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Application of matrix isolation technique in organic synthesis: I. Synthesis of deuterated cyclobutadiene; II. Approaches to the synthesis of tetrahedrane

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APPLICATION OF MATRIX ISOLATION TECHNIQUE IN ORGANIC SYNTHESIS. I. SYNTHESIS OF DEUTERATED CYCLOBUTADIENE. II. APPROACHES TO THE SYNTHESIS OF TETRAHEDRANE.

Iowa State University, Ph.D., 1974
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Application of matrix isolation technique in organic synthesis.
I. Synthesis of deuterated cyclobutadiene.
II. Approaches to the synthesis of tetrahedrane.

by

Danilo Orcilla De La Cruz

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1974

TABLE OF CONTENTS

QUOTATION

Finally, brethren, whatever is true, whatever is honorable, whatever is right, whatever is pure, whatever is lovely, whatever is of good repute, if there is any excellence and if anything worthy of praise, let your mind dwell on these things.

Phil. 4:8

INTRODUCTION

Modern organic synthesis has reached a level of sophisitication where only imagination and experimental skill can set the limits to its goals. The recent synthesis of Vitamin B_{12}, a very complex molecule, attests to this fact. In general, however, success in organic synthesis has been limited to those molecules which are stable (at ordinary laboratory conditions) for spectroscopic observation. For many decades, organic chemists have tried to synthesize reactive organic molecules such as cyclobutadiene and its isomers but to no avail because their reactivity precluded spectroscopic observation. The failure at synthesis of these reactive organic molecules is unfortunate because they have been the object of extensive theoretical predictions. Their synthesis would contribute to a fundamental understanding of their chemistry, and provide a testing ground for numerous calculations.

For many years, the challenge has been to generate these molecules at very low temperatures and at very high dilutions to prevent decomposition and bimolecular reactions. Matrix isolation has met these two conditions. This technique (traditionally used by physical chemists), in the hands of organic chemists has opened a new era of organic synthesis.

Matrix isolation technique was first applied to the synthesis of free radicals by Lewis and Lipkin (1). These workers obtained the visible spectra of triphenylmethyl radical by photolysis of hexaphenylethane in a glass matrix made from ether, isopentane, and ethanol (EPA) in the ratio of 5:5:1 at 90°K. Matrix isolation technique as we know it today was proposed independently by Norman and Porter (2) and Whittle, Dows, and Pimentel (3) in 1954. Norman and Porter used transparent glasses made by cooling dilute solutions of the desired molecule in several hydrocarbon solvents as their matrix, and followed the progress of photolysis by ultraviolet spectroscopy. Whittle, Dows and Pimentel prepared their matrix samples by vapor co-deposition of the matrix gas (CO_2, CCl_4, and methylcyclohexane) and the vapor of the guest molecule on a low temperature target, usually at 20°K or 4°K. Subsequently, Becker and Pimentel (4) used nitrogen and argon as the inert matrix. When the reactive species is formed by photolysis, the inert matrix serves to isolate the primary products, prevent secondary reactions, and act as a heat sink for exothermic reactions. The use of these effects was elegantly exploited by Pimentel (1954 to present), Milligan (1958 to present), and others in the preparation of free radicals. The early work on radical formation and trapping in a matrix has been reviewed by

Pimentel (5). More recently, Milligan and Jacox have discussed free radical spectroscopy (6).

The early workers used double Dewar cryostats which used liquid hydrogen (b.p. 20°K) or helium (b.p. 4°K) as the primary refrigerant and liquid nitrogen (b.p. 77°K) as a secondary refrigerant (4, 6). Subsequently a cryogenic device, "Cryo-Tip" (Air Products and Chemicals, Inc.) was developed which uses the open-cycle Joule-Thomson expansion of high pressure cylinder gases (7, 8). Recently, four closed-cycle cryogenic refrigerators have become commercially available. 1) "Cryogen" (North American Phillips Co. 2) "Cryomite" (Malakar Corp.). 3) "Displex" (Air Products and Chemical, Inc.). 4) "Cryodyne" (Cryogenic Technology, Inc.). These machines constitute a major technical improvement. They are smaller, easier to operate, quicker, more accurate in temperature control, and simpler than any other means of refrigeration previously known.

The matrix sample is deposited unto a substrate mounted on an oxygen-free, hard copper block maintained in good thermal contact with the source of cryogenic refrigeration. For infrared spectroscopy, alkali halide windows are used to collect the sample. Sodium chloride transmits the i.r. down to 600 cm^{-1} while cesium iodide extends to 200 cm^{-1}. For e.s.r. work, sapphire windows or copper strips are used. The window must be mounted with excellent thermal contact to the copper block to insure rapid dissipation of the heat from the sample upon condensation. Lead or indium spaces are generally used for this purpose.

Good matrix isolation depends on the matrix, the sample concentration, deposition rate, and temperature (9). The most widely used matrix materials are argon and nitrogen, but neon, krypton, and xenon also find application. These materials are in general inert with respect to the active species being isolated, and are transparent for infrared studies. They also have a high enough vapor pressure to be used in a gas handling system but have sufficiently low pressure at the temperature of the refrigerant to permit exposure to vacuum. Becker and Pimentel have found that the upper limit at which xenon, argon, and nitrogen can be used is 70°K, 35°K, and 30°K, respectively (4). Most work is done at a matrix to reagent (M/R) ratio of 500 or higher to insure good isolation of the active material. Calculations using a crystal structure where each molecule has eight nearest neighbors shows that a 100 to 1 ratio gives a probability of 0.08 that two active species will be adjacent to each other. Experimental results, however, show that a 1000:1 ratio does not give complete isolation. As a general rule, the deposition temperature should be well below half the melting point of the matrix materials (5). If the matrix gas is deposited at too cold a temperature, a great amount of light scattering occurs. For example, xenon forms a transparent matrix when deposited at 66°K, but the same amount of xenon is highly scattering when condensed below 50°K. Sample deposition times for less than 1-48 hours have been reported in the literature, although most deposition periods are near 6 hours. A rate of 1-2 mmoles per hour corresponds to an increase in sample thickness of about one molecular layer per second. This rate has been empirically established as an ideal compromise and yields for a given M/R ratio, the sharpest lines and fewest dimers (10). For i.r. work, only millimole amounts of the reactive species are necessary.

Any chemical species trapped in an inert matrix will sustain perturbation by the matrix. Pimentel and Charles have shown that both the bending and stretching modes can vary by as much as 40 cm^{-1} from the gas phase infrared (11). Andrews has found that matrix shifts are usually less than 1% for nonpolar species and as high as 10% for polar molecules (9). Dressler has further observed that the entire band system shifts rather than one particular bending or stretching mode (12). Theories on matrix shifts have been discussed by Pimentel and Charles (11), and more recently by Barnes and Hallam (8). The infrared spectrum of a matrix isolated species has very sharp spectral bands. This sharpening of bands has been found to be due to a quenching of rotational motion. Frequently doubling of infrared absorption is observed, depending upon the relative sizes of the guest molecule and host cavity. Such splittings are attributed to different orientations of a guest specie in a host cage and can be identified by the use of two different matrix materials such as krypton and argon. Further splittings of a spectral line can be caused by guest molecules in nearest or next-nearest neighbor sites in host matrix. These splittings are usually concentration dependent and can be removed by decreasing the concentration of the guest species. These effects are discussed in detail by Pimentel and Charles (11).

There are three very popular methods of detection for matrix work: e.s.r., u.v., and i.r. The e.s.r. is the most selective and most sensitive for singling out free radicals and triplet species. It has a unique potential for concentration determination. However, centering of all e.s.r. spectra around the same value of g causes a troublesome superposition of spectra. U.V. is selective for absorbing species but less sensitive than the e.s.r. method. Scattering by matrices makes u.v. rather difficult. Most work using this technique uses glassy matrices. I.R. is the most informative and versatile of these three. It gives the most complete picture of the chemistry taking place, and the spectra are a substantial aid in identifying unknown species.

Light scattering is less serious but the absorption coefficient is low in this region.

The matrix isolated species has been generated by photochemistry, pyrolysis, radiolysis or upon electron impact. The most popular method, however, is photochemistry. Irradiation of the matrix isolated species has been followed by plotting the i.r. absorbance of the starting material and the resulting product as a function of irradiation time. This clearly differentiates primary and secondary photoproducts. Identification of any new species is based on i.r. bands, chemical behavior on warming, and when possible on chemical trapping with reagents that give isolable adducts at room temperature.

Matrix isolation has numerous applications. In the hands of physical chemists, it has been used to study molecular association, molecular rotation, vibrational analysis, noble gas compounds, high temperature species, and analysis of gas mixtures. These studies have been reviewed by Barnes and Hallam (8). The most prolific application of this technique, however, is in the generation of free radicals. Pimentel and co-workers, and Milligan and Jacox have generated numerous free radicals and characterized them by i.r. Kasai and Wasserman have also generated free radicals and used e.s.r. as their probe. For a complete review of matrix isolation of free radicals, see Milligan and Jacox (13), Dressler (12), Barnes and Hallam (8), Hallam (14), and Andrews (9). Kasai et al. (15), and Miles (16) give good reviews of matrix isolation using e.s.r. Except for the work of Pimentel in the early 1960's with carbenes, no matrix isolation work on other reactive organic intermediates have been reported. The real breakthrough in the use of matrix isolation came in 1973 when O. L. Chapman et al. and Lin and Krantz independently reported the synthesis of matrix isolated cyclobutadiene. This remarkable achievement was followed by the synthesis of matrix isolated benzopropiolactone, benzyne, and methylenecyclopropene in the laboratories of O. L. Chapman. This pioneering work has clearly established matrix isolation as a useful tool in the synthesis of organic compounds. The number of organic compounds that can be synthesized using this technique is unlimited but the challenge is clearly the synthesis of precursors that can be deposited in the matrix and photolysed to yield the desired species.

The present work was undertaken to further characterize the cyclobutadiene molecule through deuterium labelling. This work also reexamined the photochemistry of known precursors to substituted tetrahedrane at 8°K. Attempts were made at synthesis of unsubstituted precursors to tetrahedrane.

PART I. SYNTHESIS OF MONO- AND DIDEUTERIOCYCLOBUTADIENE

HISTORICAL

Cyclobutadiene has been the object of significant research effort since the initial attempt at its synthesis by Kekulé one hundred years ago (17). Excellent reviews have appeared over the years dealing with cyclobutadiene and related compounds (18).

Early molecular orbital calculations on cyclobutadiene predicted that it is not stabilized by π-electron delocalization and has a triplet ground state while calculations with valence-bond wave functions predicted an exceptionally large stabilization and a singlet ground state (19). It was this striking discrepancy in prediction by two theories whose results are normally in agreement that prompted the intensive theoretical studies on the unknown cyclobutadiene.

Recent calculations are conflicting on the ground state of cyclobutadiene but are in agreement on the square planar (D_{4h}) geometry of the triplet state. M. J. S. Dewar et al. have carried out semiempirical SCF-MO calculations and predicted cyclobutadiene to have a rectangular singlet ground state with very low lying triplet (square planar), and is stable to dissociation into two acetylene molecules (20). A minimal basis <u>ab initio</u> calculation (limited CI) by Buenker and Peyerimhoff suggested a singlet ground state in a rectangular geometry and a lowest excited triplet which possesses a slightly rectangular geometry. They also concluded that the molecule is not stable with respect to two acetylene molecules (21). However, more flexible and extended ab initio calculations predicted a square triplet similar to Dewar's semiempirical result (22). More recently, calculations using the general valence bond method (GVB) indicate that the singlet lies 7.7 kcal/mole above the triplet at the triplet equilibrium geometry (square planar) and that this triplet equilibrium geometry is unstable to rectangular distortions (22). Calculations by N. L. Allinger, C. Gilardeau, and L. Chow using a modification of the Pariser-Parr Method, also predicted that the ground state is square triplet and more stable by 6.1 kcal/mole than the rectangular singlet (23).

The nonexistence of cyclobutadiene was used in the past to support the M.O. predictions, but it was pointed out that the strain energy of four trigonal carbon atoms in a square arrangement might be sufficient to account for its apparent instability. Coulson and Moffitt calculated the total strain of about 74 kcal/mole for cyclobutadiene which is not exceptionally large (24). A similar study by Weltner gave a value of about 50 kcal/mole (25). Lipscomb has pointed out that one way in which cyclobutadiene can achieve enhanced stability is through rearrangement to tetrahedrane (26). However, the strain energy for tetrahedrane has been estimated to be approximately 90 kcal/mole, which compares unfavorably with the strain energy for cyclobutadiene (25).

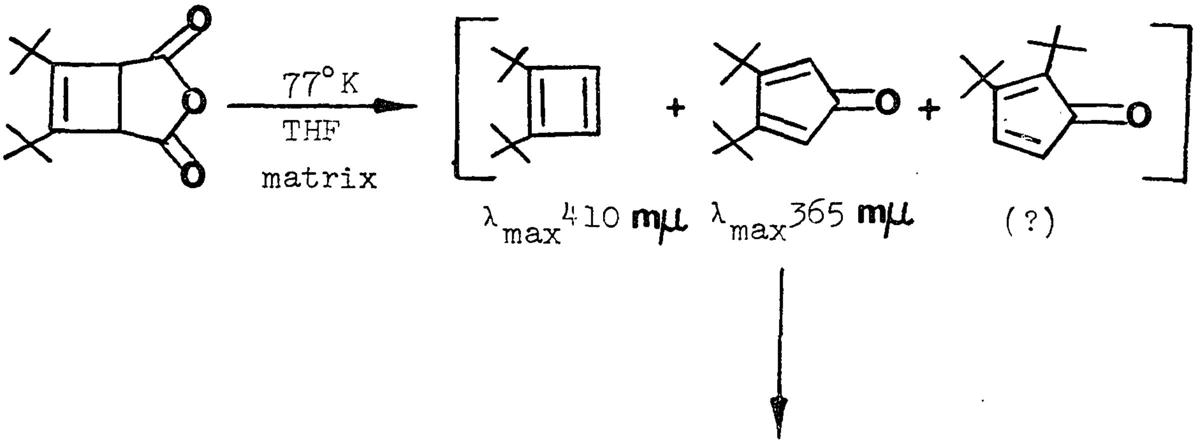
Group theory predicted four infrared active modes for square (D_{4h}) cyclobutadiene; a C-H stretch (E_μ), a framework deformation (E_μ), an in-plane C-H bend (E_μ), and an out-of-plane C-H bending deformation ($A_{2\mu}$) (27, 28). The corresponding analysis for the rectangle (D_{2h}) gives seven infrared allowed fundamentals, as a consequence of breaking the degeneracy of the $3E_\mu$ modes of the square ($E_\mu \rightarrow B_{2\mu} + B_{3\mu}$, $A_{2\mu} \rightarrow B_{1\mu}$), five of which should be observable in the non-C-H stretch region of the i.r. spectrum. All other minor distortions lead to more than four infrared allowed fundamentals: e.g. puckered cyclobutadiene (D_{2d}, 7 i.r. bands), rhomboidal (D_{2h}, 9 i.r. bands), and trapezoidal (C_{2vS}, 15 i.r. bands) (22). The structure and u.v. spectrum of cyclobutadiene have been studied theoretically by a modification of the Pariser-Parr method, which explicitly includes the effect of the sigma system in determining molecular geometry (23). It was concluded that the ground state is probably a triplet with the geometry of a regular square. The u.v. spectrum for the actual triplet molecule is predicted to show a strong absorption band at about 353 mμ (extinction coefficient of a few thousand), and the compound should be colored, probably yellow. The lowest singlet state has a rectangular geometry, and it is predicted to show no allowed transitions above 200 mμ, but because of forbidden transitions at 439 and 487 mμ (extinction coefficient of about 10-200), should appear red in color.

Woodward and Hoffman rules of conservation of orbital symmetry (29) predict that cycloreversion of cyclobutadiene to two acetylenes ($\pi_{2s} + \pi_{2s}$) is allowed photochemically but forbidden thermally. The same selection rules predict a preference for the concerted dimerization ($\pi_{2s} + \pi_{4s}$) thermally and reveals further that the endo process, leading to the syn dimer should be favored over the alternative exo process which would give the anti dimer. Hence, in those experiments in which a free cyclobutadiene is generated, the predicted endo process was observed.

The first attempt to synthesize cyclobutadiene was reported by Kekulé in 1872 (17). The early work on synthesis of cyclobutadiene has been extensively reviewed (see reviews). Of the early attempts, the work by Willstatter and Schmadel in 1905 was noteworthy (30). They heated 1,2-dibromocyclobutane in powdered KOH at 210°C and obtained acetylene presumably through a cyclobutadiene intermediate. The initial investigations were in general unrewarding until a fresh approach to the problem was advanced by Longuet-Higgins and Orgel who predicted the possibility of stabilization of cyclobutadiene through complexing with transition metals (31). Following this prediction, several synthetic methods for the generation of cyclobutadiene or its derivative as a reactive intermediate have been developed (32, 33, 34a). The question of whether or not such a cyclobutadiene intermediate is actually produced in any given case was usually answered on the basis of indirect evidence *i.e.*, through the isolation of a cyclobutadiene dimer or other Diels-Alder adduct, a cleavage product such as acetylene, or a cyclobutadiene-metal complex; or it can be a product arising from any one of these primary transformation products through further chemical change or rearrangement. Recently, however, good evidence for free cyclobutadiene has become available through experiments of Grubbs and Grey (34b).

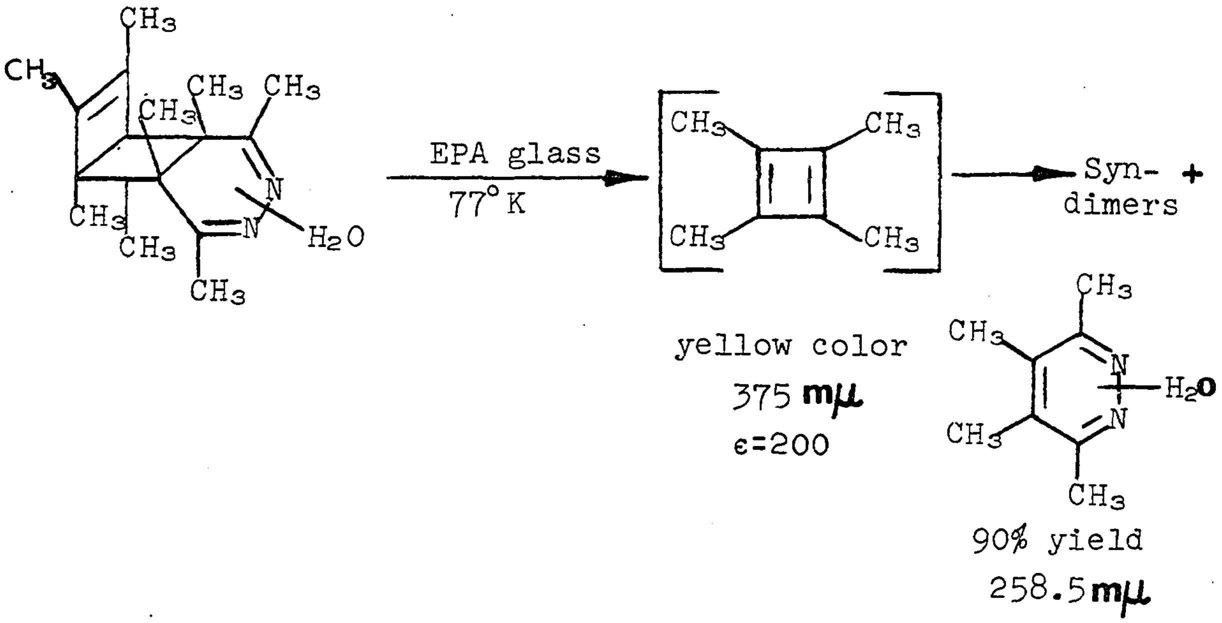
Through the years, chemists later realized that in order to determine the ground state geometry and spin multiplicity of cyclobutadiene, it has to be isolated at very low temperatures and observe spectroscopically. The 1960's was characterized by tremendous upsurge in the synthesis of precursors which upon photolysis provide cyclobutadiene in a matrix exclusively and efficiently.

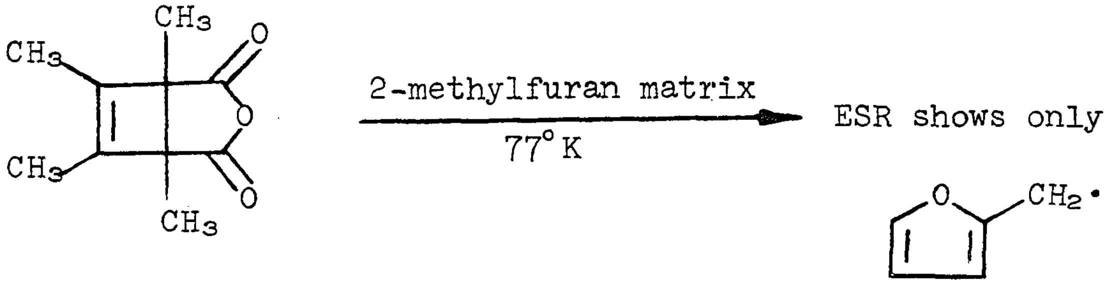
The early low temperature work utilized glass matrices for isolation and u.v. for detection. Maier and Schneider claimed to have observed the u.v. absorption of several substituted cyclobutadiene by photolyzing substituted cyclobutenedicarboxylic anhydride in a THF glass matrix at 77°K (35). For example, 3,4-di-tertiary-butylcyclobutenedicarboxylic anhydride when irradiated at 77°K in a THF glass matrix resulted in a yellow color which exhibits an absorption maximum at 410 mμ, and which disappeared immediately when the matrix melted. The cyclobutadiene-cyclopentadienone adducts and the cyclopentadienone dimers



cyclobutadiene-cyclopentadienone adducts
+
cyclopentadienone dimers

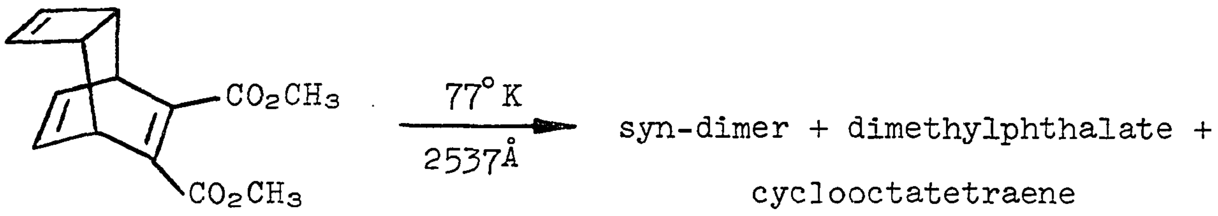
are the sole products isolated from the photolysis. The unequivocal assignment of the u.v. absorption to cyclobutadiene was however not conclusive because of the presence of cyclopentadienones. An independent route to generate substituted cyclobutadiene that avoids the formation of cyclopentadienones was then devised. The appropriate compound was photolyzed in an EPA (ether-isopentane-ethanol) glass at 77°K and resulted in the formation of a yellow color (λ_{max} 375 mμ)





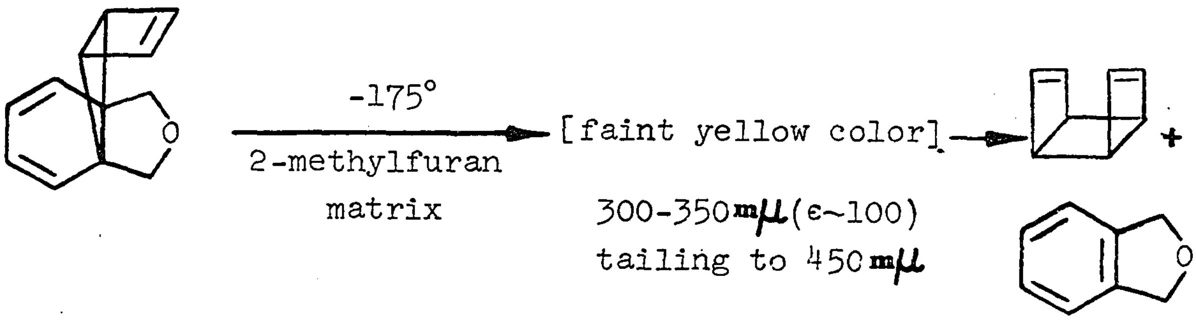
assigned to tetramethycyclobutadiene. Also, tetramethylcyclobutenedicarboxylic anhydride was photolyzed until the yellow color appeared; e.s.r. of the yellow matrix showed a signal attributed to the radical formed from 2-methylfuran.

Miller and Hedaya photolyzed the appropriate compound at 77°K in a 1:1 ether-isopentane glass matrix, and subsequent warming produced the syn-dimer, dimethylphthalate, and



cyclooctatetraene (36).

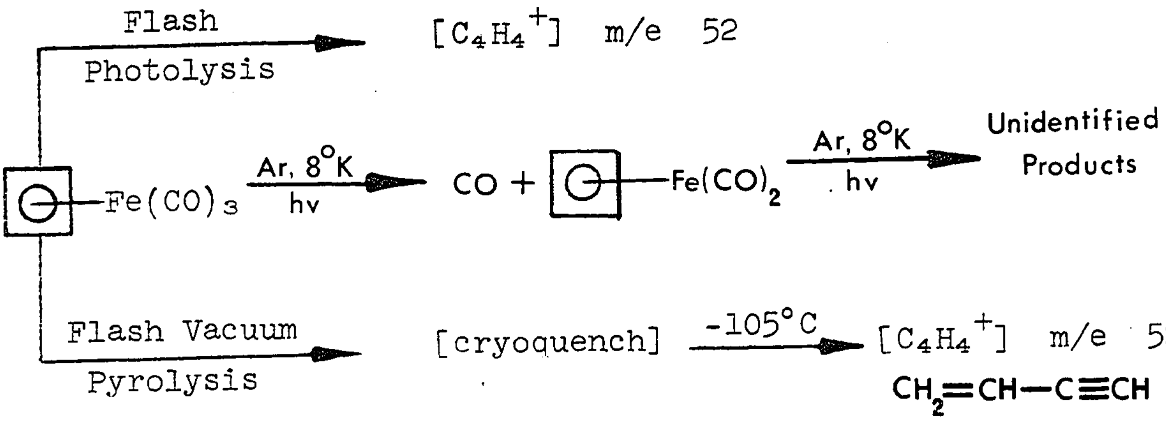
Masamune et al. photolyzed the compound shown below at -175°C in a 2-methylfuran matrix and produced a faint yellow color which disappeared upon warming to form the syn-dimer (37a). The difference between two u.v. spectra before and

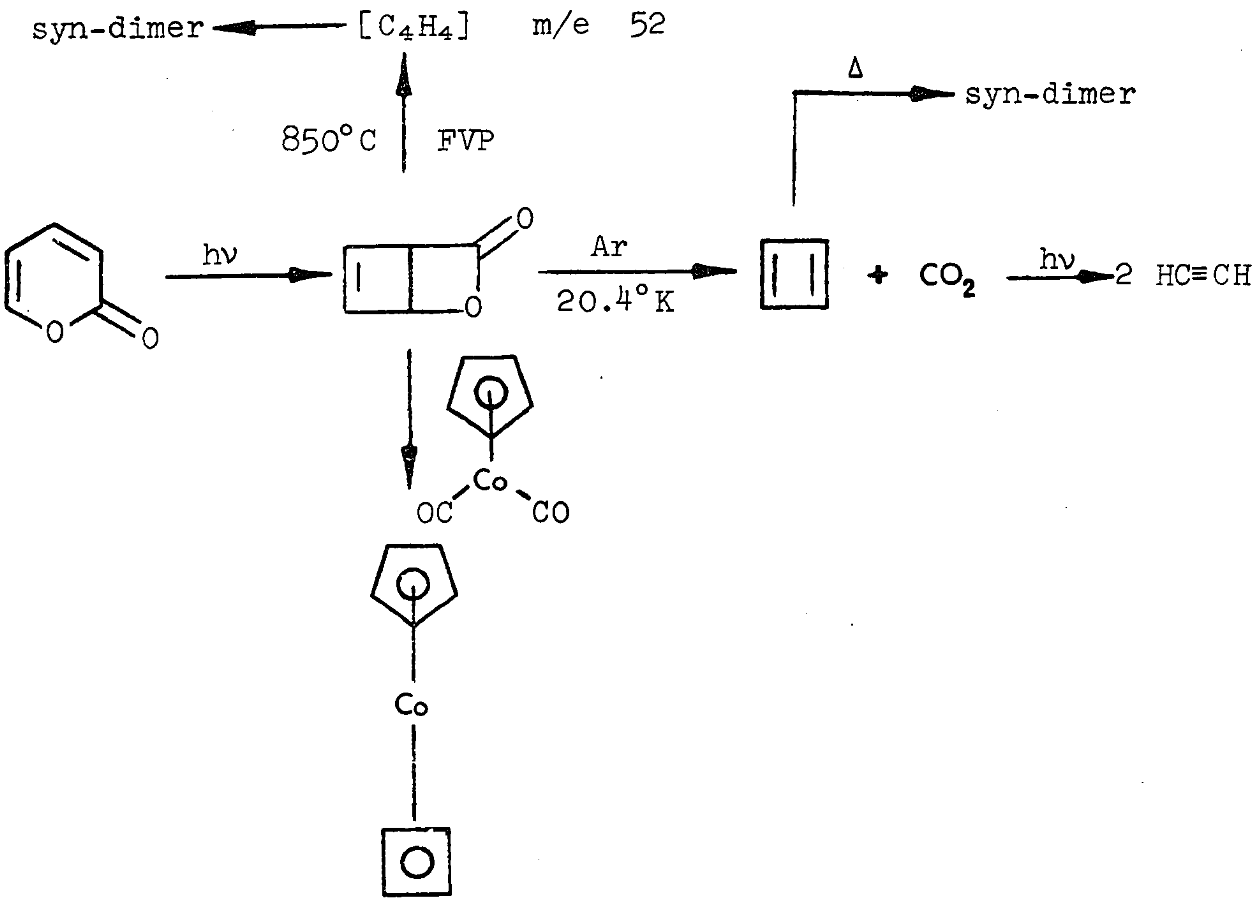


after warming was taken to represent cyclobutadiene. Thus the broad absorption with a maximum over 300-305 mμ (E ∿ 100) and tailing to 400 mμ was attributed to cyclobutadiene. Following the above result, Maier and Hoppe (37b) reported a u.v. absorption at 301 mμ (attributed to cyclobutadiene) upon photolysis of cyclobutenedicarboxylic anhydride in an ether-THF-isopentane matrix at -196°.

The first cyclobutadiene precursor to be examined using inert gas matrix and i.r. was cyclobutadieneirontricarbonyl. Several workers have claimed that upon flash photolysis (38) or flash vacuum pyrolysis (39), this iron-complex generates a $[C_4H_4^+]$ ion detected by mass spectrometry. The $[C_4H_4^+]$ ion detected in the mass-spectrometer upon flash vacuum pyrolysis of cyclobutadieneirontricarbonyl, however, was found to be due to vinylacetylene (40). Moreover, matrix isolation of this complex in argon and photolysis at 8°K resulted in the formation of carbon monoxide and cyclobutadieneirondicarbonyl which further decomposed to form uncharacterized products; there was no evidence for cyclobutadiene or cyclobutadiene-derived products (41).

