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Thermal Fragmentation Of Some Cyclic Ketones And Sulfonyl Chlorides

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THERMAL FRAGMENTATION OF SOME CYCLIC

KETONES AND SULFONYL CHLORIDES

by

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Submitted in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy

/

Faculty of Graduate Studies

The University of Western Ontario

London, Canada

June, 1971

To the successor of Sherlock Holmes

who stalks the second floor of the

Chemistry Department in search of

errant graduate students.

"Hockey game or no hockey game it seems
to me Mr. Verdun that you are not tak-
ing your problems too seriously . . .
Three in a row won't do! Not at all."

April 4, 1969

ABSTRACT

This thesis comprises two projects in the thermolysis of organic

compounds characterized by low pressure and short contact time

conditions.

In the first project the ketones cyclohexanone, cycloheptanone,

cyclooctanone, cyclopentanone, 5-nonanone, and 2-hexanone were thermo-

lysed at 1000-1050°. Product analyses were carried out. Homolysis of

a β carbon-carbon bond is found to be the most important primary

dissociative process in the thermolysis of cyclohexanone. In cyclo-

heptanone, β cleavage is also found to be a major primary thermolytic

process. The products, obtained in the thermolysis of the other ketones,

suggest that β cleavage is a general process in the low pressure thermo-

lysis of alicyclic and aliphatic ketones. The thermally induced β

cleavage in ketones found in the present study contrasts with all pre-

viously reported thermal, photolytic, and electron impact induced frag-

mentations for which α cleavage is the predominant primary dissociative

process.

The other project consisted of the thermolysis at 650° and 940° of

chlorosulfonylacetic acid. In the thermolysis at 650° sulfene is pro-

duced in greater than 50% yield and is shown to be a discrete, volatile

compound that has a finite lifetime. At 940°, sulfene again appears to

be generated in good yield but it undergoes unimolecular decomposition

to formaldehyde before escaping from the thermolysis zone.

ACKNOWLEDGMENTS

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PART I

GENERAL INTRODUCTION

The thermolysis of organic compounds has been a constituent part
of chemistry for many years (I). The many refinements, in the appa-
ratus and techniques, that have been made over the years now permit
detailed examination of the decompositions, isomerizations, and elimina-
tions that compounds can be induced to undergo when subjected to heat.

Prior to 1930, the thermolyses of compounds were generally
carried out in static systems at temperatures greater than 500°, and
the decompositions were studied by product analysis. Two factors
complicated the deduction of mechanisms for the decompositions.
Firstly, because the primary products had long residence times in the
furnace, they often underwent secondary decompositions. Secondly, the
high pressures in the reactor permitted bimolecular reactions between
primary products and/or intermediates*.

In order to reduce the residence time of compounds in the furnace,
Hurd and co-workers employed a flow system in which the thermolyses
were carried out in a heated tube (2). In a typical experiment, the
temperature was 600-700°, the pressure was about 1 atm, and the residence
time of the compounds in the furnace was about 20 msec. Because the
decompositions were carried out at atmospheric pressure, complicating

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*At that time the intermediacy of free radicals was not generally
accepted.

I

bimolecular processes probably still occurred. Rice and collaborators realized that it was necessary to use low pressures in the thermolysis zone in order to minimize bimolecular processes (3). They employed a continuously evacuated quartz reactor and carried out the thermolyses at temperatures of 700-800°, at pressures of about 10 mm, and residence times of 8-20 msec. Under these conditions, cyclohexene _I_ cleanly underwent the reverse Diels-Alder reaction to give ethylene and butadiene. No free radical chain products were found. Thus, under low pressure and short contact time conditions, product analysis can generally be used in the deduction of the mechanisms of thermal decompositions.

In the last 20 years and especially in the last 5 years, significant advances have been made in the development of systems that combine a low pressure thermolysis apparatus and modern analytical instruments (4). The use of these systems has allowed the direct observation of thermally generated, transient species and has, therefore, provided a powerful probe for the elucidation of the mechanisms of thermally induced reactions.

Some of the analytical techniques, afforded by the use of instruments in conjunction with low pressure reactors, are described. If the thermolysate that emerges from the furnace is passed directly into the electron source of a mass spectrometer, direct measurement of the molecular weight and appearance potential of the thermal fragments is possible. When the appropriate optical surface is placed at the end of the furnace, the thermolysate can be isolated in a rare gas matrix at liquid helium or nitrogen temperatures. Thus, it is possible to obtain

the infrared, ultraviolet, visible, and esr spectra of the primary thermally generated species. The chemical behaviour of primary products or intermediates can be investigated by the immediate condensation of the thermolysate at liquid nitrogen temperature as it emerges from the furnace. The thermal fragments can either react at liquid nitrogen temperature or at higher temperatures when the Dewar is allowed to warm up. Alternatively, the thermolysate can be condensed with a trapping agent in a matrix at liquid nitrogen temperature. Subsequent reaction of the primary thermal fragments with the trapping agent affords adducts. Low pressure thermolysis can be used as a synthetic method to generate reactive compounds which are exceedingly difficult to obtain in ordinary solution reactions.

During the last 20 years, Lossing and collaborators have refined the coupled thermolysis mass spectrometer system (5). They have carried out extensive mass spectrometric studies on organic free radicals generated by the thermolysis of alkyl nitrites (6). Benson and co-workers have carried out precise kinetic experiments in a system that consisted of a reactor coupled with a quadrupole mass spectrometer. This procedure, called "very low pressure pyrolysis", has been used to study the equilibrium between 1,5-hexadiene 2 and two allyl radicals (7). By measuring the equilibrium constant, they have been able to calculate accurately the resonance energy of the allyl radical. The value obtained is 9.6 kcal/mole, a quantity lower than the previous estimates of 12-25 kcal/mole.

Hedaya and co-workers, in their "flash vacuum pyrolysis experiments" (FVP), have used both a mass spectrometer and the cryoscopic technique to

$\underline{1}$ $\xrightarrow{700°}$

$\underline{2}$ $\xrightleftharpoons{700°}$ 2

$\underline{3}$ CH$_2$Br $\xrightarrow{1000°}$ $\underline{4}$ ĊH$_2$ + Br·

$\underline{5}$ $\xrightarrow{800°}$ $\underline{6}$ + CO$_2$ + other products

$\underline{7}$
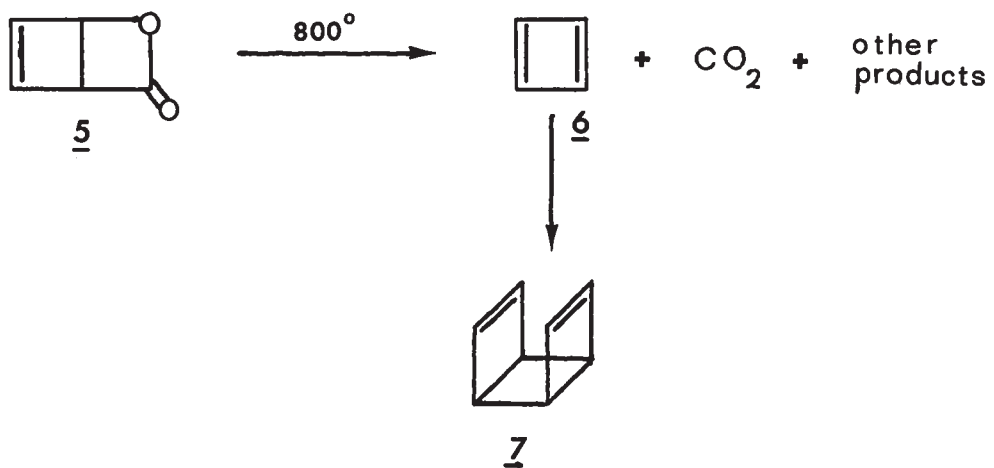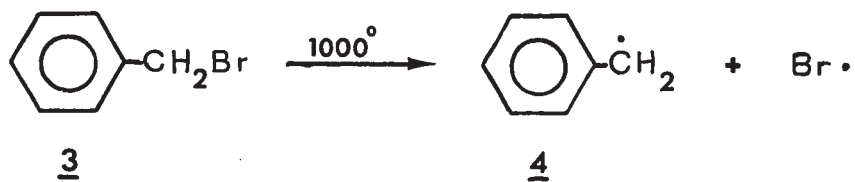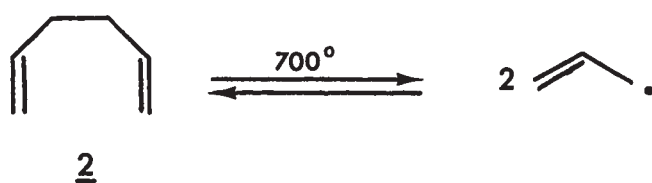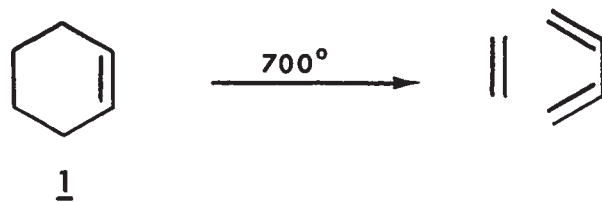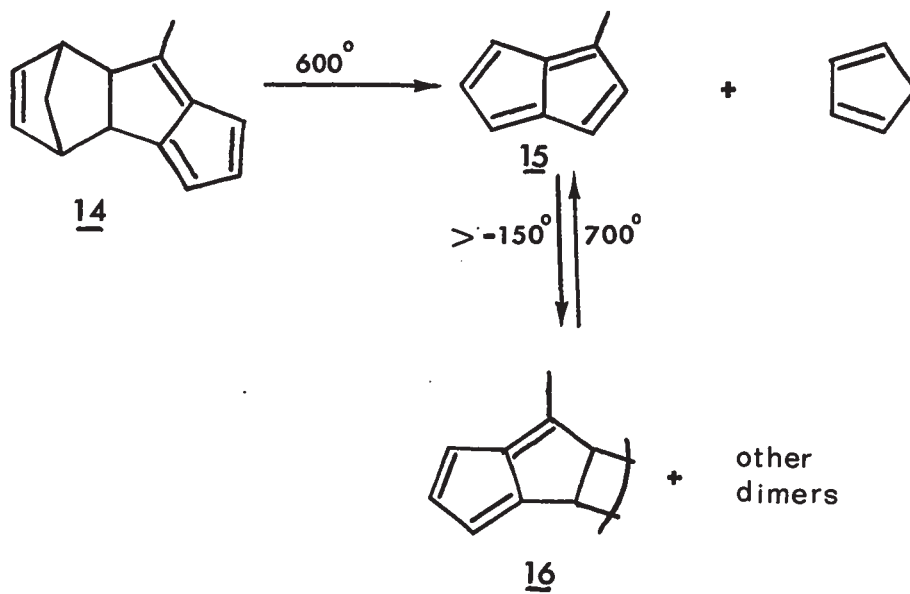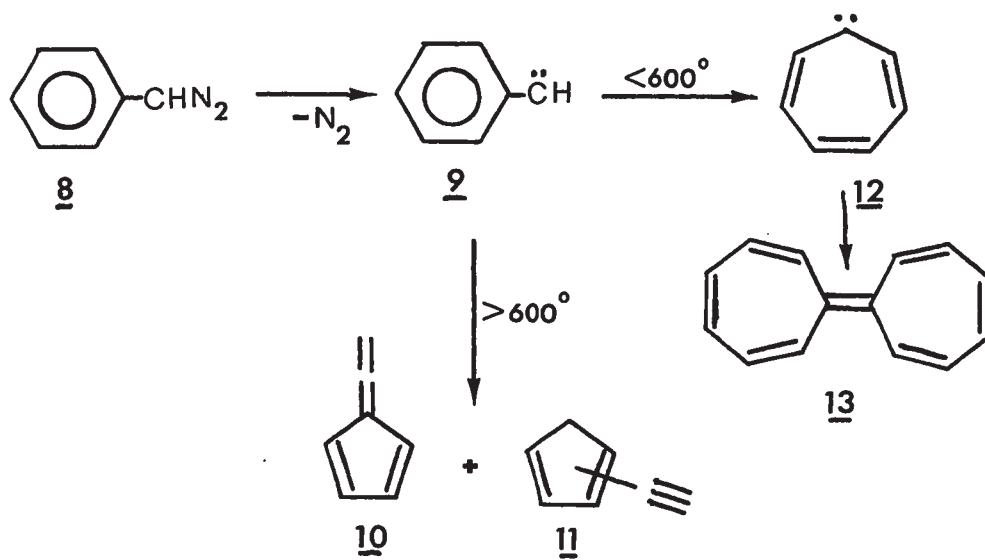
examine some interesting reactions. Benzyl radicals 4, generated by the FVP of benzyl bromide 3, were isolated in a matrix at liquid helium temperature and the ir, uv, and esr spectra were obtained (8). The FVP of photo-α-pyrone 5 gave a transient species that was shown to be cyclobutadiene 6 (9). Cyclobutadiene has an ionization potential of 8.2 ev and a lifetime, after emerging from the thermolysis zone, of about 10 msec at a pressure of 35 μ before it dimerizes to the tricyclo compound 7. Recently, Hedaya and collaborators have provided an elegant example of a reaction that gives one set of products at lower temperatures and a different set of products at higher temperatures (10). The FVP of phenyldiazomethane 8 gives initially phenylcarbene 9. At temperatures above 600°, phenylcarbene gives the ring contracted products 10 and 11. At temperatures below 600°, the ring expanded product 13 is obtained via the intermediate 12.

By a similar method, designated as "flash thermolysis", de Mayo and co-workers have recently reported the generation of 1-methylpentalene 15 which was shown to be stable at temperatures below -150°, and was characterized by its uv and ir spectra (11). The thermolysis of 14 gives, by a retro Diels-Alder reaction, 1-methylpentalene 15 and cyclopentadiene. At temperatures above -100°, 1-methylpentalene dimerizes (several isomers), but is, itself, regenerated by the thermolysis of the dimer 16.

In summary, low pressure thermolysis in conjunction with the analytical methods is used to:

1. generate and examine the physical and chemical properties of transient intermediates.

2. elucidate the mechanism and investigate the kinetics of
   thermal decompositions.

3. generate in the vapour phase and isolate at low temperatures,
   reactive compounds that are difficult to prepare in solution.

4. provide the conditions whereby products from competing pathways
   that are temperature dependent can be produced.

This thesis summarizes some new work that was carried out in low pressure thermolysis. In Part II, the investigations of the thermal decomposition of some cyclic ketones are presented. Part III summarizes the work carried out to produce sulfene, from the thermolysis of chlorosulfonylacetic acid and methanesulfonyl chloride.

PART II

THE THERMOLYSIS OF SOME CYCLIC KETONES

A.   Introduction

Thermolysis, photolysis, and electron impact are three common
processes that can impart sufficient energy to organic compounds in
order to induce unimolecular reactions such as eliminations, dissocia-
tions, and isomerizations (12). However, the nature of the excitation
in the compounds that is imparted by these processes is not identical.
Molecules, when subjected to heat, are generally excited to higher
vibrational levels of the ground state. On the other hand, the absorp-
tion of irradiation elevates molecules to their excited electronic
states, and electron impact produces, initially, the ionized species.
In spite of the differences in the nature of the excited states, some
striking analogies have been noted in the behaviour of compounds when
subjected to the three high energy conditions.

An example is presented to illustrate this analogous behaviour.
Carbonyl compounds, with chains that possess γ hydrogen atoms, undergo
cyclic six-centred eliminations when subjected to each of the high
energy conditions. Thus, the thermolysis of ethyl acetate $\underline{1}$ gives
acetic acid and ethylene. Photolysis of 2-pentanone $\underline{2}$ gives initially,
by Norrish II cleavage, ethylene and the enol of acetone. In the
McLafferty rearrangement, the ionized 2-pentanone yields ethylene and
the ionized enol of acetone. The McLafferty rearrangement also occurs

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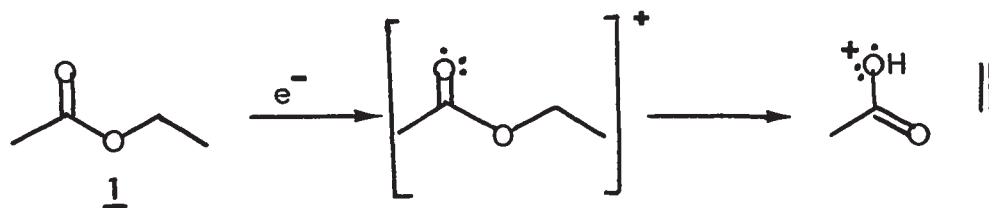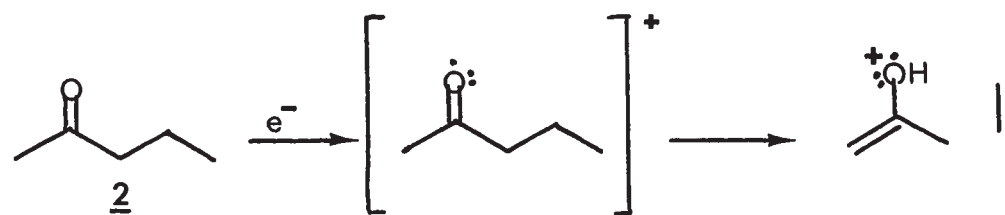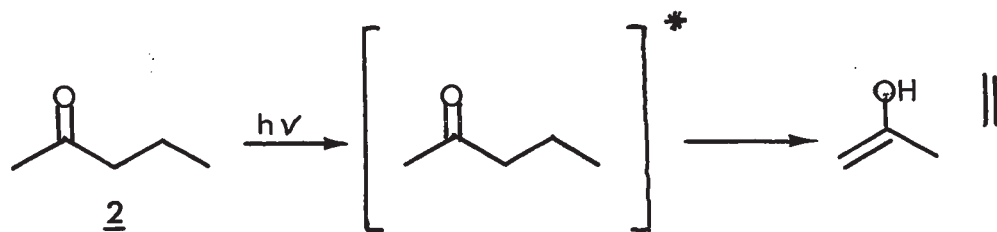
with ethyl acetate I to give ethylene and ionized acetic acid.

High Energy Chemistry of Ketones

From the high energy induced decompositions of both alicyclic and aliphatic ketones that have been reported, the products that were obtained can be satisfactorily rationalized by primary α carbon-carbon bond fission in the ketone following the initial excitation. The parallel decomposition behaviour is amply illustrated by three ketones: cyclohexanone, cyclopentanone, and 2-hexanone.

The high energy chemistry of vapourized cyclohexanone is summarized in Figure I. For all three modes of excitation, the observed products are adequately rationalized by primary α carbon-carbon bond fission following the initial excitation of the ketone.

In Figure 2, the high energy chemistry of cyclopentanone is illustrated. Parallel behaviour to cyclohexanone is noted in all cases.

The decompositions of 2-hexanone, shown in Figure 3, show more variety than the cyclic ketones. The products from the thermolysis of 2-hexanone, at 450°, in a static system were rationalized by a radical chain mechanism in which methyl radicals, derived initially from α cleavage of the ketone, were responsible for the chain propagation. The vapour phase photochemistry of 2-hexanone is characterized by Type I and Type II cleavage. The major products, induced by electron impact, arise from α fission and the McLafferty rearrangement of the ionized ketone.

From molecular orbital considerations, a rationalization of the cleavage in ketones following their electronic excitation has been

Figure I

High Energy Chemistry of Cyclohexanone

(13)

(14)

(15)

(16)

Figure 2

The High Energy Chemistry of Cyclopentanone

(17)

(18)

(16)
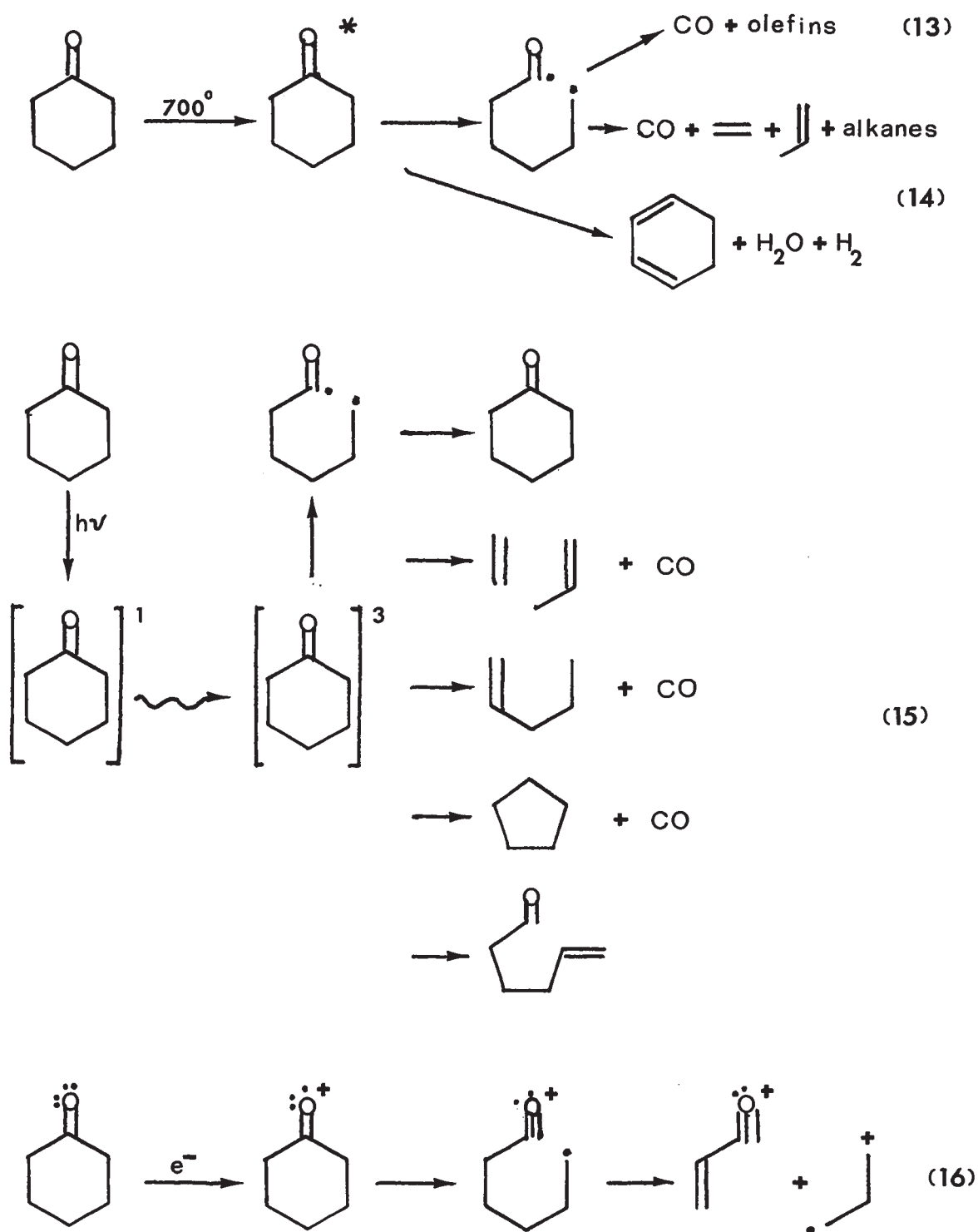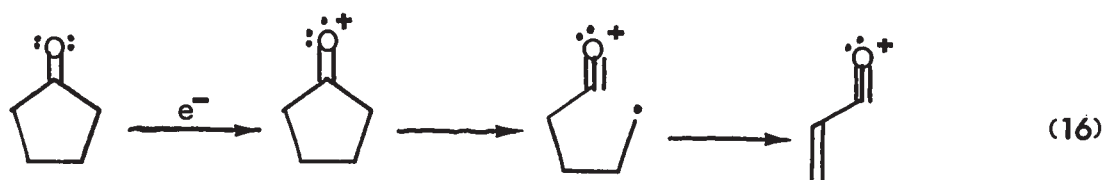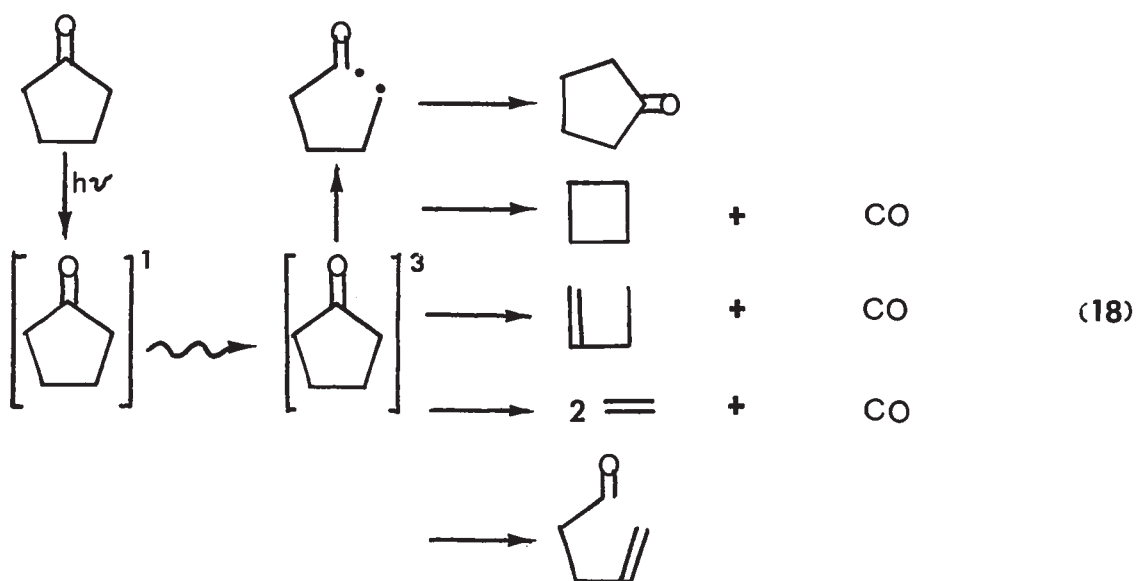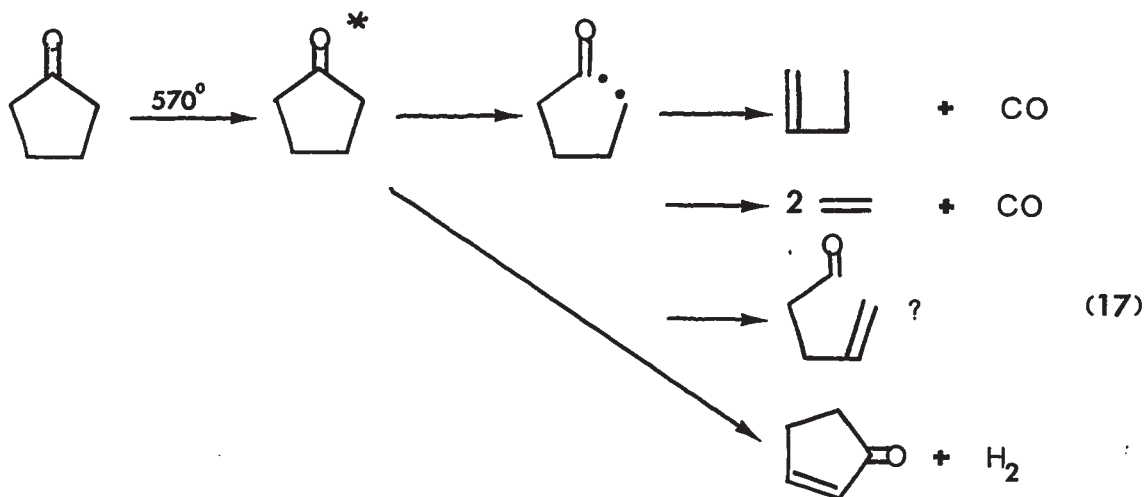
Figure 3

