

1976

Synthesis and characterization of highly reactive molecules: o-Benzyne, 2-methyl-2-sila-2-butene, benzocyclobutadiene and 9, 10-dehydeoanthracene

Cheng-Chung Chang
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Synthesis and characterization of highly reactive
molecules: o-Benzyne, 2-methyl-2-sila-2-butene,
benzocyclobutadiene and 9,10-dehydroanthracene

by

Cheng-Chung Chang

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
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1976

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GENERAL INTRODUCTION

For several decades, chemists have been developing new techniques for the investigation of reaction intermediates. When an intermediate is involved in a reaction, the successful detection of the intermediate species is the best way to elucidate the mechanism. Success in the direct observation of intermediate has been limited to those species which are relatively stable under ordinary laboratory conditions. Many intermediates are too reactive to allow direct detection. The generation and observation of such reactive species is of interest both as a challenging synthetic problem and as an extension of our understanding of the fundamental of structure and bonding. Existence of transient species often poses a formidable problem. Indeed, much of the evidence for most reactive intermediates comes from inferences based on chemical observations. The direct detection of an intermediate by some physical means is feasible only if it can be made to exist for a sufficiently long period of time. Under such conditions, the species may no longer qualify in the strictest sense as a reactive intermediate, since it either must be too stable to react readily or must be trapped in such a manner that its normal course of reaction is prohibited. In spite of these qualifications, some of the

most exciting research in organic chemistry has involved the observation and characterization of reactive intermediates.

To prevent decomposition and bimolecular reactions of reactive intermediates, low temperature and high dilution techniques have to be employed. Matrix isolation techniques meet both requirements. The cold matrix or an inert solvent serves to isolate the primary products, prevents secondary thermal reactions and acts as a heat sink for exothermic reactions. Without a matrix, there is no temperature control, and no selective reaction. The technique was first initiated by the study of absorption spectrum of triphenyl radical in glassy matrix by Lewis and Lipkin.¹ They found that a glassy matrix made from EPA (ether, isopentane and ethanol) in a ratio of 5:5:1 gave a good matrix at liquid nitrogen temperature. Work similar to that of Lewis was carried out by Norman and Porter,² who first used hydrocarbons as the matrix material to study free radicals in 1954. However, it was Whittle et al.³ and Becker and Pimentel⁴ who developed the technique and demonstrated its general applicability. Pimentel used nitrogen and argon as the inert matrix to study many radicals formed by photolysis.⁵ More recently, similar techniques were employed by Milligan and Jacox in study free radicals.⁶

The early workers used double Dewar cryostats which used liquid hydrogen (b.p. 20° K) or liquid helium (b.p. 4° K) as a primary refrigerant and liquid nitrogen (b.p. 77° K) as a secondary refrigerant.^{5,6} Subsequently a cryogenic device, the "Cryo-Tip" (Air products and Chemical, Inc.), was developed. It uses the open-cyclo Joule-Thomson expansion of high pressure cylinder gases.^{7,8} More recently, several closed-cyclo cryogenic refrigerators have become commercially available.⁹ Until recently, matrix isolation has been used primarily by physicists and physical chemists for the study of the physical properties of a variety of reactive species. Common to all these studies is the structural simplicity of the compounds investigated, e.g., HBr, HCN, NH_3 , small alkyl radicals and etc.¹⁰ Little work has been conducted with the goal of synthesizing more complex structures. Recently, the technique in hands of organic chemist has opened a new era for organic synthesis. The pioneering work of O. L. Chapman *et al.*¹¹ and Lin and Krantz¹² on the synthesis of cyclobutadiene in 1973 is clearly a breakthrough in the use of matrix isolation. The remarkable achievement was followed by the synthesis of *o*-benzyne¹³ and many other reactive compounds in the laboratories of O. L. Chapman. As a result of this work, matrix isolation

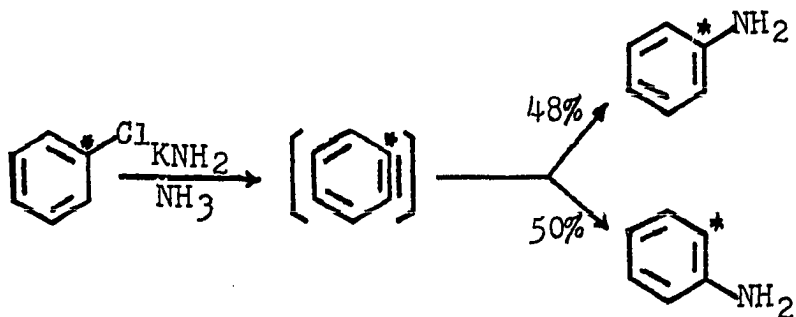
has been demonstrated to be a powerful tool in organic synthesis.

The present work was undertaken to synthesize para and ortho-benzynes, benzocyclobutadiene and silaethylenes. This involved the preparation of potential precursors for photolysis, thermolysis or other chemical reactions to generate the desired species under conditions suitable for spectroscopic observation. Since the techniques of low temperature studies such as matrix isolation have been well documented,^{10,14} the methods will not be discussed here in further detail. However, a specific description of the technique used in these studies will be given in the experimental part of Chapter I.

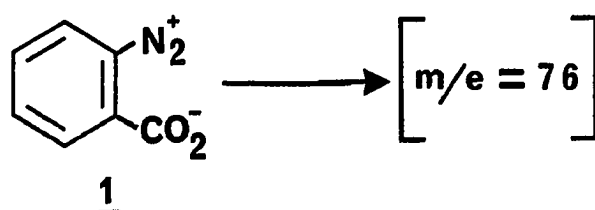
PART I. 1,2-DEHYDROBENZENE (o-BENZYNE)

INTRODUCTION

Rearrangements of aryl halides initiated by strong nucleophiles have been known for more than seventy years.¹⁵ Many papers have been published on the amination of aryl halides by metal amides in liquid ammonia.¹⁶ A C_6H_4 intermediate was first suggested by Bachmann and Clarke¹⁷ to rationalize the formation of triphenylene and polyphenyl in the Wurtz-Fittig reaction of chlorobenzene with sodium metal. Later, similar suggestions were made by Morton *et al.*¹⁸ and Lüttringhaus and Sääf¹⁹ to explain the rearrangements and aminations of aryl halides. In 1940, Wittig *et al.* attempted to classify a large number of experimental facts relating to organometallic reaction by postulating intermediate formation of dehydrobenzene.²⁰ However, the first compelling argument for occurrence of dehydrobenzene was not made until the brilliant work of Roberts and co-workers in 1953.²¹ They showed that the reaction of (1- ^{14}C)-chlorobenzene with potassium amide in liquid ammonia gave both of the expected labelled anilines in approximately equal quantities.



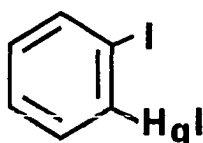
It is now known that many results can be interpreted in terms of mechanisms which involve benzyne as an intermediate. A variety of other way to generate benzyne have also been reported.²² common to these studies is the idea that benzyne is a transient intermediate and not a directly observable species. The first physical evidence was provided by Berry and his co-workers^{23,24} in 1960. They generated benzyne by flash photolysis of benzenediazonium-2-carboxylate (1) and applied the technique of time-resolved mass and ultraviolet spectroscopy.^{25,26} They combined a flash photolysis apparatus, a time-of-flight mass spectrometer, and an oscillographic recorder. In their experiment,



the molecules generated by flash photolysis are allowed to flow continuously into the mass spectrometer which probes them after short, regular time intervals. A peak at $m/e = 76$ decreases and disappears completely after 250-300 μ sec, while in the same time interval biphenylene ($m/e = 152$) appears, increases and reaches its maximum. The authors attributed the signal at 76 to dehydrobenzene. Signals for N_2 and CO_2 were also observed.

Time resolved absorption spectra have been recorded in

the same system.^{25,26} They observed a gradual development of a broad absorption at 2430 \AA between 30 and 100 μsec . This absorption is always observed independent of whether benzene-diazonium-2-carboxylate or *o*-iodophenylmercuric iodide (2) serves as the precursor. However, biphenylene is only formed

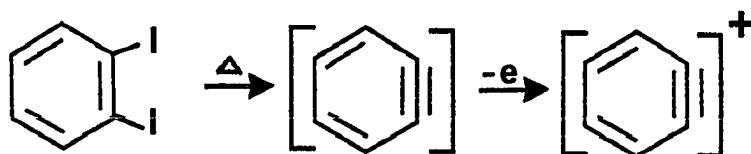


2

from the former precursor. They also reported a second order dependence on the concentration of benzyne ($k = 10^9 \text{ mole}^{-1} \text{ sec}^{-1}$) in accord with the formation of biphenylene.¹¹

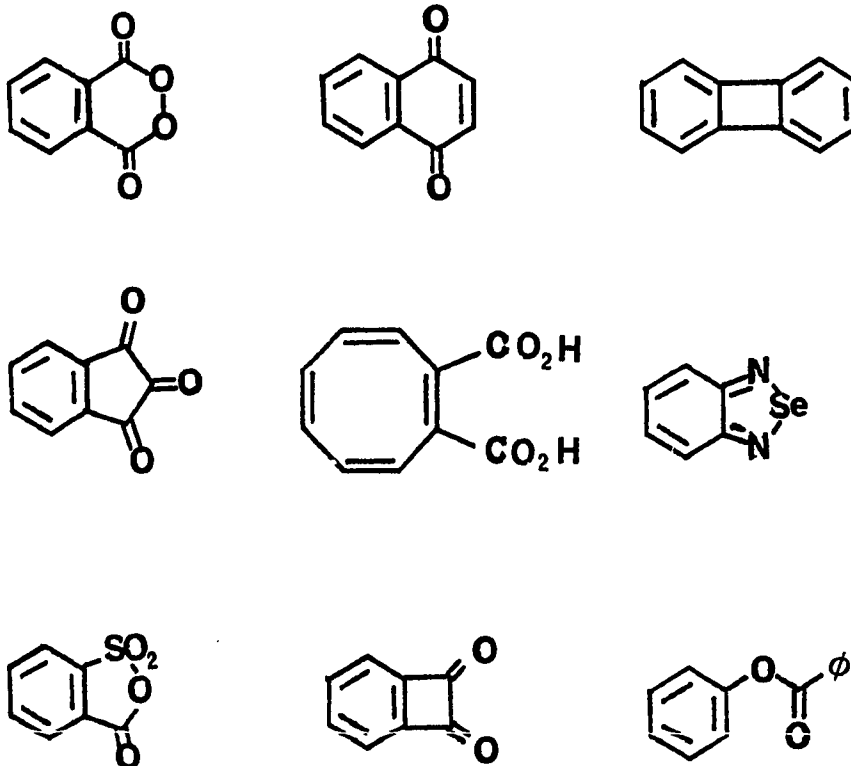
Schüler and Lutz reported the emission spectrum of dehydrobenzene in 1961.²⁷ A broad emission at $3400\text{-}4000 \text{ \AA}$ was observed in their experiments. The formation of biphenylene was observed in their studies.