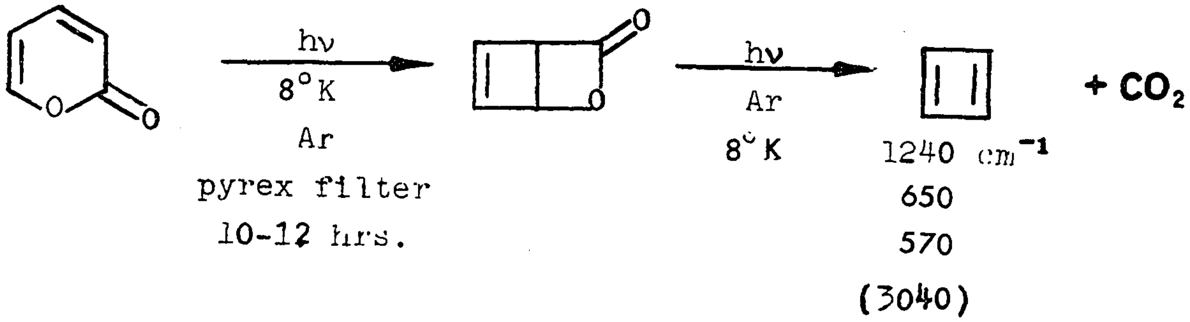
Corey and Streith have reported the photochemical conversion of α-pyrone to an isomeric β-lactone at -20°C, and suggested that the β-lactone would be a possible precursor to cyclobutadiene (42). A cobalt complex of cyclobutadiene has

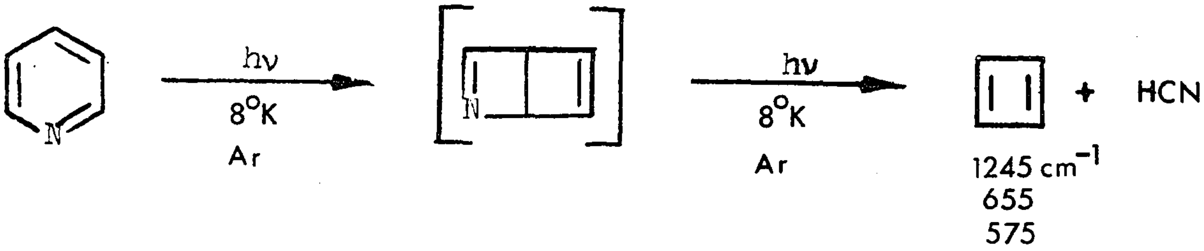

Flash
Photolysis
[C4H4+] m/e 52
Fe(CO)3
Ar, 8°K
hν
CO +
Fe(CO)2
Ar, 8°K
hν
Unidentified
Products
Flash Vacuum
Pyrolysis
[cryoquench]
-105° C
[C4H4+] m/e 52
CH2=CH—C≡CH


syn-dimer
[C4H4] m/e 52
850° C
FVP
O
O
hν
O
O
Ar
20.4° K
Δ
syn-dimer
+ CO2
hν
2 HC≡CH
Co
OC
CO
Co

been prepared by irradiation of the β-lactone in the presence of the appropriate cobalt carbonyl complex (43), and evidence has been presented that flash vacuum pyrolysis of the β-lactone give cyclobutadiene (34).

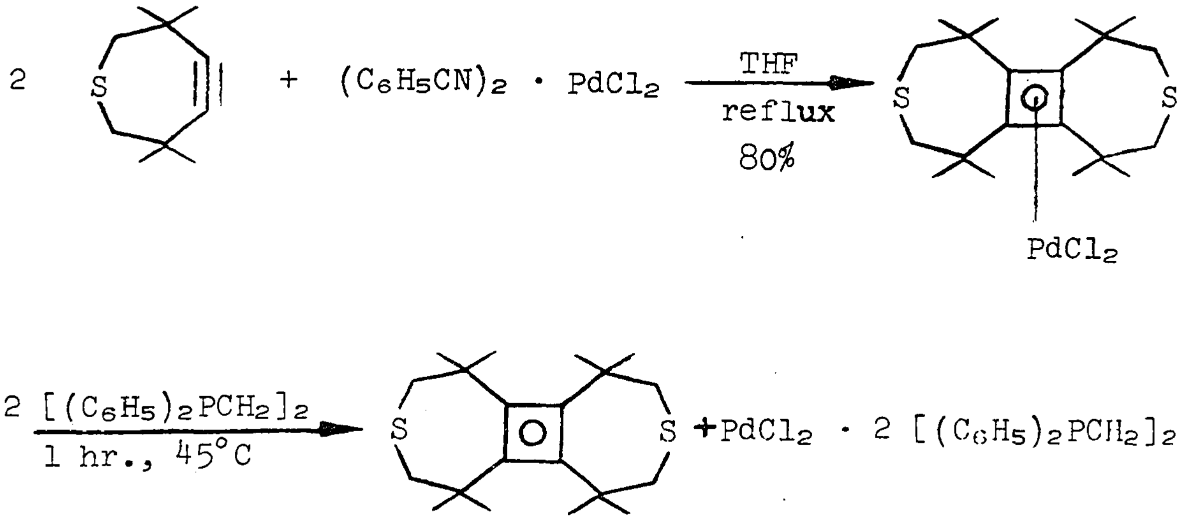
After exactly one hundred years, two groups have independently generated cyclobutadiene in an inert gas matrix and observed its i.r. absorptions. C. Y. Lin and A. Krantz (44), irradiated the β-lactone (obtained from photolysis of α-pyrone) in argon for 3.6 hr. at 20.4°K and observed the formation of carbon dioxide (2350 and 662 cm^{-1}), and the appearance of major bands at 1236, 653 and 573 cm^{-1} tentatively assigned to cyclobutadiene. Continued irradiation resulted in the formation of acetylene (747 cm^{-1}) and warming formed the syn-dimer. O. L. Chapman, C. L. McIntosh and J. Pacansky have succeeded not only in observing the i.r. bands of cyclobutadiene but also provided evidence for the square planar (D_{4h}) structure of cyclobutadiene (45-46). They generated the β-lactone <u>in situ</u> using a Pyrex filter since the β-lactone undergoes rearrangement to the tricyclo[2.1.1]pyran-2-one during matrix deposition. Removal of the Pyrex filter and continued irradiation (through quartz) caused destruction of the β-lactone and gave rise to new bands at 1240, 650, and 570 cm^{-1} in addition to the carbon dioxide bands at 2340 and 660 cm^{-1}. In experiments with an unusually thick matrix, an additional band at 3040 cm^{-1} can be observed. An intensity





versus time plot showed that the four bands were due to the same primary product. Confirmatory evidence was found in the observation that these bands disappear on over irradiation (to form acetylene), or warming above 35°K (to form the syn-dimer). Also, irradiation of pyridine isolated in argon at 8°K gave rise to HCN and cyclobutadiene but not as primary products. Presumably, the reaction proceeded via the pyridine valence tautomer reported by Wilzbach and Rausch (47). Group theory predicted four infrared active fundamental bands for D_{4h} (square, planar) cyclobutadiene and seven for D_{2h} (rectangular, planar) cyclobutadiene. The simplicity of the cyclobutadiene infrared spectra consisting of four fundamental bands led to the tentative conclusion that cyclobutadiene has D4h symmetry.

Recently, derivatives of cyclobutadiene stable at room temperature have been synthesized. Kimling and Krebs reported the synthesis and physical properties of the derivative shown below (48). Masamune *et al.* synthesized methyl tri-*tert*-butylcyclobutadiene carboxylate and tri-*tert*-butylcyclobutadiene by a classical ring-expansion method via Δ^2-cyclopropenylcarbene (49). Both compounds are extremely reactive toward oxygen and decomposed instantaneously in contact with air, giving three or more oxygen-containing compounds. They both react with dimethyl acetylenedicarboxylate to give quantitative yields of adducts which were further characterized. Using cyclopentadiene as reference, tri-*tert*-butylcyclobutadiene showed a paramagnetic contribution by induced ring current of 1.04 ppm. The same authors estimate a value of 1.18 ppm paramagnetic contribution by cyclobutadiene.



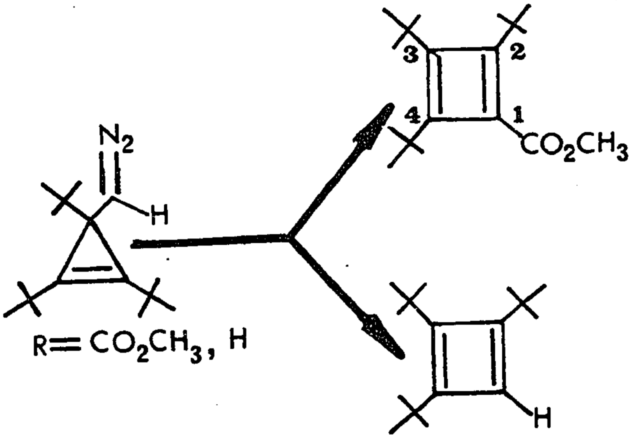
m. p. 240°C

M. S.: m/e = 336 (M)

^{1}H-NMR (60 MHz, CDCl$_3$): δ = 2.50 (s, 8H, CH$_2$), 1.26 ppm (s, 24H, CH$_3$)

^{13}C-NMR (22.63 MHz, CDCl$_3$, broad band decoupled): δ = -2.70 (CH$_3$),
-41.6 (C quat.), -52.1 (CH$_2$), -146.5 ppm (C$_{\text{olef.}}$)

Raman (cryst.) : $\nu_{c=c}$ 1590 cm^{-1}



m.p. 70.0°; nmr (methylcyclohexane-d_{14}) δ 1.13 (s, 18), 119 (s, 9), 3.45 (s, 3); cmr (methylcyclohexane-d_{14}) δ 29.73 (CH_3C), 31.6, 31.8 (quart, C of t-Bu), 50.4 (OCH_3), 147.0 (C-3), 154.3 (C-1 overlaps with C-2, C-4), 165.7 (C=0); u.v. (pentane), 425 mμ

nmr (tetrahydrofuran-d_8) δ 1.05 (s, 9), 1.22 (s, 18), 5.38 (s, 1)

RESULTS AND DISCUSSION

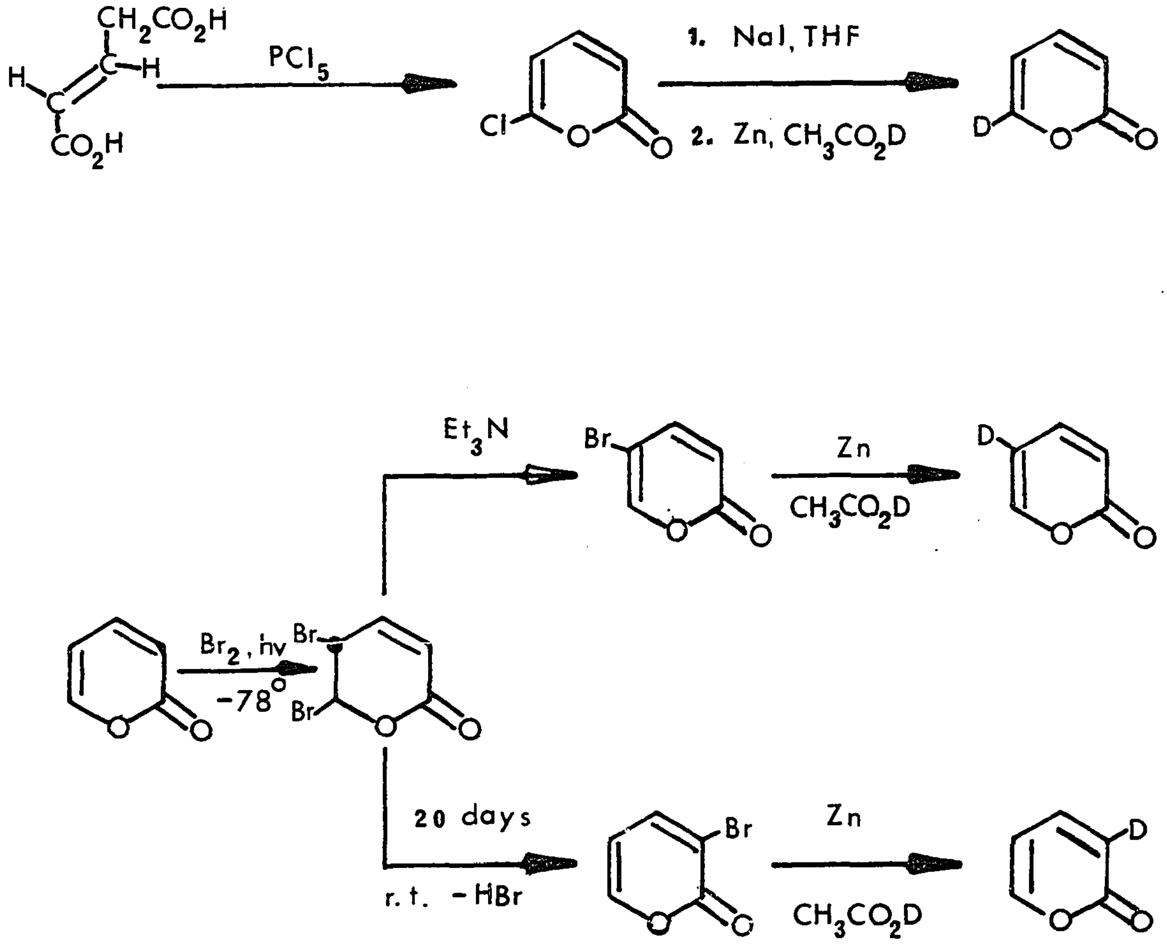
The synthesis of monodeuterio-, 1,2-dideuterio-, and 1,3-dideuteriocyclobutadiene depended on the preparation of the appropriate deuterated α-pyrones, photoisomerization to the β-lactones, and photoelimination of carbon dioxide.

The preparation of deuterated α-pyrones was accomplished by zinc/deuterioacetic acid reduction of the corresponding bromo- or chloro-α-pyrones. The bromo-α-pyrones were synthesized according to the procedure published by W. H. Pirkle and Martin Dines (50). The 4,6-dichloro-α-pyrone was synthesized from 3-chloroglutaconic acid. Schemes I, II and III illustrate the synthesis of the deuterated α-pyrones.

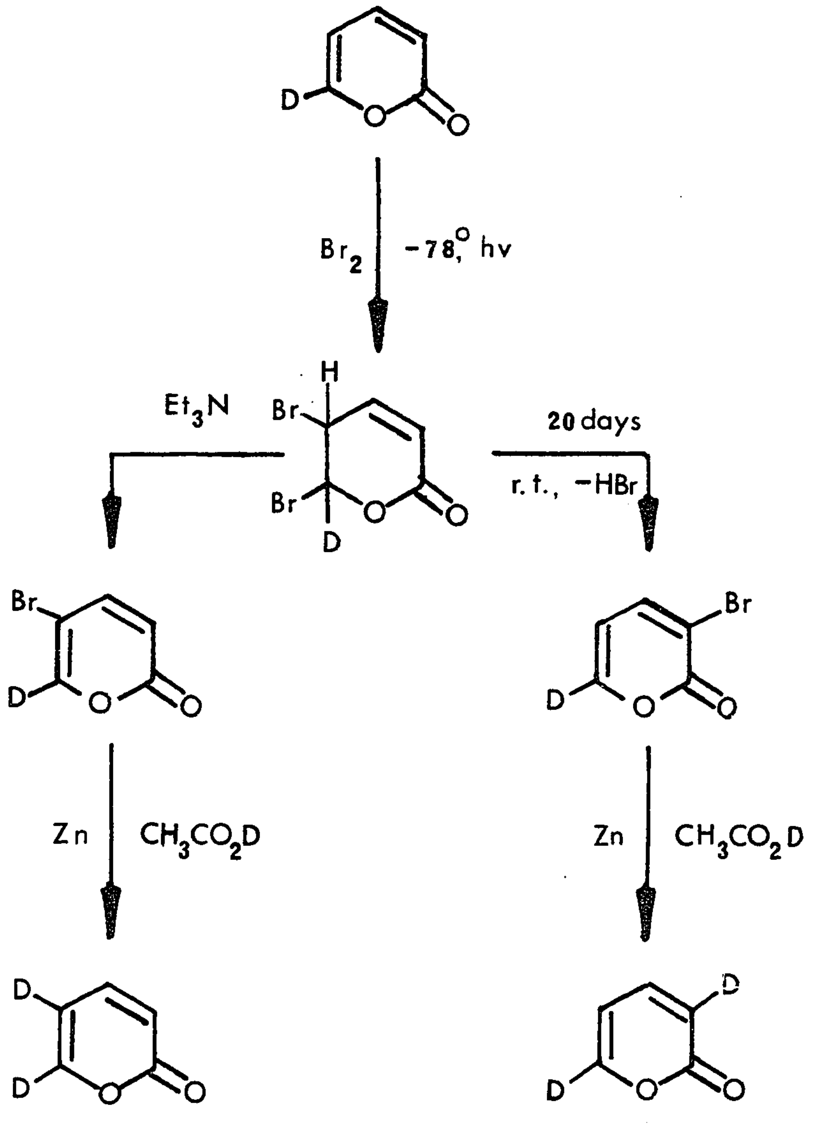
The position of deuterium and the deuterium content in the α-pyrones were ascertained from the characteristic coupling constants and integration areas observed for the remaining hydrogens (51a). Table 1 shows the nmr parameters of the deuterated α-pyrones. Figures 1, 2 and 3 shows the nuclear magnetic resonance spectra of the deuterated α-pyrones.

The exact deuterium content of the deuterated α-pyrones was determined at low ionizing voltage (at 14 e.v. where the M-1 peak is negligible) after correction for naturally occurring carbon thirteen and deuterium. In all cases when

Scheme I


CH2CO2H
H
C
C—H
CO2H
PCl5
Cl
O
O
1. NaI, THF
2. Zn, CH3CO2D
D
O
O
Et3N
Br
Zn
CH3CO2D
D
Br2, hν
−78°
Br
Br
20 days
r.t. −HBr
Br
Zn
CH3CO2D
D

Scheme II


D
Br_2
-78°, hv
H
Br
Br
D
Et_3N
20 days
r.t., -HBr
Br
D
Br
D
Zn
CH_3CO_2D
Zn
CH_3CO_2D
D
D
D
D

Scheme III

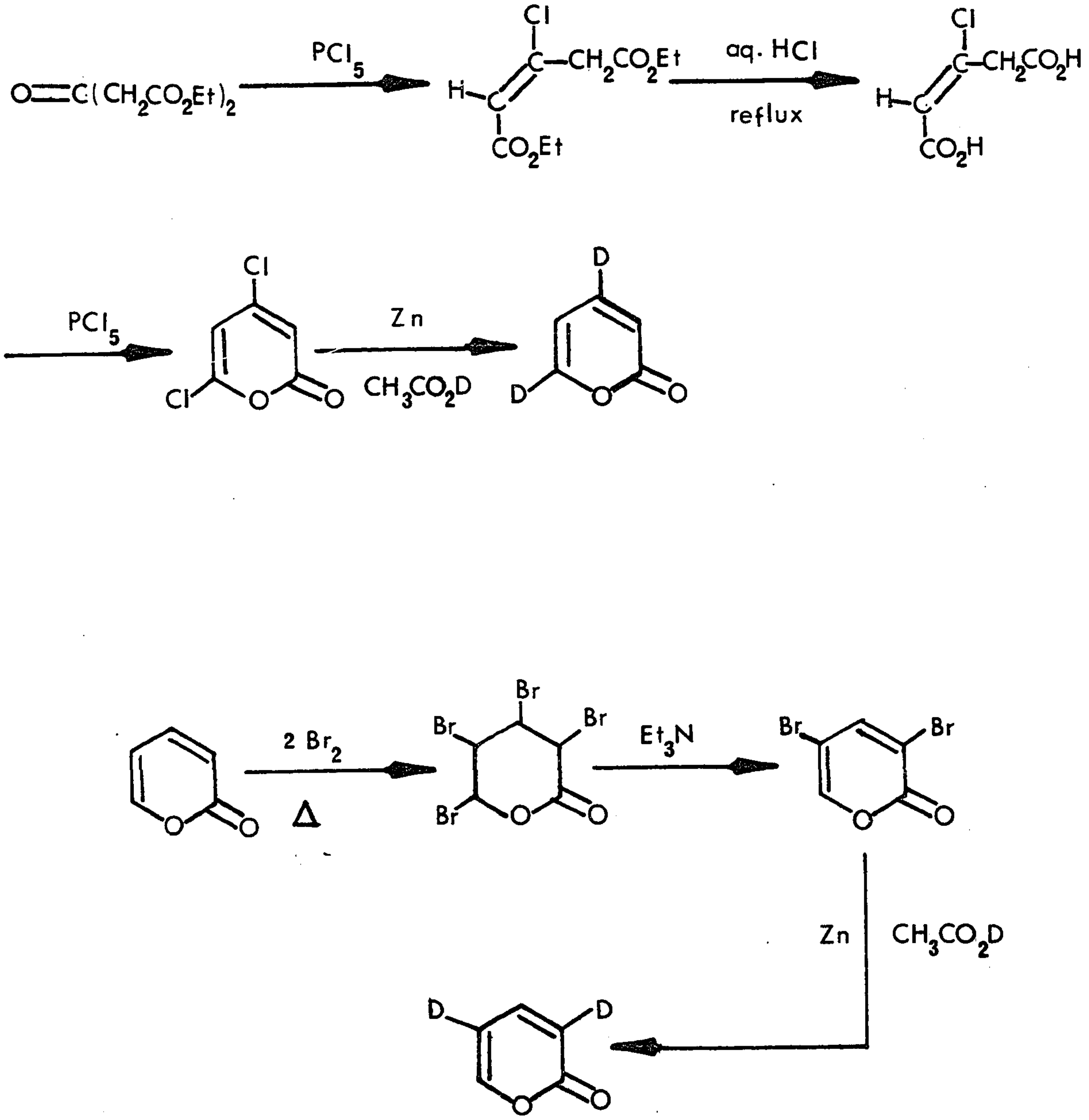
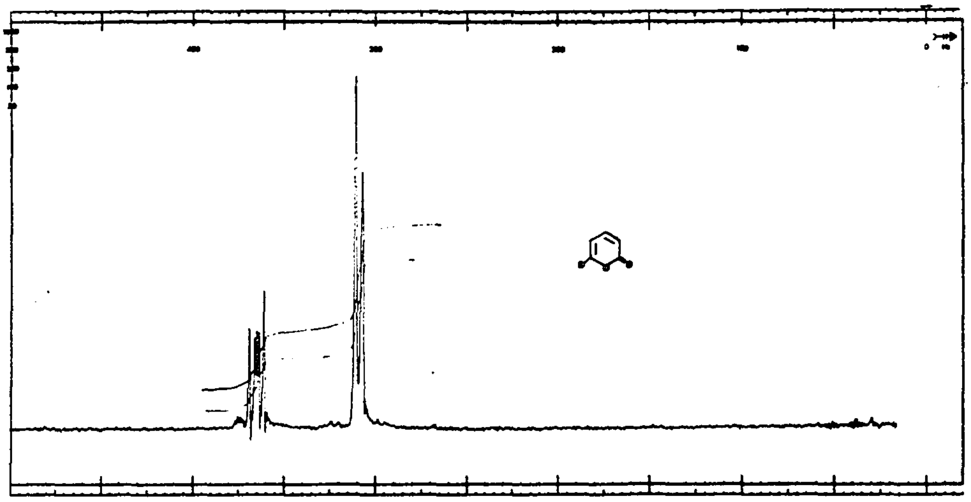

O=C(CH2CO2Et)2
PCl5
Cl
C—CH2CO2Et
H—C
CO2Et
aq. HCl
reflux
C—CH2CO2H
CO2H
PCl5
Cl
Zn
CH3CO2D
D
2 Br2
Δ
Br
Et3N
Zn
CH3CO2D
D

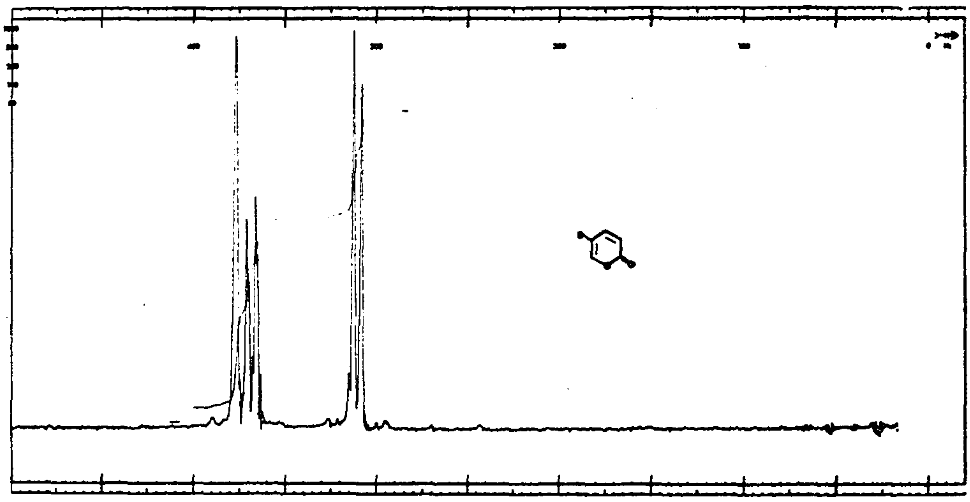
Figure 1. Nuclear magnetic resonance spectra

Top: α-pyrone-6-d_1

Middle: α-pyrone-5-d_1

Bottom: α-pyrone-3-d_1


400
300
200
100
0


400
300
200
100
0

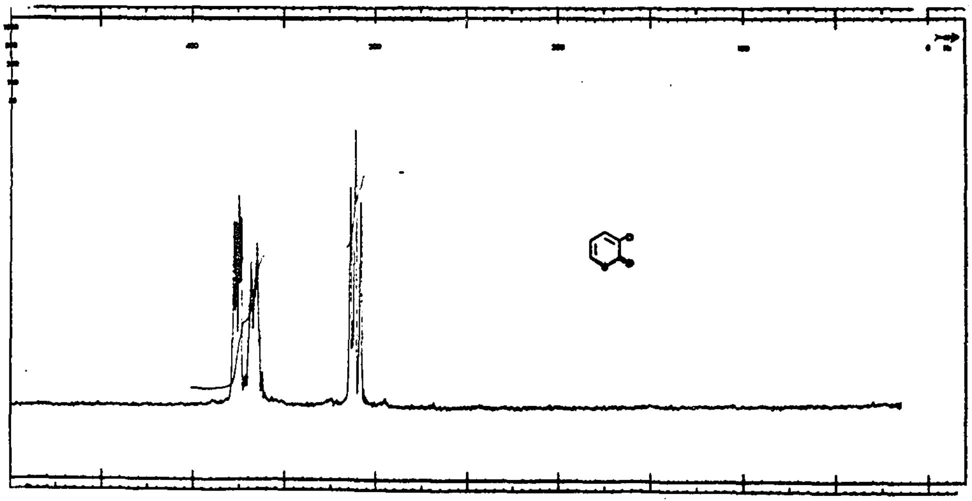
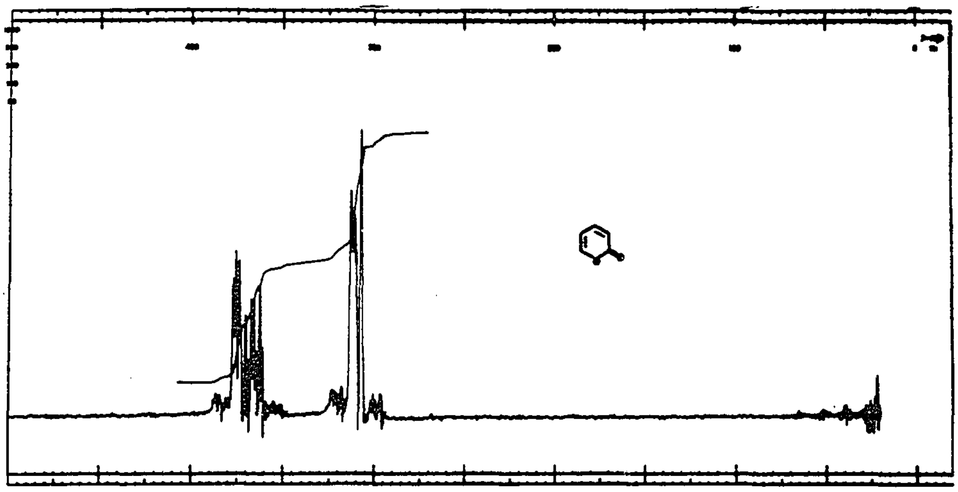

400
300
200
100
0

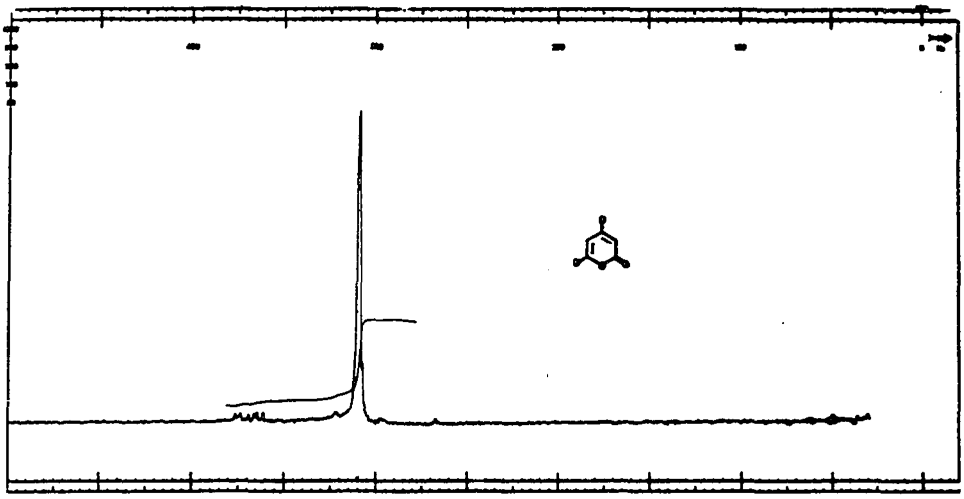
Figure 2. Nuclear magnetic resonance spectra

