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I REACTIONS OF DELOCALIZED DICARBANIONS WITH DIHALIDES.
II PREPARATION AND REACTIONS OF CYCLOHEPTATRIENYL TRIANION.

by

Joseph John Bahl

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF CHEMISTRY
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

1977
THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

I hereby recommend that this dissertation prepared under my
direction by Joseph John Bahl
entitled I Reactions of Delocalized Dicarbanions with Dihalides.
II Preparation and Reactions of Cycloheptatrieny1 Trianion.
be accepted as fulfilling the dissertation requirement for the
degree of Doctor of Philosophy

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Dissertation Director 12-21-76

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ix</td>
</tr>
<tr>
<td>PART I: REACTIONS OF DELOCALIZED DICARBANIONS WITH DIHALIDES</td>
<td>1</td>
</tr>
<tr>
<td>INTRODUCTION: I</td>
<td>2</td>
</tr>
<tr>
<td>EXPERIMENTAL: I</td>
<td>6</td>
</tr>
<tr>
<td>Instrumentation and Source of Chemicals</td>
<td>6</td>
</tr>
<tr>
<td>Preparation of Isobutylene Dianion (I)</td>
<td>6</td>
</tr>
<tr>
<td>Preparation of 2-Methyl-1,4-pentadienyl Dianion (IV)</td>
<td>7</td>
</tr>
<tr>
<td>Reactions of Dianions I and IV with Dihalides</td>
<td>7</td>
</tr>
<tr>
<td>Diiodomethane</td>
<td>8</td>
</tr>
<tr>
<td>1,2-Dibromoethane</td>
<td>11</td>
</tr>
<tr>
<td>1,3-Dibromopropane</td>
<td>11</td>
</tr>
<tr>
<td>1,4-Dibromobutane</td>
<td>14</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION: I</td>
<td>31</td>
</tr>
<tr>
<td>PART II: PREPARATION AND REACTIONS OF CYCLOHEPTATRIENYL TRIANION</td>
<td>36</td>
</tr>
<tr>
<td>INTRODUCTION: II</td>
<td>37</td>
</tr>
<tr>
<td>EXPERIMENTAL: II</td>
<td>43</td>
</tr>
<tr>
<td>Instrumentation and Source of Chemicals</td>
<td>43</td>
</tr>
<tr>
<td>Preparation of 1,3-Cycloheptadiene (XXXIV)</td>
<td>44</td>
</tr>
<tr>
<td>and 1,4-Cycloheptadiene (XXXIII)</td>
<td>44</td>
</tr>
<tr>
<td>7-Methoxycycloheptatriene (XXVI)</td>
<td>45</td>
</tr>
<tr>
<td>Preparation of Cycloheptatrienyl Trianion (XX)</td>
<td>45</td>
</tr>
<tr>
<td>Reaction of XX with D&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>46</td>
</tr>
<tr>
<td>Alkylation of XX</td>
<td>46</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION: II</td>
<td>56</td>
</tr>
</tbody>
</table>
## TABLE OF CONTENTS—Continued

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONCLUSION: II</td>
<td>76</td>
</tr>
<tr>
<td>APPENDIX A. HANDLING OF n-BUTYLLITHIUM</td>
<td>78</td>
</tr>
<tr>
<td>APPENDIX B.</td>
<td>81</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>84</td>
</tr>
</tbody>
</table>
**LIST OF ILLUSTRATIONS**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Illustration</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Methylenecyclopropane (IXa) PMR</td>
<td>9</td>
</tr>
<tr>
<td>2.</td>
<td>2-Methyl-1-butene (X) with IXa and acetone PMR</td>
<td>10</td>
</tr>
<tr>
<td>3.</td>
<td>2-Vinylmethylenecyclopropane (IXb) PMR</td>
<td>12</td>
</tr>
<tr>
<td>4.</td>
<td>2-Vinylmethylenecyclobutane (XVIa) PMR</td>
<td>13</td>
</tr>
<tr>
<td>5.</td>
<td>Methylenecyclohexane (XIa) and 1-methylcyclohexene PMR</td>
<td>15</td>
</tr>
<tr>
<td>6.</td>
<td>2-Vinylmethylenecyclohexane (XVIb) PMR</td>
<td>16</td>
</tr>
<tr>
<td>7.</td>
<td>Allylidene cyclohexane (XVII) PMR</td>
<td>17</td>
</tr>
<tr>
<td>8.</td>
<td>Methylenecycloheptane (XIIb) PMR</td>
<td>18</td>
</tr>
<tr>
<td>9.</td>
<td>Vinylmethylenecycloheptane (XVIc) PMR</td>
<td>19</td>
</tr>
<tr>
<td>10.</td>
<td>Vinylcyclopropane (XIIa) PMR</td>
<td>21</td>
</tr>
<tr>
<td>11.</td>
<td>Vinylcyclopentane (XIIb) PMR</td>
<td>22</td>
</tr>
<tr>
<td>12.</td>
<td>Vinylcyclohexane (XIIc) PMR</td>
<td>23</td>
</tr>
<tr>
<td>13.</td>
<td>1-Cyclopropyl-1,3-butadiene (XIVa) PMR</td>
<td>24</td>
</tr>
<tr>
<td>14.</td>
<td>1,3,5-Hexatriene (XIIIb) PMR</td>
<td>25</td>
</tr>
<tr>
<td>15.</td>
<td>1-Cyclopentyl-1,3-butadiene (XIVb) PMR</td>
<td>26</td>
</tr>
<tr>
<td>16.</td>
<td>(E)-1,2-divinylcyclopentane (XVb) PMR</td>
<td>27</td>
</tr>
<tr>
<td>17.</td>
<td>1-Cyclohexyl-1,3-butadiene (XIVc) PMR</td>
<td>28</td>
</tr>
<tr>
<td>18.</td>
<td>(E)-1,2-divinylcyclohexane (XVc) PMR</td>
<td>29</td>
</tr>
<tr>
<td>19.</td>
<td>(E)-1,2-divinylcyclopropane (XV) PMR</td>
<td>30</td>
</tr>
<tr>
<td>20.</td>
<td>1,4-Cycloheptadiene with 2.8D PMR</td>
<td>47</td>
</tr>
<tr>
<td>21.</td>
<td>1,3-Cycloheptadiene with 2.8D, acetone PMR</td>
<td>48</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>22.</td>
<td>7-Methylcycloheptatriene, toluene PMR</td>
<td>51</td>
</tr>
<tr>
<td>23.</td>
<td>Trimethylcycloheptadiene PMR</td>
<td>52</td>
</tr>
<tr>
<td>24.</td>
<td>7-Ethylcycloheptatriene, propylbenzene PMR</td>
<td>53</td>
</tr>
<tr>
<td>25.</td>
<td>Triethylcycloheptadiene PMR</td>
<td>54</td>
</tr>
<tr>
<td>26.</td>
<td>Cycloheptadienyl monoanion PMR</td>
<td>57</td>
</tr>
<tr>
<td>27.</td>
<td>(1) Cycloheptadienyl monoanion, cycloheptatrienyl trianion PMR</td>
<td>59</td>
</tr>
<tr>
<td>28.</td>
<td>(2) Cycloheptadienyl monoanion, cycloheptatrienyl trianion PMR</td>
<td>60</td>
</tr>
<tr>
<td>29.</td>
<td>(3) Cycloheptadienyl monoanion, cycloheptatrienyl trianion PMR</td>
<td>61</td>
</tr>
<tr>
<td>30.</td>
<td>CMR Cycloheptatrienyl trianion (XX)</td>
<td>62</td>
</tr>
<tr>
<td>31.</td>
<td>Highest resolution dilithocycloheptatrienyl dianion radical ESR</td>
<td>64</td>
</tr>
<tr>
<td>32.</td>
<td>Low resolution dilithocycloheptatrienyl dianion radical ESR</td>
<td>65</td>
</tr>
<tr>
<td>33.</td>
<td>Cycloheptatrienyl dianion radical ESR</td>
<td>66</td>
</tr>
<tr>
<td>34.</td>
<td>Dilithocycloheptatrienyl dianion radical ESR</td>
<td>67</td>
</tr>
<tr>
<td>35.</td>
<td>Computer simulation dilithocycloheptatrienyl dianion radical ESR</td>
<td>69</td>
</tr>
<tr>
<td>36.</td>
<td>IR Mixture methane and ethane</td>
<td>71</td>
</tr>
<tr>
<td>37.</td>
<td>PMR, MS Tetra substituted product</td>
<td>73</td>
</tr>
<tr>
<td>38.</td>
<td>MS Butyl triethylcycloheptadiene</td>
<td>75</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Products and yield dianions I-IV with dihalides</td>
<td>20</td>
</tr>
<tr>
<td>2. Deuteration of cycloheptatrienyl trianion (XX)</td>
<td>49</td>
</tr>
<tr>
<td>3. Alkylation of cycloheptatrienyl trianion (XX)</td>
<td>55</td>
</tr>
</tbody>
</table>
ABSTRACT

I: REACTIONS OF DELOCALIZED DICARBANIONS WITH DIHALIDES

The dianions of isobutylene, 2-z-2-butene, 1,5-hexadiene, and 2-methyl-1,4-pentadiene have recently been prepared. The reaction of these delocalized dicarbanions with dihalides of the form \( X-(CH_2)_n-X \) \((n = 1-4)\) was investigated as a possible route to cyclic olefins (the dianions of isobutylene and 2-methyl-1,4-pentadiene by this author). Ring formation was observed to favor the smaller ring size when more than one ring size was possible. This method of preparation provides access to many known cyclic olefins plus four compounds not previously reported.

