined in equation 10 should be readily accomplished. Indeed, when a solution of α-methylstyrene in hydrocarbon is added to a hydrocarbon solution of t-butyllithium in the presence of TMEDA or tetrahydrofuran at -30°C, the formation of a one-to-one adduct is quantitative²⁸,²⁷ (equation 10, R = -CH₃).

The study of benzylic lithium compounds by nmr spectroscopy has proved a fertile source of information concerning their structure and basic nature.⁶,²⁸-³² Most of the discussion has centered around the hybridization of the benzylic carbon and the amount of negative charge delocalized into the aromatic ring.⁶,³¹ Based on carbon-13 data Waack et al.²⁸,³² inferred that the benzylic carbon in diphenylmethyl- and triphenylmethyl lithium is predominantly sp² hybridized, while for benzyl lithium the benzylic carbon's variation in chemical shift with solvent indicated a concurrent variation in its hybridization. Waack et al.²⁸ and others³³ have pointed out that there are alternate explanations for this chemical shift behavior in benzyl lithium.

Worsfold et al.,⁶,³¹ van Dongen et al.,³⁰ Takahashi et al.³⁴,³⁵,³⁶ and Fraenkel et al.²⁸ have investigated the charge distribution in the aromatic ring of benzylic lithiums by both proton and carbon-13 nmr spectroscopy as a function of counter-ion, solvent and alkyl substituent at the benzylic carbon. Up to now, however, no study of the influence of conjugating para-substituents on the aromatic ring and benzylic carbon nmr chemical shifts has been reported.
The dynamic processes of benzylic lithiastics have been less extensively studied. It was noted that the aromatic ring hydrogens of unsymmetrically substituted benzylolithiastics were magnetically non-equivalent, confirming the co-planarity of the system, but before the work of Fraenkel et al. only one report of a full nmr line shape study of the dynamic rotational process around the benzylic carbon-aromatic ring carbon bond in a benzylic lithium had been made, and the data presented were not of exceptionally high quality. Of related interest are the studies of molecular structure and hindered rotation in phenylallyl metal compounds, where the rate of rotation was found to be dependent on counter-ion and solvent.

Altogether, the dnmr data indicated above suggested that unsymmetrical benzylic lithiastics exist in the ground state as some type of solvent-separated ion pairs, in a planar-conjugated conformation with some degree of sp² character at the benzylic carbon. There has been no definitive conclusion on the mechanism of rotation for these benzylic lithium compounds. Fraenkel et al. postulated a covalent tetrahedral transition state for rotation while Bates invokes imperceptible amounts of covalent species in equilibrium with the ion pairs. Any influence of conjugating para substituents on the rate of rotation of the benzylic lithiastics could be a result of either a change in the relative energy difference between the ground and transition states or a shift in the equilibrium between the conjugated and covalent species.
RESULTS AND DISCUSSION

Part I - Synthesis and Chemistry of Benzylic Lithium Compounds

In this section the reaction of α-methyl styrenes and 1-phenyl-cycloalkenes with t-butyllithium will be described together with electrophilic capture reactions and one example of oxidation of the resulting benzylic lithium compounds.

Here is the central reaction investigated in this work, (equation 1);

\[
X-H + (\text{CH}_3)_3\text{C}Li \xrightarrow{L} X-\text{CH}-(\text{CH}_3)_3\text{C}Li
\]

\(L = \text{amines, ethers, benzene}\)
\(X = -H, -\text{Si(CH}_3)_3, -\text{Si(CH}_3)_2\Phi, -\text{Ge(CH}_3)_3, -\text{Sn(CH}_3)_3\)
\(-\text{SCH}_3, -\text{SC(CH}_3)_3, -\Phi\)

\(-\text{NO}_2, -\text{Br}, -\text{OCH}_3,\)

The experimental method followed was to add one equivalent of styrene to a 1:1 t-butyllithium-ligand complex at \(-30^\circ\text{C}\) in 2,2,4-trimethylpentane ("isoctane"). The resulting benzylic lithium compound was
indicated by the formation of a dark red solution, usually but not always homogeneous.

The influence of both ligand and substituent on the course of the above reaction and its products was investigated. First, a brief description of the method of detection and analysis of benzylic lithium compounds is appropriate.

The formation of soluble benzylic lithium compounds was monitored by nmr spectroscopy. The pronounced upfield shifts of the aromatic protons of a benzylic anion served as direct evidence of its formation. Inspection of the average values for these proton resonances (Figure 1) also shows the sharp separation between ortho, meta and para positions.

![Figure 1](image-url)

Figure 1. Average proton shifts for benzylic lithums (ppm from TMS).

Examples of typical spectra are shown in Figures 2 and 3. The nmr spectra of the benzylic lithums are well resolved from those for their styrene precursors and any hydrolysate product generated by trace amounts of water (equation 2).

![Equation 2](image-url)

Figures 4 and 5 depict typical aromatic portions of spectra for these two species. Thus the relative amounts of starting material,
Figure 2. Nmr spectrum, 90 MHz, 27° C, for aromatic protons of 2, ca. 1.0 M in TMEDA-isoctane
Figure 3. Nmr spectrum, 90 MHz, 27°C for aromatic protons of \( \text{ca.} \ 1.0 \ M \) in THF-pentane.
Figure 4. Nmr spectrum, 90 MHz, 27°C, for aromatic protons of 25, 20% v/v in CDCl₃
Figure 5. Nmr spectrum, 90 MHz, 27° C, for aromatic protons of 9, 20% v/v in CDCl₃
soluble benzylic lithium and hydrolysate were determined with nmr integration techniques. In cases where the benzylic lithium species was insoluble its yield was determined by hydrolysis of the heterogeneous mixture and determination of the yield of product.

In many cases the ligand exerted a profound influence on the course of the reaction, and the yield, solubility and stability of the resulting benzylic lithium compound. Table 1 lists these effects for α-methylstyrene. The yield of 2 is seen to be fairly independent of the choice of ligand although it drops slightly when benzene is used. The variation of solubility is more interesting and deserves some comment.

Benzylic lithium compounds such as 1 are thought to exist in solution as solvent-separated ion pairs.\textsuperscript{26} X-ray crystallographic work has demonstrated that both benzyl- and triphenylmethyllithium form bidentate complexes with TMEDA, where the stability derived from a five-membered ring (see figure 6) is important.\textsuperscript{42} The TMEDA-lithium configuration in these ion pairs in solution is probably the same. The

\begin{center}
\includegraphics[width=0.2\textwidth]{benzyllic_lithium-TMEDA_complex}
\end{center}

Figure 6. Structure of benzylic lithium-TMEDA complex.

The solubility behavior depicted in Table 1 indicates that when a bidentate complex would require the formation of a four or six-membered ring (TMMDA or TMPDA) this does not occur, but rather some alternate form
### TABLE 1
Effect of Ligand on Yield, Stability and Solubility of 2

![chemical structure](image)

<table>
<thead>
<tr>
<th>LIGAND</th>
<th>n</th>
<th>yield(^a)</th>
<th>solub.(^b)</th>
<th>stab.(^c)</th>
<th>yield(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMEDA</td>
<td>1</td>
<td>95%</td>
<td>S</td>
<td>100(^\circ)C</td>
<td>85 ± 5%</td>
</tr>
<tr>
<td>TMMDA</td>
<td>1</td>
<td>--</td>
<td>IN</td>
<td>--</td>
<td>80%</td>
</tr>
<tr>
<td>TMPDA</td>
<td>1</td>
<td>--</td>
<td>IN</td>
<td>--</td>
<td>80%</td>
</tr>
<tr>
<td>(\text{N}(\text{CH}_2\text{CH}_3)_2)</td>
<td>1</td>
<td>90%</td>
<td>S</td>
<td>100(^\circ)C</td>
<td>80%</td>
</tr>
<tr>
<td>N-methyl-pyrroldidine</td>
<td>2</td>
<td>95%</td>
<td>S</td>
<td>100(^\circ)C</td>
<td>87%</td>
</tr>
<tr>
<td>benzene(^e)</td>
<td>1</td>
<td>--</td>
<td>IN</td>
<td>--</td>
<td>70%</td>
</tr>
<tr>
<td>THF</td>
<td>2</td>
<td>95%</td>
<td>S</td>
<td>45(^\circ)C</td>
<td>85 ± 5%</td>
</tr>
<tr>
<td>none(^f)</td>
<td></td>
<td>--</td>
<td>IN</td>
<td>--</td>
<td>97%</td>
</tr>
</tbody>
</table>

\(^a\) yield of 2 based on nmr integration  
\(^b\) soluble enough to obtain nmr spectrum using HA-100  
\(^c\) temperature at which sample decomposed within nmr probe  
\(^d\) yield after distillation, average of several runs when limits given  
\(^e\) reaction temperature 0\(^\circ\)C  
\(^f\) reaction temperature 50\(^\circ\)C
of interaction takes place. A likely possibility is an insoluble polymeric structure (Figure 7.)

![Polymeric structure diagram](image)

Figure 7. Possible polymeric-like structure for RLi-tertiary amine complexes. Alkyl groups around the N atoms are omitted for clarity.

Complexes of this type would surely have lower solubility than a 1:1 benzyl lithium-bidentate amine complex or a 1:2 benzyl lithium-monodentate amine complex. Interestingly enough when only 0.5 equivalents of TMEDA are present, a red precipitate forms which when filtered, hydrolized and analyzed by vapor phase chromatography, shows that no TMEDA was present in the precipitate.

The reactivity of 2 in deprotonating the ligand differs greatly between tertiary amines and ethers (equations 3 through 6).

\[
\begin{align*}
\text{2} & \quad + \quad \text{O} \quad \rightarrow \quad \text{3} \\
\text{O} \quad \text{Li} & \quad \rightarrow \quad \text{CH}_2\text{CH}_2 \quad + \quad \text{CH}_2\text{CH} \quad \text{OLi}
\end{align*}
\]
\[ \text{Li} \]
\[ 2 + (\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N} (\text{CH}_3)_2 \rightarrow 2 + (\text{CH}_3)_2\text{NCHCH}_2\text{N} (\text{CH}_3)_2 \]  \hspace{1cm} (5)

\[ \text{Li} \]
\[ (\text{CH}_3)_2\text{NCHCH}_2\text{N} (\text{CH}_3)_2 \rightarrow (\text{CH}_3)_2\text{NCHCH}_2\text{N} (\text{CH}_3)_2 + \text{LiN} (\text{CH}_3)_2 \]  \hspace{1cm} (6)

Since \( \text{N-} \text{methylpyrroolidine} \) shows the same stability towards \( \text{2} \) as TMEDA\(^4\)\(^3\), the greater reactivity of THF is probably due to the greater acidity of a proton adjacent to oxygen rather than the effect of a five membered ring.

When t-butyllithium is mixed with \( \text{1} \) at \(-30^\circ \text{C} \) in isooctane no reaction occurs. However, at \( 50^\circ \text{C} \) addition takes place as fast as the styrene is added. If one equivalent of benzene is present, the reaction occurs slowly at \(-30^\circ \text{C} \), but rapidly at \( 0^\circ \text{C} \) to yield a viscous solution which eventually precipitates a red solid. By working rather rapidly an nmr spectrum of this solution can be obtained which exhibits the same chemical shifts as the amine or ether solvated benzylic lithions. This insensitivity towards the nature of the ligand supports the premise that these benzylic lithions exist as solvent-separated ion pairs.\(^2\)\(^8\)

When the para hydrogen of \( \text{1} \) is replaced by a trimethylsilyl group changes occur in the reactivity and solubility of the resulting benzylic lithium. Figure 8 displays its proton spectrum (aromatic region only). Inspection of Table 2 illustrates these differences. The nmr spectrum of \( \text{2} \) in THF can be recorded at \( 90^\circ \text{C} \), which indicates the strong stabilizing effect of a \( p \)-trimethylsilyl group. This observation is in accord with what is known about the ability of
Figure 8. Nmr spectrum, 100 MHz, 33°C, for aromatic protons of 5, ca. 0.75 M in TMEDA-isoctane
silicon to stabilize a negative charge on an adjacent carbon both kinetically and thermodynamically.44 The solubility of the TMEDA complex is somewhat lower in this case possibly because the silicon atom's conjugative effect perturbs the charge distribution which in turn changes the lithium-nitrogen interaction responsible for solubility. The enhanced stability of 5 in THF led to an investigation of ether-benzylithium complexes which would be expected to behave in a bidentate fashion. In all three cases examined, rapid formation of benzylic lithium occurred at -30° C, but decomposition was complete at 0° C as judged by fading of the color on warming from -30° C to 0°. In the cases of dioxane and dimethoxyethane, a good yield of 6 was obtained on work-up, but the decomposition product isolated in the case of dimethoxymethane was not 6. Spectroscopic evidence indicated that addition of t-butyllithium across the double bond had occurred, followed by a nucleophilic methylation process rather than a deprotonation (equation 8) to produce 7 in 85% yield. No 6 was isolated.

\[
\text{(CH}_3\text{)}_3\text{Si-} + \text{CH}_3\text{OCH}_2\text{OCH}_3 \rightarrow \text{Li} \\
\text{5} \\
\text{(CH}_3\text{)}_3\text{Si-} + \text{CH}_3\text{+ LiOCH}_3 \\
\text{7 (8)}
\]

The investigation of substituent effects was continued by studying reactions with p-trimethylgermyl-α-methylstyrene (8), p-phenyldimethylsilyl-α-methylstyrene (9) and p-trimethylstannyl-α-
TABLE 2

Effect of Ligand on Yield, Solubility and Stability of 2

![Chemical structure](image)

<table>
<thead>
<tr>
<th>LIGAND</th>
<th>n</th>
<th>yield&lt;sup&gt;a&lt;/sup&gt;</th>
<th>solub&lt;sup&gt;b&lt;/sup&gt;</th>
<th>stab&lt;sup&gt;c&lt;/sup&gt;</th>
<th>yield&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMEDA</td>
<td>1</td>
<td>95%</td>
<td>S</td>
<td>116° C</td>
<td>80 ± 5%</td>
</tr>
<tr>
<td>(CH₃)₂N</td>
<td>2</td>
<td>90%</td>
<td>S</td>
<td>107° C</td>
<td>80%</td>
</tr>
<tr>
<td>(CH₃CH₂)₂N</td>
<td>2</td>
<td>95%</td>
<td>S</td>
<td>107° C</td>
<td>80 ± 5%</td>
</tr>
<tr>
<td>Ethyl Ether</td>
<td>2</td>
<td>90%</td>
<td>S</td>
<td>95° C</td>
<td>80%</td>
</tr>
<tr>
<td>THF&lt;sup&gt;g&lt;/sup&gt;</td>
<td>2</td>
<td>95%</td>
<td>S</td>
<td>107° C</td>
<td>80%</td>
</tr>
<tr>
<td>dioxane</td>
<td>1</td>
<td>--</td>
<td>--</td>
<td>0° C</td>
<td>71%</td>
</tr>
<tr>
<td>DMM</td>
<td>1</td>
<td>--</td>
<td>--</td>
<td>0° C</td>
<td>0%</td>
</tr>
<tr>
<td>DME</td>
<td>1</td>
<td>--</td>
<td>--</td>
<td>0° C</td>
<td>75%</td>
</tr>
<tr>
<td>none</td>
<td></td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>95%</td>
</tr>
</tbody>
</table>

<sup>a</sup> yield of 2 based on nmr integration

<sup>b</sup> soluble enough to obtain nmr spectrum using HA-100

<sup>c</sup> temperature at which sample decomposed within nmr probe

<sup>d</sup> yield after distillation, average of several runs when limits given

<sup>e</sup> reaction of temperature 0° C

<sup>f</sup> reaction temperature 50° C

<sup>g</sup> excess THF gave the same results
methylstyrene (10). The results are summarized in equations 9 through 11.

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{Ge} & \quad \text{(CH}_3\text{)}_3\text{ClLi} \quad \text{THF or TMEDA} \\
\text{-30}\degree\text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{Ge} & \quad \text{Li} \\
\text{11} & \quad (95\%) \\
\end{align*}
\]

\[
\begin{align*}
\Phi(\text{CH}_3\text{)}_2\text{Si} & \quad \text{(CH}_3\text{)}_3\text{ClLi} \\
\text{THF or TMEDA} \quad \text{-30}\degree\text{C} \\
\end{align*}
\]

\[
\begin{align*}
\Phi(\text{CH}_3\text{)}_2\text{Si} & \quad \text{Li} \\
\text{12} & \quad (95\%) \\
\end{align*}
\]

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{Sn} & \quad \text{(CH}_3\text{)}_3\text{ClLi} \\
\text{-30}\degree\text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{Sn} & \quad \text{Li} \\
\text{13} & \quad (20\%) \\
\text{THF or TMEDA} \\
\text{14} & \quad (80\%) \\
\text{Ethyl Ether} & \quad (10\%) \\
\end{align*}
\]

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{Sn} & \quad \text{(CH}_3\text{)}_3\text{ClLi} \\
\text{-30}\degree\text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{Sn} & \quad \text{Li} \\
\text{13} & \quad (90\%) \\
\end{align*}
\]
In the first two cases the benzylic lithium is generated in greater than 95% yield in the presence of both TMEDA and THF. Figure 9 displays the proton nmr spectra (aromatic portion) for 12 in TMEDA. The clear distinction between the protons in the "back" ring and in the "front" ring is worthy of note. THF solutions of both 11 and 12 exhibited greater stability than that of 2 while the solubility behavior was the same as the p-trimethylsilyl derivative.

As outlined above the p-trimethylstannyl derivative displayed distinctive behavior. When reacted with t-butyllithium in the presence of TMEDA or THF at -30°C, the desired addition across the double bond occurred, but only in approximately 10% yield; the main reaction was displacement of the trimethylstannyl group giving p-lithio derivative 1h. Figure 10 shows the nmr spectrum which clearly distinguishes the two species. The same result was observed when the reaction temperature was varied from -70°C to 0°C using TMEDA as the ligand. Surprisingly, when the reaction was attempted in the presence of two equivalents of ethyl ether, a complete reversal in relative yields occurred. The benzylic lithium was generated in greater than 90% yield with only traces of the 4-lithio-α-methylstyrene present. Two more examples of this distinctive behavior of ethyl ether will be described presently, and discussion will be deferred until later.

Sulfur is known to stabilize adjacent anion centers in the same manner as silicon.45,46 It was expected that para thioalkyl derivatives of benzylic lithiurns would show the same enhanced stability as the para silyl derivatives. These expectations were not fulfilled however, by either the p-thiomethyl or p-thio-t-butyl groups.
Figure 9. Nmr spectrum, 100 MHz, 33°C, for aromatic protons of 12, ca. 0.75 M in TMEDA-isooctane
Figure 10. Nmr spectrum, 100 MHz, 33°C, for aromatic and vinylic protons of 13 and 14, total concentration ca. 1.0 M in TMEDA-isoctane
The reaction of p-thiomethyl-α-methylstyrene (15) with t-butyl-lithium was studied extensively in the presence of both THF and TMEDA, the reaction of the p-thio-t-butyl derivative only with TMEDA but with similar results in both cases. These negative results are summarized in equations 12 and 13.

\[
\begin{align*}
\text{CH}_3\text{S}-\begin{array}{c} \text{Li} \\ \text{THF or TMEDA} \end{array} & \begin{array}{c} (\text{CH}_3)_3\text{Li} \\ 78 \text{ to } 0^\circ \text{C} \end{array} & \begin{array}{c} \text{LiCH}_2\text{S} \\ \text{X} \end{array}
\end{align*}
\]

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{CS} & \begin{array}{c} \text{Li} \\ \text{TMEDA} \end{array} & \begin{array}{c} (\text{CH}_3)_3\text{Li} \\ -30^\circ \text{C} \end{array} & \begin{array}{c} \text{Li} \\ \text{X} \end{array}
\end{align*}
\]
In both cases a heterogeneous dark red mixture was produced on mixing the reactants. Nmr analysis of the supernatant indicated that no soluble benzylic lithium compound or phenyllithium compound had been produced. Quenching the reaction mixture with either H₂O or D₂O and subsequent examination of the organic products by vapor phase chromatography and nmr indicated that the olefin had been largely consumed when the reaction temperature was above -50°C (quench taking place at reaction temperature) and that little or no reaction had occurred below -50°C. Nmr analysis of the D₂O quench showed no deuterium incorporation in the methyl group of 15 or the phenyl ring in 15 or 19. When the reaction was attempted on 15 in the presence of two equivalents of ethyl ether at -30°C a dark red heterogeneous mixture again resulted. The proton nmr spectrum of the supernatant phase showed only solvent resonances, but analysis of the quench products revealed that addition to the double bond had occurred in high yield and a 75% conversion to the appropriate hydrocarbon was realized on work-up (equation 14).

\[(\text{CH}_3)_3\text{Li}\quad 15 \xrightarrow{\text{Ethyl Ether}} 16 \xrightarrow{-30^\circ\text{C}} \text{H}_2\text{O}\quad \text{CH}_3\text{S}^-\text{C}_{\text{6}H_4}^-\text{CH}_2^-\text{H} \quad (14)\]

Here again the use of ethyl ether allows addition to the double bond to be the favored reaction while in TMEDA or THF, either some other reaction predominates or the benzylic lithium compound was unstable. In the case of the sulfur derivatives however, the results of this
alternate process could not be identified. If 16 is formed when THF, or TMEDA is used, it does not decompose by deprotonation of the solvent. The mass balance of these reactions was very poor. Typically, when 5 to 10 millimoles of 15 to 19 were reacted with t-butyllithium, only 40 to 60 milligrams of organic product was recoverable by vacuum distillation (approximately a 10% recovery). This is indicative of either polymerization or possibly some type of reaction involving benzyne as an intermediate (equation 15). Since this does not occur with thioanisole under these conditions this latter possibility seems doubtful. When the ether-insoluble salt is treated with two equivalents of THF, reaction with solvent is complete in five minutes at 0° C.

In contradistinction to the above results, when p-thiophenyl-α-methylstyrene (23) is reacted with t-butyllithium in the presence of TMEDA or THF at -30° C, benzylic lithium is the only product observed.

\[
\text{(15)}
\]

\[
\begin{align*}
\text{RS} & \quad \text{CH}_3\text{CLi} \\
\begin{array}{c}
\quad \quad \quad \quad \\
\end{array} & \quad \quad \quad \quad \\
\text{RS} & \quad \quad \quad \quad \\
\quad \text{Li} & \quad \quad \quad \quad \\
\end{align*}
\]

\[
\begin{align*}
\text{RS} & \quad \text{CH}_3\text{CLi} \\
\begin{array}{c}
\quad \quad \quad \quad \\
\end{array} & \quad \quad \quad \quad \\
\text{RS} & \quad \quad \quad \quad \\
\quad \text{Li} & \quad \quad \quad \quad \\
\end{align*}
\]

\[
\text{(16)}
\]
The benzylic lithium-TMEDA complex is almost insoluble in isooctane, while the THF complex yields one molar solutions in pentane at room temperature. The stability of this benzylic lithium is intermediate between the unsubstituted (2) and the silicon substituted (5) derivatives. After thirty minutes of 90° C nmr analysis indicated that slightly more than one-half of the salt had decomposed. This striking difference in both ease of synthesis and thermal stability between the p-thiomethyl (16) and the p-thiophenyl (2h) benzylic lithums must obviously be due to some stabilizing effect of the phenyl group. This topic will be further discussed in the following two sections.

An investigation of the effects of the cyclopropyl and phenyl groups was then undertaken. p-Cyclopropyl-a-methylstyrene (22) reacted in high yield with t-butyllithium in the presence of TMEDA or THF to give one molar benzylic lithium solutions (equation 17). The benzylic lithium-TMEDA complex was stable up to 115° C but the THF

complexed species decomposed rapidly above 25° C, showing that it was less stable than 2 in this medium. Since a cyclopropyl group in the para position lowers slightly the equilibrium constant for benzoic acid ionization (destabilization of a negative charge) this result is reasonable.47 The p-phenylbenzylic lithium (28) is also formed in

\[
\text{(17)}
\]
high yield by reaction of the para phenyl substituted α-methylstyrene (27) with t-butyllithium in the presence of THF (equation 18).

\[(\text{CH}_3)_3\text{ClLi} \quad \text{THF-isooctane} \quad -30^\circ\text{C}\]

The precursor is insoluble in hydrocarbon or TMEDA-hydrocarbon solutions, but is soluble in 1:1 THF-hydrocarbon solution. The benzylic lithium was generated in excess THF and most of the excess removed by vacuum evaporation (0.5 torr) at room temperature. If one equivalent of TMEDA was added to the THF-28 complex vacuum evaporation resulted in mainly the 28-TMEDA complex, although traces of THF remained even after three such treatments. The 28-THF complex was soluble in isooctane (one molar solutions at room temperature) but 28-TMEDA was only sparingly soluble (concentrations less than 0.5 molar). A mixed THF-TMEDA complex (2:1) was soluble in isooctane. Thus the solubility of the p-phenyl derivative (28) resembles closely that of the p-thiophenyl derivative (24) but 28 is somewhat less soluble than the p-trimethylsilyl (5) and p-phenyldimethylsilyl (12) derivatives. The stability of 28-THF complex is greater than that of the 24-THF species and at least as good as 5-THF. The nmr spectrum (Figure 11) of 28-THF can be recorded at 95\(^{\circ}\)C. At this temperature there is no discernable decomposition. Strangely enough, the mixed THF-TMEDA complex is less stable, as decomposition at 95\(^{\circ}\)C is slow but noticeable. This could result from the fact that THF molecules
Figure 11. Nmr spectrum, 100 MHz, 95° C, for aromatic protons of 28, ca. 0.9 M in THF-pentane
"floating around" outside the complex are more available for reaction than those locked into the complex.

The final three para substituents investigated all gave negative results. When p-nitro-α-methylstyrene (22) was reacted with t-butyl-lithium in the presence of TMEDA at -30° C a dark red solution resulted. Upon warming to 0° C, the entire contents of the flask turned to a dark red-brown solid. Hydrolysis of the solid and work-up yielded only a small return of starting material (5-10%) and a polymeric non-volatile residue. Addition of one equivalent of p-bromo-α-methylstyrene (30) to t-butyllithium-TMEDA complex at -30° C resulted in a dark red solution whose color faded rapidly, accompanied by the formation of a white precipitate, as the temperature rose to 0° C. Here again the recovered yield of volatile organic products was very low (< 5%) and no hydrocarbon product resulting from addition of t-butyllithium across the double-bond was identified. In this case benzyne formation seems very probable (equation 19) but there is a different mode of decomposition available as illustrated in equation 20;

\begin{align}
\text{Br-} & \text{CH-CH-CH-CH-CH} \quad (\text{CH}_3)_2\text{Li} \quad \text{TMEDA} \quad -30^\circ \text{C} \\
\text{Br} & \text{CH-CH-CH-CH} \quad -\text{LiBr} \\
\text{Br-} & \text{CH-CH-CH-CH} \quad -\text{LiBr} \quad \text{TMEDA} \quad -30^\circ \text{C} \\
\text{Br-} & \text{CH-CH-CH-CH} \\
\end{align}

\begin{align}
\text{Br-} & \text{CH-CH-CH-CH} \\
\text{Br-} & \text{CH-CH-CH-CH} \\
\end{align}

\begin{align}
\text{Br-} & \text{CH-CH-CH-CH} \\
\text{Br-} & \text{CH-CH-CH-CH} \\
\end{align}
If the dark red color generated at -30° C was due to formation of 31, quenching at this temperature should allow isolation of the corresponding hydrocarbon 32.

\[
\text{31} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{32}
\]

Reaction of the dark red solution with H$_2$O at -30° C however, yielded no discernible amounts of 32, which indicates that 31 is not present.

Placement of a methoxy group in the para position was anticipated to greatly modify the stability in the benzylic lithium compound. Here inductive effects would be expected to stabilize the benzylic lithium while the question of the existence of a conjugative destabilizing influence is open to debate. The whole question is a mute one however, since t-butyllithium could not be induced to add to the double bond of 34 in the presence of TMEDA, THF, or ethyl ether. The only reaction observed was the quantitative ring deprotonation depicted in equation 22;

\[
\text{CH}_3\text{O} \quad \xrightarrow{\text{THF, TMEDA or Ethyl Ether}} \quad \text{CH}_3\text{O} \quad \xrightarrow{-30° C} \quad \text{(22)}
\]
The proton nmr spectrum of this sample was strong evidence for structure 35 (Figure 12) and this datum coupled with a comparison of the carbon-13 data for 35 and 36 (Figures 13, 14) is conclusive.

A short summary is now in order. In general, the benzylic lithium compounds are stable toward tertiary amine ligands (TMEDA) regardless of para substituent, but show wide differences in solubility which are dependent on the nature of the para substituent. The THF-benzylic lithium complexes are all quite soluble, but differ greatly in stability. There seems to be no difference between TMEDA and THF on the yield of benzylic lithium compound; whether the addition reaction goes well or not at all depends only on the para substituent. In two cases where side reactions predominate, the use of ethyl ether has been shown to favor addition.

