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Thermal rearrangements of linear carbon chains: Theoretical and experimental studies

John Mabry

University of New Hampshire, Durham

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THERMAL REARRANGEMENTS OF LINEAR CARBON CHAINS:
THEORETICAL AND EXPERIMENTAL STUDIES

BY

JOHN MABRY
B. S. HAMPTON UNIVERSITY, 1997

DISSERTATION

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Doctor of Philosophy

in
Chemistry

December, 2003
UMI Number: 3111508

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10/3/03
Date
DEDICATION

I dedicated this dissertation to all single parent African-American mothers, and especially my mother, Barbara J. Mabry. My mother has been my pillar of strength and my source of wisdom. She instilled in my sisters and me, good work ethic, respect for others and ourselves, the importance of education, and to have faith in God. She encouraged us to set high goals and taught us how to effectively pursue them. She also taught us how to overcome barriers encountered in life. Being the ideal role model, she has always led by example. I consider her one of life’s true “warriors.” I thank you and love you with all my heart.
ACKNOWLEDGEMENTS

I would like to thank the people and organizations that have contributed to my success through this endeavor. Certainly, I could have not succeeded without the assistance of others. I have attempted to provide a list of some of those contributors.

I would like to acknowledge my advisor, Professor Richard P. Johnson, for his guidance. I appreciate the excellent scientific training that I have received and guidance on becoming an effective educator. I consider him an outstanding mentor.

I also would like to thank: Stefanie T. Mabry, James and Carol Mack, the UNH Chemistry Faculty, Amanda Burton Lapham and JoAnõ Moody of the New England Board of Higher Education, Reverend Robert Earls, Sr. and Saint John’s Baptist Church, Kathleen S. Gallagher and the University Instrumentation Center, Peg Torch and Cindi Rohwer of the Chemistry Office, Dr. Roger Beattie and the Office of the Vice President for Student and Academic Services, Dr. Harry Richards and the Graduate School, Dr. Arthur Greenberg and the College of Engineering and Physical Sciences, Bob Constantine and UNH Library Services, National Organization for the Professional Advancement of Black Chemists and Chemical Engineers (NOBCChE), Christian J. Kastrup, Susanne and David Lewis, Karelle S. Aiken, Wei-jun Niu, Martin G. Kociolek, Dhananjaya Nauduri, Mark Tetreau, Todd Ziemek, Chris and Angela Barnes, D. Nicole “Coley” Edwards. I would like to especially thank the Mabry, Mills, and Tucker families for their love, support, and prayers.
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ABSTRACT

THERMAL REARRANGEMENTS OF LINEAR CARBON CHAINS: EXPERIMENTAL AND THEORETICAL STUDIES

by

John Mabry

University of New Hampshire, December 2003

The potential energy surface of linear hydrocarbons has been extensively investigated by experiments and the use of molecular modeling. Linear C4 structures have demonstrated the potential to scramble their inner carbon atoms leading to the formation of novel strained intermediates.

Long-range carbon atom topomerization in a 1,3-diynne has been demonstrated for the first time. 1-Phenyl-4-p-tolyl-1,3-butadiyne, $^{13}$C enriched at C-1, was synthesized and subjected to flash vacuum pyrolysis. Under high temperature and at low pressure, this resulted in nearly complete $^{13}$C label equilibration among all of the $sp$ hybridized carbons, as seen by NMR analysis. It has been proposed that 1,3-diynes rearrange to form several unprecedented strained intermediates in order to support carbon transpositions. As investigated computationally, 1,3-butadiene forms trialene, (bicyclo[1.1.0]-1,3-butadiene), a highly strained organic intermediate. Trialene serves as a key intermediate in the long-range carbon scrambling. Density functional (B3LYP/6-311+G(2d,p)), and Moller-Plesset, theory calculations support the possible formation of trialene.

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Long-range carbon topomerization in butatrienes has been investigated as well. Density functional and Moller-Plesset theory calculations predict a low-energy pathway that leads to carbon scrambling of the inner sp hybridized carbons of butatriene. We predict a thermal rearrangement of butatriene to form methylenecyclopropylidene, followed by carbene insertion to form bicyclo[1.1.0]but-1(3)-ene. Ring opening and reformation of butatriene is an overall degenerate process that leads to carbon scrambling. All of these structures have been found computationally as true energy minima along this reaction pathway. Control pyrolysis experiments with tetraarylbutatrienes have established compound stability up to approximately 800 °C. A suitable synthesis of 13C labeled unsymmetrical butatriene and pyrolysis experiments are needed in order to support our calculations.
GENERAL INTRODUCTION

This dissertation is divided into three separate chapters: (1) Pericyclic and Dehydropericyclic Reactions; (2) Chemistry of C₄H₂; and (3) Chemistry of C₄H₄. Each chapter is self-contained with its own introduction, results and discussion, and conclusion.
CHAPTER 1
PERICYCLIC AND DEHYDROPERICYCLIC REACTIONS

Introduction to Pericyclic Reactions

Pericyclic reactions play a prominent role in organic chemistry. The historic 1965 series of publications by Woodward and Hoffmann which describe orbital symmetry and the associated rules dictating pericyclic reactions have had an incalculable effect on the entire field of organic chemistry. "The Conservation of Orbital Symmetry" is an exemplary publication that summarizes the principles, which may be used to understand chemical reactions and to predict mechanisms, stereochemistry, and relative reactivity of molecules. Although the Woodward-Hoffmann rules suggest what reactions may or may not occur, the rules do not serve to settle all questions of mechanism, which have initiated intense debates of the mechanisms of pericyclic reactions. The ensuing discussion fostered an enormous range of experimental and theoretical investigations.

A concerted reaction is a single-step process in which bond making and bond breaking contribute to the structure at the transition state, but the degree of contribution is not necessarily the same. These types of reactions are typically unimolecular or bimolecular processes with no intermediates. As these concepts developed, Doering and
Roth referred to the observed reactions as “no-mechanism reactions.” Pericyclic reactions are an important class of concerted reactions.

Transition states are key to understanding pericyclic reactions. Transition state theory may be used to analyze the enthalpic and entropic components of a reaction. According to this theory, the rate constant of an elementary reaction is determined by the difference between the free energy of the transition state and the reactants, as well as the rate of the passage through the region of the transition state. Experimental data allow us to deduce an approximate description of the transition state.

Transition states must be distinguished from intermediates. An intermediate is an energy minimum on a potential energy surface and will have a finite, if limited, lifetime. The lifetime of an intermediate is based upon the relative depth of the energy minimum. Transition states have a very limited lifetime and represent an energy maximum on a potential energy surface. These differences are illustrated graphically in the following potential energy diagrams (Figure 1).
In discussion of pericyclic reactions, microscopic reversibility and Hammond's postulate offer further understanding. The principle of microscopic reversibility states that the same pathway should be traveled in both the forward and reverse directions of a reaction. This is often applied in multi-step processes. Hammond has established the circumstances under which it is logical to relate a transition state structure to the structure of reactants, intermediates, and products. Hammond's postulate suggests that for a single step in a reaction, the transition state geometrically resembles the energy minimum closer in energy. This observation has allowed for insight into the description of transition states, which are referred to as being either "early" or "late" as illustrated in Figure 2. "Early" transition states occur for exothermic reactions with a low activation barrier. According to Hammond's Postulate, an "early" transition structure will
structurally resemble the reactants since they are close in energy and are interconverted by a slight structural deviation. In contrast, "late" transition structures occur for endothermic reactions with high activation barriers.

Late TS: "product-like"  
Early TS: "reactant-like"  

Figure 2. Potential energy diagrams for “late” and “early” transition states.

Pericyclic reactions constitute a wide variety of transformations that include neutral and charged species\(^1\) and have been used extensively in organic synthesis.\(^9\) Many biological and biochemical transformations involve pericyclic processes.\(^10\) The following sections focus on several selected pericyclic reactions of the simplest representative hydrocarbons. Due to the breadth of this subject, substituent effects will not be included.

The following sections will serve to classify pericyclic reactions and provide representative examples. Also presented is a description of energetics and selected structural features. Pericyclic processes may be classified in five separate categories: electrocyclic reactions, sigmatropic rearrangements, cycloaddition reactions, cheletropic reactions, and group transfer reactions.\(^1\) According to some authors, ene reactions do not fit cleanly into one of these categories. The Woodward-Hoffmann rules provide a
reliable guide to stereochemistry in pericyclic reactions that have no alternate pathways. These reactions include sigmatropic hydrogen shifts and electrocyclizations. In the case of cycloadditions, cheletropic reactions and non-hydrogen sigmatropic rearrangements, an alternative stepwise mechanistic pathway may exist that is similar, or even lower, in energy to the concerted routes. In these cases, the Woodward-Hoffmann rules are not as reliable. The extent of this debate will be discussed in the subsequent examination of cycloadditions.

Electroyclic Reactions

Electroyclic reactions form or break rings. There are two distinct modes of ring opening or closing for electrocyclcic reactions. The conrotatory mode (con) is characterized by a motion in which all substituents rotate clockwise or counterclockwise. In contrast, a disrotatory (dis) mode is characterized by a motion in which the substituents rotate in opposite directions during an electrocyclic process. These motions relate reactant and product stereochemistry.

One of the essential principles of the Woodward-Hoffmann rules is that thermal and photochemical reactions are complementary to each other. Therefore, if an electrocyclic reaction is thermally “allowed,” it will be photochemically “forbidden” and vice versa. This idea resulted in the following set of rules\(^2\)\(\text{Table 1}\).

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<td>4n</td>
<td>con</td>
<td>dis</td>
</tr>
<tr>
<td>4n + 2</td>
<td>dis</td>
<td>con</td>
</tr>
</tbody>
</table>

Table 1. General selection rules for electrocyclic reactions.
Electrocyclic reactions play a central role in organic chemistry.\textsuperscript{11} An electrocyclic reaction is characterized by the opening, or closing, of a ring within a single molecule leading to the conversion of two $\sigma$-electrons to two $\pi$-electrons, or the reverse.\textsuperscript{12} Orbital symmetry determines the stereochemistry of electrocyclizations. A classic example is the key step in the synthesis of ergosterol (3). The first step is a sigmatropic rearrangement, which will be discussed next, to vitamin D$_2$ (2) and the final step involves a six-electron electrocyclic process to form ergosterol (3) (Scheme 1).

![Scheme 1](image)

Scheme 1. Pericyclic reactions involvement in the synthesis of ergosterol (3).

The interconversion of cyclobutene and butadiene is a four-electron electrocyclic reaction and is the simplest electrocyclic reaction for a neutral system shown in Scheme 2. The thermally allowed conrotatory electrocyclic ring opening has an experimental activation energy of 32.5 kcal/mol.\textsuperscript{13} MCSCF theory predicts a barrier of 35.8 kcal/mol which is in good agreement with the MP4 value of 34.5 kcal/mol, reported by Houk and...
Evanseck. Ring opening of cyclobutene (4) to 1,3-butadiene (5) is an exothermic process with $\Delta H^\circ_{\text{rxn}} = -10$ kcal/mol.

Scheme 2. 4 $\pi$ electrocyclic reaction.

The interconversion of 1,3,5-hexatriene (6) and 1,3-cyclohexadiene (7) is a thermal, 6 $\pi$ electron, disrotatory process (Scheme 3). The optimized transition structure adopts a boat shape to maximize the interaction of the $\pi$ system and the formation of the $\sigma$ bond. The activation energy for a ring closure was predicted to be 26 kcal/mol which is in good agreement with the experimental value of 29 kcal/mol. The cyclic diene is favored by approximately 12 kcal/mol ($R = H$).

Scheme 3. Disrotatory electrocyclization of 1,3,5-hexatriene (6).
Sigmatropic Shifts

Sigmatropic shifts or rearrangements are characterized by migration of a σ bond that is adjacent to one or more π-systems, with reorganization of the π-system.\textsuperscript{2a}

Sigmatropic rearrangements can be predicted by a general set of rules seen below in Table 2.\textsuperscript{3} The orientation of interacting orbitals directs various sigmatropic rearrangements and the resulting stereochemistry. A sigmatropic rearrangement may occur in either a suprafacial or antarafacial manner. Suprafacial is the term used when the migrating group or atom remains on the same face of the conjugated π-system throughout the process. An antarafacial approach directs the migrating group or atom to the opposite face of the π-system. Sigmatropic rearrangements can be predicted using the following set of general rules.\textsuperscript{3}

<table>
<thead>
<tr>
<th>n = # of electrons</th>
<th>supra/supra</th>
<th>supra/antara</th>
<th>antara/antara</th>
</tr>
</thead>
<tbody>
<tr>
<td>4n + 2</td>
<td>allowed</td>
<td>forbidden</td>
<td>allowed</td>
</tr>
<tr>
<td>4n</td>
<td>forbidden</td>
<td>allowed</td>
<td>forbidden</td>
</tr>
</tbody>
</table>

Table 2. General selection rules for sigmatropic shifts.

The following schemes are just a few examples of the many types of sigmatropic shifts. The 1,3-sigmatropic hydrogen shift in propene (8) (Scheme 4) has been studied extensively.\textsuperscript{16} The allowed [1s,3a] transition structure is very contorted and similar in energy to an allyl radical plus a hydrogen atom which would be formed in a dissociation-recombination mechanism. At the CASSCF/6-31 G* level of theory, the parital C---H bond is 1.61 Å long and the C-C bond length is approximately halfway between that of a double and single bond. The structure resembles an allyl radical system.\textsuperscript{14} The
symmetry forbidden suprafacial [1s,3s] hydrogen shift is an unfavorable pathway. Hartree-Fock and MCSCF calculation predict a transition structure that resembles a trimethylene diradical.\textsuperscript{17} The calculated energy of this species is approximately 60 kcal/mol higher than propene (8). There is no experimental evidence for a thermal, concerted 1,3-hydrogen shift in simple hydrocarbon systems.

![Scheme 4. 1,3-sigmatropic hydrogen shift of 1-propene (8).](image)

The methyl shift of 1-butene (9) is a thermally allowed [1a, 3s] shift as illustrated in Scheme 5.\textsuperscript{18} The calculated activation energy at the MP2 level of theory is 96 kcal/mol, which is larger than the required 72 kcal/mol for the cleavage of the C-C bond.\textsuperscript{19} Both allowed and forbidden processes are calculated to have activation energies comparable to, or higher than, the energy required for C-C bond cleavage and recombination. No decisive experimental examples of 1,3-sigmatropic alkyl shifts are known in acyclic systems.
Scheme 5. 1,3-sigmatropic methyl shift of 1-butene (9).

The 1,5-sigmatropic methylene shift in bicyclo[4.1.0]-heptadiene (10) (Scheme 6) has been studied at the Hartree-Fock level of theory.\textsuperscript{20} Possible transition structures for the [1,5] methylene shift are the allowed [1s, 5s] and the forbidden [1a, 5s] rearrangements. The activation energy of the [1,5] sigmatropic methylene shift in bicyclo-[4.1.0]-heptadiene (10) itself is not experimentally known. The calculated activation energy at the MP2 level of theory is 53 kcal/mol for the allowed [1s, 5s] methylene shift and 87 kcal/mol for the forbidden [1a, 5s] methylene shift reaction.

Scheme 6. [1,5] sigmatropic methylene shift in bicyclo [4.1.0]-heptadiene (10)

The most synthetically useful sigmatropic rearrangement is the [3,3] process, which was discovered by A. C. Cope in 1940 and now bears his name. The Cope reaction is a well known and synthetically useful sigmatropic process.\textsuperscript{9,21} The
unsubstituted example (Scheme 7) is an overall degenerate process since the reactants and products are identical. In substituted examples, the rearrangement is usually stereospecific.


The aromatic transition state for the Cope rearrangement prefers the chair conformation (12) over the boat conformation (13) by approximately 5-6 kcal/mol (Figure 3). The Cope reaction activation barrier is 33.5 kcal/mol and has a negative entropy of activation of -13.8 cal/mol K, which supports a concerted, cyclic transition state, rather than a biradical (14).

Figure 3. Possible transition structures for the Cope rearrangement.
Cycloadditions

Cycloadditions are some of the most widely used reactions in organic chemistry and have been studied extensively both experimentally and theoretically. This field has been reviewed in a substantial number of books and review articles. Cycloadditions are reactions involving the addition of two or more unsaturated molecules to each other to form a new ring. This generally proceeds with a high degree of stereocontrol, which is very crucial for synthetic applications. This section serves to introduce the topic of cycloadditions and to briefly cover certain important aspects by using examples of simple hydrocarbons.

Cycloadditions are characterized by the number of electrons and the type of atoms involved in the process. A broad definition of cycloaddition reactions is reactions that involve the addition of two or more unsaturated molecules to each other, which yields a new ring. Cycloadditions can occur intermolecularly or intramolecularly. Orbital symmetry principles apply to both cycloaddition and retro-cycloaddition processes. The latter is the concerted fragmentation of one molecule into two or more smaller compounds. Scheme 8 presents an example of inter and intramolecular [4 + 2] cycloadditions.
Scheme 8. Inter and intramolecular [4 + 2] cycloadditions.

The best-known orbital symmetry controlled process in organic chemistry surely is the Diels-Alder reaction. Otto Diels and Kurt Alder discovered the [4 + 2] cycloaddition, named in their honor, in the 1920's and were later presented with a Nobel Prize. The Diels-Alder reaction is categorized as a [4 + 2] cycloaddition due to four π electrons from the diene and two π electrons from the dienophile that are directly involved in the bonding process. Several common Diels-Alder reactions are illustrated in Scheme 9.
The mechanism of the Diels-Alder reaction has been the subject of a lively debate. The parent Diels-Alder reaction of 1,3-butadiene (5) with ethylene to form cyclohexene is the prototype thermally allowed cycloaddition. The reaction is said to proceed in a concerted fashion when there is formation of the two bonds in a single transition state. Moreover, the reaction can be considered to be synchronous concerted if both the new bonds are formed simultaneously and at the same rate. If bonds are formed at different rates, the reaction is considered asynchronous concerted. Both processes are concerted and stereospecificity is expected. When unsymmetrically substituted dienes or dienophiles react, the asynchronous process should be operative (Figure 4).

The other plausible mechanism is depicted as a stepwise process. This involves formation of a single bond between the diene and dienophile to produce an intermediate, which then forms a second bond to yield the cycloadduct. The intermediate can be considered a diradical or zwitterion. Diels-Alder reactions are almost always stereospecific; therefore, if a biradical intermediate forms, it cannot have a lifetime long enough to permit successive bond rotation and loss of stereochemistry. Based upon the vast amount of literature concerning this issue, the consensus is that this process is concerted,\(^4\) however, there is still discussion about the mechanism of substituted cases.\(^{25}\)
Until recent years, only theoretical calculations could provide detailed information about transition state geometries. The emergence of femtosecond spectroscopy has allowed for the real-time studies of the retro Diels-Alder reaction of norbornene and norbornadiene. Zewail has suggested that both symmetric and nonsymmetric motions of the forming and breaking of C-C bonds are possible and the concerted and nonconcerted trajectories of the reactants are present. It was also suggested that the reactions path followed would be determined by the symmetry/asymmetry of the structure, activation barrier and available energy.

The Diels-Alder reaction's ability to form six-membered rings is accompanied by remarkable regioselectivity and stereoselectivity for a given combination of diene and dienophile. The stereochemistry can often be predicted using the Alder "endo" Rule while frontier molecular orbital theory has been commonly used to predict the regioselectivity.\textsuperscript{5,27d} Scheme 10 illustrates representative examples of regioselectivity and stereoselectivity.
Scheme 10. Regioselective and stereoselective Diels-Alder reactions.

The Woodward-Hoffman rules for cycloadditions and cycloreversions are summarized in Table 3. These generalized selection rules serve to predict whether thermal or photochemical are allowed or forbidden of such reactions. These rules can be derived by orbital correlation diagrams, frontier molecular orbital theory, or transition state aromaticity analysis.²⁷

<table>
<thead>
<tr>
<th>n = # of electrons</th>
<th>Mode</th>
<th>Thermal, Δ</th>
<th>Photochemical, hv</th>
</tr>
</thead>
<tbody>
<tr>
<td>4n</td>
<td>supra/supra</td>
<td>forbidden</td>
<td>allowed</td>
</tr>
<tr>
<td></td>
<td>antara/antara</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4n</td>
<td>supra/antara</td>
<td>allowed</td>
<td>forbidden</td>
</tr>
<tr>
<td>4n + 2</td>
<td>supra/supra</td>
<td>allowed</td>
<td>forbidden</td>
</tr>
<tr>
<td></td>
<td>antara/antara</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4n + 2</td>
<td>supra/antara</td>
<td>forbidden</td>
<td>allowed</td>
</tr>
</tbody>
</table>

Table 3. General selection rules for cycloadditions.
The thermally allowed cycloaddition of s-cis 1,3-butadiene (5) and ethylene (15) represents the prototypical Diels-Alder reaction (Scheme 11). The reaction is believed to proceed through a symmetrical transition state. The calculated transition structure possesses Cs symmetry in which the angles of attack of the approaching diene and dienophile are approximately tetrahedral with a forming bond distance of 2.285 Å. A free energy of activation of 37.18 kcal/mol and an enthalpy of activation of 25.01 kcal/mol have been calculated at the MP4/6-31G*//MP2/6-31G* level of theory for the reaction of 5 and 15. The experimental enthalpy barrier was determined to be approximately 27 kcal/mol, in excellent agreement with calculations. The stepwise mechanism is predicted to be slightly higher in energy. The difference in energy between the concerted and the stepwise processes is referred to as the energy of concert. For the cycloaddition of 5 and 15, the energy of concert is predicted to be 6 kcal/mol at the CASSSCF/6-31G* level. This is in good agreement with experimental results of 2-7 kcal/mol.