A species of $m/e = 76$ has also been detected during the thermolysis of *o*-diiodobenzene in gas phase.²⁸ The appearance potential of benzyne ion was determined to be 9.75 e.v. using both *o*-diiodobenzene²⁹ and *bis*-2-iodophenyl

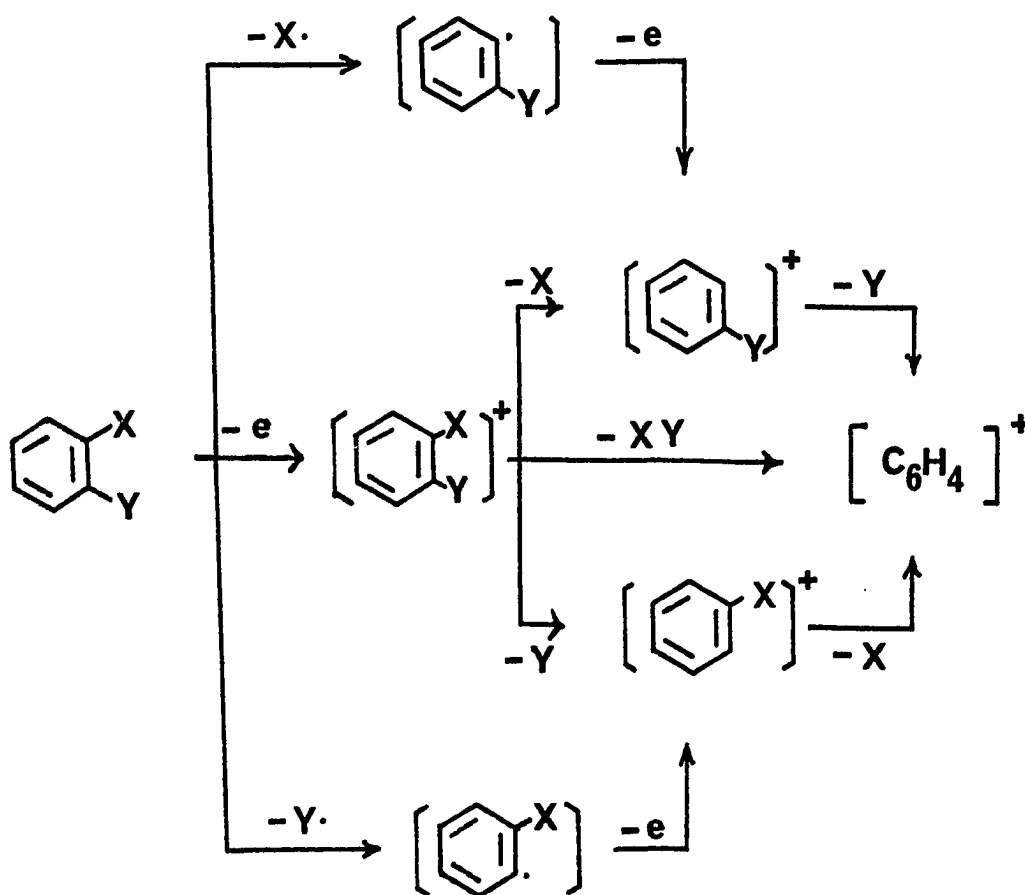


mercury.³⁰

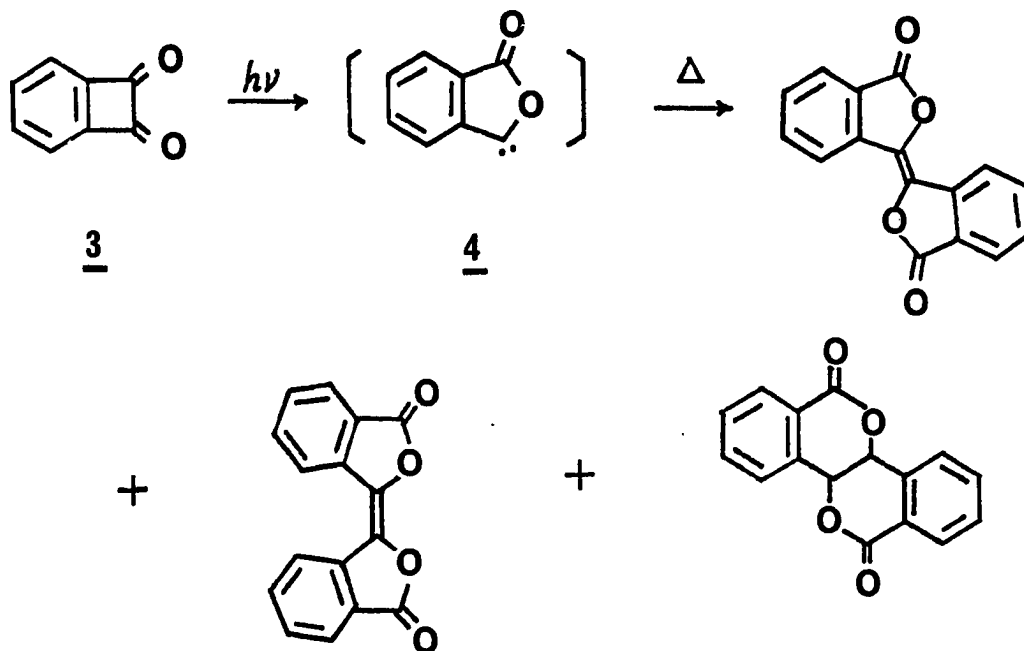
In fact, a mass spectral peak at $m/e = 76$ can be generated using as substrate any of the following compounds



as well as many other disubstituted benzenes.^{22,23} It has not been demonstrated that the precursors of these ions are a neutral species of the same molecular weight. Indeed, a variety of mechanisms can lead to an ion of $m/e = 76$ without involving benzyne.



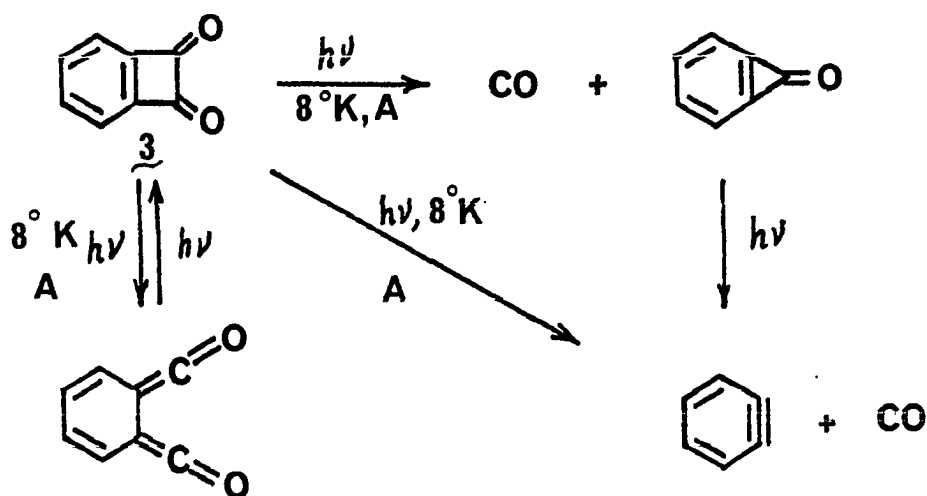
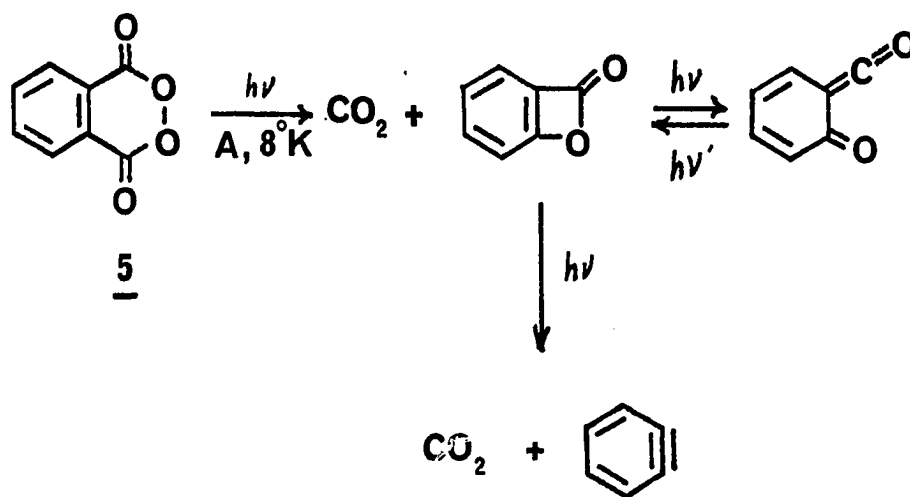
Low temperature techniques were employed by Staab and Ipaktschi³¹ and Chapman and McIntosh³² in attempts to generate benzyne. Both groups reported the photolysis of benzocyclobutenedione (3) to yield dimers, probably through the carbene intermediate. (4)



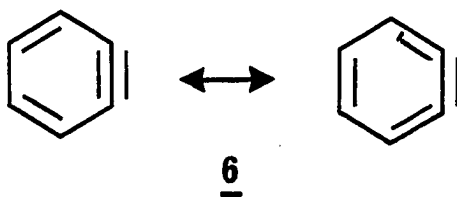
Later, decarbonylation of 1 was observed without detection of benzyne upon its irradiation in ethanol at room temperature³³ and EPA matrix at 77° K.³⁴ In the latter experiment, Kolc showed that biphenylene was formed when the matrix was warmed showing that benzyne was the decarbonylation product.

The preparation of benzyne under conditions conducive to direct spectroscopic observation was recently achieved by Chapman and co-workers, who reported that the photolysis

of both 3 and phthaloyl peroxide (5) matrix isolated in argon at 8° K gave benzyne.



The spectrum obtained from that experiment only includes the region $400\text{-}1700\text{ cm}^{-1}$. Unfortunately, the more interesting region between 1900 cm^{-1} and 2400 cm^{-1} , was not reported. This region is very instructive because it will tell the strength of the triple bond between the dehydro centers of benzyne (6).



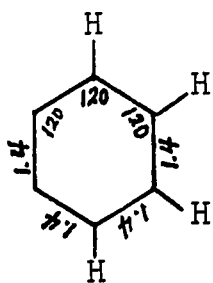
Very little experimental evidence on structure and bonding is available. On the other hand, there is abundance of theoretical studies of benzyne. Each has given rise to a different set of structural parameters, these are summarized in Figure 1.

The calculations carried out by Hoffmann and co-workers are based on idealized geometry obtained by removing two hydrogens from a D_{6h} benzene with bond lengths C-C 1.40 \AA and C-H 1.10 \AA .³⁵ Even with this assumption, the increased 1-2 overlap population (1.3685) indicates partial triple-bond character. With the same parameter an acetylene with C≡C bond length of 1.40 \AA has an overlap population of 1.6020, while a normal acetylene with C≡C at 1.21 \AA has 1.9095. If one converts the MO result into valence bond

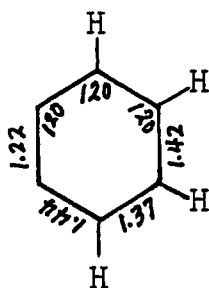
Figure 1 Structure suggested for benzyne

- I Hoffmann et al.³⁵
- II Coulson³⁶
- III Mckelvey and Washburn³⁷
- IV Fraenkel and Newton³⁸
- V Haselbach³⁹
- VI Dewar and Li⁴⁰
 - a. siglet without CI
 - b. siglet with CI
 - c. triplet
- VII Laing and Berry⁴¹

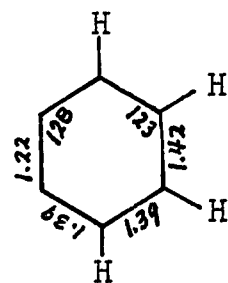
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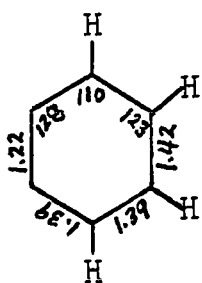
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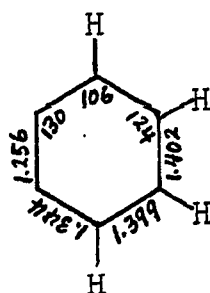
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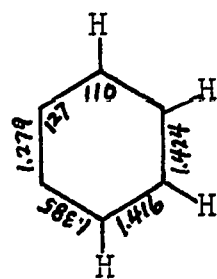
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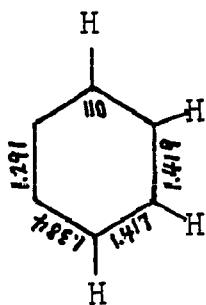
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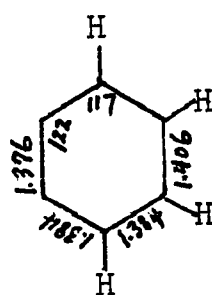
VIa



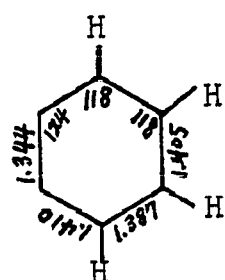
VIb



VIc



VII



representation, there should be considerable contribution from the resonance form of the cumulene-like structure, as well as from the aryne-like structure. However, these authors did not give a clear structure of benzyne.

