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LUKE KWOK TUNG LAM   for the   M. S.
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Title: SOME SYNTHETIC EFFORTS IN SMALL RING CHEMISTRY

Abstract approved: _____
                                    F. Thomas Bond

Cyclopropylcyclobutene was prepared via the intermediate dicyclopropylcarbinyl carbene which was generated by the thermal decomposition of the sodium salt of dicyclopropylketone p-toluenesulfonylhydrazone. The successive thermal isomerization of cyclopropylcyclobutene to 2-cyclopropyl-1,3-butadiene and to vinylcyclopentene was studied. Kinetic data were obtained for the cyclopropylcyclobutene to 2-cyclopropyl-1,3-butadiene isomerization in the gas phase. Decomposition of the sodium salt was studied in different solvent systems at 130°, but bicyclo(1.1.0)butane ring formation was not a major reaction pathway under conditions similar to those used in the decomposition of cyclopropylcarboxaldehyde p-toluenesulfonylhydrazone. Attempts to synthesize the compounds bicyclo-(2.2.0)hex-1(4)-ene and bicyclo(2.2.0)hex-1-ene via carbenoid intermediates were hampered by difficulties in preparing the necessary precursors.

Some Synthetic Efforts in Small Ring Chemistry

by

Luke Kwok Tung Lam

A THESIS

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in partial fulfillment of
the requirements for the
degree of

Master of Science
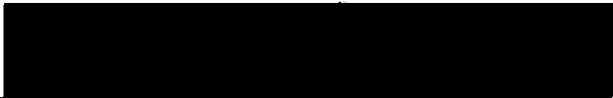
June 1968

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TABLE OF CONTENTS

LIST OF TABLES

SOME SYNTHETIC EFFORTS IN SMALL RING CHEMISTRY

INTRODUCTION

In recent years, small ring carbon compounds (three and four membered) have been studied very extensively from both synthetic and physical points of view of organic chemistry. Modern methods of synthetic organic chemistry have allowed the synthesis of many small ring systems which were once considered to be too strained to exist.

The mere existence of three and four membered ring alkanes, alkenes, and their derivatives, has been enough to arouse considerable interest among theoretical chemists. Theoretical aspects of the structures of such systems have been the center of research for the past two decades. At the same time small ring systems interested physical organic chemists in studies of the chemical nature of the strained systems and challenged the synthetic organic chemists for better and more efficient methods.

This thesis concerns synthetic routes to small ring compounds and fused strained ring systems as well as the thermal isomerizations of vinylcyclopropyl and cyclobutene systems.

Synthetic Routes to Small Ring Compounds

Synthesis of Three-Membered Ring Compounds

Recent advances in synthetic methods make the synthesis of

three and four membered ring compounds routine practices in the

laboratory (85, 68, 8). The first successful synthesis of cyclopro-

pane (or trimethylene) dated back to 1882 (27). 1, 3-dihaloalkanes

were treated with sodium or zinc to give the corresponding cyclo-

propane. Since then, numerous methods have been developed for

$$CH_2\begin{smallmatrix}CH_2Br\\[4pt]CH_2Br\end{smallmatrix} \quad + \ Zn \quad \longrightarrow \quad \triangle \ + \ ZnBr_2$$

the synthesis of cyclopropane and its derivatives. A recent review

by Vogel lists extensive references on the subject (85). Recent ex-

amples of cyclization reactions and formation of cyclopropane deriv-

atives from olefins will be given in the following paragraphs.

Cyclization Reactions. J. T. Gragson and co-workers (37)

obtained monosubstituted cyclopropanes by reacting β-ethoxypropi-

onaldehyde with a Grignard reagent.

$$CH_3CH_2OCH_2CH_2CHO \xrightarrow{RMgX} CH_3CH_2OCH_2CH_2\overset{\overset{\displaystyle OH}{|}}{C}HR \xrightarrow{PBr_3}$$

$$CH_3CH_2OCH_2CH_2\overset{\overset{\displaystyle Br}{|}}{C}HR \longrightarrow R\!-\!\triangle$$
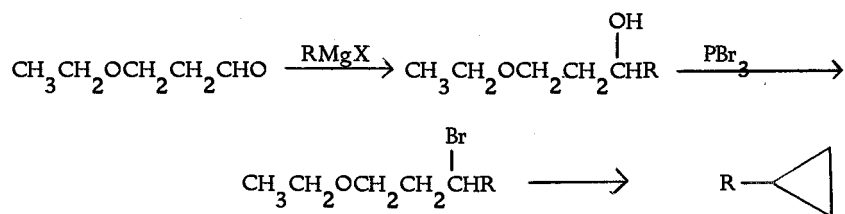
Active methylene groups, when treated with base, form carban-

ions which undergo intramolecular displacement reaction to give

three membered rings. An example of this type employed in this

thesis is the synthesis of dicyclopropyl ketone described by Hart

and Curtis (40).

Y = $-\overset{\overset{\displaystyle O}{\|}}{C}R$ X =   - Cl, Br

   $-\overset{\overset{\displaystyle O}{\|}}{C}OR$ - OTs

   $-C\equiv N$ $-O\overset{\overset{\displaystyle O}{\|}}{C}R$
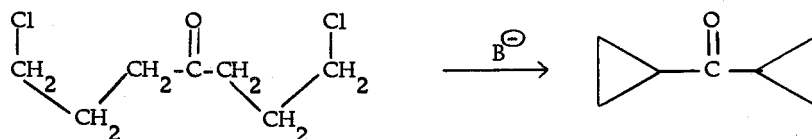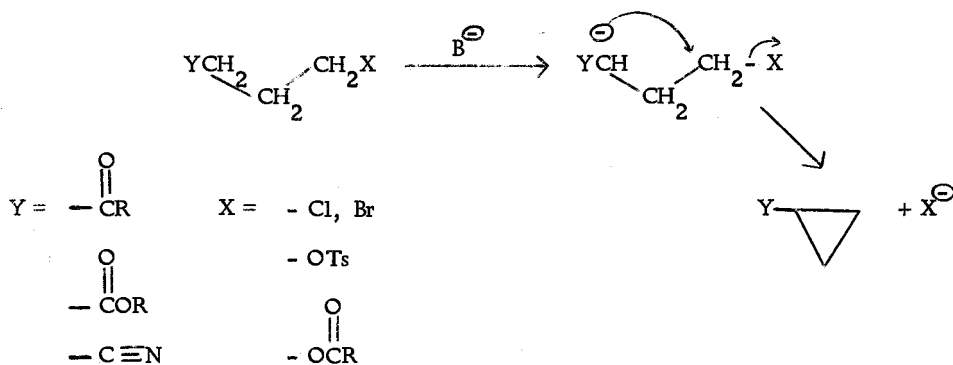
Carbene Addition to Olefins. In 1956, Doering and coworkers

(21) found that methylene undergoes addition reaction onto the double
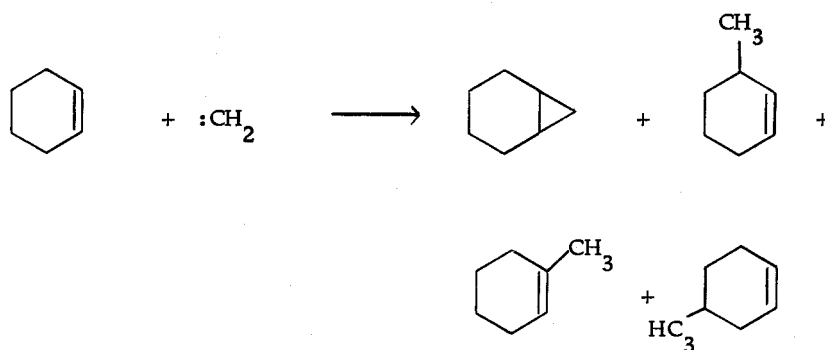
bond of an olefin. As shown by the above equation, the methylene

can, at the same time, insert into C-H bonds to give olefinic prod-

ucts. The addition product, namely, the cyclopropane is often less

than 40% of the product mixture.

One advantage of this reaction is its stereospecificity. In the absence of large amount of inert gas, it was found that the addition proceeds in a cis manner with retention of stereochemistry. When cis- and trans-2-butene are allowed to react with methylene (generated by the irradiation of diazomethane at -75°), the former gives only cis-1, 2-dimethylcyclopropane, and the latter yields only trans-1, 2-dimethylcyclopropane.
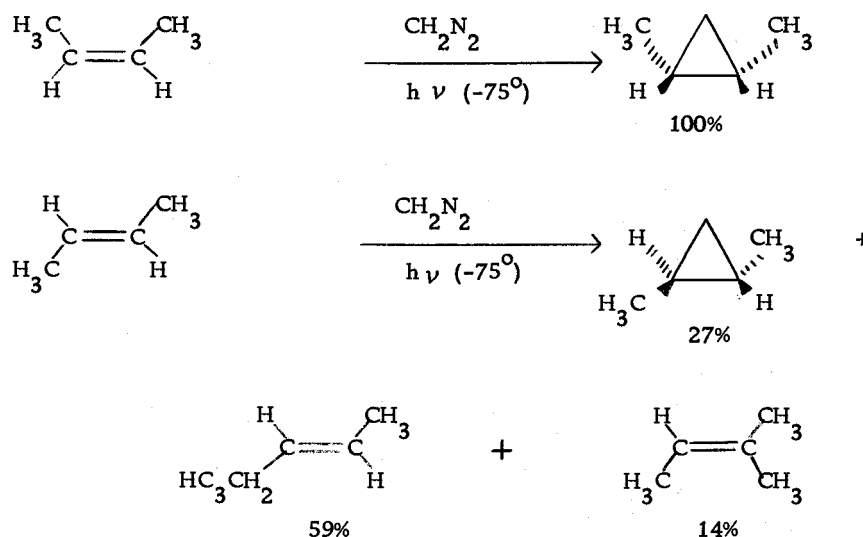
A reaction using methylene iodide and a zinc-copper couple for the synthesis of cyclopropane derivatives was developed by Simmons and Smith (72). Up to 80% yields of substituted cyclopropanes were reported using this method. Since the reaction does not involve free methylene, no insertion product is formed.
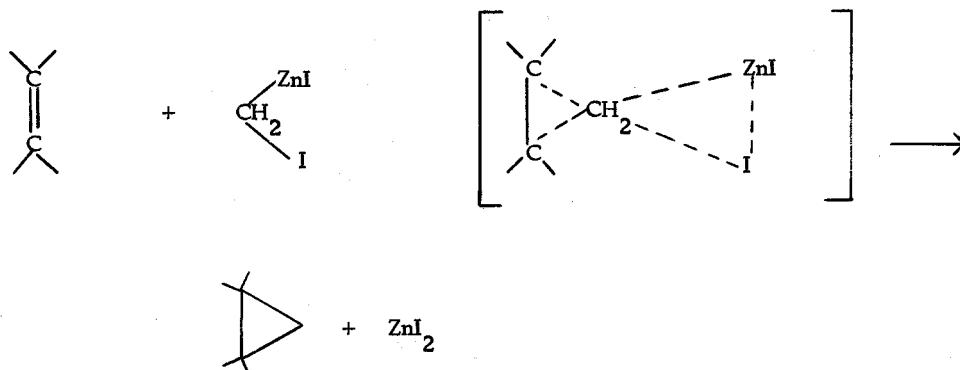
Unlike methylene, dihalocarbenes undergo addition reactions with only rare examples of insertion (45). Dihalocarbenes generated in basic media react with cis and trans olefins stereospecifically giving retention of geometrical configuration (21, 74). Dihalocarbenes generated by other methods (45) also give identical results. By far, the most efficient method synthetically, is that developed by Seyferth and coworkers (70). Making use of the fact that the
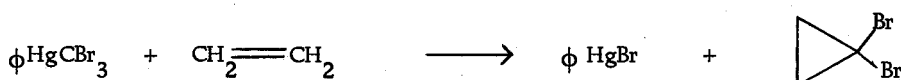
electropositive phenylmercury group attached to trihalomethyl groups has a strong tendency for α -elimination, dihalomethylenes are generated thermally from phenyltrihalomethylmercury compounds. Cyclopropane derivatives are obtained in greater than 65% yield from ethylene, stilbene, and tetrachloroethylene using this method.

Pyrazoline Decomposition. Diazomethane adds onto conjugated double bonds with retention of geometrical configuration (82). This 1,3-dipolar addition product, 1-pyrazoline, can be converted to the

$$H_3C-CH=C(CO_2CH_3)(CH_3) \xrightarrow{CH_2N_2}$$

$$\Big\downarrow \Delta \text{ or } h\nu$$
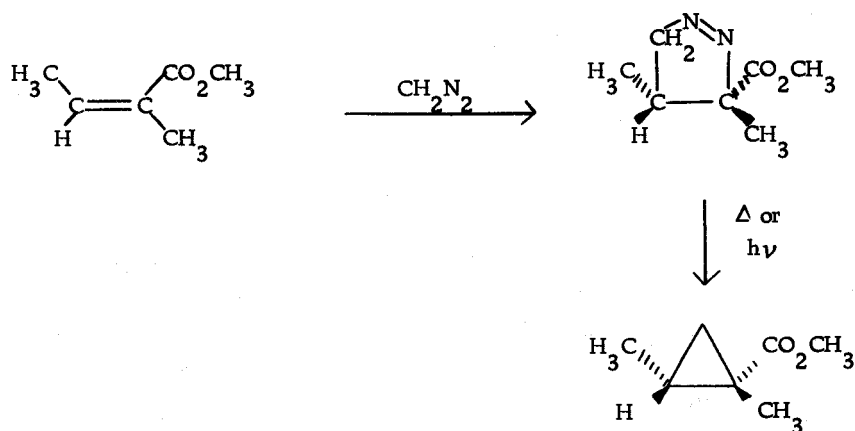
corresponding cyclopropane derivatives by either photolysis (82) or

pyrolysis (48, 56, 82). The products obtained from both reactions

have retention of geometrical configuration.

Synthesis of Four Membered Ring Compounds

Cyclobutanes. Willstätter and Bruce (94) prepared cyclobutane

by the following process. An improved synthesis was described by

$$BrCH_2CH_2CH_2Br + CH_2(CO_2CH_2CH_3)_2 \xrightarrow{NaOEt}$$

(1) H_2O, $H^{\oplus}$

(2) Δ

Br$_2$/KOH

(1) SOCl$_2$

(2) NH$_3$

(1) CH$_3$I

(2) "AgOH"

$$\frac{(1) \quad \Delta}{(2) H_2/Ni, \ 100^\circ} \longrightarrow$$
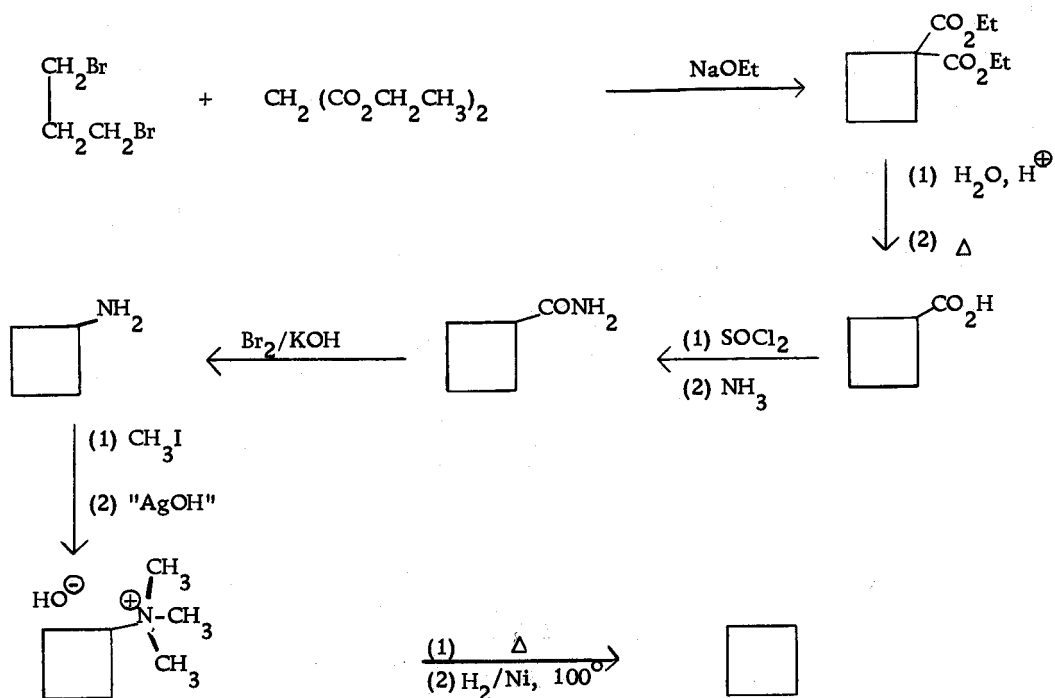
Pines and coworkers (62) with an over-all yield of cyclobutane up to

57% starting from cyclobutane carboxylic acid.
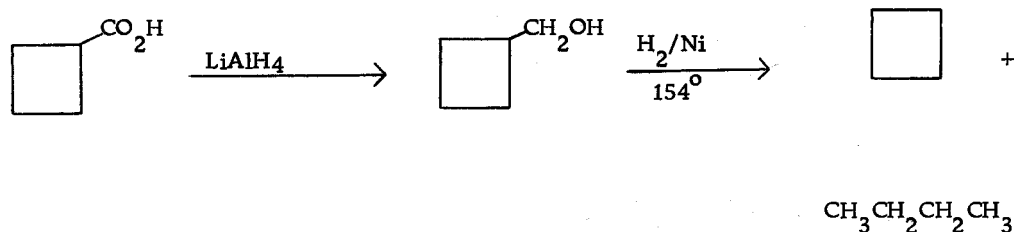
Attempts to dimerize ethylene were unsuccessful in spite of

the numerous examples of cyclobutane derivatives formed from

substituted olefins (85). For example,
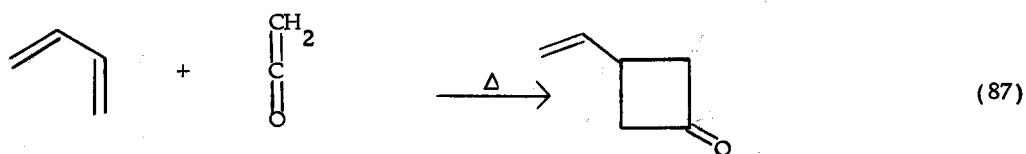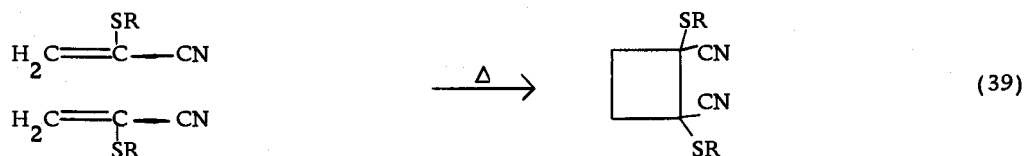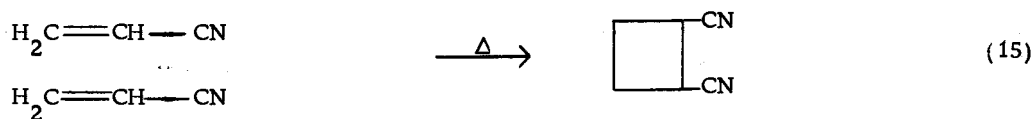
Cyclobutenes. Many cyclobutane syntheses go through cyclo-

butene as an intermediate. Willstätter's synthesis of cyclobutane

which was discussed on page 6 , has cyclobutene as the immediate

precursor. Since then, many new synthetic methods have been

developed for the formation of the cycloalkene and its derivatives.

Some recent examples of importance are given below.

Very recently, it was found that treatment of 1,4-dichloro-1,4-diphenylbutane with sodium amide in liquid ammonia produces 1,2-diphenylcyclobutene in excellent yield (20).

$$\underset{\underset{Cl}{|}}{\overset{\phi}{|}}CHCH_2CH_2-\underset{\underset{\phi}{|}}{\overset{Cl}{|}}CH \xrightarrow[aqNH_3]{NaNH_2} \quad \square \overset{\phi}{\underset{\phi}{}}$$
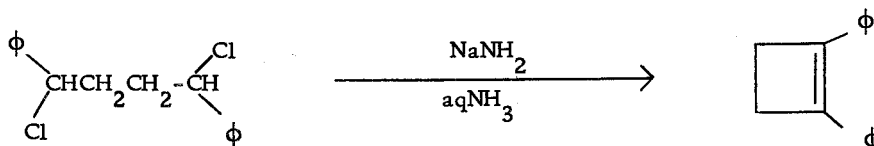
Cyclopropylcarbinyl carbene, 1, is known to undergo rearrangement reaction to give cyclobutene. The tosylhydrazones of cyclopropane carboxaldehyde, and of cyclopropyl methyl ketone, yield

$$\triangleright-CH: \longrightarrow \square$$

$$\underline{1}$$

mainly cyclobutenes when treated with sodium methoxide in an aprotic medium (31).
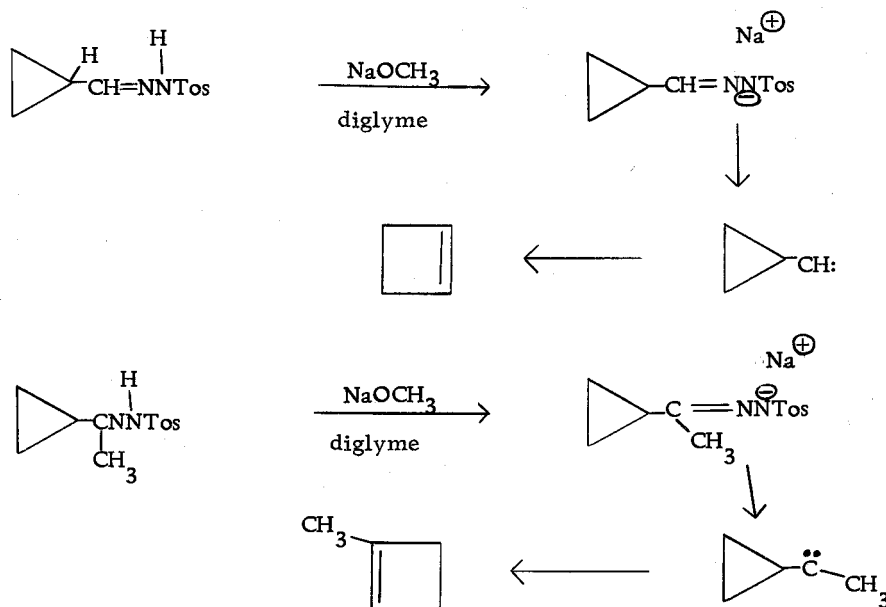
In recent years, the most widely used reaction for the synthesis of cyclobutenes has been photochemical cyclization of dienes and polyenes (88). At 2537 Å, butadiene is converted to cyclobutene in over 90% yield (79). Substituted butadienes are also converted to