Scheme 11. Prototypical Diels-Alder reaction between butadiene and ethylene.
High levels of theory are required to reproduce experimental activation parameters. Hartree-Fock methods and other methods, which consist of low levels of electron correlation, are inadequate. Semiempirical methods are inconsistent. Higher levels of theory such as MP4 and B3LYP (density functional theory) do a much better job at predicting cycloaddition reactions and pericyclic processes in general.\textsuperscript{30}

There are many other types of cycloadditions.\textsuperscript{2} An example that has been extensively examined in the [2 + 2] cycloaddition as shown in Scheme 12. The $[\pi 2s + \pi 2s]$ dimerization of two moles of ethylene (15) to cyclobutane (17) is thermally forbidden and photochemically allowed.\textsuperscript{3} Most commonly, this is a photochemical cycloaddition that produces four-membered rings. Most thermal [2 + 2] cycloadditions, which are formally symmetry forbidden, proceed by a stepwise pathway involving diradical or zwitterionic intermediates. One example is from the cycloaddition of ketene (18) and ethylene (15), which occurs readily.\textsuperscript{31} The cycloaddition is categorized as $[\pi 2s + \pi 2a]$ and the calculated transition state for the ketene cycloaddition indicates an asynchronous concerted reaction, which has a high degree of zwitterionic character. Other theoretical examples of [2 + 2] cycloadditions involving unsaturated systems, such as acetylene\textsuperscript{32} and allene,\textsuperscript{33} to ethylene have been studied.

Higher-order cycloadditions serves as useful synthetic applications in making large complex ring systems. An example is the [4 + 6] cycloaddition, which provides a route to ten-membered ring systems. The simplest example involves the reaction of 1,3,5-hexatriene (6) and 1,3-butadiene (5) to give compound 19 (Scheme 13). However, this reaction is entropically unfavorable and lacks the necessary geometric constraints needed to be an efficient cycloaddition. A more efficient example is the reaction of tropone and cyclopentadiene is shown in Scheme 14. In contrast to the Alder rule, this reaction results in the exclusive formation of the exo isomer as represented in Scheme 14.
Scheme 13. Cycloaddition to form 10-membered ring.


A more complex reaction is the [2 + 2 + 2] cycloaddition, which is a 6 \( \pi \) electron thermally allowed process,\(^3\) exemplified by the cyclotrimerization of ethylene (15) to yield cyclohexane (20) and the cyclotrimerization of acetylene (21) to yield benzene (22) (Scheme 15). In 1886, Berthelot reported that acetylene thermally cyclotrimerizes to benzene.\(^34\)
Recently, our research group found that a tethered triyne, 1,6,11-dodecatriyne (23), cyclotrimerizes to a benzene derivative, indacene (24) (Scheme 16). Even though concerted \([2 + 2 + 2]\) cyclotrimerizations are exothermic reactions, they are unfavorable due to very high entropic and enthalpic barriers. However, Johnson and Kociolek suggested a stepwise process in which a 1,4-diradical is formed followed by subsequent trapping with an alkyne. More commonly, these reactions do not occur without the use of metal catalyst as a template.
Group Transfers

Group transfers are the least explored category of pericyclic reactions. One of the most basic group transfers is the concerted dihydrogen transfer between ethylene (15) and ethane (25) as shown in Scheme 17. This group transfer reaction is categorized as \([\pi 2s + \sigma 2s + \sigma 2s]\). Computational studies predict an aromatic transition state with D_2h symmetry. The calculated activation barrier using MCSCF theory was 71 kcal/mol while MP2 theory predicted a value of 51 kcal/mol, both predicting relatively high values.

\[
\begin{align*}
\text{H} & \quad + \quad \left[ \pi 2s + \sigma 2s + \sigma 2s \right] \\
\text{H} & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ Quad
(29) using diimide (30). As shown in Scheme 18, this process can be highly selective, even in the presence of other functional groups.

Scheme 18. Representative group transfer reactions.

Cheletropic reactions are defined as pericyclic processes in which two sigma bonds that terminate at a single atom are made or broken in a concerted fashion. The fragment containing a single atom is referred to as the chelefuge. Reaction at the chelefuge position is classified as either linear or non-linear and reaction at the diene component is referred to as being suprafacial or antarafacial. The term linear implies the linear least motion path of the chelefuge. Cheletropic 1,4-additions are not common.
because 1,2-addition is usually a more favorable process. For this reason, most cheletropic reactions have been studied in the reverse process. Scheme 19 illustrates common examples of extrusion of small molecules from five-membered rings.

Scheme 19. Cheletropic elimination reactions.

Ene Reactions

The ene reaction is a pericyclic reaction, but is not easily categorized because it is a combination of a cycloaddition and a sigmatropic shift. In this reaction a \( \pi \) bond is converted to a \( \sigma \) bond, and a hydrogen atom is transferred at the same time by a 1,5-shift. The ene reaction is a concerted process that consists of a thermal intermolecular or intramolecular process between an alkene carrying an allylic hydrogen, which acts as a donor (ene), and the double bond or triple bond (enophile), which acts as an acceptor. Basic ene reactions with simple unactivated hydrocarbons such as propene (8) and ethylene (15) usually take place at high temperatures (Scheme 20). Often, the reverse fragmentation is more favorable. Due to the high activation barrier of many ene
reactions, the use of catalysts or the addition of appropriate activation groups is usually necessary. For example, Lewis acid catalyzed ene reactions with methyl acrylate are highly selective and proceed under relatively mild conditions (Scheme 20).

Scheme 20. Representative ene reactions.
This reaction has found considerable synthetic utility. **Scheme 21** represents an example of an intramolecular ene reaction of an unsaturated ketones in which the carbonyl functionality serves as the ene component, *via* its tautomer, and the olefinic moiety serves as the enophile. This is known as the Conia reaction.⁴³

Scheme 21. Intramolecular Ene reaction.
Introduction to Dehydropericyclic Reactions

The term “dehydropericyclic” reaction is a new term coined in our research group to describe classes of pericyclic reactions that form unstable intermediates. Essentially, dehydropericyclic reactions are pericyclic reactions (as discussed previously) that are formally missing two or more hydrogens in the overall process. The first examples of dehydropericyclic reaction can be found in the scientific literature dating back to the late nineteenth century. Early researchers really did not know how to characterize these observations, but knew something was very unusual about them. The following section will describe some common types of dehydropericyclic reactions.

Dehydrobenzene Chemistry

Dehydrobenzene, also known as benzyne, is the archetypal member of the class of compounds known as arynes. Arynes are aromatic compounds containing a formal carbon-carbon triple bond and often are referred to as dehydroaromatic compounds. Benzyne, the simplest and most studied aryne, is best described as “benzene with two hydrogen atoms removed.” Two \( sp^2 \) orbitals with a total of two electrons are orthogonal to the aromatic \( \pi \) system. There are three possible isomeric \( C_6H_4 \) structures: \( o \)-benzyne 31, \( m \)-benzyne 32, and \( p \)-benzyne 33 (Figure 5).
Figure 5. C₆H₄ isomeric structures.

*p*-Benzyne

Bergman is credited with providing the first experimental evidence for the existence of *p*-benzyne (33) through deuterium labeling studies on enediyne rearrangements⁴⁶ (Scheme 22). The experiment demonstrated the thermal interconversion of deuterium labeled enediyne 34 to 35 with scrambling of deuterium and subsequent intermolecular trapping. These results provided evidence for a skeletal carbon rearrangement to produce a diradical intermediate, which was further, characterized by CIDNP spectroscopy and was determined to possess singlet spin state. This reaction is commonly referred to as the Bergman cyclization and is categorized as a 6 π-electron electrocyclization, which is a thermally allowed disrotatory process. Even though this is a diradical intermediate, the activation barrier is relatively moderate and analogous to other pericyclic reactions of hydrocarbons. Bergman determined the enthalpy of activation to be 32 kcal/mol for cyclization and 18 kcal/mol for ring opening. An important observation was that incorporation of strain in the ground state structure can lower the energy of activation and in some cases, cyclization occurs at ambient temperature.⁴⁷
It has been found that the incorporation of the enediyne moiety into a ring decreases the activation barrier for cyclization. In a ten-membered ring (37), cycloaromatization readily occurs at $37^\circ$ C (Scheme 23). It has been suggested that the determining factor for reactivity is not the distance between the acetylenic termini. Magnus and coworkers concluded that the difference in strain energy between the enediyne and the transition structure leading to the diradical intermediate will determine the reactivity of the enediyne towards cyclization. This approach appears to reflect the
observed reactivity of enediynes, but does not consider substituent effects, which also
have been shown to affect reactivity.

![Scheme 23. Cycloaromatization of cyclic enynes.](image)

36  \( n = 1 \)
37  \( n = 2 \)

In recent years, there has been renewed interest in this important
electrocyclic process because potent anti-tumor agents are believed to undergo Bergman-type
cyclization as part of their essential chemistry.\(^{50}\) This discovery has resulted in a
dramatic increase in the exploration of the chemistry of enediynes and
cycloaromatizations. The five known classes of enediyne containing natural products are
calicheamicin, esperamicin, dynamicin, kedarcidin, and C-1027, which are illustrated in
Figure 6. These natural products are among the most potent antitumor and antibacterial
agents known. The mode of action is believed to involve diradicals, which abstract
hydrogens from DNA to cause double-strand DNA cleavage and cell death.\(^{51}\) In the
natural product, the enediyne moiety is contained within a nine or ten membered ring,
which facilitates chemical activation. However, the simple nine membered ring enediyne
(36) is unknown and the ten-membered ring (37) reacts at room temperature.\(^{52}\)
Figure 6. Natural products that contain the enediyne moiety.
**m-Benzyne**

1,3-Didehydrobenzene, or *m*-benzene (32), is the least understood of the three benzyynes. To date, very little has been reported about its chemical reactivity.\(^{53}\) *m*-Benzyne (32) is best described as a singlet diradical.\(^{54}\) Examination of *m*-benzyne derivatives have shown them to be generally less reactive than related phenyl radicals.\(^{55}\) Recently, Sander and coworkers reported experimental and theoretical results on the chemistry of 32, which was generated by two separate precursors (Scheme 24), isolated in an argon matrix, and characterized spectroscopically.\(^{56}\) The infrared spectrum of *m*-benzyne (32) was recorded and is in good agreement with the calculated spectrum. *m*-Benzyne (32) can be identified by the observed vibration at \(547 \text{ cm}^{-1}\) (545 cm\(^{-1}\) calculated) which is attributed to the strong ring deformation. The CCSD/6-31G* optimized geometry of *m*-benzyne (32) indicated a planar distorted hexagon.
1. 300°C  
2. Ar, 10 K

hv > 305 nm  
Ar, 10 K

Scheme 24. Thermal and photochemical generation of m-benzyne (32).

o-Benzyne

The structure of o-benzyne (31) has long held the interest of researchers. Wittig is acknowledged to have discovered o-benzyne chemistry.\textsuperscript{57} Roberts and coworkers later generated conclusive evidence by use of a \textsuperscript{14}C labeling study, which confirmed the existence of o-benzyne (31) as a reactive intermediate\textsuperscript{58} (Scheme 25). Equal amounts of \textsuperscript{14}C labeled anilines (39 and 40) were observed in the dehydrohalogenation of chlorobenzene (38), which demonstrated that a symmetrical intermediate was generated.
o-Benzyne (32) has been previously generated by trapping as a Diels-Alder adduct, observed spectroscopically, and studied in metal complexation studies.  

Scheme 25. o-Benzyne $^{14}$C labeling study.

o-Benzyne (33) is best described as a singlet, acetylenic or cumulenic compound with an estimated strain energy of 63 kcal/mol. The MP2/6-31G* optimized geometry has been reported and shows a relatively unperturbed aromatic ring. The dehydrogenated C-C triple bond length is calculated to be 1.268 Å, which is longer than a typical C-C triple bond of 1.2 Å. This is indicative of a weak triple bond. This is shown in the in-plane π bond strain energy, which is estimated to be 49.5 kcal/mol.

Figure 7. Resonance contributors of o-Benzyne (33)

Infrared stretching frequency assignment for the triple bond of o-benzyne (33) has been the subject of controversy. Nevertheless, theory and experiment have recently come to an agreement and assigned a value of 1860 ± 15 cm$^{-1}$. This value is outside the

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normal range for C-C triple bonds. Results conclude that the triple bond in 33 can be portrayed as an intermediate between a normal triple bond and a double bond. **Scheme 26** illustrates a variety of synthetic strategies to form o-benzyne (33).

![Scheme 26. Different synthetic pathways to form o-benzyne (33).](image)

The triple bond of o-benzyne (33) should be easily polarizable, \(^{44}\) consequently it should be able to undergo nucleophilic and electrophilic reactions as well as concerted processes. One of the simplest reactions of o-benzyne (33) is the hydrogenation to benzene (22), which has been demonstrated under a variety of conditions. \(^{61}\) The detection of benzene (22) under conditions found to generate o-benzyne (33) supports the

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notion that reduction of \( \alpha \)-benzyne with molecular hydrogen occurs readily. It is also evident that \( \alpha \)-benzyne is capable of being dehydrogenated under mild and forcible conditions\(^4\) (Scheme 27).

\[
\text{Reduction} + \text{H}_2 \quad \longrightarrow \quad \text{Reduction}
\]

Scheme 27. Reduction of \( \alpha \)-benzyne (33) to benzene (22).

**The Dehydro Diels-Alder Reactions**

One of the clearest examples of a dehydropericyclic reaction is the \([4 + 2]\) cycloaddition. The traditional Diels-Alder reactions proceed by two modes as shown in equations [1] and [2]. In principle, however, this pericyclic process may be extended to six new types which result in strained six membered rings as shown in equations [3] – [8]. These eight versions of the Diels-Alder reaction are listed in Figure 8.
Figure 8. Eight versions of the Diels-Alder cycloaddition.
Eneyne + Alkene Cycloaddition

Reports of “dehydro” Diels-Alder reactions of enynes with alkenes [Eq. 3] are uncommon in the literature, but recently have increasingly regained the interest of researchers. One of the first to suggest enyne reactions with alkenes was Butz and coworkers\textsuperscript{62} (Scheme 28). They speculated that a 1,2-cyclohexadiene intermediate (42) resulted from cycloaddition between 40 and 41. The unstable allenes 42 reacted further to yield the observed product 43 under thermal conditions.

\begin{center}
\begin{tikzpicture}
  \node (1) at (0,0) {40};
  \node (2) at (1,0) {41};
  \node (3) at (2,0) {42};
  \node (4) at (3,0) {43};
  \node (5) at (0,-1) {$\Delta$};
  \draw[->] (1) -- (5);\draw[->] (5) -- (2);
  \draw[->] (2) -- (3);
  \draw[->] (3) -- (4);
\end{tikzpicture}
\end{center}

Scheme 28. Eneyne cycloaddition using maleic anhydride (41).

More recently, intramolecular cycloaddition of conjugated enynes to alkenes has been reported. Danheiser and coworkers have applied enyne cycloadditions to alkenes to the synthesis of aromatic compounds. One example is shown in Scheme 29.\textsuperscript{63} The work of Danheiser has demonstrated the synthetic utility of these cycloaddition processes in solution. In most cases, enyne cycloaddition to alkenes have been observed under protic acid conditions or in the presence of Lewis acid catalysts.
In contrast, our research group has employed flash vacuum pyrolysis to investigate intramolecular cycloadditions of conjugated enynes as seen in Scheme 30. Under these conditions, Lewis and protic acid catalysis are unlikely. This issue will be further discussed later in this section.
Enyne + Alkyne Cycloaddition

The intermolecular dehydro Diels-Alder reactions (intramolecular [4 + 2] cycloadditions) of enynes with alkynes [Eq. 5] have been postulated for over a century. This, so-called, “dimerization” was discovered by Michael and Bucher, in 1895. In 1934, Dykstra reinvestigated the thermal reaction of vinylacetylene (44) and found only products from dimerizations. Non-catalytic conditions mostly yielded diethynylcyclobutane. Under catalytic acidic conditions, nearly half of the resulting product was styrene (46). At the time, trimerization of acetylenes to aromatic compounds was well known, so Dykstra hypothesized that this “represents a new type since 1,4-addition must be involved.” Dykstra also suggested that this new reaction was analogous to the Diels-Alder reaction and could be represented by Scheme 31. This is believed to be the first case in which the 1,2,4-cyclohexatriene structure 45 was documented.

\[
\begin{align*}
\text{44} & \quad \xrightarrow{\Delta} \quad \text{45} & \quad \xrightarrow{\Delta} \quad \text{46}
\end{align*}
\]

Scheme 31. Dykstra example of an intermolecular dehydro Diels-Alder reaction.

Dykstra also concluded that intermediate 45, the cyclic allene, “appeared to be practically impossible stereochemically” and it may not be actually formed as an intermediate, but that a “triad” shift occurred simultaneously in order for styrene 46 to be formed.

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Daddar and El-Assal as well as other researchers synthesized substituted phenynaphthalene 2,3-dicarboxylic anhydrides (49) by cyclization of substituted phenylpropionic anhydrides (47) (Scheme 32). This synthesis may also operate as a key step in the synthesis of natural plant products called lignins. Brown and Stevenson investigated substituent effects on cyclization of 47 to 49, still not proposing an intermediate. Whitlock and coworkers executed experiments in deuterium-labeled solvents and suggested that the phenylpropionic acid dimerization reaction may proceed through cyclobutadiene formation and expressed reservations concerning the reaction being concerted. Nevertheless, no further mechanistic explanation was given for the formation of the naphthalene derivatives and formation of the cyclic allene intermediate 48 was not proposed until the first clear example of 1,2,4-cyclohexatriene was reported by Miller and Shi, who described this as an “isoaromatic” molecule.

Scheme 32. Intramolecular Diels-Alder reactions of phenylpropionic anhydride to phenynaphthalenes.
Over the past fifteen years, there has been a considerable effort to generalize dehydro-Diels-Alder reactions. Intramolecular and intermolecular [4 + 2] cycloadditions of alkynes to endiynes to form 1,2,4-cyclohexatriene, cyclic allene, intermediates can be categorized into a type I and type II dehydro-Diels-Alder cycloadditions as illustrated in Scheme 33.

Scheme 33. Type I and Type II Dehyro Diels-Alder cycloadditions.
To date, the majority of dehydro Diels-Alder cycloadditions have been of type I. An example of the type I cycloaddition would be of Danheiser and coworkers in which, they reported on the solution phase intramolecular [4 + 2] cycloaddition reaction of in which 1-en-3-yne reacts with an alkyne.\(^6^3\) Scheme 34 illustrates that enediyne 50 intramolecularly cyclizes under thermal conditions to form the substituted indan 51.

### Scheme 34

**Scheme 34. Danheiser enyne cyloaddition in protic solvent conditions.**

Recently, Echavarren and coworkers have reported the first example of the alternative type II cycloaddition (Scheme 35).\(^7^3\) The 3-ene-1-yne substituent of the naphthalene derivative (52) reacts with the alkyne portion under thermal conditions in solvent to form fluoranthene 53. The same aromatized product, fluoranthene 53, is expected in both the type I and II processes. However, their differences may be substantial with regard to the outcome of the strained intermediates that are formed.\(^7^4\)
Scheme 35. Type II cycloaddition.

Our research group has employed flash vacuum pyrolysis (FVP) to investigate intramolecular cycloadditions of conjugated enynes as routes to strained allene intermediates.\textsuperscript{64} Flash vacuum thermolysis experiments, generally represented by [Eq. 4], are illustrated in Scheme 36. The results are consistent with [4 + 2] cycloaddition to give a strained cumulene, followed by secondary reactions.