The results from Coulson,³⁶ Mckelvey and Washburn,³⁷ and Fraenkel and Newton³⁸ are quite similar. All suggest an acetylenic C₁C₂ bond at 1.22 Å and C₄C₅ bond slightly elongated (1.42 Å) with respect to benzene. By using extended basis SCF calculation, Newton and his co-worker estimated 120 kcal/mole for the heat of formation of benzyne. The bond distance of 1.22 Å they obtained for C₁C₂ bond suggested a very strong triple bond character.

Supporting Hoffmann's data, Haselbach's MINDO/2 SCF procedure shows³⁹ a slightly better result. He calculated the strained "triple bond" to be 0.05 Å longer than that of acetylene (1.205 Å) which implies a sizable resonance contribution comes from the cumulene-like structure.

Using improved version of MINDO (MINDO/3), Dewar and Li reinvestigated the problem of benzyne.⁴⁰ Their calculations reveal that a singlet benzyne has short 1,2 bond and large 123 and 612 bond angles. They also suggested that the remaining C-C bond lengths are similar, implying retention of benzenoid aromaticity.

The most reliable structure so far comes from Laing and

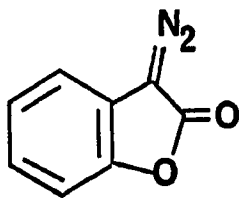
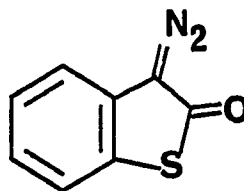
Berry's normal coordinate analysis⁴¹ of the infrared spectrum published by Chapman and co-workers.¹³ On the basis of the observed matrix-infrared spectrum between 400 and 1700 cm^{-1} , a structure, set of force constants, and bond orders are proposed by Berry and his co-workers. They predict the yet-unobserved frequencies at 2083 cm^{-1} and 2450 cm^{-1} for triple bond and infrared active frequencies of perdeuteriobenzynes.

The reactivity of benzyne reveals the species is more like a diradical. Yet there is no evidence that the ground state of benzyne is anything but a closed-shell singlet.⁴² The microwave spectrum has not been reported and the electronic spectrum shows a featureless continuum which contributes no positive information about the structure. o-Benzyne has offered a particularly challenging and intriguing problem which tests our capabilities to infer structures and bonding, ever since the first suggestion of its existence.

Therefore, continued studies of o-benzyne are clearly needed to establish the nature of bonding and geometry of this species. In particular, precursors which permit examination of the triple bond stretch region of the spectrum of benzyne are needed.

RESULTS AND DISCUSSION

To extend the spectroscopic studies of benzyne, it would be useful to design a new photochemical method for the introduction of multiple bonds which is suitable for use in its synthesis.⁴³ The 3-diazobutyrolactone and 3-diazobutyrothiolactone part structures are chosen as the precursors and

78

are designed to build in strain energy in a series of steps, such that introduction of the double bond occurs in a process involving strain relief in a high energy intermediate.

Thermodynamic driving force will be provided by elimination of a small, stable molecule (nitrogen or carbon monoxide) at each step.

Irradiation of 3-diazobenzofuranone (7) at low temperatures gives two primary products, 9 ($\lambda_{\max}^{2\text{MeTHF}}$ 255, 286, 293 nm, Figure 2; 2150 cm^{-1} , Figure 3) and 10 (2040 cm^{-1} , Figure 3; $\lambda_{\max}^{2\text{MeTHF}}$ 462 nm, Figure 2). The primary photoproducts readily interconvert photochemically with long wavelength ($>350\text{ nm}$) light favoring the ketene (9) and short wavelength light (254 nm) favoring 10. Continued irradiation

Figure 2 Irradiation of 3-diazobenzofuranone at 77° K,
uv spectrum

Dotted line, 7 in 2-MeTHF; dashed line, 10 (with
some 9) generated by photodecomposition of 7 with
ultraviolet light (250-400 nm); solid line, 9
after bleaching of 10 away with visible light.
All spectra and photochemistry at 77° K.

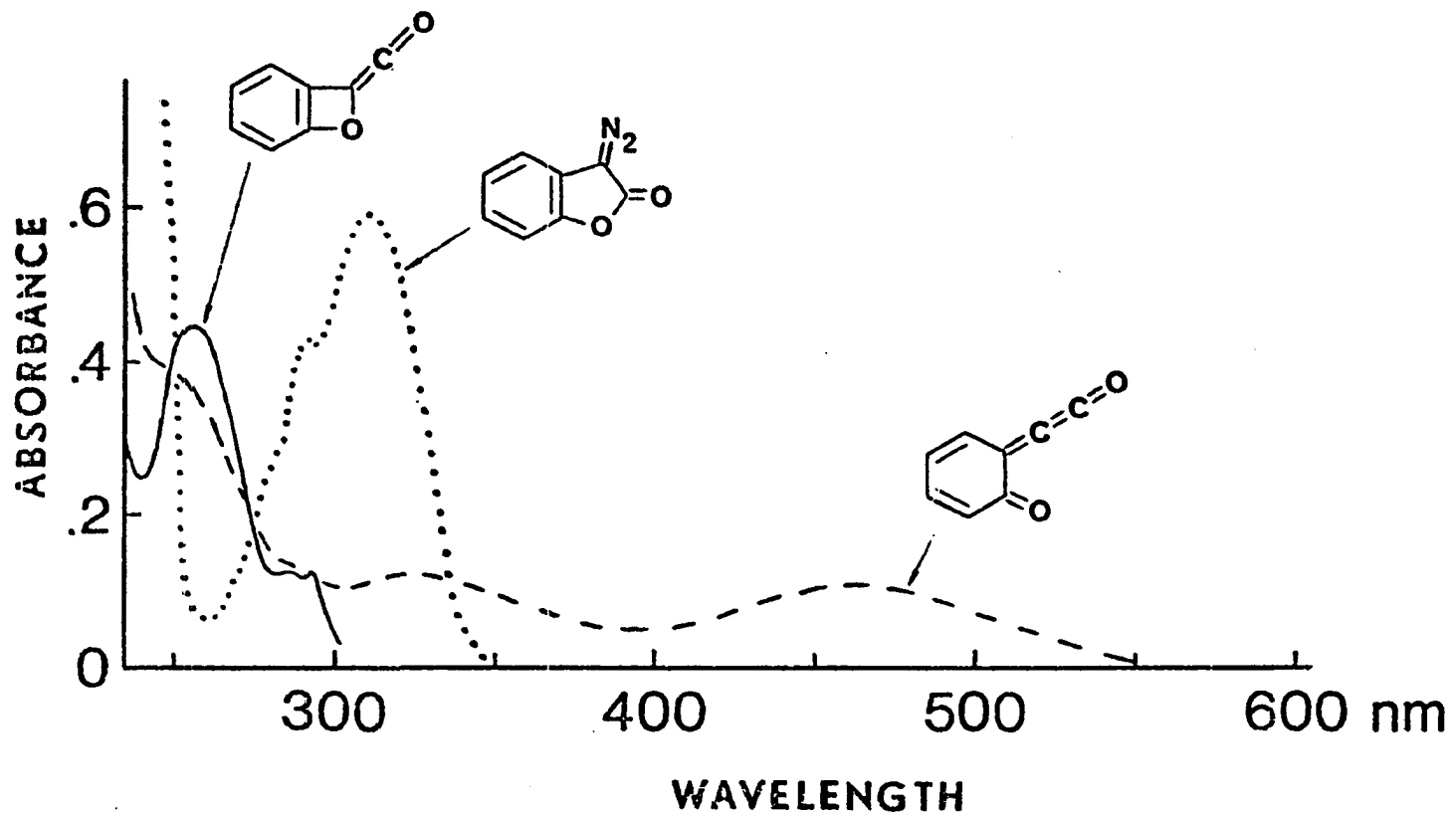
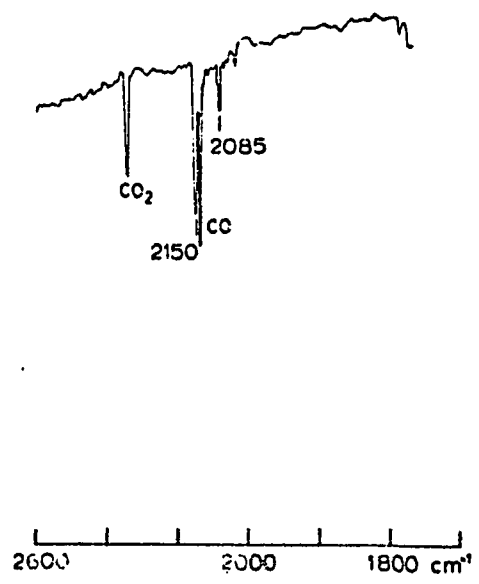
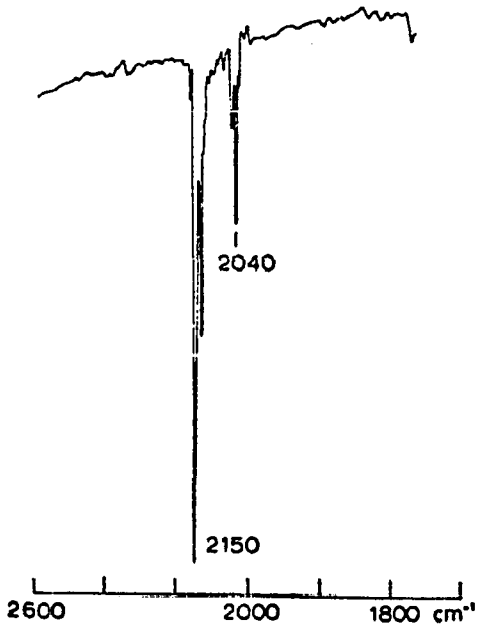
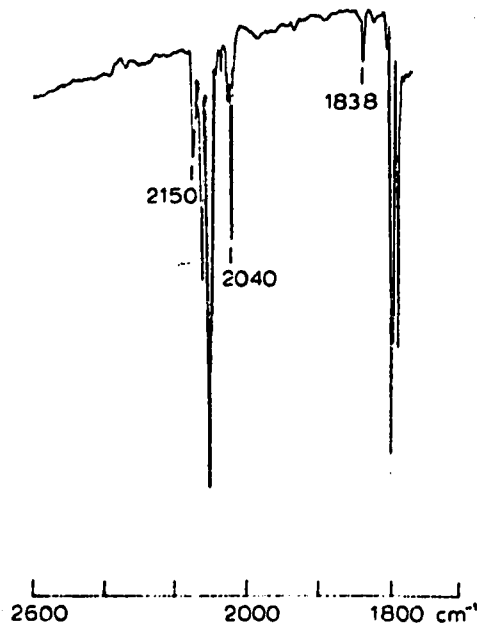
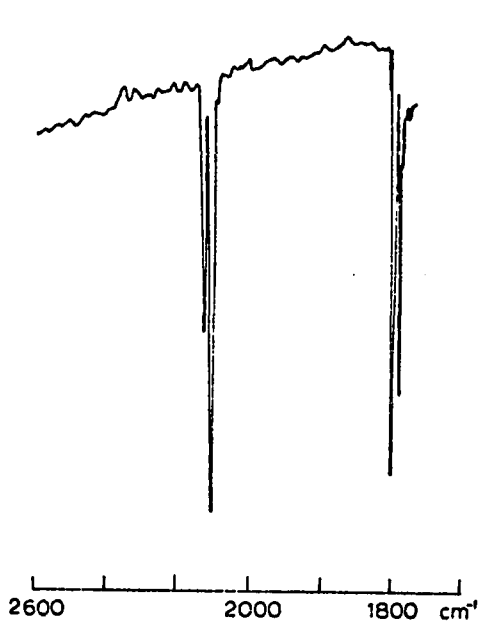
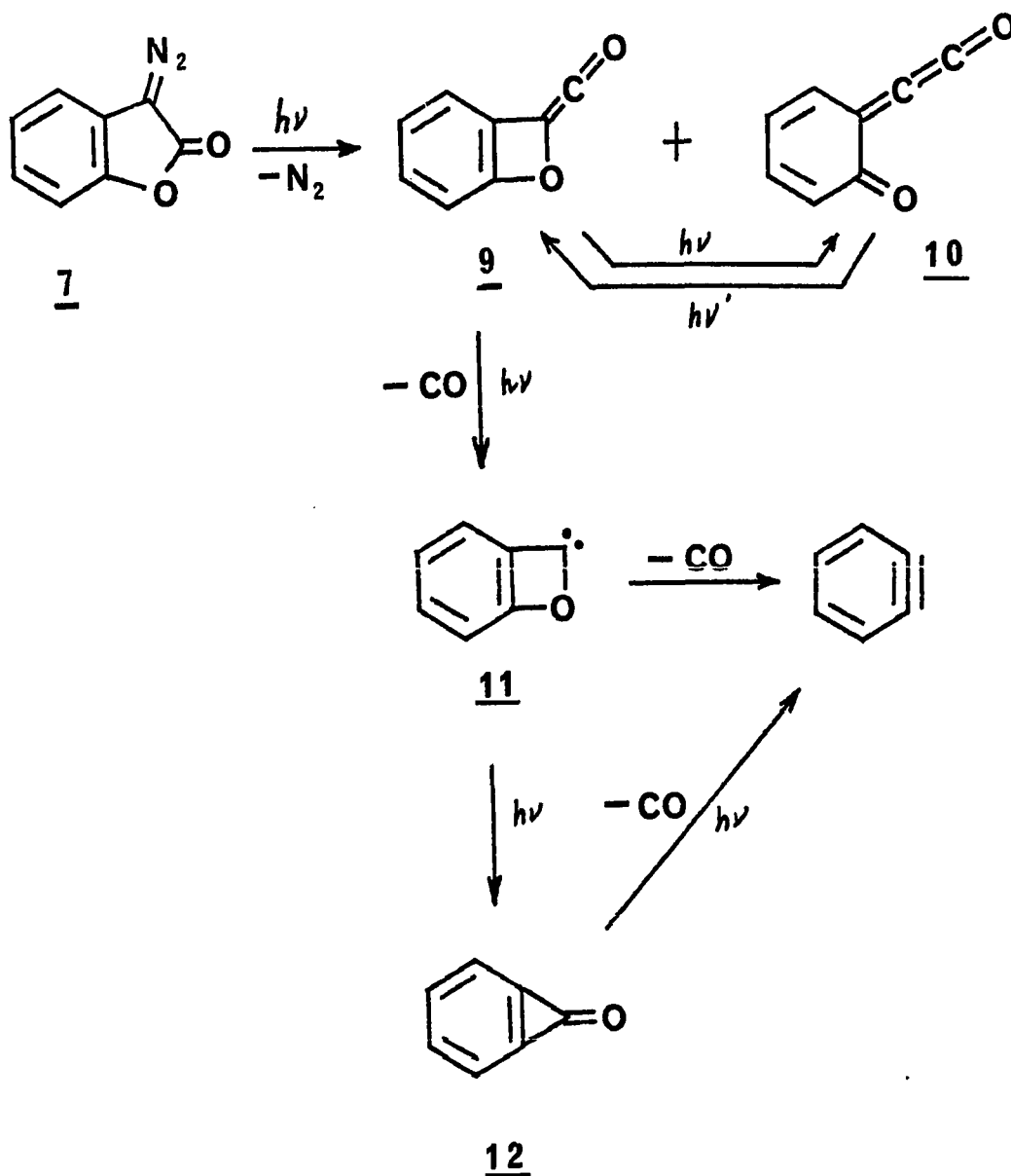