II: PREPARATION AND REACTIONS OF CYCLOHEPTATRIENYL TRIANION

Cycloheptatrienyl trianion, a novel 7-carbon-10\(\pi\)-aromatic, has been prepared from 1,4-cycloheptadiene and the strong metalating system n-butyl lithium/N,N,N',N'-tetramethylethylenediamine (TMEDA). Evidence for existence of the cycloheptatrienyl trianion includes direct measurement of proton magnetic resonance (PMR) and carbon magnetic resonance (CMR) spectra, reaction with deuterium oxide \((D_2O)\) producing trideuterated cycloheptadiene, reaction with alkylating agents to produce trialkylated...
cycloheptadiene, and the presence of minute amounts of
cycloheptatrienyl dianion radical which has as its most
probable immediate precursor the trianion.
PART I

REACTIONS OF DELOCALIZED DICARBANIONS
WITH DIHALIDES
INTRODUCTION: I

Delocalized carbanions resulting from abstraction of a proton alpha to a double bond have long been postulated as intermediates in base-catalyzed isomerizations and have been characterized by NMR and alkylation studies. Recently the use of the strong metalating system n-butyllithium/N,N,N',N'-tetramethylethlyenediamine (TMEDA) for direct dimetalation of isobutylene (1), Z-2-butene (2), 1,5-hexadiene (2), and 2-methyl-1,4-pentadiene (2) has provided access to dicarbanions I-IV respectively [CINDO calculated electron densities (3)].

\[ \text{Dianion III was the subject of an X-ray study that showed the conformation to be as drawn, with the dianion existing as an ionic and not as a covalent species (4). These dianions give dialkylated products in good yield when reacted with two equivalents of monoalkyl halides (2).} \]

As a logical extension, an investigation of ring formation from the reaction of dicarbanions I-IV with
dihalides of the form $X-(CH_2)_n-X$ ($n = 1,2,3,4$) was undertaken and is the subject of this part of the dissertation.

Several earlier studies of reactions of dianions with dihalides resulting in ring formation serve as precedent. Cyclooctatetraene dianion (V), prepared by the alkali metal reduction of cyclooctatetraene, reacts with methylene chloride (5), 1,3-dibromopropane (6), and 1,4-dibromobutane (6) to yield bicyclo[6.1.0]nonatriene (VIA), bicyclo[6.3.0]undeca-2,4,6-triene (VIB), and bicyclo[6.4.0]-dodeca-2,4,6-triene (VIC) in 45, 48.5, and 35 per cent yields, respectively.

The dianion VII prepared from the diacyl ylide diacetylmethylenetriphenylphosphorane using n-butyllithium/THF gave a 25 per cent yield of the eight-numbered ring product VIII when reacted with 1,3-dibromopropane (7).

It was of course desirable to prepare dianions I and II as solids free of monoanions, as had been done with
III and IV. However, at the start of this study this had not been done.

High concentrations of difunctional reactants were expected to favor polymeric material, and thus high dilution techniques might be necessary to favor ring formation via intramolecular displacement of halide as a second step. The factors that direct this second step, geometric considerations—proximity, orientation, and ring strain, could overwhelm the subtleties of electron densities that determined product composition and ratio for the reaction of monohalide and dianions. Ring closure via nucleophilic displacement was expected not to be thermodynamically (equilibrium) controlled, but rather kinetically (rate) controlled and favor formation of 3-, 5-, and 6-membered rings over 4-, 7-, or larger-membered rings.

An additional mode of reaction, elimination, could result in olefin formation from all of the dihalides except the dihalomethanes. Owing to the ability of halogens to help stabilize a negative charge, abstraction of a proton from X-CH₂-X might also be expected. If halide ion was expelled, products from the resulting halocarbene should be observed.

Abstraction of halogen from 1,3-dibromopropane or 1,4-dibromobutane seemed unlikely as it would involve the thermodynamically improbable formation of an anion without extensive resonance or inductive stabilization. On the
other hand, abstraction of halide from 1,2-dihaloethanes has previously been observed to be concerted with the elimination of halide, yielding ethylene, and eventually a neutral compound with two fewer electrons than the starting dianion (a net oxidation) and two halide ions (7). Also the lithium salt of the halomethyl carbanion, the product of halogen abstraction from dihalomethane, upon elimination of halide would form a reactive carbene.

This problem was worked on by Dr. William A. Beavers, Nancy S. Mills, and this author. The work done by this author involved the preparation and reactions of I and the preparation of IV and some of its reactions.
EXPERIMENTAL: I

Instrumentation and Source of Chemicals

Proton magnetic resonance (PMR) spectra were obtained on a Varian T-60 NMR.

Gas chromatography was done on a Varian Aerograph model 90-P equipped with a 25' x 0.25" O.D. copper column packed with 20 per cent Carbowax 20M on chromasorb P.

TMEDA was purchased from Aldrich, 2098 Pike Street, San Leandro, Ca. 94577, and was distilled from LiAlH₄ and stored under argon.

n-Butyllithium (2.4 M in hexane) (see Appendix A) was obtained from Alpha Ventron, 2098 Pike Street, San Leandro, Ca. 94577.

Chemical Samples Company, 4692 Kenny Road, Columbus, Ohio 43220, was the source of 2-methyl-1,4-pentadiene and 1,5-hexadiene.

Preparation of Isobutylene Dianion (I)

An oven-dried 18 x 150 mm test tube was tightly capped with a 18 x 25 mm rubber septum secured with copper wire and the tube was then filled with argon. To this, 18 ml of 2.4 M n-butyllithium (24 mmol) and 3.6 ml of anhydrous TMEDA (24 mmol) were added. The tube was cooled because of substantial heat of mixing. As the n-butyllithium and TMEDA
were mixing a white crystalline complex often formed which dissolved upon warming and did not reappear when the tube was again cooled. Isobutylene, 1.1 ml (12 mmol) distilled from a lecture bottle, was condensed in a test tube at dry ice acetone temperatures and transferred using a syringe that had been cooled in the dry ice acetone bath.

Solid dianion I began precipitating overnight and was reacted three to seven days later. Yields of 50 per cent were common, but ranged between 30 and 70 per cent.

**Preparation of 2-Methyl-1,4-pentadienyl Dianion (IV)**

Since 2-methyl-1,4-pentadiene is a liquid no special cooling was employed. The olefin, 1.4 ml (12 mmol) was added to 10 ml of 2.4 M n-butyllithium (24 mmol) and 3.6 ml of anhydrous TMEDA (24 mmol). The third day after mixing was the earliest that solid IV could be seen with two to four weeks common reaction times. Yields of 30 to 40 per cent were achieved with 30 per cent being common. With longer times yields were lowered due to decomposition of TMEDA.

**Reactions of Dianions I and IV with Dihalides**

Unless otherwise stated, all reactions were carried out at dry ice acetone temperature in a 250 ml round bottom flask fitted with a septum, and containing a magnetic stir bar and an inert atmosphere of argon. After it was
determined that simultaneous addition of dilute solutions of
dianion III and dihalides did not improve yields over
addition of dihalide in 5 ml of an appropriate solvent to a
rapidly stirred solution approximately 0.1 M in dianion, the
latter procedure was followed. THF was dried over LiAlH$_4$
and distilled just prior to use. n-Butyl ether was dried
over CaH$_2$, distilled, and stored under argon over molecular
sieves.