Scheme 36. FVP results of intramolecular enyne cycloadditions.
The proposed mechanism involves a six-membered allene, 1,2,4-cyclohexatriene (54), as the reaction intermediate (Scheme 37). The formation of such species [Eq. 4] has been shown experimentally using various trapping techniques. Six-membered ring allenes have a large calculated strain energy\(^75\). The experimental enthalpy of formation of \(\Delta H^\circ_f = 105.1 \text{ kcal/mol} \) for 1,2,4-cyclohexatriene (54) may be to that of benzene, 19.81 kcal/mol.\(^76\) The electronic structure and stability of 1,2,4-cyclohexatriene (54) have been studied with several theoretical methods. AM1 semiempirical calculations predict 1,2,4-cyclohexatriene (54) to have a \(\Delta H^\circ_f = 93.7 \text{ kcal/mol} \) compared to 22.0 kcal/mol for that of benzene.\(^77\) Recent \textit{ab initio} studies at the G2(MP2) level report similar values of \(\Delta H^\circ_f = 96.2 \text{ kcal/mol} \) and 21.1 kcal/mol for benzene (22). The energetics of cycloaddition reactions leading to allene intermediates were studied at the MP4//MP2 level of theory.\(^64\) The formation of 1,2,4-cyclohexatriene (54) was found to have a \(\Delta G^\circ_{rxn} = -13.4 \text{ kcal/mol} \) which is significantly lower than a previous estimate\(^63\) and an activation energy of \(\Delta G^\ddagger = 42.0 \text{ kcal/mol} \) for allene. Significant interest has been given to 1,2,4-cyclohexatriene (54) in its relationship to benzene isomers and related isomerization.\(^78,79\)

![Scheme 37. Dehydro Diels-Alder reaction of enyne 44 and acetylene (21).](image)

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A recent theoretical and experimental investigation of dehydro Diels-Alder reactions examined the formation of the cyclic allene intermediates under conditions for intramolecular, ionic, and radical intermolecular cycloaromatization processes.\textsuperscript{80} Computational examination of 1,2,4-cyclohexatriene (54) conversion to benzene (22) predicts the most favored intramolecular path for aromatization of 1,2,4-cyclohexatrienes as a pair of successive [1,2] H shifts rather than a [1,5] shift. Hopf and Schreiner\textsuperscript{81} and Ananikov\textsuperscript{82} have reported results that support these computational predictions. Experimental studies shows that cycloaromatization of cyclic allenes may follow both inter- and intramolecular pathways, depending on the reactions conditions. For synthetic purposes, the best procedure is to use a protic solvent to promote the ionic intermolecular route, which has shown to be the fastest and highest yielding route. Computational calculations predict that benzoannulation significantly lowers the barrier to the rate-limiting [1,2]-H transfer of the intramolecular route as shown in Scheme 38. Calculations also predict a very low barrier for the reaction of cyclohexatrienes with carbon tetrachloride, and that cyclic allenes may act as nucleophiles.
Scheme 38. Experimental and computational studies examining pathways of cyclic allenies.

**Diyne + Alkene Cycloaddition**

Our research group provided the first examples of cycloadditions in which the traditional diene compound is replaced by a diyne moiety [Eq. 5]. It is proposed that 1,3-nonadiyn-8-ene (55) undergoes cycloaddition to give intermediate 56 (Scheme 39). Subsequently, 1,2,3-cyclohexatriene derivative intermediate 56, is believed to undergo electrocyclic ring opening to dieneyne 57 (major product). The thermolysis of 55 also produced a minor amount of indan (58) and indene (59), which indicates that aromatization competes with ring opening of 1,2,3-cyclohexatriene intermediate 56. The unidentified isomeric structure was proposed to be 60. Included in this report was the predicted cyclization of 1,3-nonadiyn-8-yne (61) to form 1,2,3-cyclohexatriene or α-
benzyne derivative intermediate 62. The basic reaction is represented in Eq. 6. Pyrolysis of 61 gave indene (59), which presumably goes through indan (58).


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A fundamental goal of our research group is to explore the structural limitations of cyclic allenes. This experiment (Scheme 41) was executed in an attempt to examine the possibility of an intramolecular Diels-Alder reaction of the enyne moiety reacting with the connected phenyl ring (dienophile). As discussed previously, dehydro Diels-Alder cycloadditions have been executed using a variety of enyne and alkene or alkyne starting materials.

Recently, Saa and coworkers through theoretical and experimental studies, have shown that diynes react with a π bond in the adjacent phenyl ring in a Diels-Alder cycloaddition to yield what is believed to be cyclic allene intermediates. Phenylethynylphenylpropynone (63) was allowed to reflux in toluene using both protic and neutral conditions to yield benzofluorenone 64. The experiments were carried out in attempt to better understand the mechanism of this cycloaddition (Scheme 40).

Scheme 40. Saa Intramolecular Cycloaddition of diyne 63.
Results and Discussion

Thermal Chemistry of 1-phenyl-6-hepten-1-yne (65)

The thermal exploration of 65 was of great interest to our group. Prior to the published work of Saa and coworkers, we attempted to find similar cycloadditions using an unconjugated eneyne as illustrated in Scheme 41. 1-Phenyl-6-hepten-1-yne (65) was synthesized readily. Lithiation of phenylacetylene (70) followed by the addition of 5-bromo-1-pentene yielded 1-phenyl-6-hepten-1-yne (65) (Scheme 42). We proposed that under pyrolytic conditions, 1-phenyl-6-hepten-1-yne (65), would cyclize to form a cyclic allene intermediate 66. Through successive 1,2-hydrogen shifts or a 1,5-hydrogen shift, the intermediate, 2,3-dihydronaphthalene(67) would form and then dehydrogenate to yield 2,3-1H-cyclopentanaphthalene (68).
Scheme 41. Proposed enyne cyclization to yield cyclic allene intermediate.

Scheme 42. Synthesis of 1-phenyl-6-hepten-1-yne (65).
1-Phenyl-6-hepten-1-yne (65) was weighed out and passed through a quartz tube packed with quartz chips, maintained at 640 °C at 0.02 torr. The product was collected in a cold trap (-78°C) to give a yellow oil. The recovered material was taken up in CDCl₃ and passed through a plug of silica. The recovered material was observed by capillary GC and ¹H and ¹³C NMR. Mostly unreacted starting material (65) was observed. Trace amounts of phenylacetylene (70) were observed by GC and ¹H and ¹³C NMR. This may have been due to fragmentation of starting material during the pyrolytic process. There was no evidence that cyclization occurred to form the predicted structure 68. However, FVP at 750 °C showed evidence that cyclization of 1-phenyl-6-hepten-1-yne (65) may have led to 2,3-1H-cyclopentanaphthalene (68) as an intermediate, which further dehydrogenated, resulting in the formation of a small amount of benz[f]indene (69). The ¹H NMR spectrum showed resonances from 6.92-6.97 and 6.58-6.63 which might result from vinyl protons of benz[f]indene (69). Resonances at 3.42-3.47 ppm were also present that might show evidence for methylene protons of benz[f]indene (69). These results are in good agreement with the resonances of benz[f]indene (69) as given by the literature.¹⁷¹ ¹H NMR spectrum shows resonances from 6.80-7.05 (m, 1H) and 6.45-6.70 (m, 1H), which result from the vinyl protons, and 3.40-3.55 (m, 2H), which result from the methylene protons.

We conclude that pyrolysis of 65 may have led to the proposed intramolecular Diels-Alder reactions leading to 69. ¹H NMR shows evidence for predicted product 69. The crude material that resulted from the pyrolysis of 65 resisted several different chromatographic purification methods. Purification by rotary chromatography, column chromatography, and preparative thin layer chromatography were not successful. In the
future, more quantitative gas chromatography should be used to separate the crude mixture. If there is successful by separation by (GC), preparative gas chromatography should be employed so that pure formed products may be recovered to properly identify the produced products.
CHAPTER 2
CHEMISTRY OF C₄H₂

Introduction to High Temperature Gas Phase Chemistry of
Alkynes, Arynes, and Aryl Radicals

Application of flash vacuum pyrolysis (FVP) to the synthesis of moderately complex organic compounds has gained the interest of research laboratories worldwide since the mid-1960's. Discovery of the thermal equilibrium between alkynes with ylidencarbenes at high temperatures has led to an increase in the use of carbenes in the synthesis of polycyclic aromatic hydrocarbons (PAHs). Recent developments of the utility of high temperature gas phase pyrolytic reactions of acetylenes, precursors of arynes, and aryl radicals will be examined in this chapter.

Much of the fundamental chemistry in this field was developed in the laboratories of Australian chemist Roger Brown. Brown's involvement with acetylenic chemistry began with the generation of cumulenones such as propadienone, CH₂ = C = C = O, which were unknown at the time. Pyrolysis at 430 °C of isopropylidene benzylidenemalonate (71), which was formed from the condensation of benzaldehyde and Meldrum's acid, generated the cumulenone 72 (unlabeled). At higher temperatures (560°C), Brown and coworkers first observed the generation and rearrangement of the benzylidene carbene (73) through flash vacuum pyrolysis (FVP) of ¹³C labeled
isopropylidene benzyldenemalonate (71). Decarbonylation of propadienone 72 led
to the generation of the benzyldene carbenes (73 and 74). This reaction, at 560 °C, yielded
acetone and phenylacetylene isotopomers (75 and 76) (Scheme 43).

Scheme 43. Equilibration of acetylenes and methylcarbenes (vinylidene).

Through \(^1\)H NMR studies with a labeled substrate (75), it was determined the
benzyldene intermediate (73 or 74) undergoes a 1,2-phenyl, as well as, a 1,2-hydrogen
shift to give mixed, labeled phenylacetylenes 75 and 76. Further studies showed
evidence that the product ratio of 75 and 76 (75:25 respectively) was not a direct
reflection of the aptitude of hydrogen and phenyl migration. It was proposed that in the
temperature range of 550 to 720 °C, these 1,2-shifts are reversible. Subsequent studies have shown that acetylenes are in equilibrium with vinylidenes at this approximate temperature and this process is now known as the Brown rearrangement.

Many synthetic applications of the Brown rearrangement have been described.\textsuperscript{87,88} Generation of a carbene adjacent to a substituent bearing C-H bonds provides synthetically useful insertion reactions, as illustrated in Scheme 44. Studies by Brown and coworkers have shown that vinylidenes can be trapped in an intramolecular process.\textsuperscript{89} For example, pyrolysis of biphenyl-2-ylacetylene (77) at 700 °C gives the vinylidene (78), which can directly insert into C-H bond on the adjacent phenyl substituent to give phenanthrene (79). The vinylidene (78) can also add into the \( \pi \) system of the adjacent phenyl substituent to give intermediate 80, which rapidly rearranges to benzazulene (81). The reaction follows both pathways as illustrated in Scheme 44.

Another example of this the behavior of o-tolylacetylene (82) which at 720 °C forms the vinylidene 83, leading to indene (59) in 75% yield. Pyrolysis of 1-ethynyl-8-methylnaphthalene (84) at 750 °C yielded phenalene (85) by similar insertion to form a six-membered ring.\textsuperscript{90} Pyrolysis of 1-ethynylnaphthalene (86) led to vinylidene insertion into an aromatic C-H bond with formation of acenaphthylene (87) in 80% yield.
These syntheses usually require the initial preparation of ethynyl aromatics, but tend to behave poorly under FVP conditions because of decomposition to nonvolatile materials when sublimation is attempted. This problem becomes acute when the molecular system increases in size. The solution to this difficult problem has been to use precursors of the Ar-CX=CH$_2$ type which, on FVP, lose H-X to give the required ethynylarene system in the gas phase. Such groups are more robust during sublimation and large multi-substituted systems can be manipulated without the problem of oligomerization (Scheme 45). In an innovative approach to the construction of fullerene...
fragments, Scott and coworkers reported the synthesis of corannulene (91) by FVP of either 7,10-diethynylfluoranthene (88) or bis-2,2-dibromovinyl compound 89. In 1997, a full paper was published that describes compound 90 in which the 1-chlorovinyl group was used as a pyrolytic source of the ethynyl group. Yields of the bowl-shaped hydrocarbon increased dramatically as a result of the change. Other extensions of this approach are illustrated in the synthesis of cyclopentacorannule (93) from dichlorovinyl compound 92 and to semibuckminsterfullerene (95) from tetrachlorovinyl compound 95, by Rabideau and coworkers.
Scheme 45. Synthesis of corranulene and related systems by vinylidene insertions.
Secondary Reactions and Rearrangements

Many pyrolytic hydrocarbon syntheses are carried out at very high temperatures in the range of 900 – 1200 °C. Due to these high temperatures, the expected primary products are often transformed through secondary reactions. Scott and Necula attempted to generate the benzopyracylene (98) by FVP of the 1,5-bis(1-chlorovinyl) anthracene (96). 1,5-Bis(1-chlorovinyl) anthracene (96) could eliminate hydrogen chloride to give diethynyl anthracene (97) by carbene rearrangement and insertion. This would be expected to rearrange to benzopyracylene (98). However, FVP at 1100 °C, yielded no benzopyracylene, instead, the resulting products were isomers 100 and 101. Scott and Necula proposed that breaking of a C-C bond in 98 occurs with extrusion of a carbene to give 99, in equilibrium with the corresponding ethynyl compound. Reinsertion of the vinylidene of 99 into the left ring gives the observed cyclopent[hi]aceanthrylene (101). The subsequent deinsertion reaction is favored by strain energy of the pyracylene system of 98. The further isomerization of 101 to cyclopent[hi]aceanthrylene (100) is an example of Scott’s well-known hydrogen-shift/benzene ring contraction, which interconverts five- and six-membered rings in cyclopentarenes, and which is also involved in the automerization of naphthalene. This is described as a 6/5 rearrangement (Scheme 46).
Scheme 46. The insertion/deinsertion/reinsertion sequence leading to cyclopent[hi]aceanthrylene (100).

The preceding example illustrates a C$_2$-substituent migration from one ring to an adjacent ring, but the Jenneskens group has observed migration of an ethynyl group to an adjacent position in the same ring. 8-Ethynylfluoranthene (102) is not positioned to undergo direct isomerization/insertion to give a cyclopentarene, however, on FVP at
1100 – 1200 °C, benzo[ghi]fluoranthene (103) was a significant product (12 – 17 % yield). The other important reaction was the loss of C2 to give fluoranthene (53) in 28-31 % yield although the nature of this process is uncertain. It is proposed that ethynyl migration occurs by insertion of vinylidene in the adjacent position, followed by the alternative deinsertion reaction of the cyclobutarene (104) and insertion of the new vinylidene into the adjacent ring to form 103 (Scheme 47).

Scheme 47. Migration of the methylene group through a cyclobutarene.
In the early 1980's, Brown recognized that the equilibrium between acetylene and vinylidene might also be seen in benzyne and other arynes at high temperatures. Brown's initial approach was to anticipate and examine the $^{13}$C label scrambling of biphenylene, formed from high temperature generation of benzyne. The synthetic consequences of the interaction of exocyclic carbenes with neighboring substituents were also explored. Doubly $^{13}$C labeled phthalic anhydride (105) was synthesized and exposed to FVP conditions that gave a pyrolysate containing biphenylene (106) in which the major labeled isotopomer was $^{13}$C$_2$-biphenylene. However, $^{13}$C NMR spectroscopy showed that in this biphenylene (106), one $^{13}$C label was distributed approximately equally between the two quaternary positions (Scheme 48). This result explained alternative ring contractions of benzyne (107) leading to fulvenylidenes 109 and 110, to benzyne (108) and ultimately to scrambling of one label in biphenylene (106). The explanation of these labeling results has been challenged by Wentrup and coworkers who proposed that scrambling is due to the symmetry of loss of carbon dioxide from the anhydride (105) (Scheme 49). Brown and coworkers later concluded that both types of mechanisms are plausible.
Scheme 48. Generation and rearrangement of $[^{1,6}]_{3}^{13}C_{2}$ benzyne.
Exocyclic Vinylidene Insertion Across a Bay Region

As a tool to examine whether a vinylidene could insert into the C-H bond across the bay region, phenanthrene-3,4-dicarboxylic anhydride (111) was subjected to FVP at 870 °C. The complex product mixture included 3-ethynylacenaphthylene (113) and 1-ethynylacenaphthylene (114). Their formation were attributed to alternate modes of cleavage, a and b, in the presumed, highly strained, intermediate 112. This was the first observation of the deinsertion process. Brown failed to recognize a third important product, pyracyclene (115), which was later identified by Scott and coworkers and rationalized as the product of 6/5 hydrogen shift/ring contraction involving rings D and A of 112 in Scheme 50.
Scheme 50. Rearrangement products of FVP phenanthrene-3,4-dicarboxylic anhydride (111).
Aryl Radicals and Radical Rearrangement

1,2-Shifts of hydrogen in naphthyl radicals were first reported by Scott and Necula. Radicals were generated from bromonaphthalenes at 850 °C/0.1-0.5 torr in the presence of a 100-fold excess of maleic anhydride, which is a precursor of acetylene at this temperature. 2-Bromonaphthalene (116) gave a substantial yield of 2-ethynlnaphthalene by addition of the 2-naphthyl radical (117) to acetylene, and loss of a hydrogen atom. However, the major product was acenaphthylene (87), which was formed by the carbene insertion route from 1-ethynlnaphthalene (119) as illustrated in Scheme 51. Control experiments suggested that the major pathway to 1-ethynlnaphthylene (119) involved isomerization of the 2-naphthyl to the 1-naphthyl radical (118) and that direct isomerization of 2-ethynlnaphthalene to 119 by ethynyl migration was less important.

Scheme 51. Hydrogen migration in the 2-benzo[c]phenanthryl radical and subsequent cyclization.
A similar hydrogen shift was proposed where trapping of the new radical is intramolecular.\textsuperscript{105} FVP of 2-bromobenzo[c]phenanthrene (120) at 950-1100 °C generated the 2-benzo[c]phenanthryl radical (121) which was converted by a 1,2-shift of hydrogen in the 1-radical (122). Radical attack on the neighboring bay position 12 and loss of molecular hydrogen gave benzo[ghi]fluoranthene (103), as illustrated in Scheme 52. This result is supported by deuterium labeling studies and by BP/DN** calculations which predicts an activation energy of 58.4 kcal/mol for the 1,2-H shift. An aryne mechanism was ruled out because the very unstable cyclopenta[cd]pyrene was not detected.

![Scheme 52. Hydrogen migration in the 2-benzo[c]phenanthryl radical (122) and subsequent cyclization.](image-url)
This approach has been utilized in the synthesis of large fullerene fragments. Mehta and coworkers have developed a three-step synthesis of C\textsubscript{3}-symmetric hemibuckminsterfullerene (123).\textsuperscript{106} Similar 1,2-hydrogen shifts occurred after the initial homolytic cleavage of the bromine substituent during FVP at 1100 °C (Scheme 53).

Scheme 53. Mehta's three-step synthesis of C\textsubscript{3}-hemibuckminsterfullerene (123).

Experimental Investigation of Thermal Rearrangements of Butadiynes

A large number of polycyclic aromatic hydrocarbons (PAHs) have been found in the gaseous products of fuel-rich hydrocarbon-air/oxygen combustion.\textsuperscript{107} Homann and Pidoll have studied the formation of cyclic reaction products from the pyrolysis of a number of unsaturated aliphatic hydrocarbons, particularly the thermal decomposition of 1,3-butadiyne.\textsuperscript{108} Since 1,3-butadiyne is a very reactive hydrocarbon and has the highest concentration of all polyynes in the combustion process, these combustion scientists decided to study the pyrolysis of 1,3-butadiyne at low pressures in order to examine its behavior. Homann and Pidoll found that when butadiyne mixed with helium when
exposed to FVP at temperatures between 700 °C and 1000 °C and total pressures of 2.3 to 9.8 torr, a variety of hydrocarbons formed. The hydrocarbons that formed were (1) oligomers of \((C_4H_2)_n\) with molecular structures such as 3-methylene-1,4,6-heptatriyne and triethynylbenzene, (2) acetylene and polyynes such as and hexatriyne \((C_6H_2)\), (3) other polycyclic hydrocarbons with and without side chains which were observed at higher temperatures and longer reaction times, including diethynylbenzene \((C_{10}H_6)\), benzene \((C_6H_6)\), ethynylnapthalene \((C_{14}H_8)\), and phenanthrene or anthracene \((C_{14}H_{10})\) and finally (4) other products such as molecular hydrogen \((H_2)\), 1-buten-3-yne \((C_4H_4)\), biphenyl \((C_{12}H_{10})\), polymer, and soot. The samples were drawn through a molecular beam system and analyzed by mass-spectrometry. A movable inlet lance varied the residence time for \(C_4H_2\) with a maximum time of 45 ms.

A decade ago, Brown and coworkers studied the pyrolysis of 1,4-diphenyl-1,3-butadiyne \((124)\).\(^{109}\) The diyne was sublimed through a packed silica tube at 1120 °C/0.03 torr during 1 h. The pyrolysate was dissolved in methylene chloride and the solvent was evaporated to give a brownish-red product, which was examined by \(^1H\) NMR spectroscopy, GLC, and HPLC. The \(^1H\) NMR spectrum indicated the presence of indeno[2,1-a]indene \((125)\) (19%), fluoranthene \((53)\) (59%), and acephanthrylene \((126)\). It was found that GLC did not separate compounds 125 and 53, but showed the presence of acephanthrylene \((126)\) (13%), aceanthrylene \((127)\) (2%) and unreacted 124 (7%). HPLC confirmed the presence of 124, 126, and 127, but failed to resolve 125 and 53 (Scheme 54).
Two pathways were proposed for these isomerizations. The first pathway involves an ethylidene rearrangement involving the shift of a phenyl group to give a vinylidene, which inserts to form 1,2-didehydro-3-phenynaphthalene (128). This intermediate undergoes ring contraction and carbene insertion to give 125. The second proposed mechanistic pathway involves an electrocyclic ring closure and 1,5-H shift to form 2,3-didehydro-1-phenynaphthalene (129), which is converted into fluoranthene (53) by a radical mechanism. This experiment was repeated in our labs and results were in good agreement with those reported by Brown. This will be described later in this chapter.
Scheme 54. Brown’s FVP of 1,4-diphenylbuta-1,3-diyne (124) at 1120 °C/0.03 torr.
As noted in earlier sections, the thermal interconversion of alkynes and vinylidenes, also known as the Brown Rearrangement, is a reaction of great mechanistic and synthetic importance.\textsuperscript{92,96,110} The reverse of this reaction, the Fritsch-Buttenberg-Wiechell (FBW) Rearrangement, alkylidene carbenoids or alkylidenes (vinylidene) is a well-established method for the synthesis of acetylenes.\textsuperscript{111} Scheme 55 represents several synthetic strategies of the generation of vinylidene.