Figure 3 Irradiation of 3-diazobenzofuranone at 8° K,
ir spectrum

Irradiation of diazobenzofuranone (7) in argon matrix at 8° K. Infrared spectra of 7 isolated in argon at 8° K before irradiation (upper left), after irradiation (>274 nm) for 1 minute (upper right), after irradiation (>274 nm) for 10 minutes (lower left), and after irradiation (>200 nm) for 527 minutes (lower right)



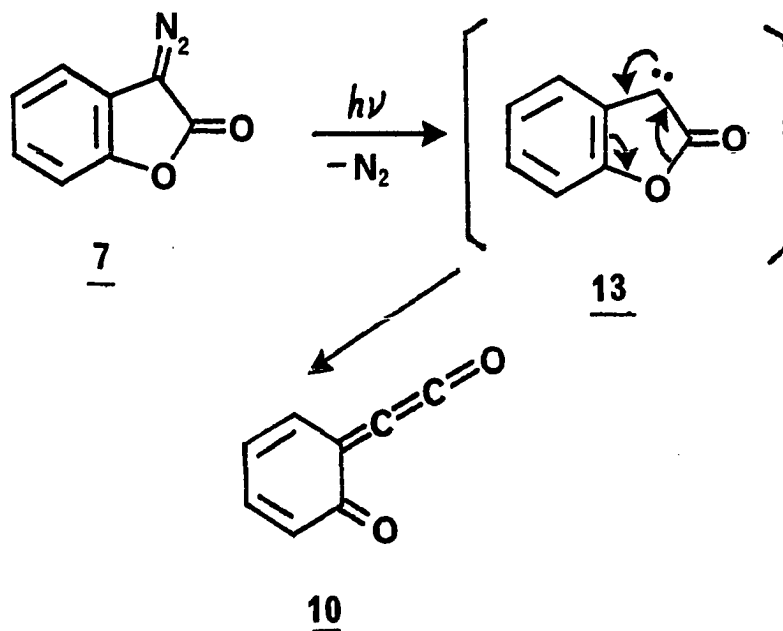
with shorter wavelength light decarbonylates the ketene (9), presumably giving carbene 11 ($\lambda_{\text{max}}^{2\text{MeTHF}}$ 398, 429, 440 nm). The carbene in turn loses carbon monoxide giving benzyne and a minor amount of a carbonyl compound (1838 cm^{-1}) which is decarbonylated by further irradiation. This minor component is probably 12. The infrared absorption is



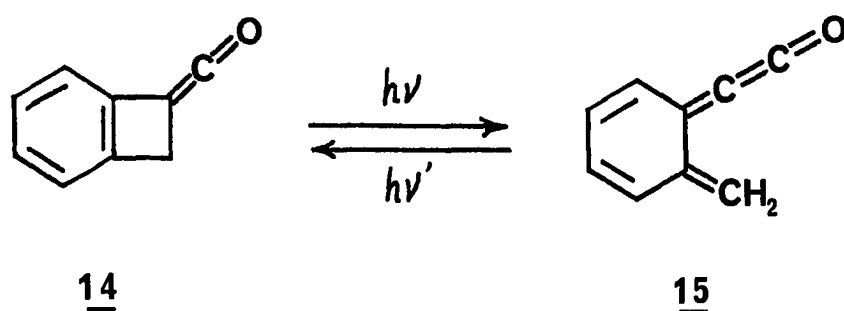
identical with that observed in the photodecarbonylation of benzocyclobutenedione (3).

The 3-diazobenzofuranone (7) is the best precursor for preparation of matrix isolated benzyne. In this experiment, it is the first time to see a carbon-carbon triple bond stretching frequency for benzyne at 2085 cm^{-1} .

Formation of 10 as a primary product was unexpected. The formation of 10 can be viewed as a concerted reaction of the initial carbene 13 (multiplicity effects are not considered in this representation). The photochemical

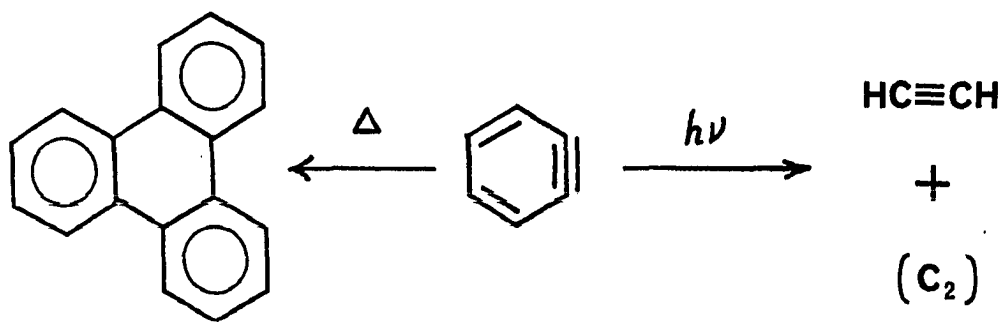


electrocyclic opening of the four-membered ring in 9 is analogous to that observed in the carbocyclic analogue 14 (Part II) which photointerconverts with 15 (vide infra).



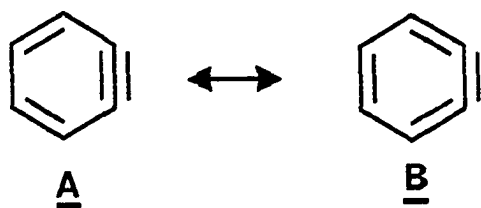
Therefore, the diazobutyrolactone part structure has shown to be an effective way to photochemically introduce a multiple bond. Other potentially interesting application of this procedure might be the synthesis of small ring cycloalkynes and trans-cycloalkenes.

Benzyne is reasonably stable photochemically, but it is slowly converted to acetylene (and presumably C_2). Warming the matrix containing benzyne to room temperature, produces triphenylene together with higher polymers.