The High Energy Chemistry of 2-Hexanone
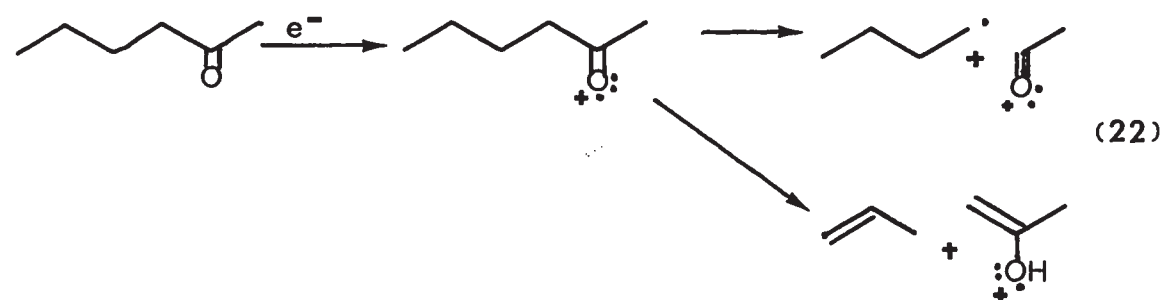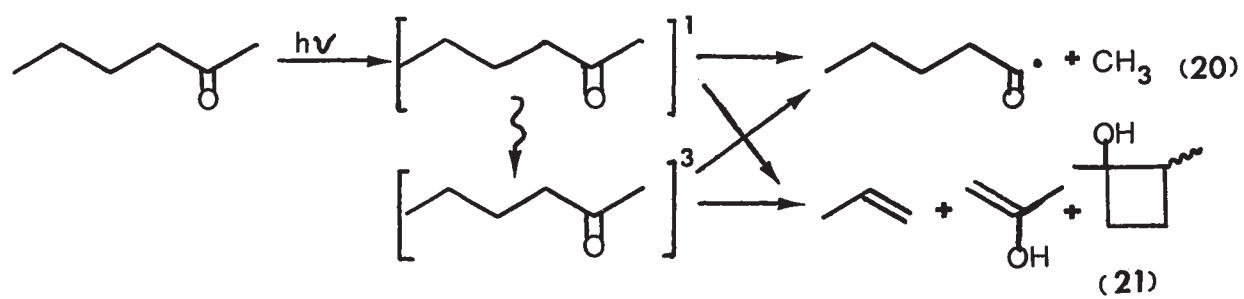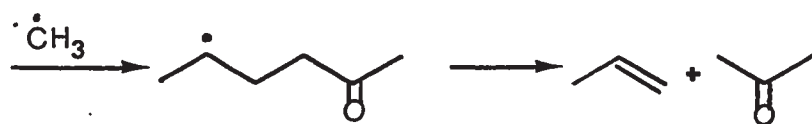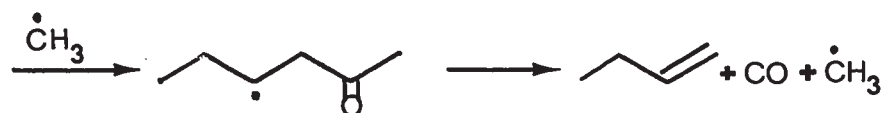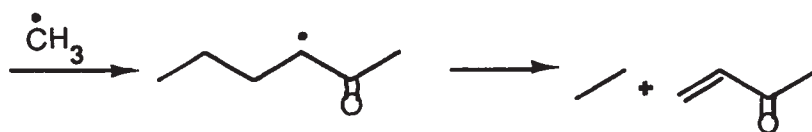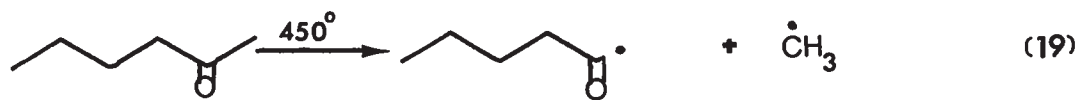
advanced (23). _Ab_ _initio_ calculations, carried out on ketones, suggest that the orbitals containing the non-bonded electron pairs on oxygen are ideally orientated for interaction with the carbon σ bond frame-work. Because absorption of irradiation excites one of the non-bonded electrons on oxygen to the n π^* molecular orbital, the interaction be-tween the orbital that contained the non-bonded electron and the C–C orbital may reduce the electron density in the α carbon-carbon bond and thereby facilitate its cleavage. An analogous situation exists for electron impact, except that the non-bonded electron is completely removed in ionization rather than merely being excited into an anti-bonding orbital. In view of the model advanced for the photochemistry of ketones, α cleavage is expected following the initial ionization of a ketone.

During his investigations of the primary processes that occur in the photolysis of cyclic ketones, Srinivasan postulated an involvement of vibrationally excited ground state molecules (24). It seemed possible that these excitation conditions might be simulated by a thermolysis process. Therefore, under suitable conditions the photochemistry of the cycloalkanones might, in part, be duplicated.

These considerations comprise the background for which the low pressure thermolysis studies of some cyclic ketones, and later, some aliphatic ketones were carried out.

B. Results and Discussion

Low pressure thermolyses, at temperatures from 950-1050°, and con-
tact times from 5-15 msec were carried out for some cycloalkanones.
Complete product analyses were performed for the thermolyses of cyclo-
hexanone, cycloheptanone, cyclooctanone, and cyclopentanone. Cyclo-
dodecanone was briefly examined. In order to elucidate the primary
decomposition processes for the cycloalkanones, a number of supple-
mentary experiments were carried out. As a final extension of the
work, product analyses for two aliphatic ketones, 5-nonanone and
2-hexanone, were done.

This part of the thesis is divided into sections that deal with
each ketone that was thermolysed. The final section summarizes the
postulated decomposition pathways of the ketones.

I. Cyclohexanone

(i) Product Analysis

The thermolyses of cyclohexanone were generally carried out at
temperatures of 1050° and pressures of about 60 μ, measured outside
the thermolysis zone. The thermolysate that emerged from the thermoly-
sis zone was immediately condensed on a liquid nitrogen Dewar face.
Under these conditions, the calculated residence time of cyclohexanone
in the thermolysis zone of the furnace was about 5 msec. The product
yields obtained for the thermolysis of cyclohexanone under these
conditions are given in Table I. At 900°, cyclohexanone decomposed
only to a minor extent and the products consisted mainly of ethylene

Table I

Thermolysis of Cyclohexanone

Products	Yields (mole %)**	
	1050°	1200°
Ethylene	85	112
Acetylene	5	16
Ethane	3	9
Propylene	16	18
Allene	7	12
1-Butene	7	3
1,3-Butadiene	3	3
Ketene	5	-
1,5-Hexadiene	3	1
Cyclopentane*	3	2
Acrolein*	2	1
Cyclopentadiene*	2	3
Benzene*	1	4
Methyl vinyl ketone	24	6

*   Products not observed in the independent thermolysis of methyl vinyl ketone.

**   Yields based on decomposed cyclohexanone.

and propylene. However, at 1200°, cyclohexanone gave increased yields of products containing 2 or 3 carbon atoms but reduced yields of compounds containing 4 or more carbon and/or oxygen atoms, relative to the products obtained from the thermolysis at 1050°. This indicates that increased secondary decomposition of the primary thermolysis products from cyclohexanone had occurred. The product yields from the thermolysis of cyclohexanone at 1200° are also given in Table I.

The stability of the products under the thermolysis conditions at 1050° was not extensively examined, but it was found that methyl vinyl ketone (MVK) itself decomposed to the extent of about 50% to give all the products observed from the thermolysis of cyclohexanone except benzene, cyclopentadiene, cyclopentane, and acrolein.

Little change was found in the product distributions for cyclohexanone when a quartz reactor tube was used in place of the ceramic tube. Reproducible product distributions were obtained from "aged" or new reactor tubes. Also, little change was noted in the product distributions when the thermolysate was condensed about 30 cm from the outlet of the reactor tube. These observations suggest that the decomposition of cyclohexanone was homogeneous following energy transfer to the molecules via their collisions with the walls of the thermolysis zone.

(ii) Deuterium Labeling Experiments

In order to ascertain the primary modes of decomposition in cyclohexanone, deuterium labeling was employed to supplement the product analysis. The thermolyses, at 1050°, of cyclohexanone-2,2,

6,6-$\underline{d}_4$, cyclohexanone-3,3,5,5-$\underline{d}_4$, and cyclohexanone-4-$\underline{d}_1$ were carried out. The products of the thermolyses were isolated by preparative gas chromatography (glc) and the deuterium distributions in the products were determined by mass spectrometry. Table 2 summarizes the deuterium distributions for the starting ketone, ethylene, and MVK for each of the three specifically labeled cycloalkanones. The complete deuterium analyses are given in the Experimental Section.
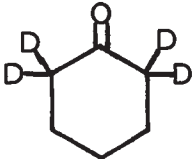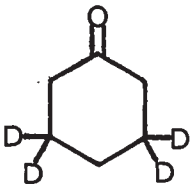
The deuterium distributions of the ketones that survived the thermolysis zone were also obtained. For recovered cyclohexanone-2,2, 6,6-$\underline{d}_4$ the deuterium content was 3.82 atoms of deuterium per molecule, as compared to 3.90 atoms of deuterium in the starting material. This loss of label indicates that some enolization, with the exchange presumably occurring on the walls of the thermolysis zone, had taken place. The deuterium distributions for the recovered cyclohexanone -3,3,5,5-$\underline{d}_4$ and cyclohexanone-4-$\underline{d}_1$ were essentially unchanged.

Cyclohexanone-2,2,6,6-$\underline{d}_4$ gave MVK with 93% overall retention of deuterium. The fragmentation mass spectrum of this MVK clearly showed that the methyl group contained 3 deuterium atoms and the α carbon of the vinyl group contained 1 deuterium atom. The deuterium content of the MVK obtained from cyclohexanone-3,3,5,5-$\underline{d}_4$ was exactly half that of the starting ketone. In addition, the fragmentation mass spectrum revealed that only the β carbon of the vinyl group of the MVK contained the deuterium label. Finally, essentially no deuterium was incorporated in the MVK that was obtained from cyclohexanone-4-$\underline{d}_1$.

These deuterium labeling studies demonstrate that a hydrogen atom (or ion) was transferred, to the extent of 72%, from one α carbon atom

Table 2

Thermolyses of Specifically Labeled Cyclohexanones

Ketone	Deuterium Distributions (%)		
	Cyclohexanone*	Ethylene	Methyl vinyl ketone
	d_0 0.0	d_0 64.5	d_0 0.3
	d_1 0.2	d_1 9.9	d_1 1.0
	d_2 0.6	d_2 22.6	d_2 3.4
	d_3 8.0	d_3 1.8	d_3 25.7
	d_4 91.2	d_4 1.2	d_4 69.6
	3.90 atom D per molecule	0.65 atom D per molecule	3.63 atom D per molecule
	d_0 0.1	d_0 7.4	d_0 2.4
	d_1 1.1	d_1 23.8	d_1 21.4
	d_2 8.0	d_2 64.3	d_2 75.0
	d_3 28.9	d_3 4.5	d_3 1.2
	d_4 61.8		
	3.51 atom D per molecule	1.66 atom D per molecule	1.75 atom D per molecule
	d_0 49.8	d_0 68.5	d_0 99.2
	d_1 50.2	d_1 31.5	d_1 0.8
	0.50 atom D per molecule	0.32 atom D per molecule	0.008 atom D per molecule

*The deuterium distribution for undecomposed cyclohexanone-2,2,6,6-d_4 was: d_1 1.0, d_2 1.7, d_3 12.6, d_4 84.9; 3.82 atom D per molecule. The deuterium distributions for undecomposed cyclohexanone-3,3,5,5-d_4 and cyclohexanone-4-d_1 were essentially unchanged.

to the other α carbon atom in the thermal decomposition of cyclo-
hexanone to give MVK. In addition, clearly no randomization of the β
and γ hydrogen atoms of cyclohexanone had occurred under the
thermolysis conditions.

(iii) <u>Beta Cleavage Mechanism</u>

Firstly, the formation of MVK in appreciable quantity in the
decomposition of cyclohexanone, and secondly, the deuterium retention
in the MVK derived from cyclohexanone-2,2,6,6-$\underline{d}_4$, suggest that β
cleavage is an important primary dissociative step in the thermolysis
of cyclohexanone. Evidence for a β cleavage mechanism is presented
in this section.

Two mechanisms (Figure 4) can be envisaged in order to rationalize
the formation of MVK from cyclohexanone. The first mechanism (path A)
requires enolization of cyclohexanone $\underline{3}$, with proton transfer presumably
occurring on the surfaces of the thermolysis zone, to give the enol $\underline{4}$.
A reverse Diels-Alder reaction of the enol $\underline{4}$ to give ethylene and the
new enol $\underline{5}$, and subsequent ketonization of $\underline{5}$, again with proton transfer
occurring on the surfaces, would give MVK. The second mechanism (path
B) involves initial homolysis of a β carbon-carbon bond of cyclohexa-
none to give the biradical $\underline{6}$. A 1,3 hydrogen transfer in $\underline{6}$ to produce
the 1,4 biradical $\underline{7}$ and its subsequent fragmentation, again would yield
MVK and ethylene. Both of these mechanisms accommodate the retention
of deuterium in the MVK by the transfer of a deuterium atom from one α
carbon to the other α carbon during the decomposition of cyclohexanone.

Further facts, deduced from the deuterium labeling experiments,
are accommodated by these mechanisms. Both mechanisms demand that

Figure 4

Fragmentation of Cyclohexanone
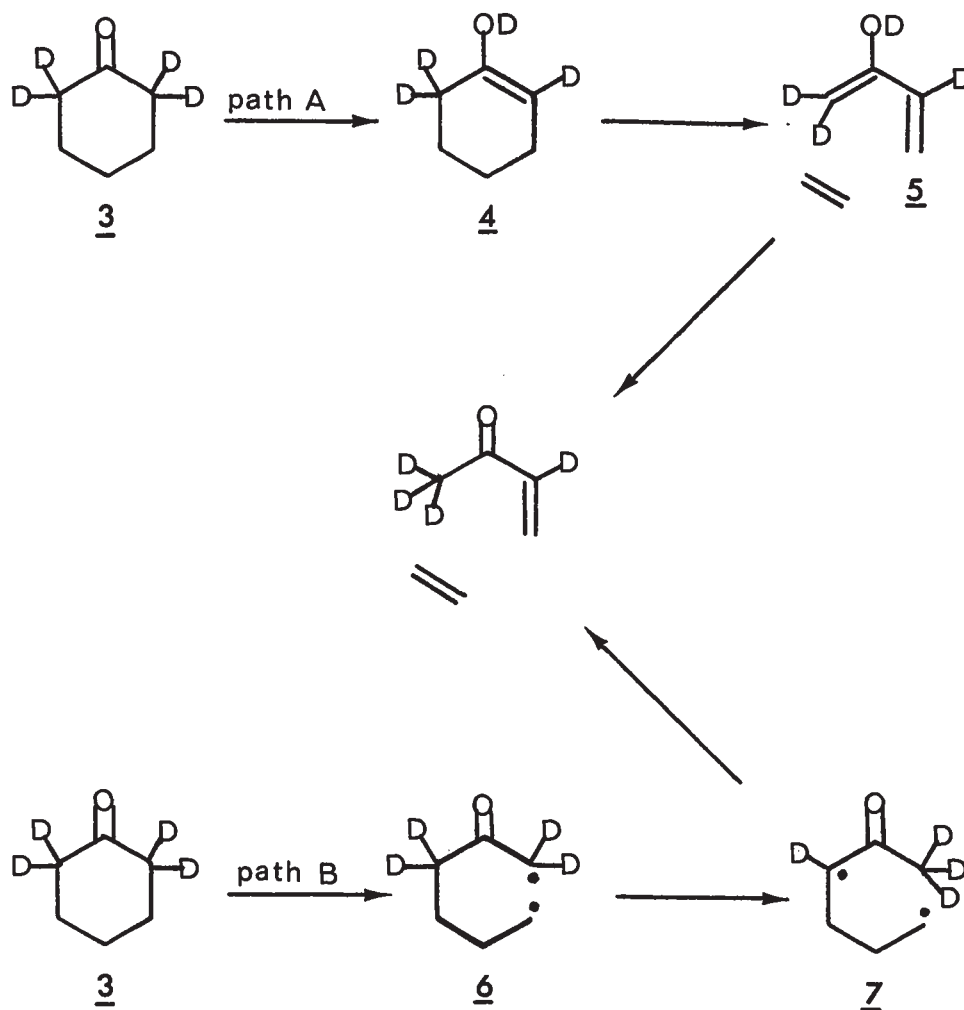
equimolar amounts of MVK and ethylene be formed. Furthermore, both mechanisms require that for the thermolysis of cyclohexanone-4-d_1, equimolar amounts of MVK and ethylene-d_1 be produced. From Table 2, the amount of ethylene-d_1 is 31.5%.* Because only 50.2% of the starting ketone was cyclohexanone-4-d_1, the adjusted amount of the ethylene-d_1 that would be expected is 63%. This expected quantity of ethylene-d_1 from cyclohexanone-4-d_1 should equal the amount of unlabeled ethylene obtained from the thermolysis of cyclohexanone-2,2,6,6-d_4. In fact, the amount of unlabeled ethylene obtained from cyclohexanone-2,2,6,6-d_4 was 64.5%,** a quantity that agrees well with the expected amount. Because the isolated yield of ethylene obtained from cyclohexanone was 85%, then the actual yield of MVK must have been 54%. This quantity is about twice the isolated yield of MVK but agrees well with the fact that MVK decomposed to an extent of about 50% under the same thermolysis conditions in the control experiments mentioned previously. Finally, because MVK is a primary product from the decomposition of cyclohexanone, then the extent of the decomposition proceeding by the pathway leading to MVK must also be 54%.

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*Ethylene can arise from both a primary fragmentation of cyclohexanone and the secondary decomposition of primary products, notably MVK. It is unlikely that carbon-4 of cyclohexanone can become a constituent atom of any ethylene which arises from the disproportionation of the biradical initially derived from α cleavage in cyclohexanone. Thus, disproportionation of the biradical produced by initial α cleavage in cyclohexanone-4-d_1 is not expected to give ethylene-d_1. In addition, any ethylene that arises from the secondary decomposition of MVK derived from the thermolysis of cyclohexanone-4-d_1 would contain no deuterium.

**In this instance, any ethylene arising from the secondary decomposition of MVK would contain at least one deuterium atom.

In an attempt to distinguish between the mechanistic pathways A and B, methylenecyclohexane and methylenecyclohexane-2,2,6,6-d_4* were prepared and thermolysed. Isoprene, the analogue of MVK in this system, was obtained in 14% yield from the thermolysis of methylenecyclohexane at 1050° (the same conditions as used for cyclohexanone). Ethylene was obtained in 57% yield. The complete product analysis is given in the Experimental Section. Methylenecyclohexane-2,2,6,6-d_4 was also thermolysed at 1050°, and isoprene, ethylene, and starting olefin that survived the thermolysis conditions were isolated by preparative glc. The deuterium distributions and average incorporations of these compounds were determined by mass spectrometry and are summarized in Table 3.

Table 3

Thermolysis of Methylenecyclohexane-2,2,6,6-d_4

Deuterium Distributions (%)

Methylenecyclohexane		Ethylene		Isoprene	
Starting Material	Recovered Material				
d_0 0.1	0.0	d_0 58.7		d_0 0.6	
d_1 0.4	1.0	d_1 13.7		d_1 1.6	
d_2 0.2	0.5	d_2 21.4		d_2 9.6	
d_3 5.1	4.8	d_3 4.9		d_3 31.8	
d_4 87.1	86.0	d_4 1.3		d_4 47.9	
d_5 6.1	6.7	inc 0.76		d_5 7.4	
d_6 1.1	1.1			d_6 1.1	
inc 4.02	4.01			inc 3.51	

*Appendix II discusses the deuterium distribution in this compound.

In the thermolysis of methylenecyclohexane-2,2,6,6-$\underline{d}_4$, essentially no change in the deuterium distribution of the material that survived the hot zone occurred. Furthermore, the isoprene contained 87.4% of the deuterium that was present in the starting olefin.

A mechanism, analogous to the β cleavage mechanism for cyclohexanone (Figure 4; path B), appears to be operative for methylenecyclohexane on the basis of the following considerations. The mechanism is outlined in Figure 5.

Homolytic β cleavage in methylenecyclohexane $\underline{8}$ would produce the biradical, consisting of canonical forms, $\underline{9}$ and $\underline{10}$. A 1,3 hydrogen transfer (paths C and D) in $\underline{9}$ and $\underline{10}$ would give the 1,4 biradicals $\underline{11}$ and $\underline{12}$ which could then decompose to yield isoprene and ethylene. The 70 ev fragmentation mass spectrum of isoprene revealed deuterium labeling consistent with both paths C and D. Because biradicals $\underline{11}$ and $\underline{12}$ can also be represented by the canonical forms $\underline{13}$ and $\underline{14}$, 1-methylcyclohexene would be an expected product according to this mechanistic scheme*. It is noted that the conformation of biradical $\underline{13}$ should prevent its closure to 1-methylcyclohexene, but biradical $\underline{14}$ would be expected to close. However, the negligible amount (less than 0.1%) of 1-methylcyclohexene actually obtained in the thermolysis of methylenecyclohexane indicates, that following the 1,3 hydrogen transfer, biradicals $\underline{11}$ and $\underline{12}$ disproportionate to ethylene and isoprene more rapidly than they undergo ring closure.

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*Frey and Ellis obtained the products isoprene-ethylene and 1-methylcyclohexene in the ratio 1.3:1.0 in the thermolysis of isopropenylcyclobutane at 325° in a static system (25). The products were rationalized by the intermediacy of biradicals $\underline{11}$, $\underline{12}$, $\underline{13}$, and $\underline{14}$.

Figure 5

Fragmentation of Methylenecyclohexane
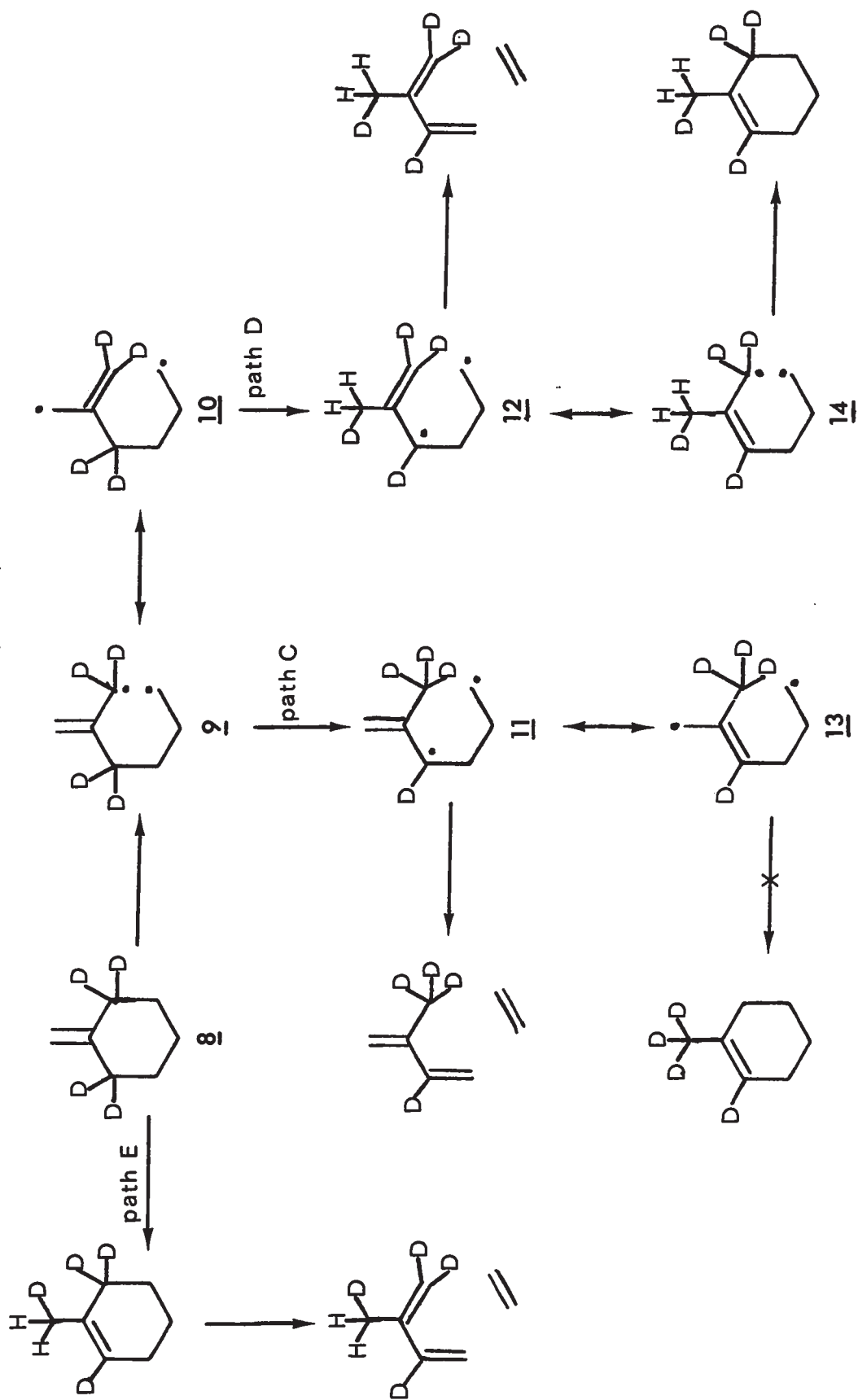
The absence of 1-methylcyclohexene as a product also indicates that the isomerization of methylenecyclohexane to 1-methylcyclhexene (path E) did not occur. If this isomerization had occurred, then all the 1-methylcyclohexene would have had to decompose (possibly by a retro Diels-Alder reaction to ethylene and isoprene). Under identical thermolytic conditions, 1-methylcyclohexene gave 15% recovered starting material and about 60% isoprene. Therefore, path E which is analogous to the enol mechanism in the cyclohexanone mechanism (Figure 1; path A) is not operative for methylenecyclohexane.

