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A STUDY OF 3-TROPYLIUM-1,5-HEXADIENE

A Thesis

Presented to

The Faculty of the Department of Chemistry

The College of William and Mary in Virginia

In Partial Fulfillment

Of the Requirements for the Degree of

Master of Arts

by

Elise Noma Hattersley

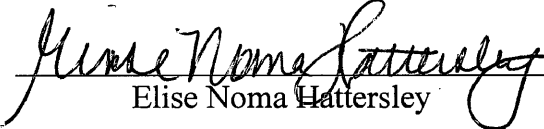
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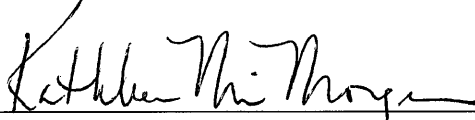
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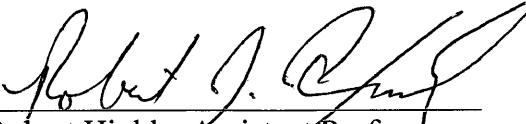
This thesis is submitted in partial fulfillment of
the requirements for the degree of

Master of Arts


Elise Noma Hattersley

Approved, July 1998


Kathleen Morgan, Director


Robert Hinkle, Assistant Professor

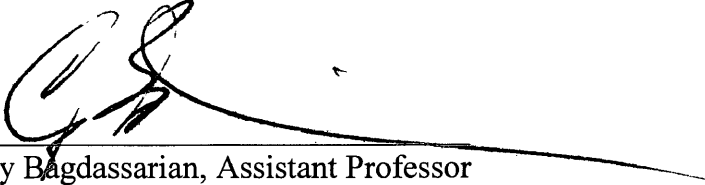

Carey Bagdassarian, Assistant Professor

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ABSTRACT

The Cope rearrangement is a thermal, pericyclic reaction which proceeds through a concerted pathway. The structure of the transition state and the rate of rearrangement are dramatically affected by substitution. Cationic substituents at the three position of 1,5-hexadiene are predicted to accelerate the rearrangement by increasing the degree of bond breaking in the transition state. The effect of a cationic substituent can be measured through kinetic and mechanistic studies by comparison with the hydrocarbon precursor. The synthesis of 3-cycloheptatrienyl-1,5-hexadiene was completed to produce the cationic species 3-tropylium-1,5-hexadiene. Several hydride abstracting agents were tested to determine the simplest method of isolating the cation as a pure, stable solid. Preliminary thermal studies were conducted to establish the stability of the cation at elevated temperatures and to determine the necessary conditions for rearrangement. Additionally, methods of reducing the cation were investigated in order to regenerate the hydrocarbon precursor, 3-cycloheptatrienyl-1,5-hexadiene, and confirm the hydride abstraction.

A STUDY OF 3-TROPYLIUM-1,5-HEXADIENE

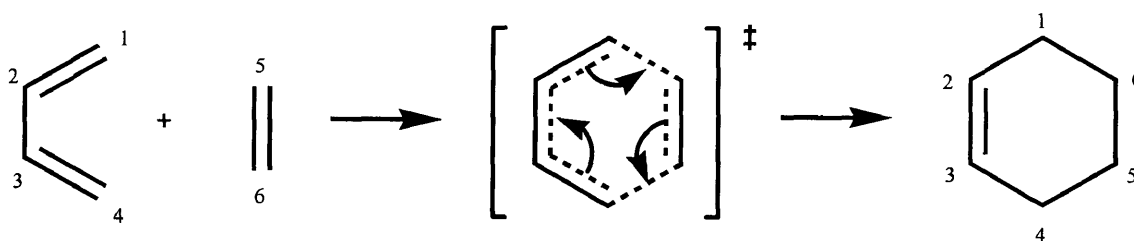
INTRODUCTION

1.1 PERICYCLIC REACTIONS

Pericyclic reactions are an important class of organic reactions. Woodward and Hoffmann defined pericyclic reactions as those "in which all first-order changes in bonding relationships take place in concert on a closed curve."¹ Their theories of the conservation of orbital symmetry demonstrated that allowed reactions would maintain bonding along a concerted pathway, while forbidden reactions would pass through a high energy non-bonding alternative along the reaction path, resulting in a step-wise mechanism. Evans and Warhurst's study of the transition state of the Diels-Alder reaction (FIGURE 1), one pericyclic process, led to a simple rule for predicting the facility of all pericyclic processes².

¹ Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

² Evans, M.G.; Warhurst, E. *Trans. Faraday Soc.* **1938**, *34*, 614.

FIGURE 1. DIELS-ALDER CYCLOADDITION

Evans determined that the reaction would proceed through a delocalized transition state similar to benzene, as opposed to a transition state resembling the corresponding localized 1,3,5-hexatriene. Preference for the delocalized transition state is due to resonance stabilization. Dewar generalized Evans's observations in the appropriately named *Evans' Principle*, which states that thermal pericyclic reactions occur through aromatic transition states.³

The early theoretical models resulted in the prevailing opinion that pericyclic reactions occur by a mechanism involving the concerted, cyclic permutation of bonds around a ring of atoms through a transition state with delocalized electrons, similar to benzene. Study of pericyclic reactions is generally concerned with describing transition states. The position, nature and number of substituents have been shown to affect the energy and structure of transition states, thereby altering the reaction rate and mechanism. The goal of this study was to measure the effects of a stable cationic

³ Dewar, M.J.S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill Book Company: New York, 1969; pp 316-339.

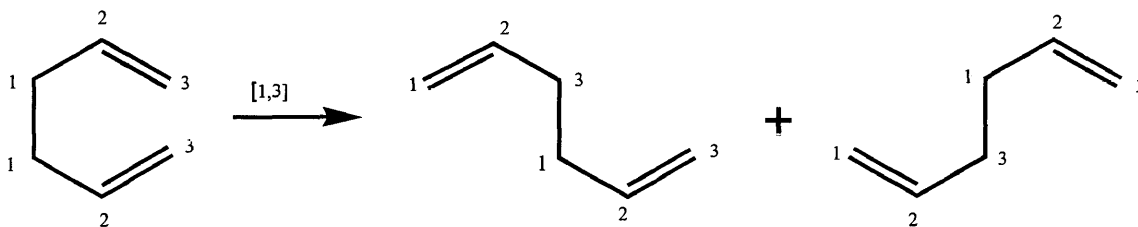
substituent on the reaction rate of the Cope rearrangement, a specific pericyclic reaction.

1.2 SIGMATROPIC REARRANGEMENTS

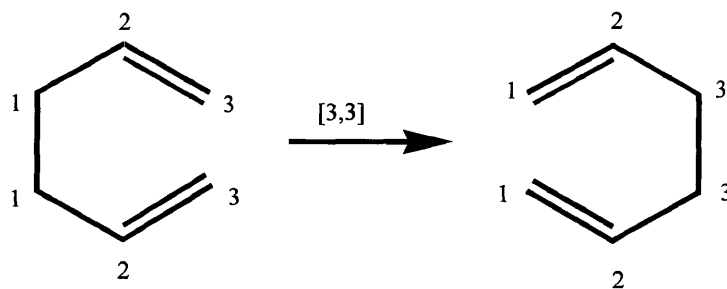
Sigmatropic rearrangements are a specific class of pericyclic reactions. These rearrangements involve the concerted reorganization of electrons, during which a sigma bond formally migrates from one end of a π -system to the other. The π bonds simultaneously rearrange in the process. Two general types of rearrangement are known, the [1,j] shift and the [i,j] shift (FIGURE 2). The numbers set in brackets represent the particular atoms in each fragment to which each end of the migrating sigma bond becomes attached. The molecule is numbered so that the carbons that form the sigma bond that breaks are numbered "one".

FIGURE 2. SIGMATROPIC REARRANGEMENTS

[1,3] sigmatropic rearrangement, an example of an [1,j] shift



[3,3] sigmatropic rearrangement, an example of an [i,j] shift



The Cope rearrangement is an example of a thermally induced [3,3] sigmatropic rearrangement. The minimum structural requirements for this rearrangement are the presence of a 1,5-hexadiene system with methylene groups in close proximity, and equilibrium between the isomeric species.⁴

The Cope rearrangement and other pericyclic processes are useful in synthetic organic chemistry because they are stereochemically reliable.⁵ The Cope rearrangement is also one of the few ways in which new carbon-carbon bonds can be formed with predictable stereo- and regio-control, especially when the reaction occurs at lower temperatures. Mechanistic study of pericyclic reactions has revealed an insensitivity to catalysis, a resistance to changes in solvent properties, such as polarity, and a lack of involvement of common intermediates, such as carbanions, free radicals, carbonium ions and carbenes.⁶ In light of these observations, Doering and

⁴ Stevens, T.S.; Watts, W.E. *Selected Molecular Rearrangements*; Van Nostrand Reinhold Company Limited: London, 1973; Chapters 7,8.

⁵ Lutz, R.P. *Chem. Rev.* **1984**, *84*(3), 205.

⁶ Doering, W. von E.; Roth, W.R. *Tetrahedron* **1962**, *18*, 67.

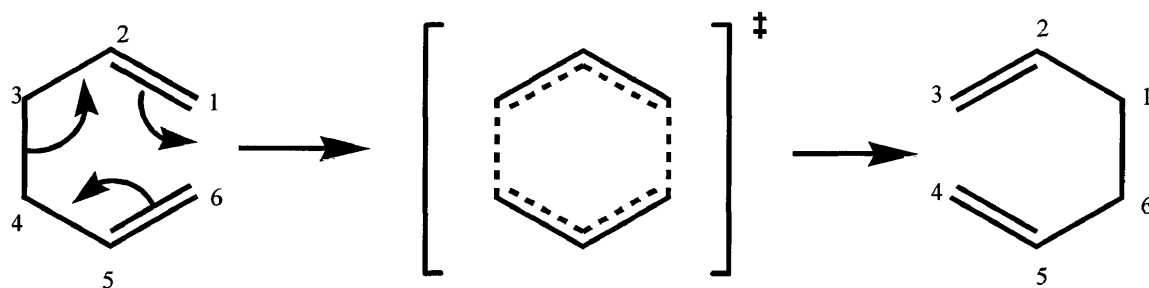
Roth dubbed, "half in jest and half in desperation", the term "no-mechanism reactions" for [3,3] sigmatropic shifts.

1.3 THE MECHANISM OF THE COPE REARRANGEMENT

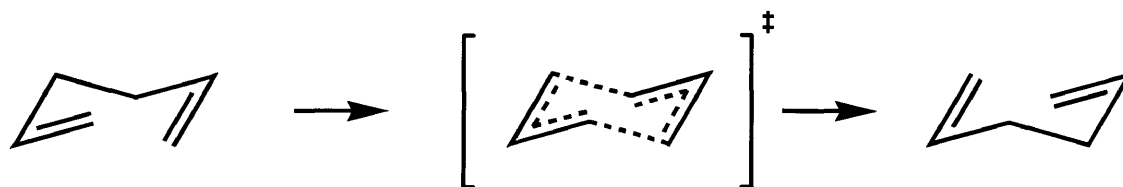
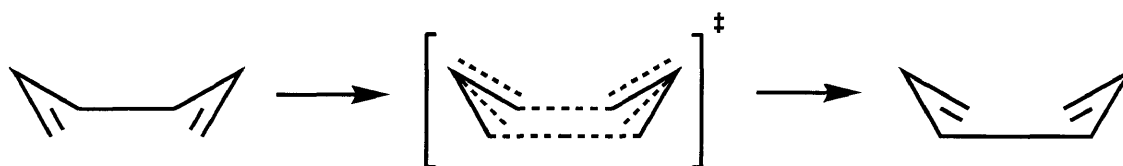
1.3.1 TRANSITION STATE GEOMETRY

The earliest mechanistic theories of the Cope rearrangement postulated a synchronous, concerted process necessarily occurring through a single, symmetrical transition state with equivalent partial bonding between C₁ and C₆ and between C₃ and C₄ (FIGURE 3). The geometry of the transition state, a cyclic, six-atom assembly, can be addressed by analogy to the conformations of cyclohexane.⁷ Although the transition state is free to adopt a variety of conformations, the chair- and boat-like transition geometries are the most likely (FIGURES 4 and 5).

FIGURE 3. CONCERTED MECHANISM OF THE COPE REARRANGEMENT

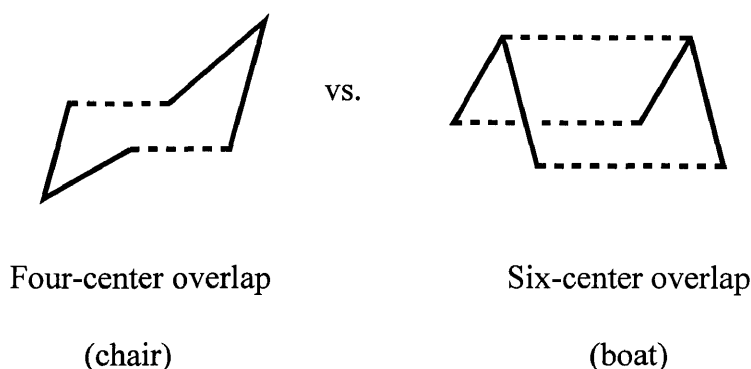


⁷ Shea, K.J.; Phillips, R.B. *J. Am. Chem. Soc.* 1980, 102, 3156.

FIGURE 4. CHAIR TRANSITION STATE OF THE COPE REARRANGEMENT**FIGURE 5. BOAT TRANSITION STATE OF THE COPE REARRANGEMENT**

The rigidity of these assemblies limits the number of stereoisomers that are observed; a looser transition state with more rotational freedom would result in stereoisomers. In addition, the relative energies of these transition states are predictable, and different enough that usually one or two stereoisomers predominate.

Doering and Roth addressed the geometry, electronic nature, and the strength of interaction between the allylic groups in the transition state of the Cope rearrangement.⁶ The most stable geometry was determined by a free energy comparison of transition states corresponding to the chair and boat conformations of cyclohexane. A six-atom overlap arrangement of the two parallel allylic groups resembled the boat conformation, and a four-atom overlap arrangement, in which only the ends of the allylic system interact, resembled the chair conformation (FIGURE 6).

FIGURE 6. FOUR-CENTER VS. SIX-CENTER OVERLAP ARRANGEMENTS

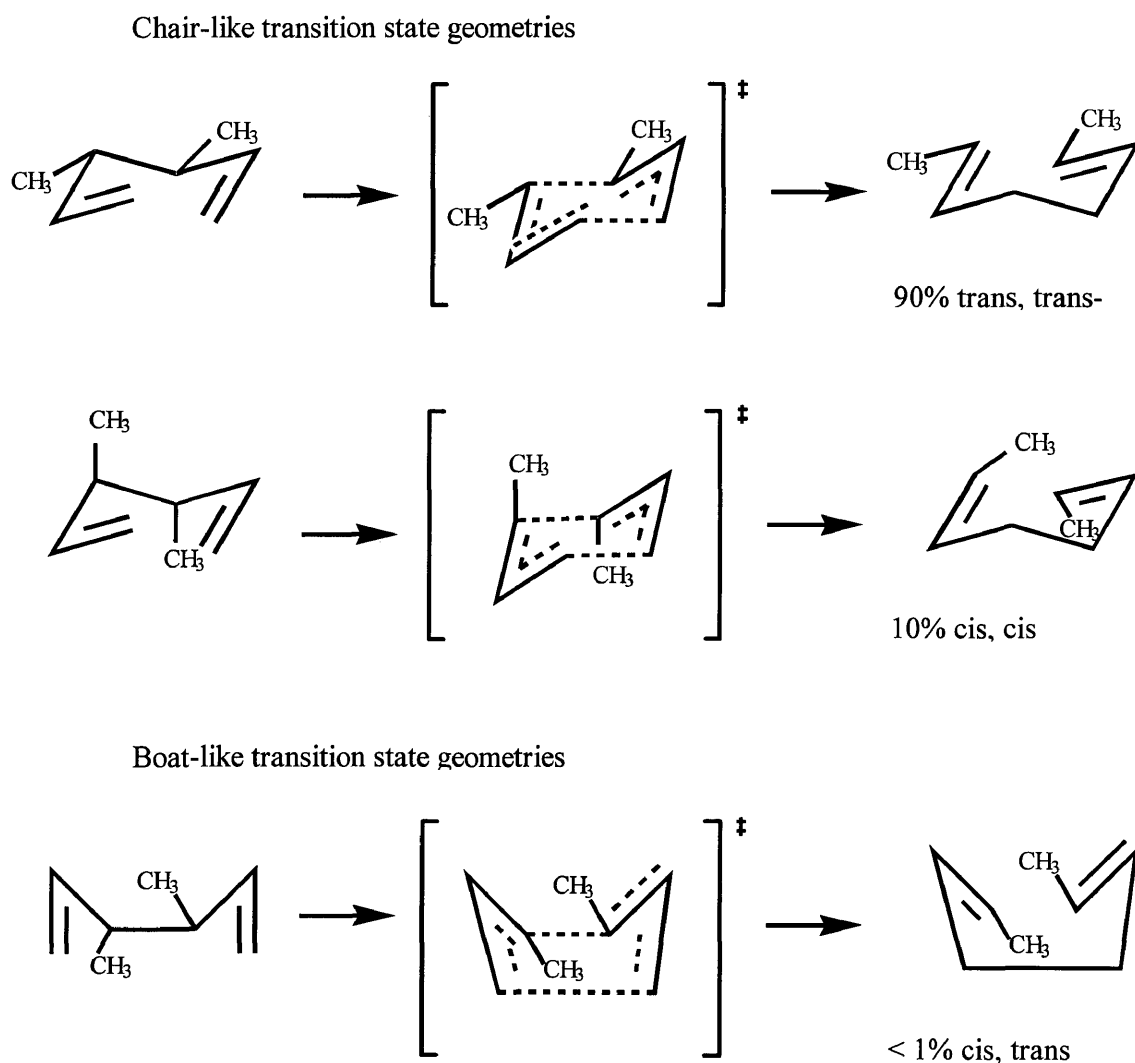
The behavior of *meso*- and *rac*-3,4-dimethylhexa-1,5-diene in the Cope rearrangement were examined in order to determine which transition state geometry is lower in free energy. The reaction products clearly indicated a kinetic preference of more than 300 to 1 for the four-center, chair-like arrangement over the six-center, boat-like arrangement of the transition state. The difference in free energy of activation between the two arrangements was determined to be at least 5.7 kcal/mole. This difference is comparable to that of the chair and boat conformations of cyclohexane, which differ in energy by 5-6 kcal/mole.⁸

The reaction products also showed a clear preference for a transition state that minimized steric interactions between the substituents. The *rac*-isomer has the choice between two four-center transition states, one leading to *trans, trans*-, the other to *cis, cis*-octa-2,6-diene. The formation of the *cis*-double bond involves a transition state

⁸ Johnson, W.S.; Bauer, V.J.; Margrave, J.L.; Frisch, M.A.; Dreger, L.H.; Hubbard, W.N. *J. Am. Chem. Soc.* **1961**, *83*, 606.

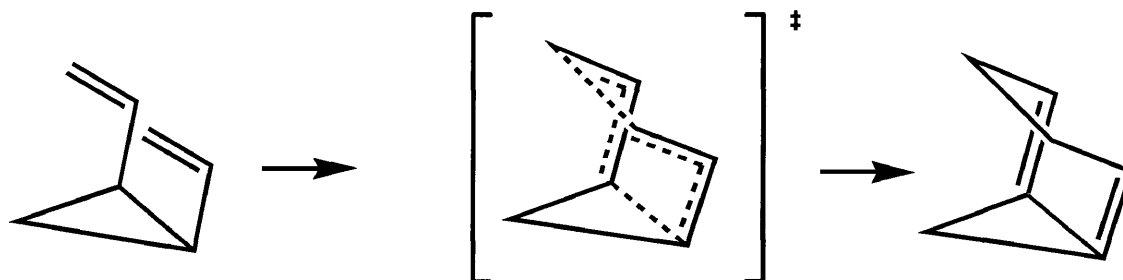
with an axially oriented methyl group, whereas the formation of a *trans*-double bond is synonymous with an equatorially oriented methyl and is favored by a difference in free energy of activation of about 2.0 kcal/mole. The *rac*-isomer rearranges with a relatively high degree of stereoselectivity to a mixture of 90% *trans, trans*- and 10% *cis, cis*-octa-2,6-diene (FIGURE 7).

FIGURE 7. COPE REARRANGEMENT OF *RAC*-3,4-DIMETHYLHEXA-1,5-DIENE



Additional studies have confirmed the preference for the chair-like transition state geometry when there is no steric barrier to reaction by either pathway, such as in the unsubstituted 1,5-hexadiene system.^{7,9} However, when the transition state conformation leads to a sterically strained product, rearrangement can occur through the boat-like conformation or by a concurrent mixture of the two geometries.⁹ *cis*-1,2-Dialkenylcyclopropane is an example of a molecule which rearranges through a six-center, boat-like transition state.¹⁰ Rearrangement through a four-center transition state would give the highly strained *cis, trans*-cycloocta-1,5-diene (FIGURE 8).

FIGURE 8. COPE REARRANGEMENT OF *CIS*-1,2-DIALKENYLCYCLOPROPANE



1.3.2 CONCERTED AND NON-CONCERTED MECHANISMS

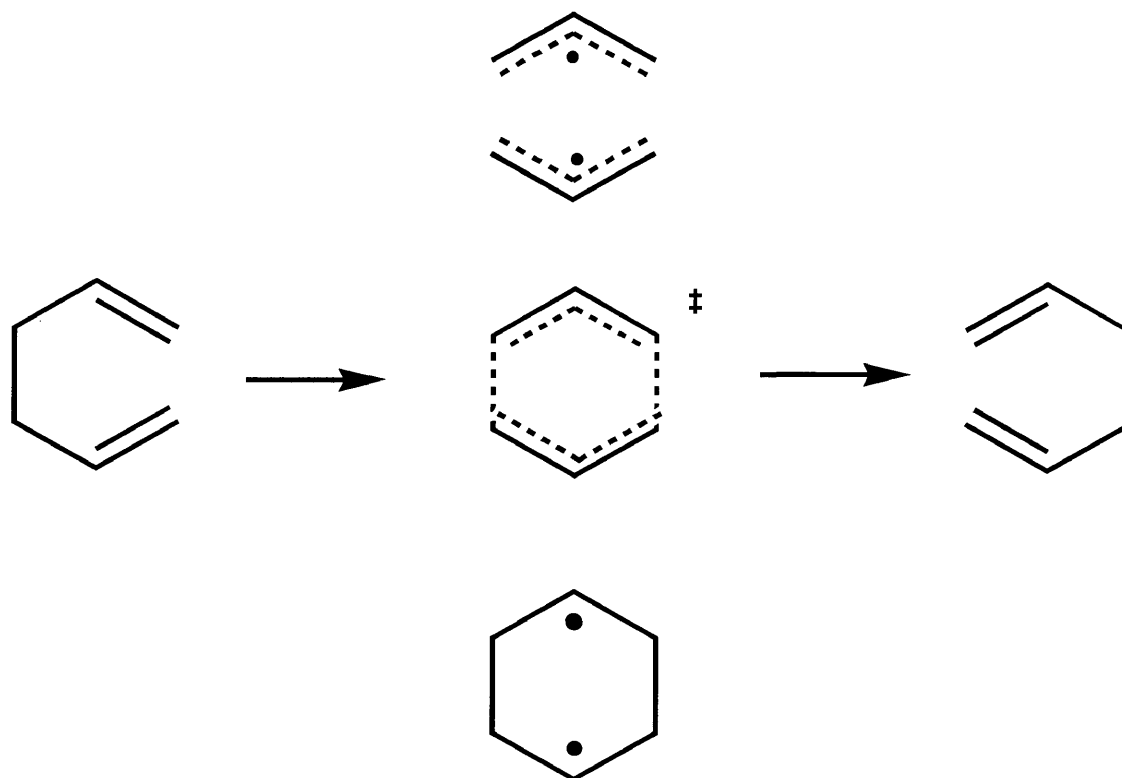
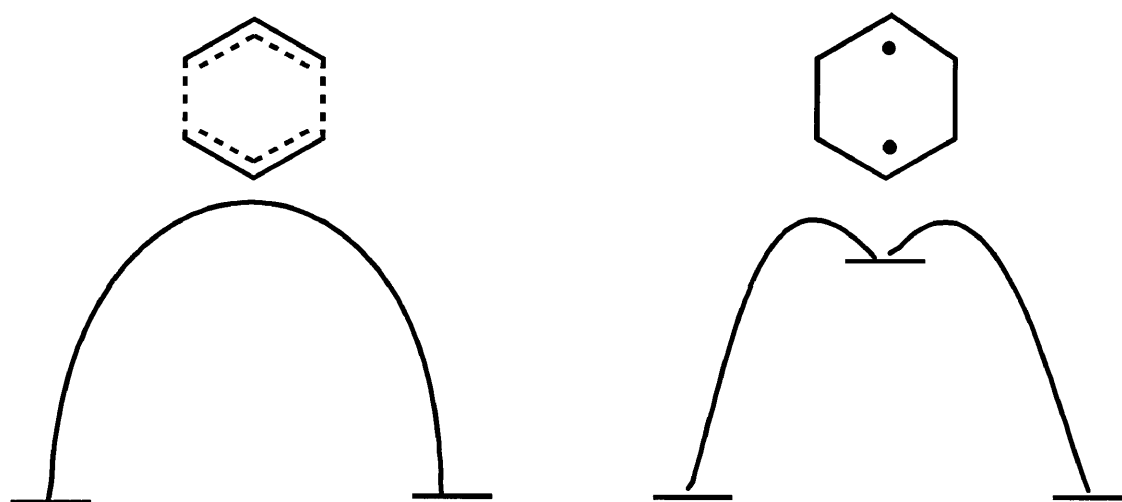
In addition to studying the geometry of the transition state, Doering *et al.* provided a detailed analysis of possible mechanisms for the Cope rearrangement.¹¹

⁹ Lutz, R.P.; Bernal, S.; Boggio, R.J.; Harris, R.O.; McNicholas, M.W. *J. Am. Chem. Soc.* **1971**, *93*, 3985.

