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THERMOLYSIS OF LITHIUM CYCLOBUTOXIDES

by

Krishnan Sundaresan

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in
The University of Michigan
1970

Doctoral Committee:

Professor R. Martin Stiles, Chairman
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Associate Professor Richard G. Lawton
Assistant Professor Paul G. Rasmussen
Assistant Professor John R. Wiseman

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ABSTRACT

THERMOLYSIS OF LITHIUM CYCLOBUTOXIDES

by

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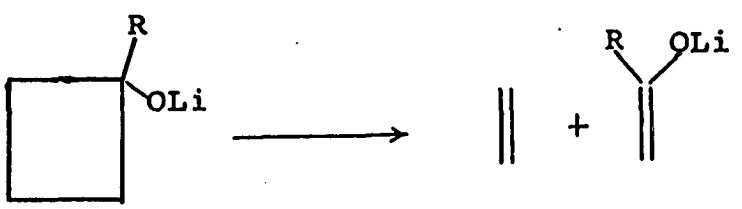
Chairman: R. Martin Stiles

The possible involvement of enolate ions in 2+2 cycloaddition reactions was studied by investigating the reverse reaction. Various cyclobutanols were converted to lithium alkoxides and these substances were heated in Triglyme. The reaction of equation 1 was shown to occur in good yield in the temperature range 150-200°.



(1)

R=H, C_6H_5

The kinetics of the reaction were studied and activation parameters $\Delta H^{\ddagger}$=23.3 kcal, $\Delta S^{\ddagger}$ = -23.2 e.u. (R=Ø) and $\Delta H^{\ddagger}$=25.5 kcal, $\Delta S^{\ddagger}$ = -21.9 e.u. (R=H) were found.

Cis- and trans-2,3-dimethylcyclobutanones were prepared and separated. Reduction of the cis with LAH yielded 80% of all cis alcohol. Reduction with tri-t-butoxy LAH yielded 90% of all cis alcohol. Thermolysis of the lithium alkoxide from the all cis alcohol at 220° in Triglyme yielded 62% olefin mixture composed of 18% propylene, 52% cis-2-butene

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and 30% trans-2-butene. Similar thermolysis of the mixture of secondary alkoxides derived from the trans ketone yielded 68% olefin mixture composed of 20% propylene, 16% cis-2-butene and 64% trans-2-butene. Analysis of incomplete reaction mixtures revealed a small amount of isomerization of the all cis-alcohol to those of the trans dimethyl series. The stereochemistry of the process thus closely resembles that of cis- and trans-dimethylcyclobutane, reported by Gerberich and Walters, even though the latter compounds required temperatures of 450-500° compared to 160-200° for the lithium alkoxides.

A mechanism involving a stepwise reaction, proceeding via intermediate anion diradicals, is proposed.

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ACKNOWLEDGMENTS

I wish to express my profound sense of appreciation to Professor R. Martin Stiles for the benefit of his exact scholarship, his patience and for his encouragements during the course of this study.

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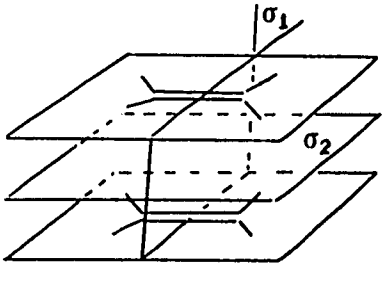
INTRODUCTION

The preparation of cyclobutanes and cyclobutenes by cycloaddition reactions[1] between two alkenes or an alkene and an alkyne has become an important synthetic reaction. Where applicable it is now the method of choice for the synthesis of four-membered carbocyclic compounds. The synthesis is achieved thermally in the presence of free-radical inhibitors or photochemically by irradiation with visible or ultraviolet light.

The mechanisms of (2+2) and (2+4) cycloaddition reactions have been and are still being investigated in detail. The statement "Orbital symmetry controls in an easily discernable manner the feasibility and stereochemical consequence of every concerted reaction" by Woodward and Hoffmann[2] has revolutionized the thinking of many research workers. If orbital symmetry is to be conserved, the two ground-state ethylene molecules cannot combine in the most obvious way in a concerted reaction to give ground state cyclobutane.

Consider the scheme below where the two ethylene molecules approach one another in parallel planes corresponding to a "suprafacial" addition to both double bonds. The four molecular orbitals that can be formulated from



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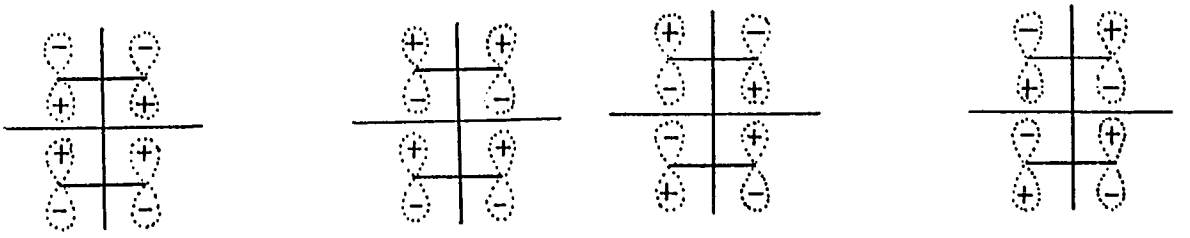

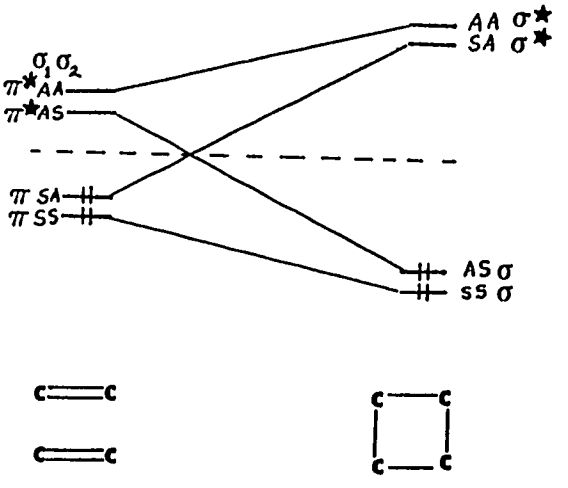

the four relevant p-orbitals are shown. Each can be classified as symmetrical (S) or antisymmetrical (A) with respect to each of the symmetry planes σ_1 and σ_2. It will be seen that SS and SA are bonding in the ethylene reactants, while AS and AA are antibonding. In the region where the sigma bonds of cyclobutane form, it will be seen that SS and AS are bonding, while SA and AA are antibonding. Thus one can construct a simple correlation diagram as shown above. From the diagram one can see that the two bonding orbitals of the reactants do not correlate with the two bonding orbitals of the product, but rather with one bonding and one antibonding. In this situation, the concerted reaction is said to be "forbidden"[3] for ground-

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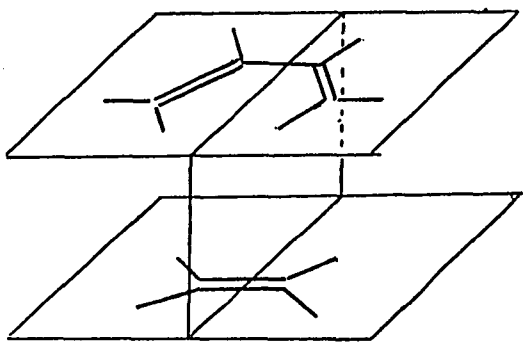
state molecules, where only the bonding orbitals are occupied. The same restrictions apply, of course, to the reverse reaction.

In contrast to the $2\pi(S)+2\pi(S)$ mode, which is symmetry forbidden, a similar process for the (4+2) (Diels-Alder) cycloaddition can be shown to be symmetry-allowed. In this case, the six possible MO's are shown below and classified as symmetric or antisymmetric with respect to the vertical symmetry plane. Construction of the correlation diagram in similar fashion illustrates the fact that the reactant bonding orbitals have the same symmetry as the product bonding orbitals, and hence the concerted reaction is allowed between ground-state molecules.



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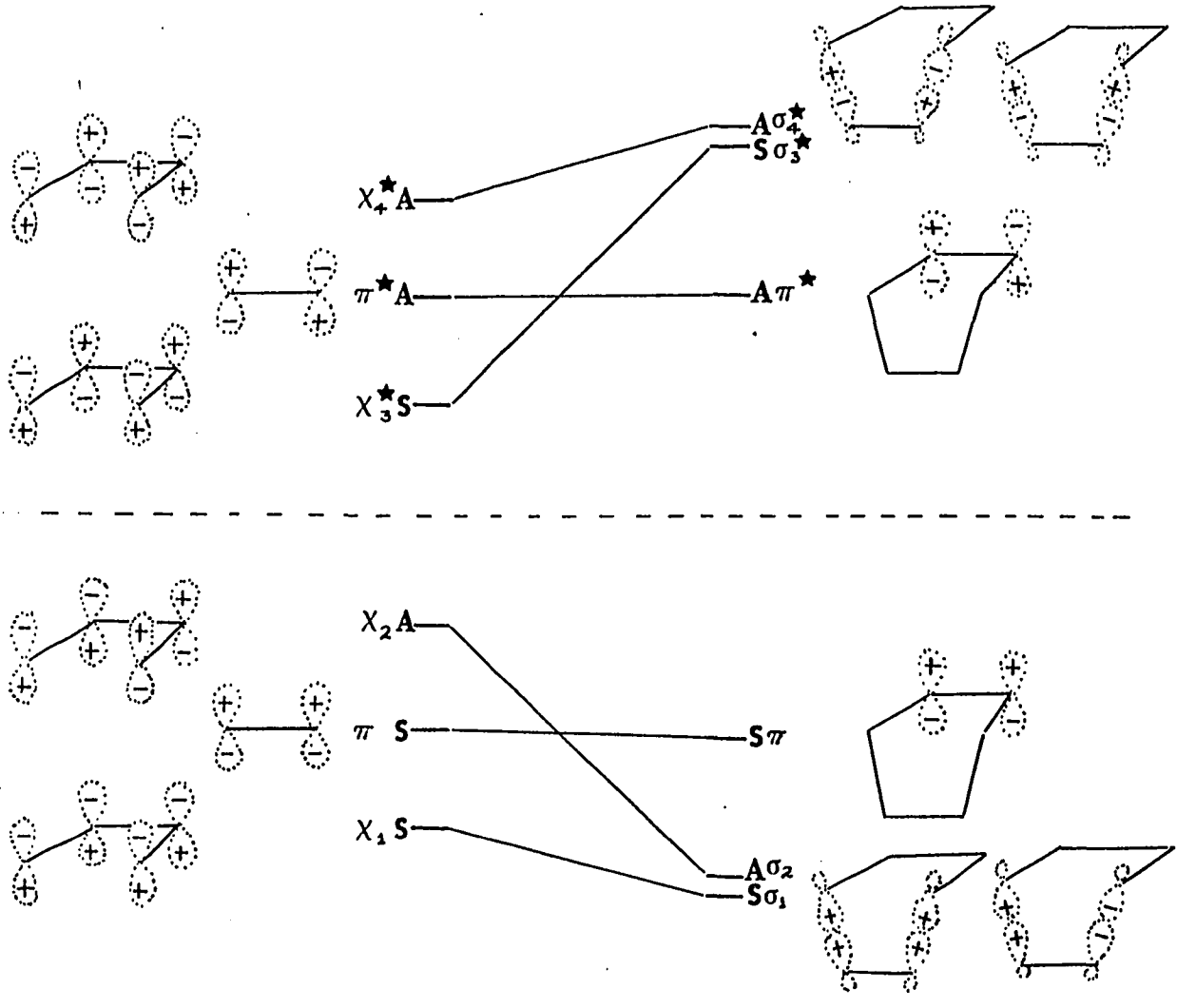

It has been pointed out by Woodward and Hoffmann[4] that a different mode of (2+2) cycloaddition is an allowed concerted reaction for ground-state ethylene. Such a mode is designed $2\pi(S)+2\pi(A)$ and corresponds to a suprafacial (S) addition to one ethylene molecule and an antarafacial (A) addition to the other. The geometry of such an allowed transition state is shown on the following page.

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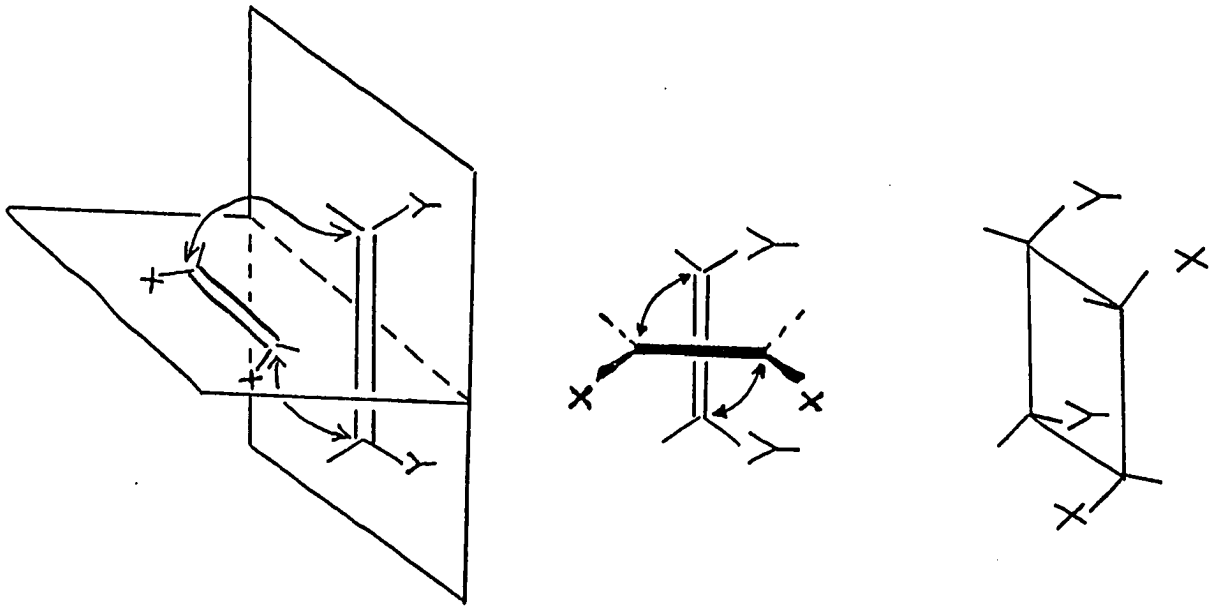
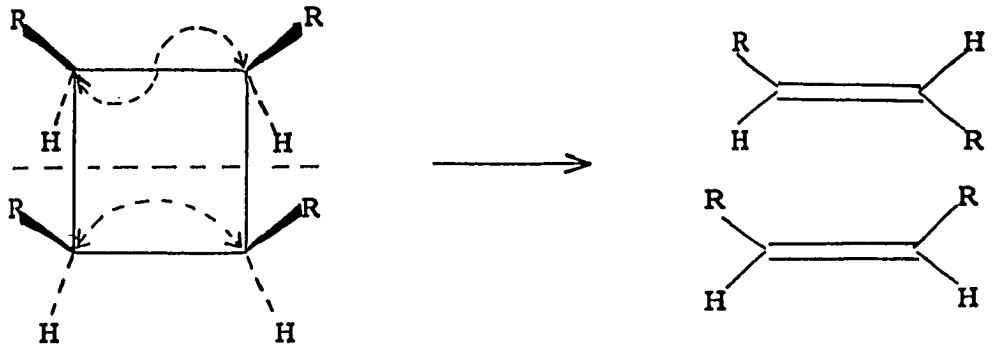


For cyclobutane fragmentation, if the process is concerted, the stereochemical relationships at three of the four carbons of the cyclobutane will be retained in the products.



Most reactions, which yield cyclobutane and cyclobutene, are not believed to be concerted and proceed with thermal energies by way of biradical or dipolar intermediates. This fact may be related to the steric problems that most olefins encounter in the transition state for a $2\pi(S)+2\pi(A)$ cycloaddition.

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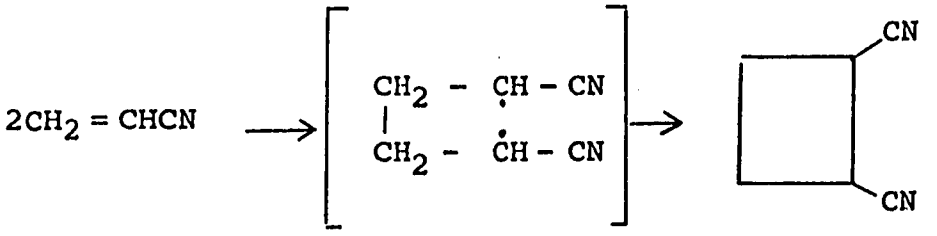
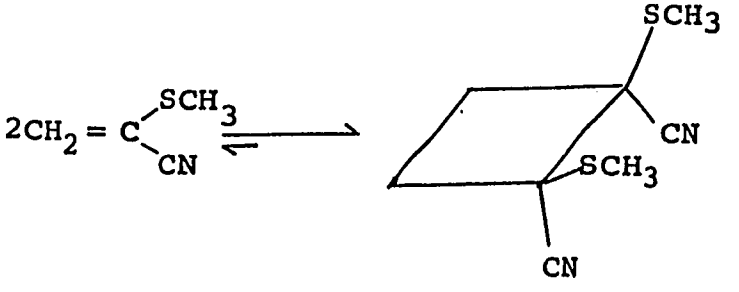
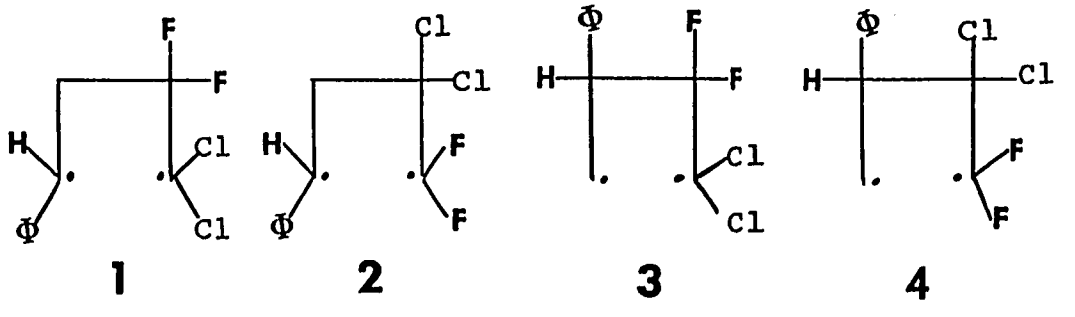
A few examples of (2+2) cycloadditions which were proven unequivocally to proceed through biradical intermediates are given below. Such a reaction is the head-to-head dimerization of acrylonitrile.[5] An equilibrium which lies well on



the side of the four membered ring is established when a thio group is introduced in the α-position of acrylonitrile. On vacuum distillation at 140° the monomer is recovered.[6]



Among the evidence for biradical mechanism is the fact that, when unsymmetrical olefins couple, the orientation of the product can always be predicted on the basis of the relative stability of the radicals; for example, styrene and 1,1-dichloro-2,2-difluoroethylene can give four intermediates.[7] On the basis of radical stability, 3 and 4 may



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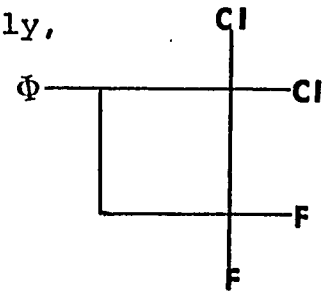
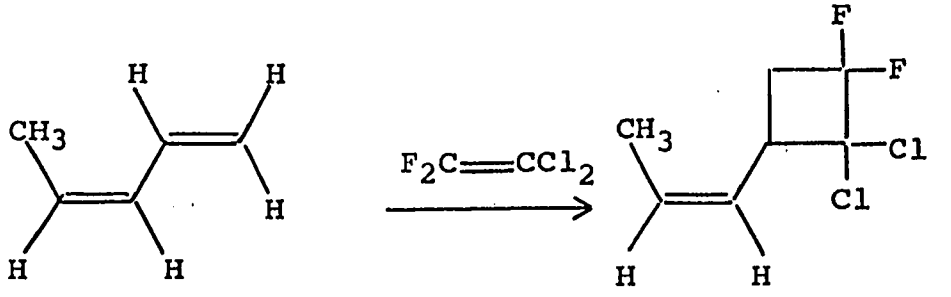
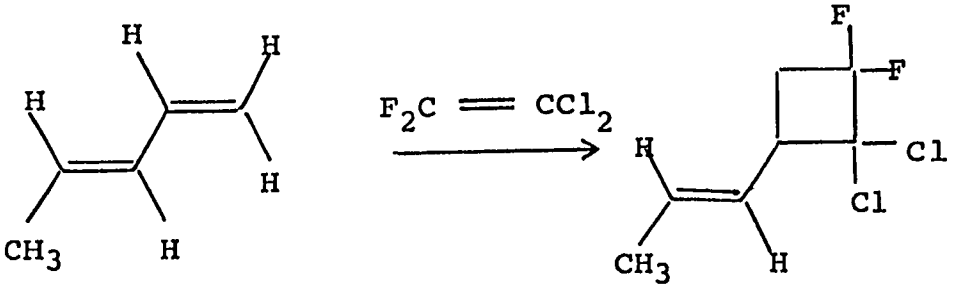
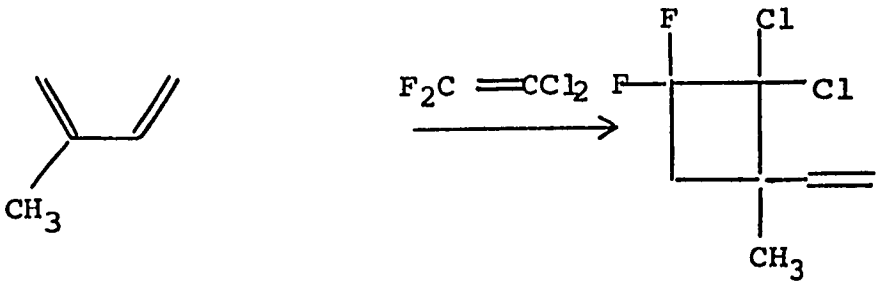
be ruled out, since in 1 and 2 there is resonance of an unpaired electron with a phenyl group. 1 is more likely than 2 since a dichloromethyl radical should be more stable than a difluoromethyl radical. In accord with the prediction, the product is actually,



In the reaction between 1,1-dichloro-2,2-difluoroethylene and cis- and trans-1,3-pentadiene and isoprene, the products were those predicted on the basis of the more stable biradical intermediate.[8]







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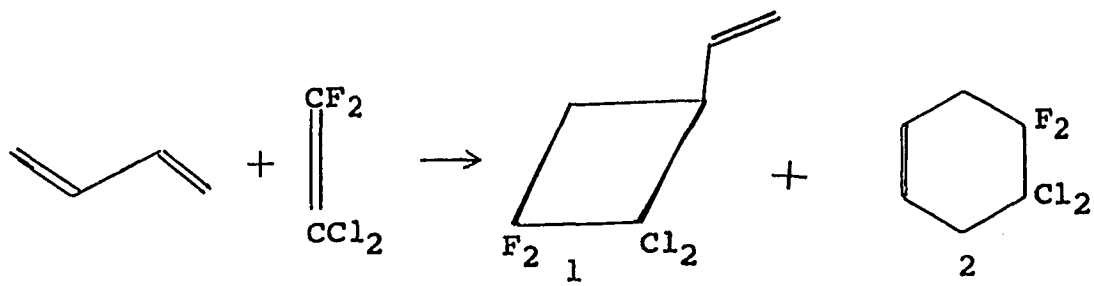
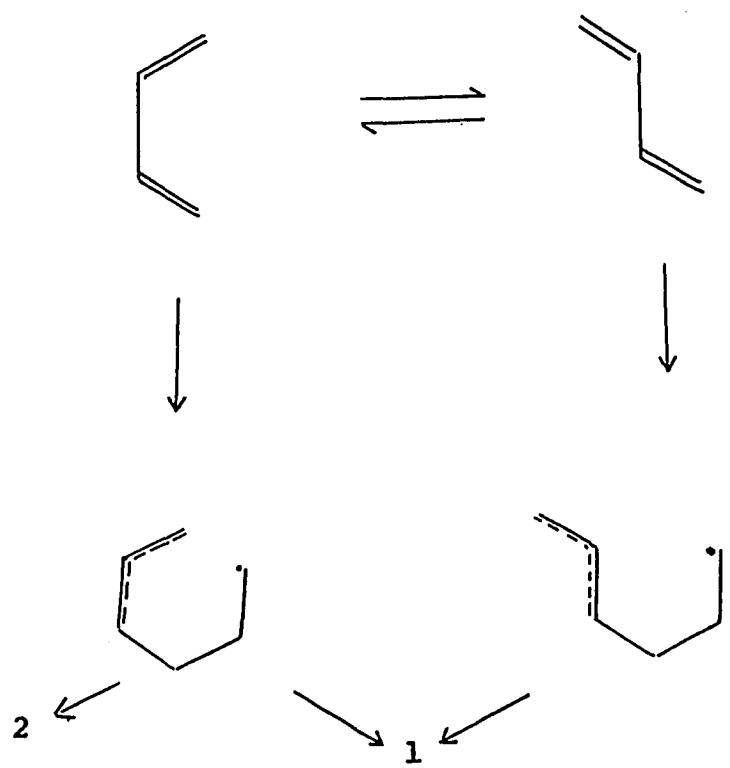
Fluorinated olefins have been observed to add to acyclic dienes with the apparent exclusive formation of vinylcyclobutanes by 1,2-cycloaddition rather than cyclohexenes by 1,4-addition.[1]

Bartlett and Swenton[9] have isolated the 1,4-adduct (2) as a minor product in the reaction of butadiene with 1,1-dichloro-2,2-difluoroethylene.



