

AN ABSTRACT OF THE THESIS OF

Stephen E. Wuerch for the degree of Master of Science

in Chemistry presented on 15 December 1986

Title: A Study of the Chemistry of Diisopropyl-
Cyclopropylisopropyl- and Dicyclopropylcarbene

Abstract approved: Redacted for Privacy
Dr. Peter K. Freeman

The effect of the conjugation with cyclopropyl rings on the activation parameters for the formation of carbenes from the corresponding diazo compounds was investigated using diisopropylcarbene (46), cyclopropylisopropylcarbene (47), and dicyclopropylcarbene (48). Each of these three carbenes was generated by the thermolysis of the parent benzenesulfonylhydrazone potassium salts using DMSO as the solvent. Each of the three carbenes underwent an intramolecular rearrangement or rearrangements to form alkene(s) as well as undergoing a reaction with the DMSO solvent to form the corresponding ketone.

Diisopropylcarbene (46) yielded two reaction products: 2,4-dimethyl-2-pentene (62) and diisopropyl

ketone (54). 62 was formed by a 1,2-hydride shift and 54 was formed by a reaction between the carbene and DMSO. Cyclopropylisopropylcarbene (47) yielded three reaction products: 1-cyclopropyl-2-methyl-1-propene (63), 1-isopropylcyclobutene (64), and cyclopropyl isopropyl ketone (55). 63 was formed by a 1,2-hydride shift, 64 was formed by ring expansion, and 55 was formed by a reaction between the carbene and DMSO. Dicyclopropylcarbene (48) yielded two reaction products: 1-cyclopropylcyclobutene (65) and dicyclopropyl ketone (56). 65 was formed by ring expansion and 56 was formed by a reaction between the carbene and DMSO.

A kinetic study was performed for each of the three carbenes. The rates for carbene formation were found to decrease in the order 48 > 47 > 46. The values for the activation energies and enthalpies of activation followed the same order. The enhanced rate of formation for the carbenes which possess cyclopropyl groups was determined to be due to their greater entropies of activation. The differences found in the entropies of activation for the formation of the three carbenes were explained by interactions of ground and transition states with the solvent (DMSO). The values for the free energies of activation for the formation of each of the three carbenes were found to be nearly the same.

A Study of the Chemistry of Diisopropyl-,
Cyclopropylisopropyl-, and Dicyclopropylcarbene

by

Stephen Edward Wuerch

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Completed 15 December 1986

Commencement June 1987

APPROVED:

Redacted for Privacy

Professor of Chemistry in charge of major

Redacted for Privacy

Head of Department of Chemistry

Redacted for Privacy

Dean of Graduate School

Date thesis is presented 15 December 1986

Thesis typed by Stephen Edward Wuerch

To Dr. Peter K. Freeman
and Dr. T. Darrah Thomas

ACKNOWLEDGEMENT

I am indeed very fortunate to have had an enthusiastic and inspiring advisor such as Prof. P. K. Freeman. His patience and understanding as well as his expertise in the field of chemistry made this thesis possible.

I wish to thank my parents, Edward and Kathryn Wuerch, and my sister, Carol Wuerch, for their love, devotion, and moral support which helped me to continue and finish my work. I would also like to thank my friends, Troy and Helen Baker, Earl and Joy Orcherton, Don and Georgiann Berger, and Ovan and Berniece Sturdivant, for their interest in this project.

I would like to thank Prof. G. J. Gleicher and Prof. R. W. Thies for their helpful comments and Dr. Violet Jonas for her technical assistance. I would also like to thank Mr. Brian Arbogast for providing the GC - mass spectra used in this research, Mr. Roger Kohnert and Dr. Larry Siggel for the proton and carbon-13 NMR spectra, and Dr. Max Deinzer and Mr. Rod Inman for assistance in using the HPLC apparatus.

TABLE OF CONTENTS

GENERAL INTRODUCTION TO CARBENES	1
Historical Background	4
Formation and Structure of Methylene	7
Reactions of Methylene	9
Stereochemistry of Carbene Addition Reactions	15
Alkyl- and Dialkylcarbenes	19
Substituent and Steric Effects	27
INTRODUCTION	35
RESULTS AND DISCUSSION: SYNTHESSES AND PRODUCTS	46
RESULTS AND DISCUSSION: KINETICS	56
RESULTS AND DISCUSSION: ACTIVATION PARAMETERS	79
EXPERIMENTAL	93
General	93
Preparation of anhydrous FeCl ₃ catalyst	94
Preparation of cyclopropanecarboxylic acid chloride (<u>57</u>)	94
Preparation of isopropylmagnesium bromide (<u>58</u>)	95
Preparation of cyclopropyl isopropyl ketone (<u>55</u>)	95
Preparation of diisopropyl ketone benzene-sulfonylhydrazone (<u>55</u>)	96
Preparation of cyclopropyl isopropyl ketone benzenesulfonylhydrazone (<u>52</u>)	97

Preparation of dicyclopropyl ketone benzene-sulfonylhydrazone (<u>53</u>)	98
Preparation of the potassium salts of the ketone benzenesulfonylhydrazones (<u>59,60,61</u>)	99
Preparation of dry DMSO	99
Thermolyses of the potassium salts of the ketone benzenesulfonylhydrazones (<u>59,60,61</u>)	100
Work-up of the products from the thermolyses for product identification and percent yield determination	102
Identification of the products obtained from the thermolysis of the potassium salt of diisopropyl ketone benzenesulfonylhydrazone (<u>59</u>)	102
Identification of the products obtained from the thermolysis of the potassium salt of cyclopropyl isopropyl ketone benzene-sulfonylhydrazone (<u>60</u>)	103
Identification of the products obtained from the thermolysis of the potassium salt of dicyclopropyl ketone benzenesulfonylhydrazone (<u>61</u>)	105
Independent determination of k_1	106
BIBLIOGRAPHY	108
APPENDIX	113

LIST OF FIGURES

FIGURE

1. Orbital representations of singlet and triplet methylene. 4
2. Singlet and triplet methylene energy levels. 9
3. Orbital representations of π -acceptors on carbenes. 28
4. Orbital representation of the bicyclobutonium cation. 36
5. Orbital representation of the bisected cyclopropylcarbinyl cation. 37
6. Plots of \ln (concentration of benzenesulfonylhydrazone) versus time for the decomposition of the potassium salt of cyclopropyl isopropyl ketone benzenesulfonylhydrazone. 78
7. Plots of $\ln k_2$ versus $1/T$ for the three benzenesulfonylhydrazone potassium salts. 85
8. Apparatus used for the pyrolysis and kinetic study of the carbenes. 101

LIST OF TABLES

TABLE

1.	The Pyrolysis of the Potassium Salt of Diisopropyl Ketone Benzenesulfonylhydrazone at 110°C.	61
2.	The Pyrolysis of the Potassium Salt of Diisopropyl Ketone Benzenesulfonylhydrazone at 115°C.	62
3.	The Pyrolysis of the Potassium Salt of Diisopropyl Ketone Benzenesulfonylhydrazone at 120°C.	63
4.	The Pyrolysis of the Potassium Salt of Diisopropyl Ketone Benzenesulfonylhydrazone at 125°C.	64
5.	The Pyrolysis of the Potassium Salt of Diisopropyl Ketone Benzenesulfonylhydrazone at 130°C.	65
6.	The Pyrolysis of the Potassium Salt of Cyclopropyl Isopropyl Ketone Benzenesulfonylhydrazone at 110°C.	66
7.	The Pyrolysis of the Potassium Salt of Cyclopropyl Isopropyl Ketone Benzenesulfonylhydrazone at 115°C.	67
8.	The Pyrolysis of the Potassium Salt of Cyclopropyl Isopropyl Ketone Benzenesulfonylhydrazone at 120°C.	68
9.	The Pyrolysis of the potassium Salt of Cyclopropyl Isopropyl Ketone Benzenesulfonylhydrazone at 125°C.	69
10.	The Pyrolysis of the Potassium Salt of Cyclopropyl Isopropyl Ketone Benzenesulfonylhydrazone at 130°C.	70
11.	The Pyrolysis of the Potassium Salt of Dicyclopropyl Ketone Benzenesulfonylhydrazone at 110°C.	71
12.	The Pyrolysis of the Potassium Salt of Dicyclopropyl Ketone Benzenesulfonylhydrazone at 115°C.	72

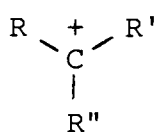
TABLE

13.	The Pyrolysis of the Potassium Salt of Dicyclopropyl Ketone Benzenesulfonylhydrazone at 120°C.	73
14.	The Pyrolysis of the Potassium Salt of Dicyclopropyl Ketone Benzenesulfonylhydrazone at 125°C.	74
15.	The Pyrolysis of the Potassium Salt of Dicyclopropyl Ketone Benzenesulfonylhydrazone at 130°C.	75
16.	Calculated values for the rate constants, k_1 and k_2 .	76
17.	HPLC peak area ratios and their logarithms for the thermal decomposition of the potassium salt of cyclopropyl isopropyl ketone benzenesulfonylhydrazone.	77
18.	Summary of data used in making plots of $\ln k_2$ versus $1/T$.	84
19.	Summary of Calculated Activation Parameters.	87

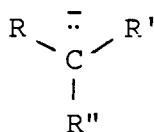
A STUDY OF THE CHEMISTRY OF DIISOPROPYL-
CYCLOPROPYLISOPROPYL-, AND DICYCLOPROPYLCARBENE

GENERAL INTRODUCTION TO CARBENES

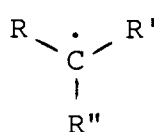
Carbenes constitute one of the four general classes of simple organic intermediates. Along with carbocations, carbanions, and free-radicals, which are the other three classes, carbenes possess a carbon atom which lacks the tetravalency associated with a stable carbon atom. The reactive center of a carbocation is a trivalent carbon atom which possesses no non-bonding valence electrons and, hence, has a positive formal charge (1). Carbanions possess a trivalent carbon atom which has a non-bonding pair of valence electrons and therefore a negative formal charge (2). Free radicals possess a trivalent carbon atom with a single, unpaired valence electron and are electrically neutral (3).



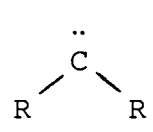
1



2



3



4

Carbenes are unique from the other three classes of organic intermediates in that their reactive centers are divalent instead of being trivalent (4). The

divalent carbon atom also possesses two non-bonding valence electrons and therefore carbenes are electrically neutral.

Carbenes can be classified as being either a singlet or a triplet. If one electron is present in each of the two low energy orbitals, and the electrons have parallel spins, the total spin quantum number $s = 1$. The multiplicity, defined as $2s + 1$, for the carbene is three and the carbene is classified as being a triplet. If the electrons are present in the same orbital, they must have antiparallel spins and a total spin quantum number $s = 0$. The multiplicity of the carbene then would be one and the carbene is classified as being a singlet (1). Singlet carbenes therefore possess an empty p-orbital.

Singlet carbenes have characteristics which are in common with both carbocations and carbanions. A singlet carbene has a vacant p-orbital and is electron deficient like a carbocation. At the same time, a singlet carbene also has a non-bonding pair of electrons like a carbanion (2).

Triplet carbenes can be considered as diradicals even though the location of the two unpaired electrons at the same carbon atom will give rise to peculiarities (2). The mechanisms of many triplet carbene reactions do involve the formation of free-radicals and diradicals.

The divalent carbon atom of a singlet carbene is approximately sp^2 -hybridized and that of a triplet carbene has more s-character than the singlet, the hybridization being sp in some cases. The three sp^2 -like orbitals of the divalent carbon atom of a singlet carbene are involved in making the two bonds and providing an orbital for the two non-bonding electrons. Again, there is also a vacant p-orbital present. The two hybridized orbitals of the divalent carbon atom of a triplet carbene are involved in making the two bonds. One of the two non-bonding electrons is in a p-orbital, the other is present in the remaining hybridized orbital (1).

Whether a carbene is in its singlet or triplet state has a significant effect upon its geometry. The H-C-H bond angle in methylene, $:CH_2$, has been experimentally determined for both the singlet and the triplet state. Herzberg observed the absorption spectrum of singlet methylene (5) and was able to determine that its center bond angle is 102.4° (3). Wasserman and co-workers used electron spin resonance (esr) spectroscopy to determine that the center bond angle of triplet methylene (6) is 136° (4).

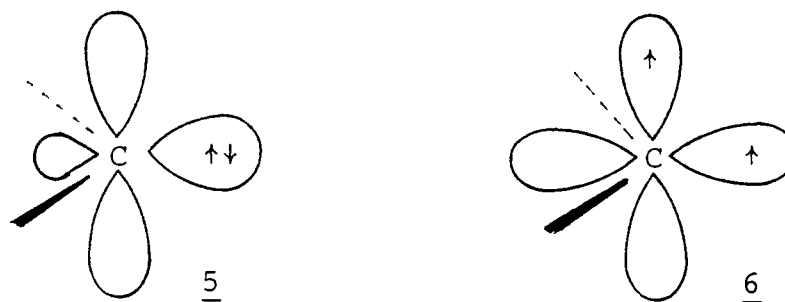


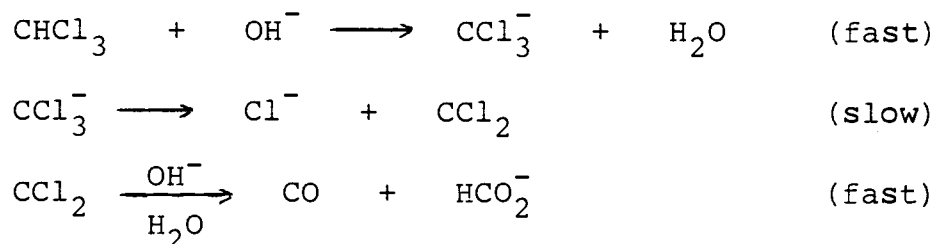
Figure 1. Orbital representations of singlet and triplet methylene.

Historical Background

Apparently, the first real carbene reaction for which a carbene was proposed as an intermediate is the reaction between chloroform and base. In 1862, Geuther suggested that dichlorocarbene could be an intermediate in the reaction between chloroform and alkali to form carbon monoxide. In his paper "Ueber die Zersetzung des Chloroforms durch alkoholische Kalilosung" (On the decomposition of chloroform by alcoholic potassium hydroxide solution), Geuther proposed that the actual formula of chloroform is $\text{CCl}_2 \cdot \text{HCl}$ (5). He proposed that the role of the base is to react with the HCl to release free CCl_2 which reacts further to form products.

In 1950, Hine provided experimental evidence to show that dichlorocarbene is indeed an intermediate in the basic hydrolysis of chloroform (6). The proposed

mechanism is given in Scheme I.

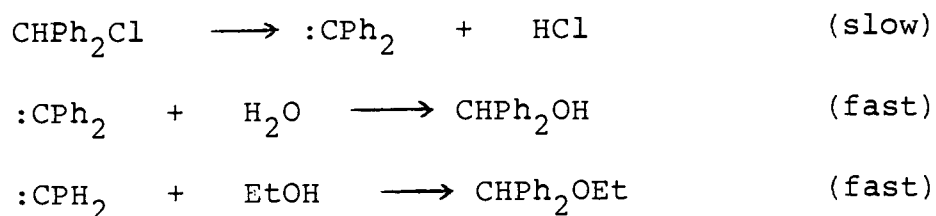


Scheme I

Following Geuther's suggestion that carbenes may be a chemical intermediate, this idea was advanced by Nef in 1897. In "Die Chemie des Methylens", the fourth paper in Nef's series of papers entitled "Ueber das zweiwerthige Kolenstoffatom" (On the divalent carbon atom), he proposed that carbenes are the chemical intermediates for many reactions (7). Most of his assumptions were incorrect and no solid evidence or reasoning was given for his assumptions. For example, part of the paper dealt with the Friedel-Craft alkylation of benzene, and he proposed that the actual species which reacts with benzene is a carbene. Part of his general theory, "Das Methylenproblem", was that pure methylene and its derivatives could be isolated and probably would be isolated in the future.

Some of Nef's ideas were still being accepted thirty years after he wrote "Die Chemie des Methylens". In 1927, Ward (8) treated diphenylchloromethane with 80% EtOH (aq) to yield

Ph₂CHOH and Ph₂CHOEt. The proposed mechanism was based upon Nef's work and is shown in Scheme II.



Scheme II

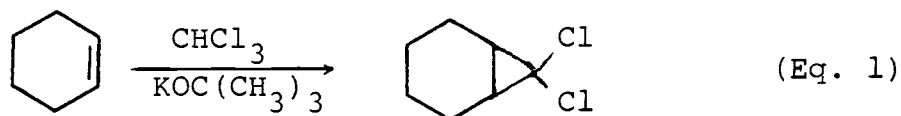
After Nef, carbene chemistry was placed on firmer ground by research involving the photochemical decomposition of diazomethane. The principal investigators were Hantzsch in 1901 and Staudinger in 1912 (1). The primary products from the photolysis of diazomethane are methylene (:CH₂) and nitrogen gas.

For many years the structure of methylene could only be dealt with on a theoretical level (9). This theoretical work on methylene's structure started in 1932 with Mulliken's work (10). He proposed that the bond angle in methylene should be approximately 110° and also did theoretical applications with :CH₂ to describe the formation of ethylene from methylene.

The period since 1950 has seen a rapid development and refinement of the understanding of carbenes. Their discrete yet fleeting existence has now been established by a large body of experimental evidence (1). The modern interest in carbenes was probably initiated by Doering's works which showed that

dichlorocarbene will undergo an addition reaction with a carbon-carbon double bond.

It was clearly recognized that halogenocarbenes could be produced by the action of bases on chloroform (11). A mixture of cyclohexene and saturated potassium t-butoxide in t-butyl alcohol was treated dropwise with chloroform. A reaction product, $C_7H_{10}Cl_2$, was isolated in 40% yield. The identity of the product was determined to be 7,7-dichloronorcaradiene (7) (7,7-dichlorobicyclo[4.1.0]heptane) as shown in Eq. 1.



Formation and Structure of Methylene

Methylene, the simplest carbene, has been the topic of a great deal of experimental and theoretical research. Methylene, $:CH_2$, has six valence electrons, two of which are non-bonding. The other four electrons are associated with the C-H σ bonds. There are two low energy levels present to accommodate the two non-bonding electrons (1).

While it is true that there are several methods by

which methylene can be prepared, the most commonly used precursors are probably ketene, $\text{CH}_2=\text{C}=\text{O}$, and diazomethane, CH_2N_2 . Ketene, when photolyzed with ultraviolet light, decomposes to form methylene and carbon monoxide. The actual mechanism of the decomposition depends on the wavelength of the light used. The photolysis or the pyrolysis of diazomethane will yield methylene and nitrogen gas (2).

Methylene probably has a triplet ground state and a low lying singlet state (12). Herzberg observed the absorption spectrum of methylene in 1961 (3). The flash photolysis of diazomethane in nitrogen gas creates a species with additional absorptions in the vacuum ultraviolet. The absorptions which occurred at 1415 Å and 1370 Å could not be observed in ketene photolysis since ketene itself absorbs strongly in this region. Methylene also has absorption bands in the far red region (8190, 7315, and 6531 Å).

Based upon his work, Herzberg was able to construct the following energy level diagram for singlet and triplet methylene, as shown in Figure 2.

The dashed line represents the energy route by which methylene is produced from excited singlet diazomethane. Methylene may react in the singlet state or may undergo spin inversion to form triplet methylene which has a somewhat lower energy content. The absorption in the red region is attributed to lowest

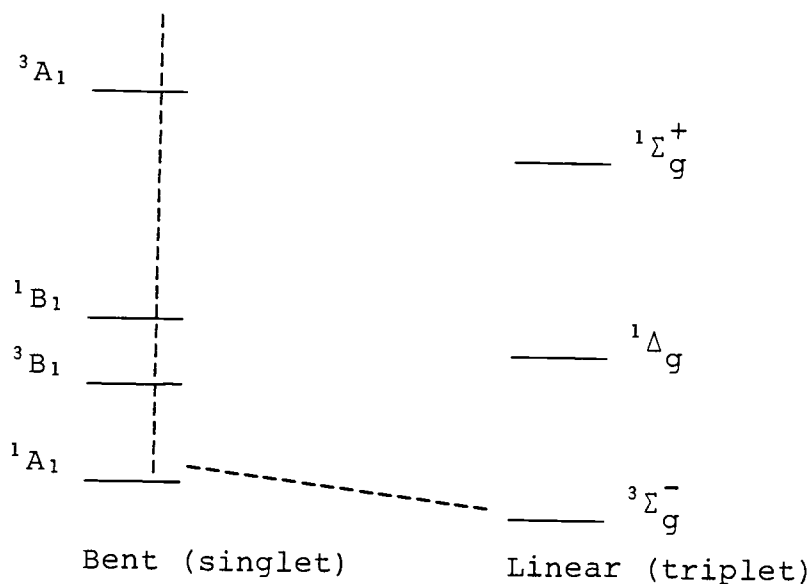


Figure 2. Singlet and triplet methylene energy levels.

energy singlet methylene (1A_1) absorbing energy to become a higher energy state singlet (1B_1).

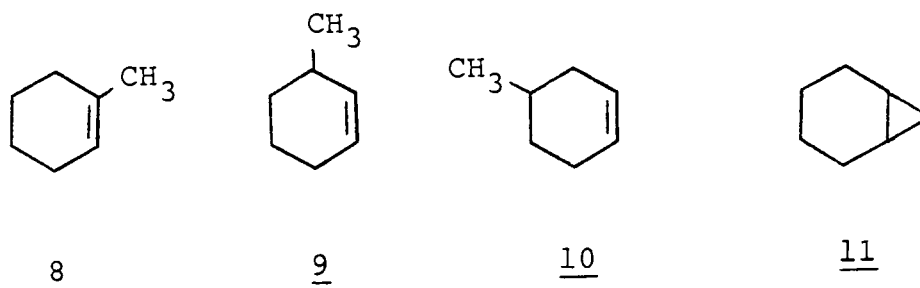
The two low lying energy states that were proposed for methylene are the bent singlet state (1A_1) and a linear triplet state ($^3\Sigma_1$). While it is true that the proposed structure for triplet methylene was linear or nearly linear, there is evidence that this is indeed not necessarily the case (4).