Scheme 55. Various Syntheses to Generate Vinylidene (Alkylidene carbene).
Research in our group has focused on the synthesis of highly strained compounds through thermal and photochemical dehydropericyclic reactions. Our work on C4 isomers compelled us to investigate whether novel atom transpositions might occur in 1,3-butadiyne. The 1,2-shift of the Brown Rearrangement in a conjugated 1,3-butadiyne (131) provides a straightforward mechanism for intrabond atom scrambling in diynes. For interbond scrambling to occur, several plausible mechanisms may be considered. In order for interbond scrambling to occur, we propose that 1,3-butadiyne (131) would first undergo a Brown Rearrangement to form an alkynylvinylidene intermediate (132) and subsequently insert into an adjacent $\pi$ bond to form bicyclo[1.1.0]buta-1,3-diene (133) [Eq. 10]. This interesting substance will be referred to its common name of trialene. In principle, when this cyclic structure forms, it can reopen with the central carbon atoms having exchanged positions. In the present work, we have used both $^{13}$C labeled material and computational modeling to study this process (Figure 9).
C₄H₂ Chemistry

There is little known about the C₄H₂ potential surface and the only shelf-stable isomer is butadiyne (131). Butatrienyldiene (135) has been studied by computation and generated in the laboratory. Stang and Fisk reported the generation and interaction of butatrienyldiene (135). Stang chose the triflate functionalized enyne (134) as a precursor to carbene 135 and trapped it with tetramethylethylene (Scheme 56). This structure 135 has also been observed in interstellar space gas clouds. The geometry and spectroscopic properties of cyclopropenylidenemethylene (136) have been predicted, but this interesting carbene remains unknown.
Bicyclo[1.1.0]buta-1,3-diene (133), more commonly known as trialene or propalene, presents an unusual $\pi$ bond topology that has generated interest in numerous theoretical studies.\textsuperscript{116} Trialene was used as an example in the classic 1961 HMO text by J. D. Roberts.\textsuperscript{116a} In addition to its obvious strain, this $4 \pi$ electron structure may be considered antiaromatic and has been predicted to be thermodynamically and kinetically unstable.\textsuperscript{117,116i} One study by Doehnert predicted that trialene (133) may exist as a biradical structure.\textsuperscript{116c} Baird and Dewar first used the semiempirical MNDO method to predict a $C_{2v}$ symmetric trialene structure, with alternating single and double bonds and with an unusually long interannular bond.\textsuperscript{118,116c} These authors further suggested that trialene might be made by photolysis of diacetylene (131) in a matrix. Schleyer and coworkers later predicted that trialene should easily convert to ethynylvinylidene (132), itself lying in a shallow energy minimum.\textsuperscript{116e} Simkin predicted that bond shift isomerization in trialene will have a low barrier, proceeding through a $D_{2h}$ structure.\textsuperscript{116h}
Several high-energy $\text{C}_4\text{H}_2$ structures are relevant to the work present (Figure 10). These isomers are 1,2,3-cyclobutatriene or cyclobutenyne (137), tetrahedrene (138), and 1,3-butadiene-1,4-diylidene (139). All of these substances are unknown. In principle, cyclobutenylidene (136) and 137 may interconvert by a 1,2-shift, much like that predicted for cyclobutyne. 1,2,3-Cyclobutatriene (137a) and cyclobutenyne (137b) represent the smallest homologues in the cyclic butatriene or cyclic enyne series. Sauer and Harris recently described calculations on tetrahedrene (138) and the related biscarbene (140) which are predicted to be high-energy species.
Results and Discussion

We began our investigation of butadiyne thermal rearrangements through preparation and pyrolysis of several different diarylbutadiyne. The particular system was chosen because the aryl groups differentiate the \( sp \) hybridized carbons and also served as “end caps”. This was expected to allow \( C_4 \) chain chemistry to occur without the fragmentations that are generally observed for alkyl-substituted alkynes.\(^{121}\)

Synthesis and Thermal Chemistry of 1,4-Diphenyl-1,3-butadiyne (124)

The thermal stability of 1,4-diphenyl-1,3-butadiynes was a key initial experiment in the investigation of butadiyne thermal rearrangements. 1,4-Diphenyl-1,3-butadiyne (124) was pyrolyzed previously by Brown and coworkers, as shown in Scheme 54. Brown and coworkers performed FVP at 1120 °C/0.03 torr\(^{102}\) and observed formation of various polycyclic aromatic hydrocarbons (PAHs). 1,4-Diphenyl-1,3-butadiyne (124) was synthesized in one step by oxidative homocoupling of phenylacetylene based on previously published literature\(^{162}\) (70) (Scheme 57).

![Scheme 57. Synthesis of 1,4-Diphenyl-1,3-butadiyne (124).](image)
Pyrolytic experiments were performed at progressively higher temperatures. Pyrolysis of 1,4-diphenyl-1,3-butadiyne (124) at 700 °C/0.01 torr resulted in only starting material. Brown rearrangements may have occurred, but without isotopic labels it would be impossible to detect this thermal rearrangement. Two $sp$ hybridized carbons are resolved in the $^{13}$C NMR spectrum of compound 124; these appear at 74.1 and 81.6 ppm. Pyrolytic experiments were next executed at 800 and 900 °C/0.01 torr. In each case, no rearrangement products were detected by $^1$H and $^{13}$C NMR. Next, FVP experiments were done at 1000 and 1100 °C/0.01 torr. Pyrolysis at 1000 °C showed some indication of product formation, but mostly diphenylbutadiyne remained. Pyrolysis at 1100 °C showed formation of mostly polycyclic aromatic hydrocarbons (PAHs) with only a small amount of starting material remaining. $^1$H NMR spectroscopy indicated products consistent with the experiments of Brown, as illustrated in Scheme 54.

**Synthesis and Thermal Chemistry of Ditolyl-1,3-butadiyne (141)**

Ditolyl-1,3-butadiyne (141) was synthesized in one step by oxidative homocoupling of $p$-tolylacetylene based on previously published literature$^{162}$ (142) (Scheme 58). This system is comparable to diphenylbutadiyne (124) with the exception of the added methyl substituents. Pyrolysis of 141 was carried out determine if the alkyl substituent would cleave at high temperatures. FVP was executed at 800–1000 °C/0.01 torr (Scheme 59). The pyrolysate was dissolved in deuterated chloroform and $^1$H and $^{13}$C NMR spectra was measured; these spectra showed only ditolyl-1,3-butadiyne (141). Importantly, the NMR spectra did not indicate any phenyltolylbutadiyne (143) or
diphenylbutadiyne (124), which would have resulted from methyl group cleavage under FVP conditions. Professor Lawrence T. Scott had suggested this possibility to us.

Scheme 58. Synthesis of 1,4-Ditoly1-1,3-butadiyne (141).

Scheme 59. FVP of ditolylbutadiyne (141) at 800-1000 °C/0.01 torr.
The previous syntheses of butadiynes produced compounds with a plane of symmetry, which is responsible for diarybutadiynes exhibiting only two different sp hybridized carbons. An unsymmetrical butadiyne would have four differentiated sp hybridized acetylenic carbons in the $^{13}$C NMR. This is an essential element in the $^{13}$C labeled diarybutadiyne pyrolytic experiments that will be described later.

The most direct route to an unsymmetrical diarylbutadiyne would be the cross coupling of two terminal arylacetylenes. This is usually achieved through differentiating one of the arylactylenes through halogenation at its terminal position. As described in the literature, phenylacetylene (70) was first brominated in situ with sodium hypobromite using aqueous sodium hydroxide and liquid bromine. This resulted in a 44.5% yield of 1-bromophenylacetylene (144). The haloalkyne 144 was used in a Cadiot-Chodkiewicz-type of cross-coupling with 4-methylphenylacetylene (142) in the presence of pyrrolidine and copper(I) iodide. Unfortunately, the reaction resulted in an intractable mixture of homocoupled and cross-coupled products: diphenylbutadiyne (124), ditolylbutadiyne (141), and phenyltolylbutadiyne (143), respectively. Thin layer chromatography (TLC) and preparative thin layer chromatography on silica did not separate the mixture.

According to the results of Alami and Ferri, these conditions produce substantially lower amounts of cross-coupled products in the presence of palladium catalysts. This catalytic method was also tried without success (Scheme 60).
We next explored the usage of a more reactive halogen. We hypothesized that metallation would occur more easily with iodine which could lead to more efficient cross-coupling. Iodination of phenylacetylene using freshly distilled morpholine and iodine in benzene produced 1-iodophenylacetylene (145) as a fragile liquid substance using previously published literature.\(^\text{164}\) Cross-coupling was attempted between 1-iodophenylacetylene (145) and 4-methylphenylacetylene (142) using the same conditions described above. Once again, the reaction resulted in an inseparable mixture of the three different types of butadiynes (Scheme 61).

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We concluded that the previous attempts to synthesize unsymmetrical butadiynes by using two arylacetylenes were probably due to the two species being too structurally similar. With minor adjustments, we decided to use a different synthesis that leads to unsymmetrical diarylbutadiynes according to previously published literature.\textsuperscript{158}

Therefore, we decided to cross-couple 1-iodophenylacetylene (145) with 2-methyl-3-butyn-2-ol (146). Due to the very low yields in the synthesis of 2-methyl-6-phenyl-3,5-hexadiyn-2-ol (147), it was decided to iodinate 2-methyl-3-butyn-2-ol (146) and react it with phenacetylene (70) in hopes of better yields. Optimal yields were highly desired to due the incorporation of expensive $^{13}$C labeled material that will be described later. 2-Methyl-3-butyn-2-ol (146) was iodinated using the conditions described in Scheme 61; this led to an 85.1\% yield of 4-iodo-2-methyl-3-butyn-2-ol (148). This substance was

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reacted with phenylacetylene (70) under cross-coupling conditions to yield 49.4% of 2-methyl-6-phenyl-3,5-hexadiyn-2-ol (147). 2-Methyl-6-phenyl-3,5-hexadiyn-2-ol (147) was then coupled with 4-iodotoluene (149) under aqueous basic conditions using the phase transfer catalysts along with catalytic amounts of palladium (II) and copper(I) iodide. After column chromatography, phenyl-p-tolylbutadiyne (143) was isolated in a 19.3% yield (Scheme 62).

Scheme 62. Synthesis of phenyl-p-tolylbutadiyne (143).
Synthesis of $^{13}$C Labeled Unsymmetrical Butadiyne

Having synthesized the desired product, phenyl-$p$-tolylbutadiyne (143), several attempts were then made to prepare phenyl-$p$-tolyl-butadiyne (143) enriched with $^{13}$C label using the same synthetic strategy.

This route began with the synthesis of $^{13}$C-enhanced phenylacetylene (76) at the terminal position. Preliminary syntheses were always executed prior to working with $^{13}$C label material. $^{13}$C labeled phenylacetylene (76) is not available commercially; therefore, we had to devise a synthetic method. Acetophenone-$m$-methyl-$^{13}$C labeled (150) is commercially available and thus was our starting point. Starting from acetophenone (150), the synthesis of unlabeled phenylacetylene was attempted by various literature methods. We first attempted the base induced elimination of phosphate ester 151 which is based on upon previously published literature. Yields as high as 26.9% were achieved, but the syntheses were not reproducible. This route to phenylacetylene was abandoned for another synthetic approach (Scheme 63).

Scheme 63. Synthesis of Phenylacetylene via Phosphate Ester (151).
The next synthetic approach to the synthesis of phenylacetylene (70) involved targeting another intermediate, \( \alpha \)-chlorostyrene (152). Acetophenone (150) was treated with phosphorus pentachloride in refluxing benzene. TLC was used to monitor the progress of conversion. After 46 h, acetophenone (150) has been fully converted to \( \alpha \)-chlorostyrene (152). NMR spectroscopy of the crude product indicated mostly \( \alpha \)-chlorostyrene (152), showing resonances at 5.6 and 5.8 ppm, and a small amount of acetophenone (150), showing a resonance at 2.5 ppm. The crude yield was 83.1%. The reaction was executed several times in which 1,1,1-dichlorophenylethane (153) was also formed as product (Scheme 64).

The mixture of \( \alpha \)-chlorostyrene (152) and 1,1,1-dichlorophenylethane (153) was then treated with commercial sodium amide and allowed to reflux. This reaction was executed several times and clean elimination did not occur to form phenylactylene (70). Therefore, a fresh solution of sodium amide was prepared using condensed liquid ammonia, with addition of sodium metal and iron (III) catalyst. The dark blue sodium amide solution was stirred for an hour after sodium metal addition. The crude mixture of \( \alpha \)-chlorostyrene (152) and 1,1,1-dichlorophenylethane (153) was then dissolved in THF and added dropwise by syringe. The reaction was worked-up and product was purified by column chromatography on silica using hexanes as an eluent to give an 80.1% yield of phenylacetylene (76) (Scheme 65).
Scheme 64. Conversion of acetophenone to α-chlorostyrene (152) and 1,1,1-dichlorophenylethane (153).

With an efficient synthetic route in hand, the synthesis of $^{13}$C labeled $p$-tolylphenylbutadiyne (143) was undertaken. This synthesis began with commercially available acetophenone-methyl-$^{13}$C, 99 atom %. This material was diluted with unlabeled acetophenone (150) to obtain acetophenone with a 20% enhancement at the methyl position. The specific amount was determined by the strength of the NMR spectroscopic signal, which would clearly differentiate itself from other signals, while not overwhelming the NMR spectrum.

$^{13}$C Labeled-methyl-acetophenone (150) was converted to α-chlorostyrene (152) and 1,1,1-dichlorophenylethane (153) using phosphorus pentachloride. The crude mixture of $^{13}$C labeled α-chlorostyrene (152) and 1,1,1-dichlorophenylethane (153) was then converted to phenylacetylene (76) by elimination with freshly prepared sodium amide to give a 71.4 % yield. The C1-$^{13}$C labeled phenylacetylene (76) was then coupled with 4-iodo-2-methyl-3-butyn-2-ol (148) under the palladium catalyzed conditions that had been previously described that produced a 46.3% yield of $^{13}$C labeled 2-methyl-6-phenyl-3,5-hexadiyn-2-ol (147). However, the homocoupled side product, doubly labeled diphenylbutadiyne (124) was observed as the major product. At first, it was thought this
was an undesired product, but after some reflection, we decided that very important preliminary FVP studies could be executed with this material. This will be described later. Based upon previous published literature, \(^{158}\, ^{13}\text{C}\)-labeled 2-methyl-6-phenyl-3,5-hexadiyn-2-ol (147) was then coupled to 4-iodotoluene (149) to produce a \(^{13}\text{C}\)-labeled \(p\)-tolylphenylbutadiyne (159) in a crude yield of 46.5%. Unfortunately, this material resisted sufficient purification. Neither, column chromatography, rotary chromatography, nor preparative GC afforded adequately pure material. \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectral analysis invariably showed the desired product along with unknown impurities, which displayed resonances in the acetylenic region of the spectrum (Scheme 65).
Scheme 65. Synthesis of $^{13}$C labeled $p$-tolylphenylbutadiyne (159).
Alternative Route to $^{13}$C labeled $p$-tolylphenylbutadiyne (143)

We decided to pursue another path to the synthesis of $^{13}$C labeled $p$-tolylphenylbutadiyne (143) (Scheme 66). This synthesis began, using unlabeled reagents, with the addition of trimethylsilylacetylene (154) to 4-methylbenzaldehyde in 87.5% yield, followed by deprotection of the TMS group by the use of tert-butylammonium fluoride (TBAF) to give 1-tolylpropyn-1-ol (155). Excess TBAF proved to be difficult to separate from the product; therefore, another deprotection method was investigated. A 3N solution of sodium chloride in methanol proved to be a very effective method of deprotecting the TMS group giving 1-tolylpropyn-1-ol (155) in 91.6% yield. This provided an attractive stable intermediate toward the desired product. Using previously published literature, the synthesis of 160 was achieved. Tolylpropyn-1-ol (155) was doubly deprotonated with $n$-butyllithium at -78 °C and reacted with 20% enriched $^{13}$C labeled benzaldehyde (carbonyl position) to give 1-$p$-tolyl-4-phenylbutyn-1,1-diol (156). Recrystallization from methanol gave 92.7% yield. The diol (156) was chlorinated using thionyl chloride to give 1,1-$p$-tolylchloro-4,4-chlorophenylbutyne. After brief storage at 0 °C, the dichloride was dissolved in THF and added dropwise into a freshly prepared suspension of sodium amide in liquid ammonia which was maintained at -78 °C. The mixture was allowed to warm to room temperature while the liquid ammonia evaporated. The product, $^{13}$C labeled $p$-tolylphenylbutadiyne (160), was extracted with hexanes and purified by column chromatography on silica gel using hexanes as eluent. The product was isolated as a crystalline solid in 35.5% yield. NMR spectroscopy confirmed the identity of the desired compound (Scheme 66).
Scheme 66. Alternate synthesis of $^{13}$C labeled $p$-tolylphenylbutadiyne (160).

**FVP Experiments on Doubly Labeled Diphenylbutadiyne (124)**

In the synthesis of $^{13}$C labeled $p$-tolylphenylbutadiyne (159), doubly labeled diphenylbutadiyne (124) was formed as a side reaction product and separated and identified (Scheme 65). Initially, this homocoupled product (124) seemed undesirable, because it decreased yields of the desired product, $^{13}$C labeled $p$-tolylphenylbutadiyne.
However, we realized that a set of FVP experiments would prove to be valuable in our investigation of atom topomerization.

Quantitative $^{13}$C NMR spectroscopy was first utilized to determine the isotopic enrichment of this sample. Due to their long relaxation times, $(T_1)$, measurement of quantitative $^{13}$C spectra for the $sp$ resonances of butadiynes is challenging. This was facilitated by addition of chromium acetonylacetonate to the sample as a relaxation agent. Quantitative $^{13}$C spectra of doubly labeled $^{13}$C diphenylbutadiyne (124) showed resonances of 81.6 ppm for C1 and C4 and 73.9 ppm for C2 and C3, respectively. Experimentally determined integrations for C1,C4 and C2,C3 resulted in a 1 to 20.2 ratio, which was in good agreement with expectations (Figure 11).

Experimentally determined integrations for C1,C4 and C2,C3 resulted in a 1 to 20.2 ratio, which was in good agreement with expectations (Figure 11).

![Figure 11. Doubly Labeled $^{13}$C Diphenylbutadiyne (124).](image)

FVP experiments were carried out at different temperatures, but with a constant pressure. The pyrolysate was isolated and analyzed by quantitative $^{13}$C NMR, as described above. FVP at 700 °C/0.01 torr resulted in approximately a 1 to 2 ratio of $^{13}$C distribution at C1,C4 and C2,C3, respectively. FVP at 800 °C/0.01 torr resulted in approximately a 1 to 1 ratio of $^{13}$C distribution of C1,C4 to C2,C3, respectively (Figure 12). These results lead to the conclusion that Brown Rearrangement occurred readily at 700 – 800 °C. These experiments, conclusively demonstrates intrabond rearrangement
It might be possible that interbond rearrangements occurred, but due to the symmetry of diphenylbutadiyne no conclusion may be drawn about these processes.

<table>
<thead>
<tr>
<th>Carbon Number (δ ppm)</th>
<th>C1,C4</th>
<th>C2,C3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreacted 13C labeled 124</td>
<td>1.0</td>
<td>20.4</td>
</tr>
<tr>
<td>Pyrolysis at 700 °C</td>
<td>1.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Pyrolysis at 800 °C</td>
<td>1.0</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 4. 13C Label Distributions from Integration.

Figure 12. Spectra of FVP of Doubly Labeled diphenylbutadiyne (124).
Scheme 67. Interbond scrambling of $^{13}$C label of diphenylbutadiyne (124).
FVP Experiments of $^{13}$C Labeled $p$-Tolylphenylbutadiyne (160).