Therefore, by analogy with the methylenecyclohexane experiments, the β cleavage mechanism (Figure 4, path B) suggested for the fragmentation of cyclohexanone seems more likely to be operative than the enol mechanism (path A). However, recent work, reported by Benson and collaborators, has cast some doubt on the strength of the analogy for the initial β cleavage in methylenecyclohexane and cyclohexanone. The resonance stabilization energy of the allyl radical was found to be 9.6 kcal/mole (7), but the acetonyl radical was found to have zero resonance stabilization energy (26)*. Because the substituted allyl biradical 9 (Figure 5) and the substituted acetonyl biradical 6 (Figure 4) would be expected to have proportional differences in resonance stabilization energies, β cleavage seems more probable in methylenecyclohexane than in cyclohexanone. Nonetheless, in the present study both compounds decomposed in a manner consistent with the β cleavage pathways as

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*However, from data reported by Kerr the resonance stabilization energy of the acetonyl radical is calculated to be 6 kcal/mole (27).

attested by product formation and deuterium labeling experiments.

The minor amount of equilibration of deuterium that occurred in the undecomposed cyclohexanone-2,2,6,6-$\underline{d}_4$ indicates that the enol was formed to some extent in the thermolysis zone. It has been noted that the enol acetate of cyclohexanone, cyclohex-1-enyl acetate 15, at 500° undergoes a rearrangement to 2-acetylcyclohexanone 16 (analogous to the Fries rearrangement) and gives no products that are consistent with a retro Diels-Alder reaction (28). However, the fragmentation of cyclohexanone by a reverse Diels-Alder reaction of its enol cannot be rigorously excluded.

Finally, further evidence is available which supports path B for the decomposition of cyclohexanone. Both 6-methyl-3,4-dihydro-2H-pyran 17 (29) and methyl cyclobutyl ketone 18 (30) decompose cleanly to MVK and ethylene at 350° in static systems. Arguments in favour of both concerted and biradical mechanisms for the decompositions have been advanced. Support for the intermedicacy of the biradical represented by canonical forms 19 and 20 has recently been put forward (31). The isolation of 6-methyl-3,4-dihydro-2H-pyran as a minor product from methyl cyclobutyl ketone, in a reinvestigation of the decomposition supports this contention (29). Thus, there is ample evidence to support the fragmentation of the 1,4 biradical 6 (Fig. 4; path B) to yield MVK and ethylene.

(iv) Direct Evidence for the β Cleavage Mechanism

In order to obtain further support for the β cleavage mechanism in the decomposition of cyclohexanone, 3-ketothiacycloheptane-1,1-dioxide 21 (KTCH) was prepared and thermolysed. Because the dissociation energy

15 → 16 + other products

17 → 19 → 20

18 → 20 → 19

17

of the carbon-sulfur bonds in KTCH is about 60 kcal/mole, it was
expected that the thermolysis of KTCH would give, by extrusion of sulfur
dioxide, the biradical 6 under milder conditions than were employed in
the thermolysis of cyclohexanone. Thus, support for path B in the
fragmentation of cyclohexanone would be obtained if KTCH decomposed to
give products (notably MVK) that were obtained from cyclohexanone. The
results of the thermolyses KTCH, carried out at 950° and 1000°, are
given in Table 4.

Table 4

Thermolysis of 3-Ketothiacycloheptane-1,1-dioxide

Products	Yields (mole %)*	
	950°	1010°
Ethylene	16	27
Ethane	3	1
Propylene	3	3
Allene	4	5
1,5-Hexadiene	3	2
Acetone	2	2
Methyl vinyl ketone	7	10
Benzene	3	3
Cyclohexanone	50	34

*Based on decomposed starting material

The products obtained from the thermolysis of KTCH do, indeed,
suggest that the biradical 6 can ultimately decompose to give products
derived from cyclohexanone as depicted in path B. Some apparent

21

22 + 23

−SO₂

−SO₂

6

products
including
MVK
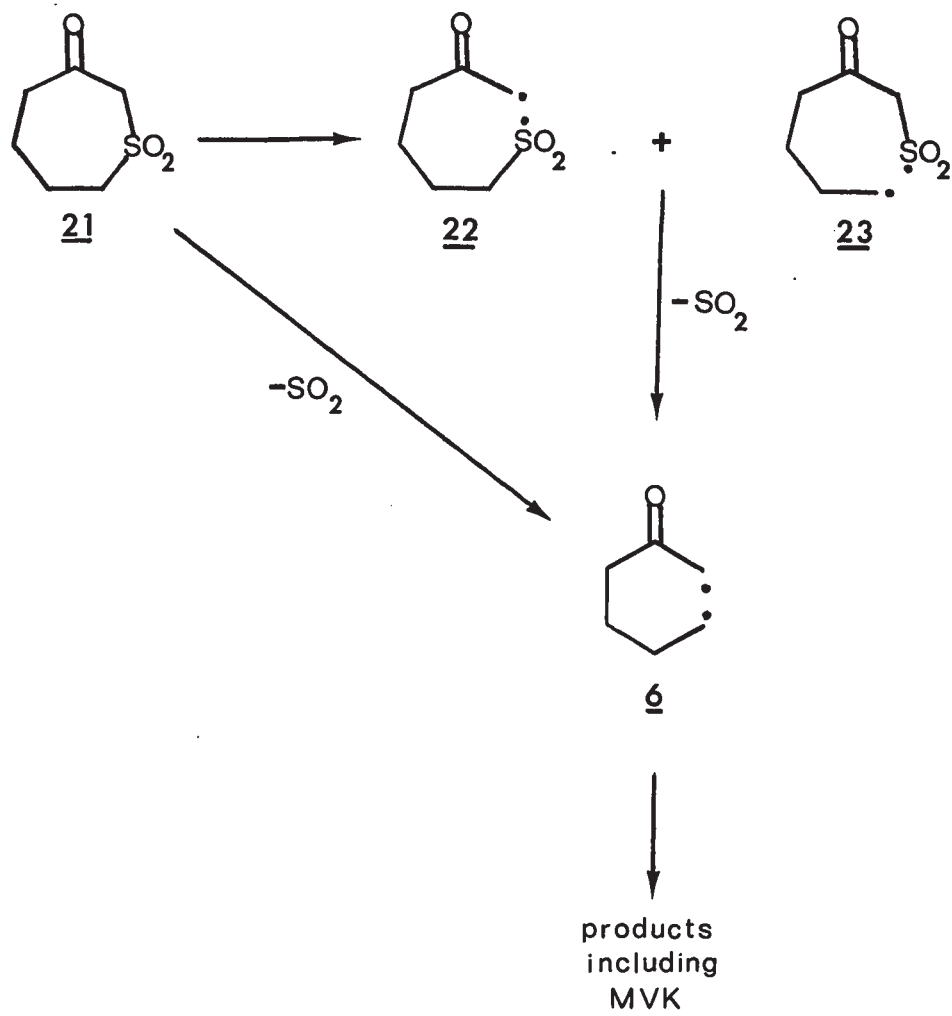
discrepancies, such as the formation of acetone, may be explained by the non-concerted expulsion of sulfur dioxide from KTCH leading initially to biradicals 22 and 23. The absence of products such as cyclopentane and cyclopentadiene shows that cyclohexanone itself did not decompose under the thermolysis conditions. Finally, the large amount of cyclohexanone (50% yield at 950°) implies that biradical 6 readily closes to cyclohexanone.

(v) Final Considerations

Considerable evidence has been accumulated which, taken together, strongly suggests that β cleavage is the most important primary process in the low pressure thermolysis of cyclohexanone at 1050°. The product analysis and deuterium labeling experiments indicate that β cleavage occurs to the extent of 54% as reflected in the actual yield of MVK. From calculations, presented in Appendix I, it seems probable that the ketene also originates from β cleavage in cyclohexanone. Finally, the total amount of initial β cleavage is not reflected by the product yields because the biradical, derived from β cleavage in cyclohexanone, can reclose.

Why has β cleavage predominated over α cleavage in the low pressure thermolysis of cyclohexanone? Calculations carried out for the standard state conditions show that the heat of formation of biradical 24 (from α cleavage in cyclohexanone) is only 4 kcal/mole less than the heat of formation of biradical 6 (from β cleavage in cyclohexanone). The fact that the acetonyl radical has zero resonance stabilization energy is used in these calculations and is largely responsible for the enthalpy difference between biradicals 24 and 6. The energy-reaction

Figure 6

Primary Thermolytic Cleavage in Cyclohexanone
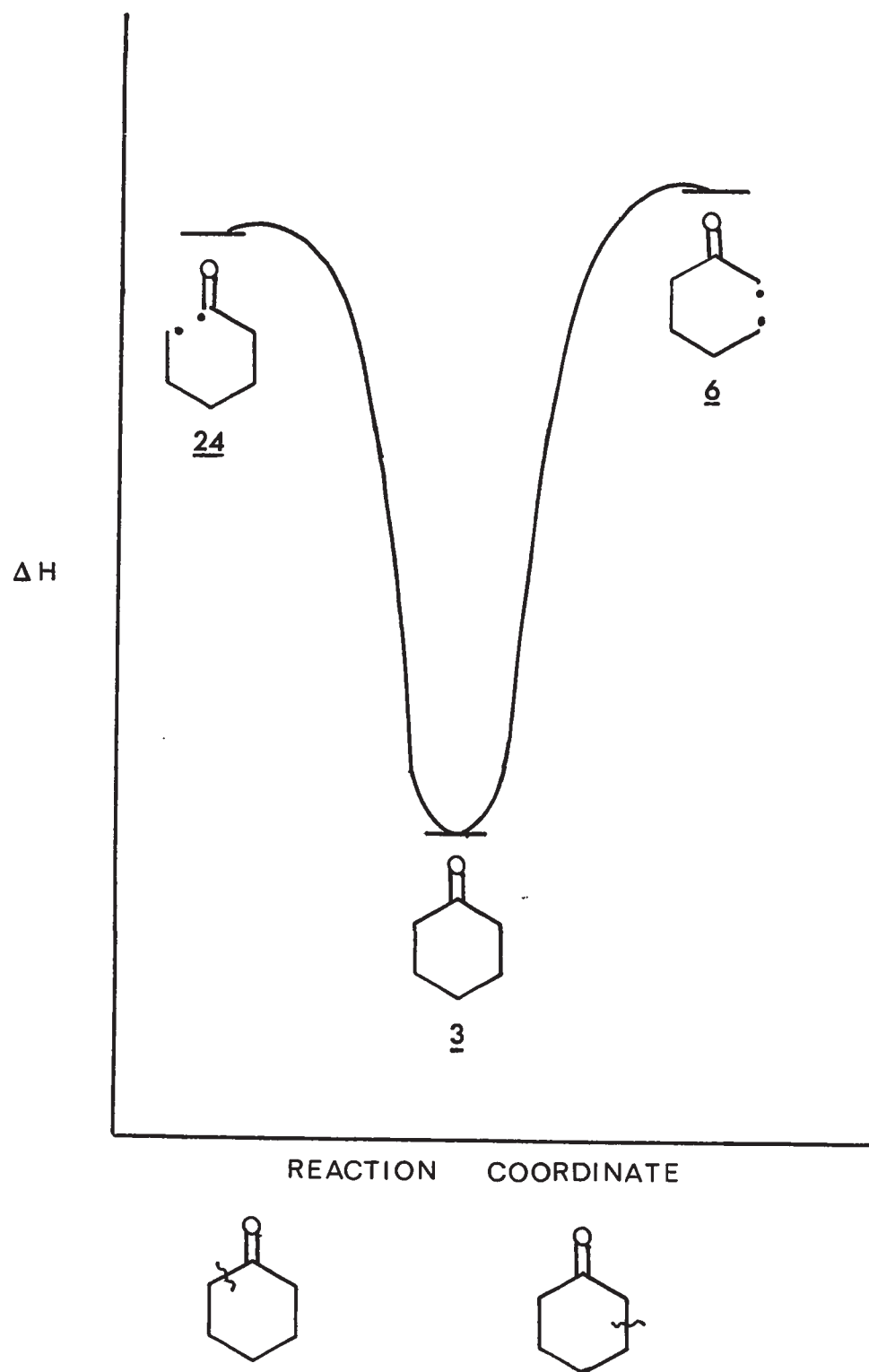
coordinate diagram for α and β cleavage is given in Figure 6. In order for β cleavage to predominate over α cleavage at 1050°, the enthalpies of the biradicals 24 and 6 must invert (that is, the enthalpy of 24 must become larger than the enthalpy of 6 at 1050°). Unfortunately, insufficient data is available to carry out these high temperature calculations in order to verify the suspected enthalpy inversion.

In Section 5, a scheme to rationalize the decomposition pathways that originate from α and β cleavage in the thermolysis of cyclohexanone is presented.

2. Cycloheptanone

(i) Product Analysis and Beta Cleavage Mechanism

The product analysis for the thermolysis of cycloheptanone at 1065° is summarized in Table 5.

The formation of MVK in the thermolysis of cycloheptanone suggests that mechanisms, similar to those considered for cyclohexanone, may be operative. Because it is known that vinylcyclopropane activated by a phenyl group (α-cyclopropylstyrene) reacts as a diene in the Diels-Alder reaction to give a seven-membered ring (32), it seemed possible that MVK might have arisen from a retro Diels-Alder reaction of the enol of cycloheptanone. This mechanism (Figure 7; path F) would require enolization of cycloheptanone 25 to give the enol 26. A subsequent reverse Diels-Alder reaction of 26 must give cyclopropane and MVK on the basis of orbital symmetry requirements (33). Despite the fact that

Table 5

Thermolysis of Cycloheptanone

Product	Yield (mole %)
Ethylene	71
Ethane	5
Acetylene	5
Propylene	29
Allene	4
1-Butene	16
1,3-Butadiene	13
Ketene	5
1,5-Hexadiene	7
Cyclohexane	9
Acetone	3
Methyl vinyl ketone	10
Benzene	1
Cyclopentanone	1
Cyclohexanone	1
3-Methylcyclohexanone	2

cyclopropane was sufficiently stable to survive the thermolysis conditions*, none was detected by mass spectrometry, infrared spectroscopy, or glc in the thermolysate from cycloheptanone. Therefore, the absence of cyclopropane represents strong evidence against mechanistic path F

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*Control experiments showed that cyclopropane isomerized to propylene to the extent of 40% at 1075° and 60% at 1205°.

Figure 7

Fragmentation of Cycloheptanone
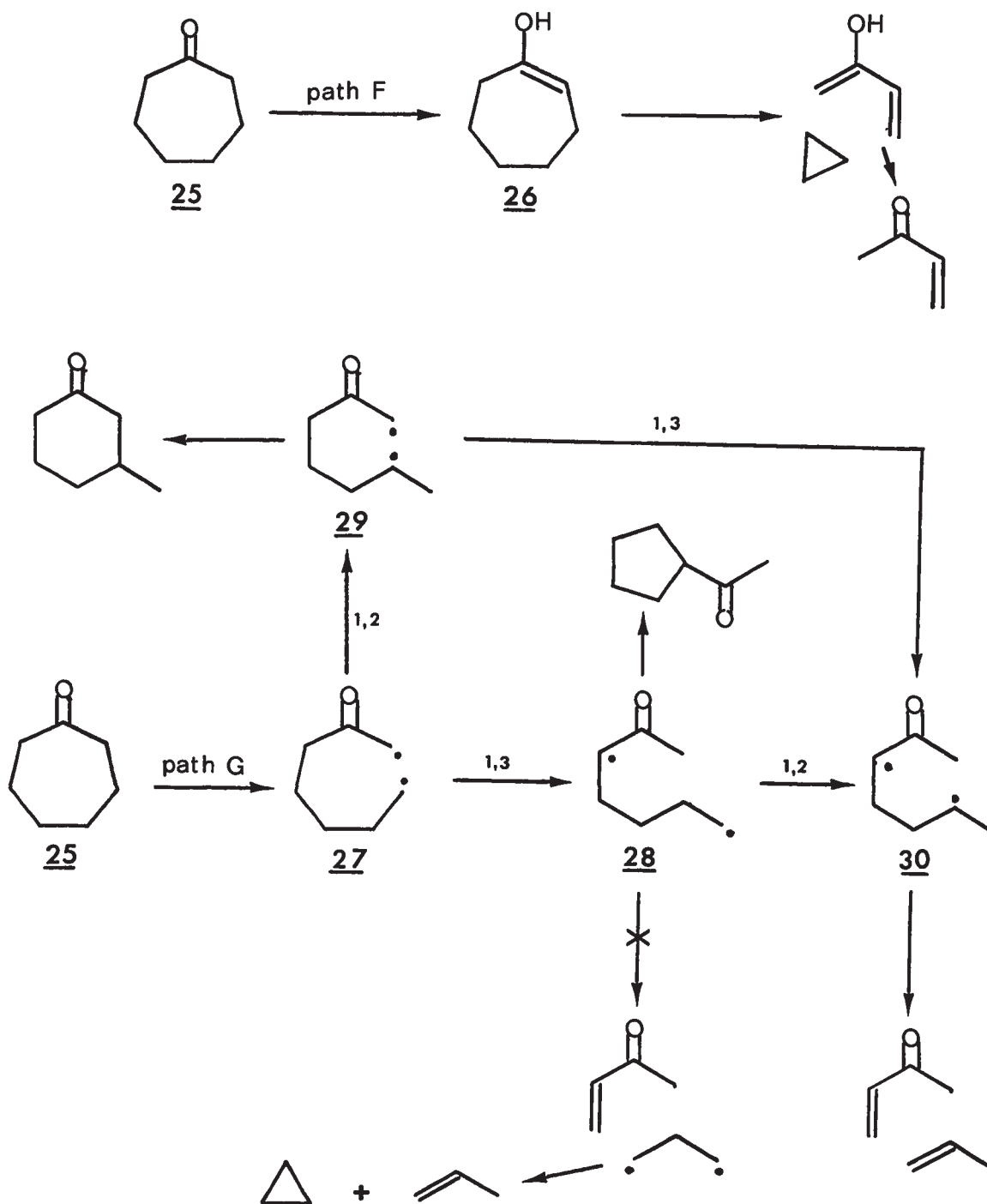
for the formation of MVK in the thermolysis of cycloheptanone. This is not surprising when it is considered that the reverse reaction for path F in which cyclopropane acts as a dienophile in the Diels-Alder reaction is not known.

As with cyclohexanone, formation of MVK is satisfactorily explained by a mechanism that is initiated by homolysis of the β carbon-carbon bond. This mechanism is given as path G in Figure 7. Initial cleavage yields the biradical 27 which can then undergo a 1,3 hydrogen transfer to give 28 or a 1,2 hydrogen transfer to give 29. Ring closure of 29 gives 3-methylcyclohexanone. Biradical 28 can either close to methyl cyclopentyl ketone or undergo a further 1,2 hydrogen shift giving the 1,4 biradical 30 which would collapse to MVK and propylene.

Sufficient evidence is available to rule out the disproportionation of biradical 28 to give MVK and trimethylene. Benson and O'Neal have reported calculations that indicate, at 500°, that trimethylene closes to cyclopropane 22 times faster than it isomerizes to propylene (34). In addition, de Mayo et al. have noted that in the thermolysis of thietane 1,1-dioxide at 960°, trimethylene gave cyclopropane and propylene in yields of about 50% each (35). Therefore, if trimethylene is a product from the thermolysis of cycloheptanone at 1050°, then some cyclopropane should be formed. Experimentally, no cyclopropane was detected and it must be concluded that biradical 28 does not disproportionate to MVK and ethylene.

It appears that formation of MVK requires both a 1,2 and 1,3 hydrogen transfer following the generation of biradical 27. The

formation of 3-methylcyclohexanone provides strong support for the

participation of the 1,2 transfer. The identification of methyl

cyclopentyl ketone (trace quantities) in the thermolysis of cyclohepta-

none and the deuterium labeling experiments that were carried out for

cyclohexanone support the 1,3 hydrogen transfer. From the information

at hand, it is impossible to specify the sequence of these two hydrogen

transfers in the fragmentation of cycloheptanone. However, on the

basis of the work of Benson et al. on the resonance stabilization energy

of the methylacetonyl radical (36), the 1,3 hydrogen shift in biradical

27 is 2.7 kcal/mole (standard state) more exothermic than the 1,2

transfer.

(ii) Direct Evidence for the Beta Cleavage Mechanism

In order to obtain further support for the β cleavage mechanism

in the fragmentation of cycloheptanone (path G), methyl cyclopentyl

ketone 31 was thermolysed. Initial cleavage of a β carbon-carbon bond

in the ring would give the biradical 28. Support for path G would be

obtained if MVK were produced with the concurrent absence of cyclopro-

pane. The thermolysis of methyl cyclopentyl ketone at 1000° and 1050°

gave MVK in about 5% yield. Significantly, no cyclopropane was detected.

In methyl cyclopentyl ketone α cleavage predominates as cyclopentane

and cyclopentadiene were obtained in combined yields of 26-28%. The

complete product yields are given in the Experimental Section.

(iii) Final Considerations

The products from the thermolysis of cycloheptanone at 1065° that

appear to arise from initial β cleavage include MVK, 3-methylcyclo-

α cleavage
products
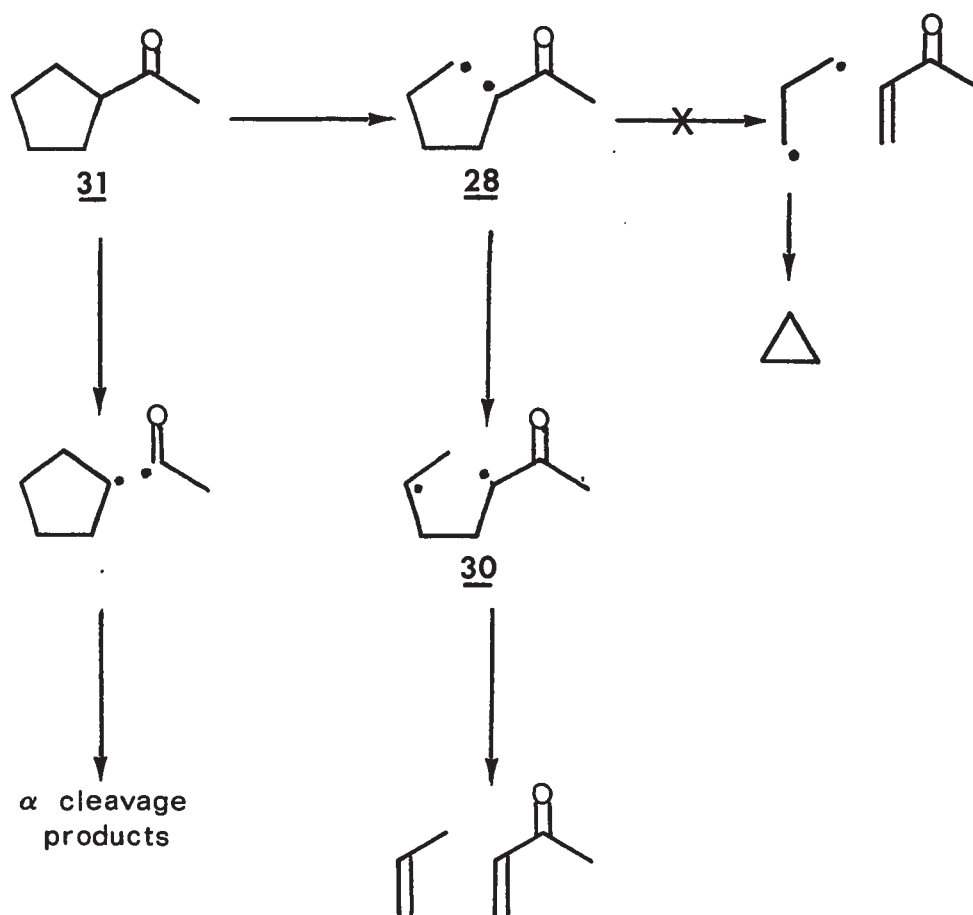
hexanone, acetone, and ketene. The various decomposition pathways in the thermolysis of cycloheptanone are discussed in Section 5.

Although the isolated yield of MVK in this case was 10%, on the basis of control experiments in which MVK was thermolysed under the same conditions, the actual yield is about 20%. The mechanistic pathway to MVK (Figure 7; path G) suggests that the essential precursor for MVK formation is an acyl substituted 1,4 biradical, in this case the biradical 30.

3.   Other Cyclic Ketones

The product analyses for the thermolyses of cyclooctanone and cyclopentanone are summarized in Table 6. Cyclooctanone was thermolysed at 1060° while cyclopentanone was thermolysed at both 1060° and 1260°.

No supplementary experiments were carried out in order to elucidate the primary processes in the decompositions of cyclopentanone or cyclooctanone.

