THE DEGENERATE VINYLCYCLOPROPANE REARRANGEMENT

A Dissertation

Presented to

the Faculty of the Department of Chemistry

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

---

by

Virgil H. Cargle

August 1969

To Sandra, Scott and Janice

ACKNOWLEDGEMENTS

For the past three years I have had the pleasurable experience of working with a scientist, teacher, and friend, in the person of Dr. M. R. Willcott, without whose help and encouragement this work could never have been completed. Dr. James R. Cox, Jr. has contributed immeasurably toward the completion of my graduate education, and I am deeply grateful.

I would like to acknowledge the efforts of Dr. Wayne Wentworth for all of the analog computer calculations, and Dr. Robert Curl and Miss Sharon Laas of Rice University for microwave data.

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ABSTRACT

The synthesis of several vinylcyclopropanes stereospecifically labelled with deuterium is presented. Several new tetrahalovinylcyclopropanes and trihalovinylcyclopropanes, which are used as precursers to some of the deuterium labelled vinylcyclopropanes, are also synthesized. Structure proofs of the deuterated and halogenated vinylcyclopropanes are accomplished by chemical and physical methods, with considerable emphasis being placed on detailed analysis of the 100 MHz nuclear magnetic resonance spectra.

Pyrolysis of trans-1-deuterio-2-vinylcyclopropane shows that the reversible, geometrical cis-trans isomerization of the cyclopropyl ring is ca. 40 times faster than the irreversible formation of cyclopentene-d_1 at 325°C. The Arrhenius Equation derived from the kinetic studies of deuterium epimerization on the cyclopropyl ring is:

$$k = 10^{14.5\pm0.1} \exp(-48{,}200\pm1{,}600/RT).$$

Interpretation of the time history of the thermolysis of 1-(cis- and trans-2-deuteriovinyl)-trans,trans-2,3-dideuteriocyclopropane shows unequivocally that the reaction does not follow any simple concerted pathway, but is best described by an intermediate diradical.

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CHAPTER I

CYCLOPROPANES AND THEIR THERMAL REACTIONS

CYCLOPROPANES AND THEIR THERMAL REACTIONS

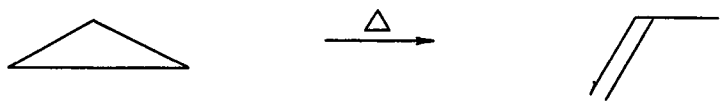
Thermal unimolecular isomerizations of cyclopropane and substituted cyclopropanes have been studied entensively during the past two decades, following the first account which appeared in 1922. Structural rearrangement to olefins and geometrical, cis-trans reactions are two types of isomerizations which cyclopropanes can undergo. A third and distinctly different reaction is the rearrangement of vinylcyclopropanes to cyclopentenes.

Investigators have studied these thermal rearrangements in attempts to develop and test theoretical models for carbon-carbon bond cleavage. Kinetic studies have been used to determine the Arrhenius parameters for a variety of cyclopropane rearrangements. Both the activation energy (E_a) and the pre-exponential "A" factor, from the Arrhenius equation ($k = A \exp(-E_a/RT)$, have been interpreted extensively in attempts to elucidate the mechanistic details of cyclopropane isomerizations. The effect of changing substituents upon the course of the reaction has been studied by analysis of the product mixtures from pyrolysis of many substituted cyclopropanes.

A variety of cyclopropanes and their thermal isomerizations are discussed in this chapter to provide a background for the new experimental work and the interpretation of it presented here.

A. STRUCTURAL ISOMERIZATIONS

The thermal isomerization of cyclopropane [1] to propylene [2] may be the most studied unimolecular reaction. Trautz and Winkler,[1]



[1] [2]

the first investigators to report the structural isomerization of cyclopropane [1], showed the reaction to be first order with an activation energy of about 64 kcal/mole in the temperature range of 550-650°C. Twelve years later, Chambers and Kistiakowsky[2] studied the kinetics of olefin formation in greater detail at temperatures from 469 to 519°C; thus supplying the more reliable Arrhenius parameters of

$$k = 10^{15.17} \exp(-65{,}000/RT)\text{sec}^{-1}$$

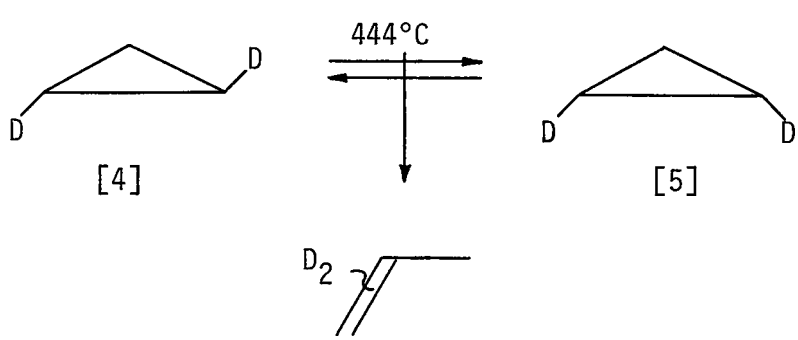
and confirming the earlier observation that the isomerization is cleanly first order. In 1961 Trotman-Dickenson, et. al.[3] pointed out one theoretical significance of the cyclopropane-propylene isomerization. "It is one of the few, clean, unimolecular reactions whose rate constant varies over an experimentally accessible pressure range." Several qualitative theories have been developed to define acceptable models for cyclopropane isomerization.[4] Along with kinetic studies of cyclopropane pyrolysis, confirming the earlier experiments,[5] investigation of deuterium,[6] tritium and carbon-13[7] isotope effects have been reported.

The next extention of experimental work was into alkyl substituted cyclopropanes. In general, reactions are more complicated since several

olefins are formed. One conclusion drawn from experimentation with alkyl substituted cyclopropanes is that they isomerize with a slightly lower activation energy than cyclopropane. Isomerizations, in all cases studied so far, at reasonable pressures, are unimolecular. Methylcyclopropane [3], an example investigated by Setser and Rabinovitch[8a] and Chesick,[8b] undergoes rearrangement to yield isobutene, cis-2-butene, trans-2-butene and 1-butene. Table I lists kinetic parameters for some alkylcyclopropanes which isomerize to olefins.

B. GEOMETRICAL ISOMERIZATIONS

Recently, geometrical isomerization of cyclopropanes, under pyrolytic conditions, has received wide attention; a situation precipitated by the observation of a reversible, geometrical isomerization of trans- and cis-cyclopropane-d_2 [4] and [5] by Rabinovitch, Schlag and Wiberg.[10] These investigators showed that the reaction is a homogeneous,



first-order, unimolecular rearrangement. Geometrical isomerization was revealed to be only slightly faster than the structural isomerization to propylene. At one half life for the appearance of cis-isomer [5] 8% of the starting material had already been converted to propylene-d_2.

TABLE I. STRUCTURAL ISOMERIZATIONS OF CYCLOPROPANES

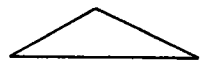
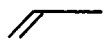
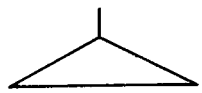
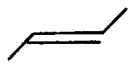
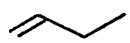
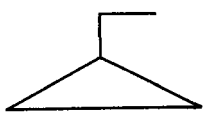
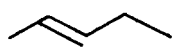
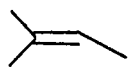
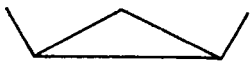
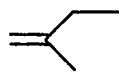
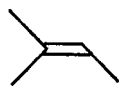
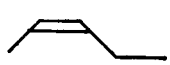
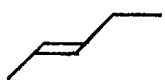
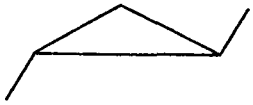
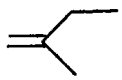
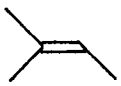
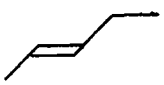
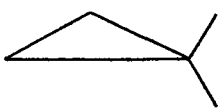
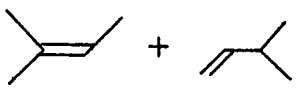
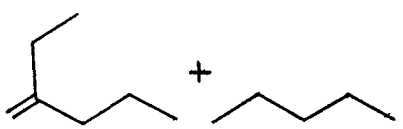
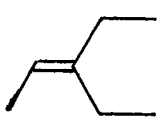
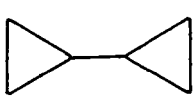
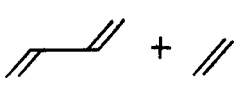
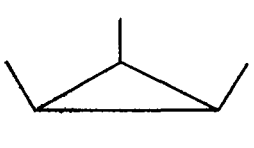
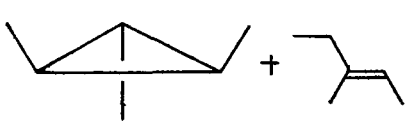
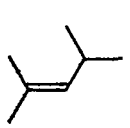
Cyclopropane	Olefin	$Log_{10}A$	E_a(kcal/mole)	Ref.
		15.17	65.0	2
		14.32	64.4	8a
		13.97	61.9	
		14.06	64.3	
		14.14	62.0	
		14.40	61.6	9a
	+ 			
	+ 			
	+ 			
		13.93	61.9	9b
		14.08	62.3	
		13.92	61.4	
		13.96	61.2	

TABLE I (CONTINUED). STRUCTURAL ISOMERIZATIONS OF CYCLOPROPANES

Cyclopropane	Olefin	$Log_{10}A$	E_a(kcal/mole)	Ref.
		13.93	61.9	9c
		14.08	62.3	
		14.40	63.9	
		14.30	62.9	
		15.05	62.6	9d
				
		15.74	64.9	9e
		16.8	70.8	9f
		15.78	60.9	9g
	cis and trans			
		15.83	64.4	9h

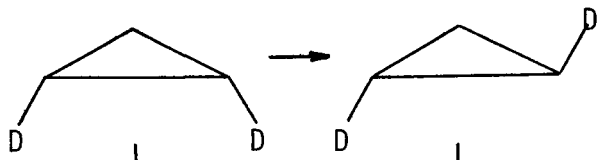
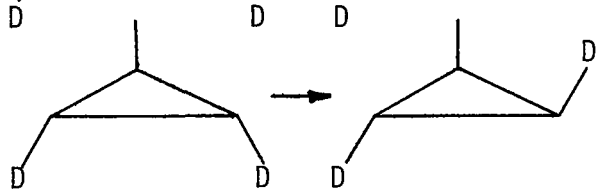
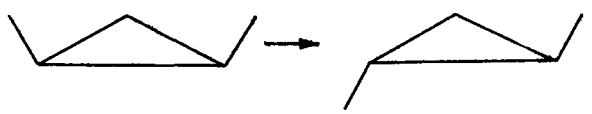
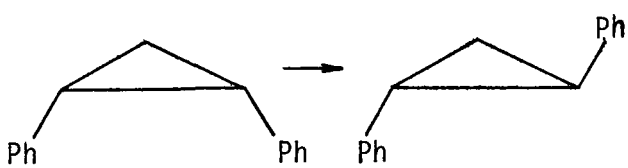
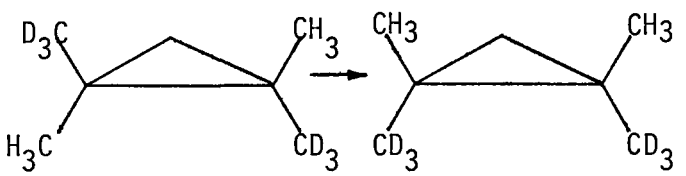
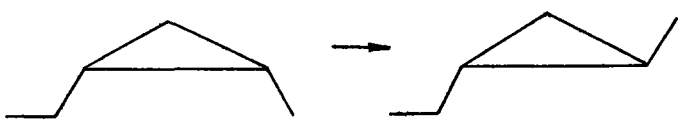
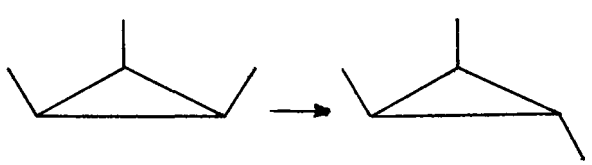
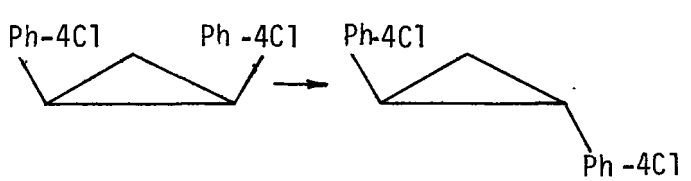
As in the structural isomerization, the absence of complicating side reactions in geometrical isomerization lends itself nicely to the construction of more sophisticated experiments. Frey, et. al. have reported the cis-trans-isomerization of 1,2-dimethylcyclopropane [6][9c,11] and the two isomers of 1,2,3-trimethylcyclopropane [7].[9g] As one might expect, their investigations showed that isomerizations of this kind are not limited to deuterated cyclopropanes. Several years later, Setser and Rabinovitch[8a] attempted to provide a mechanistic test of cis-trans-isomerization using 1,2-dideuterio-3-methylcyclopropanes [8] and [9], but the difficulties encountered in the preparation of pure isomers prevented their obtaining a definitive result.

Recently, Berson and Balquist,[12a] Carter and Bergman[12b] and Crawford and Lynch[12c] have all found evidence for racemization, along with geometrical isomerization, in optically active cyclopropyl compounds. Table II lists the kinetic parameters for geometrical isomerization of several cyclopropane derivatives.

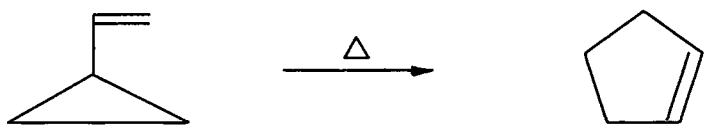
C. THE VINYLCYCLOPROPANE-CYCLOPENTENE REARRANGEMENT

Interest in the isomerization of substituted cyclopropanes leads logically to the study of olefinic substituted cyclopropanes, the most notable examples being vinylcyclopropane [10] and its derivatives. While vinylcyclopropane does undergo structural[14] and geometrical isomerization, it also has been shown to undergo a rearrangement of a type distinct from that of alkylcyclopropanes. Formation of the major pyrolysis product, cyclopentene [11], does not require the breaking of

TABLE II. GEOMETRICAL ISOMERIZATIONS OF CYCLOPROPANES

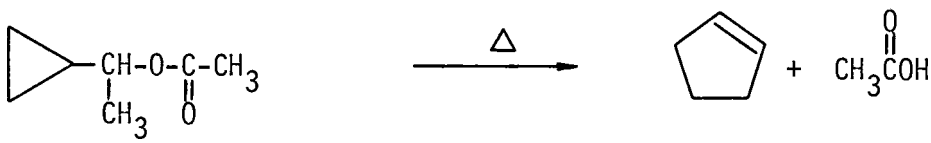
Reaction	$Log_{10}A$	E_a	Ref.
	16.41	65.1	10
	15.35	60.5	8a
	15.25	59.4	9c,11
	11.2	33.5	12c
	15.0	54.4	12a
	14.9	57.8	12b
	15.78	60.9	9g
	12.5	36.8	13

a C-H bond as do cyclopropane and alkyl derivatives of cyclopropane undergoing structural isomerization.



[10] [11]

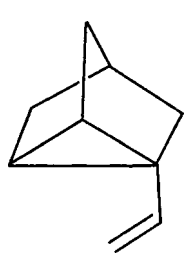
Discovery of this thermal rearrangement is generally credited to Overberger and Borchert,[15] who noted that the principal pyrolysis product of 1-cyclopropylethylacetate [12] was cyclopentene. They ration-



[12] [11]

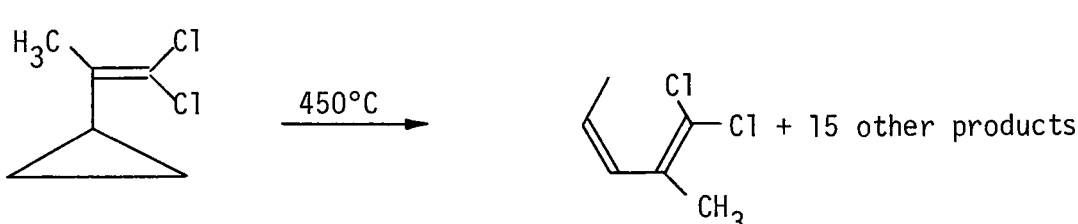
alized that vinylcyclopropane was first formed and subsequently rearranged to cyclopentene under the reaction conditions. A firm foundation was given to this explanation when a mixture of vinylcyclopropane in acetic acid was pyrolyzed under similar conditions to yield identical results. M. C. Flowers and H. M. Frey[16] and C. A. Wellington[14] reported independently that vinylcyclopropane isomerizes cleanly in a first-order reaction to cyclopentene. Both investigations dealt with the kinetics of the reaction and reported an activation energy ca. 15 kcal/mole below the cyclopropane-propylene rearrangement. Along with cyclopentene small

amounts of diolefins due to C-H bond rupture were also detected. Frey, obviously intrigued with the cyclic olefin formation and its significance in better understanding thermal rearrangements, has undertaken the study of a variety of substituted vinylcyclopropanes. Table III lists several along with their kinetic parameters. These investigations have shown that, in general, olefin formation is not significantly affected by substituents on the ring or vinyl group. However, several anomalous examples have been reported. In the low temperature range of 166-220°C, cis-1,4-hexadiene is the only observed[17d] pyrolysis product of cis-2-methylvinylcyclopropane [13], a truly unexpected result when compared to vinylcyclopropane. In contrast to the facile rearrangement of compound [13], several vinylcyclopropanes are extremely sluggish to the vinylcyclopropane-cyclopentene rearrangement. No rearrangement is observed for 1-vinylnortricyclene [14], even at 475°C.[18] Ketley, et. al.[19]



[14]

have shown that 1,1-dichloro-2-cyclopropylprop-1-ene [15] is stable at



[15]

TABLE III. VINYLCYCLOPROPANE-CYCLOPENTENE REARRANGEMENTS

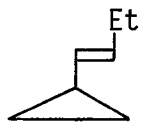
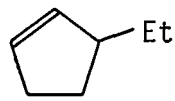
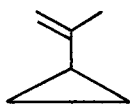
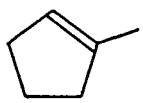
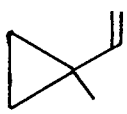
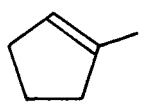
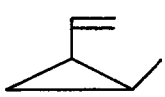
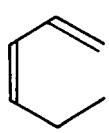
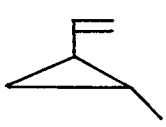
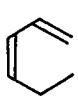
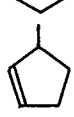
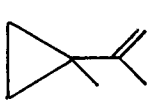
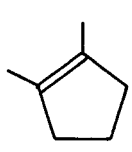
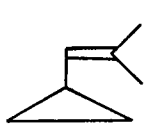
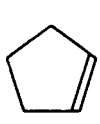
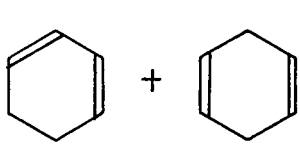
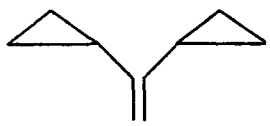
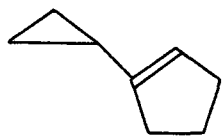
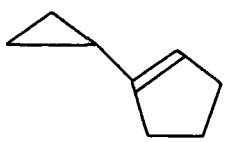
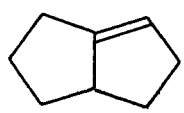
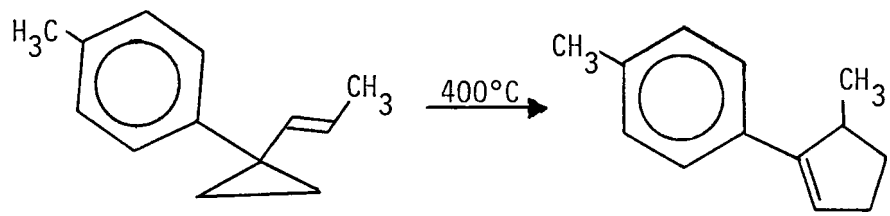
Vinylcyclopropane	Olefin	$Log_{10}A$	E_a kcal/mole	Ref.
		13.6	49.7	14, 16
		13.79	50.0	17a
		13.89	50.9	17b
		14.11	49.4	17c
		11.03	31.3	17d
	major 	14.74	48.7	17d
	minor 	13.67	48.7	
		14.14	50.5	17c
		14.00	54.6	17f
		14.50	50.2	17g

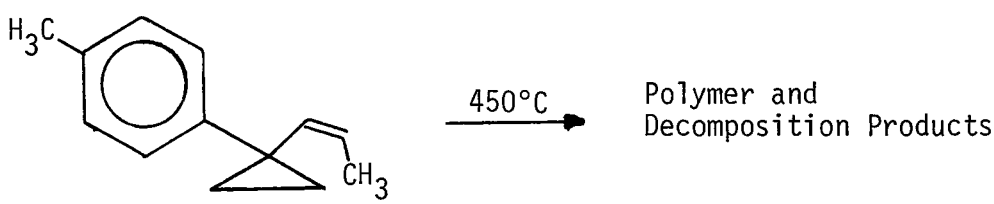
TABLE III (CONTINUED). VINYLCYCLOPROPANE-CYCLOPENTENE REARRANGEMENTS

Vinylcyclopropane	Olefin	$Log_{10}A$	E_a kcal/mole	Ref.
		14.29	51.1	17h
		14.01	51.3	17h

400°C and rapidly decomposes at 450°C to give at least 16 products. The major product of the reaction mixture was identified as 1,1-dichloro-2-methylpenta-1,4-diene. Investigations by Berlin, Fisher and Ketley,[20] dealing with the pyrolysis of geometrical isomers [16] and [17], revealed



[16]

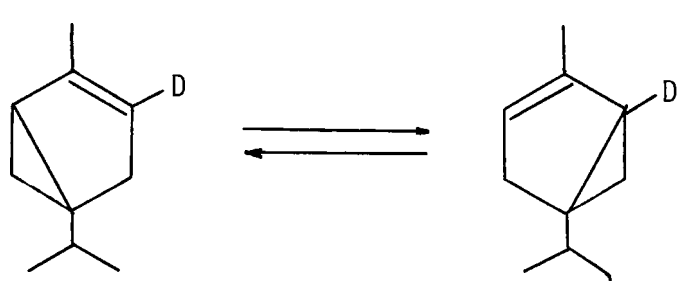


[17]

that the vinylic methyl cis (compound [17]) to the cyclopropane ring inhibits cyclopentene formation.

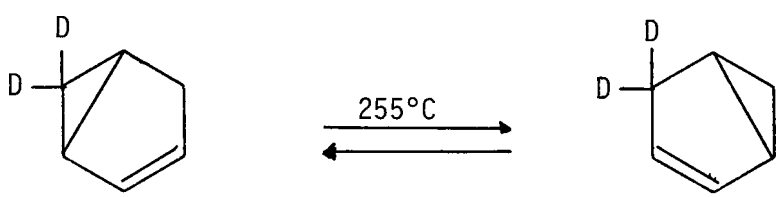
D. REARRANGEMENT OF MORE ELABORATE VINYLCYCLOPROPANES

Doering, Lambert[21] and Schmidt[63] have studied the thermal



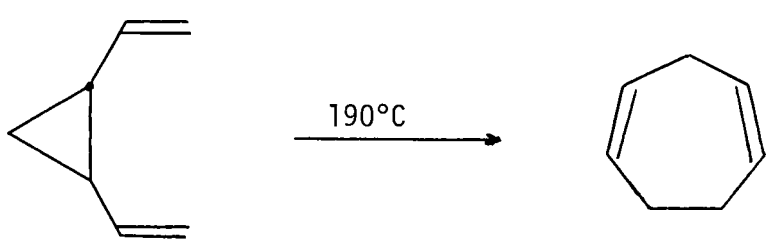
[18]

rearrangements of α-thujene-d_1 and have determined that optically active [18] can racemize and isomerize by various combinations of the vinylcyclopropane-cyclopentene rearrangement. The precise details of the rearrangement are not available from the quantitative observations first reported by Doering and Lambert. Subsequence re-examination by Schmidt has demonstrated that the rearrangement can be explain by a planar diradical. Another example of a degenerate vinylcyclopropane-cyclopentene rearrangement is the isomerization of bicyclo[3.1.0]hex-2-ene [19].[26]



[19] [19]

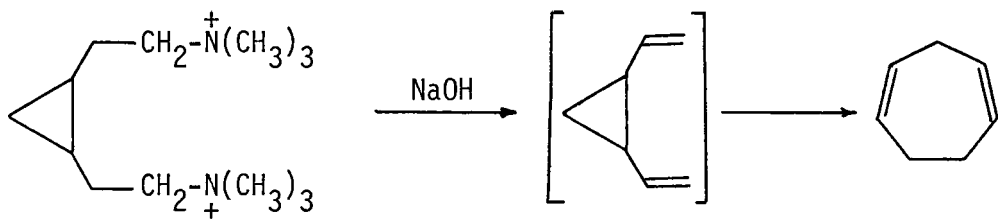
The effect of two double bonds on one cyclopropane ring has been investigated by Vogel, et. al.[23] Olefin formation from trans-1,2-divinylcyclopropane [20] proceeds nicely at 190°C with an activation



[20] [21]

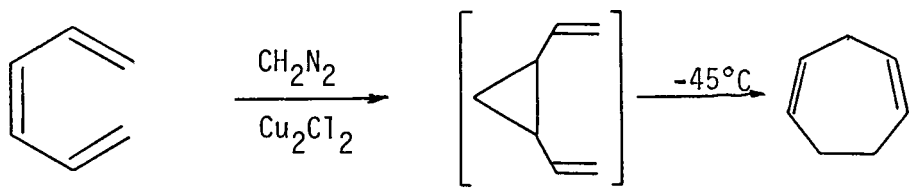
energy of 32.1 kcal/mole. Isomerizations of this type are normally visualized as Cope rearrangements. Even though the other stereoisomer,

cis-1,2-divinylcyclopropane [22], has never been prepared, it has been proposed[23c] as a highly reactive intermediate in the conversion of cis-(1,2-bis-β-dimethylaminoethyl)cyclopropane [23] to 1,4-cycloheptadiene [21].



[23] [22] [21]

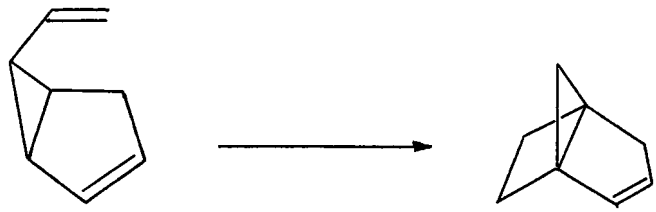
In an attempt to prepare compound [22], Doering and Roth[24] passed a dried stream of diazomethane in nitrogen into a suspension of cuprous chloride in cis-1,3,5-hexatriene [24]. The desired diolefin [22] was not detected



[24] [22] [21]

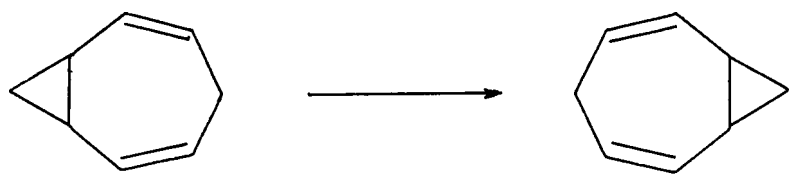
among the products of the reaction, either at room temperature or at -45°C. Instead there appeared compound [21] and products of further cyclopropanation. Again, the diolefin [22] was considered a reasonable intermediate.

The search for a stable cis-1,2-divinylcyclopropane resulted in the preparation of cis-6-vinylbicyclo[3.1.0]hex-2-ene [25], by



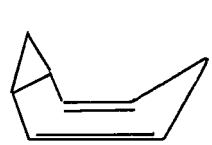
[25] [26]

J. M. Brown,[25] who reported an activation energy for rearrangement to compound [26] of 22.9 kcal/mole. Another stable cis-1,2-divinylcyclopropane is bicyclo[5.1.0]octa-2,5-diene [27] (3,4-homotropilidene).



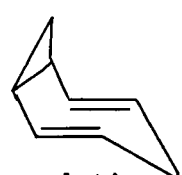
[27] [27]

Cope rearrangements within this molecule generate the starting material and lead to no permanent change. Fortunately, this degenerate reaction is observable by NMR and has been studied extensively by Doering, et. al.[24] Cope rearrangement in 3,4-homotropilidene [27] requires that the molecule be in the syn rather than the anti conformation. A molecule which



[27]

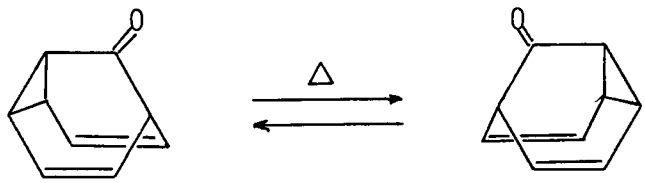
Syn



[27]

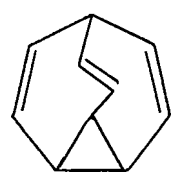
Anti

is constrained in the syn position is the tricyclic ketone [28] or



[28] [28]

"Barbaralone."[26] Rearrangements in compound [28] are much faster then in 3,4-homotropilidene [27], as was expected. An even more novel molecule is the trivinylcyclopropane tricyclo[3.3.3.$0^{4,6}$]deca-2,7,9-triene [29] or "bullvalene". Although synthesized by G. Schröder[27] in



[29]

1963, this molecule and its remarkable properties were first predicted by Doering.[26] "...the most surprising property of this hypothetical substance bullvalene is not so much the prediction of only one NMR band, but rather the fact that all its isomers can be transformed into one another. With ten carbon atoms, there are more than 1.2 million combinations that form bullvalene. The most unusual property of this molecule is that each of these arrangements can be transformed into any other one by Cope rearrangements." "The carbon atoms do not remain bound to each other in a fixed arrangement, but move statistically on the surface of a spherical molecule. Despite this extreme fluctuation, however, the structure of bullvalene does not change."

