

THERMAL ISOMERIZATIONS IN THE VINYL CYCLOPROPANE SYSTEM

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A Dissertation  
Presented to  
the Faculty of the Department of Chemistry  
College of Arts and Sciences

---

in Partial Fulfillment  
of the Requirements for the Degree  
Doctor of Philosophy

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by  
Ivar M. Rathburn, III

May 1972

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To Fran

## ACKNOWLEDGEMENTS

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## ABSTRACT

Bornylene undergoes a retro Diels-Alder reaction to give 1,5,5-trimethylcyclopentadiene and ethylene. The 1,5,5-trimethylcyclopentadiene rearranges further to 1,2,3- and 1,2,4-trimethylcyclopentadiene. Two other products identified as 1,2,3-trimethylcyclopentene and 1,2,3-trimethylbicyclo[2.2.1]heptene-2 were also isolated.

Thermolysis of two deuterated bornylenes and determination of deuterium distributions in the rearrangement products establishes the intermolecular nature of the methyl migrations. A mechanism for the radical chain process is presented and existing chemical evidence to the contrary is rationalized in terms of this pathway.

The cis-trans isomerization of 2-cyano-1-vinylcyclopropane is a unimolecular, first order process. The Arrhenius expression over the temperature range 210.0-258.54°C is

$$k = 10^{14.45 \pm .22} \exp (-41,060 \pm 1,660/RT)$$

From this kinetic study the resonance stabilization of  $\cdot\text{CH}-\text{C}\equiv\text{N}$  is found to be 7 kcal/mole.

The synthesis of 4-exo-methylene spiro[2.4]heptane is outlined. The molecule is unusually sensitive to catalysis and valid kinetic data was not obtained.

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CHAPTER I  
INTRODUCTION

## INTRODUCTION

Mechanisms in chemistry are attempts by investigators to describe the pathway which individual molecules follow during the course of a chemical reaction. Rigorous, and proper, establishment of mechanism has puzzled chemists to the present day. Organic chemists have, during the last forty years, developed various criteria to categorize two major and distinct classes of organic reactions, the ionic (heterolytic bond scission) and the free radical (homolytic bond scission) processes. However, a precise description of a long recognized but little understood third class of organic reactions has proved elusive, at best. Reactions which fall into this category resist classification by conventional criteria because the bond breaking and bond making process is so closely synchronized that the usual methods fail. These reactions are thermally induced, show little or no response to free radical initiators or inhibitors, and are relatively insensitive to solvation effects. Unanimous agreement on the mechanism of these thermally-induced reorganizations has so eluded chemists that it prompted Professor W. von E. Doering<sup>1</sup> to refer to these anomalous reactions as having a "no mechanism" mechanism.\*

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\*Perhaps it is necessary to point out that the term "no mechanism" is not to be taken literally. It simply reflects the limited success of experimental methods in attempting to shed light on the unique mechanistic character of thermal reactions.

Nevertheless, thermal isomerization reactions have provided a broadened understanding of how chemical reactions occur and a history rich in theory and experimentation. For example, the first literature account of the pyrolysis of the terpene pinene was observed in 1841 when Guy-Lussac and his assistant performed the experiment.<sup>2</sup> Simple rearrangement products were probably the minor ones. The majority of the products resulted from cracking, catalysis, decomposition or polymerization. The reason for this is the "brute-force" manner in which chemists of the time approached the problem, i.e., passing the material through red-hot steel tubes containing porcelain sticks. Since that time, methods and techniques for studying compounds under thermolytic conditions have become more sophisticated, but a good description of the thermal transformation of individual molecules is often lacking.

A simple rate process in organic chemistry is the unimolecular rupture of a carbon-carbon single bond. Consider ethane, for example, which undergoes fission to two methyl free radicals. Once the radicals are formed, each can perform free radical chemistry independent of the other. Table I lists Arrhenius parameters for the formation of free radicals from simple compounds. The limiting case at the other extreme is a synchronous bond breaking and bond making

process usually referred to as a "concerted" reaction. This involves a smooth transition from reactant to product. Table II lists Arrhenius parameters for some concerted processes.

These two models can be described pictorially by reaction coordinate diagrams as in Figures 1 and 2. The difficulty in interpreting such reactions arises when the possibility exists for an internal trap of the intermediate radicals, as when the two radicals are connected by a hydrocarbon chain, i.e., trimethylene,  $\cdot\text{CH}_2\text{-CH}_2\text{CH}_2\cdot$ . The diradical can potentially reclose the sigma bond many times faster than it can undergo radical chemistry. This shortens the lifetime of the intermediate (decreases the depth of the potential well in Fig. 1) to the extent it becomes almost experimentally inaccessible. At this point the mechanism resembles that for a concerted reaction. When such ambiguities are possible, the shape of the reaction coordinate diagram becomes exceedingly crucial.

Four tests are routinely available to distinguish between the two discrete mechanistic pathways. The first, and most obvious test, is direct observation of the intermediate. The second test is to determine the Arrhenius parameters ( $k = Ae^{-E_a/RT}$ ) for the reaction. The energy of activation,  $E_a$ , is used to determine the high point in the

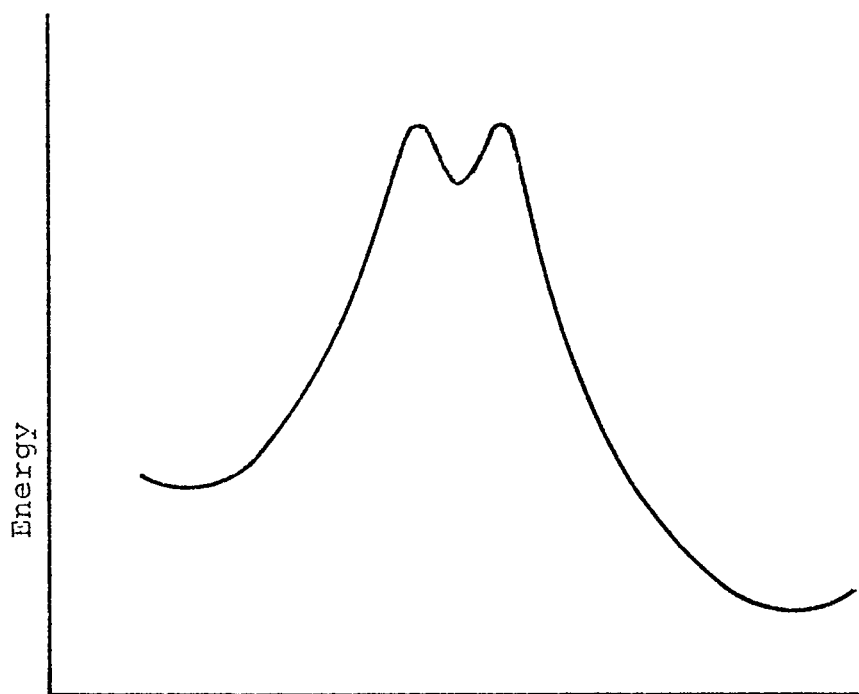


FIGURE 1. Reaction Coordinate Diagram for a Stepwise Reaction

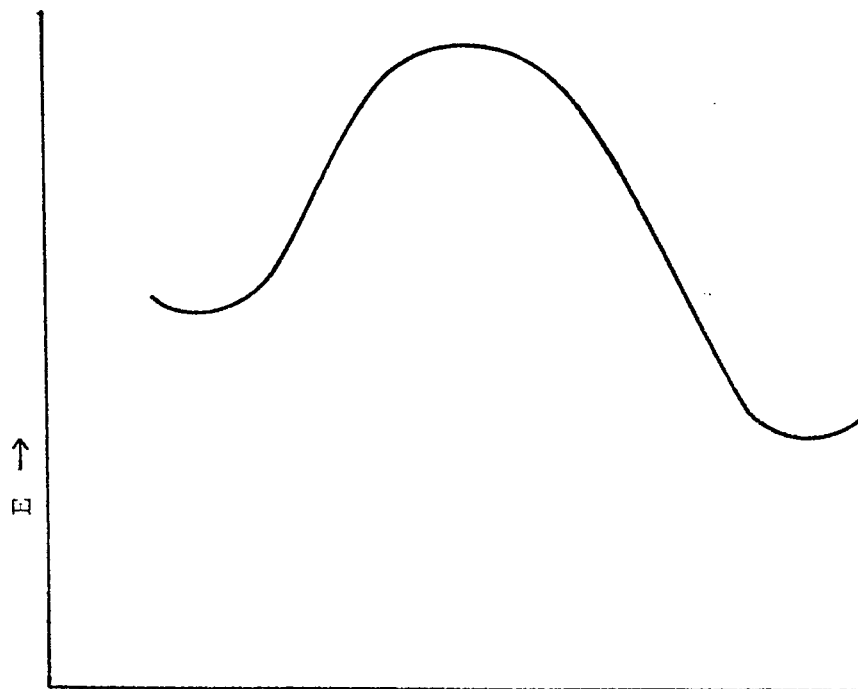


FIGURE 2. Reaction Coordinate Diagram for a Concerted Reaction

reaction coordinate diagram. It is generally assumed that the energy of activation for a stepwise process is higher than that for a concerted process. The preexponential factor "A" is a measure of the organization of the transition state. Reportedly, concerted reactions, having a highly organized transition state, have A factors lower than those for a radical process. Comparison of the Arrhenius parameters in Tables I and II shows this trend. The seemingly low values for  $E_a$  in Table I can be attributed to increased carbon substitution or some form of stabilization.

A third test is to compare the stereochemistry of the reactant with that of the product. Experimentally, this involves the thermolysis of a compound labelled in such a way that stereochemical changes can be observed. In general, a significant test of a concerted reaction is one which retains stereochemical integrity. A stepwise process is associated with mixing of stereochemical labels. For example, the highly substituted butadienes [1] and [2] are equilibrated in a concerted process through the intermediate cyclobutene [3].<sup>18</sup> After fifty-one days at 124°C, each cyclobutene molecule had undergone approximately  $2.6 \times 10^6$  ring openings without a single stereochemical mistake.

TABLE I  
FISSION OF SIMPLE COMPOUNDS INTO TWO RADICALS

Reaction	Log A (sec <sup>-1</sup> )	E <sub>a</sub> (kcal/mole)	Reference (see Bibliography)
$C_2H_6 \rightarrow 2CH_3^\bullet$	17.45	91.7	3
	16.0	86.0	4
$C_4H_{10} \rightarrow 2C_2H_5^\bullet$	17.0	82	5
$C_2F_6 \rightarrow 2CF_3^\bullet$	17.4	88 ± 3	6
$\phi CH_2CH_3 \rightarrow \phi CH_2^\bullet + CH_3^\bullet$	14.6	70.1	7
$\phi CH_2CH_2CH_3 \rightarrow \phi CH_2^\bullet + C_2H_5^\bullet$	14.9	68.6	8
$i-C_4H_{10} \rightarrow CH_3^\bullet + i-Pr^\bullet$	18.9	80.0	9
	17.8	82.5	9
$neo-C_5H_{12} \rightarrow CH_3^\bullet + tBu^\bullet$	17.4	83.0	10
	16.1	78.2	10



TABLE I CONTINUED  
FISSION OF SIMPLE COMPOUNDS INTO TWO RADICALS

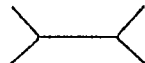
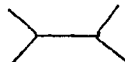
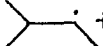
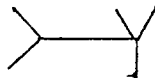
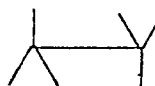
Reaction	Log A (sec <sup>-1</sup> )	E <sub>a</sub> (kcal/mole)	Reference (see Bibliography)
 → 2 i-Pr <sup>•</sup>	16.1	76.0	10
 →  + <sup>•</sup> CH <sub>3</sub>	16.6	81.1	10
 → i-Pr <sup>•</sup> + tBu	16.2	73.0	10
 → 2 tBu <sup>•</sup>	16.3	68.5	11

TABLE II  
COPE REARRANGEMENTS


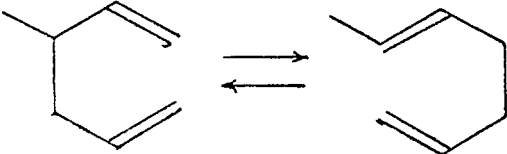

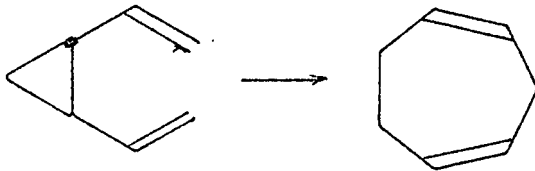
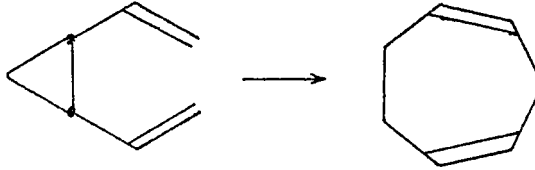
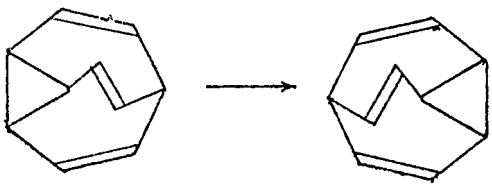
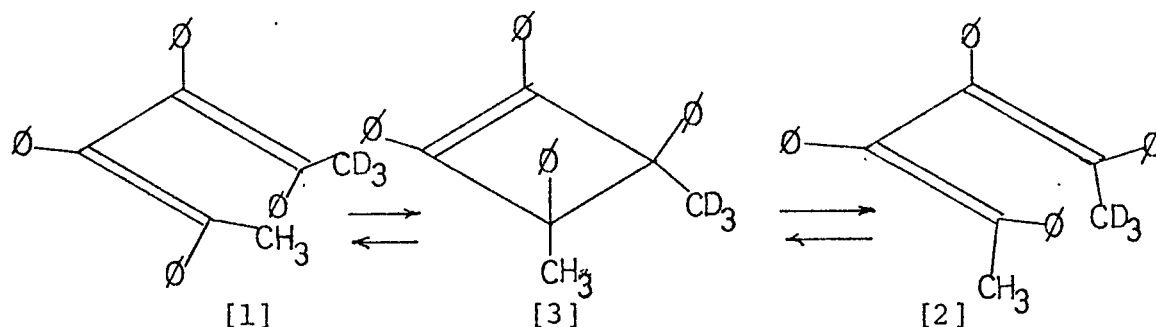
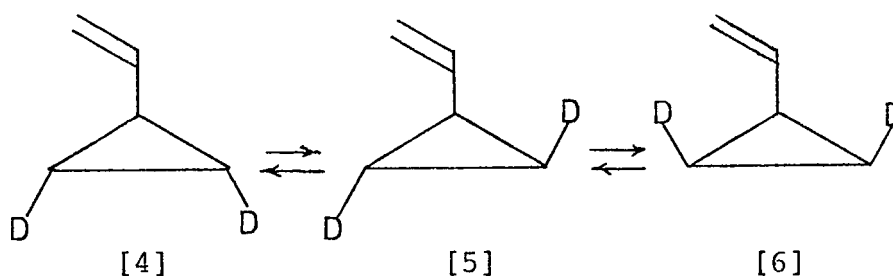
Reaction	$\text{Log}_{10} A$	$E_a$	Reference (see Bibliography)
	11.1	35.5	12
	9.84	32.5	13
	9.09	32.5	13
	11.85	29.9	14

TABLE II CONTINUED  
COPE REARRANGEMENTS

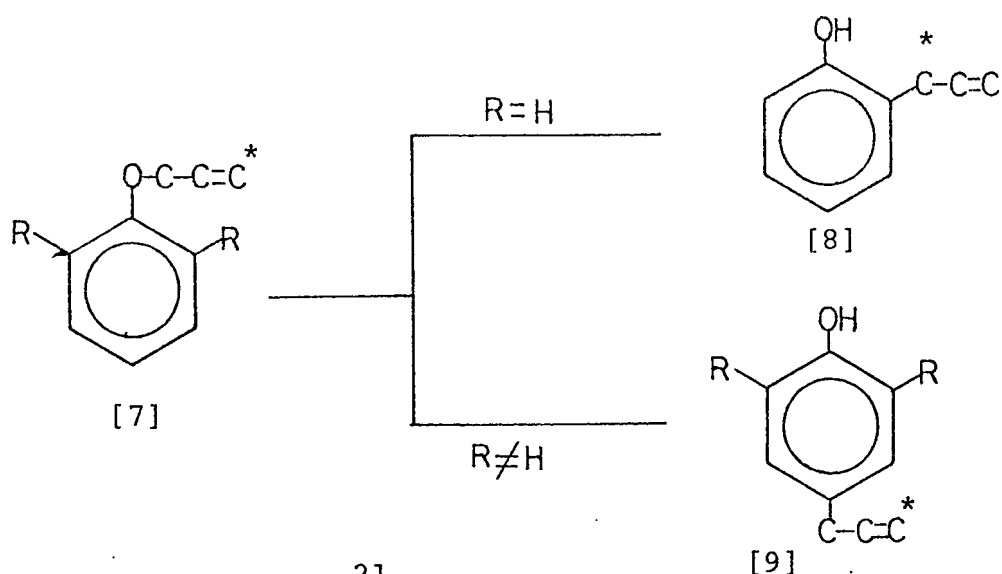
Reaction	$\text{Log}_{10} A$	$E_a$	Reference (see Bibliography)
	12.09	32.1	15
		21 (est.)	16
	12.3	11.8	17



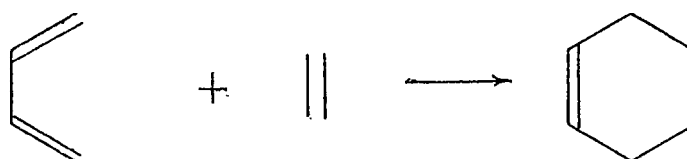
On the other hand, Willcott and Cargle<sup>19</sup> demonstrated that the mixing of the deuterium label in the degenerate vinylcyclopropane rearrangement, [4]  $\rightarrow$  [5], results from the intermediacy of a diradical.



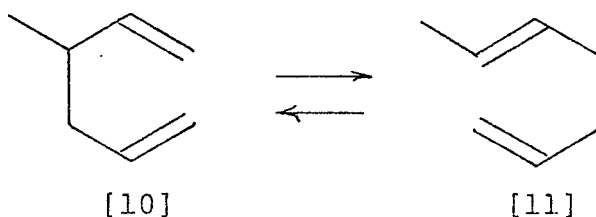
A final mechanistic criteria in determining which course a given reaction follows is based on quantum mechanics. The need for a quantum mechanical description arises from an abundance of experimental observations without a unified mechanistic explanation. For example, in 1912, Claisen<sup>20</sup> discovered a group of thermal rearrangements which now bear his name. Formally, the Claisen rearrangement is defined as a "diallylic" system such as a vinyl (or phenyl) allyl ether, i.e., [7], which rearranges to an isomeric, unsaturated system.



In 1928 Diels and Alder<sup>21</sup> discovered a class of reactions which is not only mechanistically interesting, but also widely used in synthesis. The Diels-Alder reaction requires that a 1,3 diene and an olefin react to produce a 6-membered unsaturated ring.



Another class of thermal isomerization reactions was discovered in 1940 by Cope and Hardy.<sup>22</sup> The Cope Rearrangement requires a "diallylic" system but, unlike the Claisen Rearrangement, the hetero atom is not essential.



Now that it is understood that the need for an explanation of "no mechanism" reactions existed, it must also be pointed out that the present theories describing the course of these reactions are only intellectual tools to make the observations palatable. Perhaps it is not surprising, in view of the plethora of experimental observations, that a number of alternative theoretical approaches to the problem have been developed almost simultaneously. The most notable contributions have come from Woodward and Hoffmann,<sup>23</sup> Dewar,<sup>24</sup> Fukui,<sup>25</sup> Zimmerman,<sup>26</sup> Longuet-Higgins and Abrahamson,<sup>27</sup> Salem,<sup>28</sup> and Oosterhoff and van der Lugt.<sup>29</sup> As is necessary, all of these approaches agree in the final analysis with experimental observations. The three most widely and easily used theories will be briefly discussed.