¹⁰ Schneider, M.P.; Rau, A. *J. Am. Chem. Soc.* **1979**, *101*, 4426.

¹¹ Doering, W. von E.; Toscano, V.G; Beasley, G.H. *Tetrahedron* **1971**, *27*, 299.

They challenged the concerted mechanism with the postulation of a non-concerted, two-step pathway proceeding through one of two possible radical intermediates. The intermediates were suggested in order to account for the rate accelerations observed for substituted hexadienes, and represent extremes in the extent to which bond making between C₁ and C₆ and bond breaking between C₃ and C₄ occur. The complete bond breaking pathway involves the formation of two distinct allyl radicals; the complete bond making pathway involves the formation of a symmetrical cyclohexane-1,4-diyl intermediate (FIGURE 9). The reaction mechanism predicts equivalent, high energy transition states that precede and follow the intermediate (FIGURE 10). These transition states would adopt the low energy chair conformation whenever possible.

FIGURE 9. POSSIBLE MECHANISMS OF THE COPE REARRANGEMENT**FIGURE 10.** ENERGY DIAGRAMS FOR THE CONCERTED AND NON-CONCERTED PATHWAYS

Doering *et al.* estimated the heat of formation of the biradical and found it to be consistent with the observed activation energy for the rearrangement of 1,5-cyclohexadiene.¹¹ Their support for the biradical intermediate was reinforced by Dewar and Wade's observation that 2-phenyl and 2,5-phenyl-1,5-hexadienes rearrange 69 and 4900 times faster, respectively, than 1,5-hexadiene.¹² The phenyl group is commonly used as a radical stabilizing substituent. In addition, thermal isomerization of bicyclo[2.2.0]hexanes is suggested by experiment and MINDO¹³ calculations to generate the same diyl intermediate as proposed for the Cope rearrangement.¹⁴ Computational studies by McIver using MINDO/2¹³ also supported the diradical intermediate, and ruled out the formation of symmetrical, delocalized species for transition states altogether!^{15,16}

In spite of the support for a biradical intermediate in the Cope rearrangement, detailed thermodynamic studies and advanced computational studies have reaffirmed the concerted mechanism. Gajewski *et al.*¹⁷ used Goldstein and Benzon's data for the thermal isomerization of bicyclohexane¹⁴ to reveal the inaccessibility of the cyclohexane-1,4-diyl intermediate in the low energy [3,3] rearrangement. The diyl is

¹² Dewar, M.J.S.; Wade, L.E. *J. Am. Chem. Soc.* **1977**, *99*, 4417.

¹³ MINDO and MINDO/2 are semi-empirical molecular orbital methods used to calculate molecular energies and geometries.

¹⁴ Goldstein, M.; Benzon, M.S. *J. Am. Chem. Soc.* **1972**, *94*, 5119, 7147.

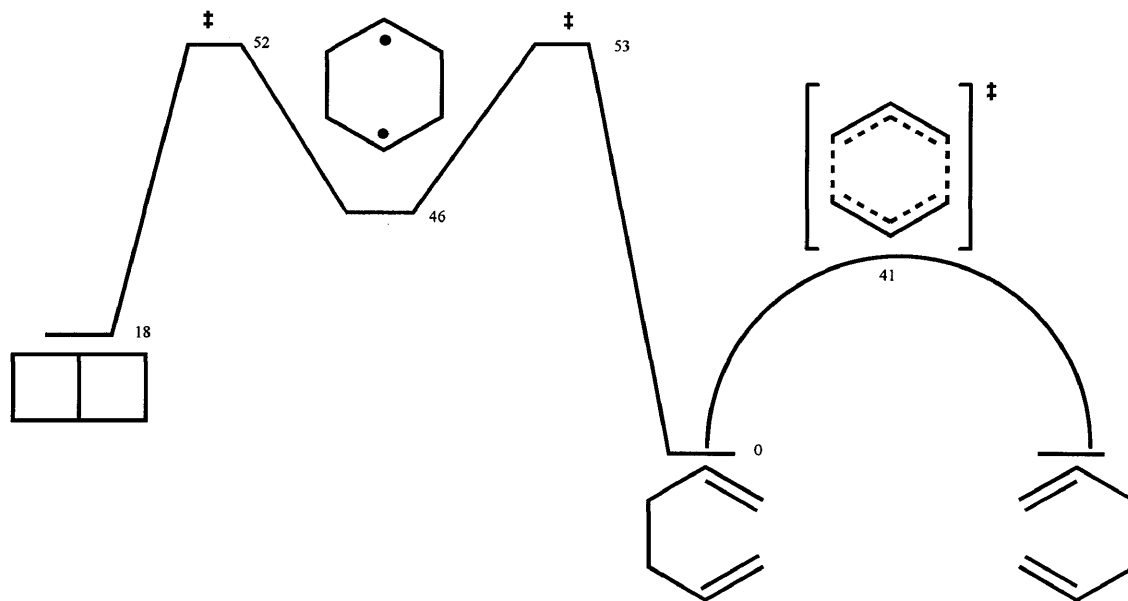
¹⁵ McIver, J.W., Jr. *Acc. Chem. Res.* **1974**, *7*, 72.

¹⁶ Komornicki, A.; McIver J.W., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 4553.

¹⁷ Gajewski, J.J.; Conrad, N.D. *J. Am. Chem. Soc.* **1978**, *100*, 6268.

the intermediate in the isomerization of bicyclohexane (BCH) to 1,5-hexadiene, and is 46 kcal/mol less stable in free energy than 1,5-hexadiene. The transition state in the cleavage of the diyl is 53 kcal/mol higher in energy than 1,5-hexadiene. Because the low-energy [3,3] transition state is only 41 kcal/mol above 1,5-hexadiene in free energy, a kinetic barrier of 12 kcal/mol (Figure 11) insulates the cyclohexane-1,4-diyl intermediate. The rearrangement must proceed through the only alternative, the single stage concerted route.

FIGURE 11. FREE ENERGY COMPARISON OF THE THERMAL ISOMERIZATION OF BCH AND THE COPE REARRANGEMENT



The question of concerted and non-concerted pathways for the Cope rearrangement still continues to be a topic of debate. Computational studies have addressed the question of transition state structure; however, different methods give

different results. Recent *ab initio*¹⁸ calculations at the CASPT2N level of theory conclude that the Cope rearrangement is concerted and does not involve a diradical intermediate.¹⁹

1.4 SUBSTITUENT EFFECTS ON THE COPE REARRANGEMENT

1.4.1 SECONDARY KINETIC ISOTOPE EFFECTS

Secondary deuterium kinetic isotope effects provide a powerful tool for evaluating the transition state structure of pericyclic reactions. They provide an experimental measure of the change in vibrational frequencies in the rate-determining transition state as compared to the reactant.²⁰ Rearrangements involving rehybridization of carbon centers can be studied by secondary kinetic isotope effects. Deuterium substitution at a carbon undergoing rehybridization affects the rate of the rearrangement relative to a hydrogen substituted carbon. A comparison of these relative rates indicates which bonds are being made or broken, and to what extent, as the reactant proceeds to the transition state.

In sigmatropic shifts, where one sigma bond is broken and a new sigma bond is made, with concomitant rehybridization, isotope effects are expected to relate to the

¹⁸ *Ab initio* calculations are iterative procedures based on self-consistent field methods. They tend to be more reliable but more complex than semi-empirical calculations.

Carey, F.A.; Sundberg, R.J. *Advanced Organic Chemistry, Part A: Structure and Mechanisms*; Plenum Press: New York, 1990; pp.20-24.

¹⁹ Hrovat, D.A.; Morokuma, K.; Borden, W.T. *J. Am. Chem. Soc.* **1994**, *116*, 1072.

²⁰ Houk, K.N.; Gonzalez, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81.

extent of bond breaking and bond making, respectively. For degenerate rearrangements of the order $[i,j]$, such as the Cope rearrangement, it is reasonable to assume that the transition state has (at least on average) equivalent partial bonds between the i th component and the j th component. These partial bonds are not necessarily half-bonds, and may have any bond order between 0 and 1.²¹ In any concerted reaction, where bonds are simultaneously broken and formed, the relative degrees of bond making and bond breaking in the transition state are dramatically affected by substitution. As the reaction proceeds from reactant to transition state, the degree of conjugation of substituent orbitals with those of the carbon framework will change, resulting in increased delocalization in the transition state of appropriately substituted molecules and an accelerated rearrangement.²² The nature and location of the substituent determines whether bond making or bond breaking pathways are accelerated.

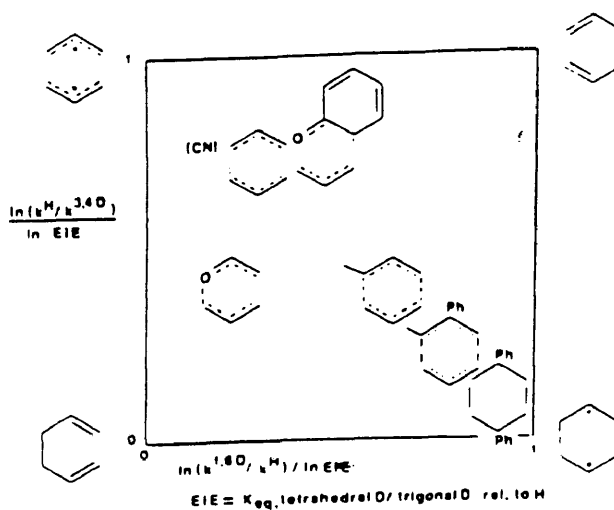
Secondary deuterium kinetic isotope effects have confirmed a variable transition state for substituted hexadienes. Gajewski and Conrad's comparison of bond making and bond breaking kinetic isotope effects on phenyl substituted hexadienes revealed a preference for bond making of 3.3 ± 1.0 times that of bond breaking for 2-phenyl substitution; 2,5-phenyl substitution demonstrated bond making 8.1 ± 2.0 times that of bond breaking.²¹ Gajewski and Gilbert attempted to correlate the rates of [3,3]-sigmatropic shifts with the free energies of formation of the

²¹ Gajewski, J.J.; Conrad, N.D. *J. Am. Chem. Soc.* **1979**, *101*, 6693.

²² Carpenter, B.K. *Tetrahedron* **1978**, *34*, 1877-1884.

transition state for nonconcerted bond breaking and bond making, and with the free energy of reaction.²³ Their empirical study determined that radical-stabilizing groups on C₃ and C₄ lower the free energy of bond breaking, while substituents placed on the C₂ and C₅ positions lower the free energy of bond formation. A More O'Ferrall-Jenks diagram compactly illustrates the relative degrees of bond making and breaking in the transition state for various substituted hexadienes (FIGURE 12). The axes of the diagram are the ratios of the secondary kinetic to the thermodynamic isotope effects at the reacting sites. The structural coordinates lead to the two nonconcerted extremes, either two allyl radicals or 1,4-cyclohexane diyl.

FIGURE 12. MORE O'FERRALL-JENKS DIAGRAM FOR SEVERAL SUBSTITUTED HEXADIENES



²³ Gajewski, J.J.; Gilbert, K.E. *J. Org Chem.* **1984**, *49*, 11.

1.4.2 THEORETICAL MODELS

Carpenter developed a simple theoretical model for understanding the qualitative effect of substituents on the rates of thermal pericyclic reactions.²² He considered the increase in delocalization of the substituted transition state to be the sole influence on the rate. For each reaction, the corresponding fully conjugated cyclic hydrocarbon was used as a model for the transition state. For example, benzene was used for the Cope rearrangement. Substituents were classified by their electronic properties, and their effects were measured at different positions. The π -electron donors were represented by a carbon bearing a doubly occupied 2p π -orbital. Similarly, π -electron acceptors were represented by an empty 2p π -orbital on carbon, while conjugating substituents were represented by a vinyl carbon. In the Cope rearrangement, the effects of substitution of π -electron donors and π -electron acceptors were predicted to have identical behavior, and were classified together as "polar substituents". Carpenter reported predictions for substitutions at the 1, 2 and 3 positions for the Cope rearrangement of 1,5-hexadiene. The greatest acceleration was observed with polar substituents at the 3 position; conjugating substituents showed only a slight rate increase at the 3 position. Substitution at the 1 and 2 positions resulted in a slower reaction rate for both conjugating and polar substituents.

1.4.3 ANIONIC SUBSTITUENTS

1.4.3A THE OXY-COPE REARRANGEMENT

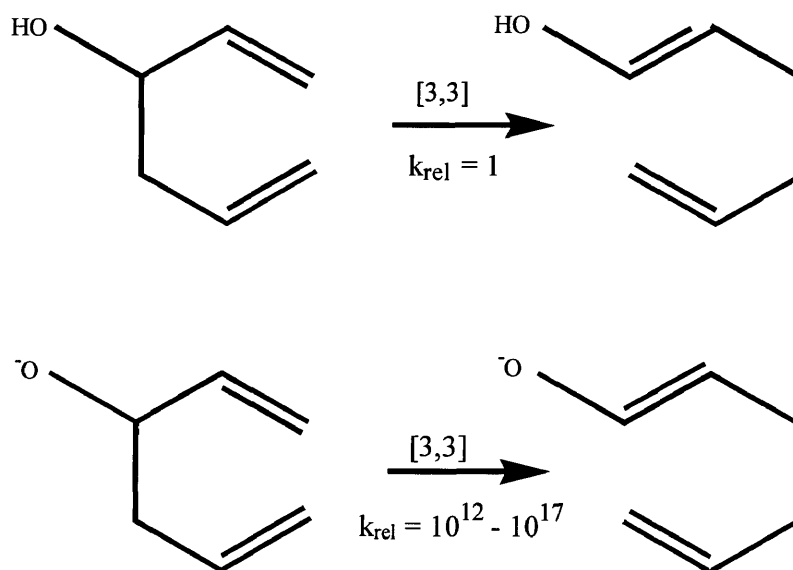
The anionic oxy-Cope rearrangement illustrates the rate accelerations predicted by Carpenter's model for a π -electron donating (polar) substituent at the 3 position of 1,5-hexadiene (FIGURE 13). Observed rate accelerations of 10^{12} - 10^{17} result with a substituent change from OH to O^- .²⁴ The absence of an alkali or other positive center on the oxygen allows the oxygen-centered electrons to delocalize, thereby increasing electron density on C_3 . A significant decrease in the dissociation energy of the C_3 - C_4 bond implies that the transition state has substantial weakening of the allylic bond and little formation of the final sigma bond, i.e., that bond breaking proceeds far beyond bond making in the transition state.²⁵ Secondary kinetic isotope effects also indicate substantial breaking of the C_3 - C_4 bond and little bond making between C_1 - C_6 in the transition state.²⁶

²⁴ Steigerwald, M.L.; Goddard III, W.A.; Evans, D.A. *J. Am. Chem. Soc.* **1979**, *101*, 1994-1997.

²⁵ Gajewski, J.J. *Acc. Chem. Res.* **1980**, *13*, 142.

²⁶ Gajewski, J.J.; Gee, K.R. *J. Am. Chem. Soc.* **1991**, *113*, 967.

FIGURE 13. THE OXY-COPE REARRANGEMENT



The anionic oxy-Cope rearrangement is one of the most well-studied [3,3] sigmatropic variants. The acceleration in rate with oxyanion substitution has greatly enhanced the synthetic utility of this rearrangement.²⁷

1.4.3B THE AMINO-COPE REARRANGEMENT

The anionic amino-Cope rearrangement presents an interesting deviation from the rate acceleration predicted by Carpenter's model. A recent investigation of anionic amino-Cope substrates found that amine anions gave dissociated and/or recombined addition products, or unreacted starting material.²⁸ The divergent

²⁷ For a good review of the oxy-Cope rearrangement, see Paquette, L.A.; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 609.

²⁸ Yoo, H.Y.; Houk, K.N.; Lee, J.K.; Scialdone, M.A.; Meyers, A.I. *J. Am. Chem. Soc.* **1998**, *120*, 205.

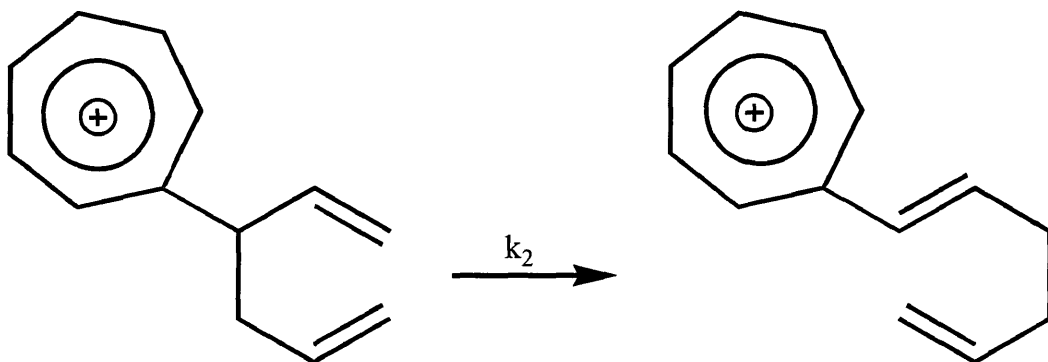
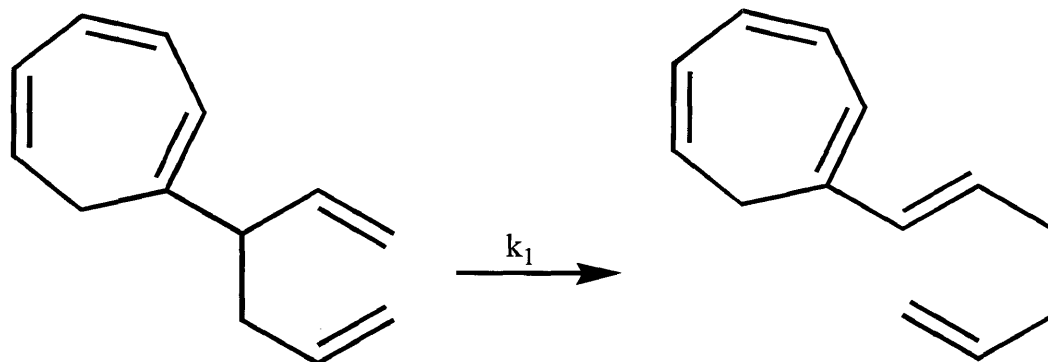
behavior of the oxy-anion and amino-anion was investigated with density functional B3LYP/6-31+G* and MP2/6-31+G* ab initio calculations. These calculations revealed that the anionic amino-Cope rearrangement proceeds through a stepwise mechanism. The intermediate is a complex of acrolein imine and allyl anion, which is substantially stabilized by weak bonding interactions. Further investigation of the mechanism revealed that the intermediate is formed by heterolytic cleavage of the C₃-C₄ bond. In the oxy-Cope rearrangement, however, low homolytic energy leads to a low-energy transition state for the concerted process. This transition state resembles two interacting allyl radicals. Heterolytic bond cleavage is substantially favored (by 18.7 kcal/mole) for the anionic amino-Cope substrate. An energetic preference for either homolysis or heterolysis therefore determines whether an anionic Cope substrate will undergo a concerted reaction or a step-wise heterolytic cleavage.

1.4.4 CATIONIC SUBSTITUENTS

Hückel Molecular Orbital theory predicts that π -electron donating and accepting, i.e. anionic and cationic, substituents will have similar rate accelerating effects on the Cope rearrangement.²² A cationic substituent may in fact be more accelerating than an anion of equal absolute charge. Hückel theory predicts the allyl cation and anion to be equally stable, while in reality the cation is more stable due to decreased electron-electron repulsion. The same reasoning may apply to the effect of a cationic substituent on the Cope rearrangement, and greater stability of the cationic substituent may result in greater rate acceleration per unit charge.

The effects of cationic substituents on pericyclic reactions have not been well developed. Catalysis by Lewis acids has been demonstrated and is attributed to the greater electrostatic stabilization of the transition state structure than the ground state.⁵ However, the transient nature of the cation in these systems makes them hard to define. The goal of this research is to determine the effect of a stable cationic substituent on the [3,3] rearrangement of 1,5-hexadiene. Two known and reasonably well understood possibilities for the cationic substituent are the cyclopropenyl and cycloheptatrienyl (tropylium) cations. The tropylium cation was selected as the substituent for several reasons. The synthetic chemistry of this system is more developed, and the cation is reported to be formed easily at room temperature with high yield and purity. In addition, the tropylium cation is a highly stabilized aromatic system, which remains stable under the conditions for rearrangement. The cationic system, 3-tropylium-1,5-hexadiene, was synthesized from the precursor, 3-cycloheptatrienyl-1,5-hexadiene. The relative rates of rearrangement have not yet been measured. The difference in rates is expected to be primarily the result of electronic differences, since steric differences between the cation and the neutral species should be small. The rearrangements of both systems are predicted to be irreversible due to the greater thermodynamic stability of the products, which results from increased conjugation (FIGURE 14).

FIGURE 14. COMPARISON OF THE RELATIVE RATES OF REARRANGEMENT OF 3-CYCLOHEPTATRIENYL-1,5-HEXADIENE AND 3-TROPYLIUM-1,5-HEXADIENE



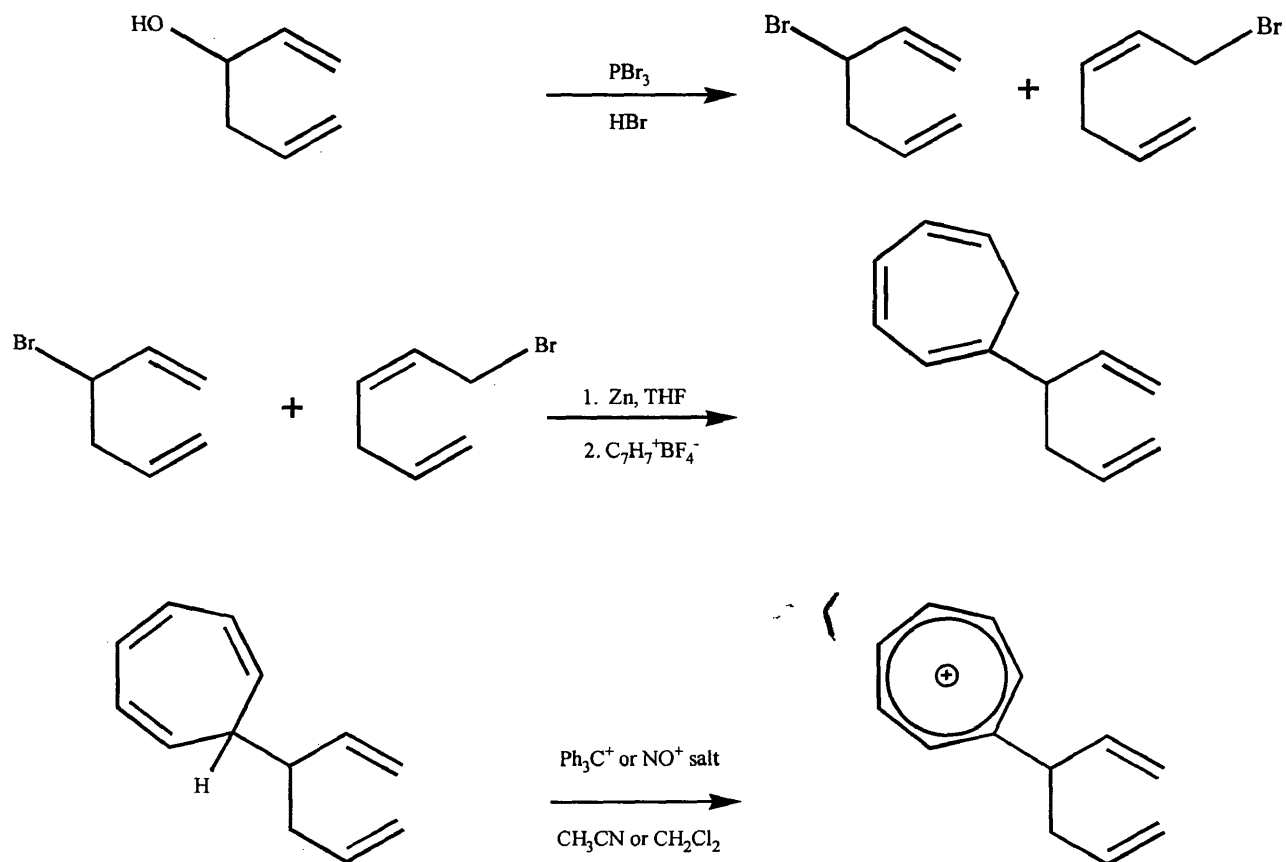
$k_2 \gg k_1?$

RESULTS

2.1 SYNTHESIS OF TARGET COMPOUNDS:

The synthesis of 3-cycloheptatrienyl-1,5-hexadiene begins with the treatment of 1,5-hexadien-3-ol with phosphorous tribromide to yield a mixture of bromohexadienes substituted at the one and three position. Tropylium tetrafluoroborate, a stable salt formed from cycloheptatriene and triphenylcarbenium tetrafluoroborate, is alkylated in a zinc mediated coupling with the bromohexadienes mixture. A hydride is removed from the product, 3-cycloheptatrienyl-1,5-hexadiene, to form 3-tropylium-1,5-hexadiene (SCHEME 1).