94%   6%
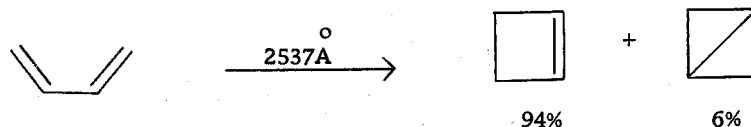
cyclobutene derivatives by irradiation of the same wavelength (78).
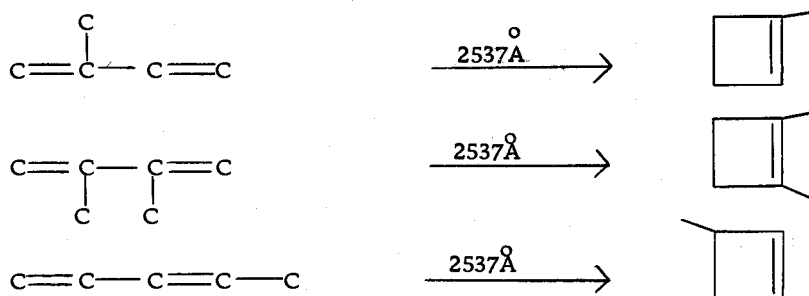
An attempt to couple ethylene with acetylene, however, was not successful (12). 3,4-disubstituted cyclobutenes can be synthesized by reacting acetylene with maleic anhydride in the presence of light (53).
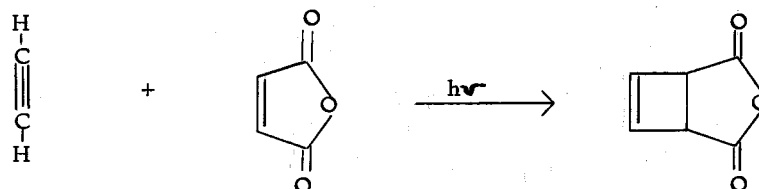
Thermally induced cyclization has also been used in the synthesis of small ring compounds. Excellent reviews have been written on the subject (86, 22). Up to 85% yields were reported for the

synthesis of 3, 4-dimethylenecyclobutenes by thermal rearrangement

of 1, 5-hexadiyne (47), and its derivatives (46). A more recent
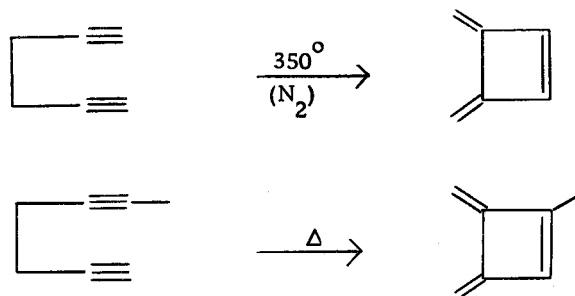
example is the thermal cyclization of a vinylallene to a cyclobutene

reported by Gil-Av and Herling (35).
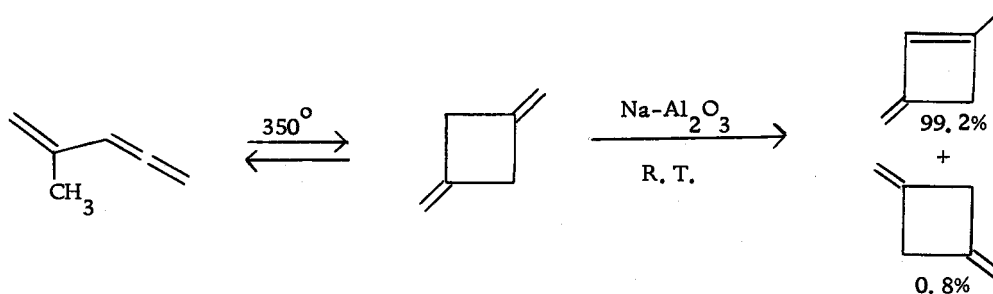
Synthesis of Fused Ring Systems

Bicyclo[2.1.0]pentanes. Criegee and Rimmelin first syn-

thesized bicyclo[2.1.0]pentane from the thermal decomposition of
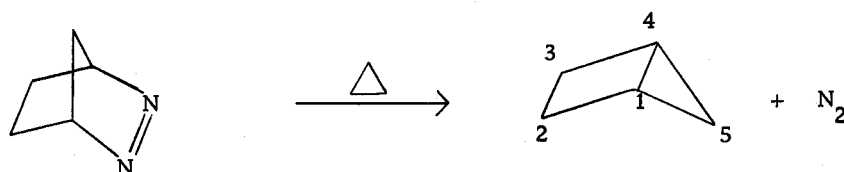
1, 3-endazocyclopentane (17). Since then, many substituted bi-

cyclo[2.1.0]pentanes have been synthesized. Chesick (10), used

the diazomethane-cuprous chloride reaction to obtain the 2-methyl

derivative 2.
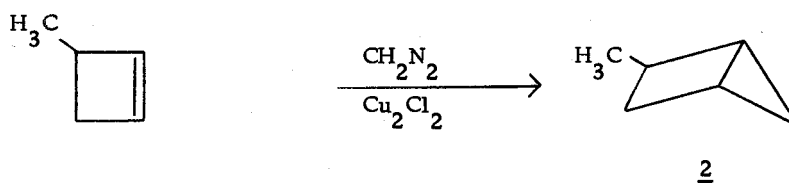
Derivatives having substituents other than alkyl groups on the

C_5 position have recently been synthesized by Wiberg and Ashe,

(91), and by Jorgenson (49).
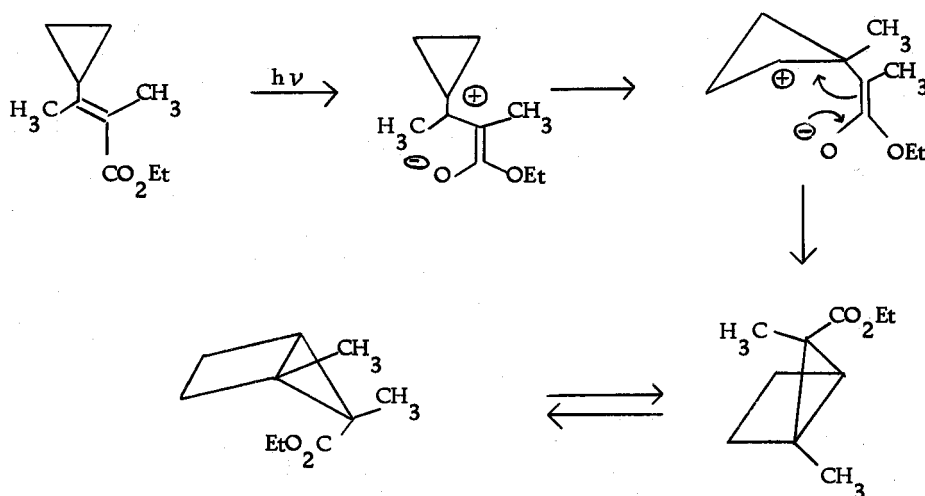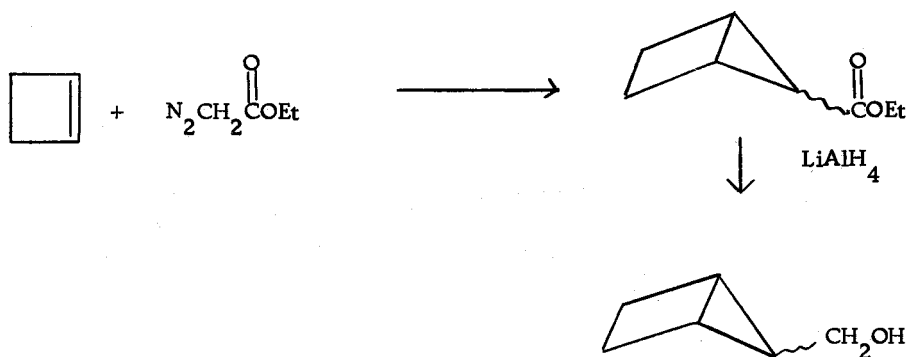
No bicyclo[2.1.0] pentanes having functional groups at the

bridgehead carbon had been reported in the literature until the

completion of the experimental work of this thesis. Methyl

bicyclo[2.1.0]pentane-1-carboxylate was prepared very recently

by Gassman and Mansfield (33) by four different routes. Two of

them which are useful synthetically are as follows.
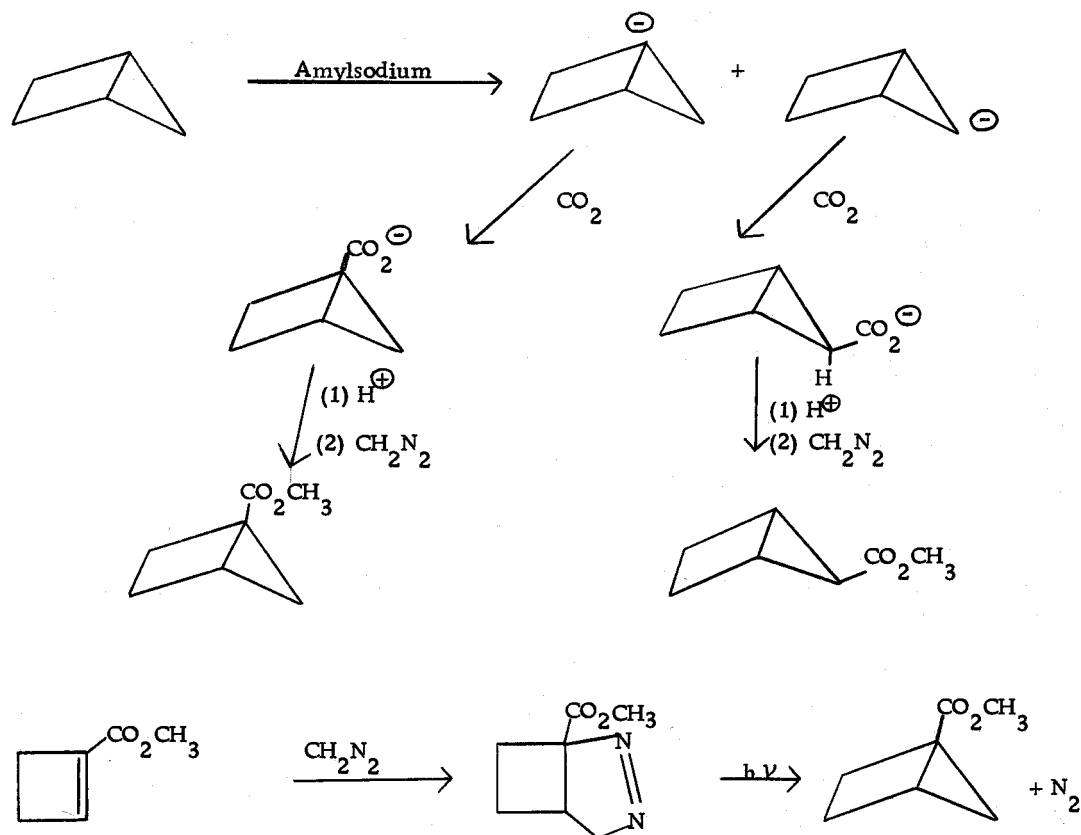
The second route is identical with that developed in this thesis though

it will be seen that small differences in experimental conditions have

a large effect on this preparation. Gassman was interested in the

system for study of cycloaddition reactions of the 1,4 bond (34).
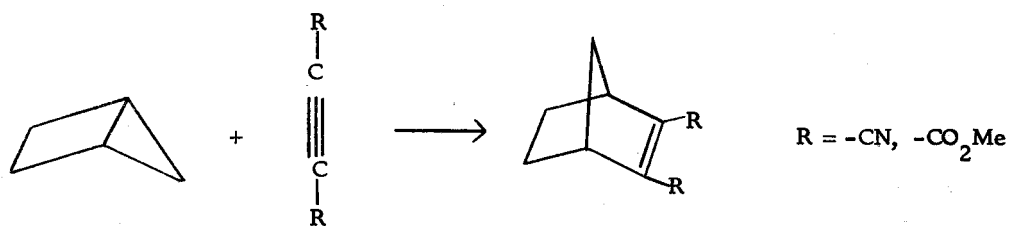
Bicyclo[2.2.0]hexanes. The hydrocarbon, bicyclo[2.2.0]hex-ane was first prepared by Cremer and Srinivasan (16) in less than 5% yield from bicyclo(3.2.0)heptan-3-one. It can now be prepared
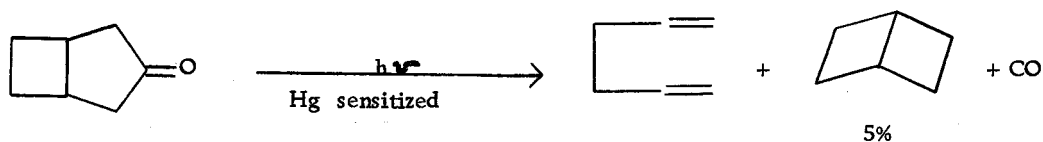
according to Griffin (38) in 60% yield from cyclohexadiene and nitro-sobenzene. This latter method of synthesis can also be used for the
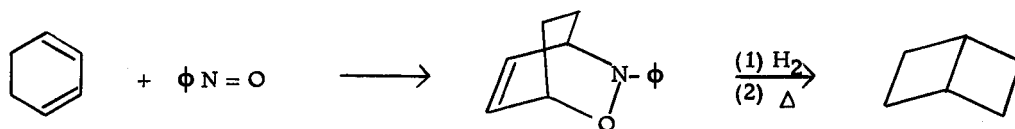
preparation of bicyclo[2.1.0]pentane. In general, this method is applicable for cyclic dienes of the type $\underline{3}$, where X = $(CH_2)_n$; n = 1 - 4.
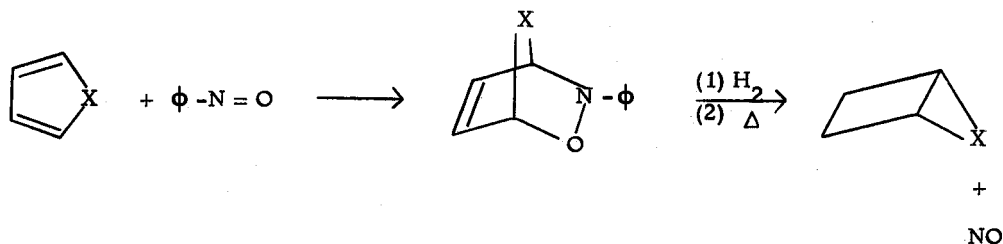
Unfortunately, attempts in our laboratories to repeat this work have been unsuccessful.

Derivatives of the (2.2.0) system have been synthesized in good yield. McDonald and Reinke (55) prepared bicyclo(2.2.0) hexane 2,3-dicarboxylic acid as follows,
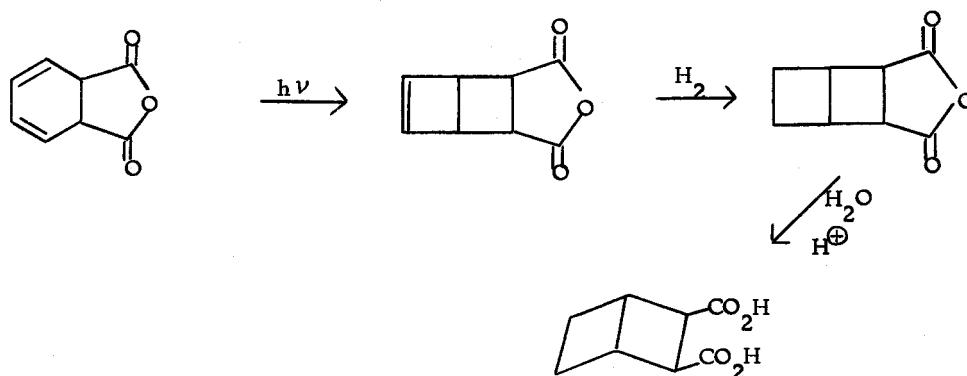
More recently a tetrasubstituted derivative was obtained from photo-sensitized cycloaddition of maleic anhydride and its derivatives to acetylene (53).
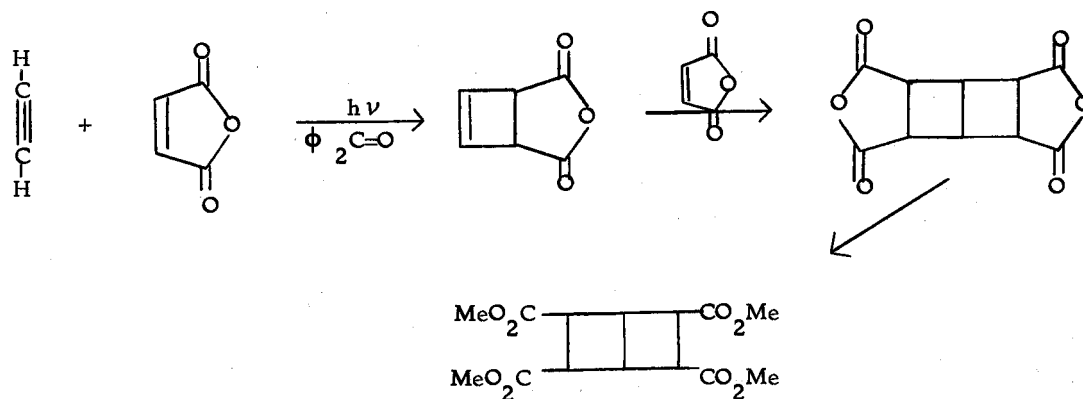
Bicyclo(2.2.0)hexadienes. According to molecular orbital calculations the structure 4 proposed by Dewar as a resonance contributing form of benzene has only slight importance. The

4

corresponding bicyclic compound - bicyclo(2.2.0)hexa-2,5-diene 5
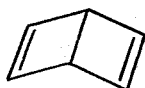
5

has been a synthetic challenge for many years.

The first successful synthesis of the hydrocarbon, 5, was reported by van Tamelen and Pappas (83). Irradiation of dihydrophthalic anhydride gives the bicyclohexene derivative 6, which upon hydrolysis and treatment with lead tetraacetate in pyridine yields the parent
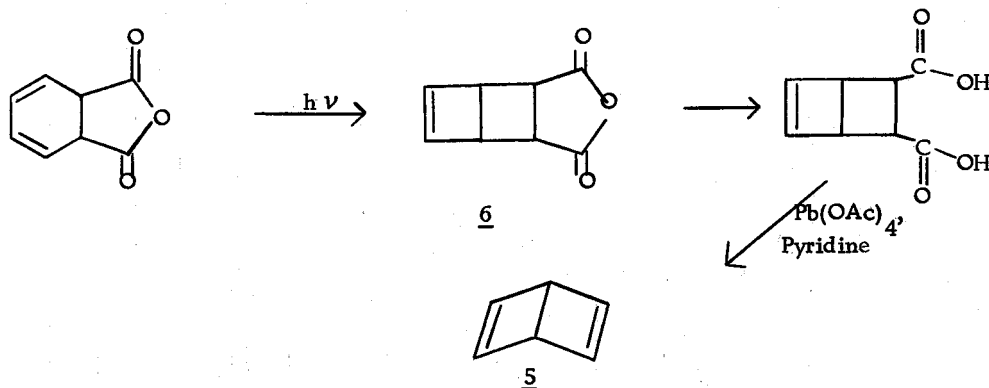
hydrocarbon. This highly strained hydrocarbon isomerizes to benzene at room temperature with a half-life of two days. A much more stable bicyclo[2.2.0] hexadiene derivative had been prepared by the same group a year before the parent compound was obtained (84). The bicyclic compound 7 is formed on irradiation of 1,2,4-tri-t-butylbenzene.

Z
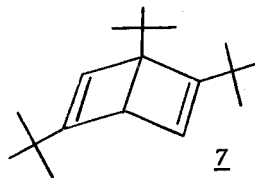
Another efficient method of preparing bicyclo (2.2.0) hexadiene

derivatives is by the reaction of cyclobutadiene complexes with acety-

lenic compounds. Pettit and coworkers (89) obtained mono- and di-

substituted bicyclo[2.2.0] hexa-2,5-dienes in this way.
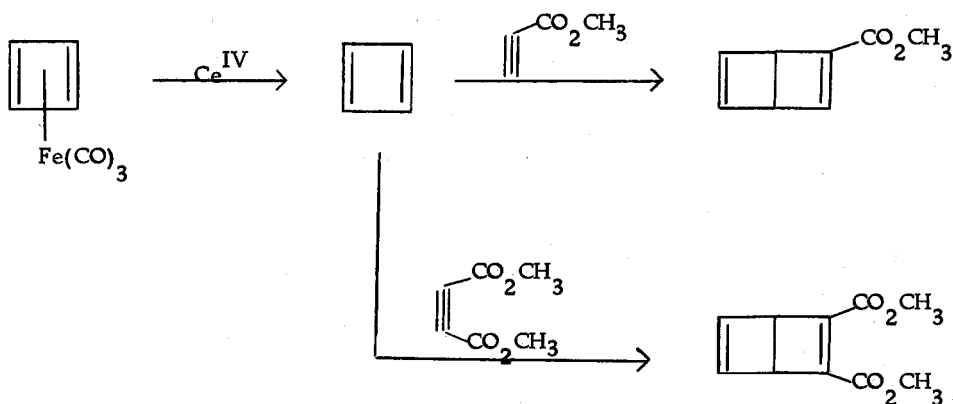
With the formula C_6H_6, one can write a few more bicyclo-

[2.2.0] hexadienes as follows,

None of these can be found in the literature.