The formation of the two products are explained by the following scheme:



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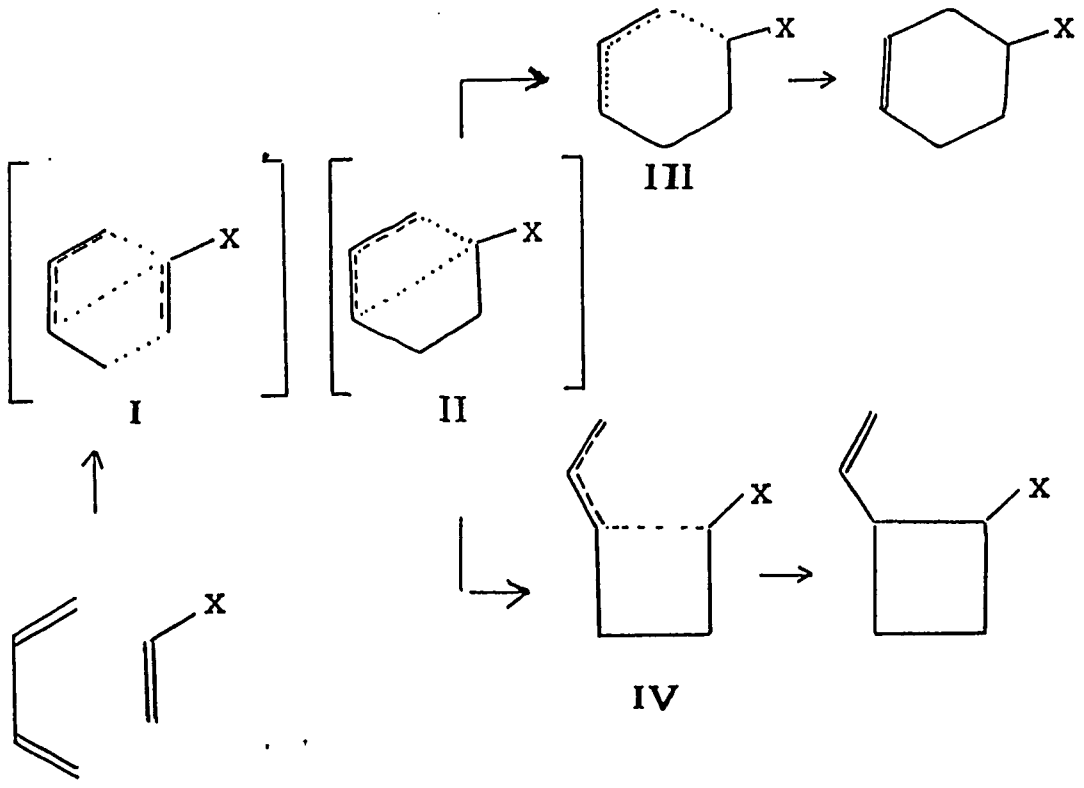
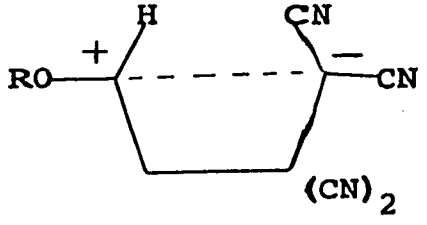
According to Little[10] the reaction of butadiene and α-acetoxyacrylonitrile proceeds through a single transition state such as I to an intermediate II. II may then continue through either of the two subsequent lower energy transitions similar to III and IV to the two observed products.



The electron rich double bonds of vinyl ethers, vinyl thioethers and enamines combine with tetracyanoethylene to form cyclobutane derivatives.[11] The reaction mechanism involves charge separation in the rate determining step with a transition state such as



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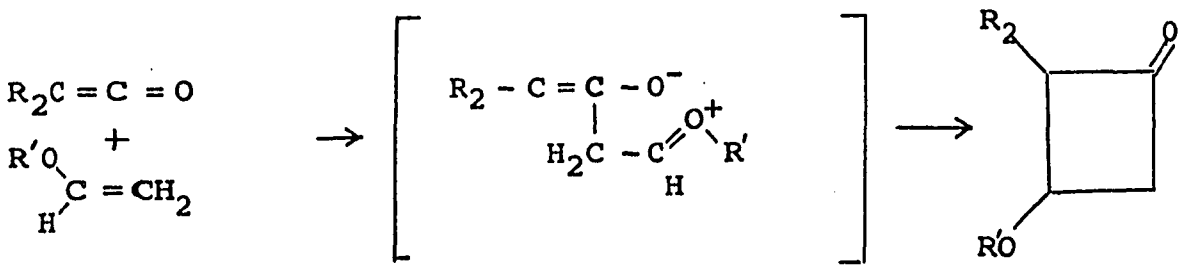
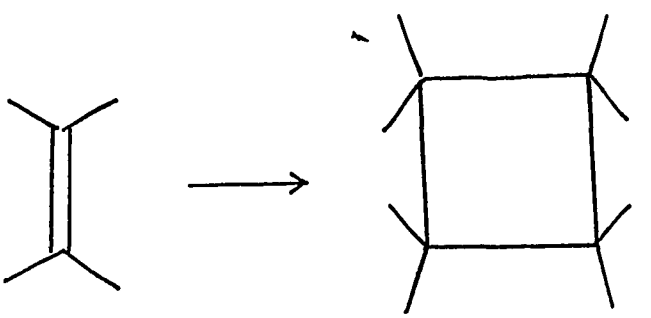
Ketenes react with enol ethers to form 3-alkoxycyclobutanones by addition in the electronically favored direction; the product being compatible with the occurrence of the resonance stabilized intermediate.[12]



There are many examples in the literature of photocycloadditions to form derivatives of cyclobutanes.[13] But there is a dearth of reported examples of photodimerizations of nonconjugated acyclic olefins in marked contrast to that of conjugated and small ring olefins. Photolysis of tetramethylethylene gives octamethylcyclobutane in a fair yield.[14]



The dimerizations of optically active and racemic 1,2-cyclononadiene reported by Moore and co-workers[15] are explained by the $2\pi(S)+2\pi(A)$ mode. The net stereochemical effect of this cycloaddition is that of <u>cis</u> (suprafacial) addition to one allene and <u>trans</u> (antarafacial) addition to the other. This is exactly the result predicted by Woodward and Hoffmann.[4] However, because of the additional π electrons,

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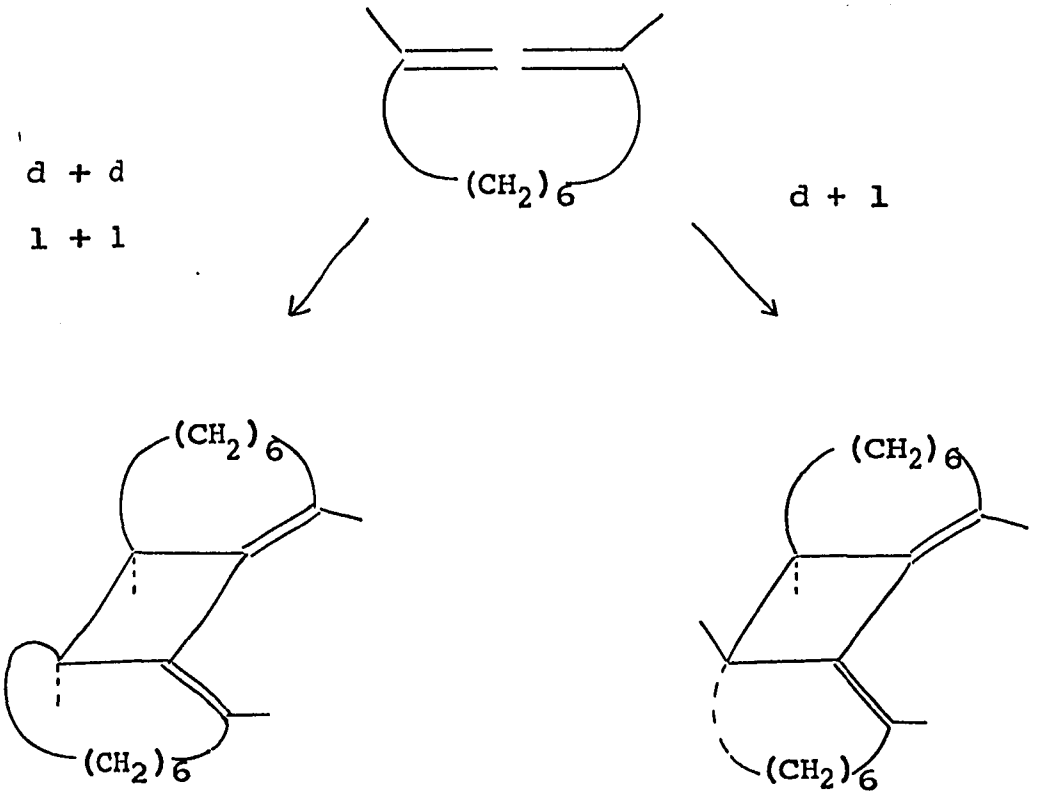

this cycloaddition may be more complex than is implied for a concerted (2+2) addition. The reaction of ketenes with olefins to give cyclobutanes has been subjected to thorough investigation recently by Huisgen and co-workers.[16] The evidence (high negative entropy of activation, the modest dependence of rate on solvent polarity, and maintenance of configurations of reactants in the products) is conclusive that it is concerted. The process involves orthogonal approach of the reacting species. For normal olefins, insurmountable difficulties would appear to be presented by steric hindrance factors and transition state strain associated with framework distortions necessary to maintain effective orbital overlap. In allene and ketene reactions, these factors may not play such a role.

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Retroaddition Reactions.

Retroaddition reactions, especially the retro Diels-Alder reaction, have been extensively reviewed.[17] The use of reverse reaction for the elucidation of the mechanism of the forward reaction is discussed in detail in the above review article. The mechanism of a (2+2) cycloaddition reaction often must be deduced from a study of the reverse process.

Pyrolysis of small ring compounds, especially of cyclobutanes, has been extensively investigated in the past two decades. The discovery of many new synthetic procedures has made numerous ring systems relatively easily available, and the advent of gas chromatography has allowed the analysis of the reaction products to be carried out with ease and precision.

The thermal unimolecular decomposition of cyclobutane to ethylene has been very thoroughly investigated.[18] In the table given on page 13 are the results of a few cyclobutane pyrolysis experiments.

Two distinct mechanisms have been proposed,[29] one involving the formation of a tetramethylene biradical intermediate which goes on to give the final products, and the other, the symmetrical stretching of two opposite C-C bonds in the ring to yield the olefins in one concerted step.

On the biradical intermediate hypothesis, it might be expected that the alkyl substitution would lead to an increase in rate. But the fact is that, if there is any

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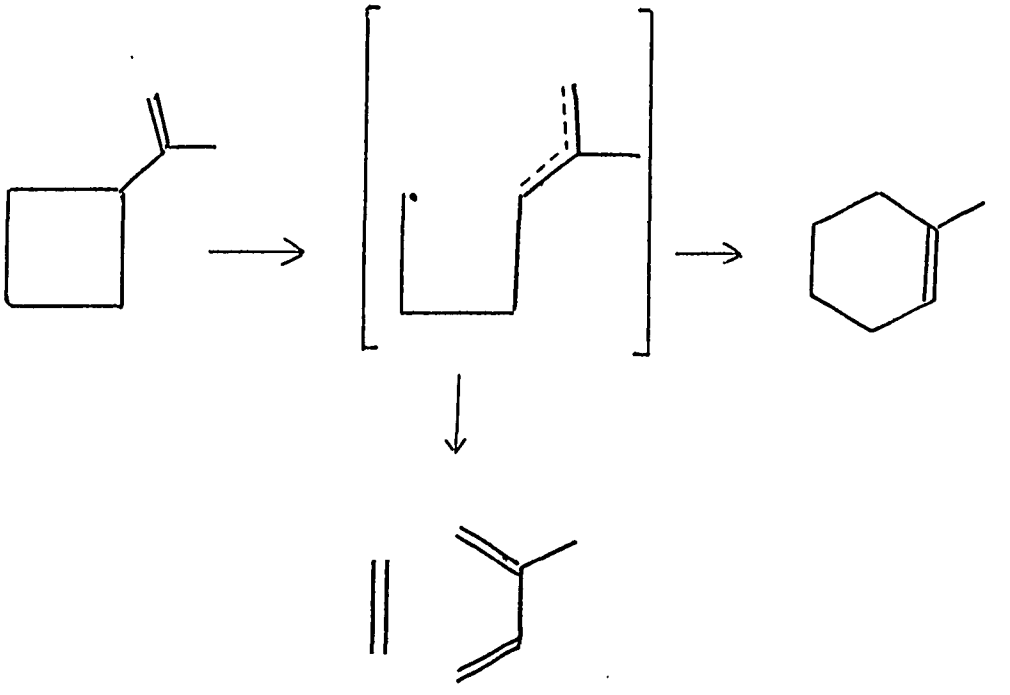
Table I*

Thermal Decomposition of Cyclobutanes

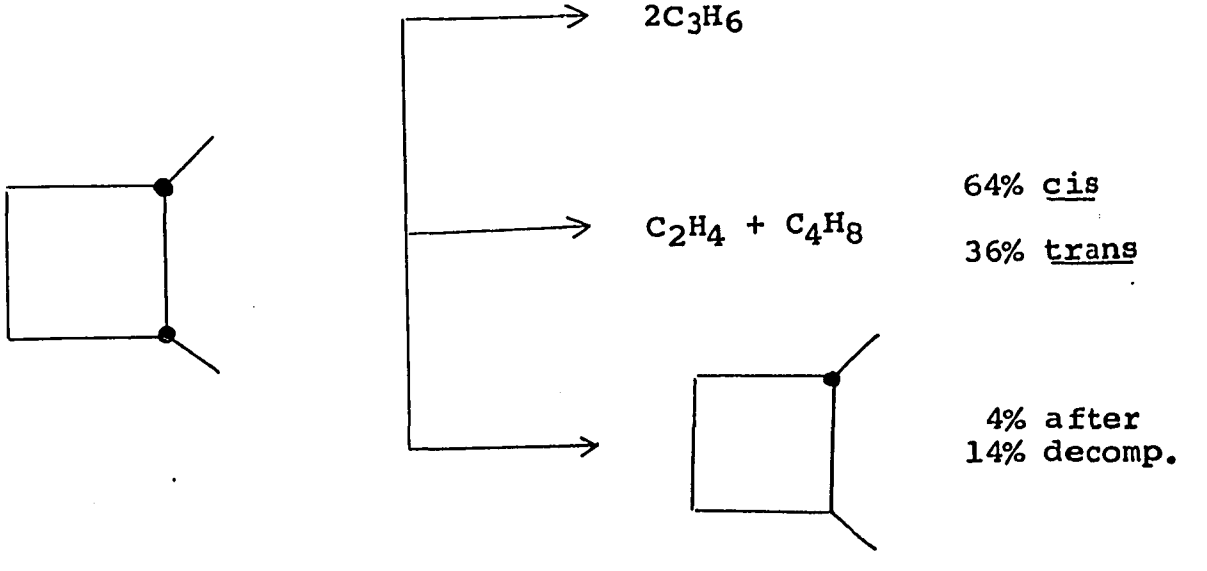
Reactant	Product	Log A, sec^{-1}	E, kcal $mole^{-1}$	Ref
Cyclobutane	Ethylene	15.62	62.5	18
Methylcyclobutane	Ethylene + propylene	15.38	61.2	19
1,1-Dimethylcyclobutane	Isobutylene + ethylene	15.68	61.0	20
cis-1,2-Dimethylcyclobutane	Butene-2 + ethylene	15.57	63.0	21
	Propylene	15.48	60.4	
trans-1,2-Dimethylcyclobutane	Butene-2 + ethylene	15.46	63.4	22
	Propylene	15.45	61.6	
Ethylcyclobutane	Butene-1 + ethylene	15.56	62.0	23
n-Propylcyclobutane	Pentene-1 + ethylene	15.53	61.6	24
Isopropylcyclobutane	3-Methylbutene-1 + ethylene	15.63	62.6	25
Isopropenylcyclobutane	Isoprene + ethylene	14.61	51.0	26
	1-Methylcyclohexane	14.53	51.0	
Acetylcyclobutane	Methyl vinyl ketone + ethylene	14.53	54.5	27

*Taken from Frey and Walsh[28]

increase, it is negligible. Isopropenylcyclobutane decomposes with a low energy of activation which according to Frey[26] is in agreement with resonance stabilized biradical.



The results of the investigation of Gerberich and Walters[21,22] on the pyrolysis of cis- and trans-1,2-dimethylcyclobutane are worth looking into in greater detail. The ring cleavage in both cases is accompanied by a slower isomerization.



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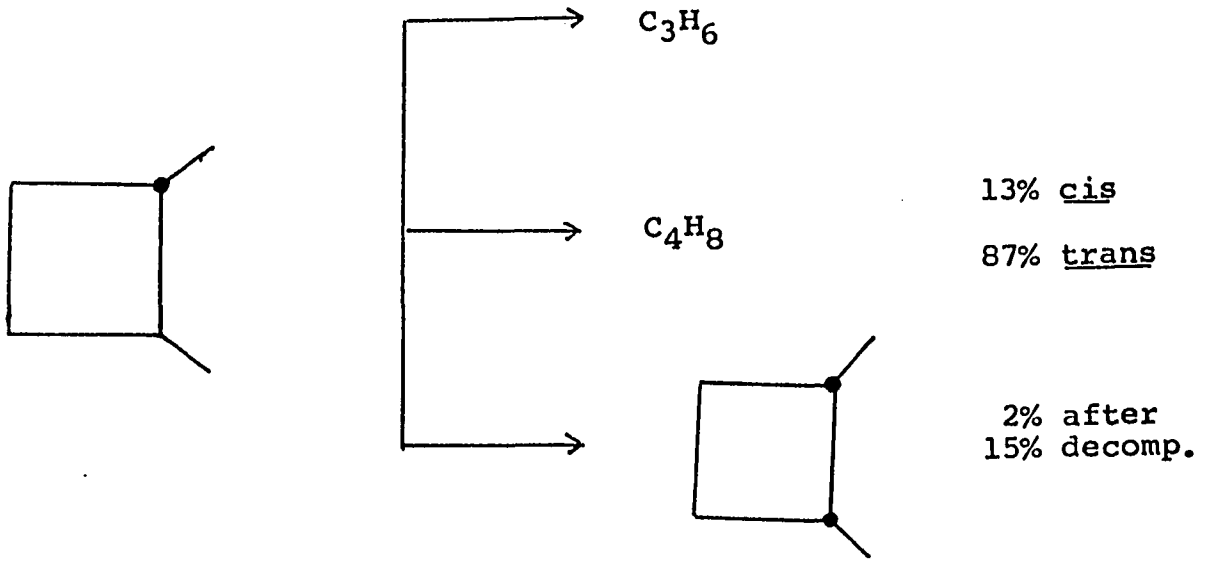
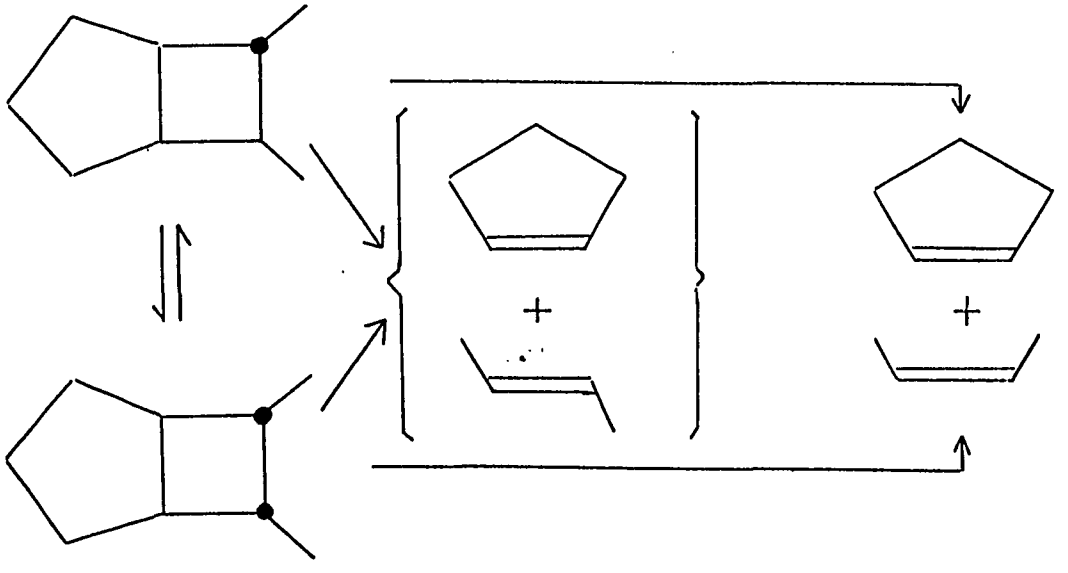


Since the product is not 100% cis-2-butene and 100% trans-2-butene in the respective experiments, the ring cleavage, according to Walters, does not occur without "some disturbance" of the geometrical features of the methyl groups.

Frey, Cocks and Stevens[29] studied the pyrolysis of trans- and cis-6,7-dimethylbicyclo(3,2,0)heptane in order to test the feasibility of the two mechanisms proposed for the pyrolysis of cyclobutanes.



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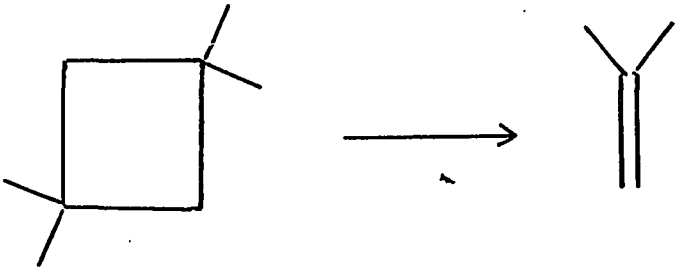
The trans dimethyl compound gave 75% trans-2-butene and the cis compound gave 50% cis-2-butene. From these results and from the fact that if there were to be a concerted process, which involves inversion taking place in one of the four carbons in the ring (inversion is limited to C_4 and C_5), Frey and co-workers have concluded that the decomposition proceeds through a biradical mechanism.

If a biradical has a momentary existence during the reaction, it decomposes before the steric configuration reaches the equilibrium conditions of cis- and trans-2-butenes at the experimental conditions.

In a recent paper,[30] Frey discusses the results of the pyrolysis study of 1,1,3,3-tetramethylcyclobutane.



The rate of decomposition of this compound is slower than that of other alkylcyclobutanes and is indeed slower than that of cyclobutane itself. This is explained as due to considerable interaction between substituents in the 1 and 3 positions, while forming the transition state. The activation energy difference between various substituted cyclobutanes depends on three factors: 1, the destabilization of the reactant due to the steric interactions involving the alkyl substituents, 2, stabilization of the incipient diradical by alkyl substituents and 3,

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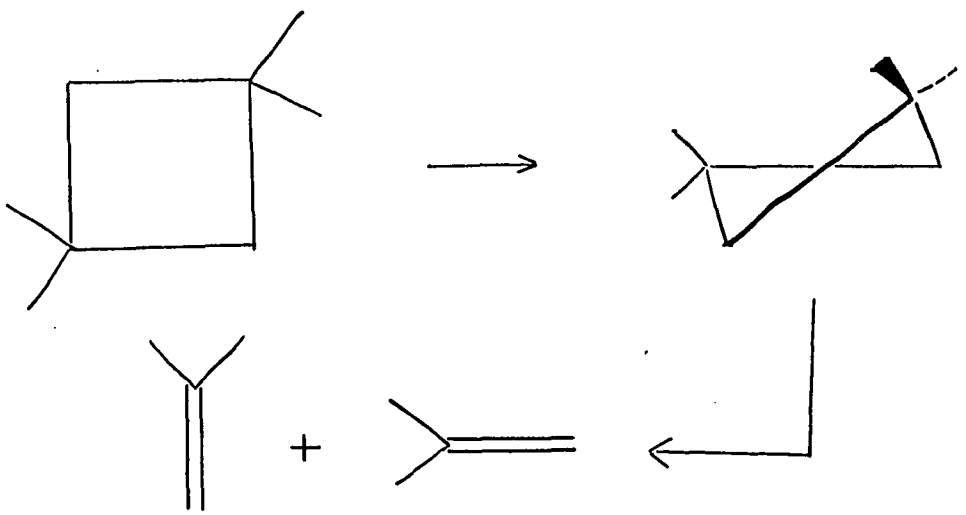
destabilization of the complex by 1,3-interaction. The order of the reaction rates Me> Et > Pr can be rationalized by assuming that the difference in the 1,3-interactions are more important than the net of the other two effects.