We now consider the reaction displayed in equation 23.

$$\text{35} \rightarrow \text{D}_2\text{O} \quad \text{CH}_3\text{O-CH}=\cdot\text{D}$$

$$\text{36}$$

We now consider the reaction displayed in equation 23.

$$\begin{align*}
\text{Ph-CH} & \cdot\text{(CH}_2\text{)}_n \quad \text{(CH}_3\text{)}_3\text{ClLi} \\
\text{Li} & \cdot\text{(CH}_2\text{)}_n + \text{Ph-CH} \cdot\text{(CH}_2\text{)}_{n-1} + \text{polymer}
\end{align*}$$

(23)
Figure 12. Nmr spectrum, 90 MHz, 27°C, for aromatic protons of 35, ca. 1.0 M in TMEDA-isoctane
Figure 13. Nmr spectrum, 22.63 MHz, 33°C, for aromatic and vinylic carbons of 34, 20% v/v in CDCl₃

Figure 14. Nmr spectrum, 22.63 MHz, 33°C, for aromatic and vinylic carbons of 36, 20% v/v in CDCl₃
The course of reaction 23 was dependent on ring size, temperature and ligand. The first example discussed is that of 1-phenylcyclopentene, which exhibited most interesting behavior.

Reaction of 1-phenylcyclopentene (37) with the t-butyllithium-THF complex at various temperatures in cyclopentane gave the results listed below.

\[
\begin{align*}
\text{1-phenylcyclopentene (37)} & \quad \text{(0° C)} & \quad \text{(50%)} & \quad \text{(30%)} \\
\text{37} & \quad \text{(CH₃)₃CLi} & \quad \text{THF} & \quad \text{-15° C} & \quad \text{(80%)} & \quad \text{(20%) (24)} \\
& \quad \text{-30° C} & \quad \text{(95%)} & \quad \text{(5%)} \\
\end{align*}
\]

At 0° C the reaction generated approximately 20% polymeric material. The major point here is the change in the ratio of allylic deprotonation to addition to the double bond with varying temperature. The relative amounts of the two anionic species were ascertained by integration of the proton nmr spectra (Figures 15 and 16). Figure 15 displays the aromatic spectrum for the reaction mixture resulting from addition at 0° C, the spectrum is recorded at 27° C. Figure 16 displays the spectrum of 38 which resulted from addition at -30° C. No 39 is present. Unfortunately the spectrum is recorded at -20° C and
Figure 15. Nmr spectrum, 90 MHz, 27° C, for aromatic protons of 28 and 39, ca. 1.0 M in THF-pentane
Figure 16. Nmr spectrum, 90 MHz, 0°C, for aromatic protons of 38, ca. 1.0 M in THF-cyclopentane
the scale is different from Figure 15, so that a direct comparison is difficult. The ortho, meta and para protons resonances for 38 and 39 are marked on Figure 15. These proton spectra are discussed further in the next sections. The fact that addition and deprotonation occur almost at the same rate at 0\(^\circ\)C and addition predominates totally at -30\(^\circ\)C is striking evidence of the subtle effects that may regulate organometallic reactions. Attempts to increase the yield of allylic species by running the reaction at still higher temperatures failed. At 10\(^\circ\)C nmr indicates that polymerization predominates. Use of TMEDA at -30\(^\circ\)C results in 100% addition at the double bond. At 0\(^\circ\)C addition again predominates but the amount of polymerization is higher than in the case of THF. This seems to indicate that the rate of initiation, either addition to the double bond or deprotonation, is slower with the \(t\)-butyllithium-TMEDA complex than with \(t\)-butyllithium-THF complex.

The solubility of 38 is sufficient to give one molar solutions at room temperature in both TMEDA in isooctane and THF in cyclopentane. The thermal stability of 38 is greater than that of its acyclic analog 2. The nmr spectrum of 38-THF can be recorded at 65\(^\circ\)C with no discernable decomposition. The TMEDA complex shows comparable stability to 2-TMEDA; its nmr spectra can be recorded at 100\(^\circ\)C. This implies that the benzylic carbon in 38 is more sterically hindered than in the acyclic derivatives, a point that will be considered again in section III.

Increasing the ring size of the olefin by one unit results in drastic changes in the chemistry of the phenylcycloalkene. When
1-phenylcyclohexene (40) is reacted with t-butyllithium-THF at $-30^\circ$C; the major product is that resulting from allylic deprotonation (equation 25).

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{C} & \overset{\text{THF}}{\text{ Li}} \overset{-30^\circ\text{C}}{\longrightarrow} \begin{array}{c}
\text{C} \\
\text{Li}
\end{array} + \begin{array}{c}
\text{C} \\
\text{Li}
\end{array}
\end{align*}
\]

(25)

This result persists at temperatures up to $0^\circ$C, while at lower temperatures ($-78^\circ$C to $-45^\circ$C) no reaction occurs at all. The proton nmr spectrum of 41 displays almost identical chemical shifts to those of 39 indicating that the phenylallylic system is perturbed very little by the change in ring size. When 1-phenylcyclohexene is reacted with t-butyllithium-TMEDA under the same temperature conditions, the yield of 41 was much lower (equation 20).

\[
\begin{align*}
\text{(CH}_3\text{)}_3\text{C} & \overset{\text{TMDA}}{\text{ Li}} \overset{-30^\circ\text{C}}{\longrightarrow} \begin{array}{c}
\text{C} \\
\text{Li}
\end{array} + \begin{array}{c}
\text{C} \\
\text{Li}
\end{array}
\end{align*}
\]

(26)

The yields were estimated by nmr analysis of the reaction solution and quench reactions to be discussed shortly. The downfield shift of the aromatic protons ortho to the lithium atom (ca. 8.0 $\delta$) identified the aromatic ring metallation products. These results indicate that the double bond in the six membered ring is much less reactive than one in a five membered ring toward $t$-butyllithium. Although there are
obviously large concentrations of olefin in the presence of small amounts of anions in t-butyllithium-phenylcyclohexene reaction solutions, polymerization occurs to a very small extent. When 1-phenylcyclohexene is reacted with t-butyllithium at 50° C in isooctane only a small amount of aromatic ring metallation occurs. Preliminary results indicate that 1-phenylcycloheptene is even more inert. Evidently steric inhibitions to reaction imposed by the larger rings are formidable.

The final cycloalkene examined was 1-phenylcyclobutene (44). The results listed below emphasize the variation in reactivity with ring

\[
\text{THF} \quad n=3, -30^\circ C \\
\text{THF} \quad n=1, 3, -45^\circ C \\
\text{THF} \quad n=1, 3, -15^\circ C \\
\text{TMEDA} \quad n=3, 0^\circ C \\
\text{TMEDA} \quad n=3, -30^\circ C \\
\text{TMEDA} \quad n=1, 3, -45^\circ C
\]
size. Under all conditions examined, the only product isolated was a polymeric material, no one-to-one adducts were isolated. Although a dark red solution was generated under all conditions, the nmr spectra of these solutions indicates that if the polymeric chains have "live" ends, they are too dilute to be seen. Indeed, the proton spectra of the reaction mixture and the hydrolysate are identical in the aromatic region. It should be emphasized that the carbon and proton magnetic resonance data are consistent with the polymer structure indicated above, but are by no means conclusive and should be considered only as a reasonable guess. The major conclusion here is that propagation is much faster than initiation even with a threefold excess of t-butyl-lithium. Overall it is evident that the reactivity of phenylcyclo-alkenes towards t-butyllithium is very dependent on ring size.

**Electrophilic Capture Processes**

The chemistry of the benzylic lithium compounds was investigated mainly for the purpose of structure proof for the one-to-one adducts and for the detection and characterization of products arising from side reactions. Protonolysis has already been mentioned in connection with the nmr analysis of the benzylic lithium species and the proton and carbon magnetic resonance spectra of the hydrocarbons resulting from the reaction of H_2O with the benzylic lithums (equation 28) was sufficient to confirm their structures.

Full proton and carbon magnetic resonance data for the hydrolysis products listed above are given in Tables 3 and 4.
A typical proton spectrum for the products of equation 28 is analyzed as follows: the non-equivalent methylene protons give an eight line AB of ABX pattern where the geminal coupling constant is $14 \text{ Hz}$, presumably negative, a methyl doublet ($J = 7.0 \text{ Hz}$), a broad envelope for the benzylic proton and a sharp singlet for the t-butylmethyls are all in accord with the aliphatic structure expected for a one-to-one adduct. The aromatic resonance was generally a collapsed AA'BB' pattern, indicative of a para substituted benzene ring. Further confirmation was obtained from the carbon spectra. The aliphatic resonances were assigned on the basis of their similarity to the shifts of 2,2,4-trimethylpentane (see below) and their multiplicities in single-frequency off resonance decoupling experiments (SFORD).
<table>
<thead>
<tr>
<th>#</th>
<th>2</th>
<th>6</th>
<th>42</th>
<th>46</th>
<th>47</th>
<th>48</th>
<th>49</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.20</td>
<td>1.19</td>
<td>1.20</td>
<td>1.22</td>
<td>1.21</td>
<td>1.19</td>
<td>1.20</td>
<td>1.19</td>
</tr>
<tr>
<td>2</td>
<td>2.78</td>
<td>2.77</td>
<td>2.76</td>
<td>2.79</td>
<td>2.80</td>
<td>2.78</td>
<td>2.77</td>
<td>2.78</td>
</tr>
<tr>
<td>3,3'</td>
<td>1.71</td>
<td>1.45</td>
<td>1.58</td>
<td>1.58</td>
<td>1.58</td>
<td>1.58</td>
<td>1.58</td>
<td>1.58</td>
</tr>
<tr>
<td>5</td>
<td>0.81</td>
<td>0.81</td>
<td>0.81</td>
<td>0.81</td>
<td>0.81</td>
<td>0.81</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>7,8</td>
<td>7.20</td>
<td>7.2</td>
<td>7.1-</td>
<td>7.1-</td>
<td>7.1-</td>
<td>6.9-</td>
<td>7.0-</td>
<td>7.17</td>
</tr>
<tr>
<td>J1,2</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>X(CH3)n</td>
<td>0.24</td>
<td>0.34</td>
<td>0.53</td>
<td></td>
<td></td>
<td>2.39</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \begin{array}{cccl}
\text{13} & 12 & 11 & \text{Si} \\
\hline
7.1- & 7.5 \\
\end{array} \]

\[ \begin{array}{cccl}
\text{13} & 12 & 11 & \\
\hline
7.1- & 7.4 \\
\end{array} \]
Table 3 - continued

<table>
<thead>
<tr>
<th>#</th>
<th>3(^b)</th>
<th>6(^b)</th>
<th>45(^c)</th>
<th>46(^d)</th>
<th>47(^d)</th>
<th>48(^b)</th>
<th>49(^b)</th>
<th>22(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
<td>7.0-7.4</td>
<td>0.65</td>
<td>1.78</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. approximately 20% v/v solutions in CDCl\(_3\)
b. 100 MHz, T ≈ 33° C
c. 60 MHz, T ≈ 40° C
d. 90 MHz, T ≈ 27° C
TABLE 4

Nmr Parameters - II

($^{13}$C, 22.63 MHz, CDCl$_3$ (20% v/v), $\delta$(ppm)/TMS, T = 35° C)

![Diagram of molecular structure]

<table>
<thead>
<tr>
<th></th>
<th>3</th>
<th>6</th>
<th>45</th>
<th>46</th>
<th>47</th>
<th>48</th>
<th>49</th>
<th>22</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.9</td>
<td>25.7</td>
<td>25.7</td>
<td>25.6</td>
<td>25.7</td>
<td>25.8</td>
<td>25.7</td>
<td>25.8</td>
</tr>
<tr>
<td>2</td>
<td>37.0</td>
<td>3.8</td>
<td>36.7</td>
<td>36.8</td>
<td>36.5</td>
<td>36.5</td>
<td>36.6</td>
<td>36.4</td>
</tr>
<tr>
<td>3</td>
<td>52.3</td>
<td>52.1</td>
<td>52.1</td>
<td>52.1</td>
<td>52.0</td>
<td>52.4</td>
<td>52.3</td>
<td>52.1</td>
</tr>
<tr>
<td>4</td>
<td>31.3</td>
<td>31.3</td>
<td>31.3</td>
<td>31.3</td>
<td>31.2</td>
<td>31.3</td>
<td>31.3</td>
<td>31.3</td>
</tr>
<tr>
<td>5</td>
<td>30.2</td>
<td>30.2</td>
<td>30.2</td>
<td>30.2</td>
<td>30.1</td>
<td>30.2</td>
<td>30.2</td>
<td>30.2</td>
</tr>
<tr>
<td>6</td>
<td>149.6</td>
<td>150.3</td>
<td>149.8</td>
<td>150.6</td>
<td>149.2</td>
<td>147.0</td>
<td>148.4</td>
<td>146.9</td>
</tr>
<tr>
<td>7</td>
<td>127.1</td>
<td>126.5</td>
<td>126.7</td>
<td>126.6</td>
<td>128.0</td>
<td>127.0</td>
<td>127.5</td>
<td>127.3</td>
</tr>
<tr>
<td>8</td>
<td>128.3</td>
<td>133.4</td>
<td>132.9</td>
<td>134.1</td>
<td>129.8</td>
<td>125.9</td>
<td>126.9</td>
<td>127.6</td>
</tr>
<tr>
<td>9</td>
<td>125.6</td>
<td>137.0</td>
<td>139.0</td>
<td>134.6</td>
<td>134.1</td>
<td>141.0</td>
<td>138.7</td>
<td>134.9</td>
</tr>
<tr>
<td>$X(CH_3)$_n</td>
<td>-1.0</td>
<td>-1.7</td>
<td>-2.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.4</td>
</tr>
<tr>
<td>$X-10^a$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X-11$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X-12$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X-13$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. numbering is from Table 3
The aromatic resonances for the hydrocarbons were assigned by comparison with the chemical shifts of the appropriate monosubstituted benzene derivatives. One interesting point is the small change in the benzylic carbon shift with para substituent, approximately 0.6 ppm. This can be contrasted with the more sizable variation in the corresponding benzylic lithium carbon shift discussed in the next section.

Further proof for their structure was obtained by treating the benzylic lithium compounds with D$_2$O, trimethylsilyl chloride and trimethyltin chloride (equation 29).

The proton and carbon magnetic resonance data for 50, 51 and 52 are listed in Table 5.
TABLE 5

Nmr Parameters - III

\(^1H\) and \(^{13}C\), CDCl\(_3\) (20% v/v), \(\delta\) (ppm)/TMS, \(J\) (Hz) \(^{a,b}\)

\[R = D, R = Si(CH_3)_3, R = Sn(CH_3)_3\]

\[J_{3,3'} \]

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.22</td>
<td>25.9</td>
<td>1.49</td>
<td>20.5</td>
</tr>
<tr>
<td>2</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>34.2</td>
</tr>
<tr>
<td>3</td>
<td>1.50</td>
<td>52.3</td>
<td>1.59</td>
<td>46.3</td>
</tr>
<tr>
<td>4</td>
<td>1.73</td>
<td>2.21</td>
<td>2.68</td>
<td>50.3</td>
</tr>
<tr>
<td>5</td>
<td>1.50</td>
<td>52.3</td>
<td>1.59</td>
<td>46.3</td>
</tr>
<tr>
<td>6</td>
<td>1.73</td>
<td>2.21</td>
<td>2.68</td>
<td>50.3</td>
</tr>
<tr>
<td>7</td>
<td>1.22</td>
<td>25.9</td>
<td>1.49</td>
<td>20.5</td>
</tr>
<tr>
<td>8</td>
<td>1.50</td>
<td>52.3</td>
<td>1.59</td>
<td>46.3</td>
</tr>
<tr>
<td>9</td>
<td>1.73</td>
<td>2.21</td>
<td>2.68</td>
<td>50.3</td>
</tr>
<tr>
<td>R</td>
<td>-0.15</td>
<td>-4.0</td>
<td>-0.10</td>
<td>-10.5</td>
</tr>
</tbody>
</table>

\(a\). \(^1H\) spectra measured at 100 MHz, \(T = 33^\circ C\)

\(b\). \(^{13}C\) spectra measured at 22.63 MHz, \(T = 33^\circ C\)
The side chain proton spectra of 50, 51 and 52 are now greatly simplified compared to 3, consisting of an aromatic pattern, an AB pattern for the non-equivalent methylene and singlets for the methyl and t-butyl groups. An interesting trend in the proton spectra is the increase in the magnitude of the methylene proton coupling constant and also the downfield shift of both the methyl and methylene resonances as the size of the group on the benzylic carbon increases. These changes are probably due to conformational differences in the aliphatic chain caused by the steric requirements of the bulkier groups. The carbon spectra of 51 and 52 reveal upfield shifts for the aliphatic carbons relative to 3 except for the quaternary and t-butyrmethyl carbons. Surprisingly, the magnitudes of the shifts are larger in the silicon substituent except for the quaternary carbon. The carbon nmr spectrum of 50 is distinguished only by the absence of resonance at 37.0 δ, since this is the shift of the benzylic carbon. The ortho and para carbons in both 51 and 52 exhibit upfield shifts relative to 31, perhaps indicative of some ionic character at the benzylic position and charge delocalization into the ring. In the case of the tin derivative, hyperconjugation has been invoked to explain the upfield aromatic shifts and also the magnitude of the aromatic carbon-tin coupling constants.48 That the magnitude of the ortho and para carbon-tin coupling constants is larger than the meta is thought to be due to some type of interaction of tin's d-orbitals with the π-system and it is known that the tin atom must be in the plane of the aromatic ring for maximum interaction to occur.49
Although the use of trimethylsilyl chloride as an electrophilic capture reagent is obviously important for proof of structure, it can also reveal data about the course of an organometallic reaction which might be missed when the reaction mixture is quenched with either H₂O or D₂O. The following data illustrate this point. When α-methyl styrene is reacted with 1.4 equivalents of t-butyllithium in isooctane at 45 to 50°C and the dark red viscous reaction mixture quenched with H₂O, a high yield of 3 is recovered (equation 30).

![](image)

When the same reaction is completed with the addition of trimethylsilyl chloride, a much different story results (equation 31).

![](image)
The relative yields of the four products are 1:2:2:4:5 as written and the total recovered yield is again 97%. The pertinent point here is that the formation of the rather interesting dilithio compound 54 is indicated by the results of the trimethylsilyl chloride quench,

while the proton quench results give no indication of its presence. Another important result revealed by the trimethylsilyl chloride quench is that ring metallation occurs only in the \textit{para} position. This can be contrasted with the results obtained when the reaction conditions are altered in the following manner;

\[
2(CH_3)_3Cl + 4\text{N} + 2 \xrightarrow{-30^\circ C, 0.5 \text{ hr.}} 0^\circ C \xrightarrow{0.5 \text{ hr.}} \text{RT} \xrightarrow{(CH_3)_3SiCl}
\]

\[
\begin{align*}
\text{3 (1\%)} & \quad + \quad \text{51 (17\%)} \\
\text{(CH}_3\text{)}_3\text{Si} & \quad + \quad \text{(CH}_3\text{)}_3\text{Si}
\end{align*}
\]
N-methylpyrrolidinone was used because of its greater inertness towards t-butyl lithium than TMEDA. Although these results could have been presented earlier in this section, their discussion has been delayed in order to dramatize the superiority of trimethylsilyl chloride as a "tag" in organo-metallic reactions.

The presence of the meta silylated derivatives (55, 56) was inferred from proton magnetic resonance data. The meta trimethylsilyl methyl resonances occurred at slightly higher field (0.05 ppm) than the para substituted ones. The aromatic pattern of the para derivative is a symmetrical AA'BB', while the meta derivative displays a complex aromatic pattern (ABCD).

The protonolysis reaction of the benzyllic lithium derived from 1-phenylcyclopentene gave two products in a 2:1 ratio (equation 32). The isomers could be separated by vapor chromatography and the major isomer was assigned on the basis of proton and carbon magnetic resonance data as trans. Table 6 lists the proton and carbon shift parameters. Even though the five membered ring carbon assignments are
not rigorous, SFORD spectra show that the ring methylene resonances in the minor isomer (cis) are all shifted upfield from those in the major isomer (trans). This is in accord with what is known about steric compression effects in five membered rings. In the proton spectra the t-butyl resonance is shifted upfield in the minor isomer by 0.11 ppm while the benzylic proton is shifted downfield by 0.4 ppm relative to the major isomer. Inspection of molecular models indicates the trans compound 57 can assume a conformation closely resembling the most stable conformation of its acyclic analogs (2 for instance). The Newman projections below illustrate this. That the benzylic and t-butyl proton shifts of the major isomer and the acyclic hydrocarbons are very similar is additional support for assigning the trans structure to the major isomer.

![Newman projections of 2 and 57.](image)

Figure 18. Newman projections of 2 and 57.

Reaction of 38 with D2O again gave a mixture of isomers (equation 33). Examination of the mixture by carbon nmr revealed that the two resonances at 48.0 and 47.4 ppm had disappeared as expected. All
TABLE 6

Nmr Parameters - IV

\(^1H\) and \(^{13}C\), CDCl\(_3\) (ca. 0.25 M), \(\delta\text{ppm)/TMS}\)\(^{a,b}\)

\begin{align*}
\begin{array}{cccc}
\text{\(^{13}C\)} & \text{trans} & \text{cis} & \text{\(^1H\)} & \text{trans} & \text{cis} \\
1 & 39.0 & 34.5 & 1.65 & 1.83 \\
2 & 48.0 & 47.5 & 2.84 & 3.24 \\
3 & 57.3 & 57.5 & 1.83 & \\
4 & 33.5 & 32.4 & & \\
5 & 28.2 & 28.8 & 0.78 & 0.67 \\
6 & 149.2 & 147.1 & & \\
7 & 128.2 & 129.3 & & \\
8 & 127.7 & 127.9 & 7.22 & 7.19 \\
9 & 125.4 & 125.6 & & \\
10 & 25.8 & 22.9 & 1.98 & 1.83 \\
11 & 28.2 & 25.1 & & \\
\end{array}
\end{align*}

\(^a\) \(^1H\) spectra measured at 90 MHz, Fourier Transform mode, T \(\approx 27^\circ C\)

\(^b\) \(^{13}C\) spectra measured at 22.63 MHz, T \(\approx 33^\circ C\)
other shifts were the same as in the protolysis product within experimental error.

\[ \text{38} \rightarrow \text{D}_2\text{O} \]

\[ \text{39} \quad + \quad \text{60} \quad \text{(33)} \]

Reaction of a sample of 32 that had been stored at -10°C for 5 months with D₂O gave slightly different results. When this mixture was examined by carbon nmr, only the resonance assigned to the benzylic carbon in the minor isomer was missing. A rather substantial resonance at 48.0 δ indicated that the benzylic position of the major isomer was partially protonated. A possible explanation for this result is that during its long storage 38 had slowly deprotonated the ligand (THF) in a stereospecific manner.⁵⁷ It is reasonable to assume that for deprotonation of the ligand to occur, the lithium atom, oxygen atom, α-hydrogen and benzylic carbon must all assume a specific arrangement.

In this case the lithium atom has the chance of approaching the benzylic carbon either on the same side of the ring as the t-butyl group or the opposite side. Since approach from the opposite side would cause the benzene ring to move into the t-butyl group, the other approach, resulting in a cis-lithium-t-butyl geometry is favored (Figure 19). As depicted in Figure 19, this approach leads to the formation of the trans product only, in agreement with the carbon magnetic resonance data. These results show how the stereochemistry of protonation of carbanions can change with proton donor, especially when steric effects become important.
Figure 19. Arrangement for stereospecific protonation.

The fact that \( p \text{-trimethylstannyl-\( \alpha \text{-methylstyrene} \) reacted with \( t \text{-butyllithium} \) in the presence of TMEDA or THF by cleaving the trimethyl-tin group instead of adding to the double bond (equation 11) led to an investigation of the benzyltin compound \( \underline{52} \) as a benzylic lithium precursor. The table below summarizes the results obtained. At room temperature, \( t \text{-butyllithium} \) cleaves the benzylic carbon-tin bond smoothly in the presence of TMEDA or THF, while in the absence of any ligand, no reaction occurs. When ethyl ether is used, no reaction occurs at room temperature after 24 hours. This is in accord with the results previously described for the \( t \text{-butyllithium-} p \text{-trimethylstannyl-\( \alpha \text{-methylstyrene} \) reaction where in the presence of ethyl ether no cleavage of the tin-carbon bond occurs. When an excess of THF is added after 24 hours, reaction occurs immediately to yield the benzylic lithium. In the presence of one equivalent of potassium \( t \text{-butoxide} \), \( t \text{-butyllithium} \) cleaves the carbon-tin bond rapidly giving a red solid. It is not known definitely what kind of benzylic anion is generated in this reaction. The product is rather insoluble and it is difficult to obtain a good nmr spectrum. Adding TMEDA does not
TABLE 7

Reaction of α-Methyl-α-Neopentylbenzyltrimethyltin and t-Dutyllithium in the Presence of co-Ligands

\[
\begin{align*}
\text{Sn(CH}_3\text{)}_3 & \quad \text{(CH}_3\text{)}_3\text{CLI} \quad \text{cyclopentane, RT} \\
\text{None} & \quad \text{N.R.} \\
\text{TMEDA (1eq)} & \quad \text{N.R.} \\
\text{Ethyl Ether (ex)} & \quad \text{N.R.} \\
\text{THF (2eq)} & \quad \text{N.R.} \\
\text{(CH}_3\text{)}_3\text{CO Li (1eq)} & \quad \text{(70-90%)} \\
\text{(CH}_3\text{)}_3\text{COK (1eq)} & \quad \text{(100%)} \\
1) \text{Ethyl Ether, 24 hrs} & \quad \text{(100%)} \\
2) \text{THF (ex)} & \quad \text{2b}
\end{align*}
\]
increase its solubility, however on adding THF to 2c at 25°C a dark red solution appears at once and then fades rapidly. This would seem to indicate that the benzylic lithium compound is not present, but rather some benzylic potassium compound or some complex (RLi)$_x$ (RK)$_y$. The fact that lithium alkoxide is much less efficient in promoting the cleavage reaction than potassium alkoxide also indicates that an RK type species is produced in the potassium alkoxide catalyzed reaction. There is also some experimental evidence that mixing alkyllithiums with potassium alkoxide generates a species which analyzes as RK.$^{51}$ The ineffectiveness of ethyl ether as a catalyst for the cleavage is somewhat more difficult to explain but must be related to the fact that ethyl ether is a somewhat weaker Lewis base than THF. Perhaps the role of ligand in these cleavage reactions is to dissociate the alkyllithium aggregates to smaller fragments.

$$(RLi)_n + nL \rightarrow n(RLi-L)$$

Clearly the ligand also solvates the product. However we already know from the t-butyllithium-styrene additions that diethylether is adequate in this respect.

The final process considered is the oxidation of the three benzylic lithium derivatives, 2, 5 and 28. It was thought that reacting these compounds with oxygen would generate alcohols (equation 34) but

$$\begin{array}{c}
\text{X-} \text{Li}^+ \quad 1) O_2 \\
\text{X-} \quad 2) \text{NH}_4\text{Cl}
\end{array} \rightarrow \begin{array}{c}
\text{X-} \text{OH}^-
\end{array} \quad (34)$$
this did not occur. Instead, three products resulted in varying yields, a styrene, a hydrocarbon and a dimer (equation 35).

\[
\begin{align*}
X\text{Li} & \xrightarrow{1) \text{O}_2} \text{Styrene} + \text{Hydrocarbon} \quad (40-60\%) \\
X\text{H} & + X\text{Li} \xrightarrow{2) \text{NH}_4\text{Cl}} \text{Dimer} \quad (0.5-3.0\%)
\end{align*}
\]

One can easily envisage a mechanism that would yield the first two products in equal amounts.

\[
\begin{align*}
X\text{Li} & \xrightarrow{\text{O}_2} \text{Styrene} - \text{LiO}_2 \\
2X & \xrightarrow{\text{dimerization (62 a-c)}} \text{Dimer} \\
2X & \xrightarrow{\text{proton transfer (61 a-c, 3, 6, 49)}} \text{Styrene} + \text{Hydrocarbon} + \text{Dimer}
\end{align*}
\]

\[
\begin{align*}
X & \\
-\text{H} & 61a \\
-\text{Si(CH}_3\text{)}_3 & 61b \\
-\Phi & 61c
\end{align*}
\]

62a

62b

62c
The fact that the relative yields of the two major products are close but never equal implies some alternate process may also be occurring.

The relative yields of major and minor products also change in a rather indeterminate manner with reaction conditions. When the oxidation is conducted at lower temperatures (-30° C to -15° C) the olefin usually but not always predominates. At higher temperatures (0° C to 25° C) the hydrocarbon usually predominates slightly. This indicates that at least one other process is occurring. A likely possibility is reaction of the radical with solvent molecules,

\[ X\text{-}C=C\text{-}H \xrightarrow{H-S} X\text{-}C=C\text{-}H + S. \]

This would explain the excess of hydrocarbon product. Another mechanism which would produce olefin is depicted below. The probability of this pathway is enhanced by a six-membered ring transition state, but suffers from the absence of precedent in the literature.

The minor product \( \text{62} \) which was depicted as a dimer is perhaps the most interesting. The yield is always small and does not seem to vary
with temperature or ligand but does with para substituent. When
X = hydrogen no 62a is discernable using nmr or vapor phase,
chromatography. When X = trimethylsilyl the yield of dimer 62b is
between 0.5% and 1.0%, and when X = phenyl the yield of 62c approaches
3% based on starting olefin. The proton nmr spectra of 61 and 62
exhibit an AB pattern for the non-equivalent methylene protons, and
singlets for the methyl and t-butyl protons. The side chain proton
shifts for the styrene and dimer products are listed below. As they
do not vary with para substituent one entry for each is sufficient.