Bicyclo(2.2.0)hexenes. Several examples of the bicyclo-

(2.2.0) hexenes are known. Among them is the hydrocarbon,

bicyclo(2.2.0)hex-2-ene 8, prepared by McDonald and Reinke (55)

from the corresponding diacid in 30-38% yield.
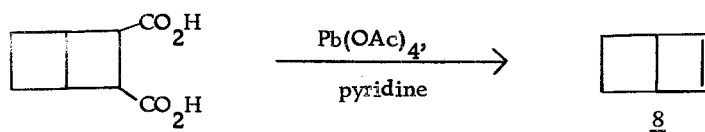
A very thermolabile bicyclohexene derivative 9 is formed in

50% yield by illuminating butyne in the presence of a 1,2-cyclobutene

dicarboxylate (69). Irradiation of the methyl ester of dihydrotere-

phthalic acid, however, does not give a bicyclohexene as originally
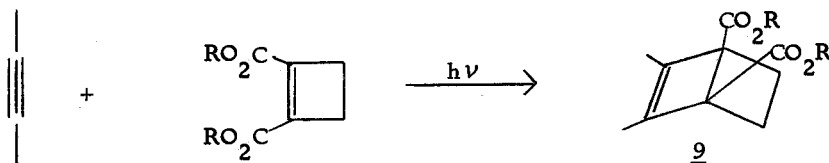
claimed (63), but gives the isomer 10 instead. Making use of
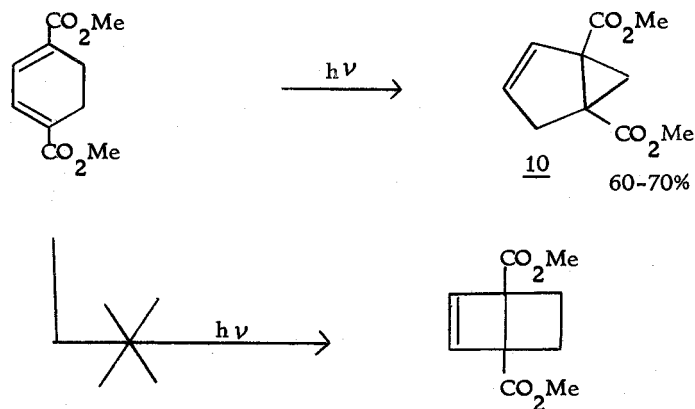
cyclobutadiene as one of the reactants and maleic anhydride the

other, Criegee and coworkers (18) were able to prepare substituted

bicyclohexenes in good yield.
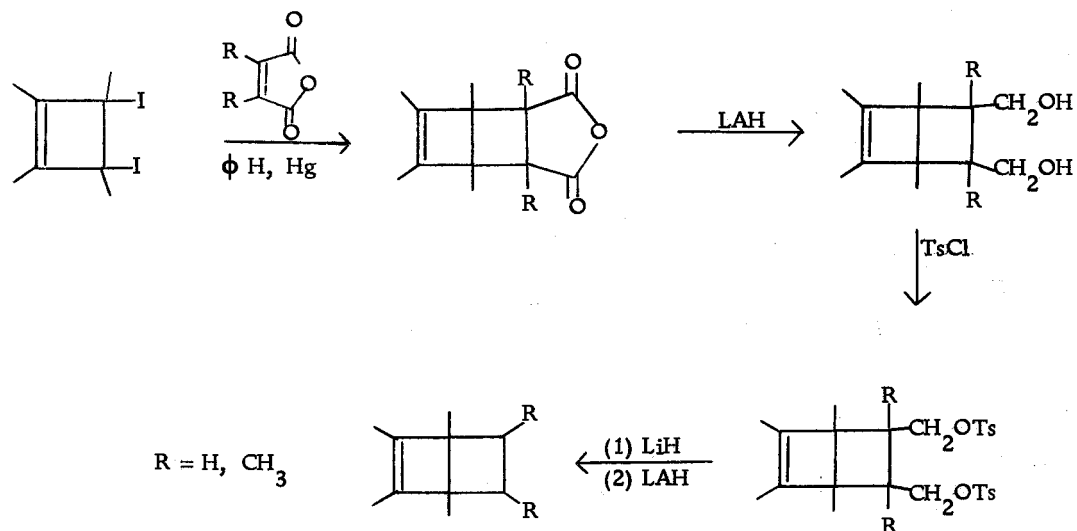
The thermally labile dimer of perchlorobutenyne prepared by Roedig and Kohlhaupt (65) was later determined to have the structure **11**. It was chosen as the more preferred structure among the other
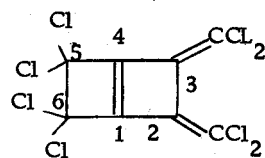
11

possibilities on the ground of extensive analytical studies.
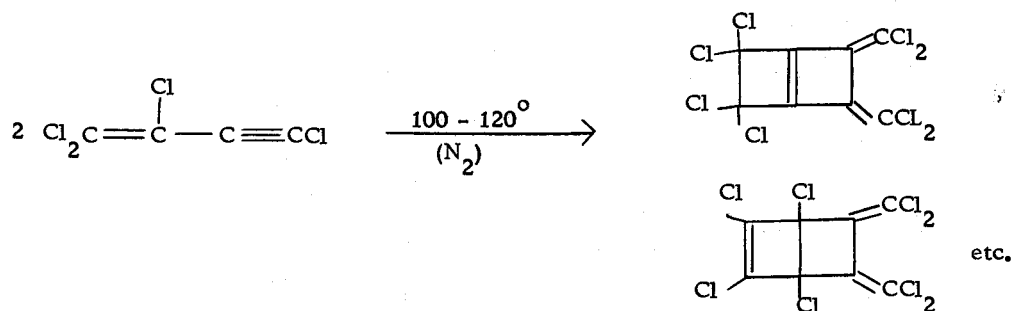
Analysis of the number of observed Raman lines, their depolarization ratios, and a comparison of the wave numbers and

intensities of the Raman and ultraviolet lines of the dimer with that

of a known compound 12 gives satisfactory evidence for the assigned

$$\text{Cl} \quad \text{CCl}_2$$
$$\text{Cl} \quad \text{CCl}_2$$
12
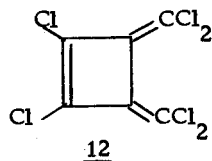
structure (97). Perhaps this is the first example of a bicyclo[2. 2. 0]

hex-1-(4)-ene. The fact that it is stable enough at room temperature

can be explained by the conjugation effect of the two double bonds at

C_2 and C_3.

No successful synthesis has been reported in the literature

regarding the preparation of compounds of the type 13. Simple

derivatives of two of the three possibly bicyclo[2. 2. 0] hexenes, 13,

14 have not been reported. Part of the work of this thesis involves

13   14

possible routes for the synthesis of these two systems.

In addition to the strained nature of these fused ring compounds,

their thermal isomerization reactions are of great interest. Bicyclo

[2. 2. 0] hex-2(3)-ene is known to isomerize to give 1, 3-cyclohexadi-

ene (55). The energy of activation for this process has not been

8
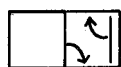
measured, but appear to be higher than that for the isomerization of

cyclobutene to butadiene (14). With cyclobutene, this process can

occur by a conrotatory process (see below) which in the case of

8, would lead to the cis-trans isomer. To get the allowed cis-cis

isomer, a higher energy disrotatory pathway must be followed. A

more detailed discussion of the Woodward-Hoffman rules governing

such reactions will be given in a later section. For bicyclo[2. 2. 0]

hex-1(4)-ene 14, the thermal isomerization would be expected to

resemble that of cyclobutene. A conrotatory process is favorable

in this case to give the known dimethylene cyclobutane (3).

Bicyclo[2. 2. 0] hex-1(2)-ene 13, would be expected to undergo

an isomerization reaction which is closely related to that of cyclo-

butene. It is also possible, however, that a complete ring opening
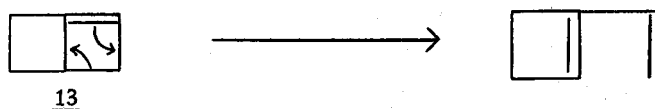
might occur in one step as follows:

It should be noted that this mode of ring opening was not re-
ported for the bicyclo[2.2.0] hex-2(3)-ene.
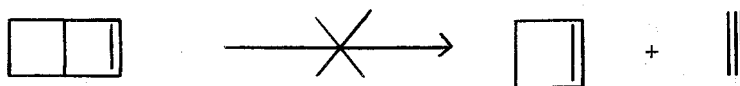
In conclusion, it can be seen that the thermochemistry of such fused
cyclobutenes should be of great interest.

Alkyl- and Dialkylcarbenes

Reactions of Alkyl- and Dialkylcarbenes

Alkyl- and dialkylcarbenes have been used very extensively
for the synthesis of strained ring systems. These highly reactive
"divalent" carbon intermediates can undergo "addition", "insertion",
and "rearrangement" reactions intramolecularly. The high energy
of these intermediate species leaves only a slight chance for inter-
molecular reactions of alkyl- and dialkyl carbenes (51).

Addition Reactions. In the presence of a double bond, alkyl-
and dialkylcarbenes can form cyclopropane ring systems by addition
onto the olefinic linkage (11, 67). The yield of such intramolecular
addition product is in general quite small.

2%
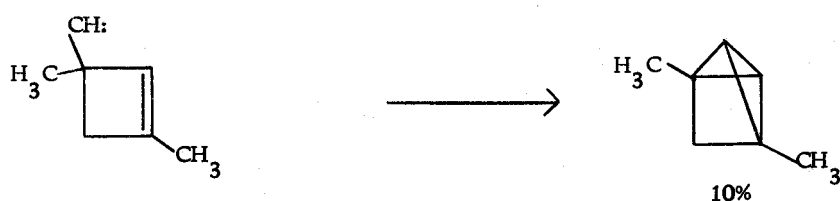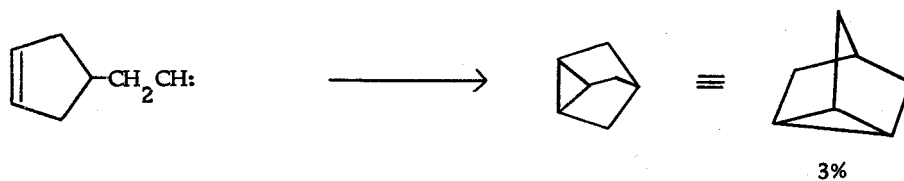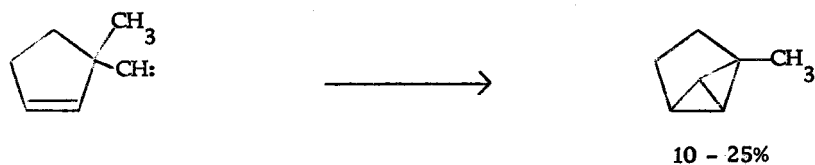
Insertion Reactions. In alkyl- and dialkylcarbenes the divalent carbon atom inserts into the β- and γ-carbon-hydrogen bonds to give olefins and cyclopropanes respectively. The relative yield of cyclopropanes increases with increased branching of the alkyl groups and appear to be governed by the proximity of a suitable carbon-hydrogen bond.
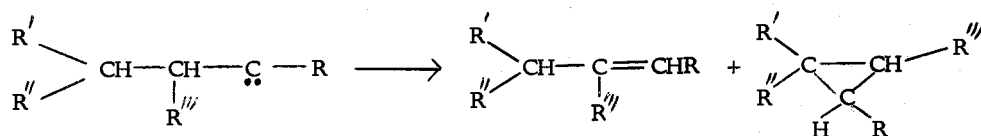
In the ring compounds, the amount of insertion varies with the ring size. Cyclobutylcarbene gives some β-insertion product (31), but no γ-insertion product was detected. Five and six membered ring carbenes undergo β-insertion reaction exclusively with no

18 - 20%   79 - 80%   1 - 2%
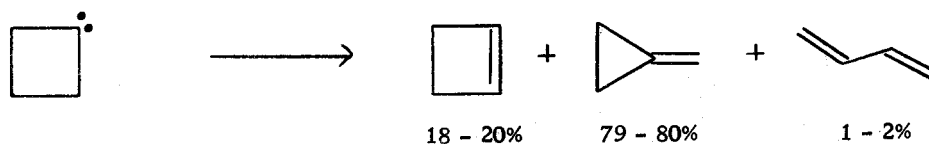
trace of other rearrangement product (32). In medium-sized rings,

100%

100%
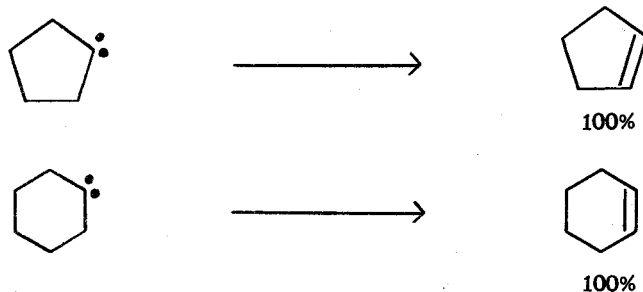
transannular insertion takes place very readily (32).

46%   9%   45%

66%   10%   22%
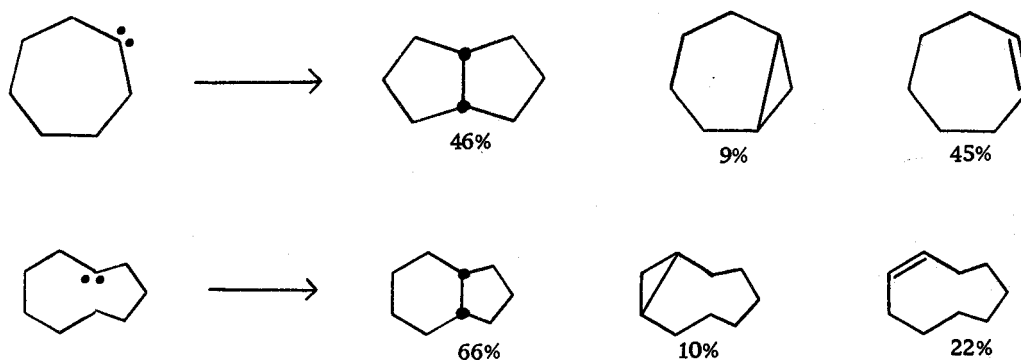
Rearrangement Reactions. Alkyl- and dialkylcarbenes contain-

ing small rings undergo rearrangement as shown on page 8.. Cyclo-

propylcarbinyl and cyclopropylmethylcarbinyl carbenes give largely

rearrangement products resulting from ring expansion. More de-

tailed discussion of the cyclopropylcarbinyl carbene system will

be given in a later section.

$\triangleright\!-CH: \longrightarrow \square \quad + \quad \diagdown\!\!\diagup \quad + \quad \boxed{\diagup} \quad +$

60 – 67%   15 – 28%   2 – 5%

$H_2C\!=\!CH_2 \quad + \quad HC\!\equiv\!CH$

10 – 13%

$\triangleright\!-C: \atop CH_3 \longrightarrow$ CH$_3$ cyclobutene   +   methylenecyclopropane   +   isoprene   +

92%   1%   2%

$CH_2\!=\!CH_2 \quad + \quad CH_3C\!\equiv\!CH$

3%   3%
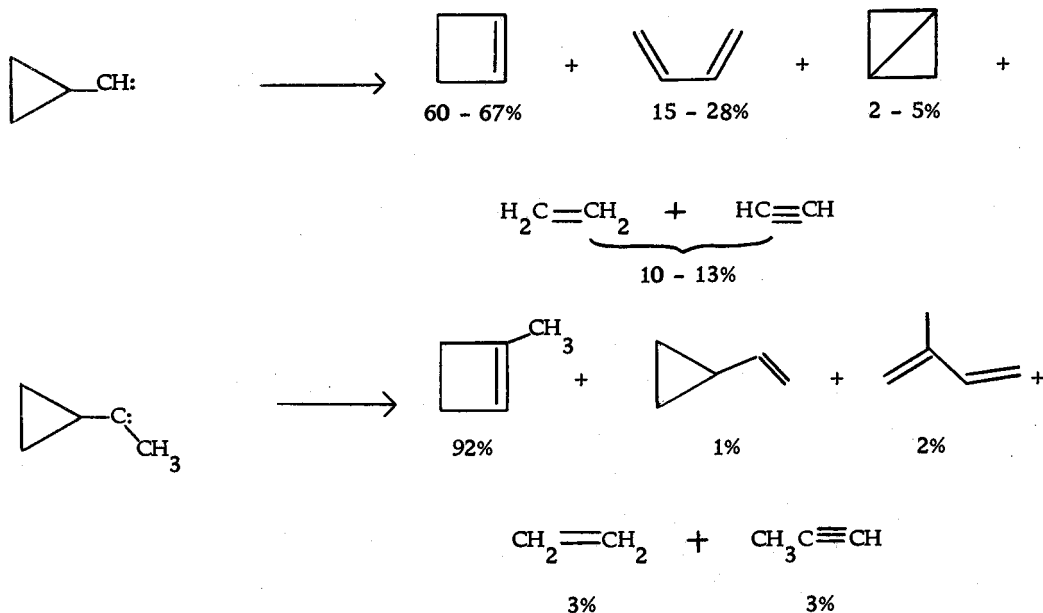
Ring contraction leading to methylenecyclopropane is the major

reaction of cyclobutylcarbene (31).

$\boxed{\bullet\bullet} \longrightarrow \triangleright\!=\ + \boxed{\square} + \diagdown\!\!\diagup\!\!\diagdown$

79 – 80%   18 – 20%   1 – 2%
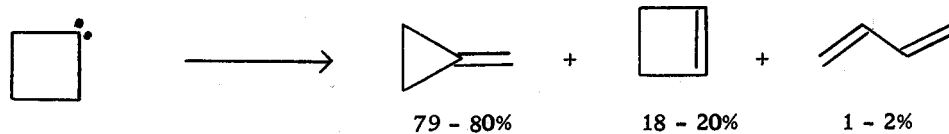
Substituted cyclobutane rings with functional groups give quite differ-

ent products (73, 9).

(EtCO–O)cyclobutane carbene $\longrightarrow$ xylylene + (EtCO–O)cyclobutene + Azine

(PHTO)cyclobutane carbene $\longrightarrow$ Azine   +   (OTHP) bicyclic

48%   26%
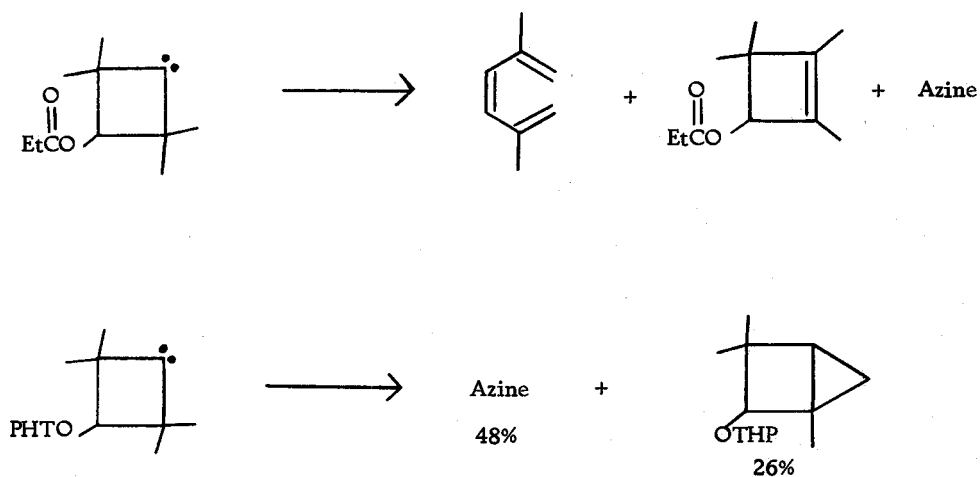
Formation of Alkyl- and Dialkylcarbenes

Alkyl- and dialkylcarbenes are frequently generated by the
decomposition of a diazocompound. The instability of many

$$ \underset{R}{\overset{R}{\diagdown}} C = \overset{\oplus}{N} = \overset{\ominus}{N} \quad \xrightarrow{\triangle \text{ or } h\nu} \quad \underset{R}{\overset{R}{\diagdown}} C\text{:} \quad + \quad N_2 $$
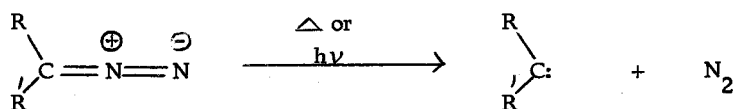
diazoalkanes does not permit their direct handling. Fortunately,
there are various methods which produce diazoalkanes in situ. Oxi-
dation of a hydrazone by mercuric oxide is among one of the classic

$$ \underset{R}{\overset{R}{\diagdown}} C = N - NH_2 \quad \xrightarrow{HgO} \quad \underset{R}{\overset{R}{\diagdown}} C = N_2 \longrightarrow \underset{R}{\overset{R}{\diagdown}} C\text{:} \quad + N_2 $$
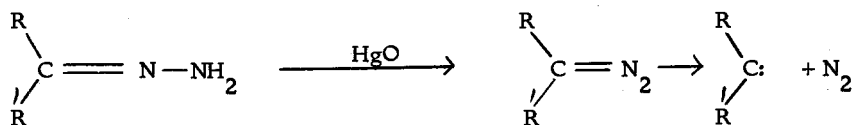
examples. Base treatment of nitrosourea derivatives has also been
used for a long time.

$$ \underset{R}{\overset{R}{\diagdown}} CH - \overset{\overset{N=O}{|}}{N} - \overset{\overset{}{\underset{||}{C}}}{\underset{O}{}} - NH_2 \quad \xrightarrow{B^\ominus} \quad \underset{R}{\overset{R}{\diagdown}} C = N_2 \quad + \quad \underset{HO}{\overset{O}{\underset{\diagup}{\overset{||}{C}}}} NH_2 $$
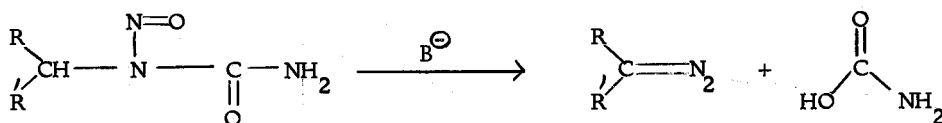
The most widely used method for carbene generation is the
thermal decomposition of the sodium salt of the p-toluenesulfonyl-
hydrazone (tosylhydrazone) of an aldehyde or ketone. This method
of generation of the diazocompound which then leads to the alkyl-
and dialkylcarbene, is quite sensitive to reaction conditions.

$$\underset{R'}{\overset{R}{>}}C=N-\underset{\underset{\ominus}{}}{\overset{\overset{\oplus}{Na}}{N}}-SO_2-\left\langle\bigcirc\right\rangle-CH_3 \xrightarrow[\triangle]{h\nu \text{ or}} \underset{R'}{\overset{R}{>}}C=N_2 +$$

$$\overset{\oplus \ominus}{NaSO_2}-\left\langle\bigcirc\right\rangle-CH_3$$
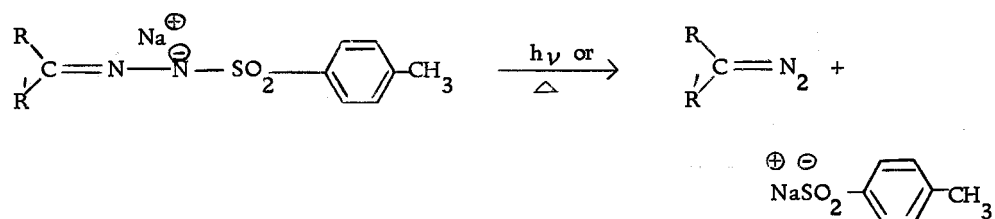
Reactions run in protic and aprotic solvent give different product compositions. The amount of base present alters the nature of the intermediate formed. A discussion of these different conditions will be illustrated by the cyclopropylcarbinyl carbene system.

Cyclopropylcarbinyl Carbene System

Cyclopropane carboxaldehyde p-toluenesulfonylhydrazone 15 was first reported by Friedman and Shechter (31) to react with sodium methoxide in aprotic solvents to give cyclobutene (60-67%) by ring expansion, 1,3-butadiene by rearrangement (presumably from cyclobutene), and ethylene and acetylene by fragmentation, along

$$\triangleright-CH=NNHTs \xrightarrow[180^\circ]{NaOCH_3} \triangleright-\underset{H}{\overset{N_2}{C}} \xrightarrow{-N_2} \triangleright-CH: \quad (I)$$

15

$$\triangleright-CH: \longrightarrow \boxed{} \xrightarrow{\triangle} \diagup\diagdown \quad (II)$$

$$\triangleright-CH: \longrightarrow \overset{\oplus}{\boxed{}}:\ominus \longrightarrow \| + \| \quad (III)$$
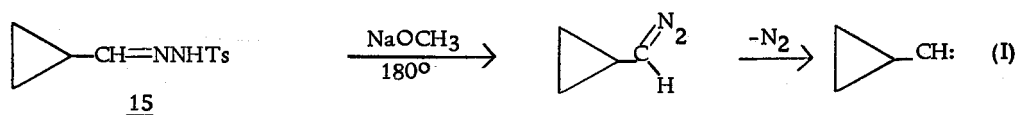
with unidentified hydrocarbons. None of the product, methylene-cyclopropane, which would arise from hydride shift, could be detected in the product mixture.

This reaction is generally considered to proceed via a carbenoid intermediate as shown in the above equations, II and III. Frey and Stevens (30), however, repeated the experiment and found that the major product of the decomposition was bicyclobutane. It was suggested that this product was formed by intramolecular insertion of cyclopropylcarbinyl carbene into one of its four equivalent secondary carbon-hydrogen bonds.
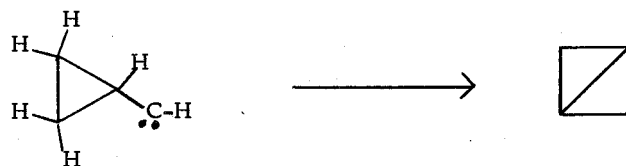
Later, Smith and coworkers (76) reinvestigated the decomposition of cyclopropane carboxaldehyde p-tosylhydrazone under various conditions. It was found that the experimental conditions affect the reaction mechanism to a large extent. The effect of the number of equivalents of base (sodium methoxide) and of the proton-donor capacity of solvents on the decomposition of the tosylhydrazone and of its sodium salt is summarized in Table 1.