A concerted mechanism for the reaction, which involves the simultaneous stretching of the two bonds to form the olefinic products directly, may be postulated. Such a process is forbidden on the basis of orbital symmetry



correlation, which makes it a relatively high energy pathway. The energy of activation for the decomposition is indeed unusually high. That makes it a good example for a concerted process.

Baldwin and Ford[31] have studied the stereochemistry of the pyrolysis of 7,8-cis,exo-dideuterio-cis-bicyclo (4.2.0)octane, giving predominantly ethylene. The system is constrained to give cis-cyclohexane and thus to force the antarafacial role upon ethylene moiety in a concerted ring opening.

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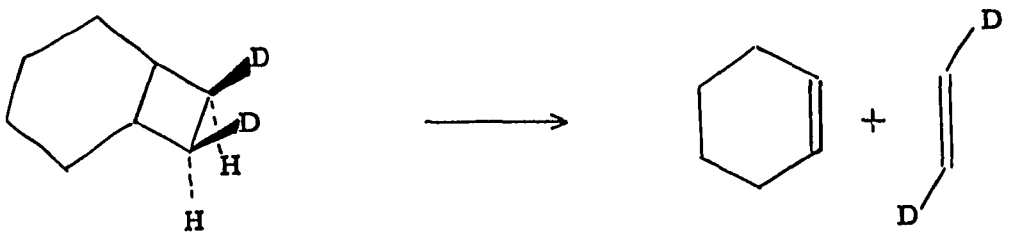

62±3%

The results, demonstrating trans-1,2-dideuterioethylene as a major isomer from the pyrolysis show that the predominant portion of the reaction occurs in a stereochemical sense incompatible with both the tetramethylene diradical hypothesis and the completely stereoselective antarafacial elimination of ethylene predicted through orbital symmetry theory.

Reactions of Enols and Enolate Ions.

Procedures that involve the formation and subsequent reaction of anions derived from active methylene compounds constitute a very important and synthetically useful class of organic reactions. Perhaps the most common reactions of this class are those in which the anion has been derived by removal of a proton from the carbon atom alpha to a carbonyl group. These anions, usually called enolate anions, are to be distinguished from enols, which are present in equilibrium with the carbonyl compounds in the presence of either acidic or basic catalysts.[32] A few of the best known reactions of enols are illustrated.

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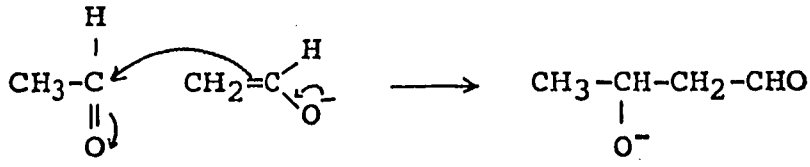
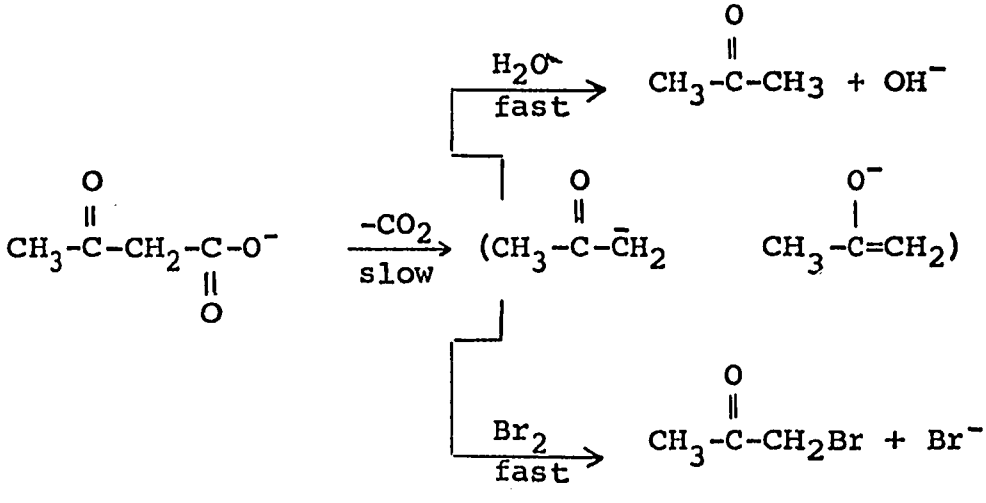
Aldol reaction is one of many organic reactions in which carbon-carbon bond is formed by the addition of an enolate-anion 'donor' to a carbonyl acceptor.[33]



The decarboxylation of β-ketoacids[34,35] is quite rapid even at room temperature and is thought to give rise to an enol or enolate anion which is rapidly converted to the ketone. Running the decarboxylation in presence of bromine gives the monobromoketone. Bromination occurs at the same rate as the decarboxylation. Under the same conditions, the ketone is not brominated. These facts indicate that decarboxylation leads to an enol which is very rapidly brominated.



The reaction of a ketone with bromine [36] proceeds by the acid catalyzed enolization of the ketone and subsequent electrophilic attack on the enol by bromine, loss of a proton from the intermediate oxonium ion leads to the bromoketone.

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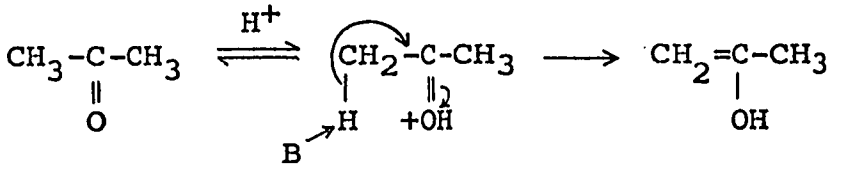
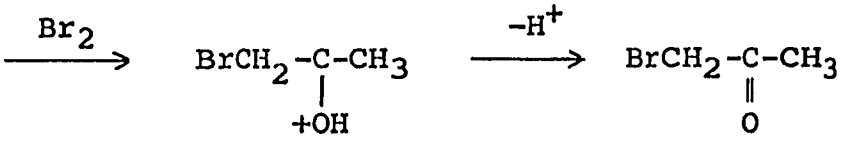
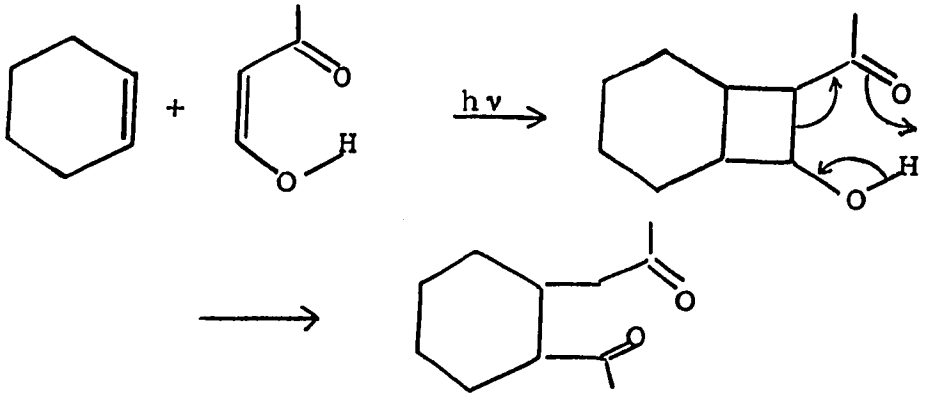
For the majority of ketones, which exist largely in the keto rather than the enol form, enolization is the rate-limiting step, and the overall rate of halogenation is independent of the nature or concentration of the halogen.





Enol ethers and enol esters have been studied extensively in (2+2) and (2+4) cycloaddition reactions. A (2+2) cycloaddition reaction which has the potential of being of considerable synthetic utility is the one reported by de Mayo and co-workers.[37]



Now the question is whether the enolate anion would participate in reactions illustrated on the next page. An important generalization of the selection rules for (m+n) cycloaddition is that these rules depend not on the total

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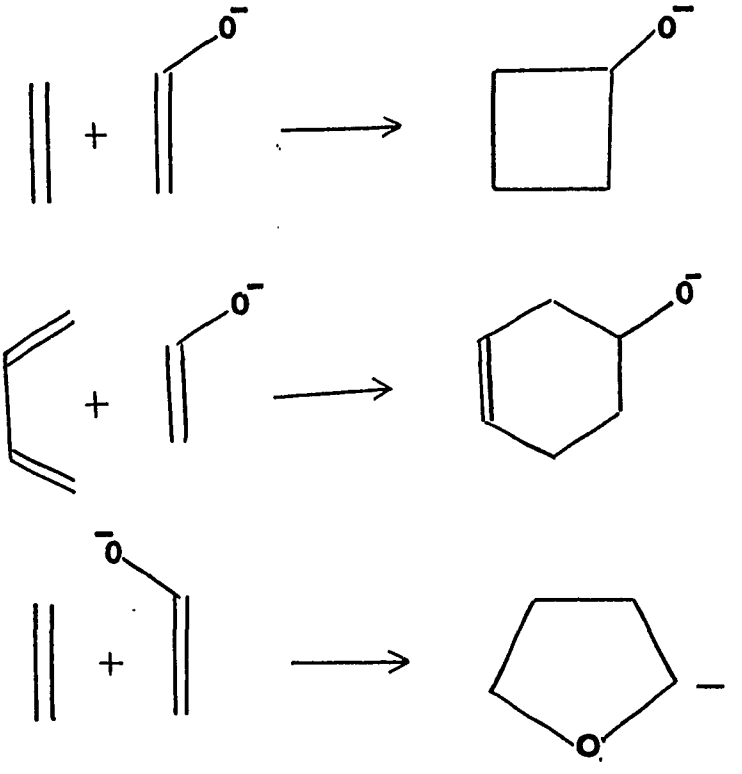
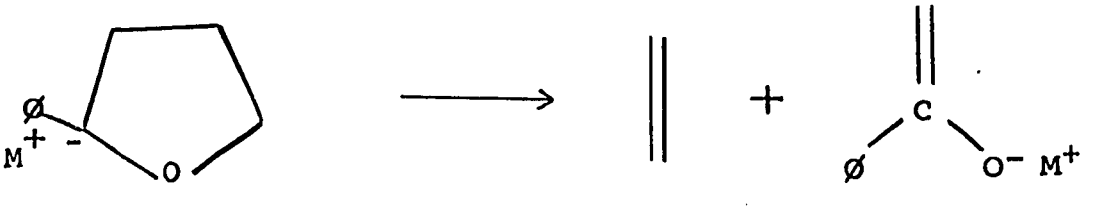
number of orbitals but on the number of electrons. Thus a (4+2) case may be achieved in the last case.



The forward reactions as shown may be extremely endothermic and are therefore likely to be observed in the opposite direction. The last case may be looked into as reverse of the observation of Letsinger and Pollart,[38] which will be discussed in detail later.



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STATEMENT OF THE PROBLEM

The research problem was aimed at investigating possible cycloaddition processes involving enolate ions. From energy considerations, it appeared that 1,2-cycloaddition reactions might be observable in the reverse, rather than the forward, direction. It was therefore decided to prepare various cyclobutanols and to determine whether thermal fragmentation reactions occurred.

Exploratory experiments indicated that such reactions did indeed occur. Further experiments were then directed toward understanding the mechanism of the process.

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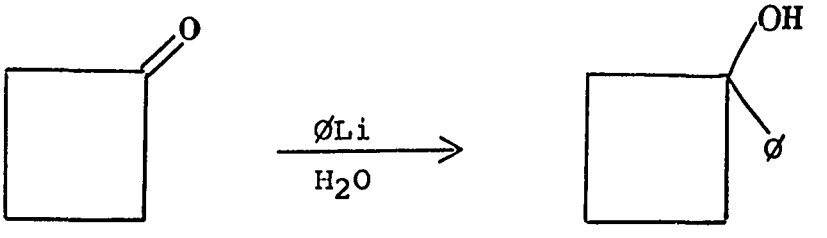
RESULTS AND DISCUSSION

Preparation of 1-Phenylcyclobutanol and Cyclobutanol.

1-Phenylcyclobutanol was prepared by Dupin and Jullien[39] by the action of phenylmagnesium bromide on cyclobutanone. A better yield of the product was obtained by the reaction with phenyllithium, which in turn was prepared from bromobenzene and lithium metal.



Cyclobutanol was prepared by the reduction of cyclobutanone at room temperature with lithium aluminum hydride, as described by Roberts and Sauer.[40] The physical and spectroscopic properties of both compounds were identical to those reported in the literature. The methylene protons of almost all cyclobutanols absorb as a complex envelope between 1.3 and 2.7 ppm in nmr.

Preparation of cis- and trans-2,3-Dimethylcyclobutanones.

Conia and co-workers[41,42] have recently studied the ring expansion of the formal two 'ring' system, ketene. They found that various substituted ketenes upon reaction with diazomethane yielded cyclobutanones with migration of the most highly substituted carbon-carbon bond. The intermediate in these reactions was confirmed by Turro and coworkers[43] to be the corresponding cyclopropanones.

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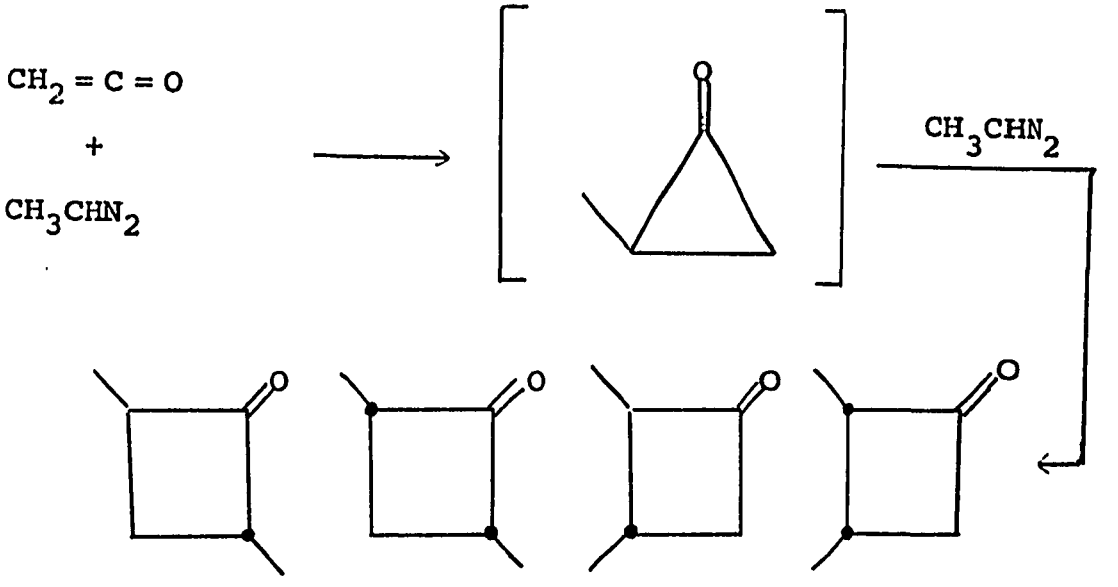
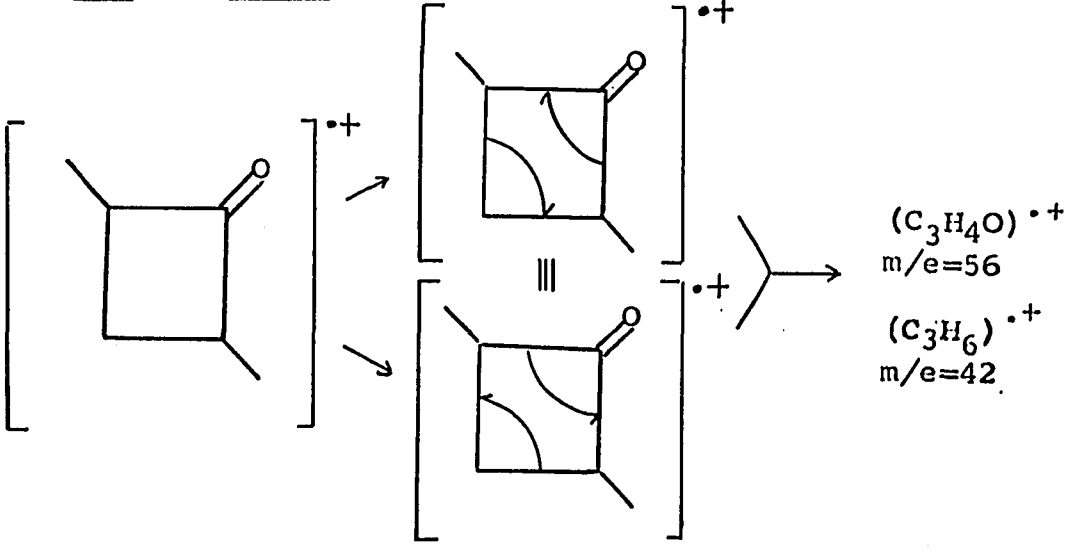
Turro and Gagosian[44] obtained a mixture of four isomers of dimethylcyclobutanone by the reaction of ketene with diazoethane at -130°. The cyclobutanones were separated by glpc.



The structural assignments were based on the following observations. Mass spectra of all four isomers had base peak at 56 ($M^+ - C_3H_6$ or C_2H_2O). Two sets of identical spectra were obtained for the four different isomers. The splitting pattern could be analyzed based on the observations of Conia and co-workers.[45]

cis and trans-2,4-Dimethylcyclobutanone.



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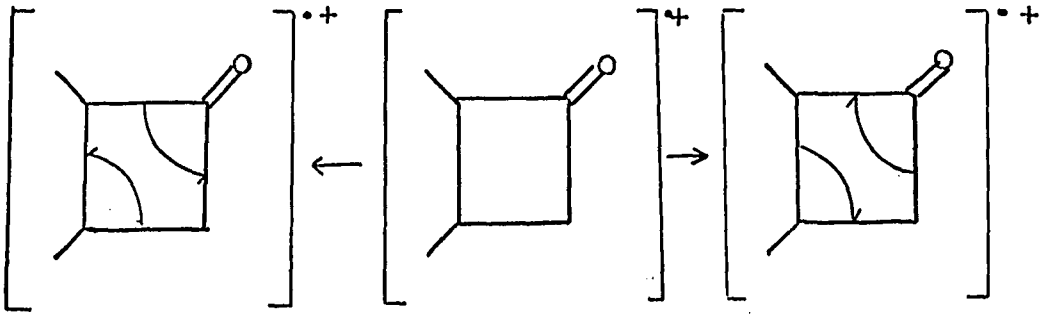
cis and trans-2,3-Dimethylcyclobutanone.



$(C_4H_8)^{\cdot+}$ m/e=56

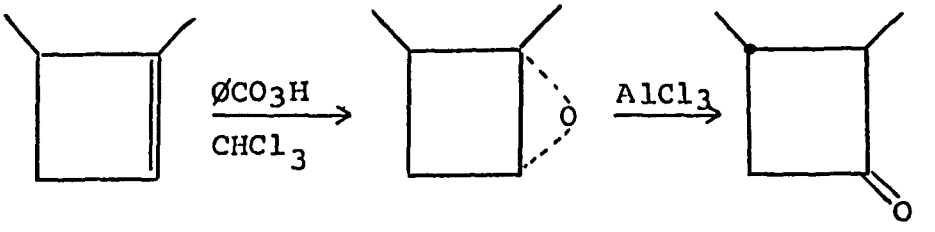
$(C_2H_2O)^{\cdot+}$ m/e=42

$(C_3H_4O)^{\cdot+}$ m/e=56

$(C_3H_6)^{\cdot+}$ m/e=42

The base peak for all three isomeric butenes is at 41 (M^+-CH_3).* The isomers which were assigned cis- and trans-2,3-dimethyl configuration had a very intense (50%) peak in the mass spectra.

Ripoll and Conia[46] isolated 2,3-dimethylcyclobutanone from the following reaction. They assigned trans configuration to the methyl groups.



One of the two isomeric cyclobutanones Turro and Gagosian separated, which had an intense peak at 41, was identical in its spectral properties to the trans-2,3-dimethylcyclobutanone reported by Ripoll and Conia.

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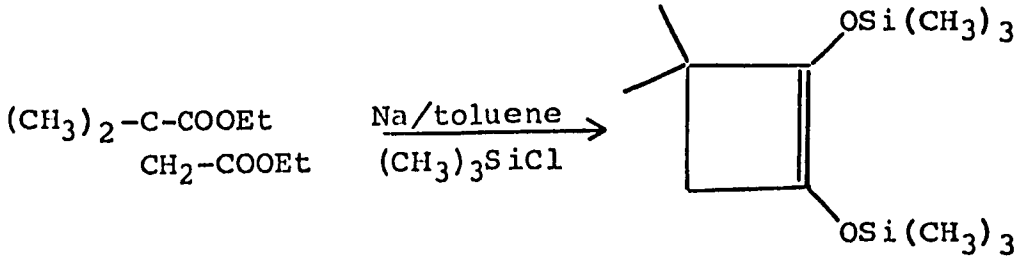
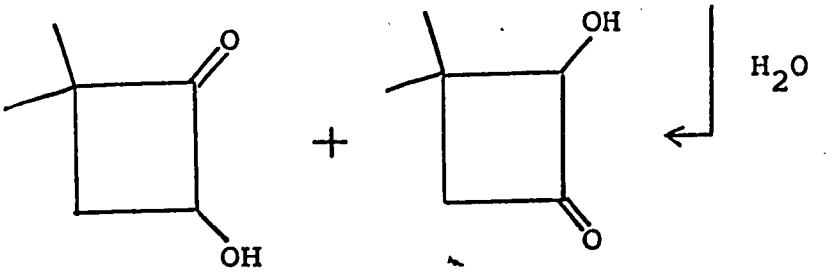
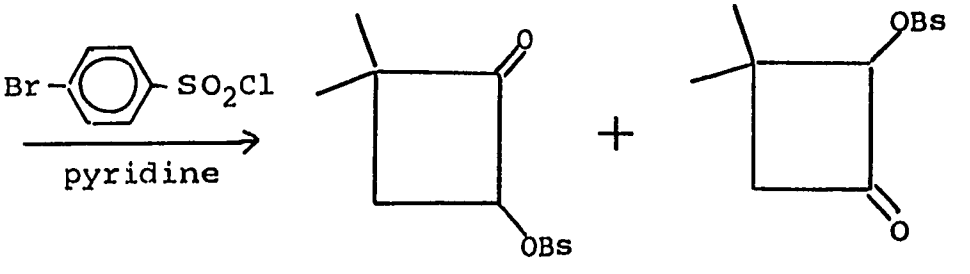
Besides, the equilibration experiment on the other isomer, using catalytic amount of sodium methoxide in methanol, gave a mixture containing 76.5% of the trans isomer.

An attempt, which turned out to be unsuccessful, was made to synthesize 2,2-dimethylcyclobutanol, via acyloin reaction.[47] It involved the following steps.