In the thermolysis of cyclooctanone trace amounts (less than 0.1%) of MVK were detected. By analogy with cycloheptanone, a plausible mechanism that is initiated by β cleavage is suggested as a pathway to MVK. This pathway, which is outlined in Figure 8, involves initial cleavage in cyclooctanone 32 and a series of one 1,3 hydrogen transfer and two 1,2 hydrogen transfers to give ultimately, the 1,4 biradical 33. Evidence of the randomness of these hydrogen shifts could be furnished by the characterization of the four indicated ring closure products. The gas chromatogram of the products from the thermolysis of cyclooctanone exhibited peaks (corresponding to trace quantities) that had retention times which were consistent with the ketones that would result

Table 6

Thermolyses of Cyclooctanone and Cyclopentanone

Products	Yields (mole %)		
	Cyclooctanone	Cyclopentanone	
	1060°	1060°	1260°
Ethylene	99	109	107
Ethane	6	0	0
Acetylene	1		
Propylene	27	1	2
Allene	7	2	5
1-Butene	19	5	1
1,3-Butadiene	13	16	11
Ketene	23	10	--
1,5-Hexadiene	10	3	1
Cyclopentadiene	4	1	1
Acetone	4	1	0
Benzene	2	0	1
Cycloheptane	6	NO	NO
2-Cyclopentenone	NO	7.	1
Cyclopentanone	1	NO	NO
Cyclohexanone	1	NO	NO

NO means that the product is not obtained from the particular ketone.

from the indicated ring closures. The mass spectra of the compounds corresponding to three of the peaks showed that each had a molecular ion at 126 amu (the same as cyclooctanone). Unfortunately, the compounds

Figure 8

Fragmentation of Cyclooctanone
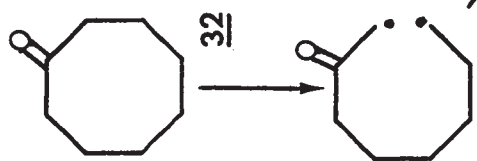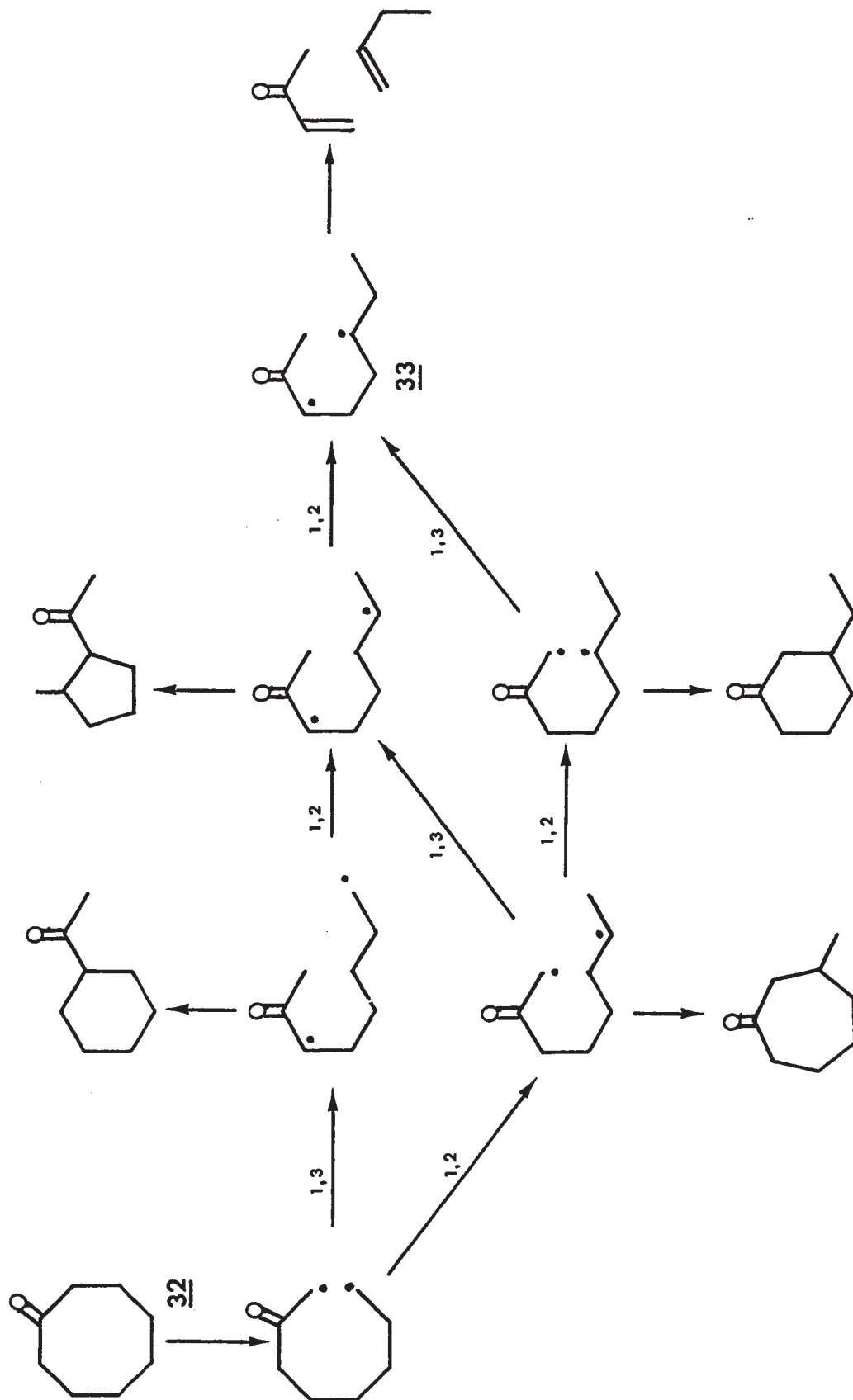
could not be obtained with sufficient purity or in sufficient amounts to permit unequivocal identification. The very low yields of MVK or any of the ring closure ketones indicate that the hydrogen shifts are slow relative to biradical disproportionation (probably to ketene and hydrocarbons).

In the thermolyses of cyclooctanone and cyclopentanone, the only products that seem to originate from initial β cleavage are acetone and ketene. Possible decomposition pathways for the ketones are outlined in Section 5.

In the thermolysis of cyclododecanone at 1050°, no oxygen containing compounds were found. Hydrocarbon products included cyclopentene, cyclopentadiene, 1,3-cyclohexadiene, benzene, and large amounts of noncondensible gases. The decomposition resembles those of aliphatic hydrocarbons.

4. Aliphatic Ketones

Thermolyses of 5-nonanone and 2-hexanone were performed and the product analyses are given in Table 7. The thermolyses were conducted at 950, 1000, and 1050° for each compounds.

Products that probably derive from initial β cleavage in 5-nonanone include 2-hexanone, MVK, acetone, and ketene. Initial β cleavage in 5-nonanone 34 gives the radical 35 which can then give MVK, acetone, ketene and 2-hexanone. Alternatively, 2-hexanone can arise from a molecular mechanism involving a six-centred transition state.

In 2-hexanone 36, ketene and acetone can arise from the initial cleavage product, the acetonyl radical 37. It is possible that acetone

Table 7

Thermolyses of 5-Nonanone and 2-Hexanone

Product	Yields (mole %)					
	5-Nonanone			2-Hexanone		
	950°	1000°	1050°	950°	1000°	1050°
Ethylene	180	185	185	95	102	120
Ethane	28	24	25	33	33	37
Propane	7	6	4	9	7	4
Propylene	29	30	29	17	18	18
1-Butene	4	3	2	2	2	1
Ketene	-	-	12	-	24	-
1,5-Hexadiene	0	0	0	1	1	0
Acetone	2	2	1	15	15	13
MVK	2	2	1	2	2	2
Valeraldehyde	1	1	1	2	2	1
2-Hexanone	5	2	1	NO	NO	NO

can also originate from a molecular mechanism. The origin of the MVK in the thermolysis of 2-hexanone is unclear. Because radical-molecule reactions are minimized by the low pressure thermolysis conditions, MVK could perhaps arise from a hydrogen abstraction, which occurs on the cold face, at carbon-3 of 2-hexanone.

A rationalization of the products from the thermolyses of 5-nonanone and 2-hexanone is presented in Section 5.
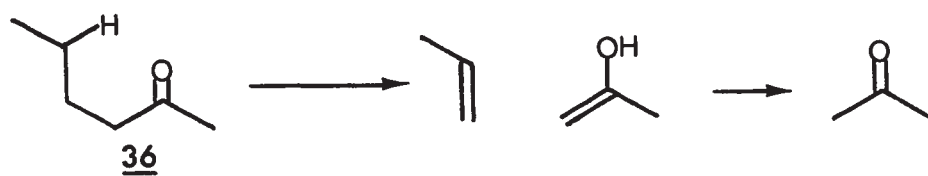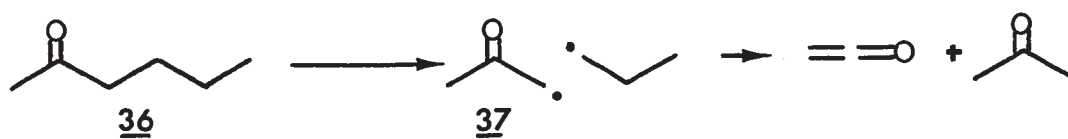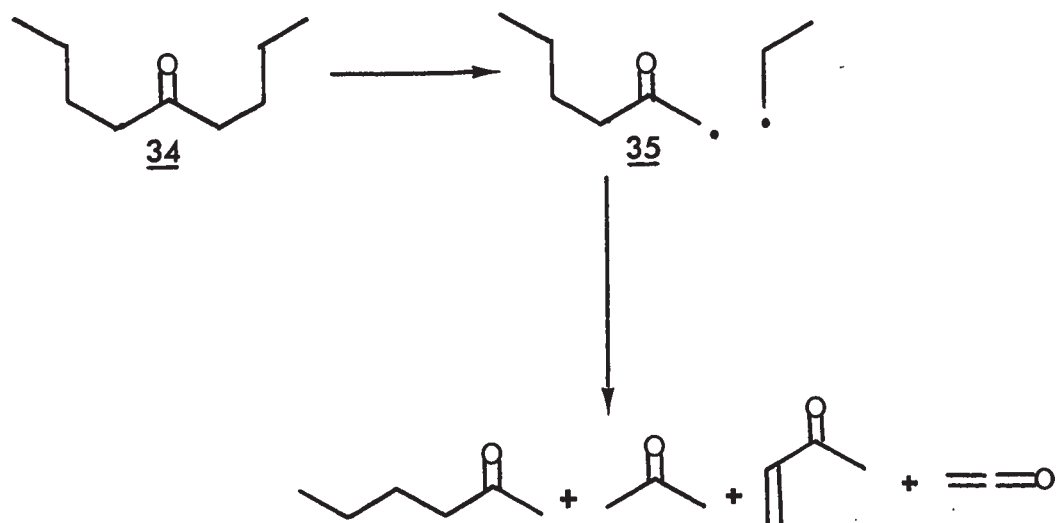
5. <u>Possible Decomposition Pathways for the Ketones</u>

In this section, an attempt to reconstruct the decomposition path-
ways for the ketones which were thermolysed is outlined. The approach
is based on product analysis and consists of identifying as far as
possible, the obtained products with initial α or β cleavage in the
ketone.

Table 8 summarizes the products for each compound which was thermo-
lysed. Gaseous hydrocarbons (C_2, C_3, C_4) are classified simply by the
number of carbon atoms that they contain. For example, allene and
propylene are taken as C_3 fragments. It is assumed that 1,5-hexadiene
arises from the coupling of two allyl radicals on the cold face.
Therefore, 1,5-hexadiene is counted with the C_3 products.

The general procedures which are followed in order to identify the
decomposition pathways are listed:

1. All products except the gaseous hydrocarbons are assigned
    to a pathway which is initiated by β or α cleavage (or no
    cleavage) in the ketone. In the previous sections, products
    that appear to originate from β cleavage have been specified.

2. Decomposition pathways which are consistent for carbon mass
    balance are identified, that is, the number of carbon atoms
    in the products of each pathway equals the number of atoms
    in the starting ketone.

3. After all obvious pathways and the extent to which they occur
    are specified, the remaining pathways are assumed to consist
    of the fragmentation of the biradicals derived from initial
    α cleavage in the ketones. These pathways assume only

Table 8

Summary of Products Obtained from the Ketone Thermolyses

Product

	Cyclo-hexanone	Cyclo-heptanone	Cyclo-octanone	Cyclo-pentanone	5-Non-anone	2-Hex-anone
C_2	86*	79*	106	109	209*	135*
C_3	27*	45*	54	9	36*	27*
C_4	8*	28*	32	21	3*	2*
Ketene	5	5	23	10	12	24
Acetone	NO	3	4	1	2	15
MVK	54**	20**	NO	NO	4**	4**
3-Methyl-cyclohexanone	NO	2	NO	NO	NO	NO
2-Hexanone	NO	NO	NO	NO	2	X
Alicyclic (n-1)	3	9	6	NO	NO	NO
Cyclopenta diene	2	NO	4	1	NO	NO
Cyclopent-anone	NO	1	1	X	NO	NO
Cyclohex-anone	X	1	1	NO	NO	NO
Acrolein	2	NO	NO	NO	NO	NO
Valeraldehyde	NO	NO	NO	NO	1	2
2-Cyclo-pentenone	NO	NO	NO	7	NO	NO
Benzene	1	1	2	NO	NO	NO

X indicates starting material. NO means that the product was not obtained for the particular ketone. *Contribution from decomposed MVK has been deducted. **Value adjusted for decomposed MVK.

reasonable radical fragmentations. When two or more choices are available, the extent to which each pathway is assumed to be operative is weighted so that the total amount of the gaseous hydrocarbons, produced by the suggested pathways, best approximates the experimental quantities of the hydrocarbons.

The possible thermal decomposition pathways for cyclohexanone, cycloheptanone, cyclooctanone, cyclopentanone, 5-nonanone and 2-hexanone are given in Tables 9, 10, 11, 12, 13, and 14 respectively.

As an example, the treatment for cyclohexanone (Table 9) may be elaborated upon. The pathways which lead to MVK, ketene, cyclopentane, cyclopentadiene, acrolein, and benzene are straightforward. The extent to which each of these pathways is operative is empirical and the amount of the hydrocarbon fragments accompanying each pathway is recorded in the appropriate hydrocarbon column. In ketene formation, a C_4 compound is arbitrarily assumed to be the accompanying hydrocarbon fragment (instead of two C_2 fragments) and, hence, the C_4 yield is enclosed in parentheses. It is found that 33% of the products are not accounted for by the already mentioned pathways. Therefore, it is assumed that 33% of the decomposition in cyclohexanone is initiated by α cleavage to yield carbon monoxide plus a C_2 and a C_3 compound. These quantities, which are not based on empirical observations, are enclosed in parentheses. Finally, the sums of the C_2, C_3, and C_4 hydrocarbon yields demanded by the decomposition pathways are obtained and are compared with the experimental quantities which are given in Table 8.

As a further illustration, three possible pathways which yield only C_2, C_3, and C_4 hydrocarbons are suggested in the decomposition of

Table 9

Decomposition Pathways in the Thermolysis of Cyclohexanone

Pathway	Clea-vage	Ex-tent	Mass Balance for Hydrocarbon Gases		
		(%)	C_2	C_3	C_4
Cyclohexanone ⟶ MVK + C_2	β	54	54		
⟶ Ketene + C_4	β	5			(5)
⟶ Cyclopentane + CO	α	3			
⟶ Cyclopentadiene + CO	α	2			
⟶ Acrolein + C_3	α	2		2	
⟶ C_2 + C_3 + CO	α	(33)	(33)	(33)	
⟶ Benzene	-	1			
Total:		100	87	35	5
Experimental Mass Balance:			86	27	8

Table 10

Decomposition Pathways in the Thermolysis of Cycloheptanone

Pathway	Cleavage	Extent (%)	Mass Balance for Hydrocarbon Gases		
			C_2	C_3	C_4
Cycloheptanone → MVK + C_3	β	20		20	
→ Acetone + C_4	β	3			(3)
→ 3-Methylcyclohexanone	β	2			
→ Ketene + C_2 + C_3	β	5	5	5	
→ Cyclohexane + CO	α	9			
→ Cyclopentanone + C_2*	α	1	1		
→ 2C_3 + CO	α	(13)		(26)	
→ C_2 + C_4 + CO	α	(29)	(29)		(29)
→ 3C_2 + CO	α	(16)	(48)		
→ Cyclohexanone + C_1*	α	1			
→ Benzene + C_1	-	1			
Total:		100	83	51	32
Experimental Mass Balance:			79	45	28

*Initial α cleavage assumed by analogy with electron impact (60).

Table II

Decomposition Pathways in the Thermolysis of Cyclooctanone

Pathway	Cleavage	Extent (%)	Mass Balance for Hydrocarbon Gases		
			C_2	C_3	C_4
Cyclooctanone ⟶ Acetone + C_2 + C_3	β	4	4	4	
⟶ Ketene + C_2 + C_4	β	23	(23)		(23)
⟶ Cycloheptane + CO	α	6			
⟶ Cyclopentadiene + C_2 + CO	α	4	4		
⟶ Cyclopentanone + C_3*	α	1		1	
⟶ Cyclohexanone + C_2*	α	1	1		
⟶ $2C_2$ + C_3	α	(59)	(118)	(59)	
⟶ Benzene + C_2	-	2	2		
Total:		100	152	64	23
Experimental Mass Balance:			106	54	32

*Initial α cleavage assumed by analogy with electron impact (60).

Table 12

Decomposition Pathways In the Thermolysis of Cyclopentanone

Pathway	Clea-vage	Ex-tent	Mass Balance for Hydrocarbon Gases		
		$(\%)$	C_2	C_3	C_4
Cyclopentanone → Acetone + C_2	β	1	1		
→ Ketene + C_3	β	10		10	
→ $2C_2$ + CO	α	(57)	(114)		
→ C_4 + CO	α	(24)			(24)
→ Cyclopentadiene	–	1			
→ 2-Cyclopentenone	–	7			
Total:		100	115	10	24
Experimental Mass Balance:			109	9	21

Table 13

Decomposition Pathways in the Thermolysis of 5-Nonanone

Pathway	Clea-vage	Ex-tent (%)	Mass Balance for Hydrocarbon Gases		
			C_2	C_3	C_4
5-Nonanone ⟶ Acetone + $2C_3$	β	2		(4)	
⟶ MVK + C_3 + C_2	β	4	4	4	
⟶ 2-Hexanone + C_3	β	2		2	
⟶ Ketene + $2C_2$ + C_3	β	12	(24)	12	
⟶ Valeraldehyde + C_4	α	1			1
⟶ C_4 + $2C_2$ + CO	α	(4)	(8)		(4)
⟶ $2C_3$ + C_2 + CO	α	(10)	(10)	(20)	
⟶ $4C_2$ + CO	α	(65)	(260)		
Total:		100	306	42	5
Experimental Mass Balance:			209	36	3

Table 14

Decomposition Pathways in the Thermolysis of 2-Hexanone

Pathway	Cleavage	Extent (%)	Mass Balance for Hydrocarbon Gases		
			C_2	C_3	C_4
2-Hexanone ⟶ Acetone + C_3	β	15		15	
⟶ Ketene + C_3 + C_1	β	24		(24)	
⟶ Valeraldehyde + C_1	α	2			
⟶ C_4 + C_1 + CO	α	(2)			(2)
⟶ $2C_2$ + C_1 + CO	α	(53)	(106)		
⟶ MVK + C_2	–	4	4		
Total:		100	110	39	2
Experimental Mass Balance:		135	135	27	2

cycloheptanone (Table 10). The extent (and, hence, the yields of the hydrocarbons) of each of these three pathways is chosen so that the total yield of each of the hydrocarbons demanded by all of the decomposition pathways best fits the experimental yields.

On the basis of the assumptions that have been made, the proposed reaction pathways are reasonably consistent with the hydrocarbon mass balance for cyclohexanone, cycloheptanone, and cyclopentanone. This agreement suggests that the proposed decomposition pathways do, indeed, approximate the real decomposition modes. Poorer agreement is noted for the aliphatic ketones and cyclooctanone. This lack of consistency suggests that the correlation of reaction pathway to an initial dissociation involving the carbonyl group is not valid for compounds of increasing hydrocarbon content. From a practical point of view, the validity of the correlations is affected by products that are not accounted for (material that was lost or not present in significant amounts), secondary decomposition of primary products, and the possible occurrence of radical chain processes*.

At any rate, these proposed pathways are useful for comparing the thermal decomposition modes of the ketones. Considerable work would have to be done to identify the pathways completely.

6. Conclusion

In all previously reported thermolytic decompositions and in the photolytic and electron impact fragmentation of alicyclic and aliphatic

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*The low pressure conditions of the thermolyses are expected to minimize radical chain processes.

ketones, α cleavage is the major primary dissociative process. Considerable evidence which indicates that β cleavage is a major primary process in the thermolysis of cyclohexanone and cycloheptanone has been accumulated in the present study. In fact, for cyclohexanone β cleavage is estimated by product analysis to occur to the extent of about 60%*. Finally, the studies on several other alicyclic and aliphatic ketones suggest that β cleavage is a general dissociative process in the low pressure thermolysis of ketones**.

*MVK, a product consistent with a β cleavage origin, has also been identified by Hedaya as a product in the "flash vacuum pyrolysis" of cyclohexanone (37).

**Crandall and collaborators have proposed that β cleavage is the primary process in the photolysis and thermolysis of 4-cyclooctenone, for which the major product is 3-vinylcyclohexanone. However, in this case the intermediate biradical, formed from α cleavage, has the added stabilization of the allyl moiety (38).

PART III

THE THERMOLYSIS OF CHLOROSULFONYLACETIC ACID

A. Introduction

Sulfenes ($RR'C=SO_2$) are now accepted as chemical intermediates to rationalize a variety of reactions and transformations. Although sulfenes have never been isolated and characterized there is ample chemical evidence to support their existence*.

The classical sulfene reaction is the tertiary amine catalysed solvolysis of an alkanesulfonyl chloride which contains an α hydrogen atom. When the reaction of equimolar amounts of an alkanesulfonyl chloride and a tertiary amine is carried out in the presence of excess water, alcohols, or amines the corresponding alkanesulfonate derivative is obtained. Independently, King and Durst (40) and Truce and Campbell (41) provided strong evidence that sulfenes are intermediates in these reactions. They used deuterium oxide and deuterated alcohols to show that the resulting alkanesulfonate derivative contained one deuterium atom which was α to the sulfonyl group. The following mechanism fits the experimental facts.

$$RR'CHSO_2Cl + B \longrightarrow [RR'C=SO_2] + \overset{+}{B}H\overset{-}{Cl}$$

$$[RR'C=SO_2] + DZ \longrightarrow RR'CDSO_2Z$$

$$B = NR_3 \text{ where R is commonly ethyl.}$$

*The development of sulfene chemistry has been reviewed by Opitz (39).

$Z = -OD, \quad -OR.$

$R,R' = $ alkyl, aryl, or hydrogen.

King and Lee (42) have examined the kinetics of sulfene formation in a number of alkanesulfonyl chloride-tertiary amine systems. Sulfene formation exhibits second order kinetics, being first order in alkanesulfonyl chloride, first order in tertiary amine, and zero order in trapping reagent when the concentration of the trapping agent is low.

A number of transformations that can be rationalized by the intermediacy of sulfenes have been reported. De Mayo et al. have noted that the irradiation of the sultone 1 gives products that can be accounted for by the intermediacy of the sulfene 2 (43). When the irradiation is carried out in methanol the sulfonate 3 is obtained, and in the presence of benzylamine, the sulfonamide 4 is produced. King and Durst have found that the irradiation of the unsaturated sultam 5 also gives products that can be explained by a sulfene intermediate (44). However, de Mayo and Charlton further reported that the flash photolysis of the sultone 6, which in methanol gives the expected sulfonate ester, exhibits no intermediate with an absorption longer than 320 mμ and a lifetime longer than 20 μ sec in cyclohexane (45). Similarly no transient with an absorption longer than 320 mμ is found for the sultam 5. As the intermediate sulfenes for these systems would be expected to have an absorption band longer than 320 mμ, it was concluded that the maximum lifetime of the sulfenes could be 20 μ sec. It is felt, therefore, that sulfenes are not the intermediates in these transformations.

Recently, King and collaborators have reported that the thermolysis

$\underline{1}$ → ($h\nu$) → $\underline{2}$

$\underline{2}$ → (CH_3OH) → $\underline{3}$

$\underline{2}$ → ($PhCH_2NH_2$) → $\underline{4}$ (SO_2NHCH_2Ph)

$\underline{5}$

$\underline{6}$

$\underline{7}$ → ($500°$, $-N_2$) → $\underline{8}$ → $\underline{9}$
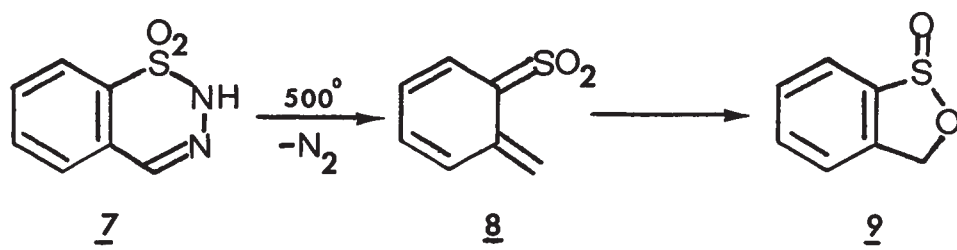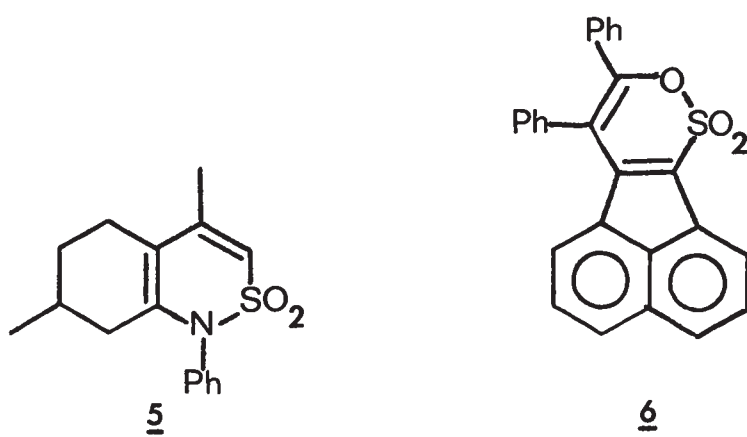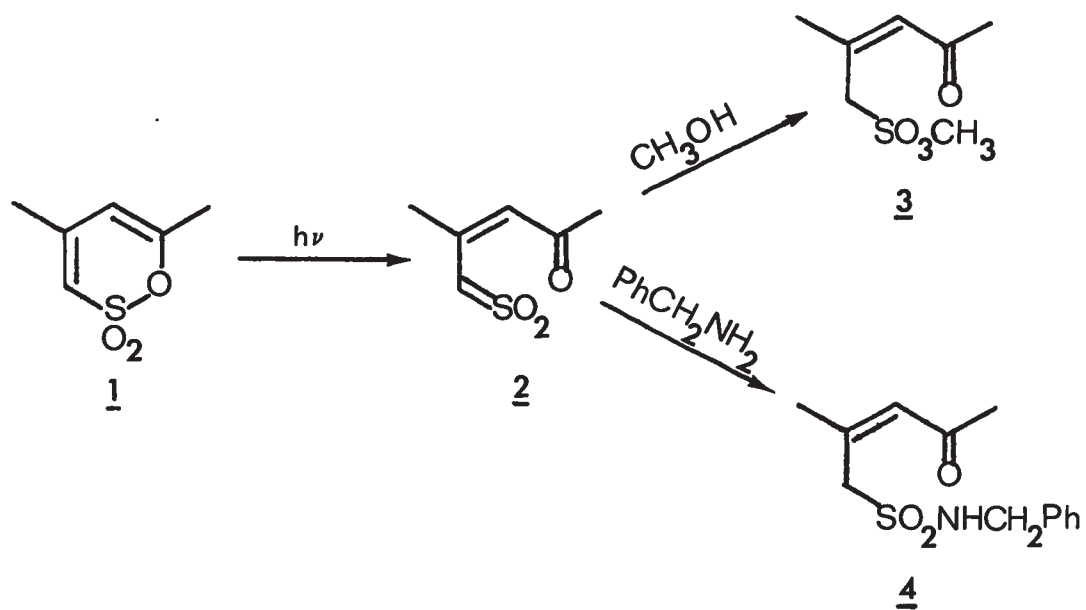
of the benzothiadiazine 7 gave the sulfinate 9. The sulfene 8 is
envisaged as the intermediate in this transformation (46).

