BUTADIENE MONOEPOXIDE AND CYCLOPROPANE CARBOXALDEHYDE: PYROLYSIS AND STRUCTURE

A Dissertation

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Presented to

the Faculty of the Department of Chemistry College of Arts and Sciences

University of Houston

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

by

John B. Sapp, Jr. December 1971

To Maxine, Christopher and Stephen

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During my enrollment at this University, I have had the enjoyable experience of working with a most inspiring chemist, Dr. M. R. Willcott. His help and advice was invaluable during the course of this work. I would also like to thank Mr. W. R. Issacs for the least squares analysis program.

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ABSTRACT

The results of pyrolyzing both butadiene monoepoxide and cyclopropane carboxaldehyde are presented. The pyrolysis temperature range was 341°C to 395°C. Rate data obtained from the pyrolysis of cyclopropane carboxaldehyde indicates that the rearrangement of cyclopropane carboxaldehyde to 2,3-dihydrofuran is first order. Arrhenius parameters for this rearrangement, containing large errors, are $E_a = 45 \pm 4$ Kcal/mole, Log A = 12 ± 1 .

Lanthanide-induced chemical shift experiments were performed on butadiene monoepoxide, cyclopropane carboxaldehyde and crotonaldehyde in solution using tris(dipivalomethanato)europium(III). The results of these experiments were interpreted to indicate the preferred ground state conformations of the molecules studied. The conformation assigned to butadiene monoepoxide is that in which the vinyl group is <u>anti</u> to the oxide ring. The conformation assigned for cyclopropane carboxaldehyde is with the carbonyl <u>anti</u> to the cyclopropyl ring. In a similar manner the conformation assigned to crotonaldehyde is <u>anti</u>. The assignments were based on correlations of ΔEu to $1/r^3$, where ΔEu is the slope of a line for a particular proton obtained by plotting the chemical shifts of that proton <u>vs</u>. the molar ratio of metal complex [Eu(DPM)₃] to substrate, and r is the vector distance from the estimated position of the europium to that proton.

Some of the products formed in the pyrolysis of cyclopropane carboxaldehyde are generated via a biradical intermediate. This

contention is supported by the thermodynamics of the system under investigation, and by careful comparison with other three membered ring systems, such as vinylcyclopropane.

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CHAPTER I

THE CHEMISTRY OF CYCLOPROPANES AND ETHYLENE OXIDES

THE CHEMISTRY OF CYCLOPROPANES AND ETHYLENE OXIDES

The isomerizations and the conditions under which certain small ring systems isomerize have been of interest to scientists for many years. Cyclopropane is probably the most studied member of this group of compounds. It has unique physical and chemical properties that have challenged the imagination of scientists. For instance, these interesting molecules have some properties which resemble those of the double bond, while other properties are more like those of alicyclic compounds. Infra-red studies indicate that for those cyclopropanes with a methylene group, the carbon-hydrogen bond is more similar to those in ethylenes than to those of alkanes. Since small threemembered rings are quite reactive as compared to other cycloalkanes, the concept of steric strain was introduced. This strain contributes to their most characteristic property--the ease with which the ring is opened. A considerable amount of effort has been expended in studying the results of ring opening by thermolysis of cyclopropane starting with the initial investigations of Trautz and Winkler,¹ who reported data for the thermal isomerization of cyclopropane to propylene.



A. ISOMERIZATIONS OF CYCLOPROPANES

1. Structural Isomerizations

The conversion of cyclopropane to propylene is an example of structural isomerization. Parameters from the Arrhenius equation together with a large number of chemical facts give considerable insight into the mechanistic possibilities for the isomerizations that occur. An informative discussion of the ring openings of cyclopropane would be most inadequate without these parameters, which are the energy of activation, E_a and Log A. For the isomerization of cyclopropane to propylene these values are 65 Kcal/mole and 15.17, respectively. One form of the Arrhenius equation from which these parameters may be obtained is $K = A \exp(-E_a/RT)$.

Although cyclopropane-propylene type rearrangements have been known for some time, it has only been in the last ten years that the real beauty of this type rearrangement has been realized. An important feature of any unimolecular rearrangement is that it must be clean, that is, it must have clearly discernible measurable products along with good material balance and some remaining starting compound.² This feature is observed in the cyclopropane-propylene rearrangement. This is not to say that other cyclopropane systems are not of interest, but only that the cyclopropane-propylene rearrangement is a good model for a unimolecular rearrangement.

Once the hydrogen atoms of cyclopropane are replaced by other substituents, the chance for a more intricate reaction description

increases. These substituents include alkyl, allyl, aromatic, halogens, deuterium,^{3a} tritium or carbon-13 isotopes.^{3b} Table I contains some selected structural isomerizations of cyclopropanes along with their recorded Arrhenius parameters.

2. <u>Geometrical Isomerizations</u>

When two substituents on the same ring change positions, relative to each other, the molecules are said to be geometrical isomers of each other, and the interconversion is called a geometrical isomerization.

In the course of observing many unimolecular rearrangements it is difficult to explain the reaction as proceeding through a single transition state.⁴ An example of this difficulty is that of the concurrent geometrical and structural isomerization of <u>cis</u>-1,2-dideuteriocyclopropane as reported by Rabinovitch, Schlag and Wiberg.⁵ Their results showed that the <u>cis</u>-dideuteriocyclopropane was isomerized to the <u>trans</u> geometrical isomer faster (12 times faster) than to the structural isomer propylene. In 1961, Benson explained the results of Rabinovitch, Schlag and Wiberg by proposing a mechanism which involved a common intermediate biradical,⁶ as shown in [3] \rightarrow [4] \rightarrow [5] and [7] \rightarrow [6] \rightarrow [4] and [5].



Furthermore, Benson notes that the rotation occurs at a rate such that the biradical reaches rotational equilibrium. 4,6

The concept of intermediate biradicals has received considerable attention in the last decade or more and is still used quite frequently to explain some reaction pathways.

The nature of the isomerization of cyclopropane might be considered the starting point of the biradical concept. Two different models, in terms of reaction coordinate diagrams have been used to explain the geometrical and structural isomerization in cyclopropane. Such diagrams contain three points of interest. Two of these points, the reactant and the product, may be obtained from thermodynamic data. The third point required is the energy of the activation which is an Arrhenius parameter that is calculated from kinetic data.

The structural isomerization of cyclopropane has been discussed from two different standpoints. On the one hand the experimental data has been interpreted as having no intermediate. In such a case a reaction coordinate diagram for the isomerization would be a smooth curve and the reaction is said to be concerted. However, another interpretation of the experimental data is that there exists, along the reaction sequence, a high energy intermediate in an energy well at the top of the reaction coordinate diagram. This intermediate is termed trimethylene. At this point we do not wish to discuss the detailed electronic properties of trimethylene.

Chambers and Kistiakowsky⁷ observed the cyclopropane-propylene isomerization and proposed two possibilities for the reaction pathway. One pathway involves rupture of a C-C bond in cyclopropane to yield trimethylene followed by hydrogen migration to form propylene. The second pathway is that of concurrent C-C bond rupture and hydrogen atom migration to form propylene.

A further attempt at elucidation of the mechanism of the cyclopropane-propylene isomerization may be seen in the isomerization of 1,2-cyclopropane-d₂, mentioned earlier, by Rabinovitch, Schlag and Wiberg.⁵ They proposed from their results that there are three possible mechanistic routes to geometrically isomerized product: (1) ring rupture and reversible recyclization, trans- ∇ -d₂ \neq C-C-C \neq cis- ∇ -d₂; (2) intermolecular exchange reaction, radical or nonradical; (3) an intramolecular hydrogen migration process. The authors state that from their observations mechanism (1) "appears established as the effective process for <u>cis-trans</u> isomerization, and formation of trimethylene thus occurs as, at least, a simultaneous process accompanying structural isomerization to propylene."

With the aid of certain thermodynamic estimates, and existing data for the cyclopropane-propylene isomerization, Benson⁶ concludes that both reactions have trimethylene as a common intermediate. From calculations obtained using estimates, Benson proposes that trimethylene is an intermediate biradical requiring an activation energy of 8.2 Kcal/ mole to reclose the cyclopropane and 9.5 Kcal/mole to form propylene. The lifetime of this biradical intermediate is estimated to be about $10^{-11.3}$ sec; however, no direct observation of its existence has been made.

The mechanics of observable geometric cyclopropane rearrangements can be classified as three limiting sets of molecular motions and can be illustrated using a report by Berson and Balquist⁸ on the racemization and geometrical isomerization of tetramethylcyclopropane-d₆.

The first of these molecular motions one can imagine synchronous conrotatory motions of the terminal methylene groups (epimerization at two centers).



This suggests from theory⁹ and indirectly supporting experiment¹⁰ that the proposed intermediate biradical may be a planar species with an antisymmetric nonbonding molecular orbital (<u>4</u>) resulting from the simultaneous conrotatory motions of the two methylene groups.

The second possibility is that bond rotations in the trimethylene biradical are fast relative to recyclization. This produces an intermediate of randomized stereochemistry which may recyclize to \underline{cis} (3) or racemic trans.



In the third mechanism, rotation of one of the substituted carbons through 180° is involved. This converts <u>trans</u> (1) to <u>cis</u> (3). The conversion of (1) to (2) requires two alternating consecutive rotations passing through the <u>cis</u> compound (3) first.



The results of this work, according to the authors, showed that neither a randomized intermediate nor an in-place rotation of one group can be the only process, but that the third of the three processes mentioned is the best for most of the time. It should be pointed out that no other geometrical isomerization is anything but random.

Bergman and Carter¹¹ studied the rates of racemization and <u>cis-trans</u> isomerization of optically active <u>cis-</u> and <u>trans-</u>1-ethy1-2methylcyclopropane in the gas phase. The rate constants obtained were similar in magnitude and were analyzed as an indication that an electrocyclic process proceeding through π -cyclopropane intermediates is energetically less favorable than a pathway involving stereoisomeric diradicals.