The brosylates were separated and were identified on the basis of their nmr spectra. The nmr absorptions of the methine protons of both isomers are doublets of doublets, in one case J=1.5 cps, indicating long-range coupling, and in the other case J=11 cps and 7.5 cps, indicating vicinal coupling. The splitting patterns of the methylene

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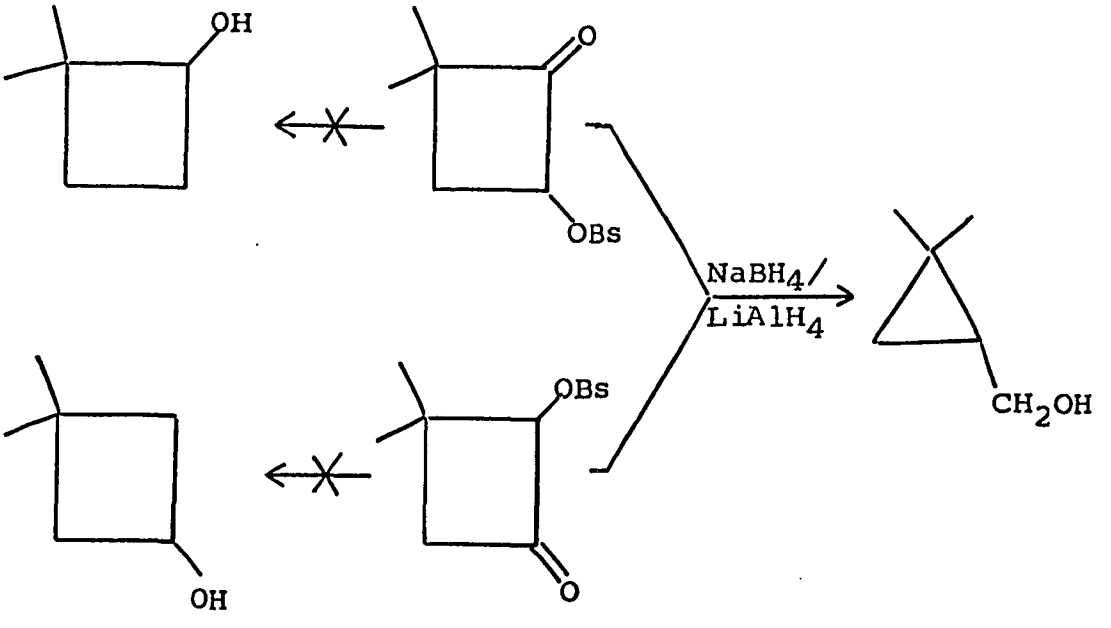
absorptions were also different due to long-range and vicinal coupling (see Figures 1 and 2).

The reduction of either brosylate gave the same compound (2,2-dimethylcyclopropyl) carbinol[48] (see Figure 3) rather than the expected cyclobutanols.



Reduction of cis- and trans-2,3-Dimethylcyclobutanones.

The reduction of cis-2,3-dimethylcyclobutanone was carried out using lithium aluminum hydride. A mixture of two isomeric cyclobutanols was obtained (see Figure 4). All attempts to separate the isomers were unsuccessful. The methine protons of both isomers were multiplets, one centered at 4.04 ppm (major isomer, 80%) and the other at 3.7 ppm (minor isomer, 20%). By using lithium tri-t-butoxy aluminum hydride, the isomer ratio was changed to 90:10 from 80:20 (see Figure 5).

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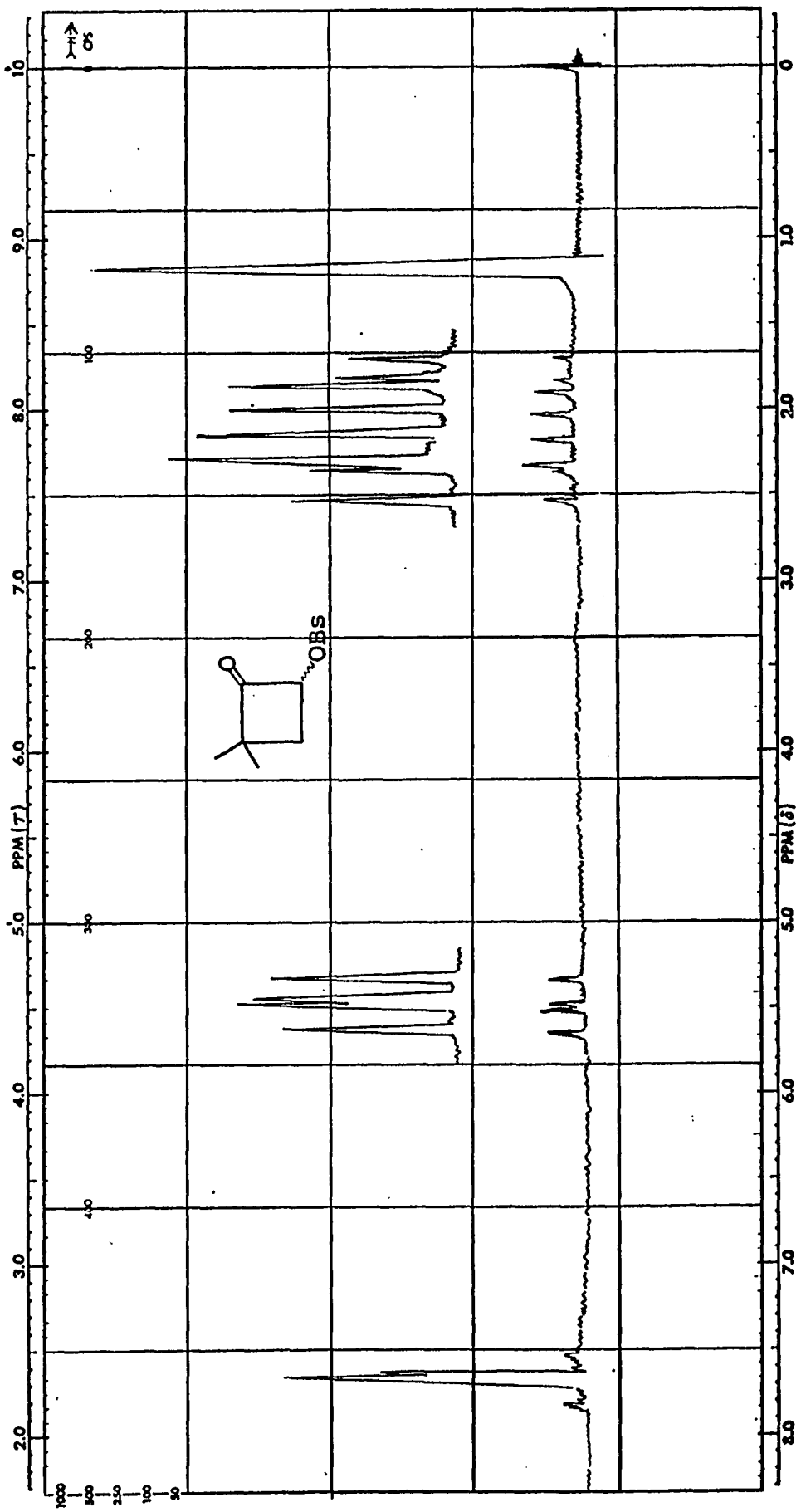

Figure 1

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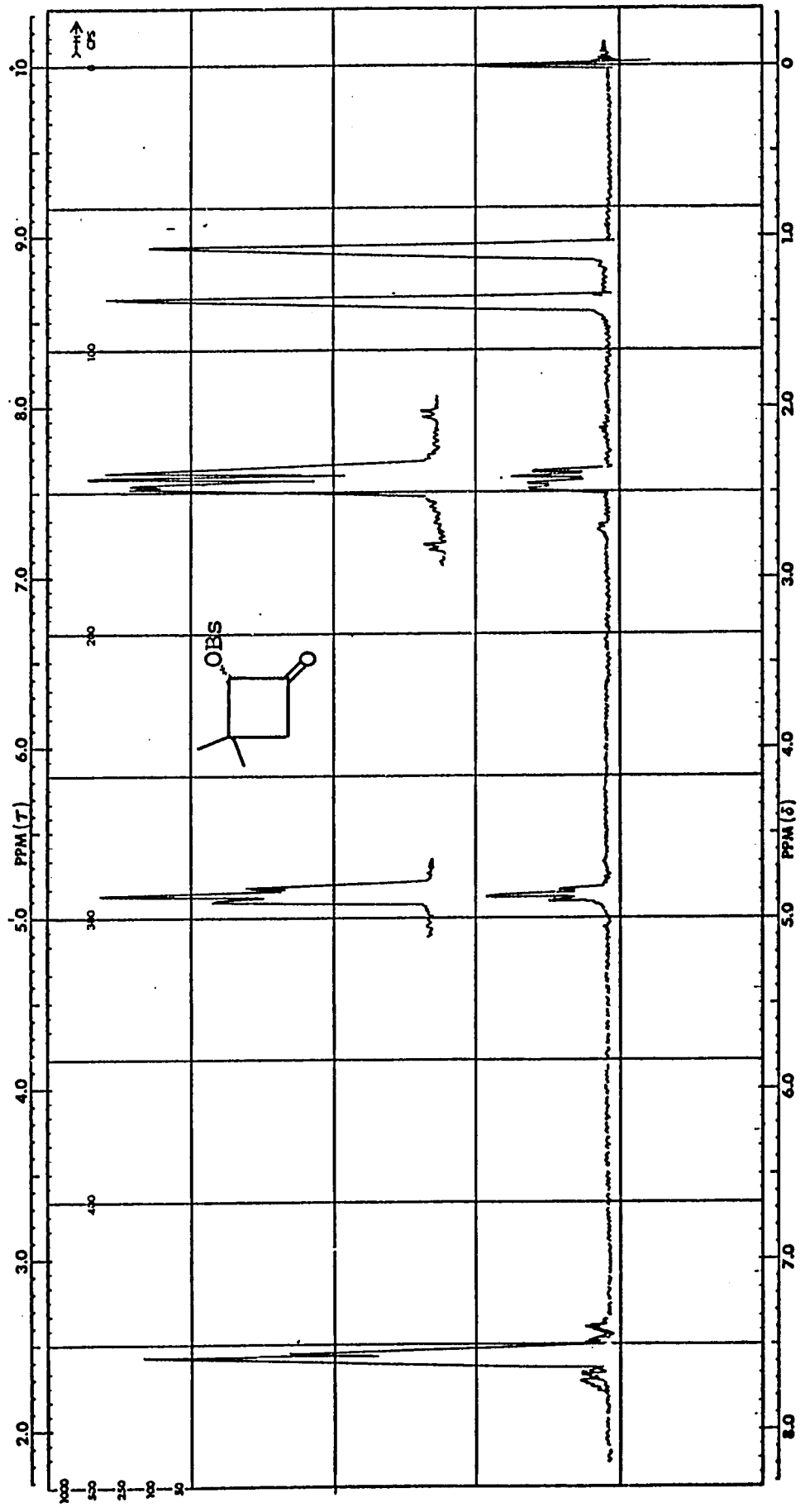

Figure 2

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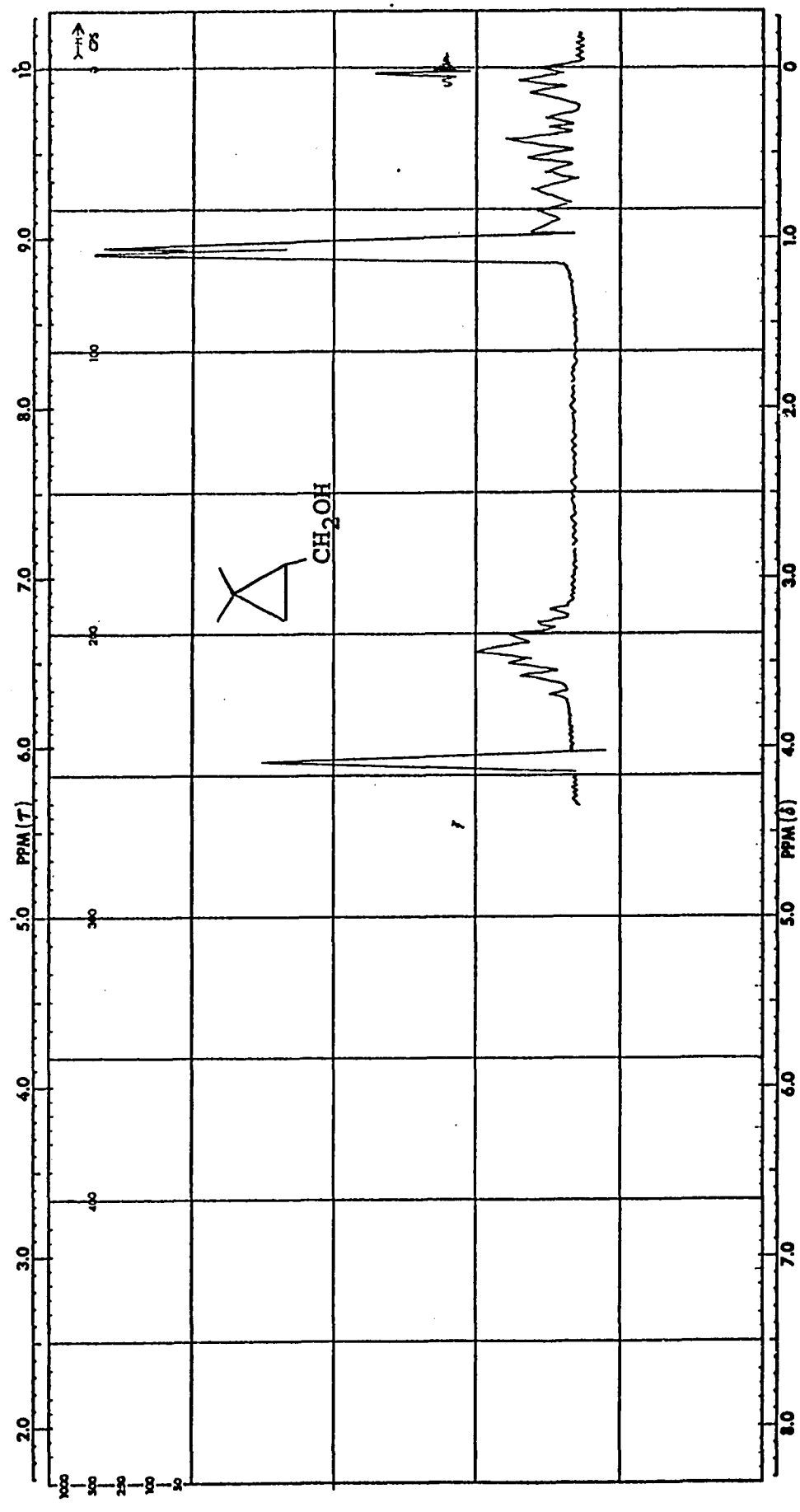

Figure 3

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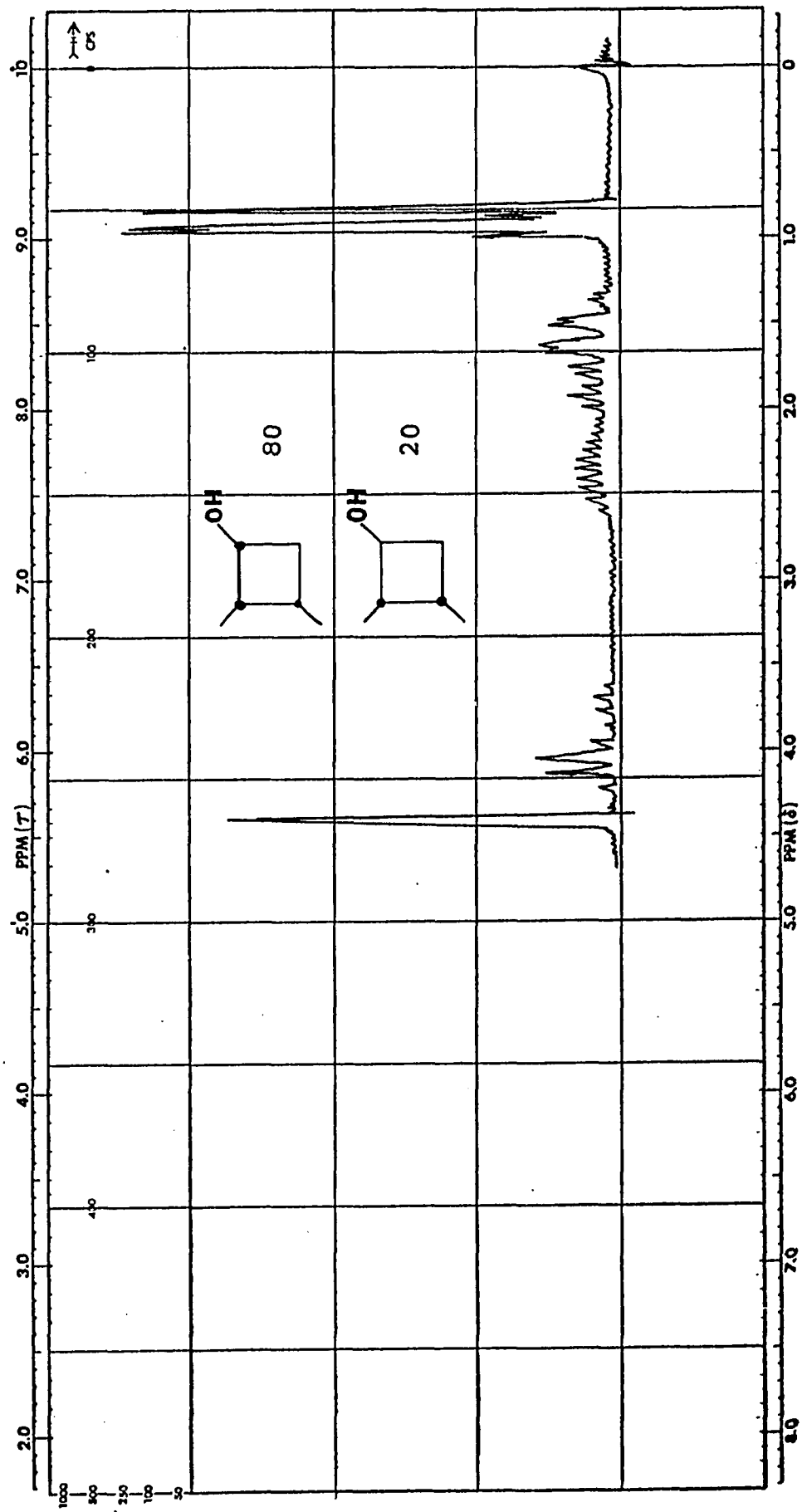

Figure 4

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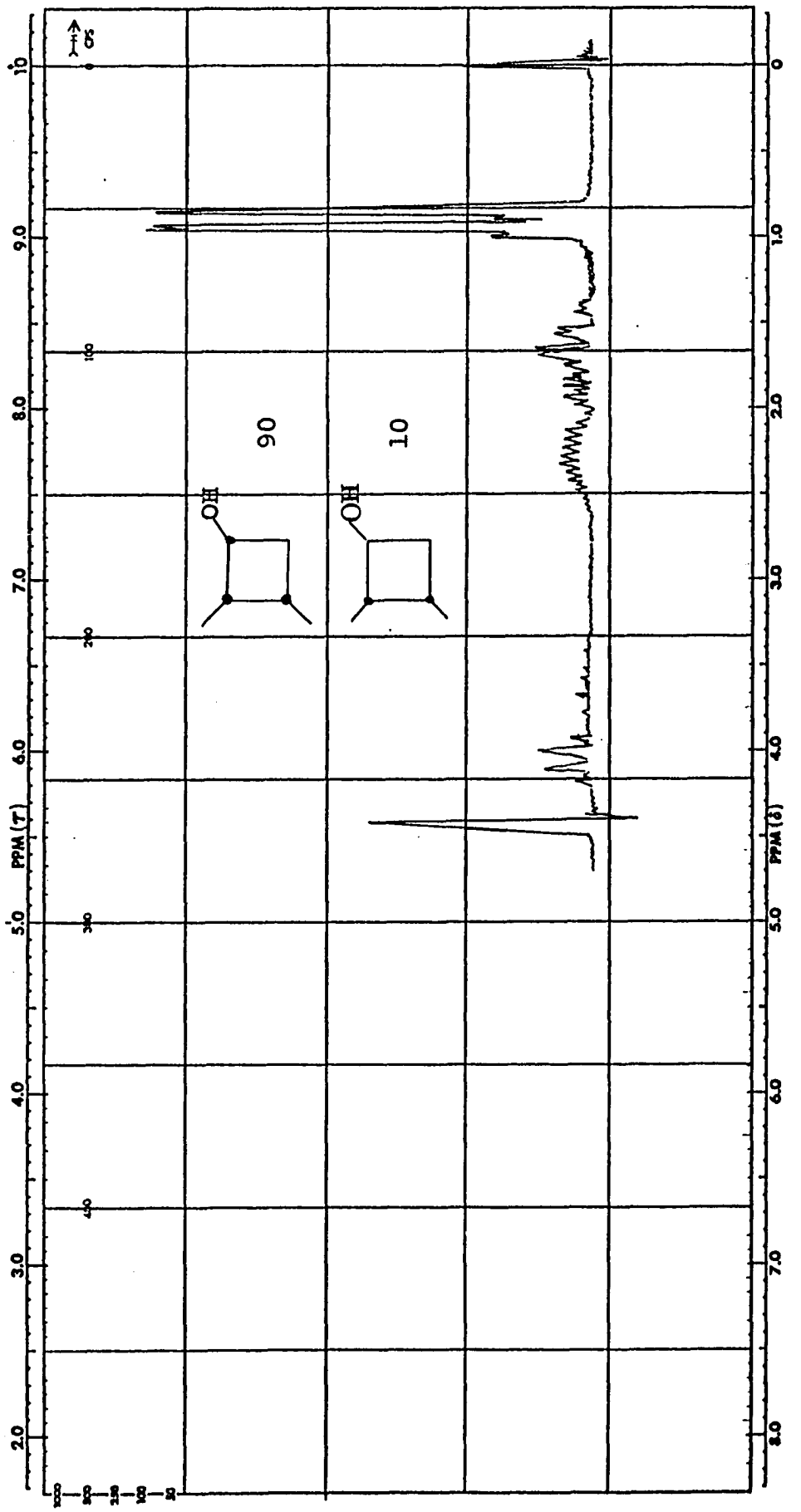

Figure 5

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Lithium tri-t-butoxy aluminum hydride is known to reduce ketones stereoselectively. Reduction of 2α-bromo-5α-cholestan-3-one with sodium borohydride gives a mixture of epimeric alcohols; reduction with lithium tri-t-butoxy aluminum hydride gives only 3β-ol.[49]

In all reported examples, the approach of the hydride is from the least hindered side. On this basis, as well as on the example cited above, it would seem safe to assume that the major isomer obtained in the reduction is the all-cis compound.

Due to the lack of sufficient amount of trans-2,3-dimethylcyclobutanone and the fact that the yield is poor due to difficulties in workup after reduction with lithium tri-t-butoxy aluminum hydride, the reduction is carried out with lithium aluminum hydride. The mixture of cyclobutanols (see Figure 6) was used for thermolysis studies.

Pyrolysis of the Lithium Salt of 1-Phenylcyclobutanol.

Lithium salt was prepared by the addition of standardized n-butyllithium from Foote to 1-phenylcyclobutanol. Initial thermolysis study was carried out at refluxing Triglyme (220°). In a matter of minutes, all the cyclobutoxide had reacted (no cyclobutanol was detected after quenching with water and workup). The mass spectrum of the gaseous substance, collected in the cold trap, was identical to the one reported* for ethylene.

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*Spectrum No. 65, National Bureau of Standards; Project No. 44.