The Woodward-Hoffmann viewpoint<sup>23</sup> should be discussed first, since the number of literature references in recent years indicates their approach is the most fashionable explanation of thermal isomerization reactions. This is developed by correlating orbital symmetry in the reactant with that in the product. The basic premise of the Woodward-Hoffmann theory is "orbital symmetry is conserved in concerted reactions."

Woodward and Hoffmann define a sigmatropic change of order [i,j] as "the migration of a  $\sigma$  bond, flanked by one or

more  $\pi$  electron systems, to a new position whose termini are  $i-1$  and  $j-1$  atoms removed from the original bond loci, in an uncatalyzed intramolecular process."<sup>23</sup> Thus, the previously discussed Claisen and Cope rearrangements are [3,3] sigmatropic shifts. There are two topologically distinct ways in which a sigmatropic shift may occur, suprafacial or antarafacial. In a suprafacial process the migrating atom is associated at all times with the same face of the  $\pi$  system. In an antarafacial process, the migrating atom passes from the top face of one carbon terminus to the bottom face of another. These changes are exemplified for a [1,5] hydrogen migration in Figure 3.

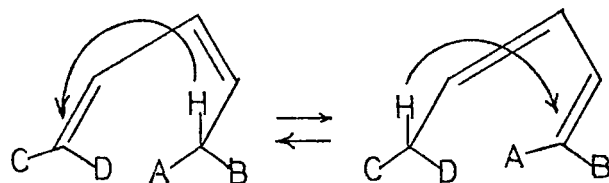


Figure 3a. Suprafacial Migration of Hydrogen Atom

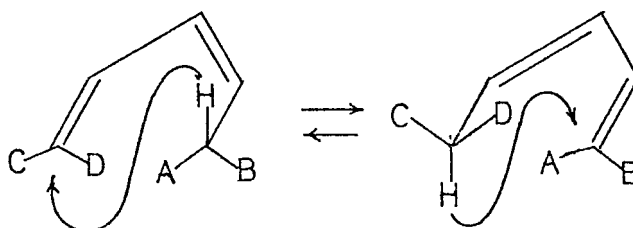
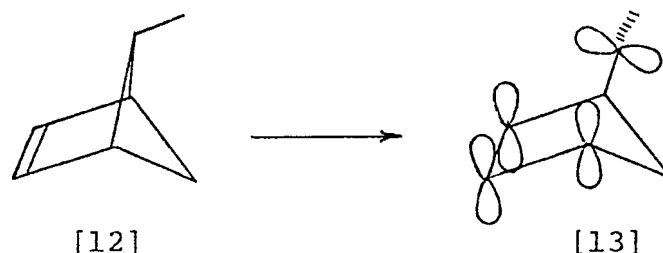
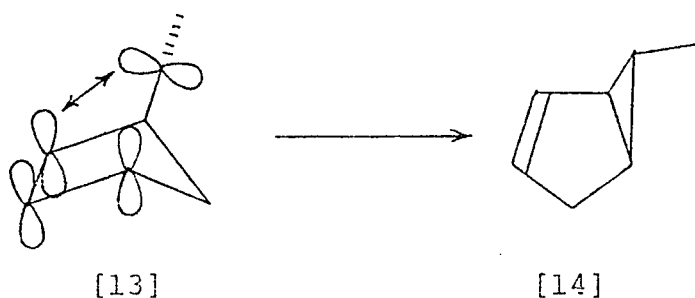


Figure 3b. Antarafacial Migration of Hydrogen Atom

Application of the Woodward-Hoffmann rules to thermal isomerizations has acquired many forms. Perhaps the simplest to use is the requirement of an "odd number of 's' events." Consider the experiment performed by Roth in which exo-5-methyl-bicyclo[2.1.1]hexene-2 [12] was thermolyzed.<sup>30</sup>



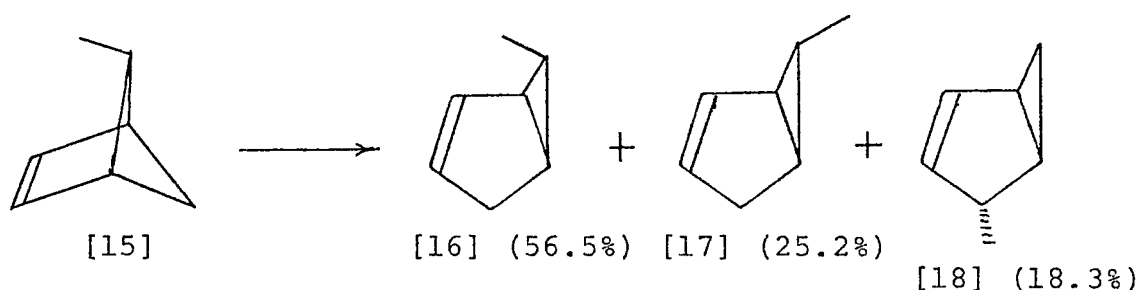
Since, in small ring systems, the antarafacial event is forbidden by geometrical constraints, the formation of the new  $\pi$  bond must be a suprafacial event. For the reaction to be "symmetry allowed" according to the "odd number of 's' events" rule, formation of the new  $\sigma$  bond must be an antarafacial event. In other words, the orbital lobe on the opposite face of the migrating carbon must be used to form the new bond.





Using this predictor, one is led to the experimentally observed product [14], composing 98.5% of the product distribution. Further, since sigmatropic reactions may be viewed as cycloadditions, the Woodward-Hoffmann notation for the [1,3]-sigmatropic shift is  $[\pi 2s + \sigma 2a]$ . This indicates the two electrons involved in the formation of the new  $\pi$  bond overlap suprafacially and the two electrons forming the sigma bond overlap antarafacially. This can easily be seen in the reaction  $[12] \rightarrow [14]$ .

However, it was found that when the methyl group is endo, as in [15], orbital symmetry control of the reaction was disrupted. The product distribution is grossly affected as evidenced by mixed stereochemistry about the methyl-bearing carbon ([16] and [17]) and migration of the carbon atom in the 6 position as a significant competing reaction ([18]).



This and other apparent violations of the Woodward-Hoffmann rules are explained as a diversion from a purely concerted reaction.

The frontier-orbital treatment developed by Fukui<sup>25</sup> is very similar in its basic principles. According to this method, the course of the reaction is controlled by the highest occupied molecular orbital (HOMO). In order to apply this method one must determine the HOMO for the system being studied. For example, returning to [12], the  $\pi$  electron system is analogous to the allyl radical.\* Figure 4 represents the ground state molecular orbitals for the allyl radical.

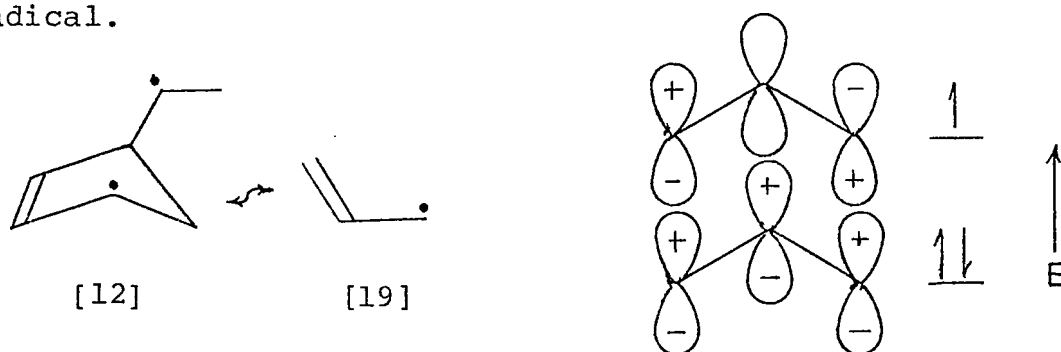


Figure 4. Molecular Orbitals for the Allyl Radical

Fukui then correlates the HOMO of the reactant with that of the product in the sense that Woodward and Hoffmann correlate all molecular orbitals of the reactant with those in the product. Fukui's insistence that the HOMO controls the reaction is the difference between the two theories.

An alternative approach to understanding electrocyclic reactions, advocated by Zimmerman<sup>26</sup> and supported by Dewar<sup>24</sup>,

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\*This does not imply that the transition state for the reaction is a diradical, but is merely the means of analysis.

maintains that the transition state is responsible for guiding the course of a reaction as opposed to correlation of symmetry elements. Giving credit to M. G. Evans<sup>31</sup> who discovered the basic ideas behind this generalization in 1936, Dewar calls this treatment the "Evans' Rule."

Simply stated, the Zimmerman viewpoint (Evans' Rule) contends that "thermal concerted electrocyclic reactions take place via aromatic transition states." In other words, a concerted reaction of this type occurs only if the corresponding transition state is aromatic. Conventionally, aromaticity in the Huckel-molecular orbital sense is associated with  $(4n+2)\pi$  electrons. However, Dewar calls attention to Perturbation Molecular Orbital theory which predicts that systems with an odd number of out-of-phase overlaps should exhibit aromaticity that is the reverse of the normal  $(4n+2)$  Huckel systems. Thus, in anti-Huckel systems  $(4n)\pi$  electrons are aromatic. Figure 5 describes phase dislocations as used in this theory. As shown in Figure 5a, a sign change in passing from one end of an orbital to another is not considered a phase dislocation. Figure 5b displays an obvious phase dislocation. If the ends of an initially planar system are twisted  $180^\circ$  with respect to each other and then reclosed, the  $\pi$  AO's at the ends will join out of phase.\*

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\*The topology of the resultant structure is that of a Mobius strip, a geometric figure with a single side.

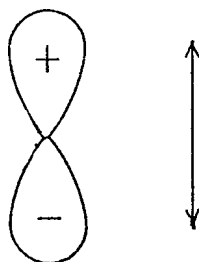


Figure 5a. No Phase Dislocation

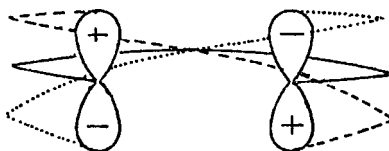
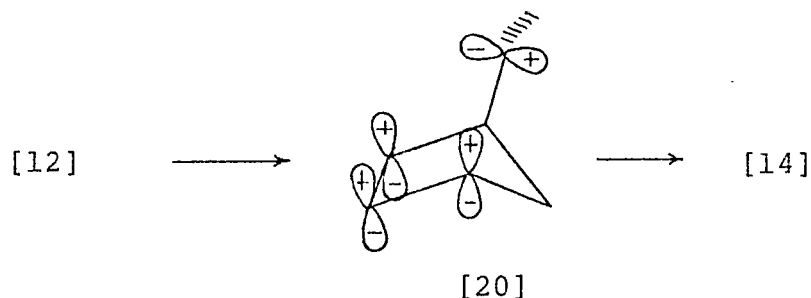


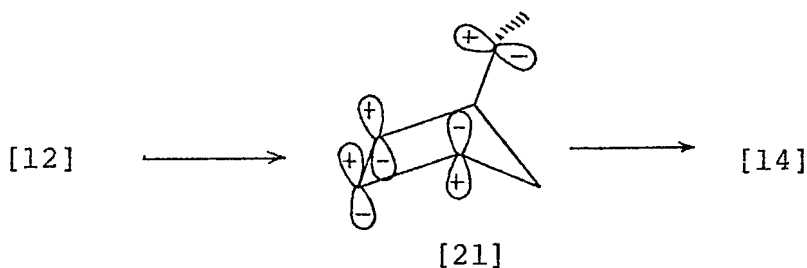
Figure 5b. Phase Dislocation

This forms the basis for predicting the course of concerted electrocyclic reactions via aromatic transition states. First, draw any arbitrary set of atomic orbitals with the smallest possible number of phase dislocations. Then, if the rearrangement involves  $4n+2$  electrons, the transition state must have an even number of phase dislocations. If  $4n$  electrons are involved in the reaction, the transition state must have an odd number of phase dislocations.

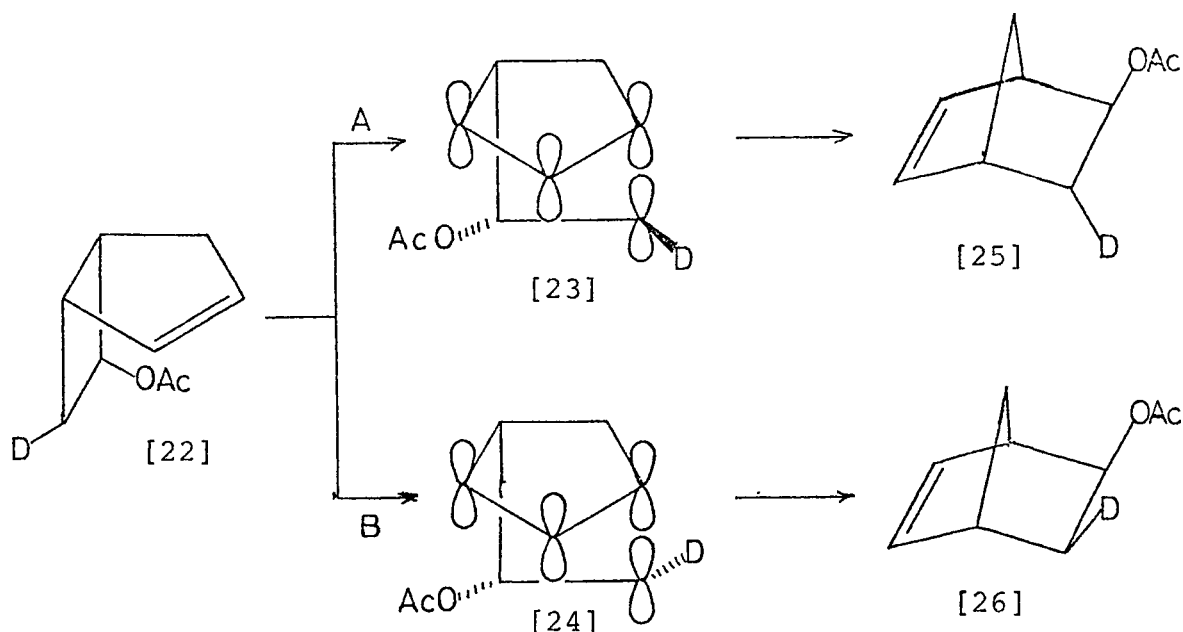
Referring to compound [12] again, it can be seen that the transition state [20] is indeed aromatic in this sense. Regardless of the assignment of phases, this particular description of the transition state is aromatic in the sense that  $4n$  electrons and 1 phase dislocation are involved.



Had we chosen the signs of the atomic orbitals differently, as in [21], the consequences would be identical to the above description.



From the foregoing discussion it can be seen that an intimate knowledge of molecular orbital theory is not necessary in order to utilize these theories. As pointed out previously, each theory arrives at the same conclusion. However, these theories might violate the principle of least motion.<sup>32</sup> Consider the experiment by Berson and Nelson<sup>33</sup> in which the bicyclo[3.2.0]heptene derivative [22] was thermolyzed. Two limiting outcomes, [25] and [26] are conceivable. Of course, any number of mixed outcomes are possible. The principle of least motion stipulates that the migrating moiety slip smoothly across the face of the



5-membered ring and bond to C3 as shown in Path A. The Woodward-Hoffmann theory of electrocyclic reactions predicts that during migration there is  $180^\circ$  rotation about the C6-C7 bond in order to effect an antarafacial event as shown in Path B, as does Zimmerman. The observed product is endo-endo [26], contrary to the principle of least motion. This result is surprising in view of the fact that most predictions based on the theories of electrocyclic reactions are in complete accord with the principle of least motion.

Once the large number of experimental observations have been unified by theory, it becomes necessary to test the theory in order to determine not only its validity, but also its applicability. Thus, the chemist is obligated to return to the laboratory to construct molecules that will test the theoretical model. Cyclopropane and substituted

cyclopropanes are well-suited for this purpose for two reasons. First, cyclopropanes can undergo both structural isomerizations to olefins and also geometrical isomerization to cis-trans isomers. Secondly, since it is a "bridged" ethane, it is the simplest case that provides an internal trap for a diradical intermediate. Indeed, cyclopropane investigations have encompassed many perturbations ranging from the simple cyclopropane to the complex bullvalene. Many of these compounds have been discussed by Cargle.<sup>34</sup>

Ultimately, the most scientific insight into the pathway of thermal, unimolecular reactions is gained by a molecular rearrangement whose mechanism is ambiguous, assuming, of course, the ambiguities can be unravelled through experiment. Perhaps, vinylcyclopropane fits this requirement. For example, consider the vinylcyclopropane - cyclopentene rearrangement whose kinetic parameters fit the equation:<sup>35</sup>

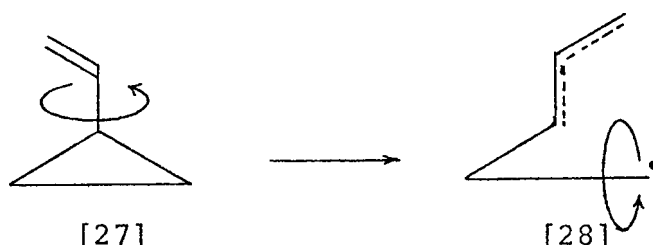
$$k = 10^{13.6} \exp(49,700/RT) \text{ sec}^{-1}$$

Flowers and Frey<sup>35</sup> contend that the reaction is concerted, i.e., the transition state involves rupture of C<sub>1</sub>-C<sub>2</sub> bond in vinylcyclopropane simultaneous with formation of cyclopentene. They believe the "normal" A factor is consistent with little increase in entropy, as is to be expected in

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\*"Normal" A factors are considered to fall in the range of 10<sup>13</sup>-10<sup>14</sup>.

concerted reactions. Further, they maintain that the low energy of activation also supports this belief. Conversely, Benson interprets the same data as consistent with an allylically stabilized diradical intermediate.<sup>36</sup> Further, he believes the allylic resonance energy ( $12.6 \pm 1$  kcal/mole)<sup>37</sup> accounts for the discrepancy in  $E_a$  between isomerization of cyclopropane to propylene and cyclopentene formation from vinylcyclopropanes (ca. 50 kcal/mole). The "normal" A factor is explained by no net change in entropy from the freely rotating vinyl group in vinylcyclopropane to the freely rotating radical in the allylically stabilized transition state.



This is because for full allylic resonance participation in the transition state the vinyl group is rigid while the  $-\text{CH}_2^\bullet$  radical is free to rotate, thus producing no net change in entropy.

This polarization of opinion regarding existing chemical data points out three facts. One, the shallower the potential well in Figure 1 the more experimentally inaccessible the intermediate becomes. Second, much of the data gathered in

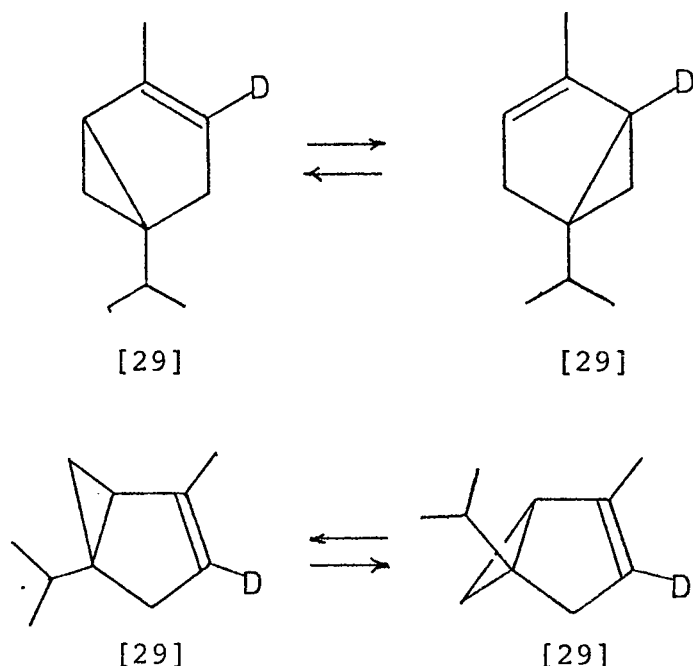


the field of thermal unimolecular rearrangements is compatible with both concerted and diradical mechanisms. Rate data alone is sufficient to prove unequivocally the existence of a nonisolable intermediate. Finally, as a consequence, there exists a need for further and more subtle investigations into the pathways available to reacting molecules.