These authors found it difficult to find precise values for the ratio of the rate of cyclization to rotation but were able to show that the

values of these rates are small, probably less than 0.3. From this it is seen that each time a diradical is formed it undergoes rotation to the isomeric diradical at least four or five times for each time it recyclizes to cyclopropane. Many of the questions concerning the structure of the diradicals produced on pyrolysis of cyclopropane cannot be completely determined on the basis of this work alone. However, in addition to the work of Bergman and Carter, the study of the geometrical isomerization of (<u>cis</u> and <u>trans</u>-2-deuterioviny1)-<u>trans</u>, <u>trans</u>-2,3-dideuterio-cyclopropane [8] by Cargle offers almost unequivocal proof for the intermediate diradical.¹²



The results of the pyrolysis of this dideuteriocyclopropane are shown in the following reaction scheme.



Analog computer plots of both the concerted and biradical model for the isomerizations showed some interesting results. The ratios of (B+C)/D for the two mechanisms show a large difference early in the reaction. The concerted model shows a (B+C)/D ratio of as much as 5:1 at about one half-life and remains larger than 2:1 for several half-lives. This same ratio in the diradical mechanism rapidly approaches 2:1 and remains constant. The experimental results showed that the ratio of B+C/D was 2:1 throughout the reaction. These results were interpreted as a randomization of stereochemistry at two of the three carbons in the ring occurring by way of an intermediate diradical along the reaction coordinate.

Similar evidence for biradical intermediates is found in the thermolysis of cyclobutanes. Gerberich and Walters showed that the geometrical isomerization of <u>cis</u>-1,2-dimethylcyclobutane takes place at a rate that is four times slower than the formation of the major products, two molecules of propylene.¹³



Cvclopropane	Olefin	Arrhenius Parameters		Peference
		Log ₁₀ A.	E _a (Kcal/mole)	
\bigtriangleup	/	15.17	65	7
\bigtriangleup	/	14.32	64.4	14
		13.97	61.9	
	=	14.06	64.3	
		14.14	62	
\checkmark		13.93	61.9	15(a)
	\succ	14.08	62.3	
		13.92	61.4	
		13.96	61.2	

TABLE I

STRUCTURAL ISOMERIZATIONS OF CERTAIN CYCLOPROPANES

TABLE I CONTINUED

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STRUCTURAL ISOMERIZATIONS OF CERTAIN CYCLOPROPANES

Cvclopropage	Olefin	Arrhenius Parameters		Poforonco
cycropropane		Log ₁₀ A	E _a (Kcal/mole)	ner er ence
		13.93	61.9	15(b)
		14.08	62.3	
		13.92	63.9	
		13.96	62.9	
\land		15.05	62.6	15(c)
\bigtriangleup	cis + trans	15.78	60.9	16

It can be seen that cleavage at <u>a</u> will give the two molecules of propylene, while cleavage at <u>b</u> will yield the minor products, a molecule of ethylene and a molecule of <u>cis</u> or <u>trans</u>-2-butene. The third of three simultaneous reactions is the geometrical isomerization of <u>cis</u>-1,2-dimethylcyclobutane to <u>trans</u>-1,2-dimethylcyclobutane. The formation of the products are explained by way of the biradical mechanism.



The literature also contains interesting accounts of geometrical isomerizations of substituted cyclopropanes, such as that of \underline{trans} -l-deuterio-2-vinylcyclopropane. This work has been well documented by

Cargle who concluded that his observation of geometrical isomerization of 1-deuterio-2-vinylcyclopropanes is consistent with a diradical mechanism.¹²



B. GENERAL FEATURES OF OXIRANES

1. Structure of Ethylene Oxide

The simplest member of the class of compounds called oxiranes is ethylene oxide. It is a three-membered ring, which differs from cyclopropane in that an oxygen atom has been substituted for a methylene group. Figure 1 shows the structure of ethylene oxide as determined by Ackerman and Mayer.¹⁷

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FIGURE 1 STRUCTURE OF ETHYLENE OXIDE 1

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The plane formed by the carbon and hydrogen atoms is perpendicular to that of the ring. The hydrogens lie above and below the ring, while the two carbons are raised above the plane that is formed by the four hydrogens. Ackerman and Mayer note that the C-C bond length (1.47 Å)is intermediate between that of a normal C-C single bond (1.54 Å), a normal C-C double bond (1.33 Å), and that the H-C-H bond angle $(116^{\circ}13')$ lies between tetrahedral $(109^{\circ}28')$ and trigonal (120°) .

2. Structural Isomerization of Ethylene Oxides

Several products have been observed from the thermolysis of ethylene oxide,¹⁸ including methyl radicals, carbon monoxide, methane, ethylene and ketene. By passing ethylene oxide over alumina at 200°C-300°C or at 500°C in the absence of catalyst, Ipatieff and Leontovitch showed that the main product was acetaldehyde.¹⁹ Table II lists some of the known thermal isomerizations of ethylene oxides.

As is evidenced by Tables I and II, both cyclopropanes and ethylene oxides undergo structural isomerizations though they differ in the kinds of atmos contained in their structures.

C. REACTIONS OF SUBSTITUTED VINYLCYCLOPROPANES AND A VINYL ETHYLENE OXIDE

Potentially interesting observations concerning three-membered rings can be found by comparing vinylcyclopropane with vinyloxirane .

STRUCTURAL ISOMERIZATIONS OF CERTAIN ETHYLENE OXIDES

Ethylene Oxide	Products Formed	Reference
	сн ₃ -сн ₂ -сно сн ₃ -со-сн ₃ сн ₂ =сн-сн ₂ он	20 .
\bigvee	сн ₃ сн ₃ сно сн ₃ сно	21
	сн _з сн ₂ сн-сно сн ₃	· 21
		22
		. 23

(butadiene monoepoxide).* Structurally, these two molecules differ



in the same way as do cyclopropane and ethylene oxide. Further, since the thermolysis of vinylcyclopropane had been studied in this laboratory,¹² it seemed appropriate to investigate butadiene monoepoxide.

The literature does not contain many accounts of butadiene monoepoxide and its isomerixations. There are, however, reports of free radical chemistry involving this molecule among other reactants. Huyser and Munson,²⁴ for example, found that the light-induced addition of bromotrichloromethane to vinylcyclopropane produced a mixture of <u>cis-</u> and <u>trans-1,1,1-trichloro-6-bromohex-3-ene</u>, [22] and [23].

Huyser and Munson investigated another method of β -elimination, to study the stereochemistry of the β -elimination and at the same time avoid the presence of free radicals capable of rapid addition and

^{*}This molecule may have several names including vinyl ethylene oxide, 1,2-epoxy-3-butene, vinyl oxirane and butadiene monoepoxide. In this dissertation we shall use the name butadiene monoepoxide.









elimination from the double bond that could cause isomerization. The method was that of di-t-butyl peroxide induced additions of cycloalkanes to butadiene monoepoxide. This system, according to the authors, "proved to be a system that not only involved a ß-elimination essentially identical to that encountered in the vinyl cyclopropane reactions, but was also free of any radicals that could cause isomerization of the products." The addition of cyclopropane, cyclohexane and cyclooctane to butadiene monoepoxide gave the corresponding trans-4-cycloalkyl-but-2-en-l-ol as the major one to one addition product. The following is an example of the proposed sequence of reactions for the formation of the unsaturated alcohols.



TABLE III

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DI-T-BUTYL PEROXIDE INDUCED FREE-RADICAL ADDITIONS

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CYCLOALKANES TO BUTADIENE MONOEPOXIDE²⁴

Adding reagent (m moles)	m moles of butadiene monoepoxide	m moles of peroxide	Product (m moles)	% Yield
Cyclopentane (2280)	143	15	trans-4-cyclo- pentylbut-2-en- l-ol (8.2)	5.8
Cyclohexane (4000)	71.5	15	<u>trans</u> -4-cyclo- hexylbut-2-en- l-ol (6.5)	13
Cyclooctane (2460)	143	18	<u>trans</u> -4-cyclo- octylbut-2-en- l-ol (25.7)	4 3

The low yield of the radical chemistry of butadiene monoepoxide is necessary as an aid in explaining the products and yields seen in our investigation of the same molecule.

Earlier, Kadesch investigated the ring opening of butadiene monoepoxide with methanol.²⁵ Butadiene monoepoxide is said to react "abnormally" with hydrogen chloride and hydrogen bromide to give the corresponding 2-halo-3-buten-1-ols [29].²⁶ However, it is said to react "normally" with respect to most epoxides, with alcohols in the presence of sodium to give 1-alkoxy-3-buten-2-ols [30].²⁷




Kadesch found in his investigation that the reaction proceeded normally or abnormally depending upon the catalyst. The reaction scheme is shown below.



The normal reaction, according to Kadesch, that occurs with methanol in the presence of a small amount of sodium is due to a bimolecular nucleophilic displacement by methoxide ion which is then regenerated.



[18]

$$\begin{array}{c} \text{CH}_2=\text{CH}-\text{CH}-\text{CH}_2-\text{OCH}_3 \\ \downarrow \\ \text{O}_{\Theta} \\ \end{array} \xrightarrow{\begin{array}{c} \text{CH}_3\text{OH} \\ \text{CH}_2=\text{CH}-\text{CH}_2\text{OCH}_3 \\ 0\text{H} \\ 0\text{H} \\ \end{array} + \begin{array}{c} \text{CH}_2^{\text{OCH}_3} \\ \text{OH} \\ + \begin{array}{c} \text{CH}_3\text{O}^{\text{O}} \\ \text{OH} \\ \end{array} \end{array}$$

The acid-catalyzed reaction may also be expected to lead to the normal product.