Reactions of Methylene

Two of the most studied and characteristic reactions of methylene are insertion into C-H bonds and addition reactions to alkenes. Other notable reactions

of methylene which will not be discussed here are its reaction with hydrogen gas to form methane (13) and its reaction with diazomethane or ketene precursor to form ethylene (2).

Doering and co-workers (14) allowed cyclohexene to react in solution with methylene produced from the photolysis of diazomethane. The isolated reaction products were 1-methylcyclohexene (8), 3-methylcyclohexene (9), 4-methylcyclohexene (10), and norbornane (11). The relative percent yields of these products, respectively, at 15°C, are 11%, 26%, 26%, and 37%.



The relative percent yields for 8, 9, and 10 are close to the 1:2:2 statistical ratio of hydrogen atoms present on cyclohexene which would lead to these products upon insertion by methylene. Doering and co-workers also investigated the reaction between methylene and pentane and the reaction between methylene and 2,3-dimethylbutane to test the apparent lack of discrimination of methylene in reactions. The three products from the C-H insertion of methylene into

pentane (i.e., hexane, 2-methylpentane, and 3-methylpentane) at 15°C were all formed within 1% of the statistical percentage. The two products from the reaction between methylene and 2,3-dimethylbutane (i.e., 2,3-dimethylpentane and 2,2,3-trimethylbutane) at 15°C were both formed within 3% of the statistical percentage.

Frey (15) carried out a similar experiment to test the indiscriminancy of methylene. While Doering and co-workers carried out the reaction in solution, Frey did his experiment in the gas phase.

Frey allowed methylene (from diazomethane) to react separately with propane, butane, and isobutane. In each case there are two possible C-H insertion products. The two products from the reaction between methylene and propane (i.e., butane and isobutane) were formed in a 2.62:1 ratio (statistical ratio = 3.0:1). The products from butane (i.e., pentane and isopentane) were formed in a 1.25:1 ratio (statistical ratio = 1.5:1). The products from isobutane (i.e., isopentane and neopentane) were formed in a 6.06:1 ratio (statistical ratio = 9:1). From this work, Frey concluded that the relative reactivities on a per bond basis for the insertion reaction of methylene into primary, secondary, and tertiary C-H is approximately 1.0:1.2:1.5.

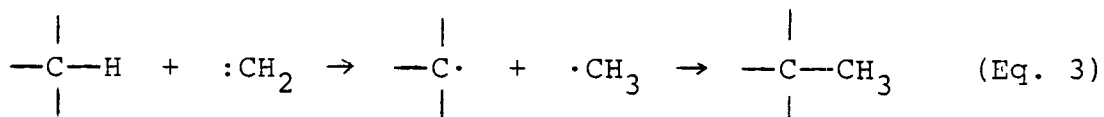
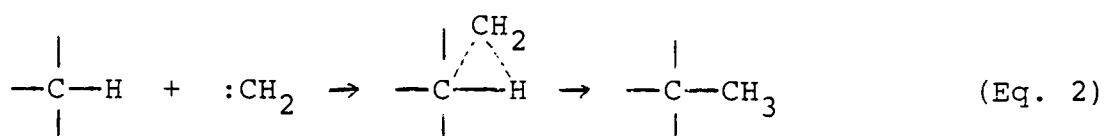
The methylene which was produced in solution in

Doering's work was singlet methylene and that produced in the gas phase by Frey was a mixture of singlet and triplet methylene. From this it should be easy to see that the triplet methylene is the spin state which is able to discriminate between the various types of C-H bonds.

Pure triplet methylene is impossible to produce (without a sensitizer). To investigate the selectivity of triplet methylene, Herzog and Carr (16) carried out the reaction between methylene and isopentane under several different conditions. The conditions which were employed in these reactions were (a) added oxygen gas which insures 0% triplet carbene present, (b) oxygen-free conditions which corresponds to approximately 15% triplet carbene present, and (c) added nitrogen gas which corresponds to approximately 40% triplet carbene present. By extrapolating the results to 100% triplet carbene production, Herzog and Carr were able to deduce the triplet product ratio for the four products from isopentane on a per bond basis. Their results showed that triplet methylene reaction rates for primary, secondary, and tertiary C-H bonds is in the ratio of 1.0:1.5:4.3, respectively.

The experimental results which suggest that singlet carbenes do not discriminate between the three types of C-H bonds whereas triplet carbenes do show some selectivity (tertiary > secondary > primary) can

be explained by the different mechanisms which are used to describe these reactions. Singlet methylene inserts into C-H bonds via a concerted mechanism (Eq. 2) whereas triplet methylene does so by the formation and reaction of two free radicals (Eq. 3) (16, 17, 18).



Additional evidence for the concerted mechanism proposed for the reaction of singlet methylene and a C-H bond is provided by the stereochemistry of the reaction. Franzen (19) determined that the insertion reaction between singlet methylene and the C-H bond of the chiral carbon in 1,2-pentanediol diacetate proceeded with 95% retention of configuration.

One further quality of the methylene produced from diazomethane and ketene which is of interest is the translational energy of the methylene produced from these precursors. Frey (20) noted that the reaction between methylene and isobutylene in the gas phase yielded different product compositions depending on

whether the methylene was produced from ketene or diazomethane. The primary addition product expected upon reaction of the methylene and the carbon-carbon double bond of isobutylene is 1,1-dimethylcyclopropane. If excess energy is present, the 1,1-dimethylcyclopropane can isomerize to form 2-methyl-2-butene and 3-methyl-1-butene. The methylene which was produced from the photolysis of diazomethane showed a greater tendency for the 1,1-dimethylcyclopropane product to isomerize to butenes and, hence, it was concluded that the methylene produced had a greater amount of translational energy than that produced from the photolysis of ketene. Frey also noted that the amount of excess translational energy seemed to be independent for the wavelength of light used in the photolysis.

A similar experiment was performed by Butler and Kistiakowsky (21). In this experiment, the alkene was propylene and the same overall conclusion was reached about the excess translational energy in the methylene which was produced from the photolysis of diazomethane.

Butler and Kistiakowsky stated that in the presence of nitrogen gas there was no difference in the relative rates of attack of the methylene towards C-H bonds or carbon-carbon double bonds regardless of the precursor used to generate the methylene (diazomethane or ketene) (22). They concluded that the excess

translational energy inherent in the methylene from diazomethane was removed by collisions with the molecules of nitrogen gas.

Herzog and Carr (16) found that there was no real difference in the reactivity of singlet methylene from diazomethane or ketene towards C-H bonds. They concluded that this could be due to the methylene from diazomethane undergoing intermolecular collisions before reacting or from the fact that there is no activation energy differences for the insertion reactions into the various types of C-H bonds.

Stereochemistry of Carbene Addition Reactions

The overall behavior of triplet methylene can be described as free-radical in nature whereas singlet methylene should be considered to be a highly reactive molecule (17). These differences in singlet and triplet methylene lead to a difference in the stereochemical outcome of the addition reactions of these carbenes to alkene carbon-carbon double bonds.

The stereochemical differences of singlet and triplet carbenes were first described and explained by Skell (18). Skell proposed that reactions which involve a change in multiplicity (singlet-triplet interconversions) under the conditions employed in

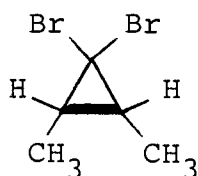
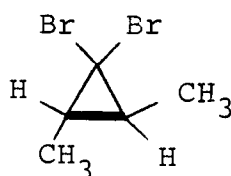
carbene reactions are slow. Based upon this assumption, Skell put forth the following statement regarding the stereochemical outcomes of carbene reactions with carbon-carbon double bonds (23).

It was suggested that the two varieties of bivalent carbon are distinguished by their singlet and triplet natures, from which derives their respective chemical properties, the singlet state species, carbenes, having non-radical properties (for the main part electrophilic), and undergoing stereospecific cis addition to olefins, the triplet state species, methylenes, undergoing non-stereospecific addition to olefins.

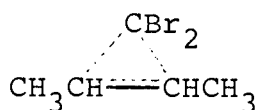
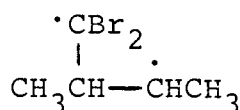
As discussed previously, the ground state of methylene is the triplet state. Regardless of this fact, it is the singlet state that is generally formed and undergoes the carbene reactions. Sensitizers, such as benzophenone, will allow for the direct formation of triplet methylene in solution (24) and it is known that the addition of nitrogen gas as a diluent in the production of methylene in the gas phase will promote spin conversion to allow the formation of a triplet enriched mixture (25).

In some of Skell's experimental work, he allowed dibromocarbene (from the basic hydrolysis of bromoform) to react with cis- and trans-2-butene in solution

(26). The reaction proceeded in a stereospecific manner. That is, cis-2-butene reacted with dibromocarbene to form cis-1,1-dibromo-2,3-dimethylcyclopropane (12) and trans-2-butene reacted with dibromocarbene to form trans-1,1-dibromo-2,3-dimethylcyclopropane (13).

1213

Skell proposed that the stereospecificity of the reaction indicated that the dibromocarbene formed was in its singlet spin state. This meant that the reaction was concerted proceeding through transition state 14 instead stepwise with the formation of a diradical species 15 (18).

1415

Skell (18) also treated cis- and trans-2-butene with methylene produced from the photolysis of diazomethane. The reaction also proceeded in a stereospecific manner, and, hence, he proposed that the

methylene produced must react as a singlet.

After Skell's work, there was some interest in the effect that reaction conditions had upon the formation of singlet versus triplet methylene. One point that became clear is that triplet methylene was quenched in the presence of oxygen gas, and that in the presence of oxygen all methylene would react as a singlet in the gas phase (16). Carr and Kistiakowsky (27) allowed trans-2-butene to react with methylene (from the photolysis of ketene) in the presence and absence of oxygen gas. They noted that there was some formation of cis-1,2-dimethylcyclopropane (resulting from the reaction of the formation of some triplet methylene) without added oxygen gas but the reaction was completely stereospecific when oxygen gas was added (i.e., only trans-1,2-dimethylcyclopropane was formed).

Carr and Kistiakowsky reported that the elimination of triplet products may be due to one of three reasons. First, it may be the result of a reaction between triplet ketene and oxygen gas. Second, it may be the result of a reaction between triplet methylene and oxygen gas. And third, it may be the result of radicals formed from triplet methylene reacting with oxygen gas.

Another aspect of Carr and Kistiakowsky's experimental work was to establish the relationship between the wavelength of light used in the photolysis

of ketene and the singlet-triplet methylene composition. Again, the methylene was allowed to react with trans-2-butene and the amount of cis-1,2-dimethylcyclopropane formed was noted. It is well known that substituted cyclopropanes can isomerize in the presence of ultraviolet light, but they reported that no isomerization of the cyclopropanes themselves would occur under the reaction conditions employed.

Carr and Kistiakowsky reported that ketene underwent photolysis in the presence of light with wavelengths of 2800 Å and 3130 Å to produce methylene which has 15% in its triplet spin state. Increasing the wavelength of light increased the yield of triplet methylene. The methylene produced from light with a wavelength of 3340 Å was 30% triplet and that produced from light with a wavelength of 3660 Å was 40% triplet.

Alkyl- and Dialkylcarbenes

Most of the discussion so far has been devoted to the formation and reactions of methylene and its halogenated derivatives. The higher carbenes will now be considered.

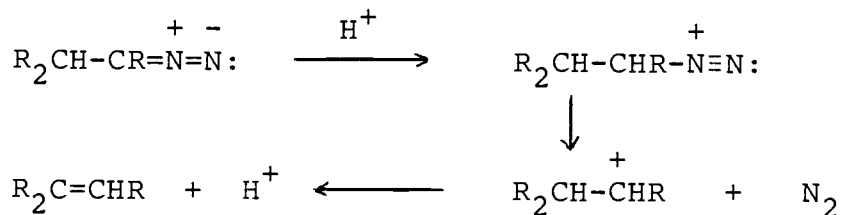
A good starting point would be to discuss the formation of the alkyl- and dialkylcarbenes. A logical choice for a precursor for the carbene would be its

corresponding diazo compound as in the production of methylene from the photolysis or pyrolysis of diazomethane. Generally speaking, however, diazo compounds are quite unstable and difficult to work with under normal laboratory conditions. With the exception of aromatic diazo compounds, most diazo compounds have not been isolated. Two notable exceptions are cyclopropyldiazomethane and dicyclopropyldiazomethane which have been prepared (28,29).

A convenient carbene precursor for general alkyl- and dialkylcarbenes are the corresponding p-toluene-sulfonylhydrazones (tosylhydrazones). Bamford and Stevens allowed nineteen different tosylhydrazones to react with alkali in ethylene glycol to form reaction products (30). A diazo intermediate could be isolated for all of the arene-substituted tosylhydrazones. It was therefore assumed that diazo compound intermediates were produced from all of the tosylhydrazone decompositions.

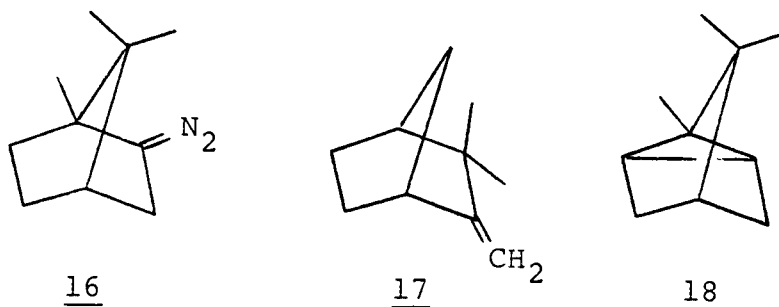
Reactions which lead to the formation of carbenes are very sensitive and reaction conditions favoring modes of decomposition other than to carbenes may need to be avoided (1). For example, the presence of proton donors often leads to the formation of carbocation formation from diazoalkanes (31). The proposed mechanism for this process is presented in Scheme III.

Since the diazoalkane intermediate is the actual



Scheme III

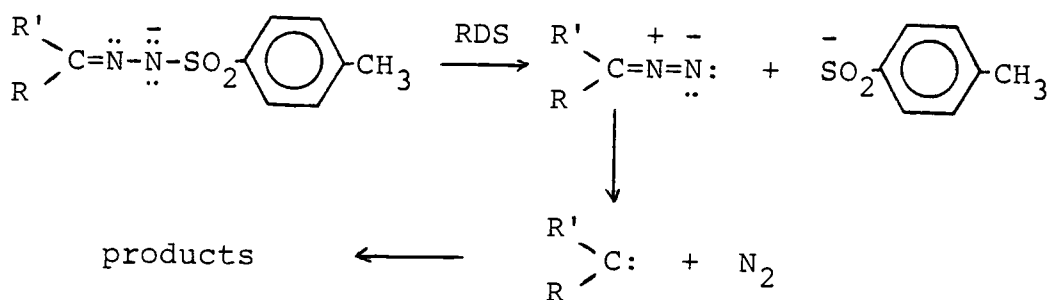
species in the decomposition of a tosylhydrazone which is capable of producing a carbene, solvents can have large effect on the mode of decomposition of a tosylhydrazone. For example, diazocamphane (16) will decompose in the presence of alkali in 2-ethoxyethanol (a protic solvent) to form a mixture which is rich in camphene (17) whereas in etherial solvents (which are aprotic) the product is mostly tricyclene (18) (31,32,33).



Dauben showed that the potassium salt of camphor tosylhydrazone underwent photolysis (Hanovia high pressure mercury lamp) to form tricyclene (18) in diglyme solvent at 25°C (33). He concluded that the mode of decomposition of the photolysis of the potassium salt of a tosylhydrazone at 25°C was similar

to that of treating a tosylhydrazone with base at elevated temperature (130 - 180°C).

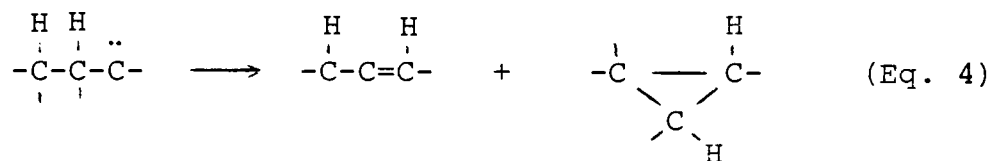
It was shown that the rate determining step in the Bamford-Stevens reaction is the unimolecular elimination of p-toluenesulfinate anion to form a secondary aliphatic diazo-compound (31). In aprotic media, this diazo-compound will decompose to form the corresponding carbene and nitrogen gas. The carbene can then react to form isolatable products. The overall mechanism is presented in Scheme IV.



Scheme IV

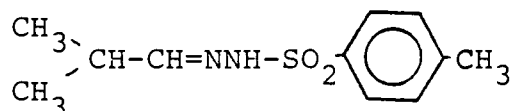
Alkyl- and dialkylcarbenes in general react predominately by insertion into the β and γ C-H bonds (Eq. 4) to give olefins and cyclopropanes, respectively (34). These insertions are mechanistically identical even though the products appear to be quite unique from each other. The insertion reaction into a β C-H is called a 1,2-hydride shift.

Apparently, the first 1,2-hydride shift from a carbene reaction was noted in 1934 by Rice and



Glasebrook (35). It was shown that the pyrolysis of diazoethane at 650°C yielded ethylene as the principle product.

A very important series of reactions involving the basic decomposition of tosylhydrazones was performed by Friedman and Shechter (32). The first reported decomposition was that of isobutyraldehyde tosylhydrazone (19) by sodium methoxide in hexadecane (C₁₆H₃₄) or diethylcarbitol ((EtOCH₂CH₂)₂O). The isolated hydrocarbon products were isobutylene (64%) and methylcyclopropane (36%).



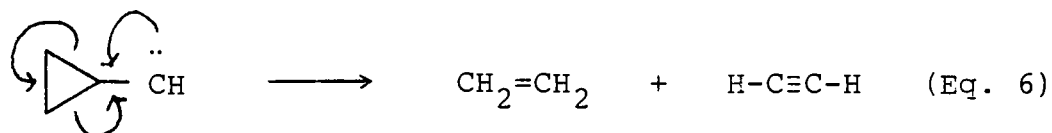
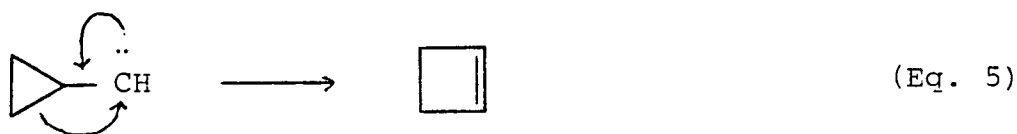
19

If a protic solvent, diethylene glycol, was used instead of hexadecane or diethylcarbitol the product composition was significantly different. The two major products were still isobutylene (65%) and methylcyclopropane (12%), but 1-butene (10%), trans-2-butene (8%), and cis-2-butene (4%) were also isolated. It was assumed that this reaction proceeded through a carbocation pathway whereas the previous

reaction (carried out in aprotic solvent) proceeded through a carbene mechanism.

In the same paper, Friedman and Shechter also presented the product result from the decomposition of several other tosylhydrazones by sodium methoxide in diethyl carbitol. The tosylhydrazones investigated were those of propionaldehyde, butyraldehyde, neovaleraldehyde, ethyl methyl ketone, and methyl tert-butyl ketone. The overall results showed that increased branching in the carbene intermediate favored the increased formation of a cyclopropane derivative over alkene formation. For example, butyraldehyde tosylhydrazone produced methylcyclopropane in 4.6% relative yield whereas neovaleraldehyde tosylhydrazone produced 1,1-dimethylcyclopropane in 92% yield.

Friedman and Shechter also investigated the chemistry of cyclopropylcarbenes by allowing the tosylhydrazones of cyclopropanecarboxaldehyde and cyclopropyl methyl ketone to decompose using sodium methoxide in diethyl carbitol (36). The cyclopropylcarbene produced from the decomposition of cyclopropanecarboxaldehyde tosylhydrazone underwent ring expansion (Eq. 5) and, to a much lesser extent, fragmentation (Eq. 6). No normal C-H insertion products were reported (methylene cyclopropane and bicyclobutane). Cyclobutene was the major product and was formed in 67% yield.

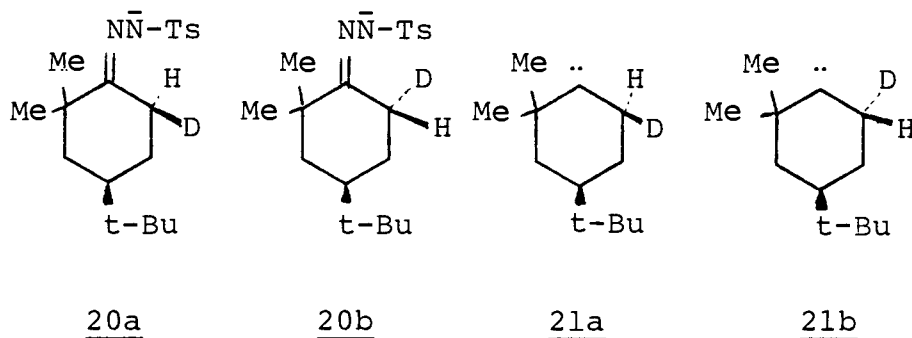


The decomposition of cyclopropyl methyl ketone tosylhydrazone yielded the ring expansion product, 1-methylcyclobutene, in even a greater yield (92%). A very minimal amount of 1,2-hydride shift product, vinylcyclopropane, was isolated (1%).