CHAPTER II

MECHANISM DISCUSSION

MECHANISM DISCUSSION

A great deal of conjecture concerning the nature of cyclopropane isomerization has arisen over the past several years. Mainly, two different models have been used to explain rearrangements. These models can be best described in terms of reaction coordinate diagrams. Three points on a reaction coordinate diagram are available experimentally. Two of these points (the reactant and product) are available from thermodynamic data, while the third point (the activation energy) is an Arrhenius parameter and calculable from kinetic data. Figures 1 and 2 are reaction coordinate diagrams for structual isomerization to propylene by both models and geometrical isomerization by both models.

One interpretive viewpoint is that there is a high energy intermediate along the reaction sequence between reactant and product. This intermediate, designated as trimethylene,* exists, in terms of energy, in a "puddle" at the top of the reaction coordinate. The other interpretation of existing experimental data is that the reaction coordinate is smooth and the reaction is concerted. An intermediate therefore plays no role if this is the case.

The activation energy (E_a) and "A" factor contain useful information about the nature of reactions. The highest point on our

---

*No particular geometry or spin state is meant to be inferred by the name trimethylene. Trimethylene, here, is a substance of molecular formula C_3H_6 that is neither cyclopropane nor propylene and should be subject to experimental tests to determine its exact nature.

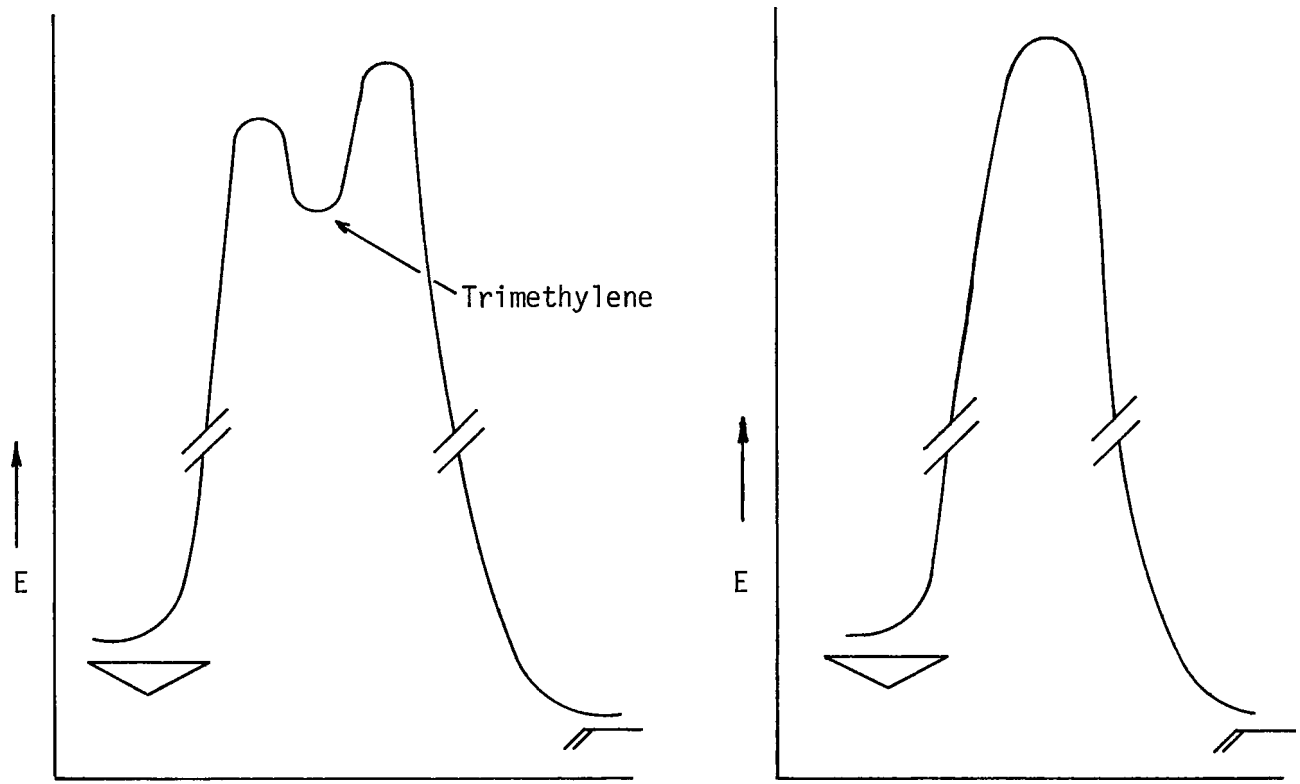


FIGURE 1. REACTION COORDINATE DIAGRAMS FOR CYCLOPROPANE-PROPYLENE ISOMERIZATION

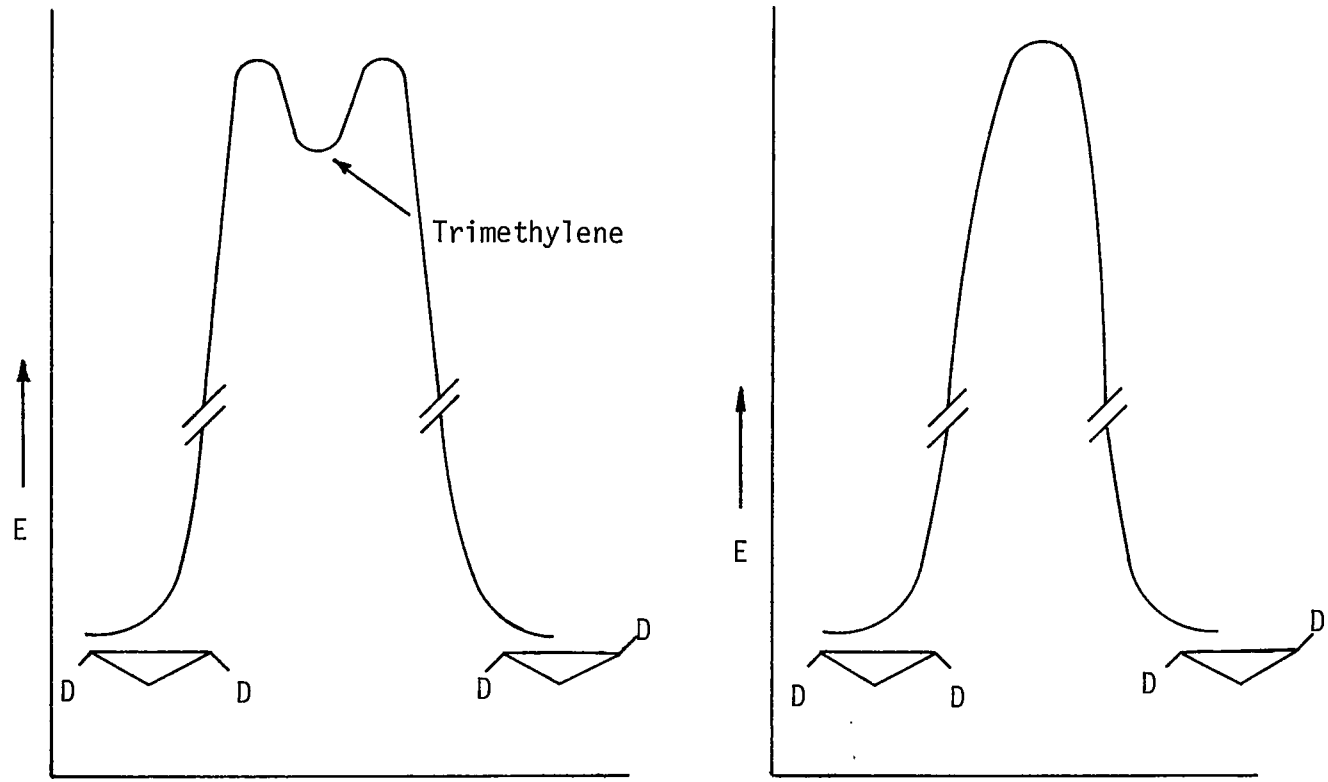
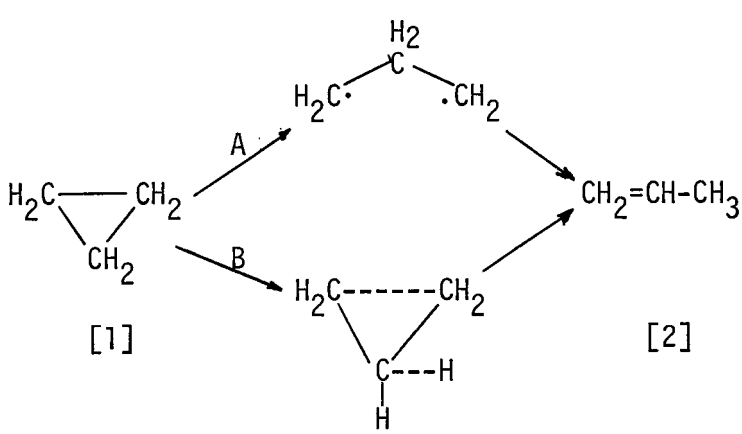


FIGURE 2. REACTION COORDINATE DIAGRAMS FOR CIS-TRANS ISOMERIZATION

reaction coordinate diagrams is E_a and measures the amount of energy necessary for carbon-carbon bond rupture. The "A" factor, in general, is a measure of the organization of the transition state. Values of 10^{10}-10^{12} for "A", are equated with a highly ordered transition state, while "A" factors of 10^{15}-10^{16} indicate a somewhat less organized transition state. "Normal" "A" factors are considered to fall in the range of 10^{13}-10^{14}. These parameters have been used by many investigators in their attempts to gain insights to pathways for thermal unimolecular rearrangements.

A. INTERPRETATION OF EXISTING CHEMICAL AND KINETIC DATA

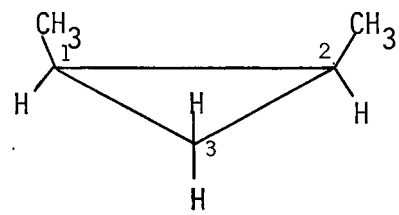
Very early in the history of the structural isomerizations of cyclopropane [1] to propylene [2], Chambers and Kistiakowsky[2] proposed



two possible courses for the reaction. Path A involves the rupture of a carbon-carbon bond in the cyclopropane ring to yield trimethylene, followed by hydrogen migration to propylene. The other path (B) involves hydrogen migration and carbon-carbon bond rupture occurring

simultaneously, without the intermediacy of trimethylene.

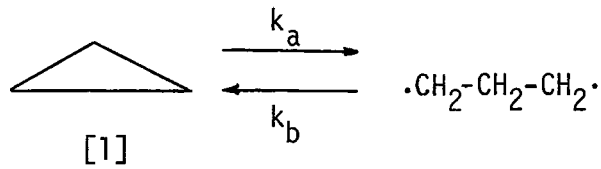
Flowers and Frey[8a] (Table I) studied the decomposition of 1,2-dimethylcyclopropane [6] to 2-methyl-1-butene, 2-methyl-2-butene and



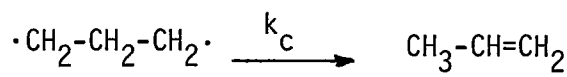
[6]

cis- and trans-2-pentene. Considerable bias was observed in favor of formation of the 2-pentenes, the result of C_1-C_2 bond rupture and hydrogen migration from C_3. Frey, et.al.[8a] interpretated these experimental results to be consistent with the existence of an intermediate like trimethylene.

Pursuing this problem from a detailed thermochemical and kinetic point of view, Benson[28] has discussed the known kinetic parameters for structural and geometrical isomerization of cyclopropane and concluded both rearrangements have a common intermediate.



[1]



[2]

Benson's interpretation of the kinetic data yields

$$\log k_a = 16.0 - 64{,}200/4.575\ T$$

$$\log k_b = 13.0 - 8{,}200/4.575\ T$$

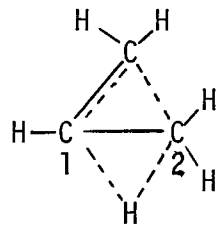
$$\log k_c = 12.2 - 9{,}500/4.575\ T.$$

Benson concludes trimethylene is an intermediate diradical which requires an activation energy of 8.2 kcal/mole to reclose to cyclopropane or needs 9.5 kcal/mole to reorganize to propylene. If this is indeed a correct interpretation then a fourth point has been placed on the reaction coordinate diagram in Figure 1 (i.e. the depth of the puddle). The life time for this diradical, calculated from the fast unimolecular step k_b is about $10^{-11.3}$ sec.[28] Since this rate is of the same order of magnitude as molecular vibrations, Benson's diradical has not lent itself, at this time, to any direct observation of its existence.

Blades,[6] studying propylene formation from both cyclopropane and cyclopropane-d_6, has observed an isotope effect of

$$\frac{k_H}{k_D} = 0.82 \exp (1{,}300/RT).$$

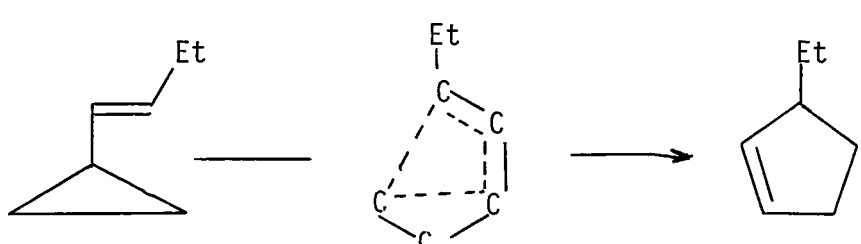
The investigators conclusion is that while trimethylene may be an intermediate, the isotope effect is consistent only with a transition state where a hydrogen atom is weakly bonded to its original carbon atom (C_1) and ultimate carbon atom (C_2).



In the same sense vinylcyclopropane [10] isomerization to cyclopentene [11] also may occur by a concerted pathway or by the intervention of an intermediate similar to trimethylene. Comparisons of Tables I and III show that vinylcyclopropane-cyclopentene isomerization proceeds with a considerably lower activation energy and with a lower "A" factor, than does cyclopropane-propylene isomerization.

Flowers and Frey[16] suggest that if the transition state involves a simultaneous rupture of the cyclopropyl ring in vinylcyclopropane and formation of the five membered ring, little entropy increase in this transition state would be expected. They state that the "normal" "A" factor (Table III) observed in their kinetics is consistent with this transition state and that the low value of the energy of activation also supports their postulate.

The Arrhenius parameters obtained by Ellis and Frey[18a] for trans-1-cyclopropyl-1-butene [30] are very similar to those of other vinyl-



[30] [31]

cyclopropanes (Table III). This difference in vinylcyclopropane-cyclopentene over cyclopropane cis-trans isomerization has been attributed to the contribution of allylic resonance energy in the transition state. Flowers and Frey[16] prefer to interpret this observation as evidence for a concerted reaction. The appreciably lower values for the "A" factor (10^{13}-10^{14}) in the vinylcyclopropane-cyclopentene rearrangement as compared with those for cyclopropane-propylene isomerization (10^{15}-10^{16}) was the basis for their conclusions.

These comparisons, however, have been used for the postulation of an allylically stabilized diradical.[29] The difference (ca. 15 kcal/mole) between the activation energy for cis-trans isomerization of cyclopropanes (ca. 65 kcal/mole) and cyclopentene formation from vinylcyclopropanes (ca. 50 kcal/mole) has been equated by many investigators with the allylic resonance energy. Recently, Benson, et. al.[29] have measured 12.6±1 kcal/mole for the allylic resonance energy from their studies of iodine catalyzed isomerization reactions. Benson's explanation of the "normal" pre-exponential "A" factors in the diradical mechanism is generally as follows: In the reactant the vinyl group can undergo essentially free rotation. However, in the transition state the allylic part of the diradical is rigid and cannot rotate. Thus, the entropy contribution of free rotation is lost in the transition state. But as a result of ring rupture the other part of the diradical is free to rotate. The net result is that on passing from reactant to the transition state there is essentially no change in entropy.

The geometrical cis-trans- isomerization of 1,2-dideuteriocyclopropane [4] observed by Rabinovitch, et. al.[10] has been cited by several investigators as evidence for the intermediacy of a trimethylene diradical.[28,30,31,32] The fact that most geometrical isomerizations of substituted cyclopropyl compounds (see Table II) have a "high" "A" factor has been interpreted as largely the result of a diradical intermediate with more freedom to rotate.[32]

Berson and Balquist[12a] in their studies with optically active tetramethylcyclopropane-d_6 [32] observed both geometrical isomerization and racemization. Unfortunately, no one mechanism explains their results. Carter and Bergman[12b] and Crawford and Lynch[12c] have found that the most convenient explanation of geometrical isomerization and racemization is the intervention of a trimethylene diradical. This conclusion was reached since it was observed that isomerization and racemization proceed at the same rate.

Geometrical isomerization will lend itself to an experimental test of mechanism. The question is what cyclopropyl substrate will allow a definitive answer. It is in this direction that our attention will now be focused.

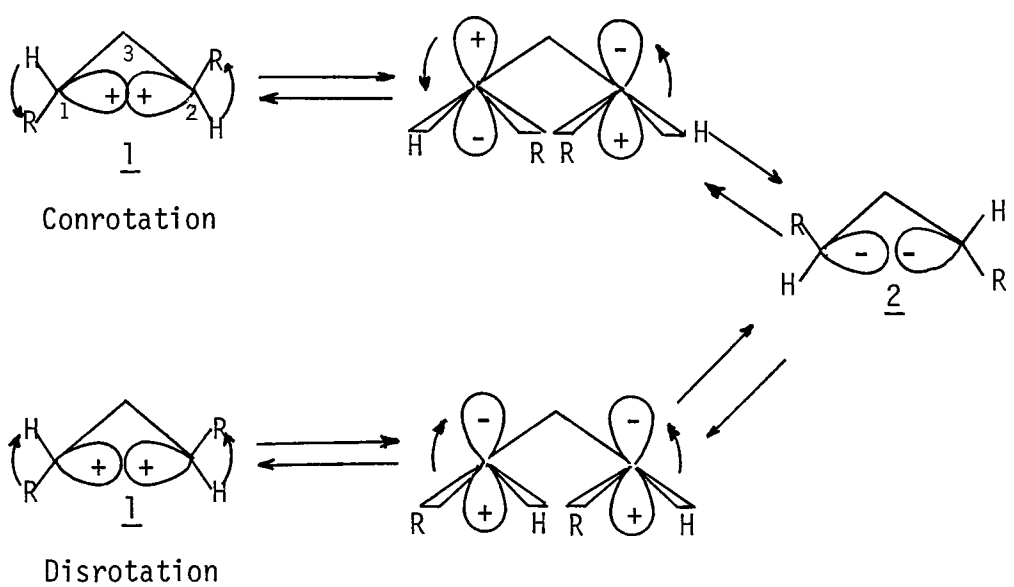
B. GEOMETRICAL ISOMERIZATION MODELS (MECHANICAL DISCRIPTION OF MOTIONS)

The description of observable, geometrical cyclopropane rearrangements, such as that of cis- to trans-1,2-dideuteriocyclopropane [4] and [5], can be classified as three limiting sets of molecular motions. At each observable event one can expect to see I) a simultaneous

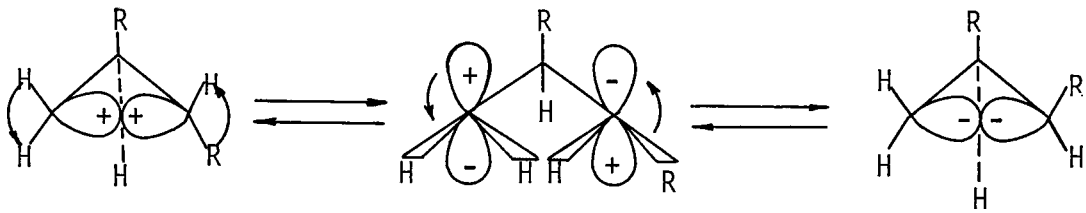
epimerization at two of the three carbon atoms in the ring, II) an epimerization exclusively at one carbon atom in the ring, or III) randomization of the stereochemistry at two of the three carbon atoms in the ring. The possibility of observing mixed mechanisms is not ruled out.

1. Simultaneous Epimerization at two Centers (Case I)

The distinguishing characteristic of this model for geometrical isomerization, is that both of the participating carbon atoms are restricted to rotate together through an angle of only 180°. The result of this operation on a vicinal disubstituted cyclopropane, in which only the most heavily substituted bond (between C_1 and C_2) breaks, is the



production of 2 from 1 and vice versa, i.e., racemization. If one of the other carbon-carbon bonds (between C_1 and C_3 or C_2 and C_3) in the three membered ring were carried through this operation, geometrical

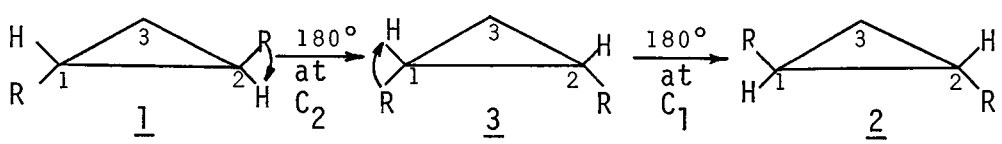


1 3

cis-trans isomerization would result. This model is identical with the concept introduced by Roald Hoffmann[33] for concerted electrocyclic isomerizations of cyclopropanes. Theoretical calculations by Hoffmann indicate that the conrotatory mode of rotation should be favored. Either rotation (disrotatory or conrotatory), however, would give the same experimental result.

2. Epimerization Exclusively at one Carbon (Case II)

This model requires the rotation of one carbon atom in the ring through 180° while the adjacent ring carbons remain stationary. Conversion of the trans compound 1 to the cis isomer 3 requires one event.

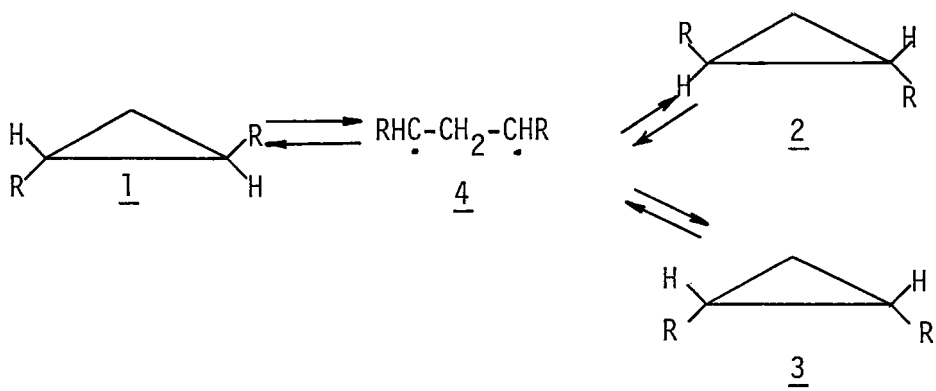


1 3 2

Note that conversion of 1 to the enantiomeric trans isomer 2 requires two consecutive rotations at C_1 and C_2 with an obligatory pause at the cis isomer 3. This model was first presented by F. T. Smith[34] as an explanation for geometrical isomerization of 1,2-dideuteriocyclopropane.

3. Randomization of Stereochemistry at two of the three Carbons (Case III)

The requirements for this model are the intervention in the reaction of an intermediate 4 in which apparent rotations about the



terminal carbons are fast relative to recyclization. As a consequence either 2 or 3 can be formed from 1 in any given event. This model fits exactly the reaction coordinate diagram discussed earlier in which trimethylene was described as the intermediate.

C. CONSEQUENCES OF THESE MECHANISTIC MODELS

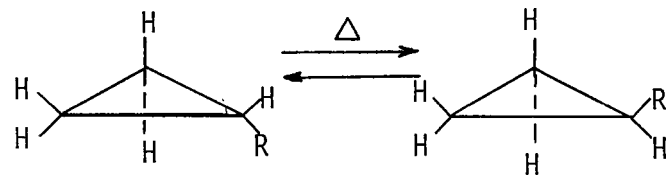
The following convenient notation will be used to describe geometrical isomerization with the reaction schemes in this section and later:

Conc - Simultaneous epimerization at two centers (Case I);

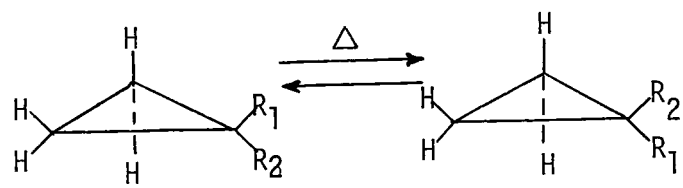
Smith - Epimerization at one center exclusively (Case II);

Random - Randomization of stereochemistry at two of the three carbons (Case III).

Monosubstituted Cyclopropanes - Geometrical isomerization of monosubstituted cyclopropyl compounds offers no mechanistic information since no observable reactions takes place.

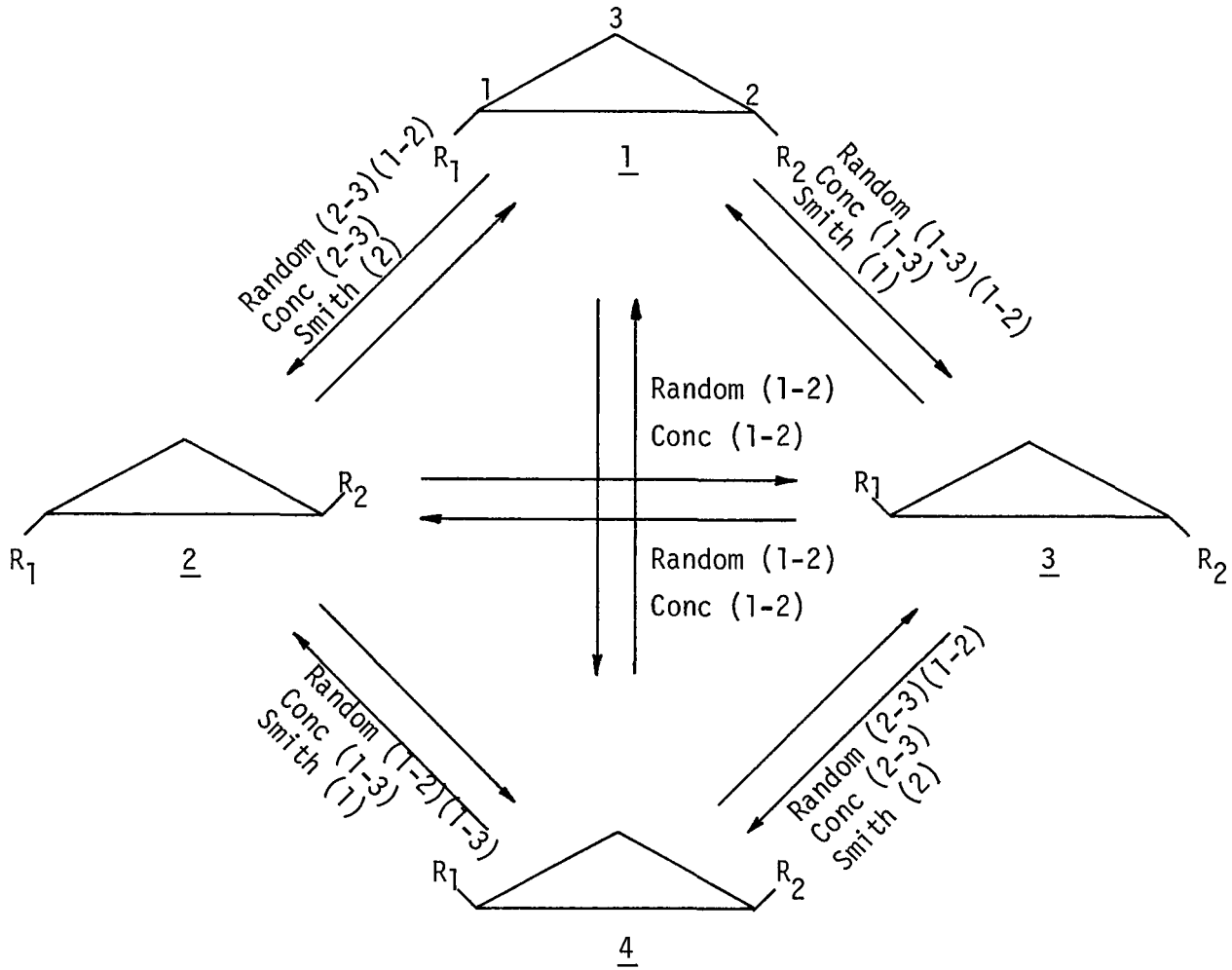


Disubstituted Cyclopropanes - Geminal disubstituted cyclopropanes fall in the same category as monosubstituted cyclopropanes. Any geometrical isomerization leads to starting material.



The simplest test case could be the geometrical isomerization of a cis-1,2-disubstituted cyclopropane as illustrated in Scheme I. If $R_1 = R_2$, isomers 1 and 2 become identical, and the observable result of isomerization is the formation of enantiomers 2 and 3. No distinction between pathways can be found, since each predicts the same products.