**Diiodomethane**

Dianion I (5 mmol), dissolved in 50 ml n-butyl ether, was transferred via syringe to a round bottom flask
cooled in a dry ice acetone bath. Rapid addition of 0.31
ml diiodomethane (5 mmol) with enough butyl ether to equal
5 ml was necessary to prevent the solution from freezing;
alternatively, slight warming to -50° circumvented the
tendency of the butyl ether to freeze. A Vigreux column
was substituted for the septum with a condenser and
receiving flask cooled by dry ice acetone completing the
system as it was allowed to warm to room temperature. A
stream of argon helped sweep all products that could be
distilled up to a pot temperature of 100°. Yields were
based on G.C. analysis at 50° on this crude mixture.

Yield: methylenecyclopropane (Figure 1, PMR) (IXa)
6%, 2-methyl-1-butene (Figure 2, PMR) (X) 7%.
Figure 1. Methylenecyclopropane (IXa) PMR.
Figure 2. 2-Methyl-1-butene (X) with IXa and acetone PMR.
Dianion IV (3.6 mmol) was dissolved in roughly 36 ml THF and cooled to dry ice acetone temperatures. Diiodomethane and enough THF to total 5 ml were added to the rapidly stirred solution. The product work-up consisted of adding 10 ml pentane, washing with two equal volumes of saturated ammonium chloride solution to remove TMEDA, and two water washes to remove THF. Back extraction of each of the washes was necessary to prevent substantial loss into the aqueous layer. The pentane fractions were combined and most of the pentane removed by distillation through a vacuum-jacketed silvered tantalum wire column and the product G.C. analysis conducted at 100 °.

Yield: 2-vinylmethylenecyclopropane (Figure 3, PMR) (IXb) 10%, 2-vinylmethylenecyclobutane (XVIa) 14% (Figure 4).

1,2-Dibromoethane

Dianion I and Dianion IV were reacted and worked up via the same procedures as with diiodomethane.

Yield Dianion I: methylenecyclopropane (IXa) 70% (PMR Figure 1); yield Dianion IV: 2-vinylmethylenecyclopropane (IXb) 100% (PMR Figure 3).

1,3-Dibromopropane

Dianions I and IV were reacted with 1,3-dibromopropane in the manner of dianion IV and diiodomethane. The product of I and 1,3-dibromopropane was determined by PMR
Figure 3. 2-Vinylmethylenecyclopropene (IXb) PMR.
Figure 4. 2-Vinylmethylenecyclobutane (XVIa) PMR.
as residual amounts of THF resulted in yields greater than 100%.

Yield Dianion I: methylenecyclohexane (XIIa) 96% (PMR, Figure 5); yield Dianion IV: 2-vinylmethylene-
cyclohexane (XVIb) 23% (PMR, Figure 6); allylidene
cyclohexane (XVII) 5% (PMR, Figure 7).

1,4-Dibromobutane

Dianions I and IV were reacted in the manner of IV
and diiodomethane.

Yield Dianion I: methylenecycloheptane (Figure 8, PMR)
(XIIb) 15%; yield Dianion IV: 2-vinylmethylene-
cycloheptane (Figure 9, PMR) (XVIc) 5%.

Table 1 lists reaction product and yields for the
reaction of dihalides with dianions I-IV (Figures 10-19, PMR
spectra of the products of dianions II and III).
Figure 5. Methylene cyclohexane (XIa) and 1-methylcyclohexene PMR.
Figure 6. 2-Vinylmethylene-cyclohexane (XVIb) PMR.
Figure 7. Allylidene cyclohexane (XVII) PMR.
Figure 8. Methylene cycloheptane (X1b) PMR.
Figure 9. Vinylethylene cycloheptane (XVIc) PMR.
Table 1. Products and yield dianions I-IV with dihalides.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂I</td>
<td><img src="CH%E2%82%82I" alt="Diagram" /></td>
<td><img src="II" alt="Diagram" /></td>
<td><img src="III" alt="Diagram" /></td>
<td><img src="IV" alt="Diagram" /></td>
</tr>
<tr>
<td></td>
<td>X, 5%</td>
<td>XIIa, 3%</td>
<td>XIVa, 20%</td>
<td>XVIa, 14%</td>
</tr>
<tr>
<td></td>
<td>IXa, 6%</td>
<td>XIIIa, 7%</td>
<td>XIIIb, 10%</td>
<td>IXb, 10%</td>
</tr>
<tr>
<td>Br(CH₂)₂Br</td>
<td><img src="Br(CH%E2%82%82)%E2%82%82Br" alt="Diagram" /></td>
<td><img src="Br(CH%E2%82%82)%E2%82%82Br" alt="Diagram" /></td>
<td><img src="Br(CH%E2%82%82)%E2%82%82Br" alt="Diagram" /></td>
<td><img src="Br(CH%E2%82%82)%E2%82%82Br" alt="Diagram" /></td>
</tr>
<tr>
<td></td>
<td>IXa, 70%</td>
<td>XIIIa, 33%</td>
<td>XIIIb, 61%</td>
<td>IXb, 100%</td>
</tr>
<tr>
<td>Br(CH₂)₃Br</td>
<td><img src="Br(CH%E2%82%82)%E2%82%83Br" alt="Diagram" /></td>
<td><img src="Br(CH%E2%82%82)%E2%82%83Br" alt="Diagram" /></td>
<td><img src="Br(CH%E2%82%82)%E2%82%83Br" alt="Diagram" /></td>
<td><img src="Br(CH%E2%82%82)%E2%82%83Br" alt="Diagram" /></td>
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<tr>
<td></td>
<td>XIA, 96%</td>
<td>XIIa, 8%</td>
<td>XIVb, 8%</td>
<td>XVIb, 23%</td>
</tr>
<tr>
<td></td>
<td>XIIb, 8%</td>
<td>XIVb, 8%</td>
<td>XVb, 9%</td>
<td>XVII, 5%</td>
</tr>
<tr>
<td>Br(CH₂)₄Br</td>
<td><img src="Br(CH%E2%82%82)%E2%82%84Br" alt="Diagram" /></td>
<td><img src="Br(CH%E2%82%82)%E2%82%84Br" alt="Diagram" /></td>
<td><img src="Br(CH%E2%82%82)%E2%82%84Br" alt="Diagram" /></td>
<td><img src="Br(CH%E2%82%82)%E2%82%84Br" alt="Diagram" /></td>
</tr>
<tr>
<td></td>
<td>XIb, 15%</td>
<td>XIIc, 3%</td>
<td>XIVc, 0.6%</td>
<td>XVC, 4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>XVIc, 5%</td>
</tr>
</tbody>
</table>

20
Figure 10. Vinylcyclopropane (XIIa) PMR.
Figure 11. Vinylcyclopentane (XIIb) PMR.
Figure 12. Vinylcyclohexane (XIIc) PMR.
Figure 13. 1-Cyclopropyl-1,3-butadiene (XIVa) PMR.
Figure 14. 1,3,5-Hexatriene (XIIIb) PMR.
Figure 15. 1-Cyclopentyl-1,3-butadiene (XIVb) PMR.
Figure 16. (E)-1,2-divinylcyclopentane (XVb) PMR.
Figure 17. 1-Cyclohexyl-1,3-butadiene (XIVc) PMR.
Figure 18. (E)-1,2-divinylcyclohexane (XVc) PMR.
Figure 19. (E)-1,2-divinylcyclopropane (XV) PMR.
RESULTS AND DISCUSSION: I

The reactions studied produced four compounds not previously reported (XIVb, XVIa, XVIb, XVIc) and provide more efficient routes to several compounds previously prepared in multistep synthesis (see Appendix B) (3). In all cases with the possibility of formation of more than one ring size, the smaller size ring was observed (e.g., 3 rather than 5, 4 than 6, 5 than 7, 6 than 8, and 7 than 9). With the exception of XVa-c all products may be rationalized as having resulted from initial alkylation at the most negatively charged carbon of the dianion to generate the most stable monoanion followed by cyclization. The exceptions suggest that the factors (mechanisms) that determine initial alkylation may be more complicated than simply nucleophilic displacement of halide such that the most stable monoanion is generated.