TABLE 8

Nmr Parameters - V

($^1$H (90 MHz), CDCl$_3$ (0.1 M), $\delta$(ppm)/TMS, J(Hz), T = 27°C)

<table>
<thead>
<tr>
<th></th>
<th>$\delta$</th>
<th>J</th>
<th>$\delta$</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-butyl-</td>
<td>0.80</td>
<td></td>
<td>t-butyl-</td>
<td>0.70</td>
</tr>
<tr>
<td>vinylic-</td>
<td>5.23, 5.02</td>
<td>2.0</td>
<td>methylene-</td>
<td>1.74, 2.36</td>
</tr>
<tr>
<td>methylene-</td>
<td>2.46</td>
<td></td>
<td>methyl-</td>
<td>1.44</td>
</tr>
</tbody>
</table>

The aromatic proton spectra for the styrenes are commonplace, but
the dimers' aromatic spectra reveal broadening of the resonances due
to the ortho (to the benzylic carbon) protons. This indicates
hindered rotation around the ring carbon-benzylic carbon bond as might
be expected for a structure as hindered as the dimer. The dimer, however, possesses two asymmetric carbons and therefore two diasteriomic forms. The nmr spectrum does not display two sets of shifts. Since the compounds were isolated by crystallization, it is possible that only one diastereomer is insoluble. Nmr spectra of the crude reaction mixtures are difficult to interpret because of the low concentration of dimer present. Nmr spectra of the mother liquors from crystallization are also heavily concentrated in the hydrocarbon and olefin products. It appears that if the third product is indeed the dimer, only one diastereomer can be detected or they fortuitously have the same chemical shifts.
Part II - Nuclear Magnetic Resonance Analysis of Benzyl Lithium Compounds

In this section the proton and carbon magnetic resonance spectra of a series of benzyl lithium compounds are discussed. Possible correlation between charge distribution, chemical shift and structure are considered. In some cases similar conclusions can be reached from both kinds of spectral parameters, but they will be treated as separate topics in order to illustrate the advantages of each.

The proton chemical shifts and coupling constants for the aromatic protons of the para substituted benzyllic lithiurns investigated in this work are listed in Table 9. The aromatic proton shifts for the phenylallyllithiums and the substituted phenyllithium species are listed in Table 10. For the most part these shifts and coupling constants were obtained by analyzing the spectra using computer techniques; full details are given in the experimental section. At temperatures from 270° K to 300° K all the benzyllic lithiurns displayed non-equivalent ortho and meta protons. The relative assignments were made by spin-decoupling experiments. When the highest field resonance (ortho to benzyllic carbon) was irradiated, the lowest field (meta to benzyllic carbon) pattern was simplified. An absolute assignment was made tentatively on the basis of the following evidence; steric effects would be pronounced with the ortho proton on the same side as the neopentyl group, and are expected to produce downfield shifts relative
### TABLE 9

**Nmr Parameters - VI**

\( ^1H (100 \text{ MHz}), \text{TMEDA-isoctane (0.5 to 1.0 M)}, \delta(\text{ppm})/\text{TMS}^a, J(\text{Hz}), T = 35^\circ \text{C} \)

![Chemical Structure](image)

<table>
<thead>
<tr>
<th></th>
<th>( \delta )</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.39</td>
<td>5.33</td>
<td>5.39</td>
<td>5.36</td>
<td>5.20</td>
<td>5.16</td>
<td>5.43</td>
</tr>
<tr>
<td>2</td>
<td>5.64</td>
<td>5.59</td>
<td>5.63</td>
<td>5.65</td>
<td>5.45</td>
<td>5.53</td>
<td>5.71</td>
</tr>
<tr>
<td>3</td>
<td>6.17</td>
<td>6.11</td>
<td>6.17</td>
<td>6.11</td>
<td>6.00</td>
<td>5.99</td>
<td>6.51</td>
</tr>
<tr>
<td>4</td>
<td>6.27</td>
<td>6.21</td>
<td>6.28</td>
<td>6.20</td>
<td>6.10</td>
<td>6.07</td>
<td>6.59</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( J_{1,2} )</th>
<th>( J_{1,3} )</th>
<th>( J_{1,4} )</th>
<th>( J_{2,3} )</th>
<th>( J_{2,4} )</th>
<th>( J_{3,4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.56</td>
<td>-0.05</td>
<td>9.04</td>
<td>9.08</td>
<td>-0.25</td>
<td>1.81</td>
</tr>
<tr>
<td>2.62</td>
<td>-0.25</td>
<td>9.05</td>
<td>9.08</td>
<td>-0.25</td>
<td>1.82</td>
</tr>
<tr>
<td>2.49</td>
<td>0.25</td>
<td>8.93</td>
<td>9.14</td>
<td>0.24</td>
<td>1.99</td>
</tr>
</tbody>
</table>

---

a. assuming methyl group of TMEDA = 2.15 \( \delta \)

b. LAOCOON-3 analysis, others estimated by inspection

c. THF-pentane, \( T = 27^\circ \text{C}, \alpha-\text{CH}_2 \) of THF assigned value of 3.63 \( \delta \)

d. \( T = 11^\circ \text{C} \)


**TABLE 10**

Nmr Parameters - VII

(\(^1\)H (90 MHz), THF-pentane (ca. 1.0 M), \(\delta (\text{ppm})/\text{TMS}^a\), \(T = 27^\circ \text{C}\))

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>41</td>
<td>39</td>
<td>38&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>6.00</td>
<td>5.95</td>
<td>5.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.00</td>
<td>5.95</td>
<td>5.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6.37</td>
<td>6.36</td>
<td>6.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6.37</td>
<td>6.36</td>
<td>6.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5.29</td>
<td>5.25</td>
<td>4.48</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14&lt;sup&gt;c&lt;/sup&gt;</td>
<td>35</td>
</tr>
<tr>
<td>1</td>
<td>7.10</td>
<td>7.10</td>
</tr>
<tr>
<td>2</td>
<td>7.10</td>
<td>7.90</td>
</tr>
<tr>
<td>3</td>
<td>7.97</td>
<td>----</td>
</tr>
<tr>
<td>4</td>
<td>7.97</td>
<td>6.50</td>
</tr>
</tbody>
</table>

---

a. assuming \(\alpha\)-CH\(_2\) of THF = 3.63 \(\delta\).

b. \(T = 0^\circ \text{C}\)

c. TMEDA-isooctane, \(T = 33^\circ \text{C}\), CH\(_3\) group of TMEDA = 2.15 \(\delta\)
to the other side of the ring. An additional steric effect is that the bulky neopentyl group could force the ortho hydrogen near it out of the plane of the aromatic ring thereby reducing the influence of the substituent on that proton's shift. In fact the downfield ortho hydrogen's shift is less sensitive to the substituent than the other one. As the data in Table 11 show, the downfield ortho resonance consistently varies less than the upfield ortho resonance with change in \textit{para} substituent and this fact provides further emphasis for assigning the downfield ortho resonances to the proton on the same side of the ring. 

\begin{table}
\centering
\caption{Variation of Ortho-Proton Resonances with \textit{Para}-Substituent in TMEDA/Isooctane at 31° C}
\begin{tabular}{llll}
Substituent & $\Delta H_1$(ppm) & $\Delta H_2$(ppm) & Ratio $\Delta H_1/\Delta H_2$ \\
\hline
(26) & -0.06\textsuperscript{a} & -0.03 & 2 \\
(2) & 0 & 0 & - \\
(11) & 0.11 & 0.03 & 3.7 \\
(5) & 0.17 & 0.08 & 2.1 \\
(24) & 0.17 & 0.07 & 2.4 \\
(13) & 0.14 & 0.09\textsuperscript{b} & 1.6 \\
(28) & 0.14 & 0.08 & 1.8 \\
\end{tabular}
\end{table}

\textsuperscript{a} negative indicates upfield shift to 2

\textsuperscript{b} benzylic lithium solution contains approximately 10% phenyllithium impurity

\textsuperscript{c} ± 0.01 ppm
ring as the neopentyl group. These shift differences \( (\delta_2, \delta_3') \) are small, indeed the most significant thing about the proton magnetic resonance behavior of these benzylic lithium compounds is the small variation in chemical shift with ligand, \( \textit{para} \) substituent or temperature.

Table 12 lists the aromatic proton shifts for \( Z \) and \( E \) in the presence of various ligands. The negligible difference in the chemical shifts of \( Z \) in the presence of one equivalent of benzene or two equivalents of THF is especially noteworthy as it indicates that a large difference in ligand solvating ability makes almost no difference in the \( \pi \)-electron density in the aromatic ring of this benzylic system. The temperature behavior is similar. At \( 284^\circ \text{K} \), in TMEDA-isooctane the \( \text{para} \) cyclopropyl derivative \( (Z) \) shifts are 5.16 and 5.53 \( \delta \) for the \( \text{ortho} \) and 5.99 and 6.07 \( \delta \) for the \( \text{meta} \). At \( 380^\circ \text{K} \) the averaged \( \text{ortho} \) shift is 5.35 \( \delta \), that for the \( \text{meta} \) is 6.04 \( \delta \), thus there is no discernable temperature shift for this species. In THF-cyclopentane \( 38 \) does exhibit small changes in certain proton shifts as a function of temperature. From \( 270^\circ \text{K} \) to \( 335^\circ \text{K} \) the \( \text{para} \) proton moves upfield approximately 0.05 ppm relative to cyclopentane while the \( \text{ortho} \) and \( \text{meta} \) proton shifts move in the same direction about 0.02 ppm. The \( \text{para} \) trimethylsilyl derivative \( (Z) \) in TMEDA-isooctane exhibits approximately the same temperature dependence.

The \( \text{ortho} \) proton shifts in these benzylic lithions are mainly due to \( \pi \)-electronic and steric effects\(^53\) and the substituents should have little direct inductive or mesomeric effect on their chemical shifts.
TABLE 12

Variation in Aromatic Proton Shifts of 2 and 2 with Ligand

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$2_{b,c,d}$</th>
<th>$2_{b,c,d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_1$</td>
<td>$H_3$</td>
</tr>
<tr>
<td></td>
<td>$H_2$</td>
<td>$H_4$</td>
</tr>
<tr>
<td>$N(CH_2CH_3)_2$</td>
<td>5.12</td>
<td>6.19</td>
</tr>
<tr>
<td></td>
<td>5.49</td>
<td>6.11</td>
</tr>
<tr>
<td>$N-CH_3$</td>
<td>5.15</td>
<td>6.20</td>
</tr>
<tr>
<td></td>
<td>5.51</td>
<td>6.10</td>
</tr>
<tr>
<td>$THF$</td>
<td>5.12</td>
<td>6.14a</td>
</tr>
<tr>
<td></td>
<td>5.52</td>
<td></td>
</tr>
<tr>
<td>$THF$</td>
<td>5.18</td>
<td>6.10a</td>
</tr>
<tr>
<td></td>
<td>5.55</td>
<td></td>
</tr>
<tr>
<td>$TMEDA$</td>
<td>5.22</td>
<td>6.17</td>
</tr>
<tr>
<td></td>
<td>5.56</td>
<td>6.10</td>
</tr>
</tbody>
</table>

a. meta protons broadened by rotation
b. ppm downfield from TMS.
c. ±0.02 ppm for worst case
d. $T = 30^\circ C$, concentration = 1.0 M for all cases
Rather substituents perturb the total charge density in the aromatic ring and thus the chemical shift of the aromatic protons. Either these substituents have very little effect on the amount of charge in the ring, or the change in the charge densities is not reflected accurately by the changes in proton chemical shift.

The direction in which the ring shifts move with para substituent is also worthy of comment. For substituents capable of accepting electrons (i.e., phenyl or trimethylsilyl), the ortho proton shift is to lower field indicating less charge in the ring and either more charge at the benzylic position or on the substituent atom or group. The change in the trimethylsilyl resonance is interesting in this respect. The olefin precursor (4) and the hydrolysis product (6) show trimethylsilyl resonances at 0.24 ppm downfield from TMS, while in the anion 5, resonance occurs at 0.02 ppm on the downfield side; this is presumably due to increased change density at the silicon atom. When the substituent is phenyl, the effect of charge transfer is much more noticeable. The proton shifts of the phenyl moiety are shifted upfield from benzene, in particular the para proton exhibits a 1.1 ppm upfield shift. The usual approximation made for the calculation charge density due to proton shifts is 10.6 ppm/e\textsuperscript{−}.\textsuperscript{54} Thus the para proton shift indicates that approximately 10% of the negative charge resides at this position, eight carbon-carbon bonds away from the benzylic carbon. These results suggested that an arylsilyl substituent might also exhibit chemical shifts indicative of charge delocalization. The aromatic proton spectra of 12 (Figure 9) has four distinct sets of resonances. The two downfield sets are centered at 7.5 \&
(integration-2 protons) and 7.1 € (integration-3 protons). Comparing these "back" ring chemical shifts with that of benzene indicates little or no charge is transferred from one ring to the other through the silicon. When looking for small amounts of charge transfer it is possibly better to compare the shifts of the anionic species with a neutral aromatic ring that more closely resembles the anion. The hydrolysate (16) is ideal but its back ring proton chemical shifts are extremely difficult to determine due to overlap of all aromatic resonances. The proton spectrum of phenyltrimethylsilane displays continuous absorption from 7.2-7.6 €, with no clear distinction between ortho, meta and para positions. The "back" ring spectra of the anion reveals a sharper distinction between the ortho protons can be clearly differentiated from the others. This suggests that the increased electron density at the silicon atom results in at least a change in the inductive effect of the silicon towards the "back" ring proton shifts. The "front" ring chemical shifts are identical with those of the para trimethylsilyl derivative (5) indicating the same degree of conjugation in both systems. These results imply that charge may travel through an aromatic ring to a silicon atom but it is not transmitted conjugatively through the silicon, at least to an extent which may be detected by proton nmr. The fact that silicon is able to expand its octet in compounds such as silicon hexafluoride, presumably through utilization of its d-orbitals, to form six bonds, but stops at five bonds, at most, in the case of the benzylic lithium is interesting.
The sulfur atom in the para thiophenyl derivative (24) displayed somewhat different behavior in its ability to transmit charge from front ring to back. The proton spectrum of 24 reveals that the center of gravity of the resonance pattern of the "back" ring protons is shifted upfield relative to both its starting material (23) and hydrolysate (17). The complex aromatic pattern remains essentially the same in all these species, but the center moves from approximately 7.2 δ in the hydrolysate (for all aromatic protons) to 6.8 δ in 24 for the "back" ring protons. This clearly indicates that the sulfur is acting as a weak electron donor towards the back ring in the benzylic lithium but whether this occurs inductively or conjugatively remains unanswered.

A comparison of the aromatic proton chemical shifts of the cyclic phenylallyllithium compounds (39, 41) with those of the acyclic benzylic lithium compounds reveals as expected that less charge is present in the aromatic ring of the phenallylic species. The aromatic proton shifts of 38 are almost identical with those of 2 indicating that the five-membered ring does not grossly effect the structure of the carbanion. The proton shifts for the cyclic phenylallylic species vary somewhat from those measured by Sandel et al.38 for phenylallyllithium in THF d-8, most noticeably for the

\[ \text{THF-d8} \]

\[ \begin{array}{ccc}
5.7 & 4.1 & 6.5 \\
6.1 & 6.7 & 3.0 \\
\end{array} \]

\[ \text{THF-cyclopentane 50-50} \]

\[ \begin{array}{ccc}
5.3 & 6.4 & 6.0 \\
6.5 & 3.6-3.7 \\
\end{array} \]
para proton of the aromatic ring end. The 0.4 ppm shift seems a little large for a solvent shift, and the fact that the phenylallylic lithuim exhibit the same chemical shifts when seated inside a five or six membered ring implies that steric requirements are not the cause, and finally the two species both exist in the transoid conformation. Possibly the replacement of the hydrogen atoms by carbon atoms at the allylic termini destabilizes this section of the conjugated system, forcing more charge into the aromatic ring.

The overwhelming conclusion reached from all the results discussed so far is that the variations studied (i.e., change in para substituent or ligand) do not effect the proton parameters of the benzylic lithuim to a very great extent. Perhaps, as already stated, proton nmr is not sensitive enough to detect the changes in the character of the anions induced by the variations imposed on them. What seems even more likely is that the changes in the character of the anions are small, second order ones and that their basic solvent separated, ion-pair structure is perturbed only slightly. Carbon nmr is known to be more sensitive to slight variations in structure and we now turn to this technique in order to investigate the benzylic lithuim with a more inquisitive probe.

Two immediate advantages of carbon nmr are that non-protonated sites are now accessible to investigation and that the focus of observation is the aromatic framework of the molecule, where the magnetic resonance behavior should be more sensitive to \( \pi \)-conjugative effects and less influenced by electric field and solvent effects. Furthermore, the conditions under which these spectra were obtained
(full proton decoupling) resulted in a single line for each non-equivalent carbon atom. Thus the chemical shifts are easily obtained and in general the observation of all benzylic lithium resonances, both aromatic and aliphatic, is possible since the problem of solvent overlap is greatly alleviated. The spectra in Figures 20 and 21 illustrate these points. Figure 20 displays the carbon-13 spectrum of 2 in TMEDA-pentane with cyclopentane added as an internal reference. All anion and solvent resonances are clearly resolved. Table 13 lists the chemical shifts and assignments for all peaks in the spectrum. The methyl group in pentane was assigned a value of 13.7 ppm. Chemical shift assignments were verified by single frequency off-resonance decoupling (SFORD) and selective proton decoupling experiments. Specifically, the latter showed that when the high field ortho proton resonance (5.22 δ) was irradiated at low power, the high field ortho carbon resonance (104.0 δ) was fully decoupled. This experiment failed for the meta carbons because of the small chemical shift difference in the proton spectrum. The resonances at 85.0 and 135.4 δ were assigned on the basis of their intensities, and the singlet nature of the resonance at 135.4 δ in the SFORD spectrum. The aliphatic resonances were also assigned on the basis of their multiplicity in the off-resonance decoupled spectrum.

The reduced intensity for non-protonated carbons relative to protonated carbons is the expected behavior for carbon-13 spectra obtained in the Fourier transform mode (full details are given in the experimental section) with full proton decoupling, because of the absence of the Nuclear Overhauser Enhancement and the longer relaxation
Figure 20. Nmr spectrum, 22.64 MHz, 33°C, for 2, ca. 1.0 M in TMEDA-pentane
Figure 21. Nmr spectrum, 22.63 MHz, 33° C, for 5, ca. 1.0 M in THF-pentane
### TABLE 13

Chemical Shift Assignment of Spectrum Depicted in Figure 20

<table>
<thead>
<tr>
<th>Chemical shift (δ, ppm from TMS)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) 13.7</td>
<td>CH$_3$—pentane</td>
</tr>
<tr>
<td>2) 21.8</td>
<td>CH$_3$—2</td>
</tr>
<tr>
<td>3) 22.4</td>
<td>CH$_2$—pentane</td>
</tr>
<tr>
<td>4) 25.8</td>
<td>cyclopentane</td>
</tr>
<tr>
<td>5) 30.3</td>
<td>t-butylmethyls—2</td>
</tr>
<tr>
<td>6) 33.3</td>
<td>CH$_2$—pentane</td>
</tr>
<tr>
<td>7) 36.0</td>
<td>t-butyl quaternary—2</td>
</tr>
<tr>
<td>8) 45.0</td>
<td>CH$_3$—TMEDA</td>
</tr>
<tr>
<td>9) 49.0</td>
<td>CH$_2$—2</td>
</tr>
<tr>
<td>10) 56.3</td>
<td>CH$_2$—TMEDA</td>
</tr>
<tr>
<td>11) 76.7</td>
<td>benzylic—2</td>
</tr>
<tr>
<td>12) 85.0</td>
<td>para—2</td>
</tr>
<tr>
<td>13) 104.0</td>
<td>ortho—2</td>
</tr>
<tr>
<td>14) 106.0</td>
<td>ortho—2</td>
</tr>
<tr>
<td>15) 127.2</td>
<td>meta—2</td>
</tr>
<tr>
<td>16) 128.1</td>
<td>meta—2</td>
</tr>
<tr>
<td>17) 135.4</td>
<td>aromatic ipso—2</td>
</tr>
</tbody>
</table>
times for carbons with no directly bonded protons. It was somewhat surprising to find that the carbon-13 absorptions for these benzylic lithiums in THF-pentane displayed more or less equal intensities and integrals for all single carbon resonances. Figure 21 displays the carbon-13 spectrum for 2 in THF-pentane. As can be seen the intensities for all aromatic carbons are roughly the same, while the aliphatic resonances of 2 have intensities proportional to their statistical occurrence. The integrals computer calculated and normalized to the benzylic carbon are listed below for 2 in THF-pentane and 2 in TMEDA-pentane. The carbon numbering is that of Table 15. Notice how in 2 the integrals are not proportional to the number of carbon atoms as expected, while 2 shows a decided leveling effect. Since both spectra

<table>
<thead>
<tr>
<th>#</th>
<th>2</th>
<th>Integral</th>
<th>#</th>
<th>2</th>
<th>Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
<td>1.00</td>
<td>2</td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>1.06</td>
<td>6</td>
<td></td>
<td>0.74</td>
</tr>
<tr>
<td>7</td>
<td>1.13, 1.40*</td>
<td>7</td>
<td>7</td>
<td>3.46, 3.21*</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1.66, 1.52*</td>
<td>8</td>
<td>8</td>
<td>4.13, 4.17*</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.65</td>
<td></td>
<td>9</td>
<td>3.81*</td>
<td></td>
</tr>
</tbody>
</table>

*Protonated carbons
were obtained under the same experimental conditions the leveling
effect observed in the integrals with THF as co-solvent must be due to
the change in the solvent system. The most reasonable interpretation
is that the relaxation times of the non-protonated carbons are shorter
in the THF-complexed species than in the TMEDA-complexed one. Since
the relaxation times are inversely proportional to the molecular cor-
relation time\textsuperscript{55} this implies that the THF-complex reorients more
slowly than does the TMEDA-complex, or alternately, the THF-complex
reorients anisotropically, that is, there is a preferred axis of
molecular reorientation. The data listed in Table 1\textsuperscript{4} strongly implies
that this axis runs through the aromatic ring as shown below. The

![Diagram of preferred axis of reorientation in tertiary benzylic lithiums]

Figure 22. Preferred axis of reorientation in tertiary benzylic lithiums

result of this preferred reorientation would be shorter relaxation
times for the benzylic, substituted aromatic and \textit{para} carbons than in
the case of random reorientation. The reason for this is that atoms
on the axis of rotation sweep through a smaller volume of the mag-
netic field as the molecule reorients than do the peripheral carbons.
One important mode of nuclear relaxation comes from field gradient effects. Anisotropic rotation (as in Figure 22) cancels these gradients more effectively on the periphery than on the axis of rotation. These latter atoms relax more efficiently than otherwise which leads to similar line intensities.

An attempt was made to measure the relaxation times of the aromatic carbons in the two complexes using an inversion-recovery pulse sequence, but experimental difficulties including bad radio-frequency homogeneity in the receiver coil and inconsistent pulse timing and repetition made it impossible to obtain reliable data. The inconsistency in pulse rate and repetition has been corrected, but the RF inhomogeneity in the receiver coil persists at the time of this writing.

The carbon-13 chemical shifts for the para substituted benzylic lithiums (1 molar solutions in THF-pentane) are listed in Table 15. Variable temperature carbon-13 data are listed in Table 16 for 38 (1 molar in THF-cyclopentane). The benzylic and para carbon positions were not observable by proton spectroscopy and thus are of considerable interest. The variation of the benzylic carbon shift of 9.3 ppm (71.0 for 2 to 80.3 for 28) is interesting when compared to the corresponding shifts in the hydrolysis products—all within 0.6 ppm (36.4 to 37.0). The ca. 40 ppm downfield shift of the benzylic carbons of the lithium compounds implies some sp2 character at this position.28 This raises the question—what does the smaller variation (9.3 ppm) of chemical shift with para substituent in the benzylic
TABLE 15

Nmr Parameters - VIII

\(^{13}\text{C} (22.63\ \text{MHz}), \ \text{THF-pentane (ca. 1.0 M)}, \ \delta(\text{ppm})/\text{TMS}^a, \ T = 33^\circ \text{C}\)

\[
\begin{array}{cccccccccc}
# & 2 & 5 & 11 & 12 & 24 & 26^b & 28 & 2^b \\
1 & 22.3 & 22.3 & 22.0 & 22.4 & 22.7 & 22.1 & 22.6 & 22.4 \\
2 & 71.0 & 74.6 & 75.2 & 76.1 & 77.0 & 73.1 & 80.3 & 76.7 \\
3 & 49.5 & 49.3 & 49.0 & 49.3 & 49.8 & 49.3 & 49.7 & 49.0 \\
4 & 36.6 & 36.1 & 36.1 & 36.1 & 36.1 & 36.3 & 36.0 & 36.0 \\
5 & 30.3 & 30.3 & 30.3 & 30.4 & 30.3 & 30.2 & 30.3 & 30.3 \\
6 & 139.1 & 138.4 & 137.0 & 137.9 & 138.4 & 135.9 & 138.1 & 135.4 \\
7 & 105.3 & 107.0 & 106.7 & 107.4 & 108.1 & 103.2 & 108.8 & 104.0 \\
7' & 107.4 & 108.5 & 108.0 & 108.8 & 109.9 & 105.3 & 110.5 & 106.0 \\
8 & 128.1 & 131.8 & 132.4 & 133.3 & 135.9 & 127.3 & 124.3 & 128.2 \\
8' & 127.2 & 132.9 & 131.4 & 132.3 & 134.8 & 126.6 & 123.5 & 127.2 \\
9 & 86.7 & 89.6 & 91.7 & 86.5 & 79.4 & 99.5 & 101.4 & 85.0 \\
X(CH_3)n & 0.1 & -1.2 & -1.5 \\
X-10^c & 144.5 & 150.8 & 14.2 & 142.6 \\
X-11 & 133.9 & 124.1 & 5.8 & 116.9
\end{array}
\]
Table 15 - continued

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>5</th>
<th>11</th>
<th>12</th>
<th>24</th>
<th>26&lt;sup&gt;b&lt;/sup&gt;</th>
<th>28</th>
<th>2&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>127.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>113.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. assuming CH₃ of pentane = 13.7 δ

b. spectrum obtained in TMEDA-pentane

c. numbering is from Table 3
<table>
<thead>
<tr>
<th>#</th>
<th>260°K</th>
<th>270°K</th>
<th>280°K</th>
<th>305°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39.0</td>
<td>38.0</td>
<td>38.9</td>
<td>38.8</td>
</tr>
<tr>
<td>2</td>
<td>82.9</td>
<td>83.3</td>
<td>83.6</td>
<td>84.6</td>
</tr>
<tr>
<td>3</td>
<td>51.7</td>
<td>51.7</td>
<td>51.7</td>
<td>51.7</td>
</tr>
<tr>
<td>4</td>
<td>31.6</td>
<td>31.6</td>
<td>31.6</td>
<td>31.3</td>
</tr>
<tr>
<td>5</td>
<td>28.5</td>
<td>28.5</td>
<td>28.6</td>
<td>28.9</td>
</tr>
<tr>
<td>6</td>
<td>137.1</td>
<td>137.0</td>
<td>137.0</td>
<td>137.1</td>
</tr>
<tr>
<td>7</td>
<td>106.6</td>
<td>106.4</td>
<td>106.3</td>
<td>107.3 (^b)</td>
</tr>
<tr>
<td>8</td>
<td>108.6</td>
<td>108.8</td>
<td>108.7</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>126.9</td>
<td>127.1</td>
<td>127.2</td>
<td>127.6 (^b)</td>
</tr>
<tr>
<td>10</td>
<td>126.3</td>
<td>126.4</td>
<td>126.5</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
</tr>
</tbody>
</table>

a. CH\(_3\) of pentane assigned value of 13.7 \(\delta\)
b. broadened by rotation, ± 0.4 ppm
c. not observed, presumably under THF resonance, assignments for #'s 10 and 11 could be reversed
lithiums signify? It is possible that the para substituents affect the amount of s-character at the benzylic position, that is, a cyclopropyl group (26) decreases the s-character-moving the chemical shift upfield, while a phenyl group (28) increases the s-character, moving the benzylic shift downfield. The usual approximation for the shift induced by the hybridization change sp$^3$-sp$^2$ is 90 ppm (essentially the benzylic shift difference between toluene and styrene), so the variation in chemical shift with para substituent would indicate approximately 10% variation in the sp$^2$ character. This is certainly not indicative of profound changes in anion structure with para substituent and becomes even less significant with the fact that there is another possible explanation for the observed trend. It is known that the paramagnetic contribution, $\sigma_p$, is the dominant factor governing carbon-13 shieldings. Variations in $\sigma_p$ may be largely responsible for the shift differences caused by the para substituents, since $\sigma_p$ is inversely related to $\Delta E$ the average excitation energy. As $\Delta E$ increases, $\sigma_p$ decreases and the total screening constant increases ($\sigma_p$ is inherently negative), thus the shift moves upfield. The variation in $\Delta E$ with para substituent is difficult to estimate for the benzylic lithiums in question but a change in $\Delta E$ of 0.5 ev (~11 kcal) could account for a 10 ppm difference in chemical shift at the benzylic carbon. The results discussed in Part III will show that this is not an unreasonable energetic change caused by a para substituent. The conclusion is that the two effects discussed above probably both contribute to the observed results. The shift difference of the benzylic carbon in 2'-THF and 2'-TMEDA is 5.7 ppm, again a small deviation which could result from either of the
above effects. The \textit{para} substituent and ligand produce little effect on the benzylic carbon as determined by nmr spectroscopy, the only perturbation left is that of the counterion. The diagram below lists the carbon-13 spectral parameters for cumylpotassium in ethyl ether. The close correspondence of these shifts with those of $2^b$-THF (the change in the benzylic carbon shift is only 0.2 ppm) demonstrates that the counterions either exert the same effects on the ring shifts, or more likely, do not appreciably influence these shifts. Hence the earlier comment that these salts largely exist as solvent separated ion pairs.