King, de Mayo and co-workers have recently attempted to generate
sulfenes in the gas phase in order to further define their physical
and chemical properties (35). For example, the flow thermolysis of the
thiete 1,1-dioxides 10 at temperatures less than 600° gives the cyclic
sulfinate esters (sultines) 12 in good yields. Under flash thermolysis
conditions at 950°, the carbonyl compounds 14 are obtained in excellent
yields. Also under these conditions, the sultines 12 cleanly give the
carbonyl compounds 14. These results are interpreted as follows:

(1) electrocyclic ring opening of 10 to give the vinylsulfene 11.

(2) rapid "abnormal" nucleophilic addition of the carbon atoms
    to an oxygen atom of the sulfene to give either the sultine
    12 or the intermediate 13 depending on the temperature.

(3) extrusion of sulfur monoxide from 13 to give the carbonyl
    compounds 14.

Attempts to trap the sulfene 11 were not very successful. Only in
the solution thermolysis of 10 at 235° in the presence of phenol has
the expected adduct 15 been obtained, even then in low yield. It seems
reasonable to assume that the vinylsulfene 11 is indeed, the common
intermediate in the thermolysis of 10, but in all likelihood it decom-
poses more rapidly than it undergoes reaction with a trapping agent.

The desulfinylation (11⟶13) that is suggested for the thermolysis
of the thiete 1,1-dioxides 10, appears to be a general reaction of
sulfene at temperatures greater than 800°. For instance, it has been
observed that the thermolysis of disulfene 16 at 900° (47) and 3-thiet-

anol 1,1-dioxide 17 at 935° (35) both give formaldehyde amongst other products. These results are rationalized by the thermal fragmentations of 16 and 17 to give sulfene 18 and its subsequent desulfinylation via the cyclic isomer 19.
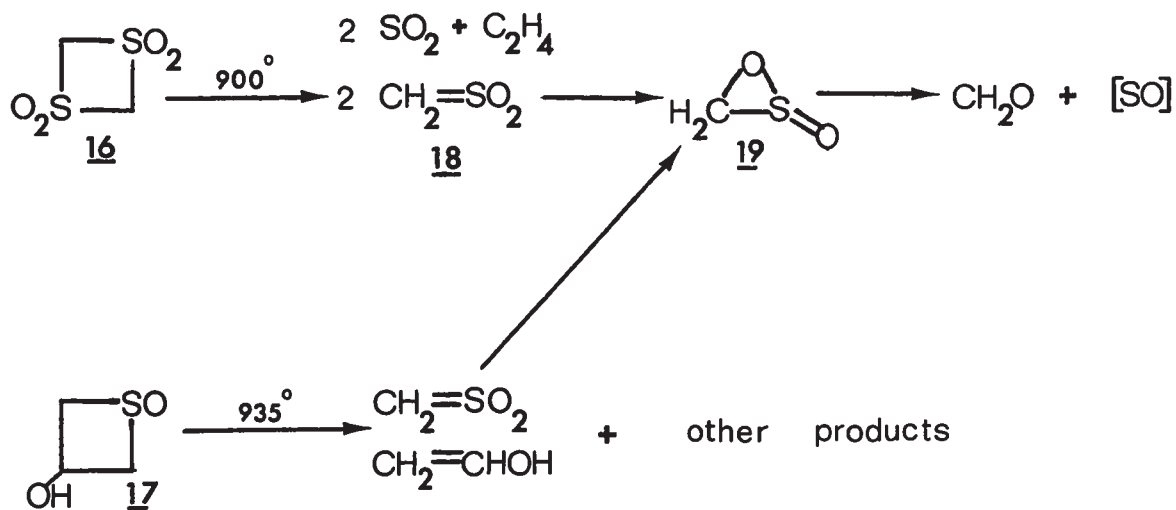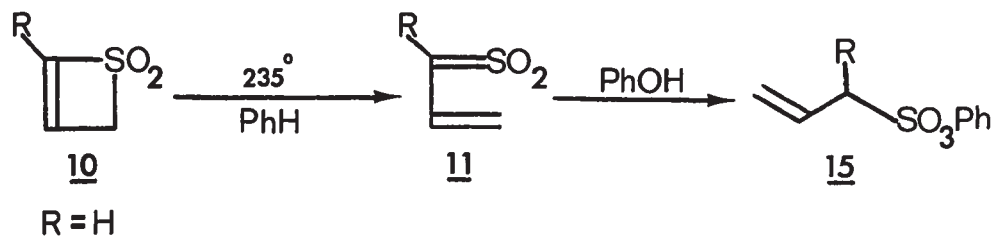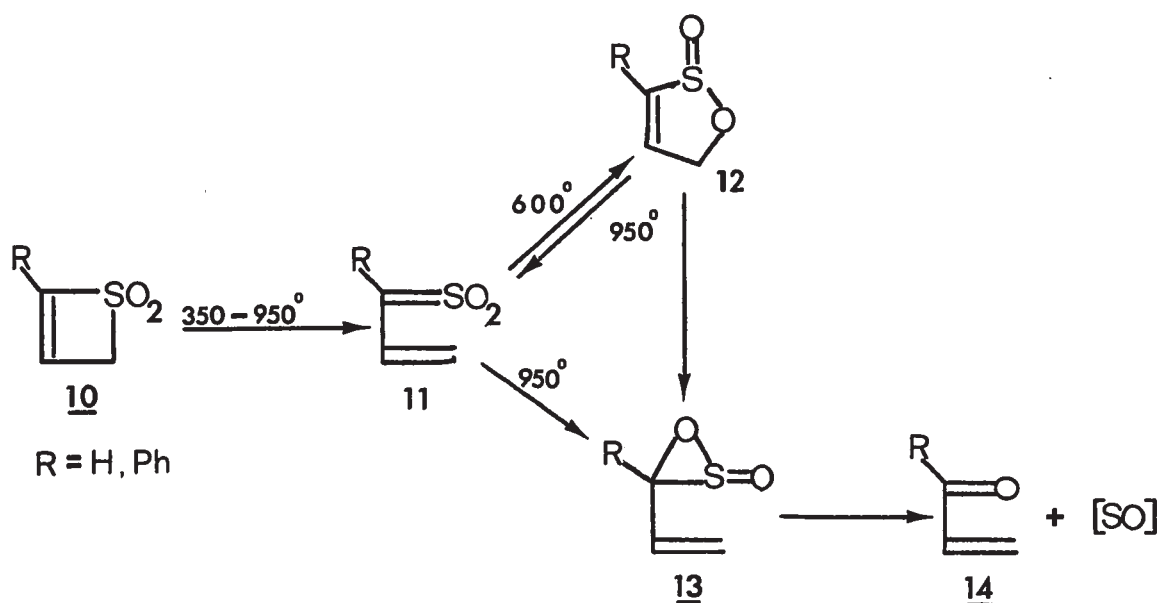
With this background information, it was desired to find a system that would undergo decomposition to give sulfene ($CH_2=SO_2$) in good yield. In addition, the thermolytic conditions employed should be mild enough that sulfene, once produced would have a sufficient lifetime to be condensed at liquid nitrogen temperature where it would be available for reaction with conventional trapping agents and, eventually spectroscopic examination.

Specifically, chlorosulfonylacetic acid 20 was thermolysed in an attempt to generate sulfene 18 in good yield under conditions where it had a lifetime of sufficient length to be intercepted by conventional reagents. The following section of this thesis summarizes the work done to achieve this goal.
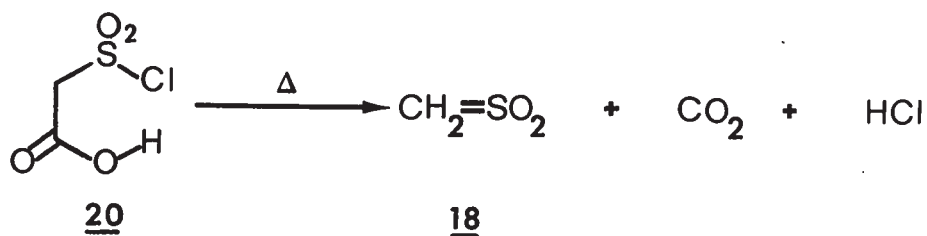
B.   Results and Discussion

I.   Product Analysis for the Thermolysis of Chlorosulfonylacetic Acid

Chlorosulfonylacetic acid was thermolysed at temperatures of 640-940° and at pressures, measured outside of the hot zone, of 10-20 μ. The thermolysate that emerged from the thermolysis zone was immediately condensed on a liquid nitrogen Dewar surface together, in most cases, with a trapping agent (methanol or hydrogen chloride). Under these conditions, the calculated residence time of chlorosulfonylacetic acid in thermolysis zone was 1-2 msec.

As experimentation progressed significant changes were made in the product handling and thermolysate trapping techniques. These alterations are pointed out in the text.

Initially, the "sandwich" method of trapping the thermolysate was employed. The cold face was first covered with a layer of methanol. Then, as the thermolysis of chlorosulfonylacetic acid progressed, thermolysate was deposited onto the methanol. Finally, the "sandwich" was completed by condensing a second layer of methanol on top of the thermolysate. The thermolysate and methanol were then distilled from the Dewar face into a sample flask mounted on the product handling manifold.

Control experiments revealed that methanesulfonyl chloride, a major product from the thermolysis of chlorosulfonylacetic acid, reacted with the methanol under the above product handling procedures to give methyl methanesulfonate. Because methyl methanesulfonate is the expected adduct when methanol intercepts sulfene, the origin of the methyl methanesulfonate that was found in the early thermolyses of chlorosulfonylacetic acid is uncertain.

A procedure was developed to separate the methanol from methanesulfonyl chloride whereby no methyl methanesulfonate was produced. The thermolysate and methanol were distilled from the cold face through a trap on the manifold that was maintained at -45° by means of a liquid nitrogen-chlorobenzene slush. Methanesulfonyl chloride and methyl methanesulfonate were quantitatively condensed, but methanol and other components of the thermolysate which were volatile at -45° were condensed in a liquid nitrogen trap at the end of the manifold. Under these conditions methanesulfonyl chloride was shown not to react with methanol to give methyl methanesulfonate.

The products identified from the thermolysis of chlorosulfonylacetic acid at 650° with methanol "sandwich" trapping included: methanesulfonyl chloride, methyl methanesulfonate, formaldehyde dimethylacetal (dimethoxymethane), sulfur dioxide, and carbon dioxide.

Quantitative analysis for the thermolyses of chlorosulfonylacetic acid at 650° and 940° were carried out. Methanol "sandwich" trapping was employed. The results are summarized in Table 15. All yields quoted in Table were based on duplicate or triplicate experiments. The variance in the product yields was chiefly attributable to the difficulty in subliming the chlorosulfonylacetic acid through the thermolysis zone at a uniform rate.

During the thermolysis at 650°, a slight amount of flaky grey, polymeric material was deposited on the cold face. The infrared spectrum of this material exhibited strong sulfur-oxygen stretching bands at 1320 and 1120 cm^{-1}. At 940°, a substantial amount of an intractable yellow gum was produced.

Table 15

Thermolysis of Chlorosulfonylacetic Acid

Product Yields with Methanol "Sandwich" Trapping

Products	Yields**	
	650°	940°
$CH_2(OCH_3)_2$	4-8	50-75
CH_3SO_2Cl	50-60	--*
$CH_3SO_2OCH_3$	2.6	--*

*negligible amount (less than 0.1%).

**mole percentages based on decomposed chlorosulfonylacetic acid.

2. Thermolysate Trapping with Methanol-d

The thermolysis of chlorosulfonylacetic acid at 650° was repeated with methanol-d (98%) as the trapping agent ("sandwich" trapping). Methanesulfonyl chloride and methyl methanesulfonate were isolated by preparative glc and analysed for deuterium incorporation by mass spectrometry. The results for duplicate experiments carried out at 650° are given in Table 16.

As a check on the accuracy of the mass spectral analyses, methyl methane-d-sulfonate ($CH_2DSO_2OCH_3$) was prepared by the reaction of methanesulfonyl chloride and triethylamine in the presence of excess methanol-d (98%). Careful integration of the nmr spectrum of the material revealed that it was 78% monodeuterated. The monodeuteration as determined by mass spectrometry was 78.9%, a number in good agreement

Table 16

Thermolysis of Chlorosulfonylacetic Acid

Deuterium Distributions with Methanol-d "Sandwich" Trapping

Run	Products	Distribution (%)*	
		$\underline{d}_0$	$\underline{d}_1$
1	$CH_3SO_2OCH_3$**	37.0	63.0
	CH_3SO_2Cl	97.0	3.0
2	$CH_3SO_2OCH_3$**	49.6	50.4
	CH_3SO_2Cl	96.7	3.3

*No significant amount of methyl methane-$\underline{d}_2$-sulfonate was found. The maximum amount was 2%.

**Deuterium incorporation for methyl methanesulfonate was in the methyl group α to the sulfonyl group.

with the value obtained by nmr*.

3. <u>Homogeneous Trapping of the Thermolysate</u>

In an attempt to get more efficient trapping of the thermolysate, the Dewar with an inlet nozzle was employed. A uniform stream of trapping agent, admitted by the nozzle, mixed with the thermolysate stream to produce homogeneous condensation of thermolysate and trapping agent on the cold face. About a twenty-fold molar excess of trapping agent was employed. Control experiments showed that methanesulfonyl chloride and methanol did not react to give methyl methanesulfonate

*King and Durst found that the methyl methane-d-sulfonate produced by the triethylamine catalysed solvolysis of methanesulfonyl chloride in the presence of methanol-d was only 72% monodeuterated (40).

under the homogeneous trapping conditions.

Thermolysis of chlorosulfonylacetic acid at 650° with methanol as trapping agent, gave methyl methanesulfonate in about 40% yield. Only trace amounts of methanesulfonyl chloride were detected. When the thermolyses were repeated with hydrogen chloride as trapping agent* the yield of methanesulfonyl chloride was about 59%. Thermolysis of chlorosulfonylacetic acid in the absence of added hydrogen chloride gave methanesulfonyl chloride in 47-56% yields.

Interesting results were obtained from the thermolysis of chlorosulfonylacetic acid at 650° when deuterium chloride (97%) was employed as the trapping agent. The methanesulfonyl chloride in the thermolysate was isolated by preparative glc and it was analysed for deuterium incorporation by mass spectrometry. The results for duplicate experiments are given in Table 17.

Duplicate control experiments were performed in which methanesulfonyl chloride was passed through the furnace (at room temperature) and condensed on the cold face in the presence of deuterium chloride. Within experimental error no incorporation of deuterium occurred in the methanesulfonyl chloride that was subsequently isolated.

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*For the trapping of sulfene, generated by a tertiary amine catalysed solvolysis of an alkanesulfonyl halide, hydrogen chloride cannot be employed as a trapping agent because it would instead form the tertiary amine hydrochloride. However, Durst has accumulated some evidence that suggests that triethylammonium hydrochloride can transfer the elements of hydrogen chloride to sulfene (48).

Table 17

Thermolysis of Chlorosulfonylacetic Acid

Deuterium Incorporation in the Methanesulfonyl Chloride

Run	Product	Distribution (%)*	
		d_0	d_1
l	CH_3SO_2Cl	12.6	87.4
d	CH_3SO_2Cl	19.9	80.1

*Negligible methane-d_2-sulfonyl chloride
(less than 0.5%) was present.

4. Sulfene Formation in the Thermolysis of Chlorosulfonylacetic Acid

In order to explain the results presented in the previous three

sections (summarized in Figure 9), a species of molecular formula CH_2SO_2

must be generated in the thermolysis zone, travel to the cold face, and

react there. This CH_2SO_2 species must be sulfene on the basis of the

following facts:

1. The expected adduct from the reaction of sulfene and methanol,

    methyl methanesulfonate, was obtained in yields of about 40%.

    It was further shown that the methyl methanesulfonate was not

    formed by the reaction of methanesulfonyl chloride and methanol

    in a displacement reaction at sulfur.

2. The formation of only methyl methane-d-sulfonate and negligible

    amounts of methyl methane-d_2-sulfonate, when the thermolysate

    was condensed in the presence of methanol-d, is in agreement

    with the work done to demonstrate the existence of sulfene in

    the base catalysed solvolyses of alkanesulfonyl chlorides

    (40) (41). The formation of methane-d-sulfonyl chloride (85%

Figure 9

Sulfene from Chlorosulfonylacetic Acid
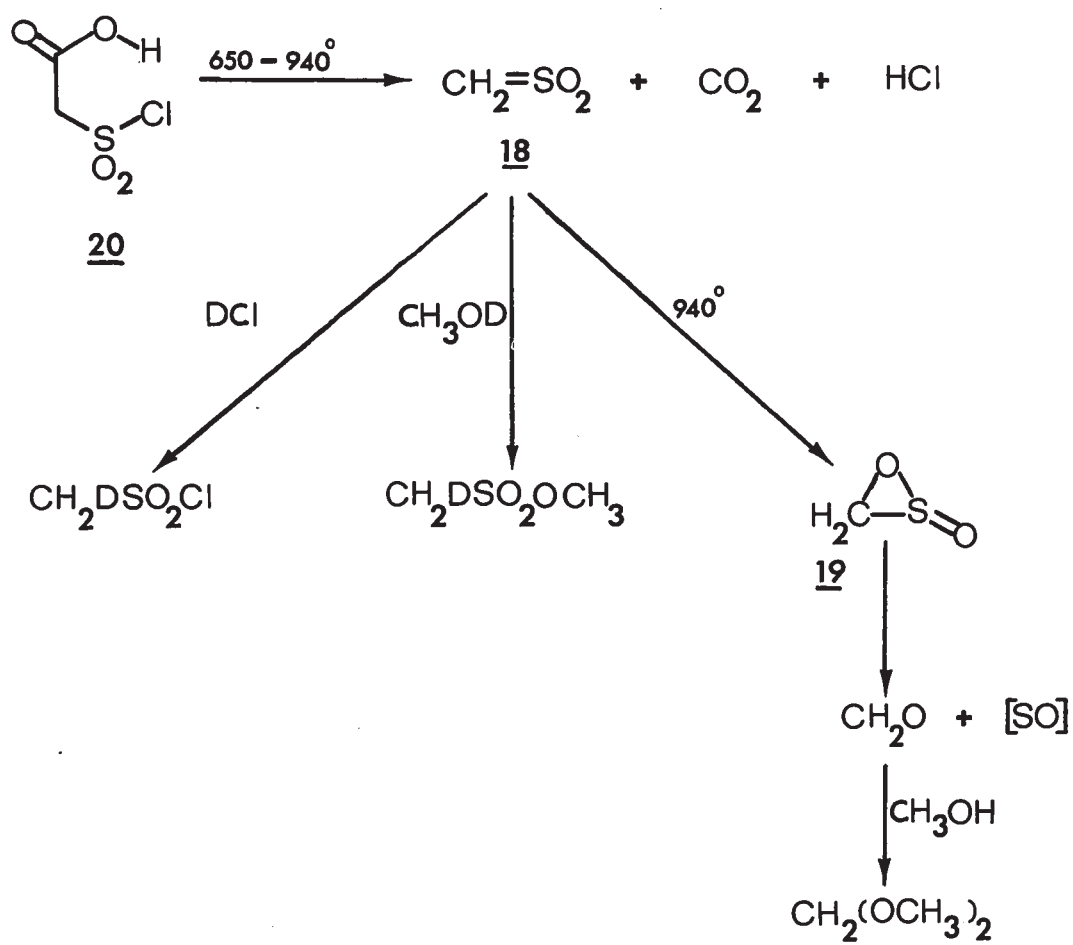
$\underline{d}_1$) when deuterium chloride was employed as the trapping agent substantiates the presence of sulfene in the thermolysate.

3. The presence of dimethoxymethane, formed by the reaction of methanol and formaldehyde, is consistent with the disproportionation of sulfene at temperatures greater than 700° (35).

Therefore, sulfene must be a discrete, volatile compound which has a finite lifetime.

The experiments described in the previous sections demonstrate that the thermolysis of chlorosulfonylacetic acid produces sulfene in the vapour phase in good yield. At 940°, sulfene is formed in 50-75% yield (the amount of dimethoxymethane) but it undergoes unimolecular decomposition before interception by methanol. At 640°, the amount of sulfene produced is represented by the yield of methane-$\underline{d}$-sulfonyl chloride (about 50%), plus the amount of dimethoxymethane (4-8%). This gives the minimum conversion to sulfene of about 55%, a number that is surely conservative. In all probability, the undeuterated methanesulfonyl chloride* also arises from sulfene. In addition, some sulfene may have polymerized to produce some of the intractable material.

5. The Thermolysis of Methanesulfonyl Chloride

Methanesulfonyl chloride is the principal product from the thermolysis of chlorosulfonylacetic acid at 640°. However, separate thermolyses of methanesulfonyl chloride revealed that it also gives products that appear to originate from sulfene.

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*The proton probably arose from addition of hydrogen chloride (a decomposition product) to sulfene.

At 660° with methanol "sandwich" trapping, methanesulfonyl chloride gave about 1% dimethoxymethane and at 940° the yield of dimethoxymethane increased to 27%*. Thermolysis of methanesulfonyl chloride at 665° with homogeneous methanol trapping gave methyl methanesulfonate in about 18% yield.

Since the thermolysis of methanesulfonyl chloride to give sulfene has not been reported, some relevant information from the literature was obtained. The thermolysis of methanesulfonyl chloride in a static system at 380-420° gives products that are consistent with a radical chain mechanism (49). No formaldehyde was detected. Sufficient information is not available for acetyl chloride, but evidence has been reported that indicates that acetyl bromide in a flow system at 600-800° gives ketene and hydrogen bromide by a molecular mechanism (50). Gas phase pyrolyses of alkyl halides give hydrogen chloride and olefins by a moderately polar four-centred transition state (51). Based on these analogies it seems possible that the thermolysis of methanesulfonyl chloride under flash conditions gives sulfene and hydrogen chloride by a four-centred ion pair mechanism.

On the basis of product analysis, it seems likely that sulfene is a product from the thermolysis of methanesulfonyl chloride at both 650° and 940°. However, it is improbable that the secondary decomposition of methanesulfonyl chloride to give sulfene is an important reaction in the decomposition of chlorosulfonylacetic acid. Because the deuterium chloride trapping experiments show that at least 85% (and possibly 100%)

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*These yields were not corrected for methanesulfonyl chloride that survived to thermolysis zone.

of the methanesulfonyl chloride produced in the thermolysis of chloro-
sulfonylacetic acid arises from sulfene, the formation of methanesulfonyl
chloride must occur on the cold face (by the addition of hydrogen
chloride to sulfene). Thus, a maximum of 15% of the methanesulfonyl
chloride obtained from the thermolysis of chlorosulfonylacetic acid at
650° can be formed by a molecular split in chlorosulfonylacetic acid.
Therefore, a maximum of about 1% of the sulfene, obtained from the
thermolysis of chlorosulfonylacetic acid can arise from the secondary
decomposition of methanesulfonyl chloride.

6. Conclusions

The principal objective of this problem has been fulfilled.
Sulfene has been generated to a minimum extent of 50% in the thermolysis
of chlorosulfonylacetic acid under conditions in which it survived the
thermolysis zone and travelled to the cold face before it was inter-
cepted by trapping agents. If the liquid nitrogen Dewar were replaced
with the electron source of a mass spectrometer, the ionization poten-
tial of sulfene could be measured. The infrared and ultraviolet spectra
of sulfene could be determined if the liquid nitrogen Dewar was replaced
with the appropriate cryoscopic optics systems*. With some of the

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*Very recently it has been reported (53) that methanesulfonic
anhydride, when heated under nitrogen at 250°, gave methanesulfonic
acid (70%), intractable material (15%), and sulfene. No experimental
evidence for the presence of sulfene was given, and it was assumed that
under the conditions of the thermolysis, the sulfene underwent further
decomposition. In these laboratories, with a thermolysis apparatus
equipped with a cryostat, the infrared spectrum of the products from
the low pressure thermolysis at 650° of methanesulfonic anhydride was
obtained. The spectrum contained several bands which were identical to
those tentatively ascribed to sulfene generated by the thermolysis at
650° of chlorosulfonylacetic acid (54).

sophisticated kinetic techniques developed by Benson and Spokes (52)

it seems possible that an estimate of the lifetime of sulfene could be

made.   Such physical data would neatly complement the already elucidated

chemical properties of sulfene.