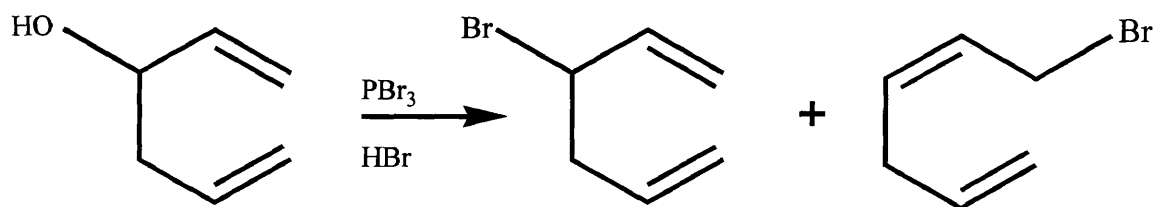
SCHEME 1.

2.1.1 1-BROMO-2,5-HEXADIENE AND 3-BROMO-1,5-HEXADIENE²⁹

The synthesis begins with treatment of commercially available 1,5-hexadien-3-ol with phosphorous tribromide (SCHEME 2). The reaction product, a mixture of bromohexadienes substituted at the 1 and 3 positions, was carried through without separation since the allyl system is regenerated in subsequent reactions.

²⁹ Hwa, J.C.H.; Sims, H. *Organic Synthesis*, 5, 608.

SCHEME 2.



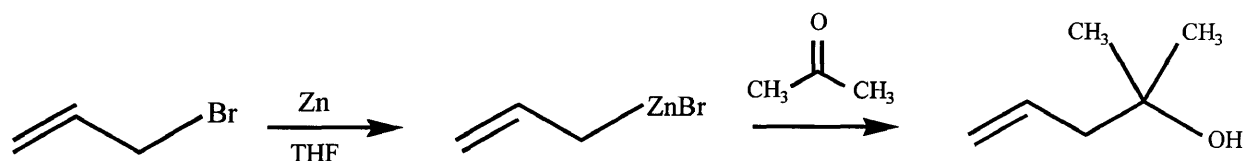
2.1.2 ZINC COUPLING REACTIONS

Picotin *et al.* studied several methods of preparing 7-alkylcyclohepta-1,3,5-trienes from the reaction of different organometallic reagents with either tropylium tetrafluoroborate or 7-ethoxycyclohepta-1,3,5-triene.³⁰ Their study determined that the reaction of organolithium and organozinc compounds with tropylium tetrafluoroborate is a reliable and relatively straightforward method of preparing 7-alkylcyclohepta-1,3,5-trienes. The reaction of organomagnesium compounds with tropylium tetrafluoroborate, however, is abnormal. Following Picotin's lead, synthesis of 3-cycloheptatrienyl-1,5-hexadiene was completed by a zinc-mediated coupling of the bromohexadiene mixture with tropylium tetrafluoroborate. The tropylium salt was selected instead of 7-ethoxy-1,3,5-cycloheptatriene, because it can be prepared easily from cycloheptatriene and triphenylcarbenium tetrafluoroborate.

³⁰ Picotin, G; Faye, A.; Migniac, P. *Bull. Soc. Chim. Fr.* **1990**, 127, 245.

A model organozinc reaction was completed to practice the technique of zinc coupling (SCHEME 3). Freshly distilled allyl bromide and tetrahydrofuran (THF) were combined with activated zinc dust, and acetone was added to the organometallic reagent to produce 2-methyl-4-penten-2-ol. Essentially all of the zinc was consumed in the reaction. The success of this reaction seemed to depend on the quality of the zinc. The initial attempts proved unsuccessful until the zinc dust was replaced with newly purchased zinc dust, which was stored in a desiccator.

SCHEME 3.

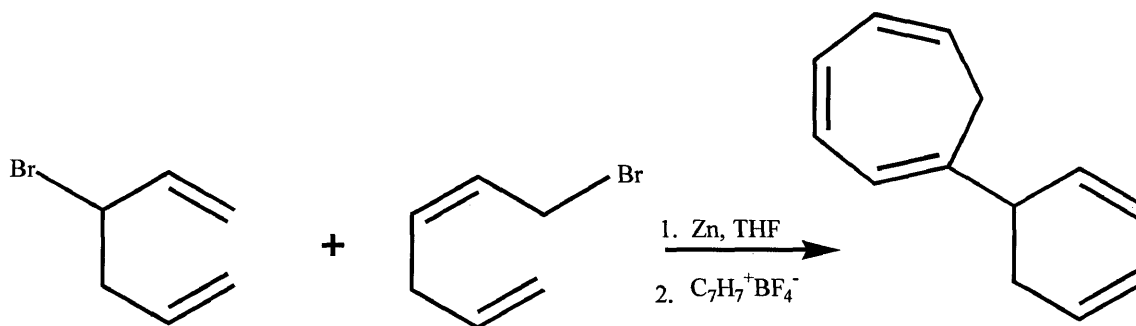


2.1.3 3-CYCLOHEPTATRIENYL-1,5-HEXADIENE

Preparation of 3-cycloheptatrienyl-1,5-hexadiene (SCHEME 4) followed essentially the same procedure as that used in the model organozinc reaction. One of several possible isomers is shown; the exact location of the double bonds in the cycloheptatrienyl ring is not established unambiguously. Tropylium tetrafluoroborate was alkylated in a zinc-mediated coupling with the bromohexadiene mixture. The conditions of the reaction were varied in an attempt to optimize the formation of the

organozinc reagent, since removal of by-products was particularly troublesome.³¹ Initially the reaction mixture was cooled to 0 °C during the addition of the bromohexadiene mixture to the zinc dust. However, over-cooling seemed to significantly inhibit or quench the reaction. The best results were obtained by controlling the reaction temperature with an ice bath. When the flask became too hot to touch, the reaction was cooled in the ice bath. The reaction was stirred until most of the zinc was consumed and the solution turned light green. Additionally, making sure that the tropylium tetrafluoroborate was a fine powder when added to the reaction mixture seemed to increase the extent of the reaction between the organozinc reagent and the tropylium salt.

SCHEME 4.

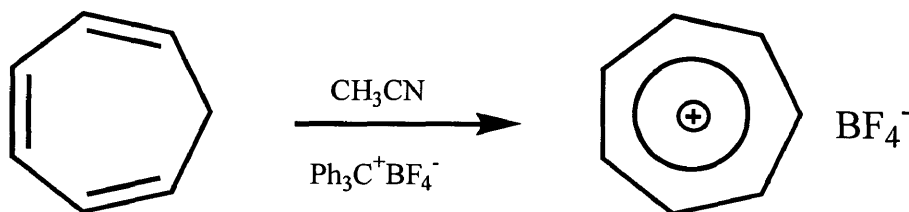


³¹ Unpublished research, Christine Beck, College of William and Mary.

2.1.4 TROPYLIUM TETRAFLUOROBORATE³²

Tropylium tetrafluoroborate was prepared by reaction of triphenylcarbenium tetrafluoroborate with cycloheptatriene in acetonitrile (SCHEME 5). Anhydrous ether was used to precipitate the solid.

SCHEME 5.



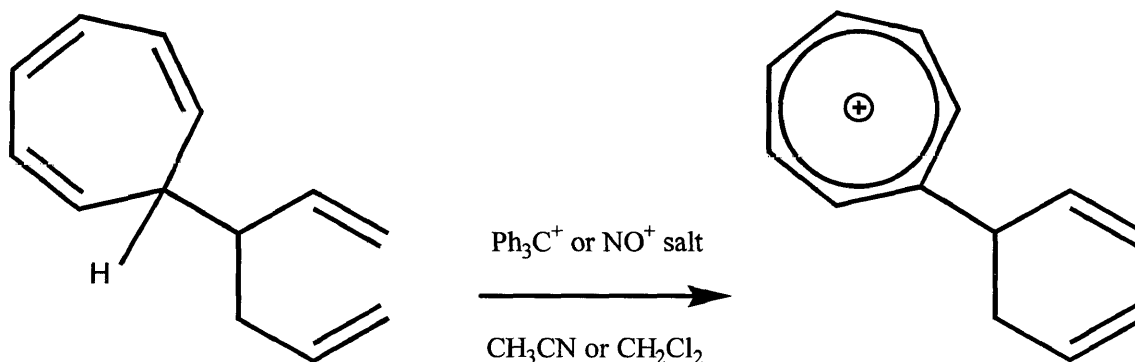
2.1.5 3-TROPYLIUM-1,5-HEXADIENE

3-Tropylium-1,5-hexadiene was synthesized by hydride abstraction from the hydrocarbon precursor, 3-cycloheptatrienyl-1,5-hexadiene (SCHEME 6).³³ Several hydride abstracting agents were tried to determine which counterion provided the most stable and easily isolated salt. Each synthesis followed the same general procedure, with some variation in solvents and reaction times. Solvents were selected for their ability to completely dissolve the hydride abstracting agents in order to

³² Harmon, K.M. *J. Am. Chem. Soc.* **1962**, *84*, 3349.

³³ a) Olah, G.A.; Salem, G.; Staral, J.S.; Ho, T. *J. Org. Chem.* **1978**, *43*, 173. b) Cavicchio, G.; Gaudiano, G.; Ponti, P. *Tetrahedron Letters* **1980**, *21*, 2333. c) Kim, E.K.; Kochi, J.K. *J. Am. Chem. Soc.* **1991**, *113*, 4962 - 4974. d) Bertelli, D.J.; Golino, C.; Dreyer, D.L. *J. Am. Chem. Soc.* **1964**, *86*, 3329.

facilitate the hydride exchange. The hydride abstracting agent was dissolved in either acetonitrile or methylene chloride; 3-cycloheptatrienyl-1,5-hexadiene was added dropwise. The mixture was stirred a maximum of three hours. The ease with which 3-tropylium-1,5-hexadiene could be isolated from the reaction mixture depended on the associated counterion. Tetrafluoroborate salts formed an oil at room temperature and a stable solid could not be isolated. Hexachloroantimonate and hexafluorophosphate salts were easily isolated by precipitating the solids with anhydrous ether. The reaction mixtures were transferred to an appropriately sized beaker, and the ether was added slowly while stirring. The solutions were then transferred to test tubes and the solids were isolated after spinning the samples in a centrifuge and decanting the solvent. An alternative method of obtaining the solid, completely removing the solvent from the reaction mixture by rotary evaporation, produced an oil from which it was often impossible to precipitate a solid.

SCHEME 6.

2.2 ANALYSIS OF PRODUCTS

The bromohexadiene mixture and 3-cycloheptatrienyl-1,5-hexadiene were analyzed with proton and carbon NMR in deuterated chloroform (APPENDIX III-A,B; APPENDIX IV-B,C). Tropylium tetrafluoroborate and the 3-tropylium-1,5-hexadiene salts were analyzed with proton NMR in deuterated acetonitrile or dimethyl sulfoxide (APPENDIX V-A,B). Gas chromatography and mass spectrometry (GC/MS) were used to determine the purity and confirm the identity of the bromohexadiene mixture and 3-cycloheptatrienyl-1,5-hexadiene. The mass spectrum of the bromohexadienes showed strong $M = 79$ and $M = 81$ mass fragments (the bromine isotopes) as well as the molecular ion peak, $M = 162$ (APPENDIX III-C). A mass spectrum of 3-cycloheptatrienyl-1,5-hexadiene identified the tropylium fragment, $M = 91$, and the molecular ion peak, $M = 172$ (APPENDIX IV-A,D). Tropylium tetrafluoroborate was analyzed by UV/Vis spectrometry in methylene chloride. This spectrum was comparable to that reported in the literature.³⁴

Two general types of impurities were consistently present in the 3-cycloheptatrienyl-1,5-hexadiene samples. These impurities were partially characterized and appear to be the result of incomplete coupling between tropylium tetrafluoroborate and the organozinc reagent. The first type of impurity was identified as a by-product of the reaction between zinc and the bromohexadiene mixture. The zinc coupling reaction was prematurely quenched with aqueous ammonium chloride

³⁴ The values determined experimentally were λ_{\min} 252.50 and λ_{\max} 277.25. These values are comparable to those reported by Harmon: λ_{\min} 253.5 and λ_{\max} 271.5.

after formation of the organozinc reagent. Analysis of the organic product by GC/MS showed two compounds, possibly isomers, which consistently appear as impurities in the 3-cycloheptatrienyl-1,5-hexadiene product (APPENDIX IV-E,F). These compounds have significantly longer retention times than either bromohexadiene isomer, although their fragmentation pattern is identical. The characteristic $M = 79$ and $M = 81$ mass fragments indicate that the impurities do contain bromine, and the bromohexadiene molecular ion peak, $M = 162$, is present. The presence of these compounds in the product implies that either they do not react with tropylium tetrafluoroborate, or that the reaction between them is incomplete.

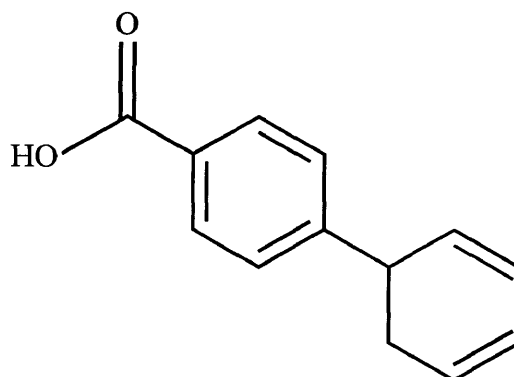
The other common impurity in the 3-cycloheptatrienyl-1,5-hexadiene samples was identified as a cycloheptatriene resin (APPENDIX IV-G,H). Cycloheptatriene is known to resinify upon exposure to air.³⁵ A sample of cycloheptatriene was exposed to air at room temperature for several days and analyzed by GC/MS. Comparison of this resin to the sample impurity confirmed the presence of the resin in the 3-cycloheptatrienyl-1,5-hexadiene product. The NMR spectrum of the resin differs slightly from cycloheptatriene, suggesting that the resin could be a dimer or oligomer of cycloheptatriene. The resin isolated from 3-cycloheptatrienyl-1,5-hexadiene samples formed a crystalline solid upon exposure to air. Attempts to remove the resin from 3-cycloheptatrienyl-1,5-hexadiene by precipitation were unsuccessful, however, since no suitable solvent system could be found.

³⁵ *Encyclopedia of Reagents for Organic Synthesis, Volume 2*: New York, 1980; pp. 1428.

2.3 PURIFICATION OF PRODUCTS

Vacuum distillation was attempted to purify the bromohexadiene mixture. The decision to purify individual samples was based on the percent composition, as determined by GC/MS. Distilling did not successfully separate the two bromohexadiene isomers from other sample impurities. Also, extensive heating of the sample may induce rearrangement (such as the Cope) or decomposition.

Various methods of purification were attempted to isolate 3-cycloheptatrienyl-1,5-hexadiene from the impurities. Column chromatography was used as the initial step in the purification process, and several combinations of solid supports and eluting solvents were tried. Samples purified with silica gel as the solid support showed an increase in impurities, suggesting that the compound decomposed on the silica gel. These impurities were isolated by column chromatography and examined by NMR and IR spectrometry (APPENDIX IV-I,K). A peak in the ^1H NMR spectrum at $\delta = 10$ ppm and another at $\delta = 10.4$ ppm suggest that the new impurity is a carboxylic acid. This was supported by the IR spectrum, which showed strong absorptions at 3383.0 cm^{-1} (OH stretch) and at 1694 cm^{-1} (C=O stretch). Additionally, peaks in the aromatic region of the NMR spectrum, between $\delta = 7$ and $\delta = 8$ ppm, suggest that a benzoic acid may have formed. The gas chromatograph shows three new peaks that could represent the three possible isomers (APPENDIX IV-J; FIGURE 15).

FIGURE 15. A POSSIBLE ISOMER OF THE OXIDATION IMPURITY

Vacuum distillation was attempted to purify 3-cycloheptatrienyl-1,5-hexadiene. The differences in the gas chromatography retention times between the sample components suggested that separation by boiling point might be possible. However, all of the sample components co-distilled to some extent with 3-cycloheptatrienyl-1,5-hexadiene; therefore, distillation did not provide a successful method of purification.³⁶ Extensive heating was avoided to prevent rearrangement.

Preparative gas chromatography was also attempted to purify 3-cycloheptatrienyl-1,5-hexadiene. The components of the sample were collected in glass tubes cooled in liquid nitrogen in order to condense the vapors. Although preparative chromatography successfully isolated most of the sample components, the results were inconsistent and therefore unreliable. It is possible that sample decomposition or rearrangement occurred.

³⁶ Percent composition of distillate fractions are tabulated in Appendix I.

Flash chromatography³⁷ with alumina as the stationary phase and hexanes as the eluting solvent gave the greatest resolution of sample components, as shown by thin layer chromatography. However, the structural similarities between 3-cycloheptatrienyl-1,5-hexadiene and the sample impurities made absolute separation difficult. Using a high ratio (100:1) of solid support to sample, packing the column tightly, and collecting fractions of approximately five milliliters made it possible to isolate pure samples (as determined by GC/MS).

2.4 THERMAL REARRANGEMENT STUDIES

Preliminary thermal rearrangement studies were conducted on both 3-cycloheptatrienyl-1,5-hexadiene and 3-tropylium-1,5-hexadiene. Two rearrangement studies were conducted on 3-cycloheptatrienyl-1,5-hexadiene. Samples were vacuum sealed in glass tubes and heated to 175 °C, either in an aluminum heating block or an oil bath, for up to 30 hours. The products were analyzed by NMR and GC/MS. The gas chromatograph of the first trial, conducted in the oil bath, showed at least twelve products. None of these sample components could be identified absolutely as a rearrangement product. The second trial was conducted in the heating block at 175 °C. The gas chromatograph showed primarily one component, which eluted at 12.8 minutes (approximately three minutes after 3-cycloheptatrienyl-1,5-hexadiene elutes and one minute before the resin elutes). The mass spectrum differed slightly from that of 3-cycloheptatrienyl-1,5-hexadiene although the molecular ion peak, $M = 172$,

³⁷ Perrin, D.D; Armarego, W.L.F., *Purification of Laboratory Chemicals, 3rd Edition*; Pergamon Press Inc.: New York, 1988; pp. 23.

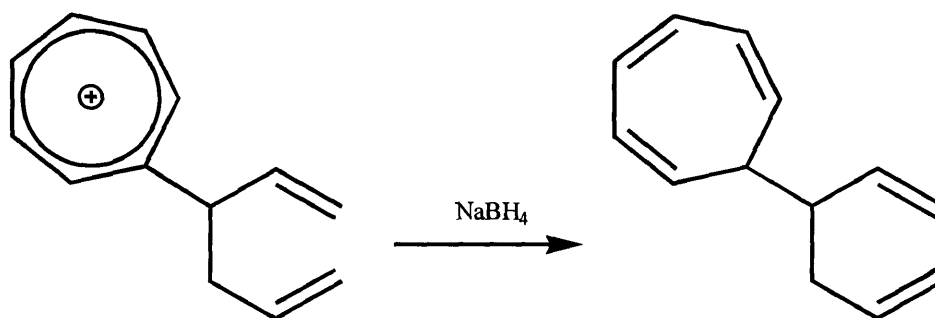
was present. Comparison by UV/Visible spectrometry also showed differences between the heated sample and 3-cycloheptatrienyl-1,5-hexadiene. 3-Cycloheptatrienyl-1,5-hexadiene had λ_{\max} 272 nm, while the rearranged product had λ_{\max} 338 nm. An increase in the λ_{\max} is consistent with increased conjugation. An NMR spectrum of the heated sample showed some differences from 3-cycloheptatrienyl-1,5-hexadiene, although the peaks were not clearly resolved. Since the rearrangement product has not yet been characterized, it is difficult to determine whether successful rearrangement occurred.

Thermal rearrangement studies of 3-tropylium-1,5-hexadiene were also conducted. This rearrangement is predicted to occur at a lower temperature than that of 3-cycloheptatrienyl-1,5-hexadiene, so the samples were only heated to 85 °C. A sample of 3-tropylium-1,5-hexadiene hexachloroantimonate in deuterated dimethyl sulfoxide was heated for up to one week without noticeable change in the NMR spectrum. The conditions required for rearrangement are still being determined. However, the cation may show a decelerated rate of rearrangement if the resonance stabilization of 3-tropylium-1,5-hexadiene is greater than the stabilization of the transition state, which results from increased conjugation. This possibility is being investigated with Hückel Molecular Orbital Theory.

2.5 REDUCTION OF CATIONIC SPECIES

Reduction of 3-tropylium-1,5-hexadiene by sodium borohydride should regenerate 3-cycloheptatrienyl-1,5-hexadiene (SCHEME 7).

SCHEME 7.



Successful reduction of tropylium to cycloheptatriene is reported in the literature,³⁸ although no procedure is described. An attempt to reduce tropylium hexachloroantimonate based on a procedure for the reduction of alkyl halides by sodium borohydride³⁹ proved moderately successful. The hexachloroantimonate salt was chosen in the interest of performing a reaction that would most closely parallel the future reduction of 3-tropylium-1,5-hexadiene with sodium borohydride. Analysis by GC/MS and NMR suggest that the cycloheptatrienyl resin was formed (APPENDIX VI-A,B). The gas chromatograph of reaction products confirms the presence of a compound with the same retention time and mass fragments as the resin. Although

³⁸ Parnes, Z.N.; Volpin, M.E.; Kursanov, D.N. *Tetrahedron Letters* **1960**, 20.

³⁹ Bell, H.M.; Brown, H.C. *J. Am. Chem. Soc.* **1966**, 88, 1473.

the NMR spectrum is complicated, the resin peaks are distinguishable. The presence of the cycloheptatrienyl resin among the reaction products suggests that the reduction of the tropylium salt did occur, although a significant number of by-products were also formed.

DISCUSSION

The synthesis of 3-cycloheptatrienyl-1,5-hexadiene was successfully completed, however, the progress of this research was limited by difficulty in isolating a pure sample. Two types of impurities consistently appeared in the product mixture. These impurities were identified and partially characterized, and appear to be the result of incomplete coupling between the bromohexadienes and tropylium tetrafluoroborate. One type of impurity was identified as a by-product of the reaction between the bromohexadienes mixture and zinc dust; the other impurity was identified as a cycloheptatrienyl resin formed from unreacted tropylium tetrafluoroborate. The zinc coupling reaction was examined in order to determine the optimal reaction conditions and increase the extent of the reaction. The original procedure was modified so that the reaction temperature is controlled with an ice bath, without overcooling the flask and quenching the reaction. Additionally, the length of time allowed for forming the organozinc reagent and for coupling between the organozinc reagent and tropylium tetrafluoroborate was increased. Care should be taken to use pure reagents and solvents and clean, dry glassware. Also, the reaction should be conducted under a nitrogen atmosphere, since the cycloheptatrienyl resin forms upon exposure to air.

Since both starting materials result in impurities, using one or the other as a limiting reagent does not simplify the purification of the product. Various methods of purification were attempted in order to separate 3-cycloheptatrienyl-1,5-hexadiene from the impurities. Unfortunately, the similarity in structure between the product and the impurities made separation difficult. Also, extensive heating is likely to cause rearrangement, making distillation or preparative gas chromatography difficult.