The minor effect (3.0 ppm) of ligand or counter-ion on the carbon-13 shift of the unsubstituted \textit{para} carbon atom can be readily seen by inspection of the entries of $2^b$ and $2^b$ in Table 15 and above.

Since the \textit{para} carbon is generally shifted upfield to the greatest extent in benzylic anion species (among the aromatic carbons) it is of interest to determine the effect of \textit{para} substituents on this carbon's chemical shift. In order to accomplish this, the "normal" substituent induced shift (SIS) must be cancelled. This is done in the following manner; first a table of \textit{para} carbon chemical shifts for the
### TABLE 17a
Para Carbon-13 Shifts of Hydrolysates and Benzyllic Lithiums ($\delta$(ppm)/TMS)

<table>
<thead>
<tr>
<th>HYD</th>
<th>$\delta_{Cp}$</th>
<th>AN</th>
<th>$\delta_{Cp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>141.0</td>
<td>26</td>
<td>99.5</td>
</tr>
<tr>
<td>3</td>
<td>125.6</td>
<td>2</td>
<td>86.7</td>
</tr>
<tr>
<td>45</td>
<td>139.0</td>
<td>11</td>
<td>91.7</td>
</tr>
<tr>
<td>6</td>
<td>137.0</td>
<td>5</td>
<td>89.5</td>
</tr>
<tr>
<td>46</td>
<td>134.6</td>
<td>12</td>
<td>86.5</td>
</tr>
<tr>
<td>47</td>
<td>131.4</td>
<td>24</td>
<td>79.4</td>
</tr>
<tr>
<td>49</td>
<td>138.0</td>
<td>28</td>
<td>101.4</td>
</tr>
</tbody>
</table>

### TABLE 18a
SIS Values for Hydrolysates and Benzyllic Lithiums

<table>
<thead>
<tr>
<th>HYD</th>
<th>$\Delta\delta_{Cp}$ HYD$^a$</th>
<th>AN</th>
<th>$\Delta\delta_{Cp}$ AN$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>+15.4</td>
<td>26</td>
<td>+12.8</td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>2</td>
<td>0.0</td>
</tr>
<tr>
<td>45</td>
<td>+13.4</td>
<td>11</td>
<td>+5.0</td>
</tr>
<tr>
<td>6</td>
<td>+11.4</td>
<td>5</td>
<td>+2.9</td>
</tr>
<tr>
<td>46</td>
<td>+9.0</td>
<td>12</td>
<td>-0.2</td>
</tr>
<tr>
<td>47</td>
<td>+5.8</td>
<td>24</td>
<td>-7.3</td>
</tr>
<tr>
<td>49</td>
<td>+13.0</td>
<td>28</td>
<td>+14.7</td>
</tr>
</tbody>
</table>

* positive values are downfield shifts
hydrolysis products is made (Table 17A). The differences between the para carbon shift of the unsubstituted compound (2) and the para substituted derivatives, $\Delta \delta C_p^{HYD}$, is calculated (Table 18A) for each substituent. These differences are considered the "normal" SIS. A similar process is repeated for the benzylic lithium species to determine $\Delta \delta C_p^{AN}$ (Tables 17B and 18B), the anionic SIS for each substituent. A comparison of the two parameter sets should reveal whether the SIS is the same for both neutral and anionic species. Table 19 lists the $(\Delta \delta C_p^{HYD} - \Delta \delta C_p^{AN})$ values. For the carbon substituents the SIS values are approximately the same in both the neutral and anionic species. Going down in group IVA results in an increase in the 

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$[\Delta \delta C_p^{HYD} - \Delta \delta C_p^{AN}]$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclopropyl-</td>
<td>+2.6</td>
</tr>
<tr>
<td>H-</td>
<td>-</td>
</tr>
<tr>
<td>$(CH_3)_3Ge-$</td>
<td>+8.4</td>
</tr>
<tr>
<td>$(CH_3)_3Si-$</td>
<td>+8.5</td>
</tr>
<tr>
<td>phenyl dimethylsilyl-</td>
<td>+9.2</td>
</tr>
<tr>
<td>thiophenyl-</td>
<td>+13.1</td>
</tr>
<tr>
<td>phenyl-</td>
<td>-1.7</td>
</tr>
</tbody>
</table>

difference between the SIS values, while the thiophenyl group possesses the largest deviation in SIS values. The values in Table 19
demonstrate that the usual additivity relationships for the carbon-13 shifts in aromatic molecules do not always hold. We believe conjugation is responsible for this effect, especially for substituents with d orbitals.

The other aromatic carbon-13 shifts of the various para substituted benzylic lithions are amenable to the same type of discussion as given the proton shifts. Considering the shifts at the non-equivalent ortho positions, the trends are the same as in the proton spectra in most cases. It has already been noted that the shifts of the ortho protons were not the same at both ortho sites and steric effects given as the reason. Table 20 lists the ortho carbon shifts of the substituted benzylic lithions relative to the unsubstituted derivative 2.

**TABLE 20**

<table>
<thead>
<tr>
<th>X</th>
<th>ΔC₁ (ppm)</th>
<th>ΔC₂ (ppm)</th>
<th>ratio ΔC₁/ΔC₂</th>
<th>ratio ΔH₁/ΔH₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>-0.8</td>
<td>-0.7</td>
<td>1.1</td>
<td>2</td>
</tr>
<tr>
<td>2 H-</td>
<td>0</td>
<td>0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8 (CH₃)₃Ge-</td>
<td>1.4</td>
<td>0.6</td>
<td>2.3</td>
<td>3.7</td>
</tr>
<tr>
<td>5 (CH₃)₃Si-</td>
<td>1.7</td>
<td>1.1</td>
<td>1.5</td>
<td>2.1</td>
</tr>
<tr>
<td>12 (CH₃)Si</td>
<td>2.1</td>
<td>1.4</td>
<td>1.5</td>
<td>2.4</td>
</tr>
<tr>
<td>24 (CH₃)S-</td>
<td>2.8</td>
<td>2.5</td>
<td>1.1</td>
<td>—</td>
</tr>
<tr>
<td>28 O-</td>
<td>3.5</td>
<td>3.1</td>
<td>1.1</td>
<td>1.8</td>
</tr>
</tbody>
</table>

a. From Table 11
Comparison of the ratios between the non-equivalent ortho carbon shifts with those of the proton shifts reveals a decided leveling effect in the carbon shifts. In the benzylic lithuim ring carbon-13 shifts should be less sensitive to steric effects than the ring proton shifts and the last two columns in the table demonstrate this fact.

The carbon spectra of the anions are a superior probe in investigating the question of charge delocalization into the back rings of derivatives 12, 24, and 28. The back ring proton spectra of 12 and 24 yielded little information because of the overlap and complexity of the spectra. In the carbon nmr spectra each individual "back" ring carbon is clearly visible. Figures 24, 25, and 26 display the carbon spectra of 28, 12, and 24. The amount of charge is usually estimated by considering the difference in carbon shift compared to benzene, but in this case it is more appropriate to consider the difference in shift between the anion and its hydrocarbon counterpart. Table 21 lists the "back" ring carbon shifts for the three benzylic lithuims and their corresponding hydrolysates. The data for 28 clearly reflects the usual chemical shift behavior for negative charge being conjugatively transferred from a substituent into an aromatic ring. The ortho and para carbons of 28 display substantial upfield shifts relative to the neutral (12) species while the meta carbon shift is relatively unchanged. For 28, using the usual approximation of 160 ppm/e⁻ one can estimate that 6% of the negative charge resides at each ortho carbon and 9% at the para carbon, or approximately 20% resides in the back ring. With these values in mind we now consider the data for 12 and 24. For 12 it is obvious that the situation is altered by
Figure 23. Nmr spectrum, 22.63 MHz, 33°C, for 12, ca. 1.0 M in THF-pentane
Figure 24. Nmr spectrum, 22.63 MHz, 33°C, for 28, ca. 1.0 M in THF-pentane
Figure 25. Nmr spectrum, 22.63 MHz, 33°C, for 24, ca. 1.0 M in THF-pentane
TABLE 21

Carbon-13 Shifts (Back Ring) of Benzylic Lithiums and Hydrolysates

<table>
<thead>
<tr>
<th>BzLi</th>
<th>HYD</th>
<th>BzLi</th>
<th>HYD</th>
<th>BzLi</th>
<th>HYD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>28</th>
<th></th>
<th>24</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>142.6</td>
<td>140.5</td>
<td>150.8</td>
<td>137.0</td>
<td>144.5</td>
</tr>
<tr>
<td>116.9</td>
<td>126.8</td>
<td>+127.4</td>
<td>132.1</td>
<td>133.9</td>
</tr>
<tr>
<td>127.8</td>
<td>128.7</td>
<td>+124.1</td>
<td>128.9</td>
<td>126.9</td>
</tr>
<tr>
<td>113.3</td>
<td>127.2</td>
<td>121.7</td>
<td>126.3</td>
<td>127.1</td>
</tr>
</tbody>
</table>

a. conditions given in Tables 4 and 15

+ assignment could be reversed

the inclusion of a silicon atom between the two rings. The only
carbon in the back ring exhibiting an appreciable shift difference
compared to the hydrolysate is the one bound to the silicon. This
shift is interesting because it goes in the direction expected for
increased electron density at the silicon atom. The other "back"
ring shifts indicate that very little charge is passed through to the
back ring. The 1.8 ppm upfield shift of the para carbon translates
to a 1% increase in the charge density at this carbon in the anion
relative to the hydrolysate. The sulfur derivative (24) displays a
13.8 ppm downfield shift at the substituted carbon. This is 0.8 ppm
larger than the C1 shift observed between phenol and phenoxide
anion\textsuperscript{84,85} and indicates a large increase in charge density at the sulfur atom in the anion relative to the hydrolysate. In this case more charge seems to be transferred into the back ring at C4 compared to the silicon derivative (12). Whether a conjugative or inductive pathway is involved is not readily apparent. The \textit{ortho} and \textit{meta} carbon resonances of the "back" ring of 2\textsubscript{4} cannot be exactly assigned. There are two choices. One is that all three aromatic shifts are upfield of the hydrolysate by 4.7 ± 1 ppm. This would correspond to a strange inductive pathway that does not diminish with distance from the substituent! The other more reasonable assignment gives upfield shifts of 8.0 ppm for the \textit{ortho}, 1.5 ppm for the \textit{meta} and 4.6 ppm for the \textit{para}, consistent with a conjugative pathway for charge transfer. In either case the shifts indicate that approximately 16% of the negative charge reaches the back ring. A final answer to the shift assignment could be obtained with suitable deuterium substitution.

Finally, we briefly consider the carbon-13 shifts of the phenylallylic species 4\textsubscript{1}. The fact that the \textit{ortho} and \textit{para} chemical shifts of the phenylallylic species (4\textsubscript{1}) occur downfield from the \textit{ortho} and \textit{para} chemical shifts of the benzylic lithium compounds (2 for example) is interesting because this corresponds to what is expected from a simple Huckel M. O. treatment.\textsuperscript{56} The charge distribution of an odd alternate anion such as benzylic or phenylallylic can be calculated from the molecular orbital coefficients of the non bonding orbital;

\[ z_1 = -c_1^2 \]
where $z_1$ is the charge on the carbon with non-bonding molecular orbital coefficient $c_1$. For ortho and para carbons of a benzylic anion,

$$z_1 = -\left(\frac{1}{\sqrt{7}}\right)^2 = -\frac{1}{7}$$

while for a phenylallylic anion

$$z = -\left(\frac{1}{\sqrt{11}}\right)^2 = -\frac{1}{11}.$$

Thus the Hückel theory predicts that $3/7$ of the negative charge should reside in the aromatic ring of a benzylic anion, while only $3/11$ should reside in the aromatic ring of a phenylallylic anion (Figure 26).

Again using the approximation of 160 ppm/e\textsuperscript{−} one would predict that the sum of upfield shift differences between benzene (128.6 ppm) and the ortho and para carbons should be 58.6 ppm for the benzylic anion and 45.6 ppm for the phenylallylic system. The experimental values (Table 22) are 90.8 ppm and 52.8 ppm in qualitative agreement. If one con-

![Figure 26. Hückel charges in odd-alternate anions.](image)
TABLE 22

Nmr Parameters - X

($^{13}$C (22.63 MHz), δ(ppm)/benzene\textsuperscript{a}, THF-pentane (ca. 1.0 M), T = 33° C)

![Diagram of a molecule]

<table>
<thead>
<tr>
<th>#</th>
<th>2</th>
<th>4\textsuperscript{f}</th>
<th>28</th>
<th>5</th>
<th>11</th>
<th>12</th>
<th>24</th>
<th>26\textsuperscript{b}</th>
<th>38\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-51.9</td>
<td>-49.2</td>
<td>-48.3</td>
<td>-54.0</td>
<td>-53.4</td>
<td>-52.5</td>
<td>-51.6</td>
<td>-55.5</td>
<td>-45.7</td>
</tr>
<tr>
<td>6</td>
<td>6.8</td>
<td>13.6</td>
<td>9.5</td>
<td>9.8</td>
<td>8.4</td>
<td>9.3</td>
<td>9.8</td>
<td>7.3</td>
<td>8.5</td>
</tr>
<tr>
<td>7\textsuperscript{d}</td>
<td>-23.6</td>
<td>-18.2</td>
<td>-19.0</td>
<td>-20.9</td>
<td>-21.3</td>
<td>-23.6</td>
<td>-19.6</td>
<td>-24.1</td>
<td>-21.0</td>
</tr>
<tr>
<td>8\textsuperscript{d}</td>
<td>-0.9</td>
<td>-1.1</td>
<td>-4.7</td>
<td>3.7</td>
<td>3.3</td>
<td>4.8</td>
<td>6.7</td>
<td>-1.6</td>
<td>-2.0</td>
</tr>
<tr>
<td>9</td>
<td>-43.6</td>
<td>-26.4</td>
<td>-27.2</td>
<td>-39.0</td>
<td>-36.9</td>
<td>-42.5</td>
<td>-49.2</td>
<td>-29.1</td>
<td>-43.0</td>
</tr>
<tr>
<td>X-10\textsuperscript{e}</td>
<td></td>
<td></td>
<td>14.0</td>
<td>13.9</td>
<td>22.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-11</td>
<td></td>
<td></td>
<td>-11.7</td>
<td>5.3</td>
<td>-4.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 22 - continued

<table>
<thead>
<tr>
<th>#</th>
<th>2</th>
<th>41</th>
<th>28</th>
<th>5</th>
<th>11</th>
<th>12</th>
<th>24</th>
<th>26</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-12</td>
<td></td>
<td>0.8</td>
<td></td>
<td></td>
<td>1.7</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-13</td>
<td></td>
<td>-15.3</td>
<td></td>
<td></td>
<td>1.5</td>
<td>6.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. chemical shift of benzene assumed as 128.6 δ

b. 1.0 M in TMEDA-pentane
c. temperature 260° K
d. average of two shifts
e. numbering of Table 3
f. terminal allylic carbon 43.6 ppm upfield from benzene
siders the ratio of the shift differences, it is seen that the Hückel theory predicts that the charge in the aromatic ring of the phenyl-allylic anion should be 64% of that in the benzylic anion. This compares fairly well with the experimental value obtained from the carbon-13 shifts (52.8/90.8) of 58%. The Hückel theory predicts only half (10%) of the charge in the "back" ring of the biphenyl anion that is indicated by the differences of the carbon-13 shifts of the back ring of 28 with benzene (22%).
Part III - Dynamic nmr Results

In this section the nmr line shapes of the tertiary benzylic lithium compounds are discussed. The mathematical techniques used in calculating the proton spectra of these exchanging systems are briefly examined (i.e., the method of deriving the equations is explained.) The thermodynamic parameters of activation derived from the kinetic studies are discussed with regard to their possible correlation with the ground state stabilities of the anionic species.

Figure 27 displays the ortho proton nmr line shapes obtained at various temperatures at the narrowest possible sweep width, of the para cyclopropyl derivative (26). As is obvious from the spectra, at low temperatures (ca. 280° K) the ortho protons are non-equivalent and give rise to an almost first order spectrum. As the temperature is increased, the two multiplets broaden, coalesce and finally begin to sharpen into the AA' portion of an AA'XX' spin system. The meta proton resonance exhibits the same behavior. These spectra show that as the temperature is increased, some process is occurring at faster rates which allows the o and o' and the m and m' aromatic protons to become equivalent on the nmr time scale. The only reasonable possibility for this process is rotation around the ring carbon-benzylic carbon bond. At lower temperatures this process is slow on the nmr time scale, hence the non-equivalence of the aromatic protons.

In order to determine the rates of rotation of the benzylic lithiurns from their proton nmr spectra it is necessary to calculate
the aromatic spectrum of the benzylic lithium species as a function of
the rate of rotation and then match the calculated with the experimental
spectra. The techniques used in calculating the spectra depend on the
type of exchange process and the complexity of the resonance pattern
(i.e., number of nuclei undergoing exchange, uncoupled or tightly
coupled spin system, degenerate or nondegenerate exchange.) The para
substituted reagents are the simpler ones to consider. They are
described as a four-spin, tightly coupled system undergoing a degenerate
exchange process (i.e., internal rotations), expressed in the following
equation,

$$ABCD = BADC,$$  \hspace{1cm} (1)

where each letter represents one proton. For this type of system, a
quantum mechanical approach in conjunction with a computer algorithm
is necessary to generate the theoretical spectra. The technique used,
a density matrix formalism, was first described by Kaplan,\textsuperscript{57,58} and
Alexander.\textsuperscript{59,60,61} A general purpose computer program based on the
density matrix approach was developed by Binsch\textsuperscript{62} and recently both
the density matrix approach and its implementation into a computer
algorithm have been improved upon by Fraenkel and Kaplan.\textsuperscript{63} In the
simplest sense this technique involves generating a set of equations
which are used to calculate the intensity of magnetization of the
system as a function of the frequency. Briefly this is accomplished
as follows. The density matrix ($\hat{\rho}$) equation in the rotating frame is

$$\dot{\hat{\rho}} = 0 = [\hat{\rho}, \hat{H}] + \frac{\hat{p}}{T} + E\hat{\rho},$$  \hspace{1cm} (2)
where $H$ is the spin hamiltonian, $T$ is the phenomenological relaxation time and $E$ the operator which simulates the exchange process. A set of equations is generated by taking all matrix elements of Eq 2;

$$\langle i|\hat{\rho}|k\rangle$$

where $m_i - m_k = +1$, meaning that the two states are connected by a transition. There are as many equations as transitions. The coupled equations contain the nmr parameters, chemical shifts, coupling constants and relaxation times, the frequency point in the spectrum, rate constants and the unknown density matrix elements, $\tilde{\rho}_{i,k}$. The amplitude of the received signal is given as a function of frequency by,

$$A_b(w) = -[Sp] \text{Im} \sum_{i,k} \tilde{\rho}_{i,k}, \quad (3)$$

where $[Sp]$ means concentration of the species and $i,k$ sums over all pairs of states connected by a transition. For a general appreciation of the complexity of a 4 spin system one of the density matrix equations is exhibited below, the rest are found in Appendix I.

$$\dot{\rho}_{2,e} = \rho_{2,e} \left[ i(\omega - \omega_C - \frac{J_{AC}}{2} - \frac{J_{BC}}{2} - \frac{J_{CD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_3, e^{\frac{i}{T_2}} - \frac{\tau}{2}$$

$$+ \rho_{2,e} \gamma \left( \frac{J_{BC}}{2} \right) + \rho_{2,g} \left( \frac{J_{BD}}{2} \right) + \rho_{2,3} \left( \frac{J_{AC}}{2} \right) + \rho_{2,10} \left( \frac{J_{AD}}{2} \right)$$

$$- \rho_{4,g} \left( \frac{J_{BD}}{2} \right) - \rho_{5,g} \left( \frac{J_{AD}}{2} \right),$$

where $\frac{1}{\tau} = k$, the rate of rotation in this instance. This example clearly illustrates why a computer is the safest and fastest way to assemble the matrix equations.
Generally the procedure goes as follows. First we analyze with iterative computer techniques the spectrum at low temperatures when rotation is slow on the nmr time scale. This provides the shifts, coupling constants and line-widths. Doing this at several low temperatures reveals whether the nmr parameters are temperature dependent. If so, one must extrapolate this temperature dependence into the temperature regions over which the line shape analysis is conducted. Once the intrinsic parameters are known then nmr line shapes are calculated over a range of rates of rotation.

Once the theoretical spectra have been obtained they must be matched with the experimental ones to determine the rate constants at different temperatures. There are various approaches for accomplishing this, ranging from visual comparison, to measuring various band shape parameters, to iterative computer matching of the experimental data obtained in digital form. Up to now, algorithms for the last technique have been developed for the simpler spin systems only. Thus the second approach was used throughout this work and will now be discussed briefly.

Figure 28 displays the theoretical spectra calculated for the p-cyclopropyl derivative at various rates of rotation. Typically peak to valley ratios and line-widths at half-peaks height were measured from the theoretical spectra and plotted versus the rate constant. Matching the experimental measurement against the theoretical curve gave first estimates of rates. Further refinement is possible by taking the first fit rates and calculating line shapes for several others near it and repeating the matching procedure. In the worst
cases all parameters can be iterated for a best fit. That, however, proved unnecessary in this work. Once this rate versus temperature match has been made, thermodynamic activation parameters such as the enthalpy of activation, $\Delta H^\ddagger$, the entropy of activation, $\Delta S^\ddagger$ and the Arrenhius activation energy, $E_a$ are obtained by the following procedures. The Eyring rate equation is given by

$$k = \kappa \left( \frac{k_bT}{h} \right) e^{-\Delta H^\ddagger / RT} e^{\Delta S^\ddagger / R}$$

where $k$ is the rate constant, $\kappa$ means the transmission coefficient (assumed to be 1), $k_b$ is Boltzmann's constant, $h$ is Planck's constant, $R$ the gas constant and $T$ the temperature. Dividing by $T$ and taking the natural logarithm of both sides yields,

$$\ln \frac{k}{T} = \ln \left( \frac{k_b}{h} \right) - \Delta H^\ddagger / RT + \Delta S^\ddagger / R$$

A plot of $\ln k/T$ vs $1/T$ gives a straight line with slope $-\Delta H^\ddagger / R$ and intercept $\ln \left( \frac{k_b}{h} \right) + \Delta S^\ddagger / R$. Similarly the Arrenhius equation,

$$k = A e^{-E_a / RT}$$

where $A$ is the frequency factor, yields equation 7,

$$\ln k = -E_a / RT + \ln A$$

A plot of $\ln k$ versus $1/T$ yields a straight line with slope $-E_a / R$ and intercept $\ln A$.

It should be mentioned at this point that while complex spin systems pose greater problems in determining the chemical shifts and coupling constants, if these difficulties can be overcome the
thermodynamic parameters derived from these systems generally are more reliable since the rate of the exchange process can be more accurately measured over a wider temperature range than in the case of simpler systems. The reason for this is that the line shapes for more complex systems are more sensitive to changes in the rates. Several different shifts and coupling constants behave like "rate clocks" running at different speeds. Inspection of the behavior of the para cyclopropyl derivative illustrates this point. As the temperature is increased, the coalescence of the small splittings due to the 1,3 coupling between the two ortho protons occurs, (bottom 3 spectra of Figure 27), yielding changes in the peak to valley ratios usable for obtaining slower rates. Then at increasing rates of rotation one sees the coalescence of the two ortho coupling constants between ortho and meta protons, (lines 4-6, Figure 27), then averaging of the chemical shift between the ortho protons which yields both peak to valley measurements and line widths as band shape parameters. Finally at fast rates the now equivalent ortho protons sharpen into their AA' subspectrum. These different features of the spectrum each provide accurate rate data within a different range of rate constants. The technique of purposely studying more complex systems and the advantages which result has been praised in the literature.64

The results of the full line shape treatment described above are listed in Table 23 for four different benzylic derivatives and one case with a different solvent. Three examples from earlier work are also listed for comparison. The thermodynamic activation parameters and their standard deviations were derived from a linear least squares
Figure 27. Nmr spectra, 100 MHz, variable temperature, for ortho protons of 26, ca. 1.0 M in TMEDA-isoctane
Figure 28. Calculated line shapes for ortho protons of $^{26}$ at different rates of rotation.
### TABLE 23

**Thermodynamic Activation Parameters**

*for Rotation in Benzyl Lithiums*

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^\ddagger$</th>
<th>$\Delta S^{\ddagger}$</th>
<th>$Ea^a$</th>
<th>$\ln A$</th>
<th>L.C.C.</th>
<th>$\Delta ^+G_{300^\circ K}^a$</th>
<th>$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>22.0</td>
<td>3.44</td>
<td>22.82</td>
<td>32.52</td>
<td>-0.9804$^f$</td>
<td>20.97</td>
<td>336-</td>
</tr>
<tr>
<td></td>
<td>±1.50</td>
<td>±4.32</td>
<td>±1.48</td>
<td>±2.04</td>
<td>-0.9836$^g$</td>
<td>±2.10</td>
<td>389°K</td>
</tr>
<tr>
<td>2</td>
<td>18.23</td>
<td>-4.72</td>
<td>18.83</td>
<td>28.16</td>
<td>-0.9934$^f$</td>
<td>19.64</td>
<td>323-</td>
</tr>
<tr>
<td></td>
<td>±0.70</td>
<td>±1.98</td>
<td>±0.68</td>
<td>±1.77</td>
<td>-0.9927$^g$</td>
<td>±1.00</td>
<td>390°K</td>
</tr>
<tr>
<td>26</td>
<td>11.82</td>
<td>-15.52</td>
<td>12.47</td>
<td>22.74</td>
<td>-0.9931$^f$</td>
<td>16.48</td>
<td>282-</td>
</tr>
<tr>
<td></td>
<td>±0.54</td>
<td>±1.64</td>
<td>±0.54</td>
<td>±0.84</td>
<td>-0.9935$^g$</td>
<td>±0.75</td>
<td>381°K</td>
</tr>
<tr>
<td>38-TMEDA</td>
<td>15.35</td>
<td>-5.22</td>
<td>16.02</td>
<td>27.96</td>
<td>-0.9970$^f$</td>
<td>16.92</td>
<td>291-</td>
</tr>
<tr>
<td></td>
<td>±0.54</td>
<td>±1.60</td>
<td>±0.54</td>
<td>±0.79</td>
<td>-0.9973$^g$</td>
<td>±0.78</td>
<td>380°K</td>
</tr>
<tr>
<td>38-THF</td>
<td>11.90</td>
<td>-10.00</td>
<td>12.50</td>
<td>25.44</td>
<td>-0.9970$^f$</td>
<td>14.90</td>
<td>270-</td>
</tr>
<tr>
<td></td>
<td>±0.36</td>
<td>±1.08</td>
<td>±0.36</td>
<td>±0.59</td>
<td>-0.9975$^g$</td>
<td>±0.60</td>
<td>349°K</td>
</tr>
<tr>
<td>2c</td>
<td>18.65</td>
<td>0.29</td>
<td>19.35</td>
<td>30.77</td>
<td>-0.9975$^g$</td>
<td>18.66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>±0.41</td>
<td>±1.14</td>
<td>±0.40</td>
<td>±0.57</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- $^a$: Uncertainties in parentheses are due to the nature of the measurement.
- $^f$: Values for free energy of activation at 300°K.
- $^g$: Values for entropy of activation at 300°K.
<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^{a}$</th>
<th>$\Delta S^{b}$</th>
<th>$E_a^{a}$</th>
<th>$\ln A$</th>
<th>L.C.C.</th>
<th>$\Delta H^{G_{300^\circ K}}^{a}$</th>
<th>$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-isopropyl</td>
<td>18.43</td>
<td>4.63</td>
<td>19.08</td>
<td>32.89</td>
<td></td>
<td>17.05</td>
<td></td>
</tr>
<tr>
<td>c,d</td>
<td>±0.41</td>
<td>±1.26</td>
<td>±0.41</td>
<td>±0.63</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-t-butyl</td>
<td>18.50</td>
<td>5.17</td>
<td>19.15</td>
<td>33.16</td>
<td></td>
<td>16.96</td>
<td></td>
</tr>
<tr>
<td>c,e</td>
<td>±0.42</td>
<td>±1.29</td>
<td>±0.42</td>
<td>±0.65</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Kcal. mole$^{-1}$

b. e.u.

c. data from reference 26

d. 2-lithio-2-(p-isopropylphenyl)-4,4-dimethylpentane

e. 2-lithio-2-(p-t-butylphenyl)-4,4-dimethylpentane

f. for Eyring plot

g. for Arrehenius plot
treatment of the rate versus temperature data. The linear correlation coefficient (L.C.C.) is an index of the "fit" of the points to the calculated line, where -1.0 or 1.0 is a perfect correlation, anything less implies scattering about the line. In general, a L.C.C. value of 0.9900 or better is considered sufficient for nmr line shape kinetics. The $\Delta G^\ddagger$ values were calculated from the equation,

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

for $T = 300^\circ$ K. Typical least squares plots are displayed in Figure 29 for the Eyring equation and Figure 30 for the Arrehenius equation. Appendix II contains a full listing of all rates and their corresponding temperatures for all line shape analyses.