The decompositions of the tosylhydrazones of cyclobutanone and cyclopentanone were also investigated. The carbenacyclobutane produced from the decomposition of cyclobutanone tosylhydrazone undergoes ring contraction to form methylenecyclopropane (80%) and a 1,2-hydride shift to form cyclobutene (20%). The carbenacyclopentane produced from the decomposition of cyclopentanone tosylhydrazone essentially only undergoes a 1,2-hydride shift to form cyclopentene.

Of course, 1,2-hydride shifts are also well known for the larger carbene-ring systems. In 1977, Kyba and John investigated the thermal decomposition of 20a and 20b which presumably forms, respectively, carbenes 21a and 21b (37). They reported that the axial hydrogen

atom migrated somewhat more freely than the equatorial hydrogen, namely, that the H(ax)/H(eq) migration ratio is approximately 1.5.



Although the 1,2-hydride shifts studied seem to proceed without stereoelectronic control, Kyba was able to show that the carbenes investigated were flexible enough to rearrange with complete stereoelectronic control using MNDO and MNDO/3 calculations. That is, the transition state from the migration of either an axial or an equatorial hydrogen atom has the migrating hydrogen atom very nearly aligned with the empty p-orbital (38).

While it is true that only intramolecular rearrangements of alkyl- and dialkylcarbenes have been considered, these carbenes can also undergo addition reactions with double bonds if the carbenes have a sufficiently long lifetime. It has been proposed that singlet carbenes with an available internal insertion or cycloaddition possible cannot be trapped by an external reagent (39). Hence, it was assumed that typical alkyl- and dialkylcarbenes could not be made to

undergo an addition reaction with a separate alkene molecule. Moss and Fantina studied the reaction between cyclopropylchlorocarbene and five different alkenes to yield addition products in moderate to fairly good overall yields (40). This particular carbene was thought to have a fairly long lifetime due to the stabilizing effect of the chlorine atom. For example, one reaction studied was that between cyclopropylchlorocarbene and 2,3-dimethyl-2-butene. The major product, 1-chloro-1-cyclopropyl-2,2,3,3-tetramethylcyclopropane, was isolated in 78% overall yield.

Substituent and Steric Effects

Substituents present on the divalent carbon in a carbene can have a profound effect upon the relative energy levels of the singlet and triplet spin states of the carbene, its electrophilicity and nucleophilicity, and steric qualities of its reactions.

Skell and Klebe (23) reported which carbenes have singlet and which have triplet ground states for eight carbenes. These were based upon how these carbenes behaved in chemical reactions. A more recent approach is to use molecular orbital calculations. For example, Mueller and co-workers reported the singlet-triplet

energy gaps for thirty different carbenes based upon STO-3G calculations (41).

Mueller and co-workers also gave a thorough explanation of the substituent effects on the singlet-triplet energy gap. A relatively high lying π -orbital of a substituent will mix with the p-orbital of the carbene. If the substituent is a π -donor, the singlet state will be stabilized more than the triplet since the two π -electrons from the donor will be stabilized through this mixing process. This stabilizing process is not as pronounced for the triplet state since there is already an electron present in the orbital of the divalent carbon that undergoes this mixing.

The influence of a π -acceptor depends on the geometry of the carbene (Figure 3). If the geometry is

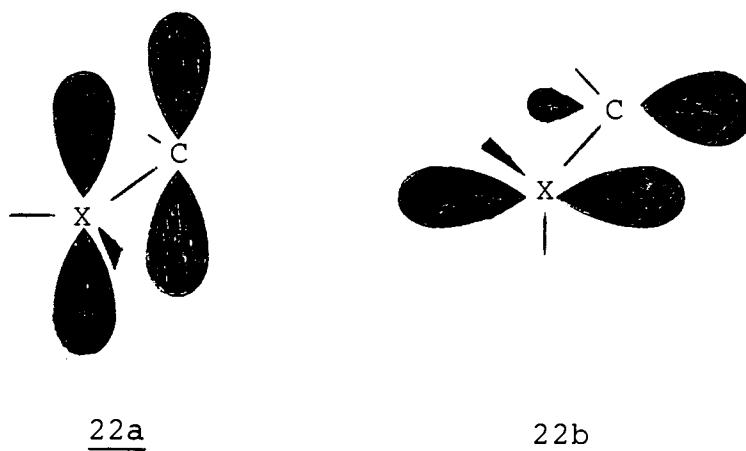


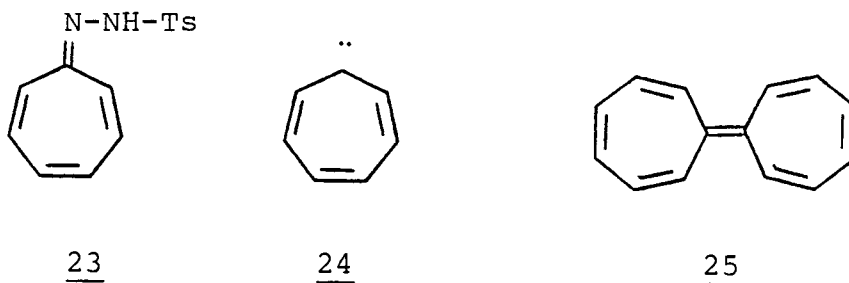
Figure 3. Orbital representations of π -acceptors on carbenes.

like that shown by 22a, only the triplet spin state can be stabilized since only a triplet carbene would have the electron in the parallel p-orbital to be stabilized. As the geometry becomes more like 22b, the singlet state will be stabilized more than the triplet state because two electrons will be stabilized by the π -accepting substituent instead of just one electron as would be with the triplet.

It has also been pointed out that π -electron donation to the divalent carbon of a carbene affects the nucleophilicity/electrophilicity of the carbene (42). Incorporation of a vacant p-orbital of a singlet carbene into a ring of such size that that it becomes part of the aromatic system will decrease the electrophilicity and increase the nucleophilicity of the carbene singlet. This is obviously due to the added electron density in the π -system which includes the formerly empty p-orbital. In addition, the triplet state of the carbene becomes destabilized because one electron would be forced to occupy a high energy anti-bonding orbital.

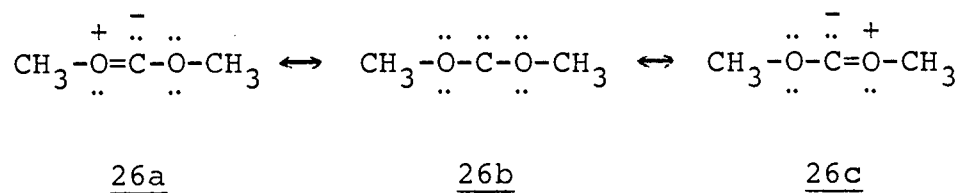
Jones and Ennis (42) allowed tropone tosylhydrazone (23) to undergo thermolysis to form cycloheptatrienyliene (24). The isolated product was the dimer of the carbene, heptafulvalene (25).

Cycloheptatrienyliene (24) does not undergo an addition reaction with "typical" electron-rich alkenes.



It does, however, undergo addition reactions readily with electron-poor alkenes such as fulmaronitrile and maleonitrile (cis and trans $N\equiv C-CH=CH-C\equiv N$). It can be readily concluded from this that the carbene is of low electrophilicity.

Dimethoxycarbene has two strong π -electron donating substituents and therefore is also expected to be a nucleophilic carbene (43). The donated electron character is perhaps best illustrated by the three resonance forms proposed, 26a-c.

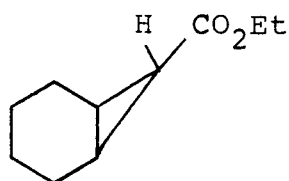
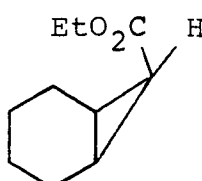


Seyferth and co-workers used a Hammett type study to show the electrophilicity of dichlorocarbene (44). Dichlorocarbene (from $\text{PhHgCCl}_2\text{Br}$) was allowed to undergo an addition reaction with styrene,

p-methylstyrene, p-fluorostyrene, p-chlorostyrene, and p-trifluoromethylstyrene. The ρ value using σ^+ constants was determined to be -0.619 ± 0.0045 . The electrophilicity of dichlorocarbene was also illustrated by its reactions with a series of aliphatic alkenes with different substitution patterns, but it was felt that steric factors were "not negligible".

Steric factors can indeed play a role in product stereochemistry in the addition of carbenes to carbon-carbon double bonds. The stereochemistry of such reactions is such that the most thermodynamically stable products may be preferred or the least thermodynamically may be preferred.

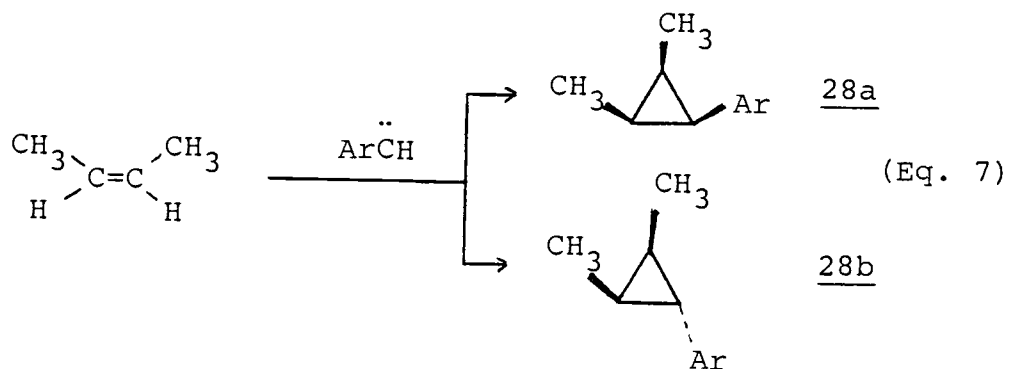
Skell and Etter (45) noted that carboethoxycarbene ($:\text{CHCO}_2\text{Et}$), from ethyl diazoacetate, adds to cyclohexene to give the more thermodynamically stable exo product (27a) in greater yield than the corresponding less thermodynamically stable endo product (27b). The product ratio for exo:endo was 1.6:1.

27a27b

If the carbethoxycarbene was obtained from ethyl diazoacetate using a copper-bronze catalyst, a copper complexed carbene is formed instead of the corresponding free carbene. This carbene complex (a carbenoid) is much more stereoselective in the addition process, forming the more thermodynamically stable exo product over the endo product in greater than a 16:1 ratio.

Perhaps a more interesting reaction of carbenes is their addition to carbon-carbon double bonds to form the less thermodynamically stable product in greater yield. Closs, Moss, and Coyle (46) produced several arene-substituted carbenes and allowed these carbenes to react with various alkenes. Of the two possible substituted cyclopropanes formed in each case, the more sterically crowded and thermodynamically less stable cyclopropane was formed preferentially. For example, the reaction between p-tolylcarbene (from the photolysis of p-tolyldiazomethane) and cis-2-butene formed the less thermodynamically stable product (28a) in greater yield than the more stable product (28b) (Eq. 7). The product ratio was 2.1:1.

Carbenes produced by treating the corresponding benzal bromide with an alkyl lithium underwent the reaction with cis-2-butene to form the less thermodynamically stable product even more preferentially. The reaction between p-tolylcarbene



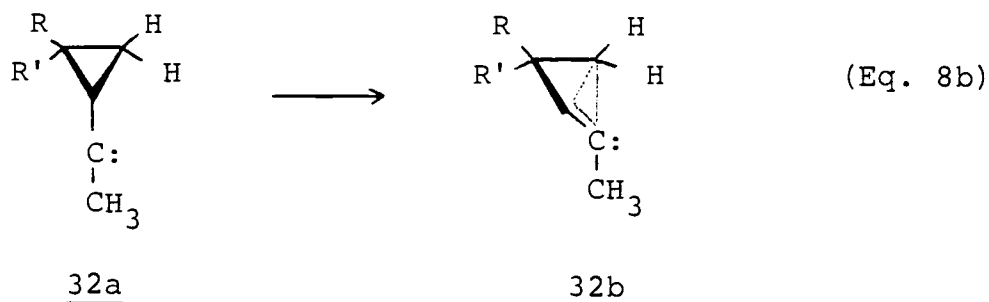
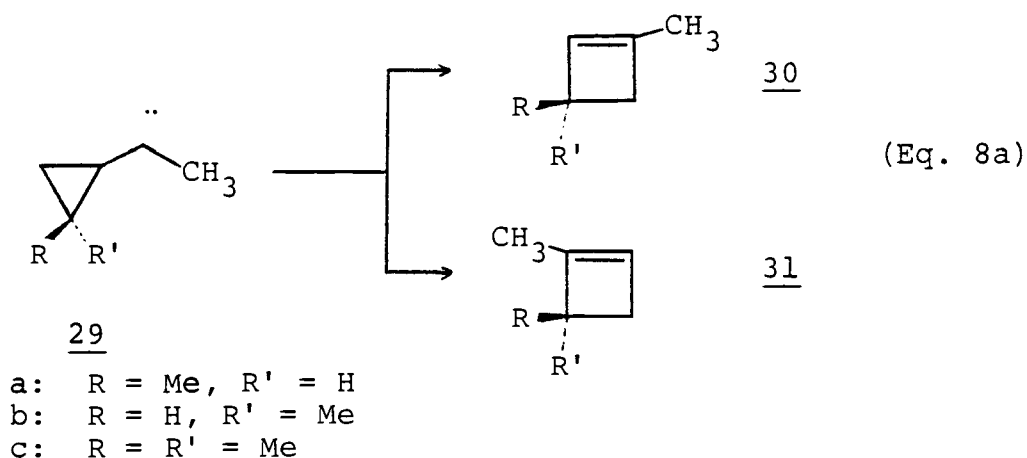
and *cis*-2-butene produced 28a and 28b in a 4.1:1 ratio if the carbene was produced from *p*-methylbenzal bromide. The difference in the magnitude of stereochemical selectivity from the different precursors was later explained by assuming that the "carbene" produced from the benzal bromide was actually an α -halolithium compound whereas the carbene produced from the photolysis of the diazo compound was a free carbene (47).

The observed contrathermodynamic stereoselectivity of the carbenes in these reactions was explained using dispersion forces (47) and molecular orbital theory (48). In either case, it must be assumed that the large arene substituent in the carbene must be well separated from the alkene fragment in the transition state so that the repulsive forces are low.

Steric effects can also play an important role in the ring expansion of cyclopropylcarbenes to form cyclobutenes. Bird, Frey, and Stevens (49) noted that carbenes 29a-c underwent ring expansion to form

cyclobutenes 30a-c and 31a-c (Eq. 8a). Cyclobutenes 30a-c were formed in greater yield than 31a-c. This meant that in each case the stronger of the two possible bonds in the three-membered ring is being broken and the reaction is sterically controlled.

The product preference can be explained by looking at the generated carbenes as shown by 32a. The divalent carbon will rotate away from the side of the cyclopropane ring which bears the substituent(s) to make the sterically less crowded transition state 32b (Eq. 8b).



INTRODUCTION

The overall goal of this research project is to study the effect that cyclopropyl groups have upon the thermodynamic characteristics of carbene production. Apparently, no study of this has been performed. The effect of cyclopropyl groups on the stabilities of carbocations and free-radicals has been well studied.

Positive charges on carbon are stabilized more by cyclopropyl groups more than other alkyl groups including vinyl groups and phenyl groups (50, 51). Roberts and Mazur (52) reported that the rate constant for the solvolysis of cyclopropylcarbinyl chloride in 50% EtOH (aq) at 50°C is 27 times that of β -methylallyl chloride and 40 times that of cyclobutyl chloride. They stated that the high reactivity of cyclopropylcarbinyl chloride is perhaps unexpected relative to cyclobutyl chloride since cyclobutyl chloride is a secondary and cyclopropylcarbinyl chloride is a primary chloride.

Roberts and co-workers proposed that the intermediate formed upon the solvolysis of cyclopropylcarbinyl chloride is the bicyclobutonium ion. This ion is resonance stabilized and has an unsymmetrical structure and its orbital representation is shown by Figure 4.

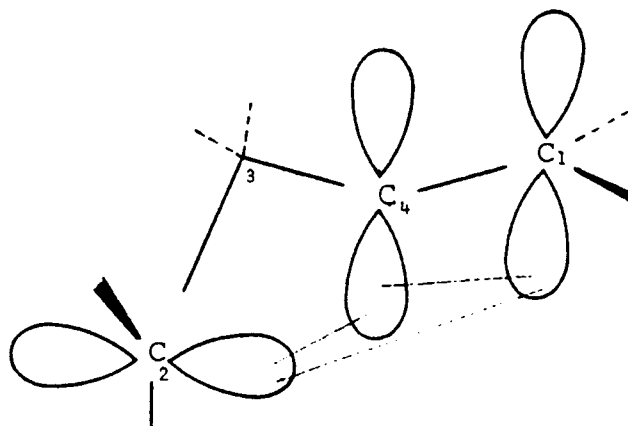


Figure 4. Orbital representation of the bicyclobutonium cation.

The bicyclobutonium ion was later refuted as the intermediate formed in the solvolysis of cyclopropylcarbinyl chloride. Schleyer and Van Dyne (53) carried out experimental work on the solvolysis of three different cyclopropylcarbinyl 3,5-dinitrobenzoates (33, 34, and 35). They noted that all three of the compounds investigated had approximately the same solvolysis rate. This result does not support the formation of a bicyclobutonium cation since the positive charge in a single bicyclobutonium cation can be delocalized to either C₂ or C₃ but not both. Hence, if the bicyclobutonium cation were the intermediate formed, the rate of solvolysis of 33 should be much greater than that of 34 or 35. The generally accepted intermediate formed in the solvolysis of cyclopropylcarbinyl chloride is now the bisected cyclopropylcarbinyl cation which has the

orbital representation given in Figure 5.

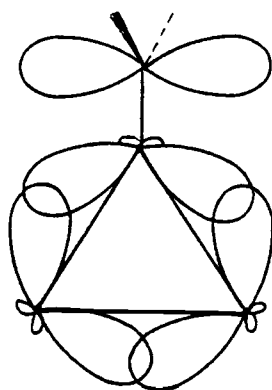
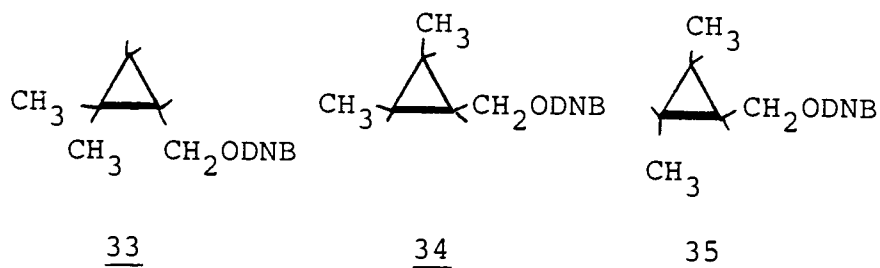
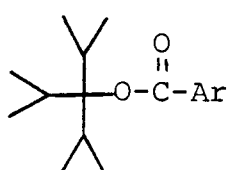
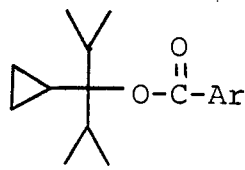
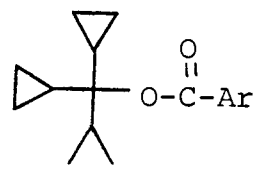


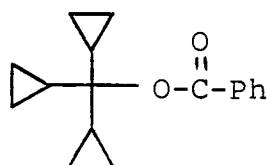
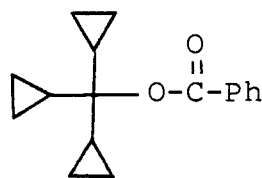
Figure 5. Orbital representation of the bisected cyclopropylcarbiny cation.

Perhaps the most illustrative works which show the stabilizing effects of cyclopropyl groups on positively charged carbon are those of Hart and Saundri (50) and Hart and Law (54). Hart and Saundri studied the solvolysis of three different p-nitrobenzoates, 36, 37, and 38, in 80% dioxane (aq) at 60°C. This particular series was studied since each solvolysis would lead to a tertiary carbocation with substituents at the trivalent carbon being of approximately the same size. The relative rates of solvolysis for 36, 37, and 38 (Ar =

p-C₆H₄-NO₂), respectively, were 1, 246, and 23,500, thus illustrating the significant stabilizing power of the cyclopropyl group.

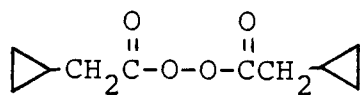
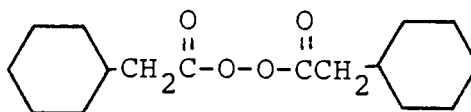
363738

Since it was of interest to determine the effect of a third cyclopropyl group and tricyclopropylcarbinyl p-nitrobenzoate was impossible to synthesize, Hart and Law (54) studied the solvolysis of two benzoates, 39 and 40, in 95% dioxane (aq) at 25°C. The relative rates of solvolysis for 39 and 40 were 1 and 1080.

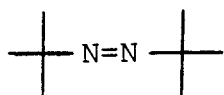
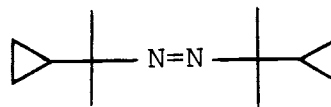
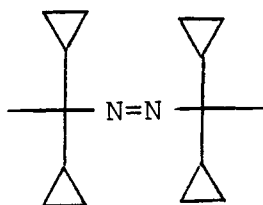
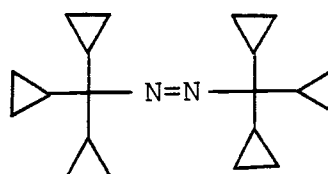
3940

There is also ample evidence for the stabilizing effects of cyclopropyl groups on free-radicals (55). For example, cyclopropaneacetyl peroxide (41a) decomposes approximately 55 times as fast as cyclohexaneacetyl peroxide (41b) in CCl₄ (56, 57). Therefore it was assumed that the cyclopropylcarbinyl free-radical

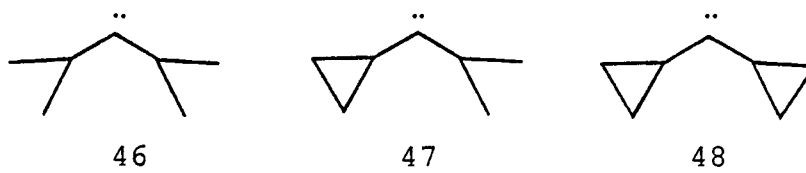
produced from 41a is more stable than the cyclohexylcarbonyl free-radical produced from 41b.