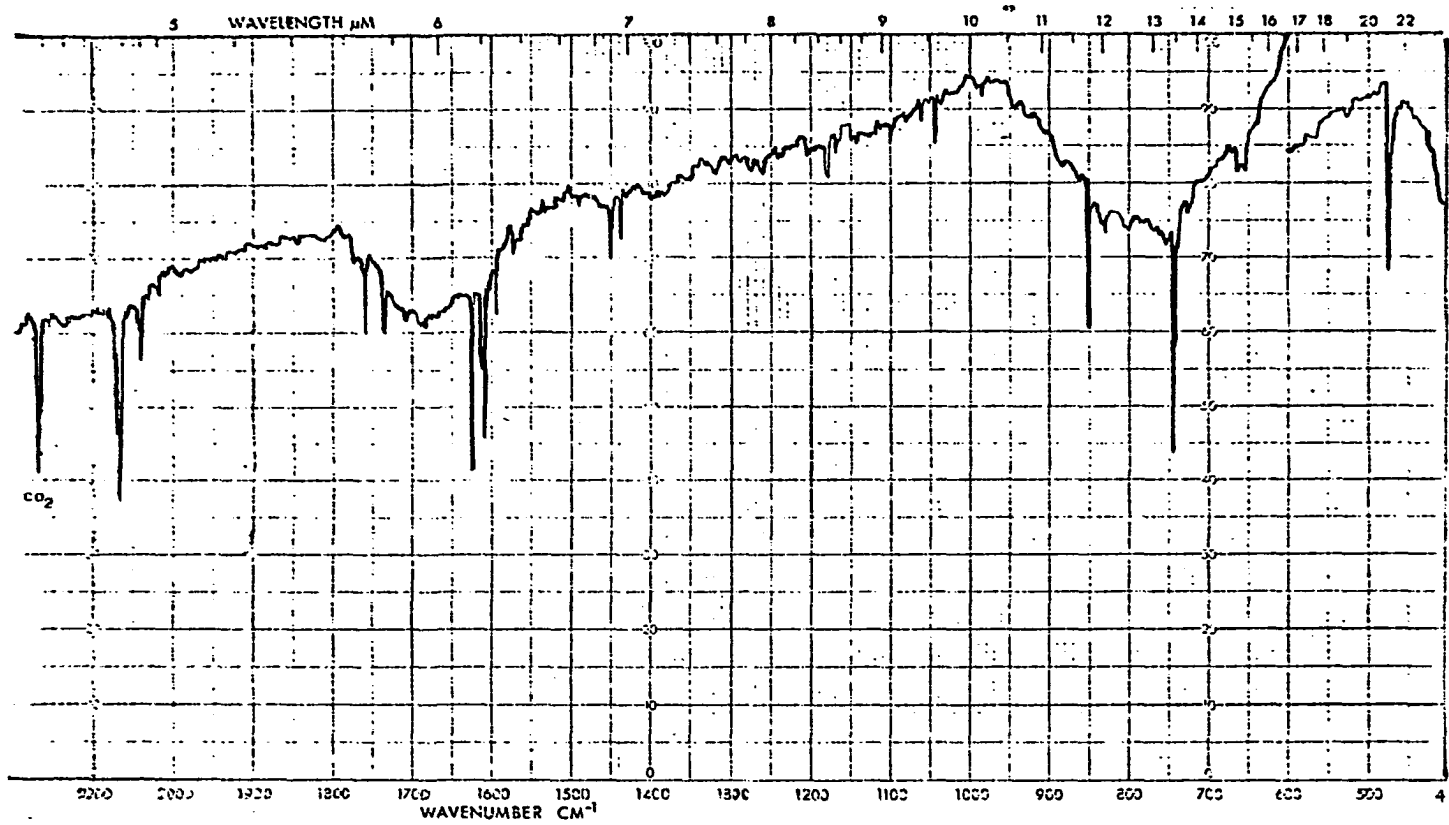
Benzyne prepared from **7** shows bands at 2085, 1607, 1451, 1253, 1038, 849, 736 and 469 cm^{-1} (Figure 4).

The infrared spectrum of benzyne provides some insight to the structure of benzyne. The out-of-plane deformation modes are similar in pattern to ortho-disubstituted benzenoid systems and the bands are shifted to lower frequency. This shift to lower frequency indicates a less rigid molecule with respect to out-of-plane distortion. Double and single carbon-carbon bond frequencies (1627, 1607, and 1451 cm^{-1}) are observed. This suggests that the molecule has more cyclohexatriene character as far as the π system is concerned. This is reasonable in terms of a shortened bond (the triple bond) which would tend to localize the π system. In terms of valence bond structures, this indicates that A is energetically favored with respect to B.



Indeed, the band at 2085 cm^{-1} shows a clearly defined triple bond for benzyne. This information plus the absence of esr signal⁴⁰ undoubtedly exclude both the cumulene-like and triplet diradical structures. The shift of the triple bond stretching to lower frequency indicates a weaker

Figure 4 Infrared spectrum of o-benzyne



triple bond.

The qualitative picture in vogue supposes that benzyne's "triple" bond is shorter than the 1.39 \AA of a normal benzenoid bond because two electrons occupy a weakly bonding orbital whose maximum electron density lies in the molecular plane. It is clear that none of structures I-V in Figure 1 offers as suitable a model as structure of benzyne since the predicted frequencies are so different from the observed spectrum. In case I and II, only very unreasonable force constant for bending and interaction could conceivably bring the calculated values into the range of the observed.

It is interesting to note that Berry correctly predicted the yet-unobserved frequencies at 2083 cm^{-1} for triple bond which we observed at 2085 cm^{-1} . The absence of the band at 2450 cm^{-1} predicted by Berry is not surprising since the dipole moment change during the 2450 cm^{-1} oscillation is considerably smaller than the change associated with the 2085 cm^{-1} band.⁴¹ The best fitting set of infrared active frequencies is shown in Table 1 together with the observed frequencies and the percent deviation of calculated from observed frequencies. The strain of benzyne can never be correctly estimated unless one knows the geometry of benzyne. It would thus be informative if one could further test, experimentally, the structure proposed by Laing and Berry.⁴¹

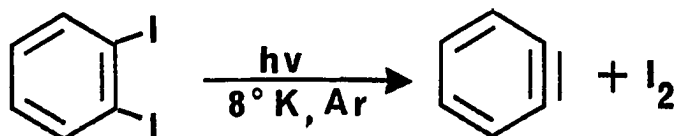
Table 1 Observed and calculated⁴¹ infrared frequencies of *o*-benzyne

Obsd. freq. (cm ⁻¹)	Calcd. freq. A ₁ representation (cm ⁻¹)	Calcd. freq. B ₂ representation (cm ⁻¹)	Calcd. freq. B ₁ representation (cm ⁻¹)
			306
469	471 (0.4%)		
		540	
735			735 (0.0%)
849		854 (0.6%)	
1038		1039 (0.1%)	
1053	1052 (0.1%)		
		1313	
1451	1444 (0.5%)		1449 (0.1%)
1607	1601 (0.4%)		
1627	1645 (1.1%)		
		1856	
		2044	
2085	2083 (0.1%)		
	2450		
		3040	
	3054		
		3087	
	3096		

Therefore, the synthesis of perdeuteriobenzynes and perfluorobenzynes and the determination of their infrared spectra would, undoubtedly, be valuable.

In this study, many other precursors were used in attempts to generate benzyne.

Since the carbon-iodine bond is a relatively weak bond it is frequently broken in photolysis reaction. It is therefore reasonable to consider photolysis of 1,2-diodobenzene as a potential route to benzyne. Photolysis of *o*-diodobenzene matrix isolated in argon at 8° K produce benzyne. Benzyne generated from this method is not practical



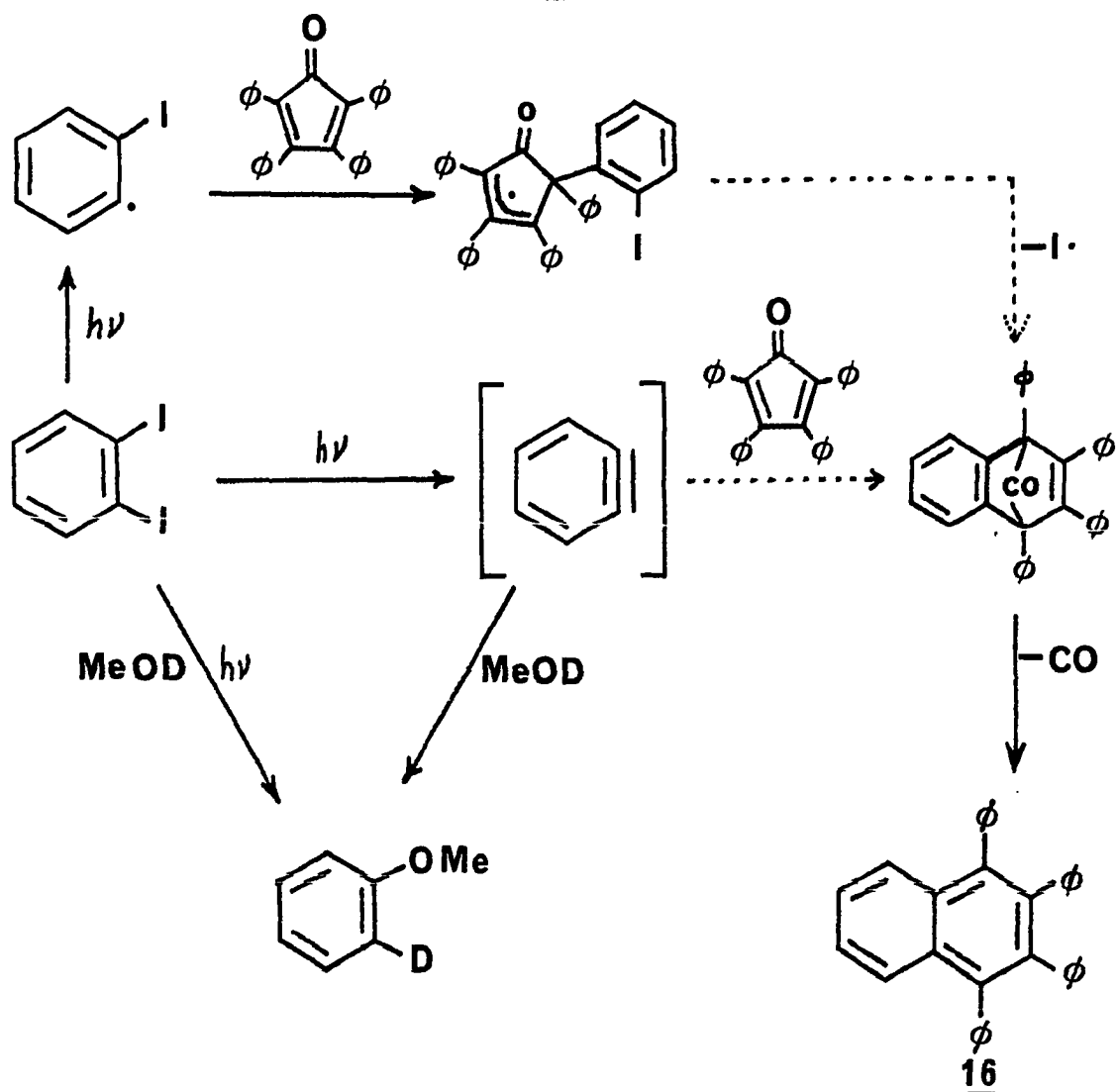
since only very small fraction of diiodobenzene is decomposed. Iodine formed along with benzyne probably absorbs most of the ultraviolet irradiation and hence stop the reaction. An attempt to photolyze using the layer-by-layer-technique was not successful.

It is interesting to note that an intermediate iodophenyl radical is not observed. This would imply that either the simultaneous photolytic cleavage of two iodine atoms is concerted or that rate of decomposition of the

phenyl radical is much faster than that of formation.