Quantitative $^{13}$C NMR spectroscopy of $p$-tolylphenylbutadiyne (160) at $^{13}$C labeled C4 showed resonances at 81.23, 74.06, 73.30, and 81.88 for C1, C2, C3, and C4, respectively. $^{13}$C labeled $p$-tolylphenylbutadiyne (160) showed integrals for the $sp$ acetylenic carbons to be in an approximate ratio of 20:1:1:1, for C1, C2, C3, and C4, respectively (Figure 13).

![Figure 13. C1-$^{13}$C labeled $p$-tolylphenylbutadiyne (160).](image)

The C1-$^{13}$C enriched $p$-tolylphenylbutadiyne (160) was then subjected to a series of FVP experiments at different temperatures, but at constant pressure (Scheme 68). FVP of $^{13}$C labeled $p$-tolylphenylbutadiyne (160) at 800 °C/0.005 torr resulted in $^{13}$C label scrambling from C1 to C2, exclusively, as shown in Figure 14. This data indicates that only 1,2-shifts occurred at this temperature, with nearly complete exchange between C1 and C2 as shown by the NMR integration ratio of 1.5 to 1.

FVP of $^{13}$C labeled $p$-tolylphenylbutadiyne (160) at 900 °C/0.01 torr was carried out next. Analysis of the pyrolysate by $^{13}$C NMR showed $^{13}$C label scrambling at all four acetylenic carbons. At higher temperatures, labeling studies indicate that two processes are occurring. The lower-energy process, 1,2-shifts, results in the distribution of $^{13}$C labeling exchange from C1 to C2 (Intrabond Rearrangements). The isotopic distributions

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observed from pyrolysis at 800 or 900 °C demonstrate that both *intrabond* and *interbond* exchange process are operative with the former passing through a lower activation barrier.

At higher temperatures, the second process indicates that *interbond* rearrangements might be occurring for this higher energy process, which proceeds through the proposed intermediate, triene (133), to achieve complete $^{13}$C scrambling. The $^{13}$C labeling distribution was found to be approximately 4:4:1:1 ratio. Integrals are measured relative to one well-resolved aromatic carbon.

<table>
<thead>
<tr>
<th>Carbon Number ($\delta$ ppm)</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreacted 143</td>
<td>20.8</td>
<td>0.72</td>
<td>0.88</td>
<td>1.40</td>
</tr>
<tr>
<td>Pyrolysis at 800 °C</td>
<td>11.6</td>
<td>7.37</td>
<td>1.16</td>
<td>0.89</td>
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<tr>
<td>Pyrolysis at 900 °C</td>
<td>8.79</td>
<td>8.76</td>
<td>3.99</td>
<td>3.01</td>
</tr>
</tbody>
</table>

Table 5. $^{13}$C Label Distributions from Integration.
Figure 14. FVP of labeled $p$-tolylphenylbutadiyne (160).
Scheme 68. *Interbond* and *Intrabond* Scrambling of C1-^{13}C label p-tolylbutadiyne (160).

R_1 = Ph; R_2 = Tol
Potential Reaction Mechanisms

Several potential mechanisms may explain the long-range atom topomerization in butadiyne. We first propose a mechanism, illustrated in Scheme 68, that passes through alkynylvinylidenes and trialenes. Initial 1,2-shift in 160 can lead to carbene 161 and, subsequently, a second shift of the opposite σ bond leads to 159. This Brown rearrangement easily explains the intrabond atom transposition that is observed from pyrolysis of 124 at 800 °C. At higher temperature, closure of the carbene 161 to trialene 162 might be followed by bond-shift isomerization, as seen by 162 → 164, via transition state TS 163, followed by reopening to carbene 165. This intermediate will rearrange to either 166 or 167. This multi-step process can achieve the entire transport of a carbon atom across the four-carbon chain. In general, 1,2-shifts should result in only alkyne intrabond atom interconversions, while trialene provides a clear mechanism for interbond atom rearrangement. An alternate route to interconnect structures 131 and 133 may be a synchronous “accordion-like”, π2s + π2a, mechanism that averts the carbene 132 (Scheme 69).

Other routes pass through high-energy structures in which the central sp carbons of the diyne become structurally equivalent. Tetrahedrene (168) and cyclobutenyne (169 or 171) both possess the requisite symmetry for interbond transposition. In principle, either structure might be formed directly from the diyne through a four-electron electrocyclic process. A reversible interconversion of 168 with vinylidene cyclopropene 170 might be expected if their energetics are favorable (Scheme 70). Alternatively, a

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biscarbene such as 139 might result from two sequential shifts or a dyotropic process, *i.e.* one in which two σ-bonds migrate simultaneously.

![Scheme 69. Accordion-like mechanism (alternate mechanism).](image)

Computational Studies

Several levels of theory were employed to investigate the energetics of potential C₄H₂ reaction mechanism. The levels of theory used were B3LYP and MP4//MP2 and these results have been summarized in Table 6. In general, these two methods provided very similar structures and relative energetics.

Computations on the existence of ethynylvinylidene (132), as with the parent vinylidene (130), provide inconclusive results. As a consequence, the surface for 1,2-
shifts is dependent on the computational level of theory. Calculations with HF, TCSCF, CASSCF, and B3LYP/6-31G(d) theories all located an energy minimum for ethynylvinylidene (132). MP2 and B3LYP calculations that we executed did not locate an energy minimum; instead the structure descends to product 131. It is not certain if ethynylvinylidene (132) represents a true stationary point; however, it is predicted that the energy of 132 should lie slightly below the transition state (TS 163) for closure to trialene.

Trialene is predicted at all levels of theory to have alternating peripheral ring bonds with an elongated central bond, which is consistent with previous lower level calculations by Dewar. The central σ bond length in 133 is dependent on the level of theory due to the strong contribution from resonance structure 133a. Calculations indicate it is not a true diradical (Figure 15). The σ bonding and antibonding orbitals which describe the transannular bond was predicted by CASSCF-(8,8)/6-31G* wave function to have occupation numbers of 1.88 and 0.126, respectively. A pure diradical would have equal values.

Figure 15. Transannular bond prediction.
Our calculations predict trialene (133) to lie in a shallow minimum at 61-65 kcal/mol above butadiyne. Low energy pathways exist for both ring opening of 133 to 132 via transition state TS1 or bond-switch isomerization through TS2. TS2 is predicted to be nonplanar with C$_{2v}$ symmetry and equal C-C bond lengths around the ring. Attempts to locate a synchronous transition state that directly connects 131 to 133 led to very high barriers and no true stationary points. Our predicted lowest energy pathway, which is in agreement with our experimental results, is illustrated in Figure 18.

Ethynylvinylidene (132) is derived from a 1,2-shift from butadiyne (131), which is predicted to be in a shallow energy minimum at 52.2 kcal/mol. Ethynylvinylidene (132) then inserts into the adjacent π bond via TS1 (66.8 kcal/mol) to generate trialene (133), which is predicted to be an energy minimum at 64.6 kcal/mol. Trialene proceeds through the delocalized transition state structure TS2 (69.0 kcal/mol) to regenerate the bond-switch isomer with the peripheral bonds transposed (Figure 16).

Figure 16. B3LYP energetics along the trialene pathway.
An intriguing alternate mechanism for the experimentally observed carbon scrambling is shown in Scheme 70. In principle, 159 might undergo four-electron pericyclic closure to 169, followed by rearrangement through cyclopropenyldienemethylene (170). Carbene 170 is approximately 70 kcal/mol above butadiyne (159) and might be energetically attainable if structure 137 undergoes a 1,2-shift. The optimized structure for 137 displays one imaginary mode with B3LYP/6-31+G(2d,p) theory but none at MP2/6-311+G(2d,p). Nevertheless, structure 137 is 89.3 kcal/mol higher in energy than carbene 136, which places this species (structure 137) out of consideration as an acceptable explanation for observed experimental results. Another possible mechanism would be the formation of the highly pyramidalized tetrahedrene (138). Our B3LYP and MP2 calculations predict tetrahedrene (138) to be an energy minimum. However, tetrahedrene (138) lies 167.2 (B3LYP) and 204.3 (MP2) kcal/mol above butadiyne, which excludes it from consideration, even if there is a low barrier for rearrangement to butadiyne.

Another high-energy species that might be considered as a possibility along the C₄H₂ surface is biscarbene 139, which could result from sequential or dyotropic hydrogen migrations. Our DFT calculations predict biscarbene 139 to be planar and lie 32.4 kcal/mol above trialene 133. MP2 optimization on biscarbene 139 led to the transition state for 1,2-migration of both hydrogens to butadiyne. Sauer and coworker have also predicted biscarbene 139 to lie at very high energy relative to butadiyne.¹²²
DFT and Moller-Plesset computations provide consistent predictions for a likely reaction mechanism (Table 6). We conclude from these calculations that the lowest energy pathway for long-range atom topomerization in butadiyne is one which follows closure to trialene (133) followed by bond-switch isomerization, and ring opening occur. The lower energy Brown Rearrangement pathway accounts for intrabond atom transpositions.
### Table 6. C₄H₂ Computational Results

<table>
<thead>
<tr>
<th>Structure</th>
<th>B3LYP&lt;sup&gt;a&lt;/sup&gt;</th>
<th>E&lt;sub&gt;rel&lt;/sub&gt;</th>
<th>NIMAG&lt;sup&gt;b&lt;/sup&gt;</th>
<th>MP4//MP2&lt;sup&gt;c&lt;/sup&gt;</th>
<th>E&lt;sub&gt;rel&lt;/sub&gt;</th>
<th>NIMAG&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-butadiyne (131)</td>
<td>-153.53412</td>
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<td>0</td>
<td>-153.14016</td>
<td>0.0</td>
<td>0</td>
</tr>
<tr>
<td>ethynylvinylidene (132)&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>52.2</td>
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<td></td>
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<td>closure TS (TS1)</td>
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<td>1</td>
<td>-153.03739</td>
<td>64.5</td>
<td>1</td>
</tr>
<tr>
<td>singlet triene (133)</td>
<td>-153.43113</td>
<td>64.6</td>
<td>0</td>
<td>-153.04295</td>
<td>61.0</td>
<td>0</td>
</tr>
<tr>
<td>bond-switch TS (TS2)</td>
<td>-153.42410</td>
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<td>0</td>
<td>-152.81456</td>
<td>204.3</td>
<td>0</td>
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<td>-152.90907</td>
<td>145.0</td>
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<td>0</td>
<td>-153.02043</td>
<td>75.1</td>
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<td>-153.46868</td>
<td>41.0</td>
<td>0</td>
<td>-153.06394</td>
<td>47.8</td>
<td>0</td>
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<tr>
<td>triplet triene</td>
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<tr>
<td>biscarbene (139)</td>
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<td>99.2</td>
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<td>-152.97663</td>
<td>102.6</td>
<td>1</td>
</tr>
<tr>
<td>bicyclobiscarbene (140)</td>
<td>-153.41430</td>
<td>75.2</td>
<td>0</td>
<td>-153.01882</td>
<td>76.1</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> B3LYP = B3LYP/6-311+G(2d,p).  
<sup>b</sup> NIMAG = number of imaginary vibrational modes from B3LYP or MP2 calculations.  
<sup>c</sup> MP4SDTQ/6-311+G(2d,p)/MP2(FC)/6-311+G(2d,p).  
<sup>d</sup> BLYP/6-31G* optimized geometry.  
Relative energies in kcal/mol, uncorrected for zero-point differences.

Table 6. Summary of C₄H₂ computational results.
Our experimental and computational results provide the first evidence for long-range atom topomerization in a polyyne chain. We observe that carbon atoms can migrate from one end of a 1,3-diyne to the other in a process that clearly passes through sequential stages of intrabond and interbond atom exchange. DFT and Møller-Plesset computations provide consistent predictions for a likely reaction mechanism. A lower energies lies a Brown rearrangement that accounts for intrabond atom transpositions. Along a slightly higher energy pathway, closure to singlet trialene (133), followed by bond-switch isomerization, and ring opening (Figure 16) presents what we believe to be the lowest energy mechanism for interbond carbon scrambling. The predicted reaction energetics are consistent with the temperature required for this rearrangement. Other logical but exotic intermediates such as 137, 138, or 139 lie at much higher energy than the trialene mechanism; therefore we believe these can be excluded. Preliminary calculations indicate that the energetics of these processes are not significantly changed in longer polyynes. Consequently, in principle, extensive carbon scrambling might occur in an $sp$ carbon chain of any length.
CHAPTER 3

CHEMISTRY OF C₄H₄

The Cyclopropylidene to Allene Rearrangement

The thermal interconversion of cyclopropylidenes and allenes, also known as the Doering-Moore-Skattlebøl Rearrangement (DMS), is a reaction of great mechanistic and synthetic importance. This rearrangement was first investigated by Doering and LaFlame. Dihalocarbeties react with alkenes to give 1,1-dihalocyclopropanes (172). Further reaction with sodium or magnesium forms the cyclopropylidene intermediate (174), which rearranges to allenes (175) in varying yields. Later, Moore and Skattlebøl replaced the amalgam by alkyllithiums, in particular n-butyllithium. Lithium-halogen exchange of 1,1-dibromocyclopropane (172) with n-butyllithium forms the lithiated compound (173). Further loss of lithium bromide gives the cyclopropylidene (174), which rearranges to the allene (175). In general, 1,1-dibromocyclopropanes (172) are preferred over the corresponding dichloro analogs because of the complete absence of acetylenic by-products (Scheme 71).
Cyclopropylidene ring-cleavage reactions can lead to remarkably strained allenes by electrocyclic ring opening\(^{75}\) (Scheme 72). Treatment of 1,1-dibromo[3.1.0]hexane (176) with methyl lithium results in the initial formation of carbene 177 which isomerizes to cyclohexa-1,2-diene (178).\(^{128}\) This strained allene has been trapped in [2 + 2] and [4 + 2] cycloaddition reactions with 1,3-butadiene to give products 179, 180, and 181. Compounds 179 and 180 undergo efficient thermal isomerization to 181. This indicates that DMS rearrangements can have synthetic and preparative value.

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Scheme 72. DMS Rearrangement to Cyclic Allenes.

Cyclopropylidene has shown to insert into geometrically proximate C-H bonds. In cases where the dibromocyclopropane is sterically crowded, as illustrated in Scheme 73, both 1-t-butyl-1-methylallene (182) and 1-t-butylbicyclo[1.1.0]butane (183) are formed in a combined yield of 70% and a 3:2 ratio, respectively. This illustrates the competition between allene formation and C-H insertion.

Scheme 73. Cyclopropylidene C-H insertion.
As previously noted, treatment of gem-dihalocyclopropanes with alkyllithiums or other metals at temperatures above –80 °C, results in the formation of cyclopropyldienes. It has been found that when there is a vinyl group attached to the cyclopropyldiene, as illustrated in Scheme 74, an alternative mode of ring-opening leads to the cyclopenyldiene (184) which subsequently forms cyclopentadiene (185) through 1,2-H shifts.

![Scheme 74. Cyclopropyldiene vinyl C-H insertion.](image)

**Thermal Rearrangements of Butatriene**

Our investigations of atom transitions in 1,3-butadiynes (Chapter 2) next led us to examine the thermal chemistry of other types of linear hydrocarbon chains. The question posed was whether the central $sp$ carbon atoms in a butatriene might interconvert and by what mechanism could this occur? [Eq. 11]
Equation 12 shows our initial plan for a reaction mechanism. Here, a reverse DMS rearrangement of butatriene (186) gives the methylenecyclopropylidene (187), which closes to a bicyclobutene (188). This process makes the central carbon atoms symmetry equivalent and thus would scramble the central atoms (Figure 17).

\[ \text{R}_1 R_1 * \text{R}_2 \Delta \text{R}_2 \]

\[ \text{R}_2 \]

\[ \text{R}_1 \]

* = $^{13}$C label

[Eq. 11]. Carbon automerization in butatrienes.

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]

186

187

188

[Eq. 12]. Proposed mechanism of butatriene carbon topomerization.

Figure 17. Carbon Topomerization of Butatriene and Mechanism.
The C₄H₄ potential energy surface is of special interest to organic chemists and has been extensively investigated both experimentally¹³⁰,¹³¹ and theoretically.¹³²,¹³³ Vinylacetylene (44) is the thermodynamically most stable C₄H₄ isomer, with a ΔH° of 70.4 kcal/mol.¹³⁴,¹³⁵ Butatriene (186) is the next most stable isomer, lying 13 kcal/mol above vinylacetylene (44).¹³⁵ The four monocyclic isomers are methylenecyclopropene (189), 1,3-cyclobutadiene (190), 1,2-cyclobutadiene (191), and cyclobutyne (192). Methylenecyclopropene (189) and 1,3-cyclobutadiene (190) have been isolated in low-temperature matrices.¹³⁶,¹³⁷ Methylenecyclopropene (189) was also synthesized at low temperature, and was shown to be stable in solutions below -75°C. This substance was characterized by NMR spectroscopy.¹³⁶,¹³⁸ There have been previous efforts by J. D. Roberts¹³⁹ and Wittig¹⁴⁰ to experimentally trap cyclobutyne (192), but then were unsuccessful. 1,2-cyclobutadiene (191) was studied computationally by Johnson and Daoust.¹⁴¹ The MCSCF(4,4)/6-31G* level of theory predicts 1,2-cyclobutadiene (191) to be chiral with vinylic hydrogens twisted 6° out of plane. 1,2-cyclobutadiene (191) is best described as a diradical with singly occupied allyl-like π nonbonding and the barrier for ring opening to vinylacetylene (44) is predicted to be low (Figure 18).
Tetrahedrane (193) is the only platonic hydrocarbon, which has not yet been prepared. As illustrated in Scheme 75, there have been many attempts to synthesize tetrahedrane (193), but it remains a challenge.\textsuperscript{142} There have also been many theoretical studies of this elusive structure.\textsuperscript{143} This may be due in part to the strain energy, which was calculated to be 132-140 kcal/mol using \textit{ab initio} level of theory.\textsuperscript{144} However, it is believed that tetrahedrane or bicyclobutyl diradical is a possible fleeting intermediate in labeling experiments.\textsuperscript{145} Tetrahedrane substituted with \textit{tert}-butyl groups at its vertices is a stable solid at room temperature, prepared by Maier and coworkers.\textsuperscript{143b}
Scheme 75. A selection of unsuccessful attempts to synthesize tetrahedrane (193).

One key $\text{C}_4\text{H}_4$ isomer in our proposed mechanism is bicyclo[1.1.0]but-1,3-ene (188). A number of molecular orbital calculations of varying levels of complexity has been performed on bicyclo[1.1.0]but-1,3-ene (188). MINDO/3 calculations by Dewar and coworkers predicted a planar structure.\textsuperscript{146} In contrast, \textit{ab initio} methods consistently predict that bicyclo[1.1.0]but-1,3-ene has a singlet ground state with a bent geometry\textsuperscript{147,148} similar to that of cyclobutane and bicyclo[1.1.0]butane, with a predicted barrier to ring inversion of 12 kcal/mol.\textsuperscript{147} Maier and Schleyer predicted the olefinic strain energy, defined as the difference in strain energy of the olefin and the saturated hydrocarbon, to be 58.7 kcal/mol.\textsuperscript{148} This value indicates that bicyclo[1.1.0]but-1,3-ene (188) is a highly destabilized molecule and not expected to persist at room temperature.
However, Hess and Schaad predict that bicyclo[1.1.0]but-1,3-ene (188) is likely to exist and might be observable in a low-temperature matrix\textsuperscript{147} (Figure 19).

![Diagram of bicyclo[1.1.0]but-1,3-ene (188)](image)

Figure 19. Bicyclo[1.1.0]but-1,3-ene (188).

The photochemistry of some matrix-isolated C\textsubscript{4}H\textsubscript{4} molecules was reported by Chapman and coworkers in 1974.\textsuperscript{130} Irradiation of methylenecyclobutene (194) produced ketene (195). At shorter wavelength, irradiation gave butatriene (186) and methylenecyclopropene (189). Allenylcarbene (196) was deduced as the primary C\textsubscript{4}H\textsubscript{4} isomer that led to the formation of butatriene (186) and methylenecyclopropene (189) via a 1,2-H shift or a vinylcarbene-cyclopropene rearrangement, respectively. Irradiation for long periods of time resulted in the formation of vinylacetylene (44) and acetylene (21). Vinylacetylene (44) was the major product of the irradiation of methylenecyclopropene (189), which was later independently confirmed by Maier and coworkers\textsuperscript{131} (Scheme 76).
Scheme 76. Photochemistry of methylenecyclobutene to produce matrixed-isolated $C_4H_4$ molecules.
Sander, Cremer and their coworkers have more recently investigated the photochemistry of butatriene (186) isolated in an argon matrix at 10K\textsuperscript{149} (Scheme 77). Butatriene (186) was irradiated at 248 nm to give vinylacetylene (44), the dimer of acetylene (21), and methylenecyclopropene (189) as the major products. The photochemical rearrangement of butatriene (186) to methylenecyclopropene (189) involves a 1,2-H shift, which produces allenylcarbene (196) as the key intermediate. The structures, thermochemical data, and IR spectra of the C\textsubscript{4}H\textsubscript{4} isomers were calculated at the MP2 and DFT/B3LYP level of theory using an extended basis set. Vinylacetylene (44) is the global minimum on the C\textsubscript{4}H\textsubscript{4} potential energy surface, with a ΔH\textsubscript{f} of 70.4 kcal/mol\textsuperscript{134}. The enthalpy of formation of butatriene (186) was calculated to be 81.9 kcal/mol, which is in good agreement with experimental measure of 83.0 kcal/mol and with previous theoretical predictions\textsuperscript{133}. 