The synthesis of 3-tropylium-1,5-hexadiene was completed by hydride abstraction from 3-cycloheptatrienyl-1,5-hexadiene. Success in isolating 3-tropylium-1,5-hexadiene as a stable solid depended on which hydride abstracting agent was used and the associated counterion. Hydrogen abstraction by nitrosonium salts is considered a superior method to triphenylcarbenium salts. The nitrosonium ion is more effective and of more general utility, and no organic by-products are formed during the reaction.⁴⁰ However, the presence of triphenylmethane in the samples that used triphenylcarbenium salts as the hydride abstracting agent verifies the hydride abstraction occurred. Tetrafluoroborate salts could not be induced to crystallize and remained an oil at room temperature. The hexafluorophosphate salt formed a solid precipitate in acetonitrile during the course of the reaction and was easily isolated. However, the insolubility of this product in readily accessible solvents prevented examination by NMR. The hexachloroantimonate salt was easily isolated by precipitation with anhydrous ether. The solubility of the hexachloroantimonate salt in

⁴⁰ Olah, G.A.; Salem, G.; Staral, J.S.; Ho, T. *J. Org Chem.* **1978**, *43*, 173.

dimethyl sulfoxide makes it suitable for rearrangement studies using variable temperature proton NMR at temperatures up to 95 °C.⁴¹

3.1 FURTHER STUDY

The synthesis of 3-cycloheptatrienyl-1,5-hexadiene can be further optimized to decrease the formation of impurities. The reaction between the organozinc reagent and tropylium tetrafluoroborate is heterogeneous, and could possibly be improved by adding a solvent in which tropylium is soluble. Also, purification methods can be further developed to find a more efficient and convenient method of isolating 3-cycloheptatrienyl-1,5-hexadiene. Purification of the bromohexadienes mixture could also be investigated.

The synthesis of 3-tropylium-1,5-hexadiene can be further developed. The appropriate stoichiometry and reaction conditions must be determined in order to maximize the extent to which the hydride abstraction occurs. A complete characterization of 3-tropylium-1,5-hexadiene with each associated counterion should be completed and include proton and carbon NMR and UV/Visible spectra, and melting points. The properties of each cationic salt in various solvents should also be recorded. The characterization could also include an x-ray crystal structure; the high stability and insolubility of the hexafluorophosphate salt may be useful for this characterization.

⁴¹ See Appendix II for a list of solubilities of the cations.

The relative rates of rearrangement of 3-cycloheptatrienyl-1,5-hexadiene and 3-tropylium-1,5-hexadiene were not measured, although preliminary attempts at thermal rearrangement were made. Future attempts at thermal rearrangement of 3-cycloheptatrienyl-1,5-hexadiene should be conducted in silated glass tubes, since unsilated glass can be acidic and cause side reactions. The rearrangement of 3-tropylium-1,5-hexadiene will be followed with variable temperature proton NMR. The solubility of the cation in various deuterated solvents will be tested to determine the optimal reaction conditions. The rearrangement product, 1-cycloheptatrienyl-1,5-hexadiene, will be independently synthesized to confirm the results of the rearrangement.

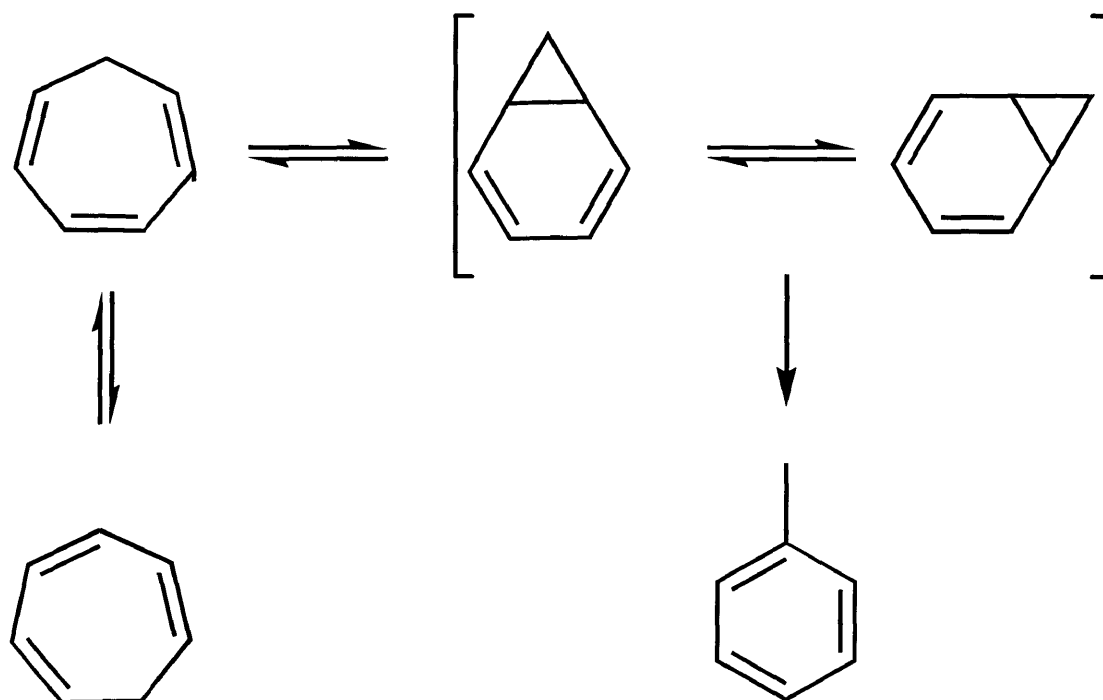
Heating cycloheptatriene results in 1,5-hydrogen shifts as well as carbon skeleton rearrangements (SCHEME 8).⁴² The hydrogen shifts occur at roughly 100 °C; the carbon rearrangements occur at temperatures close to 300 °C. These rearrangements are known to occur in substituted cycloheptatrienes as well,⁴³ and may create complications in the rearrangement of 3-cycloheptatrienyl-1,5-hexadiene. The rate of rearrangement of 3-phenyl-1,5-hexadiene is known,⁴⁴ and this system may serve as a potential alternative for comparison with 3-tropylium-1,5-hexadiene. A phenyl substituted hexadiene is valid since both systems are aromatic, are approximately the same size, and are very similar in structure.

⁴² Gajewski, J.J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981.

⁴³ Berson, J.A.; Willcott, M.R., III *J. Am. Chem. Soc.* **1966**, *88*, 2494.

⁴⁴ Levy, H.; Cope, A.C. *J. Am. Chem. Soc.* **1944**, *66*, 1684.

SCHEME 8.

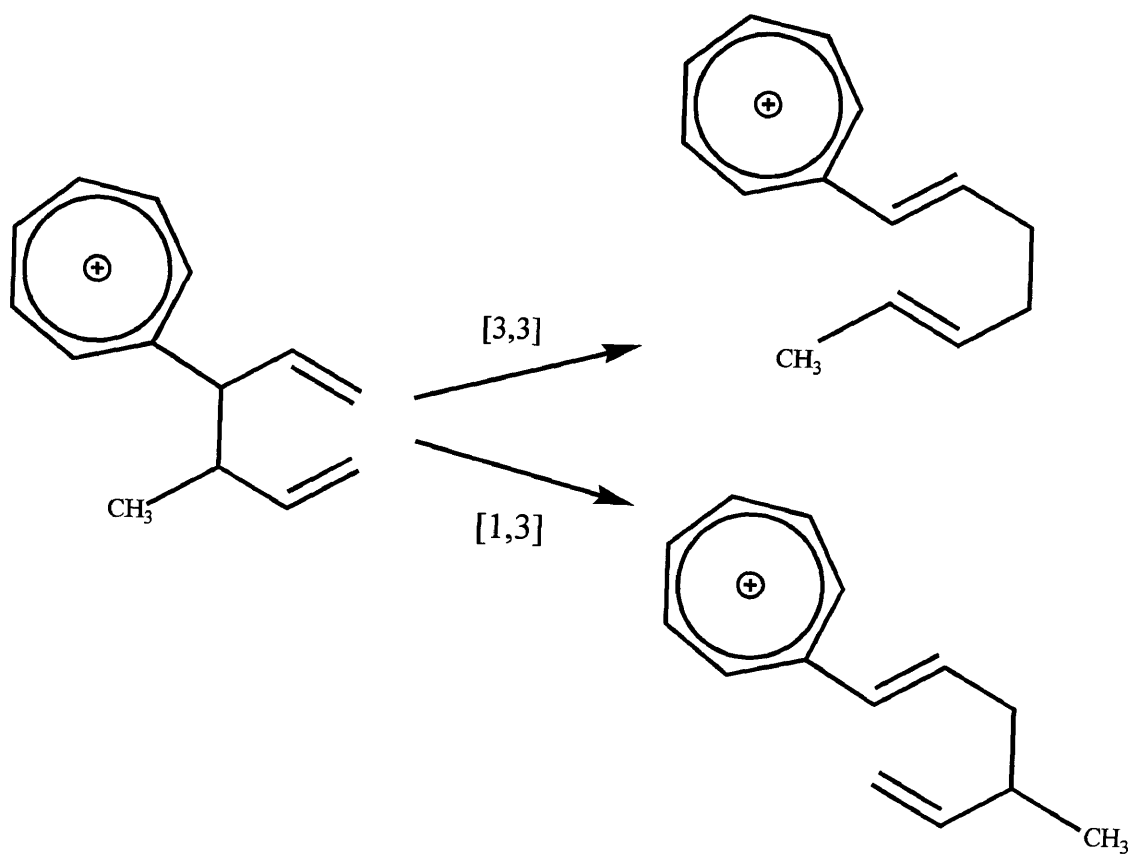


The hydride reduction of tropylium should be repeated and further developed in order to determine the optimal reaction conditions, including the appropriate solvent, stoichiometry of reactants, reaction temperature and length. Reversible hydride transfer between cycloheptatriene and tropylium is a known process, therefore hydride transfer between 3-cycloheptatrienyl-1,5-hexadiene and 3-tropylium-1,5-hexadiene is predicted to be reversible as well. This process could be used to confirm the formation of 3-tropylium-1,5-hexadiene, if the starting material is successfully regenerated.

Reversible hydride transfer may also provide a convenient method of purifying 3-cycloheptatrienyl-1,5-hexadiene. Purification of the 3-tropylium-1,5-hexadiene solid might be necessary before reduction, however, since impurities in the original 3-cycloheptatrienyl-1,5-hexadiene sample, such as the cycloheptatrienyl resin, may form stable cations (most likely tropylium) as well. These cations would also react with the sodium borohydride and regenerate their hydrocarbon precursors. Other cations could potentially be identified by differences in melting point from 3-tropylium-1,5-hexadiene, and the solid could be purified by recrystallization from an appropriate solvent. Ultimately, reduction of a pure sample of 3-tropylium-1,5-hexadiene may prove to be a convenient method for obtaining pure samples of 3-cycloheptatrienyl-1,5-hexadiene.

The [1,3] sigmatropic rearrangement presents a potentially competitive process. Carpenter's model predicts rate acceleration by substitution of cationic groups at any position for [1,3] sigmatropic rearrangements. Experiments will be conducted to determine the extent to which this potentially competitive process occurs by placing a methyl group (SCHEME 9) or a deuterium label at C₄ or C₆. Secondary deuterium kinetic isotope effects will be used to measure the change in hybridization of the carbon to which the deuterium is bound from the reactant to the transition state. Various methods of preparing deuterated compounds will be investigated.

SCHEME 9.



EXPERIMENTAL PROCEDURE

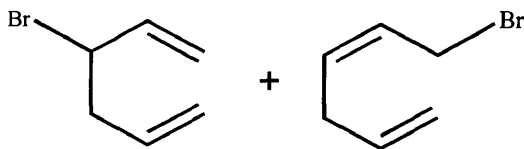
4.1 GENERAL METHODS

Reactions were conducted under nitrogen unless otherwise indicated. Acetonitrile and methylene chloride were purified by simple distillation at atmospheric pressure. Tetrahydrofuran was distilled from sodium benzophenone ketyl. Cycloheptatriene was purified by fractional distillation at atmospheric pressure. Thin layer chromatography was done on Uniplate Silica gel HLF plates, using hexanes as the eluting solvent. The plates were examined under ultraviolet light to detect unsaturated carbons before being developed in vanillin. Flash chromatography was used to purify 3-cycloheptatrienyl-1,5-hexadiene, using Fisher Scientific Alumina adsorption, 80 - 200 mesh, as the solid support and hexanes as the mobile phase. Fractions of 5 - 10 mL were collected and analyzed by thin layer chromatography. Proton NMR spectra were obtained on a GE QE-300 NMR or a Varian Mercury 400 spectrometer in CDCl_3 , CD_3CN or DMSO-d_6 . Chemical shifts were measured in parts per million and referenced to TMS in CDCl_3 and DMSO , and to the solvent reference peak in CD_3CN . Coupling constants are reported in Hertz. Preparative gas chromatography was done on a Gow Mac Series 580 preparatory gas chromatograph with the following temperature parameters: column: 100 °C; injector: 130 °C; detector: 150 °C. The detector current was set at 100 and the carrier gas was helium. A polar column was used (6' x 1/2"; 15 % OV-3, 80/100 Supelcoport). The column

was treated with triethylamine before injecting sample compounds. Capillary gas chromatography was done on a Hewlett-Packard 5890 gas chromatograph with the following temperature parameters: injector, 175 °C; detector, 250 °C. The column temperature was set at 70 °C initially, and increased 10 °C/minute to 200 °C. Gas chromatography/mass spectrometry analyses were carried out on a Hewlett-Packard 5890 gas chromatograph interfaced to a Hewlett-Packard 5971A mass selective detector. The same temperature parameters used for the capillary gas chromatography were used for 3-cycloheptatrienyl-1,5-hexadiene. For the bromohexadiene mixture, the temperature of the column was initially set at 40 °C, and increased to 100 °C at 5 °C/min; the temperatures of the injector and the detector were maintained at 175 °C and 250 °C, respectively. Ultraviolet spectra were recorded on a UV/Vis Beckman DU-70 spectrophotometer. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Densities were calculated from the weight of one milliliter of solution at room temperature (25 °C).

4.2 SYNTHESIS OF COMPOUNDS:

4.2.1 1-BROMOHEXADIENE AND 3-BROMOHEXADIENE



Phosphorous tribromide (6.06 g, 0.0224 mol, 2.13 mL), HBr (1-2 drops, 48%) and anhydrous ether (10-15 mL) were added to a 100-mL, three-necked, round-bottomed flask fitted with a thermometer, a addition funnel, and a condensing tube left open to the atmosphere for ventilation. A few grains of CaH₂ were added to prevent the PBr₃ from reacting with water. The contents of the flask were stirred with a magnetic stirrer and cooled in an ice bath to 10 - 15 °C. 1,5-Hexadien-3-ol (4.39g, 0.0447 mol, 5.00 mL) was combined with dry ether (10-15 mL) and added dropwise over 45-60 minutes at 10 - 15 °C. The mixture was stirred for 45 minutes at 10 - 15 °C and then to stand at room temperature overnight. The flask was cooled in an ice-salt bath for 20 minutes, without stirring, to allow the unreacted PBr₃ to collect on the bottom of the flask. While the contents of the flask were still cold, the upper organic layer was removed either by a cool pipet or by decanting. The organic layer was successively washed in a separatory funnel with cold deionized water (3 x 2 mL) 5% sodium bicarbonate (3 x 2 mL) and deionized water (3 x 2 mL). The funnel was vented carefully and quickly, as any residual PBr₃ will react violently with water. The organic product was dried with Na₂SO₄ and solvent was removed with rotary evaporation. The crude bromohexadiene mixture weighed 5.49 g (76% yield).

GC/MS: strong M = 79 and M = 81; molecular ion peak, M = 162 present

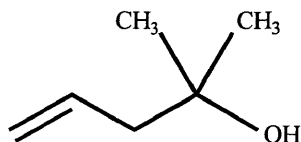
¹H NMR (CDCl₃, 300 MHz): 1.57 (s, 2H); 2.65-2.71 (t, 2H); 2.75-2.96 (m, 5H); 3.85-4.03 (m, 5H); 4.43-4.56 (q, 1H); 4.90-5.32 (m, 9H); 5.54-5.91 (m, 9H); 5.92-6.08 (m, 1H).

¹³C NMR (CDCl₃, 75 MHz): 33.3; 36.2; 43.0; 54.2; 116.3; 116.9; 118.4; 127.6; 134.0; 134.5; 135.8; 138.9

TLC: R_f = 0.65

Density: 1.22 g/mL

4.2.2 2-METHYL-4-PENTEN-2-OL: A MODEL ORGANOZINC REACTION



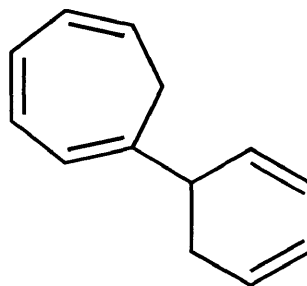
Zinc was activated in the manner described by Perrin.⁴⁵ Hydrochloric acid, (2%, 2 mL) was added to zinc dust (0.56 g, 8.6 mmol) in a 10 mL round-bottomed flask and stirred using a magnetic stirrer for one minute. The excess liquid acid was removed with a pipet. The zinc was then stirred successively with a second aliquot of HCl (2%, 2 mL), deionized water (3 x 1 mL) and punctilious ethanol (2 x 1 mL). After each addition, the mixture was stirred one minute before stirring was stopped, allowing the zinc dust to settle. The solvent was then carefully removed with a pipet, taking care not to remove the zinc dust. Ethereal rinses (2 x 1 mL) were conducted under a nitrogen atmosphere. A septum was placed over the flask and nitrogen was introduced through a needle. The system was vented to the atmosphere with a second needle placed in the septum. Anhydrous ether was added and removed with a glass syringe; residual ether was driven off with a heat gun after the second washing. Tetrahydrofuran (0.6 mL) was syringed into the flask to cover the zinc dust. Freshly distilled allyl bromide (0.21 g, 0.15 mL, 1.7 mmol) was added, neat, to the THF/zinc

⁴⁵ Perrin, D.D.; Armarego, W.L.F.; Perrin, D.R. *Purification of Laboratory Chemicals*; Pergamon Press Inc.: New York, 1980; pp 547.

slurry, with stirring. A vigorous reaction ensued, and the flask was cooled in an ice bath. A mixture of allyl bromide (0.70 g, 0.5 mL, 5.8 mmol) and THF (3.2 mL) was added dropwise to the flask from an addition funnel. The flask was warmed to room temperature and allowed to stir for 60 minutes. Most of the zinc was consumed and the solution turned light green. The flask was cooled to 0 °C, and acetone (0.44 g, 0.56 mL, .0076 mol) was added all at once by a syringe to the organozinc reagent. The temperature of the solution increased to almost 20 °C and a visible reaction ensued. The flask was stirred in the ice bath for fifteen minutes, then warmed to room temperature and stirred an additional 30 minutes. Aqueous ammonium chloride (ca. 3 - 5 mL) was added to quench the reaction, causing the unreacted zinc to precipitate. The solution was vacuum filtered to remove the zinc, using ether to rinse the flask. An emulsion resulted. The solution was transferred to a separatory funnel, and the organic layer was extracted from the aqueous layer and the emulsion with ether. The organic layer was dried overnight with Na₂SO₄, then solvent was removed by rotary evaporation.

¹H NMR (CDCl₃, 300 MHz): 1.2 (s); 1.9 (s); 3.8 (s); 4.8 (s); 5.1 (m); 5.8 (m)

4.2.3 3-CYCLOHEPTATRIENYL-1,5-HEXADIENE



Zinc metal dust was activated in the manner described by Perrin.⁴⁵ Hydrochloric acid (2%, 10.5 mL) was added to zinc dust (2.83 g, 0.0433 mol) in a 100 mL round-bottomed flask and stirred with a magnetic stirrer for 1½ - 2 minutes. The acid was removed with a pipet after allowing the zinc dust to settle. The zinc was stirred sequentially with a second aliquot of HCl (2%, 10.5 mL), deionized water (3 x 5.2 mL) and punctilious ethanol (2 x 5.2 mL). After addition of each solvent, the mixture was stirred for two minutes before allowing the mixture to settle. The solvent was then removed with a pipet, taking care not to remove the zinc dust. Ethereal rinses (2 x 5.2 mL) were conducted under a nitrogen atmosphere. Anhydrous ether was added and removed through a rubber septum using a glass syringe. The flask was vented to the atmosphere with a needle, and residual ether was removed with a heat gun. The remainder of the reaction was conducted under a nitrogen atmosphere. Reagents were added via a glass syringe except where otherwise indicated. Tetrahydrofuran (3.5 mL) was added to cover the zinc dust. The bromohexadiene mixture (0.98 g, 0.80 mL, 0.0061 mmol) was added, neat, to the slightly warm THF-zinc slurry. A visible reaction ensued, and the contents of the flask were cooled slightly (to about 20 °C) in an ice bath. A solution bromohexadienes (3.72 g, 3.05

mL, 0.0231 mol) and THF (17.5 mL) was added dropwise through an addition funnel. A nitrogen atmosphere was maintained by attaching a gas inlet to the top of the addition funnel. The temperature of the reaction was controlled with an ice bath and maintained at 25 °C. The flask was allowed to warm to room temperature and stir an additional 1½ - 2 hours under a nitrogen atmosphere, until most of the zinc dust was consumed and the solution turned light green. The flask was then cooled slightly in an ice bath and tropylium tetrafluoroborate (3.70 g, 0.0208 mol) was added through a powder funnel to the organozinc reagent. The salt was ground to a fine powder to remove any clumps before it was added. The temperature was controlled with an ice bath in the manner described above. The reaction was stirred at room temperature for 90 to 120 minutes, or until the tropylium tetrafluoroborate was no longer visible in solution. The reaction was quenched with aqueous ammonium chloride (ca. 40 mL). Two layers quickly separated and the remaining unreacted zinc metal precipitated. The solution was vacuum filtered to remove the unconsumed zinc and transferred to a separatory funnel. The aqueous layer was removed and the organic layer was washed two to three times with anhydrous ether. The organic layer was extracted and dried overnight with Na₂SO₄. The sample was stored as a solution in anhydrous ether in the refrigerator to minimize decomposition. The GC/MS indicated the sample was 83% pure.

4.2.3A PURIFICATION OF 3-CYCLOHEPTATRIENYL-1,5-HEXADIENE

The initial purification of 3-cycloheptatrienyl-1,5-hexadiene was done by flash chromatography on a 1 ½" diameter, 8" long column. The top of the column was

fitted with a ball joint connected to a nitrogen source. The lower end of the column is fitted with a glass frit and the flow is controlled with a Teflon stopcock. Hexanes were used as the mobile phase and alumina was used as the stationary phase, since silica appeared to decompose the compound. Using a mass ratio of greater than 50:1 solid support to sample afforded the best resolution. To pack the column, it was first filled with solvent. The alumina was added in several portions. After adding each portion, the stopcock was opened and the nitrogen inlet was connected, allowing the pressure from the nitrogen gas to pack the column. Each portion of alumina was packed several times: after letting most of the solvent drain from the column, the column was refilled with solvent and the nitrogen inlet was replaced. Care must be taken to keep the level of the solvent above the solid support at all times, to prevent the column from drying. Once all of the alumina was added (the column should be about one third full), about 1 cm of washed sand was layered on top of the adsorbant. 3-Cycloheptatrienyl-1,5-hexadiene was added, neat, to the top of the sand with a pipet. After allowing the sample to soak into the layer of sand by opening the stopcock, solvent was added carefully, so as not to disturb the layer of sand, to the top of the column. Fractions of about 5 mL were collected in test tubes until all of the 3-cycloheptatrienyl-1,5-hexadiene had eluted; the fractions were analyzed by thin layer chromatography. The plates were exposed to UV light to detect unsaturated carbons before being developed in vanillin. Using vanillin stain, the bromohexadienes and 3-cycloheptatrienyl-1,5-hexadiene appear as a navy blue spot; the resin appears as a purple-blue spot. The colors are similar, but the difference in the R_f values is substantial enough to distinguish the compounds. Although both impurities co-elute

to some extent with 3-cycloheptatrienyl-1,5-hexadiene, it is possible to separate the sample components by collecting small fractions. The bromo impurity elutes first, followed by 3-cycloheptatrienyl-1,5-hexadiene, and finally the resin. The resin continues to elute after all of the 3-cycloheptatrienyl-1,5-hexadiene has eluted.

Elemental Analysis (Desert Analytics) for C₁₃H₁₆: Calculated: 90.64% C; 9.36% H; Found: 89.63% C; 9.12% H

GC/MS: strong M = 91; molecular ion peak, M = 172 present

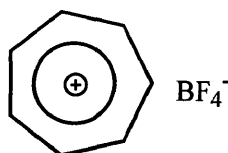
¹H NMR (CDCl₃, 400 MHz): 1.48-1.56 (m, 1.2 H); 2.13-2.21 (m, 1.7 H); 2.40-2.48 (m, 2.9 H); 4.99 (dd, J = 11, 1, 1.9 H); 5.05 (d, J = 2, 0.6 H); 5.10 (d, J = 2, 0.7 H); 5.16 (dd, J = 10, 2, 2.0 H); 5.26 (dd, J = 9, 5, 2.4 H); 5.64 -5.82 (m, 2.1 H); 6.18 - 6.25 (m, 2.2 H); 6.67 (t, J = 3, 2.1 H)

¹³C NMR (100 MHz; CDCl₃): 38.3; 43.5; 47.3; 117.1; 117.7; 125.4; 125.6; 125.6; 125.8; 131.8; 131.9; 137.5; 141.0

TLC: R_f = 0.76

Density: 0.898 g/mL

4.2.4 TROPYLIUM TETRAFLUOROBORATE²⁵



Triphenylcarbenium tetrafluoroborate (7.94 g, 0.0241 moles) was added to a 100-mL round-bottomed flask and covered with dry acetonitrile (20 mL) to effect partial solution. A magnetic stirrer was used to stir the triphenylcarbenium tetrafluoroborate in the acetonitrile. All of the salt eventually dissolved, forming a brown solution. Cycloheptatriene (3.12 g, 3.51 mL, 0.0305 moles) was added

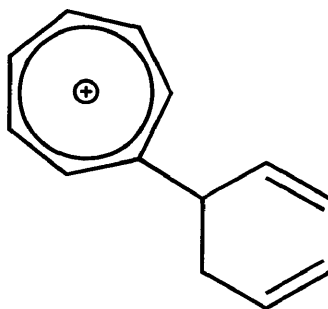
dropwise through an addition funnel while stirring. Tropylium tetrafluoroborate formed immediately. After addition of cycloheptatriene was complete, anhydrous ether (25 - 30 mL) was added through the addition funnel to complete the precipitation of tropylium tetrafluoroborate. The resulting snow-white crystals were washed with anhydrous ether (5 x 50 mL) to remove triphenylmethane, and dried *in vacuo*. The solid was dried on a watch glass overnight. The salt was examined by UV/Vis spectrometry in methylene chloride: λ_{\min} 252.50, A=0.1917; λ_{\max} 277.25, A=1.029. These values agree with those reported by Harmon for the ultraviolet spectrum in methylene chloride (λ_{\min} 253.5 and λ_{\max} 271.5).