Top: α-pyrone

Middle: α-pyrone-4,6-d_2

Bottom: α-pyrone-3,5-d_2





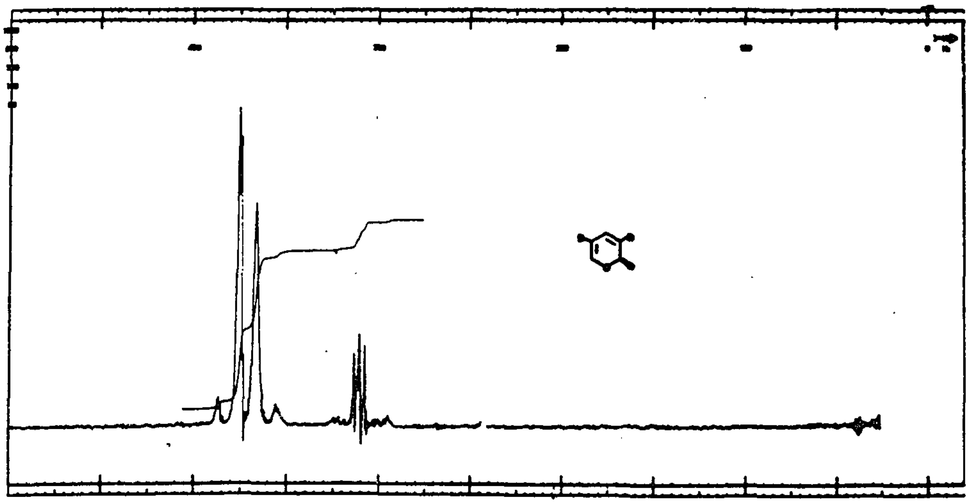
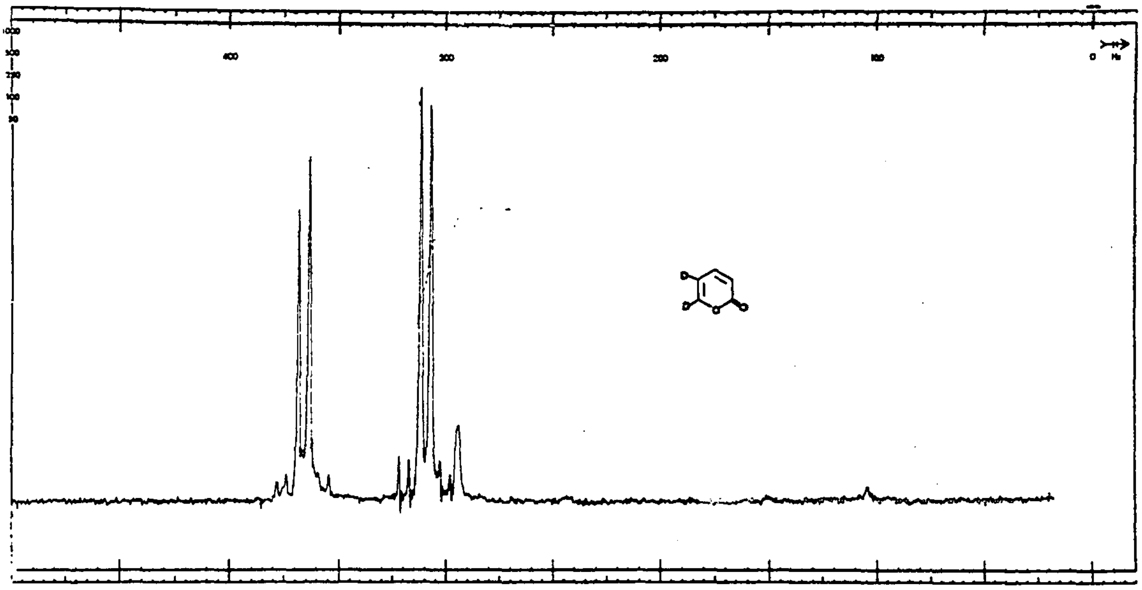


Figure 3. Nuclear magnetic resonance spectra

Top: α-pyrone-5,6-d_2

Bottom: α-pyrone-3,6-d_2


400
300
200
100
0
Hz

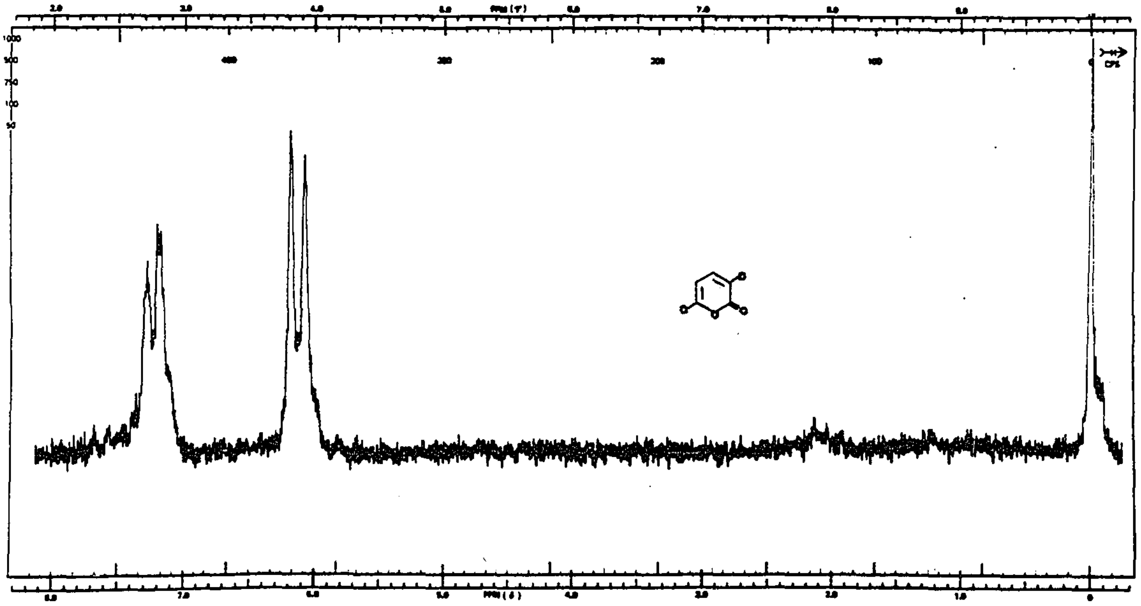

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
400
300
200
100
0
CPS
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

Table 1. NMR parameters of deuterated α-pyrones[a]

	Chemical Shifts (δ)				Coupling Constants (Hz)					
	H_3	H_4	H_5	H_6	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$
α-Pyrone	6.30	7.35	6.19	7.62	9.40	1.50	1.25	6.30	2.40	5.00
α-Pyrone-3-d_1		7.32	6.19	7.52				6.30	2.10	5.20
α-Pyrone-5-d_1	6.25	7.38		7.55	9.50		1.20		2.40	
α-Pyrone-6-d_1	6.15	7.32	6.23		9.50	–[b]		6.30		
α-Pyrone-3,5-d_2		7.34		7.52					2.10	
α-Pyrone-4,6-d_2	6.30		6.32			–[b]				
α-Pyrone-3,6-d_2		7.24	6.12					6.20		
α-Pyrone-5,6-d_2	6.27	7.50			9.50					

[a] Samples run as 10-20% solutions in CCl_4; nmr taken on Varian A-60, HA100, and Perkin-Elmer R-20B.

[b] Value could not be measured from the spectrum.

enough sample was available, the C, H analysis independently confirmed the deuterium content. Table 2 indicates the deuterium content from mass spectral measurement using the Atlas CH-4 mass spectrometer.

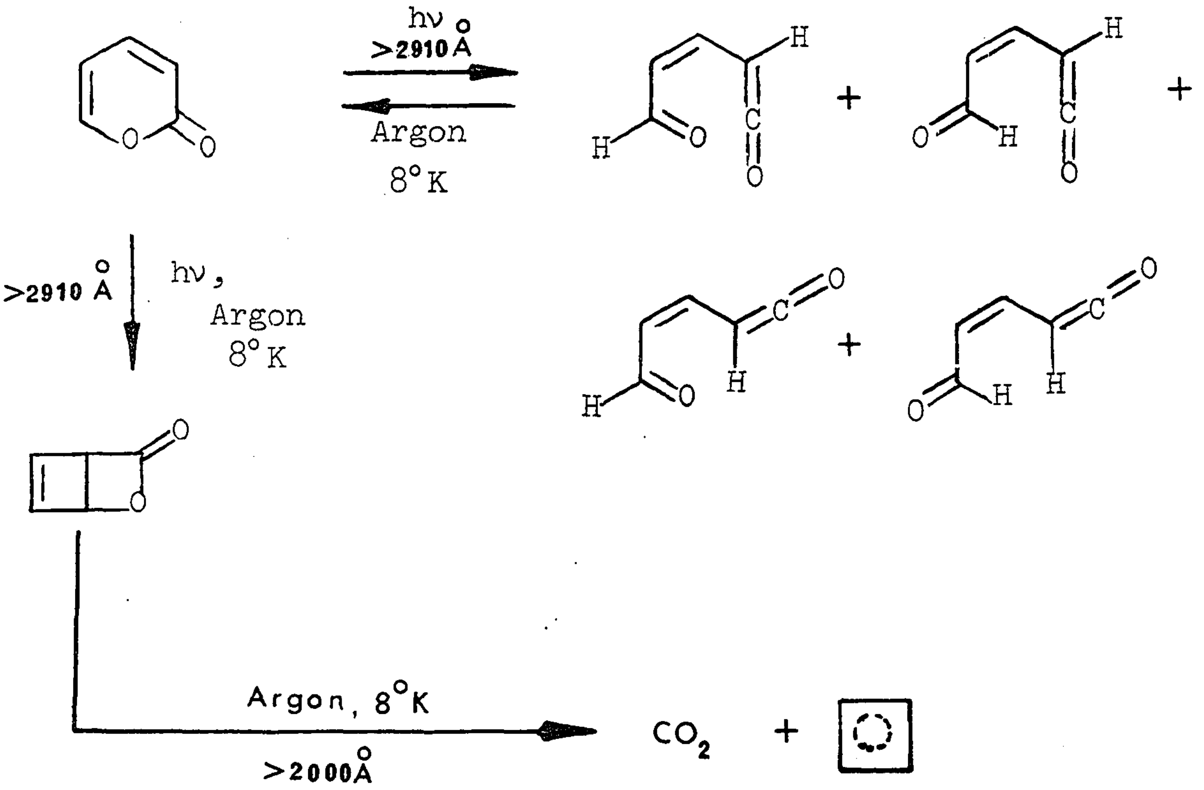
The matrix isolation and photolysis of the deuterated α-pyrones were done in the manner previously described for α-pyrone (45-46). The matrix used was argon, and the matrix to α-pyrone ratio is 500:1 to 1000:1. Irradiation of α-pyrone through a Pyrex filter (>2910Å) at 8°K initially forms the

Table 2. Per cent deuterium of deuterated α-pyrones[a]

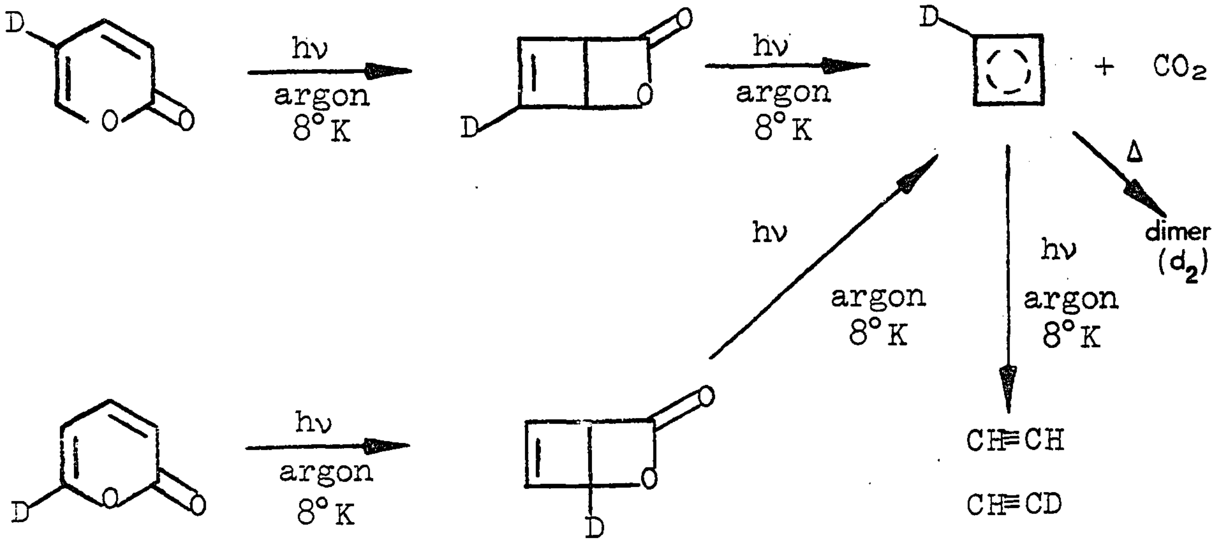
	D_0	D_1	D_2
α-Pyrone-6-d_1	8%	92%	0%
α-Pyrone -5-d_1	16%	84%	0%
α-Pyrone-3-d_1	13%	87%	0%
α-Pyrone-3,5-d_2	3%	33%	64%
α-Pyrone-4,6-d_2	1%	14%	85%
α-Pyrone-5,6-d_2	0%	14%	86%
α-Pyrone-3,6-d_2	0%	19%	81%

[a] Measured at 14 e.v. and corrected for naturally occurring carbon thirteen and deuterium.

aldehyde-ketene which equilibrates with α-pyrone and slowly converts α-pyrone to the β-lactone. After 10-12 hr. irradiation, the α-pyrone is converted solely to the β-lactone. Removal of the Pyrex filter and continued irradiation (through quartz) at 8°K causes the destruction of the matrix isolated β-lactone and gives carbon dioxide and cyclobutadiene. In all cases, the destruction of β-lactone and the formation of deuteriocyclobutadiene were followed by plotting the absorbance *versus* time of the starting material and the desired specie.

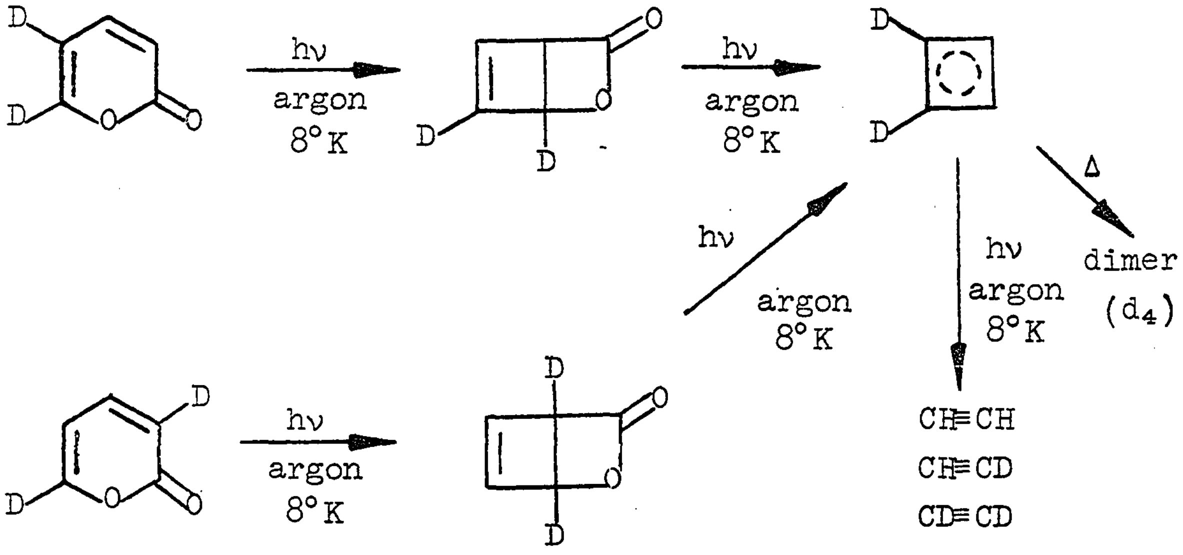


Irradiation of α-pyrone-5-d_1 (84% d_1) and 2-pyrone-6-d_1 (92% d_1) matrix isolated in argon at 8°K gives different monodeuterio β-lactones but the same monodeuteriocyclobutadiene



(1223, 780, 654, 583, 576, 535 cm^{-1}) in the region from 500 cm^{-1} to 4,000 cm^{-1}. An extra band appears at 460 cm^{-1} in the region from 200-500 cm^{-1} (22). Continued irradiation converts the monodeuteriocyclobutadiene to acetylene (3260, 735 cm^{-1}) and monodeuterioacetylene (3330, 2580, 687 cm^{-1}). The deuterium content of the acetylenes and the syn-dimer were determined by warming the matrix containing monodeuteriocyclobutadiene and acetylene and pumping the contents into a trap (77°K) and examining the trapped products by mass spectrometry. In the two cases mentioned above, the mass spectrum at 14 e.v. shows parent ions for cyclobutadiene dimer containing two deuterium atoms (m/e 106), acetylene (m/e 26) and acetylene-d_1 (m/e 27). The elemental composition of the cyclobutadiene dimer (m/e 106) was established by exact mass determination to be $C_8H_6D_2$ (calculated: 106.075154, Found: 106.074921). The ratio of acetylene to acetylene-d_1 determined at 16 e.v. was 56.6:43.4 which is consistent with the expected ratio of 58:42 based on α-pyrone-5-d_1(84% d). Similarly, the ratio of acetylene to acetylene-d_1 obtained from α-pyrone-6-d_1(92% d) was 51.7:48.3 determined at 16 e.v.) which is consistent with the expected ratio of 54:46 based on the starting α-pyrone.

In similar fashion irradiation of α-pyrone-5,6-d_2 (86% d_2, 14% d_1) and α-pyrone-3,6-d_2 (81% d_2, 19% d_1) gives



cyclobutadiene-1,2-d_2 (1212, 1188, 654, 583 cm^{-1}) in the region from 500-4,000 cm^{-1}. In a separate experiment, irradiation of α-pyrone-5,6-d_2 gives additional bands at 447 and 479 cm^{-1} in the region from 200-500 cm^{-1}. Figure 4 shows the infrared spectra (200-4,000 cm^{-1}) of matrix isolated α-pyrone-5,6-d_2 and its photolysis products. Figure 5 shows the plot of the relative intensity of significant bands as a function of irradiation time. Irradiation of cyclobutadiene-1,2-d_2 gives acetylene (3260, 735 cm^{-1}), acetylene-d_1 (3330, 2580, 687 cm^{-1}), and acetylene-d_2

Figure 4. Infrared spectra

Top: α-pyrone-5,6-d_2 matrix isolated in argon at 8°K

Middle: Photo-α-pyrone-5,6-d_2 matrix isolated in argon, prepared by 11-12 hours irradiation (>2910 A) of α-pyrone-5,6-d_2 at 8°K

Bottom: Photo-α-pyrone-5,6-d_2 after irradiation for 145 minutes through quartz at 8°K. Bands at 2340 and 660 cm^{-1} are due to carbon dioxide. Bands at 1212, 1188, 770, 654, 583, 479, and 447 cm^{-1} are due to cyclobutadiene-1,2-d_2

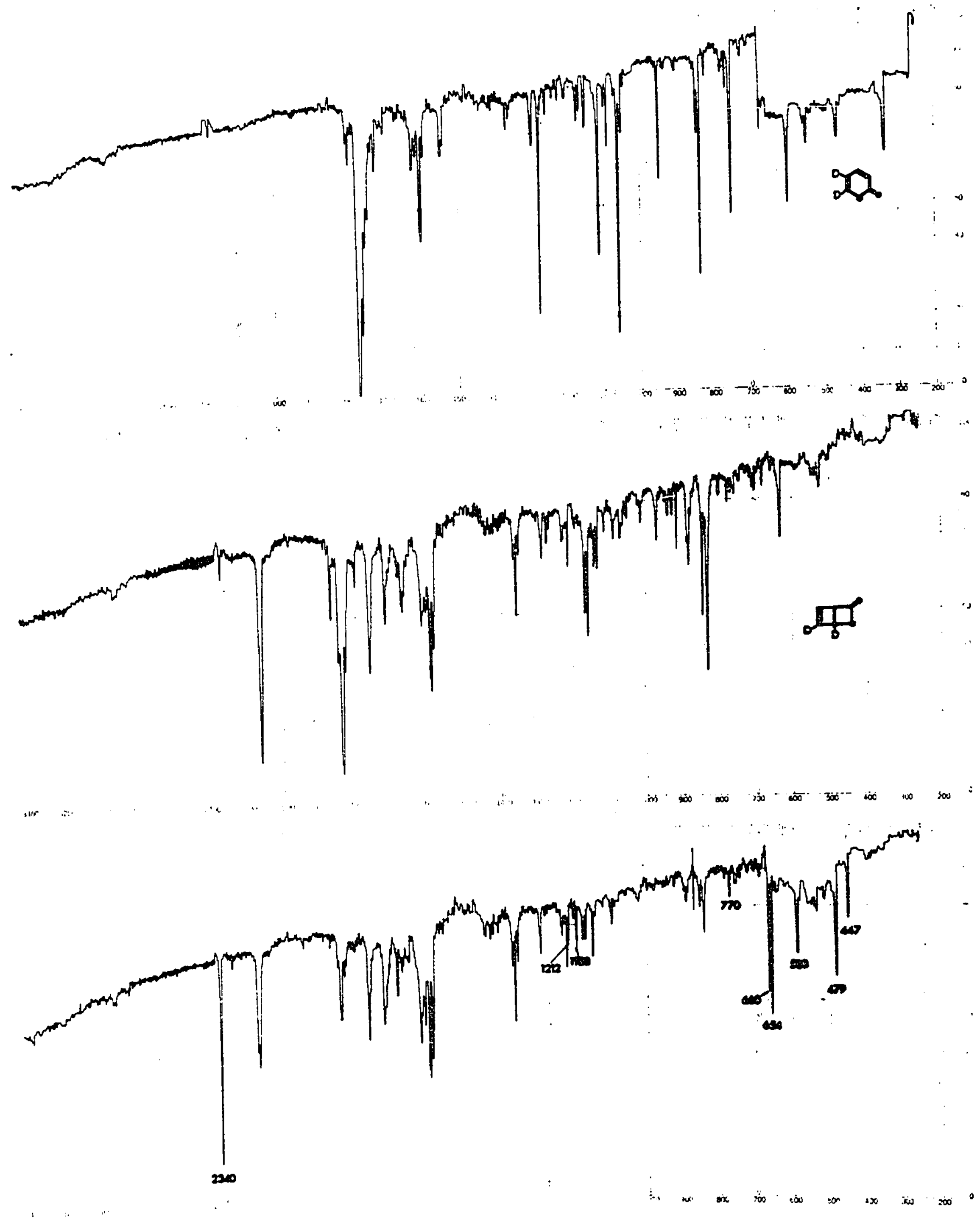
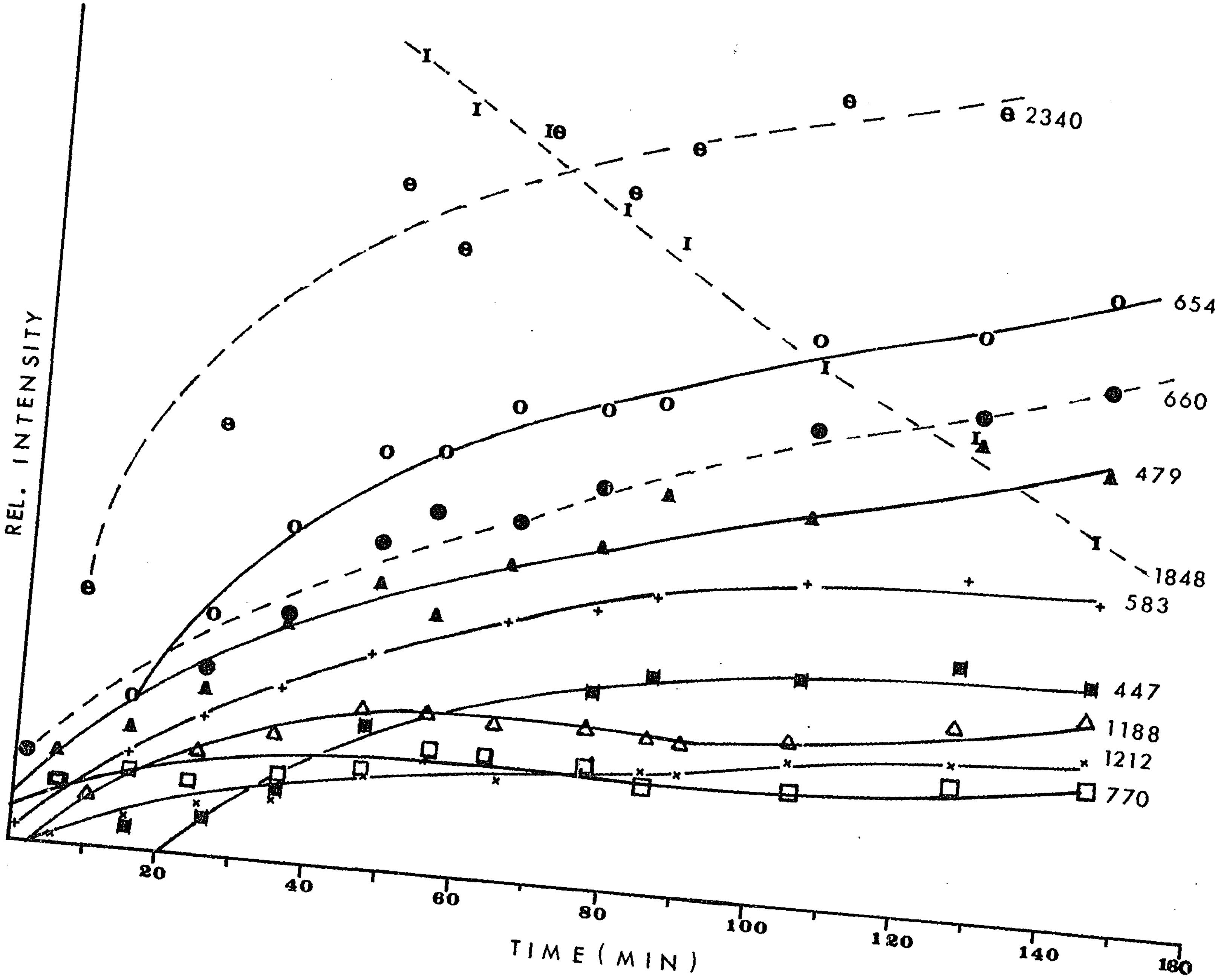

1000
900
800
700
600
500
400
300
200
2340
1212
1188
770
680
654
588
479
447

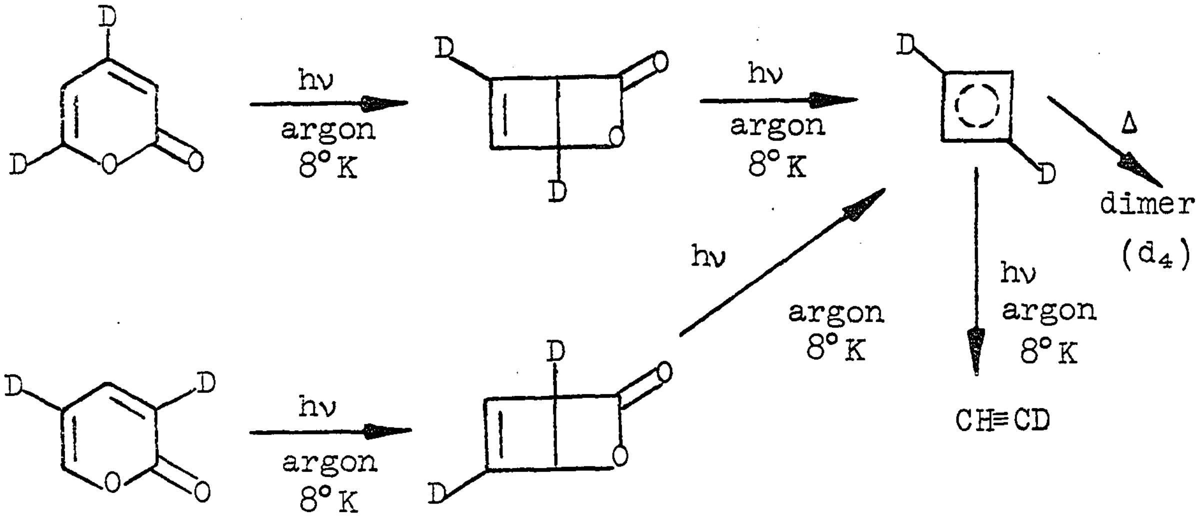
Figure 5. Plot of relative intensity of significant bands as a function of irradiation time. The 1848 cm^{-1} band is due to photo-α-pyrone-5,6-d_2 The cyclobutadiene-1,2-d_2 bands are 1212, 1188, 770, 654, 583, 479, and 447 cm^{-1}. Bands at 2340 and 660 cm^{-1} are due to carbon dioxide


REL. INTENSITY
TIME (MIN)
20
40
60
80
100
120
140
160
2340
654
660
479
1848
583
447
1188
1212
770

(2420 cm^{-1}). The mass spectrum of the product shows the cyclobutadiene-1,2-d_2 dimer (m/e 108), acetylene (m/e 26), acetylene-d_1 (m/e 27) and acetylene-d_2 (m/e 28). The elemental composition of the cyclobutadiene-1,2-d_2 dimer (m/e 108) obtained from α-pyrone-5,6-d_2 was established by exact mass determination to be $C_8H_4D_4$ (calculated: 108.096492. Found: 108.087708).

Similarly, cyclobutadiene-1,3-d_2 (1223, 1182, 781, 654, 633, 583, 535 cm^{-1}) is generated by irradiation of α-pyrone-4,6-d_2 (85% d_2, 14% d_1) and α-pyrone-3,5-d_2 (64% d_2, 33% d_1). In a separate experiment, irradiation of α-pyrone-3,5-d_2 gives additional bands at 424 and 458 cm^{-1} in the region from 200-500 cm^{-1}. Figure 6 shows the infrared spectra (200-4,000 cm^{-1}) of matrix isolated α-pyrone-3,5-d_2 and its photolysis products. Figure 7 shows the plot of the relative intensity of significant bands as a function of irradiation time. Photochemical cleavage of cyclobutadiene-1,3-d_2 gives only acetylene-d_1 (3330, 2580, 687 cm^{-1}). The mass spectrum of the product confirms the presence of acetylene-d_1 (m/e 27) and shows the parent ion of cyclobutadiene-d_2 dimer (m/e 108).