Table 1. Decomposition of cyclopropane carboxaldehyde p-toluene-
sulfonylhydrazone 15 by sodium methoxide or the sodium
salt 16 in various environments.

15 + NaOCH$_3$	Solvent	% of		
		□	▨	Others
excess base	aprotic	80-88	2-3	8-17
	protic	20	79	1
1 eq. base	aprotic	85	5	10
0.8 eq. base	aprotic	32	57	11
16	dry	100	--	--
	aprotic	66	16	15
	protic	21	74	--

Decomposition of 15 in an aprotic solvent (diethyl carbitol) with
excess sodium methoxide gives cyclobutene and 1,3-butadiene as the
principal products; bicyclo(1.1.0)-butane amounts to only 2-3%. If
insufficient sodium methoxide (0.8 equivalent) or ethylene glycol
(protic solvent) is used, bicyclo(1.1.0)butane (57-79%) becomes the
principal product. The formation of bicyclo(1.1.0)butane in the
presence of excess or equivalent base can be explained by the for-
mation of methanol which then serves as the proton donor. In the

$$\triangleright\!\!-\!CH\!\!=\!\!NNTos \ + \ NaOCH_3 \ \longrightarrow \ \triangleright\!\!-\!CH\!=\!N\overset{\ominus}{N}Tos \ Na^{\oplus} \ + \ CH_3OH$$

15   16 .

case of insufficient base, the unreacted tosylhydrazone can also
serve as the proton donor.

When the sodium salt <u>16</u> was decomposed in an aprotic solvent, 16% of the bicyclo(1.1.0)butane was obtained. With added proton source (10% ethylene glycol) or in protic medium (ethylene glycol) or in protic medium (ethylene glycol), the principal product (64-74%) was the bicyclic compound.

The formation of bicyclo(1.1.0)butane was suggested to pro-ceed via a cationic process rather than a carbenoid intermediate.
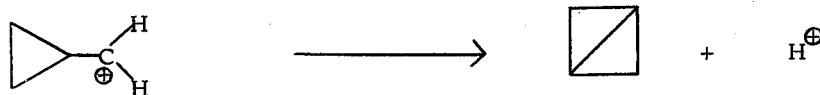
It should be pointed out that this cation is different from that formed in solvolysis of the corresponding tosylate (64).

Cook <u>et al.</u> (13), and Wiberg and Lavanish (92) used deuterium labelled tosylhydrazone and deuterated solvents to study the cationic process. Analysis of the deuterium content of bicyclo(1.1.0)butane obtained by varying the reaction conditions leads to the conclusion that protonation occurs at the diazocompound stage, or at the cyclo-propylcarbinylene <u>17</u> in specific conformations with (near) simultan-eous cationic insertion in which the stereochemistry is mostly main-tained.
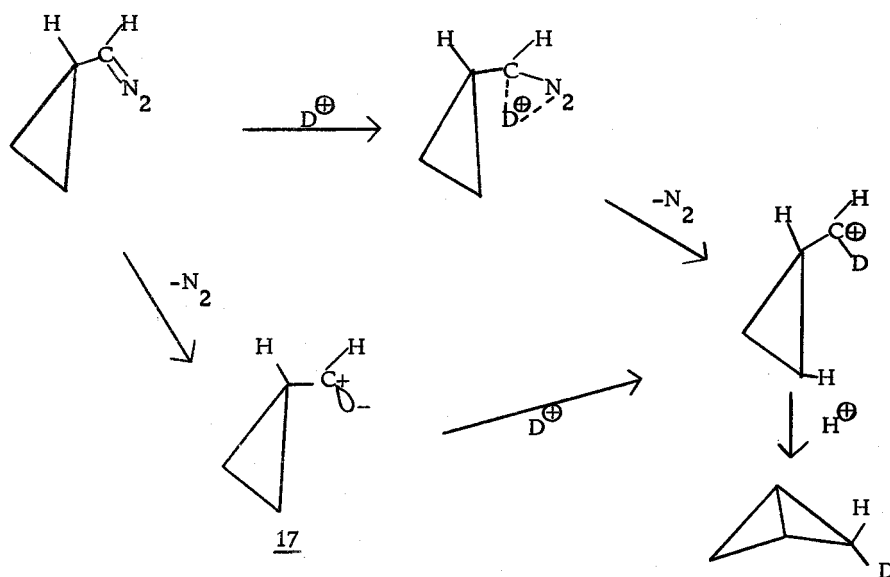
It is also believed that in protic solvent decompositions, carbenic and cationic processes occur competitively. Increase in temperature or the number of equivalents of base favors the former as evidenced by the increase in cyclobutene to bicyclo(1.1.0) butane ratio. The high percentage of bicyclo(1.1.0) butane forma- tion reported by Frey and Stevens can best be rationalized by the presence of a proton source in their reaction. Since these workers heated the tosylhydrazone in diethylene carbitol together with sodi- um methoxide, an equivalent amount of methanol would have been formed, or solvent impurities may have been involved.

Fused cyclopropylcarbinyl carbenes follow similar reaction paths as the parent system though no examples of bicyclo(1.1.0) butane formation have been reported. Sauers and co-workers (66) decomposed the lithium salt of compound 18 and obtained the

rearranged product <u>19</u>.

<u>18</u>

<u>19</u>
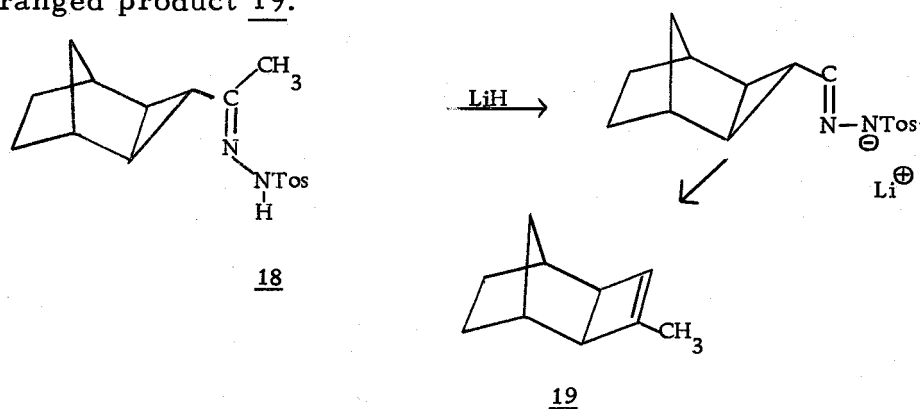
Freeman and Kuper (26) decomposed the tosylhydrazone of

bicyclo(3.1.0)hexane-6-carboxaldehyde with sodium methoxide in

"aprotic" conditions and obtained the ring enlargement compound--

bicyclo(3.2.0)heptene <u>20</u>, as the major product. Similar results

71.5%

<u>20</u>

+

28.5%
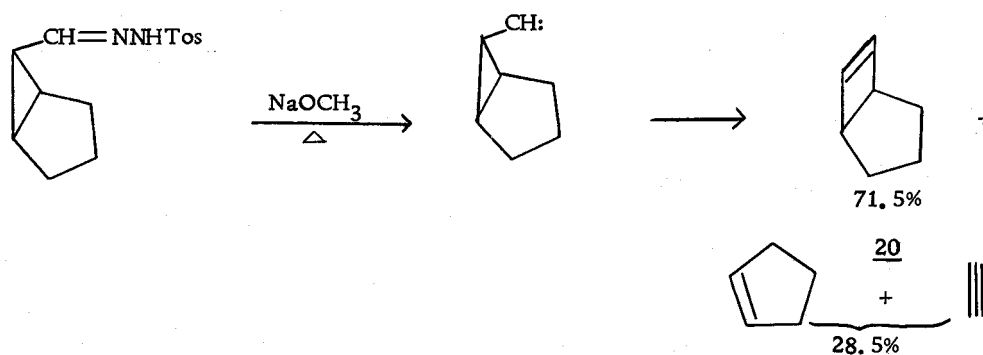
were reported by Kirmse and Pook (52) on the decomposition of the

tosylhydrazone of bicyclo(n.1.0)alkane carboxaldehydes with sodium

methoxide. For n = 3,4,5, rearrangement <u>21</u> and fragmentation

<u>22</u>, <u>23</u> products are formed in approximately 70% and 30% respec-

tively. No insertion products were detected.

$$\underline{23}$$
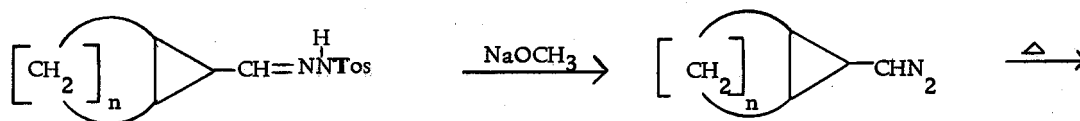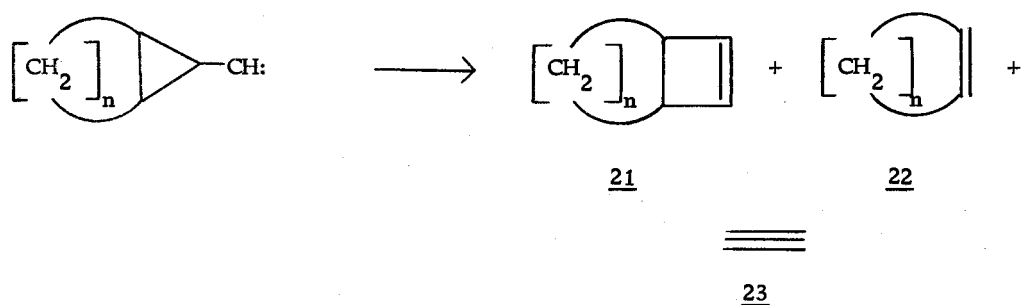
Cyclopropyl carbinyl carbene systems with the carbenoid carbon located as part of the fused ring do not give the ring enlargement product. Freeman and Kuper (26) studied the 2-bicyclo(3.1.0)hexanone p-toluenesulfonylhydrazone decomposition and obtained five

$$CH_2=CH-CH_2-CH_2-C\equiv CH$$
$$+$$
$$CH_2=CH-CH_2-CH=C=CH_2 \quad (IV)$$
$$+$$
$$CH_2=CH-CH=CHCH=CH_2$$

$$\underline{24} \qquad (V)$$

$$\text{base}$$

$$CH_2=CH-CH_2-CH=C=CH_2 \qquad (VI)$$

$$\downarrow \text{ base}$$

$$CH_2=CH-CH=CH-CH=CH_2$$

$$+ BH^{\oplus} \longrightarrow \qquad (VII)$$
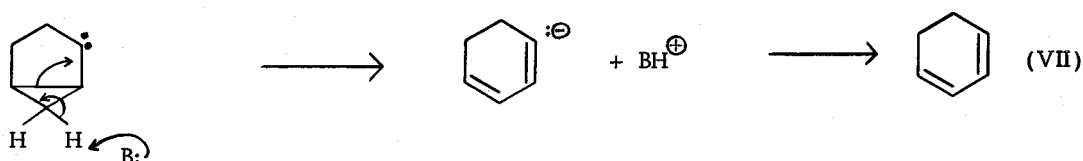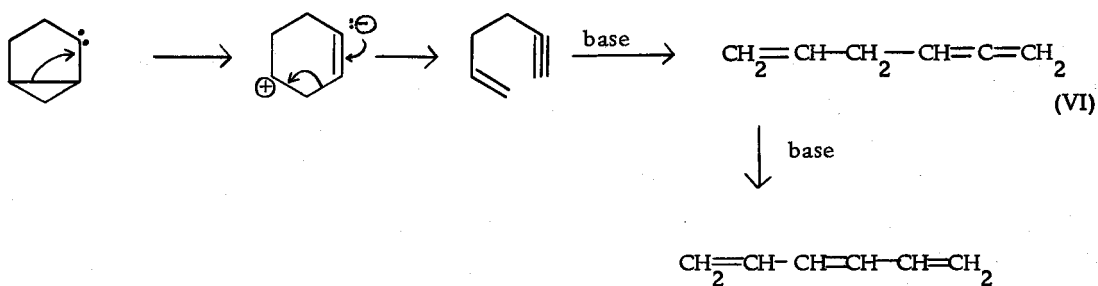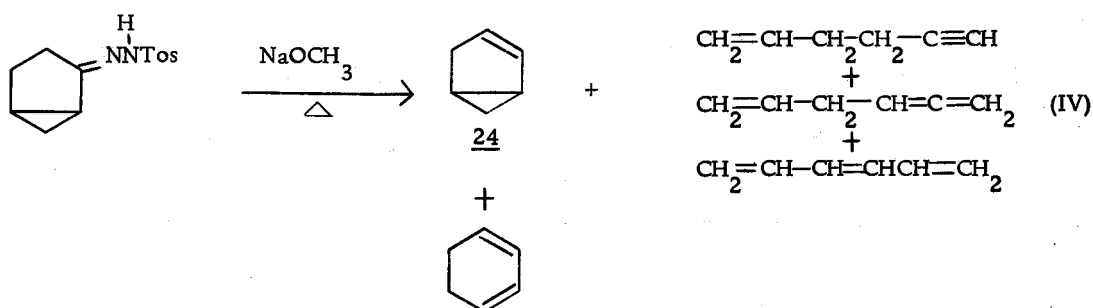
products. The formation of the bicyclo(3.1.0)hexene <u>24</u> is rationalized by a 1,2-hydride shift (β-insertion). Electronic shift followed by ring opening (eq. VI) accounts for the formation of the hexene. Subsequent base isomerization leads to the allene and the 1,3,5-hexatriene. Base participation explains the formation of the cyclohexadiene as indicated by equation VII.

A fragmentation similar to that shown in equation VI can be used to rationalize the formation of cyclopentenyl acetylene <u>25</u> from the decomposition of <u>26</u>, studied by Cristol and Harrington (19). The allene, <u>27</u>, is a base isomerized product instead of direct formation
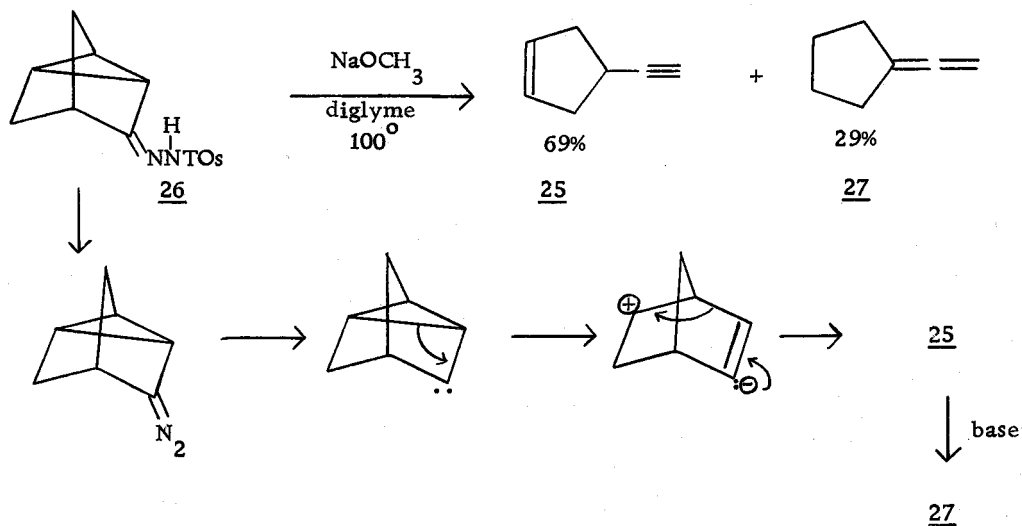
from a carbene intermediate. Irradiation of the sodium salt of <u>26</u> in aprotic solvent gave only a trace of hydrocarbon, the products being the sulfone <u>28</u> and the N-tosyl-3-nortricyclhydrazone <u>29</u>.

28

34 - 50%

4 - 52%

29
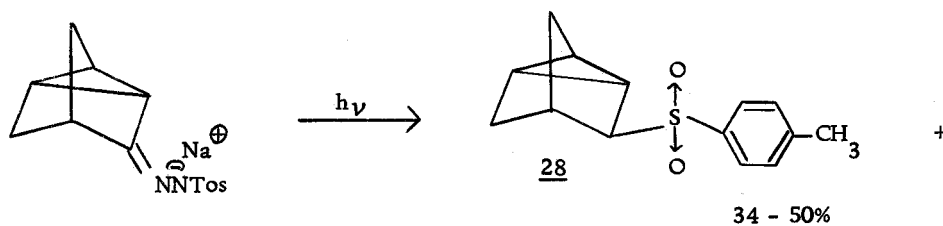
The tosylhydrazone of nortricyclene-1-carboxaldehyde, which has the cyclopropylcarbinyl skeleton incorporated into a rigidly fused ring, was investigated by Wilt and coworkers (95). No hydrocarbon 30 was found, which would be expected from a fragmentation of the carbene intermediate X. Instead, two alcohols 31 and 32, a sulfinate 33 and a tosylhydrazone 34, were obtained. The formation of these

30

32

33

31

34
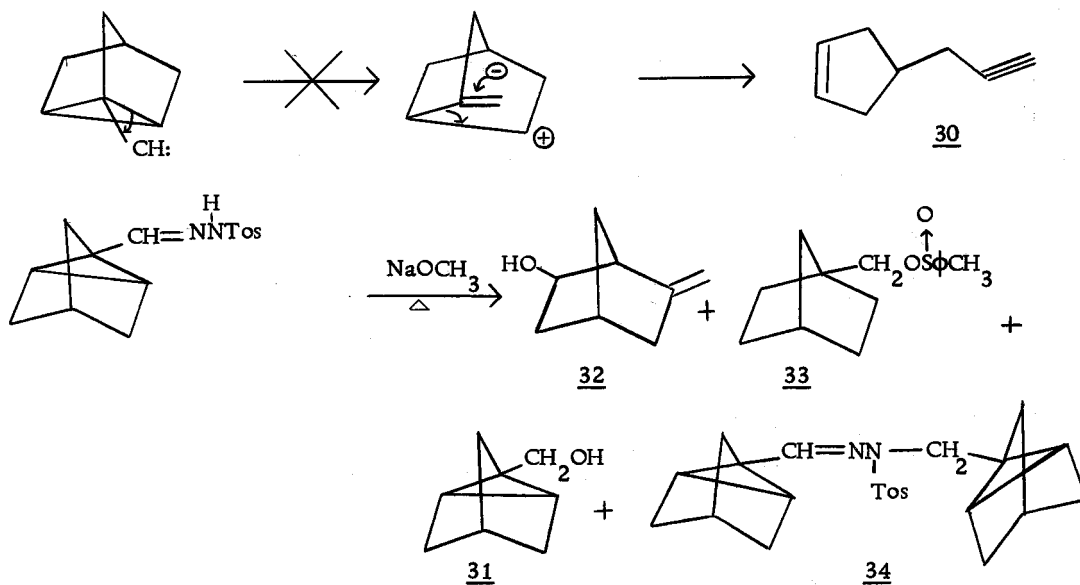
products is attributed to the longer life time of the carbene generated.
Wilt and coworkers favor the explanation that the carbene of this sys-
tem is truly constrained from intramolecular stabilization processes
and consequently undergoes protonation and sulfinate ion capture
with the eventual formation of alcohols.

In general then, cyclopropylcarbinyl carbenes tend to favor
the ring expansion process (eq. II, page 26). When this is unfavor-
able, as in the case of the nortricyclenone system shown below,
fragmentation predominates. When all three of the normal carbenoid
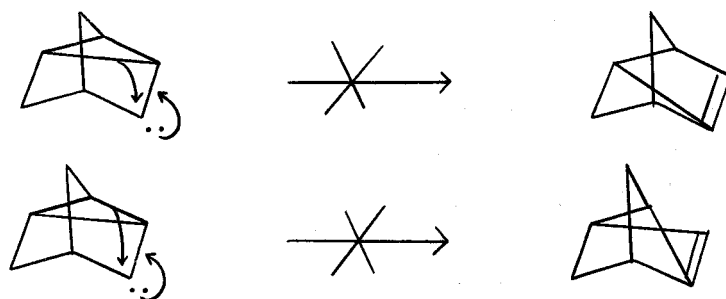
reactions, intramolecular process of hydride shifts, skeletal rear-
rangement and/or insertion, are unfavorable, intermolecular prod-
ucts can predominate.

Thermal Isomerization of Small Ring Hydrocarbons

Thermally induced isomerizations of small ring hydrocarbons
have been studied very extensively in the past decade. This develop-
ment has resulted from several distinct causes. Many of the pyroly-
ses of small ring hydrocarbons appear to be truly unimolecular

reactions. These studies have been carried out to test the well-developed theories of unimolecular reactions (75). Information on the resonance energy of systems such as allyl radicals can be estimated from the pyrolysis studies (23, 24). Stereochemical aspects of these reactions have been of much interest (29, 93). The development of the theory of electrocyclic reactions gives excellent correlations between calculated results and those obtained from experiments

These studies of small ring compound pyrolyses have been greatly facilitated by the discovery of many new synthetic procedures, which have made numerous small ring systems relatively easily available. The advent of gas liquid chromatography has allowed the analysis of the reaction products to be carried out with ease and high precision. Thermal rearrangement has been used more and more frequently for synthetic problems in various fields (6, 85). Many strained ring systems were synthesized by thermal rearrangement of molecules containing olefinic linkages (22, 86), acetylenic linkages (46, 47) and small rings (6).

Two of the most widely investigated thermolyses have involved studies of the cyclobutene to butadiene and the vinylcyclopropane to cyclopentene systems (28). Since an example which combines these two reactions has been investigated in this work, a review of relevant data is presented here.
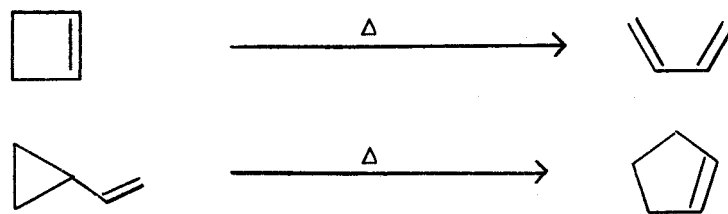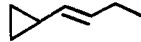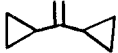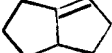
The Vinylcyclopropane to Cyclopentene Rearrangement

While cyclopropane and alkylcyclopropanes rearrange to straight chain alkenes upon pyrolysis (28), vinylcyclopropane was found by Overberger and Berchert (61) and independently by Flowers and Frey (25) to yield cyclopentene as the major product. The energies of activation for isomerizations of various vinylcyclopropanes are around 50 kcal mole^{-1}. The "A" factors of the Arrhenius equation are between 13.61 to 14.29 as shown in Table 2.

The fact that the energy of activation of the vinylcyclopropane systems is lower than that for the thermal isomerization of cyclopropane systems can be explained by the formation of an allylically stabilized biradical as the intermediate (mechanism 2). The energy diagram for this mechanism is shown in Figure 1.

Table 2. Thermal isomerization of some vinylcyclopropanes to cyclopentenes (28).