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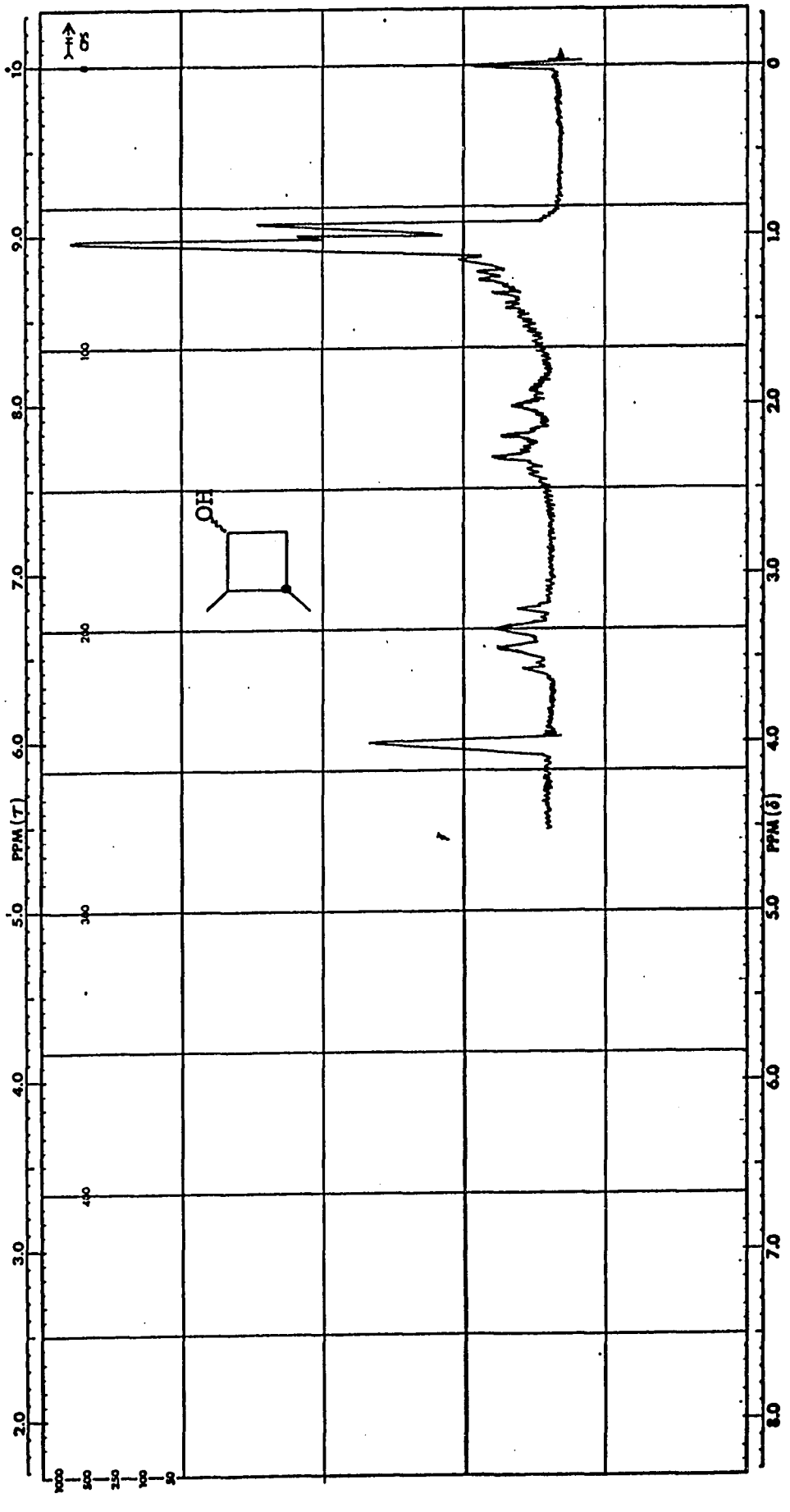

Figure 6

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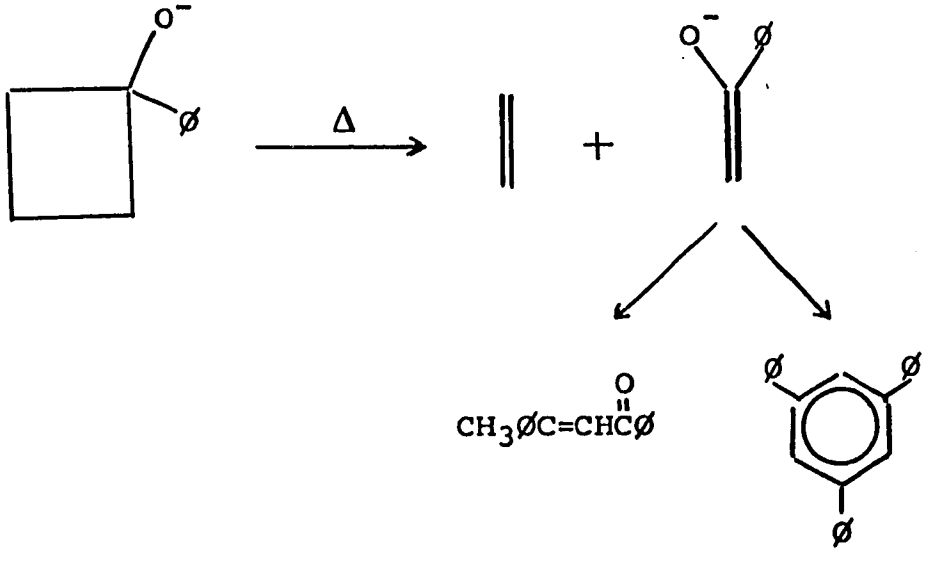
The dark brown material in the thermolysis flask on workup followed by chromatography yielded 1,3,5-triphenylbenzene[50] as the only identifiable product. The identification was based on the following facts.

The infrared spectrum[51] and the ultraviolet spectrum[52] reported were identical to those obtained for the compound. Besides, the mp 171° concurred with the reported value.[50]

Pyrolysis of the salt was carried out at lower temperatures (160° and 150°) for one hour. The results indicated partial decomposition. Longer duration of time was required for complete decomposition at lower temperatures (about 24 hr at 150°). The residue, at lower temperature experiments, on workup gave ~20% 1,3-diphenyl-2-butene-1-one (dypnone). For comparison of spectral properties, an authentic sample of dypnone was obtained from acetophenone by the reaction with sodium tertiary butoxide.[53]

The formation of dypnones and 1,3,5-triphenylbenzene from the 1-phenylcyclobutoxide can be rationalized by the following scheme.



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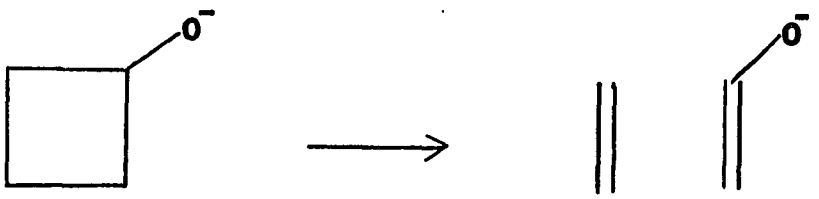
Based on the results presented, namely the formation of ethylene and the two products (dypnone and 1,3,5-triphenylbenzene) derived from the enolate of acetophenone, one could conclude that the retroaddition reaction did actually occur.

Pyrolysis of Lithium Salt of Cyclobutanol.

Pyrolysis of lithium salt of cyclobutanol was carried out at 220°. The gas evolved was identified as ethylene by mass spectral analysis. The residue in the reaction vessel was a brown solid insoluble in almost all common organic solvents. The experiment was repeated at a lower temperature, 170°, and was found to be too slow. It was found that for a comparable rate the unsubstituted compound had to be pyrolyzed 30-40° above the corresponding temperature for the 1-phenyl substituted compound. The yield of ethylene was 67%.



Pyrolysis of Lithium Salt of cis-2,3-Dimethylcyclobutanol.

Lithium salt of all cis-2,3-dimethylcyclobutanol was pyrolyzed at 220° and the gaseous products were swept into a cold-trap (liquid nitrogen) by pure and dry nitrogen. Analytical glpc[54] using n-pentane as internal standard indicated 62% yield of an olefin mixture composed of 18% propylene, 52% cis-2-butene and 30% trans-2-butene.

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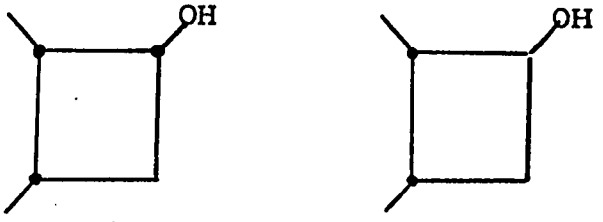
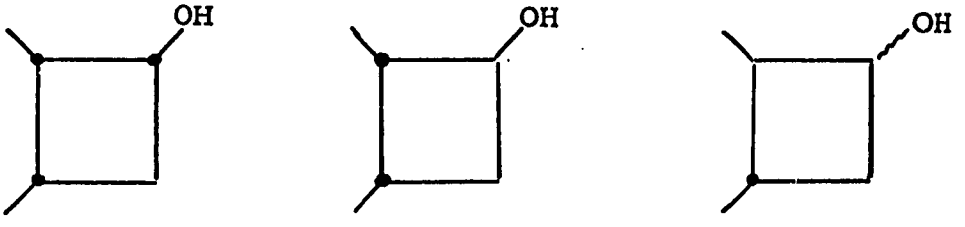
The pyrolysis experiment was repeated at 170° for different intervals of time, and the gaseous products obtained were analyzed by glpc. The results are tabulated in Table II.

In a separate experiment, a mixture containing 90% cis-cyclobutanol and 10% trans-cyclobutanol was converted to the lithium salt and was pyrolyzed at 170°. After 25% decomposition (as indicated by gas analysis), the unreacted cyclobutanols were analyzed quantitatively by glpc.

Composition before pyrolysis:



Composition after pyrolysis (25%):



Pyrolysis of Lithium Salt of trans-2,3-Dimethylcyclobutanols.

The lithium salt of the mixture of trans-2,3-dimethylcyclobutanols was pyrolyzed at 220° and the products on analysis using n-pentane as internal standard indicated 68% yield of an olefin mixture composed of 20% propylene, 16% cis-2-butene and 64% trans-2-butene.

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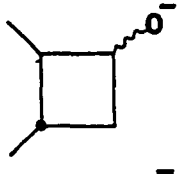
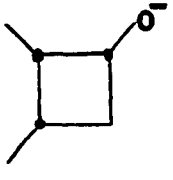
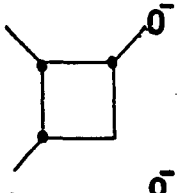
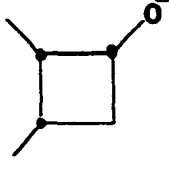
Table II

Thermolysis of Lithium cis and trans-2,3-Dimethylcyclobutoxides

Cyclobutoxide	Temp. °C	Time hr	Propylene %	trans-2-Butene %	cis-2-Butene %	Total Alkenes %
	220	3	20	64	16	68
	220	3	19	27	54	62
	170	4	18	27	55	26
	170	1	18	26	56	16
	170	24	18	27	55	16 + 50

Kinetic Studies.

After learning about the thermolysis of cyclobutoxides giving ethylene and enolate, it seemed desirable to study the mechanism of the reaction. The rates of thermolysis of substituted and unsubstituted cyclobutoxides were determined at four different temperatures in order to calculate the activation parameters.

The cyclobutoxides were thermolyzed in a closed system (see Figure 7), and the pressure differences, due to formation of ethylene, were recorded with time. The difference in pressure from the initial reading to the final reading gave a number which corresponds to the total concentration of the alcoholate, a. The difference in pressure from the initial reading to a reading at a particular interval of time gave a number corresponding to the amount of enolate that had thermolyzed, x. Plots of log a/a-x versus time (in min) were made (see Figures 8 and 9).

$$\log a/a-x \quad vs \quad t(min)$$

$$\text{slope} = k/2.3 \text{ min}^{-1}$$

$$k = 2.3 \times \text{slope}$$

$$k = A\ e^{-Ea/RT}$$

$$2.303 \log k = 2.303 \log A - Ea/RT \quad ..(1)$$

From the slope of a plot of log k vs 1/T (Arrhenius plot) (see Figure 10), the activation energies for the two systems were calculated.

$$-\text{slope} = Ea/2.3R$$

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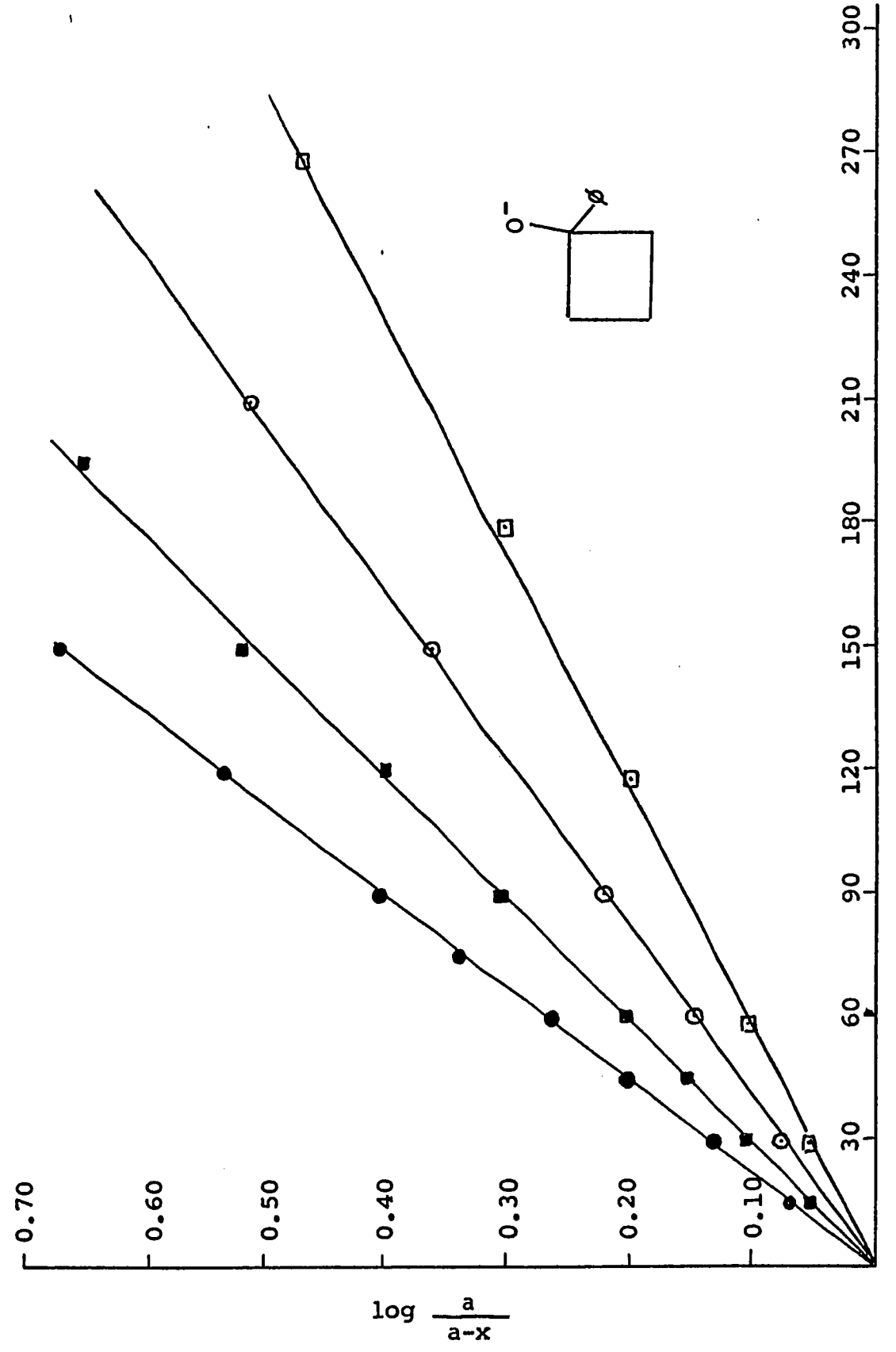

Figure 8

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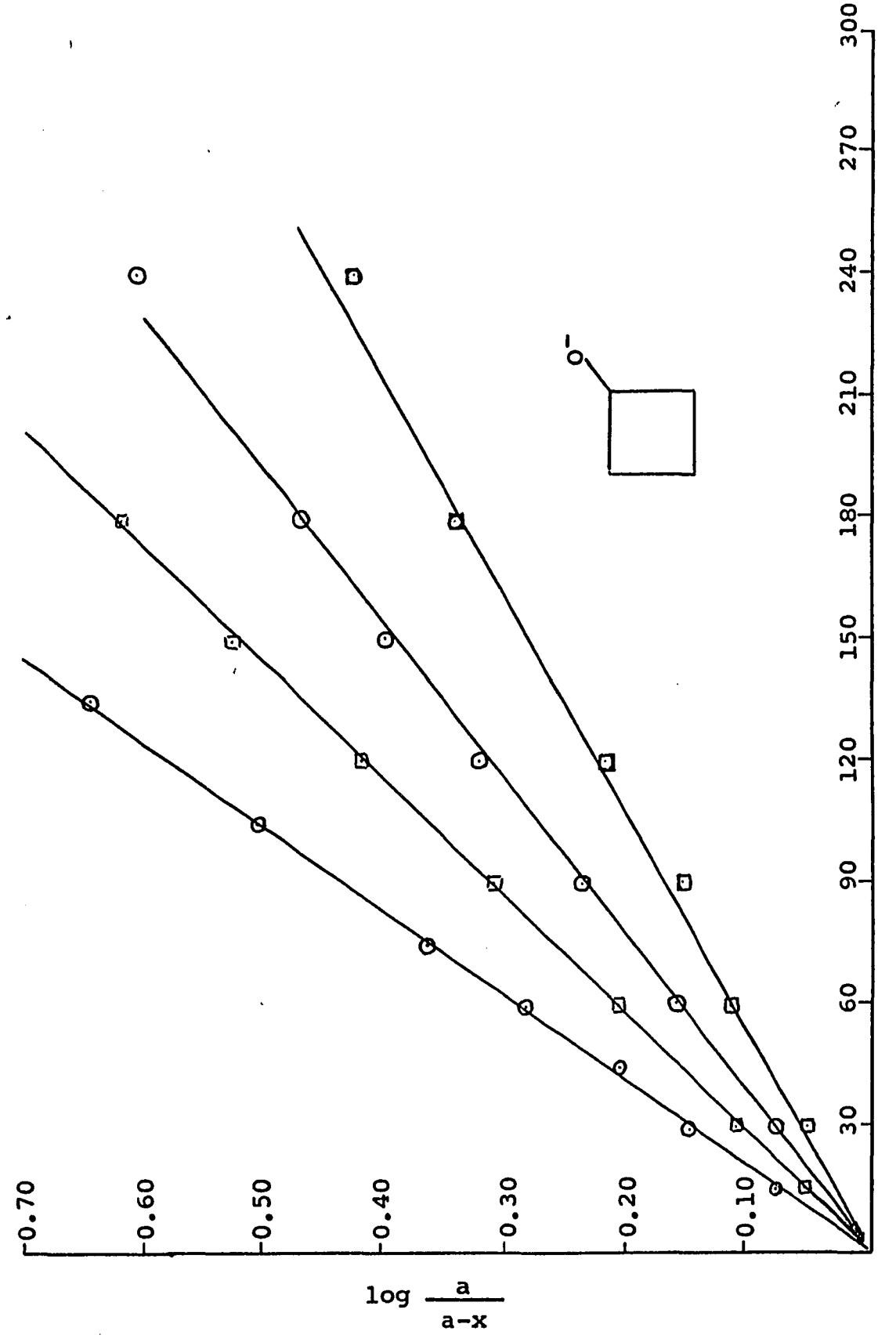

Figure 9

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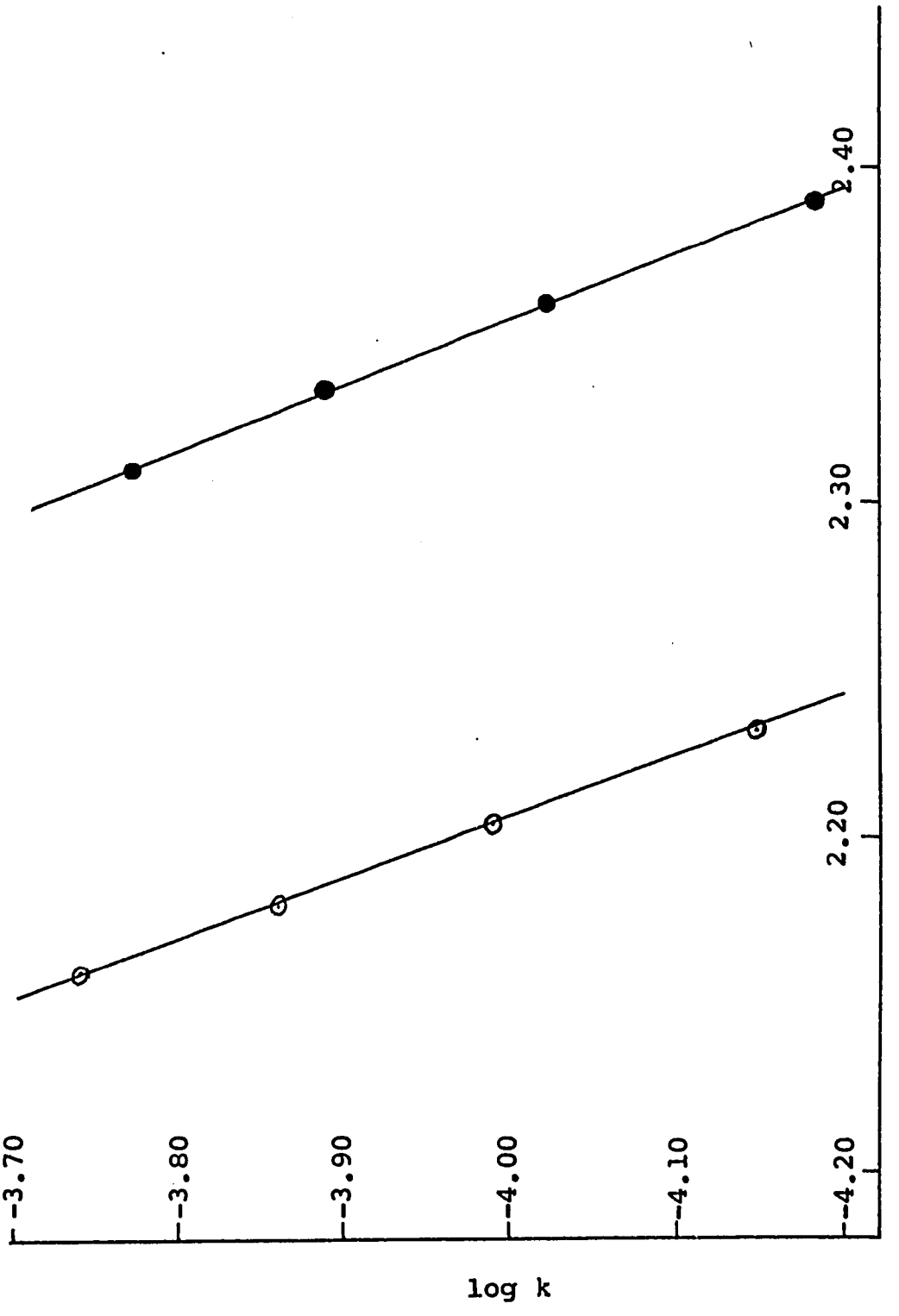

Figure 10

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A was calculated from equation (1) by substituting the values for Ea and k.

For cyclobutoxide,

$$k = 10^{9.12}\ e^{(-26{,}500/RT)}\ sec^{-1}$$

and for 1-phenylcyclobutoxide

$$k = 10^{8.44}\ e^{(-24{,}200/RT)}\ sec^{-1}$$

The temperature dependence of the rate of each cyclobutoxide was represented by an equation of the type:

$$\log (k/T) = A/T + B$$

which can be identified with the one derived from absolute reaction rate theory.[55]

$$k = K \frac{k'T}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

The constants A and B are defined as follows:

$$A = \frac{\Delta H^{\ddagger}}{2.303R}$$

$$B = \log \frac{K k'}{h} + \frac{\Delta S^{\ddagger}}{2.303R}$$

The values of constants A and B were determined graphically from a plot of log (k/T) vs 1/T for the cyclobutoxides whose rates were measured at four different temperatures. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained from A and B by assuming that K = 1.

Plots of log (k/T) vs 1/T for the two compounds measured at four different temperatures are given in Figure 11. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are recorded in Table III.