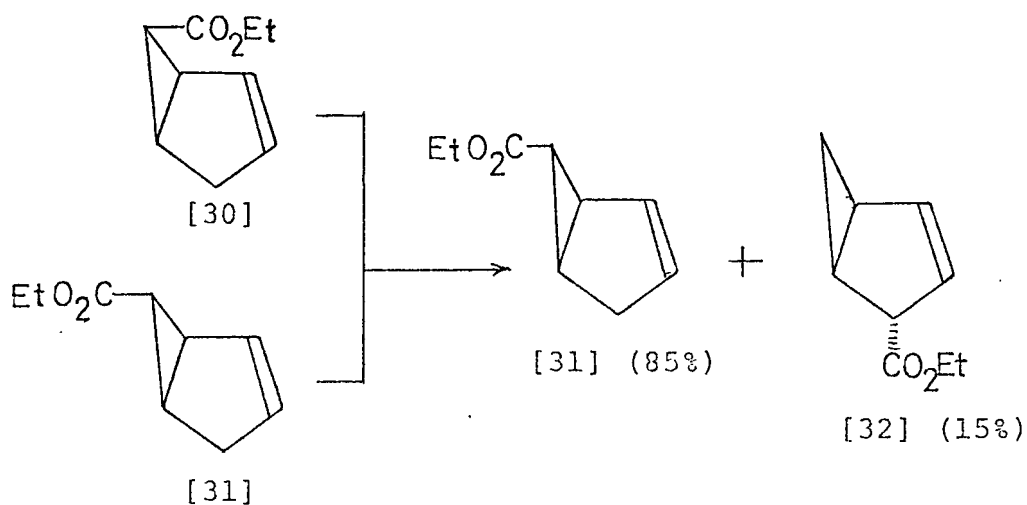
In attempts to devise more subtle experiments, the investigation into the apparent duality of mechanism in vinylcyclopropane leads to the reverse vinylcyclopropane rearrangement. As with the reverse Diels-Alder reaction, it should be possible to gain insight into the forward reaction by studying the reverse. In simple monocyclic vinylcyclopropanes this retrogression is not easily possible since isomerization to cyclopentene is favored by 10-15 kcal/mole. However, in cyclic systems it is possible to shift the relative energy of the product with respect to the reactant by incorporating strain energy. Several precedents are available for discussion.

In 1963 Doering and Lambert<sup>38</sup> and in 1970 Schmidt<sup>77</sup> studied a degenerate rearrangement with the elements of vinylcyclopropane incorporated into a ring system. This degenerate rearrangement is a special case of the reverse vinylcyclopropane rearrangement because the relative energies of the reactant and product are identical. They found racemization occurring by two processes. Schmidt, elaborating

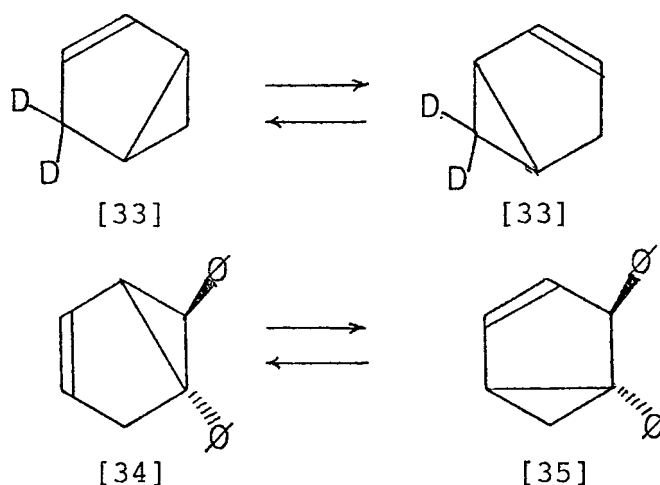
on the initial study by Doering and Lambert, believes the observations are consistent with a planar diradical.



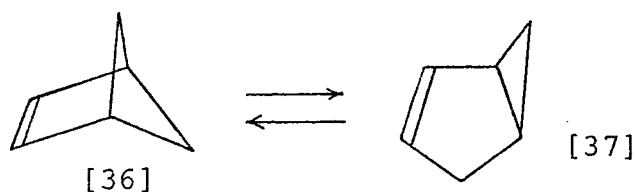
Similarly, Clark thermolyzed 6-carboethoxy-bicyclo-[3.1.0]hexene-2 [30] and [31],<sup>39</sup> observing another degenerate vinylcyclopropane rearrangement. Clark interprets both epimerization and structural isomerization as due to the intervention of an allylic-methine diradical.



Two other examples of the degenerate vinylcyclopropane-cyclopentene rearrangement are the isomerization of bicyclo[3.1.0]hexene-2 [33]<sup>40</sup> and trans-5,6-diphenyl bicyclo[3.1.0]hexene-2 [34].<sup>41</sup> The latter is interpreted by Swenton as being consistent with a diradical intermediate.



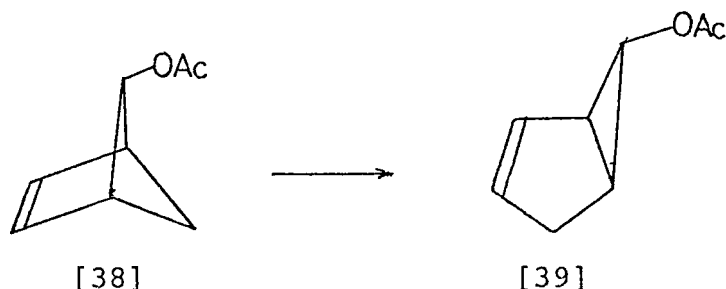
Frey, Hopkins and O'Neal reported the thermolysis of bicyclo[2.1.1]hexene-2 [36] yields bicyclo[3.1.0]hexene-2 [37]. Formally, this reaction appears to involve a cyclo-



pentene going to a vinylcyclopropane, an energetically uphill process. However, as is the case in chemical reactions, the overall process lowers the energy of the system. No mechanistic insight can be gained as the material has no label to mark its stereochemical course. Shortly after this

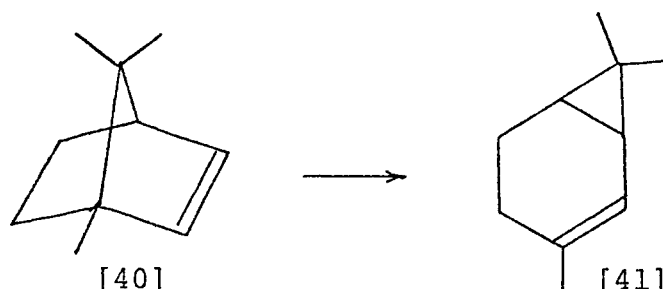
report appeared in the literature, Roth and Friedrich reported the thermolysis of exo- and endo-5-methyl-bicyclo[2.1.1]hexene-2 [12] and [15].<sup>30</sup> Here stereochemical purity of the product from [12] is interpreted as being compatible with a concerted reaction, but when the methyl group is endo, as in [15], stereospecificity in the product is lost.

Masamune and coworkers have thermolyzed bicyclo[2.1.1]hex-2-en-5-exo-acetate [38] obtaining bicyclo[3.1.0]hex-2-en-5-exo-acetate.<sup>43</sup> Once again, by interpreting the stereospecificity of the reaction as consistent only with a concerted process, they discount the possibility of a diradical.

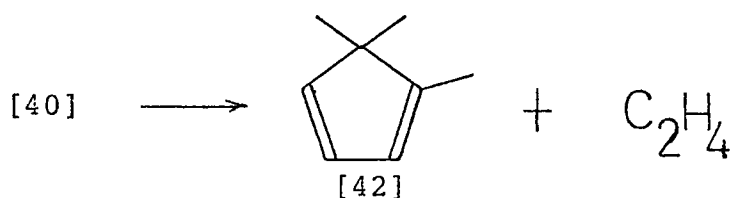


Bornylene (1,7,7-trimethyl bicyclo[2.2.1]heptene-2), [40], seems to be a good choice as a starting material for investigation of the reverse vinylcyclopropane rearrangement in a larger ring system for several reasons. First, there is some chance that  $\Delta^2$ -carene [41] may be isolated. Second, both protio and deuterio bornylene are available by

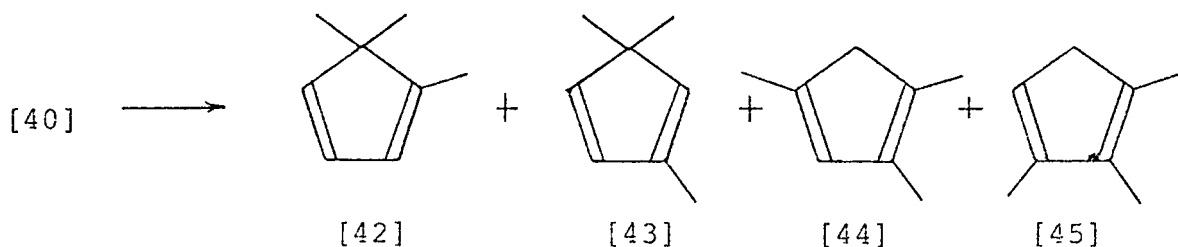
synthesis. Finally, the kinetics of the bornylene thermolysis are already documented.



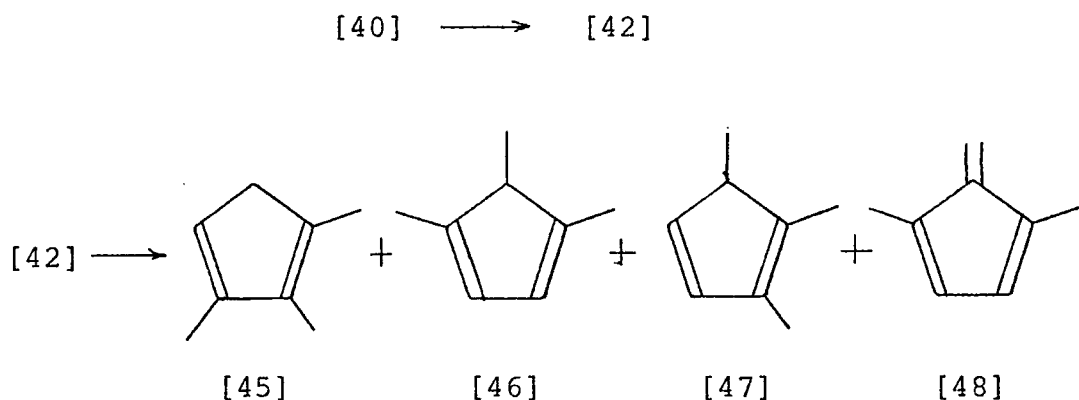
The problem is complicated by the propensity of bornylene to undergo a retrograde Diels-Alder reaction. The reaction is further complicated by the fact that 1,5,5-trimethylcyclopentadiene rearranges to a variety of compounds. These reactions are impossible to avoid.



De Haan and Kloosterziel thermolyzed bornylene in a tube reactor and obtained a number of cyclopentadienes.<sup>44a</sup> Subsequently, they reported on the thermolysis of trimethylcyclopentadienes obtained from bornylene.<sup>44b</sup>

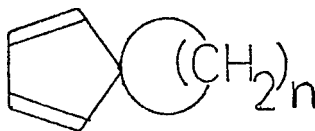


Herndon and Manion performed the same experiment in a gas phase, stirred-flow reactor and obtained similar, but not identical results.<sup>45</sup>

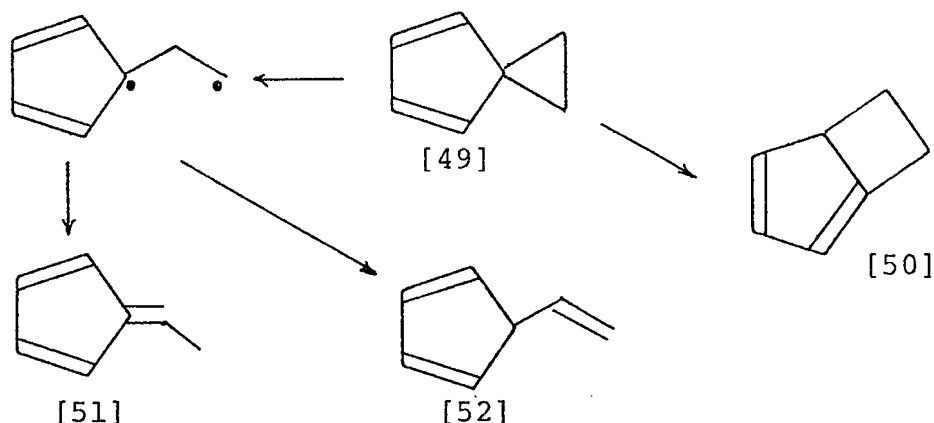


Mironov later reported the reversible skeletal isomerization of 1,2,3- and 1,2,4-trimethylcyclopentadienes and cites the absence of di- and tetramethylcyclopentadienes as evidence for intramolecularity.<sup>46</sup> All investigators maintain that the isomerization of trimethylcyclopentadienes is effectively a [1,5] sigmatropic rearrangement and interpreted as such.

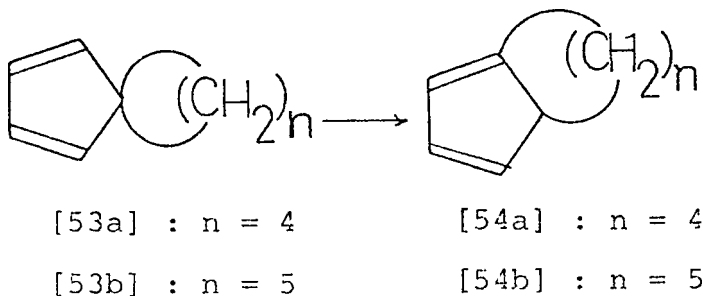
In addition, a number of spiro cyclopentadienes have been thermolyzed, being bicyclic analogues of 5,5 disubstituted cyclopentadienes.



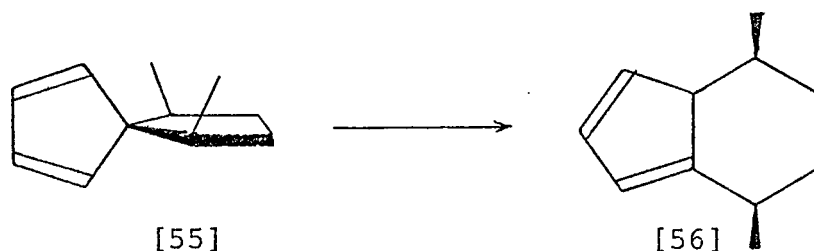
Krekels, de Haan and Kloosterziel find that spiro[2.4]heptadiene-4,6 [49] rearranges via two pathways, concerted and diradical.<sup>47</sup> The diradical mechanism is compared to the cyclopropane-propylene rearrangement.



Mironov and coworkers reported the thermal rearrangement of spiro[4.4]nonadiene-1,3 to be qualitatively compatible with a [1,5] sigmatropic shift.<sup>48</sup> In a following report, Dane, Haan and Kloosterziel obtained kinetic parameters in the thermolysis of spiro[4.4]nonadiene-1,3 [53a] and spiro[4.5]decadiene-1,3 [53b] and conclude the diradical mechanism is no longer operative.<sup>49</sup>



Their conclusions are based on differences in  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  values of their experimental results and those calculated from model systems. Following up this investigation, Klosterziel and coworkers report the stereospecificity of a thermal sigmatropic [1,5] shift in cis and trans 6,9-dimethylspiro [4.4]nonadiene-1,3 [55].<sup>50</sup>



Based on the stereospecificity of the product [56] (estimated to be better than 99% for both reactions), a stepwise process is ruled out. It is the intent of this work to show that the thermal chemistry in the cyclopentadiene system is not as simple as heretofore reported.

In the search for  $\Delta^2$ -carene, the product of the retro vinylcyclopropane cyclopentene rearrangement from bornylene, we were led, quite naturally, into the trimethylcyclopentadiene rearrangement. Pursuing this investigation, it was noted that Benson casts some doubt upon the intramolecularity and, consequently, the concertedness, of the methyl migrations.<sup>51</sup> Since these rearrangements have not been investigated with the use of isotopes, the deuterio-bornylene designed for investigation of the retro vinylcyclopropane-cyclopentene rearrangement provided a convenient tool for



entry into the problem.

Returning to the historical viewpoint of the vinylcyclopropane system, it is, as explained previously, an interesting system with which to study sigmatropic rearrangements. As in many mechanistic studies, substituent effects on the parent molecule are often employed to gain additional information about the reaction. For this reason, 2-cyano-1-vinylcyclopropane [57] and [58] would be nice because it affords a way to investigate the cis-trans isomerization in vinylcyclopropane. Although the molecule has insufficient labels to follow the stereochemical path in the vinylcyclopropane to cyclopentene rearrangement, it does have the added ability to stabilize an intermediate diradical not only through allylic resonance stabilization but also  $-\dot{\text{C}}\text{H}-\text{C}\equiv\text{N}$  stabilization. Moreover, it affords the opportunity to verify the value of this stabilization since the value presently in hand of 11.7 kcal/mole is suspect.<sup>36</sup> Indeed, the value of 11.7 kcal for conjugation energy in the  $-\dot{\text{C}}\text{H}-\text{C}\equiv\text{N}$  radical<sup>52</sup> seems somewhat high compared to 7 kcal in  $-\dot{\text{C}}\text{H}-\text{COCH}_3$  and 12.6 kcal in  $-\dot{\text{C}}\text{H}-\text{CH}=\text{CH}_2$ . Benson estimates this resonance energy to be approximately 5 kcal. The energy of activation for cis-trans isomerization in cyanovinylcyclopropane can prove the  $-\dot{\text{C}}\text{H}-\text{C}\equiv\text{N}$  radical stabilization energy (see Figures 5 and 6). Table III lists some typical vinylcyclopropane-





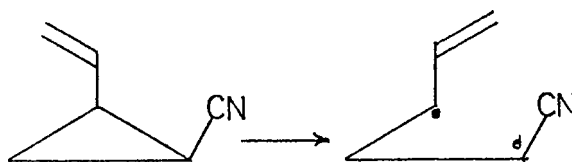
	<u>kcal/mole</u>	<u>reference</u>
C-C	85.00	53
 strain	-24.22	53
 resonance	<u>-12.60</u>	37
Total	48.12 kcal	

Figure 6a. Approximation of Bond Dissociation Energy for Formation of Diradical from Vinylcyclopropane





	<u>kcal/mole</u>	<u>reference</u>
C-C	85.00	53
 strain	-24.60	53
 resonance	-12.60	37
$\cdot\text{CH-CN}$ resonance	<u>-11.70</u>	52*
Total	36.42 kcal	

Figure 6b. Approximation of Bond Dissociation Energy for Formation of Diradical from 1-Cyano-2-Vinylcyclopropane

\*Number in present use. See reference indicated.