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Scheme 77. Irradiation of butatriene to give C₄H₄ isomers.

Individual transformations between C₄H₄ isomers have been investigated as well. In 1995, our research group reported a theoretical investigation of the interconversion of cyclobutynes (192) and vinylidene cyclopropane (197), as illustrated in Scheme 78. Cyclobutynes (192) is predicted to rearrange to 197 with a barrier of 1.8 kcal/mol and a reaction enthalpy of -20 kcal/mol according to the MCSCF(4,4)/6-31G* level of theory. Cyclobutynes is predicted to be a true minimum according to MCSCF and MP2 calculations, which contrasts the earlier calculations of Pople and Dewar where cyclobutynes (192) was predicted not to be a true minimum. Johnson and Daoust found the barrier to ring opening of cyclobutylene (192) to butatriene (186) to be 62.0 kcal/mol; this is best described as a conrotatory ring opening. This data was in agreement with
Schaefer’s estimated barriers.\textsuperscript{152} It was concluded that cyclobutyne (192) exists in a very shallow minimum and will rearrange with little or no barrier to cyclopropylidene (197), but not open to butatriene (186).

![Scheme 78. Interconversion of cyclobutyne (192) and cyclopropylidene (197).](image)

**Thermal Rearrangements of Butatrienes**

The most comprehensive theoretical investigation of the $C_4H_4$ surface, as illustrated in Scheme 79, was reported by Dewar and coworkers in 1981.\textsuperscript{153} The singlet potential energy surface for $C_4H_4$ species was extensively explored using the semiempirical MINDO/3 level of theory. Three of the major $C_4H_4$ mechanistic pathways discussed were (1) the conversion of tetrahedrane (193) to cyclobutadiene (190), (2) the conversion of tetrahedrane (193) or cyclobutadiene (190) to methylenecyclopropene (189) or vinylacetylene (44), and (3) the relationships of these species to acetylene (21). The MINDO/3 level of theory is considered inferior in reliability compared to the most current levels of theory; therefore, the results of this investigation will not be discussed in detail.
Scheme 79. Dewar's exploration of the C₄H₄ surface.
One especially relevant study was reported by Cong-Hao and Bing-Ze in 1991.\textsuperscript{154} Isomerizations of methylenecyclopropylidenes (187) were studied using the \textit{ab initio}, RHF/6-31G**/STO-3G level of theory (Scheme 80). The intermediate methylenecyclopropylidene (187) was predicted to have two possible routes for isomerization. Path 1 is a 1,2-H shift, which has a predicted activation energy of 118 kcal/mol and forms methylenecyclopentene (189). Path 2 involves ring opening of methylenecyclopropylidene (189) to butatriene (186), which has an activation energy of 24 kcal/mol. This level of theory is unlikely to yield accurate energetics and these values are almost certainly too high.

\begin{center}
\includegraphics[width=\textwidth]{scheme80.png}
\end{center}

\textbf{Scheme 80.} Ring opening and 1,2-H shift of methylenecyclopropylidene (187).
Results and Discussion

Computational Results

B3LYP and MP2 levels of theory were employed to assess the energetics of potential C$_4$H$_4$ reaction mechanisms. Results of both levels of theory are summarized in Table 7. The two methods provide very similar structures and relative energetics.

Several different mechanistic pathways have been examined in order to determine the lowest energy pathway for long-range atom topomerization. Figure 20 illustrates our proposed reaction mechanism. The lowest energy pathway, starting from butatriene (186), proceeds through closure to methylenecyclopropyldiene (187) by TS3, which lies 64.0 kcal/mol above butatriene (186). Methylenecyclopropyldiene (187) subsequently proceeds through TS4 to form bicyclo[1.1.0]butene (188). The two $sp^2$ atoms are now equivalent, hence ring opening interconverting them and leading to carbon topomerization. Alternatively, methylenecyclopropyldiene (187) can possibly perform a 1,2-H shift leading to triafulvene (189) (Figure 21). Even though triafulvene (189) is thermodynamically more stable than bicyclo[1.1.0]butene (188) (47.7 kcal/mol), its formation is improbable due to the high transition state energy along this route.
Figure 20. B3LYP/6-31G energetics of butatriene to propellane pathway.
Figure 21. B3LYP/6-31G energetics of butatriene to fulvalene pathway.

Other rearrangements might compete with the proposed long-range atom transposition mechanism. Our calculations predict that a 1,2-H shift of butatriene (186) leads to allenylcarbene (196), which lies 60.8 kcal/mol above butatriene. Allenyl carbene (196) can subsequently insert into the adjacent allenyl π bond, which forms triafulvene (189). Butatriene (186) can form cyclobutyn (192) through an electrocyclic process. Cyclobutyn (192) lies 68.4 kcal/mol higher than butatriene. Allenylcarbene (196) can possibly insert into vinyl C-H bond of the allenyl system to form 1,2-cyclobutadiene (191), which lies 69.7 – 74.2 kcal/mol higher than butatriene (186). Sander and Cremer provided experimental evidence for a similar mechanistic pathway during photolysis of butatriene at 248 nm. They predicted a 1,2-H shift of butatriene (186) forming the
allenylcarbene intermediate (196) and leading to the formation of fulvalene (189).

**Scheme 81** illustrates additional higher energy processes that we have predicted, which leads to other mechanistic possibilities for thermal rearrangement of butatriene.

Scheme 81. Alternate reaction mechanisms.
Table 7. Summary of C4H4 computational results.

<table>
<thead>
<tr>
<th>Structure</th>
<th>B3LYP $^a$</th>
<th>$E_{Tot}^{j}$</th>
<th>NIMAG $^d$</th>
<th>MP2 $^b$</th>
<th>$E_{Tot}^{j}$</th>
<th>NIMAG $^d$</th>
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<td>1,2-cyclobutadiene (191)</td>
<td>-154.61067</td>
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<td>0</td>
<td>-154.14576</td>
<td>25.6</td>
<td>0</td>
</tr>
<tr>
<td>Allenylcarbene (196)</td>
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<td>1</td>
<td>-154.07983</td>
<td>60.8</td>
<td>0</td>
</tr>
<tr>
<td>1-butene-2-yn (44)</td>
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<td>-2.57</td>
<td>0</td>
<td>-154.20563</td>
<td>-11.9</td>
<td>0</td>
</tr>
<tr>
<td>Bicyclo[1.1.0]butene (188)</td>
<td>-154.62691</td>
<td>65.3</td>
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<td>-154.10804</td>
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<td>0</td>
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<tr>
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<td>0</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>-154.08349</td>
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<td>Cyclopropenyl carbene TS (TS3)</td>
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<td>-154.09076</td>
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<tr>
<td>187 to 189 TS (TS5)</td>
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<td>1</td>
<td>-154.05309</td>
<td>81.4</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ B3LYP = B3LYP/6-31G*. $^b$ MP2 = MP2/6-31G*. $^c$ NIMAG = number of imaginary vibrational modes from both calculations. $^d$ Relative energies in kcal/mol, corrected for zero-point differences.
Syntheses and FVP of Butatrienes

Attempted Syntheses of Unsymmetrical Butatrienes

It was first necessary to establish a suitable synthetic route to an unsymmetrical butatriene to determine if each of the four sp hybridized, cumulenic carbons can be resolved by $^{13}$C NMR spectroscopy. The synthesis began with the reduction of 4,4'-dimethylbenzophenone (198) with sodium borohydride in ethanol. Purification by recrystallization with hexanes led to a 78% yield of 4,4'-ditolylmethanol (199). 4,4'-Ditolylmethanol (199) was then brominated using phosphorus tribromide in CCl$_4$ at 65 °C for 6 h to form a 63.1% crude yield of bromoditolylmethane (200), following a previously published procedure.$^{159}$ Bromoditolylmethane (200) was reacted with 1,1-diphenylethylene in refluxing benzene for 6 h to yield 1,1-diphenyl-3,3-ditolylpropene (201). TLC of the crude reaction mixture indicated that a mixture of the two starting reagents, 200 and diphenylethylene, and desired product 201 had resulted. This reaction was repeated with a longer reaction time with the same results. The reaction conditions were altered, replacing benzene with glacial acetic acid, according to previous literature.$^{160}$ The reaction was refluxed for 20 h. TLC showed a single spot and the product was recrystallized from hexanes, which resulted in 35.5% yield of 1,1-diphenyl-3,3-ditolylpropene (201). It was our plan to cyclopropanate 1,1-diphenyl-3,3-ditolylpropene (201) with dichlorocarbene, followed by treatment with tert-butoxide in order to form the target compound, ditolyldiphenylbutatriene (203). However, generation of dichlorocarbene using chloroform, phase transfer catalyst (benzyltriethylammonium chloride), and aqueous sodium chloride and alkene addition did not afford adduct 202.
All reaction conditions were modified such as varying the amounts of PTC, alkene, chloroform, lengthening reaction times, and addition of heat. Although starting material slowly disappeared, the desired product was not isolated. The same reaction conditions readily cyclopropanated 1,1-diphenylethylene resulting in a 49% yield of dichlorocyclopropanated product (Scheme 82).

Other methods were used in order to generate dihalocarbene. The formation of the dihalo compound 202 was tried using ethyltrichloroacetate and sodium methoxide, resulting in recovery of starting material. An attempt to generate dibromocarbene and subsequent addition was also attempted using bromoform and tert-butoxide in THF without success.
Scheme 82. First attempted synthesis of diphenylditolybutatriene (203).
Another strategy, illustrated in Scheme 83, was devised in order to prepare the desired compound. Trimethylsilylacetylene (154) was lithiated at -78 °C and treated with 4,4’-dimethylbenzophenone (198). Workup and purification by recrystallization from hexanes gave 49.4% of 4-methyl-α-(4-methylphenyl)-α-[(trimethylsilyl)ethynyl]benzenemethanol (204) a white solid. This was desilylated with 3N sodium hydroxide in methanol to give a 93.3% yield of propargyl alcohol 205, based upon previously published literature. Alcohol 205 was then treated with two equivalents of n-butyllithium in THF at -78 °C, followed by addition of benzophenone (206). Recrystallization of this product from chloroform gave a 65.7% yield of 207. Following previously published literature, diphenylditolybutyne diol (207) was subsequently reduced with tin(II) chloride dihydrate in concentrated hydrochloric acid to give a yield of 7.9%, of 203, after recrystallization with hexanes. The low yield on this step could probably be substantially improved.
Scheme 83. Synthesis of diphenylditolylbutatriene (203).
The position in which the $^{13}$C label is incorporated is crucial to the experiments that detect carbon scrambling in butatriene (Figure 22). $^{13}$C NMR spectroscopy of ditolyldiphenylbutatriene (203) shows four nicely resolved signals for the $sp^2$ and $sp$ hybridized carbons. Those corresponding chemical shifts are 150.71, 121.49, 123.12, and 151.99 ppm for C1, C2, C3, and C4, respectively. The $^{13}$C NMR shifts of 203 were assigned in correlation with the $^{13}$C NMR of the parent structure 219.172

![Figure 22. Ditolyldiphenylbutatriene (203).](image)

According to our proposed thermal rearrangements of an unsymmetrical butatriene, the $^{13}$C label should be incorporated at either of the internal positions (C2 or C3) in order to test our hypothesis. Therefore, syntheses were designed so that $^{13}$C label can be incorporated at positions C2 or C3. We were able to prepare the desired compound 203 and establish its suitability as a substrate. Next, $^{13}$C label had to be incorporated into the synthesis. The limited selection and expense of $^{13}$C enhanced reagents influenced our synthetic strategies. Therefore, we decided not to incorporate $^{13}$C enhanced material in Scheme 83 but rather to pursue alternate routes.
Other Attempts to Synthesize Unsymmetrical Butatrienes

Ethyl acetate is available with $^{13}$C label and we designed a route beginning with this substrate. Diphenylmethane (208) was deprotonated with $n$-butyllithium at $-78 \, ^\circ C$ and treated with ethylacetate under reflux, which yielded 82.6% of 1,1-diphenylacetone (209), based upon a published method.\textsuperscript{161} Next, attempts were made to synthesize the aldol (210). 1,1-Diphenylacetone (209) was deprotonated with sodium hydride in THF at room temperature. Once evolution of hydrogen gas ceased, $n$-butyllithium was added dropwise at room temperature over 30 min. The reaction mixture was cooled to 0 °C and a solution of 4,4'-dimethylbenzophenone (198) dissolved in THF was added dropwise, followed by stirring overnight. After workup, TLC and NMR spectroscopy indicated only very small amounts of aldol (210) had formed. This reaction was tried several additional times with slight adjustments without significant increase of yields of aldol (210). Other attempts with LDA and freshly prepared sodium ethoxide solution, in hopes of driving the reaction to the $\alpha,\beta$-unsaturated ketone (211), were also unsuccessful (Scheme 84).
Scheme 84. Attempted Synthesis using aldol-chemistry.

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A different route was attempted starting from the previously prepared 1,1-diphenylacetone (209). 1,1-Diphenylacetone (209) was added to a suspension of sodium hydride and THF at 0 °C and allowed to warm to room temperature for 2 h. Tert-butyldimethylsilylchloride (TBDMSCI) in THF was added and the mixture was stirred at ambient temperature for 48 h. Workup and purification by vacuum distillation and column chromatography gave a 64.1% yield of the silylenolether (213) following a published method. 9-Fluorenone (214) was chosen as the ketone because it would ultimately give an unsymmetrical butatriene (217) as a final product, which would give four different internal carbons by $^{13}$C NMR. The silylenolether (213) was added to LDA at 0 °C in THF followed by addition of 9-fluorenone (214). TLC and NMR showed a very complex mixture. Separation was attempted by column and rotary chromatography on silica gel with various solvent systems. This reaction gave only small amounts of allene alcohol (215) and allene diol (216). The untethered ketone, 4,4'-dimethylbenzophenone (198), was also used, but led to similar results. This route was abandoned (Scheme 85).
Ph \rightarrow 1. n-BuLi
Ph
2. ethylacetate
\[ \text{Ph} \rightarrow \text{Ph} \] 82.6%
\[ \text{CH}_3 \]

1. NaH
2. TBDMSiCl
64.1%

OSiBu(CH_3)_3

1. 3.3 eq LDA
2. 2.5 eq 9-Fluorenone
3. H_2O, H^+

Ph
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Scheme 85. Attempted synthesis via allenediol (216).

FVP Experiments of Allene, Butatriene, and Extended Cumulene Systems

As this work progressed, we explored the thermal stability of tetraaryl cumulenes. Tetraphenylallene (218) was pyrolyzed at 800 °C/0.03 torr. NMR spectroscopy showed mostly starting material with only minor products formed (Scheme 86).

Scheme 86. FVP of tetraphenylallene (218).
We next sought experimental evidence to test the hypothesis of long-range carbon topomerization occurring in cumulenes. A series of preliminary FVP experiments were carried out on cumulenic systems to detect rearrangements and thermal decomposition (Scheme 87). Tetraphenylbutatriene (219) was pyrolyzed at 700, 800, and 900 °C and 0.01 torr. Pyrolysis at 700 and 800 °C led to good recovery of starting material. Pyrolysis at 900 °C led to recovery of tetraphenylbutatriene (219) and a significant amount of unidentified product. The crude mixture was purified by preparative thin-layer chromatography using hexanes, but we were unable to identify products. It was concluded that thermal rearrangements occur around 900 °C. This was an indication of the thermal limits in which might expect to observe atom automerization without extensive formation of other products.

Scheme 87. FVP experiments of tetraphenylbutatriene (219).
FVP experiments were executed on ditolyldiphenylbutatriene (203) at 700, 800, 900 °C and 0.01 torr. Pyrolysis and 700 and 800 °C gave mostly unreacted starting material (203), while pyrolysis at 900 °C gave starting material (203) and considerable amounts of other unidentified products (Scheme 88).

Scheme 88. FVP experiments of ditolyldiphenylbutatriene (203).
Larger cumulenes were prepared for further study. Based upon previously published literature,\textsuperscript{162} 1,1-diphenyl-2-propyn-2-ol (220) was coupled under an oxygen atmosphere using catalytic copper(I) iodide in acetone to give an 80.1\% yield of 1,1,6,6-tetraphenyl-2,4-hexadiyn-1,6-diol (221), after recrystallization with toluene. The diol 221 was reduced with tin(II) chloride dehydrate in concentrated hydrochloric acid to give 49.8\% yield of 1,1,6,6-tetraphenylhexapentatriene (222) as a red solid following a published method (Scheme 89).\textsuperscript{168}

![Scheme 89. Synthesis of 222.](image)
1,1,6,6-Tetraphenylhexapentatriene (222) was set up for pyrolysis at 800 °C/0.005 torr. A heat gun along with heat tape was employed to assist in the sublimation of the solid and transport through the hot zone of the FVP apparatus. Due to the high melting point of the hexapentatriene (222), sublimation and transport did not occur and the solid carbonized to black soot. Pyrolysis of this substrate will require a different apparatus.

Conclusions

Calculations support our proposed mechanism of long-range carbon topomerization in butatrienes. A low-energy process that interconverts butatriene to methylenecyclopentadiene (187), and subsequent closure to bicyclo[1.1.0]but-1,3-ene (188) has been found as true energy minima along this reaction pathway. DFT and Møller-Plesset computations provide consistent predictions for this likely process. The desired unsymmetrical butatriene (203) was synthesized and showed four well resolved carbons resulting from the inner sp and sp² hybridized carbons. This result will allow us to follow the ¹³C label in future pyrolysis experiments with ¹³C labeled unsymmetrical butatriene. Control pyrolysis experiments of tetraaryl butatrienes were carried out and were found to have compound stability up to approximately 800 °C. A suitable synthesis of a ¹³C labeled unsymmetrical butatriene needs to be established and subsequent pyrolysis experiments remain in order to support our calculations.
EXPERIMENTAL SECTION

General Experimental

Instrumentation

$^1$H NMR Spectra were recorded on a Brucker AM-360 fourier transform spectrometer operating at 360.13 MHz, a Varian Mercury 400 fourier transform spectrometer operating at 399.77 MHz, and/or an INOVA Varian 500 fourier transform spectrometer operating at 499.76 MHz. All spectra were measured in CDCl$_3$ as solvent and (CH$_3$)$_4$Si as internal reference unless otherwise noted. Chemical shifts were reported in parts per million (ppm) relative to (CH$_3$)$_4$Si and coupling constants (J values) are in hertz (Hz).

$^{13}$C NMR Spectra were recorded on a Brucker AM-360 fourier transform spectrometer operating at 90.55 MHz, a Varian Mercury 400 fourier transform spectrometer operating at 100.52 MHz, and/or an INOVA Varian 500 fourier transform spectrometer operating at 125.67 MHz. All spectra were measured in CDCl$_3$ as solvent and (CH$_3$)$_4$Si as internal reference unless otherwise noted. Chemical shifts were reported in parts per million (ppm) relative to (CH$_3$)$_4$Si and coupling constants (J values) are in hertz (Hz).

Infrared Spectra (IR) were recorded on a Nicolet 205 fourier transform spectrometer. Absorptions were reported in wavenumbers (cm$^{-1}$) with polystyrene (1601 cm$^{-1}$) as the calibration peak.

Gas Chromatography Mass Spectra (GCMS) were obtained through the University of New Hampshire Instrumentation Center on a Hewlett-Packard 5988A-GC/MS.
quadrupolar spectrometer equipped with a 25 meter crosslinked methyl silicone capillary column. Electron impact (EI) mass spectra were obtained with an ionization voltage of 70 eV. Chemical ionization (CI) mass spectra were obtained with methane as ionization gas.

**Analytical Gas Chromatography** (GC) was performed with a Hewlett-Packard 6890 instrument equipped with a flame ionization detector connected to a Hewlett-Packard 3395 integrator. A 25 meter crosslinked methyl silicone capillary column was used.

**Preparative Gas Chromatography** was performed with a Varian 920 instrument equipped with a thermal conductivity detector connected to a Fischer Recordall 5000 chart recorder. The following columns were used: (a) 15% SE-30 20M on Supelcoport 80/100 mesh (10’ x ¼’ stainless steel) at specified temperatures, (b) 15% Carbowax 20M on Chromosorb W-HP 80/100 mesh (10’ x ¼’ stainless steel) at specified temperatures, and (c) 15% Carbowax 20M on Supelcoport 80/100 mesh (10’ x ¼’ glass) at specified temperatures.

**Molecular Modeling** calculations were performed using Spartan Pro or ’02, and Gaussian ’98 or ’03 using a Silicon Graphics O2 workstation or desktop PC.