Dihalomethanes have relatively acidic protons resulting in recovery of the diprotonated dianion I-IV in 60, 30, 10, and 15% yields, respectively. The 6-10% yields of the two electron oxidation products of dianion I-IV (IXa, XIIIa, XIIIb, IXb) presumably arise from halide abstraction and rapid nucleophilic displacement by the resulting monoanion. The resulting halomethyl carbanion can pick up a proton in solution and undergo further reaction.
(e.g., reaction with the monoanion of I to form X) or can eliminate halide ion to generate a reactive carbene (formation of X via addition of the methylcarbene to the monoanion of I to generate a very basic anion that would be quickly protonated).

\[
\begin{align*}
I + X_2CH_2 & 
\rightarrow 
\begin{array}{c}
\text{CH}_2X \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\end{array} \\
\rightarrow 
X
\end{align*}
\]

Products XIIa, XIVa, XVa, and XVIa can be rationalized by either a mechanism involving two nucleophilic displacements of halide or carbene addition to the two-electron oxidation products of dianions I, II, and IV. In general the rate of ring formation is 3>>5>>6>4 (in cases where the difference in rate is assumed to be governed by proximity and ring strain) (8), and it is thus surprising that the four-membered ring product XXIIIa is formed and not the six-membered ring product. Carbene addition to the methylene double bond of IXb would yield vinylspiropentane.

Vinylspiropentane during acidic workup or at the elevated temperature of the G.C. injection port may rearrange
(spiropentane is known to rearrange to methylenecyclobutane) (9). An alternative anionic mechanism, either concerted or stepwise, may be envisioned as the pathway to the observed product.

![Chemical diagram](image)

Katz and Garratt (5) reacted cyclooctatetraene dianion (V) with CH₂Cl₂, CHCl₃, and CCl₄ and were able to show that the mechanisms involved carbenes formed after initial abstraction of chloride and elimination of chloride ion. They went on to say, "Methylene chloride is unreactive toward SN2 displacement . . ." citing the fact that, "even a primary alkyl halide, 1-chloropentane, does not react appreciably with n-butyllithium in ether at -30° during the course of an hour" (5, p. 4876).

It is quite possible that the mechanism of reaction of diiodomethane is not the same as for methylene chloride (reported yields for reaction of III with dihalomethane were the major products of reaction with methylene chloride, other products included chlorobenzene (5%), 2,4,6-octatriene (3%), and 1,3,5-octatriene (2%); however, it was beyond the scope of this study to explore and determine the details and subtleties of the reaction mechanism.
Reaction with dibromoethane would appear to proceed via scheme Ia in which the dianion abstracts a bromine from the two carbon fragment resulting in concerted elimination of the second bromine to form ethylene (the preferred anti conformation of 1,2-dibromoethane has the geometry necessary for elimination). The resulting bromomonoanion derivatives of I-IV quickly eliminate to yield, when possible, a linear olefin or else an olefin containing a cyclopropane ring. The overall process is a net oxidation of the dianion and reduction of the dibromo compound. The dianion may act more directly by passing two electrons in a reduction (scheme Ib) reminiscent of the controlled potential electrochemical reduction of 1,3-dibromo-1,3-dimethylcyclobutane to 1,3-dimethylbicyclobutane (10).

1,3-Dibromopropane and 1,4-dibromobutane yield the cyclic product of favored ring size.
Reaction products were separated from solvents on the basis of volatility, and thus the mono and dibromo derivatives were not usually observed. However, when the solvent TMEDA was used for the reaction of I and 1,3-dibromopropane, 2-methyl-6-bromo-1-hexane and 2-(4-bromo)butyl-6-bromo-1-hexane were the major products (compared with XIA 96% as the only observed product when THF was the solvent). Dianion I reacted rapidly with dimethylformamide, dioxane, and N-methylmorpholine, exhibiting only moderate solubility in TMEDA and virtually no solubility in aliphatic hydrocarbons, and making the choice of reaction solvents very limited.

It is possible that some yields might have been increased by using techniques of higher dilution and simultaneous addition, although there does appear to be a trade off between volume used and reaction with solvent that would make such gains modest at best. Yields of some products, especially some of the conjugated dienes, might have been increased by alternative work up procedures, but in general the trends in the yields reflect ease of formation.
PART II

PREPARATION AND REACTIONS OF CYCLOHEPTATRIENYL TRIANION
Hückel using molecular orbital theory predicted that $4n+2\pi$-electron monocyclic conjugated systems would have large delocalization energies and thus additional stability over the corresponding acyclic systems. An investigation of the formation of the previously unknown $10\pi$-electron cycloheptatrienyl trianion (XX) via successive abstraction of two protons from cycloheptadienyl monoanion (XVIII) using the strong metalation system n-butyllithium/TMEDA, and the reaction of XX with several alkylation agents are the subjects of this section of the dissertation.

This novel $10\pi$-aromatic can have only six electrons in bonding orbitals and must contain the remaining four electrons in antibonding orbitals:

Even so, it is predicted to be of lower energy than the open chain $10\pi$-electron-7-carbon analog; $\beta$, the difference
in π electron delocalization energies between cyclic and linear conjugated systems, as a function of the number of π electrons, from a Hückel calculation of Breslow and Mohacsi (11) is:

\[
\begin{array}{c}
0.6 \\
0.4 \\
0.2 \\
0.0 \\
2 \\
6 \\
10 \\
\end{array}
\]

Cyclododecapentaene (XXI), cyclononatetraenyl monopropionate (XXII), and cyclooctatetraen dianion (V) begin a series of 10π-electron systems with ten, nine, and eight carbons, with XX as the next member. Although a 10π-system, XXI is not delocalized for steric reasons and does not prefer the all cis conformation drawn (12). XXII has been prepared and is reported to exhibit aromatic stabilization (13). V is an example of a 10π-delocalized aromatic system readily prepared by the addition of electrons to an existing π-system (14).

Breslow and Drury (15) reported that controlled potential electrolytic reduction of the 6π-electron tropylum ion (XXIII) resulted in dimer formation at both
the first wave (from the dimerization of cycloheptatrienyl radical [XXIV]) and as the only process at the second wave (from reaction of cycloheptatrienyl monoanion [XXV] with the starting cation XXIII). This was observed using a standard electrode even when acetic acid was used as the solvent to trap anion XXV by protonation. Breslow and Chu (16) were able to generate XXV discernible by a second clear wave by rapid scanning cyclic voltammery. The explanation of the clarity of the second wave is that the passage of the current to the surviving radicals XXIV reducing them to anions XXV is not affected by their precise chemical fate in the non-steady-state process.

Bauld and Brown (17) used both sodium and potassium metal to feed electrons into 7-methoxycycloheptatriene (XXVI) and generated the 9π-electron cycloheptatrienyl dianion radical (XXVII), but, "No unambiguous evidence for trianion was seen either in the form of attenuation of the ESR signal after prolonged reaction time in the presence of
excess metal or of alteration of the visible absorption of the dianion radical or appearance of a new maximum" (p. 4391).

Breslow and Chang (18) were able to prepare heptaphenylcycloheptatrienyl anion (XXVIII) by reduction of heptaphenyltropylium bromide with potassium metal. However, attempts to reduce it further yielded stilbene (XXIX) and pentaphenylcyclopentadienyl anion (XXXI), suggesting to those authors that the heptaphenylcycloheptatrienyl trianion (XXX) as an intermediate.

It was hoped that preparation of XX via proton abstraction would circumvent the problems encountered in attempted reductive preparations. Monoanion XVIII is formed quantitatively from 1,3,6-heptatriene (19). Monoanion XVIII is also known to be the last intermediate in the Birch reduction of cycloheptatriene (XXXII) to 1,4-cycloheptadiene (XXXIII) and 1,3-cycloheptadiene (XXXIV) [conversely it can be generated from XXXIII with n-butyllithium/TMEDA or sodamide (20) and from XXXIV with sodamide (20), but not with n-butyllithium/TMEDA].
In anions as in other substances, electron density greatly affects both PMR and CMR chemical shifts, and is very helpful in structure elucidation. For aromatic systems proton chemical shifts have been found to be proportional to $\pi$-electron density (21). Thus using the reported value for the chemical shifts for XXII ($\delta = 6.9$) and V ($\delta = 5.7$) the relation between chemical shift and electron density $\rho$ (defined as the number of pi electrons divided by the number of carbons) is:

$$\delta = 16.5 - 8.64\rho$$

O'Brien, Hart, and Russel (21) have found that for CMR not only in aromatic systems, but in general for $sp^2$ hybridized carbons in planar conjugated systems, the average chemical shift is proportional to the average electron density, thus:

$$\delta_{av} = 289.5 - 156.3\rho_{av}$$

Using these two equations for XX, where $\rho = 1.43$, the calculated values for the chemical shift are:
However, the equations as written make no allowance for variations caused by changes in counter ions and solvation.