The formation of the same cyclobutadiene from different precursors in the three cases cited above leave no room for doubt that the product formed from α-pyrone is indeed cyclo-



butadiene (44, 45-46). The photochemical cleavage of cyclobutadiene-1,2-d_2 to acetylene, acetylene-d_1, and acetylene-d_2 also provides convincing evidence that the product is cyclo-

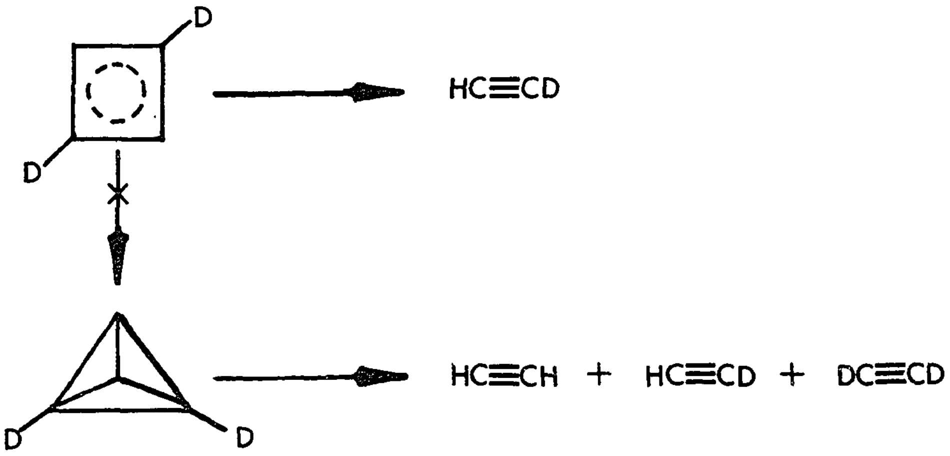
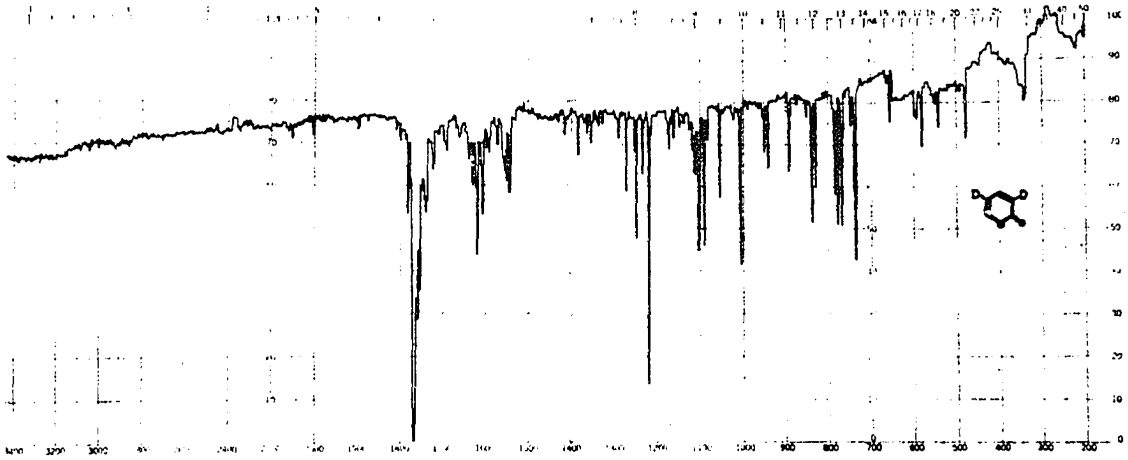


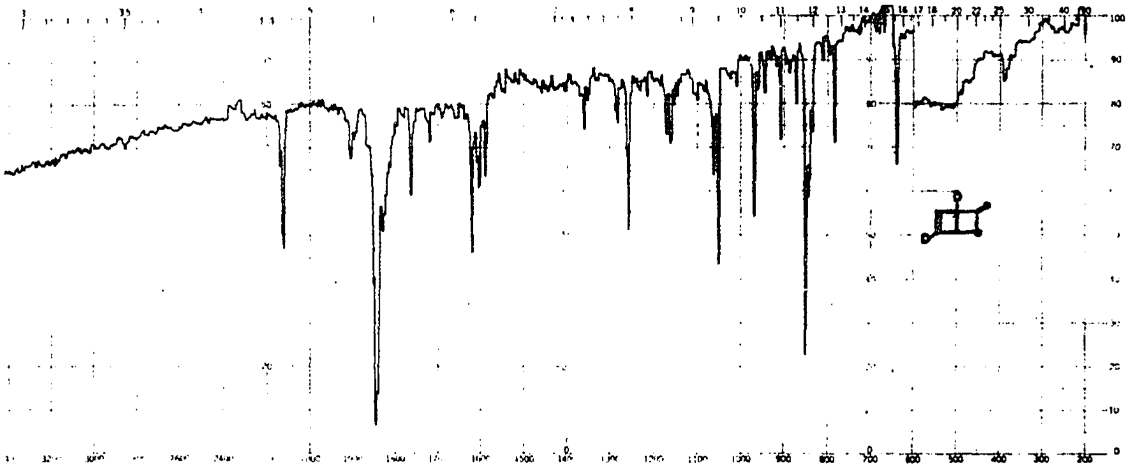
Figure 6. Infrared spectra

Top: α-pyrone-3,5-d_2 matrix isolated in argon at 8°K

Middle: Photo-α-pyrone-3,5-d_2 in argon, prepared by 11-12 hours irradiation (> 2910 Å) of α-pyrone-3,5-d_2

Bottom: Photo-α-pyrone-3,5-d_2 after irradiation for 134 minutes through quartz at 8°K. Bands at 2340 and 660 cm^{-1} are due to carbon dioxide. Bands at 1223, 1182, 781, 654, 633, 583, 535, 458, and 424 cm^{-1} are due to cyclobutadiene-1,3-d_2





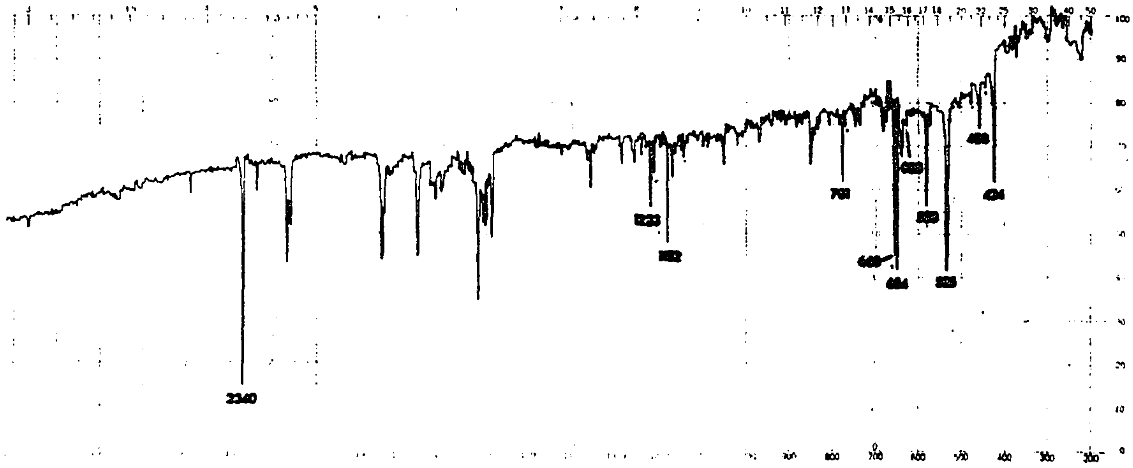
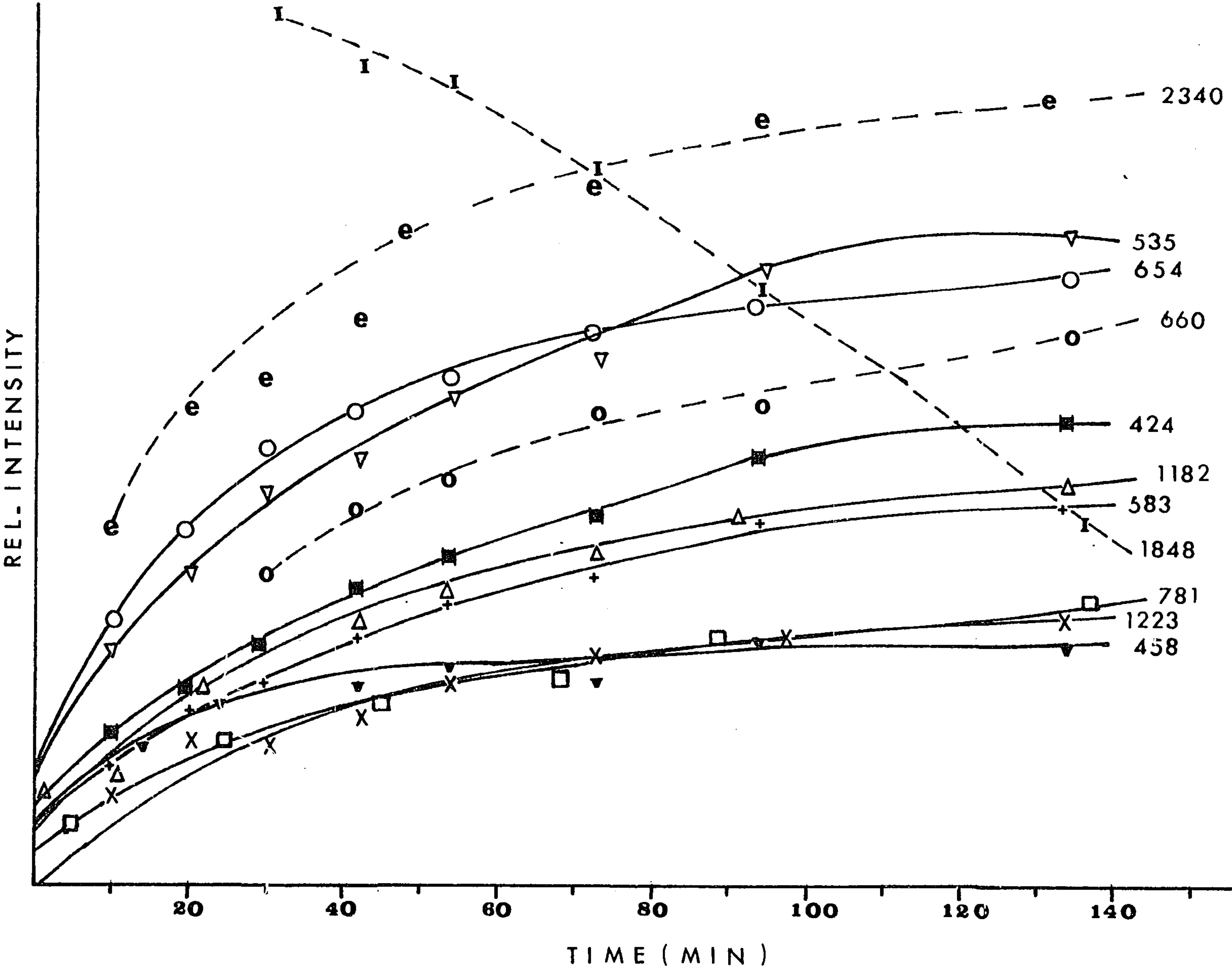

3340
1233
1182
761
648
634
620
582
535
488
434

Figure 7. Plot of relative intensity of significant bands as a function of irradiation time. The 1848 cm^{-1} band is due to photo-α-pyrone-3,5-d_2. The cyclobutadiene-1,3-d_2 bands are 1223, 1182, 781, 654, 633, 583, 535, 458, and 424 cm^{-1}. Bands at 2340 and 660 cm^{-1} are due to carbon dioxide


REL. INTENSITY
TIME (MIN)
20
40
60
80
100
120
140
160
2340
535
654
660
424
1182
583
1848
781
1223
458

butadiene. The cleavage of cyclobutadiene-1,3-d_2 to only acetylene-d_1 shows clearly that tetrahedrane is not an intermediate in the photochemical conversion of cyclobutadiene to acetylene. As shown above, a tetrahedrane intermediate would give rise to acetylene, acetylene-d_1, and acetylene-d_2. A further interesting observation comes from these studies. The rate of photochemical cleavage of the cyclobutadienes is 1,3-d_2 > 1,2-d_2 > d_1 > d_0. This could be due to an isotope effect on the rate constant for cleavage, but it is more likely due to an increase in the excited state life-time in deuterated cyclobutadiene.

Group theoretical analysis predicts four infrared active modes for the square (D_{4h}) cyclobutadiene [a C-H stretch (E_μ), a C-C stretch (E_μ), an in-plane C-H bend (E_μ), and an out-of-plane C-H bend ($A_{2\mu}$)]. The corresponding analysis for the rectangle (D_{2h}) gives seven infrared allowed fundamentals, five of which should be observable in the non-C-H stretch region of the i.r. spectrum. Merely on the basis of four bands observed above 250 cm^{-1} attributed to cyclobutadiene, the spectrum is most compatible with a square geometry, provided all of the allowed bands are observed (45-46). The location of the bands is also compatible with the analogous ordering of infrared active modes for other C_nH_n rings of D_{nh} symmetry as shown in Table 3. Support for the spectral assignment shown in Table 3 is also provided by

Table 3. Infrared-active fundamental modes for C_nH_n rings of D_{nh} symmetry[a]

Mode	$C_3H_3^+$	C_4H_4	$C_5H_5^{\bullet}$	$C_5H_5^-$	C_6H_6	$C_7H_7^+$	$C_8H_8^{2-}$
Out-of plane bend	736	570	657	701	673	633	684
In-plane bend	908	650	739	1008	1037	992	880
C-C stretch	1276	1240	1360	1442	1482	1477	1431
C-H stretch	3105	(3040)	3101	3021	3064	3020	2994

[a] Data are from reference 46 except for $C_5H_5^{\bullet}$ which is from reference 22. There is e.s.r. evidence which indicates that $C_5H_5^{\bullet}$ does not have D_{5h} symmetry (51b).

theoretical calculations employing force constants from <u>ab initio</u> calculations on cyclobutadiene and bending force constants obtained by interpolation of pertinent empirical data. These force constants (seven in all) lead to calculated frequencies in excellent agreement with the observed bands (22). These calculated frequencies are: C-C stretch (1236 cm^{-1}), in-plane bend (661 cm^{-1}) and out-of-plane bend (570 cm^{-1}).

The above assignment receive strong confirmation from the spectrum of deuteriocyclobutadiene. Table 4 shows the i.r. bands of cyclobutadiene-d_1, cyclobutadiene-1,2-d_2 and cyclobutadiene-1,3-d_2. Not surprsingly, the allowed

Table 4. Infrared bands of deuteriocyclobutadiene[a]

Cyclobutadiene-d_1		Cyclobutadiene-1,2-d_2	Cyclobutadiene-1,3-d_2
Present work	Krantz *et al.*[b]		
1223	1224	1212	1223
-	-	1188	1182
780	-	770	781
654	653(661)	654	654
-	-	-	633
583	594(616)	583	583
576	-	-	-
576	-	-	-
535	540(527)	-	535
-	460(527)	479	458
-	-	447	424

[a] Infrared bands in the region from 200-4,000 cm^{-1} except for column 1 which is in the region from 600-4,000 cm^{-1}.

[b] Values in parentheses are those calculated by Krantz *et al.* in reference 22.

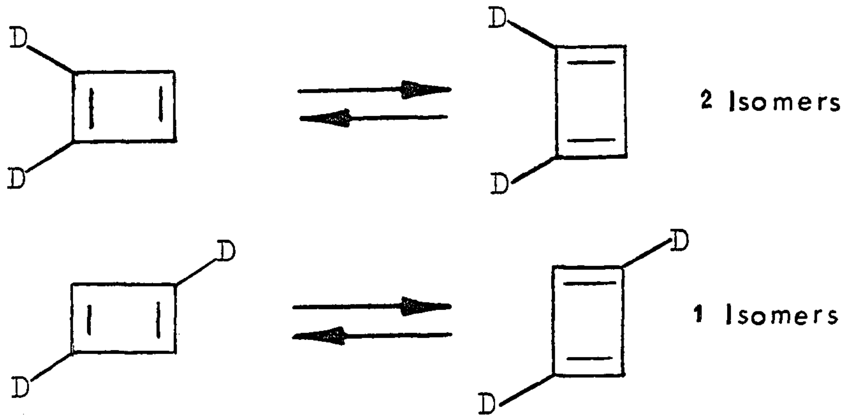
modes of the cyclobutadiene show up as strong bands, appropriately shifted and split in deuteriocyclobutadiene. The slight shift in the frequency of the band at 1224 cm^{-1} in cyclobutadiene to 1223 cm^{-1} in cyclobutadiene-d_1 confirms that it is predominantly a C-C stretch. Theoretical calculations by Krantz *et al.* (22) predicting only a small splitting of the 1224 cm-1 band confirms this assignment. Similar calculations for cyclobutadiene-1,2-d_2 and cyclobutadiene-1,3-d_2 give splittings of 17 and 32 cm^{-1}, respectively; the observed bands at 1212 cm^{-1} and 1223 cm^{-1}, respectively, are consistent with the above calculations. A much larger splitting is predicted for the in-plane and out-of-plane bending modes. The following calculated values for cyclobutadiene-d_1 are consistent with the observed values shown in Table 4: 661 cm^{-1}, 616 cm^{-1}, 527 cm^{-1}, and 477 cm^{-1}.

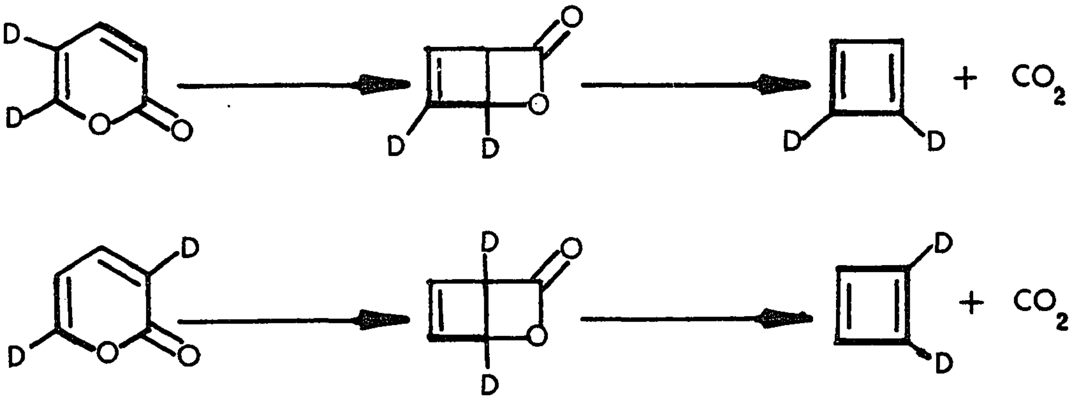
The dideuteriocyclobutadienes give further insight into the details of the cyclobutadiene structure. If the structure of cyclobutadiene has D_{4h} symmetry, only one cyclobutadiene-1,2-d_2 and one cyclobutadiene-1,3-d_2 is possible. If the

D_4h

D_2h

structure has D_{2h} symmetry, two cyclobutadiene-1,2-d_2 and one cyclobutadiene-1,3-d_2 are possible.


D
D
D
D
2 Isomers
D
D
D
D
1 Isomers


D
D
O
O
O
O
D
D
D
D
+ CO2
D
D
O
O
D
O
O
D
D
D
+ CO2

The infrared spectrum of cyclobutadiene-1,2-d_2 is very similar to that of cyclobutadiene-1,3-d_2. There is no evidence for the presence of two cyclobutadiene-1,2-d_2. Moreover, the two precursors for cyclobutadiene-1,2-d_2 would give two different cyclobutadiene-1,2-d_2 if there were any selectivity in the elimination of carbon dioxide. The observation of only cyclobutadiene-1,2-d_2 from two different precursors fits with the conclusion based on the infrared spectrum that cyclobutadiene has D_{4h} symmetry.

EXPERIMENTAL

Reagents

Common solvents and reagents were obtained from commercial sources and were generally used without purification. When anhydrous solvents were required, reagent grade materials were dried according to procedures based on Fieser and Fieser's Reagents for Organic Synthesis, Vol. I, (52).

Characterization of Compounds

All melting points were determined on a Kofler Micro Hot Stage melting point apparatus and are uncorrected. Infrared spectra were taken on a Beckman IR9, IR12, or IR18A spectrometer. NMR spectra were recorded at ambient temperatures on a Varian A-60, HA-100 or a Hitachi Perkin-Elmer R20-B. Chemical shifts are reported as parts per million (δ scale) from tetramethylsilane as an internal standard. Mass spectra were determined using an Atlas CH-4 or an AEl-MS-902 mass spectrometer. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York and Chemalytic, Inc., Tempe, Arizona. Ultraviolet spectra were obtained on a Cary 14 spectrometer or a Beckman DK-2A spectrometer.

Purification

Whenever necessary, chromatographic procedures were employed for separation and purification of products. Microanalytical, air-dried, thin-layer chromatography plates were prepared by immersion coating of microscope slides in a chloroform-methanol slurry of Merck silica gel H obtained from Merck Distributors, Brinkman Instruments, Incorporated, Westbury, New York. Column chromatography was performed on Baker analyzed silica gel (60-200 mesh). Elution solvents were established by microanalytical thin-layer chromatography, and column elution was followed by thin-layer examination of consecutive effluent aliquots. Preparative thin-layer chromatography was performed on pre-coated silica gel F-254 plates (2 mm thickness, 20x20 cm.) obtained from Brinkman Instruments, Inc., Des Plaines, Illinois.

Vapor phase chromatography was performed on either Aerograph 1520 or an F and M Scientific Corp. Model 500 gas chromatograph.

Deuterium Incorporation of α-Pyrones

The position of deuterium and the deuterium content of the α-pyrones were ascertained from the characteristic coupling constants and integration areas observed for the remaining hydrogens. Varian A-60, HA-100 or a Hitachi

Perkin-Elmer R20-B were all used for this purpose. The exact deuterium content was determined at 14 e.v. (where the M-1 peak is negligible) using an Atlas CH-4 mass spectrometer. This was corrected for contributions from naturally occurring carbon thirteen and deuterium. The percent deuterium obtained from the mass spectra were then used to calculate the percent carbon and hydrogen and compared with values by microanalysis. The percent hydrogen from microanalysis was obtained by multiplying the mgs "H_2O" reported by $\frac{5}{18+19}$ for the α-pyrone-d_1 and by $\frac{6}{18+20}$ for α-pyrone-d_2 divided by mgs. sample used times 100. This sets the upper limit for percent hydrogen since this calculation assumes that the α-pyrone-d_1 or α-pyrone-d_2 submitted for microanalysis is 100% pure. In all cases, the calculated percent carbon and hydrogen agree within experimental error with those obtained by microanalysis.

Special Equipment

Ultraviolet irradiations were conducted in two types of apparatus. Apparatus A consisted of a Rayonet photochemical reactor which is available from the Southern New England Ultraviolet Company, Middleton, Connecticut. It contains a sixteen-lamp light source rich in either

310.0 mμ or 253.7 mμ. Apparatus B consisted of a Hanovia 450 watt mercury arc lamp, and a water-cooled quartz or Pyres probe for use with reaction vessels of various sizes.

Matrix Isolation and Photolysis

Photolyses were performed using a Westinghouse 1000 watt mercury vapor lamp.

Refrigeration was achieved by a Displex Cryogenic Refrigerator Model CS202 purchased from Air Products and Chemicals, Inc. The minimum temperature achieved was 8°K. Monitoring of the temperature was accomplished using an iron-doped gold-chromel thermocouple with an ice bath as a reference junction, with the output in millivolts. The output was recorded using a millivolt meter obtained from the Data Technology Corporation.

The pumping system used a Sargent-Welch Model 1402 series. It was capable of pumping the system below 10 microns. In order to obtain pressures down to 10^{-5} mm an air-cooled oil vapor diffusion pump was used. to obtain even lower pressures, a liquid nitrogen trap was installed. Both the diffusion pump and cold trap were obtained from Edwards Vacuum Components Limited. Two vacuum gauges were employed.

For pressures down to 10 microns, a thermocouple gauge from Vacutron was used. For lower pressures either an ion gauge from Consolidated Vacuum Corporation or a cold cathode gauge from H. S. Martin and Son was employed. The pipe was hard-walled copper pipe at least 3/4" in diameter. In order to insure good vacuum and fit, the copper pipes were sweat soldered together using soft solder (Alpha Metals, Inc.) and all purpose soldering flux (J. W. Harris Company).

The method used for deposition of a matrix was as follows. Before cooling the system, the cesium iodide windows were cleaned with ethyl alcohol and tightened evenly in its holder. After putting the radiation shield on, the "O" rings were cleaned and greased. After pumping out the expander, the system is cooled to 8°K then warmed to 20°K, using the heater. The sample is then deposited at this temperature.

A matrix was deposited two ways. Method A: If the sample has at least one mm vapor pressure at room temperature, the following procedure was followed. The sample was degassed three times with liquid N_2. Then one mm of vapor was deposited into a 3-liter bulb. The pressure was then raised to 700 mm with argon gas. Mix with a magnetic stirrer for 10-15 minutes. This gives a guest to host ratio of 1 to 700. The sample was deposited at a rate of 1 mm per minute keeping the temperature at 20°K. The total amount of sample to be deposited varies from sample to sample.

Method B: If a sample has less than 1 mm. vapor pressure, direct deposition was employed. In this method the sample is connected directly to the expander head. After filling the gas handling system with argon, both the sample and argon are sprayed on the window at a rate at which good mixing results. Usually two to three depositions are tried before good isolation results.

Detailed pictures of the 1,000 watt vapor lamp, the Displex cryogenic refrigerator model CS202, the pumping system, the gas handling system, and the deposition system are contained in the master's thesis of Thomas R. Cassutt, Iowa State University (1973).

Preparations

α-Pyrone

This compound was prepared according to the procedure by Zimmerman, Grunewald, and Paufler (53). The yield from the pyrolysis of coumalic acid (Aldrich) at 650° in a Vycor tube packed with fine copper turnings is 66-70% of colorless, oily α-pyrone, b.p. 110° (15 mm). The nmr (CCl_4, TMS) exhibits two multiplets, one centered at 7.50 δ (m, 2H) and another at 6.25 δ (m, 2H). A complete analysis of the nmr of this compound is shown in Table 1. The i.r. exhibits absorptions at 1755 cm^{-1}(s), 1552 cm^{-1}(m), 1250 cm^{-1}(s), 1118 cm^{-1}(m), 1082 cm^{-1}(s). The u.v. (95% ethanol) has absorptions at 288.0 nm ($\varepsilon = 5{,}100$) and 215.0 nm ($\varepsilon = 2{,}225$).

α-Deuterioacetic acid

This was prepared according to the procedure of Thomas (54). 10.2 ml of D_2O (J. T. Baker Chemical Company, 99.5% deuterium), and 37.6 ml of glacial acetic acid (Baker, freshly opened bottle) were refluxed for 2 hours. The resulting α-deuterioacetic acid was syringed out as needed.

6-Chloro-α-pyrone

This compound was prepared according to the procedure by Pirkle and Dines (50).

Into a 50 ml r.b. flask was added 10.0 g (.077 mole) of glutaconic acid (Aldrich), the flask was cooled in an ice bath, and 30.0 g (0.147 mole) of PCl_5 was added portionwise (exothermic). The flask was heated on a steam bath for 5 minutes and fitted with a short Vigreux column, distilling head and condenser. The product distilled at 80° (0.75 mm). The clear distillate 6.34 g (0.0486 mole) crystallized on standing and melts at 27°. The yield is 67%. The average yield of two runs is 70.7%. The nmr (CCl_4, TMS) exhibits two multiplets centered at 7.48 δ (m, 1H) and 6.23 δ (m, 2H). The i.r. (neat, NaCl plates) exhibits strong absorptions at 1758, 1625, 1530, 1332, 1070, and 1010 cm^{-1}. The mass spectrum shows the molecular ion at m/e 130.

α-Pyrone-6-d_1

This compound was prepared according to the procedure of Pirkle and Dines (50).

To a solution of 3.02 g (.022 mole) of 6-chloro-α-pyrone in 15 ml. of dry THF (distilled from LAH) was added 5.8 g (.0387 mole) of NaI (vacuum-dried at 95°/0.7 mm for 2 hours). The mixture was allowed to stand for 4 hours at room temperature, and was then added to a mixture of α-deuterioacetic acid 10 ml (0.164 mole) and 15 g (0.23 mole) of zinc dust (vacuum-dried). After 12 hours at 25°, the resulting red solution was diluted with 100 ml of CH_2Cl_2 and the zinc removed by filtration. The zinc was washed with CH_2Cl_2, and the combined filtrates were washed first with water, then with 10% Na_2CO_3 solution, and finally dried over anhydrous $MgSO_4$. Evaporation of the solvent left 1.0 g of yellow oil which was chromatographed through silica gel (Bayer), and eluted with 250 ml of CH_2Cl_2. Molecular distillation (bath temperature 50°/15 mm) gave 0.31 g (0.0032 mole) of clear oil. The yield was 14%. The average yield of two runs was 24.2%. The nmr (CCl_4, TMS) exhibits two multiplets, one centered at 7.50 δ (m, 1H) and another centered at 6.34 δ (m, 2H). Deuterium content based on mass spectrum at 14 e.v. is 92% d_1 and 8% d_0.

Anal: Calcd for $C_5H_3DO_2$ (92% d_1, 8% d_0): C, 61.89; H, 5.11. Found: C, 61.71; H, 5.33.

5,6-Dibromo-5,6-dihydro-α-pyrone

In a typical preparation (50), 5.42 g (.056 mole) of freshly distilled α-pyrone was dissolved in 200 ml of CH_2Cl_2 and cooled to -78° in Dry Ice-isopropyl alcohol bath while a stream of dry nitrogen was bubbled through the solution. Bromine, 9.2 g (.057 mole), in 20 ml CH_2Cl_2, was slowly introduced into the cold solution and the mixture irradiated with a 400-W tungsten projector bulb until the bromine had been consumed (5-10 minutes). After the solvent had been removed (rotary evaporator), the amount of clear yellow oil obtained, 14.6 g, corresponded to quantitative formation of a 1:1 adduct. This adduct was purified by chromatography on Brikman silica gel with CH_2Cl_2 and yield 13.5 g (.053 mole, 94% yield) of a clear oil, which although it can be stored unchanged for several weeks at -20° evolves hydrogen at room temperature. The i.r. shows carbonyl stretching at 1760-70 cm^{-1} and no other bands between 1400 and 1700 cm^{-1}. The nmr (CCl_4, TMS) shows four equal area multiplets centered at 5.15 δ, 6.20 δ, 6.90 δ, and 7.20 δ. The coupling constants are identical with reported values (51a).

5-Bromo-α-pyrone

A magnetically stirred solution of 1.00 g (0.0039 mole) of 5,6-dibromo-5,6-dihydro-α-pyrone in 15 ml CH_2Cl_2 was treated dropwise with a solution of 0.60 ml (.0043 mole) of triethylamine in 5 ml CH_2Cl_2. The orange slush (0.794 g) left after evaporation of the ether (rotary evaporator) was chromatographed on silica gel with ether as eluant to yield 0.726 g of white crystalline product, which, after sublimation at 50° and 0.1 mm melted at 60-61°. Final yield: 0.62 g (.0036 mole, 91% yield). Nmr (CCl_4, TMS) shows three equal area multiplets centered at 6.2 δ, 7.3 δ, and 7.5 δ, identical with reported values (50, 51a).

α-Pyrone-5-d_1

In a manner exactly parallel to that described previously (50). vacuum-dried zinc dust (40.0 g) was added to a solution of 4.02 g of 5-bromo-α-pyrone in 35 ml of α-deuterioacetic acid and the mixture blanketed with dry nitrogen. After 24 hr. at room temperature and then 48 hr. at 80°, the slurry was diluted with water (75 ml), the zinc pulverized, and the mixture filtered. The zinc was washed twice with 50 ml portions of hot water and the filtrates were combined. The zinc was then washed with three 75 ml portions of CH_2Cl_2, these portions being then used for the extraction of the aqueous filtrate. The combined methylene chloride extracts were twice washed with 10% $NaHCO_3$ and dried oven anhydrous $MgSO_4$, and the solvent evaporated (rotary evaporator) to leave 0.927 g of tan oil. Molecular distillation at 50°/15 mm gave 0.674 g (64% yield) of α-pyrone-5-d_1. Deuterium content based on mass spectrum at 14 e.v.: 84% d_1, 16% d_0.