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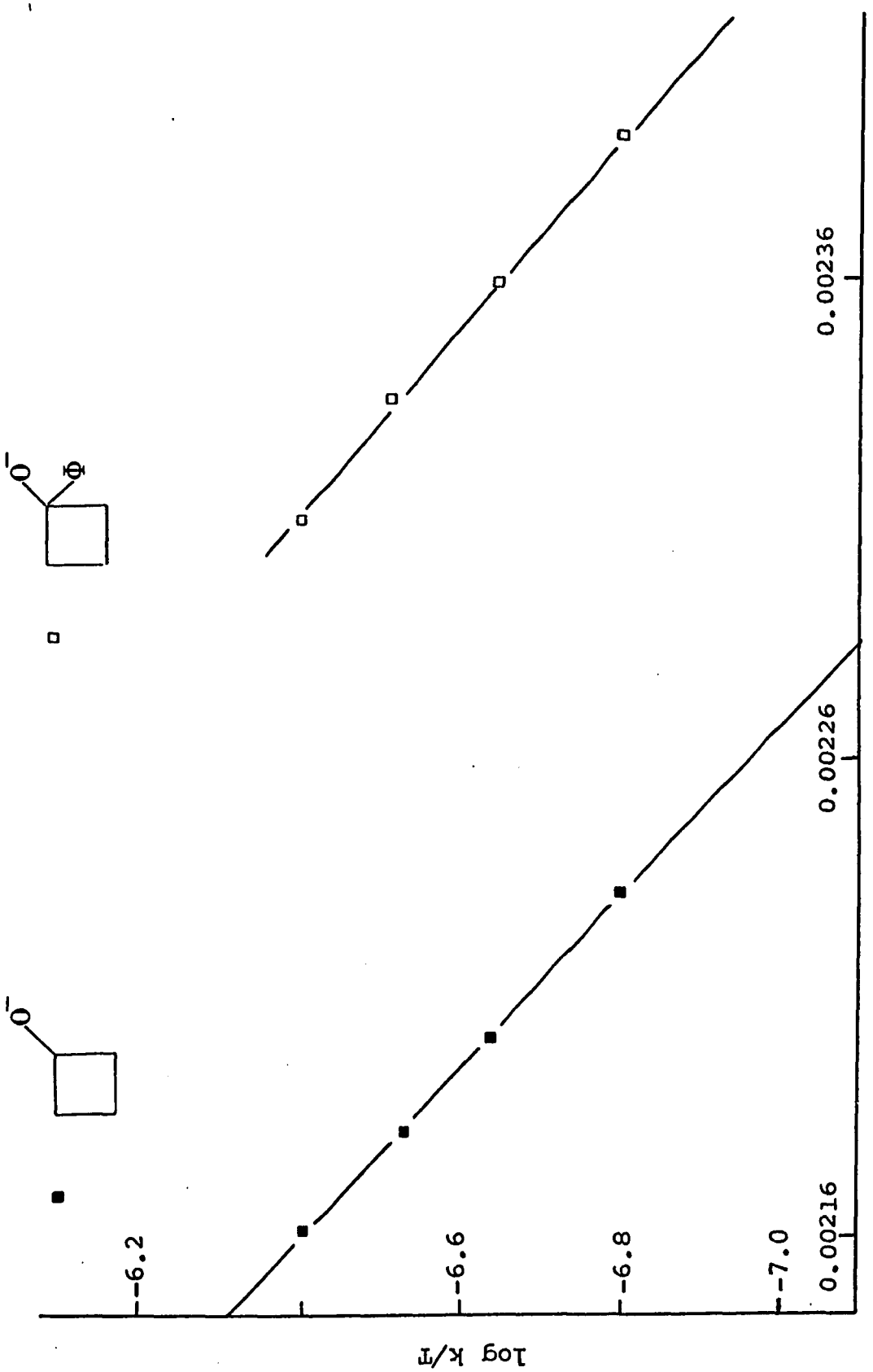

Figure 11

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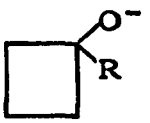
Table III

Data for Activation Parameters

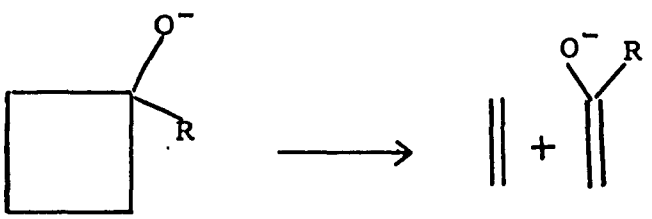
	A (slope)	B	$\Delta H^{\ddagger}$ kcal.	$\Delta S^{\ddagger}$ e.u.
R=Ø	-5060	5.25	23.3	-23.2
R=H	-5530	5.52	25.5	-21.9

In comparison, the enthalpy of activation for gas phase thermolysis of cyclobutane and derivatives is about 60 kcal. For these systems, entropy of activation is computed to be between +8 and +11 e.u., which is in accord with a process involving ring opening.

Possible Mechanisms.

One could postulate three different mechanisms by which the cyclobutoxides cleave on thermolysis.

1. Concerted mechanism:



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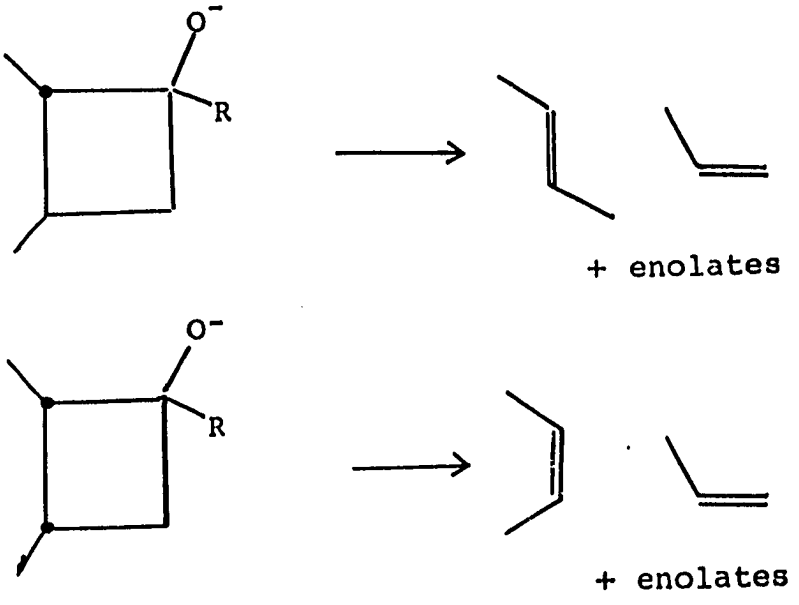
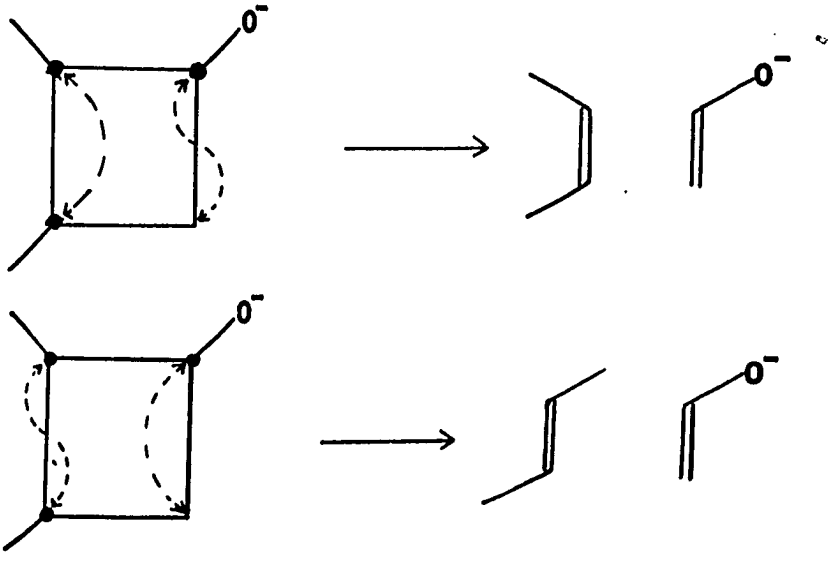
This implies that it would cleave stereospecifically, i.e.



According to Woodward and Hoffmann[4], for cyclobutane fragmentation, if the process is concerted, the stereochemical relationships at three of the four carbons of the cyclobutane will be retained in the products. Based on this, if there were to be an inversion at C-2 or C-3 of the cyclobutoxide, one would expect the reverse results, i.e. trans-2-butene from cis-2,3-cyclobutoxide and vice versa.



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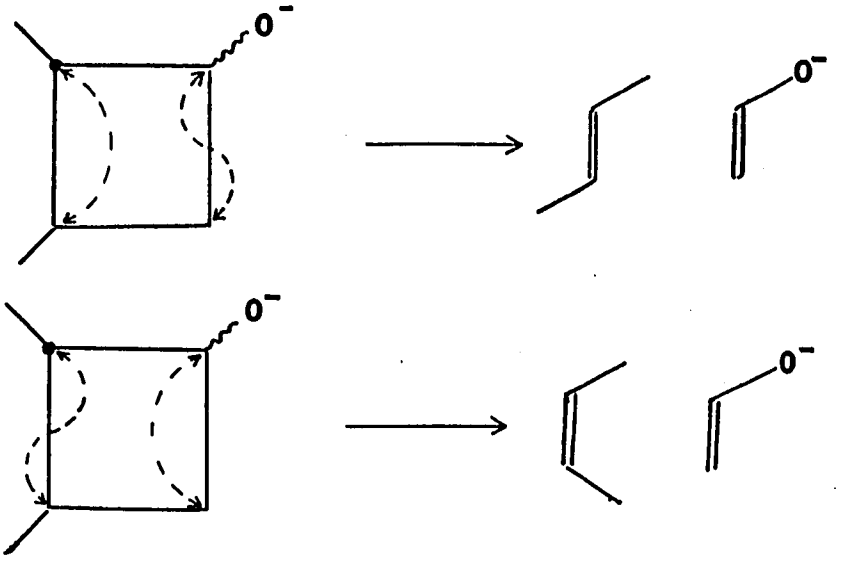
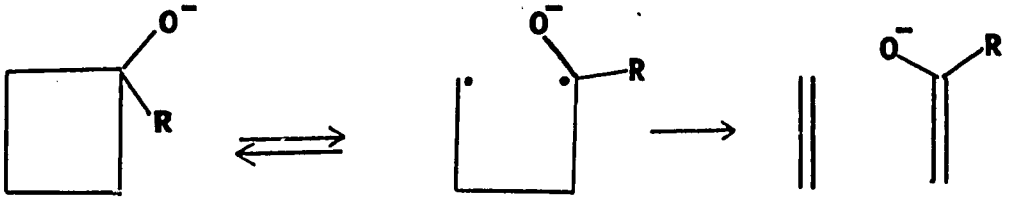
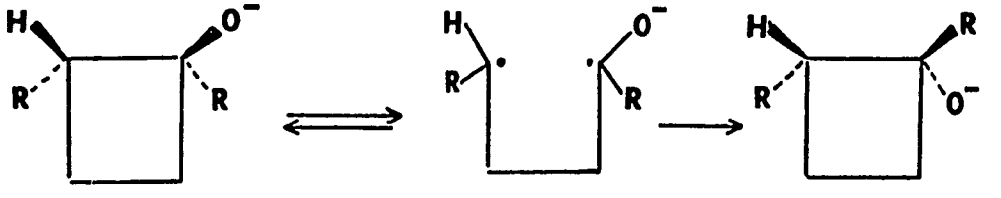
Likewise,



Stepwise Anion-Radical Mechanism.



One would expect that R=phenyl would decompose at much lower temperature than R=hydrogen by this mechanism. Also one would not expect this mechanism to be stereospecific. That is to say one would expect both cis- and trans-2-butenes from either of the dimethyl cyclobutoxides. There might also be considerable isomerization of the starting material if the second step of the reaction is not enormously faster.



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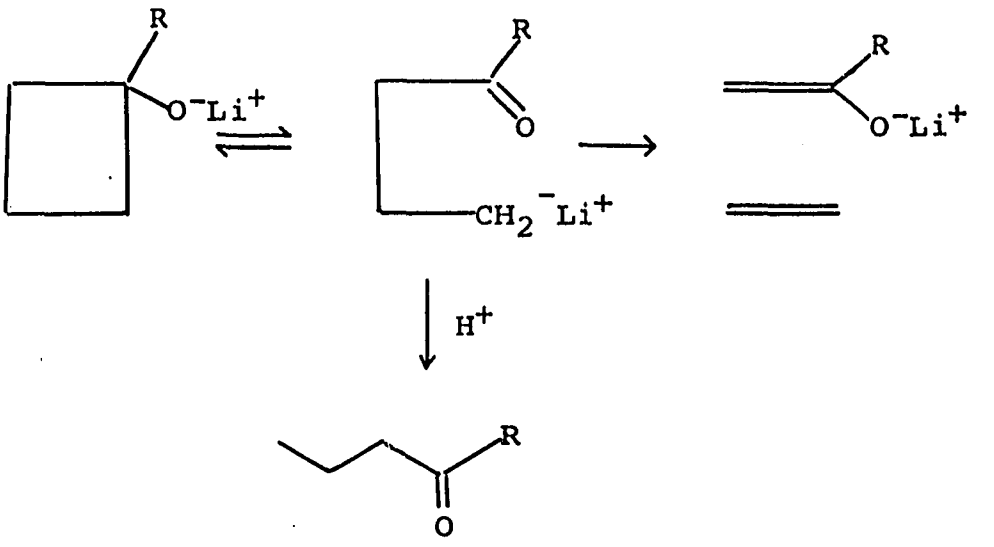
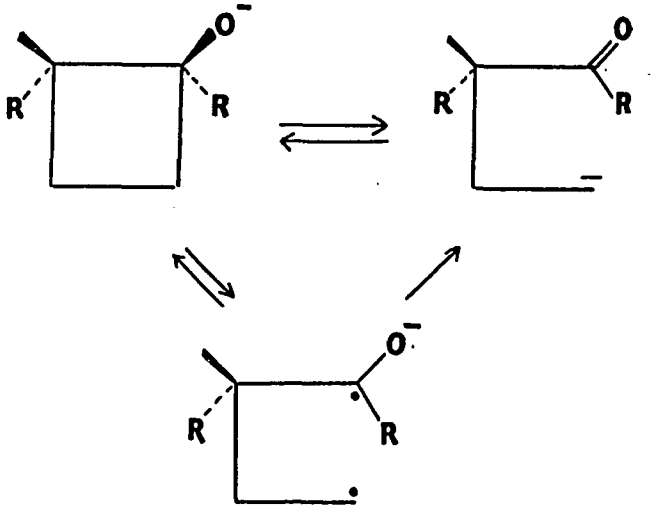
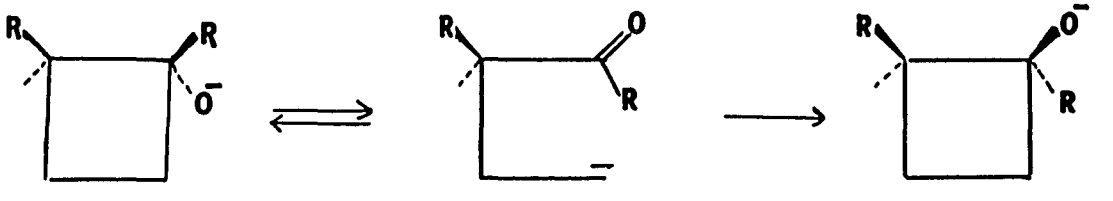
Anion Mechanism.



This mechanism might be related to the previous one in that the intermediate could arise from the anion diradical by electron transfer.



In fact since the first step of the above mechanism should be reversible, there might be isomerization of the starting material.



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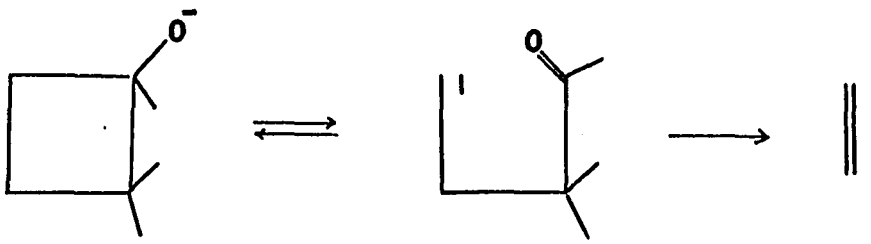
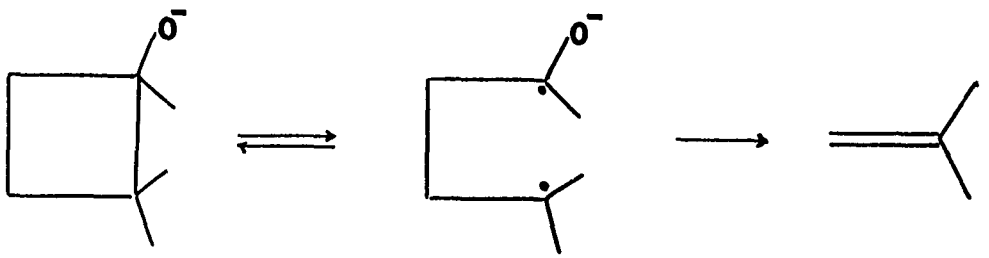
Furthermore in this mechanism the ring ought to break in such a way as to give the primary carbanion,



whereas in the radical case one would expect the other product, namely isobutylene, to predominate because of the greater stability of the 3° radical.



Mechanistic Conclusions.

Although cyclobutoxides are many orders of magnitude more reactive than simple cyclobutanes, the stereochemistry of the cleavage is remarkably similar to that found by Gerberich and Walters.[21,22] Their study showed that the thermolysis of both cis- and trans-1,2-dimethylcyclobutane proceed mainly by ring cleavage, but a cis-,trans-isomerization occur to a lesser extent.

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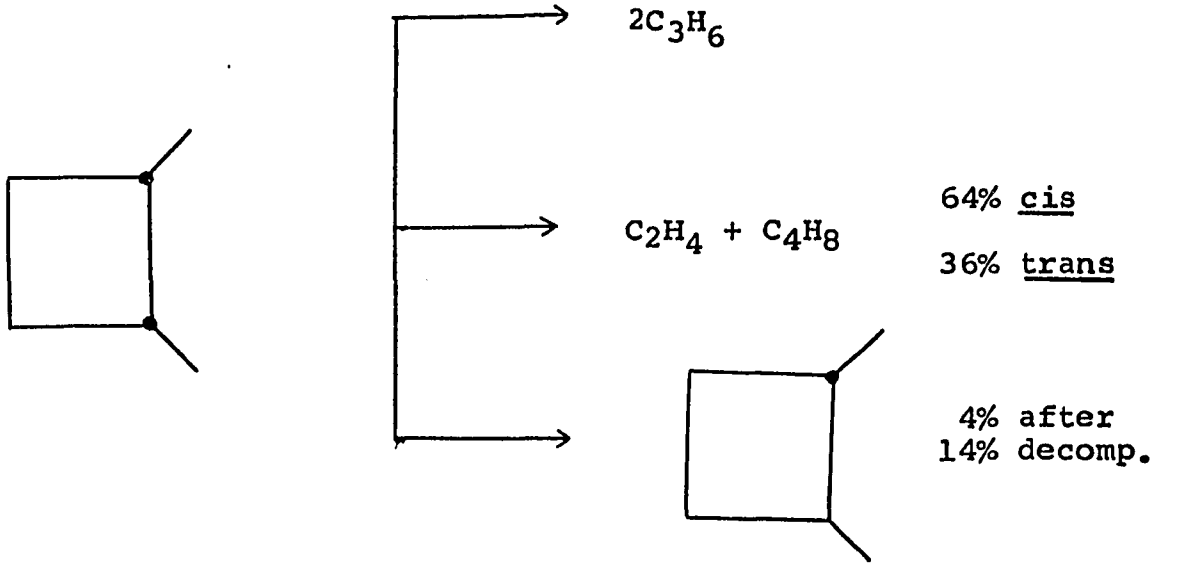

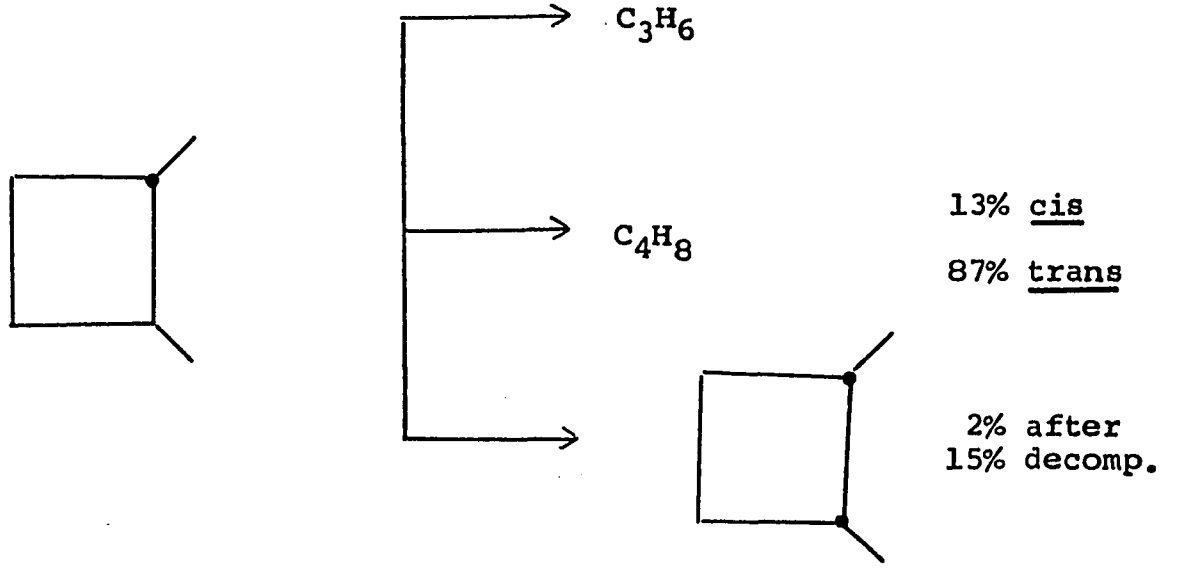

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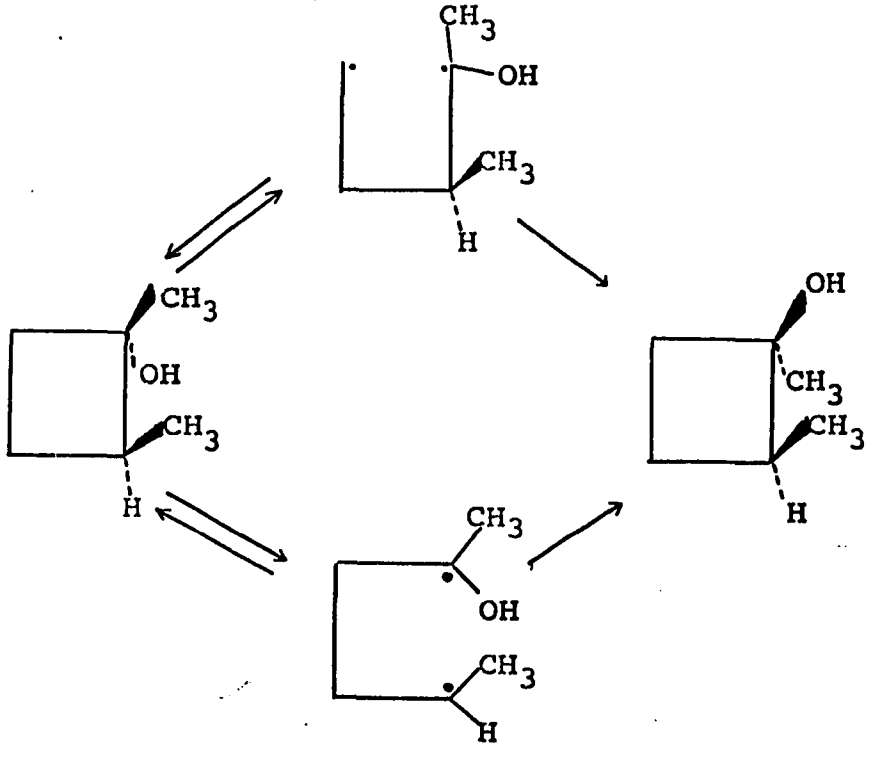
Feit's observation of the fragmentation accompanied by isomerization of cis-1,2-dimethylcyclobutanol is explained by the formation of the two different intermediates.[56]



The hypothesis that pyrolyses of cyclobutanes proceed through a tetramethylene diradical was well accepted due to absence of conflicting experimental facts. Baldwin's results,[31] on the pyrolysis of 7,8-cis,exo-dideuterio-cis-bicyclo(4.2.0)octane, are incompatible with both the tetramethylene diradical hypothesis and the completely stereoselective antarafacial elimination of ethylene predicted by the orbital symmetry theory.

Wittig rearrangement,[57] namely the rearrangement of benzylic ethers to alcohols in the presence of strong base has been known for a number of years. One of the most

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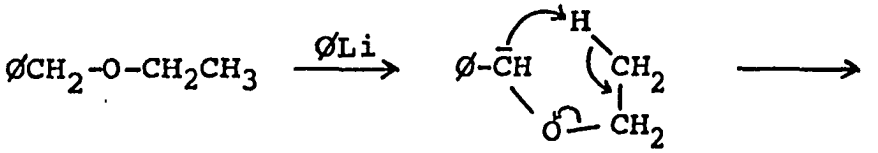
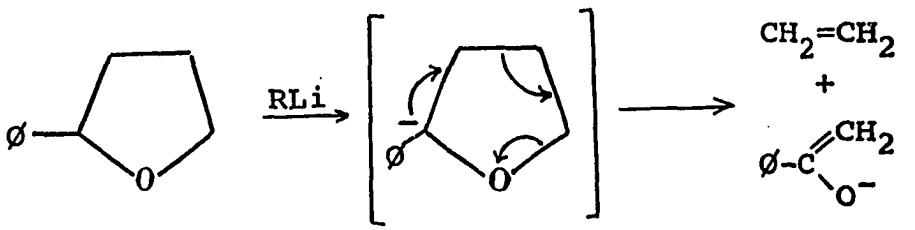
frequently encountered side reactions is elimination to give olefin and unrearranged alcohol, e.g.[58]

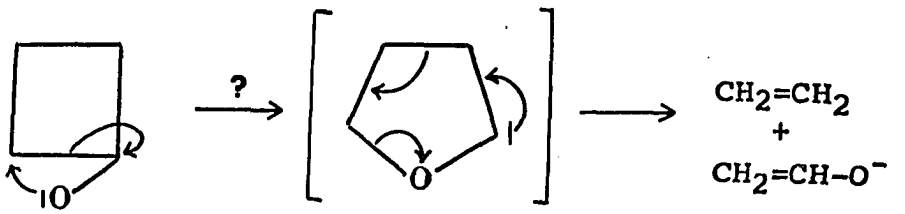


$$\text{ØCH}_2\text{O} + \text{CH}_2\text{=CH}_2$$

An interesting example of a slightly different elimination occurs with 1-phenyltetrahydrofuran.[38]



It is extremely unlikely that cyclobutoxides decompose to give ethylene by a reverse Wittig reaction.