Before discussing the results in Table 23 in detail it is worthwhile to briefly mention one mechanism of rotation for these benzylic lithiums. The proton and carbon chemical shifts for these species indicate that their ground state is always a planar, conjugated one. In order for rotation to occur, the benzylic carbon must acquire some tetrahedral character in the transition state with a concomitant loss of conjugation into the aromatic ring. This probably also involves some increase in the lithium-carbon covalency and decrease in the lithium-ligand interaction in going from the ground state to the transition state for rotation. The two diagrams in Figure 31 depict this mechanism, the lower one viewing the aromatic ring perpendicular to the plane of the paper with one ortho hydrogen staggered between the neopentyl and methyl groups and the other ortho hydrogen eclipsed with the lithium atom. This is believed to be the
Figure 29. Eyring plot of rate versus temperature data for 26
Figure 30. Arrhenius plot of rate versus temperature data for 26
Figure 31. Mechanism for rotation in benzylic lithiums
most stable conformation for the transition state. A mechanism of this type requires that both the substituent-X and the ligand show exert some influence on the observed rate of rotation and the thermodynamic activation parameters. For the time being we will consider only the effect of the former.

The thermodynamic activation parameters for the unsubstituted benzylc lithium (2) plus some para alkyl derivatives were available from earlier work.26 The values of the enthalpy of activation $\Delta H^+$ and the entropy of activation $\Delta S^+$ were 18-19 kcal/mole and 0 ± 5 entropy units for all of them. Inspection of the first three entries in Table 23 provides information on the possible conjugation effect of a para-substituent on the barrier to rotation. The result for the para trimethylsilyl derivative (2) is certainly one of the most important described in this work. The trimethylsilyl group raises both the $\Delta H^+$ and the activation energy $E_a$ by approximately 3 kcal/mole relative to the unsubstituted derivative (2) and 4 kcal/mole relative to the para t-buty1 derivative. Tentatively one could conclude that this result implies an enhanced conjugative interaction between the benzylic carbon and the aromatic ring of 2 compared to 2. The carbon-13 spectral results do not support this conclusion as the benzylic carbon-13 shift of 2 is practically the same as that of 2. However, the carbon-13 chemical shifts reveal nothing about the relative ground state stability of 2 compared to 2. This question will be discussed in greater detail later, for now it is not unreasonable to assume that the silicon atom can interact with the $\pi$-molecular orbitals of the benzylic moiety, presumably through its empty d-orbitals. This
interaction leads to a more stable ground state and higher activation parameters for rotation.

The para trimethylgermyl substituent (I) shows no effect on the activation parameters. This is a little surprising since the d-orbitals of germanium could be expected to function in the same manner as those of silicon. Perhaps the diffuse nature of 4d orbitals precludes their effective overlap with the π-orbitals of the benzylic system. Actually the entropy of activation for this derivative is slightly lower than the unsubstituted derivative (2) (by just about the experimental error in the measurement) and about the same as the para-t-butyl derivative. This indicates that the trimethylgermyl group possesses small electron releasing inductive effect but if this inductive effect destabilizes the ground state of the benzylic lithium at all, the magnitude of the destabilization is not detectable by this experimental procedure (less than 0.7 kcal/mole).

The third entry in Table 23, the para cyclopropyl derivative (26) gave results which were a little more difficult to interpret. The ΔH‡ dropped about 6 kcal/mole relative to 2 or the para isopropyl derivative. Thus, for some reason, the cyclopropyl group enhances rotation about the ring-carbon, benzylic-carbon bond. The kinetic results for solvolysis of similarly substituted cumylchloride and the ionization data of the benzoic acid show that the para cyclopropyl group strongly stabilizes the benzylic cation in the transition state while only slightly inhibiting the generation of a negative charge. The two order or magnitude increase in the solvolysis rate of cumyl chloride is thought to be due to a conjugative effect.
Cyclopropylcarbinyl anions are known to be unstable with respect to their rearrangement products. The reason for this is not clearly understood. However, the ground state of 26 is a vinyligous analog of the cyclopropylcarbinyl anion. It could be destabilized, lowering the barrier. A para cyclopropyl substituent is not expected to have much effect on the energy of the covalent transition state.

The para phenyl (28), para thiophenyl (24) and para dimethyl-phenylsilyl (12) benzylic lithuums all rotated so slowly that full line shape analysis and extraction of thermodynamic parameters was not possible. In fact, their proton nmr spectra at 102° C, 88° C and 93° C (±2° C), respectively, showed no broadening whatsoever, indicating that the rate of rotation was less than 1 sec⁻¹ at these temperatures. It is not worthwhile to estimate the thermodynamic activation parameters under these circumstances except to say that the ΔH⁺ for all three must be greater than 22.0 kcal/mole. In spite of this it is possible to draw some conclusions about the ground state stability of these anions. The carbon-13 and proton spectra of the p-phenyl derivative imply that considerable negative charge is transferred conjugatively into the "back" ring. The line-shape behavior of 28 indicates that this conjugative interaction between the two rings stabilizes the ground state of the anion by more than 4 kcal/mole. Comparison of the kinetics of rotation between the para phenyl(dimethyl)silyl derivative
Figure 32. Simplified Reaction Profile for Rotation in para-substituted Benzyllic Lithiums.

$(\text{12})$ with the para trimethylsilyl derivative (5) is difficult because at the highest temperature 12 was studied, $(93^\circ \text{ C})$, 5 was just beginning to display usable line shape data. At $93^\circ \text{ C}$ the rate of rotation of 5 is approximately 3 to 5 sec$^{-1}$ while the rate for 12 could be anywhere from 0.001 to 1 sec$^{-1}$. It is not feasible to estimate a difference in the $\Delta H^+$ between 5 and 12 from these data. Nevertheless, the replacement of a methyl group with a phenyl group retards rotation around the ring carbon-benzyllic carbon bond in 12, possibly because a conjugative interaction occurs from front ring to
back through the silicon atom stabilizing the ground state of 12 relative to 2.

The instability of the para thiomethyl derivative (16) precluded comparing the difference in ΔH‡ for rotation between thiomethyl and the thiophenyl derivative (24). Considering the slow rotation rate (< 1 sec⁻¹) at 88° C, the increased thermal stability of 24 relative to 16 and the carbon-13 chemical shifts of the back ring in 24 together provides strong evidence for ground state stabilization of 24 due to transfer of charge through the sulfur atom.

Let us now consider the effect on the enthalpy of activation by these substituents using a highly simplified quantum mechanical approach. We illustrate this by constructing molecular orbital diagrams. The ground state can be considered a seven orbital, 8 electron conjugated benzylic fragment while a six orbital, six electron benzene molecular orbital arrangement is sufficient to describe the relevant orbitals of the transition state. The substituent-X is simulated as a one orbital electron deficient moiety with the energy of the NBMO.

In the ground state, from zero order perturbation theory, mixing of the degenerate non-bonding molecular orbitals of the benzylic moiety and the substituent brings about a major splitting. Compared to this any mixing of substituent molecular orbitals and benzene-like orbitals in the transition state amounts to a relatively minor higher order interaction. We shall ignore it. This splitting in the ground state is illustrated in Figure 34 where the stabilization energy is indicated with a "→".
This perturbation treatment implies that a conjugating substituent affects only the energy of the ground state, lowering it by the amount $n c_1^* \beta_{C-X}$ where $n$ is the number of electrons in the orbital, $c_1$ is the coefficient of the non-bonding molecular orbital and $\beta_{C-X}$ is the value of the exchange integral between the carbon and substituent. This ground state stabilization is considered to be the major influence of the substituent on the barrier to rotation.
At this point some statement should be made concerning the entropy of activation, $\Delta S^\ddagger$, for the rotation process. The entropy difference between the two states of a system is basically a measure of the change in randomness or disorder between the states. A negative entropy of activation would indicate more order in the transition state relative to the ground state, a positive value the
opposite. The $\Delta S^\ddagger$ values obtained from the Eyring plots for 5 and 11 are neutral, +3.4 e.u. and -5.2 u.u., respectively. This small change in entropy between the ground state and transition state can be explained as follows. In the ground state the lithium atom is probably loosely bound to the rigid benzylic moiety but rather tightly coordinated to the TMEDA ligand restricting the movement of the lithium-TMEDA complex. In the transition state the bonding interaction between the benzylic carbon and lithium is enhanced with a subsequent decrease in the rigidity of the benzylic moiety and lessening of the TMEDA-ligand interaction, restricting the motion of the lithium atom but allowing greater mobility of the ligand molecules and benzylic moiety. Thus overall the different contributions to the entropy of ground and transition state can be envisaged to be largely the same with the result of a neutral $\Delta S^\ddagger$.

The $\pi$-cyclopropyl derivative (26) again displays distinctive behavior. Its entropy of activation, -15 e.u., is rather large and negative and just as for the enthalpy of activation, a ready explanation is lacking. The $\Delta G^\ddagger$ values of Table 23 indicate some balance between $\Delta H^\ddagger$ and $\Delta S^\ddagger$, but the Eyring plots of Figure 30 do not reveal the existence of an isokinetic relationship.65

So far we have examined the barrier to rotation as being an electronic one, but it is possible that there is a steric contribution as well. Inspection of molecular models of the ground state and the transition state (the staggered form already depicted) reveals that in the ground state there are two principle steric interactions. Both
the ortho ring hydrogen and the π-electron structure come into close
contact with the t-butylmethyl protons. In the transition state only
the t-butylmethyl--ortho proton interaction remains and it appears to
be of the same magnitude as in the ground state. The net result is
that steric effects should destabilize the ground state compared to no
steric effects at all and result in lowering the barrier to rotation.

Some insight is provided by considering the ground state and trans-

tion state geometries of the benzylic lithium nested in a five
membered ring (38). The principle steric difference between the cyclic
and acyclic derivatives is the profound steric interaction between the
t-butylmethyls and the π-structures in the ground state of the cyclic
derivative relative to the acyclic. The lower barrier to rotation in
the cyclic derivative (3 kcal/mole) is confirmation of the
destabilizing influence caused by this interaction with the
π-electronic structure in the ground state; the other interactions
appear to be similar to those discussed above.

The final topic to be considered is the effect of the ligand on
the barrier to rotation. The last entry in Table 23 displays the
results of a full line shape analysis for 28 complexed to THF. The
drop in ΔH‡ is approximately 3.5 kcal/mole relative to 38 complexed
to TMEDA. Brownstein and Worsfield measured the barrier to rotation
for 2-THF as approximately 14 kcal/mole,27 the 4 kcal/mole decrease
in ΔH‡ is consistent for both 2 and 38 in going from TMEDA to THF. A
simple interpretation of these results is readily put forward. The
fact that TMEDA displaces THF in the 28-THF complex implies that THF
does not coordinate to the lithium atom as strongly as does TMEDA. Since the lithium ligand interaction stabilizes the ground state of the benzylic lithium species the THF complex must be of higher energy than the TMEDA complex. This lowers the energy required to break-up the lithium-ligand complex and reduces the barrier to rotation. The drop in the entropy of activation may also be a reflection of the weaker ligand-lithium interaction, allowing greater freedom for both ligand and lithium in the ground state.

The line shape behavior of the \textit{para} trimethylsilyl derivative (5) was studied in trimethylamine, triethylamine, ethyl ether and THF as well as TMEDA. Although a full line shape analysis was not done on the first four examples, approximate rates of rotation could be obtained at 380° K. Table 24 lists the results.

TABLE 24

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$k$ (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA</td>
<td>$3.5 \pm 2$</td>
</tr>
<tr>
<td>TMA</td>
<td>$15 \pm 5$</td>
</tr>
<tr>
<td>TMEDA</td>
<td>$10 \pm 5$</td>
</tr>
<tr>
<td>THF</td>
<td>$40 \pm 10$</td>
</tr>
<tr>
<td>Ethyl ether</td>
<td>$20 \pm 5$</td>
</tr>
</tbody>
</table>

The pertinent point is that the rates vary with ligand to a small but measurable degree, and the ligand which retards the rotation process
to the greatest extent is the largest one, triethylamine. Presumably the relatively large size of the ligand renders the complex of lower energy. These results for \( 2 \) and \( 5 \) may imply that although these species have been grossly described as solvent separated ion pairs there may be small differences in the tightness of the ion pair or perhaps less likely some small C-Li covalency in the ground state.
Solvents Used in Benzylic Lithium Preparations.

Tetrahydrofuran, ethyl ether and dimethyloxymethane were dried by preparing a Grignard, usually n-butylmagnesium bromide, solution. When the commercial ethers were too wet to allow Grignard preparation directly, prior distillation from calcium hydride eliminated this problem. Dioxane, glyme and diglyme were distilled from calcium hydride and stored over lithium aluminum hydride. They were distilled from this reagent directly before use. N,N,N',N'-tetramethylethylene-diamine, N,N,N',N'-tetramethylpropylenediamine, triethylamine, diethylcyclohexylamine and N-methylpyrrolididine were fractionally distilled from potassium hydroxide pellets. The center cut was stored over calcium hydride and distilled from this reagent directly before use. Trimethylamine was generated from its hydrochloride salt by stirring the salt with potassium hydroxide pellets in mesitylene. The liberated amine was passed through two ten centimeter by one centimeter cylindrical columns containing potassium hydroxide pellets and oxide lumps, respectively, then trapped in a calibrated cold finger at -78° C. Pentane, cyclopentane, and 2,2,4-trimethylpentane (isooctane) were washed with concentrated sulfuric acid, water and 10% bicarbonate solution, dried over anhydrous potassium carbonate, stored over lithium aluminum hydride and distilled from this reagent directly before use. Benzene was dried by distilling 10% of its volume,
discarding the distillate, adding calcium hydride and distilling from calcium hydride directly before use. All solvents used in anion preparations and organometallic reactions were distilled under argon either directly into the reaction vessel or into a dry side-arm flask and transferred through syringes equipped with stopcocks and stainless steel needles. This equipment was baked at 120° C for at least one hour prior to use.

**Apparatus**

Syringes were Becton-Dickenson and Co. multifits or Hamilton gas tight. Stainless steel needles were from W. A. Balter. Syringe stopcocks were Becton-Dickenson MS01. Nmr tubes were Wilmad 507-PP five millimeter o.d. for proton nmr and Wilmad 513-7PP ten millimeter o.d. for carbon nmr. Some carbon spectra of benzylic lithiums were obtained using Wilmad 513A-7PP eight millimeter o.d. tubes. All product mixture analyses and separations by vapor phase chromatography were done on a Varian Aerograph A-700. Columns were either a five foot by \( \frac{1}{2} \) inch 20% SE-30 on firebrick (Column A) or a fifteen foot by \( \frac{1}{4} \) inch 20% SE-30 on Chrom P (Column B). Operations requiring an inert atmosphere were carried out in either a Kewaunee Scientific Equipment 20281-20 glove box or a Vacuum Atmospheres HE-43 glove box. Continuous wave proton spectra were obtained on the Varian A-60A (60 MHz), HA-100 (100 MHz) and Bruker HX-90 (90 MHz) spectrometers. Some proton spectra were obtained in the Fourier transform mode on the Bruker HX-90 spectrometer. Carbon spectra were obtained on the Bruker HX-90 spectrometer at 22.63 MHz in the Fourier transform mode. Auxiliary
equipment used in obtaining the Fourier transform spectra included a Nicolet BNC-12 computer containing 20,480 20-bit words of memory and a Diablo movable head disk storage unit. Disks were IBM low density 600 K word capacity.

Varibale Temperature nmr Spectra of Benzylic Lithiums.

Nmr spectra used for the kinetic analysis of rotation in benzylic lithiums were obtained on the HA-100 or HX-90 spectrometers. The temperature of the gas stream was regulated by the Varian V-6040 temperature controller for the former instrument and the Bruker BS-100/700 temperature controller for the latter. The temperature in the probe was determined from the chemical shift difference of ethylene glycol (temperature > 40°C) or methanol (temperature < 40°C) using the standard equations. At each temperature three to five spectra were obtained. The homogeneity was maximized before each scan. The sweep width was 1 Hz/cm and the sweep time was 500 seconds. The spectra for 26 were obtained using an 80 Hz sweep width (1.6 Hz/cm) generated by a Wavetek frequency unit. The temperature was determined before and after each set of measurements. If a temperature variation of greater than 2°C had occurred, the spectral measurements were repeated.

Analysis of Aromatic Proton Spectra of Benzylic Lithiums.

The chemical shifts and coupling constants necessary for the calculation of theoretical line shapes were obtained by an iterative computer technique using the program IAOCOON-3. An excellent treatise on the use and pitfalls of this program has been given by
The procedure used in this work was as follows; experimental spectra were obtained at the narrowest sweep width possible (usually 1 Hz/cm) at a sweep rate of 500 seconds. The frequency of each resolvable line was measured by stopping the recorder at the center of the resonance and reading the frequency from the frequency counter (0.1 Hz setting). The results of four to six sweeps in both directions were averaged. Constant adjustment of the homogeneity controls was made in order to maintain the highest resolution possible. Trial values for the chemical shifts and coupling constants were then obtained from these spectra. These parameters were fed into the computer program, and the output was a set of numbered resonance frequencies and intensities. Since the aromatic spectrum of the benzylic lithium was almost first order, the calculated resonance frequencies were usually very close to the experimental ones (largest deviation less than 0.6 Hz). Next the experimental resonance frequencies, numbered in the same manner as the calculated frequencies, and the chemical shifts and coupling constants were fed into the program. The deviations between experimental and calculated line frequencies were minimized by repeated iteration over all shifts and coupling constants. The output was the "best fit" set of chemical shifts and coupling constants and their probable errors. The root mean square deviation between the resonance frequencies calculated from this "best fit" set of parameters and the experimental resonance frequencies was also determined in the calculation. In actual practice the program iterates until this r.m.s. deviation changes by 3% or less. For the benzylic lithi-ums three or four iterations produced an r.m.s.
error of less than 0.12 (worst case) and probable errors of less than 0.4 Hz for the chemical shifts and coupling constants.

**Carbon-13 Spectra of Benzylic Anions.**

Solutions of benzylic lithiums were syringed into 8 mm o.d. nmr tubes fitted with stopcocks bearing ground glass joints, degassed on the vacuum line by three freeze-thaw cycles and sealed off with a torch under dynamic vacuum. Teflon tape was wrapped around the 8 mm o.d. tube so that it fitted snugly inside a 10 mm o.d. tube. Care was taken so that the smaller tube was centered inside the larger one. The annulus contained CDCl₃ for field-frequency lock. With these precautions the assembly spun inside the nmr probe with no discernable wobble. The experimental acquisition parameters were: sweep width 5000 Hz. (sampling interval 100 microseconds), delay time 200 microseconds (interval between pulse and acquisition of first data point), data Table 16,384 points and pulse width 4.0 microseconds (corresponds to a flip angle of 25°). All the carbon spectra of benzylic lithiums displayed in this thesis were the result of 1024 scans. Full proton decoupling was obtained with a center-band frequency of approximately 89.999800 MHz modulated into a band pass of greater than 1000 Hz and amplified to 10 watts of power. Before Fourier transformation each point of the free induction decay was multiplied by the exponential function,

$$e^{iTC/N}$$

where i is the index of the point, TC a constant (-1.6 was used) and N
the size of the data table (16,384), in order to improve the signal to noise ratio of the transformed spectrum. This technique is sometimes referred to as digital filtering, exponential multiplication or sensitivity enhancement. Fourier transformation resulted in a 8192 data point spectrum yielding a computer resolution of 0.610 Hz/data point. All chemical shifts, intensities and integrals were obtained using the Nicolet Tl-PRGM II Fourier Transform Program.

Preparation of Benzylic Lithium Compounds from α-methylstyrenes.

All glassware used in benzylic lithium preparations was baked out at 120°C for at least one hour, assembled and flameed with a micro-burner under a current of argon. If the density of a liquid was unknown, quantitative transfer was effected via a tarred syringe. The reactions were carried out under a positive argon pressure. All reagents were transferred via syringes equipped with stopcocks except where noted.

A. Preparation of Benzylic Lithiums in TMEDA-isoctane.

A 10 ml pear-shaped flask equipped with a "stopcock adapter" (2 mm straight bore stopcock attached to a male ground glass joint) protected with a rubber serum cap was charged with 5 mmol of the appropriate α-methylstyrene and 3 ml of isoctane. The solution was outgassed by passing argon through it via a stainless steel needle. The reaction vessel was a 50 ml roundbottom flask equipped with a "stopcock adapter", a side arm fitted with a 2 mm straight bore stopcock both protected by rubber serum caps and a magnetic stirring bar. The reaction vessel was charged with t-butyllithium in pentane
(1.33 M, 3.7 ml, 5.5 mmol, 10% excess). The pentane was removed by passing a current of argon over the rapidly stirred solution and 3 ml of isoctane added. The reaction vessel was immersed in a dry ice-isopropanol bath at -50°C and TMEDA (0.64 g, 5.5 mmol) was added. The bath temperature was allowed to rise to -30°C and the deoxygenated styrene-isoctane solution prepared as described above was added drop-wise to the rapidly stirred t-butyllithium-TMEDA slurry over a 30 minute to one hour time period. The temperature of the bath was maintained at -30°C ± 5°C during the addition. The resulting dark red solution was allowed to warm to 0°C and stirred at this temperature for 30 minutes completing the reaction. This method allowed the preparation of the following tertiary benzylic lithi ums in greater than 95% yield; 2-lithio-2-phenyl-4,4-dimethylpentane (2), 2-lithio-2-(p-trimethylsilylphenyl)-4,4-dimethylpentane (5), 2-lithio-2-(p-trimethylgermylphenyl)-4,4-dimethylpentane (11), 2-lithio-2-(p-thiophenylphenyl)-4,4-dimethylpentane (24), 2-lithio-2-(p-phenyldimethylsilylphenyl)-4,4-dimethylpentane (12) and 2-lithio-2(p-cyclopropylphenyl)-4,4-dimethylpentane (26).

B. Preparation of Benzylic Lithiums in THF-pentane.

A 10 ml pear-shaped flask equipped with a "stopcock adapter" protected with a rubber serum cap was charged with 5 mmol of the appropriate α-methylstyr ene and 3 ml of tetrahydrofuran. The solution was outgassed for at least 10 minutes by passing argon through it via a stainless steel needle.
The reaction vessel (same as in A) was charged with t-butyl-
lithium in pentane (1.33 M, 3.7 ml, 5.5 mmol, 10% excess) and immersed
in a dry ice-isopropanol bath at -50° C. THF (1.0 ml) was added and
the temperature of the bath allowed to rise to -30° C. The
deoxygenated styrene-THF solution prepared as described above was added
dropwise to the rapidly stirred t-butyllithium-THF solution over a 30
to 60 minute period. The temperature of the bath was maintained at
-30° C ± 5° C during the addition. The resulting dark red solution
was allowed to warm to 0° C and stirred at this temperature for 30
minutes completing the reaction. This method allowed the preparation
of the following tertiary benzylic lithums in greater than 95% yield;
2-lithio-2-phenyl-4,4-dimethylpentane (2), 2-lithio-2-(p-trimethyl-
silylphenyl)-4,4-dimethylpentane (2), 2-lithio-2-(p-trimethylgermyl-
phenyl)-4,4-dimethylpentane (11), 2-lithio-2-(p-phenyldimethylsilyl-
phenyl)-4,4-dimethylpentane (12), 2-lithio-2-(p-cyclopropylphenyl)-
4,4-dimethylpentane (26), and 2-lithio-2-(p-phenylphenyl)-4,4-
dimethylpentane (28).

Using method A, 2 was prepared in greater than 90% yield when
the following ligands were substituted for TMEDA; N-methylpyrroline
(0.94 g, 11.0 mmol), diethylcyclohexylamine (1.71 g, 11.0 mmol),
N,N,N',N'-tetramethyldiaminomethane (0.56 g, 5.5 mmol) and N,N,N',N'-
tetramethylpropylenediamine (0.72 g, 5.5 mmol).

Using method A, 2 was prepared in greater than 90% yield when
the following ligands were substituted for TMEDA; tetrahydrofuran
(0.79 g, 11.0 mmol), ethyl ether (0.82 g, 11.0 mmol), dioxane (0.48 g,
5.5 mmol), dimethoxymethane (0.42 g, 5.5 mmol), 1,2 dimethoxyethane
(0.50 g, 5.5 mmol) and triethylamine (1.11 g, 11.0 mmol).
Specific Examples

2-lithio-2-phenyl-4,4-dimethylpentane (2) in benzene-isoctane.---
A 10 ml pear-shaped flask equipped as described above was charged with
α-methylstyrene (0.60 g, 5 mmol) and 3 ml of isoctane. This was out-
gassed for 10 minutes by passing a stream of argon through it via a
stainless steel needle. The reaction vessel (same as in A) was charged
with t-butyllithium in pentane (1.33 M, 4.1 ml, 5.5 mmol). The pentane
was removed by passing a current of argon over the rapidly stirred
solution and 3 ml of isoctane was added. The reaction vessel was
immersed in a dry ice-isopropanol bath at -30° C and benzene (0.43 g,
5.5 mmol) was added. The deoxygenated α-methylstyrene-isoctane
solution was added dropwise to the rapidly stirred solution over a
30 minute period. During this time the bath temperature was allowed
to rise to approximately 0° C. Stirring at 0° for an additional 1 hour
resulted in a dark red very viscous solution. Nmr analysis indicated
the yield of 2 to be 65 to 75%.

2-lithio-2-(p-thiomethylphenyl)-4,4-dimethylpentane (16) in ethyl
ether-isoctane.---A stock solution of p-thiomethyl-α-methylstyrene (15)
in ethyl ether was prepared as follows: a 25 ml volumetric flask
equipped with a 2 mm straight bore stopcock and ground glass joint was
charged with 15 (5.7 g, 34.7 mmol) and then filled to the mark with
ethyl ether (conc. = 1.36 M). The solution was degassed on the vacuum
line (three freeze-thaw cycles) then filled with argon.

A 50 ml round-bottom flask equipped with two 2 mm straight bore
stopcocks protected with rubber serum caps and a magnetic stirring bar
was charged with a solution of t-butyllithium in pentane (1.33 M,
4.1 ml, 5.5 mmol). The pentane was removed by passing a current of argon through the reaction vessel and 6 ml of isoctane was added. The reaction vessel was immersed in a dry ice-isopropanol bath at -30°C. The 15-ether solution prepared as described above (3.7 ml, 5.08 mmol) was added dropwise to the rapidly stirred t-butyllithium-isoctane solution over a 10 minute period. A light red precipitate formed immediately as the solution was added. Hydrolysis of the heterogeneous reaction mixture (see section on capture reactions) and subsequent nmr analysis of the product mixture indicated that 16 had formed in 75% yield.

2-lithio-2-(p-trimethylsilylphenyl)-4,4-dimethylpentane (5) in trimethylamine-isoctane. --A three necked round-bottom flask was equipped with an argon gas inlet, a magnetic stirring bar and a condenser. The top of the condenser was attached at an angle of 90° to two 10 cm by 1 cm drying tubes containing potassium hydroxide pellets and calcium oxide lumps, respectively. The second drying tube was attached to a "Tee", one end of which was equipped with a 2 mm straight-bore stopcock and attached to an argon line, the other attached to a calibrated cold finger. All connections were made by 14/20 ground glass joints. The exit from the cold finger was attached via a short piece of tygon tubing to one side arm of a 50 ml round bottom flask equipped with a magnetic stirring bar and two sidearms protected by 2 mm straight bore stopcocks. The second side arm was protected with a rubber serum cap. The entire assembly was flushed with argon for one hour. The coldfinger and 50 ml round bottom flask were flamed with a microburner several times during this period.
The 100 ml round bottom flask was charged with trimethylamine hydrochloride (0.10 mol, 9.6 g) and 50 ml of mesitylene, the cold trap was cooled to -78°C with a dry ice-isopropanol bath and ca. 10 KOH pellets were added to the 100 ml round bottom flask. The reaction mixture was stirred at room temperature until the pellets were almost totally consumed, then ca. 10 more KOH pellets were added. The process was repeated twice more. After the fourth addition the amount of precipitated KCl made it difficult to stir the reaction mixture and also to monitor the disappearance of the KOH pellets. By this time ca. 6 ml of liquid had condensed in the cold finger.