An example will illustrate the meaning and use of the notations in Scheme I. In proceeding from 1 to 2, Random(2-3)(1-2) means that the transformation can occur by a randomization of stereochemistry at C_2 and C_3, or


3
1
2
1
R_1
R_2
Random (2-3)(1-2)
Conc (2-3)
Smith (2)
Random (1-3)(1-2)
Conc (1-3)
Smith (1)
Random (1-2)
Conc (1-2)
Random (1-2)
Conc (1-2)
R_2
R_1
2
R_1
R_2
3
Random (1-2)(1-3)
Conc (1-3)
Smith (1)
Random (2-3)(1-2)
Conc (2-3)
Smith (2)
R_1
R_2
4

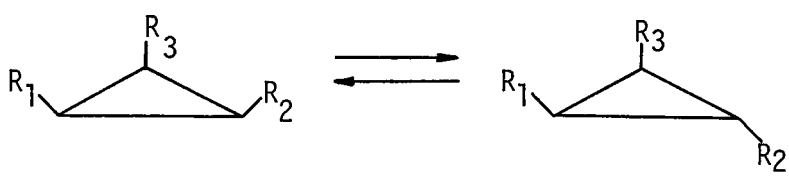
SCHEME I

at C_1 and C_2. The same transformation occurring by conc(2-3) means that C_2 and C_3 undergo simultaneous rotation of 180°C, while Smith(2) means C_2 rotates 180°, while C_1 and C_3 remain stationary.

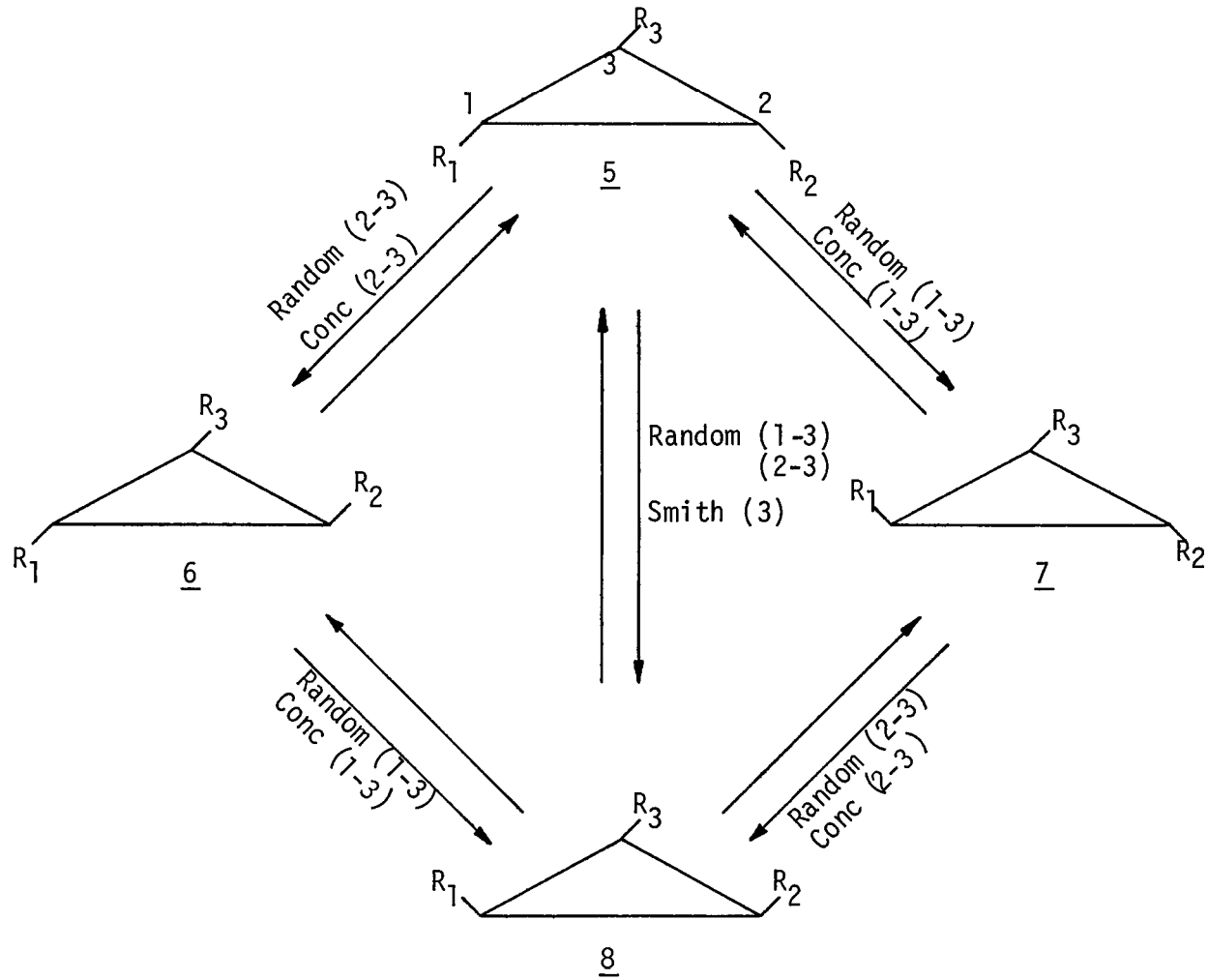
Proper substitution, i.e. $R_1 \neq R_2$, allows 1 to be transformed into its enantiomer 4 as well as isomerizing to 2 and 3. Again all three processes can mix compounds 1-4. Racemization of 1 is accomplished in one step for the random or concerted process. The Smith mechanism requires two steps in order to form 4.

Scheme I may also start from trans-1,2-disubstituted cyclopropanes and contains the same information about mechanism.

Trisubstituted Cyclopropanes - The obvious case of interest is a 1,2,3-trisubstituted cyclopropane. When $R_1 = R_2 = R_3$ no information can be generated for distinguishing our mechanisms. However, if $R_1 = R_2 \neq R_3$



and R_3 is a substituent (e.g. a vinyl group) which will favor ring openings between C_1 and C_3 or C_2 and C_3, then the resulting substrate will allow a distinction to be made between the three possible mechanisms. Scheme II is a representation of this system. If the substrate is truly biased against bond cleavage between C_1 and C_2, note that there is no direct route for 6 to be transformed into 7.


R3
3
1
2
R1
R2
5
Random (2-3)
Conc (2-3)
Random (1-3)
Conc (1-3)
Random (1-3)
(2-3)
Smith (3)
R3
R2
R1
6
R3
R1
R2
7
Random (1-3)
Conc (1-3)
Random (2-3)
Conc (2-3)
R3
R1
R2
8

SCHEME II

CHAPTER III

DISCUSSION OF EXPERIMENTS

D. KINETICS OF SCHEME II

A convenient substrate for a kinetic investigation would be one in which compounds 5, 6, 7 and 8 are thermodynamically equivalent, so that under equilibrium conditions all isomers formed would be present in equal amounts. Thus, starting with pure 5, if the Smith mechanism (Case II) is operable, the only other isomer formed would be 8. If a concerted epimerization at two centers (Case I) defines the reaction pathway, isomer 5 will form, very early in the reaction, only 6 and 7, which will subsequently rearrange to 8 and 5. Randomization at two carbons (Case III) will have kinetically a completely different outcome. Isomer 5 will rearrange to 6, 7 and 8, along with reclosure to itself, at identically equal rates. In Cases I and III isomers 5, 6, 7 and 8 would have the same concentration at equilibrium, but would have a striking different concentration very early in the reaction. In case II isomers 6 and 7 would never be formed.

The next chapter deals with the preparation and pyrolysis of some deuterated vinylcyclopropanes, designed to unravel the mechanistic problem proposed here.

DISCUSSION OF EXPERIMENTS

The mechanistic problem proposed in Chapter II can be investigated by pyrolyzing vinylcyclopropanes which have been selectively deuterated on the ring. The two carbon-carbon bonds in the ring adjacent to the vinyl group will be preferentially cleaved, lessening the complexity of rearrangements. This will allow our substrate to fit the reactions outlined in Scheme II. The synthesis of selectively deuterated vinylcyclopropanes and the proofs of structure of these compounds and their precursors will be the subject of Chapter IIIA. The thermal, geometrical isomerizations of deuterated vinylcyclopropane and associated kinetics, along with an interpretation of all NMR spectra, will be discussed in Chapter IIIB and C.

A. SYNTHESIS AND STRUCTURE PROOF OF SUBSTITUTED VINYLCYCLOPROPANES

1. 1-Deuterio-2-vinylcyclopropane

The synthetic sequence necessary for the preparation of 1-deuterio-2-vinylcyclopropane (see Scheme III), began with the isolation, in 64% yield, of 1,1-dibromo-2-vinylcyclopropane [33] from the reaction of bromoform, potassium tert-butoxide and 1,3-butadiene.[35] Vinylcyclopropane [36] was prepared from compound [33] by reaction with metallic sodium and methyl alcohol.* The reason for preparing vinylcyclopropane

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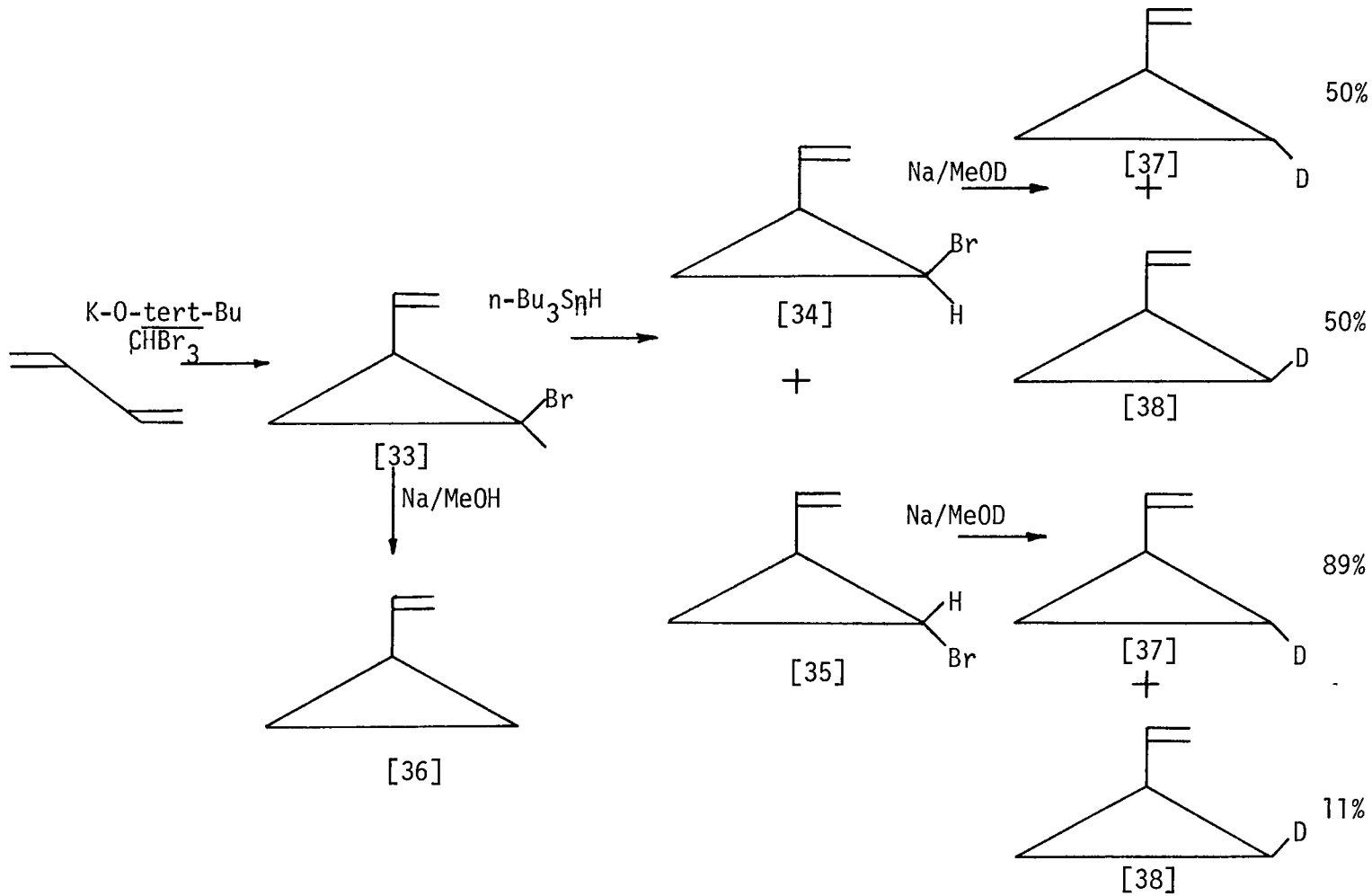
*This is a slight variation of the synthetic procedure given by Nishida, et. al.[36] who used ethanol rather than methanol.


K-O-tert-Bu
CHBr3
[33]
Na/MeOH
[36]
n-Bu3SnH
[34]
Br
H
Na/MeOD
[37]
D
50%
[38]
50%
[35]
89%
11%

SCHEME III

was two fold. First, practice was needed in preparing vinylcyclopropane by this synthetic procedure since the deuterated vinylcyclopropanes would be prepared using methyl alcohol-o-d and sodium. Second, vinylcyclopropane was needed as a comparison with the deuterated vinylcyclopropanes for vapor phase chromatography (VPC), nuclear magnetic resonance (NMR) and mass spectrometry analysis.

Thus, being assured vinylcyclopropane could be prepared, we cautiously reducted the dibromovinylcyclopropane [33] with tri-n-butyltin hydride, at ca. 30°C, to furnish, in 62% yield, the expected geometrical isomers of 1-bromo-2-vinylcyclopropane [34] and [35].[37] The ratio of isomers [34] and [35], as determined by VPC, was 7:3 respectively and identical with that reported by Seyferth. Treatment of the major isomer [34] with metallic sodium and methyl alcohol-o-d resulted in the formation of a 1:1 mixture of cis- and trans-1-deuterio-2-vinylcyclopropane, [38] and [37]. This isomeric mixture was assured when integration of the NMR peaks at 0.7 and 0.3δ (the non-allylic ring hydrogens) showed that each was representative of 1.5 hydrogens relative to one allylic ring hydrogen.

Reaction of the minor bromo isomer [35] with methyl alcohol-o-d and metallic sodium produced predominately (89%) trans-1-deuterio-2-vinylcyclopropane [37], along with only 11% of the cis-isomer [38]. (Mass spectrometry indicated that the deuterium content was ca. 96% d_1 and 4% d_0.) The isomer percentages were calculated by the area under the signals at 0.3 and 0.7δ. Pure trans [37] would have an area ratio

of 2:1 at 0.3 and 0.7δ respectively. The sample in question had an area ratio of 61:39, which is equivalent to 89% trans and 11% cis.

Modification of the synthetic procedure for trans isotopically labelled vinylcyclopropane allowed almost pure cis-1-deuterio-2-vinylcyclopropane [38] to be prepared. Scheme IV outlines this synthesis. Reaction of compound [33] with tri-n-butyltin deuteride, rather than the hydride, afforded isomers [39] and [40] in a ratio of 7:3.* The trans-bromo isomer [40] was by VPC and reduced using methyl alcohol and metallic sodium to cis-1-deuterio-2-vinylcyclopropane [38].

Structural assignments of the bromovinylcyclopropanes were made by Seyferth, et.al.[37] on the basis that cis products predominate during partial reduction of gem-dihalocyclopropanes with tri-n-butyltin hydride. This is considered consistent with a radical-chain process that transfers hydride to the least hindered side of the 1-halocyclopropyl radical.[38a,38b] Although not rigorous, Seyferth's conclusion was that the minor isomer was the trans compound [35] and the major isomer was the cis compound [34]. Several other observations confirm this assignment of configuration. Heating at 1:1 mixture of these two isomers [34] and [35] at 198°C for 60 minutes in sealed, evacuated glass ampules resulted in a predominance of isomer [35]. This is indicative of compound [35] being the thermodynamically more stable

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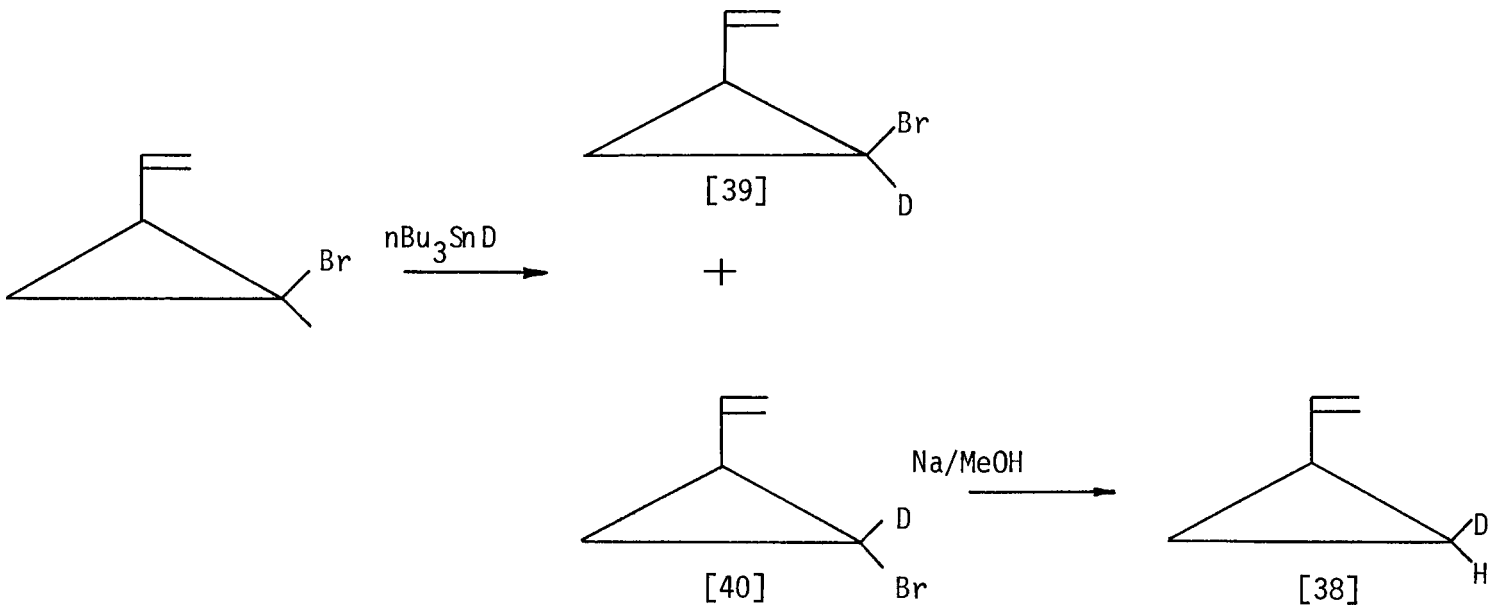
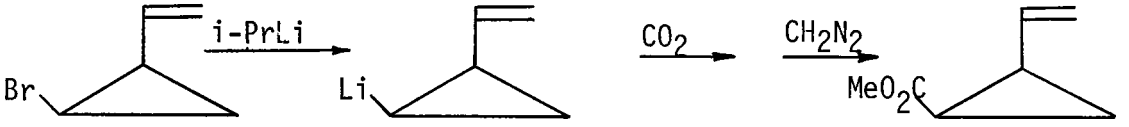
*The reaction of compound [45] with tri-n-butyltin deuteride required ca. four times longer than with tri-n-butyltin hydride, indicating a significant kinetic deuterium isotope effect.



SCHEME IV

trans isomer. NMR experiments using the Nuclear Overhauser Effect on both isomers point unambigously to [34] being cis-1-bromo-2-vinylcyclopropane.[39]

These stereochemical conclusions were reinforced by Landgrebe and Becker,[38] who noted that the chemical shift of the hydrogen on the halogen bearing carbon atom for a variety of cis-2-substituted cyclopropyl halides is ca. 0.48δ further downfield than that for the trans isomer. Finally, chemical evidence[38] was adduced by converting the cis- and trans-bromovinylcyclopropanes [34] and [35], by way of the corresponding lithium compounds to methyl cis- and trans-2-vinylcyclopropane carboxylate of known stereochemistry.



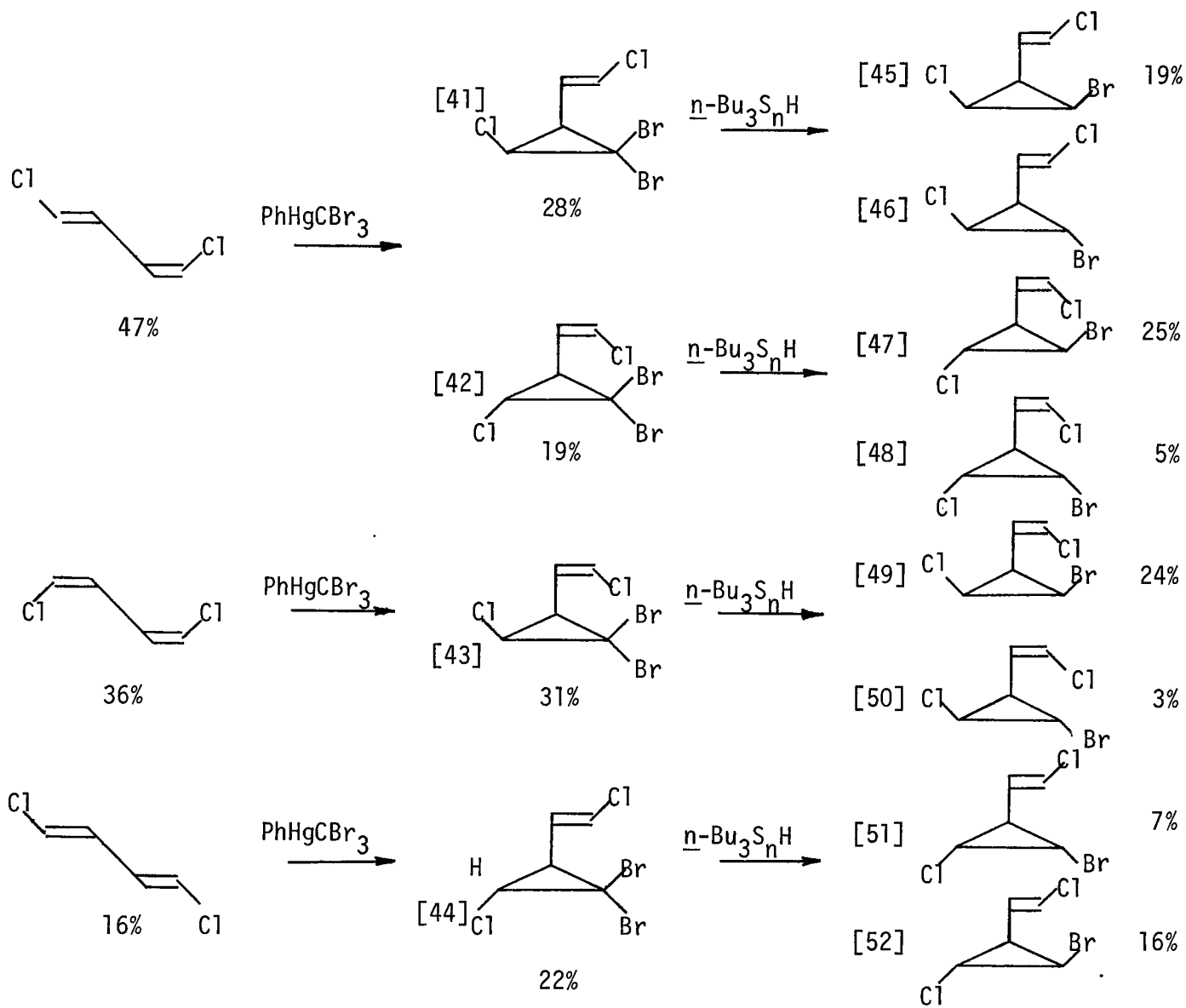
Being assured of the configuration of the bromovinylcyclopropanes we now turn our attention to the stereochemistry of the deuterated vinylcyclopropanes. It is reasonable that the stereochemically pure labelled hydrocarbon derived from trans-1-bromo-2-vinylcyclopropane [35] is almost certainly trans-1-deuterio-2-vinylcyclopropane [37]. The opposite configuration would require complete inversion of the substituent on the cyclopropyl ring. NMR parameters (coupling constants and chemical shifts, see NMR discussion, Chapter IIIC) also confirm this configuration.

A useful, but little applied tool, for structure determination is Microwave Spectroscopy. Using microwave data in the literature for unlabelled vinylcyclopropane and a sample of compound [37] R. J. Curl[40] has calculated and experimentally observed the microwave spectra of trans-1-deuterio-2-vinylcyclopropane. This has unambigously assured that the configurational assignment of [37] is correct.

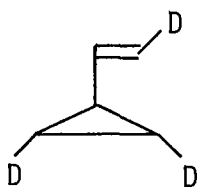
With trans-1-deuterio-2-vinylcyclopropane [37] now securely characterized and prepared, the synthesis and structure proof of a vinylcyclopropane with two deuterium labels on the ring will be considered.

2. Trideuteriovinylcyclopropane

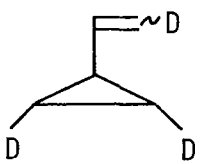
The preparation of the halogenated vinylcyclopropanes that were used as precursers to deuterium labelled vinylcyclopropane is illustrated in Scheme V. Reaction of phenyl(tribromomethyl) mercury[41] with a large excess of cis,trans-, cis,cis-, and trans,trans-1,4-dichloro-1,3-butadiene led to the expected dibromodichlorovinylcyclopropanes [41], [42], [43] and [44]. That these isomers possessed a vinylcyclopropane skeleton was shown by their metallic sodium and methanol reduction to vinylcyclopropane [10]. These four stereoisomers were isolated as three peaks by preparative VPC using a 13 ft., 10% polypropyleneglycol-4000 on chromasorb W, 60/80 mesh column. Isomers [42] and [43] were found in one peak in a ratio of 2:3 respectively, while [41] and [44] were completely separated. Mass spectra indicate that these compounds contain two bromine and two chlorine atoms. NMR (see Section IIIC) suggests two olefinic hydrogens, one allylic hydrogen and one


Cl
Cl
47%
PhHgCBr3
[41]
Cl
Br
Br
28%
n-Bu3SnH
[45]
19%
[46]
[42]
19%
[47]
25%
[48]
5%
36%
[43]
31%
[49]
24%
[50]
3%
16%
[44]
H
22%
[51]
7%
[52]
16%

SCHEME V

Compound [45] —Na/MeOD→ 

[53]

Compounds [45, 47-52] —Na/MeOD→ 

[54]

SCHEME V (CONTINUED)

hydrogen on a cyclopropyl carbon that also bears a halogen. Detailed analysis of the NMR coupling constants shows that the stereochemistry exhibited in Scheme V is correct.

Cautious reduction of a mixture of compounds [41], [42], [43] and [44] with tri-n-butyltin hydride at 30°C would be expected to produce the eight stereoisomers of bromodichlorovinylcyclopropane* [45] through [52]. Seven of the eight trihalo compounds were found to be formed in the amounts shown in Scheme V. Only isomer [46] was not detected, but must have been formed. These seven isomers were purified by preparative VPC using a 10 ft., 10% SF-96 on chromasorb W, 60/80 mesh column. Five chromatographic peaks with relative retention times of 1:1.1:1.5:1.8:2.1 were found to contain the seven isomers. Mass spectra of these five chromatographic peaks indicate all contain compounds having a molecular weight of 214. Parent, Parent + 2 and Parent + 4 lines in the mass spectra were in a ratio of 10:16:7, which confirms that all contain one chlorine and two bromine atoms.[42] The NMR spectra of these compounds indicate two olefinic hydrogens, one allylic hydrogen and two vincinal hydrogens on a cyclopropyl carbon with each hydrogen attached to a carbon atom bearing a halogen. NMR parameters were used to assign the stereochemistry shown in Scheme V (see Section IIIC for a more detailed NMR discussion).

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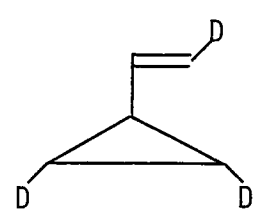
*Previous experiments by Seyferth, et. al. (ref. 37) have shown removal of chlorine by tri-n-butyltin hydride requires a much higher temperature of 140°C.

Metallic sodium and methyl alcohol reduction of a mixture of these trihalo compounds yielded vinylcyclopropane and provided the rationale for deuterium labelling using methyl alcohol-o-d.

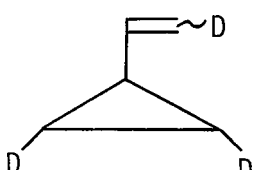
Our previous experience, in the preparation of 1-deuterio-2-vinylcyclopropane, would indicate that preparation of a vinylcyclopropane with two deuteriums placed stereospecifically on the ring would require sodium and methanol-o-d reduction of compounds containing ring halogens trans to the vinyl group (Compounds [48] or [51]). (It was shown in Section IIIA-1 that the reduction of cis-1-bromo-2-vinylcyclopropane [34] yielded a 1:1 mixture of cis- and trans-1-deuterio-2-vinylcyclopropane, while reduction of trans-1-bromo-2-vinylcyclopropane [35] yielded very nearly pure trans-1-deuterio-2-vinylcyclopropane [37].) Compound [45], which has both halogens cis to the vinyl group, was available pure from preparative VPC. To gain some practice with the sodium and methanol-o-d reduction of these bromodichlorocyclopropanes, compound [45] was reduced to the trideuteriovinylcyclopropane. A mixture of ring stereochemistry was expected, but instead compound [53] was formed almost



[53]

exclusively. Several explanations for this unsuspected event were open. First, our assignment of ring stereochemistry of compound [53] could

have been in error. This, of course, would have meant the observed chemical shifts and coupling constants were contradictory to all other cyclopropyl compounds of analogous structure. Second, the assignments of stereochemistry of trans-1-deuterio-2-vinylcyclopropane [37] could be "backwards", a situation very unlikely from the microwave data. Third, the mechanism for reduction of the trihalo compound [45] might not be the same as in the monobromovinylcyclopropanes, and inversion of the ring stereochemistry was a course in the reaction. To test the last hypothesis, a mixture of compounds [48], [49] and [51] was reduced with sodium and methanol-o-d. Compound [54] was produced which differs



[54]

from compound [53] only by the mixed stereochemistry about the olefin. Finally, reduction of a mixture of compounds [45] and [47] through [52] (all seven isomers) also produced compound [54].* This adventitious synthesis provided a route to sizeable quantities of the stereospecifically labelled trideuteriovinylcyclopropane.