Reactant	Product	$\log_{10} A$	$E(\text{kcal mole}^{-1})$
		13.61	49.7
		13.89	50.9
		14.11	49.35
		13.79	49.98
		14.14	50.5
		14.29	51.06 (4)
		14.01	51.29 (4)

Mechanism 1
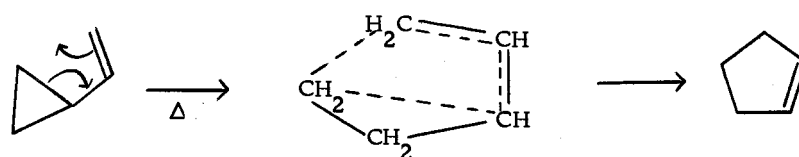
Mechanism 2
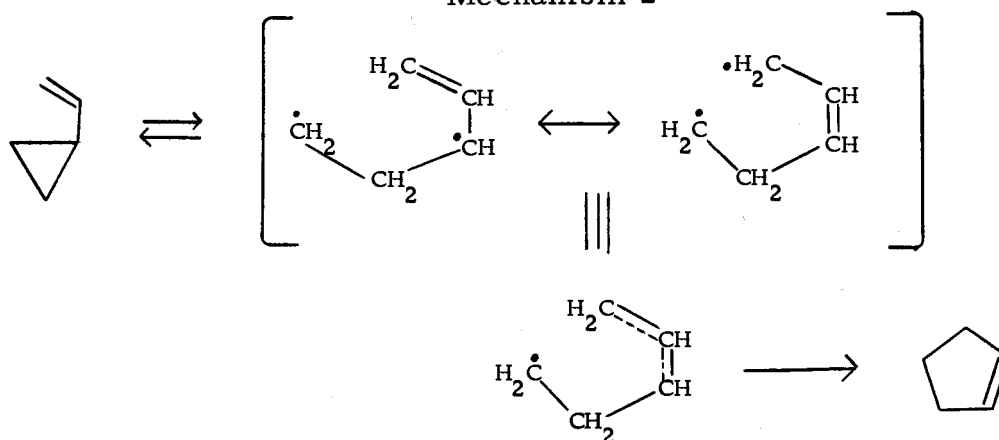
The biradical, when formed, will have sufficient energy to recyclize to the cyclopropane and, if the energy barrier is higher than pictured, it will also be energized with respect to isomerization to the cyclopentene. If the energy barrier for isomerization is lower than shown, isomerization to the cyclopentene will be faster

Reaction Coordinate
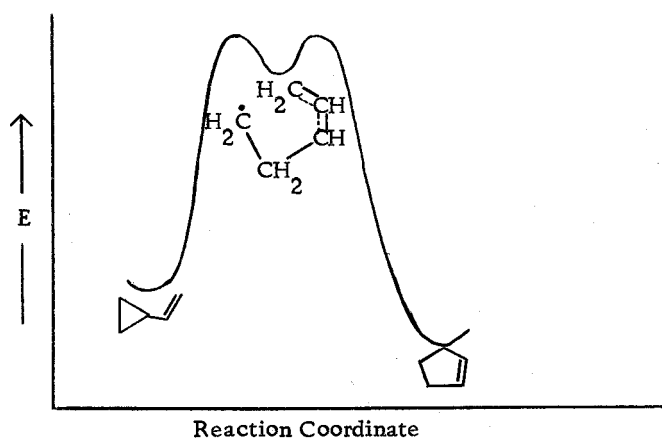
Figure 1

than the recyclization to the cyclopropane. It has been shown recently by Willcott and Cargle (93) that the recyclization to the cyclopropane process is approximately five times faster than the former. Using essentially the same potential-energy diagram for the biradical mechanism for the cis-trans isomerization of cyclopropanes, Ellis and Frey (24) compared the activation energies for the isomerization of 1, 1-dimethylcyclopropane to methylbutene and 1-methyl-1-vinylcyclopropane to 1-methylcyclopentene, and deduced a value for the allylic resonance energy of 13.2 ± 1 kcal/mole. Egger and co-workers (23) compared the activation energy for the iodine atom

catalyzed isomerization of 1-butene to 2-butene (12.4 ±0.3 kcal/mole

with that for the analogous reaction of iodine atom attack on propane

(25.0 ±0.5 kcal/mole) and obtained a resonance energy of 12.6 kcal/mole.

A concerted mechanism (mechanism 1) cannot be ruled out,

however. The "normal" A factor favors a concerted process accord-

ing to some workers studying this isomerization reaction (28).

The Cyclobutene to 1,3-Butadiene Systems

Thermal isomerization of cyclobutene to a butadiene was first

studied by Cooper and Walters (14). It was found that the reaction

is homogeneous, first order, and unaffected by the presence of rad-

ical inhibitors. The Arrhenius equation obtained was

$$k = 10^{13.08} \exp(-32,500/RT) \text{ sec}^{-1}.$$

Later, Hauser and Walters (42) reinvestigated the isomerization

over a very extended pressure range and obtained the high-pressure

rate constants by extrapolation.

$$k_\infty = 10^{13.26} \exp(-32,700/RT) \text{ sec}^{-1}.$$

Like most other pyrolyses of small ring compounds, the mech-

anism of this ring opening is a topic of debate among various workers

in the field. H. M. Frey (28), noting the low value of energy of

activation for the cyclobutene to butadiene isomerization, suggested

that the transition state involves the simultaneous deformation (twist-

ing) of the cyclobutene ring with the stretching of the carbon-carbon

bond opposite the double bond (dotted line of mechanism 1). The

"normal" A factor of the reaction (13 compared with 15 for cyclo-butane) favors this mechanism because no free internal rotation is possible in the transition state 79 as compared with 80 and 80a (mechanism 2).

<p style="text-align:center">Mechanism 1</p>

79
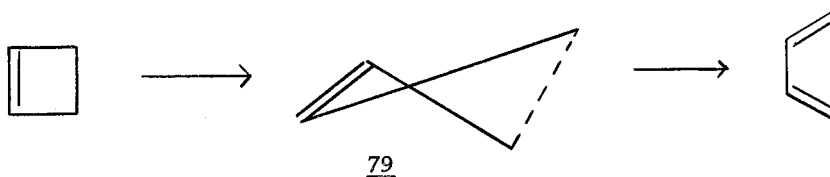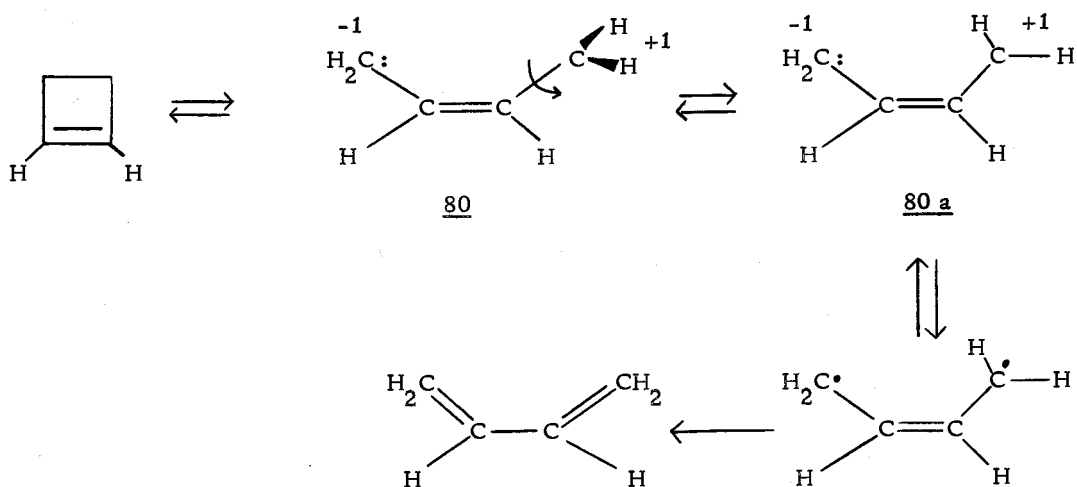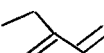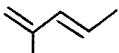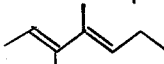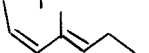
<p style="text-align:center">Mechanism 2</p>

Benson, however, has proposed a different mechanism (mech-anism 2) (2). An ion-pair of semi-ion pair intermediates such as 80 and 80a may play an important role in such cyclobutene thermoly-sis reactions where the activation energies are abnormally low (1).

Thermal isomerization of various alkyl substituted cyclobutenes has been studied. In all cases the reactions have been shown to be first order homogeneous reactions with no radical-chain components. and the Arrhenius parameters obtained were close to those found for

cyclobutene (Table 3).

Table 3. Arrhenius parameters for the isomerization of cyclobutenes (28).

Reactant	Product	$\text{Log}_{10}A$	$E(\text{kcal mole}^{-1})$
		13.79	35.10
		13.53	31.55
		13.76	34.83
		13.84	36.04
		13.65	33.00
		13.52	33.39
		14.70	37.70
		13.85	33.59

The stereochemical aspects of the reaction products of cyclo-butenes with substituents on C_3 and C_4 can be explained by the Woodward-Hoffmann rule (96). In an open-chain system containing $4n\pi$ electrons (such as butadiene), the conrotatory process is favored.
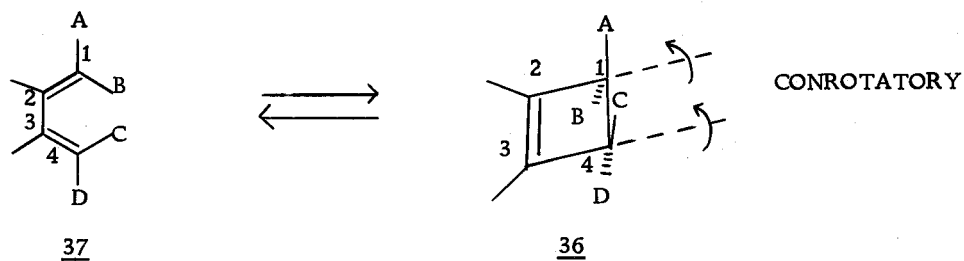
The symmetry of the highest occupied ground-state orbital is such

that a bonding interaction between the terminal orbitals must involve

overlap between orbital envelopes on opposite faces of the system,

and this can only be achieved in a conrotatory process 35. Substi-

tution groups, A and C, which are cis to each other on the cyclic

compound 36, will end up as indicated in 37.

35
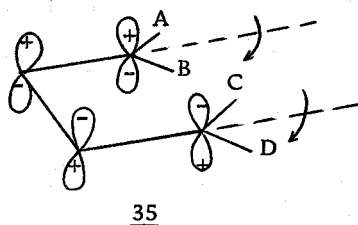
This explains the higher temperature requirement for systems

which are restricted to disrotatory processes and yet contain $4n\pi$ -

electrons in the open-chain partner such as cycloheptadiene formed

from bicyclo(3.3.0)-6-heptene. The conrotatory process, in this

38
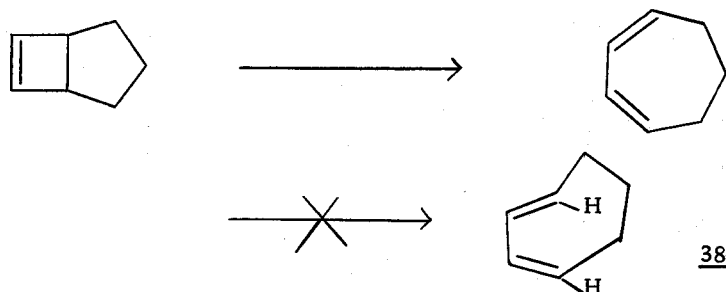
case, is energetically unfavorable because of the strain energy in

cis-trans 1,3-cycloheptadiene 38, which would be the predicted prod-

uct of this mode of opening. Likewise, the very existence of bicyclo

(2.1.0)-2-pentene (5) can be attributed to the necessity of a
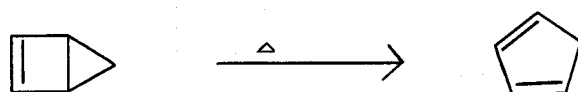
disrotatory opening to the much less strained cyclopentadiene.

RESULTS AND DISCUSSION

Cyclopropylcyclobutene

The first system investigated in this work was the carbene 40, a dicyclopropylcarbinyl carbene. It was of interest to compare this substituted system with the parent cyclopropylcarbinyl carbene which reacts (see introduction) largely by ring enlargement in aprotic media and by insertion in protic solvents. Similar reactions of 40 would give rise to 41 and 42. Such a study was expected to shed light on the
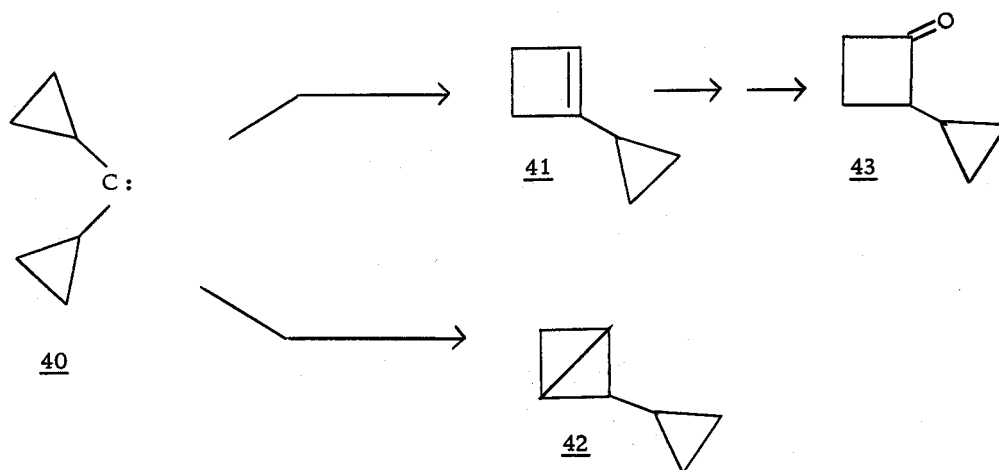
interesting and confusing properties of cyclopropylcarbinyl carbenes as well as offer a simple synthetic route to two potentially valuable intermediates. In particular, 41, should be readily converted into 43 which would be a most interesting ketone to convert into a cyclo-butylidene.

The dicyclopropylcarbinyl carbene intermediate was generated via the dicyclopropylketone p-toluenesulfonylhydrazone 44. The

sodium salt of <u>44</u> was obtained by treatment with sodium methoxide,
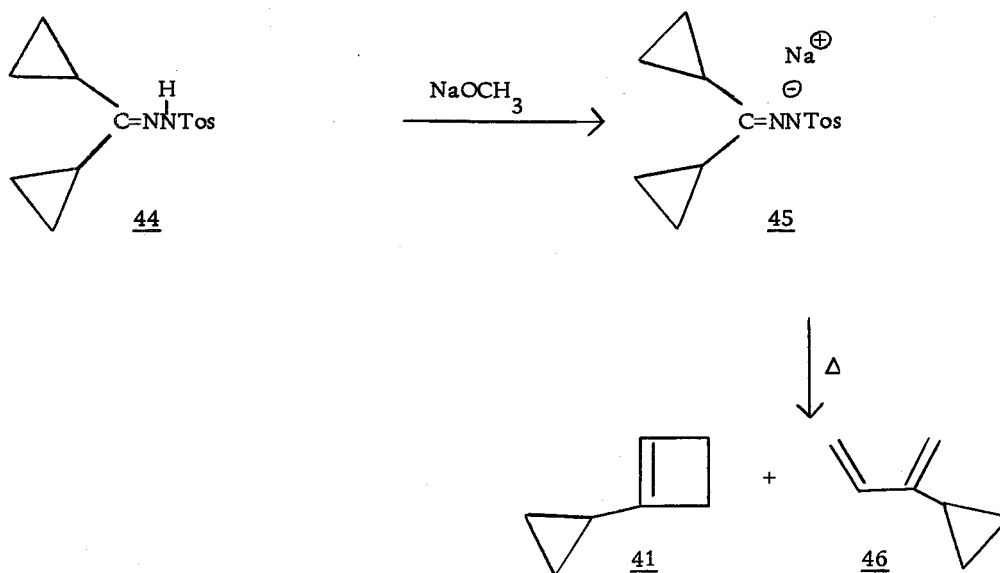
and was not isolated. Using the dry method developed in this lab-

oratory, the sodium salt <u>45</u> was suspended in celite and was decom-

posed at 128-130° in the absence of any solvent. The yield of hydro-

carbon obtained was as high as 87%. This represents the cleanest

decomposition ever achieved in our laboratories using this method.

G. l. c. analysis of the product mixture indicated three differ-

ent components. The most volatile component, though suspected to

be the fragmentation product cyclopentenylacetylene, was not iden-

tified. The major component (79%) which has the highest retention

time in g. l. c. analysis shows infrared absorptions at 3090 cm.$^{-1}$

and 3050 cm.$^{-1}$. These two bands are probably due to the carbon-

hydrogen stretching modes of a cyclopropane ring and of an olefinic

group. The presence of a carbon-carbon double bond was shown by

the absorption band at 1630 cm.$^{-1}$. The characteristic cyclopropane

absorption at 1020 cm.$^{-1}$ (71) was also present.

The n. m. r. spectrum of this compound shows a one proton

singlet at 5. 71δ, which was assigned to an olefinic hydrogen. A

sharp singlet at 2. 28δ of four protons was assigned to the two methyl-

ene groups of the cyclobutene ring (44). The lack of coupling with

the vinyl hydrogen is identical with the results obtained with cyclo-

butene. The multiplets centered at 0. 56δ with five protons was

assigned to the cyclopropane ring. The structure of this compound

was tentatively assigned as 41. No λ_{max} above 205 mμ was observed

in cyclohexane.

The second component (0.5%) with intermediate retention time

has a λ_{max} at 223 mμ (= 12,300). The infrared spectrum shows no

aliphatic carbon-hydrogen stretching bands. Characteristic absorp-

tion of olefins and cyclopropane are observed at 3010 cm.$^{-1}$, 1590

cm.$^{-1}$, 3090 cm.$^{-1}$ and 1020 cm.$^{-1}$ respectively. The n. m. r. spec-

trum shows only vinyl protons (5. 00δ-6. 85δ, 4H) and cyclopropane

ring protons (1. 60δ, 1H; 0. 72δ, 4H). The Diels-Alder adduct of 46

with maleic anhydride has a comparable melting point with that re-

ported in the literature (36) for the product 47 from 2-cyclopropyl-

1, 3-butadiene.
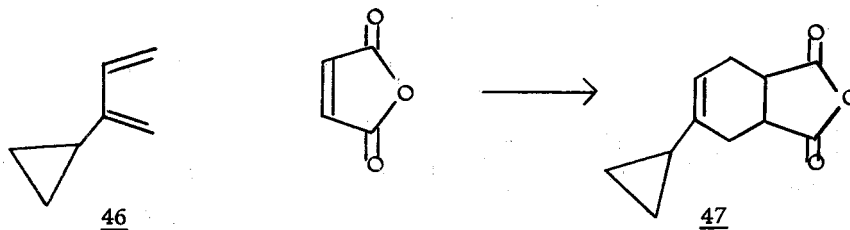
When the injector temperature of the gas liquid chromatograph used in the product analysis was raised above 250°, the peak assigned to __46__ started to increase while that assigned to __41__ decreased. At 325°, the conversion was complete. At higher temperatures a new peak was observed to build up. A thermal isomerization reaction was then carried out using a glass helices-packed pyrex column to study these phenomena.

At 265° and a carrier gas (nitrogen) flow rate of 27 ml./minute, the cyclopropylcyclobutene was completely isomerized to 2-cyclopropyl-1, 3-butadiene in 89% yield. At 380°, 87% of the

$$\underset{\underline{41}}{\qquad} \xrightarrow{265°} \underset{\underline{46}}{\qquad} \xrightarrow{450°} \underset{\underline{48}}{\qquad} \qquad (IX)$$
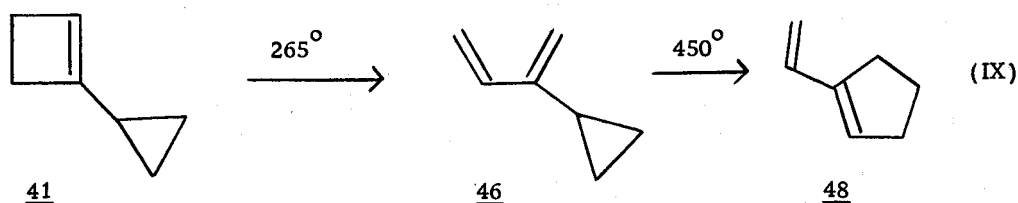
hydrocarbon was recovered, and shown by g. l. c. to contain mainly two components. The major product (77.8%) was __46__ while the minor component (21.4%) was a higher boiling hydrocarbon. Recycling this reaction product at the same temperature changed the composition to 63.9% and 36.1%. At 450°, 83.6% of the higher boiling

hydrocarbon was obtained together with 2% of 46 and approximately 14% of other unidentified products.

Since cyclobutenes and vinylcyclopropanes are known to isomerize thermally to give butadienes and cyclopentenes respectively, the high temperature isomerization product was assigned the structure 48. This structure was confirmed by comparison of its infrared, ultraviolet, and n. m. r. spectra and other physical properties with the known compound synthesized via an unambiguous route.

Cyclopentanone was allowed to react with vinyl magnesium bromide to give the vinyl alcohol 49 (57). Dehydration in the presence of iodine yielded the desired product vinylcyclopentene 48.
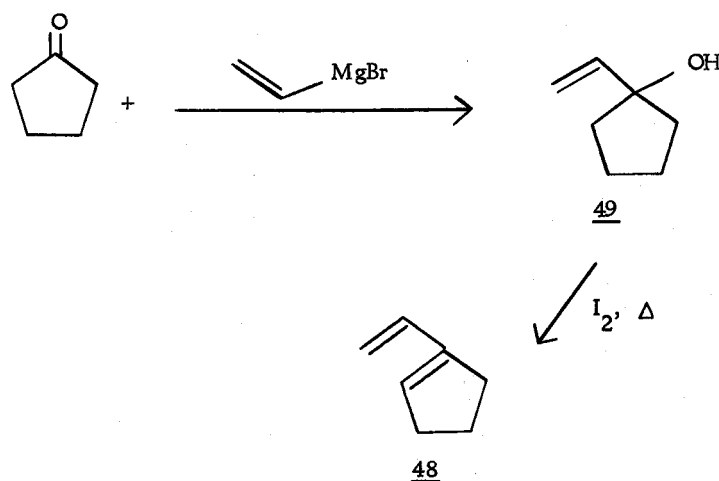
This compound was identical in all respects with the isomerization product.

The fact that at 265°, 41 isomerizes cleanly to 46 and that at higher temperatures no starting material was detected in appreciable

amount, indicates the reactions go stepwise as shown in equation IX.