In X-ray studies of the napthalene dianion (22) and the hexatriene dianion (4) the lithium counter ions are found one above the planar carbon skeleton and the other below. In the case of XX no such symmetrical arrangement with equivalent lithium counter ions is possible. If a planar skeleton is assumed, the possible combinations for anion and cations include ring whizzers and triple decker complexes (XXXV) with two cations being shared by two anions. It does not seem very probable that more than one cation would be appreciably dissociated from the highly charged anion (XXXVI). The possibility of nonplanar structures XXXVII (still aromatic using the definition of Goldstein and Hoffmann [23]) can not be excluded a priori. An X-ray study would of course allow a definitive statement about the structure of XX.
EXPERIMENTAL: II

Instrumentation and Source of Chemicals

PMR spectra were obtained on a Varian T-60 NMR. Low temperature PMR was attempted on a Varian HA-100 equipped with a variable temperature probe. CMR spectra were obtained using a Bruker 90.

Infrared spectra were obtained using a Perkin-Elmer Infracord spectrometer.

ESR spectra were recorded on a Varian E-3 ESR spectrometer.

Computer simulation using the program EPRSIM (24) was generated using a CDC-6400 computer with a CALCOMP plotter.

Gas chromatography was performed using a Varian Aerograph model 90 with columns of varying length of Carbowax 20M on 60-80 chromasorb P, and on a preparatory gas chromatograph using four 3/8 inch O.D. by 6 foot columns in tandem with the same packing.

Mass spectra were recorded on a Hitachi Perkin-Elmer Model RM4-6E double focusing mass spectrometer.

n-Butyllithium (2.4 M in hexane) was obtained from Alpha Ventron, 2098 Pike St. San Leandro, Ca. 94577.

Cycloheptatriene was obtained from Aldrich, 2098 Pike St., San Leandro, Ca. 94577, and was used without
additional purification. TMEDA also from Aldrich was distilled from LiAlH₄ and stored under argon.

Initially 1,3,6-heptatriene was obtained from Chemical Samples Company, 4692 Kenny Road, Columbus, Ohio 43220; however, upon reordering only a technical grade was available at a substantial price increase, thus 1,4-cycloheptadiene was prepared as the starting material.

Preparation of 1,3-Cycloheptadiene (XXXIV) and 1,4-Cycloheptadiene (XXXIII)

This preparation of 1,3- and 1,4-cycloheptadienes is a variation on the method of Ter Borg and Bickel (25). The following format resulted in little cycloheptene formation and thus more of the desired dienes, although occasionally not all of the cycloheptatriene was reduced. To 500 ml of anhydrous ammonia in a three neck round bottom flask, equipped with dry ice-acetone condenser and mechanical stirrer, small chunks of sodium totaling 18 g (0.783 moles) were slowly added. An additional five minutes of stirring ensured dissolution. Careful addition of 40 ml (0.385 moles) of cycloheptatriene was made during a twenty-five minute period and the reaction stirred for an equal period. The resulting red solution of cycloheptadienyl monoanion (XVIII) was poured into one pint (0.437 liter) of absolute ethanol at -78° in a 4 liter beaker (attempts to use the anion directly from the ammonia solution were not successful, presumably due to trace amounts of ammonia reacting
with butyllithium in preference to formation of dianion XIX). Addition of two 200 ml portions of H$_2$O was followed by rapid extraction with three 250 ml portions of pentane. The pentane was fractionally distilled leaving XXXIII and XXXIV (21:78). Conditions that allowed the dienes to equilibrate (e.g., quenching at a higher temperature, base-catalyzed isomerization, etc.) increased the yield of XXXIV at the expense of XXXIII.

Depending upon the needs of a particular experiment the crude mixture of dienes was either flash distilled and then separated by gas chromatography or the non-conjugated diene distilled away from conjugated diene and starting material after a Diels-Alder reaction with maleic anhydride using the procedure of Albelo, Wiger, and Rettig (26).

7-Methoxycycloheptatriene (XXVI)

Sodium (1.3 g, 0.057 mole) was added to 300 ml of anhydrous methanol after the reaction was complete, a solution of 200 ml of absolute ethanol containing 10 g (0.056 mole) tropylium fluoborate (27) was added. Extraction with pentane/water followed by fractional distillation yielded 7-methoxycycloheptatriene (XXVI).

Preparation of Cycloheptatrienyli Trianion (XX)

An oven dried 18 x 150 mm test tube was tightly capped with a 18 x 25 mm rubber septum. The septum was
secured with copper wire and the tube filled with argon. Addition of 0.1 ml (0.92 mmole) of 1,4-cycloheptadiene (XXXIII), 1.2 ml n-butyllithium (2.9 mmoles), and 0.43 (2.9 mmoles) TMEDA resulted in complete solidification of the liquid contents of the tube in 3-10 days. The resulting black solid appears to be stable indefinitely as long as air and water are excluded.

**Reaction of XX with D₂O**

Solid trianion XX was dissolved in THF and chilled to dry ice-acetone temperatures. One ml of D₂O was added and alternately allowing the tube to warm and then cool a moderate rate of reaction was obtained. Deuterium incorporation (NMR vinyl vs non-vinyl) was found to range between 2.0 and 2.9 D/molecule (Figures 20 and 21, PMR; Table 2).

**Alkylation of XX**

The solid anion from 0.1 ml (0.92 mmole) of XXXIII was dissolved in 5 ml of anhydrous THF and transferred to a 250 ml round bottom flask equipped with magnetic stir bar, rubber septum, and argon atmosphere. The solution was cooled in a dry ice-acetone bath followed by addition of the desired alkylation agent in 5 ml of THF. To prevent the alkylation agent from freezing the round bottom flask was removed from the dry ice-acetone bath and allowed to warm slightly. After the reaction was completed water was added to extract inorganic salts and pentane was added. In the
Figure 20. 1,4-Cycloheptadiene with 2.8D PMR.
Figure 21. 1,3-Cycloheptadiene with 2.8D, acetone PMR.
Table 2. Deuteration of cycloheptatrienyl trianion (XX).

<table>
<thead>
<tr>
<th>Mass</th>
<th>Abund</th>
<th>Toluene</th>
<th>Cycloheptadiene</th>
<th>Corrected abundance Abund—7.7% 13°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>.5</td>
<td></td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>91</td>
<td>7.0</td>
<td></td>
<td></td>
<td>7.0</td>
</tr>
<tr>
<td>&gt; 92</td>
<td>30.2</td>
<td>d1</td>
<td></td>
<td>30.0</td>
</tr>
<tr>
<td>&gt; 93</td>
<td>34.4</td>
<td>d2</td>
<td></td>
<td>32.8</td>
</tr>
<tr>
<td>&gt; 94</td>
<td>29.4</td>
<td>d3</td>
<td></td>
<td>27.5</td>
</tr>
<tr>
<td>&gt; 95</td>
<td>45.2</td>
<td>d1</td>
<td></td>
<td>44.2</td>
</tr>
<tr>
<td>&gt; 96</td>
<td>33.3</td>
<td>d2</td>
<td></td>
<td>30.7</td>
</tr>
<tr>
<td>&gt;&gt; 97</td>
<td>100.0</td>
<td>d3</td>
<td></td>
<td>100.0</td>
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<tr>
<td>98</td>
<td>24.8</td>
<td></td>
<td>d4</td>
<td>17.7</td>
</tr>
<tr>
<td>99</td>
<td>3.6</td>
<td></td>
<td>d5</td>
<td>1.7</td>
</tr>
<tr>
<td>100</td>
<td>.8</td>
<td></td>
<td></td>
<td>0.5</td>
</tr>
</tbody>
</table>
case of diethyl sulfate unreacted material was hydrolyzed with 10% KOH in 80% ethanol, refluxing for 3 hours prior to addition of pentane and subsequent extraction. The pentane layer was washed with ammonium chloride saturated water (removal of TMEDA) and again with water. The THF was removed by the aqueous washing, necessitating back extraction with pentane to prevent loss of olefinic product. The pentane was fractionally distilled and the crude mixture separated by gas chromatography. PMR spectra: Figure 22 7-methylcycloheptatriene; Figure 23 trimethylcycloheptadiene; Figure 24 ethyl cycloheptatriene; Figure 25 tri-ethylcycloheptadiene; Table 3 lists products and yields of alkylation.
Figure 22. 7-Methylcycloheptatriene, toluene PMR.
Figure 23. Trimethylcycloheptadiene PMR.
Figure 24. 7-Ethylcycloheptatriene, propylbenzene PMR.
Figure 25. Triethylcycloheptadiene PMR.
Table 3. Alkylation of cycloheptatrienyl trianion (XX).