^1H NMR (CD_3CN , 300 MHz): 9.2 ppm (s)

4.2.5 TROPYLIUM HEXACHLOROANTIMONATE

Triphenylcarbenium hexachloroantimonate (1.65 g, 2.85 mmol) was added to freshly distilled methylene chloride (15 mL) in a 50 mL round-bottomed flask. The mixture was stirred until the triphenylcarbenium hexachloroantimonate dissolved, resulting in a yellowish-brown solution. Cycloheptatriene (0.233 g, 2.53 mmol) in freshly distilled methylene chloride (10 mL) was added dropwise through an addition funnel, with stirring, to the methylene chloride solution. A precipitate formed during the addition. The mixture stirred for an additional thirty minutes to ensure the reaction was complete. Anhydrous ether (20 mL) was added to complete the precipitation of tropylium hexachloroantimonate, and the solvent was decanted to isolate the solid. The pale green solid was dried overnight at room temperature.

^1H NMR (CD_3CN , 300 MHz): 9.2 ppm (s)

5.2.6 3-TROPYLIUM-1,5-HEXADIENE⁴⁶4.2.6A TRIPHENYLCARBENIUM TETRAFLUOROBORATE⁴⁷

Triphenylcarbenium tetrafluoroborate (0.660 g, 0.002 mol) was added to a 50-mL round-bottomed flask and covered with dry acetonitrile (10 mL). The mixture was stirred until the salt dissolved, forming a brown solution. 3-Cycloheptatrienyl-1,5-hexadiene (0.347 g, 0.002 mol) was added dropwise via a pipet to the acetonitrile solution. After allowing the solution to stir at room temperature for two hours, the solvent was removed by rotary evaporation. ¹H NMR analysis of the crude mixture showed the presence of triphenylmethane ($\delta = 5.55$ (s); 7.09 - 7.38(m)), indicating that the hydride abstraction was successful. Ethyl acetate (10 mL) and hexanes (10 mL) were added to dissolve unreacted triphenylcarbenium tetrafluoroborate and the by-product triphenylmethane. A blue oil, presumed to be 3-tropylium-1,5-hexadiene, formed on the bottom of the flask. The oil was dissolved in acetonitrile. Attempts to precipitate a solid with ether were unsuccessful, and the oil could not be induced to crystallize.

⁴⁶ Procedures for synthesizing 3-tropylium-1,5-hexadiene are listed according to the hydride abstracting agent used.

4.2.6B NITROSONIUM TETRAFLUOROBORATE⁴⁸

Nitrosonium tetrafluoroborate (0.234 g, 2.0 mmol) was added to dry acetonitrile (25 mL) in a 50 mL round-bottomed flask. The solution was stirred with a magnetic stirrer under a nitrogen atmosphere. 3-Cycloheptatrienyl-1,5-hexadiene (0.334 g, 1.9 mmol) was added dropwise through a pipet to the acetonitrile solution. The solution turned yellow immediately after addition of the 3-cycloheptatrienyl-1,5-hexadiene was complete. After stirring for thirty minutes, the solution turned orange, and after 2 ½ hours the color deepened to a dark orange-brown. After removing most of the solvent by rotary evaporation, a bluish-gray oil remained on the bottom of the flask. The oil turned bright sapphire blue on exposure to the atmosphere. The blue color indicates the presence of triphenylmethane in the sample. Anhydrous ether was added dropwise to the flask in an attempt to precipitate 3-tropylium-1,5-hexadiene. Further attempts to induce crystallization of the solid with hexanes, ethyl acetate, and a 95 % hexanes / 5 % ethyl acetate mixture were unsuccessful.

¹H NMR (CD₃CN, 300 MHz): 2.05 - 2.85 (m); 4.08 - 4.22 (m); 4.87 - 5.38 (m); 5.59 - 5.81 (m); 6.01 - 6.26 (m); 6.65 (s); 7.78 (s); 8.29 (s); 9.01 (s); 9.21 (s); 9.42 (s)

4.2.6C TRIPHENYLCARBENIUM HEXACHLOROANTIMONATE⁴⁹

Triphenylcarbenium hexachloroantimonate (1.156 g, 0.002 moles) was added to freshly distilled methylene chloride (15 mL) in a 50 mL round-bottomed flask. The mixture was stirred with a magnetic stirrer until the triphenylcarbenium

⁴⁸ Kim, E.K.; Kochi, J.K. *J. Am. Chem. Soc.* **1991**, *113*, 4962 - 4974.

⁴⁹ Bertelli, D.J.; Golino, C.; Dreyer, D.L. *J. Am. Chem. Soc.* **1964**, *86*, 3329.

hexachloroantimonate dissolved, resulting in a yellowish-brown solution. 3-Cycloheptatrienyl-1,5-hexadiene (0.334 g, 1.9 mmol) in freshly distilled methylene chloride (10 mL) was added dropwise through a pipet, with stirring, to the methylene chloride solution. The solution and the crystals were poured into a 50 mL beaker, and cooled in an ice bath. Anhydrous ether was added slowly, with stirring, to precipitate 3-tropylium-1,5-hexadiene. The solution became cloudy and a solid was visible. The solution was transferred to a test tube, and the solid collected using a centrifuge. The solid was washed with anhydrous ether to dissolve any remaining triphenylcarbenium hexachloroantimonate or triphenylmethane. The olive green solid was dried overnight on a watch glass.

¹H NMR (CD₃CN, 300 MHz): 2.10 (s); 2.50 - 2.88 (m); 4.08 - 4.22 (m); 4.94 - 5.17 (m); 5.22 - 5.39 (m); 5.66 - 5.82 (m); 6.05 - 6.20 (m); 9.09 (s); 9.24 (s)

Melting Point: 82 - 84 °C.

4.2.6C TRIPHENYLCARBENIUM HEXAFLUOROPHOSPHATE

Triphenylcarbenium hexafluorophosphate (1.00 g, 2.68 mmol) was added to dry acetonitrile (20 mL) in a 50 mL round-bottomed flask under a nitrogen atmosphere. The mixture was stirred until the triphenylcarbenium hexafluorophosphate dissolved, resulting in an orange solution. 3-Cycloheptatrienyl-1,5-hexadiene (0.334 g, 1.92 mmol) was added dropwise through a pipet, with stirring, to the acetonitrile solution. The solution turned red upon addition of 3-cycloheptatrienyl-1,5-hexadiene. After one hour, a precipitate was visible in the flask. The solution was allowed to stir for a total of 2 ½ hours, after which it

appeared brown in color. The solution was transferred to a test tube, and the white solid collected using a centrifuge. The solid was washed with anhydrous ether to dissolve any remaining triphenylcarbenium hexafluorophosphate or triphenylmethane. The solid was insoluble in all readily available deuterated solvents, and was not examined by NMR. A large enough sample could not be isolated to obtain a melting point.

4.2.7 HYDRIDE REDUCTION OF TROPYLIUM HEXACHLOROANTIMONATE⁵⁰

In a 50 mL round-bottomed, two-necked flask fitted with a nitrogen inlet and a thermometer, aqueous ethylene glycol dimethyl ether (80 %, 10 mL) was heated to 45 °C with a mantle. Sodium borohydride (0.256 g, 6.77 mmol) was added slowly through a powder funnel. The mixture bubbled slightly, and the temperature increased so the heating mantle was removed. The mixture was stirred with a magnetic stir bar under a nitrogen atmosphere. Tropylium hexachloroantimonate (0.390 g, 0.916 mmol) was added slowly with a spatula. The pale green solid turned yellow and reacted visibly upon addition to the sodium borohydride solution. A black solid formed on the bottom of the flask. The reaction was stirred under a nitrogen atmosphere at 45 °C for four hours, during which time the tubing connected to the nitrogen inlet turned black. After four hours, the flask was cooled to 20 °C and pentane (10 mL) was added. The black solid that had formed remained in the aqueous layer as a pale gray solid. The contents of the flask were transferred to a separatory funnel, and the aqueous layer removed. The remaining organic layer was

then washed with deionized water (8 - 10 mL). A few pellets of sodium hydroxide were added to dry the organic layer. The organic product was examined by ^1H NMR in chloroform and GC/MS. Although the NMR spectrum was complex, the same peaks present in the cycloheptatrienyl resin NMR spectrum could be distinguished. Also, the GC/MS of the organic product contained a peak with the same retention time as the resin, suggesting that the hydride abstraction was successful.

⁵⁰ Bell, H.M.; Brown, H.C. *J. Am. Chem. Soc.* **1966**, *88*, 1473.

APPENDIX I**PERCENT COMPOSITION OF DISTILLATE FRACTIONS OF
3-CYCLOHEPTATRIENYL-1,5-HEXADIENE**

FRACTION	% 3-CYCLOHEPTA- TRIENYL-1,5-HEXADIENE	% BROMO IMPURITY	% RESIN
1	82	4	12
2	86	7	7
3	89	8	9
4	36	63	0.5

APPENDIX II

SOLUBILITIES OF 3-TROPYLIUM-1,5-HEXADIENE SPECIES

SOLVENT	COUNTERION		
	BF_4^-	PF_6^-	SbCl_6^-
ETHYL ETHER	INSOLUBLE	INSOLUBLE	INSOLUBLE
ACETONITRILE	SOLUBLE	INSOLUBLE	SOLUBLE
DIMETHYL SULFOXIDE (d_6)	SOLUBLE	INSOLUBLE	SOLUBLE
HEXANES	INSOLUBLE	INSOLUBLE	-----
ETHYL ACETATE	SOLUBLE	INSOLUBLE	-----
95% HEXANES, 5% ETOAC	INSOLUBLE	INSOLUBLE	-----
NITRO BENZENE (d_5)	-----	INSOLUBLE	SOLUBLE
ACETONE	SOLUBLE	INSOLUBLE	SOLUBLE
METHYLENE CHLORIDE	-----	-----	SOLUBLE

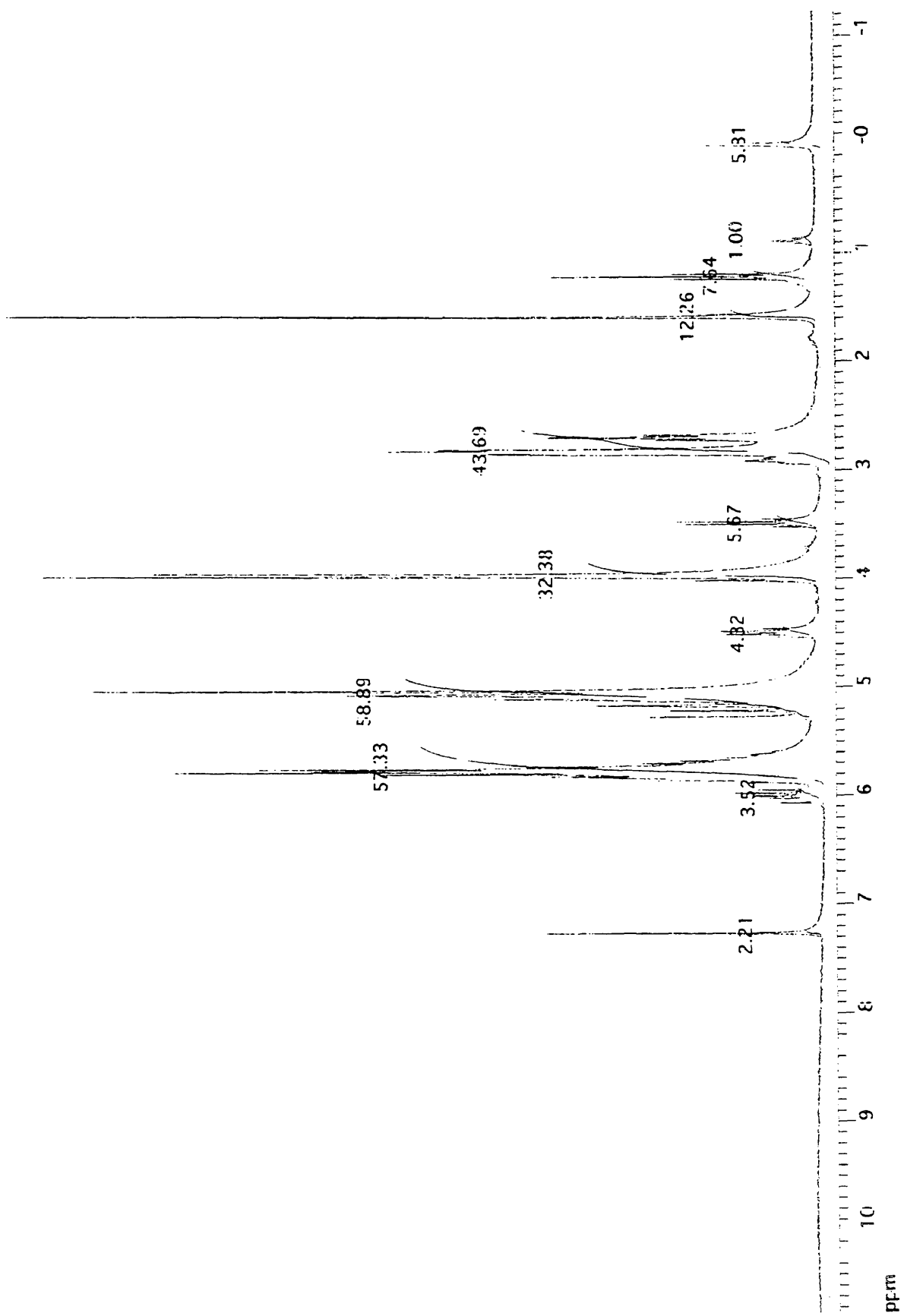
APPENDIX III

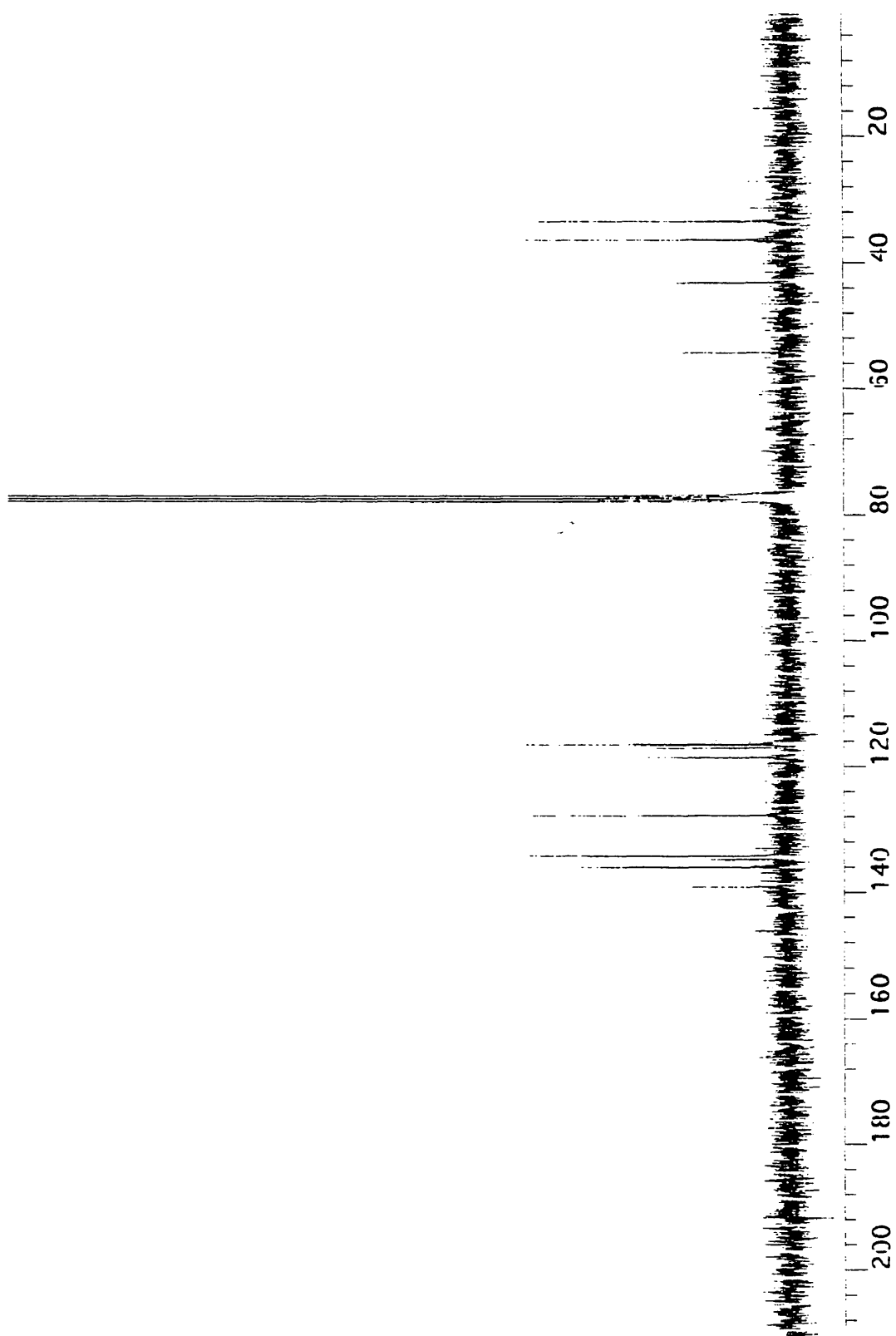
ANALYTICAL SPECTRA OF BROMOHEXADIENES

III-A ^1H NMR SPECTRUM OF BROMOHEXADIENES

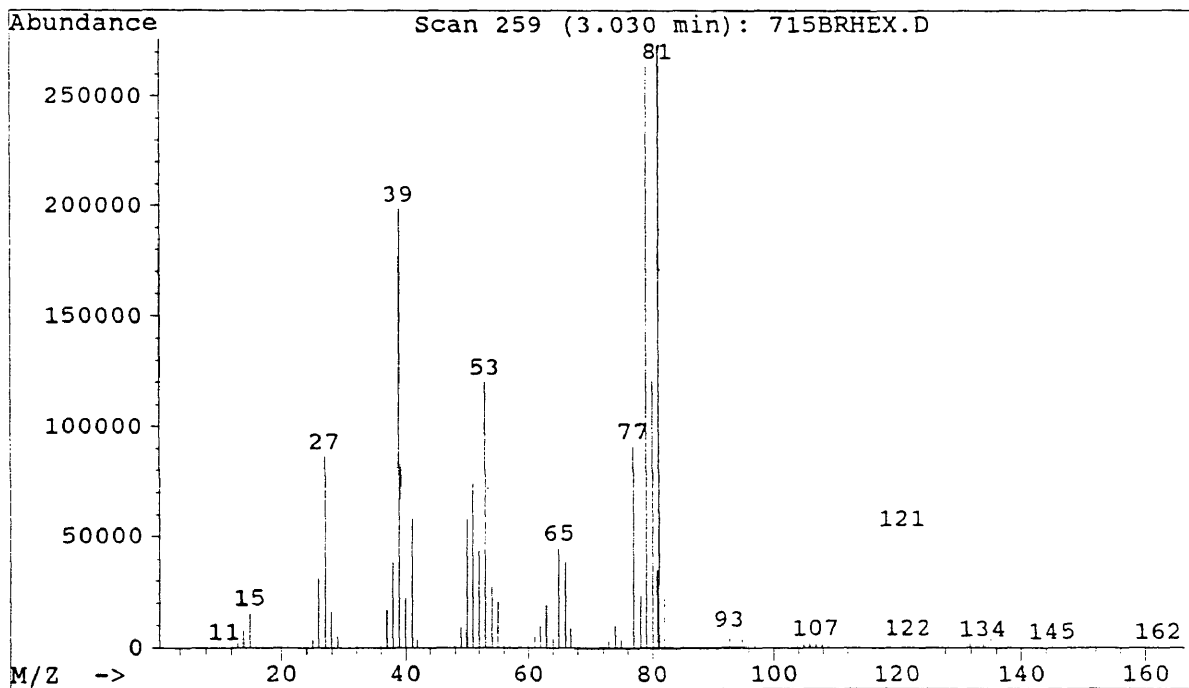
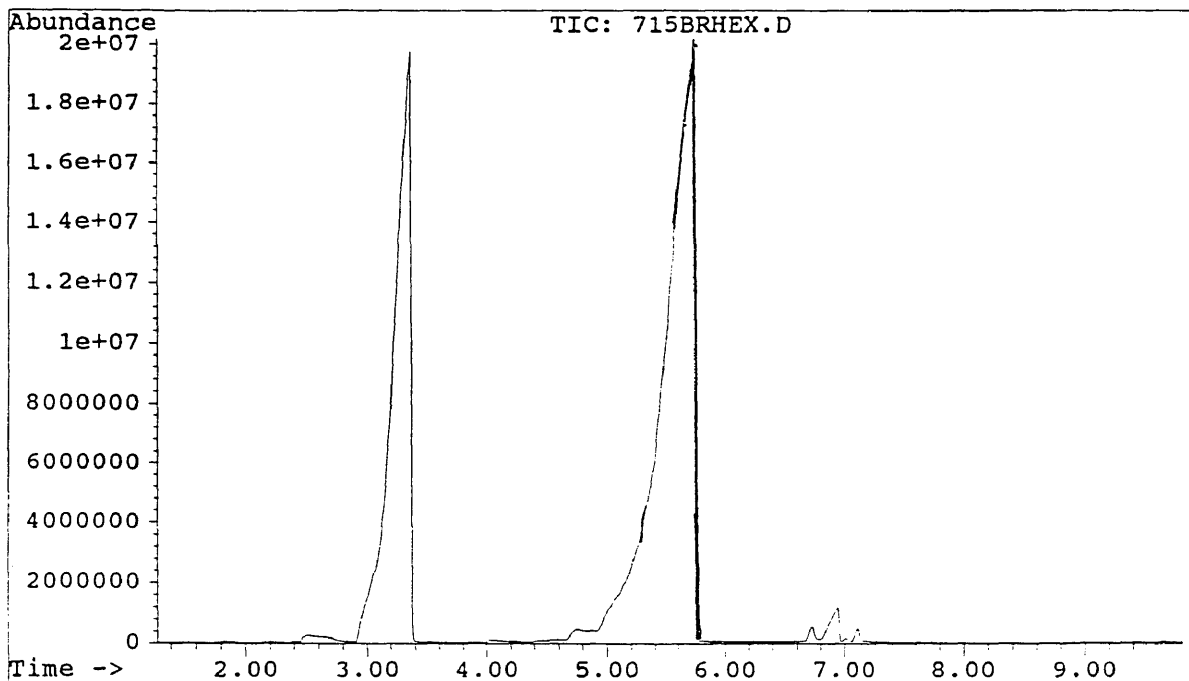
III-B ^{13}C NMR SPECTRUM OF BROMOHEXADIENES