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*The mixed stereochemistry of the vinyl group is inconsequential to the thermal reactions to which isomer [54] was later subjected.

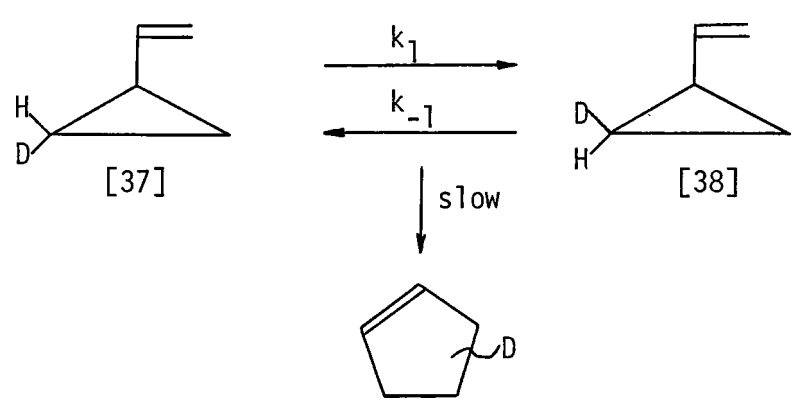
The labelled vinylcyclopropane was purified by preparative VPC using a 10 ft. 10% SF-96 on chromasorb W 60/80 mesh column.

In hand now are vinylcyclopropanes containing highly stereospecific deuterium labels, on the cyclopropyl ring. These mono and trideuterated vinylcyclopropanes will be subjected to thermal rearrangements. The pyrolysis techniques and kinetics of these isomerizations are discussed in the following section.

B. PYROLYSIS AND KINETICS

1. trans-1-Deuterio-2-vinylcyclopropane [37]

The usefulness of this substrate, in the investigation of geometrical isomerization of cyclopropyl rings, clearly hinges on whether or not deuterium epimerization on the ring is faster than cyclopentene formation. Exploratory pyrolysis of trans-1-deuterio-2-vinylcyclopropane [37] at 360°C for 20 minutes, conducted in the manner described in the kinetics part of this section, revealed that cis-trans isomerization of the cyclopropyl ring is the dominant reaction, with less than 5% cyclopentene formed when the cis:trans ratio was 1:1.



Within experimental error the ratio of deuterated vinylcyclopropane isomers is 1:1 at equilibrium, verifying that k_1 equals k_{-1}.

The establishment of rapid, geometrical isomerization, relative to cyclopentene formation, while informative, does not allow for direct comparison with the Arrhenius parameters for the irreversible rearrangement to cyclopentene. As a result, the kinetics of deuterium epimerization were studied. The pyrolysis and analytical techniques are discussed below.

Pyrolyses were carried out in sealed, evacuated, pyrex glass ampules at four temperatures in the temperature range 277.0 - 324.5°C over different time periods. All ampules, ca. 20 ml volume, were washed carefully in ammonium hydroxide and rinsed with distilled water before use. Deuterated vinylcyclopropane sample sizes were sufficient to produce pressures of ca. 100 torr. The air bath used for pyrolysis, a modified Aerograph A90-P3 gas chromatograph oven, is illustrated in Figure 3. The temperature of the oven, for each run, was maintained to ±0.5°C as monitored by a chromelalumel thermocouple. An Aerograph Model 326 Linear Temperature Programmer, operated in the isothermal mode, was used for temperature control. This air stirred oven was equipped with a chamber for preheating all samples to 250°C before insertion into the main body of the oven. This was done to lessen the time required for the samples to reach thermal equilibrium. Several experiments were carried out using soft glass ampules and pyrex ampules filled with glass wool to check for surface catalyzed reactions. No change in the rate of the reaction was observed under these conditions.

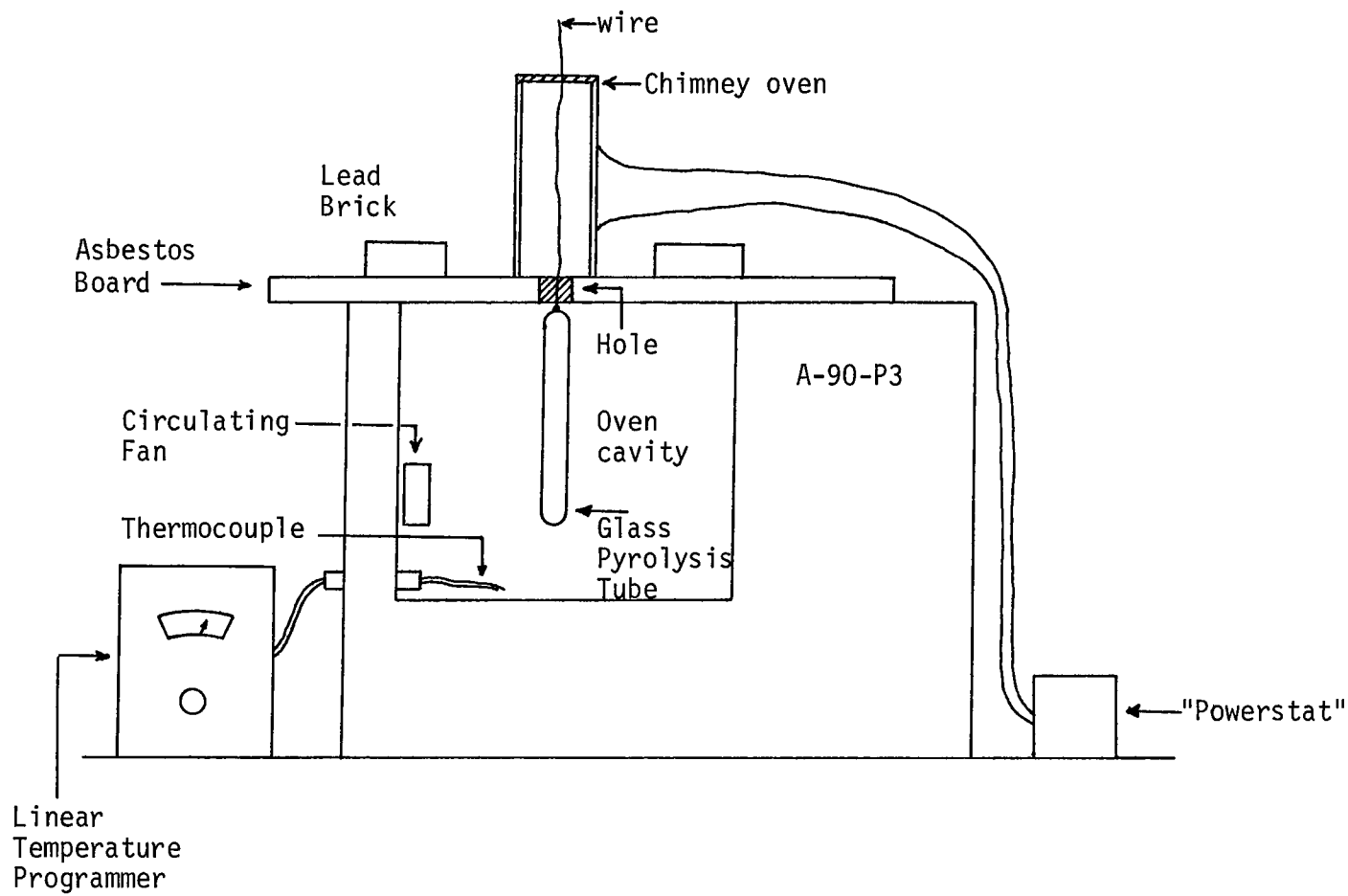
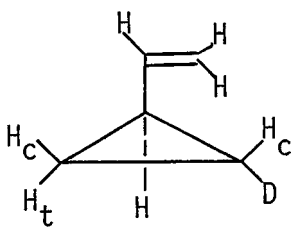


FIGURE 3. AIR BATH PYROLYSIS OVEN

The analytical method used for determining stereospecific purity of starting materials and products was 100 MHz NMR. After pyrolysis each ampule was partially immersed in liquid nitrogen to condense the gaseous material in the ampule. The ampules were opened and the water white liquid that had been frozen at the cold end of the glass ampule was dissolved in carbon tetrachloride and transferred directly to an NMR tube.

An example will best illustrate the method used for calculating the relative amounts of cis- and trans-deuteriovinylcyclopropane [38] and [37] in the reaction mixture. The areas under the NMR peaks at 0.3δ and 0.7δ (Figure 18), due to non-allylic cyclopropyl hydrogens, for 100 percent trans- isomer, would be 2.00 and 1.00 respectively.* The larger peak is due to the two hydrogens (H_c) cis to the vinyl group and the smaller peak is due to the one hydrogen (H_t) trans to the vinyl.



[37]

*This is true if the areas are normalized to the allylic hydrogen at 1.5δ being equal to 1.00 and if the vinylcyclopropane contains 1.00 atom/molecule of deuterium.

The following equations can be used to compute the percent composition of the cis-trans mixture.

$$[2/3\ (H_c) - 1/3\ (H_t)]\ 100 = \text{percent trans isomer,}$$

assuming only cis-trans isomerization.

percent cis + percent trans = 100

One form of the integrated rate expression for this first order, reversible reaction is:[43]

$$k_1 = \frac{x_e}{A_{ot}} \ln \frac{x_e}{x_{e-x}}$$

x_e = mole fraction of either isomer at equilibrium (0.5)

x = mole fraction of cis isomer at time t.

$a_o = 2\ x_e$

This equation must be reduced to a useful form because in the form above it requires the ln of an undefined number when x = 0.5.

$$k_1 = \frac{\frac{a_o}{z}}{a_{ot}} \ln \frac{0.5}{0.5-x}$$

$$2k_1t = -\ln (1-2x)$$

Table IV is a summary of the kinetic data.

TABLE IV. KINETIC DATA FOR GEOMETRICAL ISOMERIZATION OF TRANS-1-DEUTERIO-2-VINYLCYCLOPROPANE

Temperature = 277.0°C

t(sec)	Area Under Peaks* 0.7δ	0.3δ	Mole Fraction cis-isomer (x)
0	0.376	0.624	0.126
5,400	0.390	0.610	0.170
10,800	0.416	0.584	0.248
16,200	0.428	0.572	0.284

Temperature = 293.0°C

t(sec)	Area Under Peaks* 0.7δ	0.3 δ	Mole Fraction cis-isomer (x)
0	0.390	0.610	0.170
1,800	0.413	0.587	0.239
3,600	0.432	0.568	0.296
5,400	0.453	0.547	0.359
7,200	0.466	0.534	0.398

TABLE IV (CONTINUED). KINETIC DATA FOR GEOMETRICAL ISOMERIZATION OF TRANS-1-DEUTERIO-2-VINYLCYCLOPROPANE

Temperature = 309.0°C

t(sec)	Area Under Peaks* 0.7δ	0.3δ	Mole Fraction cis-isomer (x)
0	0.376	0.624	0.126
900	0.403	0.597	0.209
1,320	0.434	0.566	0.302
1,800	0.443	0.557	0.329
2,700	0.466	0.534	0.398

Temperature = 324.5°C

t(sec)	Area Under Peaks* 0.7δ	0.3δ	Mole Fraction cis-isomer (x)
0	0.390	0.610	0.170
302	0.418	0.582	0.252
603	0.441	0.559	0.323
903	0.458	0.542	0.374
1,205	0.476	0.524	0.428

TABLE IV (CONTINUED). KINETIC DATA FOR GEOMETRICAL ISOMERIZATION OF TRANS-1-DEUTERIO-2-VINYLCYCLOPROPANE

Temperature °C	$10^4 k\ sec^{-1}$
277.0	0.177±0.072
293.0	1.209±0.016
309.0	2.458±0.038
324.5	6.200±0.074

*Areas under peaks can be expressed in normalized terms, relative to the allylic hydrogen at 1.5δ, by multiplication times three.

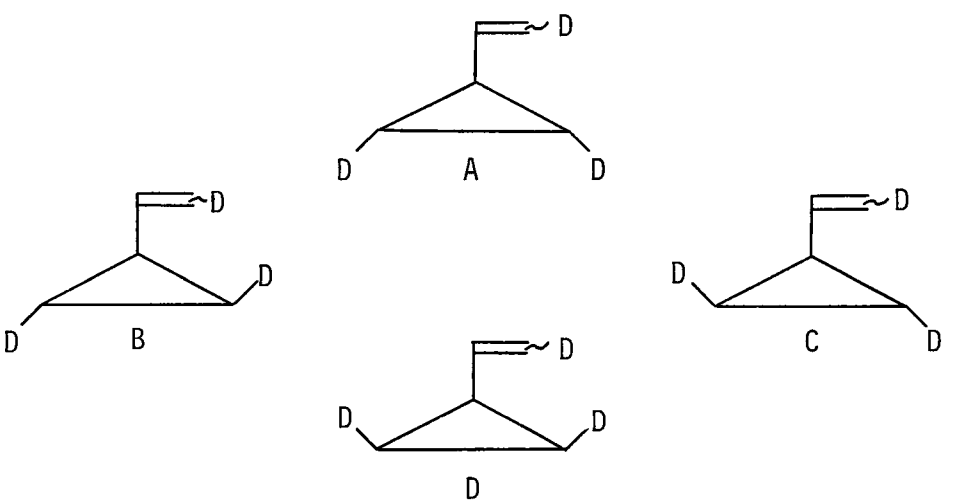
A standard least squares treatment of the data was used to determine the rate constant at each temperature. Then, a least squares fit of the rate data to the Arrhenius equation,

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

yields an activation energy, E_a, of 48.2±1.6 kcal/mole. The $\log_{10}A$ term was determined to be 14.5±.1.

2. Trideuteriovinylcyclopropane

The thermal reaction of the trideuteriovinylcyclopropane [54] was studied under conditions identical with the monodeuterated vinylcyclopropane [37]. At 324.5°C the rate of appearance of signal at 0.7δ in the NMR spectrum (due to cyclopropyl hydrogens trans to the vinyl group, but not necessarily trans to each other) was determined to be identical with the rate of epimerization of compound [37]. Even though isomers B, C and D are all formed at the same rate as the epimerization



of monodeuteratedvinylcyclopropane this does not define a mechanism. The ratio of (B+C)/D must be known in order to characterize a pathway. The analysis of the NMR spectrum of a mixture of A, B, C and D, which permits some conclusions about mechanism, are discussed in Chapters IIIC and IV.

C. NMR DISCUSSION

When used as an analytical tool, a high resolution NMR spectrum yields, in general, four useful parameters. These are chemical shifts (ν), coupling constants (J), pattern multiplicity and integrals.* The place of NMR, along side other methods of spectroscopy, is somewhat unique since with the use of quantum mechanics the exact spectral details of many compounds are predictable. However, the greatest utilization of NMR lies in the emperical manner by which the general features of the spectrum can be predicted. Because of this, many correlations have been made between the structure of organic molecules and their observed chemical shifts[45b,45c] and coupling constants.[45a,45b]**

From correlation charts and the literature, Tables V and VI list some typical chemical shifts and coupling constants for cyclopropyl compounds, which are related to the compounds of interest here. Whereas

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*An introduction to these NMR parameters can be found in ref. 44.

**Ref. 45 is, by no means, a complete listing of correlation tables.

TABLE V. TYPICAL CHEMICAL SHIFTS FOR CYCLOPROPYL H-α TO A HALOGEN

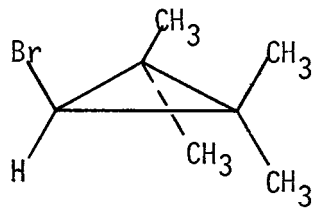
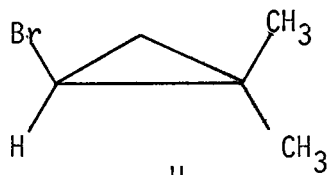
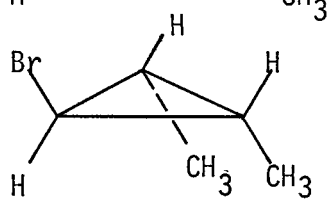
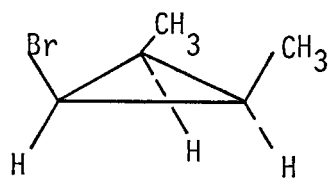
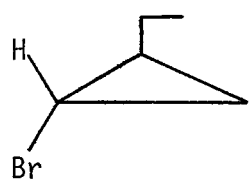
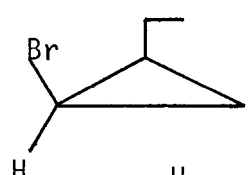
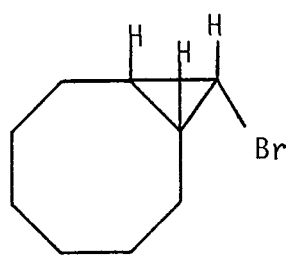
Compound	ν(δ)	Reference
	2.66	47
	2.75	47
	2.14	47
	3.18	47
	2.5	47
	3.00	47
	3.14	37

TABLE V (CONTINUED). TYPICAL CHEMICAL SHIFTS FOR CYCLOPROPYL H-α TO A HALOGEN

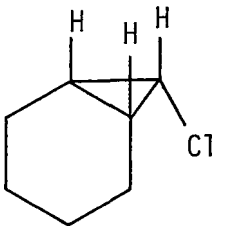
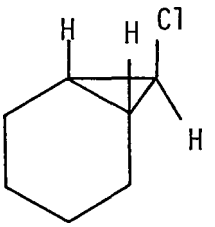
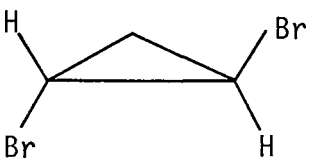
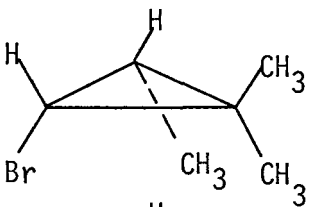
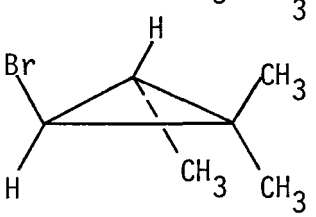
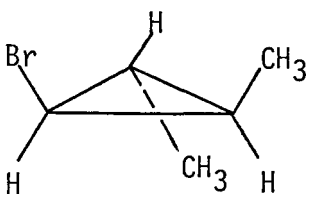
Compound	ν(δ)	Reference
	3.14	37
	2.56	37
	3.1	48
	2.88	37
	2.42	37
	2.69	47

TABLE VI. TYPICAL CIS- AND TRANS-CYCLOPROPYL RING COUPLING CONSTANTS

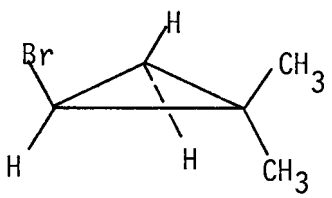
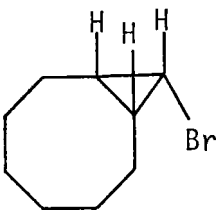
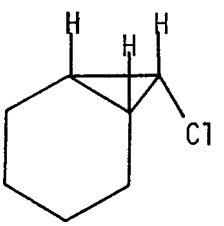
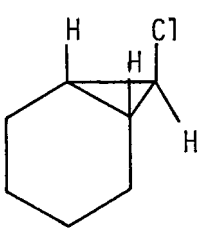
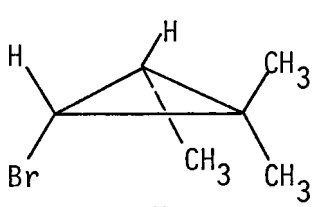
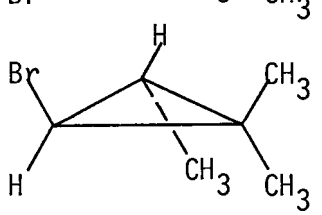
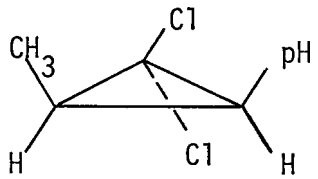
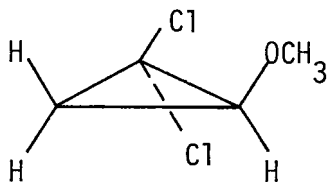
Compound	J_{cis} (Hz)	J_{trans} (Hz)	Reference
	7.68	4.12	47
	7.5		37
	7.5		37
		3.7	37
	7.2		37
		3.8	37

TABLE VI (CONTINUED). TYPICAL CIS- AND TRANS-CYCLOPROPYL RING COUPLING CONSTANTS

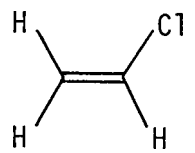
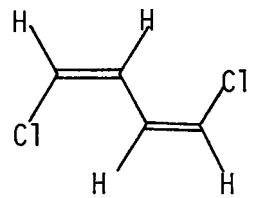
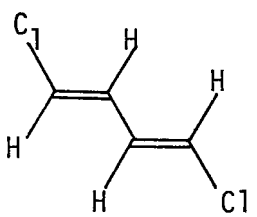
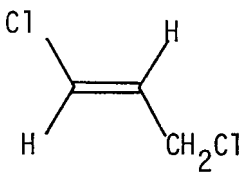
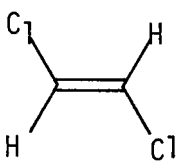
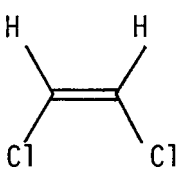
Compound	J_{cis}(Hz)	J_{trans}(Hz)	Reference
	8.28		49
	7.90	5.28	49

the hydrogens in cyclopropane appear at 0.22δ, the secondary ring hydrogens in vinylcyclopropane appear at ca. 0.2 and ca. 0.8δ.[46] A hydrogen on the same ring carbon with a bromine or chlorine atom (Table V) is observed to be shifted to between 2.1 to 3.2δ. In these same molecules, the hydrogen anti to other ring substituents normally appear at higher δ numbers by ca. 0.5δ. These are just a few examples of a widely recognized phenomenon in NMR, i.e., chemical shifts are quite sensitive to the nature of the substituents on the same carbon with the hydrogen, as well as other substituents in close proximity. The magnitude of coupling constants, on the other hand, are effected very little by the nature of the substituents in the molecule.[49]

For a large variety of substituted cyclopropanes the range of trans- and cis-cyclopropyl coupling constants is 3-5 Hz and 7-9 Hz respectively. Even when values are outside this range, as in 1,1-dichloro-2-phenylcyclopropane where J_{trans} = 8.5 Hz and J_{cis} = 10.5 Hz,[53] cis coupling constants are greater than trans coupling constants, usually by greater than 2 Hz. This is particularly useful information since it allows unambiguous identification of ring stereochemistry. Fortunately, the coupling constants of substituted olefins are also predictable. In chlorine substituted olefins trans coupling constants are 12-15 Hz and cis coupling constants are 5-7.5 Hz (Table VII). Again, unambiguous identification of olefin stereochemistry is possible.

For many simple molecules, chemical shifts and coupling constants are obvious by inspection and can, in most cases, be taken directly off the spectrum. In other simple cases (especially those possessing special

TABLE VII. TYPICAL CIS AND TRANS COUPLING CONSTANTS FOR CHLOROOLEFINS

Compound	J_{cis}	J_{trans}	Reference
	7.3	14.6	50
	7.28		45a
		13.12	45a
		13.1	51
		12.2	52
	5.2		52

symmetry properties), chemical shifts and particularly coupling constants are not readily evident. In this event considerable skill is required in the interpretation of the spectrum. Computer analysis is necessary, in more difficult systems, to obtain these NMR parameters.

The line frequency in all NMR spectra used to establish chemical shifts and coupling constants were measured using a Hewlett-Packard 5122A electronic counter to the nearest tenth of a cycle. Coupling constants are the measured spacing between lines, and chemical shifts are the center of the pattern.

1-1-Dibromo-2-vinylcyclopropane [33] - Figure 4 shows the 100 MHz NMR spectrum of compound [33]. The three upfield peaks at ca. 1.8-2.2δ are due to the cyclopropyl ring hydrogens. Vinyl hydrogens are observed at 5.2-5.5 δ. The vinyl region is very complex and would require computer analysis to obtain its NMR parameters. The parameters for the ring hydrogens, on the other hand, can be approximated by inspection. Figure 5 is an interpretation of the splitting observed for the ring hydrogens.

The peak at 2.16 δ can be assigned to the allylic hydrogen as follows: the allylic hydrogen in vinylcyclopropane [36] is found at ca. 1.3δ. The added effect of this hydrogen being adjacent to a carbon bearing two bromine atoms would be expected to shift the resonance downfield (to larger δ numbers) by ca. 0.6-0.9δ.[45a] This correlation would place H_1 at ca. 1.9-2.2δ. Confirmation of this assignment is made by the number of lines in the pattern which indicate H_1 is strongly coupled

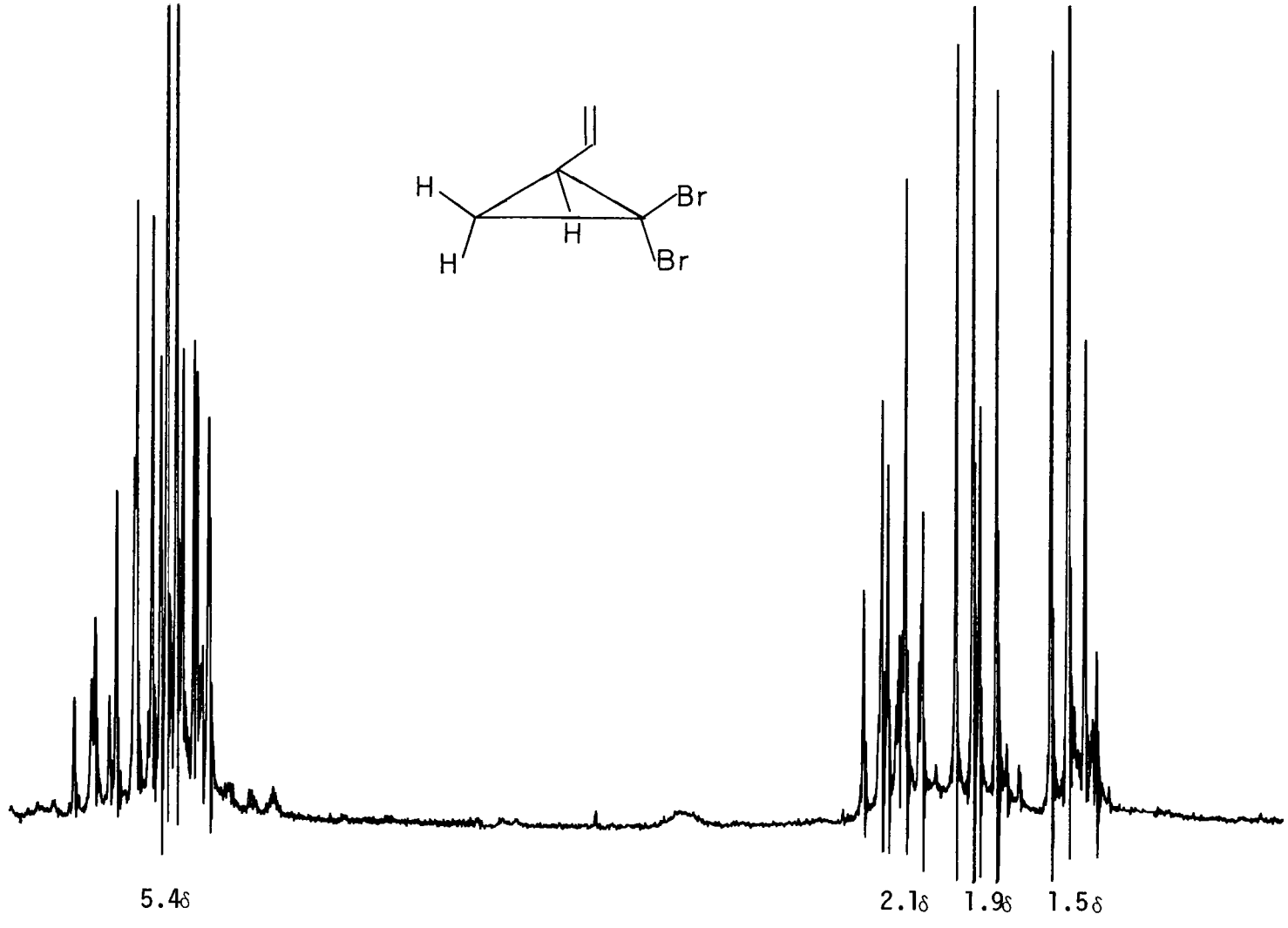


FIGURE 4. 100 MHz NMR SPECTRUM OF 1,1-DIBROMO-2-VINYLCYCLOPROPANE [33]

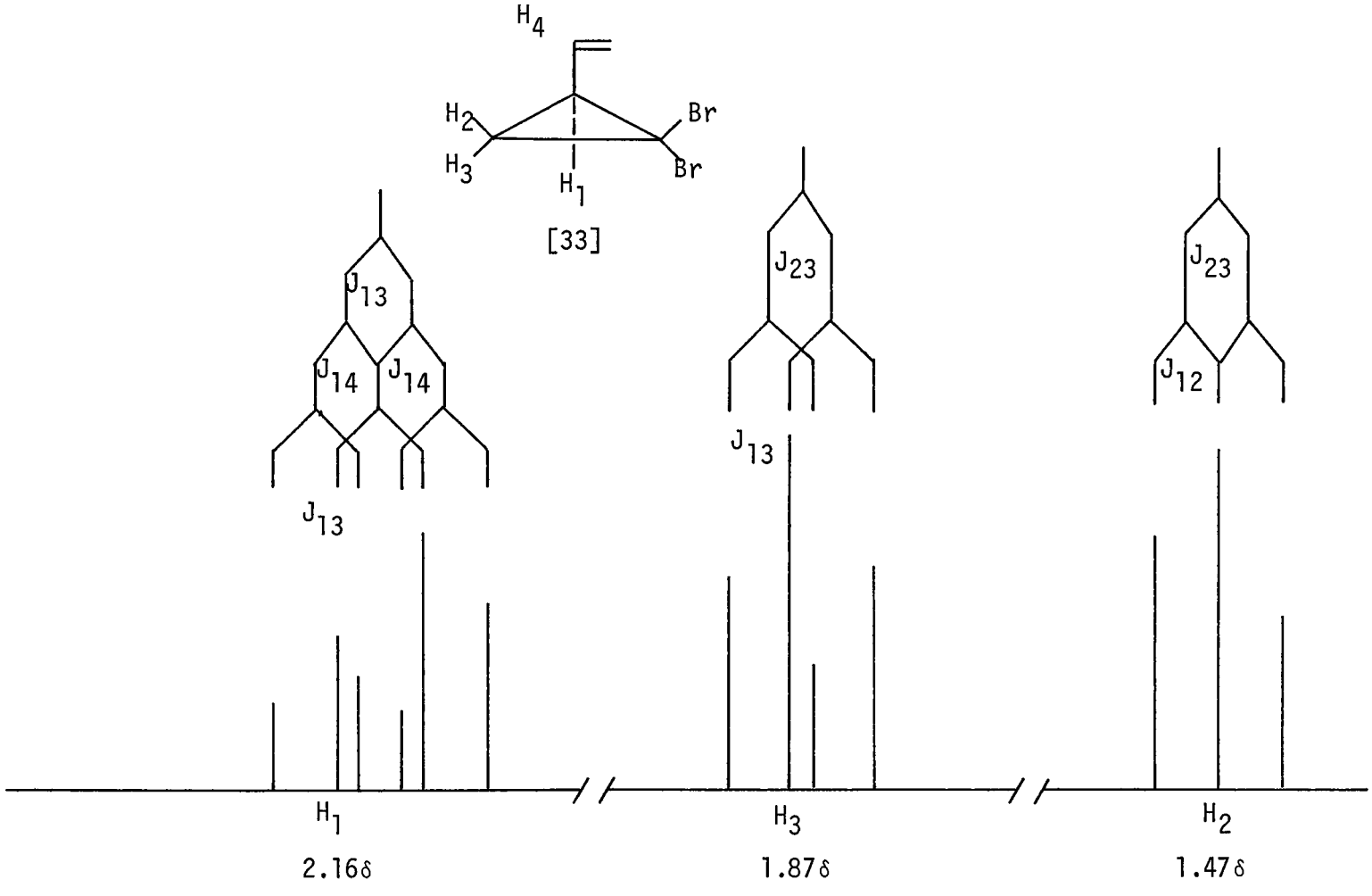


FIGURE 5. ANALYSIS OF SPLITTING PATTERNS FOR CYCLOPROPYL HYDROGENS IN 1,1-DIBROMO-2-VINYLCYCLOPROPANE [33]

to three other hydrogens H_2, H_3 and H_4. The assignment of H_2 and H_3 is made by analogy with the non-allylic ring protons in vinylcyclopropane. The ring proton in vinylcyclopropane trans to the vinyl group are approximately 0.4 δ further downfield than the cis hydrogens. Therefore, H_3 at 1.87 δ is trans to the vinyl while H_2 at 1.47 $\delta$is cis to the vinyl. Also H_3 is coupled to H_1 by 10.1 Hz (cis cyclopropyl coupling constant), while Hz is coupled to H_1 by 7.2 Hz (trans cyclopropyl coupling constant).