<table>
<thead>
<tr>
<th></th>
<th>Triene</th>
<th>Dienes Trialkylated</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeI</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>EtI</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>EtBr</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>(Et)$_2$SO$_4$</td>
<td>Trace</td>
<td>70</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION: II

Cycloheptadienyl anion (XVIII) was observed using PMR (Figure 26) shortly after mixing three equivalents of n-butyllithium/TMEDA with either 1,3,6-heptatriene or 1,4-cycloheptadiene (XXXIII). The clear liquid became dark reddish-brown immediately following mixing, and continued to darken gradually. About two hours after mixing a black precipitate was observed forming; after about twelve hours the tube was clogged with precipitate, and broadened peaks were observed in the PMR spectrum. Additional TMEDA resulted in solvent peaks sharpening, but the spectrum showed little else. However, between two and eight hours (occasionally longer) a sharp singlet was observed to increase with time as monoanion XVIII and butyllithium decreased.

TMS was not included as a reference since it reacts with strong bases. The aforementioned singlet tended to move upfield with time. Since the observed drift with time for any one sample (± 0.09δ) was not as great as the observed range for the singlet (0.30δ) other factors undetermined are important in determining the observed chemical shift. The location of the peak, δ = 4.55 ± 0.15, correlates well with the predicted value of δ = 4.16 as calculated in the introduction using the eight and nine carbon carbanion analogs.
Figure 26. Cycloheptadienyl monoanion PMR.
Figures 27 to 29 represent the important features of change in singlet position, the peaks of monoanion, hexane, and TMEDA. It is interesting to note the broadened peaks of the methyl protons of TMEDA, most likely due to an exchange phenomenon. This broadening became more pronounced with time.

It was not known if the corresponding CMR spectrum could be measured before the tube was clogged with solid, and while this did limit the total number of scans that could be collected, CMR spectra were successfully obtained. The important characteristics of Figure 30 are the peaks of butyllithium, hexane, and other hydrocarbons in the solvent (δ12.0-35 ppm), the peaks of TMEDA (δ35-60 ppm) again with broadening of the methyl peak, and in the range of δ60-70 ppm two peaks, one of which seems likely to be due to XX.

The calculated shift of δ = 66.2 ppm argues for the downfield peak (δ = 66.0 ppm) to be XX; however, the question remains unanswered as to the origin of the peak at δ = 64.6 ppm.

Attempts to correlate PMR and CMR in a selective heteronuclear spin decoupling experiment failed as the decoupling power could not be applied in a narrow range. Attempts to obtain low temperature PMR spectra were not successful because a locked signal could not be obtained.

A strong signal was observed by ESR for a paramagnetic species which correlate with the solution turning
Figure 27. (1) Cycloheptadienyl monoanion, cycloheptatrienyl trianion PMR.
Figure 28. (2) Cycloheptadienyl monoanion, cycloheptatrienyl trianion PMR.
Figure 29. (3) Cycloheptadienyl monoanion, cycloheptatrienyl trianion PMR.
Figure 30. CMR Cycloheptatrienyl trianion (XX).
black during the preparation of XX. The concentration of this radical compared to a known concentration of galvinoxyl radical indicated that it was approximately $10^{-5}$ M (maximum concentration of XX 0.5 M). Identification of the radical was hampered by the lack of resolution of the ESR spectra. Figure 31 is representative of the highest resolution ESR spectra obtained. All spectra eventually degenerated to the non-informative spectrum of Figure 32. Most spectra obtained after mixing 1,4-cycloheptadiene (XXXIII) with three equivalents of n-butyllithium/TMEDA had only the resolution of Figure 32. Dilution with TMEDA or THF did not change the resolution. Substituting 1,3-cycloheptadiene XXXIV or using less than three equivalents of n-butyllithium or TMEDA resulted in moderate to good resolution; presumably these methods provided low concentrations of the radical accompanied by little trianion XX (no PMR singlet was observed under these reaction conditions).

The most likely radical appears to be the dianion radical XXVII first reported by Bauld and Brown (17), but with two lithiurns as the associated cations. In the di-potassium salt coupling with the potassiuurns is not observed, but only the hyperfine interactions of the protons. Figure 33 is an ESR spectrum which although prepared by the action of n-butyllithium/TMEDA on cycloheptadiene does not show any coupling with lithium cations. Figure 34 appears to be intermediate between Figure 31 and Figure 33. The disodium
Figure 31. Highest resolution dilithocycloheptatrienyl dianion radical ESR.
Figure 32. Low resolution dilithocycloheptatrienyl dianion radical ESR.
Figure 33. Cycloheptatrienyl dianion radical ESR.
Figure 34. Dilithocycloheptatrienyl dianion radical ESR.
salt, however, shows coupling with each sodium (spin = 3/2) as well as the seven hydrogens. Computer simulation (24) of the ESR spectrum (Figure 35) does much to establish the radical to be the dilithium salt of cycloheptatrienyl dianion radical XXVI where the seven proton splitting (spin = 1/2) was $a = 3.52$ and the two lithium (spin = 3/2) splitting was $a = 0.83$ with a line width of 0.88.

Prior to the identification of the dianion radical XXVII by computer simulation, attempts were made to prepare it as Bauld and Brown (17) had from 7-methoxycycloheptatriene (XXVI), but due to the lower volatility of lithium it was not possible to prepare a mirrored surface for the reduction as had been done with sodium and potassium. Attempts to form the dianion radical XXVII using lithium wire, shot, and suspension produced radicals with only low resolution. Attempts to prepare the potassium and sodium dianion radical in the same manner produced equally unresolved spectra.

Formation of the dianion radical XXVII is evidence that the trianion XX had been formed, as the most likely route to XXVII is from XX via transfer of one electron to an unspecified electron receptor. One interesting possibility for the electron acceptor is monoanion XXV:

\[
\begin{align*}
\text{XIX} & \quad \xrightarrow{-H^+} \quad \text{XX} \\
\text{XX} & \quad \xrightarrow{-H^-} \quad \text{XXV} \\
\text{XXV} & \quad \xrightarrow{-H^-} \quad \text{XXV} \\
\text{XXV} & \quad \xrightarrow{2} \quad \text{(XXVII)}
\end{align*}
\]
Figure 35. Computer simulation dilithocycloheptatrienyl dianion radical ESR.
Quenching the black solid with D$_2$O resulted in a 50% yield of a 3:1 mixture of 1,3-cycloheptadiene (XXXIV) and 1,4-cycloheptadiene (XXXIII) containing an average of 2.0 to 2.9 deuteriums per molecule (based on PMR integration of non-vinyl versus vinyl protons). Mass spectral results (Table 2) indicate that either small amounts of higher melated compounds were formed or that during the quench the system underwent base-catalyzed enrichment.

Trialkylation products of the form XXXVIII provide the best evidence for the existence of trianion XX. Two

![XXXVIII](image)

![XXXVIIa](image)

![XXXVIIb](image)

isomers XXXVIIIa and XXXVIIb are the two most likely positional isomers (which have the potential of 8 different optical isomers).

Reaction of methyl iodide with the black solid anion XX was extremely vigorous. A gas evolved from the reaction mixture was identified using IR (Figure 36) as a mixture of methane and ethane. Along with trimethylated cycloheptadienes was 7-methylcycloheptatriene which seems very plausible to have proceeded via the following mechanism:
Figure 36. IR Mixture methane and ethane.
For alkylation using alkyl halides displacement on halide competes with displacement on carbon. Yields of the trialkyl derivatives of cycloheptadiene and 7-alkyl-cycloheptatriene are given in Table 3. A small (1% or less) yield of what appears to be tetra-substituted material was sometimes isolated (Figure 37, PMR-MS) from reaction with both the alkylation agents and the silylating reagent.

Using the procedure for preparation of XX except substituting cycloheptatriene (XXXII) for 1,4-cycloheptadiene (XXXIII), n-butycycloheptatrienyl trianion (XXXX) was prepared.