However, if unimolecular ring opening occurs in the acid-catalyzed reaction instead, the formation of the abnormal product may be accounted for.



This unimolecular ring opening is said to be assisted by the resonance stabilization of the intermediate carbonium ion.

$$[CH_2=CH-CH-CH_2OH \longleftrightarrow CH_2-CH=CH-CH_2OH]$$

In these simple illustrations we have pointed out that the C-O bond in butadiene monoepoxide confers special reactivity to the molecule. It is not an ordinary ether. This is further evidenced by some more complicated systems which contain the C-O bond.

Sondheimer and Shani have shown that the C-C bond in an epoxide may be severed leaving the C-O bonds intact.²⁸ They found that 1,6-oxido [10] annulene [38] could be prepared from 9,10-oxido-1,4,5,8,9,10-hexahydronaphthalene [35], in good yield. Two products were formed, one via C-O cleavage [37], and the other through C-C bond cleavage [38].



Molecules [37] and [38] were formed in yields of 20% and 50%, respectively.

Cockroft and Rhoads irradiated 4,5-dihydrooxepin [39]²⁸ and found three major photoproducts, [40], [41], and [42].



The yields of the products varied depending upon reaction conditions. In 0.15 M ether at room temperature and at 253.7 nm light, the yields for [40], [41] and [42] were 34.2%, 17.0%, and 40.8%, respectively. Cockroft and Rhoads proposed that formation of the cyclic aldehyde was due to a [1,3] shift in the enoyl system of [39], which occurs through a diradical intermediate. According to these authors, the transformations and geometrical requirements are most easily met by the diradical intermediate.

In a similar manner, Boykin and Lutz have demonstrated that ring contractions and formation of cyclic carbonyl isomers $occur^{15}$



in the photolysis of the substituted 2,5- and 2,3-dihydrofurans, [43] and [45].





[46]

D. THERMAL INTERCONVERSIONS OF STRUCTURAL ISOMERS OF BUTADIENE MONOEPOXIDES

Two structural isomers of butadiene monoepoxide are 2,3-dihydrofuran [47] and cyclopropane carboxaldehyde [48].



Wilson found that both cyclopropane carboxaldehyde and 2,3-dihydrofuran were formed in the pyrolytic decomposition of tetrahydrofuran derivatives.³⁰ He proposed that the aldehyde [48] was formed through a rearrangement of 2,3-dihydrofuran, and performed the control experiment



by passing the dihydrofuran vapor through a tube heated to 375°C and detecting crotonaldehyde [49], carbon monoxide [50], and propylene [51].³¹

At higher temperatures (550°C) the entire product consisted mainly of carbon monoxide and propylene. His results-were explained by supposing three consecutive reactions.



His attempts at establishing this sequence by further experiments with [48] and [49] proved fruitless. The aldehyde [48], when heated, gave a little 2,3-dihydrofuran and crotonaldehyde. The formation of these products gave credence to the reversibility of the first step. However, an analysis of the carbon monoxide and propylene which were formed when crotonaldehyde was pyrolyzed showed the ratio of these to be nearly two to one. These complicated facts presented a problem which Wilson and other investigators could not solve with the investigative tools available at that time. Since then, the methods for studying the structure of molecules and mechanisms of reactions have improved and are considered more advanced. However, the need for still more techniques will become evident as a description of our experience unfolds. A recent method of determining the structure of molecules in solution has received considerable attention by scientists. This new method involves the use of lanthanide complexes to produce paramagnetic shifts in the nuclear magnetic resonance spectra of most compounds which contain unpaired electrons and are reasonably strong Lewis bases.

E. HISTORICAL BACKGROUND OF PARAMAGNETIC SHIFT REAGENTS

In 1969, C. C. Hinckley³² took NMR spectra of solutions of cholesterol and the dipyridine adduct of tris(dipivalomethanato) europium(III).* A comparison of the spectrum of cholesterol in carbon tetrachloride with no $Eu(DPM)_3 \cdot 2py$, with that of a solution containing the lanthanide showed little broadening of the line in the spectrum and interesting shifts of resonance peaks. The addition of the paramagnetic shift reagent dispersed two resonances that were at first unresolved and showed them clearly resolved at a distance down field that depended upon both the concentration of the metal complex and the distance of the shifted hydrogen atom from the complexation site. The largest changes in chemical shifts were observed for the hydrogen atoms closer to the hydroxyl group and were taken as an indication of association of the shift reagent through the hydroxyl group.

^{*}Tris(dipivalomethanato)europium(III) is Eu(2,2,6,6-tetramethylhep-_tane-3,5-dione)₃, usually abbreviated Eu(<u>DPM</u>)₃. The dipyridine adduct then in Eu(DPM)₃·2py. In this thesis we shall use the above -abbreviated form.

In a subsequent report by Demarco, Elzey, Lewis and Wenkert, it was shown that the use of a high frequency spectrometer (220 MHz) and the pyridine-free complex $Eu(DPM)_3$, permitted much better resolved spectra of steroids to be obtained.³³ With spectra of the quality obtained by Demarco and his coworkers, it was possible to make assignments to every proton in androstan-2-ol. These same workers studied the effect of paramagnetic shift reagents on alcohols.³⁴ In this investigation it was found that at a molar ratio of $Eu(DPM)_3$ to 4-tert-butylcyclohexanol of 0.7 the spectrum was first order.

A plot of chemical shift <u>vs</u>. moles of Eu(DPM)₃ added showed that the relationship of chemical shift and the concentration of complex is linear. The approximate resonance positions in the solvent containing no complex was obtained by extrapolation. Then, by using the expression $\Delta_{Eu} = \delta_{solvent} - \delta_{Eu}^{n=1}$ where n = 1 is the point where the molar ratio of complex to solute is one, the paramagnetic induced shifts for each proton were determined. Δ_{Eu} can be defined as a function of $1/R^3$ where <u>R</u> is the distance from the metal atom to the proton. However, the Demarco group found that for their system, a plot of $\Delta Eu \ vs$. R (R is the vector distance between the hydroxyl oxygen atom and the proton in question) gave a straight line with a slope of -2.2 $(1/R^{2.2})$ rather than $1/R^3$.

These results, and many others, have been interpreted as being pseudo-contact shifts. Eaton has already pointed out that these paramagnetic shifts in the NMR can arise from contact interactions,

pseudo-contact interactions, or from a combination of both.³⁵ The difference between the two types of interactions can be seen from a mathematical relation. According to Eaton, two different equations can be used to describe these two effects. The contact interaction contribution is given by

$$\frac{\Delta H_{i}}{H} = \frac{\Delta v_{i}}{v} = a_{i} \frac{\gamma_{e}}{\gamma_{n}} \frac{2\beta S(S+1)}{6S'KT}$$

and the pseudo-contact contribution is given by

$$\frac{\Delta H_{i}}{H} = \frac{\Delta v_{i}}{v} = \frac{-1}{\sqrt{3}} \frac{\beta^{2} S(S+1)}{27 RT} (3 \cos^{2} \Theta - 1) X(g_{11} + 2g)(g_{11} - g)$$

The symbolisms used in the equation are as follows:

- H_i and v_i = differences in resonance field or frequency of the nucleus i at applied field H or frequency v, respectively.
- γ_e and γ_n = magnetogyric ratio of the electron and nucleus.
 - γ = distance from the metal atoms to the nucleus n.
 - e = angle between a line drawn joining the metal atom and the nucleus n and the principal magnetic axis of the molecule.

S = total spin of electrons involved in delocalization.

A convenient way of expressing the shifts caused by paramagnetic reagents is,³⁶

$$\Delta \delta_{i} = \delta_{i,[Eu\neq0]} - \delta_{i[Eu=0]} = K(3 \cos^{2} \Theta_{i} - 1)(1/R^{3}_{i})$$

where

- $\Delta \delta_i$ = change in shift in ppm of proton i.
 - δ_i = chemical shift of proton i in ppm from TMS.
 - K = a collection of constants.
 - e_i = the angle describing the position of proton i relative to the assumed effective symmetry axis of the europium complex.
- $\delta_{iEu\neq0}$ = chemical shift of proton i in ppm from TMS in presence of europium shift reagent.
 - R_i = distance from proton to europium.

With the use of this modified version of the McConnel-Robertson equation and molecular models, the distance from metal to the site of complexation may be estimated.³⁷

It is necessary to point out that the complexation takes place with atoms which contain a lone electron pair. The approximate order of functional groups which give characteristic paramagnetic shifts is³⁸

 $-NH_2 > -OH > -C=0 > -O- > CO_2R > -CN$

Eaton pointed out also that when the paramagnetic center is a rare earth ion the pseudo-contact shift should dominate the effect, especially where there is little conjugation in the substrate. Indeed the cholesterol observations of Demarco, <u>et al</u>. show that the pseudo-contact interaction appears to be the major contributor to the paramagnetic shift phenomenon.

Paramagnetic shift reagents are not limited to chelated europium. All of the rare earths have been used to induce paramagnetic shifts. Praseodymium³⁹ and ytterbium⁴⁰ are said to be especially useful. It is interesting that in the use of praseodymium, the observed shifts are upfield rather than downfield as in europium, and the magnitude of shifts is larger than those of europium.

The application of paramagnetic shift reagents is a rapidly expanding field. The first published report by Hinckley in August, 1969, has been followed by at least 57 more publications before July 15, 1971. Since reports are fragmentary and confusing, we will not discuss each of these. However, an annotated bibliography in the appendix contains all of the reports on paramagnetic shift reagents known to us at the time of this writing.

One paper we would like to discuss is that of the use of $Eu(DPM)_3$ in the structure elucidation of epoxides.⁴¹ The molecule was investigated by Willcott, Oth, Thio, Plinke and Schroder, in an attempt to determine whether or not the epoxide ring of [52] is <u>syn</u> or <u>anti</u> to the proton at carbon atom 2.