TABLE III  
VINYL-CYCLOPROPANE-CYCLOPENTENE REARRANGEMENTS

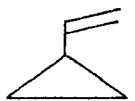
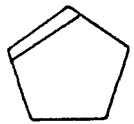
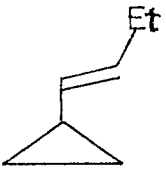
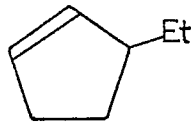
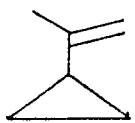
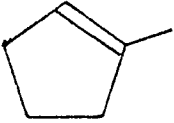
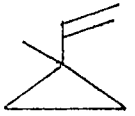
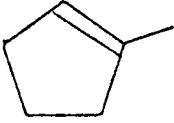
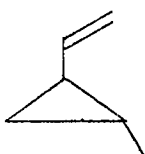
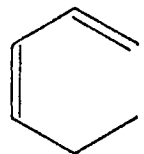
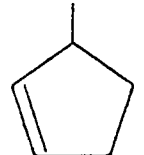
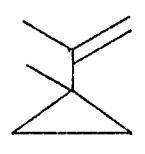
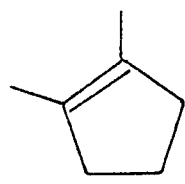
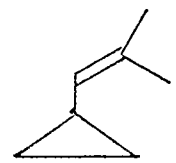
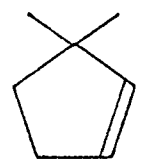
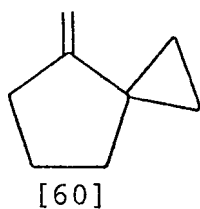
VCP	Olefin	$\text{Log}_{10} A$	$E_a$ (kcal/mole)	Reference
		13.6	49.7	35,54
		13.79	50.0	55a
		13.89	50.9	55b
		14.11	49.4	55c

TABLE III CONTINUED  
VINYL-CYCLOPROPANE-CYCLOPENTENE REARRANGEMENTS

VCP	Olefin	$\text{Log}_{10} A$	$E_a$ (kcal/mole)	Reference
	 major	14.74	48.7	55d
	 minor	13.67	48.7	
		14.14	50.5	55c
		14.00	50.2	55e

cyclopentene rearrangements and their corresponding energies of activation. Note that these compare favorably with the estimate based on thermochemical methods.

Finally, as previously discussed, there is essentially no change in entropy in passing from reactant to transition state. However, if the vinyl group were held stationary in the reactant, the entropy contribution of the freely rotating radical would manifest itself in the A factor. Additionally, if the vinyl group were to be "pinned-down" in the sterically unfavorable position cis to the cyclopropyl ring, then the energy contribution of the rotating vinyl group could be estimated from the additional lowering of the energy of activation. For these reasons, 4-exo-methylene-spiro[2.4]heptane was synthesized for study.



In this molecule the vinyl group is held stationary over the plane of the cyclopropyl ring and is in the favored conformation for allylic resonance participation in the transition state.

## STATEMENT OF THE PROBLEM

In summary, it is the intention of this work to explore several aspects of thermal isomerization reactions in the vinylcyclopropane system. First, the thermolysis of bornylene is investigated from two standpoints; the search for the unreported  $\Delta^2$ -carene [41] in a system analogous to bicyclo[2.1.1]hexene-2 and isotopic analysis of the thermolysis products. Second, the kinetics of cis-trans isomerization in 2-cyano-1-vinylcyclopropane is investigated to confirm or correct the  $\dot{\text{C}}\text{H}-\text{C}\equiv\text{N}$  stabilization energy and thus determine additional rate data supporting a diradical process. Finally, a kinetic investigation of 4-exo-methylene spiro[2.4]heptane [59] is undertaken in an attempt to determine the Arrhenius parameters for a constrained vinylcyclopropane.

## CHAPTER II

### DISCUSSION OF EXPERIMENTS AND RESULTS

## DISCUSSION OF EXPERIMENTS AND RESULTS

Bornylene, an artificially derived terpene, is a curious organic compound. Physically, it is a colorless, wet-looking, waxy solid that has a very high vapor pressure. This latter fact enables bornylene to be purified readily by bulb-to-bulb distillation. Using recently developed synthetic methods, bornylene can be prepared in excellent yields from camphor. Preliminary thermolysis in an evacuated ampoule (380°C/90 sec) revealed the propensity of bornylene to undergo a retro Diels-Alder reaction as its most significant thermal process. The products, as shown in Figure 7, were 1,5,5-trimethylcyclopentadiene, unreacted bornylene and a small amount of unknown material.

All subsequent thermolyses of bornylene were performed in the range 350-380°C in a similar manner. An ampoule, approximately 10 mls in volume, was washed with dilute ammonium hydroxide, rinsed thoroughly with distilled water and dried in an oven at 110°C. A small amount of bornylene was introduced via bulb-to-bulb distillation and the tube was sealed under vacuum. The thermolysis was accomplished using a tube furnace whose temperature was monitored with a 0-400°C thermometer and a chromel-alumel electrode connected to a Tempco Model PM-1K35 pyrometer. After thermolysis, the tubes were cooled, opened and the contents purified by bulb-



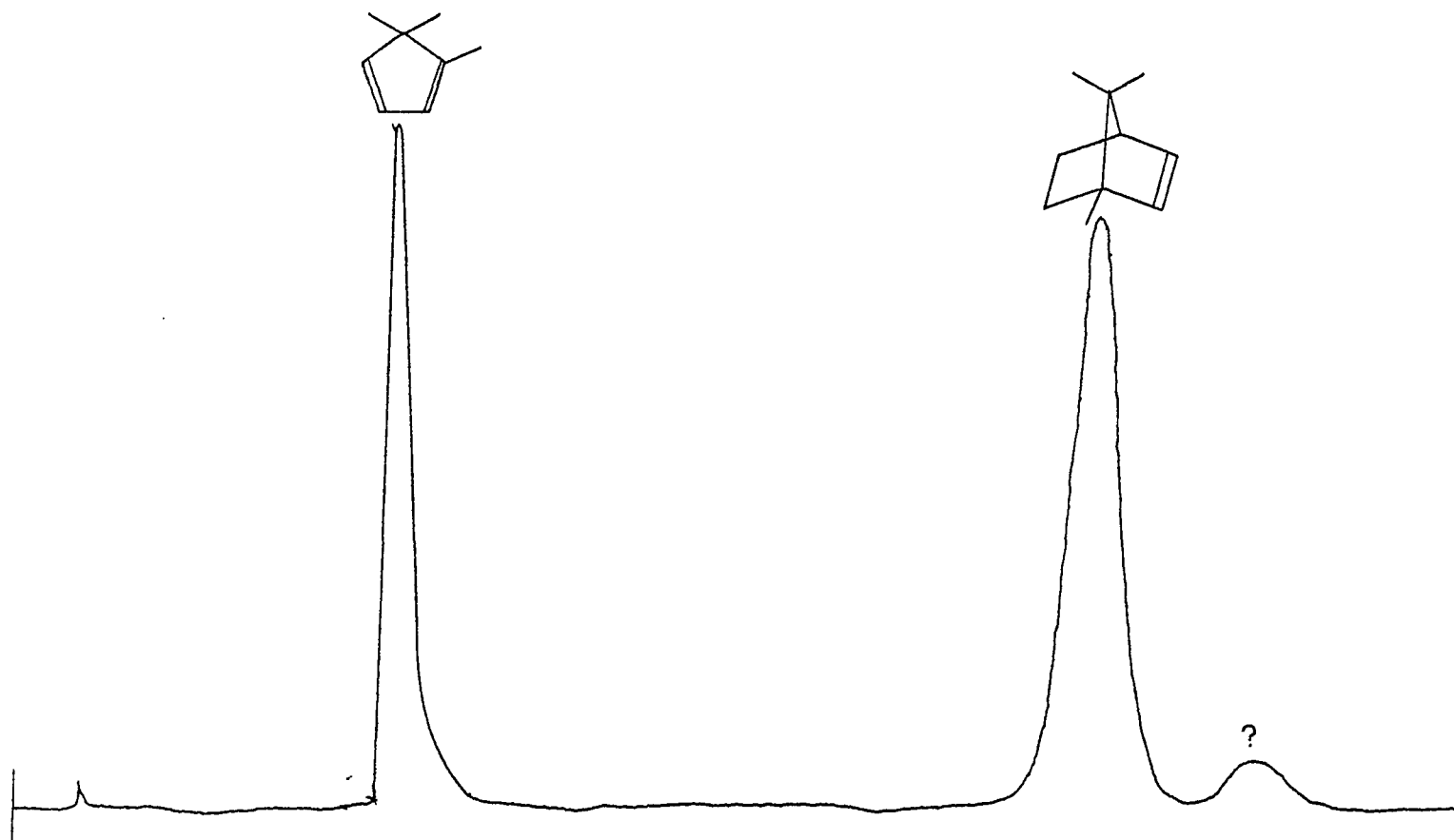


FIGURE 7. GLPC Trace of Bornylene Thermolysis Products: 380°C/90 sec

to-bulb distillation. The products were separated and collected from a preparative gas chromatograph using a 15' 20% Carbowax on 60/80 mesh Chromosorb W column operated at 100°C.

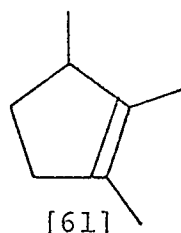
Thermolysis of bornylene [40] at low conversions yielded 1,5,5-trimethylcyclopentadiene [42] and unreacted [40]. Ethylene was also formed but under our analysis conditions was lost upon opening of the ampoule after thermolysis. Increasing the time spent in the oven to 180 sec, we observed a greatly changed product distribution. The easily identifiable products were the expected ones; 1,5,5-trimethylcyclopentadiene [42], 1,2,4-trimethylcyclopentadiene [44], and 1,2,3-trimethylcyclopentadiene [45]. Two other significant products were noted and subsequently identified.

Kloosterziel<sup>44a</sup> reported a significant amount of xylenes were formed from both 1,2,3- and 1,2,4-trimethylcyclopentadiene at temperatures above 400°C. In a test of this observation bornylene was pyrolyzed for 1.5 min at 380°C. The 1,5,5-trimethylcyclopentadiene formed was isolated by GLPC and rethermolized for 10 min at 350°C. The GLPC trace of the thermolysis products compared to one of a known mixture of xylenes indicated no aromatics were present.

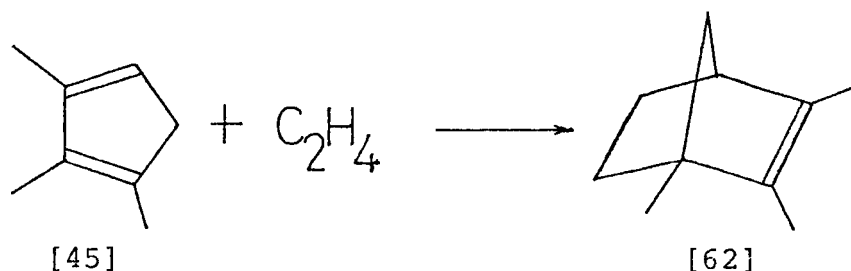
## IDENTIFICATION OF TWO UNKNOWN PRODUCTS

Initially, these two compounds posed a perplexing problem because their spectral properties were unusual. Neither compound exhibited vinyl resonances in the NMR spectrum, but yet each would decolorize a solution of bromine in  $\text{CCl}_4$ . Mass spectral analysis indicated one substance had an  $m/e = 110$  ( $\text{C}_8\text{H}_{14}$ ) and the other had an  $m/e = 136$  ( $\text{C}_{10}\text{H}_{16}$ ), isomeric with bornylene. Thermolysis of bornylene for 24 minutes at  $350^\circ\text{C}$  resulted in an almost complete conversion to the low molecular weight material. This mixture was separated into two fractions by gas liquid partition chromatography (GLPC). The  $\text{C}_8\text{H}_{14}$  hydrocarbon, obtained pure, was rethermolized for 22 minutes at  $350^\circ\text{C}$ . GLPC analysis indicated no change had occurred. The remainder of the material was sealed in an ampoule and thermolyzed similarly. The low molecular weight hydrocarbon was again the major product.

Kloosterziel,<sup>44a</sup> in a single sentence, noted the appearance of 1,2,3-trimethylcyclopentene (laurolene) [61] as a product of the thermolysis of [42]. Suspecting [61] to be the  $\text{C}_8\text{H}_{14}$  unknown, we obtained an authentic sample. Comparison of the spectral properties of the authentic material with those gathered experimentally revealed that laurolene was the low molecular weight unknown in our thermolysis.



The structure of the bornylene isomer was only slightly more difficult to establish. Its infrared spectrum was almost uninformative, being characteristic of a hydrocarbon. A clue to its identity was found in a report by Alder and Muders that "Damsky's Hydrocarbon" [45] reacts with ethylene in an autoclave at 180°C to produce 1,2,3-trimethyl bicyclo[2.2.1]heptene-2 ( $\epsilon$ -fenchene or 1-methyl santene) [62].



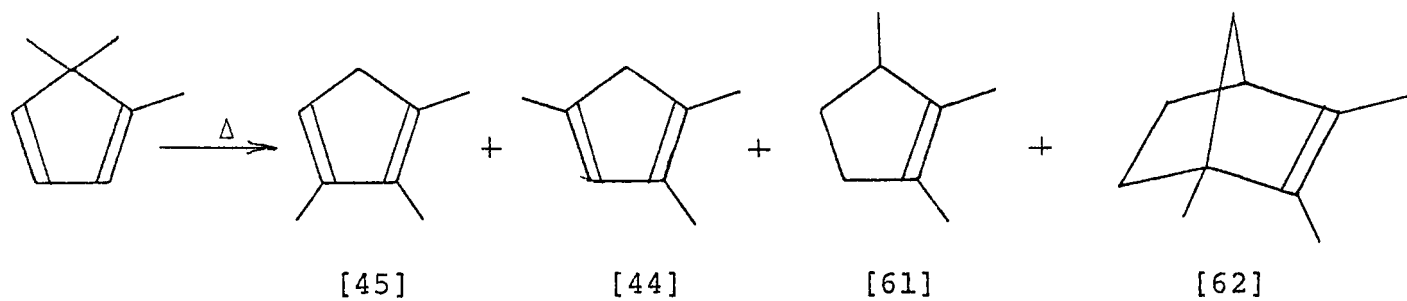
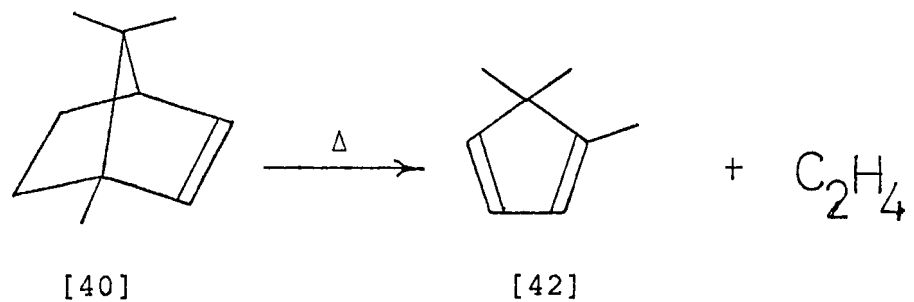
In an attempt to synthesize [62] by an independent method, fenchol was dehydrated by KHSO<sub>4</sub>. GLPC analysis indicated the expected plethora of dehydration products, none of which had spectral properties identical with the C<sub>10</sub>H<sub>16</sub> unknown. If [52] is produced by a (4+2)cycloaddition as believed, it should exhibit a marked pressure dependence, providing indirect proof of structure. To test this hypothesis, three

ampoules containing decreasing amounts of bornylene were thermolyzed under identical conditions. The amount of unknown in the thermolysis products was directly proportional to the initial amount of bornylene. Based on the information in hand, we assigned structure [62] to the  $C_{10}H_{16}$  unknown. This assignment completed the identification of the products observed in our thermolysis. The product distribution is summarized in Scheme I.

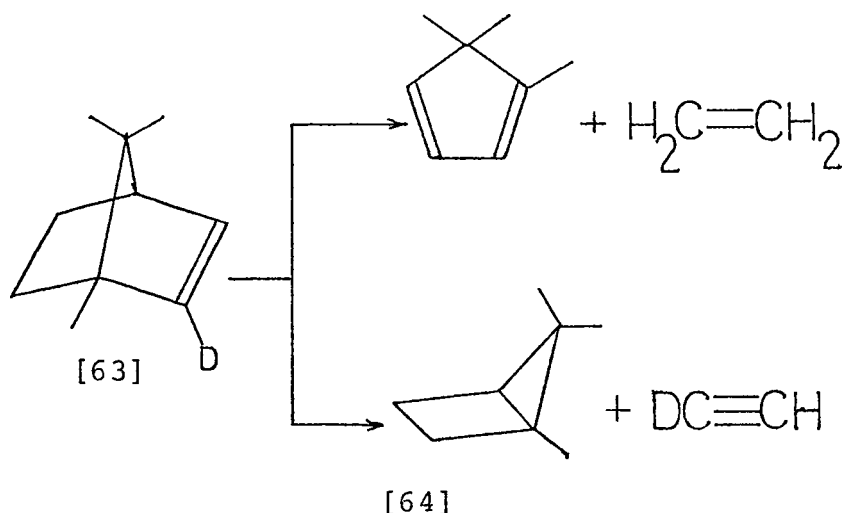
#### SYNTHESIS OF BORNYLENE AND DEUTERIO-BORNYLENE

Bornylene is most conveniently prepared by Shapiro's method.<sup>58</sup> Effectively, the procedure involves preparation of camphor tosylhydrazone, reaction of the hydrazone with an alkylolithium and subsequent hydrolysis with water. The yield becomes almost quantitative when diglyme (bis-2-methoxyethyl ether) is added to the solvent.

The preparation of 2-deuterio-bornylene [63] was deemed necessary for two reasons. First, it provided a means to study hydrogen migrations in the trimethylcyclopentadienes and second it provided a check for the intermediacy of 1,5,5-trimethyl bicyclo[2.1.0]pentane [63], which is a possible pathway to laurolene.

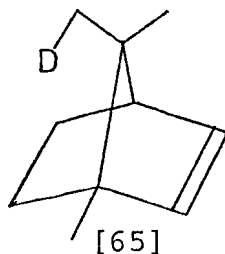


SCHEME I. Products from Thermolysis of Bornylene at 380°C for 3 min.



Bornylene-2-d is most conveniently prepared by Shapiro's olefin synthesis.<sup>58</sup> Camphor was first converted to the tosylhydrazone. The camphortosylhydrazone was suspended in ether and 2 equivalents of freshly prepared and standardized n-butyllithium in ether were added. The reaction was quenched with a large excess of  $\text{D}_2\text{O}$ . Work-up of the reaction mixture yielded bornylene with less than expected deuterium incorporation. We suspected, as did Shapiro,<sup>58</sup> that the ether was acting as a proton donor. Thus, several attempts were made to increase both yield and % deuterium incorporation. This included the use of hydrocarbon solvents ( $n\text{-C}_6$  and  $\text{C}_6\text{H}_6$ ) with and without diglyme added and reversal of the order of addition of reagents. In no case did the deuterium content exceed 65% or the yields approach 100%. Subsequent mass spectra showed that the bornylene prepared in this manner has 43.5 atom percent deuterium, lower than expected but useable nevertheless.

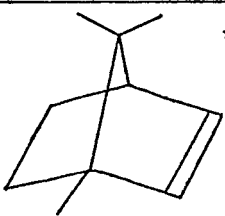
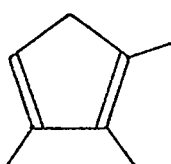
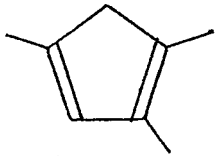
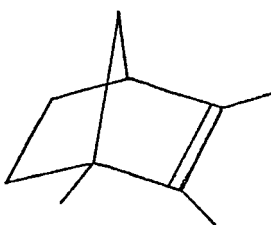
The bornylene-9-d<sub>1</sub> [65] used in this investigation was prepared according to the procedure described by Willcott and Boriack.<sup>59</sup> Mass spectral analysis indicated this material contains 97.5 atom % deuterium in the 9-methyl.



Mass spectral data was used to obtain the extent of isotopic mixing in the thermolysis products. The parent region of each product, observed from low-voltage ionization, was compared carefully with those obtained for the all protio material. In every case the non-deuterated counterparts were used as standards and were reproducible from run to run.

Tables IV, V, VI, VII, and VIII are summaries of the isotopic mixing observed in the thermolysis of [63] and [65] at various conditions. The important features are the amount of d<sub>2</sub> and d<sub>3</sub> present as compared to the standards and the total atom % d which closely resembles that for the starting material. Table IX is the isotopic mixing observed when 1,5-dimethyl-5-deuteriomethylcyclopentadiene was isolated from [65] and rethermolized for 10 minutes at 350°C.