III-C GC/MS SPECTRUM OF BROMOHEXADIENES

III-A ^1H NMR SPECTRUM OF BROMOHEXADIENES

III-B ^{13}C NMR SPECTRUM OF BROMOHEXADIENES

III-C GC/MS SPECTRUM OF BROMOHEXADIENES



APPENDIX IV

ANALYTICAL SPECTRA OF 3-CYCYLOHEPTATRIENYL-1,5-HEXADIENE

IV-A GC/MS SPECTRUM OF CRUDE 3-CYCYLOHEPTATRIENYL-1,5-HEXADIENE

IV-B ^1H NMR SPECTRUM OF 3-CYCYLOHEPTATRIENYL-1,5-HEXADIENE

IV-C ^{13}C NMR SPECTRUM OF 3-CYCYLOHEPTATRIENYL-1,5-HEXADIENE

IV-D GC/MS SPECTRUM OF 3-CYCYLOHEPTATRIENYL-1,5-HEXADIENE

ANALYTICAL SPECTRA OF IMPURITIES ISOLATED FROM 3-CYCYLOHEPTATRIENYL-1,5-HEXADIENE

BROMO IMPURITIES

IV-E GC/MS SPECTRUM OF BROMO IMPURITIES

IV-F GC/MS SPECTRUM OF QUENCHED ORGANOZINC REACTION

RESIN IMPURITY

IV-G ^1H NMR SPECTRUM OF RESIN

IV-H GC/MS SPECTRUM OF RESIN

OXIDATION IMPURITIES

IV-I ^1H NMR SPECTRUM OF OXIDATION IMPURITIES

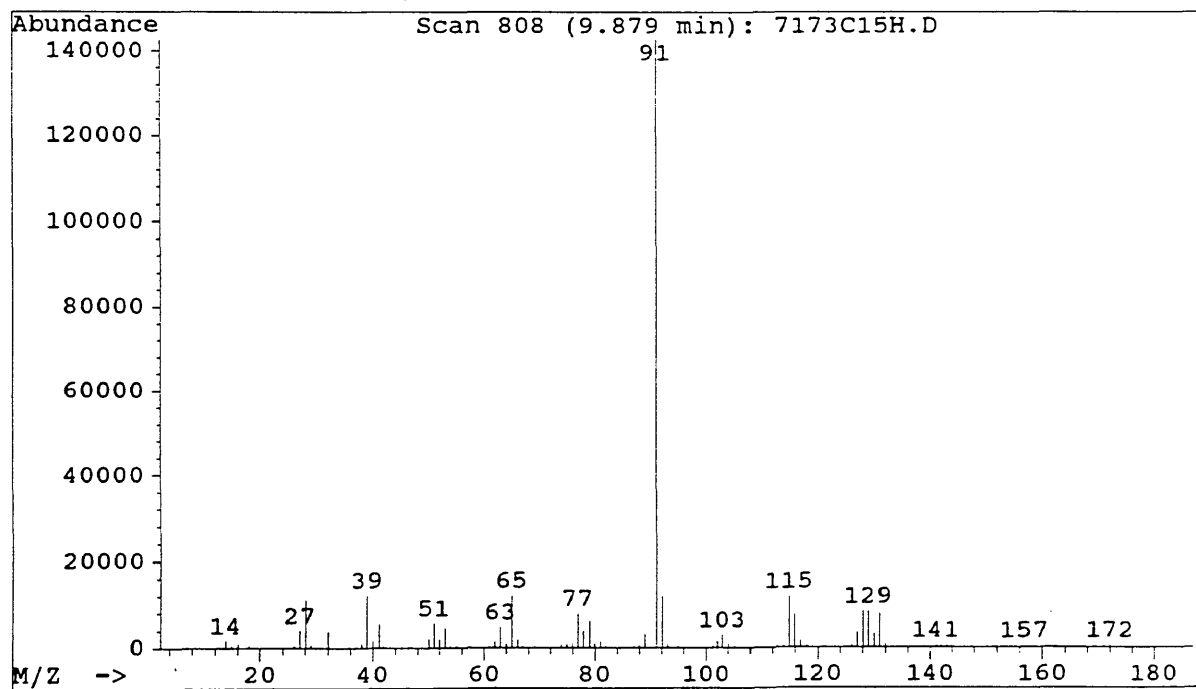
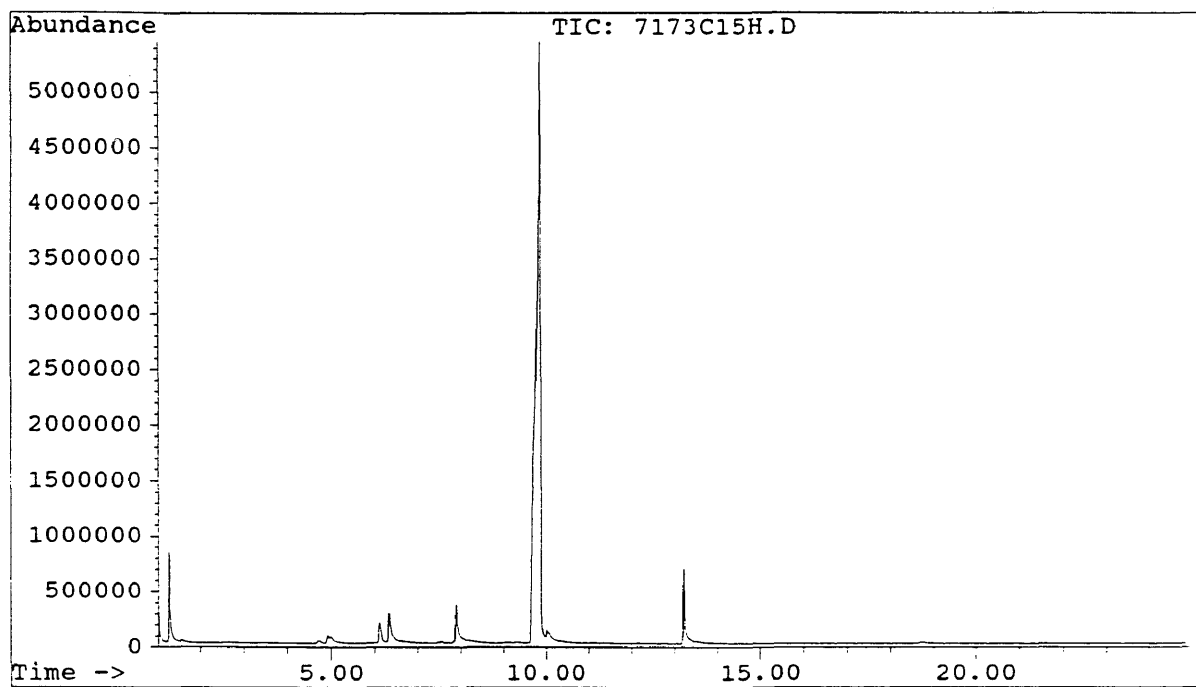
IV-J GC/MS SPECTRUM OF OXIDATION IMPURITIES

IV-K IR SPECTRUM OF OXIDATION IMPURITIES

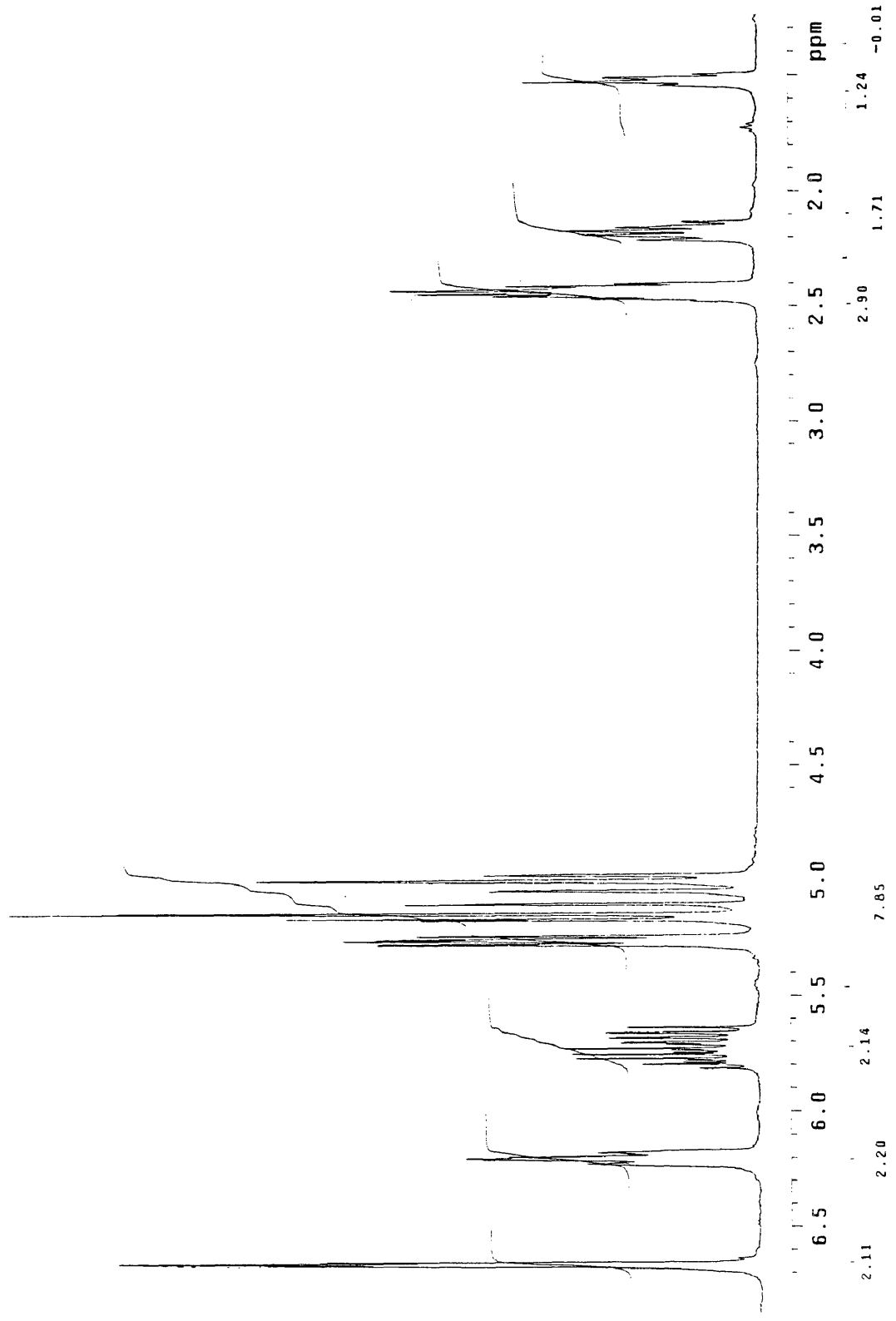
ANALYTICAL SPECTRUM OF REARRANGEMENT OF 3-
CYCYLOHEPTA-TRIENYL-1,5-HEXADIENE

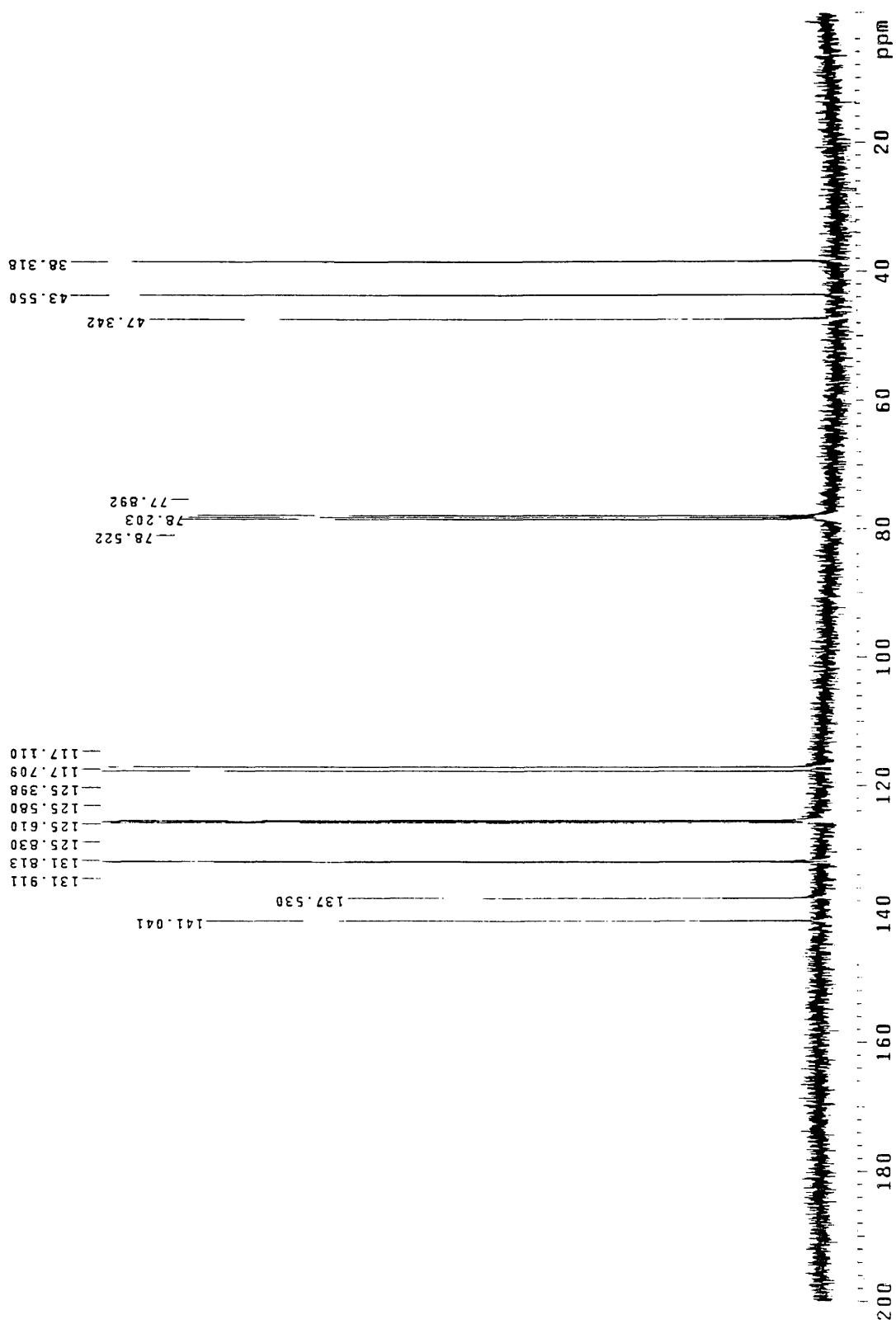
IV-L GC/MS SPECTRUM OF REARRANGEMENT PRODUCT

IV-A GC/MS SPECTRUM OF CRUDE 3-CYCLOHEPTATRIENYL-1,5-
HEXADIENE

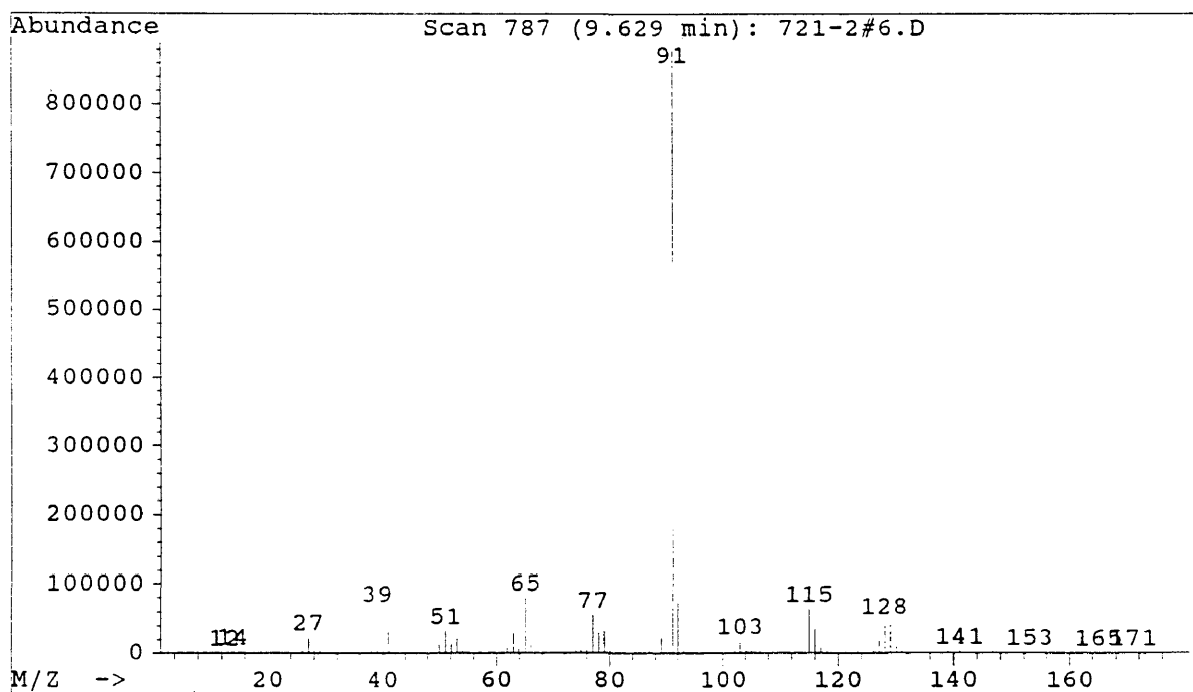
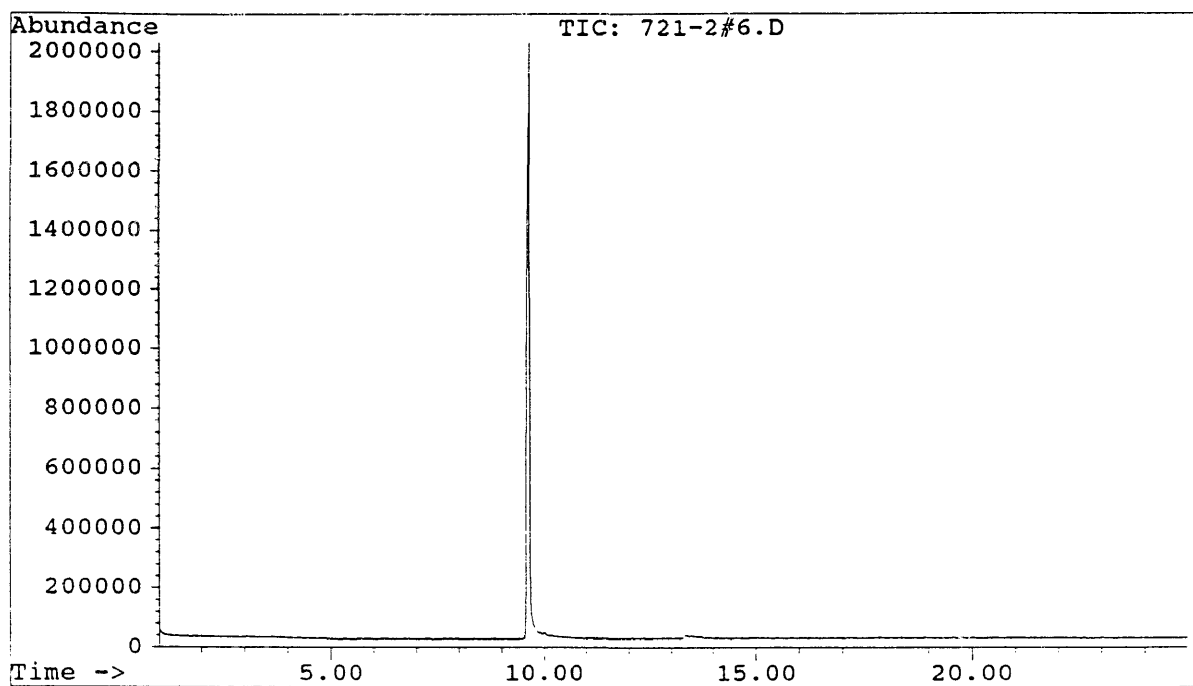


IV-B ¹H NMR SPECTRUM OF 3-CYCLOHEPTATRIENYL-1,5-HEXADIENE

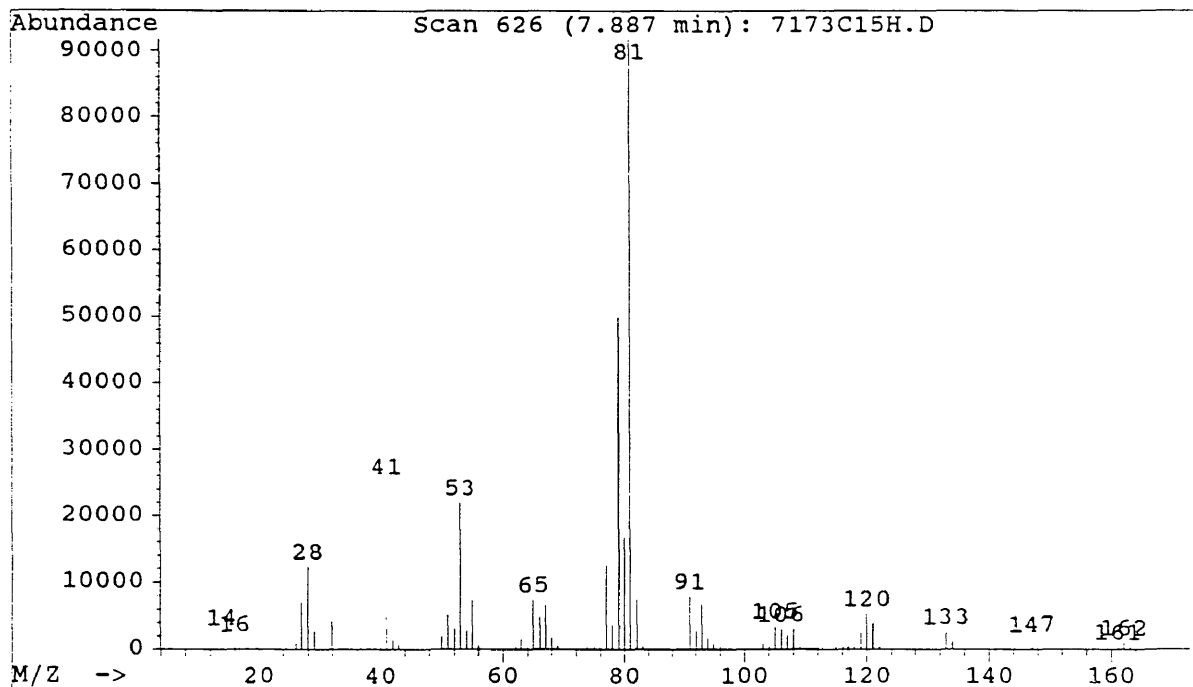
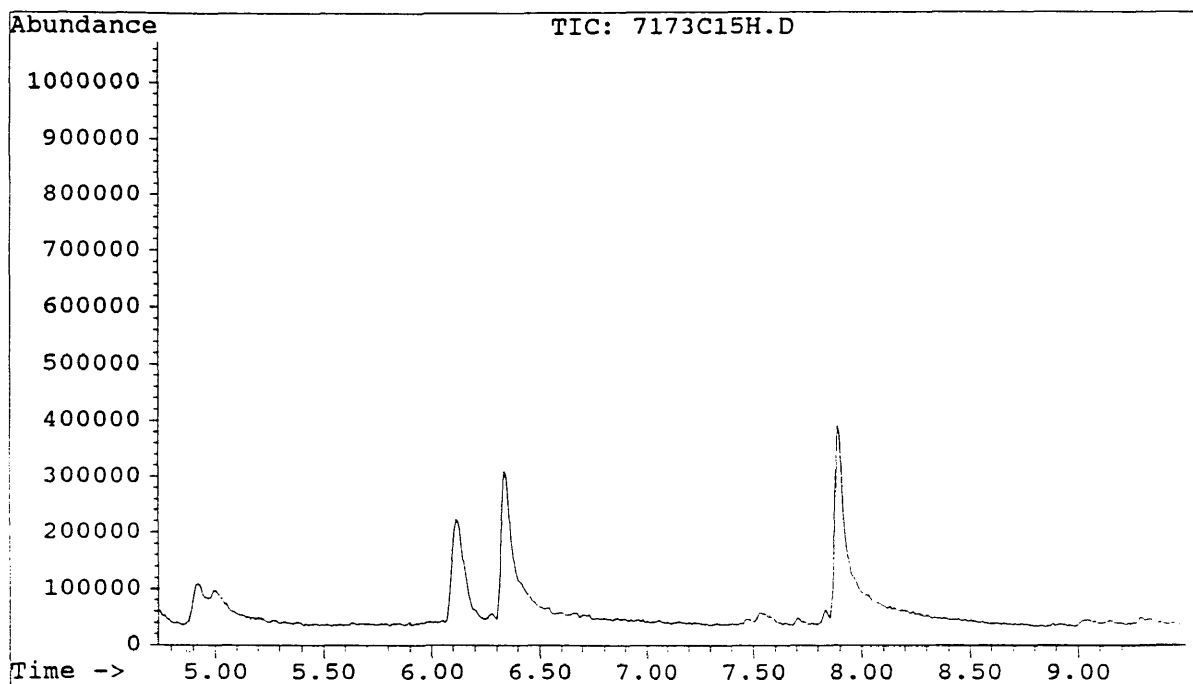