Anal: Calcd for $C_5H_3DO_2$ (84% d_1, 16% d_0): C, 61.94; H, 5.03
Found: C, 61.89; H, 5.48.

3-Bromo-α-pyrone

0.968 g (0.00379 mole) of 5,6-dibromo-5,6-dihydro-α-pyrone was allowed to stand at room temperature for 20 days, at which time evolution of HBr has subsided. The resulting crystalline material was triturated with CH_2Cl_2 and the soluble material was chromatographed on silica gel to yield 0.645 g (.00369 mole, 97.5% yield) of 3-bromo-2-pyrone. After sublimation of 50° (0.1 mm), the white crystals had mp 63.5-64°. Nmr (CCl_4, TMS) exhibits three equal are multiplets centered at 6.23 δ, 7.56 δ, and 7.77 δ identical with reported values (50).

α-Pyrone-3-d_1

In a manner exactly parallel to that described for α-pyrone-5-d_1, α-pyrone-3-d_1 (.628 g, .00648 mole, 45.3% yield) was prepared by reduction of 3-bromo-α-pyrone (2.60 g, 0.0143 mole). The nmr ($CDCl_3$, TMS) shows three equal area multiplets centered at 6.15 δ, 7.32 δ, and 7.55 δ. The deuterium content based on the mass spectrum of 14 e.v. is 87% d_1, 13% d_0.

Anal: Calcd for $C_5H_3DO_2$ (87% d_1, 13% d_0): C, 61.92; H, 5.06.

Found: C, 62.57; H, 5.49.

5-Bromo-α-pyrone-6-d_1

This compound was prepared in a manner exactly parallel to that described for 5-bromo-α-pyrone except that the photodibromide of α-pyrone-6-d_1 was used as starting material. Hence, from 2.0 g (.0078 mole) of the photodibromide of α-pyrone-6-d_1 was obtained 1.08 g (.00617 mole), 79.0% yield of white crystals. Nmr (CCl_4, TMS) exhibits two equal area doublets centered at 6.25 δ and 7.35 δ, both split by 9.5 Hz.

α-Pyrone-5,6-d_2

In a manner exactly parallel to that described for α-pyrone-5-d_1, α-pyrone-5,6-d_2 (0.147 g, .0015 mole, 31.6% yield) was prepared by reduction of 0.834 g (.00475 mole) of 5-bromo-α-pyrone-6-d_1. The nmr (CCl_4, TMS) exhibits two equal area doublets centered at 6.27 δ and 7.50 δ, both split by 9.5 Hz. The deuterium content: 86% d_2, 14% d_1.

Anal: Calcd for $C_5H_2D_2O$ (86% d_2, 14% d_1): C, 61.29; H, 6.03. Found: C, 61.20; H, 6.52.

3-Bromo-α-pyrone-6-d_1

This compound was prepared in a manner exactly parallel to that described for 3-bromo-α-pyrone except that the photodibromide of α-pyrone-6-d_1 was used as starting material. Hence, from 1.87 g (.0073 mole) of the photodibromide of α-pyrone-6-d_1 was obtained 0.209 g (.0012 mole), 16.4% yield of white crystals.

α-Pyrone-3,6-d_2

In a manner exactly parallel to that described for α-pyrone-5-d_1, α-pyrone-3,6-d_2 (.0655 g, .000670 mole, 56.3% yield) was prepared by reduction of 0.209 g (.0012 mole) of 5-bromo-α-pyrone-6-d_1. The nmr (CCl_4, TMS) exhibits two equal area doublets centered at 6.12 δ and 7.24 δ, both split by 6.20 Hz. Deuterium content: 81% d_2, 19% d_1. Not enough sample was available for a good C, H analysis but the exact elemental composition ($C_5H_2D_2O_2$) was determined by high resolution mass spectrometry.

3-Chloroglutaconic acid methyl ester

To 10 g (.0685 mole) of dimethyl acetonedicarboxylate (55) was added portionwise 14.6 g (.070 mole) of PCl_5. The temperature was kept below 50°C by cooling in an ice-bath. After HCl evolution has subsided, the reddish orange mixture was distilled to give 3.85 g (.0234 mole) of sweet-smelling oil which boils at 93.5-94°/0.25 mm. The yield was 40.5%. The nmr (CCl_4, TMS) exhibits resonances at: 3.7 δ (s, 6H, $-O\underline{CH_3}$), 4.08 δ (s, 2H, $-\underline{CH_2}-$), and 6.25 δ (s, 1H, $-\underline{C{=}CH}-$). The i.r. (neat, NaCl plates) shows strong absorption at 1745 cm^{-1} and 1645 cm^{-1}. These are consistent with literature values (55).

4,6-Dichloro-α-pyrone

To 8.9 g (.054 mole) of 3-chloroglutaconic acid (prepared by refluxing the dimethyl ester in 20% HCl for 2-1/2 hours) was added portionwise 22.4 g (0.108 mole) of PCl_5 while cooling in ice-bath. After evolution of HCl has subsided, distillation gave 5.8 g (.0351 mole), 65% yield of 4,6-dichloro-α-pyrone, b.p. 70.5-71°/0.75 mm, sublimed at 50-55°/0.25 mm which gives a m.p. 48-50°. The nmr (CCl_4, TMS) shows a singlet at 6.42 δ (the coupling constant cannot be measured from the spectrum). The mass spectrum shows molecular ion at m/e 165.

α-Pyrone-4,6-d_2

5.48 g (0.0333 mole) of 4,6-dichloro-α-pyrone was dissolved in 51 ml of α-deuterioacetic acid. 85 g (1.3 mole) of vacuum-dried zinc dust was added, then blanketed with dry nitrogen gas, and heated on steam bath for 3 days. Work-up as usual and molecular distillation gave 1.24 g (.0126 mole), 38% yield of α-pyrone-4,6-d_2. The nmr (CCl_4, TMS) shows a singlet centered at 6.31 δ (the coupling constant cannot be measured from the spectrum). The deuterium content: (85% d_2, 14% d_1, 1% d_0).

Anal: Calcd for $C_5H_2D_2O_2$ (85% d_2, 14% d_1, 1% d_0): C, 61.30; H, 5.97

Found: C, 61.21; H, 6.14.

3,5-Dibromo-α-pyrone

This compound was prepared according to the procedure of Pirkle and Dines (50). The spectral properties were identical with those reported. Sublimation at 100°/0.01 mm gave a m.p. 92-93°(lit. values 92.5-93°).

α-Pyrone-3,5-d_2

To a solution of 2.47 g (.00975 mole) of 3,5-dibromo-α-pyrone in 15 ml of α-deuterioacetic acid was added 25 g (.354 mole) of zinc dust and the nitrogen blanketed mixture heated on a steam bath for 3 days. Work-up as usual and molecular distillation gave 0.308 g (.0030 mole), 33% yield of α-pyrone-3,5-d_2. The nmr (CCl_4, TMS) contains two equal area doublets centered at 7.34 δ, and 7.52 δ, both split by 2.10 Hz. Deuterium content: 64% d_2, 33% d_1, and 3% d_0.

Anal: Calcd for $C_5H_2D_2O_2$ (64% d_2, 33% d_1, 3% d_0): C, 61.46; H, 5.77

Found: C, 61.66; H, 6.24.

General procedure for preparation of cyclobutadiene

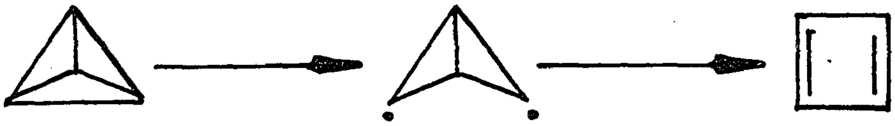
The sample (one drop) was degassed three times with liquid nitrogen. Then one mm of vapor was deposited into a 3-liter bulb. This takes 2 hours to equilibrate at room temperature since the α-pyrone is not very volatile. The pressure was then raised to 500 mm with argon gas. Mix with a magnetic stirrer for 10-15 minutes (the 3-liter bulb was covered with metal foil to protect the α-pyrone from light). This gives a guest to host ratio of 1 to 500. Deposit the sample at a rate of 1 mm per minute keeping the temperature at 20°K. A total amount of 100 mm was deposited, then the matrix was cooled down to 8°K. The i.r. of the matrix-isolated α-pyrone was then scanned from 4,000 cm^{-1} to 500 cm^{-1} (or 4,000-200 cm^{-1} in some cases). This will reveal any water absorptions or other extraneous peaks that interferes with the analysis. If the matrix-isolation looks good, the α-pyrone was photolyzed through Pyrex for 11 hours to convert it completely to the β-lactone. A scan was taken to confirm this. The bands due to β-lactone was then identified by comparison with a sample prepared previously (42). The Pyrex filter was removed and the matrix-isolated β-lactone was photolyzed through quartz for a total time of 200 min. Scans were taken every 10 min. The destruction of β-lactone causes formation of new bands at 1240, 650, and 570 cm^{-1} in addition to the carbon dioxide bands at 2340 and 660 cm^{-1}. An intensity <u>vs</u>. time plot shows that the 1240-, 650-, and 570-cm^{-1} bands are due to the same primary product (cyclobutadiene). The concentration of cyclobutadiene rises to a maximum and then slowly decreases as irradiation is continued. The photoproduct of cyclobutadiene shows bands at 3280, 3265, 745, 737, 733, and 727 cm^{-1}. Warming above 35°K causes the photoproduct to coalesce into single bands at 3260 and 735 cm^{-1} identical with those of acetylene. Warming cyclobutadiene above 35°K gives the dimer which is observed in the i.r. (by comparison with matrix isolated dimer) and by high-resolution mass spectrum (the matrix was melted and the products were trapped at 77°K and analyzed by mass spectrometry).

PART II. APPROACHES TO THE SYNTHESIS OF TETRAHEDRANE

HISTORICAL

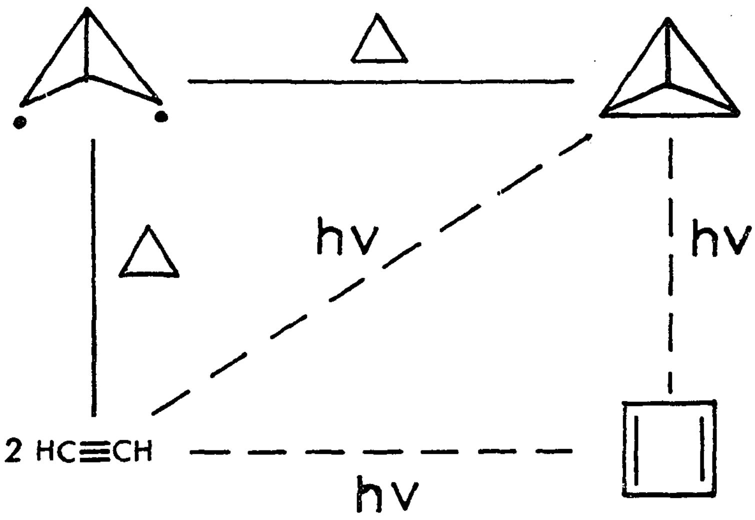
Tricyclo[1.1.0.0^{2,4}]butane (tetrahedrane) is the most highly strained saturated C_4 hydrocarbon imaginable. It has proven to be more elusive than its monocyclic isomer, cyclobutadiene, and has been of great theoretical interest because of its high degree of strain and symmetry.

The SCF-MO calculations of Baird and Dewar (56) predicted that tetrahedrane has a strain energy of 150.5 kcal/mole, 83 kcal/mole greater than bicyclobutane. Since 83 kcal/mole is approximately the same as the bond energy of a carbon-carbon single bond, Baird and Dewar claimed that the conversion of tetrahedrane to 2,4-bicyclobutyl diradical should be almost thermoneutral. Moreover, tetrahedrane was claimed to immediately isomerize via the diradical to cyclobutadiene.



R. J. Buenker and S. D. Peyerimhoff (57) undertook ab initio SCF and CI calculations for tetrahedrane to investigate its geometry and its stability relative not only to cyclobutadiene but also to two acetylene molecules. They found that cyclobutadiene (in its rectangular ground state) is more stable than tetrahedrane by 70.3 kcal/mole and that tetrahedrane is unstable with respect to dissociation into two acetylene molecules by 70-100 kcal/mole. Weltner (25) calculated the strain energy of tetrahedrane and found it to have a strain energy of 90 kcal/mole as compared to 50 kcal/mole in cyclobutadiene.

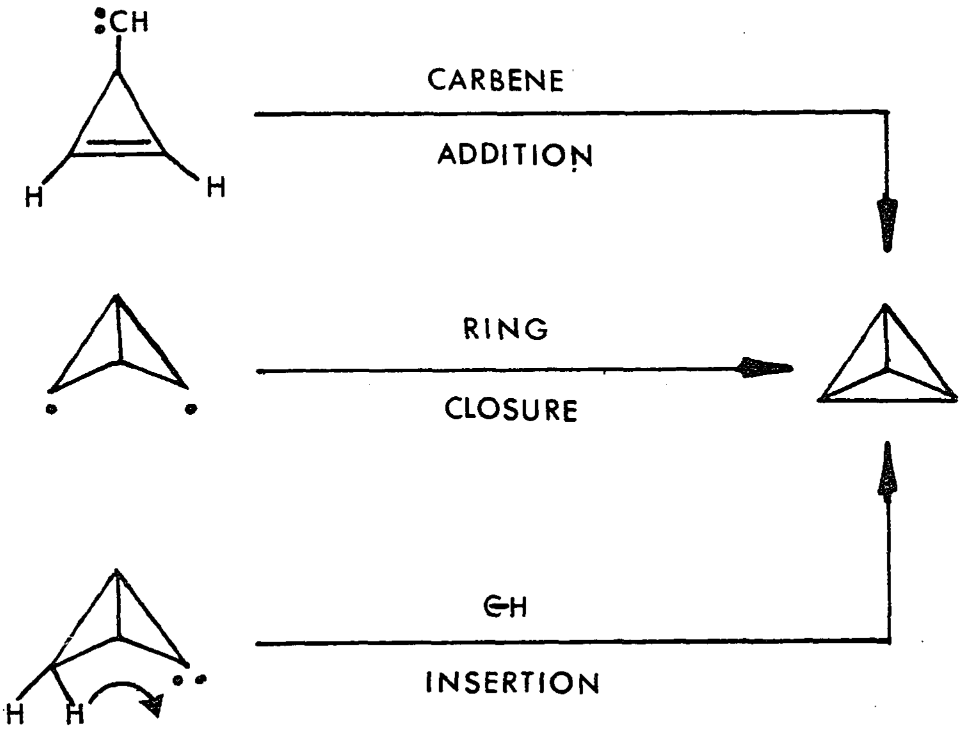
Orbital symmetry arguments (58a) predict that the concerted rearrangement of tetrahedrane to cyclobutadiene and its disproportionation to acetylene are thermally forbidden reactions. On the other hand, homolytic cleavage of a tetrahedrane single bond to a 2,4-bicyclobutyl diradical is not. Photochemically, the conversion of tetrahedrane to acetylene or cyclobutadiene are both allowed.



To date, the most rigorous theoretical study of the tetrahedrane molecule was done by Schulman and Venanzi (58b). They did an ab initio calculation in the extended Gaussian 4-31G basis set and has established that tetrahedrane is a local minimum point on the eight-atom C_4H_4 potential energy surface. After extensive geometry search, the CC and CH bond lengths were found to be 1.48 and 1.05Å, respectively. A normal coordinate analysis performed in the 4-31G basis furnished the following predicted vibrational frequencies of tetrahedrane: A_1 (3520 and 1550 cm^{-1}), E (900 and 840 cm^{-1}), T_1 (1110 cm^{-1}), and T_2 (3540, 1260, and 940 cm^{-1}). The relative intensity of the three allowed modes in the infrared (3540, 1260, and 940 cm^{-1}) was predicted to be in the ratio of 0.18:0.017:1.0. Also, a barrier of at least 18 kcal/mole for homolytic cleavage of a single bond to form a bicyclobutyl diradical (the triplet state of this diradical was found to lie 45 kcal/mole above the singlet state) was obtained. The calculated heat of formation, hybridization, photoelectron spectrum, and one-bond nuclear spin-spin coupling constants were also determined. From the calculated heat of formation, tetrahedrane was determined to be 18-26 kcal/mole higher in energy than two acetylene molecules (at 25°K) and to have a strain energy of 129-137 kcal/mole (at 0°K), consistent with previous values (56, 57).

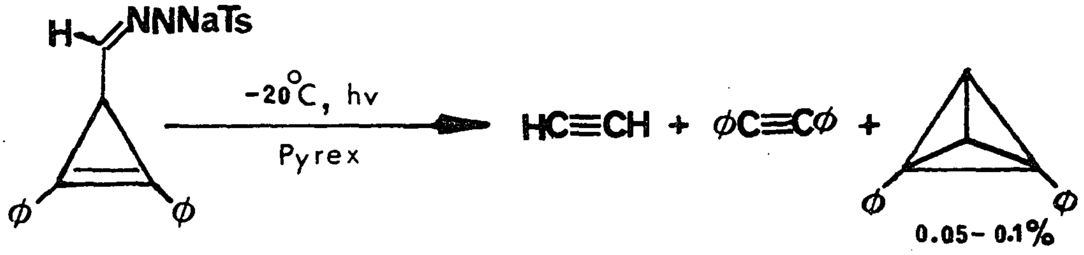
The synthesis of a derivative of tetrahedrane has been attempted by numerous workers, with no confirmed case of the isolation of tetrahedrane being reported. The earliest reported preparation of a tetrahedrane derivative was made by Beesley and Thorpe (59), who in 1920 claimed to have synthesized 1-methyl-2,3,4-tricarboxytetrahedrane from 1-methylbicyclobutane-2,3,4-tricarboxylic acid. This claim lay unchallenged for several decades until 1959 when Larson and Woodward (60) demonstrated that the synthesis was not reproducible.

Recent approaches to tetrahedrane involve three different precursors:

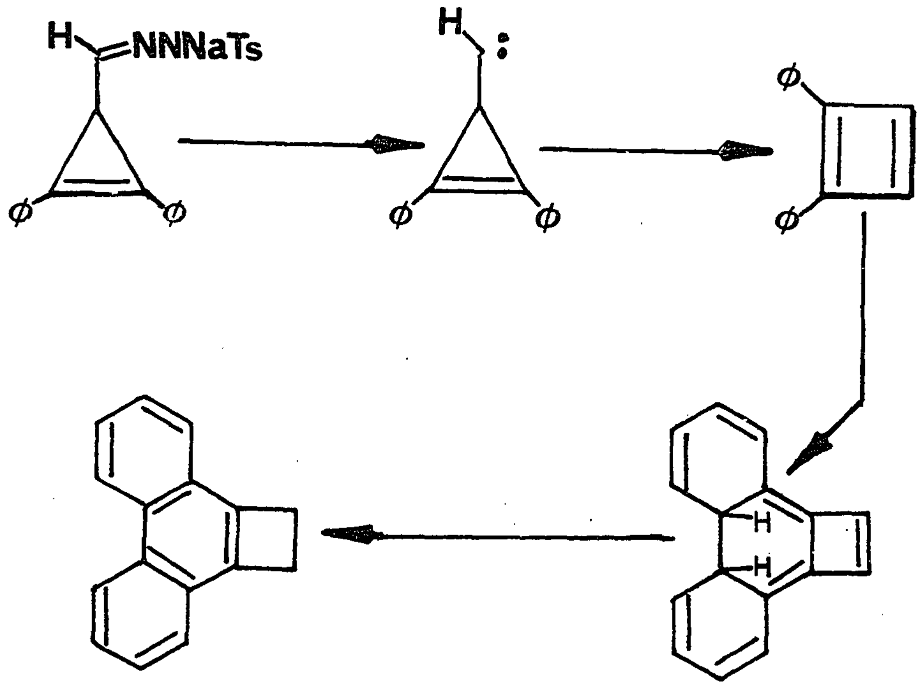


1) The Δ^2-cyclopropenylcarbene by intramolecular addition of the carbene to the double bond, 2) the 2,4-bicyclobutyl diradical by ring closure, and 3) the 2-carbenabicyclobutane by intramolecular C-H insertion.

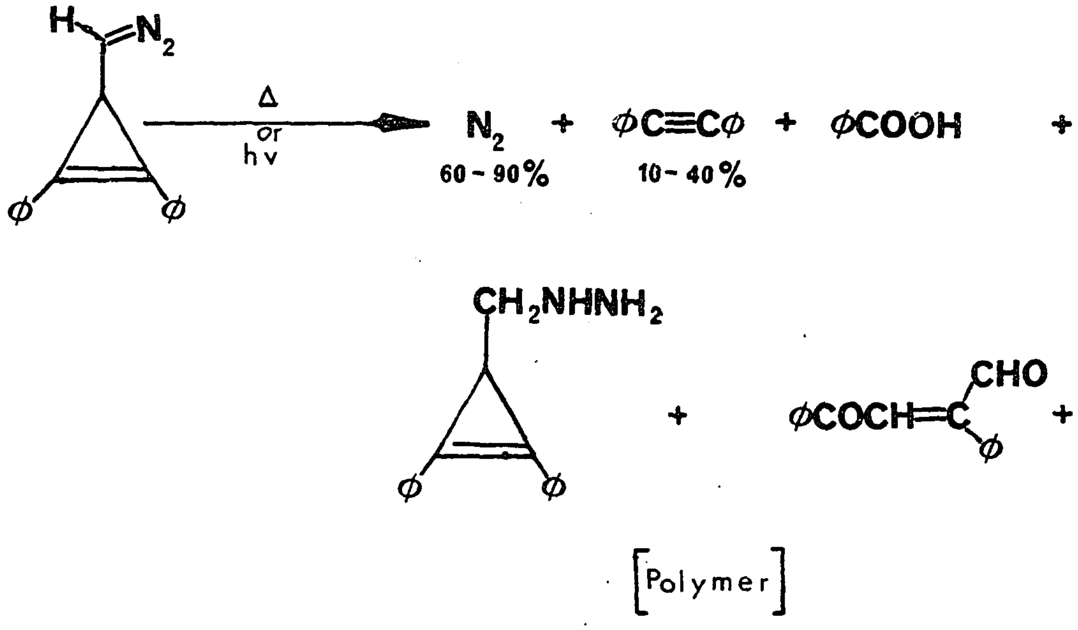
The earliest example utilizing intramolecular carbene addition appeared in 1965 when Masamune and Kato (61) reported the preparation of diphenyltetrahedrane by photolysis of the sodium salt of Δ^2-2,3-diphenylcyclopropenylcarbinyl tosylhydrazone.



This report was reinterpreted by White et al. (62) in terms of the formation of a phenanthrene derivative instead of diphenyl tetrahedrane.

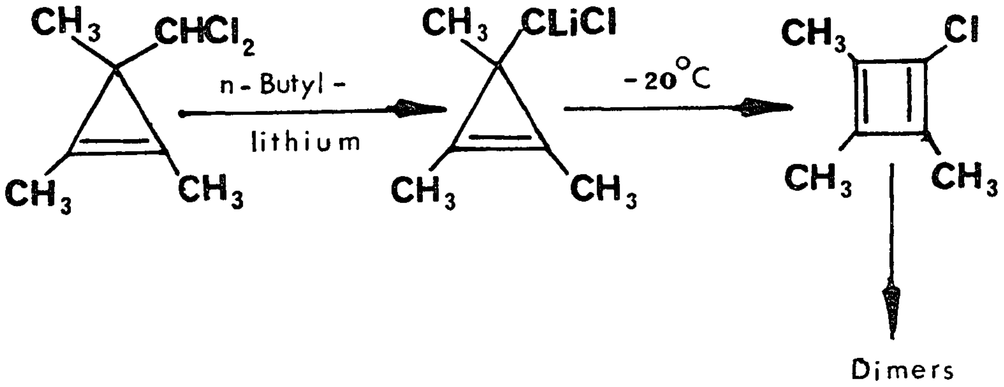


Masamune and Kato (63) retracted their original report and agreed with White's interpretation that the compound they obtained was indeed the phenanthrene derivative shown above. White _et_ _al_. (62) also found that photolysis or thermolysis of Δ^2-2,3-diphenylcyclopropenyldiazomethane did not give rise to any



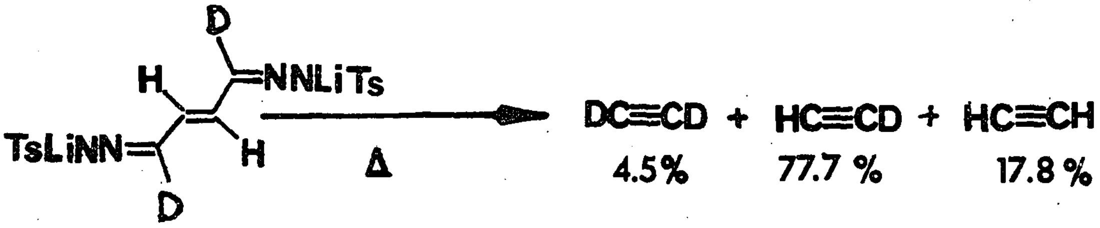
substituted tetrahedrane.

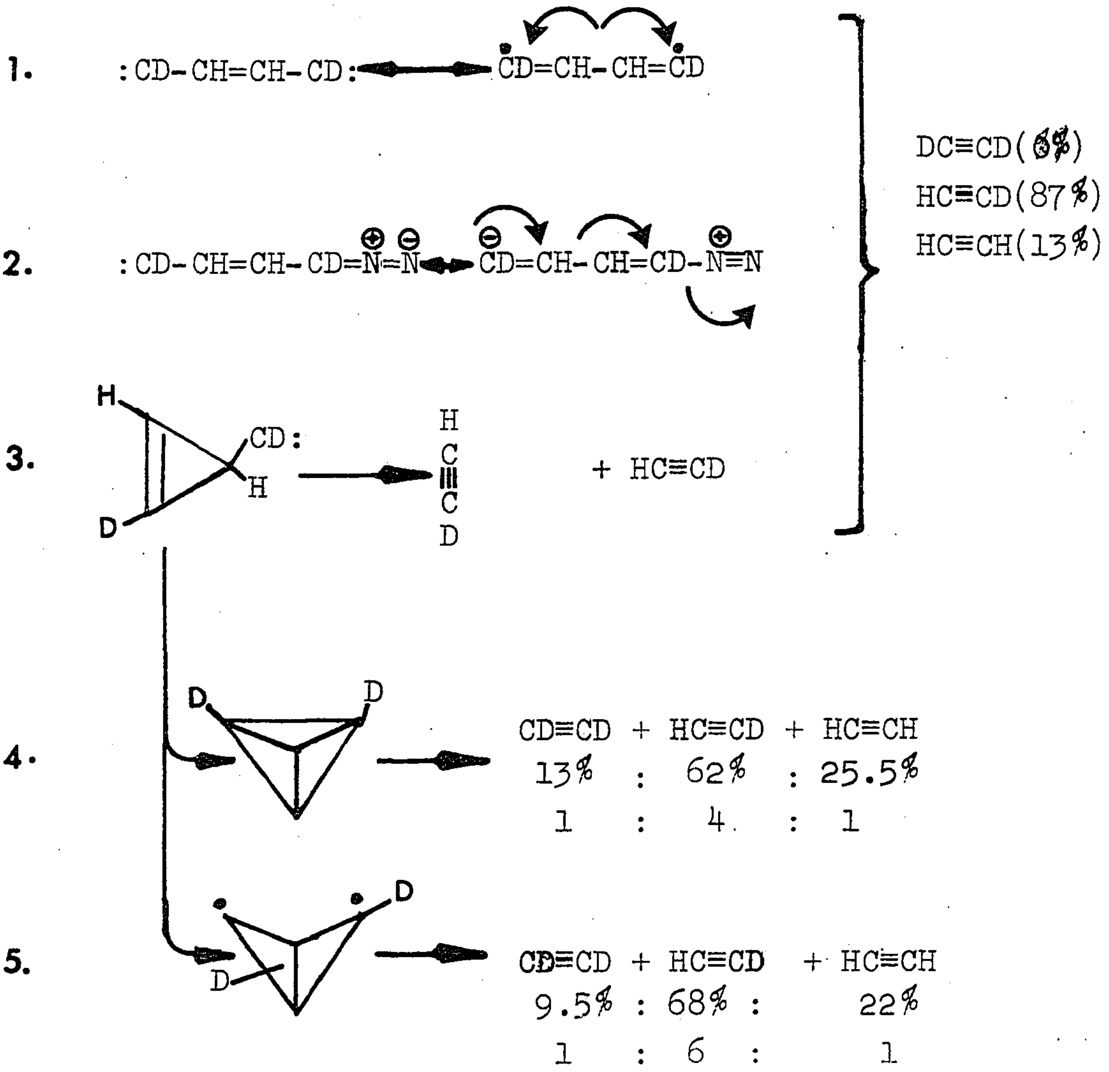
Closs and Rao (64) observed that the decomposition of Δ^2-trimethylcyclopropenyldichloromethyllithium at -20° gave an 85% yield of the tricyclooctadienes expected from the dimerization of an initially formed cyclobutadiene derivative. They suggested that although the rearrangement may proceed in a single step by ring expansion to chlorotrimethylcyclobutadiene, one cannot exclude the possible



intermediary of chlorotrimethyltetrahedrane.

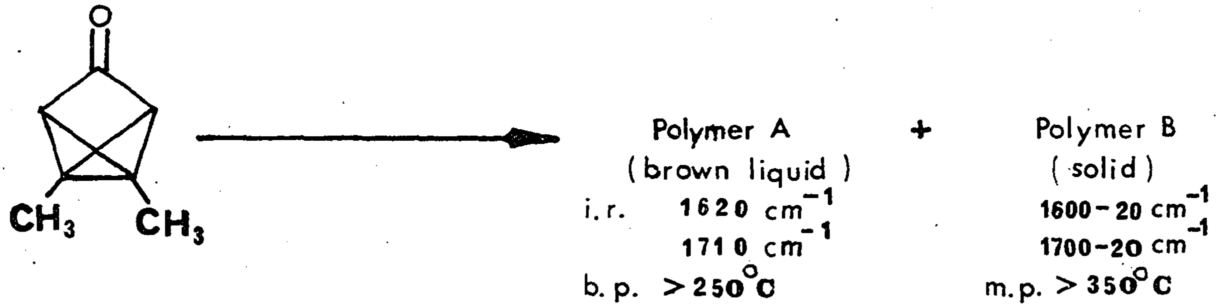
Rodewald and Lee (65) pyrolyzed the dilithium salt of trans-butenedial bistosylhydrazone and obtained 20-30% acetylene and 1-1.5% ethylene as the only volatile materials, and noted that the absence of vinylacetylene, benzene, cyclooctatetraene, and syn-dimer of cyclobutadiene, precluded the formation of cyclobutadiene. They investigated the intermediate responsible for the acetylene by deuterium labeling and obtained the results shown below.