41a41b

To investigate the cumulative effects of cyclopropyl groups on free-radical stability (similar to the work investigated for carbocations by Hart and Saundri, Hart and Law), Martin and Timberlake (58) investigated the decomposition of azo compounds 42, 43, 44, and 45 in 90:10 diphenyl ether - isoquinoline at 135°C. The relative rates of decomposition for 42, 43, 44, and 45 were 1, 26.8, 362, and 2540. Therefore, as with carbocation stabilities, increased number of cyclopropyl groups will increasingly stabilize free radicals even though the effect is not as pronounced as it is with carbocations.

42434445

The experimental work on which this thesis is largely based is to study the effect of cyclopropyl groups upon the inherent stabilities of carbenes. As in the works of Hart and Saundri, Hart and Law, isopropyl groups will be the substituent present to substitute for a cyclopropyl group to keep steric factors similar for the carbenes studied. Therefore, the carbenes studied are diisopropylcarbene (46), cyclopropylisopropylcarbene (47), and dicyclopropylcarbene (48).



These carbenes were originally going to be produced from the thermal decomposition of the potassium salts of the corresponding ketone tosylhydrazones in diglyme. A complexing agent, 18-crown-6, was added to the solvent to insure solubility of the potassium salt in the relatively non-polar solvent. The nitrogen gas was collected in an inverted burette and data was collected as volume of nitrogen gas evolved versus time. This data would then be numerically analyzed by a least-squares curve fitting computer program to yield the rate constants for the first and second mechanistic step.

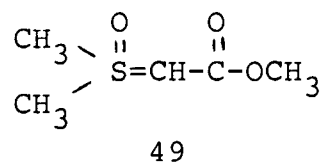
It was noted that the potassium salts of the ketone tosylhydrazones studied were not sufficiently soluble in diglyme to give satisfactory measurable amount of

nitrogen gas. This was true even in the presence of 18-crown-6. It was thought that 18-crown-6 would allow for a great enough solubility for this study since this and similar crown ethers are known for making stable complexes which are relatively soluble in non-polar media (59). For example, it was noted that potassium permanganate became soluble enough in benzene to give an intensely purple colored solution when complexed with dicyclohexano-18-crown-6. 18-crown-6 is thought to be especially good for complexing potassium cations since the center cavity of 18-crown-6 is 2.6 - 3.2 Å which is similar in size to a potassium cation, 2.66 Å (60).

A different solvent was therefore chosen in which to carry out the thermal decompositions. Because of its high dielectric constant ($\epsilon = 46.7$), dimethyl sulfoxide (DMSO) was utilized. The solubilities of the potassium salts of the ketone tosylhydrazones investigated were sufficiently soluble in DMSO to generate convenient amounts of nitrogen gas for numerical analysis of the data. With the use of DMSO as the solvent, it became unnecessary to use a complexing agent (18-crown-6) since the solubilities of the potassium salts were great enough without its use.

It should be pointed out, however, that DMSO has been shown to be capable of oxidizing carbenes. Oda and co-workers (61) allowed a series of tosylhydrazones to undergo alkaline cleavage in DMSO. In each case the

Somewhat different results are obtained between the reaction of a carbene and DMSO if the carbene is produced from an α -carbonyl or α,α -di-carbonyl diazo compound. Dost and Gosselck (62) found that for such carbenes that a stable sulfur ylide could be isolated if the carbene was generated in DMSO. For example, ylene 49 was isolated in 50 - 60% yield when $N_2=CHCOOCH_3$ was treated with DMSO and Ag_2O at $90^\circ C$.



Stable sulfur ylene such as those discussed above cannot be formed in the usual manner of treating a sulfoxide with an α -halocarbonyl compound (63). Stable sulfur ylides themselves have many valuable synthetic applications.

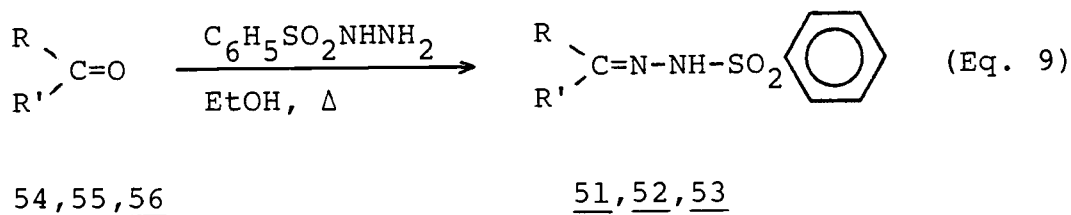
The earliest kinetics runs proved to yield rate constants which were irreproducible. It was suggested that greater reproducibility might be obtained if the two rate constants for the mechanism could be made as close as possible in numerical value (64). Assuming that the rate-determining step is the first step of the mechanism of the decomposition of a tosylhydrazone (i.e., loss of arenesulfonyl group) (31), the two rate constants could be made closer to each other in value by making the first step faster or the second step slower. Making the second

were easily synthesized and were easy handled.

Therefore, the potassium salts of benzene-sulfonylhydrazones were utilized in the experimental work as carbene precursors.

RESULTS AND DISCUSSION:
SYNTHESES AND PRODUCTS

The benzenesulfonylhydrazones utilized in this research are diisopropyl ketone benzenesulfonylhydrazone (51), cyclopropyl isopropyl ketone benzenesulfonylhydrazone (52), and dicyclopropyl ketone benzenesulfonylhydrazone (53). These benzenesulfonylhydrazones were each prepared by treating the corresponding ketone (54, 55, 56) with benzenesulfonylhydrazide in refluxing ethanol (Eq. 9). An acid catalyst was also used in the synthesis of 51.



51, 54: R = R' = isopropyl

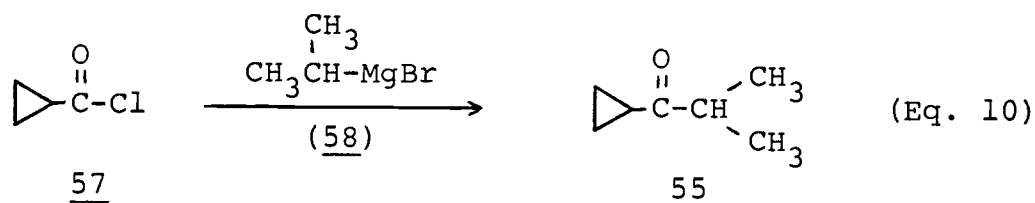
52, 55: R = isopropyl, R' = cyclopropyl

53, 56: R = R' = cyclopropyl

The NMR and IR spectra are consistent with the assigned structures of the benzenesulfonylhydrazones 51, 52, and 53. Their molecular formulae are also consistent with their percent carbon and hydrogen analysis.

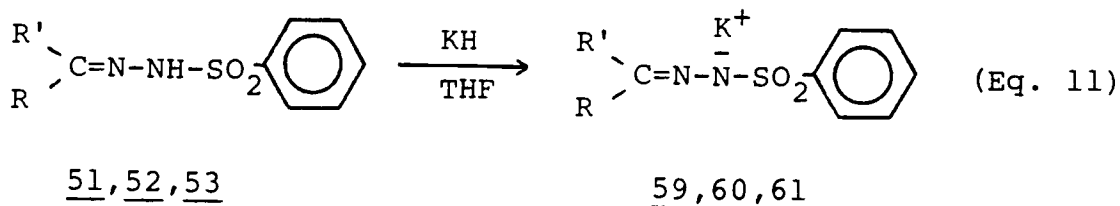
Diisopropyl ketone (54) and dicyclopropyl ketone

(56) are available commercially as is benzenesulfonylhydrazide. Cyclopropyl isopropyl ketone (55) was prepared by a Grignard reaction. Cyclopropanecarboxylic acid chloride (57) was treated with isopropylmagnesium bromide (58) in the presence of an anhydrous FeCl_3 catalyst (Eq. 10).



The NMR and IR spectra are consistent with the structure proposed for 55. 57 was prepared by treating cyclopropanecarboxylic acid chloride with thionyl chloride (SOCl_2) and 58 was prepared by treating isopropyl bromide with magnesium metal.

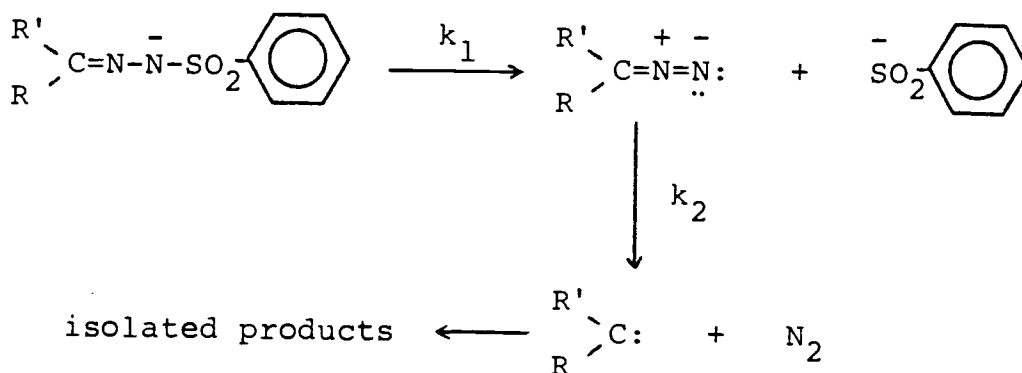
The benzenesulfonylhydrazones 51, 52, and 53 were each treated with potassium hydride in dry THF to form their corresponding potassium salts 59, 60, and 61 as shown by Eq. 11. Each benzenesulfonylhydrazone potassium salt was allowed to thermally decompose in dry DMSO. Decomposition temperatures ranged from 110 - 130°C. The mechanism for carbene formation for the three systems is assumed to be as given by Scheme VII.



51, 59: R = R' = isopropyl

52, 60: R = isopropyl, R' = cyclopropyl

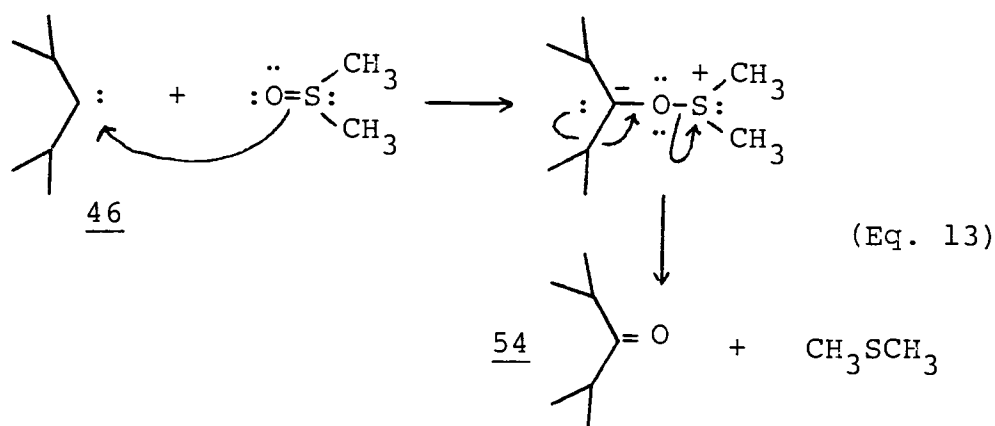
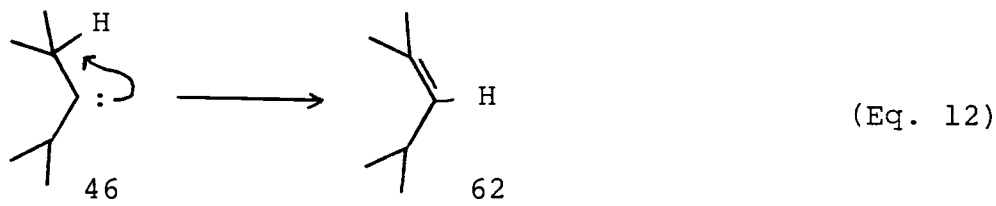
53, 61: R = R' = cyclopropyl



Scheme VII

The isolated carbene products from the thermal decomposition of 59 in DMSO were 2,4-dimethyl-2-pentene (62) and diisopropyl ketone (54). The overall yield of these products together was 60%. 62 was formed in 42% yield and 54 was formed in 18% yield. The NMR and mass spectra of 62 and 54 were consistent with the proposed structures.

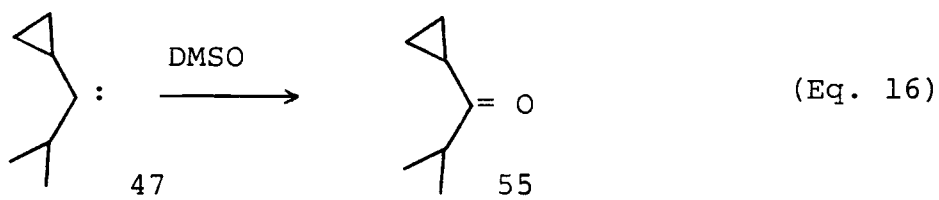
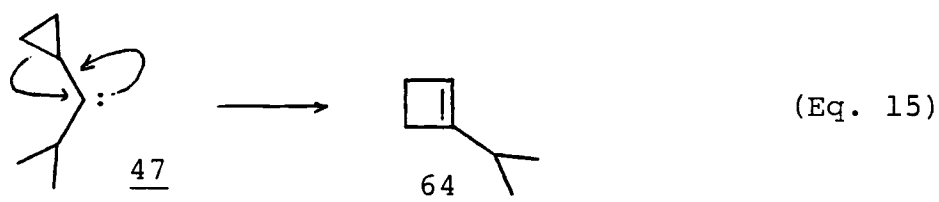
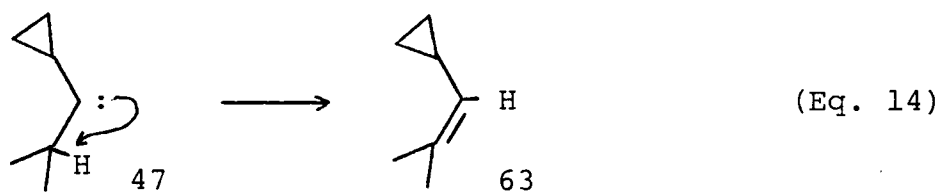
62 was formed via a 1,2-hydride shift of carbene 46 (Eq. 12) whereas 54 was formed by the carbene undergoing a reaction with DMSO (Eq. 13).



The isolated carbene products from the thermal decomposition of 60 in DMSO were 1-cyclopropyl-2-methyl-1-propene (63), 1-isopropylcyclobutene (64), and cyclopropyl isopropyl ketone (55). The total isolated yield of the three products was 56%. 63 was formed in 21% yield, 64 was formed in 16% yield, and 55 was formed in 19% yield.

63 was formed via a 1,2-hydride shift of carbene 17 (Eq. 14) whereas 64 was formed by ring expansion of the carbene (Eq. 15). 55 was formed by the reaction between the carbene and DMSO (Eq. 16) and the mechanism of this formation is similar to that shown in Eq. 13.

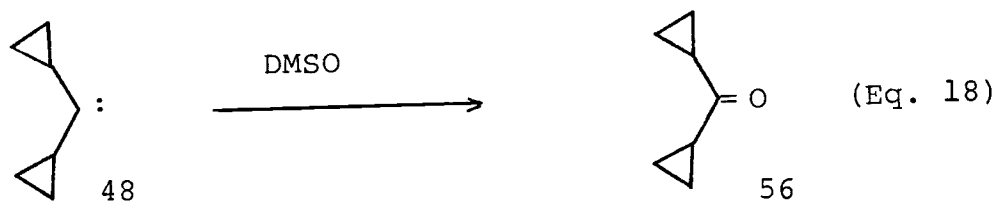
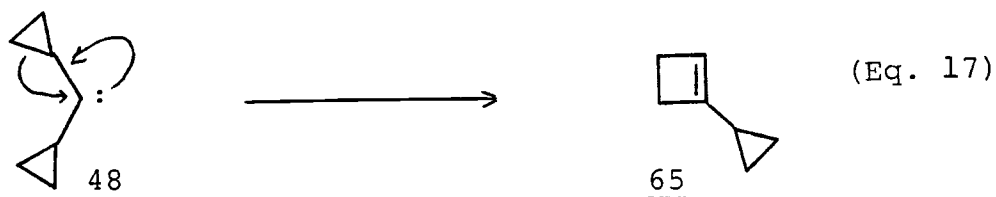
It is interesting to note that carbene 47 undergoes hydride shift and ring expansion in a 1.3:1 ratio. Hence, there does not seem to be an overwhelming preference for this carbene to rearrange by one of these mechanisms over the other.



The isolated carbene products from the thermal decomposition of 61 in DMSO were 1-cyclopropylcyclobutene (65) and dicyclopropyl ketone (56). The overall yield of these products was 58%. 65 was formed in 28% yield and 56 was formed in 30% yield. The NMR and mass spectra of the products are consistent with their assigned structures.

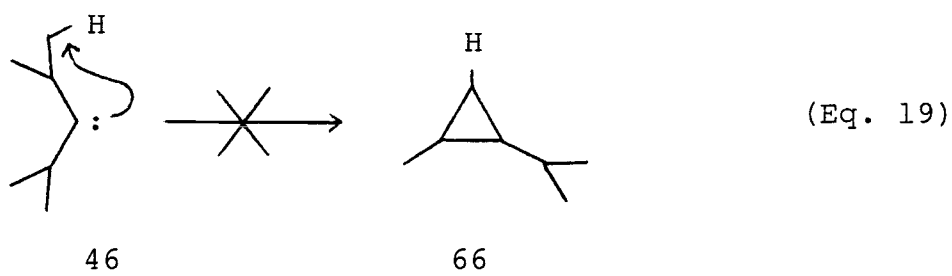
65 was formed by ring expansion of carbene 48 (Eq. 17) and 56 was formed by the reaction of the carbene with DMSO (Eq. 18) and the mechanism of this reaction with

DMSO is similar to that shown in Eq. 13.



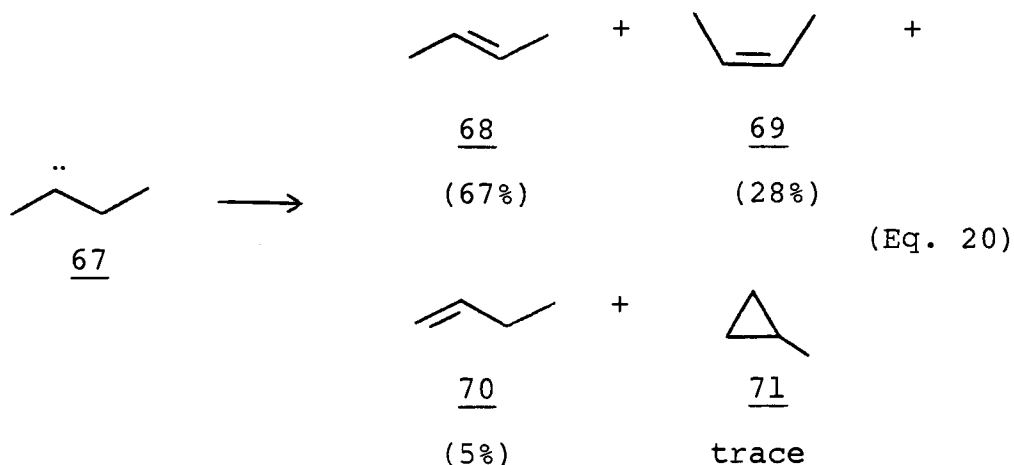
In summary, each of the carbenes studied were capable of undergoing a reaction with DMSO to form the corresponding ketone. The major difference in the reaction products from the carbenes is in their intramolecular rearrangements. Diisopropylcarbene (46) rearranged by a 1,2-hydride shift, dicyclopropylcarbene (48) rearranged by ring expansion, and cyclopropylisopropylcarbene (47) rearranged by both of these two processes.

It may seem unreasonable that diisopropylcarbene (46) should only undergo a hydride shift without any γ C-H bond insertion as shown in Eq. 19 to form 1-isopropyl-2-methylcyclopropane (66). To justify the results obtained for diisopropylcarbene (46) it will be necessary to again consider the research of Friedman and Shechter discussed earlier (32). Friedman and Shechter found that isopropylcarbene underwent a γ C-H bond



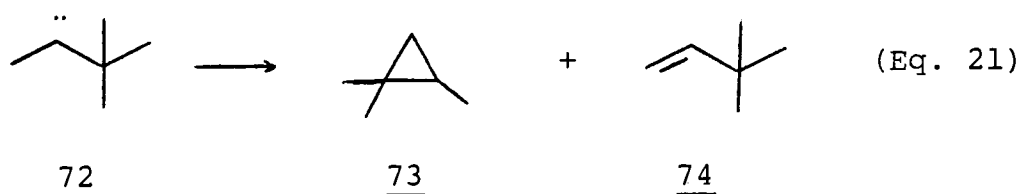
insertion to form methylcyclopropane in 33% relative yield (and isobutylene, by a 1,2-hydride shift, was formed in 67% relative yield). The fact that diisopropylcarbene (46) only undergoes a 1,2-hydride shift can be justified by the fact that the alkene formed, 2,4-dimethyl-2-pentene (62) with its internal carbon-carbon double bond is more stable than isobutylene with its terminal carbon-carbon double bond.