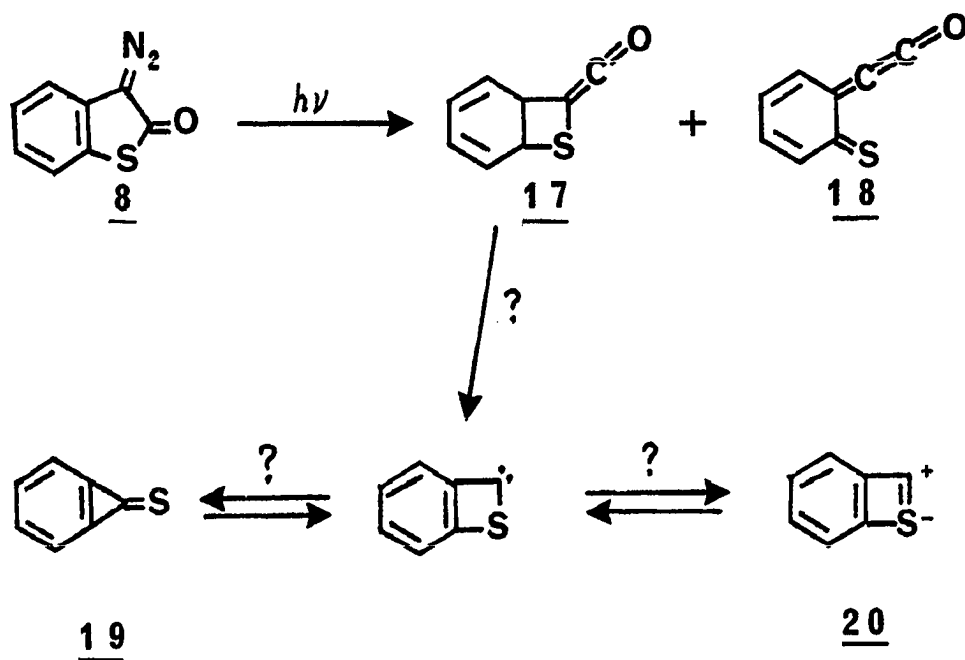
It is also interesting to compare the result of this study with those of solution photolysis previously reported. Photolysis of *o*-diiodobenzene in benzene gives mainly 2-iodobiphenyl and small amount of biphenyl and triphenylene.⁴⁴

It was shown by Kampmeiker and Hoffmeister⁴⁴ and Kharasch⁴⁵ that photolysis of *o*-diiodobenzene in the presence

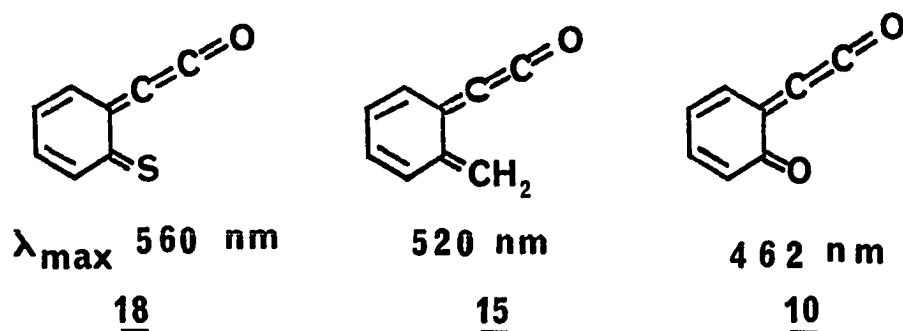


of tetracyclone gives the expected Diels-Alder adduct of benzene of tetracyclone, *i.e.*, 1,2,3,4-tetraphenylnaphthalene (6). Methanol-OD has also used to trap the possible benzyne intermediate.⁴⁶ However, production of all the observed products can be also explained without involving a benzyne intermediate.

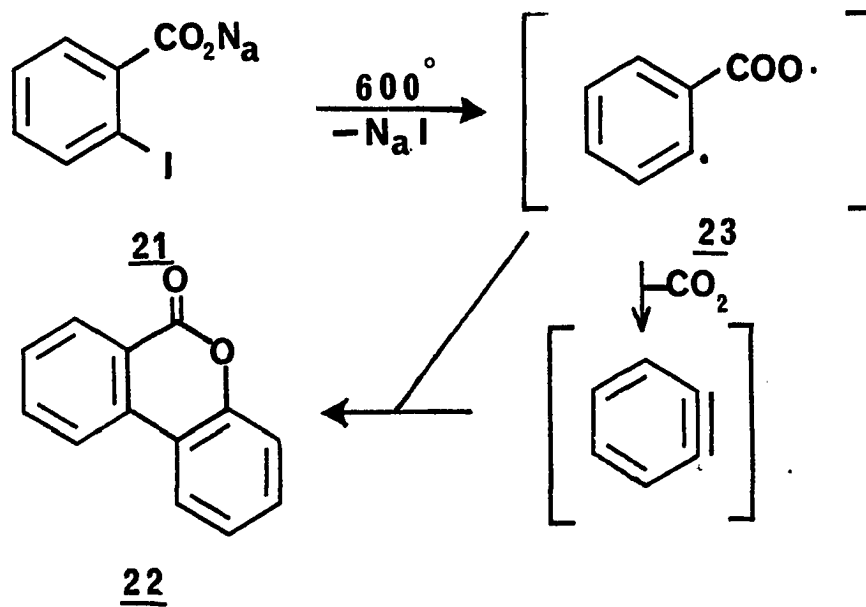
Irradiation (>350 nm, CS 7-37) of 3-diazobenzothiofuranone (8) matrix isolated at low temperature gives two primary products, 17 (2140, 1440, 1100, 732 and 705 cm^{-1}) and 18 (2070 cm^{-1} , $\lambda_{\text{max}}^{\text{2MeTHF}}$ 560 nm). Further irradiation with shorter wavelength light (>2000 Å) cause destruction of 17 and 18 with new bands arising at 1370, 1230, 1162, 743 and 450 cm^{-1} . Prolonged irradiation under this condition



caused destruction of all the previously mentioned bands with final new bands at 1970 (s), 1820 (s), 1470, 1375, 1000, 732 and 705 cm^{-1} . It is difficult to assign structure based upon this data. However, if one compares this result with that of diazobenzofuranone, 19 and 20 are possible structures for bands at 1970 and 1820 cm^{-1} . It is also interesting to note that the absorption maxima for 18, 15 and 10 are in an interesting order.



The pyrolysis of sodium salt of *o*-iodobenzoic acid (20) at 600° gave an ester (IR 1745, 1615, 1590, 1477, 1440, 1314, 1278, 1247, 1222, 1141, 1105, 1090, 1040, 1021, 903, 761, 727, 693, 665, and 638 cm^{-1}). It is tentatively assigned as 3:4-benzocoumarin (22) based on infrared spectrum. This implies that some dehydrobenzene might be formed by loss of carbon dioxide from 23 and then combined with 23 to give benzocoumarin 22.



EXPERIMENTAL

Instrumentation

The nmr spectra were recorded on a varian Associates A-60, T-60, HA-100 or a Hitachi Perkin-Elmer R 20-B. Chemical shifts are reported in parts per million (δ scale) downfield from tetramethylsilane. The infrared spectra were obtained on a Beckmann IR-9, IR-12, IR-4250, or IR-18A spectrometer. Mass spectra were obtained on an Atlas CH-4, AEI-MS-902 or DuPont 21-491 mass spectrometer. Ultraviolet spectra were obtained on a Cary 14, Beckman DK-2A or a Beckman ACTA-CV spectrometer. ESR spectra were recorded on a Varian Associates E-3, V-4500 or V-3601 spectrometer. Melting and boiling points are uncorrected.

Reagents

Common reagents and solvents were obtained from commercial sources and were generally used without purification. When anhydrous conditions were required, reagents grade solvents were dried according to procedures in Fieser and Fieser's Reagents for Organic Synthesis, Vol. 1.⁴⁷

Chromatography

Vapor phase chromatography was performed on either a Varian Aerograph 920 or an Aerograph 1520 chromatograph. Microanalytical thin-layer chromatography plates were prepared by immersion coating of microscope slides in a chloroform-methanol slurry of Merck silica gel H. Microanalytical, pre-coated, thin-layer chromatograph plastic plates with fluorescent indicator (13181 silica gel, 20 x 20 cm) were obtained from Eastman Kodak. Preparative thin-layer chromatography was performed on precoated silica gel F-254 plates (2 mm thickness, 20 cm x 20 cm) obtained from Brinkman Instruments.

Photolysis Equipment

Ultraviolet irradiation were performed in five types of apparatus: a) a Rayonet photochemical reactor, sixteen lamp model, which is available from Southern New England Ultraviolet Company, Middleton, Connecticut; b) Hanovia 450 Watt medium pressure mercury lamp equipped with water-cooled quartz immersion well; c) Westinghouse 1000 Watt medium pressure mercury street lamp; d) 800 Watt high pressure mercury lamp obtained from General Electric; e) Penlite mercury lamp obtained from Ultraviolet Products.

Matrix isolation and low temperature equipment

Refrigeration was achieved by a Displex Cryogenic Refrigerator Model CS 202 or Model DE 2025 purchased from Air Products and Chemicals, Inc. The minimum temperature achieved was 8° K. Monitoring of the temperature was accomplished using a 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 temperature can be also monitored by the indicator on the temperature controller obtained from Air Product and Chemicals.

The pumping system used a Sargent-Welch Model 1402 series equipped with an air-cooled oil vapor diffusion pump and liquid nitrogen trap (Edwards Vacuum Components Limited) which gave pressures down to 10^{-7} mm. Pressures were measured using a cold cathode gauge from H. S. Martin and Son. The glass handling system is shown in Figure 5. The valves used were 10 mm high vacuum valves obtained from Ace Glass.

The method used for deposition of a matrix was as follows: after the system was pumped down, the window (CsI for infrared experiments, sapphire for uv experiments and copper strip for esr experiment) was cooled to 8° K

then warmed to 20° K.

Two methods of deposition were employed depending on the volatility of the sample. If the sample was stable and had at least one half mm vapor pressure at room temperature, the so-called "indirect" deposition method was used.

After degassing the sample, introduced one half mm of vapor in to a 3 liter bulb (see Figure 5). The pressure was increased then to 500 mm with argon gas (ration of host to guest in 1000:1), and the sample was mixed with a magnetic stirrer for 10 minutes. The sample was deposited at a rate of 1 mm per minute keeping the window temperature constant. The total amount of sample deposited varied from sample to sample.

If a sample was unstable or had less than one half mm vapor pressure, "direct deposition" must be employed. In this method the sample was connected directly to the expander head. Both the argon and sample vapor were sprayed on the windows at a rate which good isolation resulted. The vaporization of the sample was controlled by temperature.

Apparatus for 77° K studies

For 77° K glass matrix studies a quartz Dewar and a 2 ml Suprasil cell were employed (obtained from Rontes

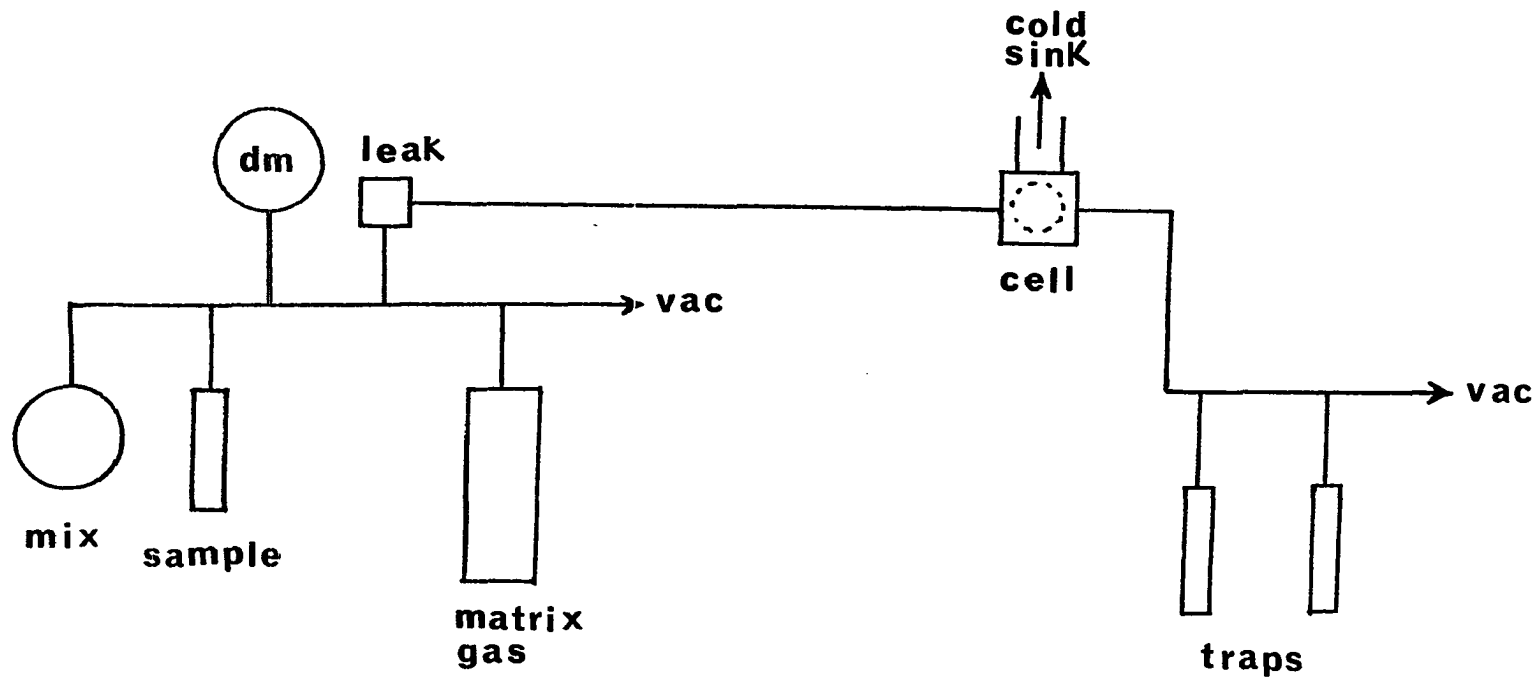


Figure 5 Schematic of apparatus for matrix isolation

Martin Co., Evanston, Illinois; see Figure 6). Anhydrous 3-methylpentane and 2-methyltetrahydrofuran were frequently used for the glass material. After distillation, these solvents were passed through the alumina column. The method used for making of a glass matrix was as follows. The Dewar was filled with ice free liquid nitrogen using a filter paper. Immerse the Suprasil cell containing degassed sample very slowly. Extreme care should also be taken when removing the cell from the liquid nitrogen Dewar (fast warming causes the cell to crack).