IV-C ^{13}C NMR SPECTRUM OF 3-CYCLOHEPTATRIENYL-1,5-HEXADIENE

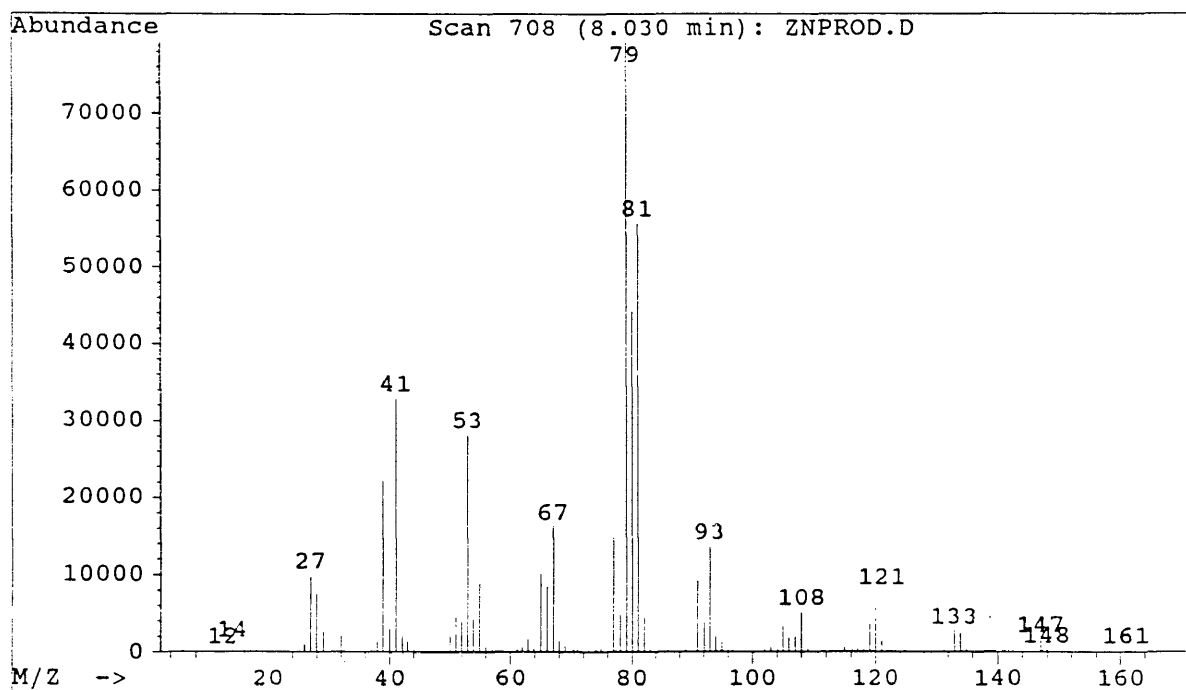
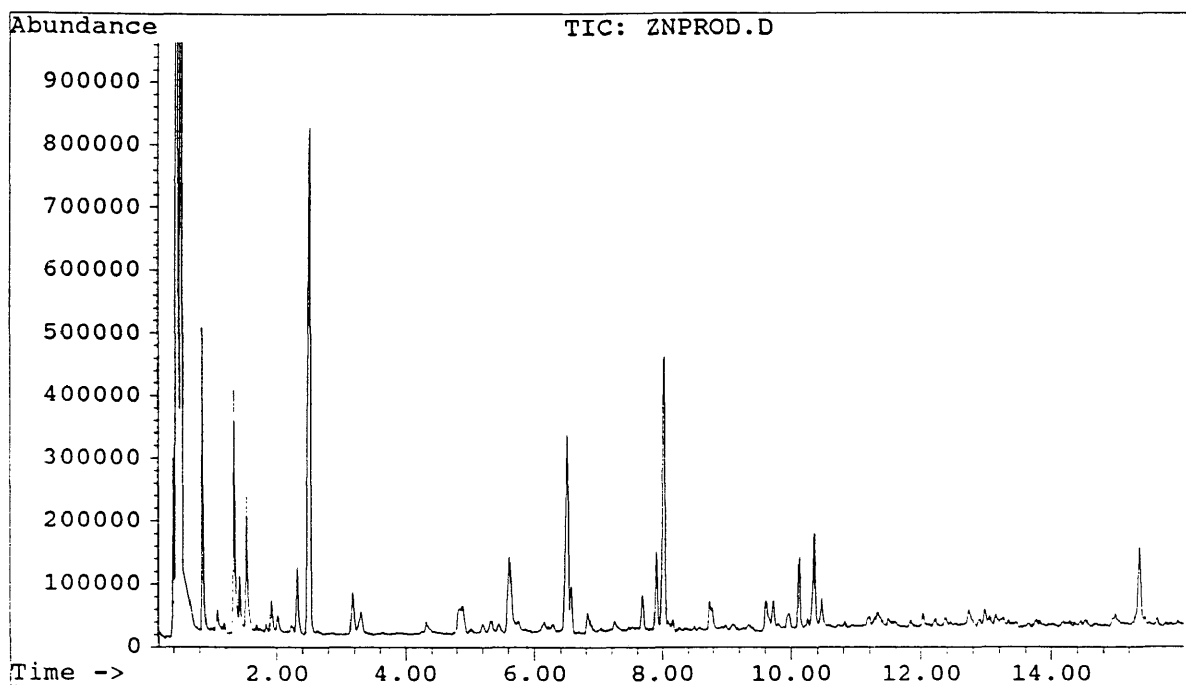
IV-D GC/MS SPECTRUM OF 3-CYCLOHEPTATRIENYL-1,5-HEXADIENE

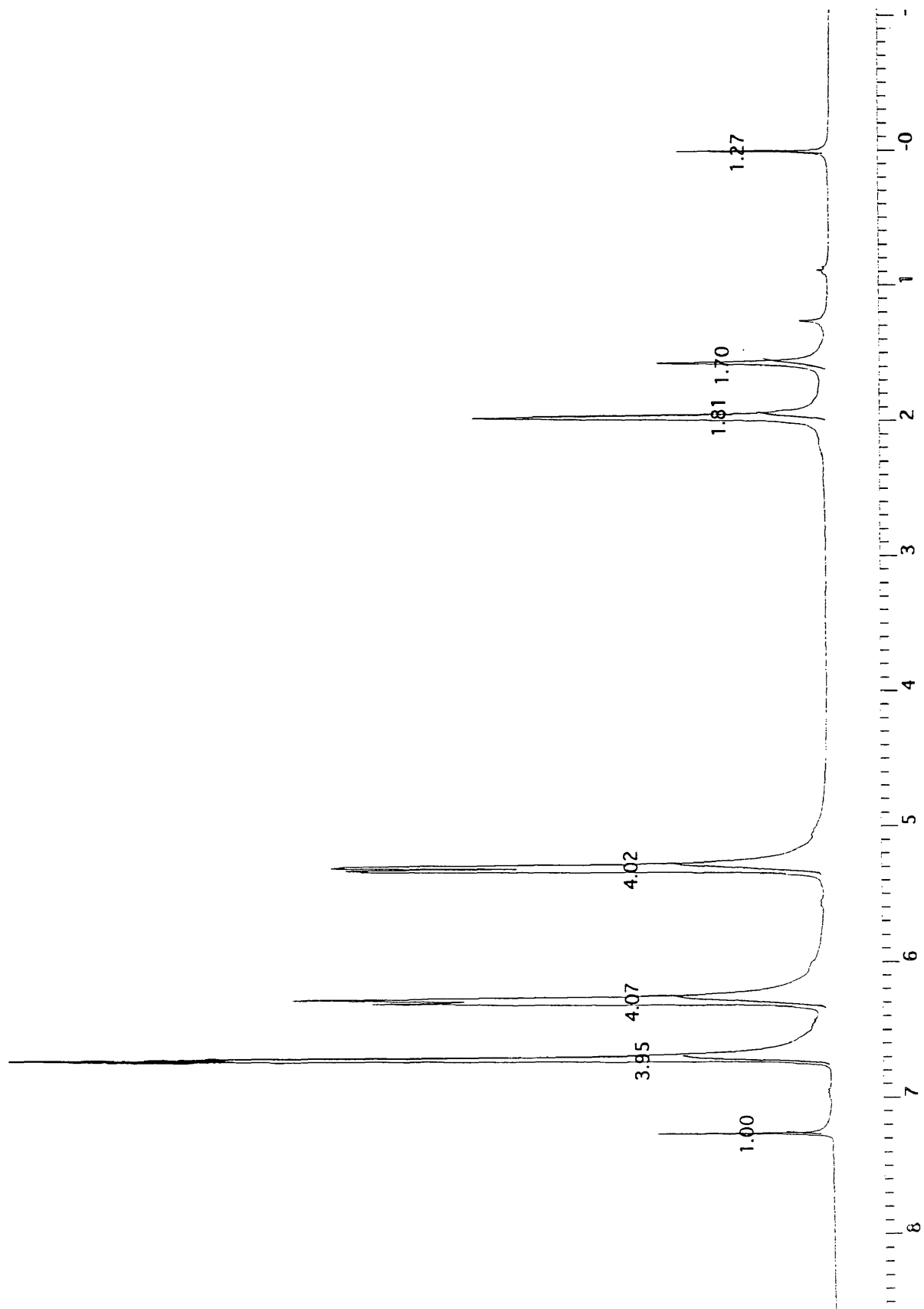


IV-E GC/MS SPECTRUM OF BROMO IMPURITIES

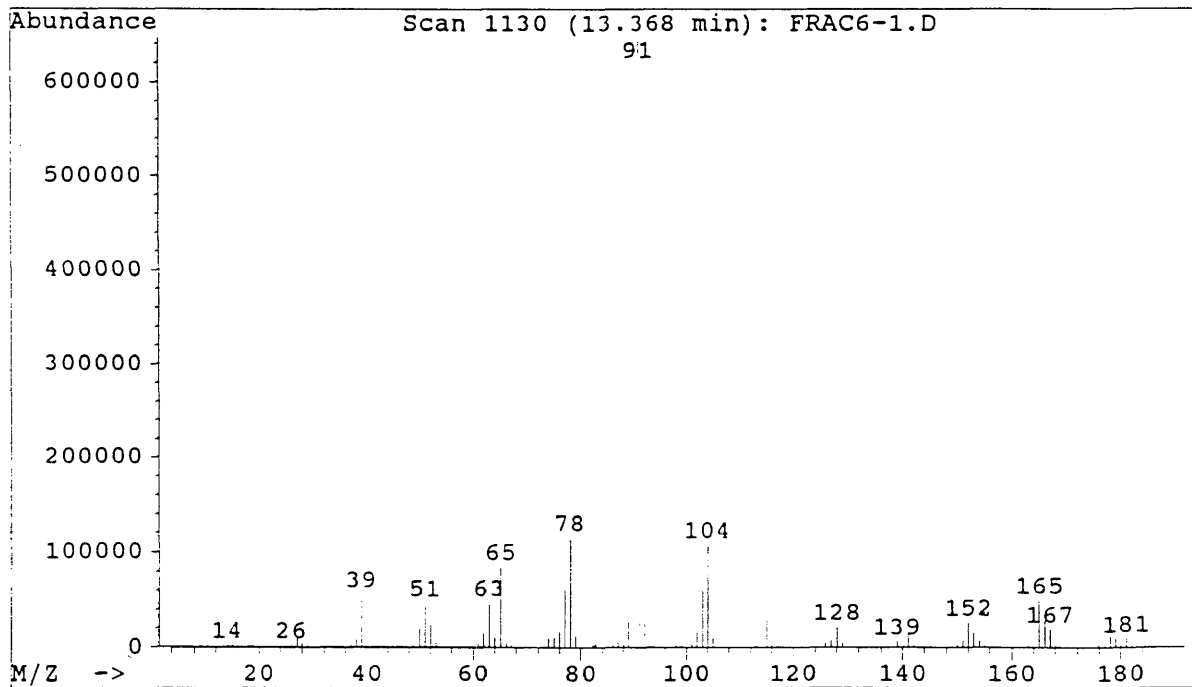
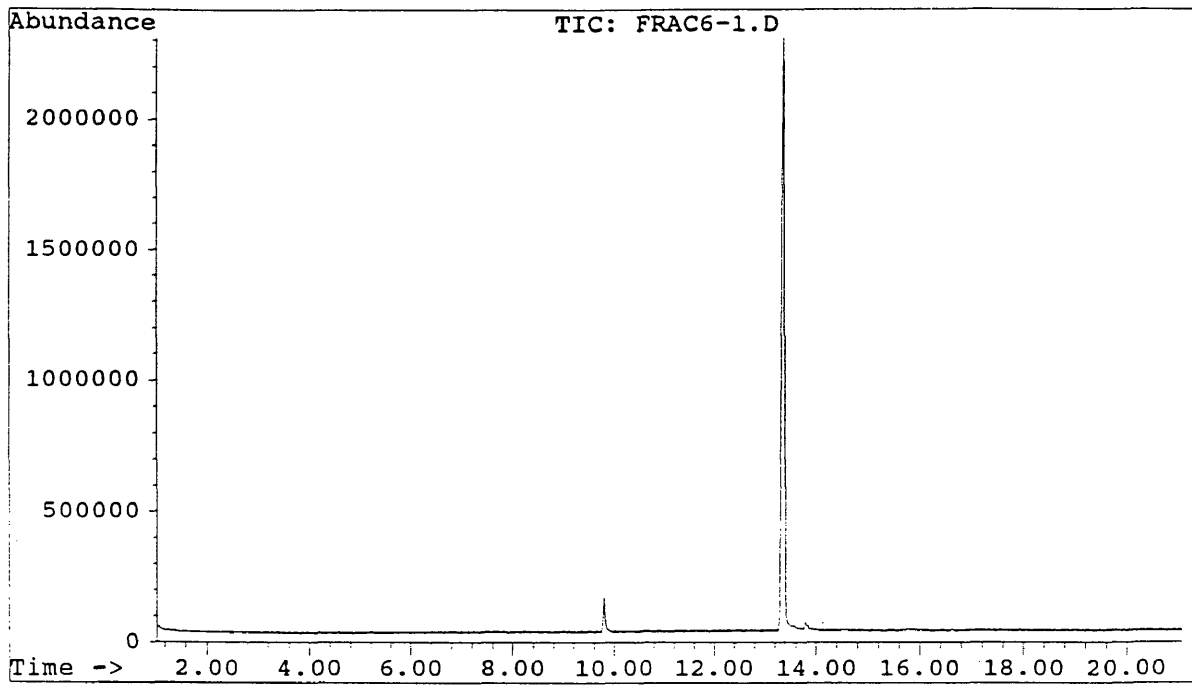


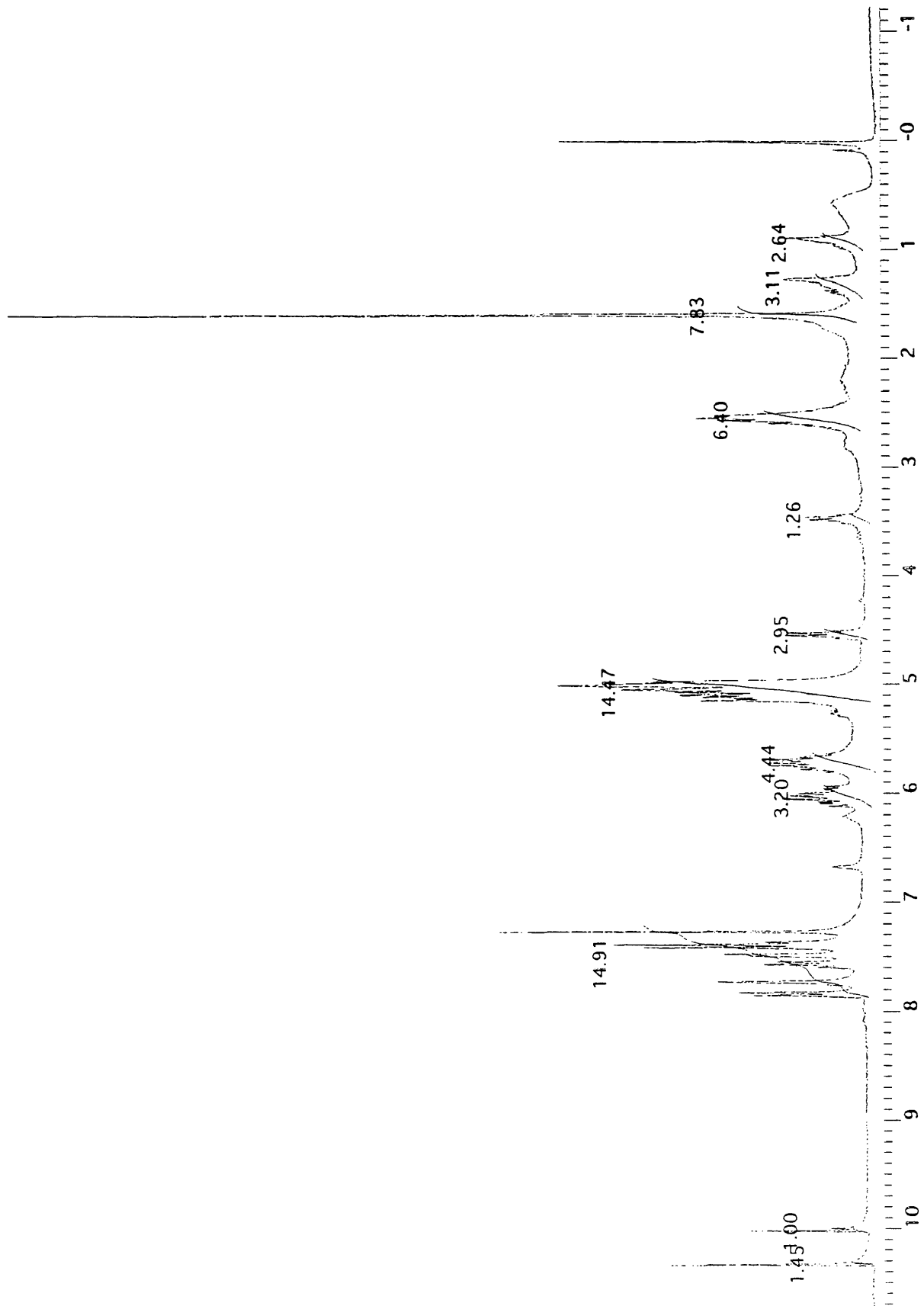
IV-F GC/MS SPECTRUM OF QUENCHED ORGANOZINC REACTION



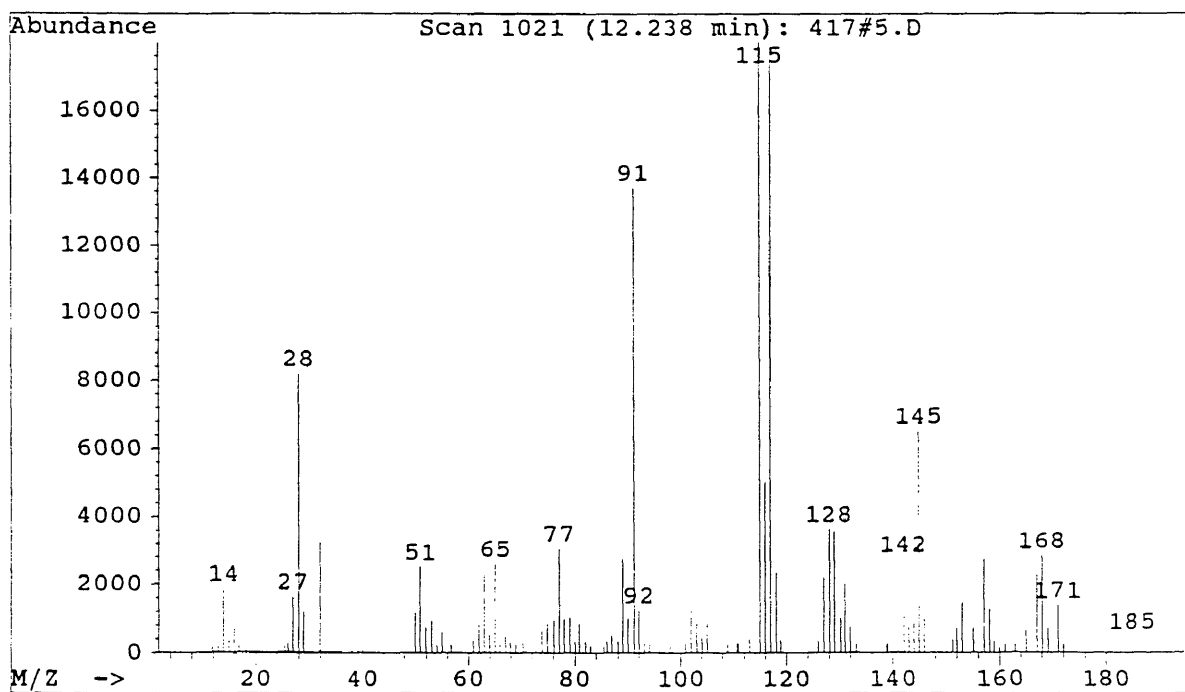
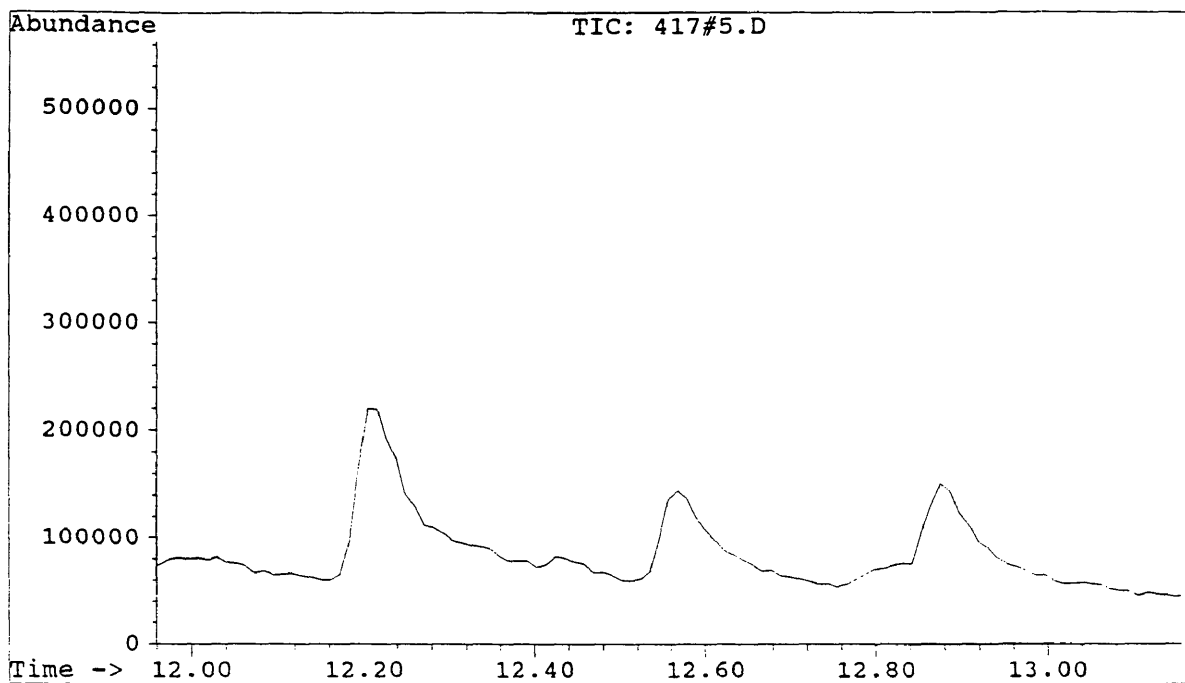
IV-G ^1H NMR SPECTRUM OF RESIN