The results of the investigation showed that the epoxide ring is situated unsymmetrically on the cyclooctatetraene dimer. This was

explained after the spectrum containing no europium complex showed signals of a ratio of five to one for the six aliphatic protons. The other protons which underwent paramagnetic shifts were 2, 6, 1, 10, 7, 17, 9, 8, 11, 12, 13 and 14, decreasing in that order. Protons 3 and 5 had the largest shifts. The shifts of all of the protons correlated with 0 . . . H_i distance γ_i for the <u>syn</u> isomer of [52]. Protons 15 and 16 showed diamagnetic shifts. This is explained by reference to the pseudo-contact shift equation $\Delta v_i \alpha (3 \cos^2 \psi_i - 1) d_i^{-3}$ where d_i is the europium and the ith proton and ψ_i is the 0 . . . Eu . . . H angle.⁴² The angles for 15 and 16 are said to be greater than 54.7° and the shifts are thus diamagnetic. This illustration alone points out the great utility of paramagnetic shift reagents in the elucidation of the structure of molecules bearing a lone-pair of electrons in solution.

CHAPTER II

STATEMENT OF THE PROBLEM

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STATEMENT OF THE PROBLEM

Butadiene monoepoxide undergoes thermal rearrangement to several products which include propylene, 2,3-dihydrofuran, cyclopropane carboxaldehyde, and crotonaldehyde. Cyclopropane carboxaldehyde forms the same products under thermal rearrangement.

The problem, then, was to investigate the thermal rearrangement of these two molecules and to characterize the products, set the analytical system, and, if feasible, perform the kinetics. This data would be useful in gaining insight into the mechanistic route(s) which lead to the several products formed, and would help to determine whether or not butadiene monoepoxide is an intermediate in the pyrolysis of cyclopropane carboxaldehyde. CHAPTER III DISCUSSION

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DISCUSSION -

The results of the pyrolysis, kinetics and lanthanide induced shift studies on butadiene monoepoxide, cyclopropane carboxaldehyde and crotonaldehyde will be presented in this section. The pyrolyses were carried out in a gas-phase stirred flow reactor. The results represent a method for a qualitative analysis of this chemical system. This data, along with the shift reagent data, comprises a reasonable picture of the molecules presented.

A. PYROLYSIS AND KINETIC STUDY OF BUTADIENE MONOEPOXIDE AND CYCLOPROPANE CARBOXALDEHYDE

The pyrolysis of butadiene monoepoxide and cyclopropane carboxaldehyde weredone in a stirred flow reactor that was a modified version of the one introduced by Lewis and Herndon.⁴⁰ Figures 2 and 3 show the system and illustrate the various parts. The system and the technique used in sampling were the same as those used by Boriack in his pyrolysis of bornadiene.⁴³ The pyrolysis of each of the two molecules was done at five different temperatures ranging from 341.5°C to 395°C. At each temperature, eleven samplings were done at five different flow rates.

The results of pyrolysis of butadiene monoepoxide and cyclopropane carboxaldehyde at each of the five temperatures indicate that thermal rearrangement of these molecules in a stirred flow reactor is, to say the least, nontrivial.

FIGURE 2

APPARATUS USED IN GAS PHASE STIRRED FLOW REACTOR

- 1. Matheson Automatic Regulator #8
- 2. Hoke 2403H Regulator
- 3. Magnesium sulfate drying tube
- 4. Sulfuric acid bath
- 5. Sodium hydroxide drying column
- 6. Magnesium sulfate drying column
- 7. Five-turn calibrated needle valve

- 8. Manometer
- 9. Water jacketed vaporizer
- 10. Reactor
- 11. Cold trap
- 12. Soap-bubble flow meter
- 13. Powerstat



FIGURE 3

CUT-AWAY VIEW OF REACTOR OVEN

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- 1. Asbestos insulation
- 2. Heating wire for temperature controller
- 3. Aluminum bath block
- 4. Pyrex glass reactor
- 5. Cartridge heaters
- 6. Chromel-alumel-thermocouple
- 7. Temperature probe for controller
- 8. Sampling port

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9. Electric heating tape

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Our original aim was to observe the rearrangements, and using equations similar to those presented by Herndon and Lowry in their study of the kinetics of the isomerization of bicyclo[2.2.1]heptadiene to toluene and tropilidene, establish rate constants and energies of activation for both molecules.⁴⁴ However, after consideration of our results, it was decidedly evident that the most that could be obtained from our pyrolysis study of butadiene monoepoxide was a simple qualitative discussion of our findings. Similar difficulties have been encountered with the same molecules by other investigators. Crawford, using a batch reactor technique for the pyrolysis of butadiene monoepoxide, gathered data which were similarly erratic.⁴⁵

The VPC traces (VPC = vapor phase chromatography) of both butadiene monoepoxide and cyclopropane carboxaldehyde were similar with the identified peaks (see Experimental section) having the same retention time. The epoxide chromatogram showed the presence of several small peaks which were not identified (See Figures 4 and 5).

1. Pyrolysis of Butadiene Monoepoxide

The pyrolysis of butadiene monoepoxide was done at four different temperatures. It was soon apparent that the component of shortest retention time comprised 75 to 80 percent of the total products. When the exit gas from the oven was allowed to pass into a solution of bromine in carbon tetrachloride, the solution was decolorized. Removal of solute and excess bromine gave a compound whose

FIGURE 4

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TYPICAL CHROMATOGRAM OF BUTADIENE MONOEPOXIDE

Peak	1	=	propylene
Peak	2	=	acetaldehyde
Peak	3	=	2,3-dihydrofuran
Peak	4	=	crotonaldehyde
Peak	5	=	cyclopropane carboxaldehyde



FIGURE 5

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TYPICAL CHROMATOGRAM OF CYCLOPROPANE CARBOXALDEHYDE

Peak 1 = propylene
Peak 2 = acetaldehyde
Peak 3 = 2,3-dihydrofuran
Peak 4 = crotonaldehyde
Peak 5 = cyclopropane



NMR spectrum was identical with that of the richly detailed 1,2dibromopropane. For positive identification passage of propylene into a solution of bromine in carbon tetrachloride gave the same result which led us to believe that either there was something wrong with the previous description of the chemical system or that the route to formation of the product was very much more complicated than supposed.

Several attempts at isolating the cause of the difficulty were made. For instance, the reaction vessel was cleaned by annealing in an oven at 535°C followed by NH₄OH washings. The data obtained after this surface treatment was essentially unchanged. Since it appeared that the reaction was surface catalyzed, the vessel was silanized with dichlorodimethylsilane. The data was still unchanged. After this, a periodic check of the reactivity of the epoxide at different temperatures was made between pyrolysis of other compounds. The results showed similar but scattered overall rates. The product distribution showed that the amount of butadiene monoepoxide remaining was, in nearly each instance, less than one percent making the system inadequate for quantitative study. Table IV shows the percentage of products formed, and epoxide remaining at the given temperatures and corresponding flow rates (average).

2. Pyrolysis of Cyclopropane Carboxaldehyde

Cyclopropane carboxaldehyde, a structural isomer formed when butadiene monoepoxide is pyrolyzed, proved to be not quite as troublesome as the epoxide. Still, the kinetic data obtained from

TABLE IV

PERCENT PYROLYSIS PRODUCTS OF BUTADIENE MONOEPOXIDE

Temperature	снСНО	\bigtriangledown	$\triangle R$	сн ₃ -сно	=/	\bigcirc	U/V x 10 ⁻⁴ sec ⁻¹
353.75°C	0.5	0.1	2.6	2.8	83.3	6.4	2.7
353.75°C	0.5	0.5	1.7	2.4	82.3	9.7	4.9
353.75°C	0.5	0.8	1.8	2.1	81.2	10.9	6.3
353.75°C	0.6	0.8	1.3	2.5	81.1	10.7	6.6
353.75°C	0.6	1.3	1.7	1.8	79.8	12.0	9.0
368.8°C	2.4	1.1	3.3	3.0	74.0	13.9	15.8
383.75°C	1.4	0.1	3.9	2.8	81.0	10.9	15.7
395.0°C	1.6	0.1	3.1	4.4	84.1	4.1	5.3

the stirred flow reactor system had large error limits (estimated to be $\pm 10\%$).

The amounts of product formed and cyclopropane carboxaldehyde remaining at different temperatures and flow rates are shown in Tables V through IX. The product distribution indicates that although propylene was a component, it did not comprise the major portion of product as was the case with butadiene monoepoxide.

After evaluating the data from the pyrolysis of the aldehyde we observed that the most useful data was that obtained by following the rate of formation of 2,3-dihydrofuran.

Using equations 1 and 2 as a model for the cyclopropane carboxaldehyde - 2,3-dihydrofuran rearrangement we were able to obtain reasonable rate constants at the different temperatures which allowed calculation of the energy of activation and the "A" factor.

$$K_1 V(CCA) = U(dHF)$$
(1)

$$\frac{U}{V} = K_1 \frac{(CCA)}{(dHF)}$$
(2)

The equations show the relation, in a stirred flow reactor, of the volume of the reactor V, the flow rate of the exit gas U (corrected), the first order rate constant K_1 , the concentration of reactants (CCA = cyclopropane carboxaldehyde) and product 2,3-dihydrofuran (dHF).