Cmpd	% d <sub>0</sub>	%d <sub>1</sub>	%d <sub>2</sub>	%d <sub>3</sub>	Total Atom %
	59.0	38.7	2.4	0	43.5
	68.7	26.5	4.5	.3	36.5
	60.8	34.9	3.6	.7	44.2
	61.9	32.5	4.6	1.0	44.7

\*Starting material

TABLE IV

MASS SPECTRAL ANALYSIS OF BORNYLENE-2-d THERMOLYSIS

PRODUCTS: 380°C/2.5 min

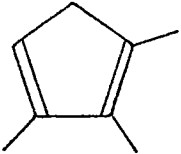
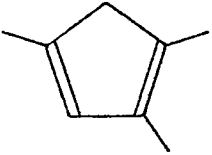
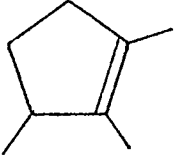
Cmpd	% d <sub>0</sub>	% d <sub>1</sub>	% d <sub>2</sub>	% d <sub>3</sub>	Total Atom %
	66.7	26.6	6.0	.7	40.9
	61.8	29.3	7.8	1.0	47.9
	60.1	31.8	6.9	1.2	49.3

TABLE V

MASS SPECTRAL ANALYSIS OF BORNYLENE-2-d THERMOLYSIS

PRODUCTS: 350°C/25 min

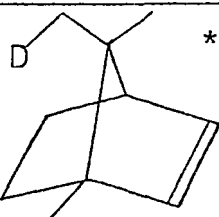
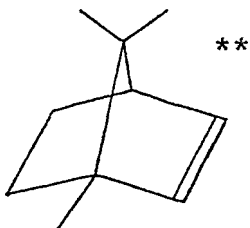
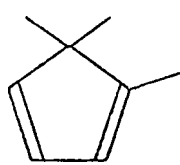
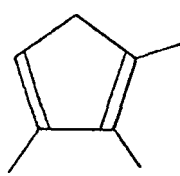
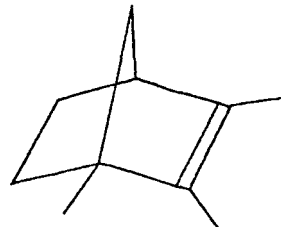
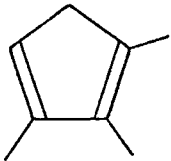
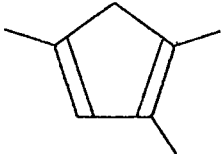
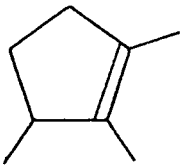
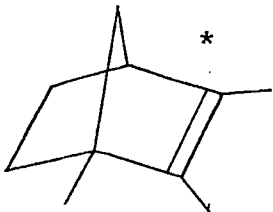
Cmpd	% d <sub>0</sub>	% d <sub>1</sub>	% d <sub>2</sub>	% d <sub>3</sub>	Total Atom %
 *	3.0	96.5	.5	0	97.5
 **	3.2	92.5	2.5	1.8	102.9
	5.4	90.4	3.7	.5	99.3
	17.1	65.4	13.6	3.9	103.1
	3.1	93.7	2.2	1.0	101.1
*Starting Material      **Recovered					

TABLE VI

MASS SPECTRAL ANALYSIS OF BORNYLENE-9-d THERMOLYSIS

PRODUCTS: 380°/2.5 min

Cmpd	%d <sub>0</sub>	%d <sub>1</sub>	%d <sub>2</sub>	%d <sub>3</sub>	Total Atom %
	19.0	62.5	14.3	3.9	102.8
	12.0	75.5	9.4	3.1	103.6
	14.0	75.6	9.2	1.2	97.6
	10.9	71.8	11.6	5.6	111.8

\*possible bornylene-9-d contamination

TABLE VII

MASS SPECTRAL ANALYSIS OF BORNYLENE-9-d THERMOLYSIS

PRODUCTS: 380°C/3.5 min

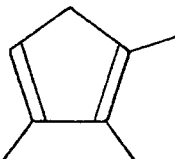
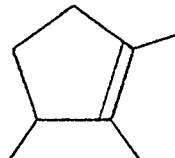
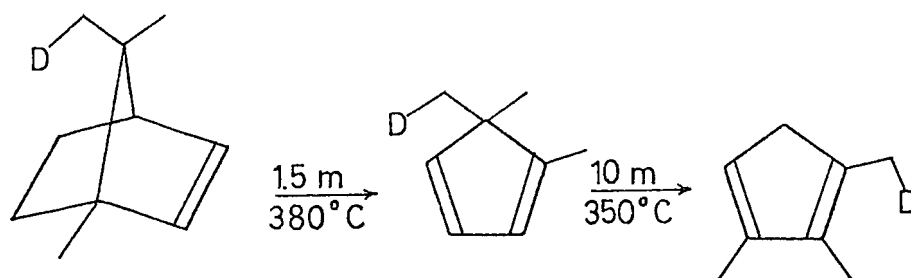
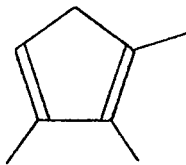
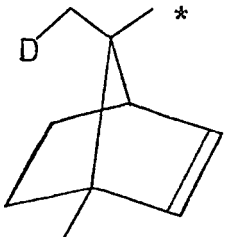
Cmpd	% d <sub>0</sub>	% d <sub>1</sub>	% d <sub>2</sub>	% d <sub>3</sub>	Total Atom %
	22.7	55.8	17.7	3.8	102.6
	16.9	67.2	12.9	3.0	102.0

TABLE VIII

MASS SPECTRAL ANALYSIS OF BORNYLENE-9-d THERMOLYSIS

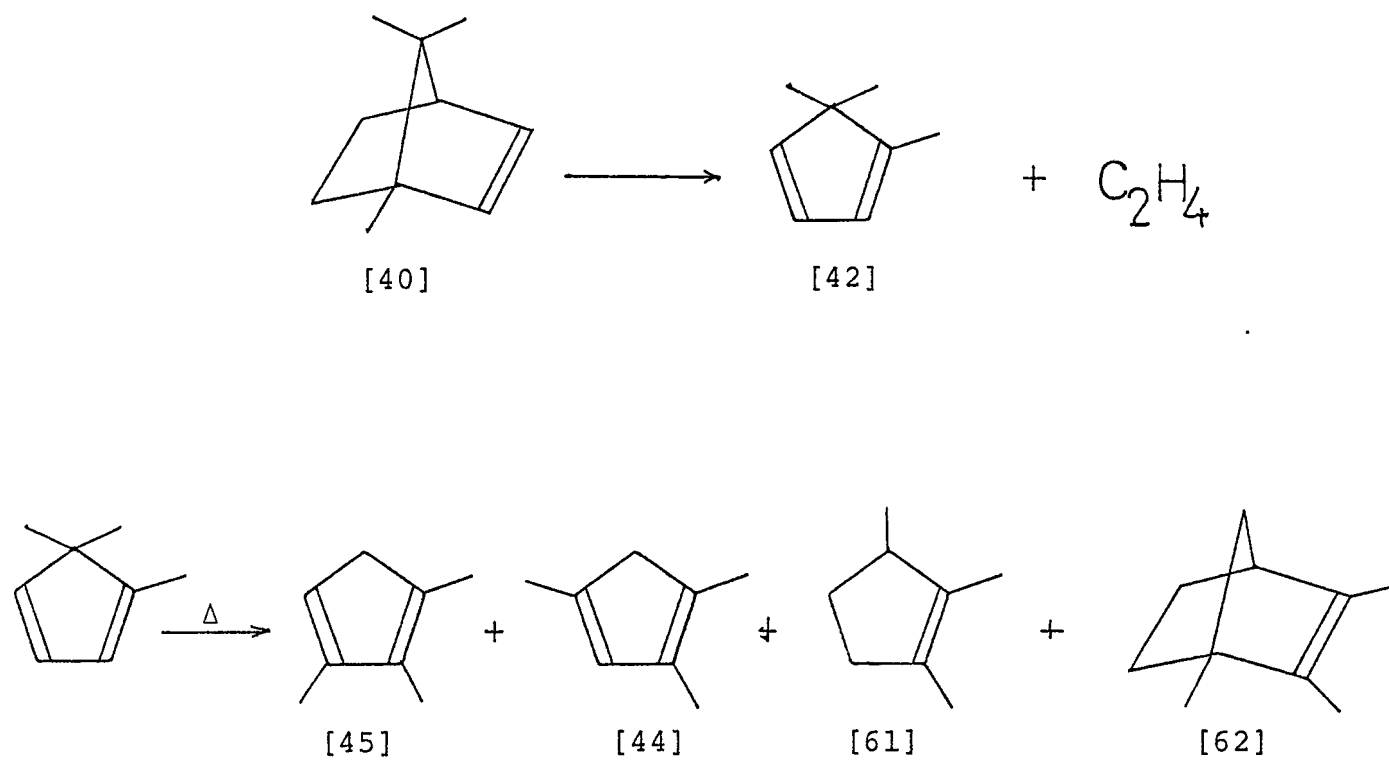
PRODUCTS: 350°/25 min



Cmpd	%d <sub>0</sub>	%d <sub>1</sub>	%d <sub>2</sub>	%d <sub>3</sub>	Total Atom %
	22.8	59.6	15.2	2.4	97.2
	3.0	96.5	1.0	0	98.5

\*Starting material

TABLE IX  
THERMOLYSIS OF 1,5-DIMETHYL-5-DEUTERIOMETHYL-  
CYCLOPENTADIENE: 350°C/10 min



SCHEME I. Products from Thermolysis of Bornylene at 380°C for 3 min.

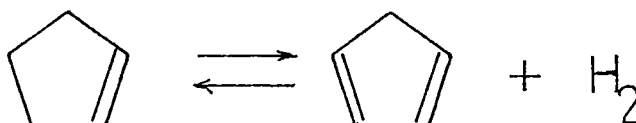
## DISCUSSION OF RESULTS

In a repeat of Scheme I, five rearrangement products were isolated from the thermolysis of bornylene. The search for  $\Delta^2$ -carene proved futile as it had to be less than 1% of the reaction products. Thus, a reverse vinylcyclopropane rearrangement, similar to that in the Roth experiment ([12]  $\rightarrow$  [14]), is not operating in this bicyclo[2.2.1]heptene system. Indeed, the propensity of bornylene to undergo a retro Diels-Alder reaction appears to be its most significant, and perhaps only, thermal process.

$\epsilon$ -Fenchene [62] and laurolene [61] are the most unexpected products, the two trimethylcyclopentadienes obviously resulting from methyl migrations. The existence of  $\epsilon$ -fenchene is an understandable recombination of 1,2,3-trimethylcyclopentadiene and ethylene. The occurrence of 1,2,3-trimethylcyclopentene is more difficult to rationalize. Conceptually, the presence of [61] could be the result of bornylene undergoing a cycloreversion to acetylene and 1,5,5-trimethyl bicyclo[2.1.0]pentane [64], followed by rearrangement of [64]  $\rightarrow$  [61]. This pathway, perhaps unlikely, can be disregarded by the observation that the thermolysis of bornylene-2-d produced laurolene with a total deuterium content virtually indistinguishable from the starting material. The deuterium should have been lost in the acetylene. Since the intermediacy of [64] is ruled out, a



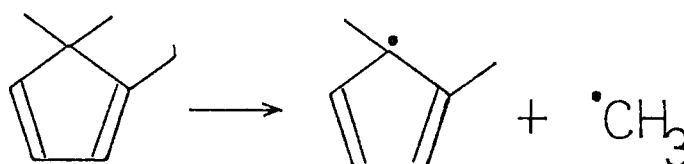
second rationale is necessary. The structural similarity between 1,2,3-trimethylcyclopentadiene and 1,2,3-trimethylcyclopentene appears as though hydrogenation of the [45] produces [61]. The source of hydrogen is not obvious but qualitatively could have arisen from decomposition, as evidenced by considerable carbonaceous material on the walls of the ampoule. It may be noted that Walsh and Grant<sup>59</sup> reported the gas phase decomposition of cyclopentene is unexpectedly reversible.



This account complements our proposed pathway for the existence of [61]. Even though this is an attractive explanation it is a conjecture in need of further investigation.

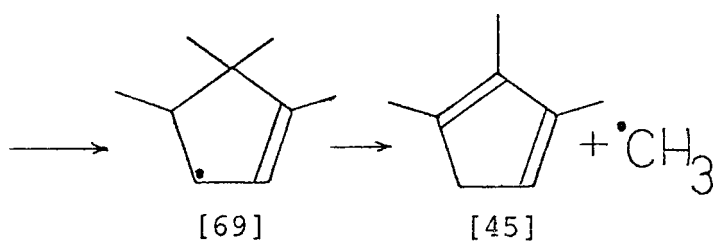
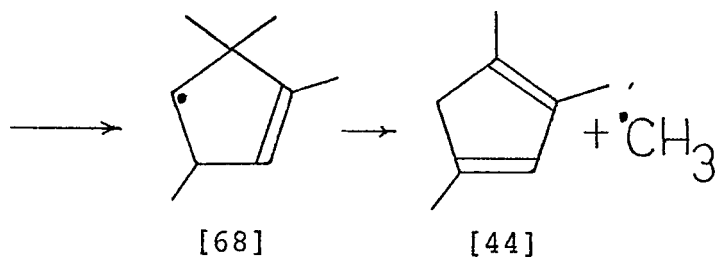
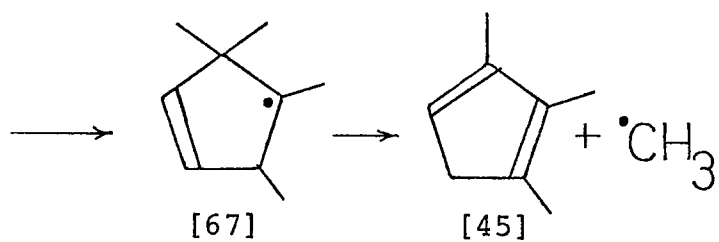
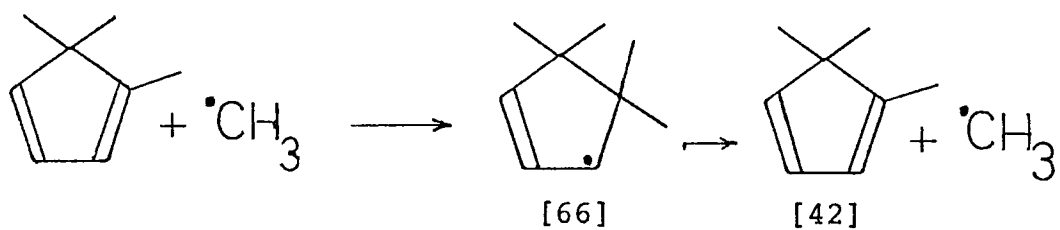
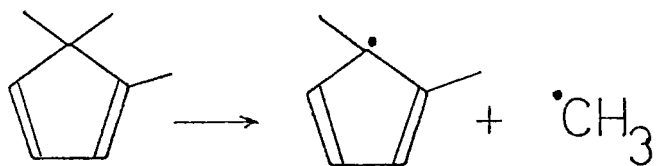
The intra- or intermolecularly of the rearrangement of 1,5,5-trimethylcyclopentadiene has not been seriously challenged experimentally. The use of isotopically labelled substrates furnishes such a challenge. Thermolysis of bornylene-9-d<sub>1</sub> provides a means to follow the methyl migrations without perturbing the system. Similarly, bornylene-2-d examines the hydrogen migrations. As can be seen from

Tables IV-IX, two features are immediately obvious. First, the vinylic hydrogens remain attached to the same molecule for a large part of the reaction time. For example, Table IV shows [45], isolated early in the reaction, to have about 5% of the molecules containing two deuteriums. Longer reaction times mix the labels only slightly more. Second, there is extensive mixing of methyl labels under all thermolysis conditions. This observation is easily rationalized by the occurrence of a radical chain reaction initiated in the following manner:



Following this chain initiating step, the methyl radical can then add to the remaining 1,5,5-trimethylcyclopentadiene molecules in one of four positions as shown in Scheme II.

It is interesting to note that loss of any methyl group from [66] gives 1,5,5-trimethylcyclopentadiene in a degenerate rearrangement. Intermediates [67] and [69] both lead to the 1,2,3-trimethyl isomer [45] while [68] yields 1,2,4-trimethylcyclopentadiene [44]. Several facts concerning product distribution become obvious on the basis of this mechanism. The preponderance of the 1,2,3 isomer is justified



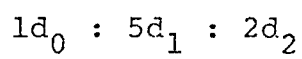
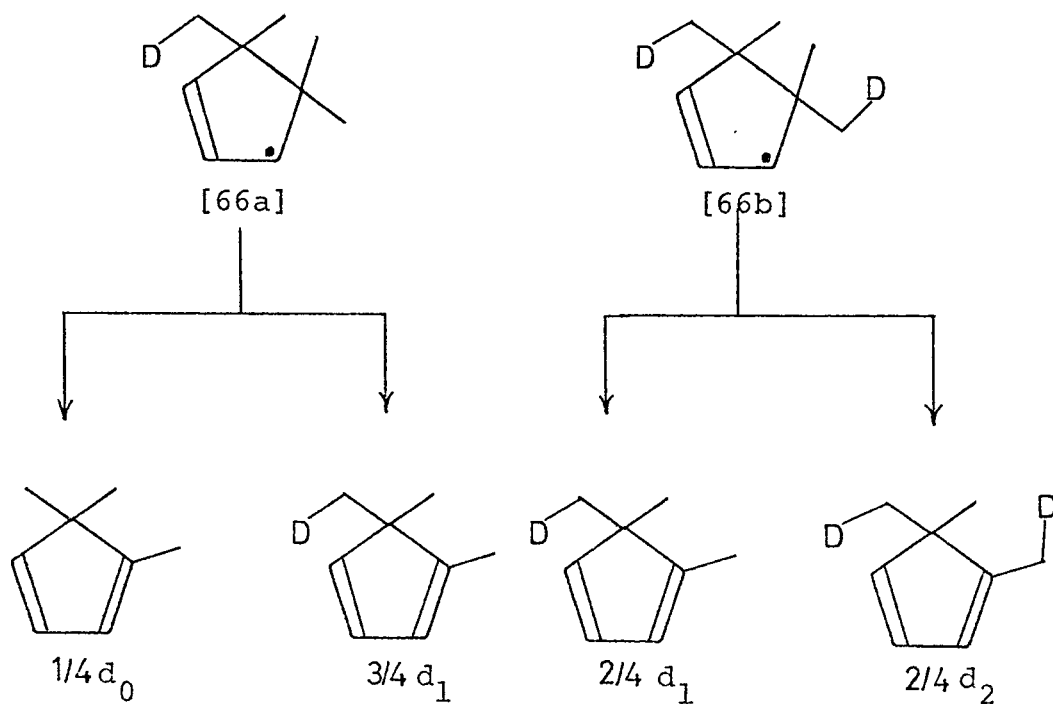
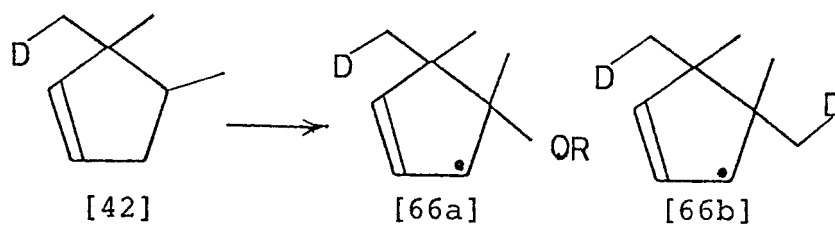
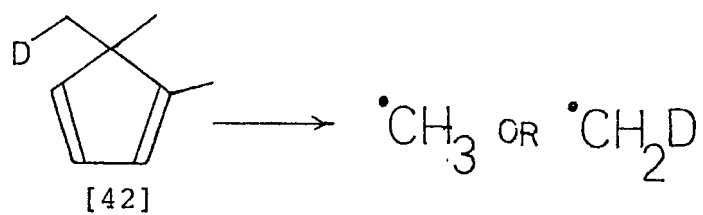
Scheme II.

by allylic radical stabilization in [69], making this a favored pathway. In addition, a second pathway is available for its formation. By the same argument, the lack of the 1,2,4-trimethyl isomer is related to the unconjugated radical [68]. Further, the 1,5,5-trimethylcyclopentadiene isolated early in the reaction should show some mixing of labels due to the availability of the degenerate 1,5,5-1,5,5 rearrangement. Once again, this coincides with experimental observations as seen in Table VI. Augmenting this is the report by Boriack<sup>6ld</sup> who, in the course of synthesizing bornadiene-9-d<sub>1</sub>, noted that the integrity of the methyl label in 1,5-dimethyl-5-deuteriomethyl cyclopentadiene had gone awry, even at very low conversions. Finally, and most importantly, the methyl migration in the cyclopentadiene system is obviously intermolecular, contrary to previous reports.