Pyrolysis Apparatus

The pyrolysis apparatus is shown in Figure 7. The two inch inner quartz tube can be heated to 1000° and can be connected to the expander head for matrix isolation experiments. The inner diameter of the quartz tube is 2.5 mm. Monitoring of the temperature was accomplished using an iron-constant thermocouple and a Leeds & Northrup potentiometer. The heater was made of Nichrome wire.

The temperature was controlled by two Varian transformers connected in series.

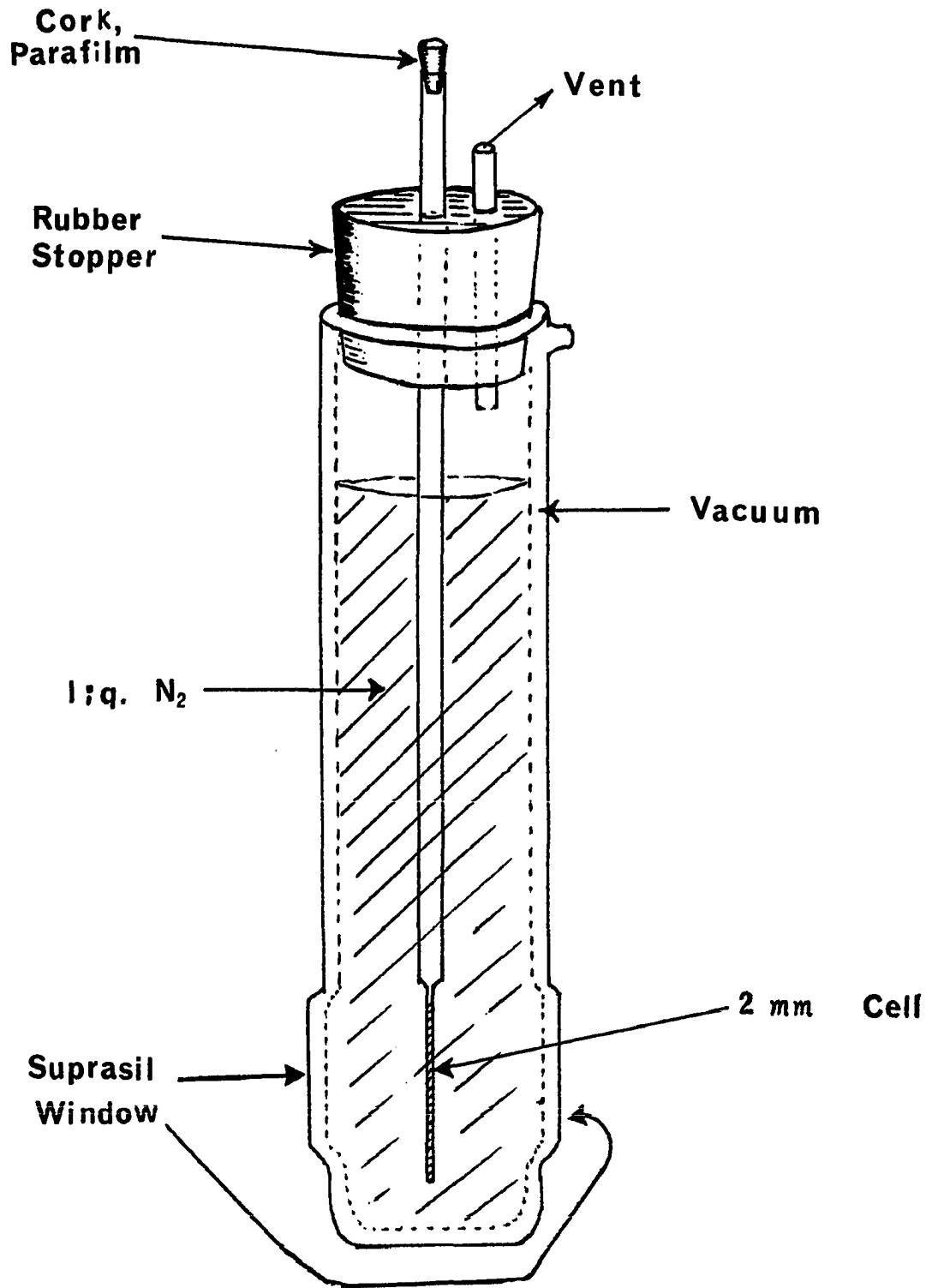


Figure 6 Apparatus for 77° K glass matrix studies

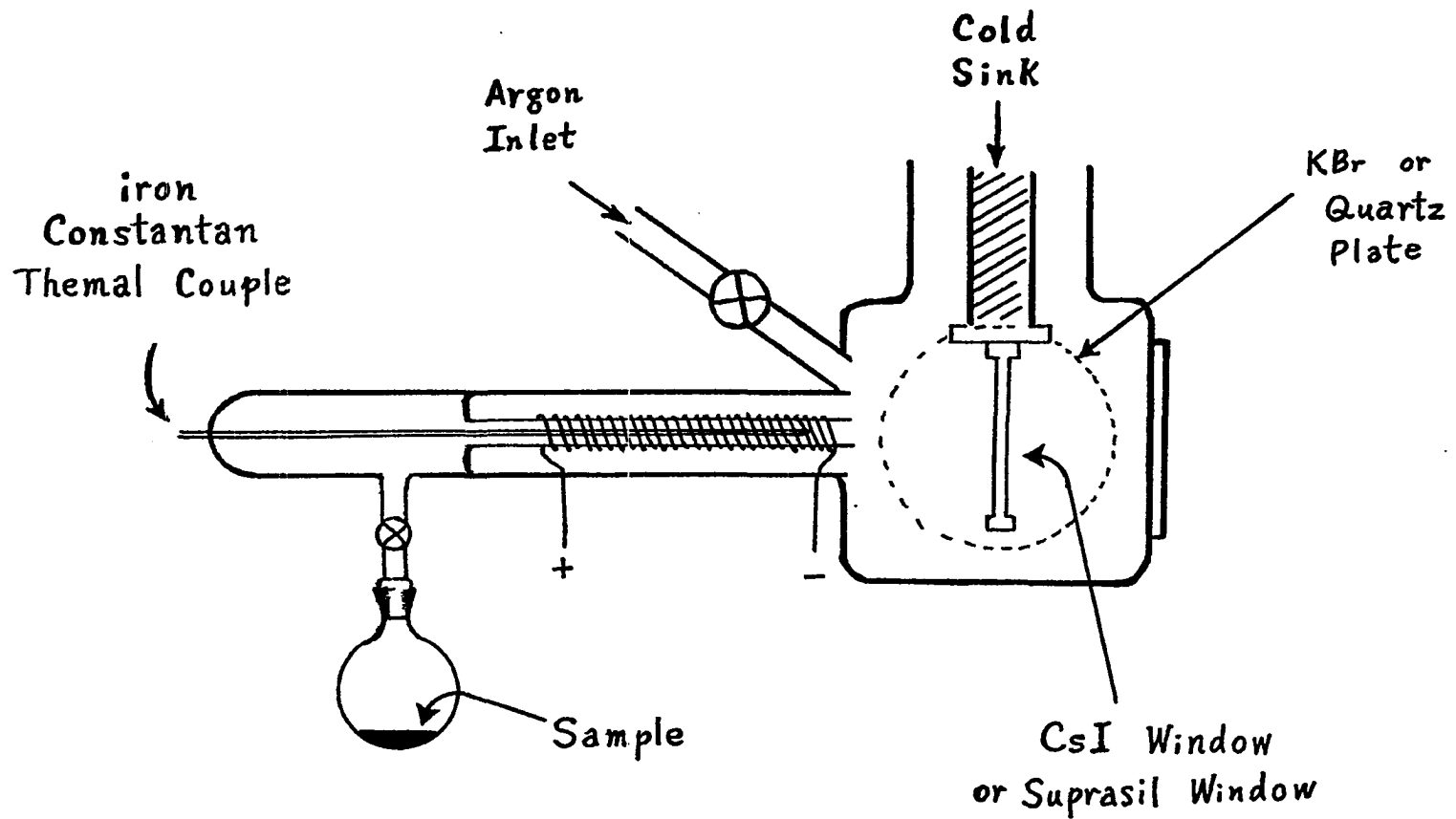


Figure 7 Apparatus for pyrolysis

o-Iodobenzoic acid sodium salt

o-Iodobenzoic acid was prepared according to the procedure by Baker, Mann, Sheppard and Tetlow.⁴⁸ It is prepared by diazotising anthranilic acid in dilute sulphuric acid, and adding the filtered solution to potassium iodide, also in the dilute acid, the crude brown acid (90%) was converted into the ethyl ester, b.p. 152-153 /14 mm (75%) which on hydrolysis with ethanolic potassium hydroxide gave the pure acid, m.p. 162°. By treating with equivalent amount sodium hydroxide and dried to give white sodium salt. (IR 1600, 1415, 1020, 755 and 485 cm^{-1} in KBr disc).

Pyrolysis of sodium salt of o-iodobenzoic acid

The pyrolysis apparatus is shown in Figure 8. The salt is heated at 600° in a quartz tube under pressure at 10^{-6} mm. The volatile product is codeposited with argon onto a cesium iodide window. During deposition the cesium iodide window is maintained at 20° K. The argon is deposited at a rate of 1 mm/min. The pyrolysis products in argon matrix at 20° K have bands at 1745, 1615, 1590, 1477, 1440, 1314, 1278, 1247, 1222, 1141, 1105, 1090, 1040, 1021, 903, 761, 727, 693, 665 and 638 cm^{-1} .