The solution turned black on mixing and an ESR signal of low resolution (identical with Figure 32) was observed, but no attempt was made to improve the resolution. Peaks corresponding to the monoanion were readily observed,
Figure 37. PMR, MS Tetra substituted product.
but no peak for trianion was observed. The black material did not precipitate rapidly or completely and yields of trialkylated butylcycloheptadiene (Figure 38 MS) were low with the largest amount of material being dialkylated butylcycloheptadiene.
Figure 38. MS Butyl triethylcycloheptadiene.
CONCLUSION: II

The observed PMR singlet at 4.55 = 0.15 correlates with the predicted value of 4.16 (with no correction made for solvent differences). Similarly the CMR peak at 66.0 correlates well with the predicted value of 66.2. A radical identified as the dilithocycloheptatrienyl dianion radical has as its most likely precursor the trianion XX. Deuteration results indicate that 2.0-2.9 D had been incorporated per cycloheptadiene molecule. Isolation of material identified by PMR and mass spectral data as tri-alkylated, cycloheptadiene provides additional proof for the existence of cycloheptatrienyl trianion.

Whereas the PMR displays a sharp singlet and there is a singlet in the CMR believed to correspond to trianion XX, it is still possible that XX is non-planar. Low temperature NMR could have been useful in showing that the singlet peak was not just a time average of the signal from a nonplanar molecule. The importance of an X-ray study can not be denied to answer this and other questions about this novel 10π-system; however, no crystals even approaching the quality needed were ever observed and attempts to re-crystallize the dark precipitate were not successful.

As better metalating systems are discovered preparation of systems even less likely than XX will be produced,
but for the moment preparation of XX reflects the state of the art and science of carbanion formation.
APPENDIX A

HANDLING OF n-BUTYLLITHIUM

n-Butyllithium is a strong base that decomposes to butane and lithium hydroxide upon contact with water and butyl peroxide on exposure to oxygen. The butyl peroxide may eventually be isolated from reaction mixtures as butanol. Some care must be taken to insure that storage is under an inert atmosphere to avoid rapid decomposition.

Commercially available n-butyllithium in hexane (Alpha Ventron, 2098 Pike St., San Leandro, Ca. 94577) is a yellow colored translucent liquid. A metal cap fitted with a rubber septum is provided, but was not used because of failure to close after repeated withdrawal of n-butyllithium. In its place a 16 x 25 mm rubber stopper was found to provide the necessary protection and ease of access required for routine handling of this pyrophoric liquid.

Removing the metal cap from a fresh bottle of n-butyllithium reveals a plastic insert which has maintained an argon atmosphere. It is easily pried loose as a stream of argon directed through a pipet prevents air from entering. As much air as possible is flushed from the bottle before the septum cap is put in place. The upper flange is turned down and stretched over the bottle's mouth
to form a tight seal. A few turns of copper wire twisted tight insures the cap will stay in place. Smearing the septum with a small amount of stopcock grease helps to ease entry and exit of needles and to retard oxygen diffusion through the cap. Periodic regreasing may be necessary between uses. To insure all oxygen has been removed, a 22 gauge needle is inserted to allow ingress of argon as a second 22 gauge needle provides egress. By removing the egress needle before the ingress needle a positive pressure of argon will be maintained. The bottle should be stored under refrigeration as prolonged periods at room temperature speed decomposition.

To withdraw liquid a small pressure (0.1-0.5 psi) of argon is introduced and maintained throughout the withdrawal procedure. The tip of a 22 gauge needle fitted on a dry syringe is inserted. The positive pressure is allowed to force the plunger back, sweeping any oxygen out the end of the barrel. Next, the plunger is pushed down the barrel and the needle advanced until the tip is below the level of the liquid. The syringe should now fill with liquid and a small bubble of argon may be trapped. Larger bubbles cause problems for upon withdrawal they expand greatly, expelling the caustic pyrophoric liquid preventing quantitative transfer. To minimize such problems a lower filling pressure may be used or alternatively the bubble can be returned to the bottle. Tipping the bottle so solvent
contacts the septum may result in the septum eventually ballooning and/or bursting (although this is more often a problem associated with TMEDA). Any spattering on the bottle should be wiped off with a damp towel and the cap regreased if necessary.

The use of a 18 gauge needle necessitates changing the septum immediately as the hole it leaves is sufficiently large to allow oxygen and moisture to enter overnight even when a liberal coating of stopcock grease has been applied. It is very important to maintain a positive pressure and to exclude oxygen and water. The residual moisture left by fingerprints on the plunger often causes lithium hydroxide to jam the plunger in the syringe barrel. However, even after the golden-yellow translucent liquid has become milky white and contains much solid material, the molarity may be greater than 2.0 and should be determined exactly by titration (28).

This procedure may be applied to the handling of other lithium alkyls, the user being advised that they are often much more pyrophoric than n-butyllithium in hexane. Solvents that have been dried may also be stored by this method with the exception of THF which quickly picks up water even when the foregoing procedure has been rigorously adhered to.
PLEASE NOTE:

Pages 81-83, Appendix B, is reprinted article with very small print. Filmed in the best possible way.

UNIVERSITY MICROFILMS.
The reaction of butadiene dianion, heptatriene dianion, 2-methylenecyclopentene dianion, and 2-methylenepenta-1,4-dienyl dianion with dihalides $X(\text{CH}_2)_2X$ gave, in variable yield, products with three to seven-membered rings as well as some acyclic products. The predominant cyclic products generally came from initial alkylation at the most negatively charged carbon of the dianion to give the most stable monoanion intermediate, followed by cyclization to give the smallest ring possible. These reactions appear to provide the most convenient route to some of the observed products.

The reaction of a carbanion with an alkyl halide is one of the most commonly used carbon-carbon bond-forming reactions. Recently delocalized dicarbanions 1-4 have been prepared and shown to react in good yield with 2 equiv of alkyl halide. The current study was undertaken to determine the feasibility of treating dianions 1-4 with dihalides to give a series of cyclic hydrocarbons, some of which are currently available only by multistep procedures using unusual starting materials.

The dianions used were $\text{CICH}_2\text{CII}$, $\text{ICCH}_2\text{I}$, and $\text{Br(\text{CH}_2)_2\text{Br}}$. To favor ring formation over polymerization, high dilution techniques were indicated. After it was determined in one case that simultaneous addition of dilute solutions of the two reagents to a large volume of vigorously stirred solvent gave only slightly better yields than adding a dilute dianion solution to a vigorously stirred 0.1 M dihalide solution, the latter technique was employed.

Excess of the products obtained are summarized in Table I. They were isolated by distillation and preparative Gc, and characterized by 'H NMR, mass spectrometry, and in many cases by comparison with authentic samples. The E configurations of 8a and 8c were demonstrated by oxidation to (E)-cyclopentane-1,2-dicarboxylic acid and (E)-cyclohexane-1,2-dicarboxylic acid, respectively. The 1,2-divinyldicyclopropane isolated must have the $E$ configuration as shown in $8a$ since it is stable to at least 125°C, whereas the Z isomer Cope rearranges above 0°C.

During the reactions involving 2 prepared by dimetalating 1,5-hexadiene with n-butyl lithium, 1-methyl-3-n-butylcyclopentane (14a) was noted among the products. That this is a minor by-product in the dimetalation step was shown by isolating it in 7% yield from the mother liquor from the preparation of 2. Similarly, when tert-butyl lithium was substituted for n-butyl lithium, 1-methyl-1,3,5-tert-butylcyclopentane (11b) was formed in 7% yield. These reactions may occur as follows, or perhaps with the first two steps concerted:

$$\text{R} \rightarrow \text{R} \rightarrow \text{R}$$

14a. $R = n$-butyl
b. $R = \text{tert}-\text{butyl}$

**Discussion**

Of the products listed in Table I, $5a-c$, $7a-c$, $8a-c$, $11a-b$, $12a-c$, and $13$, with three- to seven-membered rings, were from the desired reactions. Where total yields of these cyclization products were low, it was not due to the formation of further isomeric cyclization products (e.g., cyclohexenes in the first reaction), but to side reactions. Most of the by-products were higher boiling and no doubt arose from two intermolecular alkylation rather than an intramolecular alkylation followed by an intramolecular one; these side reactions could have been lessened by employing higher dilution.