The 50 ml round bottom flask was charged with a solution of t-butyllithium in pentane (5.7 ml, 1.0 M, 5.7 mmol) and cooled to -78°C. With the argon still flushing the system the dry ice-isopropanol bath was removed from the cold finger until 1.5 ml of trimethylamine (0.99 g, 16.5 mmol) had been transferred from the cold finger to the reaction flask, then the cold finger was reimmersed in the dry ice-isopropanol bath and held at -70°C. The reaction flask was warmed to ca. -50°C and a solution of p-trimethylsilyl-α-methyl-styrene (4) (1.0 g, 5.2 mmol), in 3 ml of isoctane was added dropwise over a 45 minute period. After the addition was completed the reaction mixture was warmed to 0°C and stirred at that temperature for 30 minutes. Most of the pentane and excess trimethylamine were removed by allowing the reaction mixture to warm to 20°C while passing a current of argon over the solution. Additional isoctane (5 ml) was added to the reaction mixture prior to the preparation of a sealed,
degassed nmr sample. The nmr analysis of the reaction mixture showed that a 90% conversion of $\frac{1}{2}$ to $\frac{5}{2}$ had occurred.

**2-lithio-2-(p-trimethylstannylphenyl)-1,4-dimethylpentane (13).**--

Using method A, a solution of p-trimethylstannyl-α-methylstyrene (10) (0.86 g, 3.1 mmol) in 3 ml of isooctane was reacted with a solution of t-butyl lithium (3.4 mmol) in isooctane (5 ml) in the presence of ethyl ether (0.7 g, 9.5 mmol) at -30° C. Nmr analysis revealed that the one-to-one adduct $\frac{13}{2}$ had formed in greater than 90% yield.

**2-lithio-2-phenyl-1,4-dimethylpentane (2) in isooctane.**--A 50 ml three-necked round bottom flask equipped with a magnetic stirring bar, immersion thermometer, "stopcock adapter" protected by a rubber serum cap and condenser was thoroughly flamed out under a rapid current of argon. The flask was charged with a solution of t-butyl lithium in pentane (10.0 ml, 0.95 M, 9.5 mmol) and most of the pentane removed by passing a rapid current of argon through the reaction vessel. Then, 15 ml of isooctane was added and the solution heated to approximately 50° C α-methylstyrene (0.8 g, 6.8 mmol) was added dropwise (neat) over a 30 minute period. During the addition the solution turned dark red and became very viscous. After the addition was completed the heating mantle was removed and the solution stirred for two hours. During that time a dark red precipitate formed. The heterogeneous mixture was hydrolyzed by adding water via syring dropwise until the solution was light orange in color (titration-like endpoint). The precipitated lithium hydroxide serves as an adequate drying agent so that the only work-up necessary is filtration and washing of inorganic salts with
three 25 ml portions of pentane. The combined pentane washings and isoctane solution were concentrated by flash evaporation at water aspirator pressure and 60° C to leave a clear, water-white liquid, 99% 2-phenyl-4,4-dimethylpentane (3) by vapor phase chromatography (Column A), and 97% overall yield. The ease of work-up and high yield and purity of product make this the preferred method for the synthesis of the hydrolysis products of the one-to-one adducts. There is some evidence that ring metallation occurs under the above conditions (see Results and Discussion). Preliminary results indicate that the amount of ring metallation is dependent on the purity of the t-butyllithium solution.

Preparation of Benzylic Lithiums from 1-Phenylcycloalkenes.

1-lithio-1-phenyl-2-t-butyln cyclopentane (38).—Using method A, a solution of 1-phenylcyclopentene (1.3 g, 9.0 mmol) in 5 ml of isoctane was reacted with t-butyllithium (0.95 M, 10.0 ml, 9.5 mmol) in the presence of TMEDA (1.16 g, 10.0 mmol) at -30° C. The yield of 38 was 95% (nmr analysis). Using method B, a solution of 1-phenylcyclo-pentene (1.3 g, 9.0 mmol) in 3 ml of tetrahydrofuran was reacted with t-butyllithium (0.95 M, 10.0 ml, 9.5 mmol) at -30° C to give 38 in 95% yield. Raising the reaction temperature resulted in mixtures of 38 and the phenylallylic lithium compound 39 (see Results and Discussion).

phenyl-cyclohexenyllithium (41).—Using method B a solution of 1-phenylcyclohexene (1.4 g, 8.9 mmol) in 3 ml of tetrahydrofuran was reacted with a solution of t-butyllithium in pentane (0.95 M, 10.0 ml,
9.5 mmol) at -30° C. Nmr analysis indicated that \( \text{H1} \) had formed in greater than 95% yield. Using method A with the same molar quantities resulted in only a 20% conversion of \( \text{H0} \) to \( \text{H1} \).

**Reaction of 1-phenylcyclobutene with t-butyllithium.**—Using method A, a solution of 1-phenylcyclobutene (0.65 g, 5.0 mmol) in 5 ml of isoctane was reacted with a solution of t-butyllithium (5.7 mmol) in isoctane (5 ml) at -30° C. A heterogeneous deep red solution resulted. Nmr analysis of the supernatant indicated no one-to-one adduct was present. Nmr analysis of the hydrolyzed reaction mixture indicated that polymerization of the 1-phenylcyclobutene had occurred. Lowering the reaction temperature to -78° C and/or diluting the 1-phenylcyclobutene by a factor of 3 gave the same results. Using method B, the same molar scale, three equivalents (ca. 17 mmol) of t-butyllithium, or diluting the 1-phenylcyclobutene-tetrahydrofuran solution with 10 ml of isoctane gave the same results.

**Reactions of Benzylic Lithiums**

1. **Capture Reactions**

   **2-(p-cyclopropylphenyl)-4,4-dimethylpentane.**—A rapidly stirred solution of 2-lithio-2-p-cyclopropylphenyl-4,4-dimethylpentane (5 mmol) in TMEDA-isoctane (prepared as described above) was treated with water (2.0 g, 11.1 mmol) added by syringe at room temperature (exo-thermic reaction). The organic phase was diluted with 50 ml of pentane and washed with 5% aqueous hydrochloric acid (25 ml, 5 times), water (25 ml, once), and saturated aqueous sodium bicarbonate (25 ml, once). Filtration through a cone of anhydrous magnesium sulfate, flash
evaporation of solvents and distillation through a short-path distillation head gave 2-p-cyclo-propylphenyl-4,4-dimethylpentane (46) (bp. 90-97°/0.1 Torr, 1.05 g, 98%). This method was used to prepare the following hydrocarbons: 3, bp. 50-60°/0.5 torr, 95%; 6, bp. 80-90°/0.5 torr, 90%; 45, bp. 95-115°/0.5 torr, 85%; 46, molecular distillation, 120° c/0.5 torr, 81%; 47, molecular distillation, 120°/0.5 torr, 76%; 22, bp. 75-90°/0.5 torr, 75%; 49, sublimed, 75° c/0.5 torr, 71% mp. 87°. See Tables 3 and 4 for nmr parameters.

2-deuterio-2-(p-trimethylsilylphenyl)-4,4-dimethylpentane. — Using the same procedure as described above, 5 mmol of 2-lithio-2-p-trimethylsilylphenyl-4,4-dimethylpentane was reacted with deuterium oxide to give the title compound in 97% yield, bp. 90-105°/0.5 torr. The carbon and proton magnetic resonance data showed that deuterium had been incorporated at the benzylic position (see Table 5). J_{13C-D} = 19.2 ± 0.6 Hz, deuterium isotope shift 0.5 ppm upfield.

2-phenyl-2-trimethylsilyl-4,4-dimethylpentane (51). — A solution of 2-lithio-2-phenyl-4,4-dimethylpentane (10 mmol) in tetrahydrofuran-isooctane (prepared using method B doubling all quantities) was treated with freshly distilled trimethylsilyl chloride (1.2 g, 11 mmol), added dropwise via syringe to 0° C. The resulting white precipitate (lithium chloride) was dissolved by the addition of 25 ml of water. The organic phase was diluted with 50 ml of pentane and washed with saturated sodium chloride solution (25 ml). Filtration through a cone of anhydrous magnesium sulfate, flash evaporation of solvents and distillation head yielded 51 (1.6 g, bp. 80-85°/0.2 torr, 65%). The nmr parameters are given in Tables 3 and 4.
2-phenyl-2-trimethylstannyl-4,4-dimethylpentane (52).--A solution of 2-lithio-2-phenyl-4,4-dimethylpentane (10 mmol) in tetrahydrofuran-pentane (prepared as described by method B with doubling of all quantities) was treated with a solution of trimethylstannyl chloride (20.0 g, 10.0 mmol) in 25 ml of tetrahydrofuran at 0° C. The same work-up as described directly above yielded 52 (19.4 g, 58%, bp. 95-105°/0.5 torr). The nmr parameters are given in Table 5.

cis and trans 1-phenyl-2-t-butylcyclopentane (57) and (58).--A rapidly stirred solution of 1-lithio-1-phenyl-2-t-butylcyclopentane in tetrahydrofuran-pentane (9.0 mmol, prepared as in method B) was treated with water (2.0 g, 11.1 mmol). The organic phase was diluted with 50 ml of pentane and washed with 5% aqueous hydrochloric acid (25 ml, 5 times), water (25 ml, once) and saturated aqueous sodium bicarbonate (25 ml, once). Filtration through a cone of anhydrous magnesium sulfate, flash evaporation of solvents and distillation at reduced pressure using a short-path distillation head gave a 60/40 mixture of 57 and 58 respectively, overall yield 90%, bp. 95-105 at 0.5 torr. The two isomers could be separated by vapor phase chromatography on column B at 165° C, the major isomer (trans) eluting first. The proton and carbon nmr data are listed in Table 6.

2. Oxidation Reactions

Reaction of 2-lithio-2-phenyl-4,4-dimethylpentane (2) with oxygen.--A solution of 2 (5 mmol) in TMEDA-isoctane was prepared as described by method A. A stream of dry air was passed through the reaction mixture via a stainless steel needle at 0° C until the dark
red solution had turned light yellow. The reaction mixture was warmed to room temperature, treated with 10 ml of saturated aqueous ammonium chloride and diluted with 50 ml of pentane. The organic layer was washed with water (25 ml, 5 times), saturated aqueous sodium bicarbonate (25 ml, twice) and filtered through a cone of anhydrous magnesium sulfate. Flash evaporation of solvents and distillation through a short-path distillation heat (bp. 50-100º/0.1 torr) yielded a mixture of 3 (60%) and 6la (40%) as shown by vapor phase chromatography (Column A, 165º C). Tables 4 and 5 list the magnetic resonance parameters for 3. Table 9 lists the proton parameters for 6la. The carbon chemical shifts for 6la are (CDCl₃, TMS); δ 150.3 (aromatic ipso carbon), δ 147.8 (C-vinyl), δ 128.2 and 126.6, ortho and meta aromatic carbons), δ 127.0 (para aromatic carbon), δ 116.2 (CH₂- vinylic), δ 149.1 (CH₂-aliphatic), δ 31.8 (C-quaternary), δ 30.1 (t-butylmethyls).

**Reaction of 2-lithio-2-biphenylyl-4,4-dimethylpentane (28) with Oxygen.**—A solution of 28 (2.5 mmol) in tetrahydrofuran-pentane was prepared as described by method B. The reaction vessel was opened to the air by removing one serum cap and replacing it with a drying tube containing anhydrous calcium chloride and allowed to stand at 0º C for two days. The color of the reaction mixture turned from dark red to light green during this time. The contents of the flask were treated with 10 ml of water and diluted with 50 ml of ethyl ether. The organic phase was washed with saturated aqueous sodium chloride and filtered through a cone of anhydrous magnesium sulfate. Flash evaporation of solvents left 0.53 g of yellow oil. This was dissolved in 5 ml of
pentane and cooled to -10°C for ten hours to yield ca. 60 mg of a white solid. The solid was separated from the mother liquor by decantation and recrystallized from one ml of pentane to yield 41 mg of $62c$, mp 108-110°C, 3.2% based on 28. The combined pentane solutions were concentrated and subjected to molecular distillation. After ca. 100 mg had been collected the distillation was stopped and the distillate, which had hardened to a glassy solid in the receiver, was analyzed by proton nmr to be a mixture of $61c$ (65%) and $49$ (35%).

Cleavage of Benzyllic Tin Compounds

Reaction of 2-phenyl-2-trimethylstannyl-4,4-dimethylpentane ($52$) with t-butyllithium. --A standard solution of $52$ was prepared as follows: A 25 ml volumetric flask equipped with a 2 mm straight bore stopcock fitted with a ground glass joint was charged with 5.5 g of $52$ (25 mmol) and filled to the mark with cyclopentane (conc. = 1 M). The solution was degassed on the vacuum line (3 freeze-thaw cycles, pressure < 1 micron) and then filled with argon.

A 25 ml round bottom flask equipped with a "stopcock adapter" protected by a rubber serum cap and magnetic stirring bar was charged with 3.5 ml of sublimed t-butyllithium in pentane (0.88 M, 3.1 mmol) and 3.0 ml (3 mmol) of the $52$-cyclopentane solution described above. At room temperature TMEDA (0.17 g, 3.0 mmol) was added dropwise. A dark red homogeneous solution resulted immediately. Nmr analysis indicated that the formation of 2-lithio-2-phenyl-4,4-dimethylpentane (2) was greater than 90%.
The following experimental variations occurred in examining the effect of various ligands on the above reaction. Using the same procedure but substituting tetrahydrofuran (0.43 g, 6 mmol) or ethyl ether (0.45 g, 6 mmol) gave the results listed in Table 7. The reaction of 3.0 mmol of 52 with a mixture of 6.2 mmol of t-butyllithium and 3.1 mmol (.2 g) of t-butanol was accomplished by adding the t-butanol to the t-butyllithium at room temperature before the addition of 52. Sublimed alcohol-free lithium t-butoxide (Alfa, .25 g, 3.1 mmol) was placed in the round bottom flask inside a dry box. The flask was removed from the dry box and the reaction completed by adding the t-butyllithium in pentane (7.0 ml, 6.2 mmol) followed by the 52-cyclopentane solution. The reaction involving potassium t-butoxide was performed in the same manner. The results of these variations are listed in Table 7.

Preparation of Benzylic Lithium Precursors.

α-Methylstyrene, 1-phenylcyclohexene and 1-phenylcyclopentene were available from commercial sources. Although experimental procedures for the preparation of most of the para substituted α-methylstyrenes are available in the literature, in general they were not followed. Hence new procedures are presented here. Figures 35, 36, and 37 display flow charts for the synthetic sequences used in this work. Tables 25, 26, 27 and 28 list proton and carbon magnetic resonance parameters for the para substituted-α-methylstyrenes and intermediates in their synthesis. Note should be made of the assignment of the carbon chemical shifts for α-methylstyrene (Table 26). Specifically
the ortho, meta and para carbon assignments are based on the carbon-13 spectrum of p-deutero-α-methylstyrene where the resonance at 127.4 ppm disappears, and the resonance at 125.6 is split into a 1:1:1 triplet, J_{13C-\text{D}} = 1.0 Hz. Since J_{13C-H} \text{meta} is approximately 7.4 Hz in benzene and the corresponding J_{13C-H} in α-methylstyrene is about 7.0 ± 0.2 Hz, the assignment of the resonance at 125.6 ppm to the ortho carbons, the resonance at 127.4 ppm to the para carbon and the resonance at 128.3 ppm to the meta carbons is unequivocal. Note that these assignments differ from those given by Stothers.

The experimental procedure for the preparation of 1-phenylcyclobutene (Figure 37) was exactly that of Koster et al. (methlene-cyclopropane), Aue et al. (1-oxaspiro[2.2]pentane and cyclobutanone) and Burger and Bennet (1-phenylcyclobutene). Since all three papers give excellent experimental, it will not be repeated here.

2-(p-bromophenyl)-2-propanol. -- A one liter round bottom three-necked flask was fitted with a pressure equalizing dropping funnel, mechanical stirrer, and condenser. The entire apparatus was flamed out under a current of argon and allowed to cool. Magnesium turnings (9.0 g, 0.37 g-atom) were placed in the flask and the dropping funnel was charged with a solution of p-dibromobenzene (75 g, 0.32 moles) in anhydrous ethyl ether (400 ml). Approximately 50 ml of the ether-bromide solution was discharged from the dropping funnel and a small crystal of iodine was added to the flask. The stirrer was started and within two minutes a vigorous reflux had commenced. The reaction was controlled with an ice bath until the reflux had subsided, the ice bath was removed, and the remainder of the ether-bromide solution was
Figure 35. Synthetic scheme for para substituted α-methylstyrenes, I.
Figure 36. Synthetic scheme for para-substituted α-methylstyrenes, II.
Figure 37. Synthetic scheme for the preparation of 1-phenylcyclobutene.
### TABLE 25 - XI

**Nmr Parameters**

\(^1\text{H} (60 \text{ MHz}), \text{CDCl}_3 (20\% \text{ v/v}), \delta(\text{ppm})/\text{TMS}\)

![Chemical Structure](image)

<table>
<thead>
<tr>
<th></th>
<th>4</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>15</th>
<th>19</th>
<th>23</th>
<th>25</th>
<th>27</th>
<th>29</th>
<th>34</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me(δ)</td>
<td>2.08</td>
<td>2.10</td>
<td>2.10</td>
<td>2.08</td>
<td>2.10</td>
<td>2.08</td>
<td>2.08</td>
<td>2.05</td>
<td>2.13</td>
<td>2.15</td>
<td>2.10</td>
</tr>
<tr>
<td>Ha</td>
<td>4.99</td>
<td>5.06</td>
<td>5.08</td>
<td>5.03</td>
<td>5.05</td>
<td>5.02</td>
<td>5.05</td>
<td>4.90</td>
<td>5.05</td>
<td>5.20</td>
<td>4.97</td>
</tr>
<tr>
<td>Hb</td>
<td>5.27</td>
<td>5.37</td>
<td>5.38</td>
<td>5.33</td>
<td>5.33</td>
<td>5.32</td>
<td>5.30</td>
<td>5.20</td>
<td>5.37</td>
<td>5.40</td>
<td>5.27</td>
</tr>
<tr>
<td>O, O'</td>
<td>7.3(^a)</td>
<td>7.4(^a)</td>
<td>7.2(^-)</td>
<td>7.4(^a)</td>
<td>7.4(^a)</td>
<td>7.4(^a)</td>
<td>7.1(^-)</td>
<td>7.0(^-)</td>
<td>7.4(^b)</td>
<td>7.4(^b)</td>
<td></td>
</tr>
<tr>
<td>m, m'</td>
<td>complex</td>
<td>complex</td>
<td>complex</td>
<td>complex</td>
<td>complex</td>
<td>complex</td>
<td>complex</td>
<td>complex</td>
<td>complex</td>
<td>complex</td>
<td>complex</td>
</tr>
</tbody>
</table>

\(^a\) Reference values for aromatic protons.

\(^b\) Additional peaks due to coupling effects.

Note: The chemical structure diagram represents the connectivity and labeling of the aromatic and olefinic protons, with 'X' indicating the position of substitution or functional group.
Table 25 - XI - continued

| X      | 0.24 | 0.38 | 0.55 | 0.23 | 2.50 | 1.20 |

\[ J_{\text{Ha-Me}} = 0.9 \text{ Hz}, J_{\text{Hb-Me}} = 1.5 \text{ Hz}, J_{\text{Ha-Hb}} = 1.5 \text{ Hz} \text{ for all cases} \]

a. collapsed AA'BB' pattern

b. center of gravity of \( \frac{1}{2} \) of AA'BB' pattern
TABLE 26

Nmr Parameters - XII

($^{13}$C (22.63 MHz), CDCl$_3$ (20% v/v), $\delta$(ppm)/TMS, $T = 35^\circ$ C)

\[
\begin{array}{cccccccccccccc}
\text{X-CH}_3 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 & 11 & 12 \\
2 & 143.3 & 143.3 & 143.2 & 143.3 & 142.5 & 142.5 & 143.3^* & 142.8 & 142.6 & 142.2 & 143.3 \\
3 & 112.6 & 112.4 & 112.7 & 112.4 & 111.9 & 112.7 & 111.4 & 112.5 & 110.6 & 113.0 & 112.4 \\
6 & 141.7 & 141.6^* & 141.9 & 141.4^* & 138.1 & 140.1 & 138.5 & 140.2 & 133.8 & 140.1 & 141.4 \\
7 & 124.9 & 125.1 & 124.9 & 125.1 & 126.5 & 126.3 & 125.4^* & 125.9 & 126.6 & 127.1 & 125.6 \\
8 & 133.4 & 132.9 & 134.2 & 135.8 & 125.9 & 130.9^* & 125.5^* & 126.9 & 113.6 & 131.3 & 128.3 \\
9 & 135.9 & 141.3^* & 137.2 & 141.2^* & 137.7 & 134.7 & 143.0^* & 140.1 & 152.9 & 121.4 & 127.4 \\
X-CH$_3$ & -1.1 & -1.8 & -2.4 & -9.6 & 15.8 & & & & & & 55.1 \\
\end{array}
\]
Table 26 - continued

<table>
<thead>
<tr>
<th></th>
<th>4</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>15</th>
<th>23</th>
<th>25</th>
<th>27</th>
<th>34</th>
<th>p-Br</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-10&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>138.2</td>
<td></td>
<td></td>
<td></td>
<td>135.9</td>
<td>15.2</td>
<td>140.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>130.9&lt;sup&gt;*&lt;/sup&gt;</td>
<td>9.2</td>
<td>126.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>129.2</td>
<td></td>
<td></td>
<td>128.8</td>
</tr>
<tr>
<td>X-13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>127.0</td>
<td></td>
<td>127.2</td>
</tr>
</tbody>
</table>

* assignments could be reversed

# assignments could be reversed

a. numbering is from Table 3
TABLE 27

Nmr Parameters - XIII

($^1$H, CDCl$_3$ (20% v/v), $\delta$(ppm)/TMS)

\[
\begin{align*}
&\text{Br} \quad \text{O} \quad \text{H} \rightarrow 2.1 \\
&1.5 \quad (\text{CH}_3)_2\text{C} \quad \{7.3 \\
&\text{Br} \quad \text{O} \quad \text{H} \rightarrow 2.1 \\
&1.5 \quad (\text{CH}_3)_2\text{C} \quad \{7.3 \\
&\text{Br} \quad \text{O} \quad \text{H} \rightarrow 2.0 \\
&1.5 \quad (\text{CH}_3)_2\text{C} \quad \{7.4 \\
&\text{Br} \quad \text{O} \quad \text{H} \rightarrow 2.1 \\
&1.8 \quad 0.6, 0.9 \\
&\text{NO}_2 \quad \text{H} \rightarrow 8.1 \\
&1.3 \quad \text{CH}_3\text{CCH}_3 \quad 7.3 \\
&\text{CO}_2\text{CH}_3 \quad \text{H} \rightarrow 3.0 \\
&7.3-7.5 \\
&\text{J} = 7.0 \text{ Hz}
\end{align*}
\]
TABLE 28

Nmr Parameters - XIV

\(^{13}\)C (22.63 MHz), CDCl\(_3\) (20\% v/v), \(\delta\) (ppm)/TMS, T - 33° C

\[
\begin{array}{cccc}
\text{#} & \# & \delta & \delta \\
1 & 1 & 31.6 & 9.3 \\
2 & 2 & 72.2 & 15.0 \\
3 & 3 & 148.2 & 143.0 \\
4 & 4 & 126.4 & 127.4 \\
5 & 5 & 131.1 & 131.2 \\
6 & 6 & 120.4 & 118.1 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{#} & \# & \delta & \delta \\
1 & 2.1 & 167.0 & 167.0 \\
2 & 2 & 52.0 & 167.0 \\
3 & 3 & 129.0 & 129.0 \\
4 & 4 & 130.1 & 130.1 \\
5 & 5 & 127.0 & 127.0 \\
6 & 6 & 145.6 & 145.6 \\
7 & 7 & 140.0 & 140.0 \\
8 & 8 & 127.3 & 127.3 \\
9 & 9 & 128.4 & 128.4 \\
10 & 10 & 128.1 & 128.1 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{#} & \# & \delta & \delta \\
1 & 5 & 132.6 & -0.81 \\
2 & 2 & 133.0 & 133.0 \\
3 & 3 & 128.1 & 128.1 \\
4 & 4 & 130.3 & 130.3 \\
5 & 5 & -0.81 & -0.81 \\
\end{array}
\]
added at such a rate as to maintain a steady reflux. The total addition time was approximately 1.25 hours. The flask was then heated so that the ether maintained a steady reflux for 4 hours, the heat removed and the flask immersed in an ice bath. A solution of acetone (19.8 g, 0.35 moles) in anhydrous ethyl ether (50 ml) was added via the dropping funnel while stirring vigorously. The ice bath was removed and the resultant white slurry was stirred at room temperature for 2 hours. The flask was again immersed in an ice bath and a saturated aqueous solution of ammonium chloride was added via the dropping funnel with vigorous stirring until the magnesium salts settled to the bottom of the flask in large clumps and a clear, light yellow ether solution was evident. The stirrer was stopped, the ice-bath removed, and the contents of the flask allowed to further settle for 30 minutes. The ether solution was decanted from the magnesium salts and the salts were washed with additional portions of ether (50 ml, 5 times). The combined ether extracts were dried over anhydrous magnesium sulfate overnight. Subsequent filtration flash evaporation of ether and distillation using a short path distillation head yielded 2-(p-bromophenyl)-2-propanol (53.2 g, 78%, bp. 75-85°/0.1 torr, Lit. 74 99-102°/2.5 torr). Tables 27 and 28 list the proton and carbon magnetic resonance data.

2-(p-bromophenyl)-propene (Method A).--A 500 ml round flask equipped with a magnetic stirring bar, Dean-Stark trap, and condenser was charged with 2-(p-bromophenyl)-2-propanol (32.5 g, 0.15 mole), benzene (300 ml) and phosphoric acid (85%, 1 ml). Refluxing the mixture for 5 hours resulted in the separation of an equivalent of
water (3.0 ml) in the trap. After cooling to room temperature the reaction mixture was poured into a separatory funnel containing ethyl ether (150 ml). The ether-benzene solution was washed twice with water (100 ml), once with a saturated aqueous solution of sodium bicarbonate (50 ml), again with water (100 ml), and once with saturated aqueous sodium chloride (100 ml), then dried over anhydrous magnesium sulfate overnight. Filtration, evaporation of volatile solvents, and distillation through a short path distillation head yielded 2-(p-bromophenyl)-propene (25.4 g, 83%, bp. 55-65°/2.3 torr, Lit. 74 58-60°/2 torr). The proton and carbon magnetic resonance spectra were in accord with the predicted structure (See Tables 25 and 26).

2-(p-bromophenyl)-propene (Method B).—A 25 ml round bottom flask equipped with a magnetic stirring bar was charged with 2-(p-bromophenyl)-2-propanol (10.5 g, 49 mmol) and potassium bisulfate (6.8 g, 50 mmol). Distillation of the mixture through a 2 inch Vigreux column at water aspirator pressure (ca. 20 torr) yielded the title compound (6.5 g, 68%, bp. 110-120°).

2-(p-trimethylsilylphenyl)-propene.—Into a flame dried 500 ml round bottom three-necked flask equipped with a magnetic stirring bar, "stopcock adapter" protected with a rubber serum cap and adapter for maintaining a positive argon pressure was added via syringe a solution of n-butyllithium in hexane (1.4 M, 20 ml, 28 mmol). The solution was cooled by immersion in a dry ice-isopropanol bath at -50° C and 100 ml of ethylether was added via syringe. The bath temperature rose to ca. -15° C while a solution of 2-(p-bromophenyl)-propene (5.0 g,
25 mmol) in 50 ml of ethyl ether was added dropwise to the vigorously stirred solution. The bath temperature was maintained at -15°C for one hour. Analysis by vapor phase chromatography on a hydrolyzed aliquot showed that the formation of 2-(p-lithiophenyl)-propene was quantitative. Then freshly distilled trimethylsilyl chloride (4.2 g, 38 mmol) was added in a thin stream from a syringe. The reaction mixture was warmed to room temperature and 50 ml of water was added to dissolve the lithium salts. The organic layer was diluted with pentane (200 ml) and washed with water (50 ml, twice) and saturated aqueous sodium chloride (50 ml, once). Filtration through a cone of anhydrous magnesium sulfate, flash evaporation of solvents and distillation through a 3-in. four-path distillation head yielded 2-(p-trimethylsilylphenyl)-propene (4.1 g, 85%, bp. 78-83°C/2.0 torr, Lit. 68-70/0.7 torr). Nmr data are listed in Tables 25 and 26.

2-(p-trimethylgermylphenyl)-propene.—A solution of 2-(p-lithiophenyl)-propene (76 mmol) in ethyl ether-hexane prepared as described above was treated with trimethylgermyl bromide (15 g, 76 mmol) at -15°C to yield after similar work-up and two distillations 2-(p-trimethylgermylphenyl)-propene (6.8 g, 30%, bp. 65-72°C/0.5 torr, Lit. 55-57°C/0.3 torr). Nmr data are listed in Tables 25 and 26.

2-(p-trimethylstannylphenyl)-propene.—A solution of 2-(p-lithiophenyl)-propene (40 mmol) in ether-hexane prepared as described above was treated with a solution of trimethylstannyl chloride (10.2 g, 51 mmol) in 50 ml of ethyl ether at -15°C. The same work-up as described above and one distillation yielded
2-(p-trimethylstannylphenyl)-propene (8.5 g, 75%, bp. 59-63°/0.1 torr, Lit.75 49-51°/0.0003 torr). The proton and carbon magnetic resonance data were in accord with the expected structure (Tables 25 and 26).