**Solvents:**

The following chromatographic solvents (Reagent/ACS grade) were obtained from Fischer Scientific or VWR Scientific and used without further purification: n-pentane, n-hexane, ethyl acetate, and diethyl ether. The following solvents used for experimentation were freshly distilled from sodium benzophenone ketyl and used immediately: diethyl ether (Et₂O) and tetrahydrofuran (THF). Anhydrous dimethyl sulfoxide (DMSO) was purchased from Aldrich and used without further purification. Methylene chloride
(CH₂Cl₂) and carbon tetrachloride (CCl₄) were stored over 4Å molecular sieves prior to use. Acetonitrile was pesticide grade and N,N-dimethylformamide (DMF) was peptide synthesis grade, both were used without further purification. Diethylamine, diisopropylamine, and pyridine were distilled from potassium hydroxide and stored over 4Å molecular sieves prior to use. HPLC grade methanol was used without further purification. The following deuterated solvents for NMR analysis were purchased from Cambridge Isotope Laboratories and stored over 4Å molecular sieves: chloroform-d (CDCl₃), benzene-d₆ (C₆D₆), and methylene chloride-d₂ (CD₂Cl₂).

**Reagents:** All reagents purchased were of sufficient quality and used as obtained from the following companies: Aldrich, Lancaster, Fischer (Acros), Farchan, Alfa Aesar, and Cambridge Isotopes Laboratories.

**Column Chromatography and Adsorbents:**

**Silica Gel:** 80-200 mesh Fischer Scientific silica gel was used as obtained from the company. 200-425 mesh Fischer Scientific “flash” silica gel was used as obtained for the company. Where necessary, the silica gel was doped with Sylvania 2282 green phosphor to allow observation with ultraviolet light in quartz chromatography columns.

**Alumina:** 80-200 mesh Fischer Scientific alumina adsorption was used as obtained from the company.

**Florisil:** 100-200 mesh Fischer Scientific florisil was used as obtained from the company.

Thin Layer Chromatography (TLC) was performed using Whatman polyester plates coated with 250 µm layer silica gel doped with phosphor. Visualization was accompanied through the use of ultraviolet light or an iodine vapor stain.
Flash Vacuum Pyrolysis Experiments (General Procedure)

Flash vacuum pyrolysis (FVP) experiments were performed using a Lindberg model 55035-thermolysis oven containing a 50 cm quartz column packed with quartz chips (Figure 23 - Flash Vacuum Pyrolysis Apparatus). One end of the quartz tube was fitted with a 50 mL round bottom tube containing the sample. The opposite end of the column was equipped with a cold trap maintained at -78 °C, which was connected to a Welch Duo-Seal model 1400 vacuum pump. The sample was cooled using solid carbon dioxide while the pyrolysis apparatus was typically maintained at 10⁻² torr while the sample was warmed at room temperature and by a heat gun and evaporated. The sample traveled through the pyrolysis oven (hot zone), which was held at a constant temperature before condensing in the cold trap. Experiments were performed in the 600 – 1100 °C range and 50 – 200 mg samples were typically pyrolyzed. Temperatures were initially started in the lower range and gradually increased depending on the particular rearrangement being studied.
Figure 23. Flash Vacuum Pyrolysis Apparatus (FVP).
Experimental Procedures for Chapter 1

1-Phenyl-6-hepten-1-yne (65)

To a 125 mL three-neck round bottom flask containing THF (25 mL), phenylacetylene (70) (3.76 mL, 3.51 g, 34.3 mmol) was added and the mixture was cooled to -78 °C under a nitrogen atmosphere. n-Butyllithium (36.2 mmol, 14.4 mL) was added dropwise to the solution while it was stirred vigorously. The mixture was stirred for 2.75 h then warmed to -30 °C and hexamethylphosphoramide, HMPA, (6.45 g, 36.2 mmol) was added dropwise. After 10 min, 5-bromo-1-pentene (5.37 g, 36.2 mmol) was added dropwise over a 20 min period. The reaction mixture was allowed to stir for 24 h and then cooled to 0 °C with an ice bath. The reaction mixture was quenched with saturated aqueous sodium chloride (25 mL) and the two layers were separated. The aqueous layer was extracted with diethylether (4 x 25 mL) and the organic extracts were combined and washed with water (3 x 15 mL), and dried over magnesium sulfate. The solvents were concentrated under vacuum and column chromatography (silica gel, hexanes) and vacuum distillation yielded 65 a yellow oil (3.83 g, 22.5 mmol, 65.7%).

$^1$H NMR (360 MHz, CDCl₃) δ 1.75 (tt, 2H, $J = 7.2, 7.2$ Hz), 2.28 (dt, 2H, $J_d = 7.2$ Hz, $J_t = 7.2$ Hz), 2.49 (t, 2H, $J = 7.2$ Hz), 5.11 (d, 1H, $J = 11.5$) 5.18 (dd, 1H, $J = 1.4, 17.1$ Hz), 5.81-5.98 (m, 1H), 7.22-7.39 (m, 3H), 7.41-7.52 (m, 2H); $^{13}$C NMR (90 MHz, CDCl₃) δ 18.8, 27.9, 32.8, 80.8, 89.9, 115.2, 124.0, 127.5, 128.2, 131.5, 137.9; IR (neat) 1491, 914, 756, 692 cm$^{-1}$. 

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Pyrolysis of 1-phenyl-6-hepten-1-yne (65)

1-Phenyl-6-hepten-1-yne (65) was weighed out and passed through a quartz tube packed with quartz chips, maintained at 640 °C at 0.02 torr. The product was collected in a cold trap (-78 °C) to give a yellow oil. The recovered material was taken up in CDCl₃ and passed through a plug of silica. The recovered material was observed by capillary GC and ¹H and ¹³C NMR. Mostly unreacted starting material was observed. Trace amounts of phenylacetylene was believe to be observed by GC and ¹H and ¹³C NMR. This may have been due to fragmentation of starting material during the pyrolytic process. There was no observable evidence for cyclization. However, FVP at 750 °C, there is evidence that cyclization of 1-phenyl-6-hepten-1-yne (65) may form 2,3-1H-cyclopentanaphthalene (68) as an intermediate and further dehydrogenate resulting in benz[f]indene (69). Pyrolysis of 65 resulted in mostly unidentified products with small amounts of starting material (65), fragmented product (70), and benz[f]indene (69). ¹H NMR showed resonances from 6.92-6.95 ppm and 6.60-6.62 ppm which might result from vinyl protons of benz[f]indene (69). Resonances at 3.36-3.45 ppm where also present that might show evidence for methylene protons of benz[f]indene (69).
Experimental Procedures for Chapter 2

Synthesis of Diphenylbutadiyne (124)

Diphenylbutadiyne (124) was prepared based on previously published literature.\textsuperscript{162} Acetone (10 mL) was placed into a 125 mL round bottom flask surrounded by a water bath at 25 °C. Copper(I) chloride (0.187 g, 9.85 mmol) and N,N-N,N-tetramethylethylenediamine, TMEDA, (0.114 g, 9.85 mmol) was added and then oxygen was bubbled through the solution while it was stirred vigorously. Once the system was fully purged with oxygen, phenylacetylene (70) (2.01 g, 19.7 mmol) was added dropwise to the stirred reaction mixture over a 15 min period. After the addition was complete, the reaction mixture stirred for an additional 20 min. The solvent was then removed under reduced pressure and dilute aqueous hydrogen chloride (10 mL) was then added until the solution was slightly acidic to pH paper. A colorless precipitate formed and was filtered in a Buchner funnel and washed with water (10 mL). The precipitate was allowed to dry and was recrystallized (hexanes) to yield 124 as a white solid (2.00 g, 19.7 mmol, quant.) \textsuperscript{1}H NMR (360 MHz, CDCl\textsubscript{3}) \( \delta \) 7.31-7.62 (m, 10H); \textsuperscript{13}C NMR (90 MHz, CDCl\textsubscript{3}) \( \delta \) 73.92, 81.56, 121.81, 128.45, 129.22, 132.52; mp 87-88 °C (lit.\textsuperscript{174} 87 °C).

Synthesis of p-Ditolylbutadiyne (141)

p-Ditolylbutadiyne (141) was prepared based on previously published literature.\textsuperscript{162} Acetone (20 mL) was place into a 250 mL round bottom flask in a water bath at 25 °C. Copper(I) chloride (0.143 g, 1.44 mmol) and N,N-N,N-tetramethylethylenediamine, TMEDA, (0.172 g, 1.48 mmol) was added and then oxygen
was bubbled through the solution while it was stirred vigorously. Once the system was fully purged with oxygen, \( p \)-tolylacetylene (141) (3.57 g, 30.7 mmol) was added dropwise to the stirred reaction mixture over a 15 min period. After the addition was complete, the reaction mixture was stirred for an additional 20 min. The solvent was then removed under pressure and dilute aqueous hydrogen chloride (10 mL) was then added until until the solution was slightly acidic to pH paper. A colorless precipitate formed and was filtered in a Buchner funnel and washed with water (10 mL). The precipitate was allowed to dry and recrystallized (hexanes) to yield a white solid (3.54 g, 30.7 mmol, quant.) \(^1\)H NMR (360 MHz, CDCl\(_3\)) \( \delta \) 2.38 (s, 3H), 7.15 (d, 2H, 7.6 Hz); \(^1\)\(^3\)C NMR (90 MHz, CDCl\(_3\)) \( \delta \) 17.51, 69.35, 77.43, 114.67, 125.11, 128.28, 135.38; mp 183-184 °C (lit.\(^{175}\) 183 °C).

**Synthesis of 1-Bromo-2-phenylacetylene (144)**

1-Bromo-2-phenylacetylene (144) was prepared by a similar method.\(^{155}\) A solution of aqueous sodium hydroxide (16 mL of 1 M NaOH) was cooled at 10 °C and liquid bromine (4.00 g, 1.29 mL, 50.1 mmol) was added using an addition funnel with vigorous stirring by a mechanical stirrer for 30 min. After the bromine dissolved, 1,2-dimethoxyethane (8 mL) and phenylacetylene (70) (2.01 g, 19.6 mmol) were added consecutively and the mixture was allowed to stir for 5 h under a nitrogen atmosphere. The reaction mixture was cooled to 0 °C and water (100 mL) was added. The mixture was extracted with diethyl ether (4 x 25 mL), washing with water (25 mL) and dried over sodium sulfate. Solvent was removed under pressure, assisted by a warm water bath, to yield an oil (1.58 g, 8.78 mmol, 44.5%) \(^1\)H NMR (360 MHz, CDCl\(_3\)) \( \delta \) 7.27-7.36 (3H,
Synthesis of 4-Iodo-2-methyl-3-Butyn-2-ol (148)

4-Iodo-2-methyl-3-Butyn-2-ol (148) was prepared using the method described previously. A mixture of morpholine (24 mL) and benzene (24 mL) was slowly added to a solution of iodine (18.1 g, 74.1 mmol) in benzene (200 mL) while stirring vigorously using a mechanical stirrer. After 20 min, 2-methyl-3-butyn-2-ol (146) (4.01 g, 47.6 mmol) was added to the dark orange morpholine complex and the reaction was allowed to stir for 48 h at 45 °C. After cooling the reaction mixture to room temperature, the hydroiodide salt was removed by filtration and washed with diethylether. The combined filtrates were washed with a saturated aqueous sodium chloride solution (2 x 100 mL), 10% sodium thiosulfate solution (2 x 100 mL), 5% sodium hydrogen carbonate solution (2 x 100 mL), and water (200 mL) and dried with sodium sulfate. The solvent was evaporated under pressure assisted with a warm water bath and trace amounts of solvent was remove under pressure using high vacuum give an oil (7.48 g, 35.6 mmol, 74.8%)

$^1$H NMR (360 MHz, CDCl$_3$) $\delta$1.51 (br s, 1H), 2.50 (s, 6H), $^{13}$C NMR (90 MHz, CDCl$_3$) $\delta$ 31.35, 66.86, 99.12.
Synthesis of 2-Methyl-6-phenyl-3,5-hexadiyn-2-ol (147)

2-Methyl-6-phenyl-3,5-hexadiyn-2-ol (147) was prepared with slight variations using the following procedure from the literature.\textsuperscript{157}

Bis(triphenylphosphine)palladium(II) dichloride (0.721 mmol, 0.506 g) and copper(I) chloride (0.721 mmol, 0.134 g) were added to a 500 mL three-neck round bottom flask and THF (150 mL) was added under a nitrogen atmosphere. A mixture of 4-iodo-2-methyl-3-butyn-2-ol (148) (24.0 mmol, 5.05 g) and phenylacetylene (70) (26.0 mmol, 2.66 g) in THF (20 mL) was added and the mixture was stirred vigorously surrounded by a room temperature water bath. Diisopropylamine (4.86 g, 6.74 mL, 8.1 mmol) was injected into the reaction flask by syringe and the reaction mixture was allowed to stir at room temperature for 2 h. The reaction mixture was then diluted with diethylether (30 mL), extracted with aqueous hydrochloric acid (20 mL of 1M solution), washed with water (20 mL), aqueous saturated sodium chloride (20 mL) and dried over magnesium sulfate. Solvent was removed under pressure. Column chromatography (silica gel, methylene chloride/hexanes 1:1 ratio) gave 147 as a white solid (4.43 g, 24.0 mmol, 49.4\%). \textsuperscript{1}H NMR (360 MHz, CDCl\textsubscript{3}) \(\delta\) 1.59 (s, 6H), 2.04 (br s, 1H), 7.44-7.54 (m, 5H); \textsuperscript{13}C NMR (90 MHz, CDCl\textsubscript{3}) \(\delta\) 30.7, 65.6, 73.1, 78.6, 86.7, 121.4, 127.6, 128.3, 132.5; IR (neat) 3594, 3155, 2983, 2254, 1466, 1381, 1164, 1099 cm\textsuperscript{-1}; mp 84-85 °C (lit.\textsuperscript{176} 85 °C).
Synthesis of Phenyl-p-tolylbutadiyne (143)

Phenyl-p-tolylbutadiyne (143) was prepared using the conditions described previously. To a 250 mL three-neck round bottom flask was added copper(I) chloride (0.211 mmol, 0.040 g), aqueous benzyltrimethyl ammonium chloride (62 mL of a 50% aqueous solution, 0.171 mmol, 0.032 g) and bis(triphenylphosphine)palladium(II) dichloride (0.211 mmol, 0.148 g). The mixture was stirred vigorously under a nitrogen atmosphere at room temperature. A de-aerated mixture of 2-methyl-6-phenyl-3,5-hexadiyn-2-ol (147) (5.27 mmol, 0.972 g) and 1-iodo-4-methylbenzene (149) (5.27 mmol, 1.15 g) in benzene (15 mL) was added rapidly to the reaction mixture by syringe. Next, a de-aerated aqueous solution of 5.5N sodium hydroxide solution (2.5 mL; 13.8 mmol) was added by syringe and the reaction mixture was allowed to reflux for 48 h. The reaction mixture was then quenched with saturated aqueous ammonium chloride and stirred at room temperature for 1 h after which was extracted with diethylether (5 x 25 mL), filtered and concentrated under vacuum. Column chromatography (silica gel, methylene chloride/hexanes, 1:10) yielded 143 as a white solid (0.221 g, 1.02 mmol, 19.3%). $^1$H NMR (360 MHz, CDCl$_3$) δ 2.38 (s, 3H), 7.15-7.55 (m, 9H); $^{13}$C NMR (90 MHz, CDCl$_3$) δ 21.65, 73.32, 74.08, 81.25, 81.90, 118.67, 121.93, 128.44, 129.13, 129.26, 132.44, 132.49, 139.64; mp 107-109 °C (lit. 177 110 °C).
Preparation of $^{13}$C Labeled 1-Chloro-1-phenylethylene (152) and 1,1-Dichloro-1-phenylethane (153)

Acetophenone (1g) labeled at C1 with $^{13}$C (Aldrich, 99%) was diluted with four parts of unlabeled acetophenone. Benzene (40 mL) was injected to a 100 mL round bottom flask under a nitrogen atmosphere. Phosphorus pentachloride (6.50 g, 31.2 mmol) was added to the reaction flask and allowed to stir for 5 min. The reaction apparatus was set up for reflux and 20% $^{13}$C labeled acetophenone (150) (2.5 mL, 20.8 mmol) was injected into the solution and allowed to reflux for 45.5 h. Thin layer chromatography, (TLC), (silica gel, methylene chloride) was used to monitor the progress of the reaction. TLC was performed at 19, 25, and 45.5 h showing complete disappearance of the starting material and formation of two products. The reaction mixture was then poured into iced water (50 mL), extracted with diethylether (3 x 20 mL), and dried over sodium sulfate. The solvent was removed under reduced pressure assisted by a warm water bath to yield 152 and 153 as an oil (2.39 g), which was used without any further purification. $^1$H NMR (360 MHz) δ 2.52 (s) indicating methyl group for 153 and δ 5.61 (d) and 5.84 (d) for methylene group for 152. $^{13}$C NMR (90 MHz, CDCl$_3$) δ 56.11 indicating methyl group for 153 and δ 112.72 for methylene group for 152.
Conversion of $^{13}$C labeled 1-Chloro-1-phenylethylene (152) and 1,1-Dichloro-1-phenylethane (153) to C1-$^{13}$C labeled Phenylacetylene (76)

A mixture of $^{13}$C labeled 1-chloro-1-phenylethylene (152) and 1,1-dichloro-1-phenylethane (153) (2.29 g) was diluted with tetrahydrofuran (10 mL) and was added over a 5 min period to a suspension of excess sodium amide, which was generated from Na° (0.4 g, 17 mmol) in liquid ammonia (30 mL) at −78 °C. The mixture was stirred for 1.5 h, ammonium chloride (2 g) was added and the ammonia was allowed to evaporate. The solvent was removed under pressure, assisted by a warm water bath, and the residue was extracted with hexanes (3 x 20 mL). The concentrated extract was purified using column chromatography (silica gel, hexanes) to yield 76 as an oil (1.55 g, 15.2 mmol, 71.4% overall yield) $^1$H NMR (360 MHz, CDCl$_3$) $\delta$ 3.09 (s, 1H), 7.31-7.52 (m, 5H); IR (neat) 3350 (s), 3070 (s), 2110 (w) cm$^{-1}$.

Preparation of p-Tolyl-3-silyl-propyn-1-ol (157)

A solution of trimethylsilylacetylene (154) (59.5 mmol, 5.85 g) in THF (52 mL) was cooled to −78 °C under a nitrogen atmosphere. n-Butyllithium (45.8 mmol, 18.32 mL of 2.5 M solution in hexane) was added dropwise by syringe and the mixture was allowed to warm to room temperature. The stirred solution was then cooled back down to −78 °C and 4-methylbenzaldehyde (45.8 mmol, 5.50 g) dissolved in THF (10 mL) was added dropwise by syringe over 15 minutes. The solution was allowed to stir for 2 h at room temperature. The reaction was then quenched with saturated ammonium chloride, extracted with diethylether (4 x 10 mL). Combined extracts were washed with saturated aqueous solution of sodium chloride (20 mL), and a saturated aqueous sodium
bicarbonate solution (20 mL) then dried with sodium sulfate. The solvent was removed under pressure, which resulted in a clear light brown oil (5.1 g, 93%). $^1$H NMR (360 MHz, CDCl$_3$) δ 0.25-0.26 (m, 9H), 2.39 (s, 1H), 2.56-3.00 (br s, 3H), 5.42 (s, 3H), 7.21 (d, 2H, J = 7.96 Hz), 7.45 (d, 2H, J = 8.06 Hz).

Preparation of 4-Methyl-1-phenyl-2-propyn-1-ol (155)

4-Methyl-1-phenyl-2-propyn-1-ol (155) was prepared based on previous published literature.$^{166}$ $p$-Tolyl-3-silyl-propyn-1-ol (157) (2.52 g, 11.5 mmol) was added to a solution of 3N sodium hydroxide in methanol (20 mL) and allowed to stir at room temperature for 3 h. The solution was quenched with 1M aqueous hydrochloric acid (10 mL), extracted successively with diethylether (3 x 10 mL), saturated aqueous sodium chloride (10 mL), and water (10 mL). The solvent was then removed under pressure, which resulted in a yellow oil (1.54 g, 92.1%). $^1$H (360 MHz, CDCl$_3$) δ 2.40 (s, 3H), 2.67-2.68 (m, 1H), 2.98 (br s, 1H), 5.41-5.42 (m, 1H), 7.22 (d, 2H, J = 8.06 Hz), 7.45 (d, 2H, J = 7.93 Hz) $^{13}$C NMR (90 MHz, CDCl$_3$) δ 21.22, 64.11, 64.15, 83.86, 126.69, 129.35, 137.32, 138.32; IR (neat) 3850, 2117 (w) cm$^{-1}$.