In summary:

$$\nu_1 = 2.16$$

$$\nu_2 = 1.47$$

$$\nu_3 = 1.87$$

$$\nu_{12} = 7.2 \text{ Hz}$$

$$\nu_{13} = 10.1 \text{ Hz}$$

$$\nu_{14} = 7.6 \text{ Hz}$$

$$\nu_{23} = 7.2 \text{ Hz}$$

cis- and trans-1-Bromo-2-vinylcyclopropane [34] and [35] - The 100 MHz NMR spectra of compounds [34] and [35] are shown in Figures 6 and 7. Analysis of these spectra is not trivial, but would require computation to obtain the NMR parameters. For purposes of differentiation between [34] and [35], the signal of the alpha bromo hydrogens are useful.

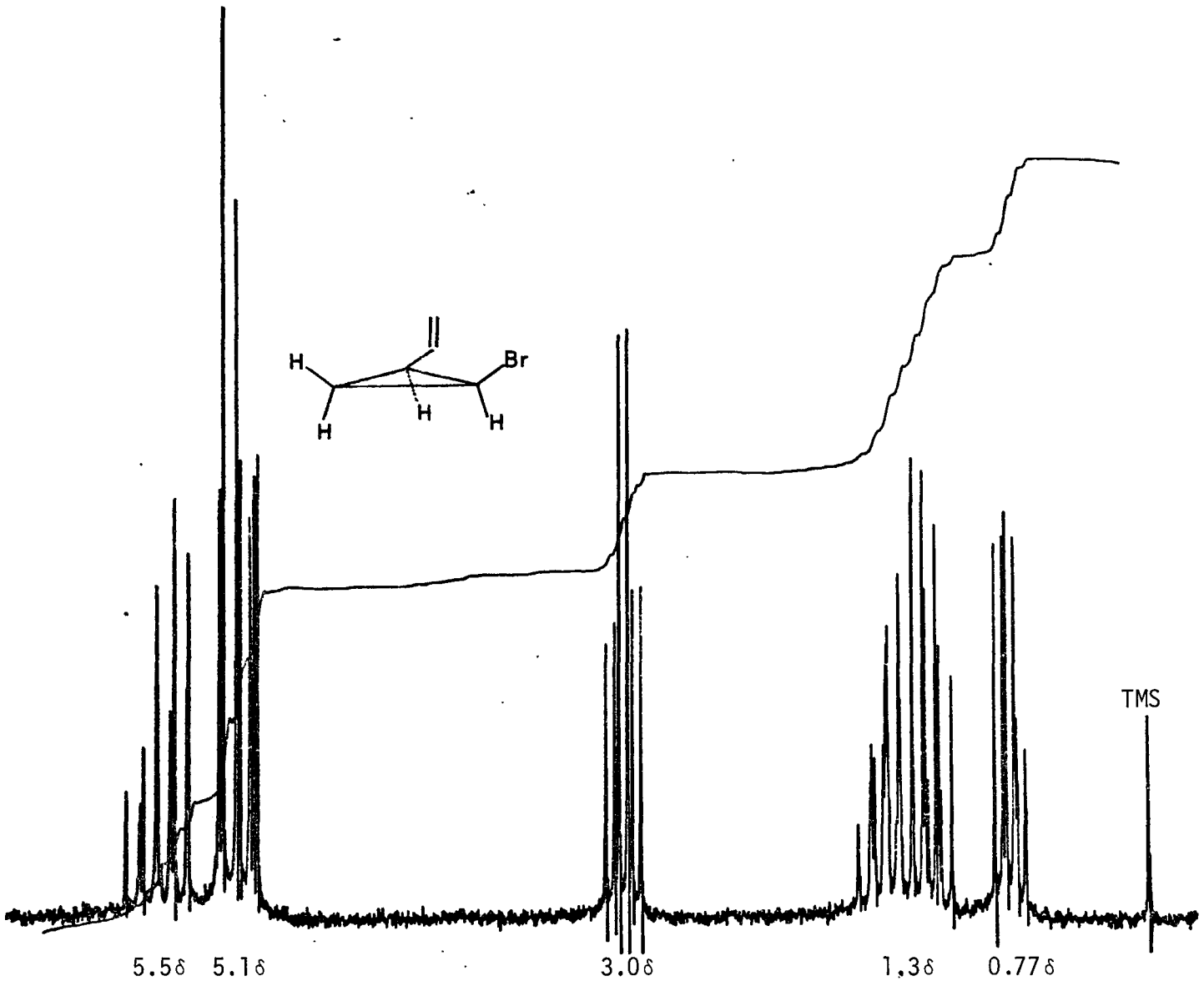


FIGURE 6. 100 MHz NMR SPECTRA OF CIS-1-BROMO-2-VINYLCYCLOPROPANE [34]

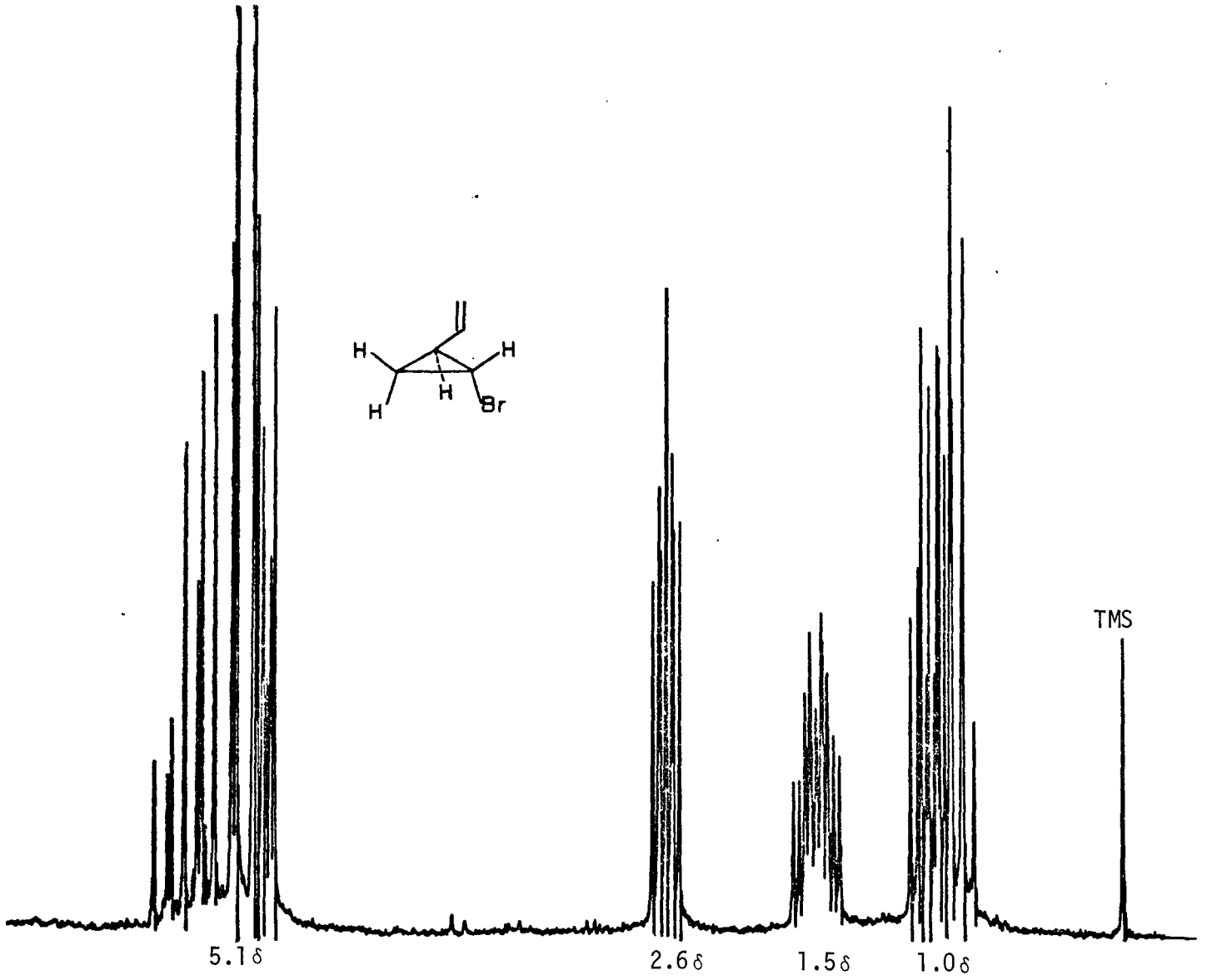


FIGURE 7. 100 MHz NMR SPECTRUM OF TRANS-1-BROMO-2-VINYLCYCLOPROPANE [35]

Table V indicates that the alpha bromo hydrogen on a cyclopropyl ring trans to an alkyl substituent appears at ca. 3δ, while if the hydrogen is cis to an alkyl substituent the signal is at ca. 2.1-2.5δ. Therefore, the compound with the furtherest downfield alpha bromo hydrogen peak (2.96δ) is cis-1-bromo-2-vinylcyclopropane [34], while the other isomer [35] (alpha bromo hydrogen signal at 2.63δ) is trans-1-bromo-2-vinylcyclopropane.* The width of these two signals also confirms this assignment. Compound [34], which has two cis and one trans coupling constants to the alpha bromo hydrogen, should and does exhibit a resonance for this hydrogen ca. 4Hz wider than the same hydrogen in [35], which has two trans and one cis couplings.

ν(α-bromo) = 2.96	ν(α-bromo) = 2.63
width of α bromo hydrogen resonance = ca. 19Hz	width of α bromo hydrogen resonance = ca. 15 Hz.
[34]	[35]

Tetrahalo and Trihalovinylcyclopropanes [41-44] and [45,47-52] - The chemical shifts and coupling constants for the tetrahalovinylcyclopropanes [41-44] and the trihalovinylcyclopropanes [45,47-52] are listed in Table VIII. These parameters were obtained from line spacings in carefully calibrated high resolution 100 MHz NMR spectra taken over the

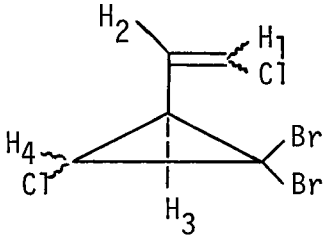
*That the peaks at 2.96δ and 2.63δ are indeed those due to the alpha bromo hydrogens is verified by the spectra of cis- and trans-1-deuterio-1-bromo-2-vinylcyclopropane [39] and [40]. The NMR spectra of these compounds do not have any peaks at 2.96δ and 2.63δ.

TABLE VIII. OBSERVED CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR TETRAHALO AND TRIHALOVINYLCYCLOPROPANES

Compd No.	ν_1	ν_2	ν_3	ν_4	ν_5	J_{12}	J_{13}	J_{14}	J_{15}	J_{23}	J_{24}	J_{25}	J_{34}	J_{35}	J_{45}
[41]	6.34	5.64	2.55	3.79		13.31	0.56	0	-	8.93	0	-	8.90	-	-
[42]	6.40	5.57	2.66	3.40		6.06	0.4	0	-	7.78	0.27	-	6.09		
[43]	6.46	5.57	2.97	3.88		7.23	1.3	0	-	7.86	0	-	8.98	-	-
[44]	6.33	5.66	2.67	3.39		13.43	0.69	0	-	8.61	0.35	-	6.00	-	-
[45]	6.20	5.75	2.02	3.37	3.37	13.43	0	0	0	8.66	0	0	8.1 or 8.6	8.6 or 8.1	
[47]	6.31	5.55	2.46	3.42	3.15	7.31	1.3	0	0	8.36	0	0	4.69	8.59	3.12
[48]	6.20	5.28	2.30	3.13	3.13	7.23	1.2	0	0	8.40	0	0	4.98	4.98	
[49]	6.35	5.68	2.46	3.47	3.47	7.12	1.1	0	0	8.21	0	0	8.78 or 8.24	8.24 or 8.78	
[50]	6.31	5.58	2.46	3.59	2.96	7.35		0	0	8.35	0	0	8.35	5.15	2.98
[51]	6.16	5.57	1.93	3.08	3.08	13.32	0.79	0	0	7.99	0	0	4.84	4.84	
[52]	6.25	5.65	2.04	3.32	3.14	13.35	0.60	0	0	8.74	0	0	4.62	8.58	3.03

region of interest at a sweep width of 250 Hz. NMR spectra of the tetrahalo compounds [41] (Figure 8), [44] and the trihalo compounds [45] (Figure 9), [49] (Figure 10) and [52] indicated that they were pure compounds, uncontaminated by any other isomers. The tetrahalo compounds [42] and [43] (Figure 11) and the trihalo compounds [47] and [50], and [48] and [51] were not physically separable on the VPC columns employed in this work and were analyzed as mixtures of two components each. This was easily accomplished since all peaks in these binary mixtures were separate enough to permit analysis.

For the spectra of the tetrahalo isomers [41-44], one would expect, and does observe a 2:2 ratio of vinyl:cyclopropyl hydrogens. Also the vinyl:cyclopropyl ring stereochemistry should be trans:cis, cis:trans, cis:cis and trans:trans. Experimental coupling constants



for vinyl (J_{12}) and cyclopropyl (J_{34}) hydrogens, listed in Table VIII, compared with those from the literature, Tables VI and VII, indicate that these configurations about the vinyl group and the cyclopropyl ring are present in compounds [41-44].

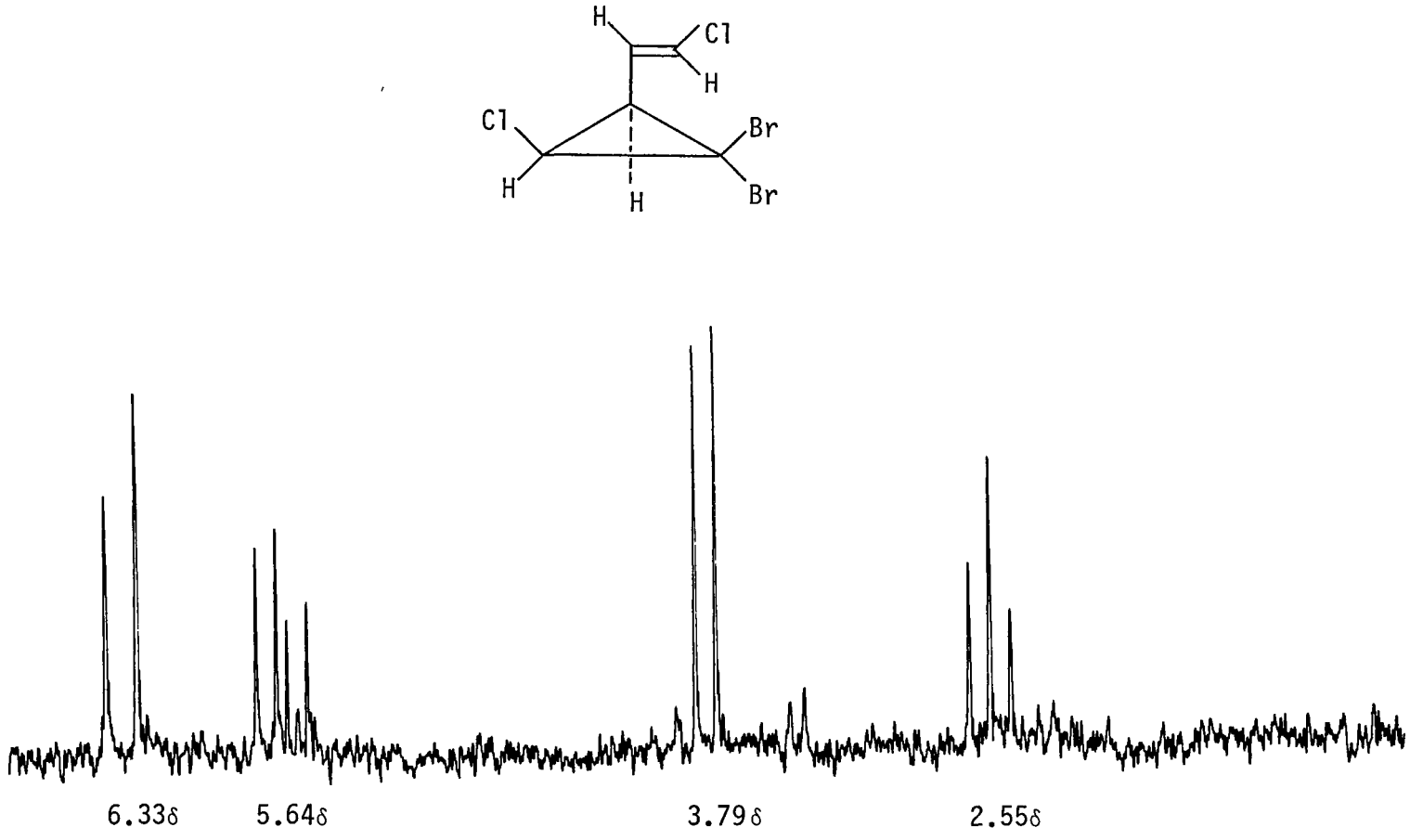


FIGURE 8. 100 MHz NMR SPECTRUM OF COMPOUND [41]

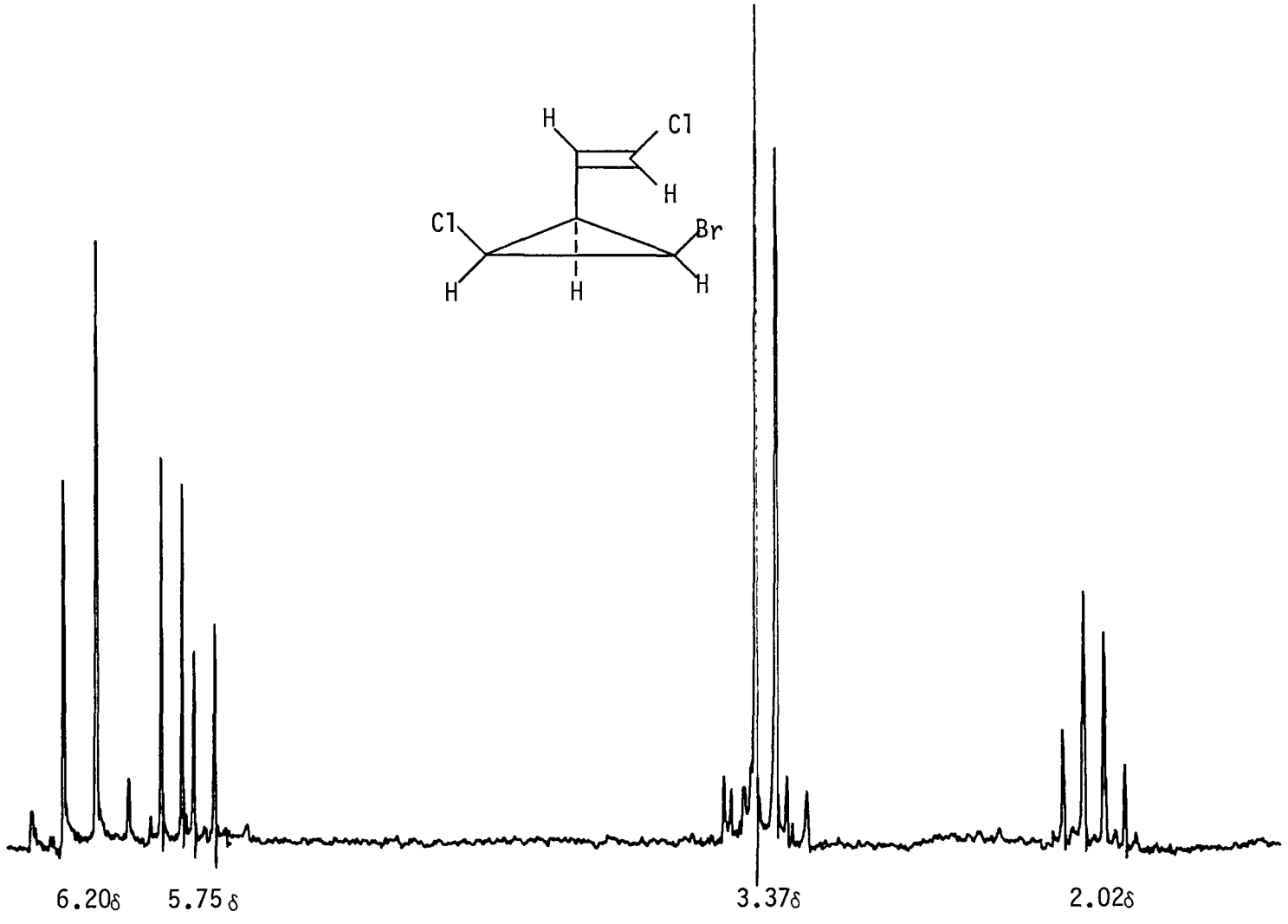


FIGURE 9. 100 MHz NMR SPECTRUM OF COMPOUND [45]

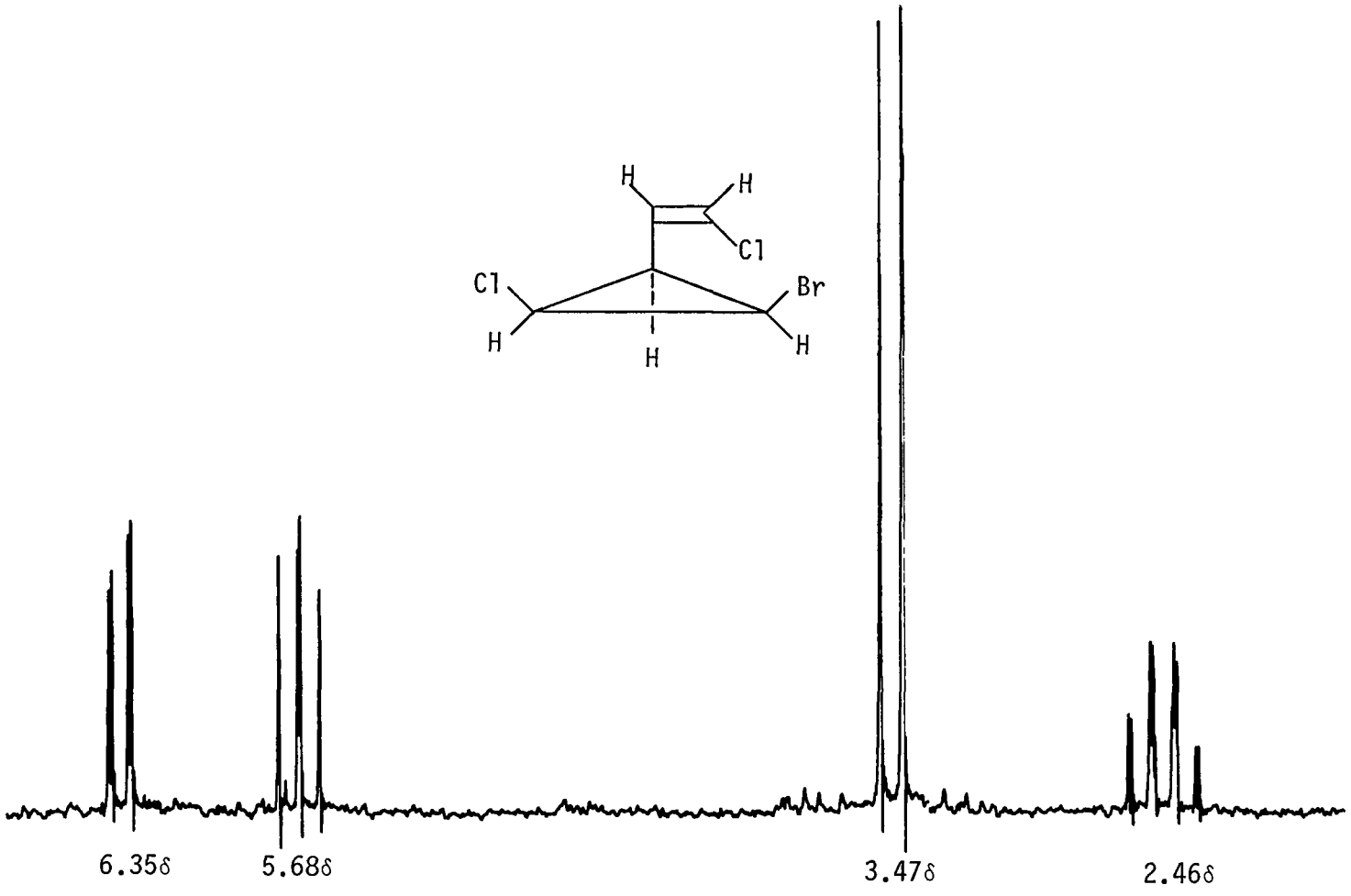


FIGURE 10. 100 MHz NMR SPECTRUM OF COMPOUND [49]

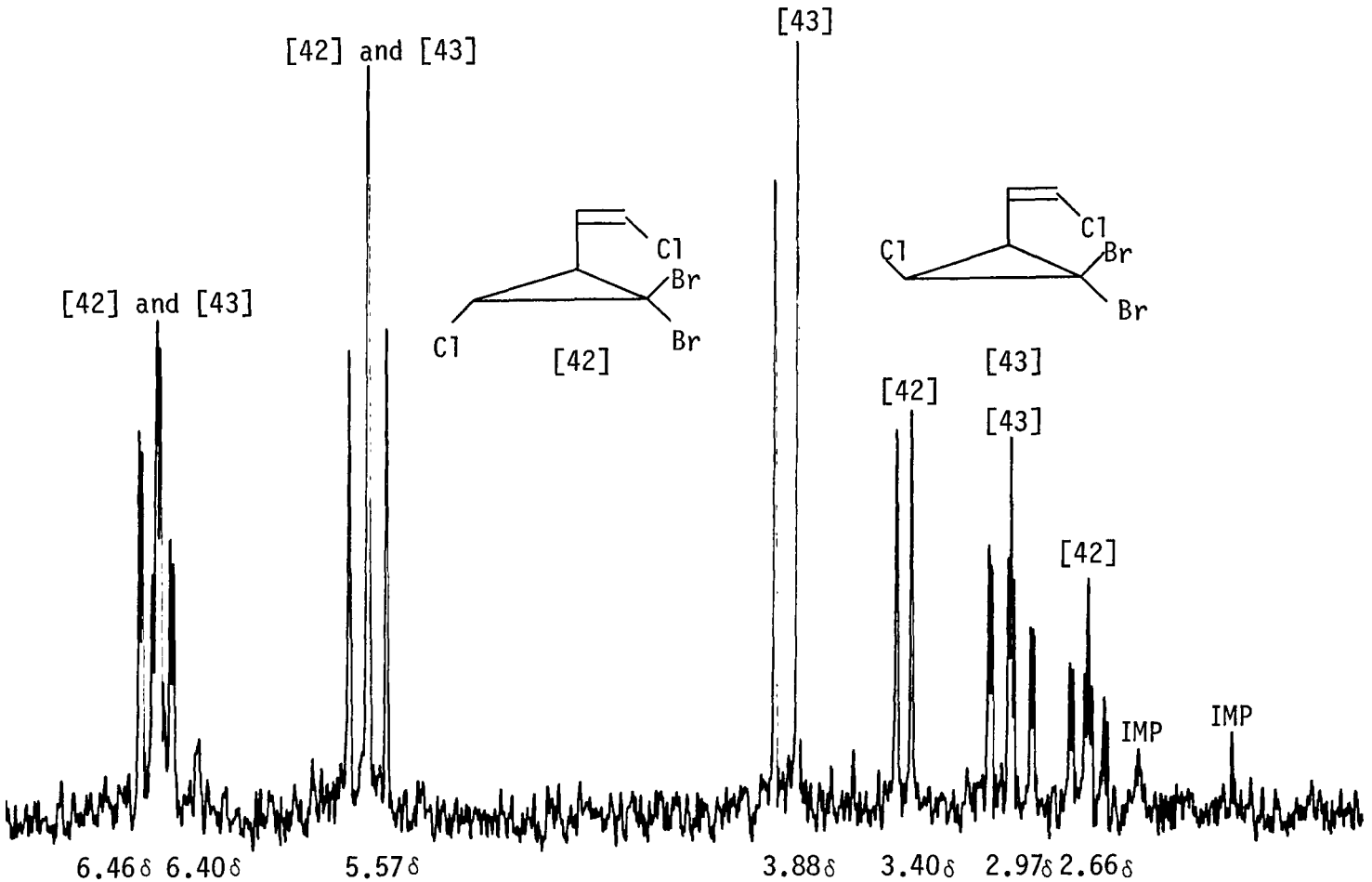
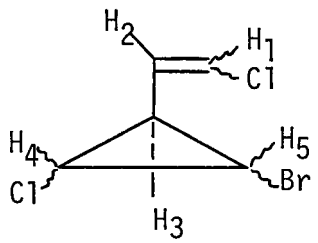


FIGURE 11. 100 MHz NMR SPECTRA OF COMPOUNDS [42] and [43]

Unlike the four tetrahalo isomers [41-44], the spectra for the seven trihalo isomers [45,47-52] are somewhat more complex. The cis and trans olefin stereochemistry should separate these isomers into two groups. Reference to Table V would indicate that when both alpha halo hydrogens are cis to the vinyl they would be ca. 0.5 δ further upfield then when both these hydrogens were trans to the vinyl group. Correlation charts[45c] and Table V suggests that a degeneracy in the chemical shift of the alpha chloro (H_4) and alpha bromo (H_5) ring hydrogens in the same compound is possible. (A fact observed in



compounds [45,48,49,51].)* When the alpha halo hydrogens are trans to each other no such degeneracy is observed and they are separated by ca. 20-60 Hz.