A stepwise anion diradical mechanism would account for the results obtained for the thermolysis of cyclobutoxides. Formation of both <u>cis</u>- and <u>trans</u>-2-butenes from either of the two 2,3-dimethylcyclobutoxides provides experimental support for this explanation.

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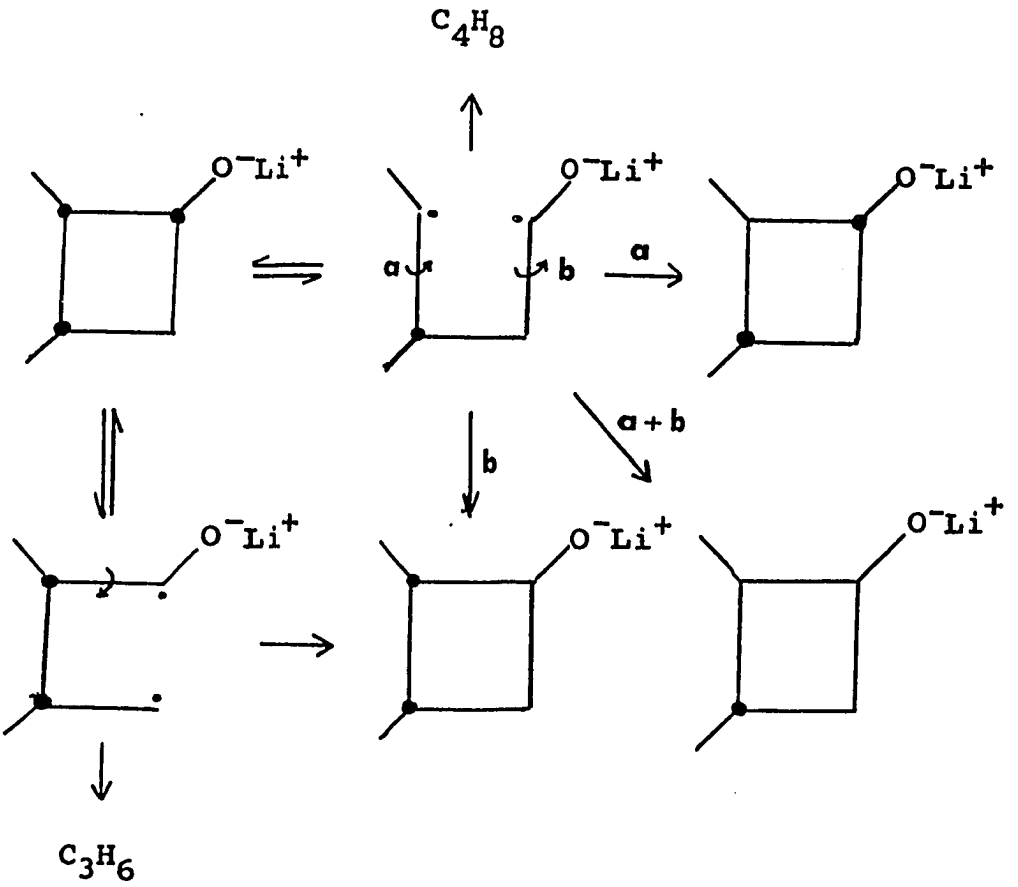
Our results are summarized in the following scheme:



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EXPERIMENTAL

All melting points were determined with a Thomas-Hoover Capillary Melting Point apparatus using open capillary tubes. Boiling points and melting points are uncorrected.

Infrared spectra were determined with a Perkin-Elmer Infracord infrared spectrophotometer. Nuclear magnetic resonance spectra, unless otherwise mentioned, were recorded on a Varian Model A-60 spectrometer using tetramethylsilane as an internal standard. Ultraviolet spectra were taken on a Cary Model II recording spectrophotometer.

Microanalysis were performed by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

1-Phenylcyclobutanol.

Phenyllithium was prepared by adding a solution of 25 g (0.16 mole) of bromobenzene in 40 ml of ether to 2.3 g (0.33 mole) of lithium metal, cut into small pieces, in 100 ml of ether. To the above solution was added slowly with stirring a solution of 5 g (0.071 mole) of cyclobutanone (Aldrich) in 10 ml of ether at 0°C. The mixture was stirred for 4 hr, and water was added to decompose the lithium salt. The ether layer was separated, washed with sodium chloride solution and was dried over sodium sulfate. Removal of the solvent and distillation provided 7.5 g (70%) of 1-phenylcyclobutanol, bp 92-94°C (1.0 mm), lit 116-118°C (20 mm), mp 40-41°C, lit[39] 40.5°C.

Infrared: $\bar{\nu}_{max}^{CCl_4}$ 3450(b), 1600 (v), 1145(s), 695 (s) cm^{-1}

nmr: $\delta_{ppm}^{CCl_4}$ 1.3-2.6 (complex absorption; 6H); 3.1 (singlet; 1H); 7.05-7.5 (multiplet; 5H).

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Purification of Triglyme.

Triglyme (Matheson, Coleman and Bell) was first percolated through a column of alumina, in order to remove peroxides, if any. It was then agitated with calcium hydride and left overnight. Distillation under reduced pressure (15 mm) afforded fairly dry triglyme. Further drying was carried out by treatment with lithium aluminum hydride, followed by distillation under reduced pressure, bp 65-67°C (0.3 mm).

Standardization of n-Butyllithium.

To 10 ml of water was added carefully 5 ml of n-butyllithium in hexane. A drop of phenolphthalein was added to the above solution, and it was titrated against standard hydrochloric acid. From the amount of acid used, the total base present was calculated.

In another titration, to 5 ml of n-butyllithium were added 10 ml of anhydrous ether and 1 ml of benzyl chloride. The mixture was allowed to stand for a minute and was then hydrolyzed with 10 ml of water. The base was titrated. This value corresponded to the amount of base other than n-butyllithium present in 5 ml of the solution. From the difference in titre values, the concentration of the n-butyllithium solution was calculated.

Thermolysis of Lithium-1-phenylcyclobutoxide.

In all thermolysis experiments, the alkoxide was taken in a 100 ml 3-neck round bottom flask, fitted with an inlet for pure and dry nitrogen, a reflux condenser and a serum cap. The condenser was connected, first to a cold

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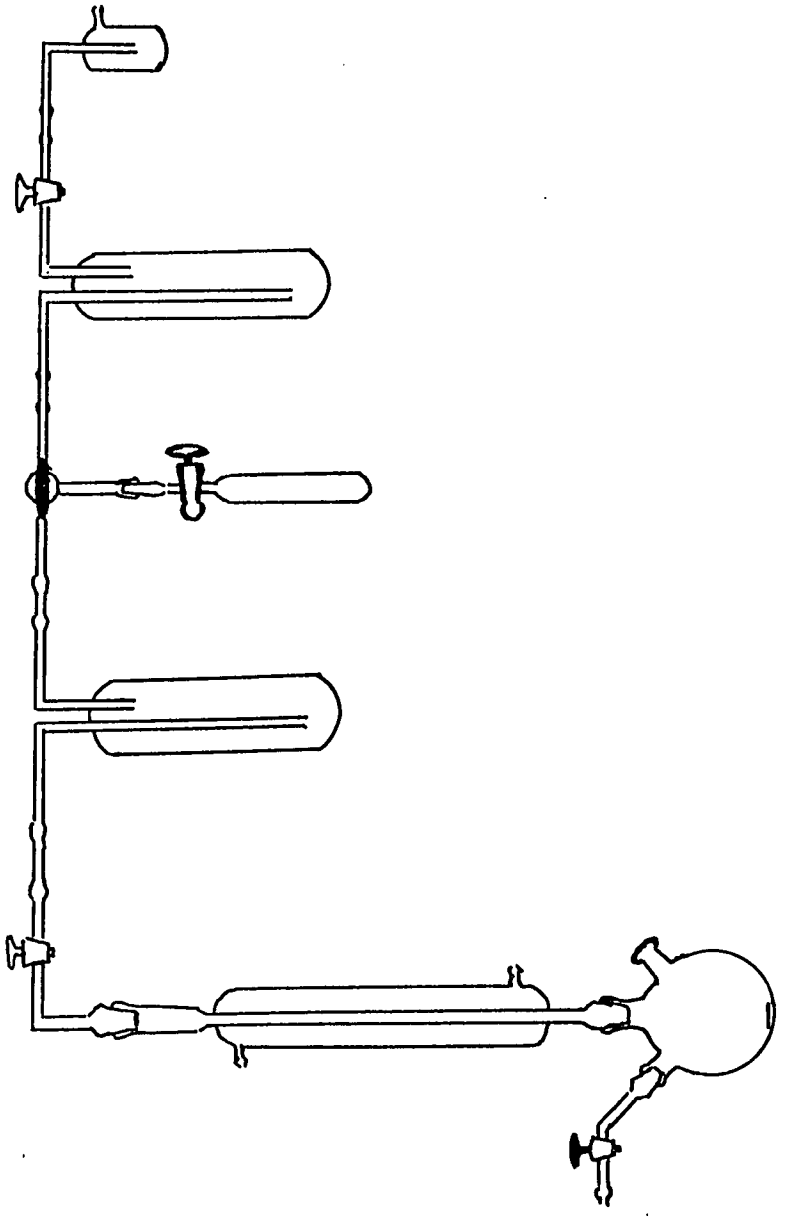

Figure 12 Special Thermolysis Apparatus

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trap (-78°C), then to a second trap cooled by liquid nitrogen and finally to a bubbler. In between the two traps, there was a three-way stop-cock, with a ₹ 10/30 female joint. A mass spectral tube fitted with a vacuum sealed stop-cock and ₹ 10/30 male joint was attached to the 3-way stop-cock.

Thermolysis at 220-222°C.

To 1 g (6.6 mmole) of 1-phenylcyclobutanol taken in the thermolysis flask, flushed with dry nitrogen, was added 4 ml (6.6 mmole) of n-butyllithium. The temperature was raised to 70°C in order to remove the hexane. The flask was now connected to the condenser. 10 ml of carefully dried triglyme was added to the alkoxide. The temperature of the mixture was raised to 220-222°C (refluxing triglyme), and it was stirred well for 3 hr. The cold traps were disconnected from the reaction flask. By means of bulb to bulb distillation, the substance in the trap cooled by liquid nitrogen was transferred to the evacuated mass spectral tube.

mass spectrum: 70 ev; m/e

26(52%); 27(59%); 28(100%; M^+);

29(2.1%; isotope peak)

(compare: spectrum No. 65, National Bureau of Standards; project No. 44)

To the reaction mixture was added enough (20 ml) water. The crude mixture was ether extracted. The etherial layer was washed several times to remove triglyme. After the removal of the solvent, the syrupy

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residue left behind was chromatographed using a column packed with 50 g of alumina, and benzene 10 ml fractions were collected. The only identifiable substance obtained was 1,3,5-tri-phenylbenzene. The yield was 112 mg (16%), mp 170-171°C, lit[50] 171°C.

Infrared: $\bar{\nu}_{max}^{CCl_4}$ 1603(s), 1510(s), 1080(m), 1042(m), 887(s), 696(s) cm^{-1}.

uv: $\lambda_{max}^{95\%\ EtOH}$ mμ, log at 250(4.8).

Thermolysis at 150°.

The previous experiment was repeated taking 0.5 g of 1-phenylcyclobutanol and equimolecular amount of n-butyl-lithium. The temperature of the flask was maintained at 150°C. After 3 hr the gas collected was analyzed and was confirmed as ethylene. The infrared spectrum of the residue indicated unreacted alcohol and also the presence of an α,β-unsaturated ketone (strong band at 1665 cm^{-1}).

In a separate thermolysis experiment, alkoxide derived from 1 g of 1-phenylcyclobutanol was allowed to react for 24 hr at 150°. The crude residue, after work up, was chromatographed using a column packed with 50 g of florisil. Dypnone was obtained as the only identifiable product, yield 1.25 mg (21%). An authentic sample of dypnone was prepared from acetophenone. The infrared and nmr spectrum were identical.

Infrared: $\bar{\nu}_{max}^{CCl_4}$ 1665(s), 1600(s), 1205(s), 955(s), 695(s) cm^{-1}.

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nmr: $\delta_{max}^{CCl_4}$ 2.50 (doublet, 3H; J=1.5)
6.90 (quartet, 1H; J=1.5)
7.28 (multiplet, 8H)
7.80 (multiplet, 2H).

Cyclobutanol.

5 g (0.071 mole) of cyclobutanone (Aldrich) dissolved in 10 ml of ether was added dropwise, in 30 minutes, to a stirred suspension of 1 g (0.025 mole) of lithium aluminum hydride in 40 ml of ether. The mixture was refluxed for 1 hr. Sufficient 10% sulfuric acid was added carefully to the mixture, cooled to 0°, to dissolve all solid matter. The aqueous layer was separated and washed several times with ether. The combined organic extract was dried over sodium sulfate. Distillation provided 3.2 g (61%) of cyclobutanol, bp 123-125°, lit[40] 124°.

Infrared: $\bar{\nu}_{max}^{neat}$ 3435(b), 1100(s) cm^{-1}.

nmr: $\delta_{ppm}^{CCl_4}$ 1.2-2.5 (complex absorption, 6H);
4.1 (quintet; 1H), 4.4 (singlet; 1H).

Thermolysis of Lithium Cyclobutoxide.

0.72 g (10 mmole) of cyclobutanol was converted to the lithium salt by the addition of 7.1 ml (10 mmole) of 1.4 M n-butyllithium. The salt was thermolyzed for 3 hr at refluxing triglyme (222°C). The gas evolved was identified (ehtylene) by mass spectrum. The yield (67%) was determined in a high vacuum line.

cis and trans-2,3-Dimethylcyclobutanones.

N-Ethyl N-nitrosourea.

To 145 g of a 70% aqueous solution of ethylamine

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(4.5 mole) in a 3-liter 3-neck flask was added 250 ml of water and 230 ml (5.6 mole) of concentrated hydrochloric acid. The total weight of the mixture was brought to 750 g. 450 g. (7.5 mole) of urea was added to the above solution, refluxed for 3 hr and then was cooled to room temperature. To the above mixture, 315 g (4.5 mole) of sodium nitrite was added. 900 g of crushed ice was mixed with 84 ml of concentrated sulfuric acid and was cooled with stirring to -20°C (isopropyl alcohol/dry ice). The mixture was siphoned out slowly with stirring to the sulfuric acid solution. The addition was completed in 2 hr. The precipitate was filtered, washed with ice-cold water, dried to constant weight and was stored in a desiccator kept in a refrigerator. The yield was 112 g (43%) based on the sodium nitrate taken.

Solution of Diazoethane in Methylene Chloride.

To a stirred mixture of 200 ml of methylene chloride and potassium hydroxide (62.5 g in enough water to make 125 ml); colled to 0°C, was added carefully 25 g (215 mmole) of ethyl nitrosourea. The resulting mixture was cooled to -78°, and the solution of diazoethane was decanted into a flask kept at -78°, containing pellets of potassium hydroxide.

Generation of Ketene.

Ketene was generated by the pyrolysis of acetone in a ketene generator and was collected at -130° (pentane/liquid nitrogen slurry). One bulb to bulb distillation on high vacuum line (-78 to -130°) gave essentially pure ketene, which was stored at -78° under nitrogen.

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cis and trans-2,3 and 2,4-Dimethylcyclobutanones.

A cold solution (-78°) of diazoethane in methylene chloride, generated from 25 g (212 mmole) of ethylnitrosourea, was added to 8 ml of ketene (~ 100 mmole) in 50 ml of methylene chloride kept at -130° (n-pentane/liquid nitrogen). After the addition, accompanied by vigorous evolution of nitrogen, was completed in 30 minutes, the reaction mixture was brought to room temperature. Removal of methylene chloride at atmospheric pressure, followed by distillation at reduced pressure, yielded a mixture of cis and trans-2,3-dimethylcyclobutanones and cis and trans-2,4-dimethylcyclobutanones, bp 37-40° (15 mm). The yield was 2 g (20%).

Separation of the cyclobutanones was carried out by gas chromatography. From the mixture of the four isomeric dimethylcyclobutanones cis-2,3-dimethylcyclobutanone was separated by preparative gas chromatography (10 ft x 3/8 in column packed with 10% FFAP on 30/60 Chromosorb W (NAW); column temperature 120°; block and injection port temperatures 200°; carrier gas flow rate 100 ml/min). Cis and trans-2,4-dimethylcyclobutanone and trans-2,3-dimethylcyclobutanone showed up in the first peak (7 min) and the cis-2,3-dimethylcyclobutanone in the second peak (10 min).

Analytical glpc (10 ft x 1/8 in column packed with 30% QF-1 on 60/80 Chromosorb (AW); column temperature 120°; injection port and block temperature 200°; carrier gas flow rate 60 ml/min) showed pure trans-2,3-dimethylcyclobutanone in the second peak.

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cis-2,3-Dimethylcyclobutanone.

Infrared: $\bar{\nu}_{max}^{CCl_4}$ 2970(s), 1780(s), 1470(s), 1375(s), 1095(s), 1075(s) cm^{-1}.

nmr: $\delta_{ppm}^{CCl_4}$ 1.00 (doublet, 3H; J=6.5)
1.08 (doublet, 3H; J=6.75)
2.50 (multiplet, 2H)
3.20 (multiplet, 2H)

mass spectrum: 75 ev
98 (25%, M^+); 56 (100%); 41 (49%).

trans-2,3-Dimethylcyclobutanone.

Infrared: $\bar{\nu}_{max}^{CCl_4}$ 1780 cm^{-1}.

nmr: $\delta_{ppm}^{CCl_4}$ 1.09 (doublet, 3H; J=7)
1.30 (doublet, 3H; J=6.5)
1.97 (multiplet, 1H)
2.78 (multiplet, 3H)

cis-2,3-Dimethylcyclobutanols.

To 10 mg (0.25 mmole) of lithium aluminum hydride, suspended in 5 ml of anhydrous ether, was added 50 mg (0.50 mmole) of cis-2,3-dimethylcyclobutanone. The mixture was stirred for 1 hr at 0°. One drop of a saturated solution of ammonium chloride was added to the reaction mixture. The precipitate formed was filtered and the etherial solution was dried over anhydrous sodium sulfate. Analytical glpc (10 ft x 1/8 in column packed with 30% QF-1 on 60/80 Chromosorb (AW), column temperature 120°, injection port and block temperature 200°, carrier gas flow rate 60 ml/min) showed only one peak other than the ether peak. (retention time 9 min; trans-2,3-

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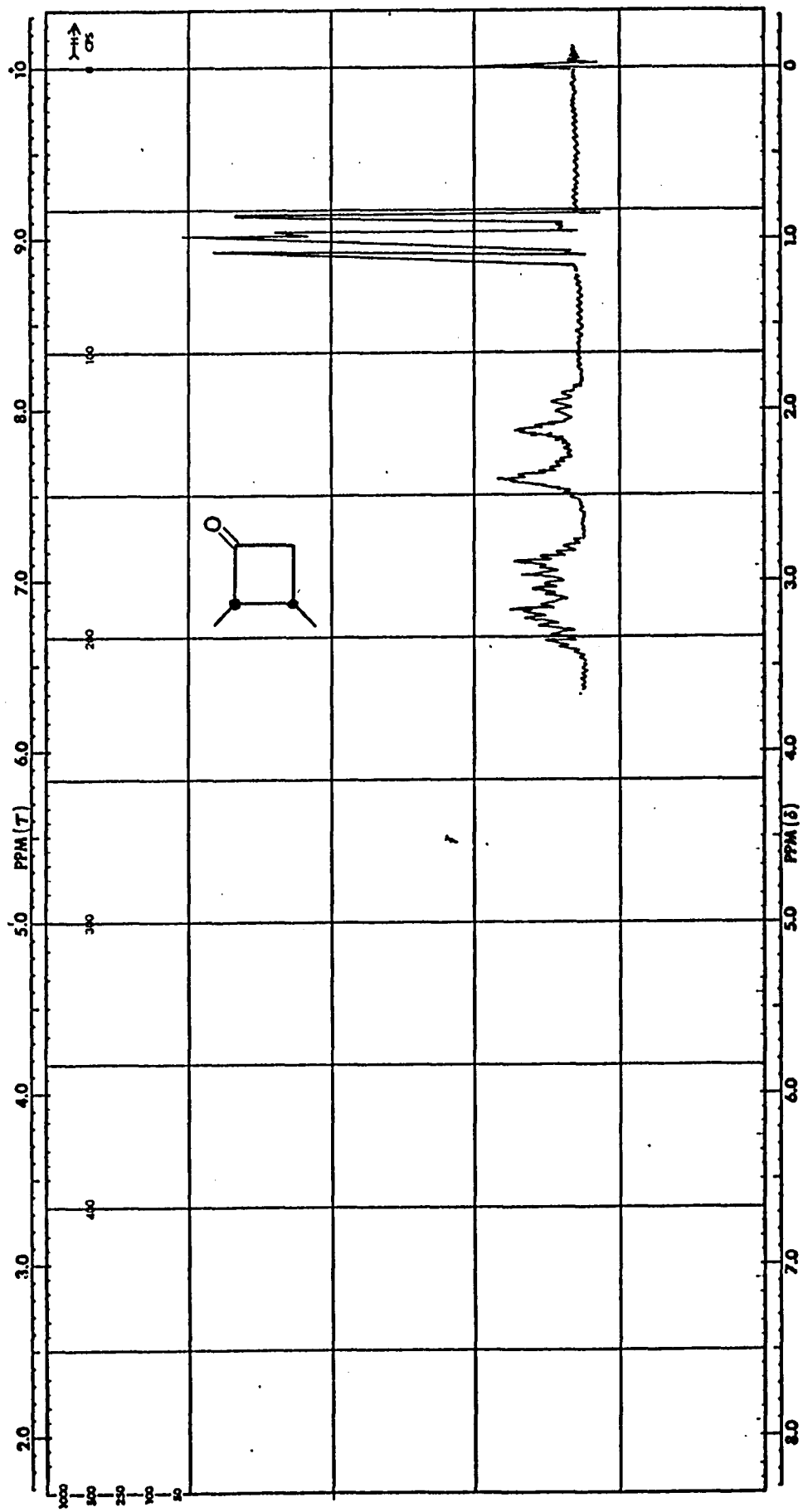

Figure 13

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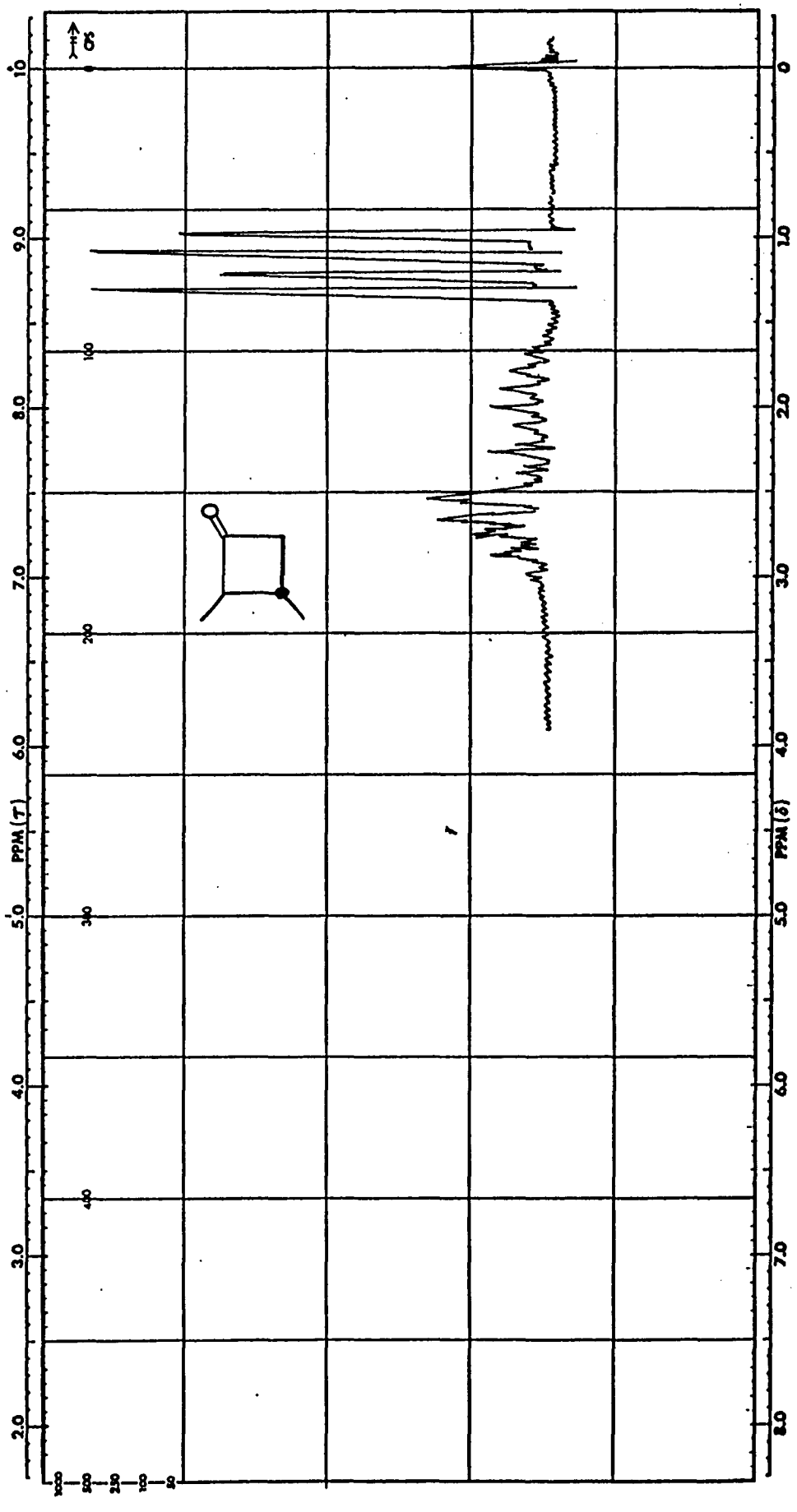

Figure 14

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dimethylcyclobutanols under the same conditions, 7 min) Analytical glpc (6 ft x 1/8 in columns packed with 3% FFAP, 5% SE-30, Carbowax 1500, silicone oil) showed only a single peak for the alcohols.