TsLiNN=
H
H
D
D
=NNLiTs
Δ
DC≡CD + HC≡CD + HC≡CH
4.5%
77.7 %
17.8 %

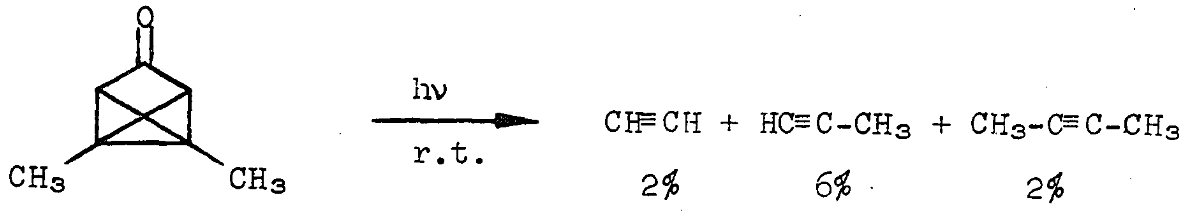

1.
:CD-CH=CH-CD:
CD=CH-CH=CD
2.
:CD-CH=CH-CD=N=N
CD=CH-CH=CD-N≡N
3.
H
D
CD:
H
H
C
C
D
+ HC≡CD
DC≡CD(0%)
HC≡CD(87%)
HC≡CH(13%)
4.
D
D
CD≡CD + HC≡CD + HC≡CH
13% : 62% : 25.5%
1 : 4 : 1
5.
D
D
CD≡CD + HC≡CD + HC≡CH
9.5% : 68% : 22%
1 : 6 : 1

Five pathways were proposed for the formation of acetylene giving the calculated distributions of acetylene. The values observed did not correspond to any of the cases proposed, 1-5. The authors concluded that although the nonscrambling reactions 1-3 are predominant, tetrahedrane or 2,4-bicyclobutyl diradical can account for some of the scrambling observed.

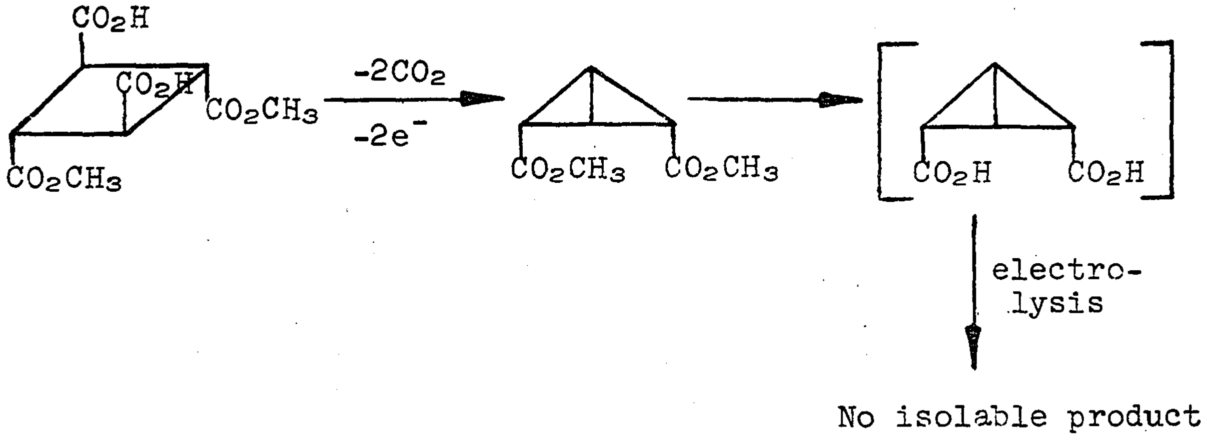
The earliest example utilizing the cyclization of 1,4-bicyclobutyl diradical was done by Pomerantz (66) in 1964. He photolyzed 15 mg. of 1,5-dimethyltricyclo[2.1.0.0^{2,5}]-pentan-3-one at 90-100° for 32 hours using a 550 watt, high



pressure, Hanovia lamp and obtained two types of polymeric material shown above. Ona, Yamaguchi, and S. Masamune (67) pyrolyzed the same tricyclicketone in THF at 106° and obtained a mixture of $C_{12}H_{16}$ compounds (m/e 160) in low yields as separable products. However, photolysis through a Corex filter for 4 hours at room temperature caused destruction of 94% of the ketone and produced acetylenic products shown below.

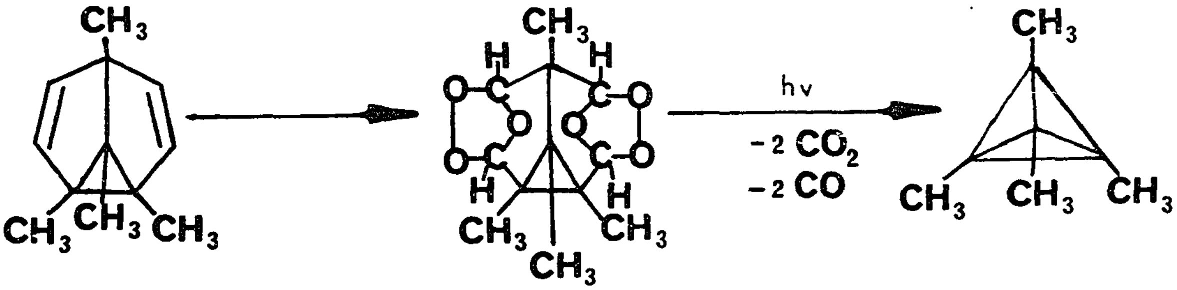


Vellturo and Griffin (68) utilized the Kolbe electrolysis as an approach to tetrahedrane but did not obtain any



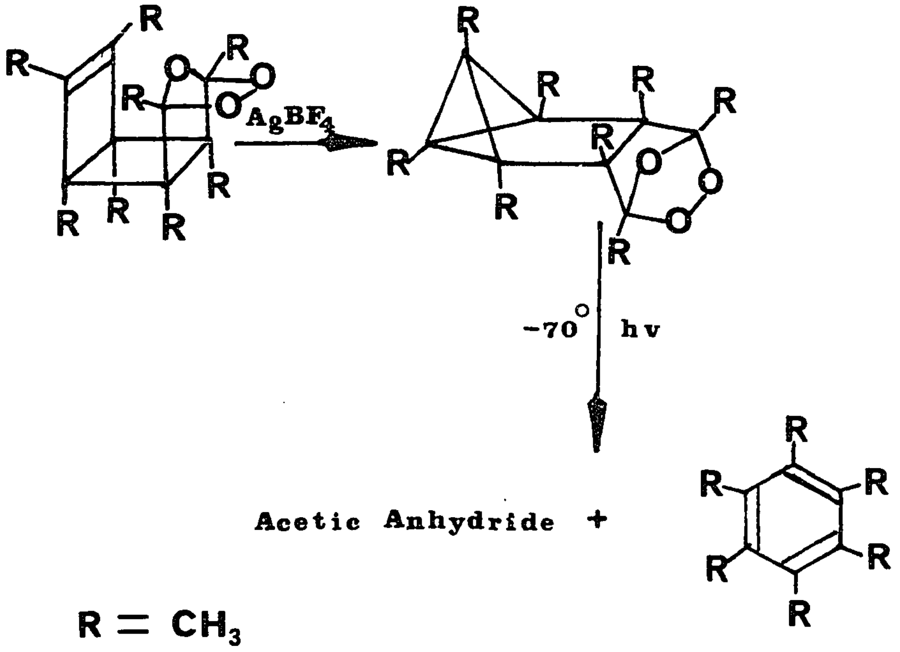
isolable product.

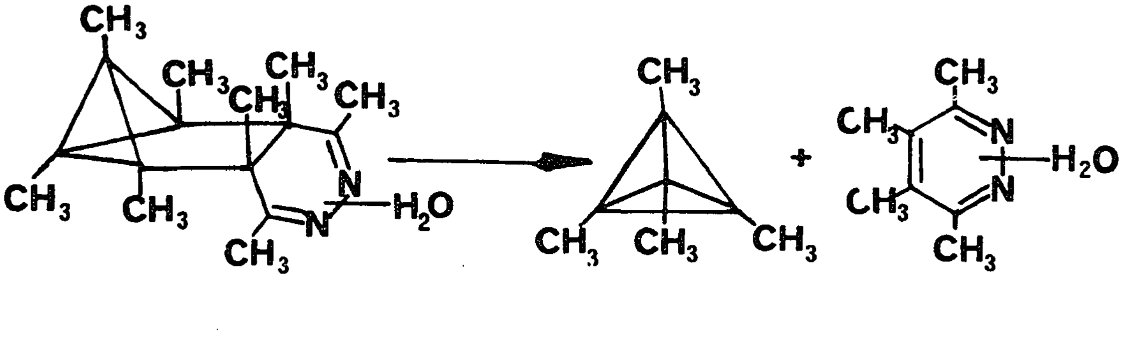
In June 1968, Criegee (69) reported that he had synthesized tetramethyltetrahedrane by ultraviolet irradiation of a diozonide of a semibullvalene derivative.



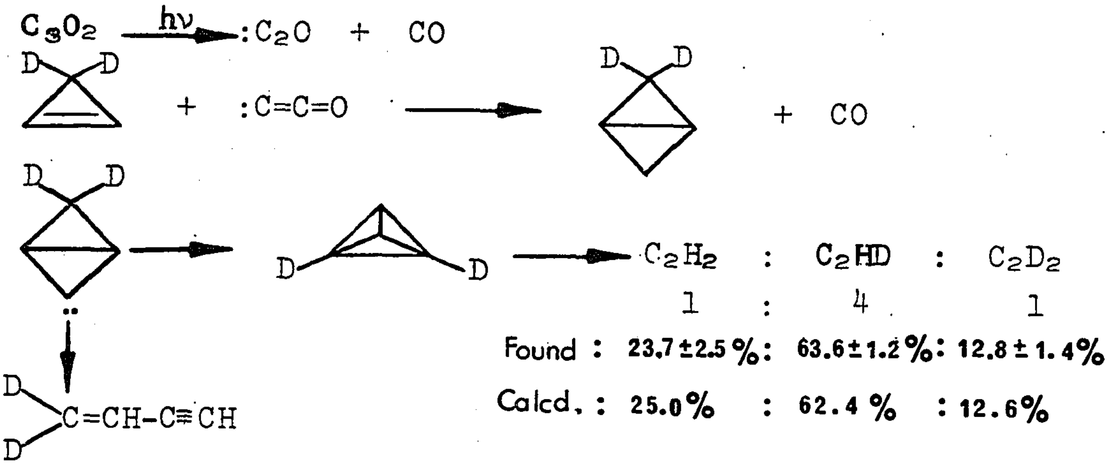
To date, this work has not appeared in the published literature.

Maier and Schneider (70) succeeded in isomerizing a cyclobutene derivative to its valence isomer, and photolyzed the resulting ozonide. He proposed that this approach would be a possible route tetramethyltetrahedrane shown below.


AgBF4
-70°
hv
Acetic Anhydride +
R = CH3


CH3
N
H2O
+

The most compelling evidence that intramolecular C-H insertion of 2-carbenabicyclobutane produces tetrahedrane was the report of Shevlin and Wolf (71). They photolyzed carbon suboxide in the presence of cyclopropene and obtained 24% acetylene and 33% vinylacetylene. Labelling studies employing deuterium-labelled cyclopropene and ^{14}C-labelled carbon suboxide gave several different isotopically labelled acetylene the relative abundances are difficult to explain



except by postulation of a symmetrical tetrahedrane intermediate. A set of competing mechanism involving the formation of both 1,2- and 1,3-dideuteriocyclobutadiene can explain the observed results, but the authors considered it unlikely.

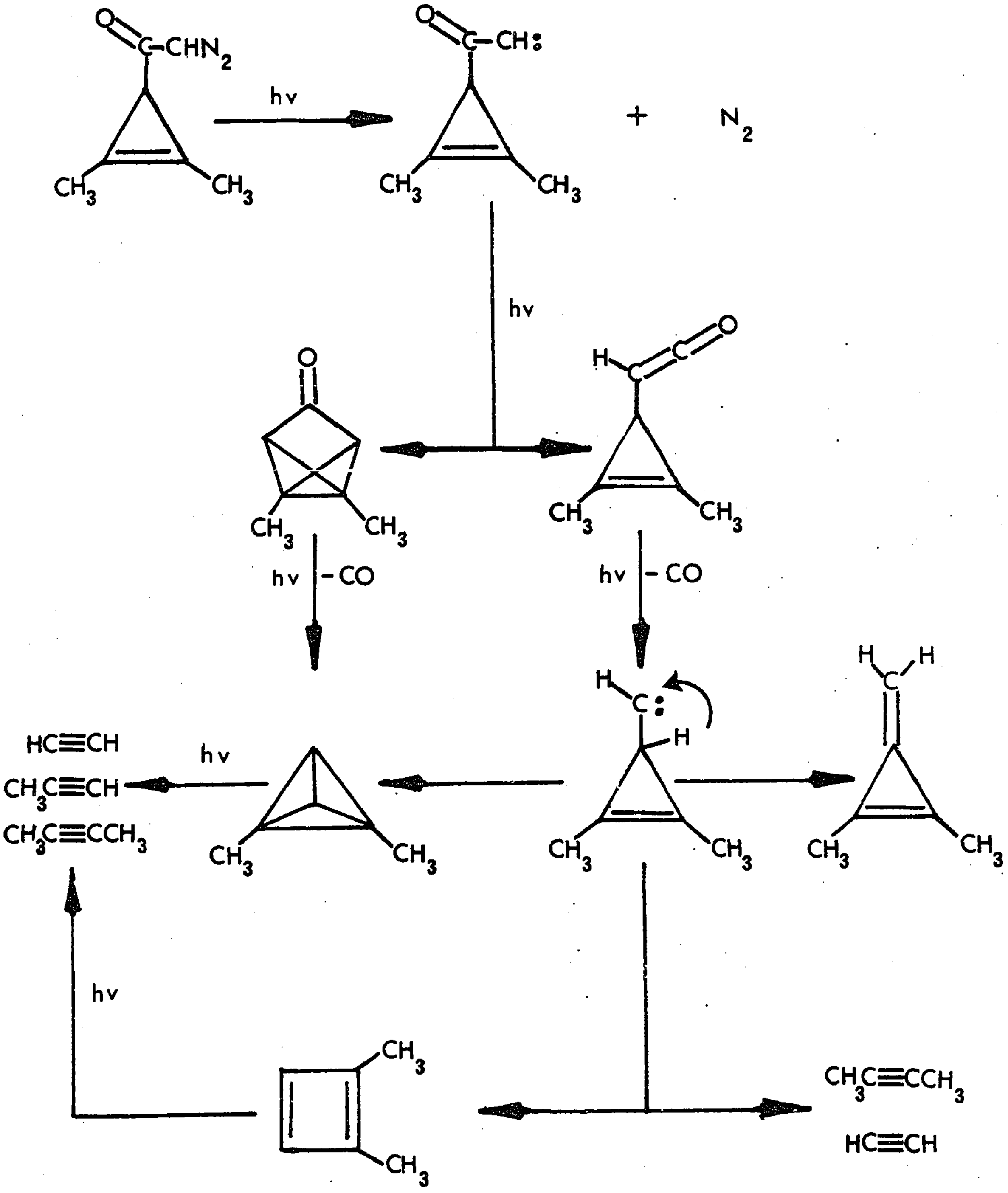
It seemed obvious from this review that one has to apply matrix isolation and photochemistry to really determine which precursor would indeed generate tetrahedrane or substituted tetrahedrane. It was therefore decided to examine known precursors to substitute tetrahedrane that have enough vapor pressure to allow deposition in a matrix and be decomposed photochemically to generate the desired compound. Moreover, attempts were made to synthesize unsubstituted precursors to simplify the analysis of the resulting infrared spectrum due to tetrahedrane. This is where the real challenge is since group theory predicts only 3 i.r. active modes for tetrahedrane and any substitution may mask these bands; consequently a great deal of effort was directed at synthesizing unsubstituted precursors to tetrahedrane.

The presence or absence of tetrahedrane was examined by plotting the absorption versus time of the destruction of the precursor, and formation of new material. New species are identified by comparison with matrix isolated spectra *e.g.* acetylene or cyclobutadiene. Warm-up experiments and detection of any decomposition products were also done to distinguish photochemical or thermal decomposition products of tetrahedrane. Finally, the mass spectra of any volatile products were taken for further characterization.

RESULTS AND DISCUSSION

The first known precursor examined was 1,2-dimethyl-3-diazoacetylcyclopropene. It was hoped that photolysis of this compound in argon at 8°K would provide two entries into dimethyltetrahedrane, namely 1,5-dimethyltricyclo[2.1.0.0^{2,5}] pentan-3-one (72) and Δ^2-2,3-dimethylcyclopropenylketene.

1,2-dimethyl-3-diazoacetylcyclopropene was deposted directly at 20°K (Method B, see Experimental of Part I) with argon (120 mm) for 4 hours at a rate of 1 mm/min, the sample tube being kept at -15°. The sample was irradiated at 8°K using a mercury vapor lamp (1,000 watts) with Pyrex filter 12 (0%-2740Å, 18%-2900Å, 68%-3100 Å). Irradiation for 500 minutes caused destruction of starting material (2108, 1928, 1662, 1370, 1359, 1350, 1310, 1320, 1117 cm^{-1}) and formation of two sets of bands: one due to 1,5-dimethyltricyclo-[2.1.0.0^{2,5}]pentan-3-one (1808, 928, and 576 cm^{-1}) and Δ^2-2,3-dimethylcyclopropenylketene (2112 cm^{-1}). Continued irradiation up to 1,800 minutes, causes a gradual increase in the bands due to the 1,5-dimethyltricyclo[2.1.0.0^{2,5}]-pentan-3-one and Δ^2-2,3-dimethylcyclopropenylketene and gradual appearance of a band at 2142 (due to carbon monoxide) and other bands at 2280, 1908, 1740, 1725, 1564, 1323, 1044, and 797 cm^{-1}. Removal of the filter and photolysis through quartz caused destruction of the tri-


C-CHN$_2$
hν
C-CH:
+
N$_2$
CH$_3$
hν
hν -CO
hν -CO
hν
HC≡CH
CH$_3$C≡CH
CH$_3$C≡CCH$_3$
hν
CH$_3$C≡CCH$_3$
HC≡CH

cyclopentanone and cyclopropenylketene band, concomittant with formation of carbon monoxide. The increase in carbon monoxide formation is parallel with the increase of the intensity of bands at 2280, 1740, 1725, 1564, 1323, 1044, and 797 cm^{-1}. Even upon continued irradiation through quartz up to 3,800 minutes, the spectra do not contain bands due to matrix isolated acetylene (3260, 737 cm^{-1}), methylacetylene (3268, 1250, 624 cm^{-1}), or dimethylacetylene (2890, 2869, 2837, 1449 cm^{-1}). Figure 8 shows the infrared spectra of 1,2-dimethyl-3-diazoacetylcyclopropene (and its photolysis products) matrix isolated in argon at 8°K. Figure 9 shows the plot of the relative intensity of significant bands as a function of time. Figure 10 shows the infrared spectra of methylacetylene and 2-butyne matrix isolated in argon at 8°K.

Warming the matrix to 35°K, 60°K, 80°K, and 100°K, and recooling to 8°K does not show any peaks due to acetylenic products expected from a dimethyltetrahedrane intermediate. The photolysis products were trapped at 77°K and submitted for mass spectral analysis. The mass spectrum is uninteresting. There are no peaks due to acetylene (m/e 26), methylacetylene (m/e 40), or dimethylacetylene (m/e 54). The only prominent peaks observable at 70 e.v. are: m/e 28, 43, 58, 78, 79, 80, and 81. The oily residue obtained from the CsI window was also analyzed. The mass spectrum at 14 e.v. shows

Figure 8. Infrared spectra

Top: 1,2-Dimethyl-3-diazoacetylcyclopropene matrix isolated in argon at 8°K showing the characteristic absorption at 1670, 1928, and 2108 cm^{-1}

Middle: 1,5-Dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one (1808 cm^{-1}) and Δ^2-2,3-dimethylcyclopropenylketene (2112 cm^{-1}) after irradiation for 20 hours through Pyrex filter 12$_o$(0%-2740 Å, 18%-2900 Å, 68%-3100 Å) of 1,2-dimethyl-3-diazoacetylcyclopropene. Two other bands appear: 2142 cm^{-1} (carbon monoxide) and 1908 cm^{-1}

Bottom: After photolysis through quartz for 65 hours

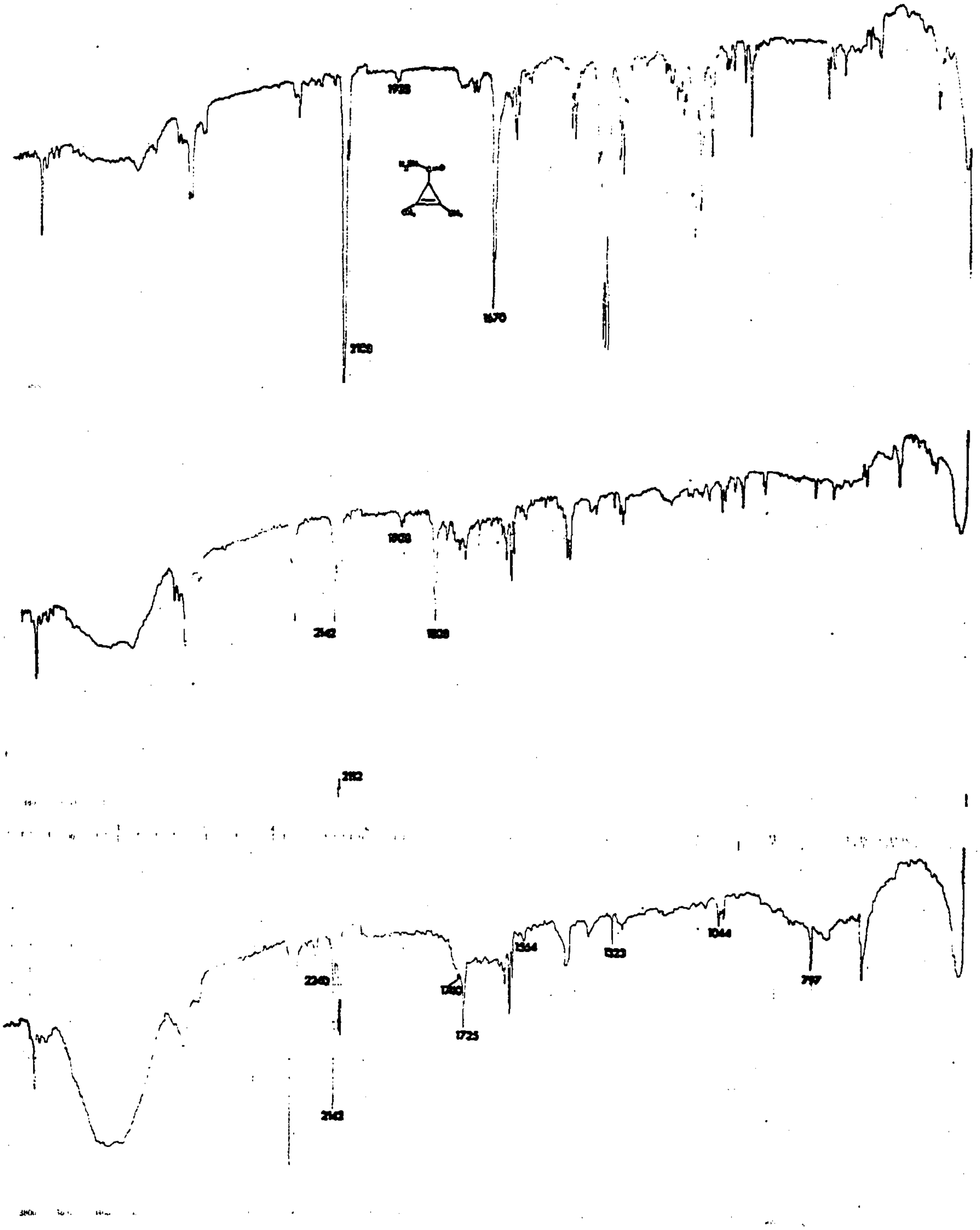

1928
2128
1670
1908
2142
1808
2182
2240
1760
1725
2143
1364
1323
1044
797

Figure 9. Plot of the relative intensity of significant bands as a function of irradiation time. The arrow denotes the time at which filter 12 was removed to allow photolysis through quartz. The 2112 cm^{-1} band is 1,2-dimethyl-3-dizoaacetylcyclopropene, 1808 cm^{-1} band is 1,5-dimethyltricyclo[2.1.0.$0^{2,5}$]pentan-3-one, and 2112 cm^{-1} band is Δ^2-2,3-dimethylcyclopropenylketene. The 2142 cm^{-1} is carbon monoxide

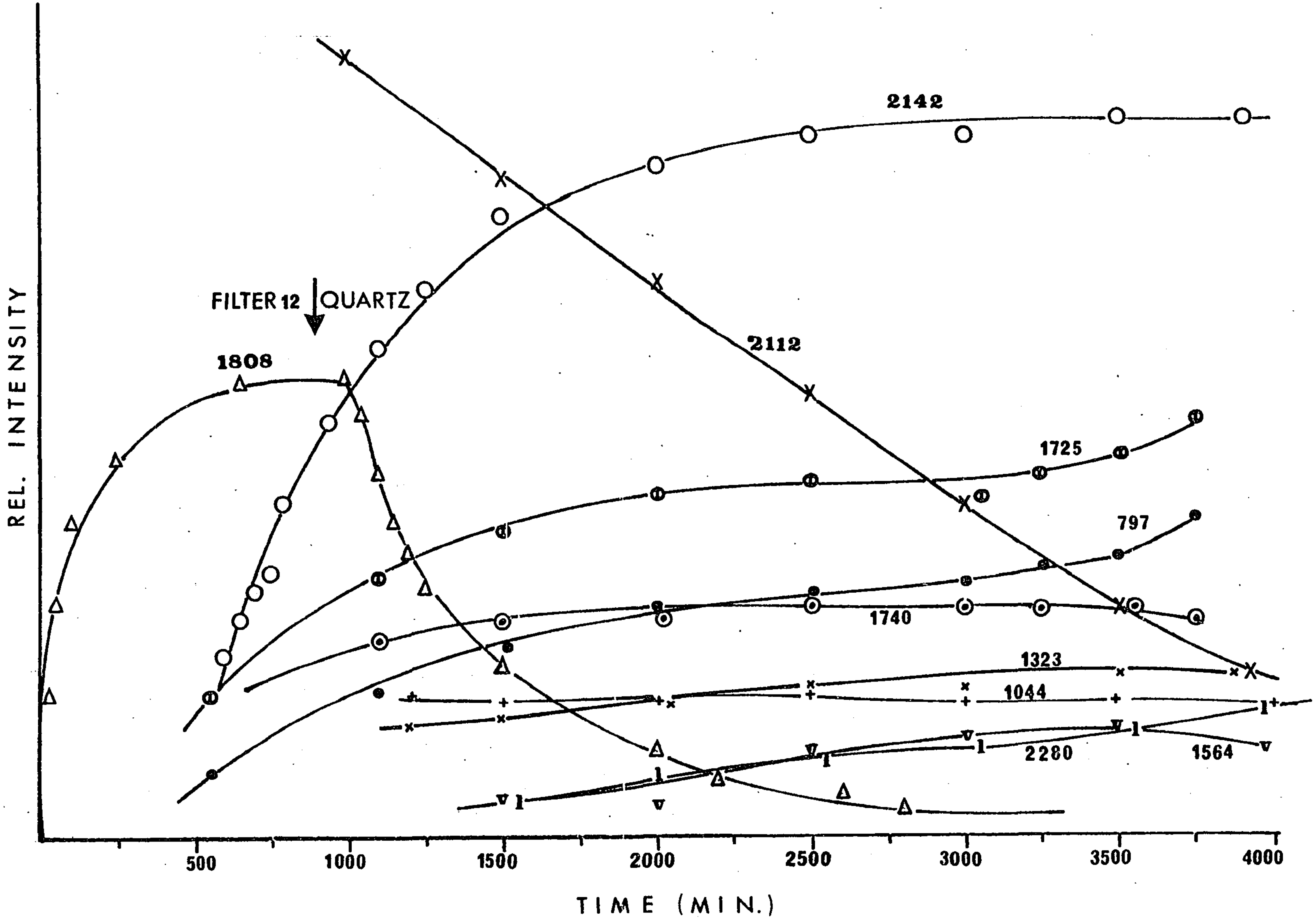
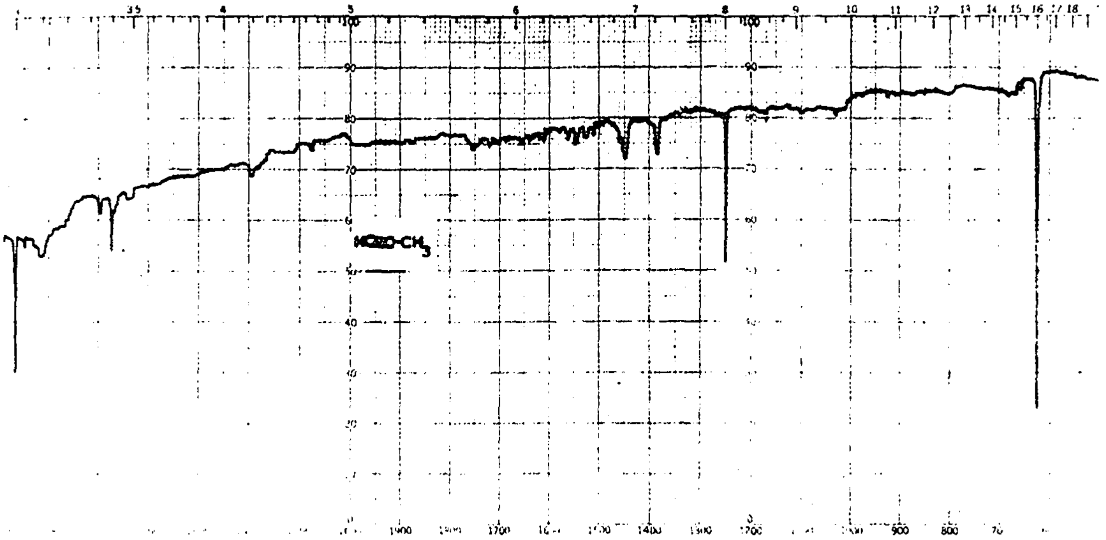
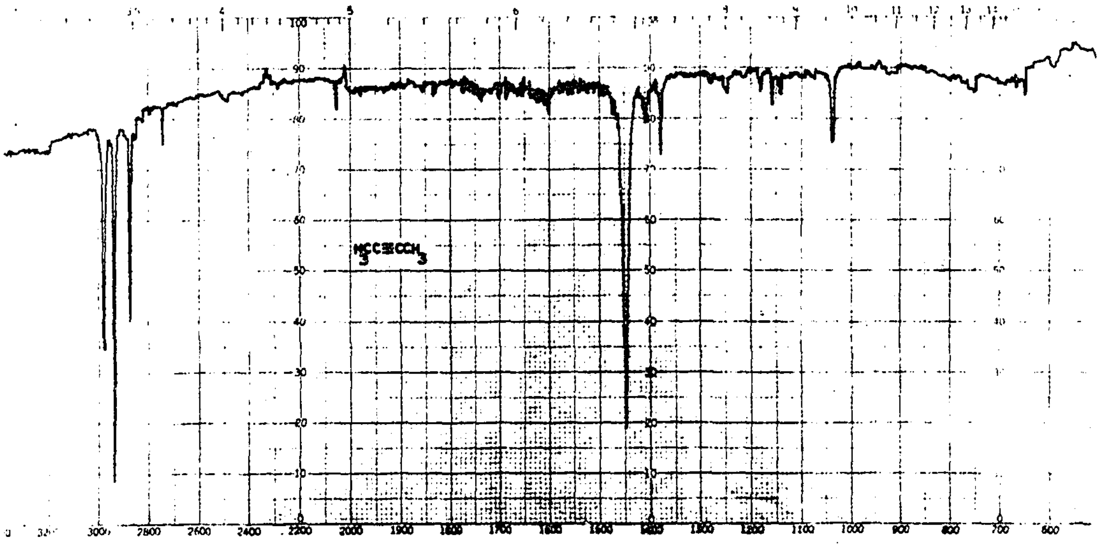

REL. INTENSITY
TIME (MIN.)
500
1000
1500
2000
2500
3000
3500
4000
FILTER 12
QUARTZ
1808
2142
2112
1725
797
1740
1323
1044
2280
1564

Figure 10. Infrared spectra

Top: Methylacetylene matrix isolated at 8°K

Bottom: Dimethylacetylene matrix isolated at 8°K


$HC\equiv C-CH_3$


$H_3CC\equiv CCH_3$

a strong ion at m/e 280. The nmr ($CDCl_3$, TMS) showed resonances at 0.88, 1.27, 2.09, 2.11, 2.14, 3.03, 4.11, and 5.04 δ. The resonance at 5.40 δ is very strong compared to the others and is indicative of an olefinic product. The very small sample available precluded further characterization.