Added justification for the observed complete preference for 1,2-hydride shift in diisopropylcarbene (46) can also be found in the Friedman and Shechter paper. It was found that ethylmethylcarbene (67), which is similar to diisopropylcarbene (46) in the fact that they are both dialkyl-substituted carbenes, only forms a trace of γ C-H bond insertion product, methylcyclopropane (71). The two more thermodynamically stable alkenes, cis- and trans-2-butene (68 and 69), together made up 95% of the isolated reaction products. 1-butene (70), which has a terminal carbon-carbon double bond, was formed in 5% relative yield (Eq. 20).

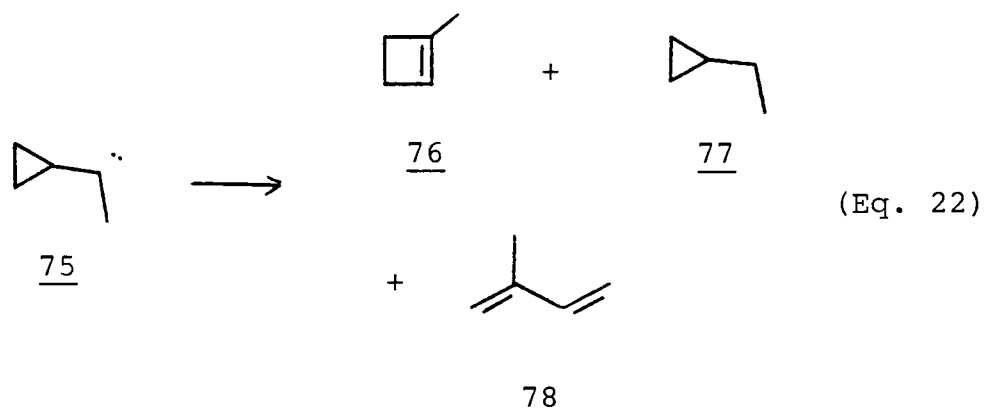


It should be pointed out, however, that Friedman and Shechter also investigated the chemistry of tert-butylmethylcarbene (72), which is also a dialkyl-substituted carbene, and found that a significant amount of γ C-H bond insertion product formed.

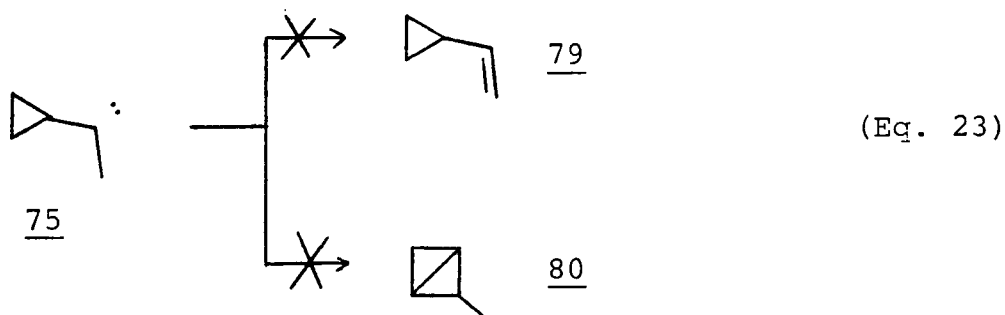
1,1,2-trimethylcyclopropane (73) was formed in 47% relative yield (Eq. 21). The 1,2-hydride shift product, 3,3-dimethyl-1-butene (74), was formed in 53% relative yield. Again note that the γ C-H insertion product is being significantly formed only when the hydride shift product is an alkene with a terminal carbon-carbon double bond.



Also recall that Friedman and Shechter performed a later work involving cyclopropylcarbenes (36). Cyclopropylmethylcarbene (75) underwent ring expansion to form 1-methylcyclobutene (76) in 92% relative yield (Eq. 22). Only 1% of the carbene rearranged by 1,2-hydride shift to form vinylcyclopropane (77). There was also



2-methyl-1,3-butadiene formed in 2% yield which probably was the result of a thermal rearrangement of 76. No product was isolated which resulted from a 1,2-hydride shift involving the cyclopropyl ring to make an exocyclic carbon-carbon double bond or a product arising from a C-H bond insertion to make a bicyclobutane (Eq. 23).



Therefore, keeping in mind that a 1,2-hydride shift on dicyclopropylcarbene would have to involve a hydrogen shift from the β position of a cyclopropyl group to make a product with a double bond exocyclic to a three-membered ring (79) and a γ C-H bond insertion would yield a bicyclobutane (80), it seems reasonable that the carbene rearranges exclusively via ring expansion to form 1-cyclopropylcyclobutene (65) (Eq. 17).

Keeping in mind that cyclopropylcarbenes undergo ring expansion readily to form cyclobutenes and that carbenes also readily undergo 1,2-hydride shifts to form double bonds which are not exocyclic to a three-membered ring, it seems reasonable that cyclopropylisopropylcarbene (47) undergoes both ring expansion to form 1-isopropylcyclobutene (64) and a 1,2-hydride shift to form 1-cyclopropyl-2-methyl-1-propene (63) as shown in Eqs. 15 and 14. As before, γ C-H bond insertion to form a new cyclopropane ring does not occur because of the possibility of forming a product with an internal carbon-carbon double bond.

RESULTS AND DISCUSSION:

KINETICS

The potassium salts of diisopropyl ketone benzene-sulfonylhydrazone (59), cyclopropyl isopropyl ketone benzenesulfonylhydrazone (60), and dicyclopropyl ketone benzenesulfonylhydrazone (61) were each allowed to undergo thermolysis in dry DMSO. In each thermolysis a known amount of the potassium salt was added to the DMSO at the thermolysis temperature in the thermolysis apparatus (see Experimental section). The decomposition of the salt was monitored by recording the volume of nitrogen gas evolved versus time as data for each of the thermolyses.

The collected data (volume of N_2 evolved versus time) were analyzed numerically by using PCNONLIN, a non-linear least squares curve-fitting computer program, to find the best estimate for the two rate constants, k_1 and k_2 , for the first two steps of the mechanism of the thermolysis. The computer program utilized the Nelder-Mead algorithm. The mechanism involved is shown in Scheme VII (p. 48).

The nitrogen gas is a product of the second step of the mechanism. Hence, the numerical analysis used is based upon an equation which relates the amount of product produced at the end of two consecutive first order steps to the two rate constants (Eq. 24) (65).

Note the the equation also involves an $[A]_0$ term. This term represents the initial concentration of potassium salt used in the thermolysis. Since the data analyzed by the computer program were entered in terms of the volume of N_2 gas instead of moles, the $[A]_0$ term involved here will actually represent the volume of nitrogen gas which could be produced from the initial amount of potassium salt utilized.

$$[C] = \frac{[A]_0}{k_2 - k_1} \left[k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t}) \right]$$

(Eq. 24)

For the purposes of this research, $[C]$ = volume of nitrogen gas evolved at time t (measured in sec), $[A]_0$ = the final volume of nitrogen gas produced by the end of the reaction, and k_1 and k_2 are the previously defined rate constants. $[C]$ versus t is the experimental data and the computer program estimates the best value for $[A]_0$, k_1 , and k_2 .

It is the value of the second rate constant, k_2 , for each thermolysis which is of particular interest. This rate constant is the one which governs the formation of the carbene (produced simultaneously with the nitrogen gas).

The thermolyses of the potassium salts were carried

out at 110, 115, 120, 125, and 130°C. One trial was carried out for each salt at each temperature except at 120°C where three trials were carried out and a standard deviation determined for the numerical values of the rate constants. Another exception is that three trials were carried out at each temperature for the thermolysis of 60, but in the error analysis for the activation parameters to be determined later, the standard deviation for the rate constant at 120°C is the one which will be used.

Tables 1 - 15 show the data regarding the volume of nitrogen gas produced versus time. For 59 and 60, the starting mass of potassium salt used was approximately 0.30 g and that for 61 was approximately 0.50 g. It was determined experimentally that the values determined for the rate constants were independent of the starting masses of the potassium salts. The reason why two different masses were employed is that it was first thought that 0.50 g of starting material would give good statistical results, but later it was determined that 0.30 g of starting material worked just as well and using less material would allow more thermolyses to be carried out from the amount of potassium salt on hand.

For thermolyses for which three trials were made, only one of these three trials are reported in Tables 1 - 15. The calculated values of the rate constants which correspond to the data in these tables is presented in

Table 16. For thermolyses for which three trials were made, the standard deviation of the values obtained is also presented.

Close observation of Eq. 24 reveals that the values of k_1 and k_2 can be switched without changing the value for $[C]$. That is, the computer program is actually unable to distinguish between the values for k_1 and k_2 . Therefore, the value for k_1 was also determined by an independent experiment so that the two rate constant values provided by the computer program could be distinguished from each other.

The independent experiment utilized was simply to monitor the disappearance of starting potassium salt versus time. This was accomplished by withdrawing and quenching aliquots from the reaction mixture and analyzing these aliquots using HPLC (high performance liquid chromatography). The data analyzed were actually the ratios of peak areas of unreacted potassium salt (converted to original benzenesulfonylhydrazone in the quenching process) and an internal standard (N,N-dimethylaniline). This process was carried out for the thermal decomposition of the potassium salt of cyclopropyl isopropyl ketone benzenesulfonylhydrazone at 110°C and 130°C.

For a first-order process involving the disappearance of starting material A, $-d[A]/dt = k[A]$ and therefore $d[A]/[A] = -k dt$ where k is the rate constant

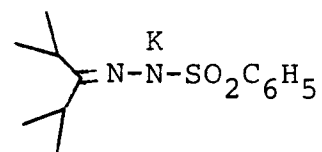
and t is time. Upon integration, this later expression becomes $\ln [A] = -k T$. Hence, a plot of $\ln [A]$ (y-axis) versus t would have a slope of $-k$.

For the procedure used here, the peak area ratio between benzenesulfonylhydrazone and internal standard will be used for the value of $[A]$. The data used in making the plots are presented in Table 17. These data were processed by Lotus 123, a computer graphics program, and the resulting graph is shown in Figure 6. Lotus 123 also was used to determine the slopes of the plots (using linear regression) and the standard deviations of the slopes.

The values obtained for the slopes of the plots gave experimental values for k_1 for the thermal decomposition of the potassium salt of cyclopropyl isopropyl ketone benzenesulfonylhydrazone as $1.24 \times 10^{-3} \pm 1.2 \times 10^{-4} \text{ s}^{-1}$ at 110°C and $6.26 \times 10^{-3} \pm 3.5 \times 10^{-4} \text{ s}^{-1}$ at 130°C . These values agree well with those recorded in Table 16. It is therefore reasonable to assume that the smaller of the two rate constants in each kinetics run provided by PCNONLIN corresponds to k_1 . Note that the first step of the mechanism of the thermal decomposition of anions of tosylhydrazones is also the rate determining step (p. 22).

TABLE 1

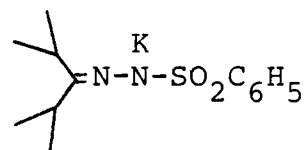
The Pyrolysis of the Potassium
Salt of Diisopropyl Ketone
Benzenesulfonylhydrazone at 110°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	1200.0	7.5
151.0	0.2	1300.0	8.3
208.0	0.4	1400.0	9.0
268.0	0.7	1500.0	9.6
312.0	0.9	1600.0	10.2
354.0	1.1	1700.0	10.8
395.0	1.4	1800.0	11.4
447.0	1.7	1900.0	11.9
495.0	2.0	2000.0	12.5
541.0	2.4	2200.0	13.4
571.0	2.7	2400.0	14.1
600.0	2.9	2600.0	15.0
657.0	3.4	2800.0	15.7
701.0	3.7	3000.0	16.3
729.0	4.0	3500.0	17.4
788.0	4.5	4000.0	18.2
860.0	5.0	4500.0	18.8
918.0	5.5	5000.0	19.2
977.0	6.0	6000.0	19.7
1060.0	6.5	7000.0	19.9
1128.0	7.0		

TABLE 2

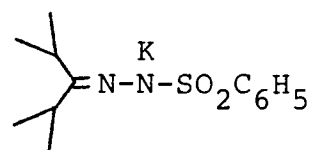
The Pyrolysis of the Potassium
Salt of Diisopropyl Ketone
Benzenesulfonylhydrazone at 115°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	895.0	9.6
70.0	0.2	936.0	10.0
107.0	0.4	970.0	10.5
143.0	0.7	1000.0	10.9
175.0	1.0	1050.0	11.4
221.0	1.5	1100.0	12.1
252.0	1.8	1150.0	12.5
295.0	2.1	1200.0	13.2
325.0	2.4	1300.0	14.2
371.0	3.1	1400.0	15.0
406.0	3.6	1500.0	15.7
444.0	4.0	1600.0	16.4
492.0	4.6	1800.0	17.7
528.0	5.1	2000.0	18.6
577.0	5.8	2200.0	19.3
624.0	6.3	2500.0	20.3
674.0	7.0	3000.0	21.2
725.0	7.6	3500.0	21.8
764.0	8.1	4000.0	22.4
816.0	8.7	5000.0	22.5
856.0	9.2		

TABLE 3

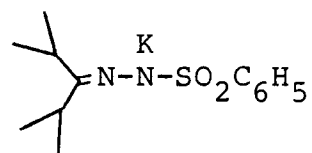
The Pyrolysis of the Potassium
Salt of Diisopropyl Ketone
Benzenesulfonylhydrazone at 120°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	650.0	10.3
63.0	0.2	691.0	10.9
107.0	0.4	722.0	11.4
129.0	0.7	760.0	11.9
160.0	1.1	795.0	12.5
180.0	1.6	850.0	13.1
200.0	1.9	876.0	13.8
225.0	2.3	910.0	14.3
249.0	2.7	950.0	14.9
275.0	3.2	1000.0	15.5
310.0	3.9	1050.0	16.1
331.0	4.4	1100.0	16.6
350.0	5.0	1150.0	17.1
381.0	5.4	1200.0	17.6
416.0	6.2	1300.0	18.2
444.0	6.8	1400.0	18.7
470.0	7.3	1500.0	19.2
499.0	7.9	1700.0	20.0
520.0	8.2	2000.0	20.9
555.0	8.7	2500.0	21.6
591.0	9.4	3000.0	21.9
620.0	9.8	4000.0	22.0

TABLE 4

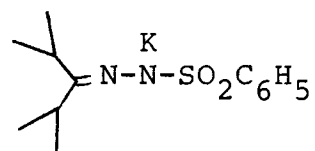
The Pyrolysis of the Potassium
Salt of Diisopropyl Ketone
Benzenesulfonylhydrazone at 125°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	500.0	9.6
55.0	0.2	529.0	10.1
84.0	0.4	566.0	10.7
106.0	0.7	602.0	11.4
124.0	1.0	631.0	11.8
141.0	1.3	672.0	12.2
165.0	1.9	717.0	12.9
184.0	2.4	752.0	13.3
205.0	2.8	802.0	13.8
223.0	3.2	850.0	14.2
247.0	3.8	900.0	14.7
270.0	4.5	946.0	15.0
295.0	5.0	1000.0	15.4
319.0	5.6	1050.0	15.7
343.0	6.2	1100.0	16.0
377.0	7.0	1200.0	16.3
399.0	7.4	1300.0	16.7
419.0	7.9	1500.0	17.2
441.0	8.5	2000.0	17.8
464.0	8.9	2500.0	18.0

TABLE 5

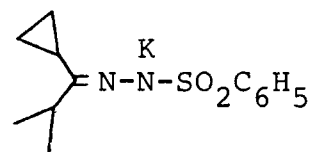
The Pyrolysis of the Potassium
Salt of Diisopropyl Ketone
Benzenesulfonylhydrazone at 130°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	343.0	11.5
38.0	0.2	364.0	12.3
54.0	0.4	383.0	12.9
68.0	0.7	403.0	13.5
83.0	1.0	427.0	14.1
95.0	1.5	450.0	14.7
110.0	2.0	473.0	15.4
123.0	2.5	499.0	15.9
139.0	3.2	526.0	16.5
152.0	3.7	552.0	17.0
167.0	4.5	584.0	17.5
184.0	5.2	615.0	18.0
200.0	6.0	646.0	18.4
216.0	6.6	700.0	19.0
231.0	7.2	800.0	20.1
258.0	8.4	900.0	20.7
275.0	9.2	1000.0	21.2
293.0	9.9	1200.0	21.9
307.0	10.4	1500.0	22.3
322.0	11.0	2000.0	22.5

TABLE 6

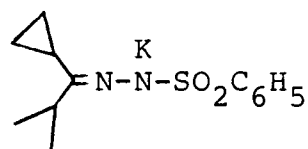
The Pyrolysis of the Potassium Salt
of Cyclopropyl Isopropyl Ketone
Benzenesulfonylhydrazone at 110°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	732.0	10.0
80.0	0.2	775.0	10.5
95.0	0.4	809.0	10.9
106.0	0.7	850.0	11.4
140.0	1.0	925.0	11.9
179.0	1.4	970.0	12.2
206.0	1.8	1000.0	12.6
224.0	2.1	1100.0	13.5
250.0	2.5	1200.0	14.2
281.0	2.9	1300.0	14.8
301.0	3.2	1400.0	15.3
336.0	3.8	1500.0	15.8
370.0	4.3	1600.0	16.2
394.0	4.8	1800.0	17.0
415.0	5.2	2000.0	17.4
446.0	5.7	2200.0	17.9
490.0	6.2	2500.0	18.5
537.0	6.7	3000.0	19.1
566.0	7.4	4000.0	19.6
600.0	8.0	5000.0	19.9
640.0	8.5	6000.0	20.1
679.0	9.1		

TABLE 7

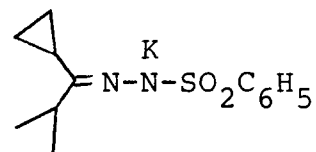
The Pyrolysis of the Potassium Salt
of Cyclopropyl Isopropyl Ketone
Benzenesulfonylhydrazone at 115°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	511.0	11.0
36.0	0.2	550.0	11.7
46.0	0.4	586.0	12.4
61.0	0.6	626.0	13.0
77.0	0.9	657.0	13.4
99.0	1.4	692.0	13.9
113.0	1.7	748.0	14.5
128.0	2.0	797.0	15.0
152.0	2.6	851.0	15.6
175.0	3.1	897.0	16.1
195.0	3.7	948.0	16.6
213.0	4.1	1000.0	17.0
238.0	4.7	1100.0	17.5
261.0	5.1	1200.0	18.0
284.0	5.9	1300.0	18.5
309.0	6.5	1400.0	19.0
343.0	7.4	1500.0	19.4
363.0	7.9	1700.0	19.9
388.0	8.5	2000.0	20.5
414.0	9.0	2500.0	20.9
447.0	9.8	3000.0	21.4
485.0	10.5	4000.0	21.7

TABLE 8

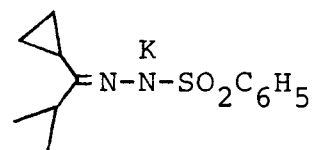
The Pyrolysis of the Potassium Salt
of Cyclopropyl Isopropyl Ketone
Benzenesulfonylhydrazone at 120°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	338.0	11.5
28.0	0.2	367.0	12.3
40.0	0.4	398.0	13.0
49.0	0.7	425.0	13.4
64.0	1.3	456.0	14.1
77.0	1.9	482.0	14.6
94.0	2.5	512.0	15.0
109.0	3.3	549.0	15.6
125.0	3.8	593.0	16.2
143.0	4.6	646.0	16.8
160.0	5.4	703.0	17.3
177.0	5.9	756.0	17.8
193.0	6.8	802.0	18.2
209.0	7.4	893.0	18.7
230.0	8.2	1000.0	19.2
254.0	9.0	1200.0	20.1
272.0	9.5	1500.0	20.5
295.0	10.4	2000.0	20.8
321.0	11.1	2500.0	21.0

TABLE 9

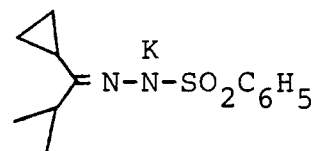
The Pyrolysis of the Potassium Salt
of Cyclopropyl Isopropyl Ketone
Benzenesulfonylhydrazone at 125°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	229.0	10.8
15.0	0.2	243.0	11.4
26.0	0.4	260.0	11.9
35.0	0.6	277.0	12.5
45.0	1.0	299.0	13.1
53.0	1.3	315.0	13.5
62.0	2.0	364.0	14.1
70.0	2.3	394.0	14.6
79.0	2.8	422.0	15.6
88.0	3.4	480.0	16.3
98.0	4.1	514.0	16.8
109.0	4.8	565.0	17.3
121.0	5.5	600.0	17.6
132.0	6.2	683.0	18.2
142.0	6.7	762.0	18.6
153.0	7.3	825.0	18.9
164.0	8.0	900.0	19.1
178.0	8.6	1000.0	19.3
189.0	9.2	1500.0	20.0
202.0	9.7	2000.0	20.1
218.0	10.4		

TABLE 10

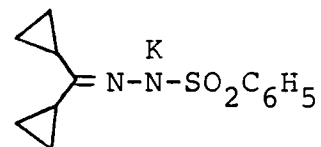
The Pyrolysis of the Potassium Salt
of Cyclopropyl Isopropyl Ketone
Benzenesulfonylhydrazone at 130°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	195.0	13.9
7.0	0.2	209.0	14.5
16.0	0.9	222.0	15.0
24.0	1.1	236.0	15.4
34.0	1.8	254.0	16.0
41.0	2.4	270.0	16.5
49.0	3.1	288.0	17.0
57.0	4.1	315.0	17.5
66.0	4.9	341.0	18.0
76.0	5.8	370.0	18.5
88.0	6.9	403.0	19.0
98.0	7.8	493.0	19.5
108.0	8.6	500.0	20.0
118.0	9.4	543.0	20.2
126.0	10.0	600.0	20.5
136.0	10.6	700.0	21.0
147.0	11.3	800.0	21.2
159.0	12.0	1000.0	21.5
170.0	12.7	1500.0	22.0
183.0	13.3		