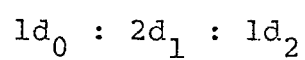
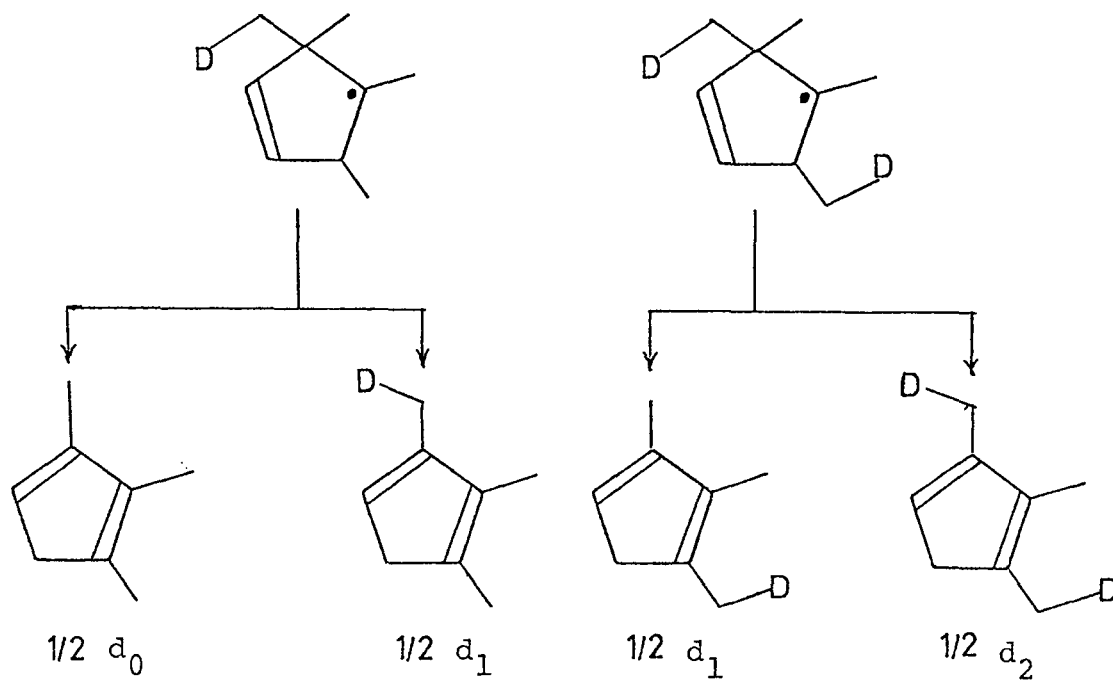
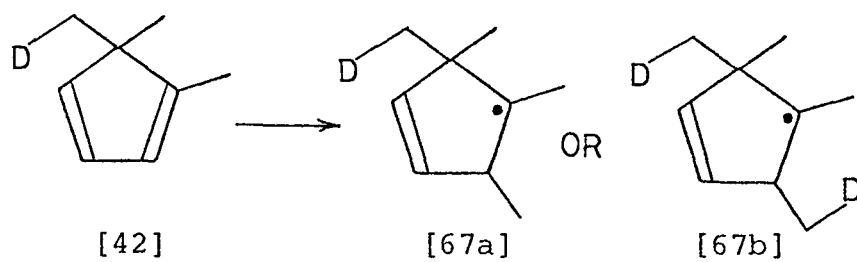
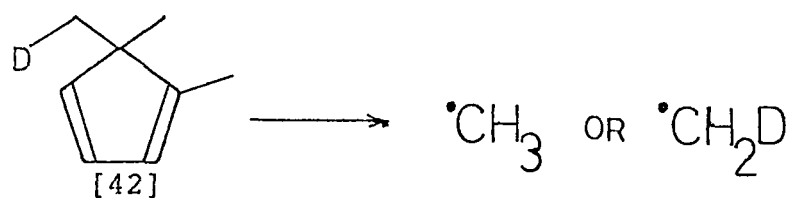
Statistically, the degenerate rearrangement with [42]-d<sub>1</sub> should lead to a different deuterium distribution than any of the other processes. These are summarized in Scheme III. Compound [42] has two modes of chain initiation available: loss of  $\cdot\text{CH}_3$  or loss of  $\cdot\text{CH}_2\text{D}$ . Each event has an equal probability of occurring, i.e., 1/2. Subsequent addition of the methyl radical to another [42]-d<sub>1</sub> molecule leads to two statistically equivalent 1,1,5,5-tetramethyl radicals.

The elimination of methyl radical has several possible outcomes in regenerating the 1,5,5-trimethyl isomer. Radical [66a] can lose any one of three non-deuterated methyls to yield [42]-d<sub>1</sub>. Loss of the deuterated methyl occurs once every four events to yield [42]-d. The second tetramethyl radical [66b] has equal probability of losing  $\cdot\text{CH}_3$  or  $\cdot\text{CH}_2\text{D}$  in any one of four events. Thus, the ratio of d<sub>0</sub>:d<sub>1</sub>:d<sub>2</sub> in the degenerate 1,5,5-1,5,5 rearrangement is 1:5:2.

Addition of methyl- or deuterio methyl radical to any one of three other positions in the cyclopentadiene skeleton leads to a different ratio. The possible outcomes are summarized in Scheme IV. Once again, the two tetramethyl radicals have different pathways in which to eliminate a methyl radical. This time, however, only one of the two geminal methyl groups can reasonably be lost, each event having equal probability. This leads to a d<sub>0</sub>:d<sub>1</sub>:d<sub>2</sub> ratio of 1:2:1. Significant deviations from either ratio (for example, the appearance of molecules containing 3 deuterium atoms) can be attributed to chain initiation from a 1,5,5-trimethylcyclopentadiene that has previously undergone a degenerate rearrangement. Understandably, the statistical deuterium distribution becomes more complicated.



Scheme III



Scheme IV

Kloosterziel<sup>44b</sup> cited the exclusive formation of 1,2,3-trimethylcyclopentadiene from the 1,5,5-trimethyl isomer as evidence in favor of intramolecularity in the reaction. Since we know small amounts of [44] exist in the thermolysis of [42], this argument is refuted. Mironov maintains that the non-appearance of di- and tetramethylcyclopentadienes is proof of intramolecularity in the reaction. Scheme II shows that disproportionated molecules can not appear except in chain termination processes. Any reasonable chain length will cause di- and tetramethyl cyclopentadienes to appear only in negligible amounts. The most critical evidence against an intermolecular pathway is that observed by Kloosterziel in the thermolysis of trans-6,9-dimethylspiro[4.4] nona-1,3-diene [55]. Reiterating, Kloosterziel interprets the stereospecificity maintained in the rearrangement product as unquestionable evidence in favor of a concerted [1,5] sigmatropic shift of an alkyl group. Even this experiment can be reconciled in terms of a radical process.

Kloosterziel's molecule has the means to trap a diradical internally. As discussed in the introduction, compounds providing an internal trap are expected to be difficult to test for concertedness. Since the radical mechanism is so well behaved in the 1,5,5-trimethylcyclopentadiene system, it is unreasonable to expect a change in mech-



anism in the closely analogous spiro[4.4]nona-1,3-diene system. This being the case, the stereospecificity observed by Kloosterziel in the reaction [55]  $\rightarrow$  [56] is due to the diradical intermediate having an extremely short lifetime. This is evidenced by the fact that the sigma bond recloses faster than rotation of the methyl group about a single bond. Comparison of proposed reaction coordinate diagrams of a reaction in Scheme II (excluding the dengerate 1,5,5-1,5,5 rearrangement) and the rearrangement [55]  $\rightarrow$  [56], as in Figures 8 and 9, leads to a potential well in the latter reaction estimated to be 1 kcal or less.

Concluding, it is frequently difficult to decide whether or not a reaction is intermolecular, much less whether or not it is concerted. We have presented direct experimental evidence that a well documented intramolecular reaction is, in actuality, intermolecular. It is not surprising, then, that Benson and O'Neal have stated that existing evidence in the trimethylcyclopentadiene system is "probably not reliable as a unimolecular process!"<sup>51</sup> Our evidence removes sigmatropic shifts of alkyl groups in cyclopentadiene from consideration as a significant thermal process. Further, it intensifies the fact that molecules providing internal traps for diradicals are extremely difficult to characterize in terms of concerted or diradical processes.

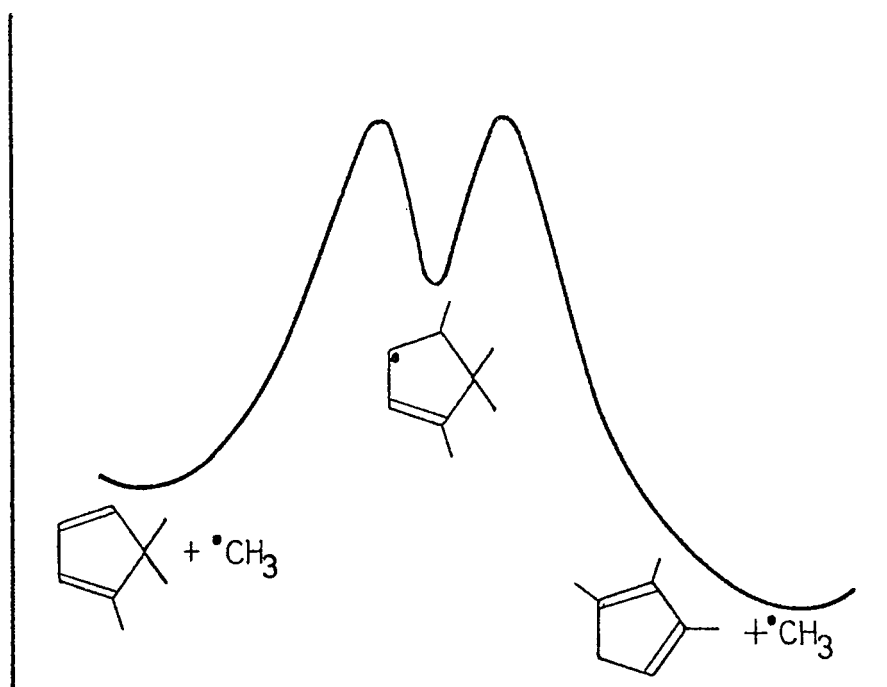


FIGURE 8. Proposed Reaction Coordinate Diagram  
Addition of Methyl Radical to [42]

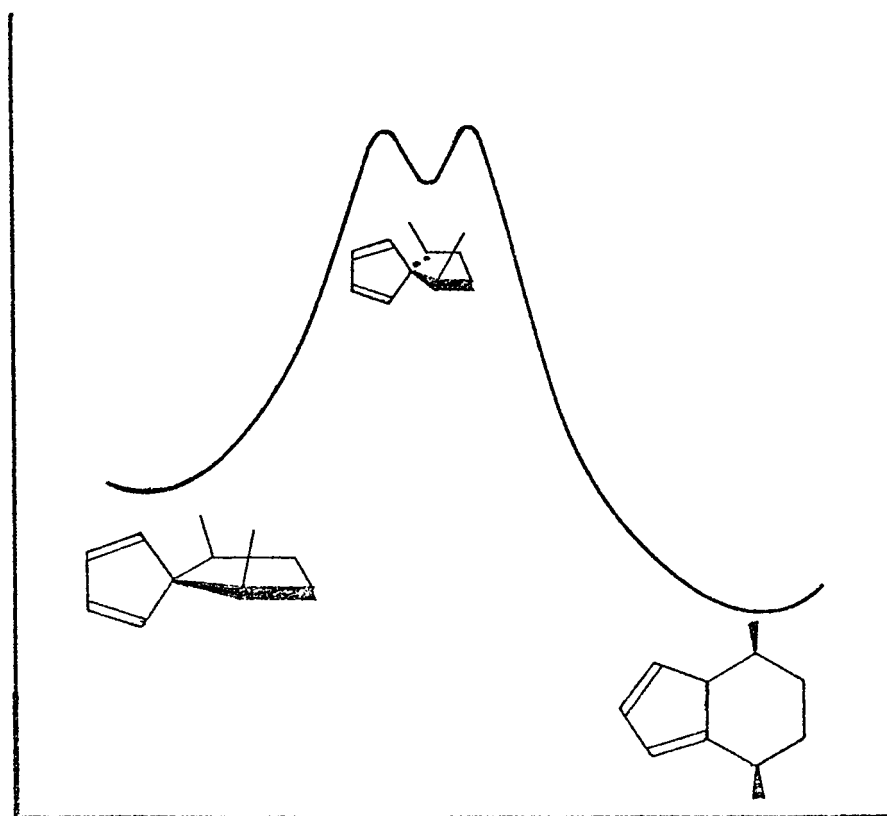


FIGURE 9. Proposed Reaction Coordinate Diagram  
for Formation of Diradical from [55]

Another compound providing such a trap is 2-cyano-1-vinylcyclopropane.

#### KINETICS OF 2-CYANO-1-VINYLCYCLOPROPANE

Preliminary investigation of the cis-trans isomerization in cyanovinylcyclopropane<sup>60</sup> indicated the proper temperature range to begin a detailed kinetic study in our gas phase stirred flow reactor. Similar flow reactors are used for kinetic studies because the accuracy obtainable over the more frequently employed evacuated ampoules is increased. The apparatus used in our laboratory was adapted from the system described by Lewis and Herndon<sup>61a,b,c</sup> and described specifically by Boriack.<sup>61d</sup>

Samples for analysis are collected in a trap cooled with dry ice and acetone. The material collected in this manner is analyzed by gas chromatography utilizing a flame ionization chromatograph. The column is a 500 ft capillary (0.02" i.d.) column coated with Co-990. The relative size of the peaks is determined by a digital readout integrator that is connected in parallel with a recorder. This provides both conventional and integral representation of the chromatograph output.

For 2-cyano-1-vinylcyclopropane the rate constants were calculated using the digital data and algebraic rela-

tionships characteristic of stirred flow reactors. These equations are based on the assumption that in a stirred flow reactor the components of a reaction reach a steady state.\* Ordinarily, when steady state is achieved, the reactant disappears at a rate equal to the formation of products. For 2-cyano-1-vinylcyclopropane, the algebraic expressions describing the system are complicated by the facile reversibility of the components as shown in Scheme V.

Mathematically, the rate constants are determined by approaching the equilibrium first from one side and then the other. Experimentally, this is accomplished by placing either the pure cis or pure trans isomer in the vaporizer. Assuming first order kinetics, the expressions governing the situation are derived in the following manner.

$$U[C_o] = U[C] + k_1V[C] - k_2V[T] \quad (\text{Equation 1})$$

$$[C_o] = [C] + [T]**$$

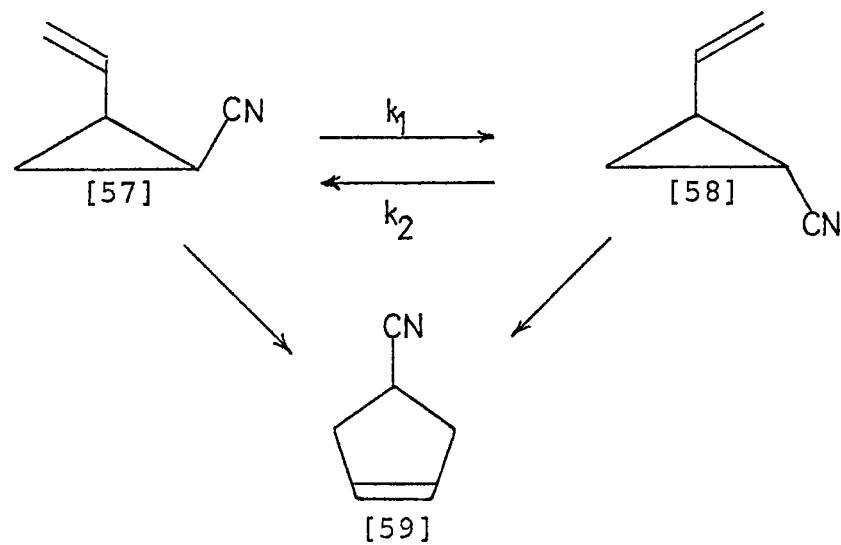
Substituting into Equation (1)

$$\begin{aligned} U[C] + U[T] &= U[C] + k_1V[C] - k_2V[T] \\ k_1V[C] &= U[T] + k_2V[T] \\ k_1\frac{[C]}{[T]} &= \frac{U}{V} + k_2 \end{aligned} \quad (\text{Equation 2})$$

---

\*Steady state means the composition of the vapors within the reactor does not vary with time.

\*\*This expression is a material balance equation, i.e., the total amount of material entering the reactor has to equal the sum of the material exiting the reactor.



Scheme V

A similar expression may be derived for the trans isomer,

$$U[T_O] = U[T] + k_2V[T] - k_1V[C] \quad (\text{Equation 3})$$

$$k_2 \frac{[T]}{[C]} = \frac{U}{V} + k_1 \quad (\text{Equation 4})$$

where  $[C_O]$  and  $[T_O]$  are initial concentrations of cis and trans-2-cyano-1-vinylcyclopropane,  $V$  is the volume of the reactor,  $U$  is the flow rate,  $k_1$  and  $k_2$  are the first order rate constants, and  $[C]$  and  $[T]$  are concentrations of the cis and trans isomers. Thus, to use these expressions, only the ratio of the concentrations of cis and trans-2-cyano-1-vinylcyclopropane are necessary and these can be obtained from integrated areas of the GLPC trace.

Values for the rate constants are determined in the following manner.

$$\begin{array}{ll} k_1 \frac{C}{T} = \frac{U}{V} + k_2 & k_2 \frac{T}{C} = \frac{U}{V} + k_1 \\ k_1 = 0, k_2 = -\frac{U}{V} & k_1 = 0, k_2 = \frac{U/V}{T/C} \\ k_2 = 0, k_1 = \frac{U/V}{C/T} & k_2 = 0, k_1 = -\frac{U}{V} \end{array}$$

Beginning with the pure cis isomer in the vaporizer and a given temperature and flow rate,  $k_1$  is set equal to zero and a value for  $k_2$  is determined. Setting  $k_2 = 0$ , a value for  $k_1$  is obtained. Values for  $k_1$  and  $k_2$  are obtained similarly for several flow rates. The cis isomer is replaced with

trans in the vaporizer and the process is repeated. The values thus obtained are plotted on a graph of  $k_1$  vs.  $k_2$  (see Figure 10). The intersection of the lines determines the values of  $k_1$  and  $k_2$  for the specified temperature.

Testing the model for possible second order complications was accomplished by varying the partial pressure of the isomer in the vaporizer. This was achieved by varying the temperature of the water circulating in the vaporizer, i.e., 32°C → 45°C → 58.5°C. The ratio of concentrations remained essentially constant indicating the first order model is correct. A test for fractionation revealed a surprising result. For this test the vaporizer was charged with a 50:50 mixture of cis and trans-2-cyano-1-vinylcyclopropane. Sampling the vaporizer contents about 1 1/2 hours apart revealed that the trans isomer is removed much faster than the cis isomer. Fortunately, the kinetic parameters are determined by charging the vaporizer with either pure cis- or pure trans-2-cyano-1-vinylcyclopropane, thus eliminating any problems of fractionation.