The absence of acetylenic products upon photodestruction of both 1,5-dimethyltricyclo[2.1.0.0^{2,5}]pentan-3-one and Δ^2-2,3-dimethylcyclopropenylketene precludes the intermediacy of dimethyltetrahedrane or 1,2-dimethylcyclobutadiene.

1-Methyl-3-diazoacetylcyclopropene was synthesized and similarly deposited in argon at 20°K. Photolysis at 8°K through filter 8 (> 3400 Å) for 50 minutes caused destruction of starting material and formation of Δ^2-2-methylcyclopropenylketene. Unlike the dimethyl derivative no tricyclic ketone was formed. Photolysis of the ketene through quartz caused a very slow decrease in ketene absorption; however, there are no peaks attributable to acetylene or methylacetylene even upon prolonged irradiation. Figure 11 shows the infrared spectra of 1-methyl-3-diazoacetylcyclpropene matrix isolated at 8°K.

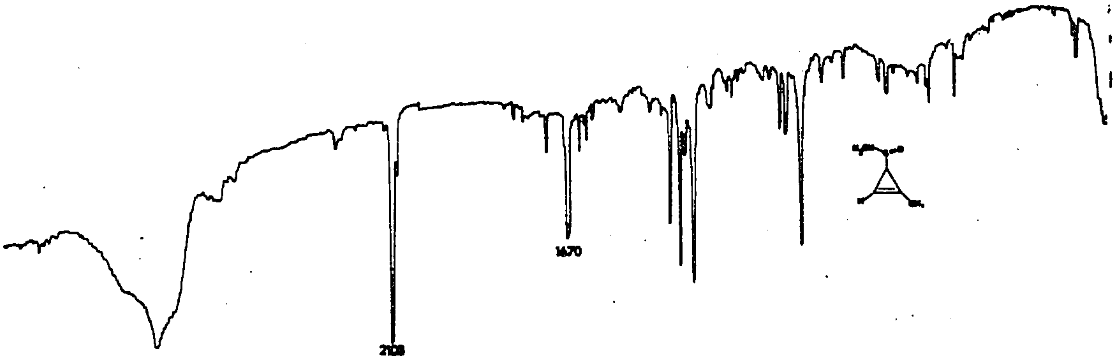
An attempt was made at the synthesis of cyclopropene-3-carboxylic acid as a route to 3-diazoacetylcyclopropene and

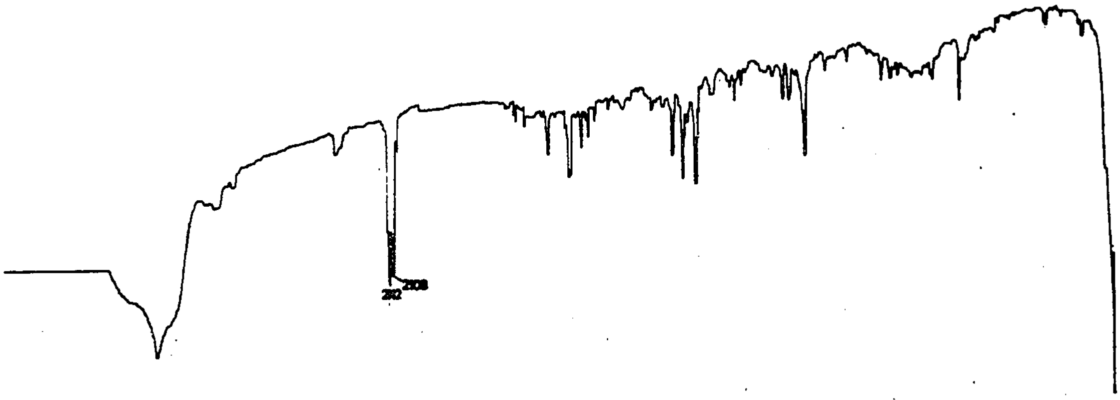
Figure 11. Infrared spectra

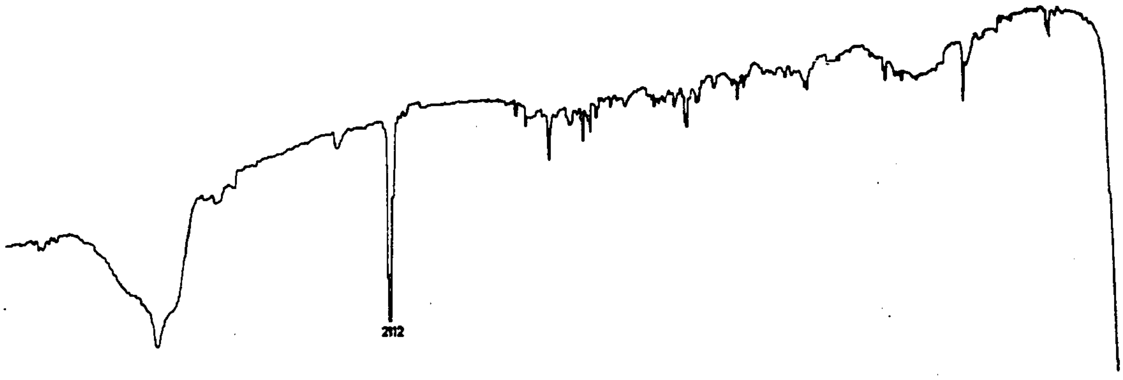
Top: 1-Methyl-3-diazoacetylcyclopropene matrix isolated at 8°K showing the characteristic band at 2108 cm^{-1} and 1670 cm^{-1}

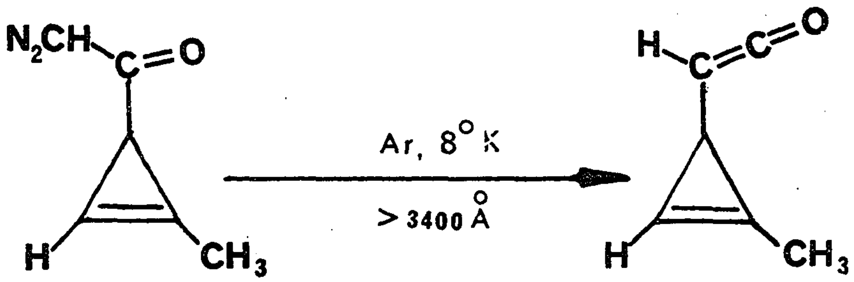
Middle: After photolysis through filter 8 (> 3400 Å) for 13 minutes. The 2112 cm^{-1} band is due to Δ^2-2-methylcyclopropenylketene

Bottom: After photolysis through quartz for 53 minutes

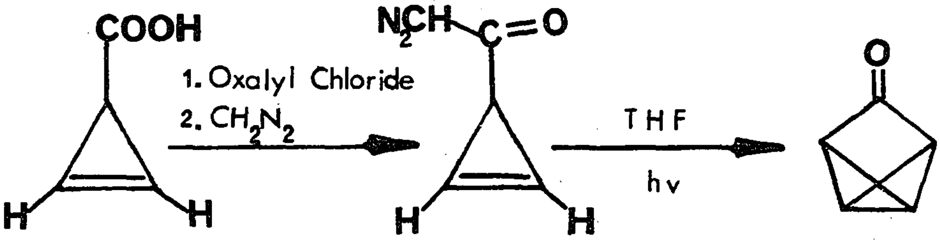

2108
1670


2112
2108

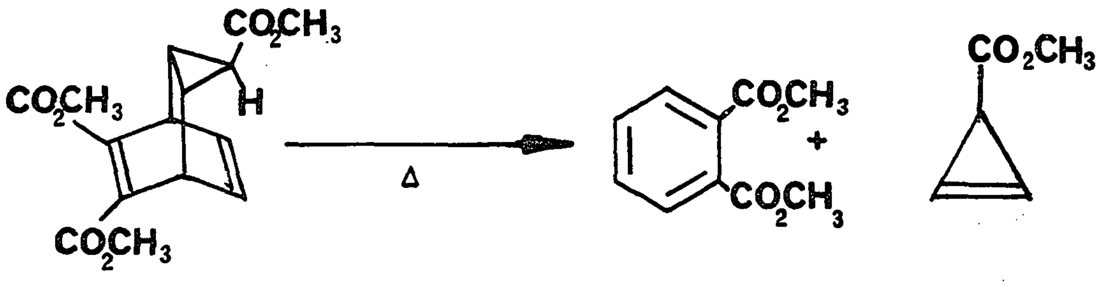

2112



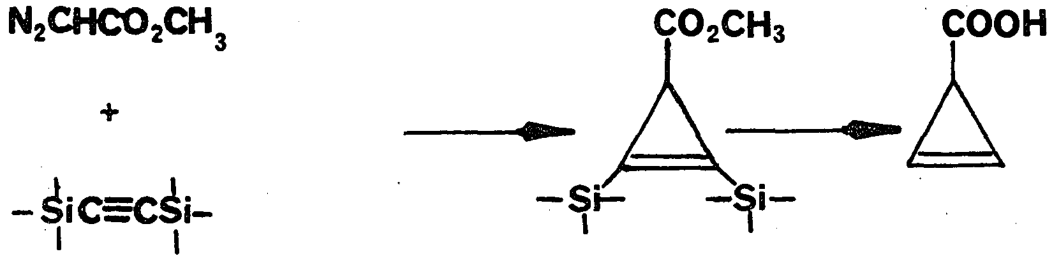
tricyclo[2.1.0.0^{2,5}]pentan-3-one. There are two known reports of the preparation of this compound. Doering *et al.*



(73) has observed that 7-carbomethoxytropilidine upon heating with dimethyl acetylenedicarboxylate gave both dimethyl phthalate and 3-carbomethoxycyclopropene, identified by hydrogenation and saponification to the known cyclopropane carboxylic acid. The yield was not reported but analogous synthesis of cyclopropene by heating the adduct of tropilidine with dimethyl acetylenedicarboxylate gave 1% yield (74). Nefedov *et al.* (75) claimed the preparation

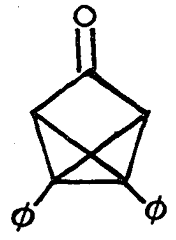


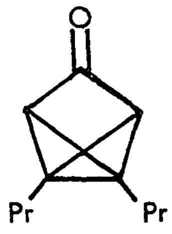
of cyclopropene-3-carboxylic acid in 5-8% yield by reaction of bis(trimethylsilyl)acetylene with methyl diazoacetate

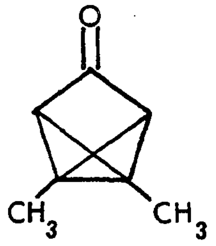


followed by basic hydrolysis. The melting point of the acid was given as 147-148° but no i.r. or nmr parameters were reported to support the structure. The reported synthesis was repeated several times but was unsuccessful. The reported procedure, however, succeeded when 1-trimethylsilylpropyne was reacted with methyldiazoacetate to give a 31% yield of 1-methylcyclopropene-3-carboxylic acid after basic hydrolysis and neutralization. Hence, it was concluded that the preparation of cyclopropene-3-carboxylic acid was not reproducible; no further attempts were made at its preparation.

The next precursors examined were the substituted tricyclic ketones. The 1,5-diphenyl- and 1,5-dipropyltricyclo[2.1.0.0^{2,5}]pentan-3-one were synthesized by photolyzing the appropriate diazoketone in THF (76). The 1,5-diphenyltricyclo[2.1.0.0^{2,5}]pentan-3-one, however, did not have enough vapor pressure to allow deposition in a matrix.

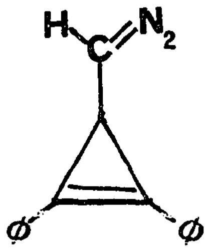


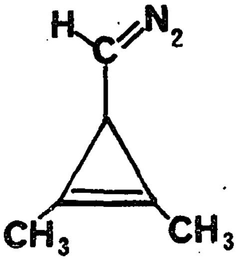


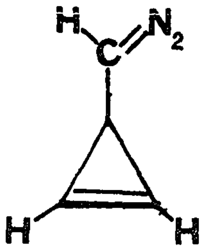


The 1,5-dipropyltricyclo[2.1.0.0^{2,5}]pentan-3-one, on the other hand, condenses in the gas handling system upon deposition. Even direct deposition did not give a satisfactory matrix isolation. Photolysis through quartz at 8°K showed the formation of carbon monoxide bands but the spectra were too poor to allow further analysis. The 1,5-dimethyltricyclo-[2.1.0.0^{2,5}]pentan-3-one was expected to give a good matrix isolation. This compound has been synthesized by Pomerantz (66) but the yield is variable, averaging about 1%. The synthesis was attempted twice according to the exact procedure but was unsuccessful. Private communications with Pomerantz revealed that he had modified the procedure ever since and obtained an average yield of 5-10%. He has also collaborated with Krantz who photolyzed the compound in argon at 8°K. They claim that although the results are interesting, they are not in publishable form. Moreover, they do not observe any evidence for dimethyltetrahedrane.

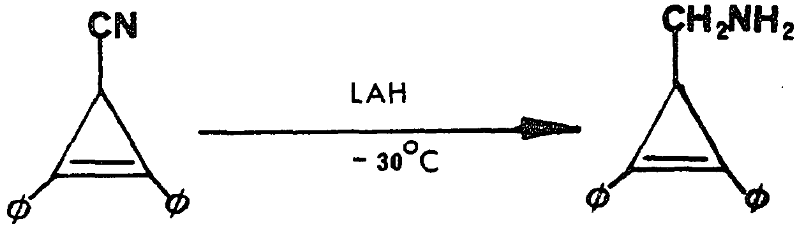
Among the Δ^2-cyclopropenyldiazomethane precursors, Δ^2-2,3-



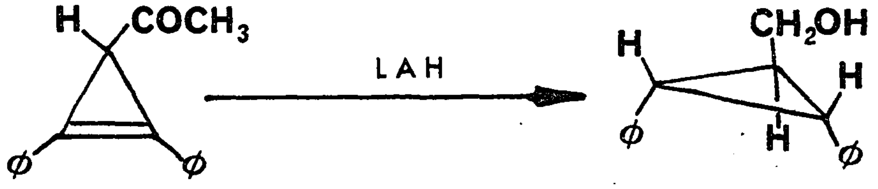


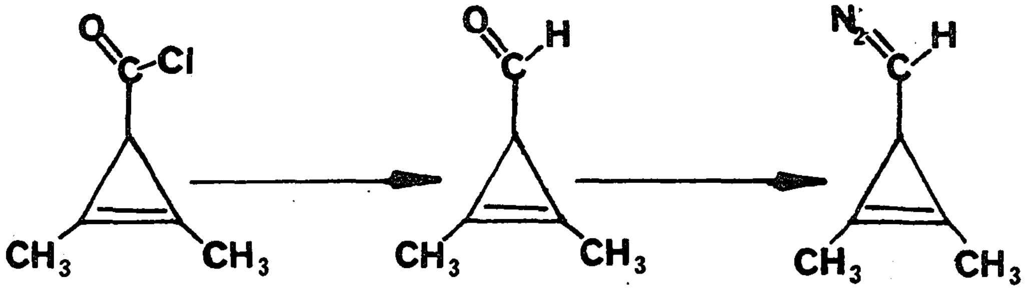


diphenylcyclopropenyldiazomethane is the only precursor known in the literature (62). This compound has been synthesized in seven steps starting with 1,2-diphenyl-3-carboxycyclopropene. Repetition of the synthesis (77) failed because the fourth step, namely the reduction of 1,2-diphenyl-3-cyanocyclopropene did not yield the expected amine.

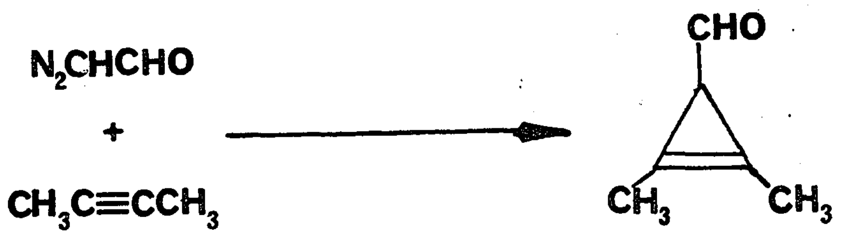


Lithium aluminum hydride seemed to reduce the double band instead of the nitrile function, even when reaction temperature was varied. This is not surprising since both 1,2-diphenyl-3-carbomethoxycyclopropene and the corresponding acid are reduced to cis-1,2-diphenyl-trans-3-hydroxymethylcyclopropane by lithium aluminum hydride (78). Pomerantz (66) had attempted to prepare 1,2-dimethyl-3-formylcyclopropene as a route to Δ^2-2,3-dimethylcyclopropenyldiazomethane by reduction of the acid chloride with lithium aluminum tri-

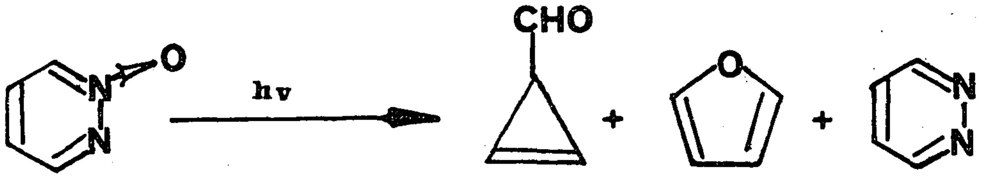




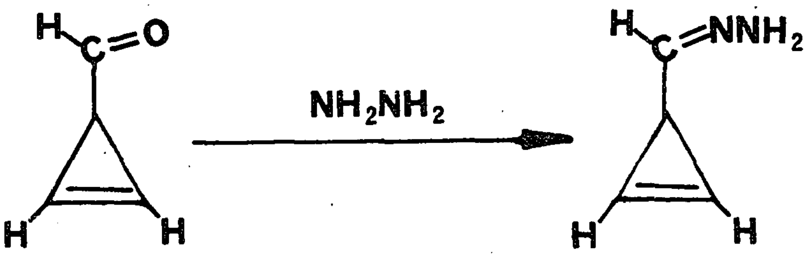
tertiarybutoxyhydride but was unsuccessful. A more promising route to 1,2-dimethyl-3-formylcyclopropene was attempted in



the present work. Dropwise addition of formyldiazomethane to excess 2-butyne containing the palladium complex at 0°C caused evolution of nitrogen and ketene. The excess 2-butyne was distilled at room temperature and the residue analyzed by i.r., n.m.r., and mass spectrometry. The residue shows a broad absorption at 1730 cm^{-1} in the i.r. and trace resonances at 9.6 δ and 9.8 δ in the n.m.r. Several peaks are present in the mass spectrum including the expected ion at m/e 96. The liquid darkens at room temperature. Attempted distillation at 10 mm did not yield any product even after heating over 100°C. The reaction was not repeated when 3-formylcyclopropene became available in 8%

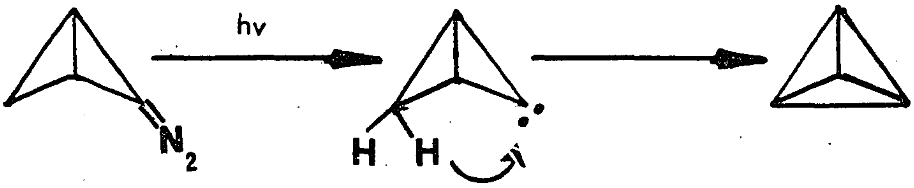


yield via photolysis of pyridazine N-oxide (79). The 3-formylcyclopropene was trapped at -78° and reacted with excess hydrazine. However, no isolable product corresponding

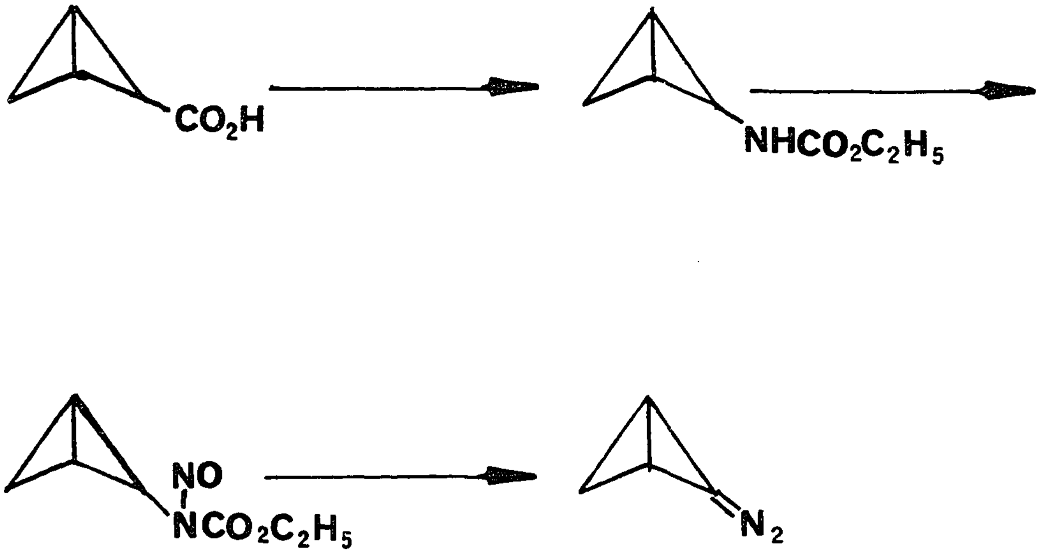


to the hydrazone was obtained (77).

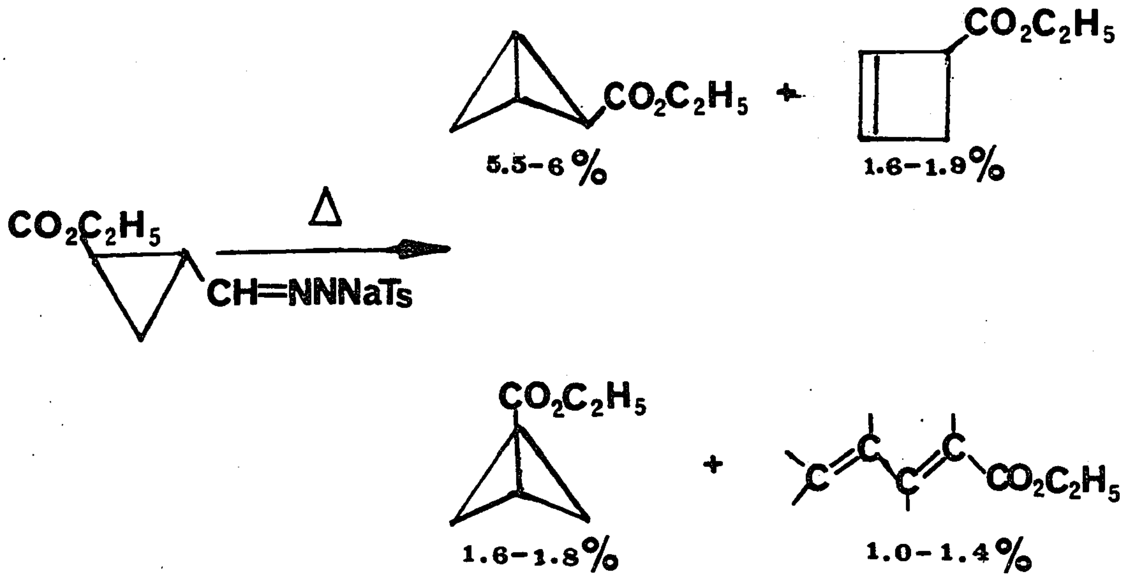
The most promising precursor to tetrahedrane is 2-diazabicyclo[1.1.0]butane.



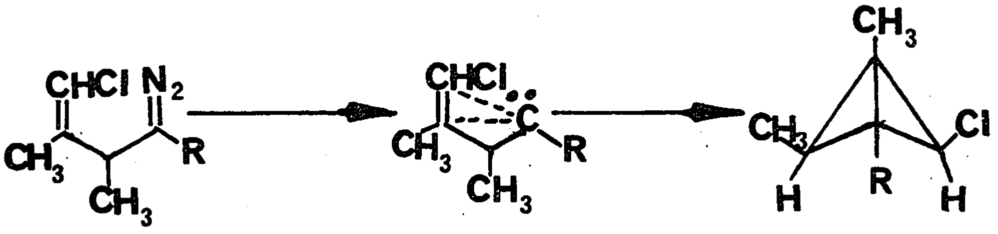
Attempts were tried toward the synthesis 2-carboxybicyclo[1.1.0]butane or N-methyl-2-bicyclo[1.1.0]butanecarbamate as the starting material towards the synthesis of 2-diazobicyclo[1.1.0]butane. There are only two reports in



the literature on attempted preparation of bicyclo[1.1.0]butane substituted at the 2 position. Kirmse and Lechte (80) have reported the preparation of ethyl bicyclo[1.1.0]butane-2-carboxylate in 5-6% yield. Atkins and Trost (81) have synthesized 1-chloro-4-diazo-2,3-dimethyl-1-pentene (R=CH_3) and 1-chloro-4-diazo-2,3-dimethyl-1-butene (R=H) as a route to 2-chlorobicyclo[1.1.0]butane. However, catalytic or photolytic decomposition of 1-chloro-4-diazo-2,3-dimethyl-1-pentene (R=CH_3) and 1-chloro-4-diazo-2,3-dimethyl-1-butene (R=H) gave a mixture of dienes and cyclobutene product; no

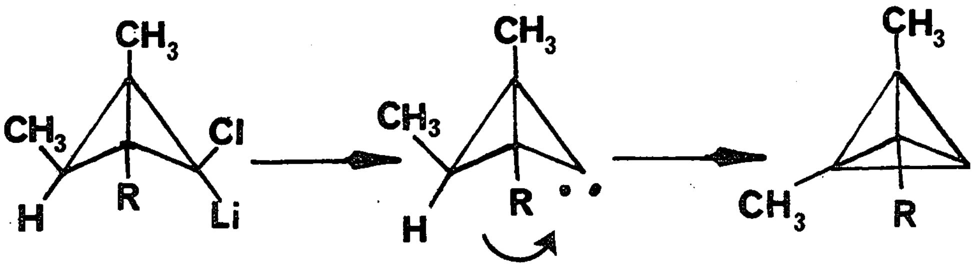


$CO_2C_2H_5$
CH=NNNaTs
Δ
$CO_2C_2H_5$
5.5-6 %
+
$CO_2C_2H_5$
1.6-1.9%
$CO_2C_2H_5$
1.6-1.8%
+
$CO_2C_2H_5$
1.0-1.4%



CHCl
N_2
CH_3
R
CH_3
CHCl
C
CH_3
R
CH_3
CH_3
CH_3
Cl
H
R
H

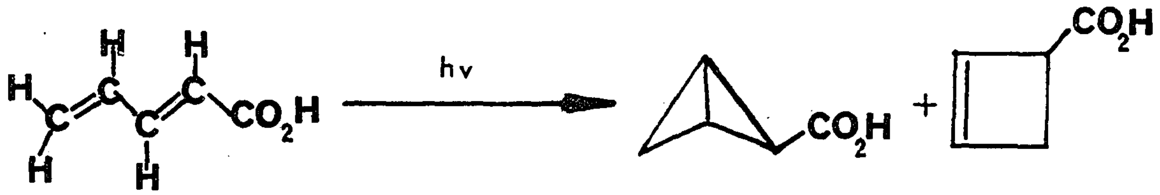
R = CH_3, H



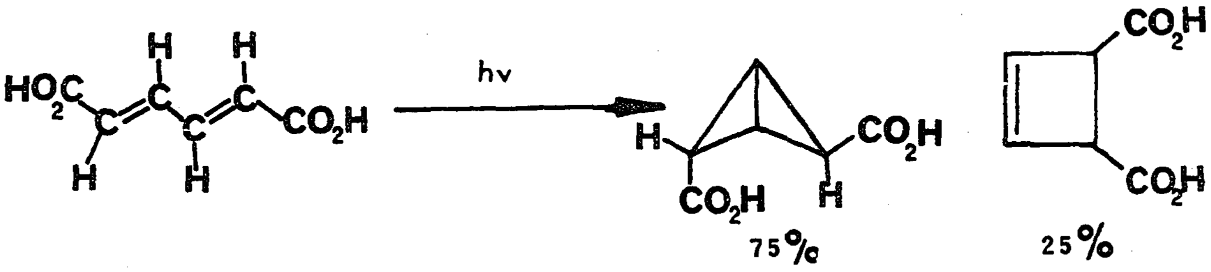
CH_3
CH_3
Cl
H
R
Li
CH_3
CH_3
H
R
CH_3
CH_3
R

chlorobicyclobutane derivate was obtained even upon careful isolation.

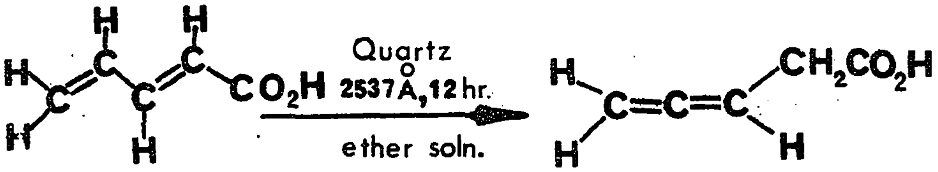
We have elected to synthesize 2-carboxybicyclo[1.1.0]-butane by photolysis of 2,4-pentadienoic acid.