PART IV

EXPERIMENTAL SECTION

A.   General Considerations

Infrared spectra were obtained with either a Beckman   IR-5 or IR-10 instrument. The mass spectra were recorded on a Varian M-66 instrument. Analytical and preparative gas chromatography was carried out with a Varian 1520-IB gas chromatograph with thermal conductivity detectors. Helium was the carrier gas and the columns and conditions are specified in the text. The nuclear magnetic resonance spectra were obtained on a Varian HA-100 or a T-60 spectrometer. The ultraviolet spectra were run on a Cary 14 instrument. Indexes of refraction were measured on a Bausch and Lomb refractometer. Melting points were obtained on a Kofler hot stage and are uncorrected.

All solvents and calibrating compounds that were used for analytical work were distilled.

The microanalysis was performed by A. Gygli, Toronto, Ont. Deuterium analyses by the combustion method were done by J. Nemeth, Urbana, Ill.

B.   Low Pressure Thermolysis

I.   Thermolysis Apparatus

The thermolyses were carried out in an apparatus that consisted of the following parts:

1.   the inlet manifold.

2.   the furnace.

3.   the Dewar.

4.   the product handling manifold.

5.   the pumping system.

A schematic diagram of the furnace and Dewar is given in Figure 10. The letters on the diagram correspond to descriptions given in the text.

The inlet manifold contained a mercury manometer, a gas storage bulb, a calibrated gas bulb (35.04 ml), and three sample tubes with taps. A teflon needle valve (B) which regulated the flow rate of compounds into the furnace connected the inlet manifold to the furnace (A).

The furnace consisted of an outer brass housing and an inner ceramic reactor tube.

The housing consisted of a cylinder with terminal flanges to which were bolted two end plates. The cylinder, of 1/8 in. thick brass, was 11 in. long and 2 1/2 in. in diameter. It was encircled with 9 coils of copper tubing (H) in order to provide water cooling and was terminated by flanges 3/8 in. thick by 5 in. in diameter. The inlet end plate, 5 in. in diameter by 3/8 in. in thickness, had a centred 1/2 in. O-ring connector, a Hastings vacuum gauge (D), and two pairs of metal-to-porcelain through connectors (C). The outlet end plate had a centred 1 in. O-ring butt connector. A vacuum seal between the flanges and end
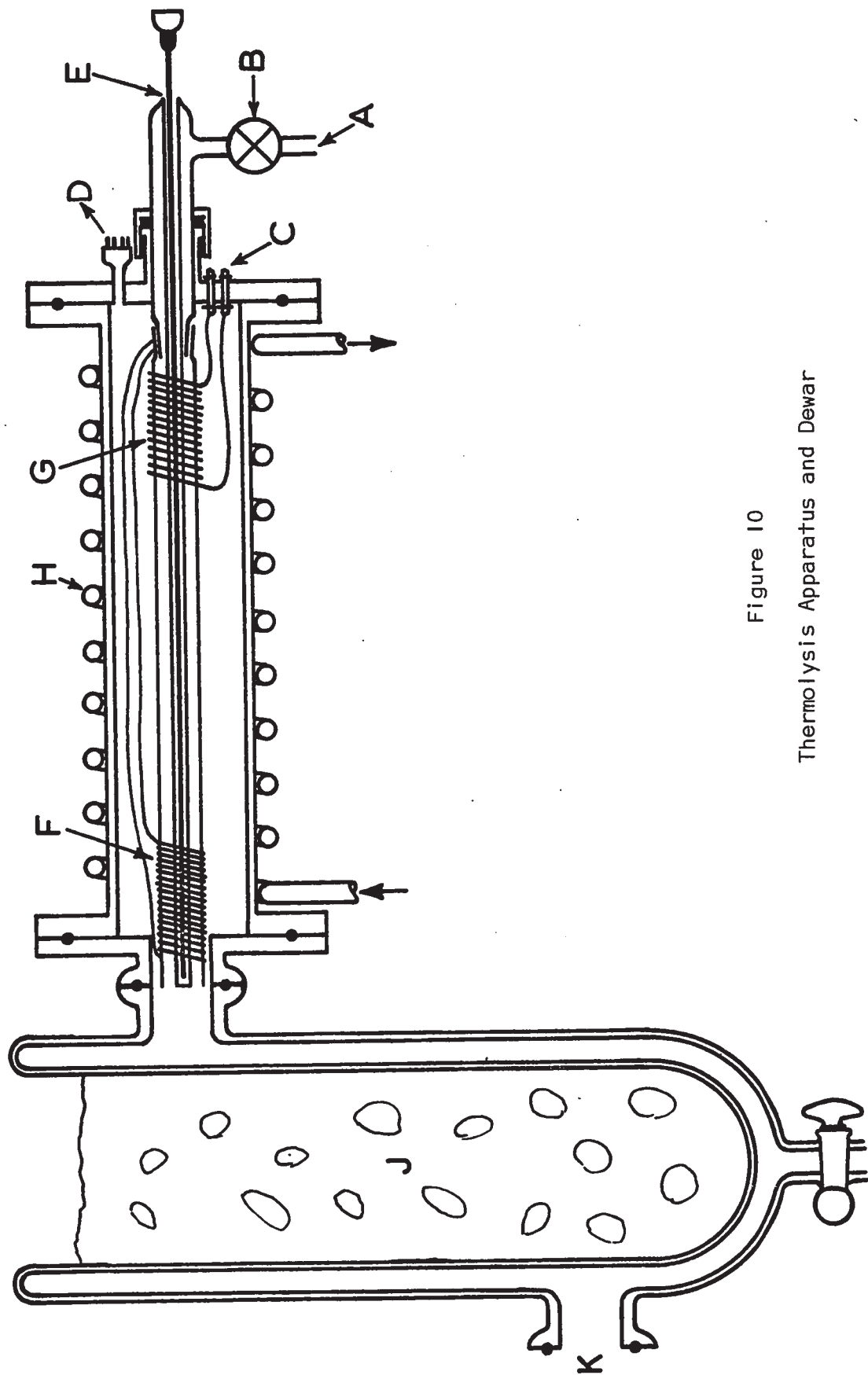
Figure 10

Thermolysis Apparatus and Dewar

plates was provided by 1/8 in. Viton O-rings.

The reactor tube was inserted into the housing through the 1/2 in. O-ring connector of the inlet end plate. The tube consisted of two concentric tubes of Coors Mullite fused to Pyrex glass and joined together outside the housing. The inner tube, of 1/4 in. o.d., was closed at the outlet end to provide the thermocouple well (E). A 1/8 in. stainless steel shielded, MgO insulated, chromel-alumel thermocouple occupied the thermocouple well and was connected to a Barber-Coleman Model 471 temperature controller. The outer tube, of 1/2 in. o.d., was open at the outlet end. The first 4 in. of the outer tube (F) were wound with 6 ft. of 18 gauge Nichrome wire, spaced by turns of asbestos rope and covered by moulded asbestos. The last 4 in. of the outer tube (G) within the housing were loosely wrapped with 4 ft. of 22 gauge Nichrome wire. The ends of both windings were attached to the through connector pairs. Variac transformers regulated the voltage across the connector terminal pairs and hence the temperatures in the thermolysis zone (F) and the sublimation zone (G).

A Dewar (J), of Pyrex glass, was attached to the O-ring butt connector of the housing. The liquid nitrogen cooled cold face of this dewar was 5.0 cm. from the aperture of the reactor tube.

A special Dewar equipped with an inlet nozzle was employed in some experiments in order to allow continuous mixing of the thermolysate and a trapping agent. The nozzle, centred between the cold face and the aperture of the reactor tube, contained three small holes to disperse the trapping agent uniformly into the thermolysate stream that emerged from the reactor tube. A schematic diagram of the Dewar equipped with

Figure II

Dewar with Inlet Nozzle
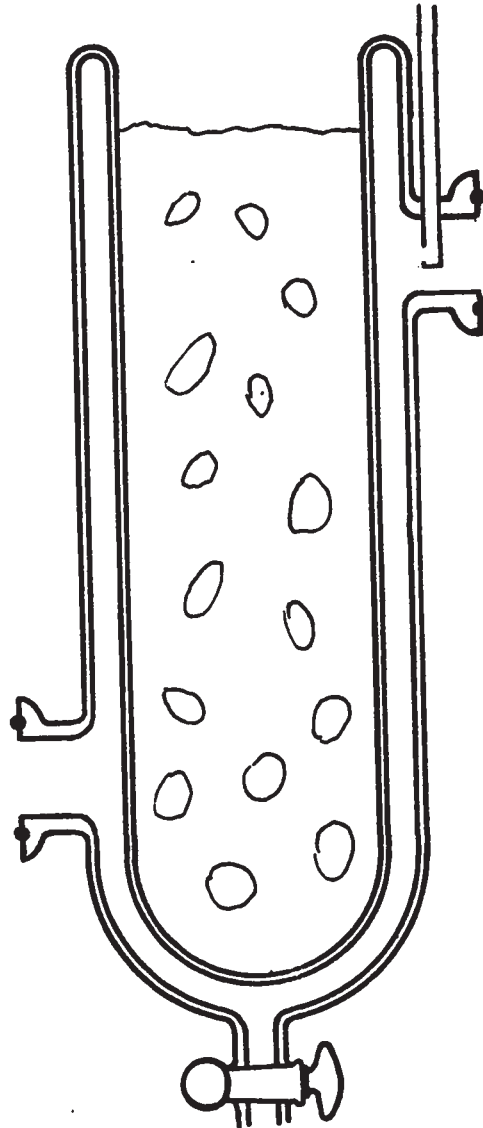
Figure 12

Temperature Profile of the Thermolysis Zone

Temp (°C) vs. Distance from cold face (cm)
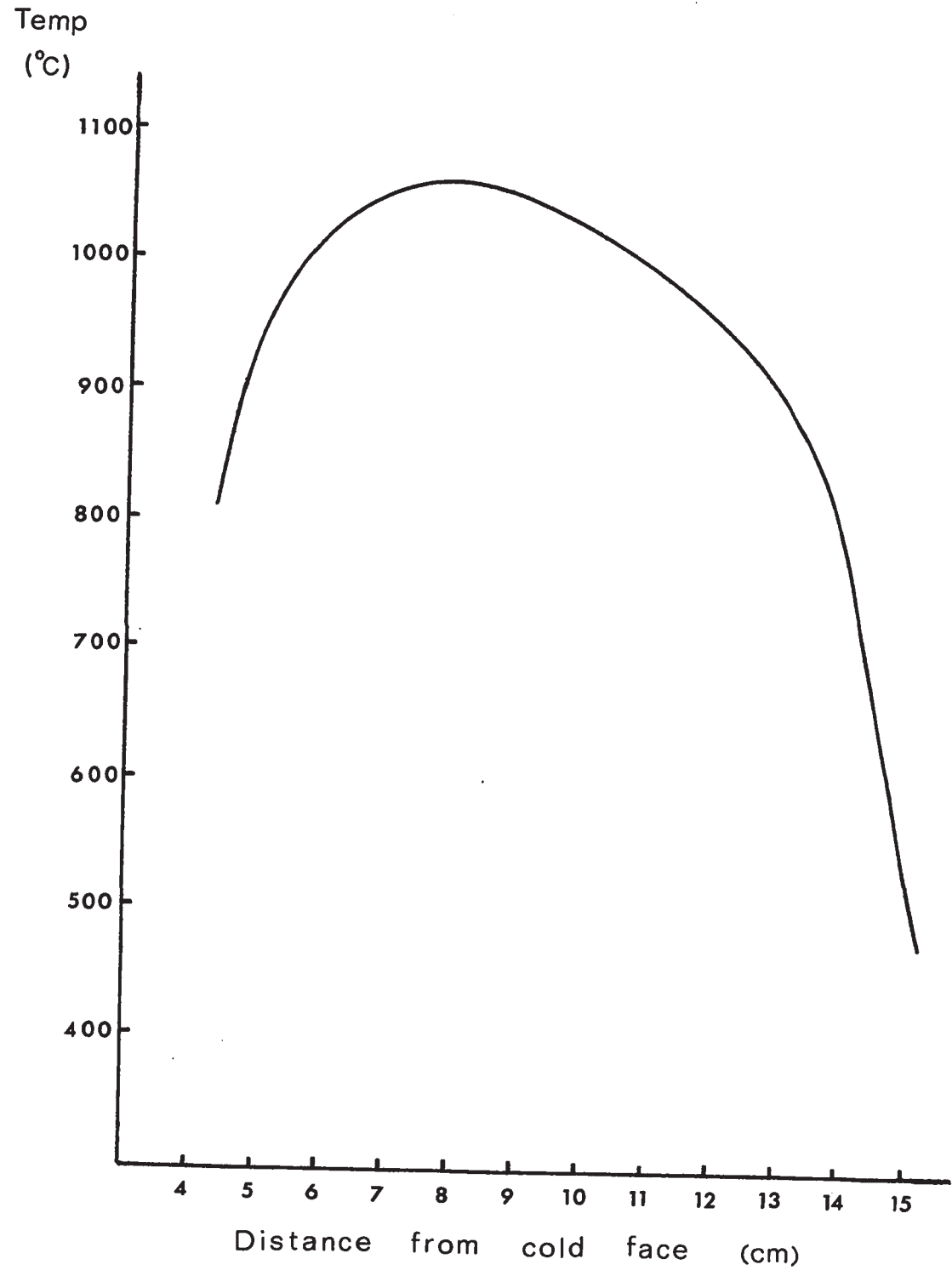
the inlet nozzle is given in Figure II.

A temperature profile which shows the temperature in the thermolysis zone at various distances from the liquid nitrogen Dewar face is given in Figure 12.

The product handling manifold consisted of two large U-tubes, a series of five outlet taps, and Hastings vacuum gauge.

The system was maintained under continuous evacuation during thermolyses by a Welch Model 1403 pump and a Consolidated Vacuum Corporation VMF-20 oil diffusion pump.

2. Thermolytic Procedures

(i) Thermolysis of Volatile Compounds

Prior to thermolysis the temperature in the thermolysis zone was allowed to stabilize, during which time the residual pressure in the furnace dropped to about 10 μ.   Degassed samples were slowly distilled from the inlet manifold, through the needle valve, and into the reactor tube.   The flow rate was regulated so that the pressure of the thermolysate outside the thermolysis zone was maintained at a constant value throughout the run.   Pressures were usually 50-100 μ.   The time required to thermolyse 0.004 moles was about 120 min.   The thermolysate that emerged from the reactor tube was condensed on the cold face.

(ii) Thermolysis of Non-volatile Compounds

A known weight of compound, wrapped in aluminum foil, was placed in the sublimation zone of the reactor tube.   After the temperature in the thermolysis zone had stabilized and the minimum residual furnace pressure was obtained, the compound was slowly sublimed into the

thermolysis zone and the emerging thermolysate was condensed on the cold face. Conditions were employed so that the compounds were not decomposed on sublimation. Compound that back-sublimed was washed out and weighed.

(iii) Residence Time in the Thermolysis Zone

The length of time that the volatilized compounds spend in the thermolysis zone is called the contact time and is defined by the following equation:

$$\Gamma = \frac{V_R}{v}$$

where V_R = the volume of the thermolysis zone.

v = the volume of compound passed per second through the hot zone at the temperature of the thermolysis.

When the volatilized compound is assumed to be an ideal gas the expression for the contact time becomes:

$$\Gamma = \frac{V_R \cdot P \cdot t}{n \cdot R \cdot T}$$

where V_R = the volume of the thermolysis zone (0.00520 l).

P = the pressure of the compound in the thermolysis zone (atm).

t = the time required for the compound to pass through the thermolysis zone (sec).

n = the number of moles of compound passed.

R = the ideal gas constant (0.0821 l atm mole^{-1} °K^{-1}).

T = the temperature in the thermolysis zone (°K).

The only quantity in the above expression that was difficult to measure was the pressure of the compound in the thermolysis zone. For

computational purposes, the pressure of the thermolysate as measured outside of the thermolysis zone was used. As this is not the true pressure of the starting material inside the thermolysis zone, the values quoted for the contact time have significance only in the relative sense. Values of the contact time were calculated at about 10 msec for volatile compounds and about 1-2 msec for solids. Undoubtedly, the pressure of the thermolysate was greater than the pressure of the starting material in the thermolysis zone because the thermolysate contained non-condensible gases such as methane and carbon monoxide. Thus, the true contact times must be lower than the quoted values.

(iv) Handling of the Thermolysate

After the thermolysis was completed and the furnace had cooled to room temperature, the internal calibrating compounds for the gas and liquid glc analyses were distilled from the inlet manifold onto cold face.

In order to get separate samples for gas and liquid analyses a splitter was employed. The slitter was a T-shaped device that contained identical tubes and taps on either side of the T-joint. The thermoly-sate and calibrating compounds were freely distilled into both tubes of the splitter which was mounted on the sample handling manifold. Control experiments showed that this proportioning of reaction products and calibrating compounds provided representative samples for gas and liquid analyses respectively.

For gas sample analysis, the contents of one of the splitter tubes were distilled into a 250 ml stainless steel gas bottle. The gas bottle contents were pressurized to 20 psi with helium prior to glc

analysis.

The contents of the other splitter tube were distilled into a small detachable flask on the manifold for liquid analysis. To facilitate handling, a small amount of an inert solvent was usually distilled into the flask as well. The flask was removed from the manifold and stored at 0° until analysis.

3. Analysis of the Products from the Thermolyses

(i) Qualitative Analysis

The products of the thermolysis of each compound were isolated by preparative glc. The columns and conditions employed for isolation were the same as those employed for quantitative analysis and are described in the quantitative analysis tables. Identification of each product was made by the comparison of the glc retention time, the infrared spectrum (usually gas phase), the 70 ev fragmentation mass spectrum, and the ultraviolet spectrum with the corresponding measurements for an authentic sample. At least two of these comparisons were made in order to identify each compound.

(ii) Quantitative Analysis

Product yields for each thermolysis were obtained by glc. A calibrating compound was added to the thermolysate to permit quantitative analysis.

The gas chromatograph was calibrated for the products of each compound that was thermolysed. Several samples containing known weight of the products and calibrating compound were injected into the chromatograph and the areas under the peaks of the chromatograms were obtained

by planimetry. A plot of the ratio of product weight to calibrating compound weight against the ratio of product area to calibrating compound area was linear and the slope of this graph was the response factor for that particular product. The weights of compounds used approximated the weights of products encountered in the thermolyses.

For each thermolysis the calibrating compounds were introduced as described in the product handling section. The chromatogram was obtained under the same operating conditions that were used for calibration and again the integrated responses were obtained by planimetry. The weight of each product in the thermolysis was obtained from the following formula:

$$wt_{prod} = wt_{cal\ cmpd} \times response\ factor_{prod} \times \frac{Area_{prod}}{Area_{cal\ cmpd}}$$

Usually three injections were made in each analysis and the average of the integrated response ratio was used. This type of analysis was used for both gases and liquids.

The weight of starting compound that survived the thermolysis conditions was also estimated by glc. The weight of compound that was thermolysed was obtained by subtracting the weight of the material that survived the thermolysis conditions from the total amount of compound that was passed through the thermolysis zone. All yields of products are reported as mole percentages based on reacted starting material.

The glc column conditions and calibrating compounds employed are summarized in the tables that contain the product yields for each compound that was thermolysed.

(iii) Mass Spectrometric Analysis

In the mechanistic studies involving deuterium labeling, the deuterium distributions and average incorporations were obtained by mass spectrometry. Compounds for deuterium analysis were isolated by preparative glc under conditions where deuterium exchange on the column was minimal. The mass spectra were obtained under source ionization conditions where fragmentation of the compounds was minimal. Identical source conditions were employed for the unlabeled standards and the deuterated samples. The pressure of the compound in the instrument was kept constant while the spectrum was scanned. Normally, the average of three or more scans were used to calculate the deuterium distribution for each compound. Standard calculations were carried out in order to eliminate the contributions of naturally occurring isotopes in the deuterium labeled samples (55).

In several instances, the accuracy of the mass spectrometrically obtained deuterium incorporations was checked by nmr spectroscopy or by the combustion method. Satisfactory agreement was noted for the average deuterium incorporations obtained by independent methods.

C.   Thermolyses of the Ketones and Related Compounds

1.   Materials

The source and preparation of the compounds that were thermolysed for quantitative analysis are given in this section.

Compounds from Commercial Sources

Cyclohexanone, methyl vinyl ketone, 1-methylcyclohexene, cycloheptanone, cyclopropane, cyclooctanone, cyclopentanone, 5-nonanone, and 2-hexanone were obtained commercially. Each of these compounds was fractionated and was analysed for purity by glc. In all cases, the material that was thermolysed contained less than 0.3% of impurities.

Methylenecylcohexane

Methylenecyclohexane was prepared by the Wittig reaction from cyclohexanone and the ylide of triphenylmethylphosphonium bromide as outlined in Organic Syntheses (56). The material was fractioned on a spinning band column, bp 100-101°, and found, by glc analysis to contain less than 0.3% of impurities, $n^{25}_D 1.4468$ (lit. bp 99-101°; $n^{25}_D 1.4470$ (56)).

3-Ketothiacycloheptane-1,1-Dioxide

To a stirred solution of 3-ketothioacycloheptane (2.6 g) (57) in glacial acetic acid (30 ml) was added dropwise over a period of 1 hr, 33% hydrogen peroxide (6 ml). The solution was refluxed for 4 hr and then the acetic acid was removed by distillation. The residue was then sublimed to give 3-ketothiacycloheptane-1,1-dioxide (2.0 g; 60%). The compound has the following physical properties: mp 107.5-108.5°;

ir (CHCl$_3$) 3009 (m), 2917 (m), 1709 (s), 1323 (s), 1304 (s), 1133 (s),

and 854 (m) cm^{-1}; nmr (CDCl$_3$) 2.13 (4H,m), 2.77 (2H,t), 3.33 (2H,t), and

4.14 (2H,s) ppm.

Analysis: Calcd for C$_6$H$_{10}$O$_3$S: C, 44.43; H, 6.21; S, 19.77.

        Found   C, 44.68; H, 6.14; S, 19.61.

Methyl Cyclopentyl Ketone

Methyl cyclopentyl ketone was prepared by the addition of cyclo-
pentyl magnesium bromide to acetic anhydride as described previously by
Overberger and Lebovits (58). The material was purified by fractiona-
tion at reduced pressure, bp 100-102° (100 mm), and contained less than
0.3% impurities by glc analysis, n^{25}_D1.4405 (lit bp 95° (99 mm);
n^{25}_D1.4409 (58)).

2. Conditions and Product Analyses of the Thermolyses

The compounds that are listed in the previous section were thermo-
lysed and the yields of the products were obtained. Products, volatile
at low pressures at liquid nitrogen temperature, could not be determined.
Such products included carbon monoxide, hydrogen, and methane. Ketene
was determined as methyl acetate; the methanol having been introduced
by the Dewar containing the trapping agent inlet nozzle. The conditions
of the thermolyses and the product yields are given in Tables 18 to 29.
The tables are arranged in the same order as the thermolyses are dis-
cussed in Part II.

The variance in the temperatures during the thermolyses was about
7°. Also, the variance in the pressures recorded during the thermolyses
was about 10 μ. The reproducibility of the product yields for dupli-

cate experiments is good, in view of the difficulties incurred in maintaining constant flow of starting material through the furnace during the thermolyses. Yields agree within 5% for major products and the agreement is somewhat poorer for minor products. Product yields are expressed as mole percentages and are based on decomposed starting material.

3. Specifically Deuterated Compounds

The preparation details and deuterium distributions of the specifically labeled compounds which were thermolysed are given in this section. All of the compounds were purified by distillation and glc analysis revealed that they were greater than 99.7% pure.

Cyclohexanone-2,2,6,6-d_4

Cyclohexanone-2,2,6,6-d_4 was prepared by the base catalysed deuterium exchange in cyclohexanone with the procedure of Anet (59). The deuterium distribution and average incorporation was: d_1 0.2%, d_2 0.6%, d_3 8.0%, and d_4 91.2%; 3.90 atom D per molecule.

Cyclohexanone-3,3,5,5-d_4

Cyclohexanone-3,3,5,5-d_4 was prepared by method reported by Djerassi et al. (60). 4-Hydroxycyclohexanone underwent base catalysed deuterium exchange before being converted into its tosylhydrzone. Lithium aluminum hydride reduction of the tosylhydrzone and subsequent oxidation of the deuterated cyclohexanol gave cyclohexanone-3,3,5,5-d_4. The deuterium distribution and average incorporation was: d_0 0.1%, d_1 1.1%, d_2 8.0%, d_3 28.9%, and d_4 61.8%; 3.51 atom D per molecule.

Cyclohexanone-4-d$_1$

Cyclohexanone-4-$\underline{d}_1$ was prepared by the procedure of Djerassi $\underline{et}$ $\underline{al}$. (61). The tosylhydrazone of 4-hydroxycyclohexanone was reduced with lithium aluminum hydride and the reduction was quenched with deuterium oxide. Oxidation of the deuterated cyclohexanol gave cyclohexanone-4-$\underline{d}_1$: $\underline{d}_0$ 49.8%, $\underline{d}_1$ 50.2%; 0.50 atom D per molecule.

Methylenecyclohexane-2,2,6,6-d$_4$

Methylenecyclohexane-2,2,6,6-$\underline{d}_4$ was prepared by the Wittig reaction of cyclohexanone-2,2,6,6-$\underline{d}_4$ ($\underline{d}_1$ 0.4%, $\underline{d}_2$ 0.8%, $\underline{d}_3$ 7.8%, $\underline{d}_4$ 90.9%; 3.89 atom D per molecule) and the ylide of triphenylmethylphosphonium bromide as outlined in Organic Syntheses (56). The deuterium distribution and average incorporation was: $\underline{d}_0$ 0.1%, $\underline{d}_1$ 0.4%, $\underline{d}_2$ 0.2%, $\underline{d}_3$ 5.1%, $\underline{d}_4$ 87.1%, $\underline{d}_5$ 6.1%, $\underline{d}_6$ 1.1%; 4.02 atom D per molecule; independently by the combustion method 4.02 atom D per molecule.

4. Thermolyses of the Deuterated Compounds

The deuterated compounds were thermolysed and the major products were isolated by preparative glc. Duplicate experiments were carried out for each compound. The compounds were isolated on columns which were shown by control experiments not to cause deuterium exchange. The columns which were used are listed below. The conditions for the thermolyses and the deuterium analyses of the products are given in Tables 30 to 33.

Preparative Glc for Deuterium Analyses

Cyclohexanone, MVK: 20% Se30, 5' × 1/4", 75°.

Ethylene, propylene: Porasil B, 6' × 3/16", r. t.