Equation 1 is derived by remembering that at a steady state in a stirred flow reactor the rate of disappearance of any molecule is

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17	٦D	L	С,	V

PRODUCT DISTRIBUTION FROM PYROLYSIS OF CYCLOPROPANE CARBOXALDEHYDE AT 341.5°C

CCA/DHF	$\bigtriangleup R_{H}$	сно	сн ₃ с́≤ ⁰ Н		//	U/V x 10 ⁻⁴
5.35	69.13	0	2.84	12.93	10.77	2.43
7.37	79.51	0	1.91	10.79	7.77	6.36
7.67	80.15	0	1.89	10.93	7.03	7.24
9.42	87.69	0	.37	9.31	2.61	9.13
10.87	89.99	0	.27	8.28	1.46	11.49

	ΤA	BL	E	٧I	
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PRODUCT DISTRIBUTION FROM PYROLYSIS OF CYCLOPROPANE CARBOXALDEHYDE AT 353.75°C

CCA/DHF	<u>∧</u> R _H	сн ₃	^о сн ₃ с=0 Н	$\langle \mathcal{A} \rangle$	/-	U/V x 10 ⁻⁴
1.78	34.50	2.69	9.72	19.42	31.03	2.73
3.08	58.96	1.57	5.32	19.14	14.78	5.33
3.75	68.24	1.28	3.48	18.21	8.67	7.11
4.54	74.29	1.26	2.53	16.36	5.48	8.86
4.79	76.66	1.05	1.40	16.01	4.83	10.10

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TABLE VII

PRODUCT DISTRIBUTION FROM PYROLYSIS OF CYCLOPROPANE CARBOXALDEHYDE AT 376.43°C

CCA/DHF	<u>∧</u> R _H	сн ₃ Сно	^{СН} 3 ^{С=0} Н	\bigcirc	/	U/V x 10 ⁻⁴
2.58	43.84	4.83	6.53	16.27	10.82	8.13
2.45	56.62	4.45	4.64	20.36	13.92	11.34
2.64	60.77	5.51	2,26	23.07	8.94	13.84
3.05	64.42	3.37	2.25	21.06	8.64	18.03
3.38	67.25	2.90	1.03	21.65	5.82	21.97

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TABLE VIII

PRODUCT DISTRIBUTION FROM PYROLYSIS OF CYCLOPROPANE CARBOXALDEHYDE AT 383.75°C

CCA/DHF	<u>∧</u> R _H	сно	сн ₃ с=0 Н	\bigcirc	/	U/V x 10 ⁻⁴
1.99	40.27	6.85	4.53	20.22	26.31	6.58
2.03	45.43	7.68	3.76	22.36	19.86	10.88
2.32	45.34	3.44	2,29	23.41	15.39	13.38
2.84	60.31	4.47	1.74	21.26	12.62	16.01
2.86	60.82	5.60	1.01	21.26	10.91	17.48

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TABLE IX

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PRODUCT DISTRIBUTION FROM PYROLYSIS OF CYCLOPROPANE CARBOXALDEHYDE AT 395.0°C

CCA/DHF	<u> </u>	сно сн ₃	сн ₃ с=0 Н	$\langle \mathcal{A} \rangle$	/	U/V x 10 ⁻⁴
1.40	14.05	3.65	3.52	5.81	68.01	2.52
1.63	28.89	9.09	4.98	17.71	37.74	7.74
1.69	31.13	11.08	4.17	18.35	33.94	8.82
1.79	37.00	10.52	2.36	21.51	26.65	10.50
1.98	42.62	10.94	3.53	20.74	22.23	13.4

equal to its rate of appearance. By sampling the reactor at various flow rates at the same temperature, one obtains straight-line data from which the slope K_1 can be determined. A plot of log k vs 1/T for the formation of 2,3-dihydrofuran from cyclopropane carboxaldehyde is shown in Figure 6. The activation energy ascertained from this data was 45.3 (±4) kcal/mole with a log A value of 12.2 (±1). The rate data for this reaction is contained in Table X.

From our investigation of the conversion of cyclopropane carboxaldehyde to 2,3-dihydrofuran, it would appear that this reaction is first order. To test this, the temperature of the sample vaporizer was altered from 20°C to 40°C, changing the vapor pressure of the aldehyde. The results showed no significant change in the rate of formation of the dihydrofuran from the aldehyde. From equation 2, one can see that if the concentration of cyclopropane carboxaldehyde is increased while the concentration of 2,3-dihydrofuran remains the same, a different value for K_1 would be obtained. Since this was not observed, then the conversion must be first order.

B. LANTHANIDE INDUCED SHIFTS IN SOLUTIONS OF BUTADIENE MONOEPOXIDE, CYCLOPROPANE CARBOXALDEHYDE AND CROTONALDEHYDE

As we have pointed out earlier in this thesis, the use of paramagnetic shift reagents has received tremendous attention in the last eight months. Further, the use of these reagents is limited to molecules bearing long pairs of electrons. Since the molecules we have studied in the pyrolysis procedure met these requirements we decided to investigate the influence of paramagnetic shift reagents on them.

PLOT OF LOG K VS. 1/T FOR FORMATION OF 2,3-DIHYDROFURAN

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FIGURE 6

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T °C	T ⁰K	$\frac{1}{T} \times 10^{-3}$	K x 10 ⁻⁴	Log K
341.5	614.66	1.625	1.47	-3.832
353.75	626.91	1.595	2.14	-3.670
376.43	649.59	1.541	11.22	-2.95
383.75	656.91	1.523	13.8	-2.910
395.0	668.16	1.495	20.1	-2.697

RATE AND TEMPERATURE DATA FOR CYCLOPROPANE CARBOXALDEHYDE ISOMERIZATION

TABLE X

E_a Kcal/mole

Log A

45.3 ± 5

12.17 ± 1



The usual method for treating a molecule bearing a lone-pair of electrons with a paramagnetic shift reagent is to dissolve a known amount of substrate in a suitable solvent, take an NMR spectrum, then dissolve small weighed amounts of shift reagent in the same substrate solution. After each addition, an NMR spectrum is taken and the chemical shifts are plotted. Our method was different, but similar results were obtained. The method we used involved adding a large amount of shift reagent to a known concentration of substrate in solvent. After the spectrum of the solution containing the substrate and large amounts of shift reagent was obtained, then a small amount of stock solution of known concentration of substrate was added. In the method of adding $Eu(DPM)_3$, the effect is to observe incremental shifts of protons from their original (no complex added) positions to some distance downfield, usually depending upon the amount of Eu(DPM), added. In our method, the chemical shifts were observed first downfield. The gradual addition of stock substrate solution, which dilutes the concentration of $Eu(DPM)_3$, while S is unchanged (S = substrate) caused the chemical shifts of each proton to move in an upfield direction toward the position each proton would occupy in a solution containing no shift reagent. Although the methods differ in technique, the results observed are the same. A plot of chemical shift vs. molar ratio of shift reagent to concentration of butadiene monoepoxide, cyclopropane carboxaldehyde and crotonaldehyde gives the same information using either method.

For the region of molar ratio (.2 - .7) of shift reagent to substrate which we investigated, a plot of chemical shift (Hz from TMS) vs. mole ratio gave straight lines for each of the protons (see Figures 7, 8, and 9). In each instance the amount of shift reagent used was 50 milligrams of Eu(DPM)₃, the solvent used was carbon tetrachloride, and the substrate concentration was about .2M. The chemical shift behavior of the protons in butadiene monoepoxide were the first investigated by substrate addition method. A least squares analysis input data assumes x (chemical shift) to be errorless, calculates y (mole ratio), gives the slope, and the standard deviation of the slope. 46 From the data obtained, it was possible to qualitatively make assignments for each proton in the molecule. The slope (l/slope x frequency in MHz) is given as an output in the least squares program. In general, the closer a proton is to the site of complexation, the larger should be the slope number and this value is related to the distance of the proton from the metal complex.⁴⁷

In our procedure we relate the slope of the line to the change in chemical shifts. By relating the slope of the line for each proton to r, where r is the measured distance from the metal complex to the proton, we were able to show that our assignments for each proton were correct and the preferred ground state conformation of the molecule in carbon tetrachloride at 30°C is <u>anti</u>. For instance, in butadiene monoepoxide, the vinyl group may be either <u>anti</u> or <u>syn</u> to the epoxide. However, with the approximate distance of proton to europium,

FIGURE 7

PLOT OF CHEMICAL SHIFT IN H_z FROM TMS <u>VS</u>. MOLAR RATIO OF Eu(DPM)₃ TO BUTADIENE MONOEPOXIDE

Extrapolation indicates intercepts of protons as obtained from least squares analysis.

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<u>Mole Ratio</u>

FIGURE 8 PLOT OF CHEMICAL SHIFT <u>VS</u>. MOLAR RATIO OF Eu(DPM)₃ TO CYCLOPROPANE CARBOXALDEHYDE

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Extrapolation indicates intercepts of protons as obtained from least squares analysis.



FIGURE 9 PLOT OF CHEMICAL SHIFT <u>VS</u>. MOLAR RATIO OF Eu(DPM)₃ TO CROTONALDEHYDE

Extrapolation indicates intercepts of protons as obtained from least squares analysis.



it can be shown that the preferred conformation is with the epoxide ring <u>anti</u> to the vinyl group. In the cases used the approximate distance was 2.5 Å. The correlation of ΔEu values and $1/R^3$ is good for all of the protons in the <u>anti</u> conformer. This is not the case for measured distances in the <u>syn</u> conformer. Table XI shows the correlations obtained for each conformation in butadiene monoepoxide. Although it is more clearly seen from models, the correlation tables point out that for each molecule the intermediate protons are the ones most sensitive in changing the conformations from <u>anti</u> to <u>syn</u>.

Using the same procedure, it can be shown that the preferred conformation of cyclopropane carboxaldehyde is that in which the carbonyl is <u>anti</u> to the cyclopropane ring rather than <u>syn</u>. In the same manner crotonaldehyde is shown to prefer the carbonyl <u>anti</u> to the double bond and not syn.

Tables XII and XIII show the correlation of ΔEu to r in the <u>syn</u> and anti forms of cyclopropane carboxaldehyde and crotonaldehyde.