Comparisons of Table VI with Table VIII show that cis and trans ring stereochemistry are easily differentiated by the size of coupling constants.

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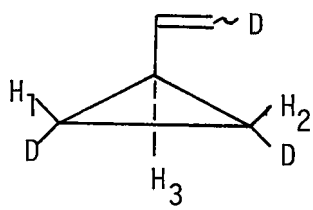
*At a lower sweep width the peaks for H_4 and H_5 can be resolved.

As mentioned before, the chemical shifts of the alpha halo hydrogens are different when these hydrogens are trans to each other on the ring. There is, however, no indication as to which resonance in the spectrum arises from which alpha halo hydrogen. In other words the spectra assigned to [47] might be that of [50] and vice versa. The assignment made is preferred because of the difference in the chemical shift of H_4 in [47] and [52]. The reason for the difference in the chemical shift of H_4 in [47] and [52] is probably due to the stereochemistry of the chlorine on the vinyl. H_4 in [52] in ca. 20 Hz further downfield than in [47]. H_5, on the other hand, has approximately the same chemical shift in [47] and [52], while in [50] H_4 is further upfield.

Other than the above mentioned ambiguity, the NMR parameters indicate that the structures assigned to [45,47-52] are correct.

Trideuteriovinylcyclopropane [54] - Since the deuterium stereochemistry of trans-1-deuterio-2-vinylcyclopropane [37] has been established by microwave spectroscopy,[40] the ring stereochemistry of the trideuteriovinyl cyclopropane [54] is also assured to be trans. (Figure 12 shows the NMR



of compound [54].) This follows necessarily from the absence of a signal

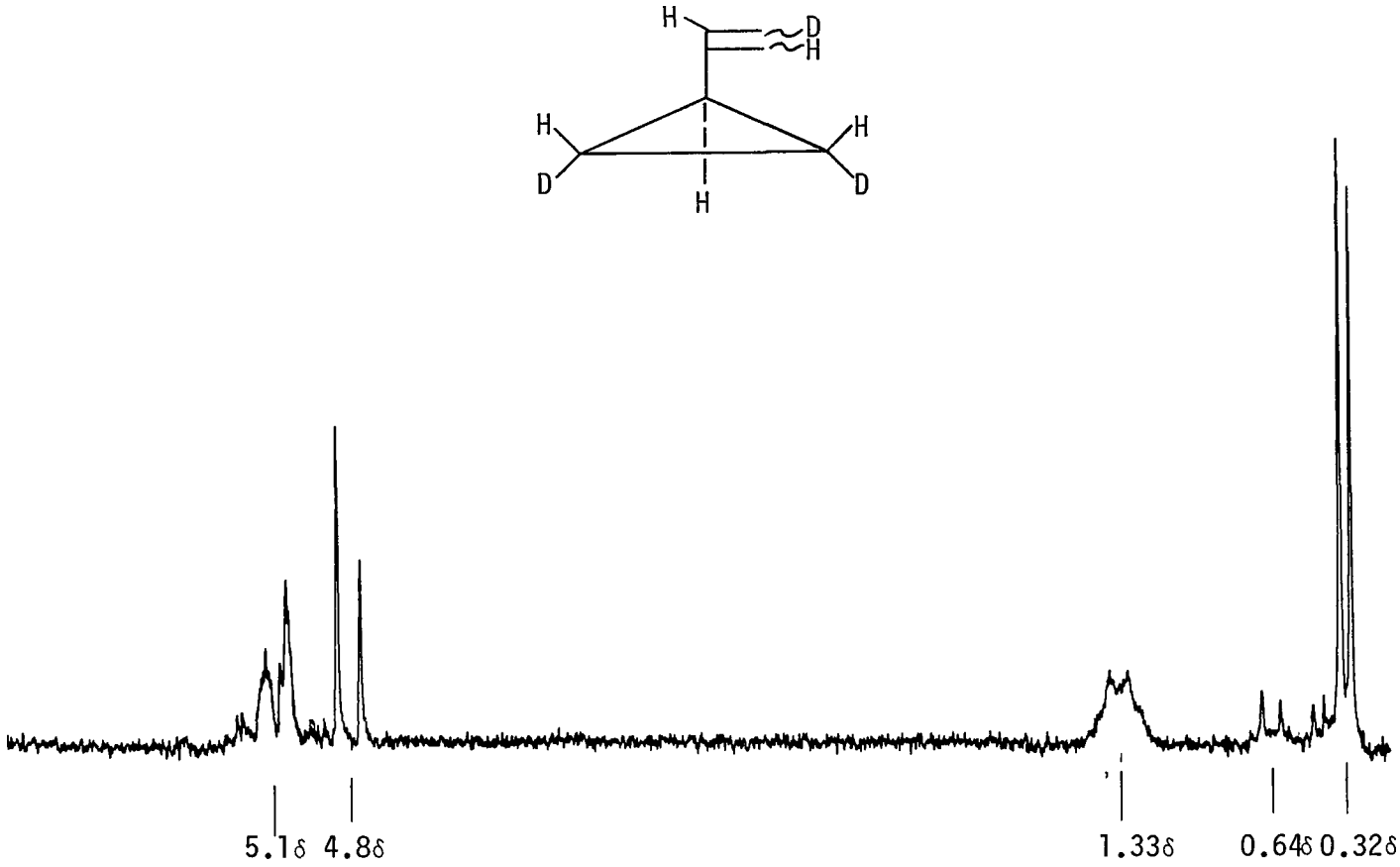
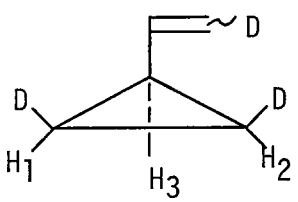
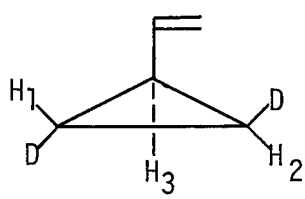


FIGURE 12. 100 MHz NMR SPECTRUM OF TRIDEUTERIOVINYLCYCLOPROPANE [54]

at 0.7δ (in a 100% pure isomer). The lack of definition observed in the peaks at 0.3δ (Figure 13) is due to the quadrupole coupling of the ring hydrogens with the ring deuteriums.[54] The small signal at 0.7δ is due to a small amount of the isomers [55 and 56] which have hydrogens trans to the vinyl group. Irradiation of the sample at the resonance



[55]



[56]

frequency for deuterium (deuterium decoupling: 15.346 MHz at 23,480 gauss)[54] while recording the protium spectrum allows observation of the hydrogens decoupled from deuterium. Figure 14 shows the upfield region of isomer [54] (contaminated with small amounts of [55 and 56]), after deuterium decoupling. The ring hydrogens H_1, H_2 and H_3 (in [54 and 55]) after deuterium decoupling constitute an AX_2 spin system.* Compound [56] is an AMX spin system. In the AX_2 and AMX limit the coupling constants can be measured to a reasonable accuracy from a calibrated spectrum.

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*An introduction to this nomenclature and its significance in NMR is found in ref. 45b.

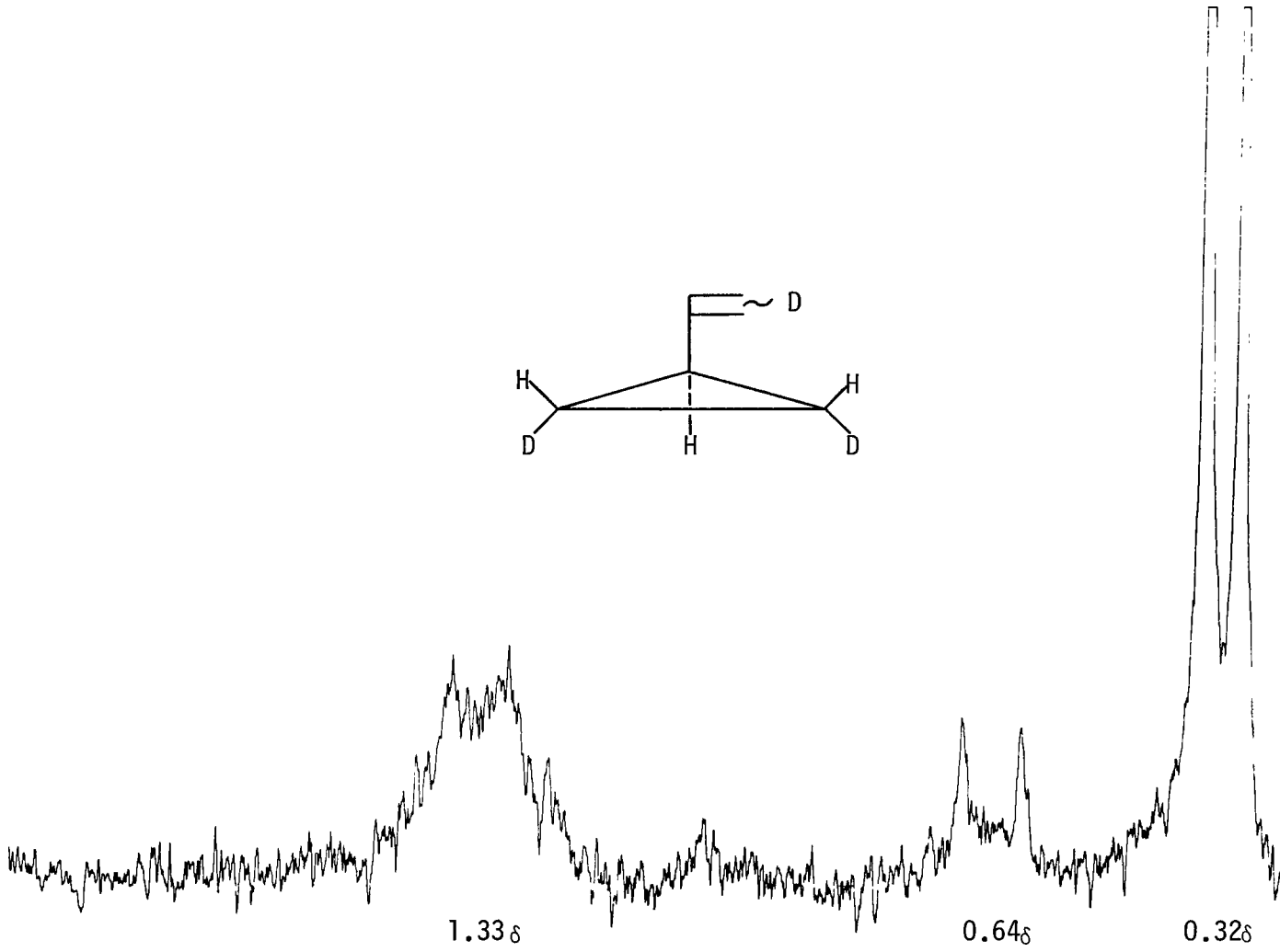


FIGURE 13. 100 MHz NMR SPECTRA OF CYCLOPROPYL HYDROGENS IN COMPOUND [54] (250 Hz SWEEP WIDTH)

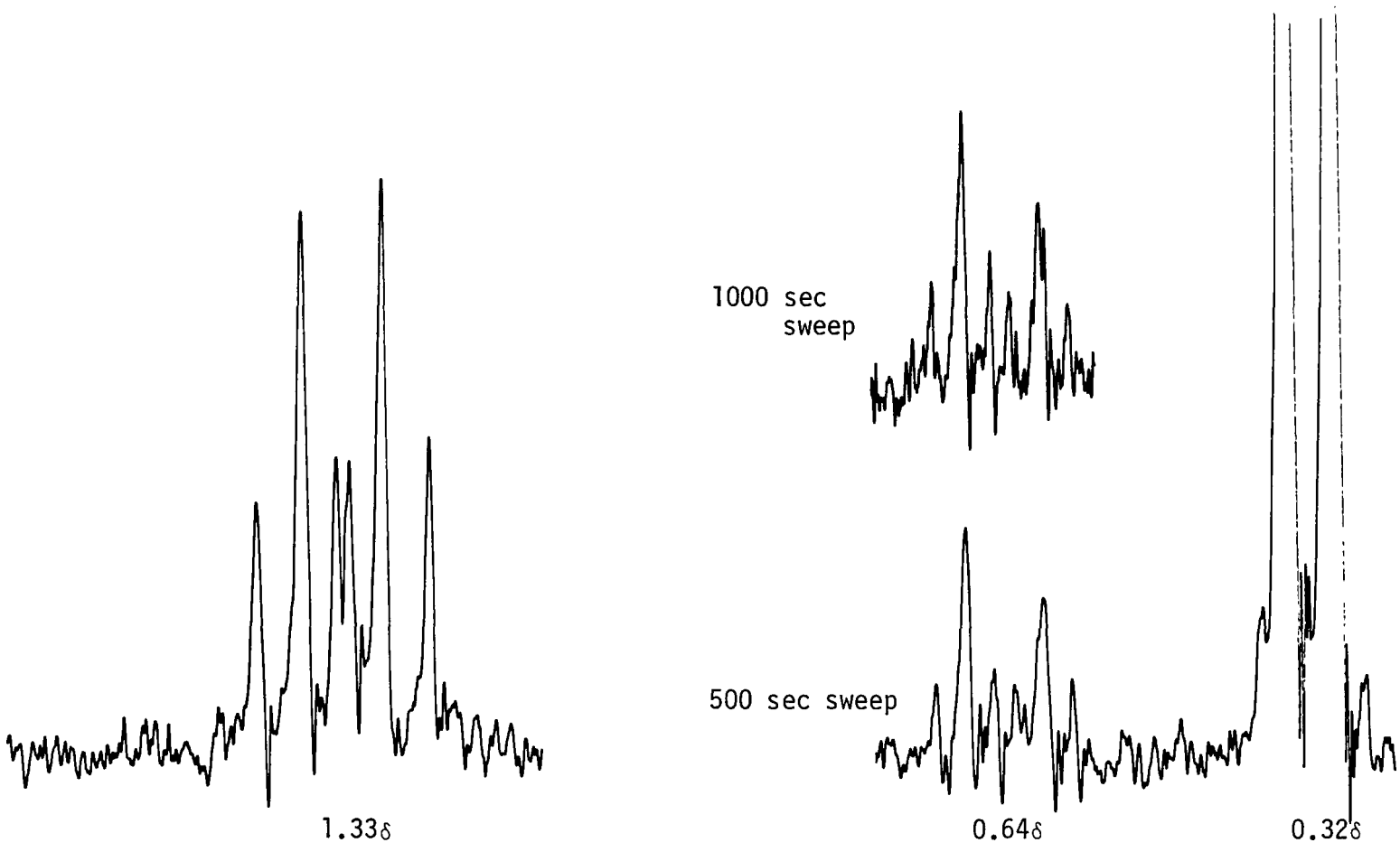


FIGURE 14. DEUTERIUM DECOUPLED 100 MHz NMR SPECTRA OF CYCLOPROPYL HYDROGENS IN COMPOUND [54] (250 Hz SWEEP WIDTH)

Table IX lists some typical spin systems and the observable or calculable parameters available from a spectra of each.

In a mixture of [54,55,56] all three isomers are easily distinguished in the 0.3-0.7δ region of the spectra by deuterium decoupling. As mentioned earlier trans cyclopropyl coupling constants are normally 3-5 Hz while cis cyclopropyl coupling constants are normally 7-8.5δ. Listed below are the observed cyclopropyl ring coupling constants and more accurate chemical shifts (non-allylic hydrogens H_1 and H_2) for isomers [54,55 and 56]. Figure 15 is an illustration of the patterns

Isomer	J_{12}	J_{13}	J_{23}	ν_1	ν_2
54		4.82 Hz	4.82 Hz	0.32	0.32
55		8.10 Hz	8.10 Hz	0.64	0.64
56	6.1	4.65	8.07	0.32	0.64

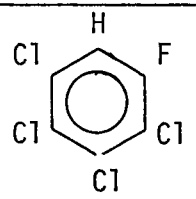
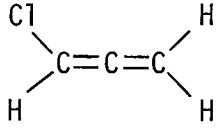
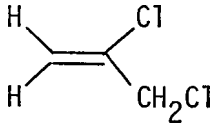
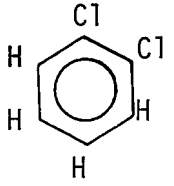
observed for H_1 and H_2.

Calculation of relative amounts of [55 and 56] can be accomplished as follows by considering the peaks at 0.7δ:

$$\frac{2x(\text{area at } H_1 \text{ for } [56])}{\text{area at } H_1+H_2 \text{ for } [55]} = \text{ratio of } \frac{[56]}{[55]}$$

In compound [56] H_1 is the four lines indicated in Figure 15 at 0.64δ while for [55] H_1 and H_2 are the other two lines in that pattern. These calculations indicate that compound [55 and 56] each make up

TABLE IX* NMR SPIN SYSTEMS

Spin Designation	Typical Example	Observable Parameters	Calculable Parameters	Unavailable Parameters
AX		ν_A, ν_X, J_{AX}		
AMX	Ring Hydrogens Furyl methyl ketone	ν_A, ν_M, ν_X, J_{AM}, J_{AX}, J_{MX}		
AXX' or AX_2		ν_A, ν_X	$(J_{AX} + J_{AX'})/2$	$J_{XX'}$
AMXX'		ν_A, ν_M, ν_X	J_{AM}, J_{AX}, J_{MX}	$J_{XX'}$
AA'BB'			ν_A, ν_B, J_{AA}; J_{AX}, $J_{XX'}$, $J_{AX'}$	

*A mathematical discussion of these and other spin systems is discussed in ref. 55

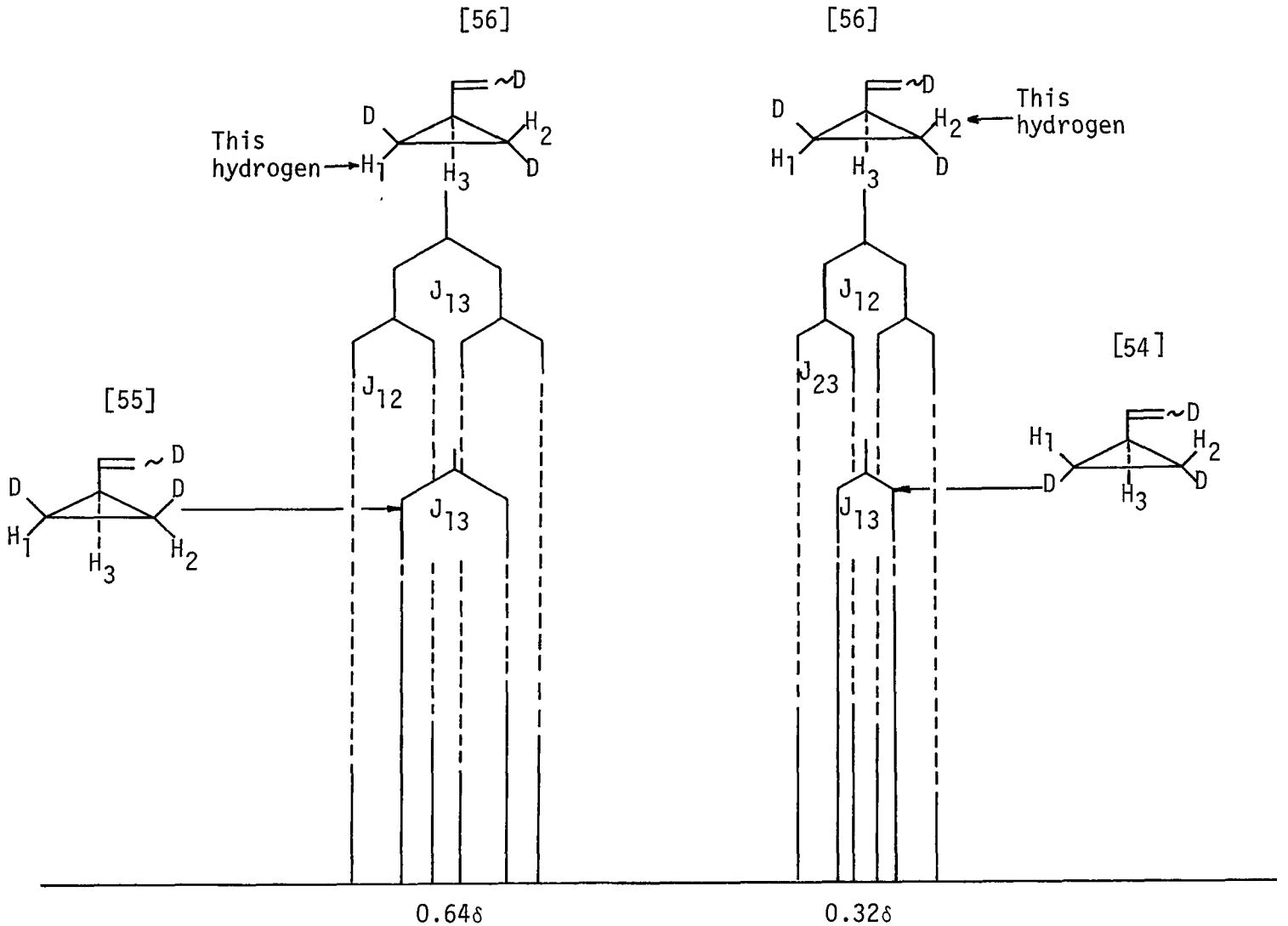
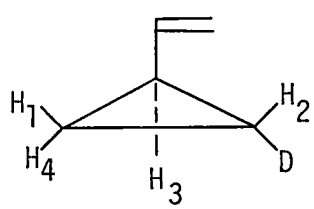


FIGURE 15. SPLITTING PATTERNS OF CYCLOPROPYL HYDROGENS IN A 1:2:1 MIXTURE OF COMPOUNDS [54, 56 and 55] DEUTERIUM DECOUPLED

ca. 5% of the composition of the trideuteriovinylcyclopropane before pyrolysis.

Since all lines are resolved in the cyclopropyl region of interest, each isomer is distinguishable and a useful analytical technique has now been established for quantitative analysis of isomer mixtures of compounds [54,55 and 56].

Trans-1-deuterio-2-vinylcyclopropane [37] - On the surface the NMR spectrum of trans-1-deuterio-2-vinylcyclopropane (Figure 16) does not appear any more complex than that for the trideuteriovinylcyclopropane [54] even though another spin (H_4) has been added to the cyclopropyl

[37] 

ring. In terms of spin systems compound [37] can be designated AMXX'. Rather than the doublet for H_1 and H_2 (by symmetry H_1 and H_2 are magnetically equivalent) and the doublet for H_4 one would expect a very complex pair of signals. Deuterium decoupling this spectrum reveals that these pairs of doublets are essentially still doublets with only a small splitting observed. This simplicity can be easily explained in terms of the geminal coupling constant J_{14} and the trans coupling constant J_{24}. Geminal coupling constants on cyclopropyl rings are almost always negative and normally fall in the range of -4 to -8 Hz.[45a] The

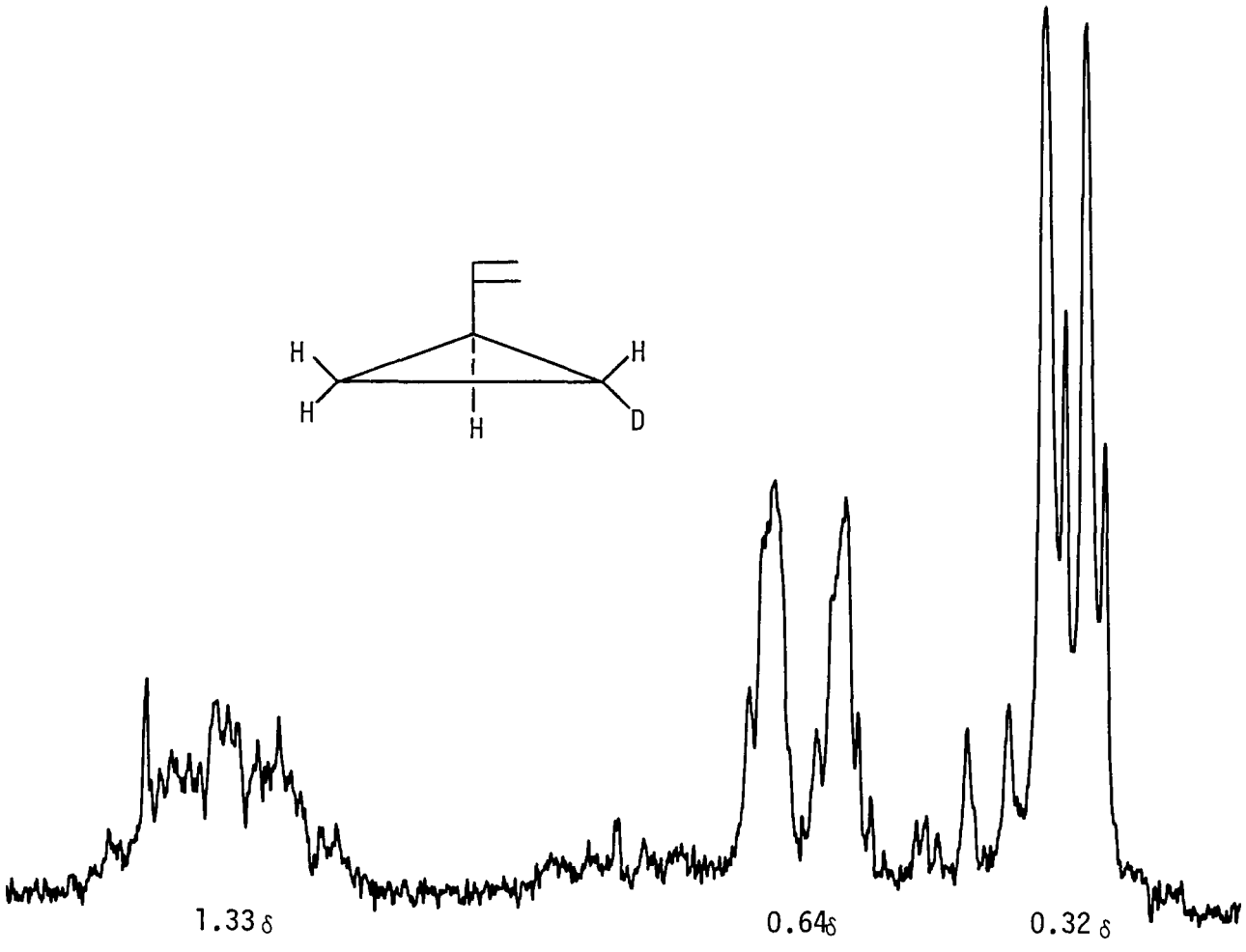


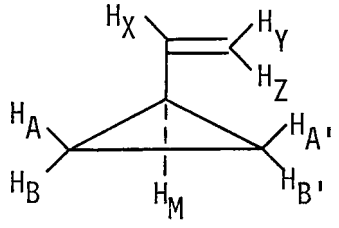
FIGURE 16. 100 MHz NMR SPECTRUM OF CYCLOPROPYL HYDROGENS IN TRANS-1-DEUTERIO-2-VINYLCYCLOPROPANE [37] (250 Hz SWEEP WIDTH)

trans coupling constant J_{12} in compound [56] was 6.1 Hz and it is reasonable to assume J_{24} in [37] is also this value. In order to observe doublets for the non-allylic cyclopropyl hydrogens H_1-H_2 and H_4 the geminal coupling constant J_{24} must necessarily be ca. -6.1 Hz.