2-(p-themethylphenyl)-propene. — A solution of 2-(p-lithiophenyl)-propene (40 mmol) in ethyl ether-hexane prepared as described above was treated with dimethyldisulfide (5.3 g, 57 mmol) added neat via syringe at 0° C. After a similar work-up to that for the para-silyl derivative (CAUTION—EXTREMELY MALODOROUS REACTION) the yield of 2-(p-thiomethylphenyl)-propene was 85% (5.7 g, bp. 85-89°/0.7 torr, Lit.76 85°/1.0 torr). The product solidified in the receiving flask (mp 45-47°, Lit.76 51°). Nmr data are given in Tables 25 and 26.

2-(p-thiophenylphenyl)-propene. — A solution of 2-(p-lithiophenyl)-propene (26 mmol) in ethyl ether-hexane prepared as described above was treated with a solution of diphenyl disulfide (6.0 g, 27.5 mmol) in 25 ml of ethyl ether at 0° C. The reaction mixture was stirred at room temperature for 24 hours. After the normal work-up and distillation the yield of 2-(p-thiophenylphenyl)-propene was 4.1 g, 71%, bp. 115-122°/0.1 torr. Tables 25 and 26 list the proton and carbon magnetic resonance data.

p-phenylmethylbenzoate. — Into a 250 ml round bottom flask equipped with a magnetic stirrer and condenser was added p-phenylbenzoic acid (25 g, 0.125 mole), thionyl chloride (16.2 g, 0.138 mole), and pyridine (2 ml). The top of the condenser was connected to a funnel inverted over a beaker containing 10% aqueous sodium hydroxide. The reaction mixture was warmed to approximately 60° C, the mixture became
a dark syrup, the stirrer was started and the mixture heated for an additional 30 minutes. The reaction flask was cooled to room temperature and its treated with methanol (10 ml, 8 g, 0.25 moles) containing 3 drops of pyridine and stirred until the reaction mixture solidified into a clump. The dark brown solid was broken-up, washed with pentane and suction filtered to leave a light brown powder. The solid was washed with 500 ml of water and dried in a vacuum dessicator over anhydrous calcium chloride overnight to yield p-phenylmethylbenzoate (22.8 g, 85%, mp 114-116°C Lit. 117-118°C). A one gram portion was recrystallized from methanol and dried in a vacuum dessicator for 3 hours to yield 0.4 g of product, mp 117-118°C, proton and carbon magnetic resonance spectra were in agreement with the predicted structure (See Tables 27 and 28).

2-(p-biphenylyl)-2-propanol.—A one liter round bottom three-necked flask was equipped with a mechanical stirrer, addition funnel, condenser, and adapter for maintaining a positive argon pressure. Magnesium chips (6.1 g, 0.25 g-atom) and approximately 50 ml of a solution of methyl iodide (28.4 g, 0.2 mole) in ethyl ether (200 ml) were added to the flask and the stirrer started. A vigorous reaction began immediately and was moderated by immersing the flask in an ice-water bath until the ether reflux had subsided. The bath was removed and the remainder of the halide-ether solution was added from the dropping funnel at such a rate as to maintain a steady reflux. After the addition had been completed the Grignard solution was refluxed for 30 minutes, then a solution of p-phenylmethylbenzoate
(20 g, 0.095 mole) in ethyl ether (400 ml) was dripped into the refluxing solution. The addition took 5 hours and was followed by 5 hours of reflux then stirring at room temperature overnight. The flask was immersed in an ice-water bath, stirred vigorously, and a saturated solution of aqueous ammonium chloride was added via the dropping funnel until the magnesium salts settled to the bottom of the flask in large clumps. The stirrer was stopped and the contents of the flask allowed to settle for 30 minutes. The ether was decanted through a glass wool plug, the magnesium salts washed with three 100 ml portions of ethyl ether, and the combined ether solutions dried over anhydrous magnesium sulfate for eight hours. Flash evaporation of ether left 19.5 g (95%) of a yellow-orange solid which displayed no carbonyl absorption in the infrared and whose proton nmr spectrum (Table 27) was consistent with the predicted structure.

2-(p-biphenylyl)-propene.--Into a 500 ml round bottom flask equipped with a magnetic stirring bar, Dean-Stark trap and condenser was added 2-(p-biphenylyl)-2-propanol (19.0 g, 0.09 mole) dry benzene (200 ml), and 85% phosphoric acid (1 ml). The solution was refluxed until no more water was observed separating from the condensate (1.5 hours, 1.4 ml water collected, 87.5%). After cooling to room temperature the contents of the flask were poured into a separatory funnel containing 200 ml of pentane and washed with water (50 ml, 3 times), saturated aqueous sodium bicarbonate (50 ml, 3 times), water (50 ml, once), saturated aqueous sodium chloride (50 ml, once) and dried over anhydrous magnesium sulfate overnight. The solution was concentrated by rotary evaporation until the volume was approximately
30 ml, poured onto a column of alumina (Woelm, activity 1, basic, column dimensions 3 cm by 20 cm), and eluted with pentane. The first 500 ml of eluate were evaporated to leave a slightly yellow solid (17.3 g, 102%) which was recrystallized three times from 50/50 ether-hexane to yield 2-(p-biphenyl)-propene (8.5 g, 49%, mp. 114-118°, Lit.78 115°). Tables 25 and 26 list the nmr parameters.

**p-bromophenyl-cyclopropane.**—A 250 ml round bottom three-necked flask equipped with a magnetic stirring bar, dropping funnel and immersion thermometer was charged with cyclopropylbenzene (10.5 g, 0.089 mole), potassium acetate (11.0 g, 0.11 mole) and acetic anhydride (100 ml). The reaction flask was immersed in an ice-bath and the contents of the flask stirred rapidly. Bromine (5.3 ml, 16.0 g, 0.10 mole) was added from the dropping funnel over a 30 minute interval while the temperature of the reaction mixture was maintained at 5-10° C. After the addition of Bromine was completed the solution was stirred at 5-10° C for five hours, poured onto 250 ml of water, and the oil which formed as an upper layer was taken up in 50 ml of pentane. The aqueous phase was extracted three times with 50 ml portions of pentane then the combined pentane solution was washed with water (50 ml, 5 times), saturated aqueous sodium bicarbonate (50 ml, 3 times), water (50 ml, once) and saturated aqueous sodium chloride (50 ml, once). Filtration through a cone of anhydrous magnesium sulfate, flash evaporation of pentane and two distillations at reduced pressure yielded **p-bromophenylcyclopropane** (6.9 g, bp. 62-68°/0.75 torr, Lit.18 61-63°/1 torr, 38%). Tables 27 and 28 list the proton and carbon nmr data.
2-(p-cyclopropylphenyl)-2-propanol.\textsuperscript{47}--A 250 ml round bottom three-neck flask was equipped with a magnetic stirring bar, condenser, side arm fitted with a "stopcock adapter", and argon gas inlet adapter. The flask was charged with magnesium powder (0.83 g, 0.034 g-atom) and 30 ml of tetrahydrofuran. The stirrer was started and a solution of p-bromophenylcyclopropane (6.7 g, 0.034 mole) in 15 ml of tetrahydrofuran was added rapidly via syringe. The mixture was refluxed for 5 hours, cooled to room temperature, and treated with acetone (9 ml, 7.1 g, 0.12 mole). The reaction mixture was stirred for ten hours at room temperature, immersed in an ice-water bath, stirred rapidly and hydrolyzed by adding saturated aqueous ammonium chloride dropwise via syringe until the magnesium salts settled to the bottom of the flask in a clump. The precipitated salts were allowed to settle for 30 minutes, the supernatant liquid was decanted through a cone of anhydrous potassium carbonate, the salts were washed with three 50 ml portions of ethyl ether and the combined tetrahydrofuran-ethyl ether solutions were flash distilled at water aspirator pressure to leave a yellow-orange oil (4.5 g, 73\%, containing a trace of tetrahydrofuran) whose proton magnetic spectrum (Table 27) was in accord with the predicted structure.

2-(p-cyclopropylphenyl)-propene.\textsuperscript{47}--Into a 500 ml round bottom flask equipped with a magnetic stirring bar, Dean-Stark trap, and condenser was added 2-(p-cyclopropylphenyl)-2-propanol (4.5 g, 0.0256 mole), benzene (300 ml) and phosphoric acid (1 ml, 8\%). Refluxing the solution for one hour resulted in the separation of one
equivalent of water. Work-up in the same manner as already described for the previous tertiary carbinol dehydrations yielded 2-\((p\text{-cyclopropylphenyl})\)-propene (2.07 g, 51\%, bp. 72-78°/0.75 torr, Lit.\(^47\) 84-85°/1-2 torr). See Tables 25 and 26 for nmr data.

2-\((p\text{-methoxyphenyl})\)-propene.\(^79\)--A 250 ml round-bottom flask equipped with a magnetic stirring bar, side-arm "stopcock adapter" and condenser was charged with magnesium powder (0.93 g, 0.049 g-atom) and 30 ml of anhydrous tetrahydrofuran. A solution of \(p\)-bromoanisole (9.2 g, 0.048 mole) in 20 ml of tetrahydrofuran was added rapidly via syringe. After an initial exothermic reaction had subsided the solution was refluxed for five hours, cooled to room temperature, and treated with acetone (9 ml, 7.1 g, 0.12 moles) added via syringe at such a rate as to maintain a gentle reflux. The reaction mixture was stirred for ten hours, cooled in an ice bath and treated with saturated aqueous ammonium chloride in the same manner as previously described. Filtration of the clear tetrahydrofuran solution through a cone of anhydrous potassium carbonate, removal of most of the tetrahydrofuran on the rotary evaporator, and distillation yielded 2-\((p\text{-methoxyphenyl})\)-propene (5.0 g, 65\%, bp. 60-65°/0.1 torr, mp. 33, Lit.\(^79\) 34-35°) which was stored under argon at -5° C. The structure of the product was verified by its proton and carbon magnetic resonance spectra, (see Tables 25 and 26).

2-\((p\text{-nitrophenyl})\)-propane.\(^80\)--A 500 ml Erlenmyer flask equipped with a magnetic stirring bar was charged with cumene (50 g, 0.38 mole) and cooled in an ice-salt bath at -10° C. A mixture of nitric acid
(50 g, 70%) and sulfuric acid (100 g, 95%) was cooled to 0°C, then added to the rapidly stirred cumene over a two hour period. After all the acid was added the reaction mixture was stirred at 0°C for one hour. The resulting two phase mixture was poured into a separatory funnel, the acid layer discarded and 100 ml of water was added cautiously. The reaction mixture was washed with two more 100 ml portions of water, then diluted with 300 ml of ethyl ether. The organic solution was washed with water (50 ml, 3 times), saturated aqueous sodium bicarbonate (50 ml, 3 times), then dried over anhydrous magnesium sulfate. Filtration, flash distillation to remove solvent and distillation at reduced pressure yielded a mixture of 2-(p-nitropheryl)-propane and 2-(o-nitropheryl)-propane (48 g, bp. 85-120°C/9 torr) collected in two fractions. Nmr showed that the higher boiling fraction was mostly the para-derivative. The entire mixture was redistilled three times, each time discarding the first 5 ml of distillate (bp. 92-110°C/2.2 torr). After the third distillation the product was greater than 95% 2-(p-nitrophenyl)-propane (30 g, 45%, bp. 100-110°C/2.2 torr, Lit. 80 128°C/12 torr). The proton and carbon-13 nmr parameters (Tables 27 and 28) were in accord with the predicted structure.

2-bromo-2-(p-nitropheryl)-propane.81—A 100 ml round bottom flask equipped with a magnetic stirring bar and condenser was charged with N-bromosuccinimide (6.38 g, 35 mmol), a solution of 2-(p-nitrophenyl)-propane (5.86 g, 35 mmol) in 16 ml of carbon tetrachloride and benzoyl peroxide (41 mg). The mixture was refluxed for 6 hours, cooled to
room temperature, filtered from the succinimide and the carbon tetrachloride removed by flash distillation. The resulting red oil (7.5 g, 86%) was used without further purification in the next step.

2-(p-nitrophenyl)-propene.\textsuperscript{81}--The red oil was dissolved in 50 ml of 10% potassium hydroxide in ethanol in a 100 ml round bottom flask and stirred at room temperature for 3 days. The solution was filtered to remove potassium bromide, reduced to one-half its volume and diluted with 200 ml of water. This ethanol-water solution was extracted with three 100 ml portions of ethyl ether. The combined ether extracts were washed with water (50 ml, 5 times). The ether solution was neutral to litmus paper. The ether solution was washed with saturated aqueous sodium chloride (50 ml, once) and filtered through a cone of anhydrous magnesium sulfate. Flash evaporation of ether and distillation through a 2 inch Vigreux column gave a yellow oil which solidified in the receiver (2.46 g, 50%, mp. 41-46°). A 1.5 g portion was recrystallized from anhydrous ethanol then dried in a vacuum dissicator over anhydrous calcium chloride to give 0.92 g (19%) of 2-(p-nitrophenyl)-propene (mp 54-55°, Lit.\textsuperscript{81} 54-55°). Table 25 list the proton chemical shifts.

phenyldimethylchlorosilane.\textsuperscript{82}--A solution of phenylmagnesium bromide in a 250 ml round bottom flask was prepared from phenylbromide (17.3 g, 0.11 mole) and magnesium turnings (3.9 g, 0.12 g-atom) in 100 ml of ethyl ether. This solution was added via syringe to a solution of dimethyl dichlorosilane (19.5 g, 0.15 mole) in 100 ml of ethyl ether at 0° C. The reaction mixture was warmed to room
temperature and the ethyl ether removed by distillation. Excess dimethyldichlorosilane was distilled at atmospheric pressure (bp. 68-72°C, Lit. 70.5°C) through a 6 inch Vigreux column, the residue cooled to room temperature, and the pressure reduced to ca. 10 torr. Distillation at this pressure gave phenyldimethylchlorosilane (13.1 g, 70%, bp. 70-80°C/10 torr, Lit. 198-201°C/760 torr). The carbon spectrum agreed with the published data (Table 28).

2-(p-dimethyl(phenylsilyl)-propene. —To a solution of 2-(p-lithiophenyl)-propene (50 mmol) prepared as described previously was added a solution of dimethylphenylchlorosilane (8.5 g, 50 mmol) in 25 ml of ethyl ether at 0°C. The reaction mixture was warmed to room temperature and stirred for one hour. The precipitated lithium chloride was dissolved by adding 100 ml of water. Separation of the two phases followed by the normal work-up (see preparation of 2-(p-trimethylsilylphenyl)-propene) gave 2-(p-dimethylphenylsilyl)-propene (7.6 g, 60%, bp. 110-125°C/0.1 torr). Tables 26 and 27 display the nmr parameters.
REFERENCES

13. G. J. Murphy, Massachusetts Institute of Technology, 1972, Private Communication.
43. G. Fraenkel and B. Hidy, The Ohio State University, unpublished results.
53. ibid., pp. 751-2.


APPENDIX A

Density Matrix Equations for a Four Spin System Undergoing Mutual Exchange.

\[
[\dot{\rho}_{i,j} = i\hbar \omega_i \omega_j \sum_s \langle i | J | j \rangle]
\]

\[
\begin{align*}
\dot{\rho}_{1,2} &= \rho_{1,2} \left[ i(\omega - \omega_D) - \frac{J_{AD}}{2} - \frac{J_{BD}}{2} - \frac{J_{CD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{1,3} \left( \frac{iJ_{CD}}{2} + \frac{1}{\tau} \right) \\
&+ \rho_{1,4} \left( \frac{iJ_{BD}}{2} \right) + \rho_{1,5} \left( \frac{iJ_{AD}}{2} \right) = 1
\end{align*}
\]

\[
\begin{align*}
\dot{\rho}_{1,3} &= \rho_{1,3} \left[ i(\omega - \omega_C) - \frac{J_{AC}}{2} - \frac{J_{BC}}{2} - \frac{J_{CD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{1,2} \left( \frac{iJ_{CD}}{2} + \frac{1}{\tau} \right) \\
&+ \rho_{1,4} \left( \frac{iJ_{BC}}{2} \right) + \rho_{1,5} \left( \frac{iJ_{AC}}{2} \right) = 1
\end{align*}
\]

\[
\begin{align*}
\dot{\rho}_{1,4} &= \rho_{1,4} \left[ i(\omega - \omega_B) - \frac{J_{AB}}{2} - \frac{J_{BC}}{2} - \frac{J_{CD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{1,3} \left( \frac{iJ_{AB}}{2} + \frac{1}{\tau} \right) \\
&+ \rho_{1,2} \left( \frac{iJ_{BD}}{2} \right) + \rho_{1,5} \left( \frac{iJ_{BC}}{2} \right) = 1
\end{align*}
\]

\[
\begin{align*}
\dot{\rho}_{1,5} &= \rho_{1,5} \left[ i(\omega - \omega_A) - \frac{J_{AB}}{2} - \frac{J_{AC}}{2} - \frac{J_{AD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{1,4} \left( \frac{iJ_{AB}}{2} + \frac{1}{\tau} \right) \\
&+ \rho_{1,2} \left( \frac{iJ_{AD}}{2} \right) + \rho_{1,3} \left( \frac{iJ_{AC}}{2} \right) = 1
\end{align*}
\]
\[ \dot{p}_{2,8} = p_{2,8}[i(\omega - \omega_C - \frac{\text{JAC}}{2} - \frac{\text{JBC}}{2} - \frac{\text{JCD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau}] + p_{3,8}(\frac{1}{\tau} - \frac{i\text{JCD}}{2}) \\
+ p_{2,7}(\frac{i\text{JBC}}{2}) + p_{2,9}(\frac{i\text{JBD}}{2}) + p_{2,10}(\frac{i\text{JAC}}{2}) + p_{2,10}(\frac{i\text{JAD}}{2}) \\
- p_{4,8}(\frac{i\text{JAD}}{2}) - p_{5,8}(\frac{i\text{JAD}}{2}) = 0 \]

\[ \dot{p}_{2,7} = p_{2,7}[i(\omega - \omega_B - \frac{\text{JAB}}{2} - \frac{\text{JAC}}{2} - \frac{\text{JBD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau}] + p_{3,10}(\frac{1}{\tau}) \\
+ p_{2,8}(\frac{i\text{JBC}}{2}) + p_{2,9}(\frac{i\text{JBD}}{2}) + p_{2,10}(\frac{i\text{JAB}}{2}) + p_{2,10}(\frac{i\text{JAD}}{2}) \\
- p_{3,7}(\frac{i\text{JCD}}{2}) - p_{4,7}(\frac{i\text{JBD}}{2}) - p_{5,7}(\frac{i\text{JAD}}{2}) = 0 \]

\[ \dot{p}_{2,8} = p_{2,8}[i(\omega - \omega_B - \omega_D - \text{JAS} - \frac{\text{JAC}}{2} - \frac{\text{JAD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau}] + p_{3,9}(\frac{1}{\tau}) \\
+ p_{2,8}(\frac{i\text{JBD}}{2}) + p_{2,7}(\frac{i\text{JCD}}{2}) + p_{2,10}(\frac{i\text{JAB}}{2}) + p_{2,11}(\frac{i\text{JAC}}{2}) \\
- p_{3,8}(\frac{i\text{JCD}}{2}) - p_{4,8}(\frac{i\text{JBD}}{2}) - p_{5,8}(\frac{i\text{JAD}}{2}) = 0 \]
\[
\rho_{2,9} [i(w - w_A - \frac{J_{AB}}{2} - \frac{J_{AC}}{2} - \frac{J_{AD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{3,8} (\frac{1}{\tau})
\]

\[
+ \rho_{2,8} (\frac{iJ_{AC}}{2}) + \rho_{2,7} (\frac{iJ_{AB}}{2}) + \rho_{2,10} (\frac{iJ_{AB}}{2}) + \rho_{2,11} (\frac{iJ_{BD}}{2})
\]

\[
- \rho_{3,9} (\frac{iJ_{CD}}{2}) - \rho_{4,9} (\frac{iJ_{BD}}{2}) - \rho_{5,9} (\frac{iJ_{AD}}{2}) =
\]

\[
\rho_{2,10} [i(w - w_A - w_C + w_B - \frac{J_{AB}}{2} - \frac{J_{BC}}{2} - \frac{J_{BD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{3,7} (\frac{1}{\tau})
\]

\[
+ \rho_{2,8} (\frac{iJ_{AD}}{2}) + \rho_{2,8} (\frac{iJ_{AB}}{2}) + \rho_{2,8} (\frac{iJ_{CD}}{2}) + \rho_{2,11} (\frac{iJ_{BC}}{2})
\]

\[
- \rho_{3,10} (\frac{iJ_{CD}}{2}) - \rho_{4,10} (\frac{iJ_{BD}}{2}) - \rho_{5,10} (\frac{iJ_{AD}}{2}) =
\]

\[
\rho_{2,11} [i(w - w_A - w_B - w_C - \frac{J_{AC}}{2} - \frac{J_{BC}}{2} + \frac{J_{CD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{3,11} (\frac{1}{\tau})
\]

\[
+ \rho_{2,7} (\frac{iJ_{AD}}{2}) + \rho_{2,8} (\frac{iJ_{AB}}{2}) + \rho_{2,8} (\frac{iJ_{BD}}{2}) + \rho_{2,10} (\frac{iJ_{BC}}{2})
\]

\[
- \rho_{3,11} (\frac{iJ_{CD}}{2}) - \rho_{4,11} (\frac{iJ_{BD}}{2}) - \rho_{5,11} (\frac{iJ_{AD}}{2}) =
\]
\[ \dot{\rho}_{3,8} = \rho_{3,9}[i(w - w_B - \frac{J_{\text{AD}}}{2} - \frac{J_{\text{BD}}}{2} + \frac{J_{\text{CD}}}{2}) - \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{3,11}\left(\frac{1}{\tau}\right) \\
+ \rho_{3,7}\left(\frac{iJ_{\text{BC}}}{2}\right) + \rho_{3,8}\left(\frac{iJ_{\text{BD}}}{2}\right) + \rho_{3,9}\left(\frac{iJ_{\text{AC}}}{2}\right) + \rho_{3,10}\left(\frac{iJ_{\text{AD}}}{2}\right) \\
- \rho_{2,8}\left(\frac{iJ_{\text{CD}}}{2}\right) - \rho_{4,8}\left(\frac{iJ_{\text{BC}}}{2}\right) - \rho_{5,8}\left(\frac{iJ_{\text{AC}}}{2}\right) = \]

\[ \dot{\rho}_{3,7} = \rho_{3,7}[i(w - w_B + w_C - w_D - \frac{J_{\text{AB}}}{2} + \frac{J_{\text{AC}}}{2} - \frac{J_{\text{AD}}}{2}) - \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{2,10}\left(\frac{1}{\tau}\right) \\
+ \rho_{3,7}\left(\frac{iJ_{\text{BC}}}{2}\right) + \rho_{3,8}\left(\frac{iJ_{\text{CD}}}{2}\right) + \rho_{3,9}\left(\frac{iJ_{\text{AB}}}{2}\right) + \rho_{3,10}\left(\frac{iJ_{\text{AD}}}{2}\right) \\
- \rho_{2,7}\left(\frac{iJ_{\text{CD}}}{2}\right) - \rho_{4,7}\left(\frac{iJ_{\text{BC}}}{2}\right) - \rho_{5,7}\left(\frac{iJ_{\text{AC}}}{2}\right) = \]

\[ \dot{\rho}_{3,8} = \rho_{3,9}[i(w - w_B + \frac{J_{\text{AB}}}{2} + \frac{J_{\text{BC}}}{2} - \frac{J_{\text{BD}}}{2}) - \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{2,8}\left(\frac{1}{\tau}\right) \\
+ \rho_{3,7}\left(\frac{iJ_{\text{BD}}}{2}\right) + \rho_{3,8}\left(\frac{iJ_{\text{CD}}}{2}\right) + \rho_{3,9}\left(\frac{iJ_{\text{AC}}}{2}\right) + \rho_{3,10}\left(\frac{iJ_{\text{AD}}}{2}\right) \\
- \rho_{2,8}\left(\frac{iJ_{\text{CD}}}{2}\right) - \rho_{4,8}\left(\frac{iJ_{\text{BC}}}{2}\right) - \rho_{5,8}\left(\frac{iJ_{\text{AC}}}{2}\right) = \]
\begin{align*}
\dot{\rho}_{3,9} &= \rho_{3,9} \left[ i \left( \omega - \omega_A + \omega_C - \frac{J_{AB}}{2} + \frac{J_{BC}}{2} - \frac{J_{BD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right) \right] + \rho_{2,9} \left( \frac{1}{\tau} \right) \\
&\quad + \rho_{3,9} \left( \frac{iJ_{AC}}{2} \right) + \rho_{3,7} \left( \frac{iJ_{AB}}{2} \right) + \rho_{3,10} \left( \frac{iJ_{CD}}{2} \right) + \rho_{3,11} \left( \frac{iJ_{BD}}{2} \right) \\
&\quad - \rho_{2,9} \left( \frac{iJ_{CD}}{2} \right) - \rho_{4,9} \left( \frac{iJ_{BC}}{2} \right) - \rho_{5,9} \left( \frac{iJ_{AC}}{2} \right) = \\
\dot{\rho}_{3,10} &= \rho_{3,10} \left[ i \left( \omega - \omega_A - \frac{J_{AB}}{2} + \frac{J_{AC}}{2} - \frac{J_{AD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right) \right] + \rho_{2,7} \left( \frac{1}{\tau} \right) \\
&\quad + \rho_{3,8} \left( \frac{iJ_{AD}}{2} \right) + \rho_{3,9} \left( \frac{iJ_{AB}}{2} \right) + \rho_{3,9} \left( \frac{iJ_{CD}}{2} \right) + \rho_{3,11} \left( \frac{iJ_{BC}}{2} \right) \\
&\quad - \rho_{2,10} \left( \frac{iJ_{CD}}{2} \right) - \rho_{4,10} \left( \frac{iJ_{BC}}{2} \right) - \rho_{5,10} \left( \frac{iJ_{AC}}{2} \right) = \\
\dot{\rho}_{3,11} &= \rho_{3,11} \left[ i \left( \omega - \omega_A - \omega_B + \omega_C - \frac{J_{AD}}{2} - \frac{J_{BD}}{2} + \frac{J_{CD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right) \right] + \rho_{2,11} \left( \frac{1}{\tau} \right) \\
&\quad + \rho_{3,7} \left( \frac{iJ_{AD}}{2} \right) + \rho_{3,8} \left( \frac{iJ_{AC}}{2} \right) + \rho_{3,9} \left( \frac{iJ_{BD}}{2} \right) + \rho_{3,10} \left( \frac{iJ_{BC}}{2} \right) \\
&\quad - \rho_{2,11} \left( \frac{iJ_{CD}}{2} \right) - \rho_{4,11} \left( \frac{iJ_{BC}}{2} \right) - \rho_{5,11} \left( \frac{iJ_{AC}}{2} \right) =
\end{align*}
\[ \rho_{4,8} [i(\omega - \omega_c - \omega_B - \omega_D + \frac{J_{AB}}{2} - \frac{J_{AC}}{2} - \frac{J_{BD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{5,8}(\frac{1}{\tau}) \]

\[ + \rho_{4,7}(\frac{iJ_{BC}}{2}) + \rho_{4,8}(\frac{iJ_{BD}}{2}) + \rho_{4,9}(\frac{iJ_{AC}}{2}) + \rho_{4,10}(\frac{iJ_{AD}}{2}) \]

\[ - \rho_{2,8}(\frac{iJ_{CD}}{2}) - \rho_{3,8}(\frac{iJ_{BC}}{2}) - \rho_{5,8}(\frac{iJ_{AC}}{2}) = \]

\[ \rho_{4,7} [i(\omega - \omega_B - \omega_D + \frac{J_{AD}}{2} + \frac{J_{BD}}{2} - \frac{J_{CD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{5,10}(\frac{1}{\tau}) \]

\[ + \rho_{4,8}(\frac{iJ_{BC}}{2}) + \rho_{4,9}(\frac{iJ_{CD}}{2}) + \rho_{4,10}(\frac{iJ_{AB}}{2}) + \rho_{4,11}(\frac{iJ_{AD}}{2}) \]

\[ - \rho_{2,7}(\frac{iJ_{BD}}{2}) - \rho_{3,7}(\frac{iJ_{BC}}{2}) - \rho_{5,7}(\frac{iJ_{AB}}{2}) = \]

\[ \rho_{4,8} [i(\omega - \omega_C - \omega_D + \frac{J_{AC}}{2} + \frac{J_{BC}}{2} - \frac{J_{CD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{5,9}(\frac{1}{\tau}) \]

\[ + \rho_{4,7}(\frac{iJ_{BD}}{2}) + \rho_{4,8}(\frac{iJ_{CD}}{2}) + \rho_{4,10}(\frac{iJ_{AB}}{2}) + \rho_{4,11}(\frac{iJ_{AC}}{2}) \]

\[ - \rho_{2,8}(\frac{iJ_{CD}}{2}) - \rho_{3,8}(\frac{iJ_{BC}}{2}) - \rho_{5,8}(\frac{iJ_{AB}}{2}) = \]
\[ \dot{\rho}_{4,9} = \rho_{4,9} \left[ i (w - w_A + \omega_B - \omega_D - \frac{J_{AC}}{2} - \frac{J_{BC}}{2} - \frac{J_{CD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{5,9} \left( \frac{i}{2} \right) \\
+ \rho_{4,6} \left( \frac{i J_{AC}}{2} \right) + \rho_{4,7} \left( \frac{i J_{AB}}{2} \right) + \rho_{4,10} \left( \frac{i J_{CD}}{2} \right) + \rho_{4,11} \left( \frac{i J_{BD}}{2} \right) \\
- \rho_{2,6} \left( \frac{i J_{BD}}{2} \right) - \rho_{3,9} \left( \frac{i J_{BC}}{2} \right) - \rho_{5,9} \left( \frac{i J_{AB}}{2} \right) = 0 \]

\[ \dot{\rho}_{4,10} = \rho_{4,10} \left[ i (w - w_A + \omega_B - \omega_C - \frac{J_{AD}}{2} + \frac{J_{BD}}{2} - \frac{J_{CD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{5,10} \left( \frac{i}{2} \right) \\
+ \rho_{4,6} \left( \frac{i J_{AD}}{2} \right) + \rho_{4,8} \left( \frac{i J_{AB}}{2} \right) + \rho_{4,9} \left( \frac{i J_{CD}}{2} \right) + \rho_{4,11} \left( \frac{i J_{BC}}{2} \right) \\
- \rho_{2,10} \left( \frac{i J_{BD}}{2} \right) - \rho_{3,10} \left( \frac{i J_{BC}}{2} \right) - \rho_{5,10} \left( \frac{i J_{AB}}{2} \right) = 0 \]

\[ \dot{\rho}_{4,11} = \rho_{4,11} \left[ i (w - w_A + \frac{J_{AB}}{2} + \frac{J_{AC}}{2} - \frac{J_{AD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{5,11} \left( \frac{i}{2} \right) \\
+ \rho_{4,7} \left( \frac{i J_{AD}}{2} \right) + \rho_{4,8} \left( \frac{i J_{AC}}{2} \right) + \rho_{4,9} \left( \frac{i J_{BC}}{2} \right) + \rho_{4,10} \left( \frac{i J_{BD}}{2} \right) \\
- \rho_{2,11} \left( \frac{i J_{BD}}{2} \right) - \rho_{3,11} \left( \frac{i J_{BC}}{2} \right) - \rho_{5,11} \left( \frac{i J_{AB}}{2} \right) = 1 \]
\[ \begin{align*}
\dot{\rho}_{5,8} &= \rho_{5,8}[1(\omega + \omega_A - \omega_B - \omega_C - \omega_D + J_{AB} - J_{BC} - J_{CD}) \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{4,8}(\frac{1}{\tau}) \\
&+ \rho_{5,8,7}(\frac{iJ_{BC}}{2}) + \rho_{5,8,6}(\frac{iJ_{BD}}{2}) + \rho_{5,8,1}(\frac{iJ_{AC}}{2}) + \rho_{5,8,10}(\frac{iJ_{AD}}{2}) \\
&- \rho_{2,8,7}(\frac{iJ_{AD}}{2}) + \rho_{3,8,6}(\frac{iJ_{AC}}{2}) - \rho_{4,8,5}(\frac{iJ_{AB}}{2}) \\