A stepwise isomerization of 1, 1-dicyclopropylethylene to 1-cyclo-

propylcyclopentene and to bicyclo(3.3.0)octene-1 was favored over
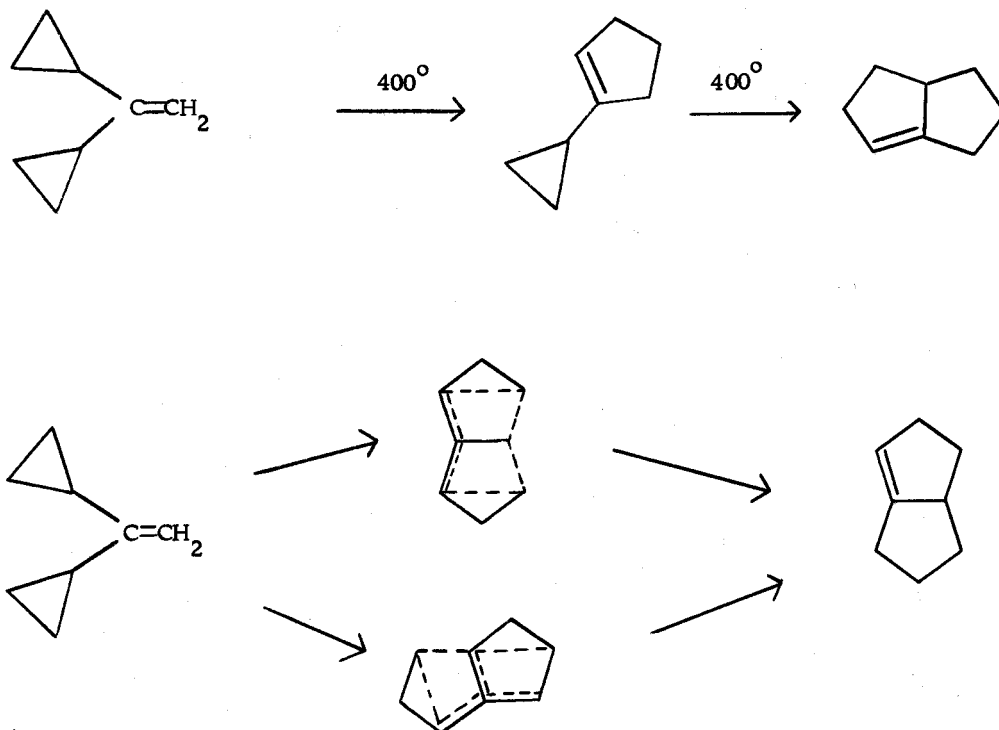
a concerted reaction by Ketley and McClanahan (50). Detailed

kinetic studies of the above system also lead to the same conclu-

sion (4).

Kinetic studies of the cyclopropylcyclobutene to 2-cyclopropyl-

1, 3–butadiene isomerization were carried out at four different tem-

peratures. The results are summarized in Table 4. A plot of ln k

against 1/T gives a slope of -1.68 $\times$ 10^4 °K. The energy of activation

E_a, for this reaction is calculated to be 33.5 kcal/mole. By extrapol-

ation to (1/T) = 0, the A factor for the Arrhenius equation was

Table 4. Rates of the thermal isomerization of cyclopropylcyclobutene to 2-cyclopropyl-1,3-butadiene.

Temperature

146.0 ±0.2°	Time in min.	10	25	40	60	90	120	150	
	$k \times 10^4$	(1.26)	0.767	0.796	0.742	0.588	0.585	0.655	
152.8 ±0.2°	Time in min.	10	20	35	50	70	90	120	
	$k \times 10^4$	1.65	1.46	1.34	1.30	1.32	1.33	1.32	
158.5 ±0.2°	Time in min.	5	10	20	30	40	60	90	
	$k \times 10^4$	2.92	2.53	2.34	(305)	2.27	2.31	2.36	
166.3 ±0.2°	Time in min.	5	15	25	35	45	60	90	120
	$k \times 10^4$	9.21	6.52	4.93	7.80	-	6.26	3.48	4.19
170.0 ±0.2°	Time in min.	3	5	10	15	25	35	45	60	90
	$k \times 10^4$	6.27	6.06	5.48	5.62	5.72	6.00	6.11	6.68	(9.16)

determined to be 13.90. The Arrhenius equation thus obtained is:

$$k = 10^{13.90} \exp(-33.50/RT) \text{ sec.}^{-1}$$

When the sodium salt <u>45</u> was decomposed in dry diglyme, the yield of hydrocarbon was 57%, considerably lower than that of the dry run in celite. The composition of cyclopropyclyclobutene and cyclopropylbutadiene was 91% and 9%. Decomposition in 1.25% water in diglyme gave 78% yield of hydrocarbon contaminated by more than one gram of water. The composition of the two products was 95% and 5%. The failure of added proton source to deviate the reaction from the carbene pathway can be explained by the following observation.

When the reaction flask was lowered into the heat source at 130-140°, the water present in the reaction mixture was distilled in less than two minutes. The decomposition however, was only beginning. Therefore, the added water did not stay in solution long enough to have actual contact with the reaction species. In the case of the decomposition of <u>15</u> studied by Friedman and Schechter, the reaction was run at atmospheric pressure at 130-150°. In such reaction conditions the water added would have remained in the reaction mixture.

When the sodium salt was decomposed in 10% ethylene glycol in diglyme and in diethylene glycol, only 3% of hydrocarbon was

obtained in the former run and less than 0.1% in the latter. The results of these runs are summarized in Table 5. When the reaction mixture was extracted with pentane after the completion of the decomposition, high boiling liquids were obtained in both cases. These liquids were different from the expected azine 50 or the dicyclopropylcarbinol 51 synthesized from the corresponding ketone.
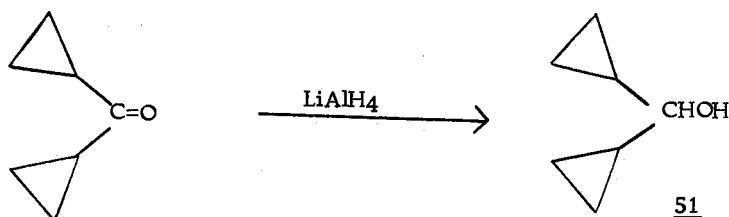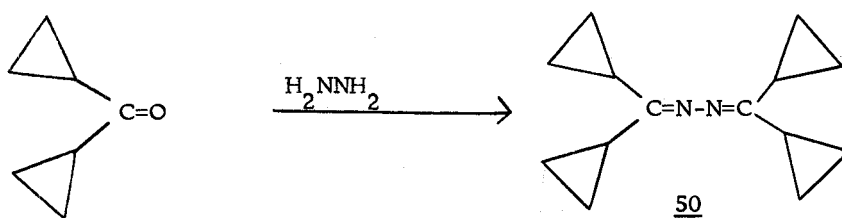
The liquid from the 10% ethylene glycol run showed the presence of a cyclopropyl group both in the infrared (3100 cm.$^{-1}$, 3010 cm.$^{-1}$) and n.m.r. (0.5δ) spectra.

Under these protic conditions, decomposition of the sodium salt of cyclopropylcarboxaldehyde p-toluenesulfonylhydrazone gives bicyclo(1.1.0)butane as the major product (76). For the present system, no 2-cyclopropylbicyclo(1.1.0)butane 42 was obtained. An

Table 5. Thermal decomposition of the sodium salt of <u>44</u> in various solvents at 130°.

Solvent	Yield of hydrocarbon	Product distribution		
		<u>41</u>	<u>46</u>	<u>42</u> ?
diglyme	57%	91%	9%	--
diglyme + 1.25% H_2O	78%	95%	5%	--
diglyme + 10% EG	3%	52%	28.4%	19.6%
DEG	<0.1%	--	--	--

unidentified compound was obtained in the diglyme-ethylene glycol

run, but in too low a yield to characterize. Thus 40 behaves differ-

ently than its simple analog. A "constrained carbene", as proposed

by Wilt for the systems he studied (95), is not suitable because the

fact that excellent "carbene product" had been obtained in the aprotic

conditions. No alcohol such as 51 was detected and the presence of

any sulfinate 52 or tosylhydrazone 53 in the pentane extract can be

ruled out by the absence of aromatic protons in the n.m.r. spectrum.
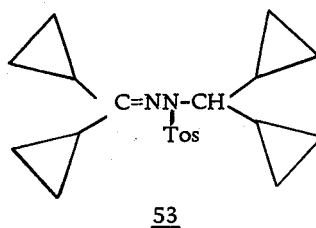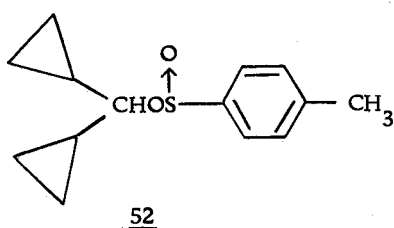
One remaining possibility is the intermolecular reaction of the car-

bene with the solvent as reported by Moore and coworkers (59, 60).

This possibility was not further investigated due to the small amount

of material available. In conclusion, the dicyclopropylcarbene 40

behaves like its monocyclopropyl analog only under true carbenoid

conditions. Conditions which give bicyclobutane with the simple

system, however, do not give a useful synthesis of 42, unfortunately.

Bicyclo(2. 2. 0)hexenes

Since ring enlargement in the carbene 40 proceeded in such high

40   41
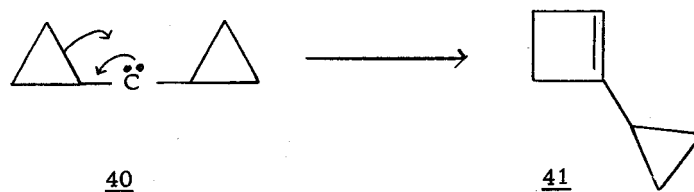
yield, we decided to try to extend this type of reaction to the synthe-

sis of a fused ring bicyclic system. The two pathways illustrated

below seemed most promising for the preparation of the unknown

bicyclo(2.2.0)hexenes 13 and 14. Three problems are associated

54   55   13   (X)

56   57   14   (XI)
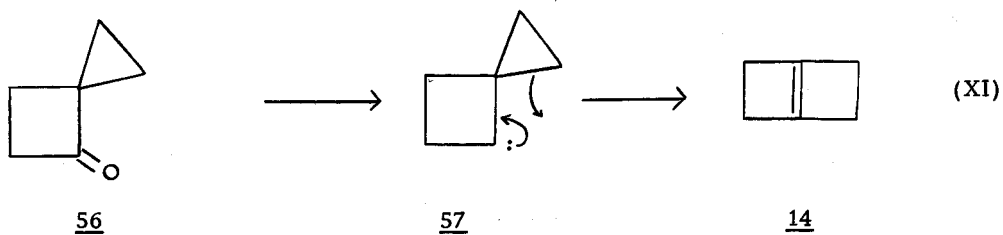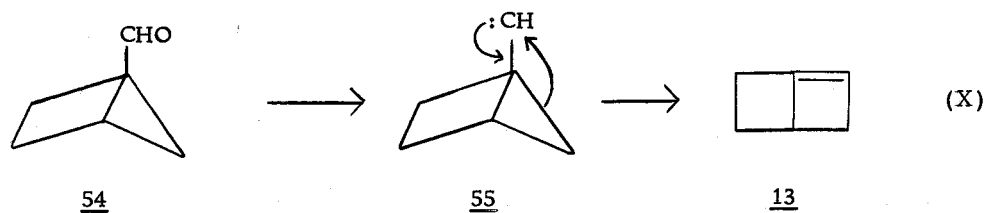
with these synthetic routes. First, the carbonyl precursors are

unknown compounds and synthetic routes to them were expected,

and proved to be, quite difficult. Second, the carbenoid species

have alternate pathways for decomposition, some of which are shown

below.
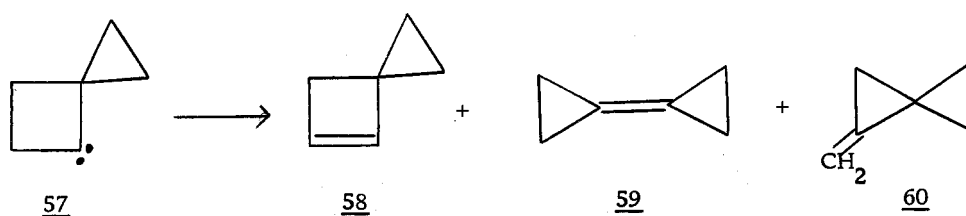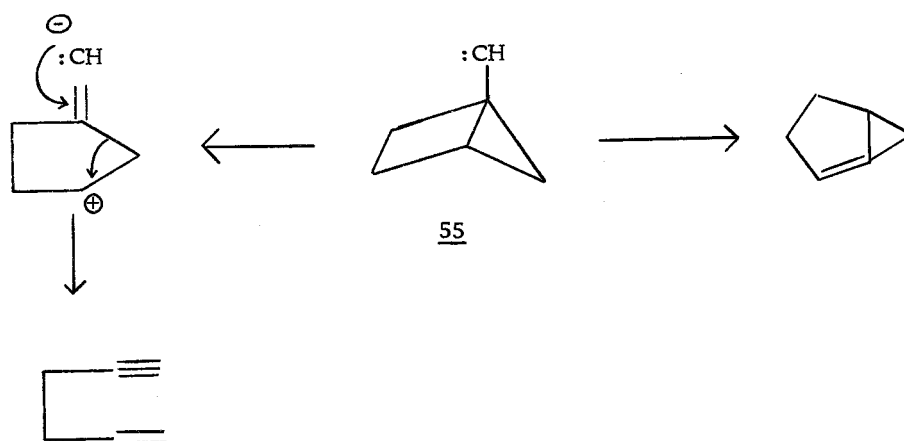
In the case of the cyclopropylcyclobutylidene 57, we were en-

couraged by the results of Dr. Judson McClure in these laboratories,

namely that carbene 61 gave the olefin 62 as its only product and in

high yield. Nevertheless, the carbene 57, while still a cyclopropyl-

carbinyl system is also a cyclobutyl carbene and products 58 through
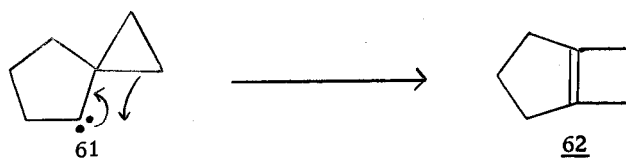
60 might also be expected. This interesting system thus combines

the features of cyclobutyl and cyclopropylcarbinyl carbenes.

The third problem anticipated was the predicted thermal instability of the cyclobutenes (see Introduction). Since even 1-cyclopropylcyclobutene had ring opened slightly during its thermal preparation, this was quite a serious problem. Unfortunately, in this study only the synthetic routes to the precursors 54 and 56 could be investigated.

An approach to the synthesis of the precursor 56 is given in scheme 1. The preparation of the dienolacetate 63 of biacetyl was reported by Hagemeyer (40) in very low yield. Attempts in this laboratory to repeat the experiment only led to the formation of polymers. Using pyridine as the base and only one equivalent of acetic anhydride at room temperature the monoenolacetate, 3-acetoxy-3-buten-2-one, 66 was obtained in 33% yield. Using triethylamine as the base or lithium hydride to form the enolate anion resulted in polymerization. The procedure given by Wharton and Aw (90) for the preparation of the same compound gave only 12% yield.

Scheme 1
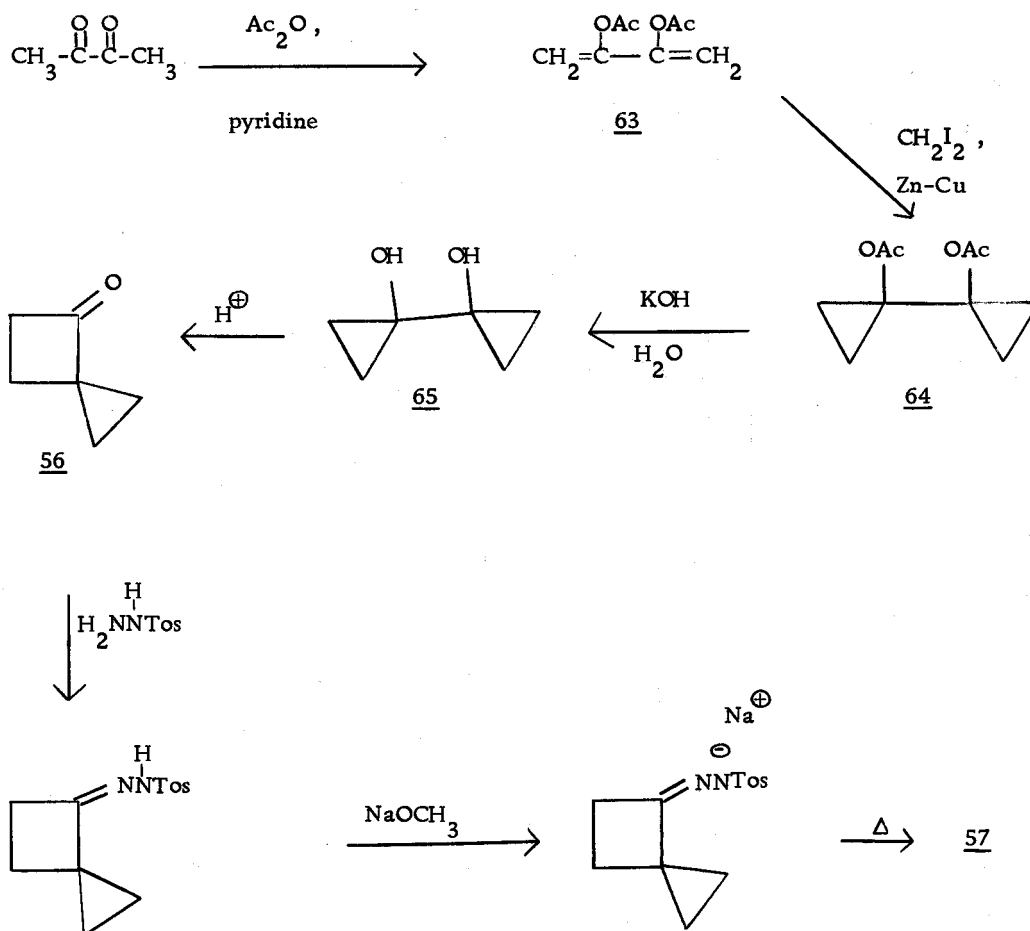
When **66** was treated under Simmons-Smith reaction conditions, no cyclopropane derivative **67** was obtained. Instead, an alcohol was obtained in less than 10% yield in a mixture of more than five components. This alcohol was collected by g.l.c. and its solution infrared spectrum shows absorption bands at 3620 and 3400 cm.$^{-1}$, indicating the presence of a hydroxyl group. Absorption at 3080 cm.$^{-1}$ indicates the presence of a cyclopropane ring.

$$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{pyridine, R.T.}]{Ac_2O} \underset{\underline{66}}{CH_2=\overset{\overset{OAc}{|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3}$$

$$\Big\downarrow \begin{array}{l} CH_2I_2 \\ Zn-Cu \end{array}$$

$$\underline{67}$$
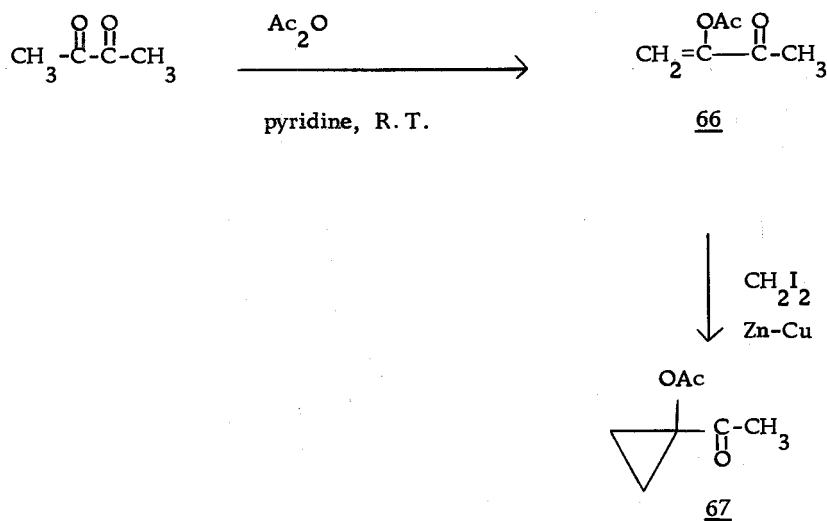
Its n. m. r. spectrum exhibits a sharp singlet at 1.20δ. There are

two multiplets on each side centered at 0.50δ and at 2.00δ. The

integration ratio was 1:2:2. From the above data, the structure of

this alcohol is tentatively assigned as 65.

The formation of 65 probably resulted from two successive

additions onto 66. The first methylene addition is most likely to

give 67 which can exist in the enol form 68. A second methylene

addition onto the carbon-carbon double bond would have given the

bicyclo-propyl compound 69, which was hydrolyzed to the diol 65

upon work up. If the assigned structure, 65, is correct this would

offer a simple route to this desired intermediate, however, the low

yield and isolation problems precluded its use in further studies of

the synthesis of 56. There are no reports in the literature of

CH$_2$=C—C-CH$_3$ with OAc and O groups; $\xrightarrow[\text{Zn-Cu}]{\text{CH}_2\text{I}_2}$; structure **67**

(equilibrium arrows)

structure **69** (OAc and OH) ; $\xleftarrow[\text{Zn-Cu}]{\text{CH}_2\text{I}_2}$; structure **68** (OAc, C=CH$_2$, OH)

↓

structure **65** (HO and OH)
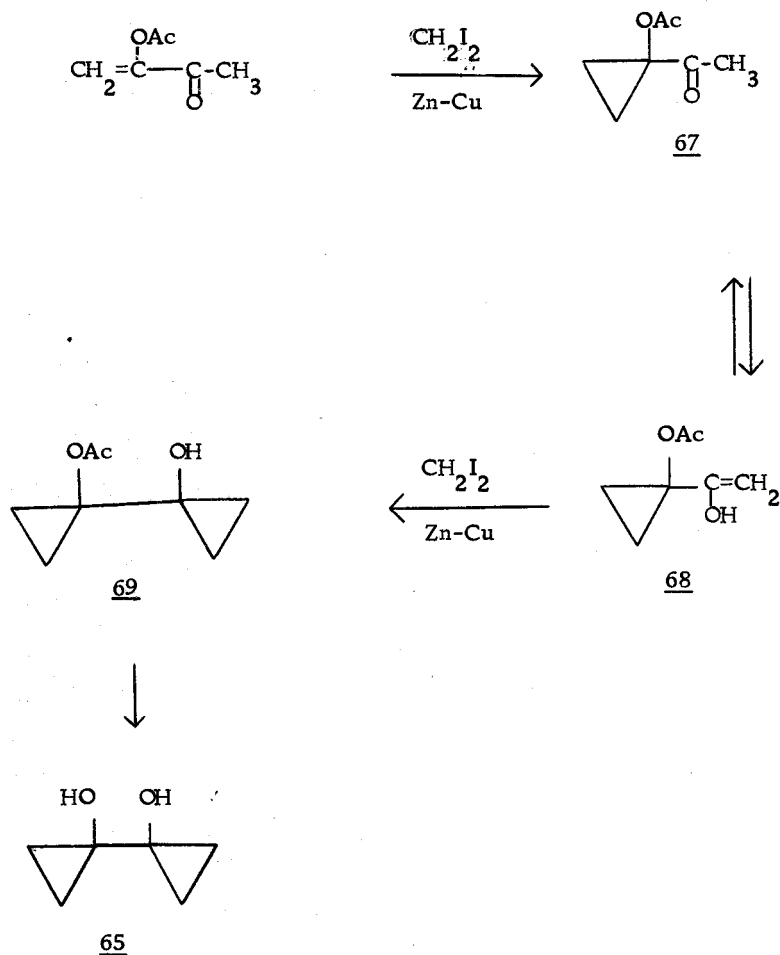
addition of any carbenoid species to a keto-enol mixture although

such addition does not seem unreasonable.