Isoprene, methylenecyclohexane: 15% FFAP, 18' × 1/4", 60°.

Table 18

Thermolysis of Cyclohexanone

Conditions	Run #1	Run #2	Run #3
Temperature (°C)	1062	1055	1195
Pressure before run (μ)	16	19	70
Pressure during run (μ)	80	90	160
Duration of run (min)	120	110	120
Contact time (msec)	5.0	4.9	6.9

Starting Material

	Run #1	Run #2	Run #3
Cyclohexanone passed (g)	0.5683	0.5307	0.5235
Cyclohexanone undecomposed (g)	0.1910	0.1552	0.0666
Cyclohexanone decomposed (g)	0.3953	0.3755	0.4569

Products

	Run #1	Run #2	Run #3
Ethylene	82.6	87.8	112.1
Ethane	3.3	2.9	8.8
Acetylene	4.6	4.7	16.2
Propylene	16.7	16.5	18.0
Allene	6.5	6.8	11.6
1-Butene	7.4	6.7	2.9
1,3-Butadiene	3.0	3.2	3.4
Ketene	4.6	4.9	---
Methyl vinyl ketone	24.1	23.7	6.4
1,5-Hexadiene	2.7	2.6	0.7
Cyclopentane	2.6	2.8	1.7
Acrolein	2.4	2.1	1.3
Benzene	0.9	1.4	4.4
Cyclopentadiene	1.3	2.3	3.9

Analysis Conditions

Liquids: 10% FFAP, 18' x 1/4", 145°; toluene.
Gases: Porapak S, 6' x 3/16", 83°; isobutane.

Table 19

Thermolysis of Methyl Vinyl Ketone

Conditions	Run #1
Temperature (°C)	1067
Pressure before run (μ)	12
Pressure during run (μ)	90
Duration of run (min)	90
Contact time (msec)	4.9

Starting Material	
Methyl vinyl ketone passed (g)	0.3409
Methyl vinyl ketone undecomposed (g)	0.1633
Methyl vinyl ketone decomposed (g)	0.1769

Products	
Ethylene	25.8
Ethane	4.2
Acetylene	5.5
Propylene	22.5
Allene	3.6
1-Butene	5.8
1,3-Butadiene	3.3
1,5-Hexadiene	---
Ketene	---

Analysis Conditions

Liquids: 10% FFAP, 18' x 1/4", 145°; toluene.
Gases: Porapak S, 6' x 3/16", 83°, isobutane.

Table 20

Thermolysis of Methylenecyclohexane

Conditions	Run #1	Run #2
Temperature (°C)	1065	1060
Pressure before run (μ)	11	7
Pressure during run (μ)	70	60
Duration of run (min)	80	60
Contact time (msec)	3.9	4.3

Starting Material		
Methylenecyclohexane passed (g)	0.4022	0.2528
Methylenecyclohexane undecomposed (g)	0.1605	0.1171
Methylenecyclohexane decomposed (g)	0.2417	0.1357

Products		
Ethylene	56.7	57.2
Ethane	10.0	6.7
Acetylene	5.2	3.6
Propylene	8.4	8.9
Allene	40.4	40.5
Propyne	9.1	9.3
1-Butene	17.6	17.6
1,3-Butadiene	5.2	4.9
2-Butene	4.2	4.3
2-Methyl-1-butene	11.1	7.2
Isopropene	13.8	14.7
1,5-Hexadiene	6.8	7.8
Cyclopentadiene	3.6	3.2
2-Methyl-1,5-hexadiene	3.0	3.5
Benzene	4.0	6.0
Toluene	1.2	1.8

Analysis Conditions

Liquids: 15% FFAP, 18' × 1/4", 80°; methyl formate.
Gases: Porapak S, 6' × 3/16", 80°; isobutane.

Table 21

Thermolysis of I-Methylcyclohexene

Conditions	Run #1
Temperature (°C)	1060
Pressure before run (μ)	11
Pressure during run (μ)	70
Duration of run (min)	50
Contact time (msec)	4.6

Starting Material	
I-Methylcyclohexene passed (g)	0.2356
I-Methylcyclohexene undecomposed (g)	0.0334
I-Methylcyclohexene decomposed (g)	0.2012

Products	
Isoprene	57.8
Benzene	6.3

Table 22

Thermolysis of Cyclopropane

Conditions	Run #1	Run #2
Temperature (°C)	1075	1205
Pressure before run (μ)	10	45
Pressure during run (μ)	75	110
Duration of run (min)	180	190
Contact time (msec)	4.2	3.7

Starting Material		
Cyclopropane passed (g)	0.43	0.48
Cyclopropane undecomposed (g)	0.26	0.19
Cyclopropane decomposed (g)	0.17	0.28

Products		
Ethylene	trace	10
Propylene	40	50

Analysis Conditions

Liquids: 15% FFAP, 18' × 1/4", 80°; decane.
Gases: Porapak S, 6' × 3/16", 83°; isobutane.

Table 23

Thermolysis of 3-Ketothiacycloheptane-1,1-Dioxide

Conditions	Run #1	Run #2	Run #3	Run #4
Temperature (°C)	940	950	1010	1005
Pressure before run (μ)	17	15	30	20
Pressure during run (μ)	50	55	70	50
Duration of run (min)	20	30	30	28
Contact time (msec)	6.0	6.9	6.8	5.0

Starting Material	Run #1	Run #2	Run #3	Run #4
3-KTCH passed (g)	0.0780	0.1148	0.1091	0.1063
3-KTCH back sublimed (g)	0.0337	0.0578	0.0615	0.0653
3-KTCH decomposed (g)	0.0443	0.0570	0.0476	0.0410

Products	Run #1	Run #2	Run #3	Run #4
Ethylene	14.1	18.1	27.1	27.0
Ethane	1.7	3.5	0.8	0.9
Propylene	1.8	3.7	3.1	3.5
Allene	5.1	3.9	6.6	4.2
1,5-Hexadiene	2.0	3.1	2.3	1.6
Acetone	1.9	1.7	1.4	2.5
Methyl vinyl ketone	5.9	8.2	9.5	11.0
Benzene	1.8	2.8	3.3	2.5
Cyclohexanone	49.0	51.7	36.3	32.1

Analysis Conditions

Liquids: 15% FFAP, 18' × 1/4", 150°; toluene.
Gases: Porapak S, 6' × 3/16", 80°; isobutane.

Table 24

Thermolysis of Cycloheptanone

Conditions	Run #1	Run #2
Temperature (°C)	1065	1065
Pressure before run (μ)	15	11
Pressure during run (μ)	80	80
Duration of run (min)	172	148
Contact time (msec)	9.8	9.1

Starting Material

	Run #1	Run #2
Cycloheptanone passed (g)	0.4788	0.3936
Cycloheptanone undecomposed (g)	0.1553	0.1327
Cycloheptanone decomposed (g)	0.3235	0.2609

Products

	Run #1	Run #2
Ethylene	71.6	70.3
Ethane	4.9	4.7
Acetylene	5.8	5.0
Propylene	28.4	28.9
Allene	4.0	4.7
1-Butene	15.8	16.1
1,3-Butadiene	13.6	12.9
Ketene	5.1	5.0
1,5-Hexadiene	6.2	7.3
Cyclohexane	8.2	9.6
Acetone	2.8	3.1
Methyl vinyl ketone	9.8	10.7
Benzene	1.1	0.8
Cyclopentanone	1.1	1.1
Cyclohexanone	1.4	1.3
3-Methylcyclohexanone	2.3	2.3

Analysis Conditions

Liquids: 15% FFAP, 18' x 1/4", 155°; 1,2,4-trimethylbenzene.
Gases: Porapak S, 6' x 3/16", 80°; isobutane.

Table 25

Thermolysis of Methyl Cyclopentyl Ketone

Conditions	Run #1	Run #2	Run #3	Run #4
Temperature (°C)	1000	1005	1055	1065
Pressure before run (μ)	20	20	20	20
Pressure during run (μ)	80	80	80	80
Duration of run (min)	65	60	65	75
Contact time (msec)	8.1	8.4	8.3	8.9

Starting Material

	Run #1	Run #2	Run #3	Run #4
MCK passed (g)	0.2151	0.2045	0.1991	0.2050
MCK undecomposed (g)	0.0482	0.0453	0.0173	0.0221
MCK decomposed (g)	0.1669	0.1592	0.1818	0.1869

Products

	Run #1	Run #2	Run #3	Run #4
Ethylene	70.3	79.5	95.7	102.4
Ethane	20.3	19.4	20.2	26.4
Propylene	9.7	9.1	9.8	9.6
1-Butene	14.5	14.0	5.3	5.7
1,3-Butadiene	4.5	5.2	4.3	4.1
Cyclopentene	19.8	17.4	11.3	11.4
Cyclopentadiene	8.7	9.4	16.0	14.8
Methyl vinyl ketone	5.7	5.1	5.5	4.6

Analysis Conditions

Liquids: 15% FFAP, 18' × 1/4", 155°; o-xylene.
Gases: Porapak S, 6' × 3/16", 80°; isobutane.

Table 26

Thermolysis of Cyclooctanone

Conditions	Run #1	Run #2
Temperature (°C)	1055	1065
Pressure before run (μ)	15	12
Pressure during run (μ)	80	80
Duration of run (min)	240	240
Contact time (msec)	15	14

Starting Material

Cyclooctanone passed (g)	0.5240	0.5233
Cyclooctanone undecomposed (g)	0.0292	0.0214
Cyclooctanone decomposed (g)	0.4948	0.5019

Products

Ethylene	97.9	100.9
Ethane	7.0	4.9
Acetylene	1.3	0.9
Propylene	26.4	27.5
Allene	6.1	7.4
1-Butene	18.6	18.7
1,3-Butadiene	12.4	12.7
Ketene	22.1	24.3
1,5-Hexadiene	10.0	9.3
Cyclopentadiene	3.7	4.0
Acetone	3.5	3.8
Cycloheptane	5.5	5.6
Benzene	1.7	2.0
Cyclopentanone	1.1	1.3
Cyclohexanone	1.6	1.1

Analysis Conditions

Liquids: 15% FFAP, 18' x 1/4", 155°; cycloheptanone.
Gases: Porapak S, 6' x 3/16", 80°; isobutane.

Table 27

Thermolysis of Cyclopentanone

Conditions	Run #1	Run #2	Run #3	Run #4
Temperature (°C)	1055	1065	1255	1265
Pressure before run (μ)	15	15	95	90
Pressure during run (μ)	80	80	200	190
Duration of run (min)	170	98	155	120
Contact time (msec)	5.5	5.6	12	9.9

Starting Material

	Run #1	Run #2	Run #3	Run #4
Cyclopentanone passed (g)	0.6356	0.3586	0.3633	0.3310
Cyclopentanone undecomposed (g)	0.4986	0.2730	0.0320	0.0368
Cyclopentanone decomposed (g)	0.1370	0.0856	0.3313	0.2942

Products

	Run #1	Run #2	Run #3	Run #4
Ethylene	106.6	110.4	109.6	104.1
Propylene	0.7	0.4	1.7	1.5
Allene	2.2	2.2	4.5	5.3
1-Butene	4.9	5.3	1.4	1.4
1,3-Butadiene	16.0	15.3	10.3	10.7
Ketene	10.2	9.3	---	---
1,5-Hexadiene	2.3	2.8	0.6	0.7
Cyclopentadiene	0.9	1.2	1.0	1.0
Acetone	1.5	0.7	0.4	0.3
Benzene	0.2	0.2	0.6	0.6
2-Cyclopentenone	8.7	6.0	1.2	1.1

Analysis Conditions

Liquids: 15% FFAP, 18' x 1/4", 155°; 1,2,4-trimethylbenzene.
Gases: Porapak S, 6' x 3/16", 80°; isobutane.

Table 28

Thermolysis of 5-Nonanone

Conditions	Run #1	Run #2	Run #3	Run #4
Temperature (°C)	955	995	1010	1060
Pressure before run (μ)	15	15	19	25
Pressure during run (μ)	85	50	55	75
Duration of run (min)	100	222	212	175
Contact time (msec)	14	18	16	16

Starting Material				
5-Nonanone passed (g)	0.2448	0.2300	0.2495	0.2810
5-Nonanone undecomposed (g)	0.0320	0.0136	0.0145	0.0027
5-Nonanone reacted (g)	0.2128	0.2164	0.2350	0.2783

Products				
Ethylene	180.3	183.9	186.1	185.0
Ethane	24.5	28.3	19.1	24.7
Propane	6.3	7.1	4.9	3.9
Propylene	32.2	28.9	30.5	28.5
1-Butene	3.3	3.7	2.9	1.8
Ketene	---	---	11.3	12.4
Acetone	1.8	1.8	1.8	1.3
Methyl vinyl ketone	1.8	1.7	1.9	0.8
Valeraldehyde	1.2	1.0	1.2	1.2
2-Hexanone	4.7	2.8	2.1	0.8

Analysis Conditions

Liquids: 15% FFAP, 18' x 1/4", 155°; anisole.
Gases: Porapak S, 6' x 3/16", 80°; isobutane.

Table 29

Thermolysis of 2-Hexanone

Conditions	Run #1	Run #2	Run #3	Run #4
Temperature (°C)	965	995	1005	1055
Pressure before run (μ)	12	15	15	20
Pressure during run (μ)	55	75	80	80
Duration of run (min)	110	142	125	182
Contact time (msec)	11	13	15	16

Starting Material

	Run #1	Run #2	Run #3	Run #4
2-Hexanone passed (g)	0.1606	0.2559	0.2219	0.2473
2-Hexanone undecomposed (g)	0.0606	0.0796	0.0518	0.0303
2-Hexanone decomposed (g)	0.1000	0.1763	0.1701	0.2170

Products

	Run #1	Run #2	Run #3	Run #4
Ethylene	95.0	102.0	102.0	120.2
Ethane	32.9	31.2	34.2	36.9
Propane	8.7	6.4	6.7	4.3
Propylene	16.7	18.4	17.0	18.2
1-Butene	1.9	2.2	1.7	1.4
Ketene	---	22.6	24.6	---
1,5-Hexadiene	0.8	0.7	0.4	0.3
Acetone	14.9	15.2	13.9	12.5
Methyl vinyl ketone	1.5	1.7	1.7	2.3
Valeraldehyde	1.8	1.9	1.6	1.1

Analysis Conditions

Liquids: 15% FFAP, 18' x 1/4", 155°; o-xylene.
Gases: Porapak S, 6' x 3/16", 80°; isobutane.

Table 30

Thermolysis of Cyclohexanone-2,2,6,6-d_4

Conditions		Run #1	Run #2
Temperature (°C)		1065	1065
Pressure before run (μ)		15	17
Pressure during run (μ)		90	90
Duration of run (min)		85	95
Cyclohexanone-2,2,6,6-d_4 passed (g)		0.3989	0.4155
Contact time (msec)		6.1	6.1

Deuterium Distributions (%)

		Run #1	Run #2
Starting Cyclohexanone-2,2,6,6-d_4	d_1	0.2	0.2
	d_2	0.6	0.6
	d_3	8.0	8.0
	d_4	91.2	91.2
	incorp	3.90	3.90
Cyclohexanone-2,2,6,6-d_4 that survived the thermolysis zone	d_1	1.0	0.9
	d_2	1.6	1.7
	d_3	12.3	12.8
	d_4	85.1	84.7
	incorp	3.81	3.82
Ethylene	d_0	63.1	66.1
	d_1	10.5	9.3
	d_2	23.4	21.7
	d_3	1.9	1.7
	d_4	1.2	1.2
	incorp	0.68	0.63
Methyl vinyl ketone	d_0	0.4	0.4
	d_1	1.0	1.0
	d_2	3.4	3.4
	d_3	27.0	24.3
	d_4	68.3	70.8
	incorp	3.62	3.62
Propylene	d_0	4.9	5.0
	d_1	6.2	5.9
	d_2	15.5	14.9
	d_3	29.0	29.5
	d_4	43.1	43.5
	d_5	1.3	1.2
	incorp	2.73	2.74

Table 31

Thermolysis of Cyclohexanone-3,3,5,5-d_4

Conditions		Run #1	Run #2
Temperature (°C)		1055	1057
Pressure before run (µ)		16	16
Pressure during run (µ)		80	80
Duration of run (min)		85	80
Cyclohexanone-3,3,5,5-d_4 passed (g)		0.3860	0.3511
Contact time (msec)		5.5	5.8

Deuterium Distributions (%)

		Run #1	Run #2
Starting Cyclohexanone-3,3,5,5-d_4	d_0	0.1	0.1
	d_1	1.1	1.1
	d_2	8.0	8.0
	d_3	28.9	28.9
	d_4	61.8	61.8
	incorp	3.51	3.51
Cyclohexanone-3,3,5,5-d_4 that survived the thermolysis zone	d_0	0.2	0.6
	d_1	1.3	1.6
	d_2	7.6	8.1
	d_3	28.5	28.8
	d_4	62.4	60.9
	incorp	3.52	3.49
Ethylene	d_0	8.0	6.8
	d_1	24.1	23.4
	d_2	63.6	65.0
	d_3	4.3	4.8
	incorp	1.64	1.68
Methyl vinyl ketone	d_0	2.5	2.3
	d_1	21.4	21.5
	d_2	74.8	75.2
	d_3	1.3	1.1
	incorp	1.75	1.75
Propylene	d_0	7.3	7.9
	d_1	33.2	32.4
	d_2	50.7	50.4
	d_3	5.6	5.7
	d_4	3.2	3.1
	incorp	1.64	1.63

Table 32

Thermolysis of Cyclohexanone-4-d_1

Conditions		Run #1	Run #2
Temperature (°C)		1060	1055
Pressure before run (μ)		14	17
Pressure during run (μ)		80	80
Duration of run (min)		85	88
Cyclohexanone-4-d_1 passed (g)		0.3919	0.3623
Contact time (msec)		5.2	5.9

Deuterium Distributions (%)

		Run #1	Run #2
Starting Cyclohexanone-4-d_1	d_0	49.8	49.8
	d_1	50.2	50.2
	incorp	0.50	0.50
Cyclohexanone-4-d_1 that survived the thermolysis zone	d_0	49.7	49.3
	d_1	50.3	50.7
	incorp	0.50	0.51
Ethylene	d_0	68.6	68.5
	d_1	31.4	31.5
	incorp	0.31	0.32
Methyl vinyl ketone	d_0	99.2	99.2
	d_1	0.8	0.8
	incorp	0.008	0.008
Propylene	d_0	81.2	80.5
	d_1	18.3	19.0
	d_2	0.5	0.5
	incorp	0.20	0.20

Table 33

Thermolysis of Methylenecyclohexane-2,2,6,6-d_4

Conditions	Run #1	Run #2
Temperature (°C)	1060	1065
Pressure before run (μ)	8	13
Pressure during run (μ)	50	75
Duration of run (min)	80	75
Starting material passed (g)	0.2715	0.3097
Contact time (msec)	4.6	5.6

Deuterium Distributions (%)

		Run #1	Run #2
Starting Methylenecyclohexane-2,2,6,6-d_4	d_0	0.1	0.1
	d_1	0.4	0.4
	d_2	0.2	0.2
	d_3	5.1	5.1
	d_4	87.1	87.1
	d_5	6.1	6.1
	d_6	1.1	1.1
	incorp	4.02	4.02
Methylenecyclohexane-2,2,6,6-d_4 that survived thermolysis zone	d_0	0.0	0.0
	d_1	1.6	0.4
	d_2	0.6	0.3
	d_3	4.8	4.7
	d_4	85.6	86.4
	d_5	6.3	7.1
	d_6	1.0	1.1
	incorp	3.98	4.03
Ethylene	d_0		58.7
	d_1		13.7
	d_2		21.4
	d_3		4.9
	d_4		1.3
	incorp		0.76
Isoprene	d_0	1.1	0.6
	d_1	1.1	2.0
	d_2	8.3	10.7
	d_3	30.5	33.1
	d_4	50.6	45.1
	d_5	7.2	7.6
	d_6	1.2	0.9
	incorp	3.55	3.47

D.   The Thermolysis of Chlorosulfonylacetic Acid

I.   Materials

Chlorosulfonylacetic Acid

To a stirred solution of chlorosulfonylacetyl chloride (28.8 g) in ether (80 ml) was added dropwise water (3.l g). After an 1/2 hour the solvent was removed under reduced pressure to yield a solid residue. Recrystallization from chloroform-carbon tetrachloride gave chloro-sulfonylacetic acid (l4.2 g; 55%). The material used for thermolysis was recrystallized to a constant melting point of 77-78°; reported melting point 77-78° (62).

Methyl Methane-d-sulfonate

To a stirred solution maintained under nitrogen of methanol-$\underline{d}$ (98%) and triethylamine (l.4 ml) in methylene chloride (20 ml) was added drop-wise methanesulfonyl chloride (0.75 ml). After l0 min the methylene chloride was washed with aqueous HCl and $NaHCO_3$ and then evaporated under reduced pressure. The residue was distilled in a bulb-to-bulb apparatus under reduced pressure to yield methyl methane-$\underline{d}$-sulfonate that was greater than 99.7% pure by glc.

Accurate proton integration on a HA-l00 nmr spectrometer revealed that the methyl group α to the sulfonyl group contained 2.22 hydrogen atoms. This corresponds to 78.0% monodeuteration. By mass spectrometry the same sample was found to be 78.9% monodeuterated.

Methanesulfonyl Chloride

Methanesulfonyl chloride, obtained commercially, was fractionally distilled under reduced pressure. The material was shown to be greater

than 99.7% pure by glc analysis.

2. The Thermolysis of Chlorosulfonylacetic Acid

Chlorosulfonylacetic acid was thermolysed as described in the section on the thermolysis of non-volatile compounds.

Because major revisions were made in the product handling and thermolysate trapping procedures as the experimentation progressed, the results are arranged to reflect these changes.

(i) "Sandwich" Trapping of the Thermolysate

In the experiments described in this section 1 ml of methanol was used as a trap to react with the thermolysate. Before the thermolysis was commenced, half of the methanol was distilled onto the Dewar cold face. After the completion of the thermolysis, the remaining methanol was condensed on top of the thermolysate layer to complete the "sandwich". As the Dewar was allowed to warm to room temperature the thermolysate and methanol distilled into a flask on the manifold. The calibrating compounds were added to the sample flask directly in the chlorosulfonylacetic acid experiments.

With these product handling procedures it was found that methanesulfonyl chloride reacted with methanol to give methyl methanesulfonate. Hence all yields for methyl methanesulfonate determined under these conditions were meaningless and have been omitted.

Experiments conducted under these conditions gave the yields for dimethoxymethane and these results are summarized in Table 34.

(ii) "Sandwich" Trapping of the Thermolysate and the Subsequent
Removal of Methanol

Thermolysis of chlorosulfonylacetic acid and "sandwich" trapping of
the thermolysate were carried out as described in the previous section.
However, the methanol and thermolysate were now distilled through a
-45° trap (chlorobenzene-liquid nitrogen slush) on the product handling
manifold. Methanesulfonyl chloride and methyl methanesulfonate were
retained in the -45° trap but methanol and other volatile components in
the thermolysate were condensed in a liquid nitrogen trap at the end of
the manifold. Methanesulfonyl chloride, methyl methanesulfonate, and a
solvent (ether) were then distilled into a flask on the manifold. After
addition of an external calibrating compound, glc analysis was carried
out.

Control experiments were performed in which methanesulfonyl
chloride was passed through the furnace and trapped under simulated
thermolytic conditions. Under the described product isolation conditions
no methyl methanesulfonate was produced.

Experiments carried out under these conditions gave yields for
methyl methanesulfonate and methanesulfonyl chloride. These experiments
are summarized in Table 35.

Duplicate experiments were repeated using methanol-d (98%) as the
trapping agent and identical thermolysis and product isolation conditions.
Methanesulfonyl chloride and methyl methanesulfonate were isolated by
preparative glc and the deuterium distributions of these compounds
were determined by mass spectrometry. Table 36 summarizes these exper-
ments.

(iii) <u>Homogeneous Trapping of the Thermolysate and the Subsequent</u>

     <u>Removal of the Trapping Agents</u>

Chlorosulfonylacetic acid was thermolysed so that the thermolysate was intercepted by a continuous stream of trapping agent that was admitted by the nozzle of the previously described dewar. The trapping agents and volatile thermolysate components were separated by the technique described in the previous section. Again control experiments showed that under these procedures methanesulfonyl chloride did not react with methanol to give methyl methanesulfonate.

The conditions and results of experiments carried out under these procedures with methanol and hydrogen chloride as trapping agents are tabulated in Table 37.

Thermolyses of chlorosulfonylacetic acid were repeated in which deuterium chloride (97%) was the trapping agent. The deuterium chloride was prepared by the addition of deuterium oxide to phosphorus penta-chloride. The deuterium chloride was purified by double distillation through a -63° trap (chloroform-liquid nitrogen slush) and was shown by mass spectrometry to be 97% deuterated.

Methanesulfonyl chloride was isolated from the thermolysate by preparative glc and analysed for deuterium incorporation by mass spectro-metry. The results are reported in Table 38.

3. <u>The Thermolysis of Methanesulfonyl Chloride</u>

(i) <u>Analysis for Dimethoxymethane</u>

Methanesulfonyl chloride was thermolysed by the procedure previously described for volatile compounds. The thermolysate was trapped by a methanol "sandwich". The experimental conditions and the yields for

dimethoxymethane are given in Table 39.

(ii) <u>Analysis for Methyl Methanesulfonate</u>

The thermolyses of methanesulfonyl chloride were repeated under conditions whereby the thermolysate was trapped homogeneously with methanol. The experimental conditions and the yields of methyl methanesulfonate are summarized in Table 40.

Table 34

Thermolysis of Chlorosulfonylacetic Acid

Methanol "Sandwich" Trapping

Yields for Dimethoxymethane

$ClSO_2CH_2COOH$ Thermolysed[**] (g)	Temp (°C)	Pressure Before	During (μ)	Duration of Run (min)	Contact Time (msec)	Yield of $CH_2(OCH_3)_2$ (%[*])
1. 0.2119	932	18	35	20	1.1	58.7
2. 0.2145	938	20	35	15	0.7	76.1
3. 0.1715	943	14	35	15	1.2	51.7
4. 0.1738	627	20	30	15	0.8	4.7
5. 0.2358	646	20	33	30	1.4	4.2
6. 0.1716	632	10	23	15	1.0	8.1

*Mole percentages based on thermolysed chlorosulfonylacetic acid.