There is a successful precedent to this approach. Kelly (82) has photolyzed a 1% solution of <u>trans</u>, <u>trans</u>-muconic acid in a quartz vessel with low pressure mercury lamp for 3 days and obtained 75% <u>endo</u>, <u>exo</u>-2,4-dicarboxy-bicyclo[1.1.0]butane and 25% 3,4-dicarboxycyclobutene. The same product mixture was obtained with or without Cu(I)Cl

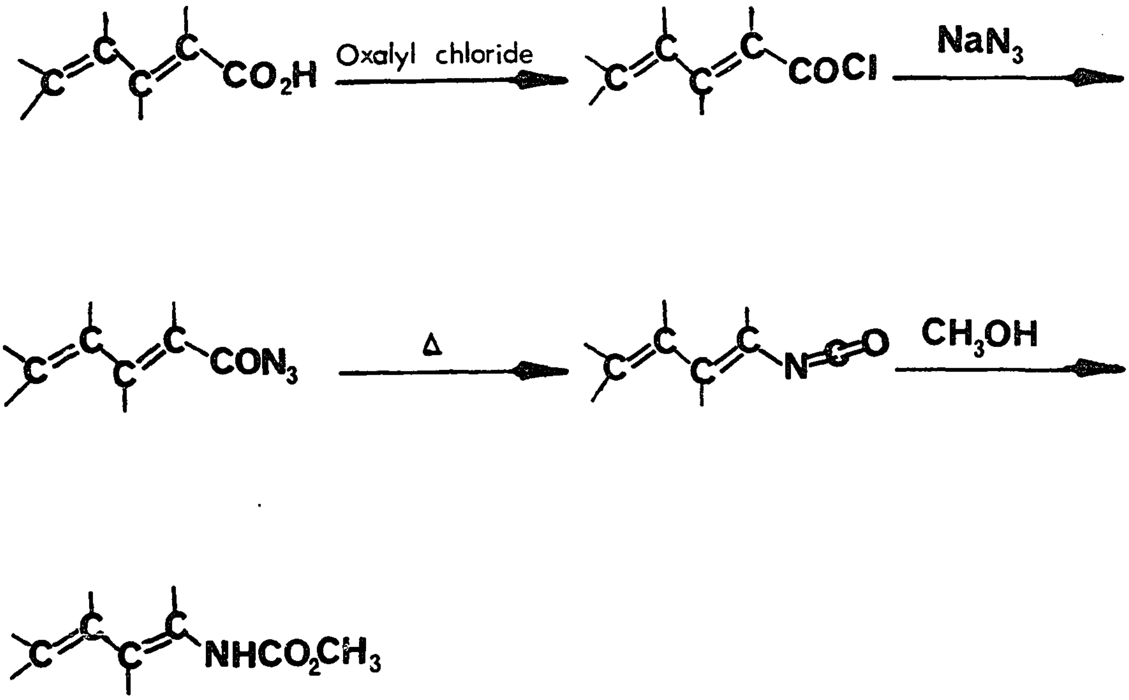


catalyst. Similar irradiation of 2,4-pentadienoic acid using a Rayonet apparatus, however, gave solely 3,4-pentadienoic acid (32% isolated yield). The acid was identified by comparison of its i.r., n.m.r., and u.v. with reported values (83).



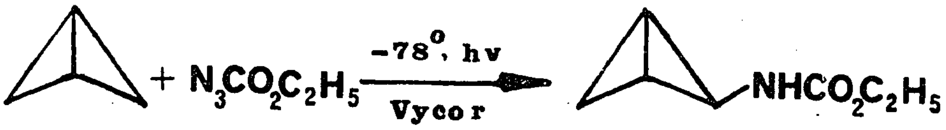
Moreover, the acid in ethyl acetate over PtO_2 catalyst, absorbed two equivalents of hydrogen (the resulting saturated acid was identified by i.r. and n.m.r.) and when heated with 1% aqueous NaOH at 70° for 15 minutes, re-isomerized to 2,4-pentadienoic acid.

Conversion of 2,3-pentadienoic acid to the methyl ester and photolysis as before yields a dark brown oil. Unlike the acid, however, the nmr does not show any allenic product. Moreover, the nmr does not show any bicyclobutyl or cyclobutene products by comparison with known resonances for ethyl *exo*-bicyclo[1.1.0]butane-2-carboxylate and ethyl cyclobutene-3-carboxylate (80). 2,3-Pentadienoic acid was also converted to the methylcarbamate. The methylcarbamate cannot be isolated neat without decomposition, hence,

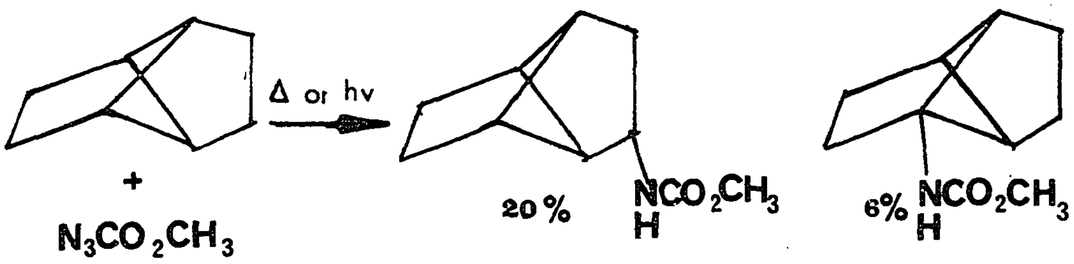


characterization was done on the more stable isocyanate. The methylcarbamate was prepared by dissolving the isocyanate in 5% MeOH-ether solution. Photolysis was started after 4 hours stirring at room temperature (quantitative formation of methylcarbamate). Photolysis was followed by u.v. and solution i.r. Photolytic decomposition of the methylcarbamate was very slow but even after continued irradiation for 3 days, no bicyclobutyl or cyclobutenyl derivative can be observed in the nmr. Instead, a copius amount of yellow brown precipitate was obtained. The nmr shows a very strong methoxyl resonance (not present in the starting material) perhaps due to addition of methanol to the diene of the methylcarbamate.

A final attempt at the synthesis of methyl bicyclo[1.1.0]-butane-2-carbamate was attempted by nitrene insertion to bicyclo-



[1.1.0]butane. There is a successful precedent to this approach. J. Meinwald and D. Aue (84) have functionalized tricyclo[3.3.0.0.^{2,6}]octane by thermolysis or photolysis with methyl azidoformate. Photolysis of ethyl azidoformate



with bicyclo[1.1.0]butane (b.p. 8°) at -78° using a Vycor filter with Hanovia medium pressure lamp took 5 days for a sufficient amount of the azidoformate to decompose. Dark-brown residue coated the photolyzing tube during the duration of photolysis and had to be continually washed. Analysis of the reaction mixture by i.r. and nmr does not indicate the formation of the expected carbamate. The limited amount of bicyclo[1.1.0]butane available precluded a second attempt.

The 2-diazobicyclo[1.1.0]butane still remains to be synthesized. This preliminary work indicates that compared to Δ^2-cyclopropenylcarbene and 2,4-bicyclobutane diradical, 2-carbenabicyclo[1.1.0]butane remains the most promising precursor of the elusive tetrahedrane.

EXPERIMENTAL

Reagents, characterization of compounds, purification, special equipment, matrix isolation and photolysis were similar to the ones mentioned in Part I of this thesis.

Preparations

Methyl diazoacetate

This compound was prepared according to the procedure by Womack and Nelson (85).

A solution of 504 g (4.03 mole) of glycine methyl ester hydrochloride (Aldrich) and 12 g (0.146 mole) in 600 ml water, was cooled to about 0-2° (ice-salt), and treated with a cold solution of 3.20 g (4.64 mole) in 400 ml of water. To the cooled (ca. 5°) solution, 300 ml of ether and 12 ml of 10% sulfuric acid were added and the reaction mixture was stirred for 5 min. The mixture was forced into a separatory funnel under pressure; the ether layer was separated and the aqueous layer returned back into the reaction flask. Once again 300 ml of ether and 60-70 ml of 10% sulfuric acid were added, the mixture was stirred for 5 min, and forced into the separatory funnel; the ether layer was separated and the aqueous layer returned to the reaction flask. The procedure was repeated eight or nine times until the ether layer no longer became colored. Each ether extract was washed immediately three times with 170-200 ml of 10% aqueous sodium carbonate solution. The combined ether solutions were dried over magnesium sulfate and concentrated by rotoevaporation (water bath temperature should be less than 40°). Distillation of the residue at 4 mm gave methyl diazoacetate, b.p. 27-28° (243 g, 2.43 mole, 60.5% yield). The i.r. (neat, NaCl plates) shows strong absorptions at 2120 cm^{-1} and 1720 cm^{-1}. The nmr (CCl_4, TMS) shows two singlets at 3.70 δ (3H) and 4.80 δ (1H).

Note: Use rubber gloves at all times and run the reaction under the hood. Methyl diazoacetate causes severe itching and blisters upon contact with skin.

di-μ-Chlorodi-π-allyldipalladium complex

This complex was prepared according to the procedure published by Dent, Long, and Wilkinson (86).

To a 500 ml Erlenmeyer flask is added 17.7 g (0.10 mole) of $PdCl_2$ (Ventron) and 11.1 g (0.074 mole) of $CaCl_2 \cdot 2H_2O$ in 150 ml methanol. After adding 30 ml (27.7 g, 0.363 mole) of allyl chloride, carbon monoxide was passed for 30 minutes. The mixture was poured into 800 ml of water and extracted with eight 100 ml portions of chloroform. After filtration and separation of the yellow chloroform layer from the colored extract that appeared at the interface, the solution was dried over magnesium sulfate. Evaporation of the chloroform after filtration gave the yellow π-allyl complex, m.p. 151-53° (dec.), 13.3 g (.0364 mole), 18.2% yield.

Ethyl 1,2-dimethylcyclopropene-3-carboxylate

This compound was prepared according to the procedure published by Armstrong (87).

A three-necked 500 ml round bottomed flask is fitted with a Dry Ice-acetone condenser, immersion thermometer and a 250 ml dropping funnel. To a mixture of 145 g (2.70 mole) 2-butyne, 1 g di-μ-chloro-di-π-allyldipalladium and 5 mg of $NaHCO_3$, that had been cooled to 0° was added dropwise a solution 57 g (0.500 mole) of ethyl diazoacetate (Aldrich, distilled before use at 35°/5-6 mm) in 100 g (1.85 mole) of 2-butyne over a 4-1/2 hour period. The reddish orange mixture was distilled and 203.2 g of 2-butyne was recovered. The residue was diluted with methylene chloride, filtered and evapoarted to yield a deep brown oil. Distillation at 3.4 mm yielded a light yellow oil, b.p. 46-48°, 12.20 g (.0880 mole), 17.5% yield based on ethyl diazoacetate. The i.r. (neat, NaCl plates) shows bands at 1730 cm^{-1} (strong) and 1920 cm^{-1} (weak). The nmr (CCl_4, TMS) shows the following resonances: 4.02 δ (quartet, 2H), 2.02 δ (singlet, 6H), 1.89 δ (singlet, H) and 1.20 δ (triplet, 3H).

1,2-dimethylcyclopropene-3-carboxylic acid

This compound was prepared according to the procedure published by Doering and Pomerantz (88).

To a 250 ml r.b. flask was added 100 ml 95% ethanol and 10 g KOH. After heating to 50° to dissolve the KOH, 2 g (0.0143 mole) of ethyl 1,2-dimethylcyclopropene-3-carboxylate was added forming a bright yellow solution. The mixture was refluxed for 2 hours. The ethanol was removed in the rotary-evaporator, the residue dissolved in 35 ml of water and extracted twice with 25 ml portions of benzene. The aqueous solution was acidified with 10% aqueous HCl and extracted with three 35-30 ml portions of ether. After drying the combined extracts over $MgSO_4$, the ether was removed in the rotary evaporator. The residue was extracted with 200 ml of pentane, and this solution was concentrated by blowing off the pentane with a stream of nitrogen. Upon cooling, the pentane solution yielded, 1,2-dimethyl-3-carboxycyclopropene (0.84 g, .00750 mole, 52.5% yield), m.p. 73.5-75° C (73.5-76.5° lit. value, reference (88). The i.r. (KBr pellet) shows two broad bands centered at 1680 and 3000 cm^{-1} and a weak band at 1920 cm^{-1}. The nmr (CCl_4, TMS) shows resonances at 1.89 δ (singlet, 1H), 2.40 δ (singlet, 6H), and 12.0 δ (singlet, 1H, disappears upon addition of D_2O).

1,2-Dimethyl-3-chlorocarbonylcyclopropene

This compound was prepared according to the procedure by Doering and Pomerantz (88).

Oxalyl chloride (8.9 ml, 13.5 g, 0.107 mole) was mixed with 3.03 g (.0271 mole) of 1,2-dimethylcyclopropene-3-carboxylic acid and since the solution began to reflux almost immediately, it was cooled in ice. When the initial reaction subsided, the mixture was refluxed on a steam bath for two more hours. The excess oxalyl chloride was distilled through a 9 cm Vigreux column at 195 mm, b.p. 26-27°. The residue was distilled at 21 mm and 3.15 g (0.233 mole, 85.8% yield), of 1,2-dimethyl-3-chlorocarbonylcyclopropene, b.p. 71-75°, was obtained (b.p. 62-65°/21 mm, reference 88). The i.r. (neat, NaCl plates) shows absorption at 1780 cm^{-1} (strong) and 1920 cm^{-1} (weak). There is no -OH absorption present.

1,2-Dimethyl-3-diazoacetylcyclopropene

This compound was prepared according to the procedure published by Doering and Pomerantz (88).

A solution of diazomethane in ether was made in the usual manner (89) from 7.1 g of EXR-101 (contains 5.0 g of bis(N-methyl-N-nitroso)terephthalamide), 60 ml of 40% aqueous NaOH solution, and 100 ml ether. An aliquot of the

CH_2N_2 ether solution was reacted with excess benzoic acid, and back-titrated with standardized solution of NaOH to the phenolphthalein end point. This titration revealed that the entire solution contains 0.04 moles of CH_2N_2.

To 250 ml of ether containing 50 mmoles of CH_2N_2, cooled in ice, was added 3.0 g (23 mmoles) of 1,2-dimethyl-3-chlorocarbonylcyclopropene in 2 ml of ether over a two hour period. The ether was blown off, on a steam bath, with a stream of nitrogen. The crude yield was 3.8 g. Crystallization of 1,2-dimethyl-3-diazoacetylcyclopropene from ether at -85° to -90° afforded, after centrifugal and removal of the last traces of ether at 1 mm, 2.10 g (15.4 mole), 67% yield. A small sample was chromatographed on a Prep. TLC plate and developed in CH_2Cl_2, extracted with ether, and crystallized at -85 to -90°. After centrifugation, and removal of the last traces of ether, the pure compound was submitted for matrix isolation and photolysis.

The nmr (D_6-benzene, TMS) exhibits resonances at: 1.60 δ (s, 6H), 2.12 δ (s, 1H) and 4.61 δ (s, 1H, $-\underline{CH}N_2$). The i.r. (neat, NaCl plates) exhibits the diazo peak at 2120 cm^{-1} and the cyclopropene double bond at 1910 cm^{-1}. The u.v. (95% ethanol) shows a maximum at 246 mμ ($\varepsilon = 9.67 \times 10^3$).

1-Trimethylsilylpropyne

This compound was readily prepared by refluxing 50 g (0.46 mole) of trimethylchlorosilane with 25.1 g (0.545 mole) of propynyllithium (Foote Mineral Company) in 500 ml anhydrous ether for 30 hours. The reaction mixture was filtered and the filtrate distilled. The product 27.3 g (0.244 mole, 53% yield), boils at 94-95°C (98-99°, lit. value, reference 90). The i.r. shows a strong absorption at 2200 cm^{-1}. The nmr (CCl_4, TMS) shows two singlets at 1.8 δ (s, 3H) and d 0.10 (s, 9H).

Methyl 1-methyl-2-trimethylsilylcyclopropene-3-carboxylate

This compound was prepared according to the procedure published by Nefedov et al. (75).

A three-necked 250 ml round bottomed flask is fitted with a condenser with a drying tube, a 250 ml dropping funnel, and a magnetic stirring bar. To a refluxing solution of 233.9 g (2.08 mole) 1-trimethylsilylpropyne containing 0.03 g $CuSO_4$ was added dropwise a solution of 29.6 g (0.296 mole) methyl diazoacetate in 30 g (0.268 mole) of 1-trimethylsilylpropyne over a 6 hour period. The reddish brown solution was distilled under vacuum and 236 g (b.p. 33°/55 mm) of 1-trimethylsilylpropyne was recovered. Distillation at 10 mm yielded a colorless oil, b.p. 77-81° (lit. value is 85-87°/10 mm, reference 75), 16.9 g (0.0918 mole), 31% yield based on methyl diazoacetate. The i.r. (neat, NaCl plates) shows band at 1715 cm^{-1} (strong) and 1830 cm^{-1} (medium). The nmr (CCl_4, TMS) shows the following resonances: 0.20 δ (singlet, 9H, $-s_i(C\underline{H_3})_3$), and 3.50 δ (singlet, 1H, $-C\underline{H}$), 2.18 δ (singlet, 3H, $-C\underline{H_3}$), and 3.50 δ (singlet, 3H, $-OC\underline{H}_3$).

1-methyl-3-carboxycyclopropene

In a reaction similar to that used for 1,2-dimethyl-3-carboxycyclopropene, a solution of 20 g (0.36 mole) of KOH and 17.4 g (0.0945 mole) of methyl 1-methyl-2-trimethylsilylcyclopropene-3-carboxylate in 250 ml of methanol was refluxed for 4 hours. The methanol was removed in vacuum (rotary evaporator), the residue dissolved in 50 ml water, and extracted twice with 25 ml portions of benzene. The aqueous solution was acidified with 10% aqueous HCl and extracted with three 75-100 ml portions of ether. After drying the combined extracts over $MgSO_4$, the ether was evaporated in vacuum (rotary evaporator) yielding 8.1 g of yellow orange oil. This was chromatographed on a 20 cm column (6 cm diameter) of silica gel (Baker) and eluted with chloroform. Crystallization in hexane gave 3.3 g (.0337 mole), 35.6% yield of white crystals, m.p. 42-44° (lit. value 42.5-43°, reference 75). The i.r. (KBr pellet) shows a weak band at 1830 cm^{-1}, a strong band at 1700 cm^{-1} and a broad band centered at 3160 cm^{-1}. The nmr (CCl_4, TMS) shows resonances at 2.03 δ

(doublet, 2 Hz, 1H, -C$\underline{H}$), 2.20 δ (singlet, 3H, -C$\underline{H}_3$), 6.19 δ (doublet, 2 Hz, 1H, -C =C-$\underline{H}$) and 12.2 δ (singlet, 1H, -$CO_2\underline{H}$, disappears upon addition of D_2O).

1-Methyl-3-chlorocarbonylcyclopropene

0.5 g (.0051 mole) of 1-methyl-3-carboxycyclopropene was dissolved in 10 ml of benzene (distilled over sodium metal). To this mixture was added 3.18 g (0.025 mole) of oxalyl chloride. After evolution of gas has subsided (2 hours), the solvent and excess oxalyl chloride was evaporated *in vacuo*. The i.r. (neat, NaCl plates) of the residue shows acid chloride band at 1780 cm^{-1} and the cyclopenyl band at 1825 cm^{-1}, there is no -OH absorption due to the starting acid. The crude product was used without further purification in the preparation of 1-methyl-3-diazoacetylcyclopropene.

1-Methyl-3-diazoacetylcyclopropene

This compound was prepared using procedure exactly similar to the preparation of 1,2-dimethyl-3-diazoacetylcyclopropene. The i.r. (neat, NaCl) shows strong absorptions at 2110 cm^{-1}, 1825 cm^{-1}, and 1640 cm^{-1}. The nmr (CCl_4, TMS) shows that the -CH_3 resonance superimposes with -CH proton at 2.19 δ (4H), 5.15 δ (singlet, 1H, -C$\underline{H}$-N_2), 6.3 δ (doublet, J=2 Hz, 1H, -C=C-$\underline{H}$).

Attempted preparation of cyclopropene-3-carboxylic acid

In a reaction similar to that used for methyl 1-methyl-2-trimetylsilylcyclopropene-3-carboxylate, 25.0 g (0.25 mole) of methyl diazoacetate in equal volume of bis(trimethylsilyl)-acetylene (91) was added dropwise to a refluxing solution of 258.0 g (1.51 mole) bis(trimethylsilyl)acetylene containing 0.024 g of $CuSO_4$ over a period of 2-1/2 hours. The excess bis(trimethyl)acetylene was distilled at 35°/10 mm (246.8 g recovered). The residue prior to final distillation was examined by i.r. and nmr. The i.r. shows a very broad absorption at 1740 cm^{-1} but no absorption at 1900 cm^{-1} characteristic of the cyclopropenyl double bond. The nmr (CCl_4, TMS) shows several resonances from 0.18 d to 6.2 δ but no resonances attributed to the expected product. The mass spectrum shows only the bis(trimethylsilyl)acetylene. Distillation at 10 mm gave 0.5 g of material but i.r., nmr, and mass spectral analysis proved negative. The reaction was repeated twice but the same negative results were obtained.

1,5-Diphenyl-tricyclo[2.1.0.0^{1,5}]pentan-3-one

This compound was synthesized following the exact procedure published by Masamune (76). The i.r. (KBr pellet) shows a very strong carbonyl absorption at 1770 cm^{-1}. The nmr (CCl_4, TMS) shows the two equivalent aliphatic protons at 2.76 δ and the phenyl protons at 7.30 δ (10 H).

1,5-Dipropyl-tricyclo[2.1.0.0^{1,5}]pentan-3-one

This compound was prepared following the exact procedure published by Masamune (76) starting from the 1,2-dipropylcyclopropene-3-carboxylic acid (92). The nmr (CCl_4, TMS) shows a singlet at 1.83 δ (2H) in addition to the typical *n*-propyl resonance.

Attempted preparation of 1,5-dimethyl-tricyclo[2.1.0.0$^{1.5}$]-pentan-3-one

Following the exact procedure from the Ph.D. thesis of Pomerantz (66), to a stirred suspension of about 400 mg of copper powder in 50 ml *n*-hexane, in a three-necked, round-bottomed flask equipped with a reflux condenser, nitrogen inlet and outlet, dropping funnel and stirrer was added, dropwise, over a three hour period, 1.0 g of 1,2-dimethyl-3-diazoacetylcyclopropene in 50 ml of *n*-hexane. The solution was kept at reflux and small portions of copper powder were added periodically during the reaction until a total of 1 g had been added. After an additional half hour of refluxing, the reaction mixture was filtered and the solution concentrated by distilling the hexane at 142 mm through a 37 cm column packed with "heli-pak" until about 10 ml remained. This solution was analyzed by i.r. and nmr for the presence of the expected product. Analysis does not show the characteristic carbonyl absorption at 1786 and 1766 cm^{-1} in the i.r., nor the characteristic resonances at δ 2.05 ($-CH_3$)

and 1.73 δ (C-H) in the nmr.

Repetition of the same reaction using 4.0 g of 1,2-dimethyl-3-diazoacetylcyclopropene only gave copious amount a dark-brown material insoluble in most organic solvents. The same result was obtained when 1,2-dimethyl-3-diazoacetylcyclopropene was photolyzed in tetrahydrofuran following the procedure for the successful synthesis of 1,5-diphenyl-tricyclo[2.1.1.$0^{1,5}$]pentan-3-one.

Attempted synthesis of 1,2-dimethylcyclopropene-3-carboxaldehyde

2.0 g (.0286 mole) α-diazoacetaldehyde (93) in chloroform was slowly added to excess 2-butyne containing catalytic amount of the Pd-allyl complex. Copious amount of gas (N_2 and ketene) was evolved. The solution which turned reddish brown was filtered, and then distilled at room temperature to recover excess 2-butyne. The residue was analyzed by i.r., nmr, and mass spectrometry. Analysis shows a broad absorption at 1730 cm^{-1} in the i.r. and trace resonances at 9.6 δ and 9.8 δ in the nmr for the aldehydic proton. Several peaks are present in the mass spectrum including the expected ion at m/e 96. The residue darkens at room temperature. Attempted distillation at 10 mm did not yield any product even after heating over 100°.

Attempted preparation of 2-carboxybicyclo[1.1.0]butane

A mixture of 4.0 g (0.0408 mole) of 2,4-pentadienoic acid (94) and 500 ml of anhydrous ether (Fisher) was placed in a 1 liter quartz vessel fitted with a reflux condenser, $CaCl_2$ drying tube, and magnetic stirring, and degassed with purified nitrogen for 30 minutes. Irradiation (2537 Å) for 24 hours in the Rayonet apparatus caused the disappearance of most of the starting material evidenced by conversion of the yellow solution into a colorless reaction mixture. The solvent was evaporated and the nmr of the crude product shows three multiplets at 3.1, 4.8, and 5.3 δ integrating at 2:2:1. Distillation gave 1.3 g (.0133 mole), 32.4% yield of colorless oil, b.p. 114.5-115.5°/26 mm. The i.r. shows the allene absorption at 1935 cm^{-1}. The nmr (CCl_4, TMS) shows resonances at: 3.2 δ (multiplet, 2H, $-C\underline{H_2}-$), 4.83 δ (multiplet, 2H, $C\underline{H_2}=C=C$), 5.25 δ (quintuplet, 1H, $C=C\underline{H}-$), and 10.9 δ (singlet, 1H, $CO_2\underline{H}$). The mass spectrum shows the molecular ion at m/e 98. The compound consumed 2 moles of hydrogen upon reduction using PtO_2 as catalyst and the resulting saturated acid identified by i.r. and nmr. Heating the acid for 15 minutes at 70° in 10% NaOH gave the 2,3-pentadienoic acid identified by i.r. and nmr. Photolysis with Cu(I)Cl catalyst gave the same result.

Attempted preparation of methylbicyclo[1.1.0]butane-2-carboxylate

1.0 g (.0102 mole) of 2,4-pentadienoic acid was dissolved in ether and reacted with 1.34 g (.032 mole) of CH_2N_2 in ether at 0°C. After stirring for 30 minutes, excess CH_2N_2 was removed by bubbling nitrogen gas into the yellow solution. The solvent was evaporated (rotary evaporator), the residue (confirmed by nmr to be quantitatively the methyl ester) was triturated with ether, and filtered through a Celite pad. The filtrate was diluted with ether to make a 1% solution and then photolyzed (2537 Å), in a Rayonet apparatus. After 2 days, yellow precipitate has collected on the walls of the photolyzing well. This precipitate was dissolved in methanol and combined with the ether solution. Evaporation of the solvent (rotary evaporator) left a residue which was analyzed by i.r. and nmr. The i.r. (neat, NaCl) shows a strong carbony absorption at 1740 cm^{-1}; the allene absorption at 1935 cm^{-1} and the diene absorption at 1620 cm^{-1} are absent. The nmr (CCl_4, TMS) also revealed the conspicuous absence of any allenic resonance due to methyl 3,4-pentadienate or dienic resonance due to methyl 2,3-pentadienoate. The only significant feature of the nmr is a broad resonance at 3.8 δ and 1.10 δ. Closer analysis of the resonance at 1.10 δ revealed that it is not due to the expected product or its cyclobutene isomer by comparison with published spectra of ethyl bicyclo[1.1.0]butane-2-carboxylate and ethyl cyclobentene-3-carboxylate.

Conversion of 2,3-pentadienoic acid to 1,3-butadienyl isocyanate

5.0 g (0.051 mole) of 2,3-pentadienoic acid was dissolved in 30 ml anhydrous benzene. To this was added 6.62 g (0.051 mole) of oxalyl chloride (Aldrich, 98%). Intermittent cooling with an ice-water bath was necessary to control the vigorous evolution of gas. The mixture was stirred at room temperature until gas evolution has subsided (*ca.* 4 hours). The i.r. (neat, NaCl plates) of the reaction mixture shows the acid chloride absorption at 1770 cm^{-1}, confirming the quantitative formation of 2,3-pentadienoic acid chloride.

Into a 3-necked round bottomed flask provided with a mechanical stirrer and thermometer, 4.07 g (0.0626 mole) of sodium azide in 25 ml water was added and cooled to 0°. To this solution was added drop by drop and with stirring, the 2,3-pentadienoic acid chloride-benzene solution over a 15 minute period. After addition, the mixture was stirred further for 30 minutes at 0°. The benzene layer was separated, washed once with 10% aqueous Na_2CO_3 and then with saturated NaCl solution. After drying over magnesium sulfate the solution was filtered and evaporated (rotary evaporator) with no heating to give a colorless oil. An infrared spectrum of the crude material (4.6 g) showed a strong azide band at 2158 cm^{-1} as well as some isocyanate present (2270 cm^{-1}).

The neat azide was dissolved in 30 ml nitrobenzene and the solution heated in a flask (85°-120°) provided with two traps, ice-bath and Dry Ice-acetone bath trap. The trapped material was distilled to give 2.7 g (.0284 mole), 55.6% yield, b.p. 42.5°/58 mm. The i.r. (neat, NaCl plates) shows a very strong band at 2270 cm^{-1}. The nmr ($CDCl_3$, TMS) shows two multiplets: 4.90-5.40 δ (2H) and 5.80 δ-6.6 δ (3H). The u.v. (Hexane) shows a maximum at 237.5 mμ ($\varepsilon = 2.50 \times 10^5$). The reactivity of this compound precluded C,H microanalysis but the exact elemental composition was determined to be C_5H_5NO, 95.0369 (calculated: 95.037) by high resolution mass spectroscopy.

Attempted preparation of N-methyl 2-bicyclo[1.1.0]butanecarbamate

0.265 g (.00279 mole) of 1,3-butadienyl isocyanate was dissolved in 30 ml anhydrous ether containing 5% methanol, and stirred under nitrogen for 10 hours at room temperature. After this time, the isocyanate is quantitatively converted to the desired carbamate as evidenced by the disappearance of the 2270 cm^{-1} band and appearance of 1750 cm^{-1} band in the infrared. Photolysis (2573 Å) of the solution in a quartz vessel was complete in 24 hours as monitored by the disappearance of the u.v. maximum and i.r. absorptions of starting material. Copious amount dark-brown material was formed. Evaporation of the solvent and nmr analysis revealed a very strong resonance at 3.75 δ. The region around 1.2-1.75 d was examined closely by comparison with published spectra of bicyclic or cyclobutene derivates. There is no evidence for a monomeric bicyclic or cyclobutene derivative.

Attempted nitrene insertion to bicyclobutane

A mixture of 8.0 g (0.148 mole) of bicyclo[1.1.0]butane (95), 2.0 g (.0148 mole) of ethyl azidoformate (96) and 0.5 g (.0037 mole) of nitrobenzene was cooled in Dry Ice-isopropanol bath in a quartz tube. It was photolyzed using a Hanovia mercury lamp, medium pressure, 450 watts, through a Vycor filter. The reaction was monitored by infrared to detect the formation of any insertion product. The inside of the tube was coated with a dark brown residue and was continually cleaned and resumed the photolysis. The infrared of the dark brown residue showed a carbonyl absorption at 1740 cm^{-1} and azide absorption at 2117 and 2190 cm^{-1} due to ethyl azidoformate. Continued irradiation for a week did not result in any new product detected by i.r.

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