The spectra for cis-1-deuterio-2-vinylcyclopropane is in all respects identical with that of compound [37] except for size of the signals at 0.3 and 0.7δ, which are reversed.

Vinylcyclopropane [36] - The NMR spectra of vinylcyclopropane [36], represented in Figure 17, is very complex. Including the three vinyl hydrogens this is an eight spin system, AA'BB'MXYZ.

[36]



The only detailed NMR investigations of vinylcyclopropane have been confined to temperature studies of the coupling constant J_{MX}[56] to determine the rotational conformer population about the vinyl-cyclopropyl bond. At room temperature, J_{MX} was determined to be ca. 8.4 Hz. DeMare and Martin[56c] reported the chemical shifts of HX and Hz, in carbon tetrachloride at 31°C, to be 5.271 and 4.996δ respectively. The other vinyl hydrogen appears in the same region.[45c]

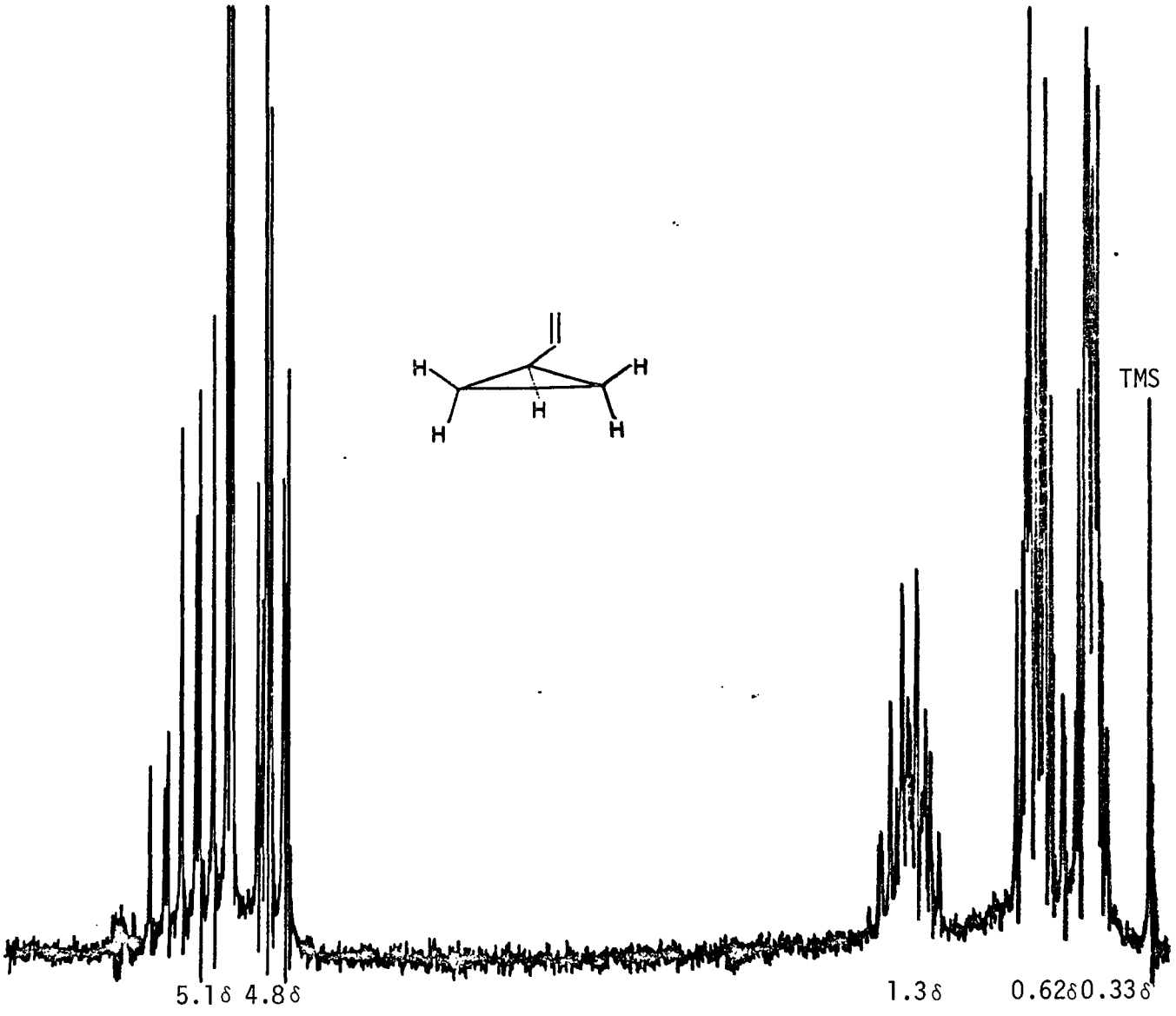


FIGURE 17. 100 MHz NMR SPECTRUM OF VINYLCYCLOPROPANE [36]

Determination of all the parameters in vinylcyclopropane would require a considerable amount of computer computation and this has not appeared necessary to the problem presented in this work.

In summary, NMR spectra of several halogenated and deuterated vinylcyclopropanes have been taken. Chemical shifts and coupling constants, critical to the assignment of vinyl and ring stereochemistry, were determined and found to be in excellent agreement with similar systems reported in the literature. This study points out the usefulness of NMR as an analytical tool, since in all probability, the stereochemistry of the tetrahalo and trihalovinylcyclopropanes could not have been determined conveniently by any other technique.

CHAPTER IV

INTERPRETATION OF THERMAL REACTIONS

INTERPRETATION OF THERMAL REACTIONS

As was pointed out in Chapter I, the concerted or diradical nature of the thermal isomerizations of cyclopropanes has, of late, aroused considerable interest. Unfortunately due to choice of substrates, most investigations of these rearrangements have led to no definitve conclusion concerning the pathway for bond reorganization of cyclopropane rings. The results of the study of the degenerate vinylcyclopropane rearrangement, presented here, have defined the nature of geometrical isomerization of the cyclopropyl ring in vinylcyclopropane.

Geometrical isomerizations have been represented in terms of reaction coordinate diagrams (Figure 2). Figure 18 represents the reaction coordinate diagram for geometrical isomerization of 1-deuterio-2-vinylcyclopropanes. The well at the top of the curve is equated with

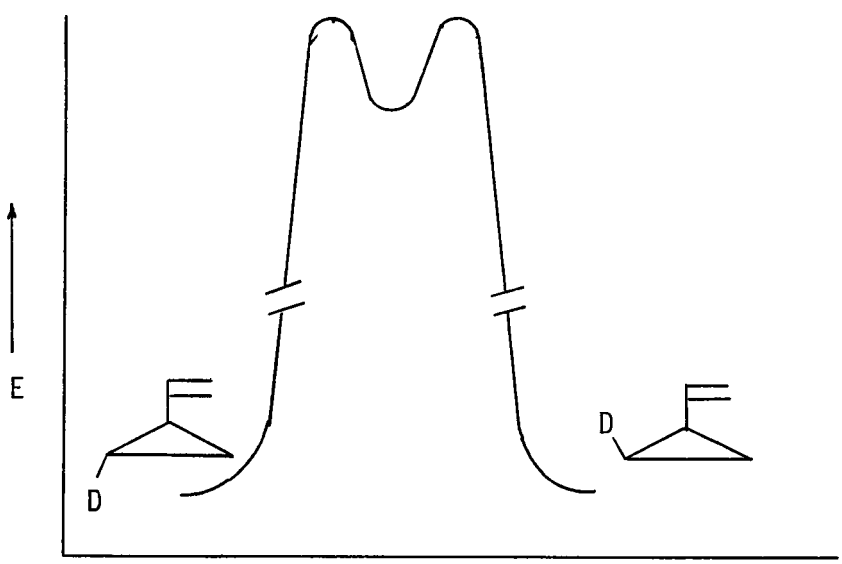


FIGURE 18. REACTION COORDINATE DIAGRAM FOR GEOMETRICAL ISOMERIZATION OF 1-DEUTERIO-2-VINYLCYCLOPROPANE

a diradical intermediate and the depth of this well is indicative of the stability of the intermediate. A concerted reaction, on the other hand, is viewed as having a smooth reaction coordinate diagram (no well), and to proceed without the intervention of any intermediate.

Initial concern, in our investigation of 1-deuterio-2-vinylcylopropane, was to determine whether epimerization of the deuterium label would be fast relative to cyclopentene formation. This question was answered by our observation that trans-1-deuterio-2-vinylcyclopropane [37] isomerized to the cis isomer [38] faster than cyclopentene was formed.[57] Comparison of the kinetic parameters for cyclopentene formation with the kinetic parameters for deuterium epimerization indicates that epimerization is ca. 40 times faster than cyclopentene formation at 325°C.

$$\frac{k_{epim}}{k_{cyclopentene}} = \frac{10^{14.5}\exp(-48{,}200/RT}{10^{13.5}\exp(-49{,}600/RT} \approx 40$$

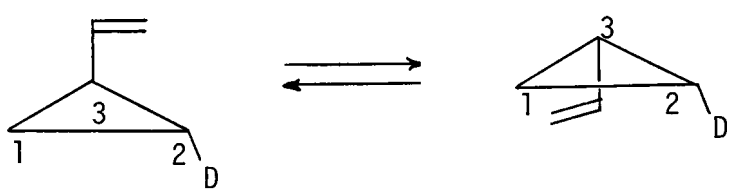
Several factors have led H. M. Frey and S. W. Benson to invoke the intermediacy of a diradical in cyclopropane rearrangements. The very observation of geometrical isomerization in 1,2-dideuteriocyclopropanes[10] has been viewed as evidence in favor of a diradical intermediate. The high pre-exponential "A" factor ($10^{16.0}$) for this isomerization is indicative of a loss of organization in the transition state relative to the ground state. This "A" factor has led Benson[24] to conclude that the intermediate is a freely rotating diradical and

precludes a concerted mechanism. The normal "A" factor in the vinylcyclopropane-cyclopentene rearrangement ($10^{13.5}$) has also been explained in terms of a diradical pathway, by invoking the intermediacy of an allylically stabilized diradical. Frey suggests that the loss of the rotation of the vinyl group in forming the allyl radical is compensated, as a result of cyclopropyl ring rupture, by the ability of the other part of the diradical to rotate. The net result is that on passing from reactant to the transition state there is essentially no change in entropy.

In attempting to understand geometrical isomerization in cyclopropanes considerable emphasis has been placed of the activation energy for these rearrangements. The fact that the activation energy of the vinylcyclopropane-cyclopentene rearrangement (ca. 50 kcal/mole) lies below that for structural isomerization of alkyl substituted cyclopropanes (ca. 63 kcal/mole) has led Ellis and Frey[17c] to equate this difference of 13 kcal/mole to the allylic resonance energy in the formation of an allylically stabilized diradical in the vinylcyclopropane-cyclopentene rearrangement. From quite different studies Benson[24] has arrived at 12.6 ± 1 kcal/mole for this resonance energy. However, by comparing the structural isomerization of cyclopropanes with the vinylcyclopropane-cyclopentene rearrangement one is equating two completely different reactions, since the former requires C-H bond cleavage while the latter does not. A much better comparison would be the activation energy for the geometrical isomerizations of 1,2-dideuterio-3-methylcyclopropanes

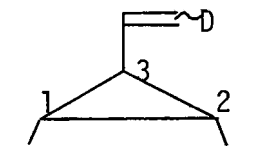
(60.5 kcal/mole) and 1-deuterio-2-vinylcyclopropanes (48.2 kcal/mole). This difference of 12.3 kcal/mole, is essentially the same as 13 kcal/mole, but was obtained by using the proper models. The difference in the "A" factors for geometrical isomerization of trans-1-deuterio-2-vinylcyclopropane ($10^{14.5}$) and the vinylcyclopropane-cyclopentene rearrangemnt ($10^{13.5}$) is probably due to the orientation of the vinyl group in the transition states for these reactions. For cyclopentene formation the vinyl group must be over the ring and therefore is somewhat more ordered than the transition state for geometrical isomerization which does not have this requirement.

Our observation of geometrical isomerization of 1-deuterio-2-vinylcyclopropanes are consistent with a diradical mechanism, but can also be explained with the concerted mechanism proposed by Hoffman.[33] By this concerted mechanism trans-1-deuterio-2-vinylcyclopropane could epimerize to the cis isomer by a simultaneous conrotatory rotation of



C_1 and C_3 through 180°. Since intellectually, both a concerted and diradical mechanism can be used to explain this geometrical isomerization, a somewhat more subtle experiment is needed.

This question of mechanism can be more nearly answered by thermolysis of (cis and trans-2-deuteriovinyl)-trans,trans-2,3-dideuteriocyclopropane [54]. Choice of this compound was made for several reasons.



[54]

The bonds obliged to break during rearrangement are the ones between C_1 and C_3 or C_2 and C_3 and not the ones between C_1 and C_2. This cleavage of the most substituted bond in cyclopropyl systems was noted earlier in the thermolysis of 1,2-dimethylcyclopropanes. The major structural isomerization products, cis and trans-2-pentene are a result of rupture of the bond between the carbons bearing the two methyl groups. Added assurance that the bonds between more substituted carbon atoms are easier to break can be seen by the low activation energy (33.5 kcal/mole) for geometrical isomerization of 1,2-diphenylcyclopropanes.

This preferential rupture of bonds between C_1 and C_3 or C_2 and C_3 (and the absence of C_1-C_2 bond breaking) simplifies the number of modes of reaction, since cleavage of either bond will yield identical reacting species due to the symmetry of the molecule. With only deuterium substituted for hydrogen all isomers should have the same energy (neglecting very small secondary isotope effects) and therefore should be present in equal amounts at equilibrium. With identical thermodynamic

reactants and products we can assume the rate constants for the operable mechanism (k_1-k_8 in concerted mechanism or k_1-k_{10} in diradical mechanism, Figure 19) are equal. Thus, starting with A in Figure 19 the reaction could follow three distinctly different courses. A could be transformed directly into D with the exclusion of B and C (Chapter II, Smith Mechanism, Case II). A could rearrange to yield B, C and D at equal rates (Chapter II, Randomization, Case III). Finally, A could be transformed into B and C, which in turn could form D (Chapter II, Concerted Process, Case I). It should be noted that B cannot form C directly by any possible breaking and reformation of C_1-C_2 or C_1-C_3 bonds.

It was realized early in the experiments that a Smith mechanism at C_1 was not dominant since the trans isomers B and C were observed as products of the reaction. The distinguishing feature between a concerted and diradical mechanism is the time history of the pyrolysis. Intuitively, early in the reaction (ca. one half-life for deuterium epimerization or about four minutes at 325°C) the relative amounts of B, C and D should be very different. If a concerted pathway is operative B and C would build up a considerable concentration relative to D early in the reaction, while a diradical mechanism would produce B, C and D at equal rates throughout the reaction.

The diradical and concerted models were tested using an analog computer to plot the time history of the two reactions represented in Figure 19. In the concerted model k_1-k_8 were set equal, while k_9 and k_{10} were set equal to zero (Figure 20). In the diradical model all

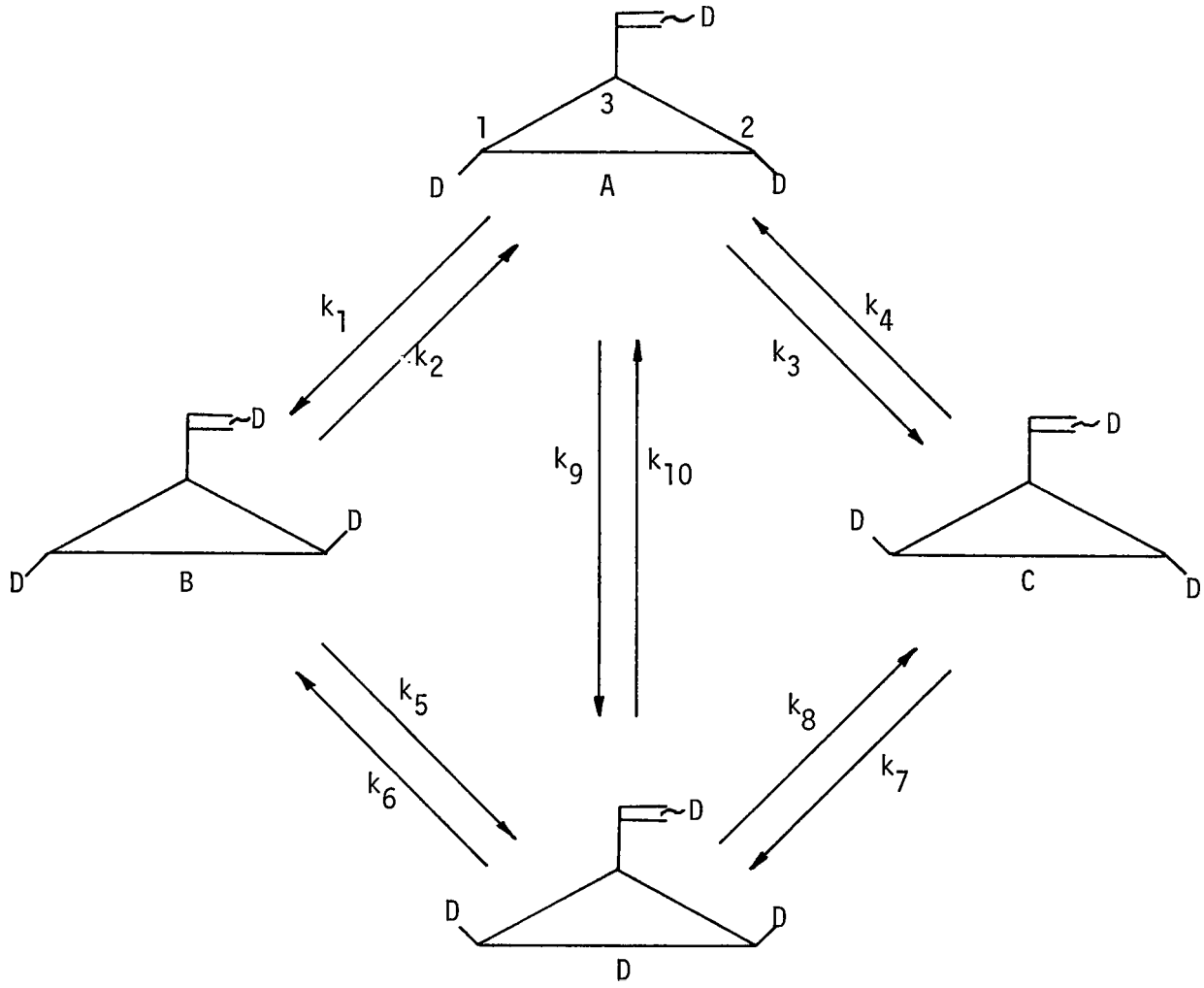


FIGURE 19. REACTION SCHEME FOR TRIDEUTERIOVINYLCYCLOPROPANES [54,55 and 56]

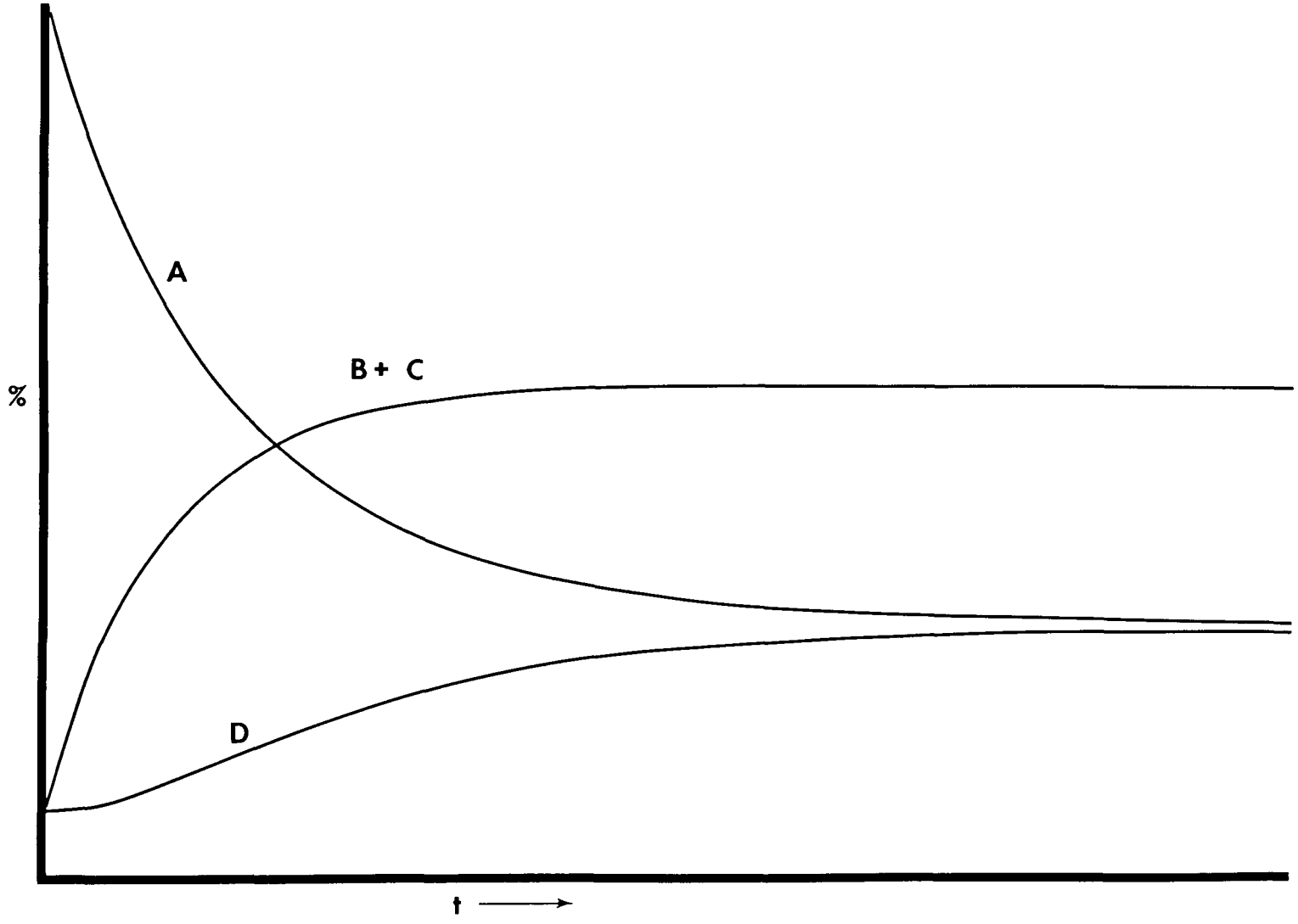


FIGURE 20. ANALOG COMPUTER PLOT FOR CONCERTED MODEL

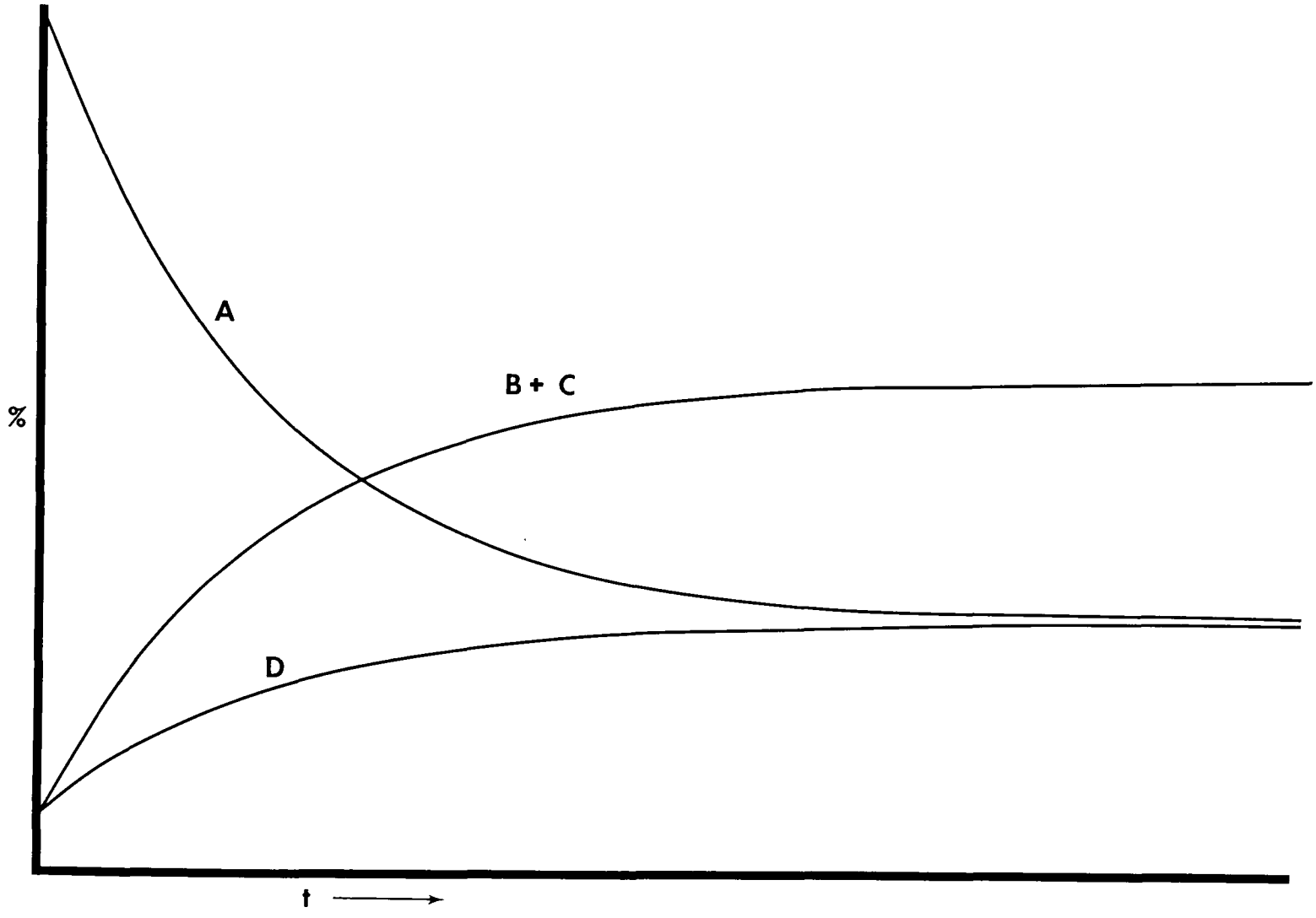


FIGURE 21. ANALOG COMPUTER PLOT FOR DIRADICAL MODEL

rate constants, k_1-k_{10}, were set equal (Figure 21). Figure 22 shows the ratio of (B+C)/D for both mechanisms.* As can be seen there is a large difference in the ratio of (B+C)/D for the two mechanisms early in the reaction. For the concerted reaction the ratio of (B+C)/D is as much as 5:1 at ca. one half-life and remains larger than 2:1 for several halflives. In the diradical mechanism (B+C)/D rapidly approaches 2:1 and then remains constant. The experimental results indicate that the ratio of (B+C)/D is 2:1 throughout the reaction. Table X contains the ratios of (B+C)/D at various times during the reaction. An example

TABLE X. RATIO OF (B+C)/D AT VARIOUS REACTION DURATIONS

Ratio at 324.5°C	Time (minutes)
1.0	0
2.1	4
2.0	10
2.0	25
2.0	50

*These computations take into account the small amounts of B, C and D present in the starting material. The relative ratios of A, B, C and D in the starting materialwere 88:3:3:6, respectively.