Another interesting question about $Eu(DPM)_3$ is its behavior in solution. Does it act as a unit or does it dissociate? This question is still unanswered, but our preliminary observations of the molecular weight of this complex, determined by the cryoscopic method, were from .5 to 2 times the molecular weight calculated from the formula (701). The most common values were those between 320 and 450. This may have been caused by precipitation of some of the complex during the determination or several other factors. But the fact remains that the calculated value is never obtained. This is a very good point to be investigated.

CORRELATIONS* FOR SYN AND ANTI CONFORMATIONS OF BUTADIENE MONOEPOXIDE

Eu	rA°	<u>1/3√∆Eu</u> r	Eu	rA°	<u>1/3√∆Eu</u> r
4.2	5.13	1.2	4.2	4.88	1.2
7.0	4.63	1.1	7.0	4.00	1.2
11.8	3.75	1.1	11.8	4.25	.95
19.4	3.44	1.0	19.4	3.44	1.0
21.5	3.38	1.0	21.5	3.38	1.0
21.5	3.38	1.0	21.5	3.38 Sum	1.0
	Anti			<u>Syn</u>	
*The -	<u>1/3√∆Eu</u> va r va	lues are norm	nalized		

TABLE XII -

CORRELATIONS*FOR SYN AND ANTI CONFORMATIONS OF

└── └CYCLO PROPANE CARBOXALDI	DEHYDE	
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∆Eu	rA°	<u>1/3/\Eu</u> r	۵Eu	rA°	. <u>1/3√∆Eu</u> r
7.40	5.63	.91	7.40	4.88	1.1
11.5	5.13	.90	11.5	3.13	1.4
15.12	3.75	1.1	15.12	4.75	.88
23.5	3.38	1.0	23.5	3.38	1.0 .
	<u>Anti</u>			Syn	

*The $\frac{1/3\sqrt{\Delta E u}}{r}$ values are normalized

T/	\BL	E	XI	I	Ι

CORRELATIONS*FOR SYN AND ANTI CONFORMATIONS OF CROTONALDEHYDE

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∆Eu	rA°	<u>1/3√∆Eu</u> r	۵Eu	rA°	<u>1/3√∆Eu</u> r
4.5	6.25	0.97	4.5	. 5.38	1.13
7.9	5.38	0.94	7.9	3.25	1.55
15.2	3.88	1.04	15.2	4.75	0,85
22.7	3.5	1.00	22.7	3.5	1.00
	<u>Anti</u>	· .		<u>Syn</u>	
The <u>1/</u>	<u>3√∆Eu</u> val	ues are normaliz	ed	. ·	

C. INTERPRETATION OF RESULTS

In the investigation of butadiene monoepoxide, cyclopropane carboxaldehyde, and crotonaldehyde we have shown, through the use of - Eu(DPM)₃, their preferred ground state conformations in solution at room temperature. The conclusions drawn about the respective conformations of the molecules are based on acceptable correlations of ΔEu (i.e., slope) and l/r^3 , where r is the vector distance from the approximate position of Eu(DPM)₃ to the proton in question. These correlations determined using models indicate that the conformations of butadiene monoepoxide, cyclopropane carboxaldehyde, and crotonaldehyde are those shown in Figures 10, 11, and 12, respectively. Figure 10 shows the ΔEu values in butadiene monoepoxide obtained from the least squares data in Tables XIV through XIX: The ∆Eu values in Figure 11 for cyclopropane carboxaldehyde were obtained from the least squares data in Tables XX through XXIII. Tables XXIV through XXVII contain data for crotonaldehyde. While the use of paramagnetic shift reagents has expanded rapidly, there are still many unanswered questions concerning their utility. For example, typical molecular weights obtained for Eu(DPM)₃ determined cryoscopically were 327, 347, 500, 427 and 380. As a result of these values many speculative explanations exist. One such explanation is that formation of precipitate during the cryoscopic determination causes the observed values to be less than the expected value. Another explanation and probably the best for the moment is

FIGURE 10

△Eu ASSIGNMENTS IN BUTADIENE MONOEPOXIDE

$$H_a = 21.5$$

 $H_b = 19.4$
 $H_c = 11.8$
 $H_d = 7.0$
 $H_e = 4.2$



TABLE XIV ~

LEAST SQUARES DATA FOR PROTON WITH SLOPE 4.2 IN

BUTADIENE MONOEPOXIDE

	Input Data			
Χ	Y			
530	.789			
471	.564			
454 ·	• .494			
441	.438			
429	.394			
413	.328			
407	.303			
401	.282			
398	.263			
Number of Point Pairs = 9				
Slope = 4.190 ± 0.007				
$X = Chemical Shift from TMS in H_Z$				
$Y = Molar ratio of Eu(DPM)_3$	to butadiene monoepoxide			

TABLE XV

LEAST SQUARES DATA FOR PROTON WITH SLOPE 7.0 IN

BUTADIENE MONOEPOXIDE

X	<u>Input Data</u> Y
619	657
575	.564
546	.494
529	.438
506	.394
495	.359
468	.303
457	.282
452	.263
Number of Point Pairs = 9	• ·
Slope = 7.03 ± .0202	
X = Chemical Shift from TMS	in Hz
Y = Molar ratio of $Eu(DPM)_3$	to butadiene monoepoxide

TABLE XVI -

LEAST SQUARES DATA FOR PROTON WITH SLOPE 11.8 IN

- ----BUTADIENE MONOEPOXIDE

χ	<u>Input Data</u> . Y		
898	.789		
. 816	•657		
748 •	• • • 564		
700	.494		
660	.438		
624	.394		
613	.358		
580	.328		
554	.303		
535	.263		
Number of Point Pairs = 10			
Slope = 11.84 ± .051			
X = Chemical Shift from TMS in Hz			
Y = Molar ratio of Eu(DPM) ₃ to butadiene monoepoxide			

TABLE XVII

LEAST SQUARES DATA FOR PROTON WITH SLOPE 19.4 IN

BUTADIENE MONOEPOXIDE

Ī	nput Data	
Χ	Υ	
1075	.789	
817	.564	
725	.494	
656	.438	
617	.395	
. 580	.358	
504	.303	
487	.282	
466	.263	
Number of Point Pairs = 9		
Slope = 19.38 ⁺ .096		
X = Chemical Shift from TMS in	Hz	
Y = Molar ratio of Eu(DPM) ₃ to butadiene monoepoxide		

TABLE XVIII -

LEAST SQUARES DATA FOR PROTON WITH SLOPE 21.5 IN

BUTADIENE MONOEPOXIDE

Input Data			
X	Y		
1220	.789		
1065	.657		
940 •	564		
840	.494		
760	.438		
707	.394		
655	.358		
561	.282		
538	.263		
Number of Point Pairs = 9			
Slope = 21.54 ⁺ .046			
X = Chemical Shift from TMS in Hz			
$Y = Molar ratio of Eu(DPM)_3$	to butadiene monoepoxide		

.

TABLE XIX -

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LEAST SQUARES DATA FOR PROTON WITH SLOPE 21.5 IN

<u>Ir</u> X	nput Data Y
1190	.789
909	•564
720 .	438
580	.328
560	.303
547	.282
523	.263
Number of Point Pairs = 7	
Slope = 21.503 ± .210	
X = Chemical Shift from TMS in	Hz ·
Y = Molar ratio of $Eu(DPM)_3$ to	butadiene monoepoxide

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BUTADIENE MONOEPOXIDE

FIGURE 11

△Eu ASSIGNMENTS IN CYCLOPROPANE CARBOXALDEHYDE

 $H_a = 23.5$ $H_b = 15.12$ $H_c = 11.50$ $H_d = 7.40$



TABLE XX

LEAST SQUARES DATA FOR PROTON WITH SLOPE 7.4 IN

--- CYCLOPROPANE CARBOXALDEHYDE

<u>II</u>	n <u>put Data</u> Y
334	.717
294	.598
250	.512
200	.398
181	.358
167	.326
153	.299
143	.279
137	.256
126	.239
Number of Point Pairs = 10	
Slope = 7.403 ⁺ .071	
X = Chemical Shift from TMS in	Hz
$Y = Molar ratio of Eu(DPM)_3$ to	cyclopropane carboxaldehyde

TABLE XXI

LEAST SQUARES DATA FOR PROTON WITH SLOPE 11.5 IN

CYCLOPROPANE C	ARBOXALDEHYDE
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v	Input Data
X	Y
498	.717
364	.512
286	.398
254	.358
230	.326
209	.299
196	.276
181	.256
178	.239
Number of Point Pairs = 9	
Slope = 21.503 ⁺ 210	
X = Chemical Shift from TMS i	n Hz
$Y = Molar ratio of Eu(DPM)_3 t$	o cyclopropane carboxaldehyde

TABLE XXII

LEAST SQUARES DATA FOR PROTON WITH SLOPE 15.12 IN

CYCLOPROPANE CARBOXALDEHYDE

Input Data	
Χ	Y
622	.717
566	.598
483	.512
385	.398
348	.358
316	.326
298	.299
256	.256
237	.239
Number of Point Pairs = 9	• ·
Slope = 15.126 ⁺ .071	
X = Chemical Shift from TMS in	Hz
Y = Molar ratio of $Eu(DPM)_3$ to	cyclopropane carboxaldehyde

TABLE XXIII

LEAST SQUARES DATA FOR PROTON WITH SLOPE 23.5 IN

CYCLOPROPANE CARBOXALDEHYDE

	Input Data
Χ	Υ
1454	.717
. 1015	.398
954	.358
905	.326
862	.299
· 840	.279
807	.256
777	.239
Number of Point Pairs = 8	
Slope = 23.503 ± .088	
X = Chemical Shift from TMS	in Hz
$Y = Molar ratio of Eu(DPM)_3$	to cyclopropane carboxaldehyde