The diethylations of these same four dianions are far from perfect models for these cyclizations, especially in the case of 2, which gives only 1,4 and 1,6 diethylation, but only 1,2 and 3,4 dialkylation in its cyclic reactions. However, it might be expected that the formation of the first carbon-carbon bond would occur with essentially the same distribution over the carbons of the dianion, whereas in the second alkylation, the distribution pattern could differ greatly between the intermolecular and intramolecular cases. The diethylation products could in all cases be rationalized by initial attack at an end of the dianion system to give the most stable monoanion intermediate, e.g., pentadienyl anion 15a from 2. However, although no 3,4-diethyl-1,5-hexadiene was found in the diethylation of 2, 8a-c, the analogous cyclic products, were found in significant amounts and prove that some of the initial alkylation of 2 by a dihalide occurs at carbon 3, the site of second highest electron density, giving an s-alkylation intermediate 15b. Probably some of the 81% of diethylation products of 2 which could have come from initial attack at either carbon 1 or 3 similarly came from initial attack at carbon 3 rather than all at 1 as was previously assumed. All of the cyclization products other than 8a-c can be rationalized as coming from initial alkylation at the most negatively charged carbon of the dianion to give the most stable monoanion intermediate, followed by cyclization to give the smaller of two possible ring sizes, i.e., three rather than
Table I. Isolated Products and Yields

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>ICH,I</th>
<th>Br(CH,3)Br</th>
<th>Br(CH,3)Br</th>
<th>Br(CH,3)Br</th>
</tr>
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<tr>
<td>1</td>
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<td>2</td>
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<td>3</td>
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<tr>
<td>4</td>
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</tr>
</tbody>
</table>

*In this case, CH,Ct was used instead of ICH,I. The yields of these products might have been higher with ICH,I. Other products included chlorobenzene (5%), 2,4,6-octatriene (3%), and 1,3,5-octatriene (2%).

These displacements on bromine occur readily with ethylene dibromide because the leaving group is bromide ion, and most of the time this dihalide is in the anti-conformation, favoring this reaction and hindering displacement on carbon. Only the E stereoisomer of 6b was observed, probably reflecting a very large predominance of E configuration for the central bond of 2.

The methylene halides are sufficiently acidic to protonate these dihalides, especially the very basic I and 3. Yields of diprotonation products from 1-4 were 30, 10, 60, and 15%, respectively. With methylene chloride, 4 gave a 20% yield of diprotonation products and virtually no 10b or 12a. An unusual product from 3 was 2-methyl-1-butane (9), apparently formed by alkylation of the monoanion with methyl iodide formed from methylene chloride.

Among the unexpected products was chlorobenzene, obtained in 5% yield from the reaction of 2 with methylene chloride; this is reminiscent of the formation of biphenyl (77% yield) by heating 3-phenylhexatriene dianion at 60 °C. Other unusual products from the reaction of 2 with methylene chloride were 1,3,5- and 2,4,6-octatrienes (2 and 3%, respectively).

Owing to the shortness of these syntheses and the ease in separating the products (most side reactions lead to higher molecular weight substances readily removed by distillation), these reactions may serve as the most convenient ways of preparing some of these substances. For example, the previous syntheses of 9a,12b,13b, and 8c each required many steps. 6b was prepared previously in considerably lower yield by a several-step procedure which gives a mixture of stereoisomers rather than E only. 6b and its thermolysis product 3-methylenecyclopentene may be more readily prepared by the procedure described herein than by earlier methods. 10b and its other thermolysis product 3-methylenecyclopentene may be more readily prepared by the procedure described herein than by earlier methods.

Experimental Section

All solvents and starting alkenes were distilled from either CaH or LiAlH, and stored under argon over molecular sieves. The gases, 1,2-2-butenes and isobutylene, were distilled from lecture bottles just prior to use and not further purified. n-Butyllithium and tert-butyllithium solutions in hexane or pentane were used as received from Alfa Inorganics. Columns for preparative GC were 15-25 ft × 0.25 in., packed with 20% Carbowax 20M on Chromosorb P, and operated at 50-160 °C.

Preparation of Dicarbanions 1-4. Each diion was prepared and crystallized in 18 × 150 mm test tubes filled with argon and tightly capped with a rubber septum. To these tubes was added 10.0 ml (24 mmol) of 2,4-M n-butyllithium. The tubes were cooled in an ice-acetone bath and 3.6 ml (24 mmol) of anhydrous TMEDA was added. Upon warming to room temperature, the white, crystalline diion complex dissolved whenupon 12 mmol of the corresponding precursor alkene was added via syringe. This mixture was set aside at room temperature until crystallization was complete. Just prior to use, the crystallized diion was purified by removing the supernatant solution by syringing, washing the rec-
The yield, necessary for the determination of the amount of dibutyl ether used, was determined by weighing the dried anion. The procedures crystallization time, solvents, and yield for each di- anion follow: (Z)-2-butenol, 5–6 weeks; TEDMA, 25–35% (5.5–6.5°C overnight). TEDMA or TIP (100:1), 2:1 (isobutylenes); TEDMA or THF; 50:70:1; 4:1 methyl-
1,4-pentadiene; 2:4 weeks; TEDMA or THF; 3:7:4.

Reaction of Dianion 4 with Dibutyl Ether. To an anion-filled, septum-capped, 450 ml round-bottom flask equipped with a magnetic stirring bar and cooled by a dry ice-acetone bath was added 50–30 ml of anhydrous solvent and a 10% excess of dibutyl ether. The solvent used depended on the properties of the desired product. For products boiling below 50°C, THF or TMEDA was used. For products with melting points up to 115°C, THF and hexanes were used for products with boiling points above 50 °C, while THF and hexanes were used for products with boiling points above 115°C, THF and hexanes were used for products with boiling points above 163°C, THF and hexanes were used for products with boiling points above 163°C. The solvent was removed under vacuum.

The reaction was conducted with rapid stirring at −78 °C by adding diazomethane dropwise via a syringe through the septum cap. Dibutyl ether tended to crystallize at these temperatures but this problem was avoided by either conducting the reaction rapidly or warming to no higher than −50 °C. The product was worked up in ways depending on the product’s boiling point. The low-boiling 4a, 5a, 7a and 7f were isolated by fractional distilla-
tion through a short Vigreux column, collecting all material until the distillation head temperature exceeded 100 °C. A slow stream of argon swept out further product, which was collected in a series of traps cooled in acetonitrile-dry ice baths. The crude product was further purified by preparative GC. Products boiling above 50 °C were worked up by quenching with 20 ml of water and removing dibutyl ether. THF was not used. The organic layer was separated and the aqueous phase was treated as above to remove impurities except that the flash distillation was unnecessary. Starting with 3 g (12 mmol) of 1,6-
hexadiene, the yield of both 4a and 4b after preparative GC was 25%.

Cycloaddition of 4a and 4b. In a 100 ml round-bottom flask equipped with a magnetic stirring bar and a septum cap, 1.65 g (17.67 mmol) of sodium periodate, 20 mg (0.13 mmol) of per-
tassium permanganate, and 45 ml of water. After 6 days, the reac-
tion was worked up by filtering off the inorganic solids, extracting the organic phase exhaustively with ether, evaporating the ether, and dissolving the solid residue in 1 ml of hot water. In a few days crystals of acid formed with mp 160–162 °C [lit. for (E)-1,2-
cyclopentanedicarboxylic acid, 133–140 °C; (E)-1,2-cyclo-
pentanedicarboxylic acid, 162–163 °C]. These crystals showed no melting point depression on mixing with an authentic sample of (E)-1,2-cyclopentanedicarboxylic acid.

The ideal procedure using 6.55 mm (0.48 mmol) of 4a gave product with mp 223–226 °C [lit. for (E)-1,2-cyclohexanedicarboxylic acid, 192 °C; (Z)-1,2-cyclohexanedicarboxylic acid, 227–229 °C].

Acknowledgment. Financial support from the National Science Foundation (GP-38970X) is gratefully acknowledged.

References and Notes

(3) Only one dianion (2) is positively known to have (E,Z) composition, but the stereochemistry of this dianion appears to be still under study.
(9) The reaction was conducted with each carbon atom in diene 4b that is shown in a formula, an HDO program was used and since hydrogen was included, the sum of charges on carbon atoms is 0.
(16) The crystalline form of 1 was isolated by reaction with diene 4b that is shown in a formula, an HDO program was used and since hydrogen was included, the sum of charges on carbon atoms is 0.
(17) Elemental analyses on 1a and 1b were 2–3% low on carbon, presumably owing to partial oxidation on exposure to air.
REFERENCES