Preparation of $^{13}$C labeled 4-(4-Methvlphenyl)-1-phenyl-2-butyn-1,4-diol (156)

A 2.5 M solution of n-butyllithium (31.4 mmol, 12.56 mL) in hexane was added by syringe over a period of 30 min, to a stirred solution of 4-methyl-1-phenyl-2-propyn-1-ol (155) (2.30 g, 15.7 mmol) in THF (17 mL) under a nitrogen atmosphere at −78 °C. The solution was allowed to warm to room temperature and cool back down to −78 °C. A mixture of benzaldehyde 20% $^{13}$C enhanced at the carbonyl position (1.53 mL, 15.0...
mmol) diluted with THF (10mL) was added over a 20 min period. The reaction mixture gradually warmed to room temperature was allowed to stir for 3 h. The reaction mixture was then treated with 2 M sulfuric acid until the solution was acidic and extracted with diethylether (3 x 20mL). Combined extracts were washed successively with saturated aqueous sodium chloride (20 mL) and saturated aqueous sodium bicarbonate solution (20 mL), and then dried with sodium sulfate. Solvent removal under vacuum resulted in a thick, dark red oil (3.24 g, 82.2%). $^1$H NMR (360 MHz, CDCl$_3$) $\delta$ 2.36 (s, 3H), 2.91 (br s, 2H), 5.49 (s, 1H), 5.52 (s, 1H), 7.12-7.54 (m, 9H); $^{13}$C NMR (90 MHz, CDCl$_3$) $\delta$ 21.3, 74.62, 74.81, 89.80, 90.6, 126.15, 126.38, 127.98, 128.55, 129.21, 137.99, 142.11, 145.61. An enhanced $^{13}$C resonance was observed at $\delta$ 74.81.
Synthesis of $^{13}$C labeled Phenyl-$p$-tolylbutadiyne (160)

$^{13}$C labeled Phenyl-$p$-tolylbutadiyne (160) was synthesized according to slight modification of a previously published procedure.$^{167}$ To a mixture of $^{13}$C labeled 4-methyl-1-phenyl-2-butyn-1,4-diol (156) (2.5 g, 9.91 mmol), pyridine (2.40 mL), and THF (25 mL) at 0 °C, a solution of thionyl chloride (2.17 mL, 30.0 mmol) in THF (10 mL) was added dropwise over a 30 min period. The reaction mixture was allowed to warm to room temperature and crushed ice was then added. The reaction mixture was extracted with diethylether (3 x 20 mL). The extract was washed successively with water (15 mL) and saturated aqueous sodium hydrogen carbonate (20 mL), and then dried with sodium sulfate. The crude dichloride (2.4 g) was obtained by evaporating the solvent under pressure and was subjected to dehydrochlorination without further purification.

A solution of the crude dichloride (1.66 g, 5.74 mmol) in THF (10 mL) was added over a 5 min period to a suspension of sodium amide, which was generated from sodium metal (0.41 g, 17.22 mmol) in liquid ammonia (30 mL) at -78 °C. The mixture was stirred for 1.5 h, and then the ammonia was allowed to evaporate after the addition of ammonia chloride (2 g). The solvent was removed under reduced pressure. The residue was extracted with hexanes (3 x 25 mL). The concentrated extract was purified using column chromatography (silica gel, hexanes) to give a white solid (0.31 g, 20.1%). $^1$H NMR (360 MHz, CDCl$_3$) $\delta$ 2.39 (s, 3H), 7.15-7.57 (m, 9H); $^{13}$C NMR (90 MHz, CDCl$_3$) $\delta$ 21.65, 73.30, 74.06, 81.23, 81.88, 118.67, 121.93, 128.44, 129.13, 129.26, 132.44, 132.49, 139.64; mp 107-109 °C (lit.$^{177}$ 110 °C). An enriched $^{13}$C resonance was observed at $\delta$ 81.23.
Pyrolysis of C1-$^{13}$C labeled Phenyl-$p$-tolylbutadiyne (160)

The C1-$^{13}$C enriched $p$-tolylphenylbutadiyne (160) was subjected to a series of FVP experiments at different temperatures and at constant pressure. $^{13}$C Labeled diyne 160 (51.1 mg) was passed through a horizontal quartz tube packed with quartz chips, maintained at 800 °C and at a pressure of 0.005 torr. The product was collected in a cold trap (-78 °C) to give a yellow solid. The crude product was dissolved in CDCl$_3$ and quantitative $^{13}$C NMR spectrum was taken (facilitated by addition of chromium acetonylacetonate to the sample as a relaxation agent) and showed $^{13}$C label scrambling from C1 to C2, exclusively. The integration showed a 11.6 : 7.37 : 1.16 : 0.89 ratio for C1(δ 81.23), C2(δ 74.06), C3(δ 73.30), and C4(δ 81.88).

$^{13}$C Labeled diyne 160 (49.5 mg) was passed through a horizontal quartz tube packed with quartz chips, maintained at 900 °C and at a pressure of 0.005 torr. The product was collected in a cold trap (-78 °C) to give a dark yellow solid. The crude product was dissolved in CDCl$_3$ and quantitative $^{13}$C NMR spectrum showed $^{13}$C label scrambling at all $sp$ hybridized carbons. The integration showed a 8.79 : 8.76 : 3.99 : 3.01 ratio for C1(δ 81.23), C2(δ 74.06), C3(δ 73.30), and C4(δ 81.88), respectively.

Pyrolysis of Doubled $^{13}$C labeled Diphenylbutadiyne (124)

Doubled $^{13}$C labeled Diphenylbutadiyne (124) was then subjected to a series of FVP experiments at different temperatures at constant pressure. Diyne 124 (50.8 mg) was passed through a horizontal quartz tube packed with quartz chips, maintained at 700 °C and at a pressure of 0.01 torr. The crude product was dissolved in CDCl$_3$ and quantitative $^{13}$C NMR spectrum was taken (facilitated by addition of chromium acetonylacetonate to
the sample as a relaxation agent) and showed $^{13}$C label scrambling from C1,C4 to C2,C3. The integration showed 1 : 2.1 ratio for C1,C4 (δ81.6) and C2,C3 (δ73.9), respectively.

Diyne 124 (52.5 mg) was passed through a horizontal quartz tube packed with quartz chips, maintained at 800 °C and at a pressure of 0.01 torr. The crude product was dissolved in CDCl$_3$ and quantitative $^{13}$C NMR spectrum was taken, showed $^{13}$C label scrambling from C1,C4 to C2,C3. The integration showed 1 : 1.3 ratio for C1,C4 (δ81.6) and C2,C3 (δ73.9), respectively.

**Experimental Procedures for Chapter 3**

4,4'-Dimethyl-benzhydrol (199)

4,4'-Dimethylbenzophenone (198) (2.01 g, 9.51 mmol) was dissolved in ethanol (24 mL) in a 100 mL round bottom flask. The solution was magnetically stirred while sodium borohydride (0.410 g, 10.5 mmol) was added slowly to the ethanolic solution at room temperature, which was then allowed to stir for 2 h. The solution was slowly poured in to 50 mL of iced water and 5 mL of concentrated hydrochloric acid. After several minutes, the precipitated product was collected by vacuum filtration and washed with water (2 x 5 mL). Recrystallized from hexanes yielded 199 as white solid (1.551 g, 77.55%). $^1$H NMR (400 MHz, CDCl$_3$) δ 2.16 (m, 1H), 2.32 (s, 3H), 5.76 (m, 1H), 7.12 (d, J = 2H, 7.78 Hz), 7.24 (d, 2H, J = 7.95); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.36, 76.15, 126.69, 129.36, 137.35, 141.37; IR (neat) 3355 (br), 2361 (s), 1508 (s) cm$^{-1}$; mp 67-68 °C (lit.$^{178}$ 67-68 °C).
Synthesis of 4,4'-Dimethylbenzhydryl bromide (200)

4,4'-Dimethyl-benzhydryl bromide (200) was prepared by slight variation of a literature procedure. 159 4,4'-Dimethyl-benzhydrol (199) (5.001 g, 23.55 mmol) was dissolved in 8 mL of CCl₄ and phosphorus tribromide (0.963 mL, 10.241 mmol) was added slowly at 0 °C. The mixture was allowed to stand for 42 h and then was heated to 65 °C for 6 h. The reaction mixture was filtered and the solid was washed with 10 mL iced water then with 15 mL of dilute sodium acetate solution, dried over sodium sulfate. A white solid (2.9403 g, 45.37%) was collected and used without further purification. ¹H NMR (400 MHz, CDCl₃) δ 2.30 (s, 3H), 6.24 (s, 1H), 7.09 (d, 2H, J = 7.80 Hz), 7.31 (d, 2H, J = 7.92); ¹³C NMR (100 MHz, CDCl₃) δ 21.43, 56.06, 128.62, 129.49, 138.16, 138.66; IR (neat) 3620 (m), 1494 (s), 1449 (s) cm⁻¹; mp 48-49 °C (lit. 179 48.5-49 °C).

3,3-Bis(4-methylphenyl)-1,1-diphenylpropene (201)

3,3-Bis(4-methylphenyl)-1,1-diphenylpropene (201) was prepared using a combination of literature methods. 160 A solution of 1,1-diphenylethylenne (1.37 mL, 7.75 mmol) and 4,4'-dimethylbenzhydryl bromide (200) (2.13 g, 7.75 mmol) in 15 mL of glacial acetic acid was refluxed under nitrogen for 20 h. The reaction mixture was allowed to cool to room temperature and 50 mL of water was added. The solution was extracted with diethyl ether (4 x 25 mL). Extracts were combined, dried and concentrated under reduced pressure using a water bath. A yellow solid resulted which was allowed to digest in a sodium hydroxide solution of ethanol of (1.003 g, 30 mL ethanol) for 30 min. The mixture was then placed into an ice bath and crystals precipitated and vacuum

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filtered to yield white solid (2.34 g, 80.7 %) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 2.32\) (s, 3H), 4.74 (d, 1H, \(J = 10.74\) Hz), 6.51 (d, 1H, \(J = 10.69\) Hz); mp 135-136.5 °C (lit.\(^{180}\) 139-140 °C).

**Synthesis of 1,1-Ditoly1-3-trimethylsilyl-2-propyn-1-ol (204)**

A solution of trimethylsilylacetylene (154) (59.5 mmol, 5.85 g) in THF (52mL) was cooled to \(-78\) °C under a nitrogen atmosphere. A 2.5 M solution of \(n\)-butyllithium (45.8 mmol, 18.32 mL) in hexane was added dropwise by syringe and the mixture was allowed to warm to room temperature. The stirred solution was then cooled back down to \(-78\) °C and 4,4'-dimethylbenzaldehyde (198) (45.8 mmol, 5.50 g) in THF (10 mL) was added dropwise by syringe over 15 minutes. The solution was allowed to stir for 2 h at room temperature. The reaction was then quenched with saturated ammonium chloride, and extracted with diethyl ether (4 x 10 mL). Extracts were washed with saturated aqueous sodium chloride (20 mL), and a saturated aqueous sodium bicarbonate solution (20 mL) and dried with sodium sulfate. The solvent was removed under reduced pressure, which resulted in a clear light brown oil (5.1 g, 93.1%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 0.003\) (s, 9H), 2.09 (s, 6H), 2.49 (m, 1H), 6.89 (d, 2H, \(J = 8.02\) Hz), 7.25 (d, 2H, \(J = 7.37\)); \(^{13}\)C (100 MHz, CDCl\(_3\)) \(\delta 0.005\), 21.17, 74.50, 91.58, 108.21, 125.99, 128.98, 137.38, 142.24.
Synthesis of 1,1-Ditoly1-2-propyn-l-ol (205)

1,1-Ditolyl-2-propyn-1-ol (205) was prepared with slight modification of previously published method.\(^{166}\) 4-methyl-\(\alpha\)-(4-methylphenyl)-\(\alpha\)-[(trimethylsilyl)ethynyl]benzenemethanol (204) (2.52 g, 11.5 mmol) was added to a solution of 3N sodium hydroxide in methanol (20 mL) and allowed to stir at room temperature for 3 h. The solution was quenched with a 1M aqueous hydrochloric acid (10 mL), extracted successively with diethyl ether (3 x 10 mL), saturated aqueous sodium chloride (10 mL), and water (10 mL). The solvent was then removed under pressure, which resulted in a yellow oil (1.54 g, 92.1%). \(^1\)H NMR (400 MHz, \(\text{CDCl}_3\)) \(\delta\) 2.41 (s, 6H), 2.90 (s, 1H), 2.95 (s, 1H), 7.21 (m, 2H), 7.56 (m, 2H); \(^{13}\)C (100 MHz, \(\text{CDCl}_3\)) \(\delta\) 21.39, 74.35, 75.55, 87.04, 126.25, 129.25, 137.78, 142.09.

Synthesis of 1,1-Ditoly1-4,4-diphenyl-2-propyn-1,4-diol (207)

1,1-Ditoly1-4,4-diphenyl-2-propyn-1,4-diol (207) was synthesized with slight modification of previously published method.\(^{167}\) 1,1-Ditoly1-2-propyn-1-ol (205) (1.16 g, 4.91 mmol) was dissolved in THF (20 mL) under a nitrogen atmosphere. The solution was cooled to \(-78^\circ\)C and a solution of 2.5 M of \(n\)-butyllithium (10.80 mmol, 4.32 mL) in hexane was added dropwise and the reaction mixture was allowed to warm to 0 °C for 20 min then cooled back down to \(-78^\circ\)C. Benzophenone (206) (0.895 g, 4.91 mmol) was dissolved in THF (5 mL) and added to the reaction flask dropwise and stirred for 6 h at room temperature. The reaction mixture was cooled to 0 °C and quenched with water (15 mL). Aqueous sulfuric acid (1M) was added to the mixture until the solution turned acidic to pH paper. The aqueous layer was separated and extracted with diethyl ether (3

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x 15 mL) and the organic layers were combined, washed with saturated aqueous sodium chloride solution (15 mL), water (15 mL) and then dried using sodium sulfate. The solvent was removed under reduced pressure. Column chromatography (silica gel, hexanes/ethylacetate 10:1) yielded 207 as a white solid (2.051 g, 0.049 mmol, 62.93%)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.30 (s, 6H), 2.80 (s, 1H), 2.89 (s, 1H), 7.08-7.59 (m, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.27, 74.60, 74.82, 89.83, 90.59, 126.12, 126.24, 127.97, 128.51, 129.19, 137.67, 142.25, 144.99; mp 126-127 °C.

Synthesis of 1,1-Ditoly1-4,4-diphenylbutatriene (203)

1,1-Ditolyl-4,4-diphenylbutatriene (203) was synthesized according to previously published literature. A solution of 1,1-ditolyl-4,4-diphenyl-2-propyn-1,4-diol (207) (0.239 g, 0.571 mmol) was dissolved in diethylether (3 mL) in a 50 mL two-neck round bottom flask under a nitrogen atmosphere at −60 °C. Finely powdered tin (II) chloride dihydrate (0.918g, 4.07 mmol) was added slowly to the solution in portions. The reaction was allowed to stir at −60 °C for 30 min. The reaction mixture was then extracted with diethylether (3 x 10 mL). Extracts were washed with ice cold water (10 mL), ice cold saturated aqueous sodium hydrogen carbonate solution (10 mL), and dried with sodium sulfate and concentrated under reduced pressure at 0 °C. Recrystallization (hexanes) yielded 1,1-Ditoly1-4,4-diphenylbutatriene (203) as a yellow solid (0.0174 g, 0.0452 mmol, 7.921%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.40 (s, 6H), 7.18-7.58 (m, 18 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.55, 121.49, 123.12, 127.92, 128.58, 129.34, 129.57, 129.62, 136.28, 138.20, 139.12, 150.71, 151.99; mp 215-215.5 °C.
Synthesis of 1,1-Diphenylacetone (209)

The preparation of 209 followed a previously published procedure with slight modifications. In a 250-mL three-neck round bottom flask, diphenylmethane (208) (68.1 mmol, 11.3 mL) was added to 127 mL of THF. The mixture was cooled to -78 °C under a nitrogen atmosphere and 2.5 M n-Butyllithium (28.05 mL, 70.10 mmol) in hexane was added dropwise. After addition, the solution was allowed to warm to room temperature and the color gradually became a dark red-orange color. Ethylacetate (34.0 mmol, 3.33 mL) was placed in another 500 mL three-neck with THF (85 mL) at room temperature under nitrogen. The diphenylmethyllithium solution was added dropwise via cannula. After complete addition, the reaction mixture was allowed to stir for 10 min and was then refluxed for an additional 10 min and allowed to reach room temperature. The reaction mixture was quenched with saturated aqueous ammonium chloride (50 mL), extracted with diethylether (3 x 25 mL). The ethereal extracts were washed with water (20 mL), brine (20 mL), and dried using sodium sulfate. The solvent was removed under reduced pressure. Column chromatography (silica gel, hexanes) yielded 1,1-diphenylacetone (209) as a yellow oil (5.90 g, 28.1 mmol, 82.6 %). $^1$H NMR (400 MHz, CDCl$_3$) δ 2.28 (s, 3H), 5.18 (s, 1H), 7.30-7.40 (m, 10H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 30.30, 65.29, 127.48, 128.95, 129.21, 138.53, 206.68; IR (neat) 1712 (s), 1600 (m) cm$^{-1}$.

tert-Butyldimethyl[(1-methyl-2,2-diphenylethenyl)oxy]silane (213)

tert-Butyldimethyl[(1-methyl-2,2-diphenylethenyl)oxy]silane (213) was synthesized according to previously published literature. To a suspension of potassium
hydride (8.86 mmol, 0.355 g) in THF (20 mL) was added to a solution of 1,1-
diphenylacetone (209) (8.06 mmol, 1.69 g) in THF (16 mL) at 0 °C. The color of the
solution became orange-red and the evolution of hydrogen was observed. After stirring
at 20 °C for 2 h, a solution of tert-butyldimethylsilyl chloride (1.82 g, 8.06 mmol) in THF
(5 mL) was added and precipitation of LiCl was observed. The reaction mixture was
stirred for 48 h at room temperature. The solvent was removed under reduced pressure
and the remaining solid was extracted with hexanes (3 x 20 mL). The organic layer was
filtered through Celite and the solvent was removed under reduced pressure. Column
chromatography (Florisil, hexanes) yielded 213 as a yellow oil (1.68 g, 5.18 mmol,
64.1%). \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 0.001 (s, 6H), 0.85 (s, 9H), 7.16-7.35 (m, 10H);
IR (neat) 3075 (m), 3015 (m), 2965 (s), 2910 (m), 1615 (s), 1490 (s), 1440 (s), 1400 (m),
1270 (s), 1230 (s), 1190 (s), 1105 (s) cm\(^{-1}\).

**Pyrolysis of Tetraphenylallene**

Tetraphenylallene (218) (100.2 mg) was passed through a horizontal quartz tube
packed with quartz chips, maintained at 800 °C and at a constant pressure of 0.03 torr.
The product was collected in a cold trap (-78 °C) to give a white solid. The product was
dissolved in CDCl\(_3\) and \(^1\)H and \(^{13}\)C NMR spectroscopy showed mostly starting material
with only formation of minor unidentified products. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.29-
7.48 (m, 20 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) 113.98, 127.95, 128.92, 128.98, 136.72,
208.75.
Pyrolysis of Tetraphenylbutatriene (219)

A series of pyrolysis experiments were carried out on tetraphenylbutatriene (219). Exactly (100 mg) of tetraphenylbutatriene was passed through a horizontal quartz tube packed with quartz chips, maintained at 700, 800, 900 °C and at a pressure of 0.01 torr for three separate experiments. The products were collected in a cold trap (-78 °C) to give a yellow solid in each case. Pyrolysis at 700 and 800 °C led to good recovery of starting material. Pyrolysis at 900 °C led to recovery of tetraphenylbutatriene (219) and the formation a significant amount of unidentified products. Purification of the crude mixture by preparative thin-layer chromatography using hexanes did not afford good separation for spectroscopic identification.

Pyrolysis of Ditolyldiphenylbutatriene (203)

A series of pyrolysis experiments were carried out on ditolyldiphenylbutatriene (203). Butatriene 203 was weigh out (50.2 mg, 52.3 mg, 51.6 mg) and passed through a horizontal quartz tube packed with quartz chips, maintained at 700, 800, 900 °C, respectively, at a constant pressure of 0.01 torr. The products were collected in a cold trap (-78 °C) to give a yellow solid in each case. Pyrolysis at 700 and 800 °C led to good recovery of starting material. Pyrolysis at 900 °C led to recovery of ditolyldiphenylbutatriene (203) and the formation a significant amount of unidentified products. Purification of the crude mixture by preparative thin-layer chromatography using hexanes led to insufficient separation for identification.
APPENDIX A
SPECTRA FOR SELECTED COMPOUNDS
CH₃

141

H₂C
APPENDIX B

B3LYP OPTIMIZED GEOMETRIES

1,3-butadiyne (131)

closure TS (TS1)

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1,2,3-cyclobutatriene (137)

bond switch TS (TS2) C$_2$h
tetrahedrene (168)

singlet trialene (133) $C_2h$
allenylcarbene (196)
bicyclo[1.1.0]butene (188) $C_2v$

butatriene (186) $D_2h$

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187 to 188 closure TS (TS4)
cyclopropenyl carbene TS (TS3)
methylene cyclopropylidene (187)
1,2-cyclobutadiene (191)
187 to 189 TS (TS 5)
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