TABLE 11

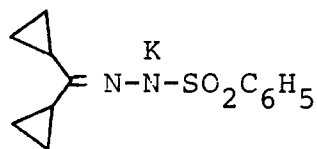
The Pyrolysis of the Potassium
Salt of Dicyclopropyl Ketone
Benzenesulfonylhydrazone at 110°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	1012.0	12.1
55.0	0.2	1047.0	12.5
74.0	0.4	1113.0	13.1
116.0	1.0	1165.0	13.6
143.0	1.4	1218.0	14.1
168.0	1.8	1329.0	15.0
195.0	2.3	1389.0	15.5
250.0	3.0	1486.0	16.0
307.0	3.8	1549.0	16.7
370.0	4.5	1658.0	17.5
399.0	4.9	1748.0	18.1
458.0	5.6	1820.0	18.5
514.0	6.3	1915.0	19.1
544.0	6.6	2129.0	20.1
571.0	7.0	2241.0	20.8
630.0	7.8	2387.0	21.5
669.0	8.3	2673.0	22.6
713.0	8.8	2820.0	23.2
773.0	9.5	3302.0	24.5
819.0	10.1	3755.0	25.5
865.0	10.6	4500.0	26.8
963.0	11.4	6000.0	28.0

TABLE 12

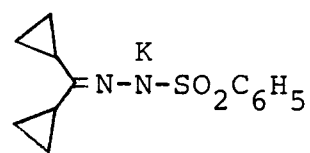
The Pyrolysis of the Potassium
Salt of Dicyclopropyl Ketone
Benzenesulfonylhydrazone at 115°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	714.0	11.1
32.0	0.2	771.0	12.0
53.0	0.4	846.0	12.9
67.0	0.6	908.0	13.5
93.0	0.9	982.0	14.4
118.0	1.3	1049.0	15.0
143.0	1.9	1115.0	15.8
175.0	2.6	1187.0	16.5
207.0	3.4	1242.0	17.0
228.0	4.0	1338.0	17.8
252.0	4.4	1394.0	18.3
275.0	4.9	1473.0	18.9
303.0	5.3	1561.0	19.5
330.0	5.8	1652.0	20.1
368.0	6.4	1755.0	20.9
410.0	7.0	1848.0	21.5
449.0	7.5	1949.0	22.1
477.0	8.0	2057.0	22.6
518.0	8.5	2271.0	23.6
574.0	9.3	2511.0	24.5
615.0	9.9	3150.0	26.5
658.0	10.5	4000.0	28.0

TABLE 13

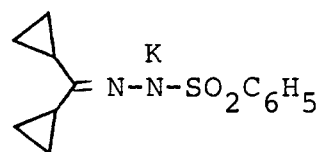
The Pyrolysis of the Potassium
Salt of Dicyclopropyl Ketone
Benzenesulfonylhydrazone at 120°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	409.0	13.1
17.0	0.2	439.0	13.8
27.0	0.4	461.0	14.4
39.0	0.8	490.0	15.2
51.0	1.3	515.0	15.7
61.0	1.8	547.0	16.4
71.0	2.2	591.0	17.3
88.0	2.9	624.0	18.0
104.0	3.6	662.0	18.6
126.0	4.6	705.0	19.3
142.0	5.2	743.0	20.0
159.0	5.9	789.0	20.6
185.0	6.6	835.0	21.2
205.0	7.3	882.0	21.9
225.0	7.9	952.0	22.6
244.0	8.5	1008.0	23.2
264.0	9.1	1109.0	24.2
285.0	9.6	1212.0	25.1
306.0	10.2	1408.0	26.3
334.0	11.0	1631.0	27.3
359.0	11.8	2047.0	28.4
386.0	12.6	3000.0	29.2

TABLE 14

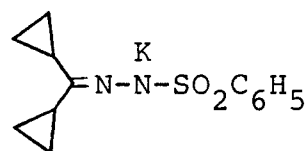
The Pyrolysis of the Potassium
Salt of Dicyclopropyl Ketone
Benzenesulfonylhydrazone at 125°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	316.0	15.1
10.0	0.3	343.0	16.1
21.0	0.6	372.0	17.1
30.0	1.1	390.0	17.6
41.0	1.9	416.0	18.4
53.0	2.6	441.0	19.1
64.0	3.5	465.0	19.9
73.0	4.2	500.0	20.7
84.0	5.0	537.0	21.5
95.0	5.6	575.0	22.4
107.0	6.5	616.0	23.1
122.0	7.1	659.0	24.0
137.0	7.7	703.0	24.7
152.0	8.4	741.0	25.4
167.0	9.1	796.0	26.0
182.0	9.7	894.0	27.1
197.0	10.4	1000.0	28.0
217.0	11.2	1210.0	29.3
232.0	11.9	1518.0	30.2
254.0	12.6	1812.0	30.7
275.0	13.5	2150.0	31.0
295.0	14.3		

TABLE 15

The Pyrolysis of the Potassium
Salt of Dicyclopropyl Ketone
Benzenesulfonylhydrazone at 130°C.



Time (s)	Volume of N ₂ evolved (mL)	Time (s)	Volume of N ₂ evolved (mL)
0.0	0.0	275.0	16.2
14.0	0.2	287.0	16.7
23.0	0.8	311.0	17.6
32.0	1.7	325.0	18.1
41.0	2.6	352.0	19.0
50.0	3.5	365.0	19.5
59.0	4.5	380.0	19.9
69.0	5.4	395.0	20.4
79.0	6.2	419.0	21.1
89.0	7.1	471.0	22.4
107.0	8.1	500.0	23.1
126.0	9.2	532.0	23.7
136.0	9.7	566.0	24.3
147.0	10.2	601.0	24.9
157.0	10.7	639.0	25.4
179.0	11.7	730.0	26.4
189.0	12.2	798.0	27.0
199.0	12.7	909.0	27.8
219.0	13.7	1030.0	28.3
230.0	14.2	1250.0	29.0
240.0	14.7	1500.0	29.4
263.0	15.6	2000.0	29.6

TABLE 16

Calculated values for the rate constants, k_1 and k_2 .
(All k values are in s^{-1} .)

Potassium salt of diisopropyl ketone benzenesulfonyl-
hydrazone (59).

<u>Temperature (°C)</u>	<u>$k_1 \times 10^3$</u>	<u>$k_2 \times 10^3$</u>
110	0.687	1.92
115	1.09	2.70
120	1.99 ± 0.03	3.18 ± 0.2
125	3.10	4.14
130	4.32	5.92

Potassium salt of cyclopropyl isopropyl ketone benzene-
sulfonyl hydrazone (60).

<u>Temperature (°C)</u>	<u>$k_1 \times 10^3$</u>	<u>$k_2 \times 10^3$</u>
110	1.20 ± 0.06	6.52 ± 1.0
115	1.78 ± 0.02	11.9 ± 2.7
120	2.90 ± 0.04	18.4 ± 0.8
125	4.23 ± 0.05	24.1 ± 1.9
130	6.13 ± 0.19	47.0 ± 2.4

Potassium salt of dicyclopropyl ketone benzenesulfonyl-
hydrazone (61).

<u>Temperature (°C)</u>	<u>$k_1 \times 10^3$</u>	<u>$k_2 \times 10^3$</u>
110	0.578	12.9
115	0.699	28.2
120	1.52 ± 0.0	48.9 ± 3.2
125	2.17	97.3
130	3.03	150.

TABLE 17

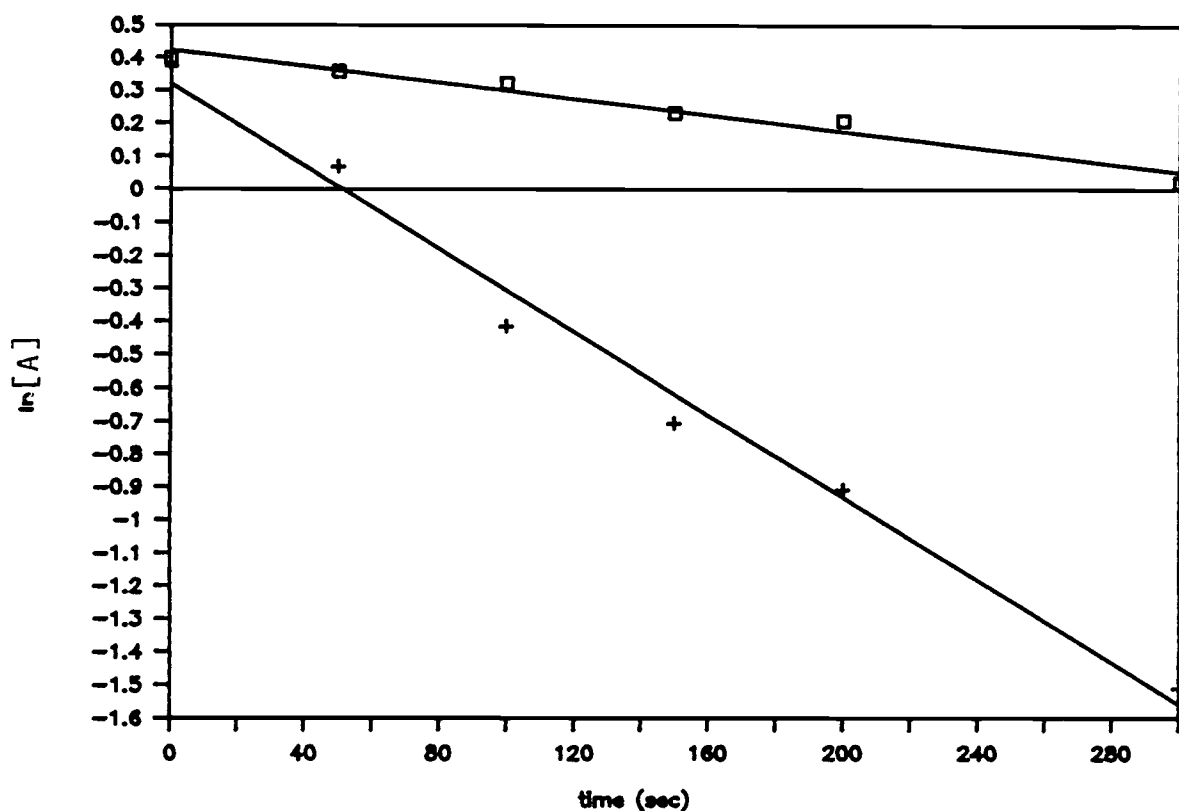
HPLC peak area ratios and their logarithms for the thermal decomposition of the potassium salt of cyclopropyl isopropyl ketone benzenesulfonylhydrazone.

110°C

<u>Time, s</u>	<u>Area ratio</u>	<u>Ln (area ratio)</u>
0	1.49	0.399
50	1.43	0.358
100	1.38	0.322
150	1.26	0.231
200	1.23	0.207
300	1.02	0.0198

130°C

<u>Time, s</u>	<u>Area ratio</u>	<u>Ln (area ratio)</u>
0	1.45	0.372
50	1.07	0.0677
100	0.661	-0.416
150	0.493	-0.707
200	0.403	-0.910
300	0.221	-1.51



□ 110°C

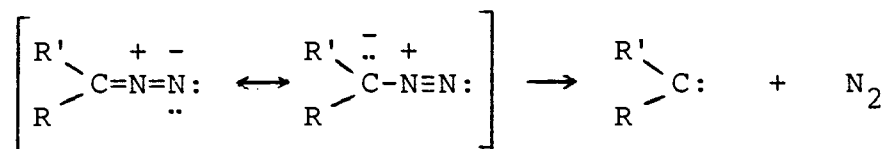
+ 130°C

Figure 6. Plots of \ln (concentration of benzenesulfonylhydrazone) versus time for the decomposition of the potassium salt of cyclopropyl isopropyl ketone benzenesulfonylhydrazone.

RESULTS AND DISCUSSION:

ACTIVATION PARAMETERS

Knowing the numerical values for the rate constants of a chemical process at different temperatures allows for the determination of the activation energy of that process. The activation energy of interest here is that of the second step of each benzenesulfonylhydrazone potassium salt thermolysis. That is, the reaction by which a diazo compound is converted to the corresponding carbene and nitrogen gas (Eq. 25).



(Eq. 25)

The activation energy is a measure of the stability of the carbene produced. In general, the lower the value of the activation energy, the greater the stability of the carbene. Actually, a more precise statement would be to say that the activation energy is a measure of the stability of the carbene with respect to the corresponding diazo compound, assuming that the transition state energy and the carbene energy are close in value.

Other activation parameters to be calculated are

state and the diazo compound. Since entropy is more precisely associated with disorder, a positive value for ΔS^\ddagger means that the transition state has less order (more disorder) than the diazo compound and a negative value for ΔS^\ddagger means that the transition state has more order (less disorder) than the diazo compound.

It would generally be assumed that the dissociation of a molecule into two separate species such as the dissociation of a diazo compound would have a positive value for ΔS^\ddagger . However, a change in the ordering of solvent molecules can have a profound effect upon the numerical value obtained for ΔS^\ddagger . An increase in the ordering of two solvent molecules can result in an entropy decrease of 30 - 40 cal/mol·K (66).

The activation energy, E_a , of the dissociation of the diazo compound is related to the rate constant for the dissociation, k_2 , by the Arrhenius equation (Eq. 26).

$$k_2 = Ae^{-E_a/RT} \quad (\text{Eq. 26})$$

and, hence,

$$\ln k_2 = -E_a/RT + \ln A \quad (\text{Eq. 27})$$

where A = frequency factor, T = absolute temperature, R = general gas constant = 1.99 cal/mol·K, E_a = activation

energy, and k_2 = rate constant for the dissociation at temperature T . Note that a plot of $\ln k_2$ (y-axis) versus $1/T$ would yield a straight line with slope $-E_a/R$. Therefore, the activation energy of the dissociation of a diazo compound can be easily calculated.

The enthalpy of activation, ΔH^\ddagger , is related to the activation energy, E_a , by Eq. 28 (67).

$$\Delta H^\ddagger = E_a - RT \quad (\text{Eq. 28})$$

In turn, the entropy of activation, ΔS^\ddagger , is related to ΔH^\ddagger by Eq. 29.

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger}{T} + R \ln \frac{k_2}{T} - 47.4 \quad (\text{Eq. 29})$$

Knowing the numerical values for ΔH^\ddagger and ΔS^\ddagger allows for the calculation of the free energy of activation using Eq. 30.

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (\text{Eq. 30})$$

The value for T , the temperature in kelvins, used for each diazo compound in Eqs. 28 - 30 will be 393 K (120°C) which is the average temperature of the five temperatures used for each thermolysis. Likewise, the value for k_2

in Eq. 29 will be the k_2 value of the corresponding diazo compound measured at 120°C.

The values for k_2 from Table 16 for the thermolyses of 59, 60, and 61 were used to plot $\ln k_2$ versus $1/T$ for each of the three benzenesulfonylhydrazone potassium salts. The data used, which are summarized in Table 18, were processed using Lotus 123 and the resulting plots for 59, 60, and 61 are shown in Figure 7. Lotus 123 was also used to determine the slope (using linear regression) and the standard deviation of the slope of the line in each case.

The slope of the line for the thermolysis of 59 is $-8.27 \times 10^3 \pm 550$ K. This slope can be used to determine the activation energy (E_a) for the production of diisopropylcarbene (46) from diisopropyldiazomethane ($E_a = -R \cdot (\text{slope})$). The value for E_a can be used to determine the enthalpy of activation, ΔH^\ddagger , using Eq. 28. The value for ΔH^\ddagger can be used to determine the entropy of activation, ΔS^\ddagger , using Eq. 29. And finally, the values for ΔH^\ddagger and ΔS^\ddagger can be used to determine the free energy of activation, ΔG^\ddagger , using Eq. 30.

In the same manner as above, the activation parameters for the production of cyclopropylisopropylcarbene (47) from cyclopropylisopropyldiazomethane can be determined from the slope of the line for the thermolysis of 60. The slope of this line is $-14.4 \times 10^3 \pm 1000$ K. Likewise, the activation parameters for the

TABLE 18

Summary of data used in making plots of $\ln k_2$ versus $1/T$.

Potassium salt of diisopropyl ketone benzenesulfonylhydrazone (59).

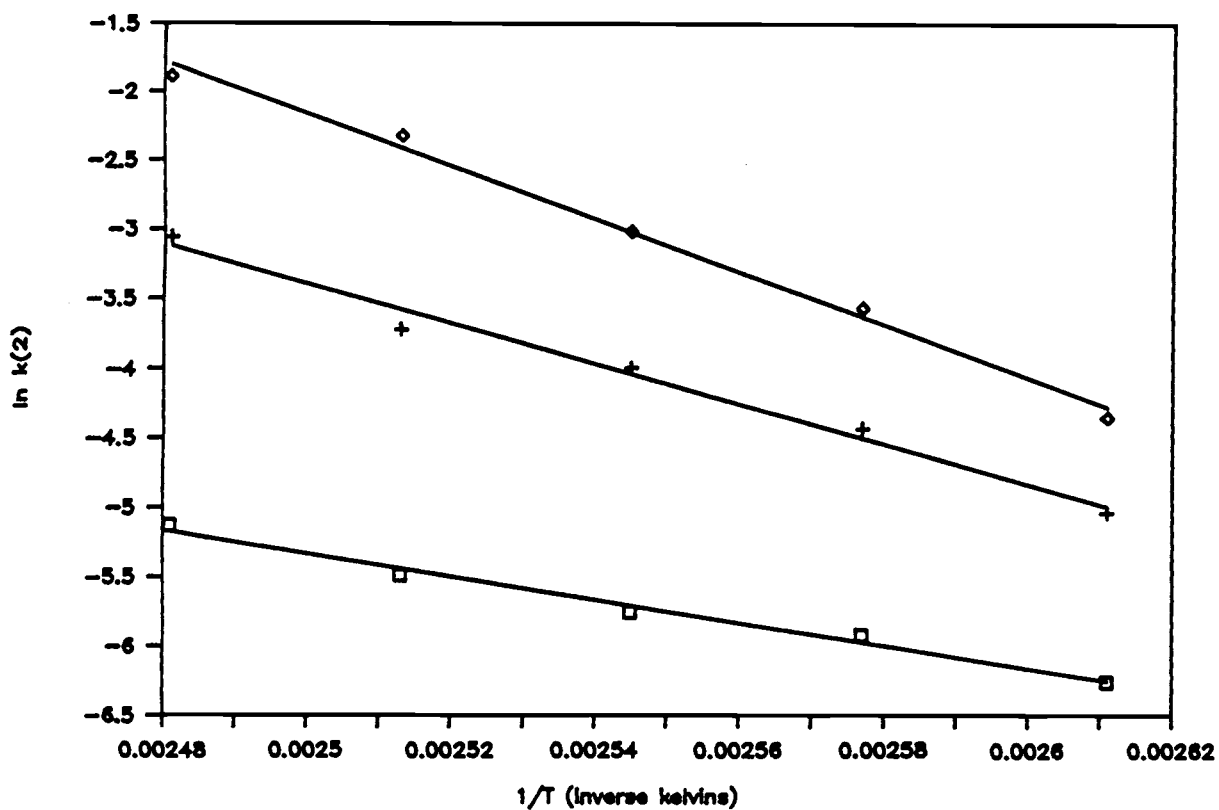
<u>T, K</u>	<u>$1/T \times 10^3, K^{-1}$</u>	<u>$k_2 \times 10^3, s^{-1}$</u>	<u>$\ln k_2$</u>
383	2.61	1.92	-6.26
388	2.58	2.70	-5.91
393	2.54	3.18	-5.75
398	2.51	4.14	-5.49
403	2.48	5.92	-5.13

Potassium salt of cyclopropyl isopropyl ketone benzenesulfonylhydrazone (60).

<u>T, K</u>	<u>$1/T \times 10^3, K^{-1}$</u>	<u>$k_2 \times 10^3, s^{-1}$</u>	<u>$\ln k_2$</u>
383	2.61	6.52	-5.03
388	2.58	11.9	-4.43
393	2.54	18.4	-4.00
398	2.51	24.1	-3.73
403	2.48	47.0	-3.06

Potassium salt of dicyclopropyl ketone benzenesulfonylhydrazone (61).

<u>T, K</u>	<u>$1/T \times 10^3, K^{-1}$</u>	<u>$k_2 \times 10^3, s^{-1}$</u>	<u>$\ln k_2$</u>
383	2.61	12.9	-4.35
388	2.58	28.2	-3.57
393	2.54	48.9	-3.01
398	2.51	97.3	-2.33
403	2.48	150.	-1.90



□ 59
+ 60
◇ 61

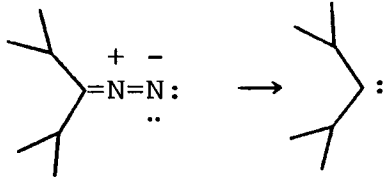
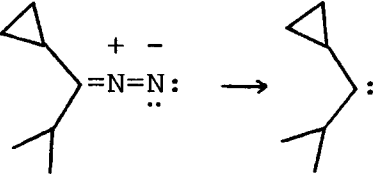
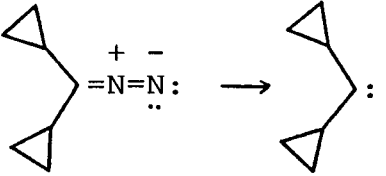
Figure 7. Plots of $\ln k_2$ versus $1/T$ for the three benzenesulfonylhydrazone potassium salts.

production of dicyclopropylcarbene, (48), from dicyclopropyldiazomethane can be determined from the slope of the line for the thermolysis of 61. The slope of this line is $-19.0 \times 10^3 \pm 900$ K.