FIGURE 12

ΔEu ASSIGNMENTS IN CROTONALDEHYDE

 $H_a = 22.7$ $H_b = 15.2$ $H_c = 7.9$ $H_d = 4.5$



TABLE XXIV -

LEAST SQUARES DATA FOR PROTON WITH SLOPE 4.5 IN

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• CROTONALDEHYDE

X	<u>Input Data</u> Y
299	.713
263	.594
23 8 •	509
213	.396
197	.357
191	.324
185	.297
166	.274
175	.255
168	.237
Number of Point Pairs = 10	
Slope = 4.504 ± .0355	
X = Chemical Shift from TMS	in Hz ·
$Y = Molar ratio of Eu(DPM)_3$	to crotonaldehyde

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TABLE XXV

LEAST SQUARES DATA FOR PROTON WITH SLOPE 7.9 IN

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	Input Data
Χ	ΥΥ
647	.594
596	.509
564	.445
550	.396
522	.367
511	.324
502	.297
489	.274
487	.255
471	.237
Number of Point Pairs = 10	
Slope = 7.933 ± .0644	
X = Chemical Shift from TMS	in Hz
$Y = Molar ratio of Eu(DPM)_3$	to crotonaldehyde

CROTONALDEHYDE

TABLE XXVI

LEAST SQUARES DATA FOR PROTON WITH SLOPE 15.2 IN

CROTONAL DEHYDE

	<u>Input Data</u>
Χ	Y
839	. 594
764	.509
700	.445
664	.396
611	.357
591	.324
574	.294
453	.274
538	.255
507	.237
Number of Point Pairs = 10	
Slope = 15.22 ⁺ .123	
X = Chemical Shift from TMS	in H _z
Y = Molar ratio of $Eu(DPM)_3$	to Crotonaldehyde

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TABLE XXVII

LEAST SQUARES DATA FOR PROTON WITH SLOPE 22J7 IN

CROTONALDEHYDE

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Input Data	
X	Υ
1268	. 594
1153	. 509
1064	.445
1015	.396
945	.357
908	.324
831	.274
782	.237
Number of Point Pairs = 8	
Slope = 22.680 ± .131	
X -= Chemical Shift from TMS in	n H _z
Y + Molar ratio of $Eu(DPM)_3$ to	o crotonaldehyde

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that the complex dissociates somewhat, perhaps according to the equation

 $Eu(DPM)_3 \ddagger Eu(DPM)_2 + (DPM)$

If dissociation does occur then this would increase the number of species in solution and thereby cause a lowering of the molecular weight value.

Before making any decisions concerning the mechanism for the cyclopropane carboxaldehyde-2,3-dihydrofuran isomerization even with the gound state conformational data at hand, one must ultimately consider the kinetics involved. The kinetics studies of these molecules proved to be interesting. For example, the energy of activation for the formation of 2,3-dihydrofuran from cyclopropane carboxaldehyde obtained in this study was 45 Kcal/mole, as shown in Figure 6. This is not the same but similar to that observed for the vinylcyclopropane-cyclopentene rearrangement (50 Kcal/mole). The vinylchclopropane-cyclopentene isomerization has been shown to proceed by way of a biradical intermediate.¹² The precursor to all of the isomerizations is that of the cyclopropane-propylene rearrangement. The energy of activation for the cyclopropane-propylene rearrangement is known to be about 65 Kcal. Indeed, this is the case in our investigation of the cyclopropane carboxaldehyde-2,3-dihydrofuran isomeri-Tables XXVIII through XXX list the estimated heats of formazation. tion for all of the compounds identified in the pyrolysis of cyclopropane carboxaldehyde.
TABLE XXVIII

	APPROXIMATION	OF ∆H _f ° OF CYCLOPROPANE_C/	ARBOXALDEHYDE	
AND 2,3-DIHYDROFURAN				
Group		۵H _f °	Reference	
СН		-1.09	49	
^{2CH} 2		~ 9.86	49	
)C=0		-33.9	49	
\triangle	(correction)	24.4	49	
)	-17.25 Kcal/mole	total	
<u>^</u>		-27.2	49	
2CH ₂		-9.86	49	
) н н		18.88	49	
\bigcirc		-18.88 Kcal/mole	total	

TABLE XXIX

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APPROXIMATION OF ΔH_{f}° OF BUTADIENE MONOEPOXIDE

AND CROTONALDEHYDE

Group	۵H _f °	Reference
<u>A</u>	-27.2	49
сн ₂	- 4.93	49
СН	- 1.09	49
C=CH ₂	15.00	49
<u>^</u>	-17.13	49
, Н	17.83	49
сн _з	-10.12	49
)C=0	-33.90	49
н _з сн=сн-сно	-26.19	
H ₃ CH=CH ₂	4.9*	48
н _з сно	-39.7*	48

TABLE XXX

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GROUP ADDITIVES USED IN CALCULATING ENERGY WELL FOR CYCLOPROPANE CARBOXALDEHYDE DIRADICAL

Group	۵H _f °	Reference
[•C-(c)(H ₂)]	35.82 Kcal/mole	48
[•c-(c _d)(H ₂)]	35.82 Kcal/mole	48
[•C-(CO)(C)(H)]	36.35 Kcal/mole	48
[•C-(C ₂)(H)]	37.45 Kcal/mole	48
Correction for Δ	24.4 Kcal/mole	49

With this information in mind we shall now turn our attention to a discussion of the kinetics of the isomerizations of cyclopropane, vinylcyclopropane and cyclopropane carboxaldehyde.

The existence of a biradical intermediate in the cyclopropanepropylene isomerization is proposed and explained by Benson.⁴⁸ The reaction mechanism is proposed to be



A reaction coordinate diagram for the isomerization is shown below.



Reaction Coordinate

From the reaction coordinate diagram it may be seen that the energy required for reclosing of the biradical is given as 9.3 Kcal/mole while the energy for hydrogen atom migration is 10.8 Kcal/mole. This then makes the depth of the energy well about 10 Kcal for the cyclopropane-propylene isomerization. It should be pointed out, however, that the estimate of 10 Kcal for the energy well for this isomerization is based on other estimates to which Benson fixed the value of 54 Kcal for the energy from ground state cyclopropane to biradical. It should be further noted that as has been pointed out earlier recyclization takes place at a faster rate than does the formation of propylene, thus the highest point of the diagram is on the back side. The difference in the energy required to recyclize and that to form propylene according to Benson is 1.5 Kcal.

In the vinylcyclopropane-cyclopentene isomerization a somewhat similar situation exists except in this case one has to account for the resonance energy of the vinyl group which is estimated, according to Benson, at 12.6 Kcal/mole. The reaction coordinate diagram for this isomerization is shown on the next page. For this reaction the energy of activation has been found to be about 50 Kcal/mole.¹² Benson calculates the energy difference from ground state vinylcyclopropane to the biradical to be about 41 Kcal which means that the energy for cyclizing to cyclopentene is about 9 Kcal. Benson's method of calculating the thermodynamic path from the reactant to the transition state involves estimates in at least five steps. The first step is

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Reaction Coordinate

the estimation of ring opening to the corresponding biradical at room temperature through the use of group additives of hydrocarbons and free radicals. Step 2 incorporates resonance (if any exists) in the biradical. The third step is a correction of the thermodynamics of the ring-opening reaction from 298°K to the reaction temperature using estimated heat capacities of this range. Step 4 is the formation of the transition state from the biradical and step 5 incorporates estimates of the total symmetry change between the reactant and the transition state. Thus, upon considering all of the estimates, Benson indicates as shown on the reaction coordinate diagram that the total energy difference between ground state vinylcyclopropane and the biradical is about 41 Kcal. Using Benson's method of calculations we should now like to turn our attention to energy estimates for the cyclopropane carboxaldehyde-2,3-dihydrofuran isomerization. Our observed value for the energy of activation for this isomerization is 45 Kcal. Using Benson's estimates of group additivity of radicals, hydrocarbons and nonhydrocarbons, the calculated difference between the energy of ground state cyclopropane carboxaldehyde and the biradical is about 42 Kcal. This value is obtained by use of Benson's group additives, correcting for the cyclopropyl ring and the resonance energy of the carbonyl group (8.7 Kcal/mole). Thus, the reaction coordinate diagram for the reaction would be as shown below.



Reaction Coordinate

From the estimates it appears that the energy well for the biradical is only about 3 Kcal deep. However, several factors should be kept in mind in looking at the 3 Kcal energy well. One of these, and probably foremost, is that the 45 Kcal value is only an approximate value and contains some error. The estimates also contain errors. Further, with few exceptions, reactions of the type just described all have been proposed to proceed by way of a biradical intermediate. We feel, even though a 3 Kcal energy well is not conclusive evidence, that when one considers the possible errors that may exist, and the close analogy of this system to vinylcyclopropane, this isomerization may also proceed via a biradical. As indicated by the heats of formation for the products in the pyrolysis of cyclopropane carboxaldehyde, once crotonaldehyde and acetaldehyde are formed there is little possibility of their re-entering the reaction. A reaction pathway to all of the products produced in the pyrolysis may be that of



The formation of crotonaldehyde via the intermediate biradical is also possible.



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The production of carbon monoxide and propylene from the intermediate has several possibilities. One is a bond cleavage and hydrogen atom transfer to form the products.



A possibility for the formation of acetaldehyde may be through vinylacetaldehyde with acetylene and acetaldehyde as products. Although neither acetylene nor vinylacetaldehyde were detected as products, vinylacetaldehyde is reported to be a product in the pyrolysis of butadiene monoepoxide.



On observing the behavior of butadiene monoepoxide in the pyrolysis it seems evident that there is present a surface catalyzed or radical chain process. This is indicated by the erratic product distribution and the complete destruction of the molecule during the pyrolysis. In each instance the products showed a range of reactant remaining of less than one percent to zero percent.