The rate constants for the isomerization of cis- and trans-2-cyano-1-vinylcyclopropane were determined over the range of 210.0-258.54°C, using equations (2) and (4). Conversion to 4-cyanocyclopentene was a negligible side reaction even at the highest temperature studied. The rate constants, obtained graphically, were subjected to error analysis.<sup>62</sup>

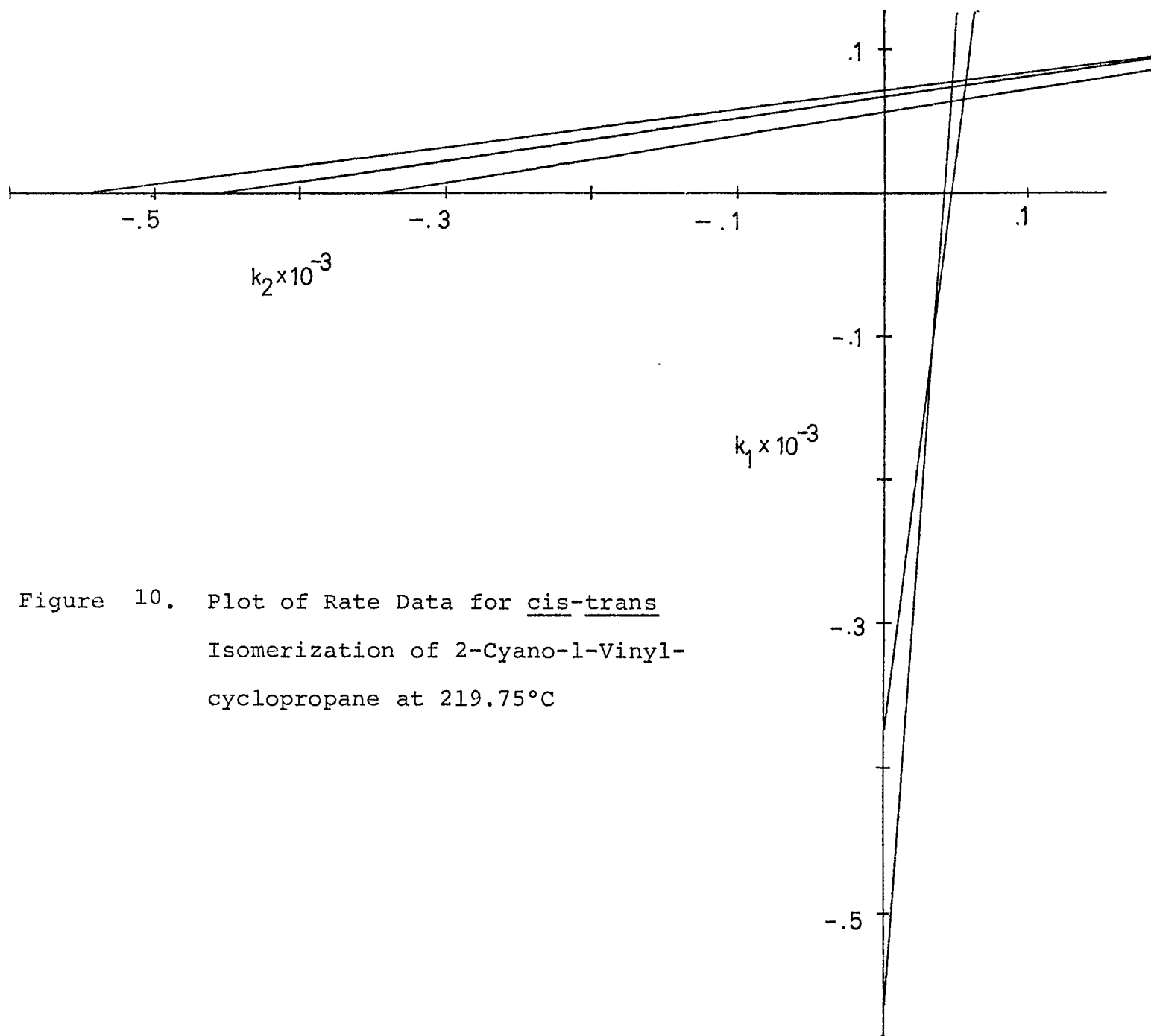


Figure 10. Plot of Rate Data for cis-trans  
Isomerization of 2-Cyano-1-Vinyl-  
cyclopropane at 219.75°C



The Arrhenius parameters, calculated from a linear least squares analysis of  $\log [(k_1 \pm \sigma_1) + (k_2 \pm \sigma_2)]$  vs.  $1/T$  where  $\sigma$  represents standard deviation obtained from the error analysis, were fit to the equation

$$\log_{10} k = \log_{10} A - E_a/2.303RT$$

Values obtained in this manner are shown in Table IV. A graph of this data is shown in Figure 11.

#### DISCUSSION OF RESULTS

The geometrical isomerization of 2-cyano-1-vinylcyclopropane was found to fit the equation

$$k = 10^{14.45 \pm .22} \exp (-41,060 \pm 1660/RT)$$

As is the case in the report by Willcott and Cargle<sup>19</sup> concerning randomization of stereochemistry in cis-1,2-dideuteriovinylcyclopropane, we wish to test the kinetic results on the basis of a trimethylene intermediate. In view of the fact that kinetic data for structural isomerization of vinylcyclopropane to cyclopentene is consistent with an allylically stabilized intermediate, as explained in the introduction, it is logical to rationalize our lower energy of activation as consistent with an intermediate diradical stabilized by allylic and cyano resonances. Further, since

TABLE IV  
AVERAGE RATE CONSTANTS FOR CIS-TRANS ISOMERIZATION  
OF 2-CYANO-1-VINYLCYCLOPROPANE

Temperature	$k_1 \times 10^{-4}$	$k_2 \times 10^{-4}$
210.00°C	.425 ± .01	.335 ± .09
219.75°C	.713 ± .06	.520 ± .05
227.50°C	1.74 ± .21	1.39 ± .18
239.90°C	4.99 ± .65	3.81 ± .37
258.54°C	20.99 ± 1.83	15.60 ± 1.88

TABLE V  
ARRHENIUS PARAMETERS FOR CIS-TRANS ISOMERIZATION  
OF 2-CYANO-1-VINYLCYCLOPROPANE

log A	$E_a$ , kcal/mole
14.45 ± .22	41.06 ± 1.66

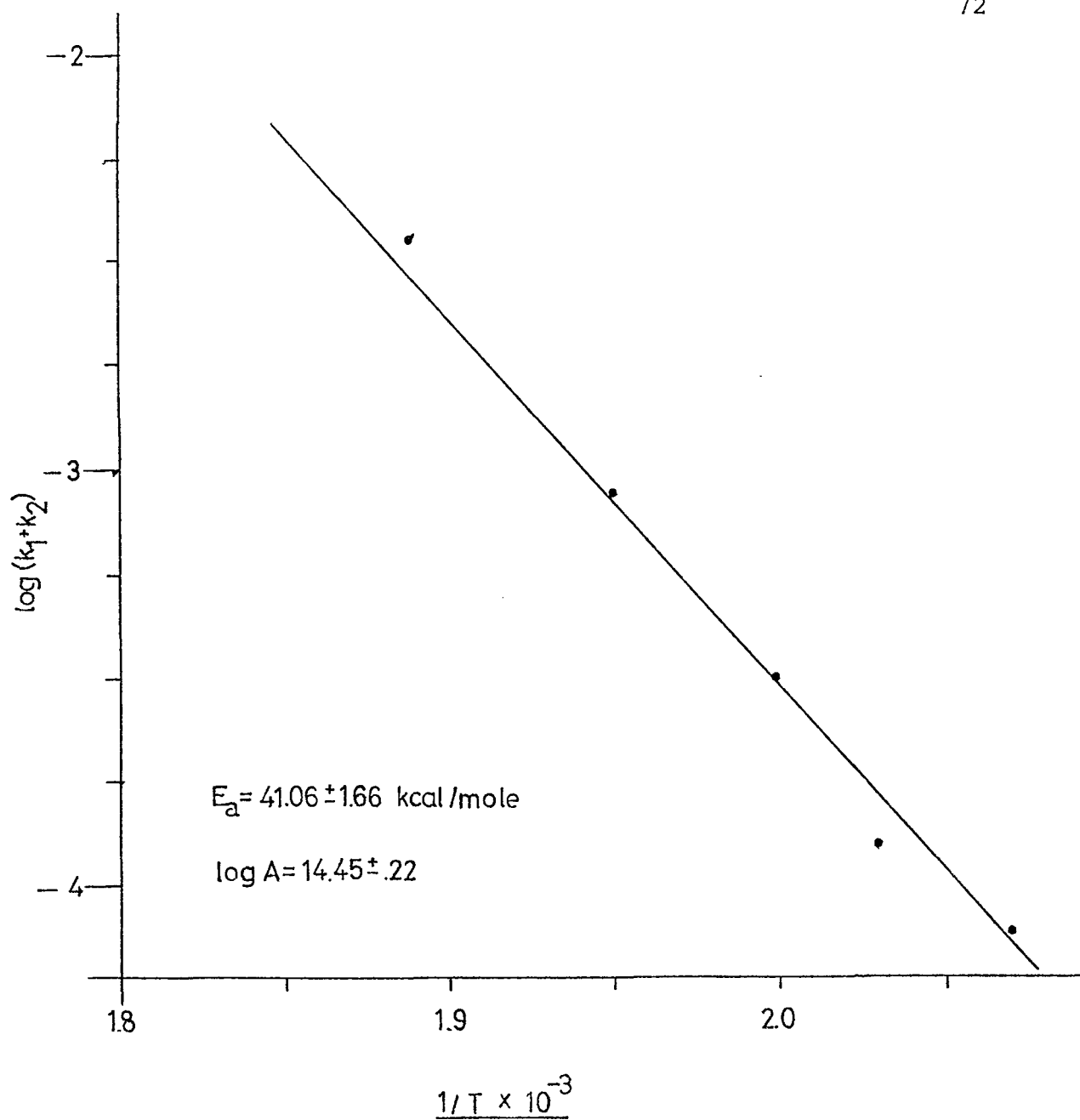
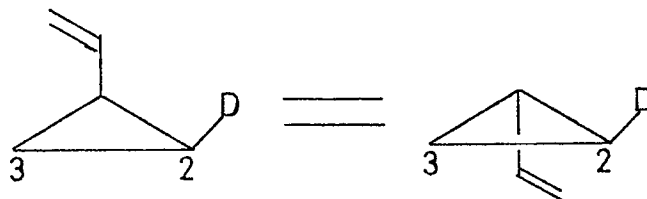


Figure 11. Plot of Rate Constants vs.  $1/T$  for cis-trans Isomerization of 2-Cyano-1-Vinylcyclopropane

the  $E_a$  for the isomerization [57]  $\rightarrow$  [58] is lower than that expected for vinylcyclopropanes (see Table II), the difference can be attributed to cyano resonance stabilization. Comparing this with the energy of activation for geometrical isomerization of trans-1-deuterio-2-vinylcyclopropane ( $E_a = 48.2$ ),<sup>34</sup> an appropriate model, a value of 7 is obtained for the  $\cdot\text{CH}-\text{C}\equiv\text{N}$  resonance stabilization.

The diradical viewpoint is supported by previous work in both cyclopropanes and substituted cyclopropanes. The very observation of a geometrical isomerization in 2-cyano-1-vinylcyclopropane is evidence in favor of this mechanism. In trans-1-deuterio-2-vinylcyclopropane a concerted process involving epimerization at C1 and C3 would lead to geometrical isomerization. The outcome is indistinguishable from a radical process leading to isomerization.



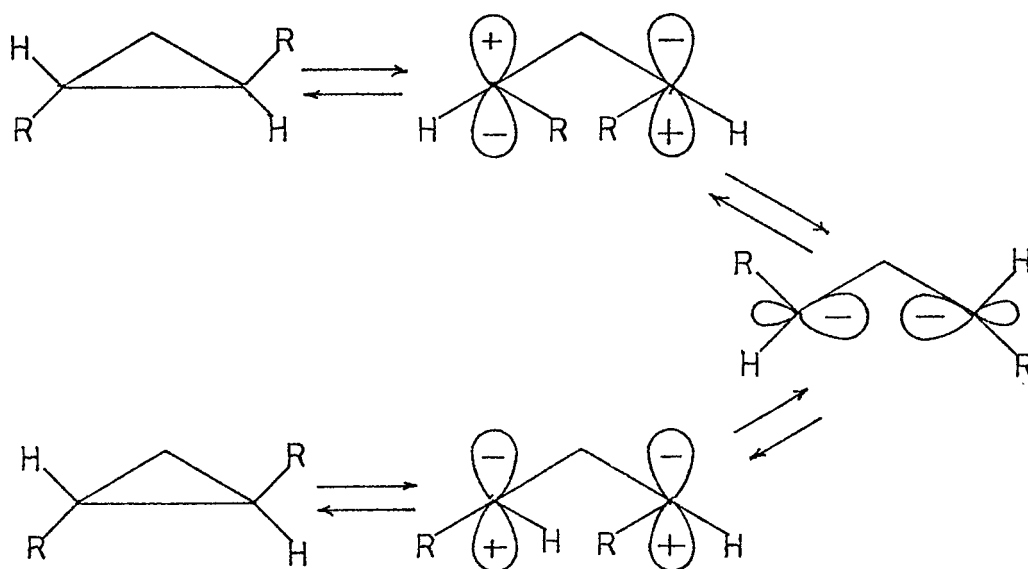
A similar situation exists in 2-cyano-1-vinylcyclopropane because it lacks an optimum labelling scheme. However, since the C1-C2 bond is evidently the weakest, it is obligated to break first.\* This would preclude a concerted reaction since

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\*Even in concerted reactions, the bond that breaks is the same one that would lead to the most stable diradical intermediate.

it does not afford a pathway for cis-trans interconversion when rupture of the C1-C2 bond occurs.

The scheme below shows that concerted disrotatory or conrotatory motions involving C1 and C2 cannot produce cis-trans isomerization.



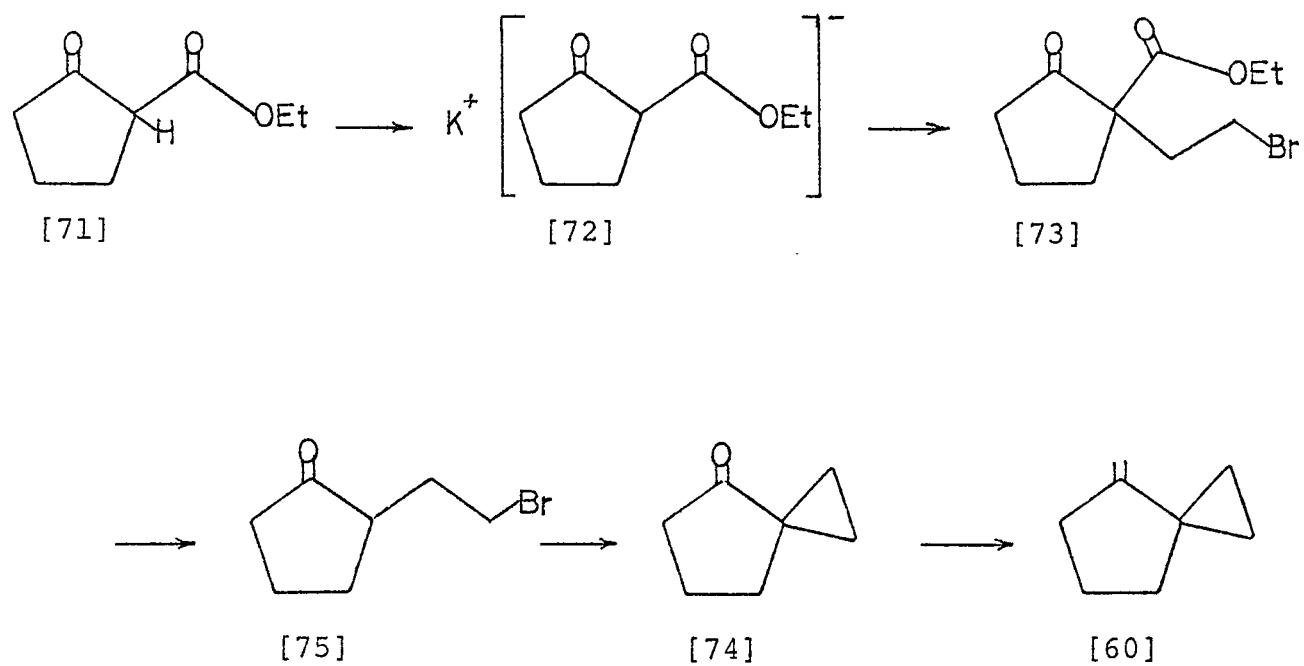
We interpret the evidence presented in favor of a diradical intermediate similar to that proposed for cis-1,2-dideuteriovinylcyclopropane [4]. Secondly, the value 7 kcal for  $\dot{\text{C}}\text{H}-\text{C}\equiv\text{N}$  stabilization is the most accurate estimate available. It is intended to replace the 11.7 kcal presently in use.

THE SYNTHESIS OF 4-exo-METHYLENE-SPIRO[2.4]HEPTANE [60]

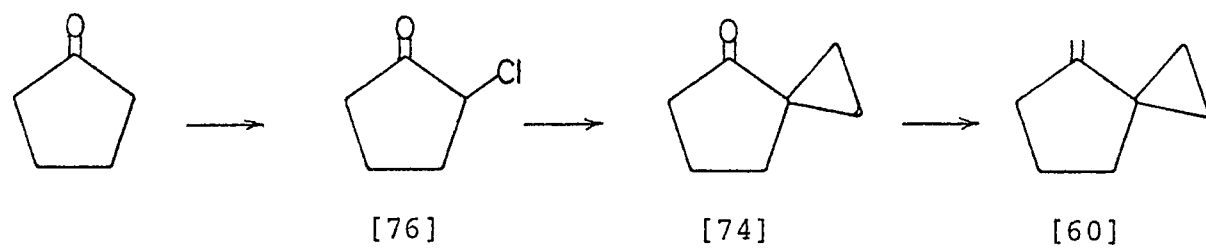
This simple but unusual hydrocarbon was synthesized by two routes. Overall yields in each case were essentially identical.

Scheme VI outlines the method adapted from a procedure by Mayer and Alder.<sup>64</sup> Beginning with 2-carbethoxy cyclopentanone, the potassium salt [71] was obtained and subsequently heated in the presence of an excess of 1,2-dibromoethane to give 2-( $\beta$ -bromoethyl)-2-carbethoxy cyclopentanone [72]. This material was decarboxylated with 47% HBr yielding 2-( $\beta$ -bromoethyl)-cyclopentanone [73]. Internal nucleophilic displacement of bromide was accomplished with potassium hydroxide to yield the spiro ketone [74]. Spiro[2.4] heptane-2-one was converted to the exo-methylene compound [60] via the Wittig reaction.

Scheme VII arrives at the same product but by quite a different route. Cyclopentanone was chlorinated directly by chlorine gas to give 2-chlorocyclopentanone[76]. Treatment of [76] with trimethyloxosulfonium iodide, a reagent described by Corey,<sup>65</sup> yielded spiro[2.4]heptane-2-one in a single step. According to the literature report,<sup>66</sup> the mechanism of this reaction is not, as yet, fully understood.



Scheme VI

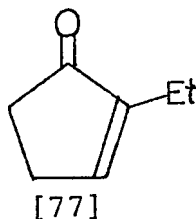


Scheme VII



THERMOLYSIS OF SPIRO[2.4]HEPTANE-2-ONE [74] AND 4-exo-METHYLENE SPIRO[2.4]HEPTANE [60]

The spiroketone [74] was an intermediate in the synthesis of [60]. The availability of [74] made it desirable to thermolyze it in order to establish the similarity, if any, to the studies by Willcott and Sapp<sup>68</sup> on cyclopropane carboxaldehyde. Compound [74] was thermolyzed in an evacuated ampoule for 100 minutes at 400°C. The reaction mixture had two products in approximately equal amounts as indicated by GLPC. NMR analysis indicated one component was unchanged ketone and the second was consistent with the structure 2-ethyl-2-cyclopentenone [77]. Subsequent UV analysis confirmed this suspicion.