**Amount of material that back-sublimed varied from 5-25 mg.

Analysis: 10% FFAP, 18' x 1/4", 45°; cyclopentane.

Table 35

Thermolysis of Chlorosulfonylacetic Acid

Methanol "Sandwich" Trapping

Yields for Methanesulfonyl Chloride and Methyl Methanesulfonate

$ClSO_2CH_2COOH$ Thermolysed (g)	Temp (°C)	Pressure Before (μ)	During	Time (min)	Contact Time (msec)	Yields of CH_3SO_2Cl (%)*	$CH_3SO_2OCH_3$
1. 0.1110	652	8	17	7	0.5	5·9.2	2.6
2. 0.1554	649	8	20	11	0.7	51.1	2.6

*Mole percentages based on thermolysed chlorosulfonylacetic acid.

Analysis: 3% Butanediol succinate, 6' x 1/4", 107°; methyl benzoate.

Table 36

Thermolysis of Chlorosulfonylacetic Acid

Methanol-d "Sandwich" Trapping

Deuterium Distributions for

Methanesulfonyl Chloride and Methyl Methanesulfonate

$ClSO_2CH_2COOH$ Thermolysed (g)	Temp (°C)	Pressure Before (μ)	During	Time (min)	Contact Time (msec)	Deuterium Content* CH_3SO_2Cl d_0	d_1	$CH_3SO_2OCH_3$ d_0	d_1
1. 0.1927	649	8	19	18	0.9	96.7	3.3	37.0	63.0
2. 0.2113	652	4	14	19	0.8	97.0	3.0	49.6	50.4

*Maximum methyl methane-d_2-sulfonate was 2%.

Isolation: 3% Butanediol succinate, 12' x 1/4", 130°.

Table 37

Thermolysis of Chlorosulfonylacetic Acid

Homogeneous Trapping

Yields for Methanesulfonyl Chloride and Methyl Methanesulfonate

$ClSO_2CH_2COOH$ Thermolysed[**] (g)	Temp (°C)	Pressure		Time (min)	Contact Time (msec)	Yields of	
		Before	During			CH_3SO_2Cl	$CH_3SO_2OCH_3$
		(μ)				(%*)	
Methanol trap							
1. 0.1665	660	40	55	18	1.4	0.3	38.2
2. 0.1784	645	45	60	25	1.8	0.5	43.6
Hydrogen chloride trap							
3. 0.1980	655	20	40	15	1.3	59.1	--
4. 0.1850	655	30	50	21	1.0	58.4	--
No trap							
5. 0.1967	655	13	25	23	1.2	47.5	--
6. 0.1505	649	13	23	15	0.9	47.7	--
7. 0.1391	644	11	18	15	0.7	55.9	--

*Mole percentages based on thermolysed chlorosulfonylacetic acid.

**Amount of material that back-sublimed varied from 5-25 mg.

Analysis: 3% Butanediol succinate, 12' x 1/4", 150°; methyl benzoate.

Table 38

Thermolysis of Chlorosulfonylacetic Acid

Homogeneous Deuterium Chloride Trapping

Deuterium Distribution for Methanesulfonyl Chloride

$ClSO_2CH_2COOH$ Thermolysed (g)	Temp (°C)	Pressure Before	During (μ)	Time (min)	Contact Time (msec)	Deuterium* CH_3SO_2Cl $\underline{d}_0$	$\underline{d}_1$
1. 0.1825	655	40	60	15	1.4	12.6	87.4
2. 0.1334	665	30	50	10	1.3	19.9	80.1

*Maximum methane-$\underline{d}_2$-sulfonyl chloride was 0.5%.

Isolation: 3% Butanediol succinate, 12' × 1/4", 150°.

Table 39

Thermolysis of Methanesulfonyl Chloride

Methanol "Sandwich" Trapping

Yields for Dimethoxymethane

CH_3SO_2Cl Passed[**] (g)	Temp (°C)	Pressure		Time (min)	Contact Time (msec)	Yield of $CH_2(OCH_3)_2$ (%[*])
		Before	During			
		(μ)				
1. 0.2739	660	10	15	110	1.7	1.3
2. 0.3627	932	15	22	120	1.5	27.8
3. 0.3506	949	4	12	110	1.6	26.6
4. 0.3035	943	12	22	95	2.0	25.6

[*]Yields based on the amount of CH_3SO_2Cl passed through furnace.

[**]Weight of material passed through furnace.

Analysis: 10% FFAP, 18' × 1/4", 45°; cyclopentane.

Table 40

Thermolysis of Methanesulfonyl Chloride

Homogeneous Methanol Trapping

Yields for Methyl Methanesulfonate

CH_3SO_2Cl Thermolysed (g)	Temp (°C)	Pressure		Time (min)	Contact Time (msec)	Yield of $CH_3SO_2OCH_3$ (%)[***]
		Before	During			
		(μ)				
1. 0.0156[*]	665	40	47	15	1.4	16.7
2. 0.0549[**]	665	50	60	29	1.3	19.9

[*]CH_3SO_2Cl passed was 0.0604 g. [**]CH_3SO_2Cl passed was 0.1865 g.

[***]Yields based on decomposed methanesulfonyl chloride.

Analysis: 3% Butanediol succinate, 12' × 1/4", 150°; methyl benzoate.

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APPENDIX I

THE ORIGIN OF KETENE IN THE KETONE THERMOLYSES

Ketene was obtained as a product from all the ketones which were thermolysed. In order to determine whether the reaction pathway to ketene originated from an initial α or β cleavage in the ketone, some pertinent examples from the literature were obtained, and the enthalpies of the species in the reactions were calculated.
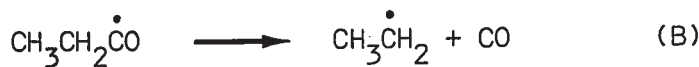
The decomposition of the acetonyl radical and two possible decomposition modes of the propionyl radical are considered. On the basis of these decompositions, projections are made for the six carbon biradicals which are generated by α and β cleavage in cyclohexanone.

The decomposition of the acetonyl and propionyl radicals, together with the reaction enthalpy changes (for standard state conditions) (63) and activation energies, are summarized below.

$$CH_3CO\dot{C}H_2 \longrightarrow \dot{C}H_3 + CH_2CO \qquad (A)$$
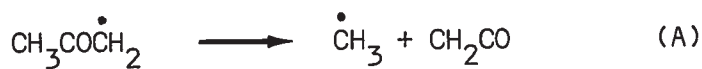
$$\Delta H = 25.2 \text{ kcal/mole}$$

$$E_a = 41 \text{ kcal/mole}$$

$$CH_3CH_2\dot{C}O \longrightarrow CH_3\dot{C}H_2 + CO \qquad (B)$$

$$\Delta H = 10.6 \text{ kcal/mole}$$

$$E_a = 12 \text{ kcal/mole}$$

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$$CH_3CH_2\overset{\bullet}{C}O \longrightarrow \overset{\bullet}{C}H_3 + CH_2CO \qquad (C)$$
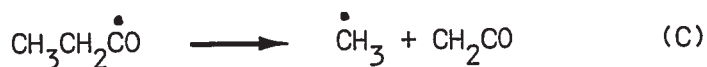
$$\Delta H = 30.8 \text{ kcal/mole}$$

$$E_a = 45 \text{ kcal/mole (estimated)}$$

The formation of ketene and methyl radicals from the unimolecular decomposition of acetonyl radicals requires an activation energy of 41 kcal/mole (64). However, propionyl radicals decompose unimolecularly to carbon monoxide and ethyl radicals with an activation energy of about 12 kcal/mole (65). Ketene is not a product of the unimolecular decomposition of propionyl (or acetyl) radicals. If it is assumed that the transition states in reactions A and C are similar, then, the activation energy for ketene formation from propionyl radicals is about 45 kcal/mole. Therefore, propionyl radicals decompose preferentially to carbon monoxide and ethyl radicals with the lower activation energy of 12 kcal/mole.

The analogous decompositions for the six carbon biradicals which are produced by β and α cleavage in cyclohexanone are summarized as reactions D to F

$$C_6H_{10}O \xrightarrow{\beta} \overset{\bullet}{C}H_2CH_2CH_2CH_2CO\overset{\bullet}{C}H_2 \longrightarrow \overset{\bullet}{C}H_2CH_2CH_2\overset{\bullet}{C}H_2 + CH_2CO \qquad (D)$$

$$\underline{1}$$

$$\Delta H = 78.9 \text{ kcal/mole} \qquad\qquad \Delta H = 22.3 \text{ kcal/mole}$$

$$C_6H_{10}O \xrightarrow{\alpha} \overset{\bullet}{C}H_2CH_2CH_2CH_2CH_2\overset{\bullet}{C}O \longrightarrow \overset{\bullet}{C}H_2CH_2CH_2CH_2\overset{\bullet}{C}H_2 + CO \qquad (E)$$

$$\underline{2}$$

$$\Delta H = 74.8 \text{ kcal/mole} \qquad\qquad \Delta H = 9.5 \text{ kcal/mole}$$

$$C_6H_{10}O \xrightarrow{\alpha} \overset{\bullet}{C}H_2CH_2CH_2CH_2CH_2\overset{\bullet}{C}O \longrightarrow \overset{\bullet}{C}H_2CH_2CH_2\overset{\bullet}{C}H_2 + CH_2CO \quad (F)$$

<u>2</u>
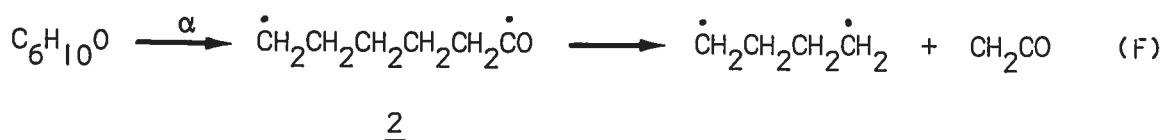
$\Delta H = 74.8$ kcal/mole $\Delta H = 26.4$ kcal/mole

Because the biradicals <u>1</u> and <u>2</u> differ from the acetonyl and pro-pionyl radicals by only a three carbon fragment, it is reasonable to assume that the activation energies for the reactions D-F are proportional to the activation energies for the reactions A-C respectively. There-fore, biradical <u>1</u> gives rise to the ketene in the decomposition of cyclohexanone, while biradical <u>2</u> merely decarbonylates. Because the activation energy difference for the two alternative pathways for biradi-cal <u>2</u> is significant, it is very unlikely that the reaction pathways intersect at 1050°. Thus, it is probable that the ketene obtained in the thermolysis of each ketone is derived from the unimolecular decomposition of a β carbonyl biradical or radical. Because β carbonyl radicals must arise from initial β cleavage in the ketone, then β cleavage must be the primary step that leads to ketene under conditions where the β carbonyl radical decomposes unimolecularly.

Calculations

The heats of formation of the radical and biradical species in reactions A-F are obtained from the following relationship:

$$A-B \longrightarrow A\cdot + B\cdot$$

$$D(AB) = \Delta H(A) + \Delta H(B) - \Delta H(AB)$$

where: A-B is the bond which is cleaved.

D is the bond dissociation energy.

ΔH are the heats of formation of the species.

The heats of formation and bond dissociation energies which are required to calculate the enthalpy changes in reactions A-F are summarized in Tables 41 and 42 respectively.

Table 41

Heats of Formation

Species	ΔH (kcal/mole)	Reference
CH_3COCH_3	-51.9	(66)
CH_3CH_2CHO	-45.5	(66)
CH_2CO	-14.2	(66)
CO	-26.4	(66)
$CH_3CH_2CH_3CH_2COCH_3$	-66.9	(66)
$CH_3CH_2CH_2CH_2CH_2CHO$	-59.5	(63)
$C_6H_{10}O$	-54.0	(66)
$CH_3CH_2CH_2CH_3$	-30.4	(66)
$CH_3CH_2CH_2CH_2CH_3$	-35.1	(66)
$H_3C\cdot$	34.0	(63)
$CH_3\dot{C}H_2$	26.0	(63)
$H\cdot$	52.1	(63)

Table 42

Bond Dissociation Energies

Bond	D (kcal/mole)	Reference
$RCOCH_2-H$	98	(26)
$RCO-H$	86.5	(27)
RCH_2-H	98	(27)
$RR'CH-H$	95	(27)

APPENDIX II

PREPARATION OF METHYLENECYCLOHEXANE-2,2,6,6-$\underline{d}_4$

BY THE WITTIG REACTION

A. Discussion

A potentially useful application of the Wittig reaction (67) is the preparation of olefins which are specifically deuterated in the vinylic or allylic positions. However, a loss and/or scrambling of the deuterium in the olefin has been noted in several instances when easily enolizable ketones had been used. In the present work, the Wittig reaction of cyclohexanone-2,2,6,6-$\underline{d}_4$ gave methylenecyclohexane-2,2,6,6-$\underline{d}_4$ for which considerable scrambling of the deuterium in the olefin had occurred.

In Figure 13, the accepted mechanism of the Wittig reaction and a partial scheme to rationalize the loss and/or scrambling of deuterium is given for the system triphenylmethylphosphonium halide $\underline{1}$ and cyclo-hexanone-2,2,6,6-$\underline{d}_4$ $\underline{3}$. In the Wittig reaction the alkylidenephosphorane ylide $\underline{2}$, derived from the reaction of the base with triphenylmethyl-phosphonium halide $\underline{1}$, reacts reversibly with the ketone $\underline{3}$ to give the betaine $\underline{4}$. Subsequent oxygen-phosphorus bond formation to give the oxaphosphetane $\underline{5}$ and its decomposition gives the olefin $\underline{6}$. Alternatively, the alkylidenephophorane ylide $\underline{2}$, acting as a base, can abstract an acidic α proton from the ketone to give the enolate anion of the ketone and monodeuterated triphenylmethylphosphonium halide. A couple of steps are given to rationalize the loss and scrambling of the deuterium

Figure 13

Mechanism of the Wittig Reaction
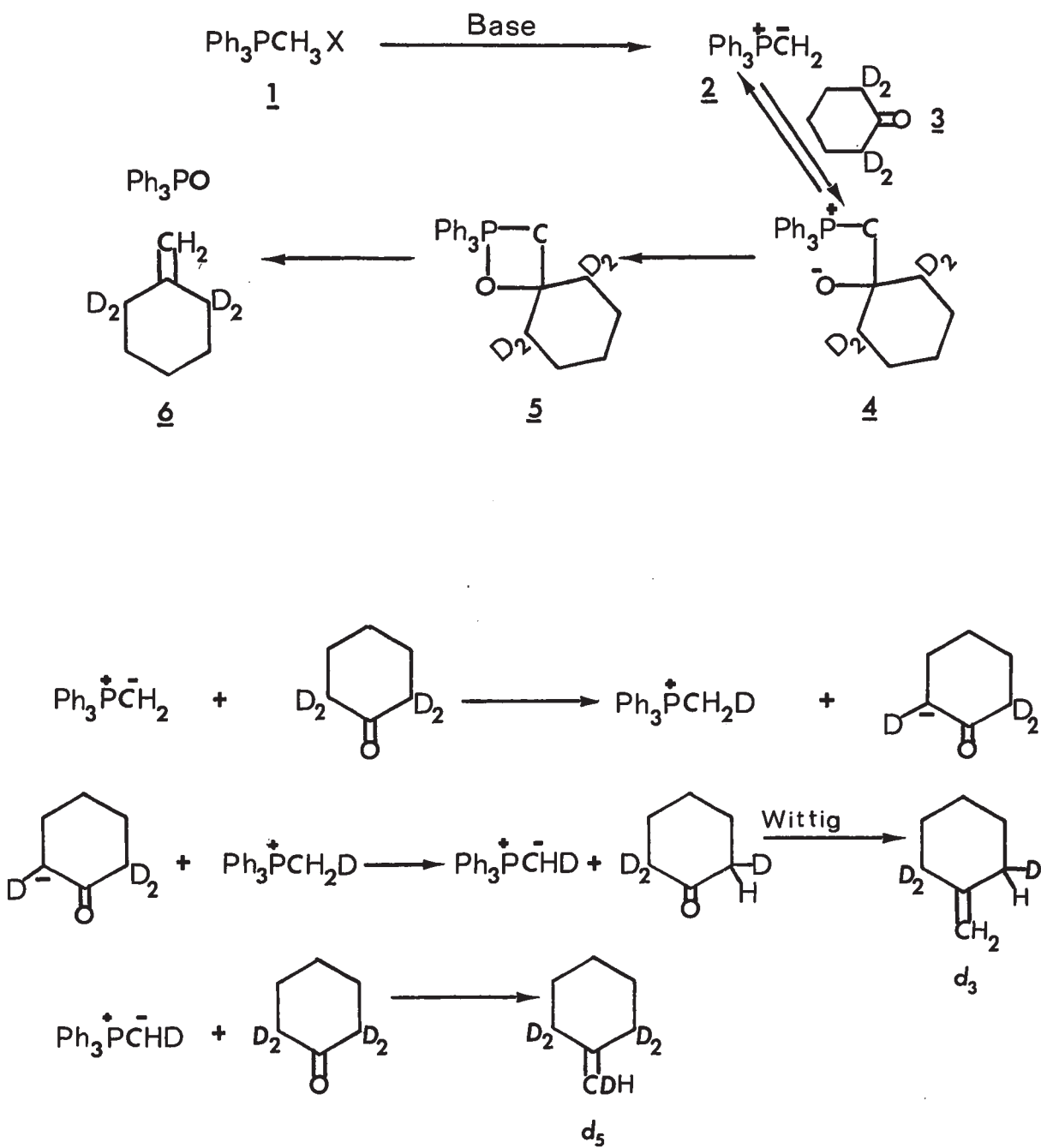
in the olefin.

Table 43 contains several relevant examples from the literature. When the methylsulfinyl carbanion (from the reaction of sodium hydride and dimethyl sulfoxide) is used to generate the ylide, exchange and/or scrambling of deuterium occurs (reactions 1, 2, 4, and 5). In all probability, both the methylsulfinyl carbanion and the ylide act as bases to abstract α protons (deuterons) from the ketones. The resulting exchange competes favorably with the Wittig reaction as reflected by the observed scrambling.

It is known, however, that the use of solvents which do not have acidic protons (for example, ethers) reduces the amount of exchange and scrambling. For the system propyllithium-ether (reaction 3) no scrambling occurred, but, the reason for the slight loss of label (5%) is uncertain. Some exchange and scrambling must have occurred in reaction 8, because of the greater deuterium content in the olefin than in the ketone. The difference of the results in reactions 6 and 7 is striking because only the base used to generate the ylide is different. It is unclear why scrambling of the label occurred in reaction 6 but not in reaction 7 when the solvent, the ketone, and presumably the alkylidenephosphorane ylide were identical, and only the cation was different. No rationalization was given for the apparent deuteron abstraction by the ylide in reaction 6 resulting in scrambled labeling in the olefin and the lack of deuteron abstraction in reaction 7. Furthermore, in the present work, the Wittig reaction for cyclohexanone-2,2,6,6-d_4 carried out on ether with the ylide generated by butyllithium, gave olefin with considerable scrambling of the label. Perhaps

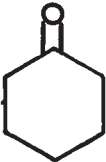Table 43
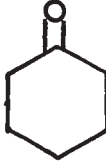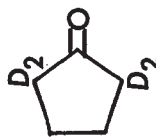
Selective Deuteration with the Wittig Reaction
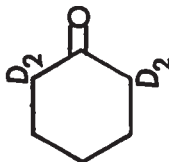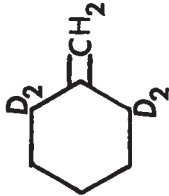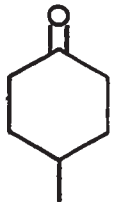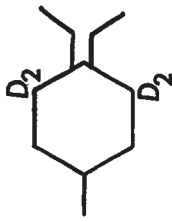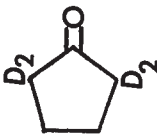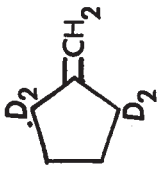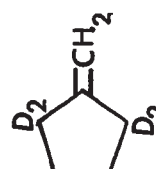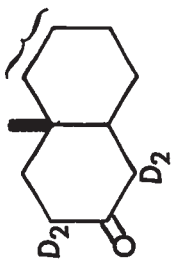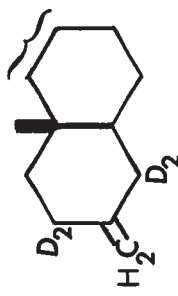
No.	Phosphonium Salt	Base/ Solvent	Ketone	Product (Expected)	Analysis		Ref.
1	Ph_3PCH_3I	NaH/DMSO	CD_3CDO		d_3 25 d_4 50 d_5 25		(68)
2	Ph_3PCD_3I	NaH/DMSO			d_1 83 d_2 15.5		(68)
3	Ph_3PCD_3Br	PrLi/Ether			d_1 11.4 d_2 88.6 d_3 0.0		(68)
4	Ph_3PCH_3I	NaH/DMSO			d_3 15 d_4 74		(68)

Table 43 (continued)

#	Reagent	Base/Solvent	Product D content	Ref.
5	Ph$_3$PCH(CH$_3$)$_2$Br	NaH/DMSO-d$_6$	d$_2$ 5 — d$_3$ 20 — d$_4$ 70	(69)
6	Ph$_3$PCH$_3$Br	NaH/DEE*	allylic 80%D — vinylic 40%D	(70)
7	Ph$_3$PCH$_3$Br	BuLi/DEE*	allylic 98%D — vinylic 0%D	(70)
8	Ph$_3$PCH$_3$Br	PhLi/ether	4.08 atom D per molecule	(71)

*Diethoxyethane

the effect of solvent, acidity of the α protons of the ketones, and the effect of the cations produced from the bases in the generation of the ylide should be investigated further in order to substantiate the claim of the authors of reaction 7. These authors state that the conditions specified in the table prevent exchange and scrambling during the generation of the olefin.

Table 44 summarizes the present work. The Wittig reaction of cyclohexanone-2,2,6,6-$\underline{d}_4$ (3.89 atom D per molecule) gave methylene-cyclohexane-2,2,6,6-$\underline{d}_4$ $\underline{6}$ (4.01 atom D per molecule). Ozonolysis of the methylenecyclohexane-2,2,6,6-$\underline{d}_4$ $\underline{6}$ gave cyclohexanone-2,2,6,6-$\underline{d}_4$ $\underline{7}$ (3.45 atom D per molecule). Thus, the Wittig reaction gave methylene-cyclohexane that had 86% allylic deuteration (3.45 atom D per molecule) and 28% vinylic deuteration (0.56 atom D per molecule). Therefore, deuterium exchange and scrambling had occurred in the Wittig reaction and, in fact, there was 3.1% greater deuteration in the olefin than in the starting ketone.

B. Experimental

Preparation of Cyclohexanone-2,2,6,6-d$_4$

The preparation of this compound is identical to that described in Section C of the Experimental Section. The distribution and average incorporation of deuterium for this compound is given in Table 44. No combustion analysis for deuterium incorporation was obtained for this compound.

In order to check the accuracy of the mass spectrometric deuterium analysis, a different sample of cyclohexanone-2,2,6,6-$\underline{d}_4$ was analysed by both mass spectrometry and the combustion method. Good agreement

between the analyses was found. The deuterium distribution by mass spectrometry was: d_0 0.0%, d_1 0.5%, d_2 1.9%, d_3 16.6%, d_4 81.0%. This distribution corresponded to 3.78 atom D per molecule. By combustion analysis, the incorporation was 3.77 atom D per molecule.

Preparation of Methylenecyclohexane-2,2,6,6-d_4

The preparation of this compound is given in Section C of the Experimental Section. The deuterium analyses are given in Table 44.

Ozonolysis of Methylenecylcohexane-2,2,6,6-d_4

Methylenecyclohexane-2,2,6,6-d_4 (0.122 g) in ethyl acetate (3.0 ml) was ozonized at -78° until the solution turned blue. The solution was then added to a -78° mixture of 10% palladium on charcoal (0.5 g) in ethyl acetate (3.0 ml). The mixture was allowed to warm to room temperature, with shaking, under a hydrogen atmosphere. After filtration, most of the ethyl acetate was removed by distillation, and the residue was distilled in a bulb-to-bulb apparatus. Pure cyclohexanone-2,2,6,6-d_4 (0.020 g; 16%) was obtained by preparative glc with a column on which enolization of cyclohexanone did not occur (20% Se 30, 5' × 1/4", 70°). The deuterium analyses are summarized in Table 44.

Table 44

Deuterium Scrambling in the Synthesis

of Methylenecyclohexane-2,2,6,6-$\underline{d}_4$
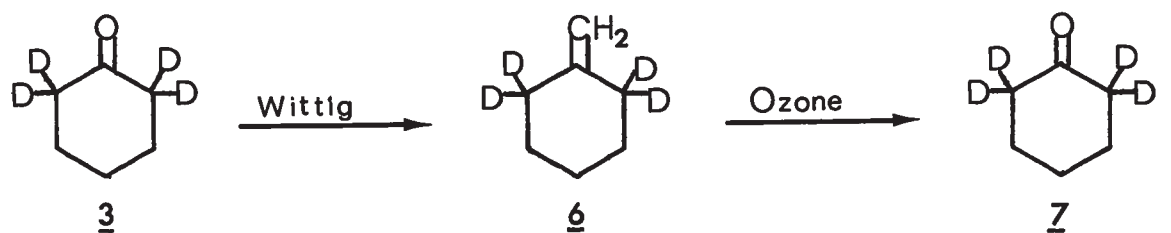
	3		**6**		**7**
$\underline{d}_0$	0.0	$\underline{d}_0$	0.1	$\underline{d}_0$	0.0
$\underline{d}_1$	0.4	$\underline{d}_1$	0.4	$\underline{d}_1$	1.6
$\underline{d}_2$	0.8	$\underline{d}_2$	0.2	$\underline{d}_2$	6.2
$\underline{d}_3$	7.8	$\underline{d}_3$	5.1	$\underline{d}_3$	25.1
$\underline{d}_4$	90.9	$\underline{d}_4$	87.1	$\underline{d}_4$	67.1
		$\underline{d}_5$	6.1		
		$\underline{d}_6$	1.1		

3.89 atom D/
  molecule*

4.02 atom D/
  molecule*

4.02 atom D/
  molecule**

3.48 atom D/
  molecule*

3.41 atom D/
  molecule**

*Deuterium incorporation calculated from the mass spectrum.

**Deuterium incorporation determined by the combustion method.