The original reason for attempting the pyrolysis of butadiene was to determine whether or not it is an intermediate in the isomerization of cyclopropane carboxaldehyde to 2,3-dihydrofuran. It is apparent from the thermochemical data presented that it is not an intermediate.

Summary

The use of shift reagents in conformational studies of molecules containing sites for complexation has shown to be a valuable and useful tool. Although there is still much to be learned about the way the shift reagents really work, their use as a qualitative tool for ground state conformational studies is invaluable.

Our studies show that the preferred ground state conformation of cyclopropane carboxaldehyde is <u>anti</u>. However, it is evident that for the major product, 2,3-dihydrofuran, to be formed the molecule must assume the <u>syn</u> conformation. Another worthwhile observation is that most of the good thermal isomerizations involve pure hydrocarbons. Our system is not in this category and it appears that non-pure hydrocarbon systems lend themselves to many difficulties as we have shown. Another difficulty is seen in the fact that our isomerization of cyclopropane carboxaldehyde to 2,3-dihydrofuran is an equilibrium type isomerization since the product upon thermolysis produces the reactant. Butadiene monoepoxide, contrary to our original thought, is not an intermediate in the isomerization and upon pyrolysis produces radicals and fragments to form primarily propylene and carbon monoxide. The shallow energy well seen in the reaction coordinate diagram for the cyclopropane carboxaldehyde-2,3-dihydrofuran isomerization must be observed while keeping in mind that the value for the energy of activation is a good estimate that contains some error.

Although we have discussed the isomerization of cyclopropane carboxaldehyde as proceeding by was of an intermediate biradical we cannot totally disregard the fact that the reaction may be occurring through a concerted pathway.

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EXPERIMENTAL

CHAPTER IV

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EXPERIMENTAL

<u>Butadiene Monoepoxide</u> [19] was purchased from Columbia Organic Chemicals, Inc., Columbia, South Carolina.

<u>Pyrolysis of Butadiene Monoepoxide</u>. The procedure used for the pyrolysis was the same as that used by Boriack in the pyrolysis of bornadiene. The apparatus is shown in Figures 2 and 3 and the data from the pyrolysis may be found in Table IV.

<u>Cyclopropane Carboxaldehyde</u> [49]. The method used in the preparation of cyclopropane carboxaldehyde was a modified form of that used by Rogier and Smith.⁵⁰ The aldehyde was synthesized from cyclopropyl cyanide.

<u>Pyrolysis of Cyclopropane Carboxaldehyde</u>. The pyrolysis procedure was the same as that for butadiene monoepoxide. The kinetic data obtained from the pyrolysis if cyclopropane carboxaldehyde is contained in Tables V through IX.

Lanthanide Shift Reagent. Tris(dipivalomethanato)europium(III) was obtained from Diaprep, Inc., Houston, Texas.

<u>Preparation of the Stock Substrate Solution</u>. To a weighed 10 ml volumetric flask was added the required weight of aldehyde or epoxide to give the desired concentration (13 mg/ml). The flask was then filled to the mark with carbon tetrachloride. <u>Procedure for Lanthanide Induced Shift Experiment</u>. To an NMR tube was added .5 ml of stock solution from a l ml syringe. To the solution in the NMR tube 50 mg of Eu(DPM)₃ was added. The tube was warmed with a heat gun and thoroughly mixed until all of the shift reagent was dissolved. An NMR spectrum was then taken. Upon completing the spectrum, the tube was removed from the instrument and 100 microliters of stock solution were added. The tube was then shaken to assure mixing and a second spectrum-was taken. This same procedure of aliquot addition of stock solution was repeated until the total number of mls of stock solution contained in the NMR tube was 1.5 ml.

The NMR instrument used in the lanthanide shift reagent experiment was the T-60 Nuclear Magnetic Resonance Spectrometer by Varian.

Identification of Pyrolysis Products. Individually sealed pyrex tubes of butadiene monoepoxide and cyclopropane carboxaldehyde were pyrolyzed for 10 minutes at about 380°C. The components were separated on a Varian Aerograph A-90P3 chromatograph with a thermal conductivity detector and helium as the carrier gas. The columns used were .25 inch diameter carbowax packed columns. The NMR spectra of the components were identified by comparison with authentic spectra of crotonaldehyde and 2,3-dihydrofuran. A sample of these mixed with exit gas from the reactor oven and injected into the Aerograph Hy-Fi Model 600 flame ionization chromatograph showed an increase in the size of those two individual peaks. Tables XXXI

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through XXXV show the ratio of percentage of cyclopropane carboxaldehyde to acetaldehyde at various flow rates. Tables XXXVI through XXXIX show the ratio of percent cyclopropane carboxaldehyde to crotonaldehyde. No crotonaldehyde was observed at 341°C.

Propylene was identified by the method mentioned in Chapter III.

<u>Acetaldehyde</u> was identified by retention time on the Aerograph Hi-Fy Chromatograph, and by identification from an NMR of trapped pyrolysate from the stirred flow reactor.

TABLE XXXI THE PYROLYSIS OF $AT 395^{\circ}C$			
37.0	3.53	10.5	10.5
14.05	3.52	3.99	2.52
28.89	4.98	5.8	7.74
31.13	4.17	7.48	8.2
42.62	2.36	18.1	13.4

Percent and ratio of cyclopropane carboxaldehyde to acetaldehyde at _395°C and various flow rates.

CCA = cyclopropane carboxaldehyde ACT = acetaldehyde

THE PYROLYSIS OF AT 383.75°C			
Percent CCA	Percent ACT	CCA/ACT	U/V x 10 ⁻⁴
41.66	4.41	9.45	6.58
47.02	3.45	13.65	10.88
54.34	2.29	23.7	13.38
60.31	1.74	34.6	16.01
60.82	1.01	60.3	17.48

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Percent and ratio of cyclopropane carboxaldehyde to acetaldehyde at 383.75°C and various flow rates.

CCA = cyclopropane carboxaldehyde ACT = acetaldehyde

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TABLE XXXIII THE PYROLYSIS OF AT 376.43°C			
67.25	1.03	65.2	21.97
64.42	2.35	28.6	18.03
60.77	2.26	26.9	13.84
43.84	6.94	6.32	8.13
56.62	4.64	12.2	11.34

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Percent and ratio of cyclopropane carboxaldehyde to acetaldehyde at 376.43°C and various flow rates.

CCA = cyclopropane carboxaldehyde ACT = acetaldehyde

TABLE XXXIV THE PYROLYSIS OF AT 353.75°C			
34.50	9.72	3.55	2.73
58.96	5.32	11.1	5.33
68.24	3.48	19.6	7.11
74.29	2.53	29.3	8.86
76.6	1.4	54.8	10.1

Percent and ratio of cyclopropane carboxaldehyde to acetaldehyde at 353.75°C and various flow rates.

CCA = cyclopropane carboxaldehyde ACT = acetaldehyde

	TABLE XXXV			
•		THE PYROLYSIS OF	AT 341°C	
	Percent CCA	Percent ACT	CCA/ACT	U/V x 10 ⁻⁴
	69.13	4.30	16.1	2.43
	79.51	1.91	41.7	6.36
	87.69	.37	237.0	9.13
	89.99	.27	333.0	11.49
	80.15	1.89	42.4	7.24

Percent and ratio of cyclopropane carboxaldehyde to acetaldehyde at 341°C and various flow rates.

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CCA = cyclopropane carboxaldehyde ACT = acetaldehyde

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THE PYROLYSIS OF AT 395°C			
Percent CROT	Percent CCA	CCA/CROT	U/V x 10 ⁻⁴
10.94	37.0	3.38	10.5
3.95	14.05	3.56	2.52
9.09	28.89	3.56	7.74
11.08	31.13	2.8	8.2
10.52	42.62	4.05	13.4

TABLE XXXVI

Percent and ratio of cyclopropane carboxaldehyde to crotonaldehyde at 395°C and various flow rates.

-

CROT = crotonaldehyde CCA = cyclopropane carboxaldehyde

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•

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TABLE XXXVII				
THE PYROLYSIS OF AT 383.75°C				
Percent CROT	Percent CCA	CCA/CROT	U/V x 10 ⁻⁴	
6.85	41.66	6.1	6.58	
7.68	46.29	6.03	10.88	
3.60	54.34	15.1	13.38	
4.47	60.31	13.5	16.01	
5.60	60.82	10.8	17.48	

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Percent and ratio of cyclopropane carboxaldehyde to crotonaldehyde at 383.75°C and various flow rates.

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CROT = crotonaldehyde CCA = cyclopropane carboxaldehyde

THE PYROLYSIS OF AT 376.43°C			
Percent CROT	Percent CCA	CCA/CROT	U/V x 10 ⁻⁴
4.45	56.62	12.7	11.34
4.83	43.84	9.1	8.13
5.51	60.77	11.0	13.84
3.37	64.42	19.1	18.03
2.90	67.25	23.2	21.97

TABLE XXXVIII

Percent and ratio of cyclopropane carboxaldehyde to crotonaldehyde at 376.43°C and various flow rates.

CROT = crotonaldehyde CCA = cyclopropane carboxaldehyde

	THE PYROLYSIS OF	AT 353.50°C	
Percent CROT	Percent CCA	CCA/CROT	U/V x 10 ⁻⁴
2.69	34.50	12.9	2.73
1.57	58.96	37.5	5.33
1.28	68.24	53.3	7.11
1.26	74.29	58.9	8.86
1.05	76.66	73.0	10.1

TABLE XXXIX

Percent and ratio of cyclopropane carboxaldehyde to crotonaldehyde at 353.50° C and various flow rates.

CROT = crotonaldehyde CCA = cyclopropane carboxaldehyde

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APPENDIX

APPLICATIONS OF LANTHANIDE SHIFT REAGENTS

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