214    base

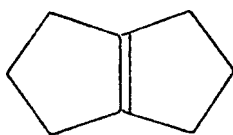
10    α-substituent

224 mμ predicted

220 mμ observed

The spiro olefin [60] was subjected to preliminary thermolysis in a similar manner. The sealed tube was removed from the oven after 60 minutes at 350°C. NMR analysis of the

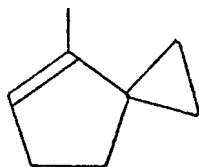
only product showed a broad singlet at 2.1  $\delta$ . A report in the literature<sup>74</sup> confirms that this material is, as suspected,  $\Delta^{1,5}$ -bicyclo[3.3.0]



[78]

#### KINETICS OF 4-exo-METHYLENE SPIRO[2.4]HEPTANE [60]

The attempt to determine the kinetic parameters for the reaction [60]  $\rightarrow$  [78] was made in the previously described kinetics oven. However, [60] was unusually sensitive in its rearrangement to [78]. At any given temperature, the extent of conversion to  $\Delta^{1,5}$ -bicyclo[3.3.0]octene was almost identical at the different flow rates. In addition, a third component identified as 4-methyl spiro[2.4] was found in the thermolysis products. We suspected a



[79]

reactive site was catalyzing the reaction. Several attempts were made to pacify the vessel. These included sweeping it with dry ammonia gas, passing trimethylsilyl chloride through

the reactor and a combination of the two. The data was well-behaved only briefly after such treatments. The pyrex vessel was removed from the oven and washed thoroughly with chromic acid, distilled water, dilute  $\text{NH}_4\text{OH}$ , rinsed and replaced in the oven. Even such drastic measures did little to improve the data. Finally, the entire glass reaction vessel was replaced by a new one. Even this substitution did not remedy the problem. This problem was surprising in view of the fact that the apparatus had been used in kinetic studies previously by other investigators<sup>61d,68,75</sup> and in this work<sup>75,68</sup> all with satisfactory results. Since that time the oven has been used in thermolysis of other hydrocarbons, also with reasonable outcomes.<sup>76</sup>

We conclude therefore that the molecule [60] is unexpectedly sensitive to a catalytic effect suffered in the reactor. Thus, only the qualitative aspect that this is another example of the vinylcyclopropane-cyclopentene rearrangement was obtained from this study.

## CHAPTER III

## CONCLUSIONS

## CONCLUSIONS

The evidence presented in this work establishes the fact that the study of chemical bond breaking and making processes is a difficult task. As stated previously it is not easy to determine if a reaction is intramolecular or intermolecular, much less concerted. The abundance of experimental evidence in the bornylene rearrangement was unable to ascertain the molecularity of the reaction until the present study of the isotopic distribution in the thermolysis products. This implies that the proper choice of label and labelling scheme is also an arduous proposition.

To aid in the selection of proper labels, the stabilization energy of  $\text{-}\dot{\text{C}}\text{H-C}\equiv\text{N}$  has been determined to be 7 kcal/mole. The innocuous cyano group is often overlooked when choosing a label to follow the course of a thermal reaction. The relatively small size of the cyano group decreases the amount of steric interaction as compared to some labels such as acetate. Indeed, it would not be surprising to find that the cyano group is used more frequently in future studies of thermal reactions.

CHAPTER IV  
DESCRIPTION OF THE EXPERIMENTS

## DESCRIPTION OF THE EXPERIMENTS

Infrared (IR) spectra were recorded on either a Beckman Model IR-10 or Perkin-Elmer Model 700 infrared spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained from either a Varian Associates Model HA-100 or T-60 spectrometer. Chemical shifts are reported as parts per million downfield from TMS using the  $\delta$  scale. NMR data are presented in the order (chemical shift) : multiplicity, s = singlet, d = doublet, t = triplet, q = quartet; m = multiplet, b = broadened; integration, assignment. Mass spectra were obtained from a Hitachi Perkin-Elmer Model RMU-6H mass spectrometer operated near the ionization potential. Ultraviolet spectra were recorded on a Cary Model 15 spectrometer. Preparative gas chromatography was performed using a Varian Aerograph A-90-P3 chromatograph equipped with a thermal conductivity detector. Helium was used as a carrier gas in several 0.25 inch diameter packed columns. Analytical gas chromatography was performed on an Aerograph Hy-Fi Model 600 hydrogen flame chromatograph equipped with a 500' .02 i.d. column coated with CO-990. Integration of the GLPC peaks was accomplished with an Infotronics Model CRS-10HB digital readout integrator.

Tosylhydrazine.<sup>73</sup> One hundred grams of p-toluene-sulfonyl chloride was dissolved in 200 mls benzene. The reaction flask was cooled in ice and 60 grams hydrazine in 10 mls H<sub>2</sub>O were added over a period of 40 minutes. The solution was allowed to stir for 3 hours at room temperature. The white solid in the flask was collected by filtration and then recrystallized rapidly from water. The yield was 50 grams (61%); mp 105-108°C, lit. mp<sup>73</sup> 104-107°C.

Camphor Tosylhydrazone. Adapting the procedure of Depuy and Froemsdorf,<sup>75</sup> a two liter reaction flask was fitted with a mechanical stirrer, condensor, and addition funnel. Five hundred mls 1% ethanolic HCl was placed in the flask and to this was added 56 grams of tosylhydrazine. Forty-five grams of camphor were added and the mixture was heated to reflux for 40 minutes. After cooling the reaction mixture was poured into 500 mls of H<sub>2</sub>O. A precipitate formed immediately and was collected by vacuum filtration. The material was recrystallized once from ethanol/water. The yield was 58.1 grams (60.4%).

n-Butyllithium. A mixture of 4.3 grams of lithium (cut into small pieces) and 200 mls anhydrous ether was placed in a flask that had been swept out with dry nitrogen.



A gentle flow of nitrogen was maintained throughout the reaction. A solution of 35 grams of n-butylbromide in 75 mls of anhydrous ether was added slowly. When the reaction began the internal temperature was controlled at  $-10^{\circ}\text{C}$  with a bath of methanol and dry ice. The remainder of the solution of n-butylbromide was added over a 30 min period. The mixture was allowed to warm to  $0-10^{\circ}\text{C}$  while being stirred for 1-2 hours. The mixture was then decanted through a glass tube containing a glass wool plug into a suitable container. The transfer was made under a nitrogen blanket.

Standardization of n-Butyllithium.<sup>70</sup> The n-butyl-lithium, prepared as described, was standardized by the titration method of Gilman and Haubein.<sup>71</sup>

Bornylene-2-d [63]. A flame dried two liter three-neck flask was fitted with a nitrogen inlet, rubber septum, and dry ice condensor protected with a drying tube ( $\text{MgSO}_4$ ). Three hundred mls anhydrous ether and 32 grams of camphor tosylhydrazone was added. Approximately 0.2 mole n-butyl-lithium in ether was added in small portions. The mixture was stirred for 1 hour. The brilliant orange solution became colorless upon addition of an excess  $\text{D}_2\text{O}$ . The ether solution was washed with water and dried with  $\text{Na}_2\text{SO}_4$ . The

solvent was removed by distillation. Pure bornylene-2-d was obtained by preparative gas chromatography; nmr ( $\text{CCl}_4$ ) 0.76 (s, 3H, methyl), 1.02 (s, 6H, methyl), 1.43 (broad, 4H, aliphatic), 2.26 (bt, 1H, bridgehead), 5.62 (bd, 1/2H, olefin), and 5.88 (bq, 1H, olefin). (43.5 atom % d).

Bornylene-9-d<sub>1</sub> [65]. This material was obtained by the method of Willcott and Boriack.<sup>60</sup> The nmr is identical with that of 2-bornylene except the resonance at 0.76 $\delta$  is shifted to 0.78 $\delta$  and is a 1:1:1 triplet ( $-\text{CH}_2\text{D}$ ).

1,2,3-Trimethylcyclopentene [61]. 1,2,3-trimethylcyclopentene was obtained from Chemical Samples Company.

2-Cyano-1-vinylcyclopropane [57] and [58]<sup>62</sup>. The cis and trans isomers used in this investigation were provided by R. S. Cooke.

Potassium 2-carbethoxy cyclopentanone [72]<sup>64a</sup>. Fifty-six grams of potassium hydroxide was mixed in 15 mls water and added to 250 mls 95% ethanol in a 1-liter reaction flask fitted with a mechanical stirrer. The flask was then immersed in an ice bath. 156 grams 2-carbethoxy cyclopentanone was added over a 3 minute period to the chilled solution of base. About 3 minutes after addition of the ketone, the white solid that had formed was diluted with

50 mls chilled ether. The mixture was then vacuum filtered. The white material collected was washed successively with cold ether and cold ethanol. The salt was placed in a desiccator to dry. The yield of potassium 2-carbethoxy cyclopentanone was 111.0 grams (57% yield).

2-Carbethoxy-2-( $\beta$ -bromoethyl) cyclopentanone [73]<sup>64a</sup>.

One hundred ten grams of potassium 2-carbethoxy cyclopentanone was placed in a 2 liter 3-necked flask equipped with thermometer, condensor, and mechanical stirrer. Fifteen hundred grams of 1,2-dibromoethane was added and the mixture heated to 90°C for 7 hrs. The reaction mixture was vacuum filtered to remove solid potassium bromide. The majority of the 1,2-dibromoethane was removed by a rotary evaporator. The yield was 22 g (20%).

2-( $\beta$ -Bromoethyl) cyclopentanone [75]<sup>64a</sup>. About 110 grams 2-carbethoxy-2-( $\beta$ -bromoethyl) cyclopentanone containing some 1,2-dibromoethane was placed in a 1-liter 1-neck flask equipped with a condensor. 185 mls 47% HBr was added, the mixture stirred with a magnetic stirrer and heated in an oil bath to 80-85°C. Small bubbles began to evolve indicating decarboxylation was occurring. After gas evolution ceased, the mixture was cooled, diluted with 200 mls H<sub>2</sub>O and extracted 3 times with ether. The ether

was dried with sodium sulfate and removed by distillation. The 1,2-dibromoethane was removed by vacuum distillation (4mm at 160°C) through a Vigreux column. The pot residue containing the desired product was purified by molecular distillation ( $1 \times 10^{-4}$  mm at 70-80°C). The yield of 2-( $\beta$ -bromoethyl) cyclopentanone was 27 grams.

Spiro[2.4]heptane-4-one [74]<sup>64b</sup>. About 27 grams of 2-( $\beta$ -bromoethyl) cyclopentanone was placed in a 500 ml flask equipped with a mechanical stirrer and condensor. To this was added 160 mls 30% potassium hydroxide. The mixture was stirred and refluxed for 1.5 hours. The mixture was cooled and extracted with 3 50-ml portions of ether. The ether was dried with sodium sulfate and removed by distillation. The spiro ketone was purified by bulb-to-bulb distillation to yield 12.0 grams of product: ir (neat) 2965, 2870, 1730, 1345, 1285, 1080, 965 and 814  $\text{cm}^{-1}$ ; nmr ( $\text{CHCl}_3$ ) 2.2 (m, 2H,  $\alpha$  to carbonyl), 1.95 (m, 4H, aliphatic), 1.05 (m, 2H, cyclopropyl) and 0.75 (m, 2H, cyclopropyl).

Triphenylmethylphosphonium Bromide.<sup>68</sup> Fifty five grams of triphenylphosphine was dissolved in benzene that had been distilled from sodium. The solution was placed in a pressure bottle and chilled in an ice-salt mixture.

Approximately 23 mls methyl bromide was added and the bottle sealed. The contents were allowed to stand for 3 days at room temperature. At the end of this time the pressure bottle contained a white solid. The solid was removed and washed with benzene. The material was dried over  $P_2O_5$  in an Abderhalen drying pistol at  $100^\circ C$ . The yield was 71 grams (98%): mp  $230-232^\circ C$ , lit. mp  $232-233^\circ C$ .

4-exo-Methylene spiro[2.4]heptane [59]<sup>68</sup>. A 500 ml 4-neck flask was fitted with a gas inlet tube, condensor, mechanical stirrer, and septum. About 225 mls anhydrous ether was placed in the flask and a positive pressure of dry nitrogen was maintained by a mercury-filled U-tube. The n-butyllithium was added with a syringe and the septum replaced with a means for addition of a solid. To this solution was added 54 grams triphenylmethylphosphonium bromide as rapidly as possible (Caution: frothing!). At this point the solution was orange-red. When the solid material had dissolved, the solid addition apparatus was replaced by a pressure compensated dropping funnel containing 11.7 g spiro[2.4]heptan-2-one. The ketone was added to the ylide solution slowly. After all the ketone had been added, the solution was stirred at room temperature for 1 hour and then heated at reflux for 12 hours.

The reaction was cooled and the solid material removed by filtration. The precipitate was washed with ether and the washings combined with the ethereal filtrates. The ether was extracted with water until neutral and then dried over  $\text{CaCl}_2$ . The ether was removed by careful distillation through a Vigreux column and the remaining solution purified by preparative GC. The yield of the spiro-olefin was about 4-5 grams: ir (neat); 3060, 1650 and 1010  $\text{cm}^{-1}$ ; nmr ( $\text{C}_6\text{H}_6$ ); 4.5 (t, 1H, olefin), 4.2 (t, 1H, olefin), 2.45 (complex m, 2H, allylic), 1.2 (m, 4H, aliphatic) and .7 (m, 4H, cyclopropyl).

2-Chlorocyclopentanone [76]<sup>71</sup>. A two liter, three-necked flask was fitted with a gas inlet tube reaching deep into the flask, a mechanical stirrer and an outlet tube connected to a water filled U-tube. 252 grams of cyclopentanone and 900 mls of water were added to the flask. The chlorine gas was collected from a lecture bottle into a 500 ml pre-weighed flask immersed in a dry ice-acetone cold trap. The liquid chlorine was weighed on a single pan balance. Approximately 231 grams of chlorine were collected in this manner. When the required amount of chlorine was collected, the flask was raised from the cold trap and the chlorine vapors passed through

a liquid trap into the reaction flask which had been cooled in an ice bath. Control of the chlorine addition was maintained by raising and lowering the cold trap surrounding the liquid chlorine. After addition of chlorine was complete, the mixture was allowed to stir for one hour.

The heavier chlorocyclopentanone layer was separated and combined with 3-150 ml ether extractions of the aqueous phase. The combined ether extracts were washed once with 150 mls of water and once with 200 mls of saturated sodium chloride solution. The ether was removed by distillation. The pot residue was then vacuum distilled to yield 213 grams (60%) of 2-chlorocyclopentanone: nmr ( $\text{CCl}_4$ ) 4.0 (t, 1H,  $\text{CHCl}$ ) and 1.2 (m, 6H,  $\alpha$  to carbonyl and aliphatic).

Trimethyloxosulfonium iodide (TMOSI)<sup>65</sup>. 156 grams of dimethylsulfoxide, distilled from calcium hydride, and 293 mls of iodomethane were placed in a flask and the air purged with dry nitrogen. The flask was stoppered and placed under a can to exclude light. After 3 days, the trimethyloxosulfonium iodide was filtered. The solid was recrystallized from water containing a small amount of potassium carbonate to retard decomposition. The large white crystals were dried in a drying pistol and stored in a desiccator.

4-exo-Methylene spiro[2.4]heptane [59]<sup>66</sup>. Twenty-four grams of sodium hydride (50% in mineral oil) was placed in a 1-liter 4-necked flask fitted with a mechanical stirrer, pressure compensated addition funnel, an inlet for dry nitrogen and an exit connected to a mercury filled U-tube. The NaH was washed three times with dry petroleum ether, decanted each washing. The flask was evacuated to remove traces of pet ether, the vacuum was broken and 110 grams TMOSI added and mixed thoroughly. The system was purged of air by evacuating the flask and then filling with nitrogen. Finally, a slight pressure of nitrogen was maintained as evidenced by a difference in the mercury levels in the U-tube. Dry dimethylsulfoxide was added very slowly (Caution!) and gas evolution was noted in the U-tube. About 400 mls DMSO was added and at this point the sulfonium ylide solution was milky-white and gritty looking. The mixture was allowed to stir at room temperature for 15 minutes and then immersed in an ice bath. To this chilled solution was added 50 grams of 2-chlorocyclopentanone. After addition of the ketone, the reaction mixture was blood red. The ice bath was removed and as the solution warmed to room temperature, it became dark brown with some solid material present. This mixture was allowed to stir at room temperature for 3.5 hours.



The mixture was poured over ice/water mixture and extracted with ether. The ether was filtered as it was collected from the separatory funnel. The ether was carefully distilled. The pot residue was purified by bulb-to-bulb distillation and molecular distillation ( $1 \times 10^{-4}$  mm/70-80°C). The yield was about 10 grams.

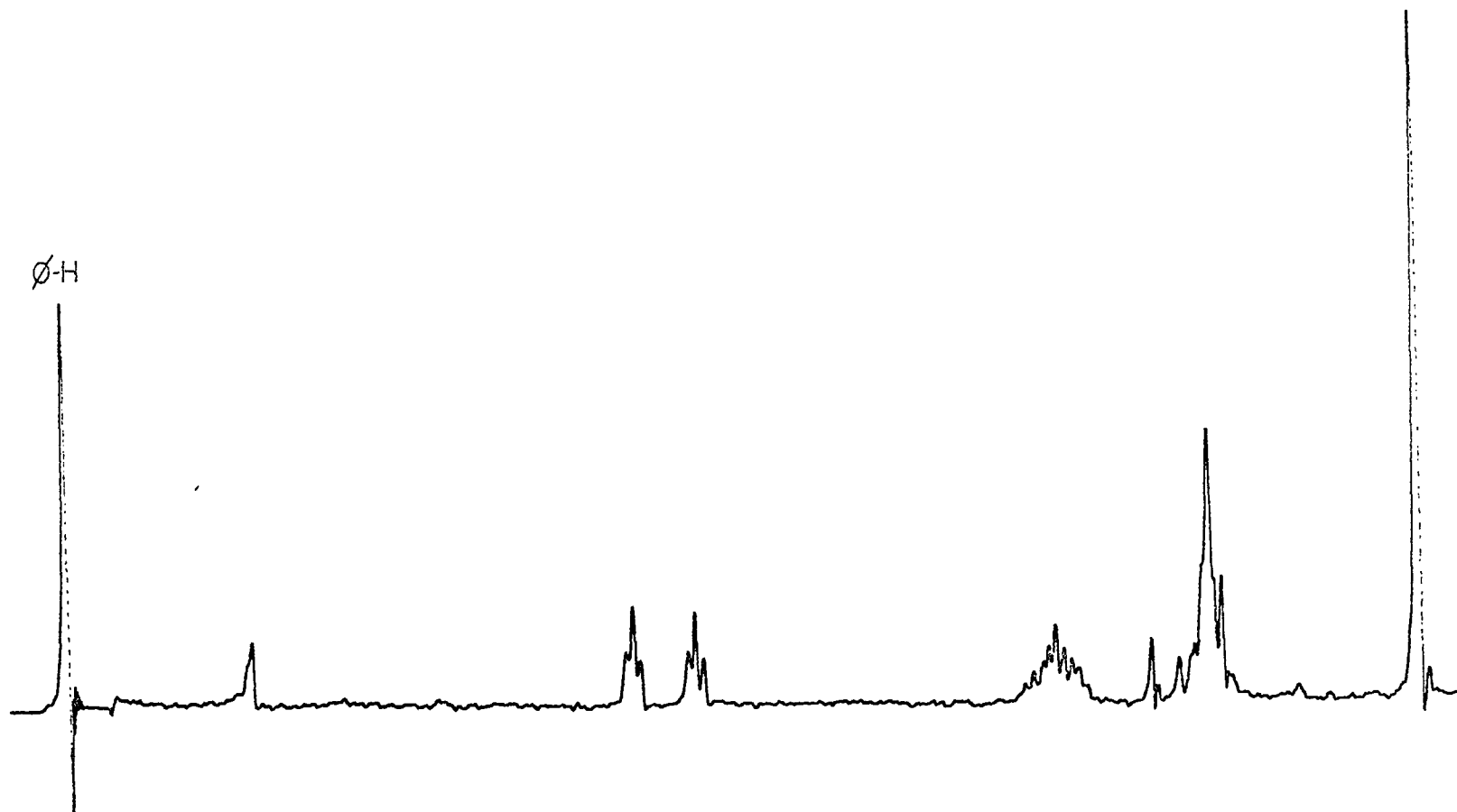


FIGURE 12. NMR Spectrum of [60]

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