The approach for the synthesis of the precursor to 55 is given

in scheme 2. The cyclobutenecarbinol 72 was successfully prepared

according to the scheme developed by Heyns and coworkers (43) in an

over-all yield of 17%.

Scheme 2

(1) SOCl$_2$

(2) Br$_2$, P

(3) CH$_3$OH

COOH

COCH$_3$
Br

KOH
φCH$_3$

COOH

70

CH$_2$N$_2$
Et$_2$O

CH$_2$OH
Br
Br

LiAlH$_4$

COCH$_3$
Br
Br

Br$_2$

COCH$_3$

71

Zn, CH$_3$OH

CH$_2$OH

72

CH$_2$I$_2$
Zn-Cu

CH$_2$OH

73

[o]

CHO

54
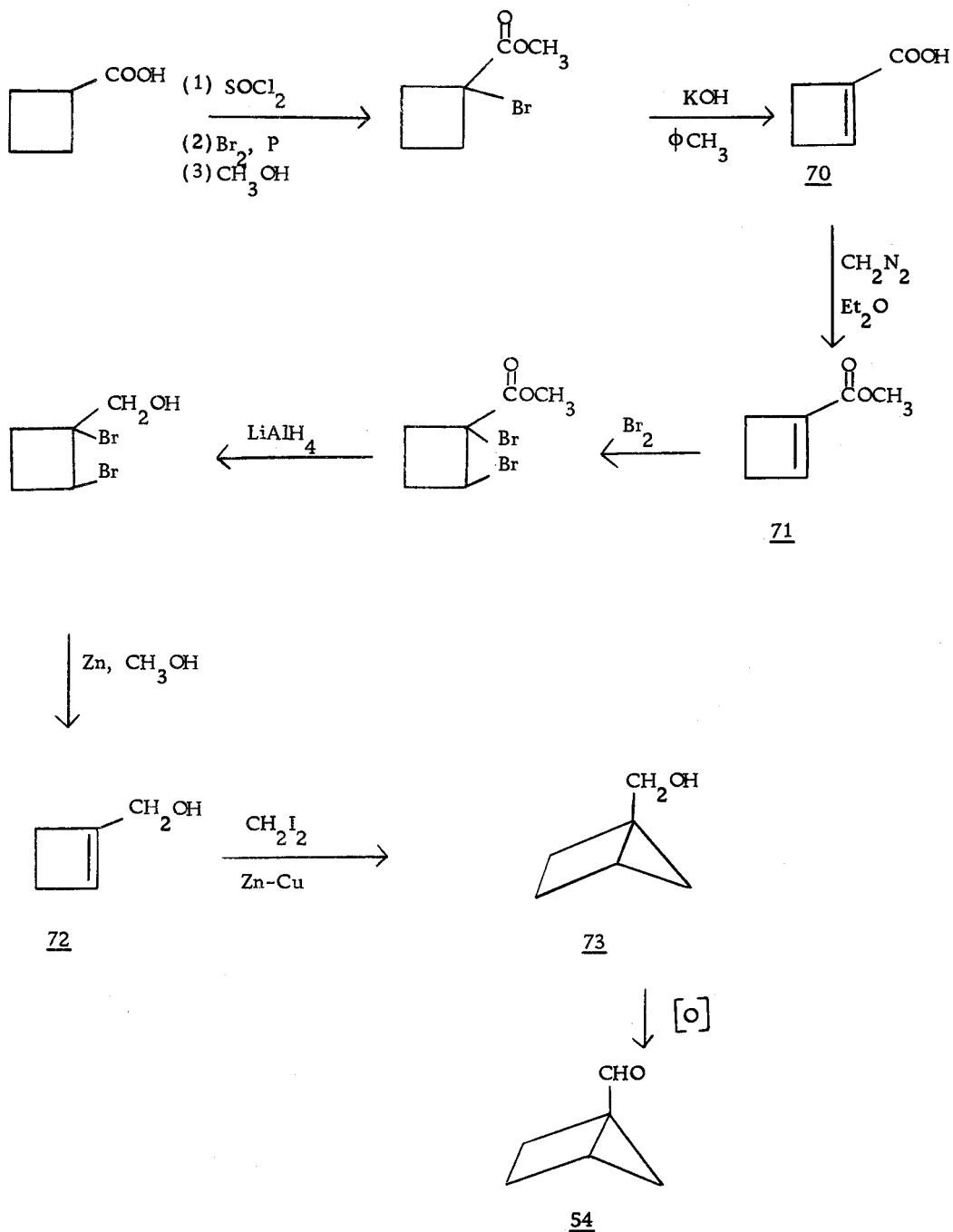
A Simmons-Smith reaction on **72** was expected to give the bicyclo-
(2.1.0)pentane carbinol **73**, which upon oxidation should give the
carboxaldehyde **54**.

In our hands, during the esterification of the cyclobutene

carboxylic acid 70, it was found that in the presence of two equiva-

lents of diazomethane, a pyrazoline 74 was obtained in 74% yield.
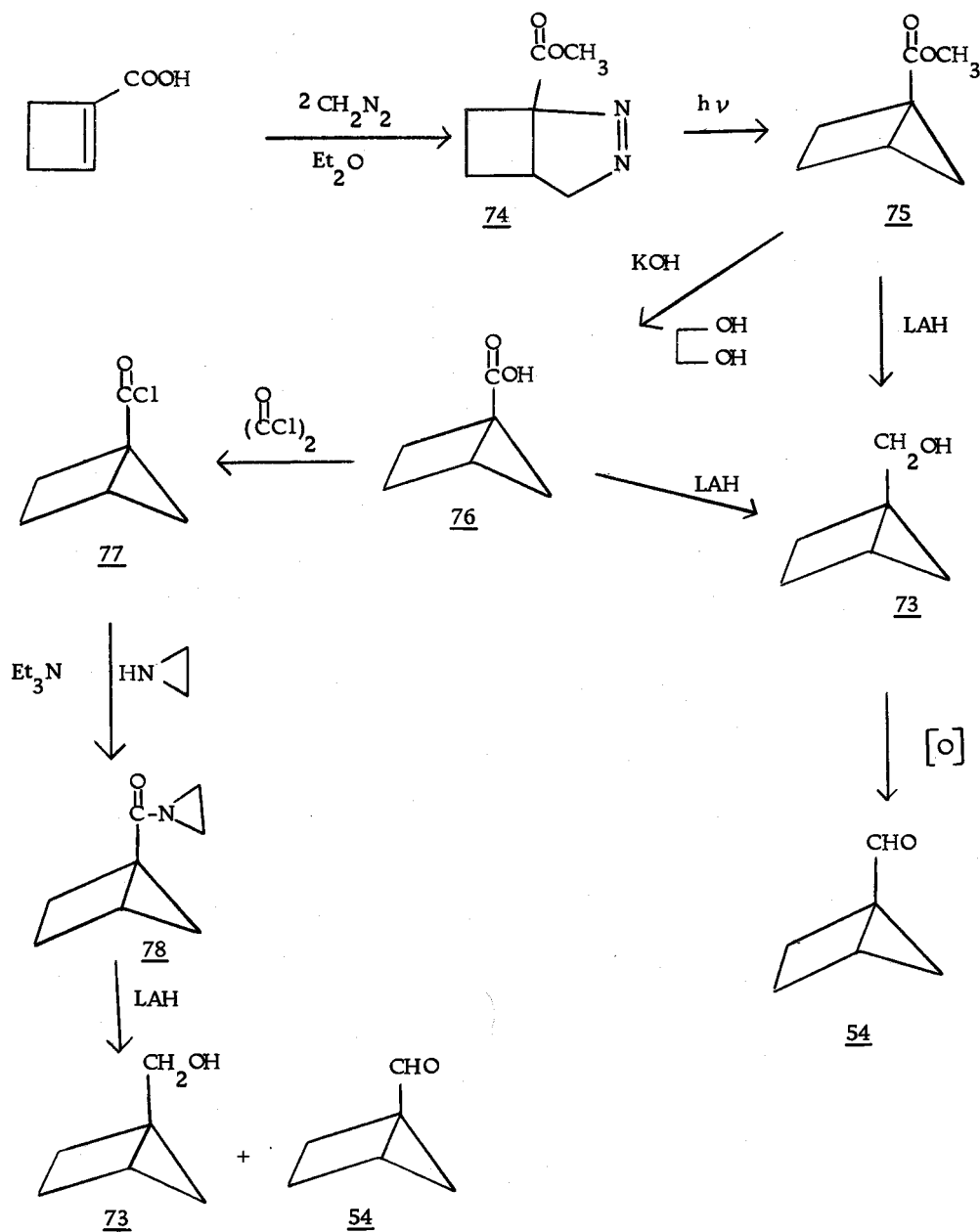
This was formed evidently by a 1,3-dipolar addition of the diazo-

methane to the α-β unsaturated carbon-carbon double bond of the

ester 71. Irradiation of the pyrazoline 74 in pentane with a medium

pressure Hanovia mercury lamp through a quartz probe gave four

different products (60%) in a ratio of 4:12:4:80. The major compo-

nent was identified as the desired product, methyl bicyclo(2.1.0)pen-

tane-1-carboxylate 75, by its spectral data as well as comparison

with recently reported literature values (33). Its n.m.r. spectrum

shows a singlet at 3.60δ containing three protons. This was assigned

to the methyl ester group. Multiplets centered at 2.20, 1.55 and

1.08δ which have a sum of seven protons were attributed to those

hydrogens of the bicyclo(2.1.0)pentane skeleton.

The over-all yield of 75 is calculated to be 30% from the cyclo-

butane carboxylic acid. This promised to be a better route to the

bicyclo(2.1.0)pentane carboxaldehyde 54. The original approach

was abandoned at this point.

The 12% component from the photolysis experiment was identi-

fied by conversion to the corresponding acid and reesterified by

diazomethane. The ester obtained has identical properties with

the methyl 2-methylcyclobutene-1-carboxylate reported recently

in a similar photolysis reaction of the pyrazoline (33).

When a pyrex filter was used in the photolysis as reported by

Gassmann (33), to cut off wavelengths below 300 mμ, the same four

products were obtained in a ration of 9:17:23:51. The major product,

75 was therefore formed in about 40% yield from the pyrazoline. The

second largest component was shown to be again methyl 2-methyl-cyclobutene-1-carboxylate. Photolysis without a pyrex filter, therefore gives a much cleaner product mixture and a better yield for the desired compound 75.

Upon saponification of the photolysis product mixture the acid 76, was separated by distillation. The structure was established by infrared and n.m.r. spectroscopy and by carbon-hydrogen analysis. It was also reconverted to pure 75. Attempts to convert the acid to its acid chloride 77 using thionyl chloride led to a mixture of more than three components. The infrared spectrum of the reaction mixture showed more than three carbonyl absorptions with almost equal intensities. The presence of an olefinic methyl in the n.m.r. and the loss of cyclopropane protons suggested that ring opening had occurred.

Since oxalyl chloride has been used to convert acid sensitive compounds to their corresponding acid chloride (80), it was used on this system. The acid chloride obtained was not isolated. Its structure was established by its infrared (3050, 1775, and 1020 cm.$^{-1}$) and n.m.r. (no acid proton, multiplets from 1.20-2.70δ) spectra.

An efficient synthesis of aldehydes from the corresponding acid chlorides was reported by Brown and Tsukamoto (7). Using this method, cyclopropylcarboxaldehyde was obtained in very good yield. Similar procedures were employed for the conversion of 77 to 54. The aziridine 78 was reduced with lithium aluminum hydride

directly. A mixture of products was obtained which was analyzed
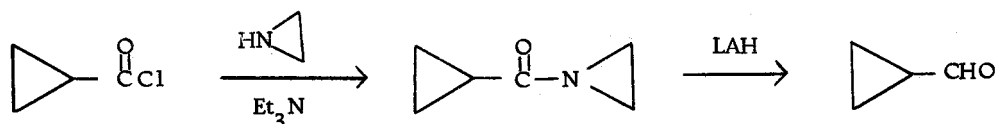
by g.l.c., and infrared and n.m.r. spectroscopy. Aldehyde bands

were observed at 2730 and 2800 cm.$^{-1}$ in the infrared, and an alde-

hyde proton was detected at 9,676 in the n.m.r. spectrum. The

infrared spectrum also showed the presence of a hydroxyl group

(3410 cm.$^{-1}$) which is most likely due to the alcohol 73 formed by

further reduction by the lithium aluminum hydride. The estimated

aldehyde to alcohol ratio by g.l.c. was 1.35:1.0.

An attempt to convert the aldehyde in the crude mixture to the

p-toluenesulfonylhydrazone resulted in an oily product. No crystal-

line material was obtained upon purification by recrystallization.

Due to the small amount of material available, no further experi-

ments were tried to purify the starting aldehyde nor to separate the

crude p-toluenesulfonylhydrazone by physical methods such as

column chromatography.

Gassman and Mansfield (33) reported the reduction of the acid

76 to the carbinol 73 in low yield. Should the yield leading to the

carbinol be improved, the oxidation pathway to the aldehyde via 73

using mild oxidation reagents in basic media might have been better

than the acid chloride route. The bicyclo(2.1.0)pentane system is very sensitive to acidic conditions as shown in our acid chloride synthesis.

Summary

In summary, cyclopropylcyclobutene was synthesized in excellent yield via the dicyclopropylcarbinyl carbene formed under dry conditions. In the presence of protic and aprotic solvents, the reaction is believed to behave differently. The thermal isomerization of cyclopropylcyclobutene went smoothly, as expected, to give first the 2-cyclopropyl-1,3-butadiene, and then the vinylcyclopentene. Kinetic data for the first isomerization agree with those of closely related cyclobutene systems. The cyclopropyl group behaves as a normal substituent in this isomerization.

Synthetic efforts towards the two unknown bicyclo(2.2.0)-hexenes were not completed, but the major problems in these routes have been overcome. Lengthy, large scale preparations using fairly expensive reagents will be necessary to complete these studies.

EXPERIMENTAL

All melting points were recorded on a Büchi melting point

apparatus and are uncorrected. Proton n.m.r. spectra were run

in carbon tetrachloride or deuterochloroform and are reported as

parts per million from the internal standard tetramethylsilane. In-

frared absorption spectra were determined using a Beckman IR-8

spectrophotometer. Ultraviolet absorption spectra were measured

with a Cary-15 spectrophotometer. The gas chromatograms were

taken on the Aerograph A-90P using helium as the carrier gas. Type

of column and temperature settings are specified in each case.

p-Toluenesulfonylhydrazone of Dicyclopropylketone 44 . A

solution of dicyclopropyl ketone (44 g., 0.4 mole) and p-toluene-

sulfonylhydrazine (75 g., 0.4 mole) in 1 l. of methanol was heated

under reflux for 1.5 hours. The solvent was evaporated and the

solid residue, 118.8 g., m.p. 96-100° was recrystallized from

ether. The product, 82.6 g. (74%) has m.p. 102-103.5°. An an-

alytical sample was obtained by further recrystallization from ether,

m.p. 103-104.5°.

Anal. Calcd. for $C_{14}H_{18}N_2O_2S$: C, 60.41; H, 6.52; N, 10.06

Found: C, 60.71; H, 6.86; N, 9.71

Its infrared spectrum shows absorption bands at 3310, 3100,

3000, 1600, 1490, 1300 and 1160 cm.$^{-1}$.

Its n.m.r. spectrum shows a multiplet at 0.75δ, a singlet at 2.42δ and a quartet at 7.55δ.

1-Cyclopropylcyclobutene 41. Metallic sodium (0.46 g., 0.02 mole) was dissolved in 50 ml. of anhydrous methanol with stirring. A solution of dicyclopropylketone tosylhydrazone (5.52 g., 0.0198 mole) dissolved in 100 ml. of anhydrous methanol was added dropwise with constant stirring. The reaction flask was kept at room temperature in a water bath. The mixture was stirred for an additional 0.5 hour after addition, and was then transferred into a 250 ml. round-bottom flask containing 6 g. of dry celite. The methanol was evaporated and the sodium salt-celite mixture was dried under reduced pressure (0.02 mm.) for two days at room temperature.

The flask containing the sodium salt-celite mixture was immersed into a Fischer bath, the temperature of which was raised gradually to 128°. A goose neck was used to connect the flask to two consecutive dry ice-acetone cooled traps evacuated to a pressure of 9 mm. The temperature of the bath was maintained at 128-130° and the decomposition carried out for 1.5 hours. The volatile products thus obtained weighed 1.515 g. (87%). The first trap contained 1.397 g., and the second trap contained 0.218 g.

A 20 foot 15% diisodecylphthalate on firebrick column (120°) was used for the g.l.c. analysis of the decomposition products. Three peaks were obtained for products in the first trap with

retention time 4.16, 6.28 and 8.16 minutes respectively. Their composition was 1.75, 5.76 and 92.5%.

The products in the second trap gave also three peaks with retention time 4.12, 6.22 and 8.17 minutes respectively. Their composition was 11.9, 3.55 and 84.6%.

The first peak (4.16 minutes) was not identified. The second and third peaks were later identified as 2-cyclopropyl-1,3-butadiene 46 and 1-cyclopropylcyclobutene 41 respectively.

The yield of 46 was calculated to be 88 mg. (0.05%), n_D^{24} 1.4790, cyclohexane
λ_{max} = 223 mμ (ϵ 12,300).

Its infrared spectrum shows absorption bands at 3090, 3010, 1590 and 1020 cm.$^{-1}$.

Its n.m.r. spectrum shows vinyl protons from 5.0 to 6.85δ, multiplets at 1.60 and 0.72δ.

The yield of 41 was calculated to be 1.48 g. (78.8%), b.p. 104-105°, $n_D^{23.5}$ 1.4635.

Its infrared spectrum shows absorption bands at 3090, 3050, 2995, 2920, 1630 and 1020 cm.$^{-1}$.

Its n.m.r. spectrum shows two singlets at 5.71δ (1 H), 2.28δ (4H) and a multiplet centered at 0.56δ (5H).

Sodium Salt of Dicyclopropylketone p-Toluenesulfonylhydrazone

45. Metallic sodium (0.83 g., 0.036 g. atom) was dissolved in 50 ml. absolute methanol in a 100 ml. round-bottom flask.

Dicyclopropylketone p-toluenesulfonylhydrazone 44 (10.0 g., 0.036

mole) was added with stirring until the solution turned clear. The

methanol solution was stirred for an additional hour. The solvent

was then removed in vacuo, and the flask attached to a vacuum and

was evacuated overnight at 0.02 mm to remove any trace of methanol.

The dried sodium salt 45 thus obtained was used immediately for the

following decomposition experiments.

Thermal Decomposition of Dicyclopropylketone p-Toluene-

sulfonylhydrazone Sodium Salt 45. The decomposition of the sodium

salt was carried out in four different solvent systems, diglyme (dried

over sodium and lithium aluminum hydride), 1.25% water in diglyme,

10% ethylene glycol in diglyme, and diethylene glycol. A typical ex-

periment is as follows.

The appropriate solvent (50 ml.) was introduced into the flask

containing the dried sodium salt from the previous experiment. The

mixture was stirred until homogeneity was obtained. The reaction

flask was connected by a goose neck to a dry ice-acetone cooled trap

and was evacuated at a pressure of 130 ± 3 mm. It was then lowered

into an oil bath maintained at a temperature of 130° for two hours.

The volatile material collected in the trap was analyzed by g.l.c.

using a 15 foot 15% diisodecylphthalate on firebrick column (120°).

No significant amount of volatile substance was collected in

the diethylene glycol run. For the other solvent systems, diglyme

was present in the trap along with the hydrocarbons. The yield of

hydrocarbons estimated by g. l. c. was 1.93 g. (57.0%) for the

diglyme run; 2.65 g. (78.5%) for the 1.25% water in diglyme run,

and only 0.1 g. (3%) for the 10% ethylene glycol in diglyme run.

The products were identified by comparison of retention time on

g.l.c. with known samples. In the 10% ethylene glycol run, an

additional peak with lower retention time than that of the two olefins

was obtained. This was suspected to be the cyclopropylbicyclo(1.1.0)

butane.

Solvent			(?)
diglyme	91%	9%	--
diglyme + 1.25% H_2O	95%	5%	--
diglyme + 10% EG	52%	28.4%	19.6%
diethylene glycol	--	--	--

Diels-Alder adduct of 2-Cyclopropyl-1,3-butadiene with maleic

anhydride 47. A solution of 2-cyclopropyl-1,3-butadiene (0.18 g.,

0.80193 mole) and maleic anhydride (1.9 g., 0.00193 mole) in 5 ml.

of benzene was heated under reflux for 0.5 hour. The solvent was

removed by evaporation. The solid obtained was recrystallized from

pet-ether (30-60), yield 0.25 g. (69%), m.p. 85.5-86°. [Lit. (36)

m.p. 83-84].

Its infrared spectrum shows absorption bands at 3110, 3030,

2980, 2920, 2870, 1845, 1775 and 1640 cm.$^{-1}$.

Thermal isomerization of 1-Cyclopropylcyclobutene 41.

1-Cyclopropylcyclobutene 41 was injected through a Tygon tubing

into a pear-shape flask which was connected to a column packed with

glass helices (17 cm. in length). The tygon tubing was connected to

a nitrogen source and the column connected to a dry ice-acetone

cooled trap. The column was heated by a heating coil jacket and the

temperature measured by a thermocouple. The nitrogen flow was

maintained at 27 ml./min. Temperature fluctuation for the 265°

run was ±2° and that for 380° and 450° was ±5°. Four runs were

made. The first one at 265°, the second and third at 380° and the

fourth one at 450°. The materials for the first, second, and fourth

runs were 99.5% pure cyclopropylcyclobutene 41, while that for the

third run was the isomerized product from the second run. All the

products were analyzed by g.l.c. with a 20 foot 15% diisodecylphthal-

ate on firebricks column.

Injector temperature = 155°

Detector temperature = 178°
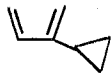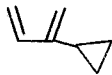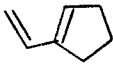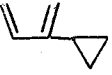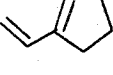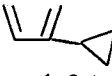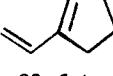
Collector temperature = 155°

Column temperature = 100°

Flow rate of helium was 50 ml./min.

The isomerization products were identified by the comparison

of their retention times on g.l.c. with those of authentic samples.

The vinylcyclopentene was synthesized independently by a known

procedure.

Table 6. Thermal isomerization of 1-cyclopropylcyclobutene.

	Wt.	m moles	Temp.	N$_2$ flow rate	Yield	Yield %	Product distribution			
1.	0.323 g.	3.43	265°	27 ml./min.	0.288 g. (3.06 m moles)	89.2	99.2%	2 more volatile + 1 less volatile products. 0.8%		
2.	0.339 g.	3.61	380°	27 ml./min.	0.294 g. (3.12 m moles)	86.7%	77.8%	21.4%	< 0.23%	+ 2 more volatile products. 0.59%
3.	0.269 g.	2.86	380°	27 ml./min.	0.229 g. (2.44 m moles)	85.2%	63.9%	36.1%		
4.	0.293 g.	3.11	450°	27 ml./min.	0.244 g. (2.59 m moles)	83.4%	1.8%	83.6%	more volatile products 5.67%	+ 8.6% others.