\dot{\rho}_{5,7} &= \rho_{5,7}[1(\omega + \omega_A - \omega_B - \omega_C + J_{AC} - J_{BC} - J_{CD}) \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{4,10}(\frac{1}{\tau}) \\
&+ \rho_{5,7,6}(\frac{iJ_{BC}}{2}) + \rho_{5,7,5}(\frac{iJ_{CD}}{2}) + \rho_{5,7,1}(\frac{iJ_{AC}}{2}) + \rho_{5,7,10}(\frac{iJ_{AD}}{2}) \\
&- \rho_{2,7,6}(\frac{iJ_{AD}}{2}) - \rho_{3,7,5}(\frac{iJ_{AC}}{2}) - \rho_{4,7,4}(\frac{iJ_{AB}}{2}) \\

\dot{\rho}_{5,8} &= \rho_{5,8}[1(\omega + \omega_A - \omega_B - \omega_C + J_{AD} - J_{BD} - J_{CD}) \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{4,9}(\frac{1}{\tau}) \\
&+ \rho_{5,8,7}(\frac{iJ_{AC}}{2}) + \rho_{5,8,6}(\frac{iJ_{CD}}{2}) + \rho_{5,8,1}(\frac{iJ_{AB}}{2}) + \rho_{5,8,11}(\frac{iJ_{AD}}{2}) \\
&- \rho_{2,8,6}(\frac{iJ_{AD}}{2}) - \rho_{3,8,5}(\frac{iJ_{AC}}{2}) - \rho_{4,8,4}(\frac{iJ_{AB}}{2}) \\
\end{align*} \]
\[ \dot{\rho}_{5,9} = \rho_{5,9} \left[ \frac{i(w - \omega_D)}{2} + \frac{J_{AD}}{2} - \frac{J_{BD}}{2} - \frac{J_{CD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{4,9} \left( \frac{1}{2} \right) \]
\[ + \rho_{5,6} \left( \frac{iJ_{AC}}{2} \right) + \rho_{5,7} \left( \frac{iJ_{AB}}{2} \right) + \rho_{5,10} \left( \frac{iJ_{CD}}{2} \right) + \rho_{5,11} \left( \frac{iJ_{BD}}{2} \right) \]
\[ - \rho_{2,9} \left( \frac{iJ_{AD}}{2} \right) - \rho_{3,9} \left( \frac{iJ_{AC}}{2} \right) - \rho_{4,9} \left( \frac{iJ_{AB}}{2} \right) = \]

\[ \dot{\rho}_{5,10} = \rho_{5,10} \left[ \frac{i(w - \omega_C)}{2} + \frac{J_{AC}}{2} - \frac{J_{BC}}{2} - \frac{J_{CD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{4,10} \left( \frac{1}{2} \right) \]
\[ + \rho_{5,6} \left( \frac{iJ_{AD}}{2} \right) + \rho_{5,8} \left( \frac{iJ_{AB}}{2} \right) + \rho_{5,9} \left( \frac{iJ_{CD}}{2} \right) + \rho_{5,11} \left( \frac{iJ_{BC}}{2} \right) \]
\[ - \rho_{2,10} \left( \frac{iJ_{AD}}{2} \right) - \rho_{3,10} \left( \frac{iJ_{AC}}{2} \right) + \rho_{4,10} \left( \frac{iJ_{AB}}{2} \right) = \]

\[ \dot{\rho}_{5,11} = \rho_{5,11} \left[ \frac{i(w - \omega_B)}{2} + \frac{J_{AB}}{2} - \frac{J_{BC}}{2} - \frac{J_{BD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{4,11} \left( \frac{1}{2} \right) \]
\[ + \rho_{5,7} \left( \frac{iJ_{AD}}{2} \right) + \rho_{5,8} \left( \frac{iJ_{AC}}{2} \right) + \rho_{5,9} \left( \frac{iJ_{BD}}{2} \right) + \rho_{5,10} \left( \frac{iJ_{BC}}{2} \right) \]
\[ - \rho_{2,11} \left( \frac{iJ_{AD}}{2} \right) - \rho_{3,11} \left( \frac{iJ_{AC}}{2} \right) - \rho_{4,11} \left( \frac{iJ_{AB}}{2} \right) = \]
\[ \dot{\rho}_{e,12} = \rho_{e,12} \left[ \frac{1}{2}(w - w_B - \frac{J_{AB}}{2} + \frac{J_{BC}}{2} + \frac{J_{BD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{e,13} \left( \frac{1}{\tau} \right) + \rho_{e,13} \left( \frac{J_{AB}}{2} \right) + \rho_{e,14} \left( \frac{J_{AC}}{2} \right) + \rho_{e,15} \left( \frac{J_{AD}}{2} \right) - \rho_{7,12} \left( \frac{J_{BC}}{2} \right) - \rho_{8,12} \left( \frac{J_{BD}}{2} \right) - \rho_{9,12} \left( \frac{J_{AC}}{2} \right) - \rho_{10,12} \left( \frac{J_{AD}}{2} \right) = \]

\[ \dot{\rho}_{e,13} = \rho_{e,13} \left[ \frac{1}{2}(w - w_A - \frac{J_{AB}}{2} + \frac{J_{AC}}{2} + \frac{J_{AD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{e,12} \left( \frac{1}{\tau} \right) + \rho_{e,12} \left( \frac{J_{AB}}{2} \right) + \rho_{e,14} \left( \frac{J_{BC}}{2} \right) + \rho_{e,15} \left( \frac{J_{BD}}{2} \right) - \rho_{7,13} \left( \frac{J_{BC}}{2} \right) - \rho_{8,13} \left( \frac{J_{BD}}{2} \right) - \rho_{9,13} \left( \frac{J_{AC}}{2} \right) - \rho_{10,13} \left( \frac{J_{AD}}{2} \right) = \]

\[ \dot{\rho}_{e,14} = \rho_{e,14} \left[ \frac{1}{2}(w - w_A - w_B + w_C + \frac{J_{AD}}{2} + \frac{J_{BD}}{2} - \frac{J_{CD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{e,15} \left( \frac{1}{\tau} \right) + \rho_{e,12} \left( \frac{J_{AC}}{2} \right) + \rho_{e,13} \left( \frac{J_{BC}}{2} \right) + \rho_{e,15} \left( \frac{J_{CD}}{2} \right) - \rho_{7,14} \left( \frac{J_{BC}}{2} \right) - \rho_{8,14} \left( \frac{J_{BD}}{2} \right) - \rho_{9,14} \left( \frac{J_{AC}}{2} \right) - \rho_{10,14} \left( \frac{J_{AD}}{2} \right) = \]
\[
\dot{\rho}_{e,15} = \rho_{e,15}\left[i(w - w_A - w_B + w_D + \frac{J_{AC}}{2} + \frac{J_{BC}}{2} - \frac{J_{CD}}{2} - \frac{1}{T_2} - \frac{1}{\tau}) + \rho_{e,14}\left(\frac{1}{\tau}\right)\right] \\
+ \rho_{e,12}\left(\frac{iJ_{AD}}{2}\right) + \rho_{e,13}\left(\frac{iJ_{BD}}{2}\right) + \rho_{e,14}\left(\frac{iJ_{CD}}{2}\right) \\
- \rho_{7,15}\left(\frac{iJ_{BC}}{2}\right) - \rho_{e,15}\left(\frac{iJ_{BD}}{2}\right) - \rho_{e,15}\left(\frac{iJ_{AC}}{2}\right) - \rho_{10,15}\left(\frac{iJ_{AD}}{2}\right) = 0
\]

\[
\dot{\rho}_{7,12} = \rho_{7,12}\left[i(w - w_C - \frac{J_{AC}}{2} + \frac{J_{BC}}{2} + \frac{J_{CD}}{2} - \frac{1}{T_2} - \frac{1}{\tau}) + \rho_{10,15}\left(\frac{1}{\tau}\right)\right] \\
+ \rho_{7,13}\left(\frac{iJ_{AB}}{2}\right) + \rho_{7,14}\left(\frac{iJ_{AC}}{2}\right) + \rho_{7,15}\left(\frac{iJ_{AD}}{2}\right) \\
- \rho_{e,12}\left(\frac{iJ_{BC}}{2}\right) - \rho_{e,12}\left(\frac{iJ_{CD}}{2}\right) - \rho_{e,12}\left(\frac{iJ_{AB}}{2}\right) - \rho_{11,12}\left(\frac{iJ_{AD}}{2}\right) = 0
\]

\[
\dot{\rho}_{7,13} = \rho_{7,13}\left[i(w - w_A + w_B - w_C + \frac{J_{AD}}{2} - \frac{J_{BD}}{2} + \frac{J_{CD}}{2} - \frac{1}{T_2} - \frac{1}{\tau}) + \rho_{10,12}\left(\frac{1}{\tau}\right)\right] \\
+ \rho_{7,12}\left(\frac{iJ_{AB}}{2}\right) + \rho_{7,14}\left(\frac{iJ_{BC}}{2}\right) + \rho_{7,15}\left(\frac{iJ_{BD}}{2}\right) \\
- \rho_{e,13}\left(\frac{iJ_{BC}}{2}\right) - \rho_{e,13}\left(\frac{iJ_{CD}}{2}\right) - \rho_{e,13}\left(\frac{iJ_{AB}}{2}\right) - \rho_{11,13}\left(\frac{iJ_{AD}}{2}\right) = 0
\]
\[
\dot{\rho}_{7,14} = \rho_{7,14}[i(\omega - \omega_A + \frac{J_{AB}}{2} - \frac{J_{AC}}{2} + \frac{J_{AD}}{2}) - \frac{1}{T_2} - \frac{1}{T}] + \rho_{10,15}(\frac{1}{T})
\]

\[
+ \rho_{7,12}(\frac{iJ_{AC}}{2}) + \rho_{7,13}(\frac{iJ_{BC}}{2}) + \rho_{7,15}(\frac{iJ_{CD}}{2})
\]

\[
- \rho_{8,14}(\frac{iJ_{BC}}{2}) - \rho_{8,14}(\frac{iJ_{CD}}{2}) - \rho_{9,14}(\frac{iJ_{AB}}{2}) - \rho_{11,14}(\frac{iJ_{AD}}{2})
\]

\[
\dot{\rho}_{7,15} = \rho_{7,15}[i(\omega - \omega_A - \omega_C + \omega_D + \frac{J_{AB}}{2} + \frac{J_{BC}}{2} - \frac{J_{CD}}{2}) - \frac{1}{T_2} - \frac{1}{T}] + \rho_{10,14}(\frac{1}{T})
\]

\[
+ \rho_{7,12}(\frac{iJ_{AD}}{2}) + \rho_{7,13}(\frac{iJ_{BD}}{2}) + \rho_{7,14}(\frac{iJ_{CD}}{2})
\]

\[
- \rho_{8,15}(\frac{iJ_{BC}}{2}) - \rho_{8,15}(\frac{iJ_{CD}}{2}) - \rho_{9,15}(\frac{iJ_{AB}}{2}) - \rho_{11,15}(\frac{iJ_{AD}}{2})
\]

\[
\dot{\rho}_{8,12} = \rho_{8,12}[i(\omega - \omega_D - \frac{J_{AD}}{2} + \frac{J_{BD}}{2} + \frac{J_{CD}}{2}) - \frac{1}{T_2} - \frac{1}{T}] + \rho_{9,13}(\frac{1}{T})
\]

\[
+ \rho_{8,12}(\frac{iJ_{AB}}{2}) + \rho_{8,14}(\frac{iJ_{AC}}{2}) + \rho_{8,15}(\frac{iJ_{AD}}{2}) - \rho_{8,12}(\frac{iJ_{BD}}{2})
\]

\[
- \rho_{7,12}(\frac{iJ_{CD}}{2}) - \rho_{10,12}(\frac{iJ_{AB}}{2}) - \rho_{11,12}(\frac{iJ_{AC}}{2})
\]
\[ \dot{p}_{8,13} \left[ \frac{1}{2} (w - w_A + w_B - w_D + \frac{J_{AC}}{2} - \frac{J_{BC}}{2} + \frac{J_{CD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau} \right] + p_{9,12} \left( \frac{1}{\tau} \right) = 0 \]

\[ + p_{8,12} \left( \frac{iJ_{AB}}{2} \right) + p_{8,14} \left( \frac{iJ_{BC}}{2} \right) + p_{3,15} \left( \frac{iJ_{CD}}{2} \right) \]

\[ - p_{8,13} \left( \frac{iJ_{BD}}{2} \right) - p_{7,13} \left( \frac{iJ_{CD}}{2} \right) - p_{10,13} \left( \frac{iJ_{AB}}{2} \right) - p_{11,13} \left( \frac{iJ_{AC}}{2} \right) = \]

\[ \dot{p}_{8,14} \left[ \frac{1}{2} (w - w_A + w_C - w_D + \frac{J_{AB}}{2} - \frac{J_{BC}}{2} + \frac{J_{BD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau} \right] + p_{8,15} \left( \frac{1}{\tau} \right) = 0 \]

\[ + p_{8,12} \left( \frac{iJ_{AC}}{2} \right) + p_{8,13} \left( \frac{iJ_{BC}}{2} \right) + p_{3,15} \left( \frac{iJ_{CD}}{2} \right) \]

\[ - p_{8,14} \left( \frac{iJ_{BD}}{2} \right) - p_{7,14} \left( \frac{iJ_{CD}}{2} \right) - p_{10,14} \left( \frac{iJ_{AB}}{2} \right) - p_{11,14} \left( \frac{iJ_{AC}}{2} \right) = \]

\[ \dot{p}_{8,15} \left[ \frac{1}{2} (w - w_A + \frac{J_{AB}}{2} + \frac{J_{AC}}{2} - \frac{J_{AD}}{2}) - \frac{1}{T_2} - \frac{1}{\tau} \right] + p_{9,14} \left( \frac{1}{\tau} \right) = 1 \]

\[ + p_{8,12} \left( \frac{iJ_{AD}}{2} \right) + p_{8,13} \left( \frac{iJ_{BD}}{2} \right) + p_{8,14} \left( \frac{iJ_{CD}}{2} \right) \]

\[ - p_{8,15} \left( \frac{iJ_{BD}}{2} \right) - p_{7,15} \left( \frac{iJ_{CD}}{2} \right) - p_{10,15} \left( \frac{iJ_{AB}}{2} \right) - p_{11,15} \left( \frac{iJ_{AC}}{2} \right) = \]
\[ \dot{\rho}_{9,12} = \rho_{9,12} \left[ i(w + w_A - w_B - w_C - J_{AD} - J_{BD} + J_{CD}) - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{8,13} \left( \frac{1}{\tau} \right) \\
+ \rho_{8,13} \left( \frac{iJ_{AB}}{2} \right) + \rho_{8,14} \left( \frac{iJ_{AC}}{2} \right) + \rho_{9,15} \left( \frac{iJ_{AD}}{2} \right) \\
- \rho_{8,12} \left( \frac{iJ_{AC}}{2} \right) - \rho_{7,12} \left( \frac{iJ_{AB}}{2} \right) - \rho_{10,12} \left( \frac{iJ_{CD}}{2} \right) - \rho_{11,12} \left( \frac{iJ_{BD}}{2} \right) = \]

\[ \dot{\rho}_{9,13} = \rho_{9,13} \left[ i(w - w_C + J_{AC} - J_{BC} + J_{CD}) - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{8,12} \left( \frac{1}{\tau} \right) \\
+ \rho_{8,12} \left( \frac{iJ_{AB}}{2} \right) + \rho_{8,14} \left( \frac{iJ_{BC}}{2} \right) + \rho_{9,15} \left( \frac{iJ_{BD}}{2} \right) \\
- \rho_{8,13} \left( \frac{iJ_{AC}}{2} \right) - \rho_{7,13} \left( \frac{iJ_{AB}}{2} \right) - \rho_{10,13} \left( \frac{iJ_{CD}}{2} \right) - \rho_{11,13} \left( \frac{iJ_{BD}}{2} \right) = \]

\[ \dot{\rho}_{9,14} = \rho_{9,14} \left[ i(w - w_B + J_{AB} - J_{BC} + J_{HD}) - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{8,15} \left( \frac{1}{\tau} \right) \\
+ \rho_{9,12} \left( \frac{iJ_{AC}}{2} \right) + \rho_{9,13} \left( \frac{iJ_{BC}}{2} \right) + \rho_{9,15} \left( \frac{iJ_{CD}}{2} \right) \\
- \rho_{8,14} \left( \frac{iJ_{AC}}{2} \right) - \rho_{7,14} \left( \frac{iJ_{AB}}{2} \right) - \rho_{10,14} \left( \frac{iJ_{CD}}{2} \right) - \rho_{10,15} \left( \frac{iJ_{BD}}{2} \right) = \]
\[ \rho_{9,15} = \rho_{9,15}'[i(\omega - \omega_B - \omega_D + J_{AB} \frac{1}{2} + J_{AC} \frac{1}{2} - J_{AD} \frac{1}{2} - \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{8,14}(\frac{1}{\tau}) + \rho_{9,12}(\frac{iJ_{AD}}{2}) + \rho_{9,13}(\frac{iJ_{BD}}{2}) + \rho_{9,14}(\frac{iJ_{CD}}{2}) - \rho_{8,15}(\frac{iJ_{AC}}{2}) - \rho_{7,15}(\frac{iJ_{AB}}{2}) - \rho_{10,15}(\frac{iJ_{CD}}{2}) - \rho_{11,15}(\frac{iJ_{BD}}{2}) = 0 \]

\[ \rho_{10,12} = \rho_{10,12}'[i(\omega + \omega_A - \omega_B - \omega_D - J_{AC} \frac{1}{2} + J_{BC} \frac{1}{2} + J_{CD} \frac{1}{2} - \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{7,13}(\frac{1}{\tau}) + \rho_{10,13}(\frac{iJ_{AB}}{2}) + \rho_{10,14}(\frac{iJ_{AC}}{2}) + \rho(\frac{iJ_{AD}}{2}) - \rho_{8,12}(\frac{iJ_{AD}}{2}) - \rho_{8,12}(\frac{iJ_{BD}}{2}) - \rho_{9,12}(\frac{iJ_{CD}}{2}) - \rho_{11,12}(\frac{iJ_{BC}}{2}) = 0 \]

\[ \rho_{10,13} = \rho_{10,13}'[i(\omega - \omega_D + J_{AD} \frac{1}{2} - J_{BD} \frac{1}{2} + J_{CD} \frac{1}{2} - \frac{1}{T_2} - \frac{1}{\tau}] + \rho_{7,12}(\frac{1}{\tau}) + \rho_{10,12}(\frac{iJ_{AB}}{2}) + \rho_{10,14}(\frac{iJ_{BC}}{2}) + \rho_{10,15}(\frac{iJ_{BD}}{2}) - \rho_{8,13}(\frac{iJ_{AD}}{2}) - \rho_{8,13}(\frac{iJ_{AB}}{2}) - \rho_{8,13}(\frac{iJ_{CD}}{2}) - \rho_{11,13}(\frac{iJ_{BC}}{2}) = 1 \]
\[
\dot{\rho}_{11,13} = \rho_{11,13} \left[ i(\omega_B - \omega_C - \omega_D - \frac{J_{AB}}{2} + \frac{J_{AC}}{2} + \frac{J_{AD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{11,12} \left( \frac{1}{\tau} \right)
\]

\[
+ \rho_{11,12} \left(\frac{iJ_{AC}}{2}\right) + \rho_{11,14} \left(\frac{iJ_{BC}}{2}\right) + \rho_{11,15} \left(\frac{iJ_{BD}}{2}\right)
\]

\[
- \rho_{7,13} \left(\frac{iJ_{AD}}{2}\right) - \rho_{8,13} \left(\frac{iJ_{AC}}{2}\right) - \rho_{9,13} \left(\frac{iJ_{BD}}{2}\right) - \rho_{10,13} \left(\frac{iJ_{BC}}{2}\right) = 0
\]

\[
\dot{\rho}_{11,14} = \rho_{11,14} \left[ i(\omega_C - \omega_D - \frac{J_{AC}}{2} + \frac{J_{BD}}{2} - \frac{J_{CD}}{2} - \frac{1}{T_2} - \frac{1}{\tau} \right] + \rho_{11,15} \left(\frac{1}{\tau} \right)
\]

\[
+ \rho_{11,12} \left(\frac{iJ_{AD}}{2}\right) + \rho_{11,13} \left(\frac{iJ_{BC}}{2}\right) + \rho_{11,15} \left(\frac{iJ_{CD}}{2}\right)
\]

\[
- \rho_{7,14} \left(\frac{iJ_{AD}}{2}\right) - \rho_{8,14} \left(\frac{iJ_{AC}}{2}\right) - \rho_{9,14} \left(\frac{iJ_{BD}}{2}\right) - \rho_{10,14} \left(\frac{iJ_{BC}}{2}\right) = 1
\]

\[
\dot{\rho}_{11,15} = \rho_{11,15} \left[ i(\omega_C - \omega_D - \frac{J_{AC}}{2} + \frac{J_{BC}}{2} - \frac{J_{CD}}{2}) + \rho_{11,14} \left(\frac{1}{\tau} \right) \right]
\]

\[
+ \rho_{11,12} \left(\frac{iJ_{AD}}{2}\right) + \rho_{11,13} \left(\frac{iJ_{BD}}{2}\right) + \rho_{11,14} \left(\frac{iJ_{CD}}{2}\right)
\]

\[
- \rho_{7,15} \left(\frac{iJ_{AD}}{2}\right) - \rho_{8,15} \left(\frac{iJ_{AC}}{2}\right) - \rho_{9,15} \left(\frac{iJ_{BD}}{2}\right) - \rho_{10,15} \left(\frac{iJ_{BC}}{2}\right) = 1
\]
\[\begin{align*}
\dot{p}_{12,10} &= \rho_{12,10} \left[ \frac{1}{2} \left( w_B - w_A \right) + \frac{J_{AB}}{2} + \frac{J_{AC}}{2} + \frac{J_{AD}}{2} \right] - \frac{1}{2} \left[ \rho_{11,10} \left( \frac{J_{AB}}{2} \right) \right] - \frac{1}{2} \left[ \rho_{13,10} \left( \frac{J_{AC}}{2} \right) \right] - \frac{1}{2} \left[ \rho_{15,10} \left( \frac{J_{AD}}{2} \right) \right] = \\
\dot{p}_{13,10} &= \rho_{13,10} \left[ \frac{1}{2} \left( w_B - w_A \right) + \frac{J_{AB}}{2} + \frac{J_{AC}}{2} + \frac{J_{AD}}{2} \right] - \frac{1}{2} \left[ \rho_{11,10} \left( \frac{J_{AB}}{2} \right) \right] - \frac{1}{2} \left[ \rho_{14,10} \left( \frac{J_{AC}}{2} \right) \right] - \frac{1}{2} \left[ \rho_{15,10} \left( \frac{J_{AD}}{2} \right) \right] = \\
\dot{p}_{14,10} &= \rho_{14,10} \left[ \frac{1}{2} \left( w_B - w_A \right) + \frac{J_{AB}}{2} + \frac{J_{AC}}{2} + \frac{J_{AD}}{2} \right] - \frac{1}{2} \left[ \rho_{11,10} \left( \frac{J_{AB}}{2} \right) \right] - \frac{1}{2} \left[ \rho_{15,10} \left( \frac{J_{AC}}{2} \right) \right] - \frac{1}{2} \left[ \rho_{14,10} \left( \frac{J_{AD}}{2} \right) \right] = \\
\dot{p}_{15,10} &= \rho_{15,10} \left[ \frac{1}{2} \left( w_B - w_A \right) + \frac{J_{AB}}{2} + \frac{J_{AC}}{2} + \frac{J_{AD}}{2} \right] - \frac{1}{2} \left[ \rho_{11,10} \left( \frac{J_{AB}}{2} \right) \right] - \frac{1}{2} \left[ \rho_{14,10} \left( \frac{J_{AC}}{2} \right) \right] - \frac{1}{2} \left[ \rho_{15,10} \left( \frac{J_{AD}}{2} \right) \right] = \\
\end{align*}\]
APPENDIX B

Kinetic Data used to Calculate Activation Parameters in Table 23

<table>
<thead>
<tr>
<th>k (sec⁻¹)</th>
<th>T (°K)</th>
<th>k (sec⁻¹)</th>
<th>T (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>336.1</td>
<td>0.26</td>
<td>323.3</td>
</tr>
<tr>
<td>0.77</td>
<td>348.9</td>
<td>0.60</td>
<td>334.0</td>
</tr>
<tr>
<td>0.85</td>
<td>350.5</td>
<td>1.38</td>
<td>337.0</td>
</tr>
<tr>
<td>2.18</td>
<td>356.7</td>
<td>2.75</td>
<td>346.1</td>
</tr>
<tr>
<td>2.40</td>
<td>362.6</td>
<td>3.43</td>
<td>351.4</td>
</tr>
<tr>
<td>4.65</td>
<td>366.8</td>
<td>5.78</td>
<td>359.6</td>
</tr>
<tr>
<td>6.75</td>
<td>374.5</td>
<td>10.9</td>
<td>364.7</td>
</tr>
<tr>
<td>6.95</td>
<td>376.3</td>
<td>17.5</td>
<td>375.1</td>
</tr>
<tr>
<td>8.57</td>
<td>382.1</td>
<td>26.8</td>
<td>382.1</td>
</tr>
<tr>
<td>16.5</td>
<td>388.6</td>
<td>40.0</td>
<td>390.0</td>
</tr>
<tr>
<td>$k \text{ (sec}^{-1}\text{)}$</td>
<td>$T \text{ (°K)}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>-----------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.21</td>
<td>281.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.81</td>
<td>292.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.00</td>
<td>307.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.8</td>
<td>317.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.5</td>
<td>327.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>52.6</td>
<td>336.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>98.8</td>
<td>346.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>171.9</td>
<td>358.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>758.0</td>
<td>381.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$28$-TWEDA</th>
<th>$28$-THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k \text{ (sec}^{-1}\text{)}$</td>
<td>$T \text{ (°K)}$</td>
</tr>
<tr>
<td>------------------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>3.00</td>
<td>301.0</td>
</tr>
<tr>
<td>8.00</td>
<td>312.0</td>
</tr>
<tr>
<td>15.0</td>
<td>320.0</td>
</tr>
<tr>
<td>87.5</td>
<td>340.0</td>
</tr>
<tr>
<td>300.0</td>
<td>360.0</td>
</tr>
<tr>
<td>500.0</td>
<td>370.0</td>
</tr>
<tr>
<td>650.0</td>
<td>380.0</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>