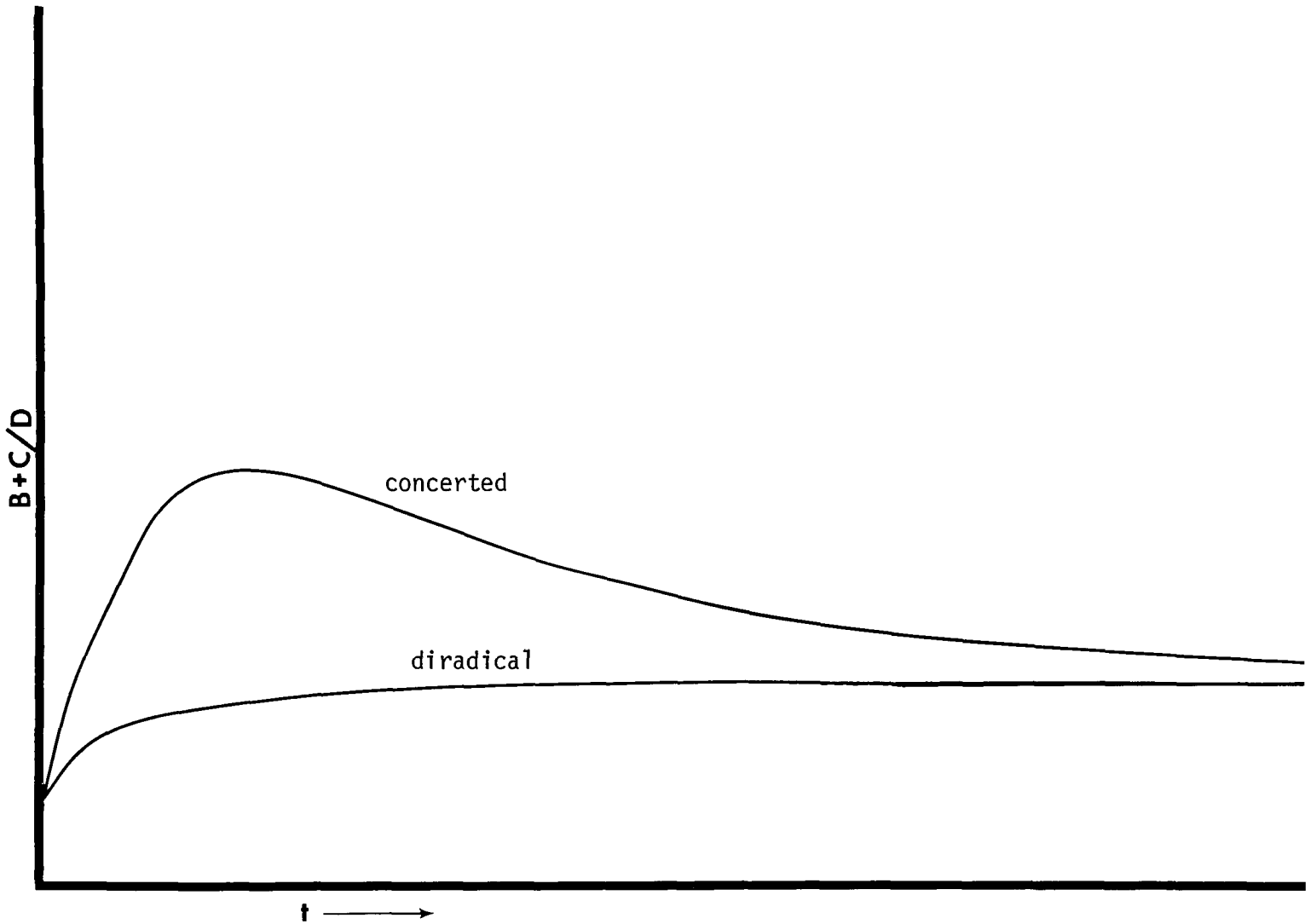
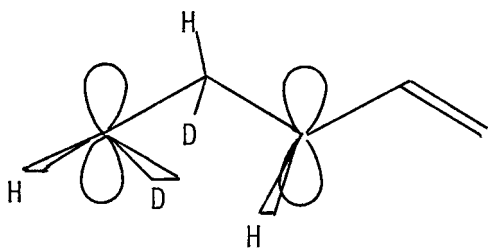


FIGURE 22. RATIO OF (B+C)/D VERSUS TIME FOR CONCERTED AND DIRADICAL MODELS

of the deuterium decoupled spectra at 0.64δ, used to calculate the relative amounts of B, C and D are shown in Figure 23.

This result offers conclusive proof that the pathway taken by the reaction can be described by our mechanistic model in which there is a randomization of stereochemistry at two of the three carbons in the cyclopropyl ring (Case III). The most obvious interpretation is that the degenerate vinylcyclopropane rearrangement has an intermediate diradical along the reaction coordinate. The life-time of a diradical (specifically that derived from cyclopropane) has been estimated by Benson[24] to be ca. $10^{-11.3}$ sec, for an 8 kcal/mole potential well. This is about 100 times shorter than the time between molecular collision at 1 atm. Thus, using this estimate of life-time, the diradical, once formed, must react adiabatically to form products. This means that the potential well in the reaction coordinate diagram (Figure 18) is not very populated and moreover, that number of times the ends of the diradical can rotate during $10^{-11.3}$ sec or less, must be small. The diradical intermediate discussed here might just as easily be a planar species [57] that recloses in a random manner to the vinylcyclopropanes.



[57]

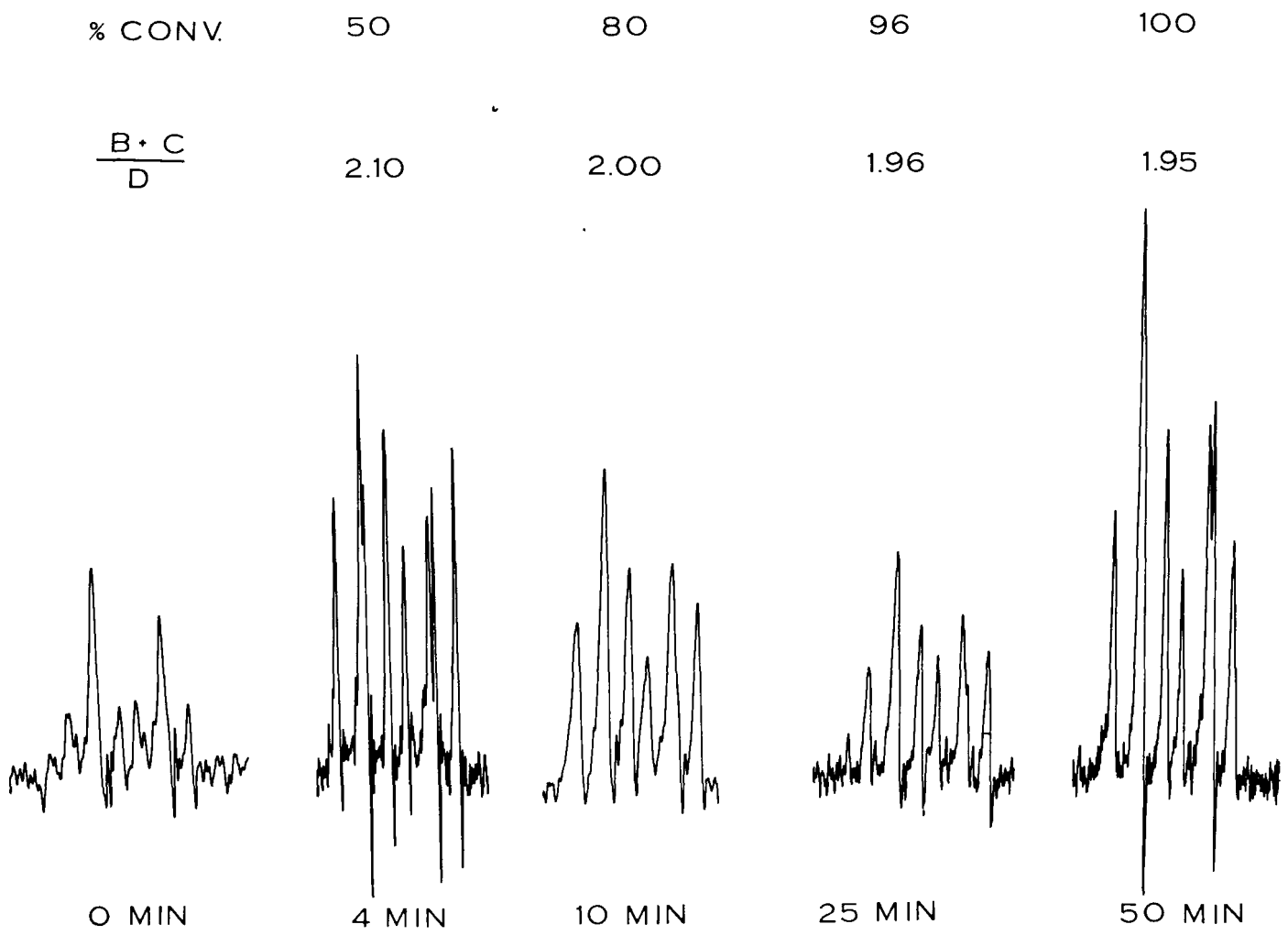


FIGURE 23. DEUTERIUM DECOUPLED SPECTRA AT 0.64δ USED TO CALCULATE (B+C)/D AT TIME t

CHAPTER V

EXPERIMENTAL

EXPERIMENTAL

All infrared spectra were obtained on a Beckman IR10 Infrared Spectrometer. Mass spectra were taken on an LKB model 9000 Mass Spectrometer and a Consolidated Electrodynamics Corporation Model 21-110B High Resolution Mass Spectrometer. Preparative and analytical VPC were conducted using various columns on an Aerograph A90-P3 Gas Chromatograph. NMR spectra were obtained using a Varian HA-100 Nuclear Magnetic Resonance Spectrometer operated at 100.00 MHz. Deuterium decoupling of NMR samples was accomplished using an NMR Specialties HD-60 Heteronuclear Spin Decoupler.

1,1-Dibromo-2-vinylcyclopropane [33] - Following the procedure of Woodworth and Skell,[35] a 500 ml three neck roundbottom flask, fitted with a mechanical stirrer, dropping funnel and dry ice-acetone cold finger, was cooled in a dry ice-acetone bath. 183 ml (2.2 moles) of butadiene (Matheson, C.P. grade) and 44 g of potassium tert-butoxide (0.4 mole) (MSA Research Corporation, Evans City, Pennsylvania) were stirred together in the flask. 98 g (0.38 mole) of bromo form (J. T. Baker, U.S.P. grade) was added with stirring over a one hour period at such a rate that the reaction temperature never exceeded -10°C. The reactants were stirred for an additional hour at ca. -10°C. Then 100 ml of pentane and 100 ml of water was added and the layers separated. The organic layer was heated with a water bath to remove excess butadiene. The water layer was washed with two 50 ml portions of pentane and the organic layers were combined. The organic portion was washed with two

100 ml portions of cold saturated sodium chloride solution and placed over anhydrous sodium sulfate for 24 hours. The pentane was removed using a flash evaporator and the residue was distilled under vacuum (24-27 torr). A light smoky yellow, oily fraction, 67 g (64% yield from bromoformed) boiling at 73-78°C was identified as 1,1-dibromo-2-vinylcyclopropane [33] using I.R. and NMR. I.R. Spectra: 3070 (m), 3026 (m); 1635 (m); 1000 (s), 975 (s), 910 (s), 705 (s), 640 (s). NMR Spectra, see Figure 5.

tri-Butyltin hydride - The procedure of Kuivila and Beumel[58] was used. To 150 ml of anhydrous ether in a three neck 250 ml flask, which was cooled in an ice-water bath and fitted with a nitrogen inlet tube, a dropping funnel and stirrer, was added 1.56 g (0.0409 moles) of lithium aluminum hydride (Alpha Inorganics, Inc., Beverly, Mass.). tri-n-Butyltin chloride (Columbia Organic Chemicals, Columbia, S.C.), 32.5 g (0.10 moles) was added dropwise over a 30 minute period with stirring. The mixture was stirred for three more hours at room temperature and then slowly hydrolyzed with 100 ml of water with cooling by an ice bath. The ether layer, after washing with 100 ml cold water, was dried overnight over anhydrous sodium sulfate. The ether was removed using a flash evaporator and the hydride distilled very rapidly, using an oil bath preheated to 110°C. The yield amounted to 21.5 g (74%) bp 70-85°C (ca. 2 torr).

1-Bromo-2-vinylcyclopropanes [34 and 35] - Using the procedure of Seyferth, et. al.,[37] 10 g (0.044 mole) of 1,1-dibromo-2-vinylcyclopropane

was placed in a 25 ml three-neck flask equipped with a thermometer, a magnetic stirrer, a pressure equalizing dropping funnel and a nitrogen inlet. To this was added dropwise 20.4 g (.07 mole) of tri-n-butyltin hydride with stirring under nitrogen over a one hour period. (Seyferth used a 1:1 mole ratio of hydride and dibromo compound.) The temperature was maintained at 10°C by external cooling with an ice bath. Distillation at 37 torr gave 4 g (62% yield) of material boiling at 43°C. VPC analysis with a 40 ft. carbowax 20 M on chromasorb W 60/80 mesh showed two components in a ratio or 3:7 with relative retention times of 1.0:1.7. These two components were collected on a preparative scale and labelled compounds [34 and 35].

I.R. Spectra: Compound [35], 3080 (m), 3000 (m), 1640 (s), 1230 (s), 1020 (m), 980 (s), 900 (s), 800 (w), 675 (m). Compound [34], 3080 (m), 3000 (m), 640 (s), 1260 (s), 1030 (m), 980 (s), 900 (s), 800 (m), 680 (m). NMR spectra, see Figures 6 and 7.

tri-n-Butyltin deuteride - The same procedure was used as in the preparation of tri-n-butyltin hydride. Lithium aluminum deuteride (Columbia Organic Chemicals, Columbia, S.C.), 0.82 g (0.02 mole), was used rather than the hydride along with 13 g tri-n-butyltin chloride and 75 ml anhydrous ethyl ether, yield 8.7 g (75%).

1-Bromo-1-deuterio-2-vinylcyclopropanes [39 and 40] - The same procedure was used as in the preparation of the 1-bromo-2-vinylcyclopropanes [34] and [35] except that 8.7 g (0.036 mole) tri-n-butyltin deuteride was used in place of the hydride along with 8.2 g (0.03 mole, 1,1-dibromo-2-vinylcyclopropane. Where the reaction using tri-n-butyltin hydride required ca. one hour for complete reaction, ca. four hours were required

to carry this synthesis to completion. Introduction over the reaction of atmospheric oxygen caused a significant increase in the rate of the reaction as monitored by the temperature rise. The reaction mixture was worked up and cis- and trans-bromo isomers were purified in the same manner as the 1-bromo-2-vinylcyclopropanes. These two isomers had the same relative retention time chromatographically as the protonated isomers and were also in a ratio of 3:7, yield 2 g (48%).

Methanol-o-d - 1 mole methanol and 2 moles D_2O (99.8%, Columbia Organic Chemicals, Columbia, S.C.) were mixed in a 200 ml flask and distilled. The recovered alcohol was mixed with another mole of D_2O and again distilled. The alcohol was dried over anhydrous magnesium sulfate. NMR analysis revealed the alcohol to be 96% + methanol-o-d.

Vinylcyclopropane [36] - By varying the procedure of Nishida, et. al.,[36] a 250 ml three-neck flask was fitted with a dropping funnel and a tube leading to a u-tube immersed in a dry ice-acetone bath. The other end of the u-tube was connected to a drying tube containing "Dyrerite". Stirring was effected with a magnetic stirrer. The reaction was cooled with an ice bath. 10 g (0.044 mole) of 1,1-dibromo-2-vinylcyclopropane [33] and 25 ml methyl alcohol was placed in the reaction flask. A total of 15 g of granular sodium metal (prepared by the method of Fieser[59]) was added over a one hour period, along with 135 ml more methyl alcohol. After the reaction of sodium was complete, the ice bath was replaced with an oil bath and the reaction mixture heated at 65°C for ca. four hours. The material in the trap was dissolved in 10 ml of cyclohexane,

extracted twice with 5 ml of cold water and dried over anhydrous sodium sulfate. Proparative scale VPC purification on a 40 ft., 10% carbowax 20 M 60/80 column operated at 70°C yielded ca. 0.3 ml of vinylcyclopropane [33] (7% yield)(The actual synthetic yield is probably much higher with most of the loss taking place during VPC purification.)
I.R. - Identical with Sadtler Standard, Spectra No. 2808.

N.M.R. Spectra - Figure 18

M.S. - (Normalize to largest Peak in Parent Ion Region equal to 100)

M/e	Intensity
66	8.5
67	100.0
68	63.7
69	3.1

---

trans-1-Deuterio-2-vinylcyclopropane [37] - 50 μl of trans-1-bromo-2-vinylcyclopropane [35] and one ml of methyl alcohol-o-d was introduced into a 10 ml two-neck flask. The same trapping apparatus used in the preparation of vinylcyclopropane was employed. The reation was cooled using an ice-salt bath at -15°C. A total of 2.5 ml of methyl alcohol-o-d was added over a 30 minute period. Sufficient granular sodium metal to react completely with the alcohol was added periodically. After the reaction was complete 2 ml of D_2O and 0.3 ml cyclohexane were added.

The layers were separated and the cyclohexane layer was washed twice with 1 ml of water. Anhydrous sodium sulfate was used to dry the separated organic layer. The yield of [37] after VPC purification (see preparation of vinylcyclopropane) was ca. 12 μl (32% yield).
NMR Spectra - Figure 17.

M.S. - (Normalized to largest Peak in Parent Ion Region equal to 100)

M/e	Intensity
66	11.1
67	23.8
69	100.0
69	66.7
70	3.2

---

cis-1-Deuterio-2-vinylcyclopropane [38] - The synthetic sequence and apparatus was identical with that used in the preparation of the cis isomer. 50 μl of trans-1-bromo-1-deuterio-2-vinylcyclopropane [40] was used to obtain 8 1 of cis-1-deuterio-2-vinylcyclopropane [38]. (ca. 20% yield after VPC purification).

M.S. - (Normalized to Largest Peak in Parent Ion Region Equal to 100)

M/e	Intensity
66	10.2
67	19.3
68	100.0
69	68.2
70	3.4

---

cis- and trans-1,3,4,4-Tetrachloro-1-butene - The synthesis was carried out in a manner identical with that given by Frank and Blackham.[60] The monomer, cis-dichloroethylene, was obtained from Eastman Organic Chemicals, Rochester, N.Y.

1,4-Dichloro-1,3-butadienes - The basic procedure of Ol'dekop and Kaberoin[61] was used. 95.5 g of cis- and trans-1,3,4,4-tetrachloro-1-butene (0.5 mole) and one l of methyl alcohol were placed in a two liter three-neck flask fitted with a mechanical stirrer and reflux condenser. To this was added 25 ml of glacial acetic acid and 5 ml of concentrated hydrochloric acid. 38 g of zinc dust was added in portions over a 15 minute period. During this time the reaction temperature rose to 35°C. After one hour 10 g of zinc dust was added with no elevation of temperature. Distilled water (1.5ℓ) was added and the reaction mixture became cloudy. This mixture was then extracted with two 500 ml portions of ethyl ether. The ether layer was washed twice with two 150 ml portions of cold water and dried over anhydrous sodium sulfate. The

ether was distilled off to yield 35 g (58% yield) of cis,cis; cis, trans and trans,trans-1,4-dichloro-1,3-butadiene. Less than one percent of starting materials cis and trans-1,3,4,4-tetrachloro-1-butane was present as shown by VPC. Triangulation of the Vapor Phase Chromatogram obtained using a 13 ft. polypropylene glycol-4000 on chromasorb W 60/80 mesh column shows cis,trans-:cis,cis-:trans,trans-1,4-dichloro-1,3-butadienes were present in 47, 36 and 16 percent, respectively.

Phenyl mercuric bromide - Phenyl mercuric bromide was prepared identically according to the procedure of Seyferth and Burlitch.[62] 100 g of tetraphenyltin (Eastman Organic Chemicals, Rochester, N.Y.), yielded 155 g (69% yield) of phenyl mercuric bromide, MP 280-282°C.

Phenyl(tribromomethyl)mercury - Preparation of phenyl(tribromomethyl) mercury was accomplished using identically the procedure of Seyferth and Burlitch.[62] 35.8g(.1 mole) of phenyl mercuric bromide, 102 g bromoform and 37.2 g of 1:1 potassium tert-butoxide:tert-butanol complex yielded 38.5 g (74% yield) of a very fine crystalline solid that decomposed on melting at 114-120°C.

Reaction of phenyl(tribromomethyl)mercury with 1,4-dichloro-1,3-butadienes - This procedure is patterned after a halogenated cyclopropane synthesis by Seyferth, et. al.[41] Into a 1 liter three-neck flask, fitted with a mechanical stirrer, reflux condenser and nitrogen inlet, was placed 450 g of trans,trans-, cis-cis-, and cis,trans-1,4-dichloro-1,3-butadiene (isomer ratio 1:2.2:3 respectively) (3.7 mole) and 196 g of phenyl (tribromomethyl) mercury (0.37 mole). This mixture was heated

slowly with an oil bath. All phenyl(tribromomethyl)mercury had dissolved when the bath temperature reached 60°C yielding a clear yellow solution. Precipitation of phenyl mercuric bromide began at ca. 90°C. The mixture was heated at 90°C for one hour, at which time the color of the solution was black and filled with solid precipitate. The reaction mixture was cooled to room temperature and ca. 200 ml of n-pentane was added. The solid phenyl mercuric bromide was filtered from the reaction mixture. 120.6 grams (0.33 mole) of phenyl mercuric bromide (ca. 90% yield) was recovered. The n-pentane and excess dichlorobutadiene was stripped using a flash evaporator (water pump first then vacuum pump). The thick black residue was molecular distilled, yielding 74 grams of a bluish liquid that turned black again on setting in a refrigerator for several days. VPC analysis indicates this liquid contains 1,3,4,4-tetrachloro-1-butene (concentrated starting material from preparation of dichlorobutadienes), and three peaks which contain the four isomers of dibromodichlorovinylcyclopropane [41,42,43,44]. NMR - see NMR discussion (Chapter IIIC).

M.S. (Peaks at 213, 215 and 215 and 217 are normalized to peak 213 = 100. Peaks at 257, 259, 261 and 263 are normalized to peak 257 = 100)

VPC Peak 1		VPC Peak 2		VPC Peak 3	
M/e	Intensity	M/e	Intensity	M/e	Intensity
213	100	213	100	213	100
215	164	215	182	215	168
217	78	217	74	217	71
257	100	257	100	257	100
259	239	259	205	259	210
261	159	261	124	261	147
263	30	263	20	263	30

Reaction of [41,42,43 and 44] with tri-n-butyltin hydride - The four isomers of dibromodichlorovinylcyclopropane (31.5 g of bluish liquid from molecular distillation) were placed in a three-neck 500 ml flask fitted with a dropping funnel, thermometer and nitrogen inlet. The reaction was stirred with a magnetic stirrer. 31.5 g of freshly prepared tri-n-butyltin hydride was added dropwise over ca. one hour. The temperature was maintained below 40°C by external cooling with an ice bath. After stirring 24 hours, the reaction was vacuum distilled (ca. 2 torr) using a 20 inch silvered, vacuum jacketed distillation column.

Three fractions were collected at 25-32°C, 32-85°C and 85°C-100°C. Fraction three (85-100°C) contained almost exclusively tri-n-butyltin bromide. Fraction one contained 1,3,4,4-tetrachloro-1-butene and compounds [47,50 and 52]. Fraction two contained 1,3,4,4-tetrachloro-1-butene and seven isomers [45,47,48,49,50,51 and 52]. (Compound [45] was a solid. All other isomers were liquids at room temperature.) These seven isomers were purified by preparative VPC using a 10 ft., 10% SF-96 on chromasorb W, 60/80 mesh column. Five chromatographic peaks with relative retention times of 1:1.1:1.5:1.8:2.1 were found to contain the seven isomers. During the preparative VPC,chromatographic peak 1 also contained a considerable amount of 1,3,4,4-tetrachloro-1-butene.

Chromatographic Peak	Relative Retention Time	Isomers
1	1	47,50
2	1.1	52
3	1.5	48,51
4	1.8	49
5	2.1	45

NMR - see NMR Discussion (Chapter IIIC).

M.S. (Peaks at 214, 216 and 217 are normalized to peak at 214 equal to 100)

Chromatographic Peak	M/e	Intensity
1	214	*
2	214	100
	216	175
	218	62
3	214	100
	216	164
	218	81
4	214	100
	216	183
	218	83
5	Not determined	

*This M.S. sample contained mostly 1,3,4,4-tetrachloro-1-butene but the trihalovinylcyclopropanes were evident by a small parent peak at 214

Reaction of compound [45] with metallic sodium and methyl alcohol-o-d - Ca. 30 mg of [45] (an off color solid) was dissolved in ca. 2 ml methyl alcohol-o-d in a 10 ml two-neck flask. The same U-tube trapping apparatus

as used in the preparation of vinylcyclopropane was employed. The flask was cooled in a methanol ice bath (ca. -20°C). Granular sodium metal was added until no further reaction took place. One ml cyclohexane and two ml deuterium oxide were added to the reaction mixture. The material in the U-tube was dissolved in cyclohexane. The cyclohexane layer from the reaction mixture and trap were combined and dried over anhydrous sodium sulfate. The vinylcyclopropane-d_3 was purified by preparative VPC using a 25 ft. 10% polypropylene glycol-4000 on chromasorb W, 60/80 mesh column operated at 70°C with a flow rate of 60 ml/min., vinylcyclopropane-d_3 retention time was six minutes. Four μl of the trideuterated vinylcyclopropane [53] was collected.

NMR Spectra was identical with Figure 13 except for vinyl stereochemistry.

Reaction of isomers [45,47-51] with metallic sodium and methyl alcohol-o-d - This reaction was carried out using the same procedure as used with isomer [45] alone. 500 μl of distillation fraction two (from reaction of isomers [41,42,43 and 44] with tri-n-butyltin hydride) was used along with ca. 15 ml methyl alcohol-o-d and sufficient granular sodium metal to react completely with the alcohol. Yield ca. 20 μl of the trideuteratedvinylcyclopropane [54] with mixed deuterium stereochemistry at the olefin.

NMR Spectra - see Figures 13, 14 and 15.

Reaction of [47,50 and 52] with metallic sodium and methyl alcohol-o-d - This reaction was carried out identically with the proceeding synthesis, except that distillation fraction one, from the reaction of tri-n-butyltin

hydride with compounds [41,42,43 and 44] was used. Yield ca. 15 µl of the trideuterated vinylcyclopropane [54] with mixed stereochemistry at the olefin. NMR spectrum is identical with the preceeding sample.

M.S. - (Normalized to largest Peak in Parent Ion Region Equal to 100)

M/e	Intensity
67	5.8
68	6.4
69	35.0
70	85.4
71	100.0
72	5.6
73	2.9

Pyrolysis of vinylcyclopropanes - The oven used for all pyrolysis (see Figure 3) was the column heating chamber of an Aerograph A-90-P3 gas chromatograph. The top of the oven was a one inch thick asbestos board provided with a hole for introduction of glass ampules containing the material to be pyrolyzed. The temperature in the oven was maintained to ±0.5°C using an Aerograph Model 326 Linear Temperature Programmer operated in the isothermal mode. A Chromel-alumel thermocouple referenced to an ice-water bath at 0°C was used to determine the oven temperature. That the temperature was constant at all points within the oven was determined by placing the thermocouple atdifferent places

and observing no temperature gradient. Thermocouple voltages were measured using a Leeds and Northrup Model 8686 millivolt potentiometer. The preheating chamber was a one foot piece of 2.5 inch diameter pyrex tubing wrapped with resistance wire and coated with asbestos. The voltage necessary to achieve 250°C (as measured by a thermometer), was applied through a "Powerstat".

Preparation of vinylcyclopropanes for pyrolysis - The monodeuterated vinylcyclopropane [37] (5 μl) was placed in a 12 mm x 180 mm pyrex tube previously washed with ammonium hydroxide, rinsed with distilled water, and dried at 110°C for two hours) and connected to a vacuum line. The deuterated vinylcyclopropane was frozen with a liquid nitrogen bath the tube evacuated to ca. 0.005 torr and sealed.

Trideuterated vinylcyclopropanes [54] were collected directly from preparative VPC (10 ft., 10% SF-96 on chromasorb W, 60/80 mesh column) into a pyrolysis tube (12 mm x 180 mm) and sealed as above.

Preparation of pyrolysis samples for NMR - The pyrolysate from the deuterated vinylcyclopropanes was collected at one of the glass ampules by partially immersing one end of the ampules in liquid nitrogen. The ampules were opened and the frozen material was dissolved in carbon tetrachloride and benzene (lock signal for NMR).

The monodeuterated vinylcyclopropanes, carbon tetrachloride and benzene were transferred directly to a "micro" NMR sample tube for analysis. The trideuterated vinylcyclopropanes, carbon tetrachloride and benzene were transferred to thin wall NMR tubes and sealed under vacuum.

Analog computation of diradical and concerted models - An Electronic Associates, Inc., Model TR-20 analog computer was used to test the two mechanisms in question.

The kinetic equations for the concentrations of A, B, C and D in Figure 19 are as follows:

$$\frac{-d[A]}{dt} = k_1[A] + k_3[A] + k_9[A] - k_2[B] - k_4[D] - k_{10}[D]$$

$$\frac{-d[B]}{dt} = k_2[B] + k_5[B] - k_1[A] - k_6[D]$$

$$\frac{-d[C]}{dt} = k_4[C] + k_7[C] - k_3[A] - k_8[D]$$

$$\frac{-d[D]}{dt} = k_6[D] + k_8[D] + k_{10}[D] - k_5[B] - k_4[C] - k_9[A]$$

These computations were carried out by Dr. W. E. Wentworth, University of Houston, Houston, Texas. For the diradical process k_1 through k_{10} were assigned equal values, while for the concerted process k_1 through k_8 were equal and k_9 and k_{10} were set equal to zero. Initial concentrations used for the four components were:

A = 88%
B = 3%
C = 3%
D = 6%

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