Anal: Calculated for $C_6H_{12}O$: C, 71.95; H, 12.07; O, 15.98.
Found: C, 71.69; H, 11.93.

Infrared: $\bar{\nu}^{CCl_4}_{max}$ 3450(b), 1100(s) cm^{-1}.

nmr: $\delta^{CCl_4}_{ppm}$ 0.90 (doublet, 3H; J=6.5)
0.92 (doublet, 3H; J=7).
1.4-2.7 (complex absorption, 4H)
4.04 (quartet, 1H; J=7)
4.25 (singlet, 1H)

mass spectrum: 70 ev; m/e
58(100%); 60(84%); 41(75%); 100(2%)

The nmr spectrum indicated the presence of two isomeric alcohols in the ratio 80:20. Reduction carried out using lithium aluminum tri-t-butoxy hydride gave a 90:10 ratio for the isomer composition. The methine protons for the two isomers give quartets, one centered at 4.04 ppm for the isomer. (The methine proton absorption for the trans-2,3-dimethylcyclobutanol is at 3.4 ppm.)

To 20 mg (0.2 mmole) of cis-2,3-dimethylcyclobutanol in 2 ml of pyridine was added 69 mg (0.3 mmole) of freshly recrystallized 3,5-dinitrobenzoyl chloride. The mixture was agitated well for 1 hr and was then poured into 10 ml of ice cold water. The precipitate formed was filtered and washed with dilute sodium carbonate solution. Recrystallization from alcohol yielded 50 mg (90%) of the derivative, mp 90-96°.

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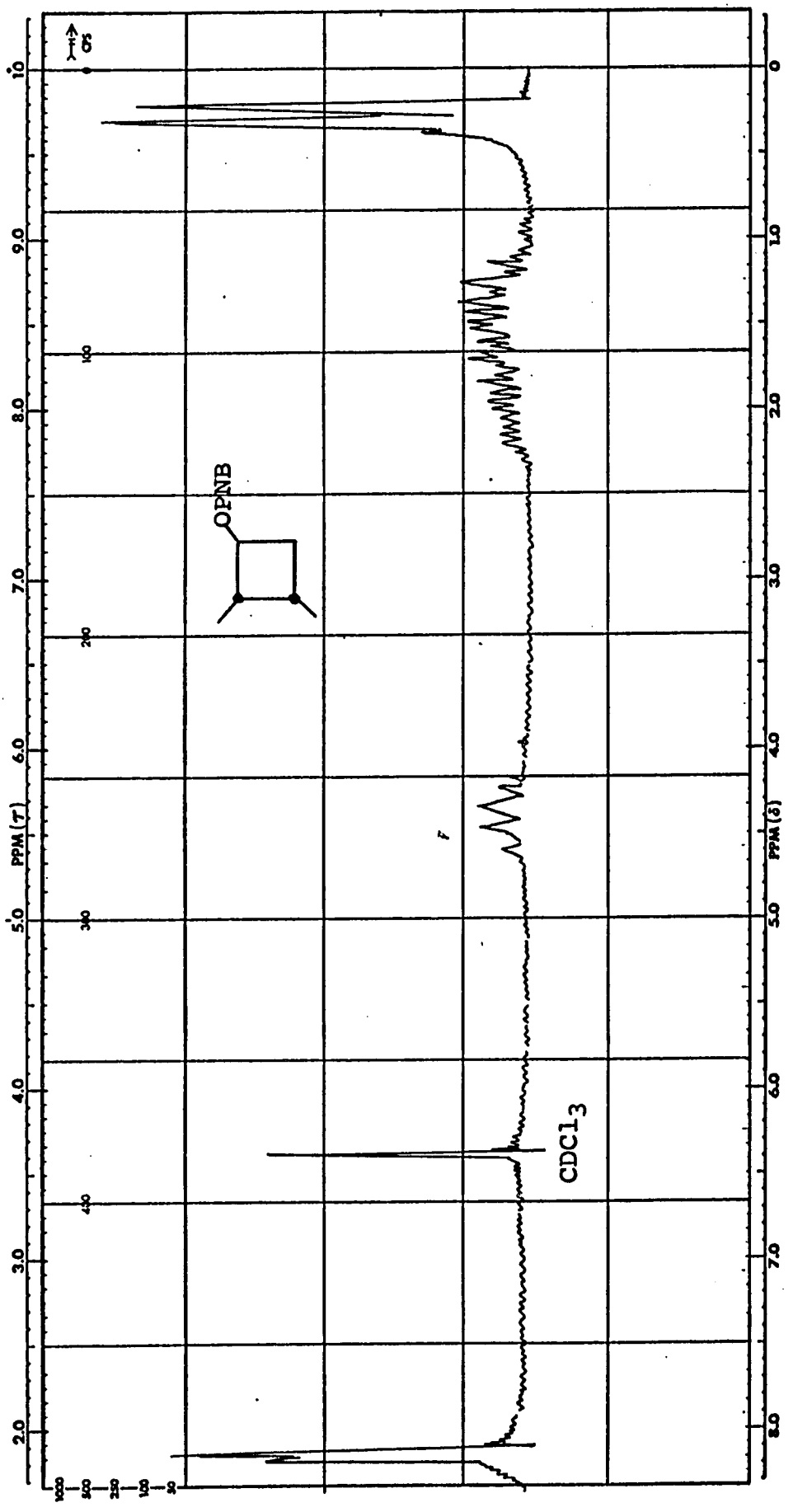

Figure 15

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Anal: Calculated for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.80; N, 9.52; O, 32.62.

Found: C, 52.76; H, 4.71; N, 9.42.

Infrared: $\bar{\nu}_{max}^{CHCl_3}$ 1740(s), 1545(s), 1350(s) cm^{-1}.

nmr: $\delta_{ppm}^{CDCl_3}$ 1.0 (doublet, 3H; J=6.5)
1.05 (doublet, 3H; J=6.5)
1.9-3 (complex absorption, 4H)
5.2 (quartet, 1H)
9.0 (multiplet, 3H).

trans-2,3-Dimethylcyclobutanols.

The reduction and work up were the same as in the previous case.

Infrared: $\bar{\nu}_{max}^{CCl_4}$ 3455(b), 1100(s) cm^{-1}.

nmr: $\delta_{ppm}^{CCl_4}$ 0.98-1.08 (complex absorption, 6H)
1.08-1.35 (complex multiplet, 2H)
1.60 (multiplet, 1H)
2.30 (multiplet, 1H)
4.40 (singlet, 1H).

Thermolysis of Lithium trans-2,3-Dimethylcyclobutoxides.

To 200 mg (2 mmole) of the alcohol, 1.4 ml of 1.4 molar n-butyllithium was added. The alkoxide was heated to 80° in order to remove all the solvent (hexane). 2 ml of carefully dried triglyme was added to the alkoxide and the mixture was heated with stirring for 3 hr at 222°. The gaseous materials formed were collected in the trap, cooled by liquid nitrogen. The gases were transferred into an evacuated mass spectral tube. Analytical glpc

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(50 ft x 1/4 in column* packed with 20% by weight mixture of bis (2-ethylhexyl) sebacate and 80% by weight of bis (2-methoxyethyl)adipate) on Chromosorb W DMCS; column temperature 4°; injection port and block temperature 30° and the carrier gas flow rate 100 ml/min), showed 3 peaks besides the air peak. The substances were identified as propylene, trans-2-butene and cis-2-butene by comparing the retention times with authentic materials.

Thermolysis experiments were carried out at temperatures 222° and 170° with the alkoxide derived from cis-2,3-dimethylcyclobutanol. n-Pentane was used as an internal standard in the glpc analysis of the olefins. The results are tabulated in Table

Experiment to Check Isomerization of cis-2-butene at Thermolysis Conditions.

A sealed tube containing lithium cyclobutoxide in triglyme and pure cis-2-butene was heated in an oil bath for 24 hr at 170°. After 24 hr gas analysis indicated only ethylene and cis-2-butene.

*This column was kindly supplied by Professor D. W. Emerson of the University of Michigan Dearborn Campus.

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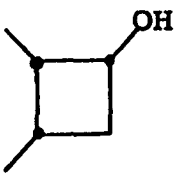
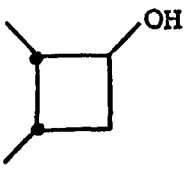
Experiment to Verify Isomerization of Cyclobutoxide During Thermolysis.

Cyclobutoxide, obtained from 0.40 mg of cis-2,3-dimethylcyclobutanol, was thermolyzed for 1 hr at 170°. The cyclobutanol mixture that was obtained after quenching was analyzed by glpc (5 ft x 1/4 in, 5% FFAP at 80°).

The composition of the butanols before thermolysis was:

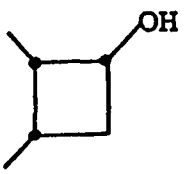


90%

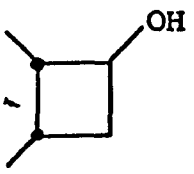


10%

after thermolysis was:



78%



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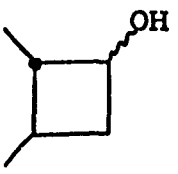

7%

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KINETIC EXPERIMENTS

All kinetic experiments were carried out in a special system shown here. A solution of the alkoxide in triglyme was introduced into the system using a hypodermic syringe. The system was then evacuated and was sealed before being heated in an oil bath maintained at a constant temperature. Readings were taken fifteen minutes after the system was introduced into the oil bath, at regular intervals of time. The study was carried out at four different temperatures, 145, 150, 155 and 160° for the lithium salt of 1-phenylcyclobutanol and at 175, 180, 185 and 190° for the salt of cyclobutanol. Readings were taken until manometer showed a constant reading indicating the end of the reaction. (The difference in the zero-reading and the end-reading gives a number corresponding to the total concentration, a, and the difference in the zero-reading and a reading at a particular interval of time gives a number corresponding to the amount that has reacted, x). Log a/a-x was plotted against time. A straight line indicating first order reaction was obtained for each set of conditions.

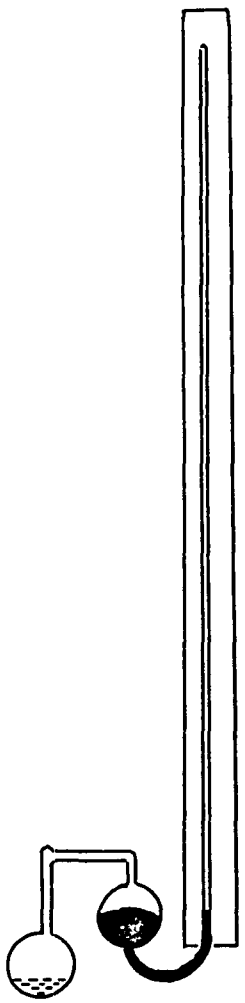

Figure 7

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Table IV

Lithium 1-Phenylcyclobutoxide

Run 1: Temp. 160°		Run 2: Temp. 155°	
Time	log a/a-x	Time	log a/a-x
15 min	0.0652	15 min	0.0502
30	0.1260	30	0.1004
45	0.1974	45	0.1500
60	0.2553	60	0.1990
90	0.4052	90	0.3002
120	0.5304	120	0.3804
150	0.7253	150	0.5152
180	0.8508	195	0.7002
240	1.1105	240	0.8648
		330	1.1520
Run 3: Temp. 150°		**Run 4: Temp. 145°**	
30 min	0.0710	30 min	0.0502
60	0.1454	60	0.0996
90	0.2158	120	0.2012
150	0.3602	180	0.3004
210	0.5120	270	0.4750
300	0.7452	360	0.6746
420	1.0450	480	0.8750

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Table V

Lithium Cyclobutoxide

Run 1: Temp. 190°		Run 2: Temp. 185°	
Time	log a/a-x	Time	log a/a-x
15 min	0.0760	15 min	0.0540
30	0.1480	30	0.1122
45	0.2102	60	0.2048
60	0.2824	90	0.3102
75	0.3620	120	0.4218
105	0.5024	150	0.5342
135	0.6458	180	0.6210
165	0.7842	225	0.7942
200	0.8382	270	0.8532
240	0.9284	360	0.9972
Run 3: Temp. 180°		**Run 4: Temp. 175°**	
30 min	0.0762	30 min	0.0540
60	0.1620	60	0.1123
90	0.2352	90	0.1554
120	0.3224	120	0.2210
150	0.4042	180	0.3452
180	0.4728	240	0.4280
240	0.6142	300	0.5482
300	0.7854	420	0.6542

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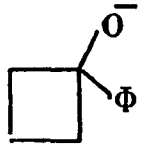
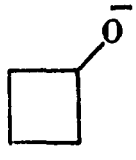
Table VI

Data for Arrhenius Plot

Cyclobutoxide	Temperature °A	$\frac{1000}{T}$	Rate Constant, k	log k
	433	2.310	16.90×10^{-5}	-3.7710
	428	2.335	12.90×10^{-5}	-3.8902
	423	2.360	9.46×10^{-5}	-4.0242
	418	2.390	6.53×10^{-5}	-4.1854
	463	2.160	18.20×10^{-5}	-3.7423
	458	2.183	13.80×10^{-5}	-3.8601
	453	2.205	10.10×10^{-5}	-3.9957
	448	2.232	7.13×10^{-5}	-4.1469

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APPENDIX

Attempt to Synthesize 2,2-Dimethylcyclobutanol.

bis-1,2-Trimethylsilyloxy-3,3-dimethylcyclobutene.

11.5 g (0.5 g-atom) of sodium metal was suspended in 150 ml of toluene in a 3-neck flask, fitted with a reflux condenser, a pressure-equalized funnel and a high speed stirrer. An argon bubbler was attached to the condenser. Toluene was heated to reflux and the stirrer was started at a low speed. The speed was gradually increased to 3000 rpm in order to obtain finely dispersed sodium. The system was cooled to 20-30°. 110 g (0.5 mole) of trimethylsilylchloride was added to sodium dispersion. 25 g (0.225 mole) of ethyl-2,2-dimethylsuccinate was added a little at a time with stirring. The addition was completed in 2 hr. The mixture was then refluxed for 4 hr and the sodium chloride formed was filtered. The filtrate was fractionally distilled at reduced pressure. 28.5 g (88%) of the silyl ether was collected, bp 65-70 (5 mm).

Anal: Calculated for $C_{12}H_{26}O_2Si_2$: C, 55.76; H, 10.14; O, 12.37; Si, 21.73.

Found: C, 55.95; H, 10.30.

Infrared: $\bar{\nu}_{max}^{neat}$ 3000(s), 1730(s), 1250(s), 1170(s), 1090(s), 960(s), 870(b) cm^{-1}.

nmr: $\delta_{ppm}^{CCl_4}$ 0.16 (singlet, 9H)
0.19 (singlet, 9H)
1.02 (singlet, 6H)
1.83 (singlet, 2H)

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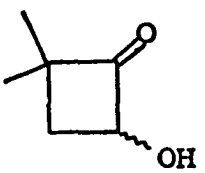
2-Oxo-3,3-dimethylcyclobutanol and 2-Oxo-4,4-dimethylcyclobutanol.

26 g (0.20 mole) of silyl ether was added to a solution of 20 ml of water in 150 ml of tetrahydrofuran. The mixture was stirred well at room temperature for 24 hr. The reaction mixture was dried over anhydrous sodium sulfate. Preparative gas chromatography (10 ft x 3/8 in in column packed with 10% FFAP on 30/60 Chromosorb W (NAW), column temperature 180°, block and injection port temperature 250°, carrier gas flow 100 ml/min) gave a mixture of succinoins.

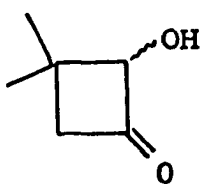
Anal. Calculated for $C_6H_{10}O_2$: C, 63.12; H, 8.84; O, 28.03.
Found: C, 63.19; H, 8.78.

Infrared: $\tilde{\nu}_{max}^{neat}$ 3450(b), 1776(s) cm^{-1}.

nmr: $\delta_{ppm}^{CCl_4}$



1.08 (singlet, 3H)
1.13 (singlet, 3H)
1.80 (multiplet, 2H)
4.65 (singlet, 1H)
4.92 (doublet of doublet, 1H; $\begin{matrix} J=9 \\ J=8 \end{matrix}$.



0.97 (singlet, 3H)
1.32 (singlet, 3H)
2.25 (multiplet, 2H)
4.30 (triplet, 1H; J=1.5)
4.65 (singlet, 1H).

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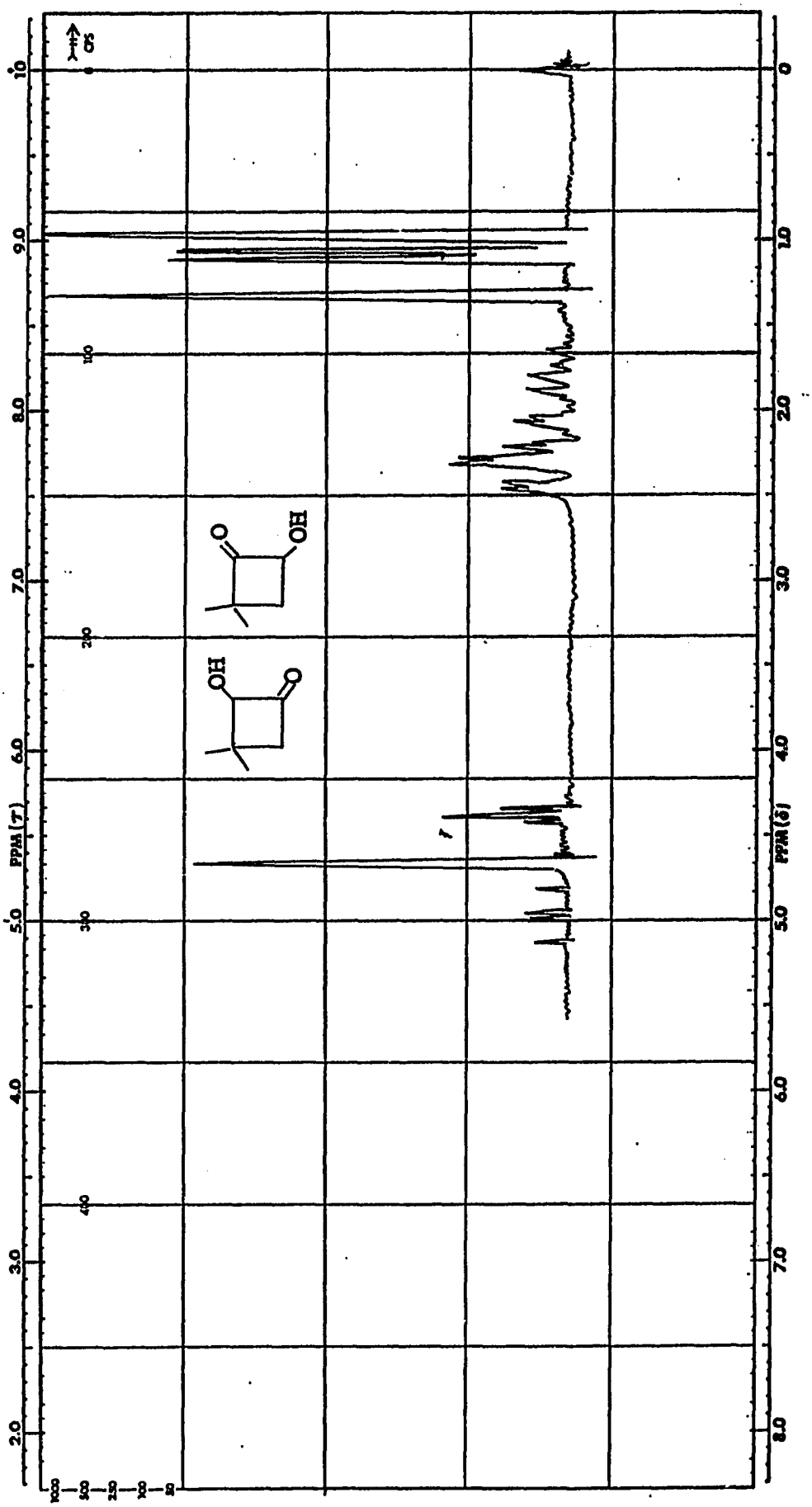

Figure 16

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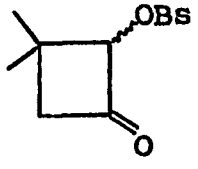
2-Oxo-3,3-dimethylcyclobutylbrosylate and 2-Oxo-4,4-dimethylcyclobutylbrosylate.

0.05 mole (based on the silyl ether taken) of the mixture of succinoins was added to 14.0 g (0.052 mole) of p-bromobenzene sulfonylchloride in 50 ml of dry pyridine. The mixture was shaken vigorously for 1 hr and was then poured into 200 ml of cold dilute hydrochloric acid. The solid derivative was washed successively with dilute sodium bicarbonate solution and water. The two isomers were fractionally crystallized from benzene:hexane (20:80).



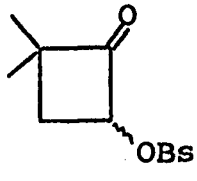
mp 96-98°

Anal: Calculated for $C_{12}H_{13}BrO_4S$: C, 43.26; H, 3.93; Br, 23.98; O, 19.20; S, 9.62.

Found: C, 43.10; H, 3.91.

Infrared: $\bar{\nu}_{max}^{CHCl_3}$ 3030(s), 1780(s), 1585(s), 1190(s), 1060(s) cm^{-1}.

nmr: $\delta_{ppm}^{CDCl_3}$ 1.20 (singlet, 6H)



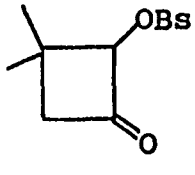
1.87 (doublet of doublet, 1H; J=10, J=7.5)

2.36 (doublet of doublet, 1H; J=11, J=10)

5.50 (doublet of doublet, 1H; J=11, J=7.5)

7.65 (multiplet, 4H).

Infrared: $\bar{\nu}_{max}^{CDCl_3}$ 3030(s), 1775(s) cm^{-1}.



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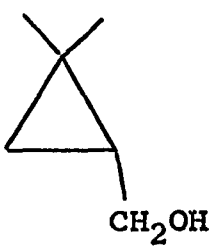
nmr: $\delta_{ppm}^{CDCl_3}$ 1.18 (singlet, 3H)
1.47 (singlet, 3H)
2.47 (doublet, 1H; J=1.5)
2.52 (doublet, 1H; J=1.5)
5.00 (triplet, 1H; J=1.5)
7.63 (multiplet, 4H)

Reduction of Brosylate.

A solution of 3.33 g (0.01 mole) of brosylate in 25 ml of ether was added dropwise to a cold suspension of 0.22 g (0.0055 mole) of lithium aluminum hydride in 10 ml of anhydrous ether with stirring. After the addition, the mixture was refluxed for 2 hr. A saturated solution of ammonium chloride was added to the reaction mixture, and the organic layer was separated and dried over sodium sulfate.

Infrared: $\bar{\nu}_{max}^{CCl_4}$ 3460(b), (3010(s), 1450(s), 1375(s), 1255(s) cm^{-1}.

nmr: $\delta_{max}^{CCl_4}$ -0.05 to 1.1 (complex multiplet, 3H)
1.07 (singlet, 3H)
1.10 (singlet, 3H)
3.40 (septet, 2H)
4.10 (singlet, 1H).



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