The numerical values obtained for the activation parameters with their corresponding standard deviations are presented in Table 19. Example calculations of the parameters and the error analysis used to determine their standard deviations are presented in the appendix.

In looking at Table 19, it can be readily noted that for the series of diisopropyl- to cyclopropylisopropyl- to dicyclopropylcarbene there is an increase in the activation energy, E_a , and the enthalpy of activation, ΔH^\ddagger , for the formation of the carbene from the corresponding diazo compound. The results shown in Table 16 show that there is also an increase in the reaction rate, k_2 , at any given temperature for the same series. These observations are opposite of what would normally be anticipated. That is, a reaction with a high rate constant would normally have a low activation energy and enthalpy of activation. This apparent anomaly can be justified by noting the results for the numerical values obtained for the entropies of activation, ΔS^\ddagger . A large positive value for ΔS^\ddagger would correspond to a large increase in molecular disorder which allows for a faster reaction. The comparatively high rate of formation of dicyclopropylcarbene (48) therefore is due to the large

TABLE 19. Summary of Calculated Activation Parameters.

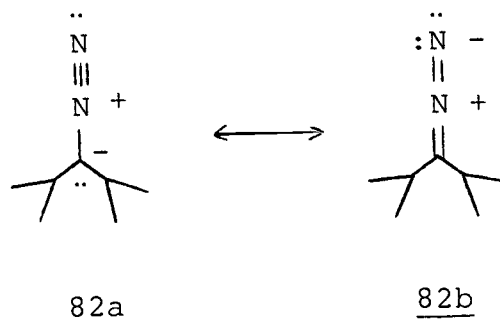
Reaction ^a	E_a (kcal/mol)	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (cal/mol·K)	ΔG^\ddagger (kcal/mol)
	16.4 ± 1.1	15.6 ± 1.1	-30.9 ± 2.8	27.7 ± 1.6
	28.5 ± 2.0	27.7 ± 2.0	3.34 ± 5.1	26.4 ± 2.8
	37.6 ± 1.8	36.8 ± 1.8	28.4 ± 4.6	25.6 ± 2.5

^aEach reaction also involves a nitrogen gas by product.

positive value for the corresponding entropy of activation, ΔS^\ddagger . Hence, the relative rates of formation of the carbene series studied are entropy controlled.

In looking at the numerical values for ΔS^\ddagger it can be noted that the entropy of formation of diisopropylcarbene (46) from diisopropyldiazomethane has a rather large negative value ($\Delta S^\ddagger = -30.9$ cal/mol·K). This result is actually not to be expected for a dissociation reaction since the transition state in such a reaction would have greater molecular disorder than the ground state. Negative entropies of activation for the formation of carbenes in DMSO have been reported previously (68) and the explanation given was that the transition state for the formation of carbenes from diazo compounds is accompanied by an overall net increase in order of the polar solvent molecules and an overall net increase in molecular order.

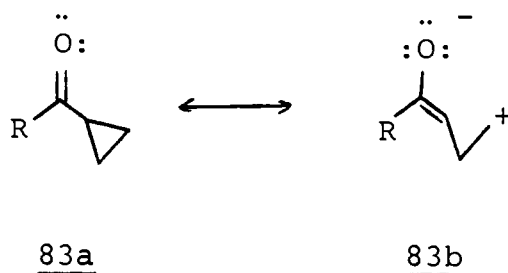
The structure of diisopropyldiazomethane can essentially be represented by resonance forms 82a and 82b. These two resonance forms are approximately of equal stability and therefore there is only a small dipole present since there is a fairly even distribution of negative charge about the positive nitrogen atom. Hence, the molecule has rather slight polarity and only a small degree of ordering of the polar DMSO solvent molecules.



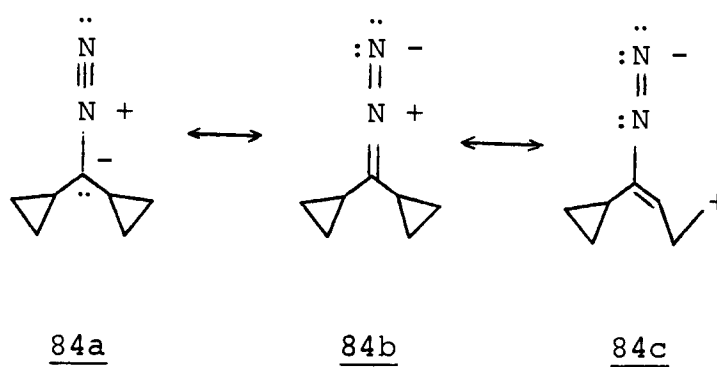
As the transition state is reached, resonance form 82b becomes much less important. This is because the carbon-nitrogen bond is breaking in the course of the dissociation and therefore the carbon-nitrogen bond length is greater in the transition state than in the diazo compound. As interatomic distances increase, the overlap integral for p- π bonding decreases drastically compared to that of σ bonding (69). Since resonance form 82b shows p- π bonding for the carbon-nitrogen bond, it becomes much less important in the transition state and the transition state more closely resembles 82a. In the transition state, therefore, the C-N-N system has a much greater dipole than in the diazo compound since the transition state resembles a single charge-separated resonance form. Because of this, the polarity of the molecule increases as the transition state is reached and this is accompanied by an increase of the ordering of the polar solvent molecules, and therefore a negative value for ΔS^\ddagger .

It can also be seen from Table 19 that the formation

of dicyclopropylcarbene (48) from dicyclopropyl-diazomethane has a positive value for ΔS^\ddagger . This cannot be explained by virtue of the fact that it is a dissociation reaction since the formation of diisopropylcarbene has a negative value for ΔS^\ddagger . The differences in the entropies of activation between these two carbene formations is again based upon the ordering of solvent molecules. Cyclopropyl groups can have a large influence upon the polarity of a molecular species. For example, it is noted in the Experimental section of this thesis that the retention times of diisopropyl ketone (54), cyclopropyl isopropyl ketone (55), and dicyclopropyl ketone (56) are 10.9 min., 20.9 min., and 56.0 min., respectively, under the same conditions on a polar GC column (carbowax). Hence, it can be concluded that dicyclopropyl ketone (56) is more polar than cyclopropyl isopropyl ketone (55) which is more polar than diisopropyl ketone (54). The enhanced polarities for cyclopropyl ketones show that charge-separated resonance forms such as 83b are important contributors.



In the same manner as for ketones, cyclopropyl groups might allow for additional important resonance forms in diazo compounds. If this is the case, charge-separated resonance forms such as 84c would be important contributors for dicyclopropyldiazomethane. Because of this, the diazo compound would have an enhanced polarity as observed in a cyclopropyl ketone.



As the transition state is reached, the carbon-nitrogen bond increases in length as before and the transition state will closely resemble 84a. The cyclopropyl groups then would lose their strong resonance influence and therefore the molecule would become less polar as the transition state is reached. This would be accompanied by less ordering of the polar solvent molecules and a positive value for ΔS^\ddagger .

The proposed resonance effect of the cyclopropyl groups would also explain why the formation of dicyclopropylcarbene occurs with a higher value for E_a and ΔH^\ddagger . The cyclopropyl groups would stabilize the

diazo compound more than they would the transition state and therefore more energy would be needed to reach the transition state. Because the presence of a cyclopropyl group increases both ΔH^\ddagger and ΔS^\ddagger , the overall change in ΔG^\ddagger due to the presence of the cyclopropyl group would be small and this is also consistent with the data presented in Table 19.

EXPERIMENTAL

General.

The melting points reported were determined using a Buchi melting point apparatus. Melting and boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer 727B apparatus. The spectra of solids were obtained using KBr pellets and those of liquids were obtained in CCl_4 solution using NaCl plates. Proton NMR spectra were recorded using a Varian Associates FT-80 and Bruker AIN-400 spectrometers (80 and 400 MHz). C-13 NMR spectra were recorded on the FT-80 spectrometer at 20 MHz. The GC - mass spectra were obtained using a Finnigan 4023 mass spectrometer equipped with a 9610 Finnigan gas chromatograph. Elemental analyses were obtained from Mic Anal Organic Microanalysis (Tuscon, Arizona). Vapor phase chromatography analyses were carried out on a Hewlett-Packard F & M Scientific 700 Laboratory Chromatograph using a thermal conductivity detector. The column utilized was a 20 ft. x 0.25 in. aluminum column containing 10% 20M carbowax on chromosorb P, 60/80 mesh. The column temperature was 110°C, the injector temperature was 200°C, and the detector temperature was 220°C.

Preparation of anhydrous FeCl₃ catalyst.

To a 200 mL round bottom flask fitted with a heating mantle was added 20 g (0.0740 mol) of finely ground FeCl₃·6H₂O and 50 mL of freshly distilled thionyl chloride. After HCl and SO₂ gas evolution had ceased, the flask was fitted with a reflux condenser and drying tube. An additional 25 mL of thionyl chloride was added to the flask and then the contents of the flask was heated at reflux for 2 h. The thionyl chloride was distilled off in vacuum to leave 8.3 g of the black anhydrous powder (0.0511 mol, 69%).

Preparation of cyclopropanecarboxylic acid chloride (57).

To a three-necked round bottom flask fitted with a reflux condenser, a drying tube, a dropping funnel, a heating mantle, and a magnetic stirrer, was added 216 mL (357 g, 3.0 mol) of freshly distilled thionyl chloride which was then brought to reflux. To the dropping funnel was added 119 mL (129 g, 1.5 mol) of cyclopropanecarboxylic acid which was added to the thionyl chloride at the rate of 1 drop per sec. After addition was complete, the reaction mixture was distilled at atmospheric pressure using a Vigreux column. The fraction at 117 - 120 °C was collected and redistilled (lit. boiling point = 119 °C). The distillate, which was not characterized but assumed to be cyclopropanecarboxylic acid chloride, has a mass of 103 g (0.99 mol,

66%).

Preparation of isopropylmagnesium bromide (58).

To a nitrogen purged and heated three-necked round bottom flask fitted with a reflux condenser, a mechanical stirrer, and a drying tube was added 72.9 g (3.0 mol) of Mg shavings, which were previously washed with anhydrous ether, and 800 mL of anhydrous ether. To the dropping funnel was added 123 g (1.0 mol) of isopropyl bromide dissolved in 200 mL of anhydrous ether. The flask was set into a hot water bath and the isopropyl bromide solution was added dropwise to maintain reflux. After addition was complete, the flask was heated at reflux for 2 additional hours. The mixture was filtered to remove magnesium shavings.

Preparation of cyclopropyl isopropyl ketone (55).

To a 3-liter three-necked round bottom flask fitted with a reflux condenser with drying tube, a mechanical stirrer, and a dropping funnel, was added 103 g (0.99 mol) of cyclopropanecarboxylic acid chloride (57), 900 mL of anhydrous ether, and 1.0 g of anhydrous FeCl_3 catalyst. To the dropping funnel was added the isopropylmagnesium bromide (58) solution prepared previously, which was added to the flask dropwise with stirring. After addition was complete, the mixture was allowed to be stirred for an additional hour. Then 500

mL of 1.0 M HCl solution was added dropwise with stirring, the aqueous and organic layers were separated, and the aqueous layer extracted with two 100 mL aliquots of ether and the ether extracts added to the organic layer. The organic layer was stirred with 1500 mL of 10% NaHCO₃ solution, the layers were then separated, and the organic layer washed with 100 mL of fresh NaHCO₃ solution. The organic layer was reduced in volume on a rotovac to a volume of approximately 100 mL and dried over anhydrous MgSO₄. The ether solution was distilled and the fraction at 137 - 140 °C collected. The mass of collected cyclopropyl isopropyl ketone was 29.0 g (0.26 mole, 26%). The product has the following spectral characteristics, which are consistent with the proposed structure: ¹H-NMR (CDCl₃): δ 0.65 - 1.00 (m, 4 H, cyclopropyl protons), 1.10 (d, J = 7 Hz, 6 H, protons from two methyl groups), 1.75 - 2.00 (m, 1 H, cyclopropyl proton adjacent to carbonyl group), and 2.5 - 2.8 (septet, J = 7 Hz, 1 H, isopropyl center proton). IR: 2950 cm⁻¹ (strong), 1705 cm⁻¹ (C=O stretch, strong), 1475 cm⁻¹ (strong), 1395 cm⁻¹ (strong), 1280 cm⁻¹ (medium), 1190 cm⁻¹ (strong).

Preparation of diisopropyl ketone benzenesulfonyl-hydrazone (51).

A mixture of 8.6 g (0.05 mol) of benzenesulfonyl-hydrazide and 5.7 g (0.05 mol) of diisopropyl ketone

dissolved in 50 mL of 95% ethanol with two drops of concentrated HCl was allowed to reflux for 3 h. The reaction mixture was cooled to room temperature and then refrigerated. The crystals formed were recrystallized from 95% ethanol to yield 9.1 g (0.034 mol, 69%) of a white crystalline product which has the following spectral characteristics which are consistent with the proposed structure: $^1\text{H-NMR}$ (DMSO- d_6): δ 1.1 (two doublets, 12 H, methyl protons of isopropyl groups), 2.4 - 2.9 (m, 2 H, tertiary isopropyl hydrogens), 7.4 - 8.0 (m, 5 H, aromatic protons). IR (KBr pellet): 3200 cm^{-1} (strong, N-H stretch), 2930 cm^{-1} (strong), 1460 cm^{-1} (medium), 1340 cm^{-1} (strong), 1180 cm^{-1} (strong), 1020 cm^{-1} (medium), 940 cm^{-1} (medium). Anal. calcd. for $\text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$: C, 58.18,; H, 7.51. Found: C, 58.15; H, 7.59.

Preparation of cyclopropyl isopropyl ketone benzenesulfonylhydrazone (52).

A mixture of 8.6 g (0.05 mol) of benzenesulfonylhydrazide and 5.6 g (0.05 mol) of cyclopropyl isopropyl ketone (55) dissolved in 50 mL of 95% ethanol was allowed to reflux for 12 h. The reaction mixture was cooled to room temperature and then refrigerated. The crystals formed were recrystallized from 95% ethanol to yield 8.6 g (0.032 mol, 65%) of a white crystalline product which has the following spectral characteristics which are

consistent with the proposed structure: $^1\text{H-NMR}$
 (DMSO- d_6): δ 0.3 - 0.8 (m, 4H, cyclopropyl ring protons), 1.0 (d, $J = 10$ Hz, 6 H, methyls of isopropyl group), 1.3 - 1.5 (1 H, m, cyclopropyl ring proton adjacent to carbonyl group), 1.9 - 2.3 (m, $J = 10$ Hz, 1 H, tertiary isopropyl hydrogen), 7.4 - 8.0 (m, 5 H, aromatic protons). IR (KBr pellet): 3200 cm^{-1} (strong, N-H stretch), 2970 cm^{-1} (medium), 1630 cm^{-1} (weak), 1460 cm^{-1} (medium), 1410 cm^{-1} (medium), 1350 cm^{-1} (strong), 1180 cm^{-1} (strong), 1100 cm^{-1} (medium), 1010 cm^{-1} (medium), 960 cm^{-1} (medium).
 Anal. calcd. for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$: C, 58.55; H, 6.89. Found: C, 58.62; H, 6.81.

Preparation of dicyclopropyl ketone benzenesulfonylhydrazone (53).

A mixture of 8.6 g (0.05 mol) of benzenesulfonylhydrazide and 5.5 g (0.05 mol) of dicyclopropyl ketone (56) dissolved in 50 mL of 95% ethanol was allowed to reflux for 12 h. The reaction mixture was cooled to room temperature and then was refrigerated. The crystals formed were recrystallized from 95% ethanol to yield 6.9 g (0.026 mol, 51%) of a white crystalline product which exhibits the following spectral characteristics which are consistent with the proposed structure: $^1\text{H-NMR}$
 (DMSO- d_6): δ 0.5 - 1.0 (m, 8 H, cyclopropyl ring protons), 1.0 - 1.6 (m, 2 H, cyclopropyl ring protons

adjacent to C=N), 7.4 - 8.0 (m, 5 H, aromatic protons).
IR (KBr pellet): 3170 cm^{-1} (strong, N-H stretch), 3000 cm^{-1} (weak), 1620 cm^{-1} (medium), 1460 cm^{-1} (medium), 1420 cm^{-1} (medium), 1320 cm^{-1} (strong), 1260 cm^{-1} (medium), 1160 cm^{-1} (strong), 1100 cm^{-1} (medium), 1060 cm^{-1} (medium), 1000 cm^{-1} (medium), 950 cm^{-1} (medium). Anal. calcd. for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$: C, 59.07; H, 6.10. Found: C, 58.94; H, 6.09.

Preparation of the potassium salts of the ketone benzenesulfonylhydrazones (59, 60, 61).

Each of the three ketone benzenesulfonylhydrazones prepared (51, 52, 53) were converted into their corresponding potassium salts (59, 60, 61) using the following general procedure: 2.0 g of 35% wt./wt. KH in mineral oil (0.70 g of KH, 0.0175 mol) was washed four times with dry THF and the KH allowed to react with approximately 0.0175 mol (4.6 - 4.7 g) of the ketone benzenesulfonylhydrazone dissolved in 20 mL of dry THF. The THF solvent was removed under vacuum in a desiccator and the solid product washed with dry THF and redried under vacuum. In each case the product was obtained in greater than 90% yield and was not characterized.

Preparation of dry DMSO.

To a three-necked round bottom flask equipped with a mechanical stirrer and a drying tube (drierite) was added

approximately 800 mL of reagent grade DMSO and 10 g of calcium hydride. The mixture was allowed to stir for two days and then was distilled under vacuum. The first 100 mL of distillate was discarded and distillation was stopped when only 100 mL of material remained in the distilling flask. The 500 - 600 mL of dry DMSO obtained was stored over type-4a molecular sieves.

Thermolyses of the potassium salts of the ketone benzenesulfonylhydrazones (59, 60, 61).

The basic set-up used is shown in Figure 8 on the next page. The oil in the oil bath was first brought up to the desired temperature and then 30 mL of dry DMSO was then transferred to the flask in the bath via syringe and the stopper quickly put into place. The DMSO in the flask was allowed to stand 45 minutes in order to reach thermal equilibrium with the oil in the oil bath. The sample of potassium salt (59, 60, or 61) was then added quickly to the DMSO in the flask. For reasons previously discussed, the approximate sample sizes used were 0.3 g for 59 and 60 and 0.5 g for 61. The nitrogen gas evolved was collected in the burette over diethyl phthalate and the volume of nitrogen gas evolved versus time was recorded as data (Tables 1 - 15).

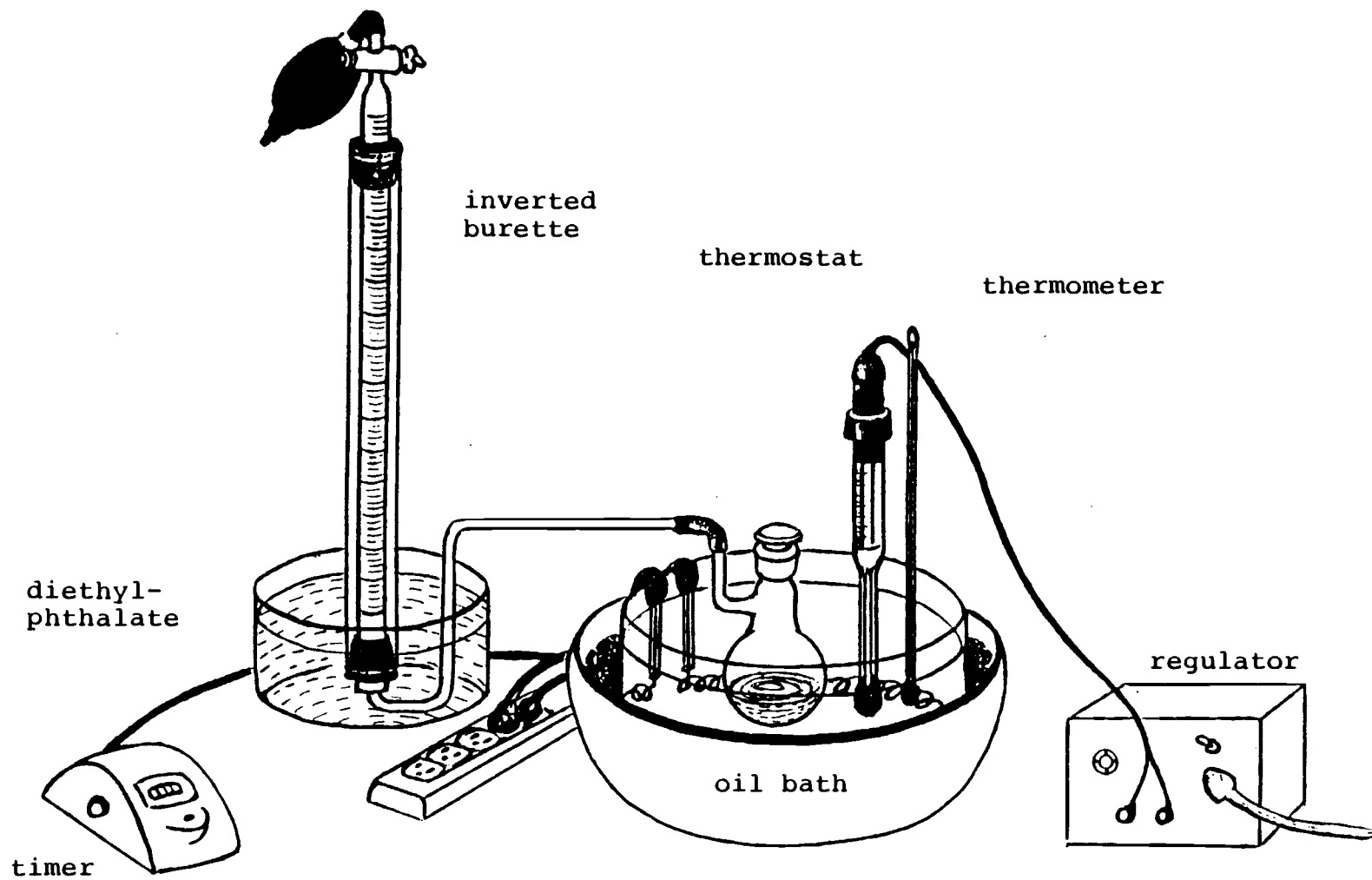


Figure 8. Apparatus used for the pyrolysis and kinetic study of the carbenes.