IV-H GC/MS SPECTRUM OF RESIN

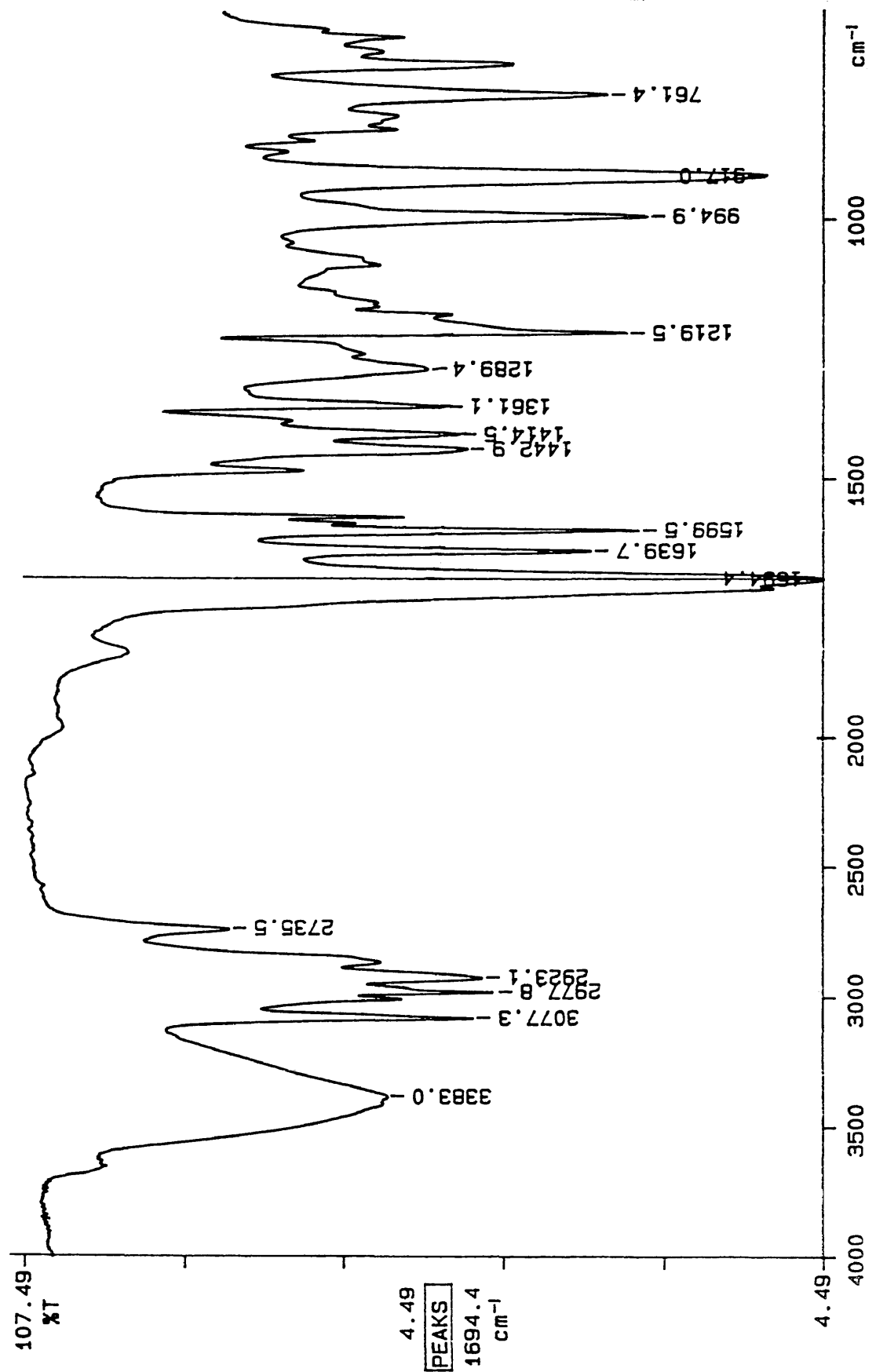


IV-I ^1H NMR SPECTRUM OF OXIDATION IMPURITY

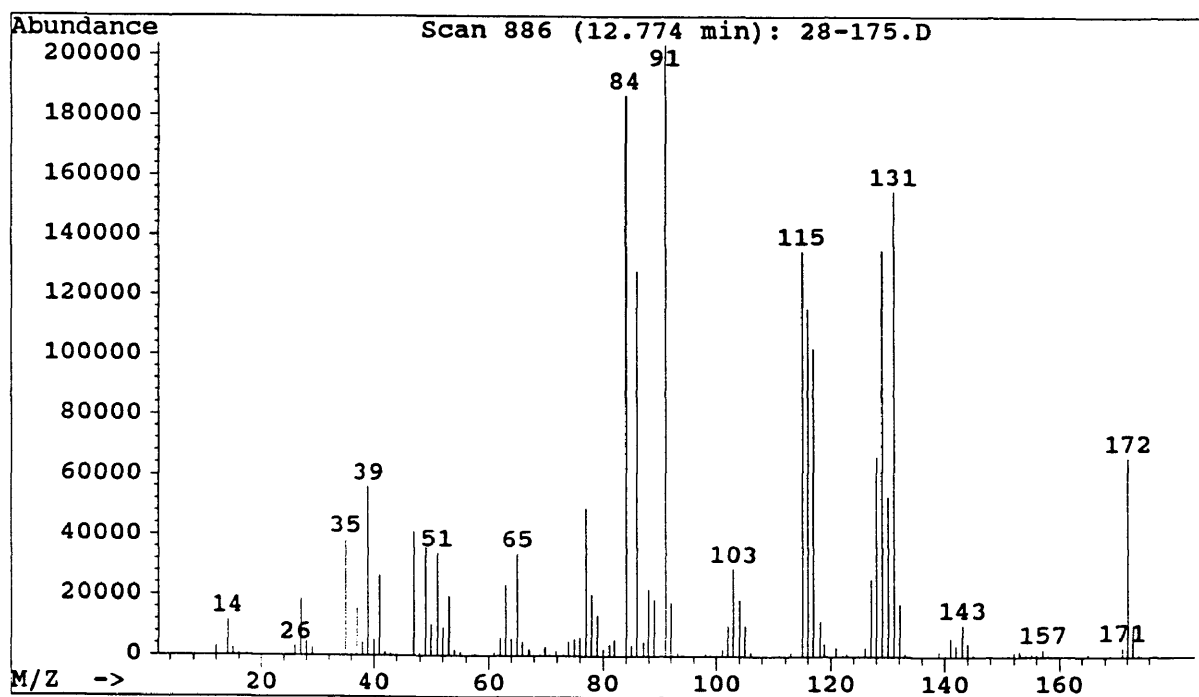
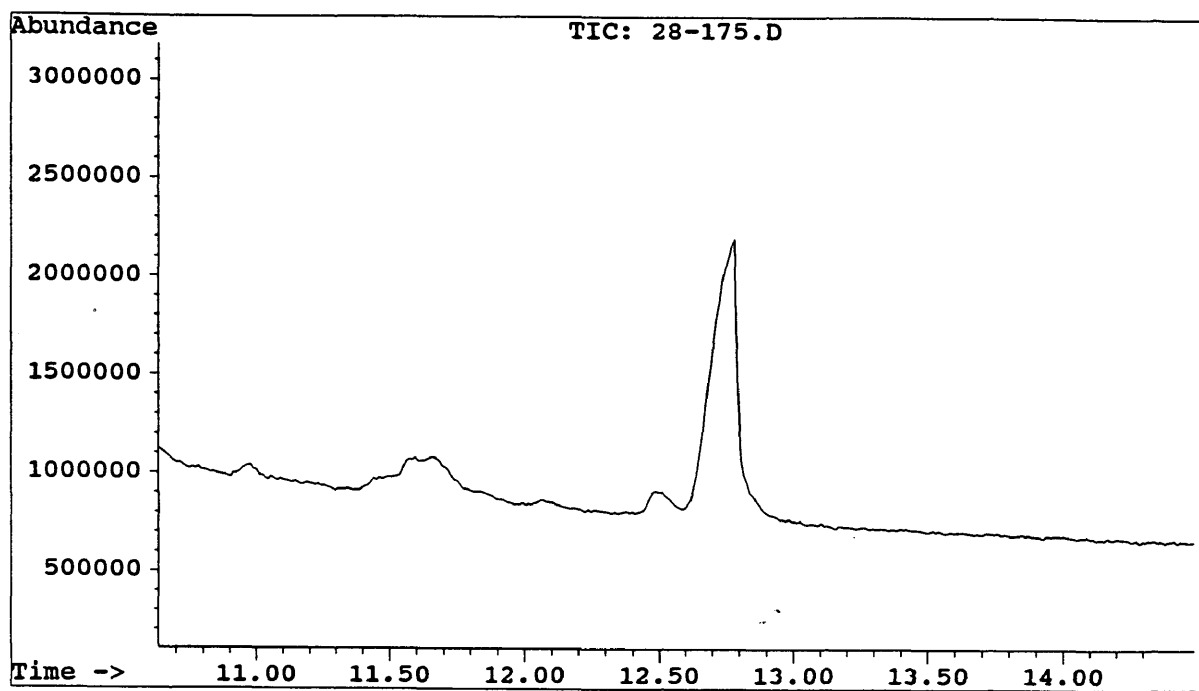
IV-J GC/MS SPECTRUM OF OXIDATION IMPURITY



IV-K IR SPECTRUM OF OXIDATION IMPURITY



IV-L GC/MS SPECTRUM OF REARRANGEMENT PRODUCT



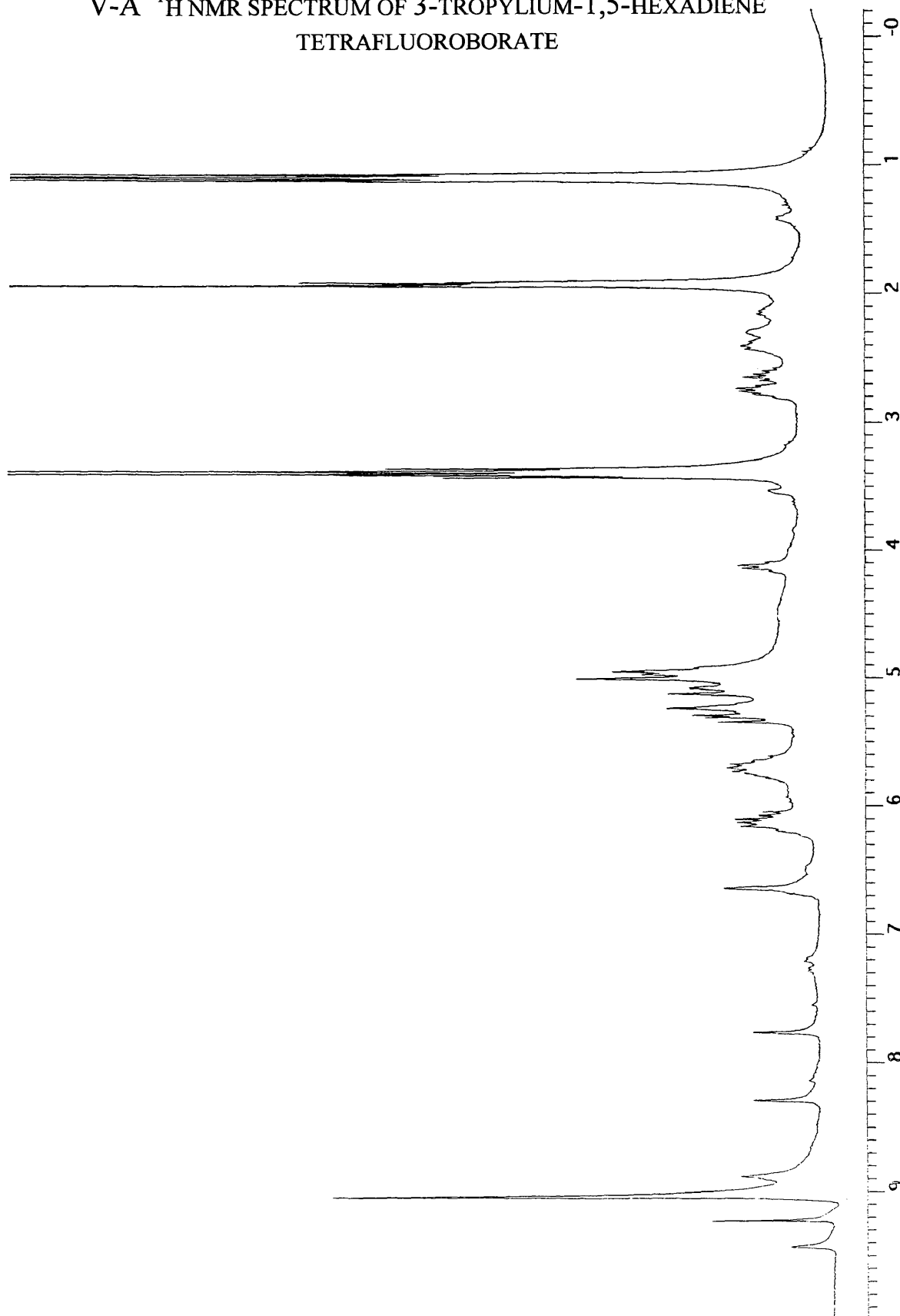
APPENDIX V

ANALYTICAL SPECTRA OF 3-TROPYLIUM-1,5-HEXADIENE

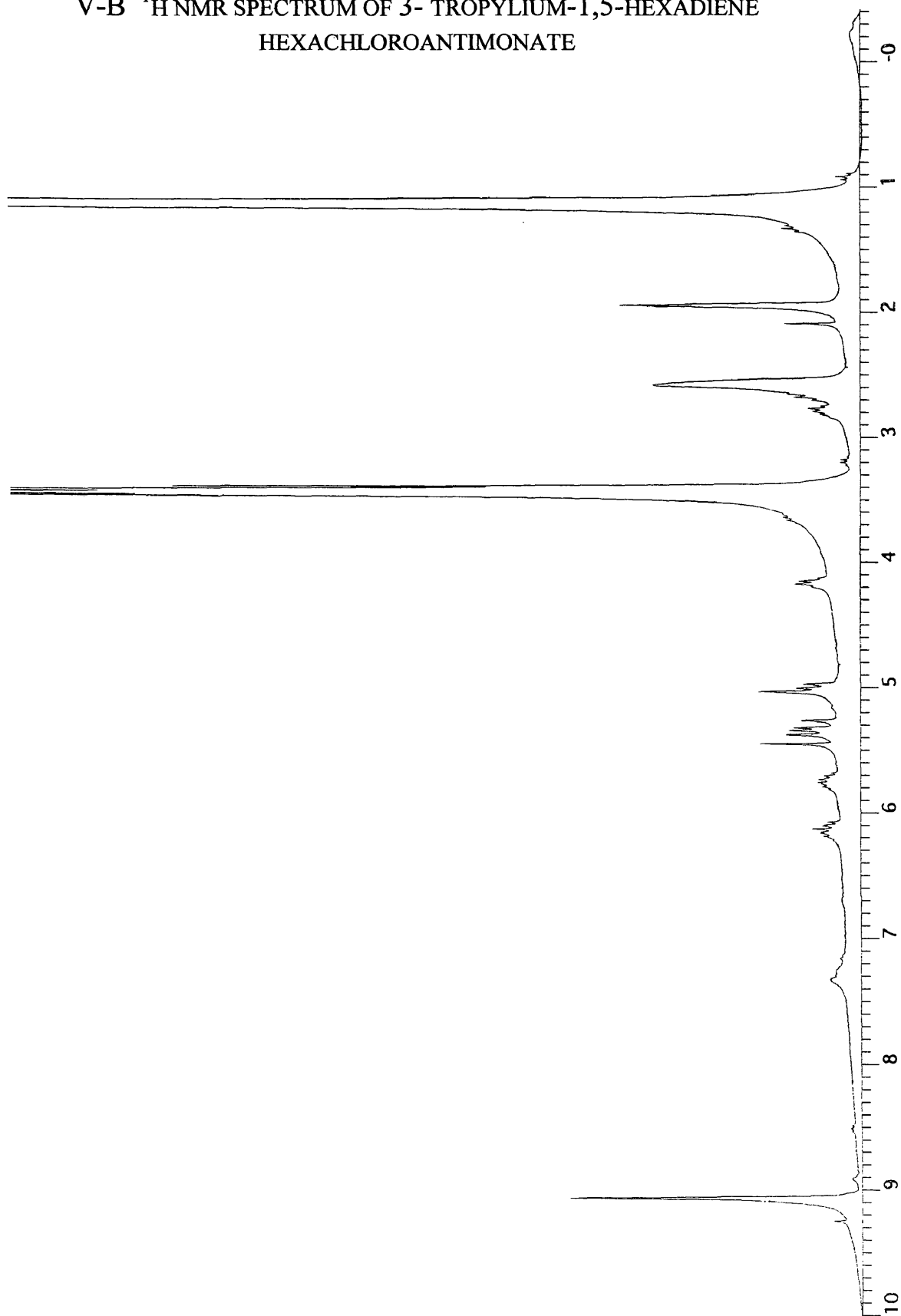
V-A ^1H NMR SPECTRUM OF 3-TROPYLIUM-1,5-HEXADIENE
TETRAFLUOROBORATE

V-B ^1H NMR SPECTRUM OF 3- TROPYLIUM-1,5-HEXADIENE
HEXACHLOROANTIMONATE

V-A ^1H NMR SPECTRUM OF 3-TROPYLIUM-1,5-HEXADIENE
TETRAFLUOROBORATE



V-B ^1H NMR SPECTRUM OF 3-TROPYLIUM-1,5-HEXADIENE
HEXACHLOROANTIMONATE

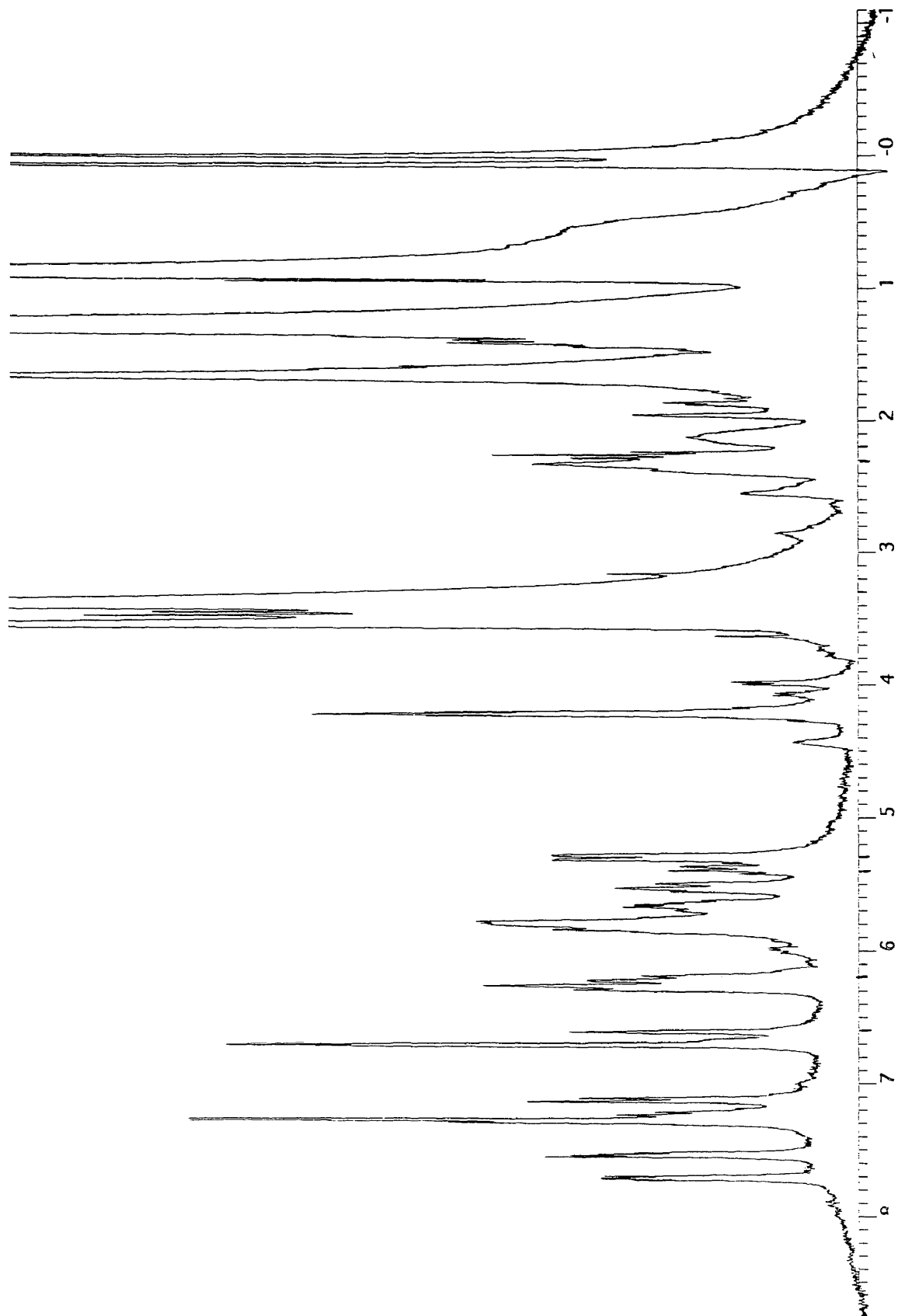


APPENDIX VI

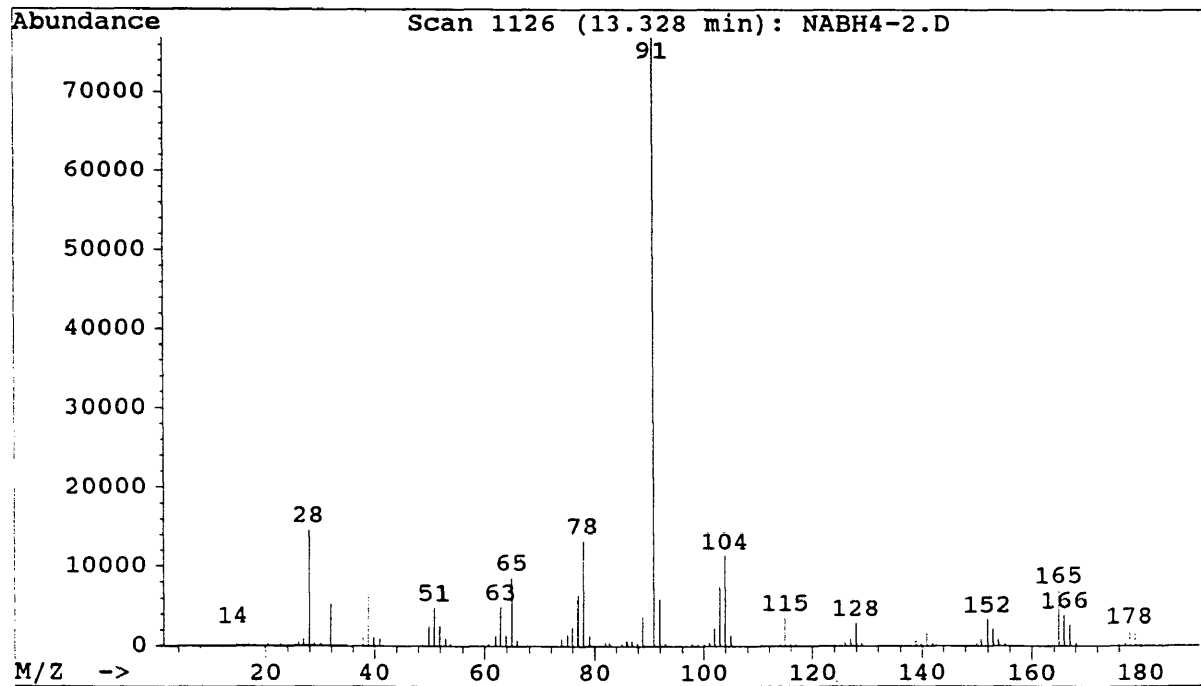
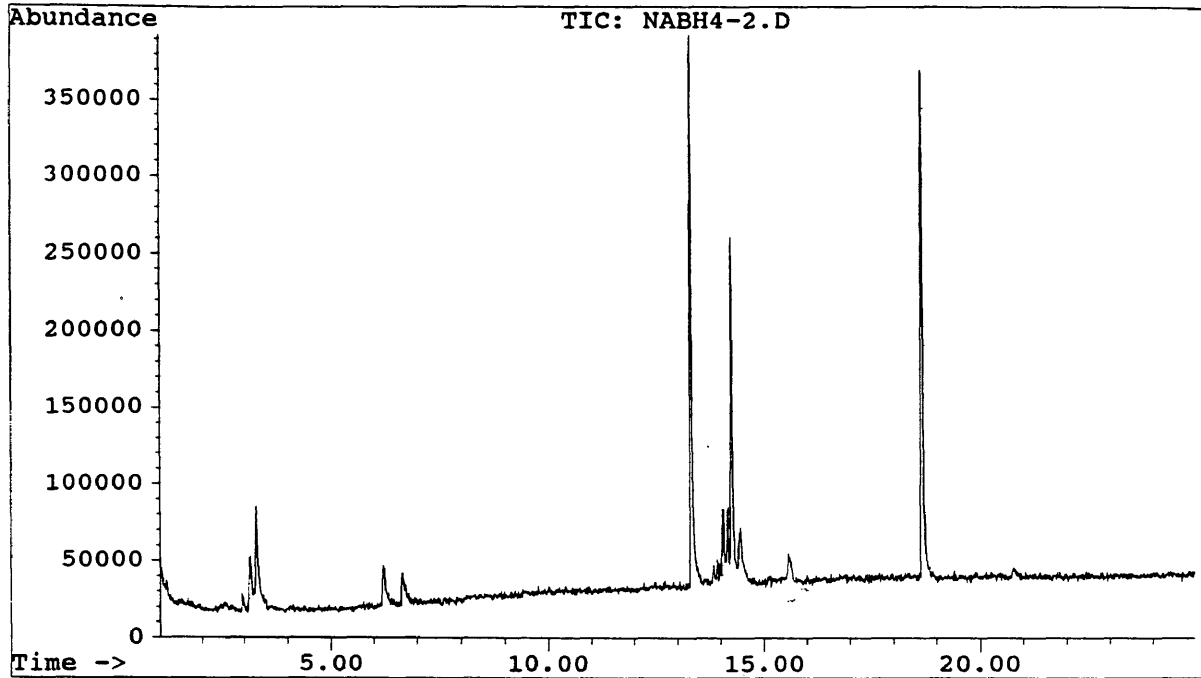
ANALYTICAL SPECTRA OF REDUCTION OF 3-TROPYLIUM-1,5-HEXADIENE

VI-A ^1H NMR SPECTRUM OF REDUCTION PRODUCTS

VI-B GC/MS SPECTRUM OF REDUCTION PRODUCTS

VI-A ^1H NMR SPECTRUM OF REDUCTION PRODUCTS

VI-B GC/MS SPECTRUM OF REDUCTION PRODUCTS



VITA

ELISE NOMA HATTERSLEY

The author was born on September 18, 1975, in Hagerstown, MD. She graduated in 1993 from Smithsburg High School in Smithsburg, MD; in 1997 she graduated from the College of William and Mary with a degree in Chemistry. She completed the Masters program at the College of William and Mary in July 1998. In August 1998, the author entered medical school at the University of Maryland at Baltimore.