74

Kinetics of pyrolysis of 1-Cyclopropylcyclobutene 41. A solution of 1-cyclopropylcyclobutene 41 in cyclohexane (0.041 mole) was pipetted by means of a calibrated micro pipette into small capillary tubes. The tubes were frozen in liquid nitrogen, degassed, and were sealed. They were totally immersed into the kinetic bath controlled at ±0.2°. They were then drawn out at certain time intervals, quenched immediately in cold water and the content diluted with cyclohexane into a 10 ml. volumetric flasks. The reaction was followed spectrophotometrically at 223 mμ. Five runs were made at temperatures 166.3°, 170.0°, 158.5°, 152.8° and 146.0° respectively. (See Table 7 for typical data)

1-Vinylcyclopentanol 49. A small portion of vinylbromide (32.1 g., 0.3 mole) in 220 ml. of tetrahydrofuran (dried over lithium aluminum hydride) was poured into a 500 ml. round-bottomed flask containing magnesium turnings (7.3 g., 0.3 mole). The flask was equipped with a mechanical stirrer and a dry ice-acetone condenser, and the entire system was kept under a nitrogen atmosphere. The remaining portion of vinylbromide was added dropwise with gentle reflux over a period of 0.5 hour. After the completion of addition, the solution was heated under reflux for an additional 0.5 hour. The Grignard reagent thus obtained was cooled to -10° to -5° by means of a salt-ice bath.

A solution of cyclopentanone (21.05 g., 0.25 mole) in 40 ml. of

Table 7. Typical data of the thermal isomerization of $\underline{41}$ to $\underline{46}$[i]. [A_o[ii] $- A_\infty$[iii] $= 1.249$.]

Tube No.	Time (min.)	A(cor.)[iv]	$A - A_\infty$	$\dfrac{A - A_\infty}{A_o - A_\infty}$	$k \times 10^4 \, \mathrm{sec}^{-1}$
1	3	0.134	1.115	0.893	6.27
2	5	0.207	1.042	0.835	6.06
3	10	0.360	0.899	0.720	5.48
5	15	0.497	0.752	0.602	5.62
4	25	0.720	0.529	0.424	5.72
6	35	0.893	0.356	0.285	6.00
8	45	1.009	0.240	0.192	6.11
7	60	1.137	0.112	0.090	6.68
10	90	1.240	0.009	0.007	(9.16)
9	∞	1.249	0.000	0.000	--

(i) These data were those taken from the 170°-0 run.
(ii) A_o = Absorbancy at t = 0.
(iii) A_∞ = Absorbancy at infinite time.
(iv) Absorbancy corrected for the solvent base line.

dry tetrahydrofuran was added dropwise into the cooled Grignard

reagent with constant stirring. The mixture was stirred for an

additional three hours before it was allowed to warm up to room

temperature. The mixture was then poured into an Erlenmeyer

flask containing 20 g. of ammonium chloride and 100 g. of ice.

After stirring for 15 minutes, it was extracted with ether three

times (50 ml.), the ether layer was washed with three portions of

distilled water (20 ml.), and was dried over potassium carbonate.

The ether was distilled and the yellowish residue distilled through

a Vigreux column under reduced pressure. The major fraction,

b. p. 53-55° (13-23 mm.) was collected, yield 16.38 g. (58.7%),

n_D^{24} 1.4701 [Lit. (57) b. p. 54° (13 mm.), n_D^{17} 1.4730] .

Its infrared spectrum taken in carbon tetrachloride exhibits

bands at 3710, 3450, 3160, 3020, 1670, 1005 and 926 cm^{-1}. An

n. m. r. spectrum in carbon tetrachloride shows a broad singlet at

1.69δ, a singlet at 2.85δ and an ABX pattern centered at 5.50δ.

1-Vinylcyclopentene 48. 1-Vinylcyclopentanol 49 (10.0 g.

0.0893 mole) was heated under reflux with 0.02 g. iodine for 0.5 hr.

The solution turned dark and two phases began to separate. Distil-

lation with an oil bath temperature of 130-135° gave a two phase

distillate. The upper organic layer was separated from the water

layer. Yield 7.7 g. (91.2%).

This yellowish crude product was dried over anhydrous

magnesium sulfate and was molecularly distilled. The product,

a colorless liquid, amounted to 7.3 g. (87.0%), b.p. 114°, n_D^{24} 1.4850

[Lit (81) b.p. 114-115, n_D^{18} 1.4870]

The ultraviolet spectrum of the product has absorption peaks

at 228 mμ (ε 19,400) and at 234.5 mμ (ε 21,500).

The infrared spectrum shows absorption bands at 3110, 3060,

1635 and 1590 cm^{-1}.

Its n.m.r. spectrum in carbon tetrachloride exhibits two

multiplets at 1.95 and 2.40δ, and vinyl portions at 4.85, 5.08,

6.27, 6.43, 6.56 and 7.74δ. The ratio of vinyl to methylene pro-

tons is 4:6.1.

Dicyclopropyl Ketone Azine 50. A solution of 5% hydrazine

hydrate was prepared by adding 3.85 ml. (0.0795 mole) of 99-100%

hydrazine hydrate to 50 ml. of 100% ethanol containing 10 drops of

glacial acetic acid. This solution was added dropwise to dicyclo-

propyl ketone (17.6 g., 0.16 mole). The stirred solution was

warmed at 80-90° for two hours. It was then dried over anhydrous

magnesium sulfate and the solvent removed in vacuo. The white

solid was collected. The yield was 7.8 g. (46%), m.p. 86-88.5°.

Recrystallization from ethanol gave 7.0 g. (41%), m.p. 89-90°.

Its infrared spectrum shows absorption bands at 3100, 3010,

1610, 1030 and 910 cm^{-1}.

Its n.m.r. spectrum shows multiplets centered at 2.44 and

0.82δ respectively.

Dicyclopropyl Carbinol <u>51</u>. A solution of lithium aluminum

hydride (0.95 g., 0.025 mole) in dry ether was added dropwise to a

cooled solution of dicyclopropyl ketone (11 g., 0.1 mole) in 100 ml.

of dry ether. The reaction mixture was heated under gentle reflux

for two hours. It was then acidified with dilute hydrochloric acid and

the two layers separated. The aqueous layer was washed with two

portions (20 ml.) of ether. The ether extracts were combined,

washed with water, sodium bicarbonate, water and was dried over

anhydrous magnesium sulfate. The ether was removed <u>in vacuo</u>, to

yield 11.4 g. of crude product. G.l.c. analysis showed 8.9 g. (80%)

of <u>51</u>. Simple distillation did not separate the alcohol <u>51</u> from the

starting ketone.

The infrared spectrum of the distilled mixture shows absorp-

tions at 3420, 3100, 3010, 2880 and 1670 cm^{-1}. The 1670 cm^{-1}

band showed only medium intensity which indicates the presence of

the unreacted ketone. Its n.m.r. spectrum shows multiplets cen-

tered at 0.35, 0.92, 1.95δ. A sharp triplet at 2.50δ (assigned to

the hydrogen of the alcohol) and a broad hydroxyl proton at 2.85δ,

which shifts upfield upon dilution of the sample.

3-Acetoxy-3-buten-2-one <u>66</u>. A mixture of 2,3-butanedione

(172 g., 2 moles), acetic anhydride (204 g., 2 moles) and pyridine

(400 g., 5 moles) was stirred at room temperature for three days.

At the end of this time, the unreacted starting materials were distilled through a Vigreux column at reduced pressure (12 mm), which amounted to 253 g. A second fraction was obtained at 0.08 mm, b.p. 20-30°, weighed 400 g. The third fraction weighed 50 g., b.p. 30-35° (0.08 mm). The fourth fraction weighed 10 g., b.p. 35-40° (0.08 mm). The residue remained in the pot weighed 43 g.

G.l.c. analysis (10 foot 10% Apiezon K on 40-80 mesh firebrick) of the third and fourth fractions indicated 99.8% of the desired product.

Redistillation of the second fraction at 11-12 mm gave 28.5 g. of product, b.p. 60-68°, containing 22.5 g. of the acetate.

The total yield of acetate thus obtained was 82.5 g. (32.3%). b.p. 72-73° (7-8 mm). [Lit. (90) b.p. 71-72° (7 mm.)]

Its infrared spectrum shows absorption bands at 1755, 1695 and 1640 cm $^{-1}$. Its n.m.r. spectrum shows two singlets at 2.12 (3H) and 2.22δ (3H) respectively, and a doublet at 4.39δ (2H).

Preparation of Zinc-Copper Couple. The Zinc-Copper Couple was prepared according to the procedure of Smith and Simmons (77). In a 500 ml. Erlenmeyer flask fitted with a magnetic stirrer were placed 49.2 g. (0.75 g. atom) of zinc powder and 40 ml. of 3% hydrochloric acid. The mixture was stirred rapidly for one minute, then the supernatant liquid was decanted. In a similar manner, the zinc powder was washed successively with three additional 40 ml. portions

of 3% hydrochloric acid, five 100 ml. portions of distilled water,

two 75 ml. portions of 2% aqueous copper sulfate solution, five

100 ml. portions of distilled water, four 100 ml. portions of abso-

lute ethanol, and five 100 ml. portions of absolute ether. The couple

was finally transferred to a Büchner funnel, washed with additional

anhydrous ether, covered tightly with a rubber dam, and suction

dried until it reached room temperature. The couple was used

immediately in the following experiment.

Simmons-Smith Reaction of 3-Acetoxy-3-buten-2-one. The

freshly prepared zinc-copper couple (50 g.) was put into a 500 ml.

round-bottom flask containing freshly distilled methylene iodide

(193 g., 0.72 mole), and iodine (0.2 g.) in 150 ml. of dry ether (dried

over lithium aluminum hydride). The mixture was heated under re-

flux with stirring for 30 minutes. A solution of the acetate 66 (10 g.,

0.0782 mole) in 20 ml. of dry ether was added dropwise. Refluxing

and stirring were continued for 20 hours. The reaction mixture was

then cooled, filtered, and washed with saturated ammonium chloride

solution, saturated sodium bicarbonate solution, and water succes-

sively. The ether solution was dried over anhydrous magnesium

sulfate and was concentrated in vacuo. This crude product weighed

18.5 g. G.l.c. analysis of this crude product using a 10 foot 15%

Apieson K column (110°) indicated five components other than ether.

Peaks	Retention time	Relative mole ratio
A	0. 5 min,	4
B	0. 7 min.	1
C	1 min.	2. 25
D	6 min,	1. 1
E	11. 5 min.	9. 0

The first three peaks were not identified. Peak E was determined to be a mixture of methylene iodide and the starting acetate by comparison with authentic samples both in retention times and their infrared spectra.

Peak D was collected through g. l. c. Its infrared spectrum shows absorption bands at 3620, 3400, 3080, 1350, 1180 and 1010 cm^{-1}.

Its n. m. r. spectrum exhibits a sharp singlet at 1. 2δ, two multiplets centered at 0. 5 and 2. 0δ respectively. The integration ratio is 1:2:2. The structure was tentatively assigned as 65. The yield of peak D was estimated to be less than 10%.

Cyclobutane carboxylic acid 79. 1, 1-cyclobutane dicarboxylic acid (200 g., 1. 39 mole) was heated in a 500 ml. round bottom flask to a temperature of 160-180° for three hours. The decarboxylated acid was distilled at reduced pressure (150-160mm), yield 141.3 g.

The crude product was distilled at 21 mm. The yield was 123. 1 g. (88. 6%) b. p. 104-106°.

The infrared spectrum of the product, which is identical with that of an authentic sample (Columbia Organic Chemicals Co., Inc), shows absorptions at 3300-2500 cm^{-1} (broad shoulder, CO_2H), 1710, 1420, 1260 and 920 cm^{-1}.

Methyl-α-bromocyclobutane carboxylate 80. Cyclobutane carboxylic acid 79 (116.5 g., 1.165 mole) was put in a 1 l. three-necked round bottom flask equipped with a mechanical stirrer, a condenser and a dropping funnel. The top of the condenser was connected to a drying tube filled with anhydrous calcium chloride. Thionyl chloride (150 g., 1.26 mole) was introduced dropwise with stirring. An endothermic reaction was noticed with acidic gas evolved. The reaction flask was warmed at 100° for one hour.

After cooling to room temperature, red phosphorus (2 g., 0.0645 g. atom) and bromine (180 g., 1.125 mole) were added to the mixture with constant stirring. When addition had been completed, heating was resumed for an additional three hours at 130-135°.

The reaction mixture was cooled before being dropped into 300 ml. of anhydrous methanol in a 1 l. round-bottomed flask cooled in an ice bath. The solution was allowed to warm to room temperature. Approximately 300 ml. of distilled water was then introduced. The organic layer was separated from the aqueous layer and washed with two 50 ml. portions of distilled water. The

water washes were combined with the aqueous layer and extracted with ether.

The ether extract and the organic layer were combined, dried over anhydrous magnesium sulfate, and the ether evaporated _in vacuo._ The remaining residue was distilled through a Vigreux column.

The fraction with boiling point 64-65° (8 mm.) was collected. The yield was 182.8 g. (81.2%), n_D^{24} 1.4760[Lit. (43) n_D^{20} 1.4777] .

1-Cyclobutene carboxylic acid 70.   Methyl 1-bromocyclo-butane carboxylate 80 (8.4 g., 0.0435 mole) was added dropwise to molten potassium hydroxide (10 g. 0.178 mole) in 150 ml. of re-fluxing toluene with vigorous stirring.   The source of heat was re-moved during the addition when a vigorous exothermic reaction oc-curred.   Solid potassium salt was noticed to separate.   After the addition, heating was resumed for a further 40 minutes, and the mixture was cooled before addition of 100 ml. of distilled water. The aqueous solution was separated, washed with light petroleum ether (30-60°), acidified with 30% (w/w) sulfuric acid, and was ex-tracted with four 50 ml. portions of ether.

The ether solution was dried over anhydrous magnesium sulfate and the solvent evaporated.   The solid thus obtained was recrystal-lized from petroleum ether (30-60°).   The yield was 3.0 g. (70%), m.p. 62-68°.   A second recrystallization from petroleum ether raised the melting point to 67-68° [Lit. (43) m.p. 67°] .

Since the 1-cyclobutene carboxylic acid was very sensitive to air, it was not isolated in later experiments. Instead, it was stored in ether (stabilized with hydroquinone) for use in subsequent experiments.

Diazomethane. Procedures according to Moore and Reed (58) were used for the generation of diazomethane.

A long condenser (50 cm) was fitted with an adapter to which was sealed a length of 8 mm pyrex tubing extending nearly to the bottom of a 5 l. round-bottom flask, which served as the distillation receiver. The tubing was connected to the receiver with a two-hole stopper carrying a drying tube filled with anhydrous calcium chloride and Drierite. The receiver was cooled in an ice-salt bath. Anhydrous ether (approximately 150 ml.) was added to cover the tip of the adapter.

In a 5 l. round-bottom flask were placed 3 l. of U.S.P. ether, 500 ml. of diethylene glycol monoethyl ether and 600 ml. of 30% sodium hydroxide solution. The mixture was chilled in an ice-salt bath to 0°. Bis(N-methyl-N-nitroso)-terephthalamide (Du Pont product, EXR-101) (180 g. 70% dispersion in mineral oil, 0.5 mole) was added in one portion. The flask was immediately transferred to a heating mantle and connected by a goose neck to the condenser. The ether solution turned yellow immediately.

The reaction flask was warmed up gradually. Approximately

1.5 l. of ether was distilled in 4-6 hours. The tip of the adapter was kept just below the surface of the distillate during the distillation. The distillate, containing 0.76-0.86 mole (76-86%) of diazomethane according to Moore and Reed, was used immediately in the next experiment.

Methyl 2, 3 -Diazabicyclo[3. 2. 0]hept-2-ene-1-carboxylate 74.

A solution of 1-cyclobutene carboxylic acid, 70 (prepared from 60 g. of methyl 1-bromocyclobutane carboxylate, 0.311 mole) in ether was added dropwise to an ether solution of diazomethane (0.76-0.86 mole) cooled in an ice-salt bath. The mixture was stirred for an additional 18-24 hours and was then warmed to room temperature.

The ether was distilled and the residue obtained weighed 42.1 g. (88%).

Distillation through a Vigreux column gave 35.2 g. (74%), b.p. 64-65 (0.08 mm), $n_D^{22.5}$ 1.4768, $\lambda_{max}^{pentane}$ 324.2 mμ . (ϵ 244) [Lit. (33) b.p. 66° (0-20 mm), N_D^{26} 1-4750, λ_{max} 322 mμ (ϵ 216)] .

Anal. Calcd. for $C_7H_{10}N_2O_2$: C, 54.54; H, 6.54; N, 18.17

Found: C, 54.52; H, 6.72; N, 18.36

Its infrared spectrum shows major absorption bands at 2970, 1720, 1540, 1435 and 1310 cm^{-1}. The n.m.r. spectrum in carbon tetrachloride consists of a singlet at 4.62δ(1H), a doublet at 4.53δ (1H), a singlet at 3.73δ(3H), and three complex multiplets centered at 2.75(2H), 2.19(2H) and 1.33δ(1H).

Photolysis of Methyl 2,3-Diazabicyclo(3.2.0)hept-2-ene-1-

carboxylate 74.   A solution of methyl 2,3-diazadicyclo(3.2.0)hept-

2-ene-1-carboxylate 74 (10 g., 0.0648 mole) in 1 l. of dry pentane

was irradiated with a Hanovia medium pressure mercury lamp through

a quartz probe for 22 hours. The completion of the reaction was de-

termined by the disappearance of the pyrazoline absorption at 324 mμ.

The solvent was then evaporated in vacuo, and the residue molecular-

ly distilled to give 4.9 g. (60%) of a colorless liquid.

G.l.c. analysis using a 10 foot 5% diethylene glycol succinate on

Chromosorb G column (135°) gave four components. The composition

of the components was 4:12:4: 80%. The major component was later

identified as methyl bicyclo(2.1.0)-pentane-1-carboxylate 75, b.p.

45-48° (10 mm.), n_D^{24} 1.4558 [Lit. (33) b.p. 78° (43 mm.), n_D^{20}

1.4573] .

Anal. calcd. for $C_7H_{10}O_2$:   C, 66.65; H, 7.99

Found: C, 66.46; H, 8.06

Its infrared spectrum shows absorption bands at 3070, 3000,

1720 and 1160 cm.$^{-1}$ Its n.m.r. spectrum shows a singlet at 3.60δ

(3 H.), and multiplets centered at 2.20, 1.55 and 1.08δ (7 H.).

When a pyrex filter was used to cut off wavelengths below 300

mμ the product composition changed to 9, 17, 23 and 51%. The dis-

tilled colorless liquid weighed 6.4 g. (78%).

One other product was identified by saponification of the crude

product mixture. The solid acid obtained has m. p. 92-93.5°. The

yield ranged from 2% to 9% depending on the photolysis method.

Its infrared spectrum exhibits absorption bands at 2500 cm.$^{-1}$

to 3150 cm.$^{-1}$ (broad shoulder), 1670 and 900 cm.$^{-1}$ Its n. m. r.

spectrum shows an acidic proton peak at 11.91δ, two multiplets

centered at 2.05 and 2.45δ respectively.

Esterification of this acid with diazomethane gave a liquid

which was identified as methyl 2-methylcyclobutene-1-carboxylate

by comparison with the reported spectral properties (33). Its infra-

red spectrum shows absorption bands at 1720 and 1665 cm.$^{-1}$ Its

n. m. r. spectrum exhibits a sharp singlet at 3.63δ (3 H.), two multi-

plets centered at 2.40 (4 H.) and 1.97δ (3 H.).

Pyrolysis of Methyl 2, 3-Diazabicyclo[3. 2. 0] hept-2-ene-1-

carboxylate 74. Methyl 2.3-Diazabicyclo[3. 2. 0] hep5-2-ene-1-

carboxylate (5 g., 0.0324 mole) was heated at 170° in a 10 ml. pear

shape flask equipped with a Vigreux column. Nitrogen was bled

through a capillary leak and the system was evacuated by an aspirator

to a pressure of 30-35 mm.

The slightly yellowish liquid formed was distilled very slowly

for 2.5 hours, to give 2.40 g. crude product.

G. l. c. analysis shows the major product (84%) to be methyl

[2. 1. 0] pentane-1-carboxylate, with five other components.

The infrared spectrum of the crude product shows absorptions

at 1660 cm^{-1} (C=C), and at 1540 cm^{-1} (N=N).

The n.m.r. spectrum showed at least three components of approximately 1:1:1 composition. Three singlets at the 3.5δ region indicates the presence of three different methyl groups of a methyl ester.

Bicyclo[2.1.0] pentane-1-carboxylic acid 76. The crude mixture from the photolysis of the pyrazoline (8.8 g. 0.697 mole) was saponified with 5.0 g. of potassium hydroxide in 50 ml. of ethylene glycol at 100° for 25 minutes. 30 ml. of distilled water was introduced while the flask was still warm.

The reaction mixture was acidified with hydrochloric acid and was extracted four times (20 ml.) with pentane. The pentane solution was dried over anhydrous sodium sulfate and the solvent evaporated in vacuo. The crude product, 4.0 g. (51%), was a thick yellowish oil.

Distillation gave a clear liquid, 1.8 g., (23%), b.p. 70-72° (0.25 mm.), n$_D^{24}$ 1.4805.

Anal. Calcd. for C$_6$H$_8$O$_2$, M.W. 112.1: C, 64.27%; H, 7.19%

Found: C, 64.38%; H, 7.25%

Its infrared spectrum shows a broad shoulder band around 3000 cm^{-1}, a carbonyl band at 1680 cm^{-1}.

Its n.m.r. spectrum shows a complicated multiplet from 1.18δ-2.75δ. The acidic proton is at 12.2δ. The integrated ratio

is 6.95:1.

Other runs gave as high as 74% crude acid and 65% distilled product.

Bicyclo(2.1.0)pentane-1-carboxaldehyde 54. A solution of oxalyl chloride (16.5 g., 0.131 mole) in 50 ml. of chloroform was added dropwise to the acid 76 (7.5 g., 0.067 mole) in 25 ml. of chloroform with stirring. The mixture was heated under reflux for two hours. The chloroform was removed in vacuo to yield 8.40 g. (97%) of crude product.

The infrared spectrum of this crude product shows absorption bands at 3050, 1775 (broad), 1625 (C=C?) and 1020 cm^{-1}.

The n.m.r. spectrum shows no acid proton.

With no further purification, this crude product was diluted with 20 ml. of dry ether and was added dropwise to a solution of triethylamine (6.77 g., 0.067 mole) and ethylenimine (2.88 g., 0.067 mole) in 100 ml. of dry ether, cooled in an ice-salt bath. The mixture was stirred for an additional two hours. The solid triethylamine hydrochloride was filtered and washed with 100 ml. of ether. The combined ether solution was cooled to 0° and 21 ml. of 1.25 M lithium aluminum hydride in ether was added to the stirred solution over 0.5 hour. After stirring for an additional hour, cold 5 N sulfuric acid was added, and the ether layer was separated, and the aqueous layer extracted. The combined ether extracts were washed with

water, sodium bicarbonate, water again, and dried over anhydrous

sodium sulfate. The ether was removed in vacuo. Molecular dis-

tillation gave 2.20 g. of clear liquid.

G. l. c. analysis (ten feet, 15% carbowax 20 M column, 98°)

indicated two components with retention times of two minutes and

15 minutes respectively. The relative mole ratio was 1.35:1.0.

The major component was assigned as the aldehyde by its n. m. r.

spectrum.

The n. m. r. spectrum shows a quartet (?) centered at 9.67δ

(J=1.2 cps), complex multiplets at up field, and a relatively distinct

quartet at 4.41δ. Relative proton ratio of the quartets is 1.7:1.0,

which is believed to be the relative ratio of the aldehyde to the alco-

hol.

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