Work-up of the products from the thermolyses for product identification and percent yield determination.

The following general procedure was used for each benzenesulfonylhydrazone potassium salt: Approximately 1.00 g of the salt was allowed to undergo thermolysis in 70 mL of dry DMSO at 120°C. A weighed amount of an internal standard (dodecane for thermolysis of 59, decane for 60 and 61) was also present in the reaction system. Upon complete reaction, the reaction mixture was mixed with 100 mL of distilled water and the resulting solution extracted with two 100 mL aliquots of pentane. The pentane extracts were combined and washed with two 100 mL aliquots each of 10% H₂SO₄ (aq), saturated NaHCO₃ (aq), and distilled water. The pentane extract was then dried over MgSO₄ and then most of the solvent removed by simple distillation through a Vigreux column. The remaining liquid residue in each case was subjected to gas-liquid chromatography for analysis. The GC conditions employed are described at the beginning of the Experimental section.

Identification of the products obtained from the thermolysis of the potassium salt of diisopropyl ketone benzenesulfonylhydrazone (59).

The GC analysis of the reaction mixture of the thermolysis of 59 after work-up just described shows that the mixture contains two components (other than residual

solvent and dodecane internal standard). The yields of these two products were determined by comparing their peak areas to that of the dodecane (retention time = 25.9 min) and adjusting the areas to take into the account that the components each have different molecular weights (70).

The first peak, which had a retention time of 4.4 min, was identified as 2,4-dimethyl-2-pentene, 62 (42% yield). The GC - mass spectral data shows that this peak corresponds to a compound with molecular weight of 98 amu. The compound was collected by preparative GC and exhibits a $^1\text{H-NMR}$ spectrum identical to that found in the literature (71).

The second peak, which had a retention time of 10.9 min, was identified as diisopropyl ketone, 54 (18% yield). The retention time of this peak is the same as that of an authentic sample. The GC - mass spectral data shows that this peak corresponds to a compound with molecular weight of 114 amu. The compound was collected by preparative GC and exhibits a $^1\text{H-NMR}$ spectrum identical to an authentic sample.

Identification of the products obtained from the thermolysis of the potassium salt of cyclopropyl isopropyl ketone benzenesulfonylhydrazone (60).

The GC analysis of the reaction mixture obtained from the thermolysis of 60 after work-up shows shows that

the mixture contains three components (other than residual solvent or decane internal standard). Percent yields of the products were determined using decane (retention time = 11.1 min) as the internal standard and following the procedure described for the product identification for the thermolysis of 59.

The first product peak, which had a retention time of 5.3 min, was identified as 1-isopropylcyclobutene, 64 (16% yield). The GC - mass spectral data show that this peak corresponds to a compound with molecular weight of 96 amu. The compound was collected by preparative GC and exhibits a $^1\text{H-NMR}$ spectrum consistent with the proposed structure: δ 0.95 (d, $J = 12$ Hz, 6 H, methyl protons of isopropyl group), 2.2 - 2.4 (m, 5 H, methylene protons of cyclobutene ring plus center proton of isopropyl group), 5.3 (s, 1 H, vinylic proton). This compound has been previously isolated (72).

The second product peak, which had a retention time of 7.3 min, was identified as 1-cyclopropyl-2-methyl-1-propene, 63 (21% yield). The GC - mass spectral data shows that this peak corresponds to a compound with molecular weight of 96 amu. The compound was collected by preparative GC and exhibits a $^1\text{H-NMR}$ spectrum identical to that described in the literature (73).

The third product peak, which had a retention time of 20.9 min, was identified as cyclopropyl isopropyl ketone, 55 (19% yield). The retention time of this peak

is the same as that of synthetic cyclopropyl isopropyl ketone. The GC - mass spectral data show that this peak corresponds to a compound with molecular weight of 112 amu. The compound was collected by preparative GC and exhibits a $^1\text{H-NMR}$ spectrum identical to the synthetic cyclopropyl isopropyl ketone prepared earlier.

Identification of the products obtained from the thermolysis of the potassium salt of dicyclopropyl ketone benzenesulfonylhydrazone (61).

The GC analysis of the reaction mixture obtained from the thermolysis of 61 after work-up shows that the mixture contains two components (other than residual solvent and decane internal standard). The percent yields of the products were determined as outlined previously.

The first product peak, which had a retention time of 9.6 min, was identified as 1-cyclopropylcyclobutene, 65 (28% yield). The GC - mass spectral data show that this peak corresponds to a compound with molecular weight of 94 amu. The compound was collected by preparative GC and exhibits a $^1\text{H-NMR}$ spectrum identical to that described in the literature (74).

The second product peak, which had a retention time of 56.0 min, was identified as dicyclopropyl ketone, 56 (30% yield). The retention time of this peak is the same as that of an authentic sample. The GC - mass spectral

data show that this peak corresponds to a compound with molecular weight of 110 amu. The compound was collected by preparative GC and exhibits a $^1\text{H-NMR}$ spectrum identical to that of an authentic sample.

Independent determination of k_1 .

The following procedure was performed for the thermal decomposition of the potassium salt of cyclopropyl isopropyl ketone benzenesulfonylhydrazone (60) at 110°C and 130°C: The thermolysis procedure was identical to that described on p. 100 except that one drop (approximately 0.02 g (2×10^{-4} mol)) of N,N-dimethylaniline was added prior to the potassium salt to serve as an internal standard. After the potassium salt had dissolved completely, 1 mL aliquots were withdrawn at 0, 50, 100, 150, 200, and 300 sec and transferred to test tubes in an ice bath. Two drops of glacial acetic acid were added to each aliquot to convert the potassium salt present into the corresponding benzenesulfonylhydrazone.

Each aliquot was then analyzed by HPLC using a Waters Associates liquid chromatograph equipped with a reversed liquid phase column (Hamilton PRP-1, 150 mm x 4.1 mm) and a Waters Associates model 440 absorbance detector. Absorbance was measured at 254 nm. The solvent used was 58% acetonitrile in water at a flow rate of 2.0 mL/min. The retention times of cyclopropyl

isopropyl ketone benzenesulfonylhydrazone (53) and N,N-dimethylaniline were 8.4 min and 12.0 min, respectively. The peak area ratios are presented in Table 17 (p. 77).

BIBLIOGRAPHY

1. Bethell, D. In "Organic Reactive Intermediates", McManus, S. P., Ed., Academic Press: New York, 1973; pp. 61-126.
2. Kirmse, W. "Carbene Chemistry"; Academic Press: New York; 1964.
3. Herzberg, G. Proc. Roy. Chem. Soc. 1961, 262A, 291-317.
4. Wasserman, E.; Kuck, V. J.; Hutton, R. S.; Yager W. A. J. Am. Chem. Soc. 1970, 92, 7491.
5. Geuther, A. Justus Liebigs Ann. Chem. 1862, 123, 121-2.
6. Hine, J. J. Am. Chem. Soc. 1950, 72, 6162-5.
7. Nef, J. U. Ann. Chem. Pharm. 1897, 298, 202-374.
8. Ward, A. M. J. Chem. Soc. 1927, 2285-95.
9. Harrison, J. F. Acc. Chem. Res. 1974, 7, 378-84.
10. Mulliken, R. S. Phys. Rev. 1932, 41, 378-84.
11. Doering, W. von E.; Hoffmann, A. K. J. Am. Chem. Soc. 1954, 76, 6162-5.
12. Foster, J. M.; Boys, S.F. Rev. Mod. Phys. 1960, 32, 305.
13. Kirkbridge, F. W.; Norrish, R. G. W. J. Chem. Soc. 1933, 119.
14. Doering, W. von E.; Buttery, R. G.; Laughlin, R. G.; Chaudhuri, N. J. Am. Chem. Soc. 1956, 78, 3224.
15. Frey, H. M. J. Am. Chem. Soc. 1958, 80, 5005-6.
16. Herzog, B. M.; Carr, Jr., R. W. J. Phys. Chem. 1967, 71, 2688-93.
17. Carr, R. W. J. Phys. Chem. 1966, 70, 1970-4.
18. Skell, P. S.; Woodworth, R. C. J. Am. Chem. Soc. 1956, 78, 4496-7.
19. Franzen, V. 141st Meeting of The American Chemical Society; Abstracts, 1962, p. 23-0.

20. Frey, H. M. Proc. Roy. Chem. Soc. 1959, 250A, 409-21.
21. Butler, J. N.; Kistiakowsky, G. B. J. Am. Chem. Soc. 1960, 82, 759-65.
22. Butler, J. N.; Kistiakowsky, G. B. J. Am. Chem. Soc. 1961, 83, 1324-6.
23. Skell, P. S.; Klebe, J. J. Am. Chem. Soc. 1960, 82, 247-8.
24. Kopecky, K. R., Hammond, G. S., Leermakers, P. A. J. Am. Chem. Soc. 1961, 83, 2397-8.
25. Frey, H. M. J. Am. Chem. Soc. 1968, 82, 5947.
26. Skell, P. S.; Garner, A. Y. J. Am. Chem. Soc. 1956, 78, 3409-11.
27. Carr, R. W.; Kistiakowsky, G. B. J. Phys. Chem. 1966, 70, 118-25.
28. Moss, H. A.; Shulman, F. C., Chem. Commun. 1966, 373.
29. Ensslin, H. M.; Hanack, M.; Angew. Chem. Int. Ed. 1967, 6, 702-3.
30. Bamford, W. R.; Stevens, T. S. J. Chem. Soc. 1952, 4735-40.
31. Powell, J. W.; Whiting, M. C. Tetrahedron. 1959, 7, 305-10.
32. Friedman, L.; Shechter, H. J. Am. Chem. Soc. 1959, 81, 5512-3.
33. Dauben, W. G.; Willey, F. G. J. Am. Chem. Soc. 1962, 84, 1497-8.
34. Kirmse, W. "Carbene Chemistry" (2nd Ed.); Academic Press, New York, 1971.
35. Rice, F. O.; Glasebrook, A. L. J. Am. Chem. Soc. 1934, 56, 741-3.
36. Freidman, L.; Shechter, H. J. Am. Chem. Soc. 1960, 82, 1002-3.
37. Kyba, E. P.; John, M. J. Am. Chem. Soc. 1977, 99, 8329-30.
38. Kyba, E. P. J. Am. Chem. Soc. 1977, 99, 8330-2.

39. Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, Jr., M.; Levin, R. H.; Sohn, M. B. in "Carbenes", Vol. 1; Jones, Jr., M.; Moss, R. A. (Eds.); Wiley: New York, 1973; p. 20.
40. Moss, R. A.; Fantina, M. E. J. Am. Chem. Soc. 1978, 100, 6788-90.
41. Mueller, P. H.; Rondan, N. G.; Honk, K. N.; Harrison, J. F.; Hooper, D.; Willen, B. H.; Liebman, J. F. J. Am. Chem. Soc. 1981, 103, 1049-52.
42. Jones, W. M.; Ennis, C. L.; J. Am. Chem. Soc. 1969, 91, 6391-7.
43. Moss, R. A. Acc. Chem. Res. 1980, 13, 58-64.
44. Seyferth, D.; Mui, J. Y.-P.; Dumrauer, R.; J. Am. Chem. Soc. 1968, 90, 6182-6.
45. Skell, P. S.; Etter, R. M. Proc. Chem. Soc. 1961, 443-4.
46. Closs, G. L.; Moss, R. A.; Coyle, J. J.; J. Am. Chem. Soc. 1962, 84, 4985-6.
47. Closs, G. L.; Moss, R. A. J. Am. Chem. Soc. 1964, 86, 4042-53.
47. Hoffmann, R.; Levin, C.S.; Moss, R.A. J. Am. Chem. Soc. 1973, 95, 629-31.
48. Bird, C. L.; Frey, H. M.; Stevens, I. D. R. Chem. Commun. 1967, 707-8.
50. Hart, H.; Saundri, J. M. J. Am. Chem. Soc. 1959, 81, 320-6.
51. Richey, Jr., H. G.; "Cyclopropylcarbonium Ions" in "Carbonium Ions", Vol. 3; Wiley, New York; 1972, pp. 1201-94.
52. Roberts, J. D.; Mazur, R. H. J. Am. Chem. Soc. 1951, 73, 2509-20.
53. Schleyer, P. v. R.; Van Dyne, G. W. J. Am. Chem. Soc. 1966, 88, 2321.
54. Hart, H.; Law, P. A. J. Am. Chem. Soc. 1964, 86, 1957-9.

55. Nonhebel, D. C.; Walton, J. C., "Free-Radical Chemistry"; Cambridge University Press: Cambridge, England; 1974.
56. Hart, H.; Wyman, D. P. J. Am. Chem. Soc. 1959, 81, 4891-6.
57. Hart, H.; Cipriani, R. A. J. Am. Chem. Soc. 1962, 84, 3697-700.
58. Martin, J. C.; Timberlake, J. W. J. Am. Chem. Soc. 1970, 92, 978-83.
59. Pedersen, C. J. J. Am. Chem. Soc. 1967, 89, 7017.
60. Hiraoka, M., "Crown Compounds: Their Characteristics and Applications"; Kodansha, Ltd., Tokyo; 1982, pp. 74-5.
61. Oda, R.; Meino, M.; Hayashi, Y. Tetrahedron Letters 1967, 25, 2363-65.
62. Dost, B. M.; Gosselck, J. Tetrahedron Letters 1970, 58, 5091-3.
63. Trost, B. M.; Melvin, Jr., L. S. "Sulfur Ylides: Emerging Synthetic Intermediates"; Academic Press: New York, 1975; p. 23.
64. Lindstrom, F. T., Oregon State University, personal communication, 1980.
65. Laidler, K. J. "Chemical Kinetics"; M^CGraw-Hill, New York: 1965; p. 323.
66. Streitwieser, Jr, A.; Heathcock, C. H. "Introduction to Organic Chemistry"; Macmillan: New York, 1985; p. 80.
67. Carey, F. A.; Sundberg, R. J. "Advanced Organic Chemistry, Part A" (2nd Ed); Plenum Press: New York, 1984; pp. 173-7.
68. Tafesh, A. M.; M.S. Thesis, Oregon State University, 1984.
69. Roberts, J. D. "Molecular Orbital Calculations"; W. A. Benjamin, Inc.: New York, 1961; p.30.
70. Eastman, R. H. J. Am. Chem. Soc. 1957, 79, 4243.
71. "The Sadtler Standard Spectra", Vol. 7, #4316; Sadtler Research Laboratory: Philadelphia, 1968.

72. Dickens, D; Frey, H. M.; Skinner, R. F. Trans. Farad. Soc. 1968, 65, 453-7.
73. Rosseau, G; Le Perchec, P.; Conia, J. M. Tetrahedron 1978, 34, 3475-82.
74. Teraji, T.; Moritani, I; Tsuda, E.; Nishida, S. J. Chem. Soc. 1971c, 3252-57.
75. Overman, R. T.; Clark, H. M. "Radioisotope Techniques"; M^CGraw-Hill: New York, 1969; pp. 108-9.

APPENDIX

APPENDIX

Calculation of Activation Parameters and Their Standard Deviations.1. Determination of E_a and σE_a .

The activation energies were all calculated using the formula, $E_a = - R \cdot m$ where $R =$ general gas constant = 1.98 cal/mol·K and $m =$ slope of the line obtained by plotting $\ln k_2$ (y-axis) versus $1/T$ (Figure 7 presented on p. 85).

Since R is a constant which is assumed to have zero standard deviation, the standard deviation of the activation energy, σE_a , is given by Eq. 31:

$$\sigma E_a = R \cdot \sigma m \quad (\text{Eq. 31})$$

where $\sigma m =$ standard deviation of the slope of the line as determined by the computer program (p. 80).

2. Determination of ΔH^\ddagger and $\sigma \Delta H^\ddagger$.

The enthalpies of activation were calculated using Eq. 28 (p. 82). Since R is a constant and T is assumed to be a constant, ΔH^\ddagger differs from E_a by a constant. Therefore, $\sigma \Delta H^\ddagger = \sigma E_a$.

3. Determination of ΔS^\ddagger and $\sigma\Delta S^\ddagger$.

The entropies of activation were calculated using Eq. 29 (p. 82). Rearranging Eq 29, it is easily possible to obtain Eq. 32:

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger}{T} + R \ln k_2 - (47.4 + R \ln T)$$

(Eq. 32)

Since $(47.4 + R \ln T)$ is a subtracted constant, it has no effect upon the standard deviation of the entropy of activation, $\sigma\Delta S^\ddagger$.

Using Eq. 33 and 34 which are general formulae for determining standard deviations of values, it is possible to derive Eq. 35 which allows for the calculation of the standard deviation of the entropy of activation (75). For quantity $Q = aX + bY$, where a and b are constants,

$$\sigma Q = [a^2(\sigma X)^2 + b^2(\sigma Y)^2]^{\frac{1}{2}} \quad (\text{Eq. 33})$$

and for quantity $Z = \ln N$,

$$\sigma Z = \frac{\sigma N}{N} \quad (\text{Eq. 34})$$

Using Eqs. 33, 34, and 32 (ignoring the parenthetical constant), it is possible to derive Eq. 35.

$$\sigma\Delta S^\ddagger = \left[\left(\frac{\sigma\Delta H^\ddagger}{T} \right)^2 + R^2 \left(\frac{\sigma k_2}{k_2} \right)^2 \right]^{1/2} \quad (\text{Eq. 35})$$

4. Determination of ΔG^\ddagger and $\sigma\Delta G^\ddagger$.

The free energies of activation were calculated using Eq. 30 (p. 82). Using Eqs. 30 and 33, it is possible to derive Eq. 36 which allows for the calculation of the standard deviations of free energies.

$$\sigma\Delta G^\ddagger = \left[(\sigma\Delta H^\ddagger)^2 + T^2 (\sigma\Delta S^\ddagger)^2 \right]^{1/2} \quad (\text{Eq. 36})$$

5. Example Calculations.

The calculations of activation parameters and their standard deviations for the formation of diisopropylcarbene (46) from diisopropyldiazomethane in the thermal decomposition of 59 will be shown here. The calculations for the other two carbenes were performed similarly.

The slope of the line for $\ln k_2$ versus $1/T$ for the thermolysis of 59 is $-8.27 \times 10^3 \pm 550$ K. Since $E_a = -R \cdot m$, we can determine E_a .

$$\begin{aligned} E_a &= -(1.98 \text{ cal/mol}\cdot\text{K})(-8.27 \times 10^3 \text{ K}) \\ &= 16.4 \times 10^3 \text{ cal/mol} = 16.4 \text{ kcal/mol.} \end{aligned}$$

Using Eq. 31,

$$\begin{aligned}\sigma E_a &= (1.98 \text{ cal/mol}\cdot\text{K})(550 \text{ K}) \\ &= 1100 \text{ cal/mol} = 1.1 \text{ kcal/mol.}\end{aligned}$$

Using Eq. 28,

$$\begin{aligned}\Delta H^\ddagger &= 16.4 \times 10^3 \text{ cal/mol} - (1.98 \text{ cal/mol}\cdot\text{K}) \\ &\quad \cdot (393 \text{ K}) \\ &= 15.6 \times 10^3 \text{ cal/mol} = 15.6 \text{ kcal/mol.}\end{aligned}$$

The value for T at 393 K was chosen because this was the average temperature used in the thermolyses.

Since $\sigma\Delta H^\ddagger = \sigma E_a$, the numerical value for $\sigma\Delta H^\ddagger$ is 1100 cal/mol = 1.1 kcal/mol.

Using Eq. 29,

$$\begin{aligned}\Delta S^\ddagger &= \left(\frac{15.5 \times 10^3 \text{ cal/mol}}{393\text{K}} \right) \\ &\quad + 1.98 \text{ cal/mol}\cdot\text{K} \left(\ln \left(\frac{3.18 \times 10^{-3}}{393} \right) \right) \\ &\quad - 47.4 \text{ cal/mol}\cdot\text{K} \\ &= -30.9 \text{ cal/mol}\cdot\text{K.}\end{aligned}$$

The value used for k_2 is the rate constant at 393 K (120°C) from Table 16 (p. 76).

Using Eq. 35,

$$\begin{aligned}\sigma\Delta S^\ddagger &= \left[\left(\frac{1100 \text{ cal/mol}\cdot\text{K}}{393 \text{ K}} \right)^2 + \right. \\ &\quad \left. (1.98 \text{ cal/mol}\cdot\text{K})^2 \left(\frac{0.2}{3.18} \right)^2 \right]^{\frac{1}{2}} \\ &= 2.8 \text{ cal/mol}\cdot\text{K}.\end{aligned}$$

Using Eq. 30,

$$\begin{aligned}\Delta G^\ddagger &= (15.6 \times 10^3 \text{ cal/mol}) \\ &\quad - (393 \text{ K}) (-30.9 \text{ cal/mol}\cdot\text{K}) \\ &= 27.7 \times 10^3 \text{ cal/mol} = 27.7 \text{ kcal/mol}.\end{aligned}$$

Using Eq. 36,

$$\begin{aligned}\sigma\Delta G^\ddagger &= \left[(1100 \text{ cal/mol})^2 + \right. \\ &\quad \left. (393 \text{ K})^2 (2.8 \text{ cal/mol}\cdot\text{K})^2 \right]^{\frac{1}{2}} \\ &= 1600 \text{ cal/mol} = 1.6 \text{ kcal/mol}.\end{aligned}$$

The numerical values for all activation parameters and their standard deviations are presented in Table 19.