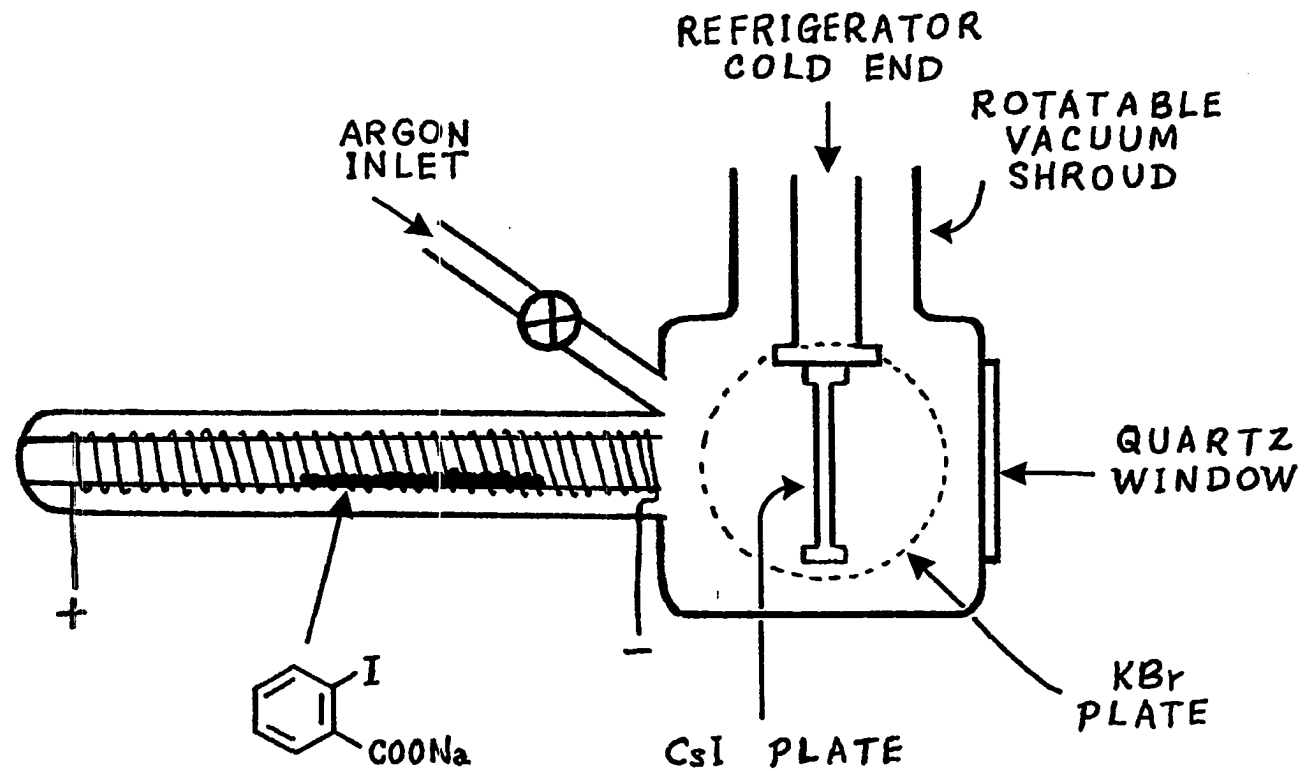


Figure 8 Apparatus for pyrolysis of sodium salt of iodobenzoic acid

Photolysis of o-diiodobenzene matrix isolated in argon at 8° K

An argon matrix of o-diiodobenzene was made by using direct deposition technique. The diiodobenzene was slowly evaporated at 50° onto the cesium iodide window during deposition. Irradiation ($\lambda > 2740 \text{ \AA}$) using a 1000 Watt mercury vapor lamp showed no change. Irradiation using quartz filter caused new bands to appear at 849, 736 and 469 cm^{-1} . The conversion of the reaction is very small over 2000 minutes.

Attempted preparation of benzyne from o-diiodobenzene and zinc

The reaction set up is quite similar to that for benzocyclobutadiene synthesis. Zinc powder (Mallinckrodt) is used directly without activation. The diiodobenzene is heated to 50° in a warm water at 10^{-6} mm to provide a sufficient rate of vaporization. The diiodobenzene vapor is passed over zinc powder at 320° and then codeposited with argon on a cesium iodide window at 20° K. The infrared spectrum shows that the compound collected on the window is essentially all starting material without reaction.

3-Diazobenzofuranone

3-Diazobenzofuranone was prepared followed the procedure of W. M. Horspool and G. D. Khandelwal,⁴⁹ by Dr. H. Tomioka.

The yellow crystal has melting point at 116-117°. (lit.⁴⁹ 116-118°)

Photolysis of matrix isolated 3-diazobenzofuranone in argon at 8° K

Argon and 3-diazobenzofuranone were codeposited on a cesium iodide window at 20° K by direct deposition. Irradiation was accomplished using a 1000 Watt medium pressure mercury vapor lamp with a Pyrex filter ($>2740 \text{ \AA}$). In the first minute of irradiation new bands grew at 2150 (s), 2040 (ss), 1838 (s), 1441, 1305, 1279, 1200, 1185, 1145, 1134, 1090, 1065, 964, 785, 775 and 735 cm^{-1} . Further irradiation caused complete destruction of starting material as well as the band previously mentioned at 1838 cm^{-1} with bands growing at 2150, 1441, 1430, 1426, 1279, 1185, 1175, 1155, 1113, 990, 950, 840, 775, 765, 735 and 730 cm^{-1} . Further irradiation with shorter wavelength light ($>2000 \text{ \AA}$) caused destruction of previously mentioned bands with final new bands arising at 2085, 1607, 1451, 1253, 1038, 849, 736 and 469 cm^{-1} .

Photolysis of 3-diazobenzofuranone in 3-methyltetrahydrofuran glass

The photolysis was carried out by the assistance of Dr. J. Kolc. Photolysis of 3-diazobenzofuranone in

3-methyltetrahydrofuran was carried out in 2 mm Suprasil cell at 77° K. An 800 Watt high-pressure mercury arc was used throughout. Irradiation of the glass (250 nm λ 400 nm, Corning filter CS 7-54) gave products with absorption maxima at 255, 286, 293 and 462 nm. These primary photoproducts readily interconvert photochemically with long wavelength (>350 nm) light favoring one with absorption with λ_{\max} 255, 286 and 293 nm and short wavelength light (254 nm Penlite) favoring the other (λ_{\max} 462 nm).

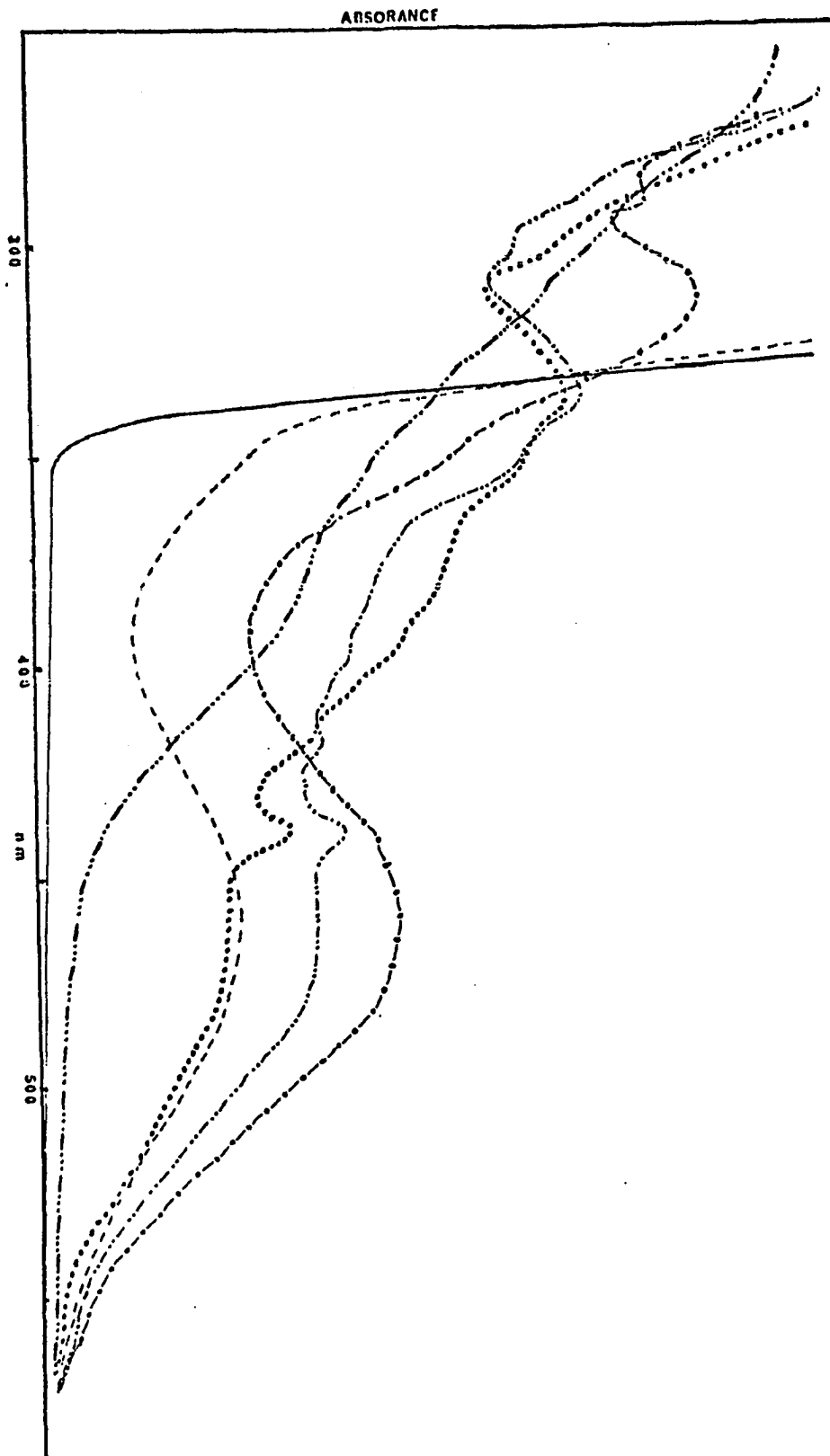
When a low pressure mercury lamp (2537 Å, Penlite) was used throughout, one more intermediate was produced on consumption of the two previously mentioned products. This intermediate has a broad absorption spectrum at λ_{\max} 337, 355, 398, 407, 429, 440 and 520 nm. Warmed up the glass gave no identified products. (see Figure 9)

Photolysis of 3-diazobenzofuranone with methanol in glass

3-Diazobenzofuranone in 2-methyltetrahydrofuran glass containing 10% of methanol was prepared as previously at 77° K. The reaction was followed by ultraviolet spectroscopy. After the species with absorption maxima at 255, 286, and 293 nm was maximized, the sample was warmed up and recooled to 77° K giving new absorption maxima at 260, 276, 283, 304,

Figure 9 Irradiation (2537 Å) of 3-diazobenzofuranone at 77° K, uv spectrum

3-Diazobenzofuranone (7) in 2-Me-THF (solid line); after 2 minutes irradiation (254 nm) (---); after 10 minutes irradiation (-...-); after 40 minutes irradiation (-...-...-); after 100 minutes irradiation (.....); warmed to room temperature and recooled (-...-...-)
All spectra and photochemistry at 77° K.



340 and 356 nm.

Photolysis of 3-diazobenzothiofuranone matrix isolated in argon at 8° K

An argon matrix of 3-diazobenzothiofuranone was made by direct deposition. The sample tube was heated to 35° by a heater during deposition. Photolysis was accomplished using a 1000 Watt medium pressure mercury with a filter (CS 7-37, > 3500 Å). The reaction was monitored by infrared spectroscopy. New bands were formed at 2140, 2070, 1440, 1100, 732 and 705 cm⁻¹). Continued irradiation through quartz optics caused new bands arising at 1370, 1230, 1162, 743 and 450 cm⁻¹ which converted to final bands at 1970, 1820, 1470, 1375, 1000, 732 and 705 cm⁻¹ upon prolonged irradiation.

Photolysis of 3-diazobenzothiofuranone in 2-methyltetrahydrofuran glass at 77° K

Irradiation of 3-diazobenzothiofuranone in 2-methyltetrahydrofuran by high pressure Hg arc with CS 7-37 filter (>3400 Å) destroyed the starting material. Irradiation by 2537 Å light (Penlite) gave a purple product (λ_{\max} 560 nm). The formation of this colored product rapidly reached its maximum (~5 min.) and slowly converted to a lower wavelength absorbing species. The warming up experiment did not give any identified product.

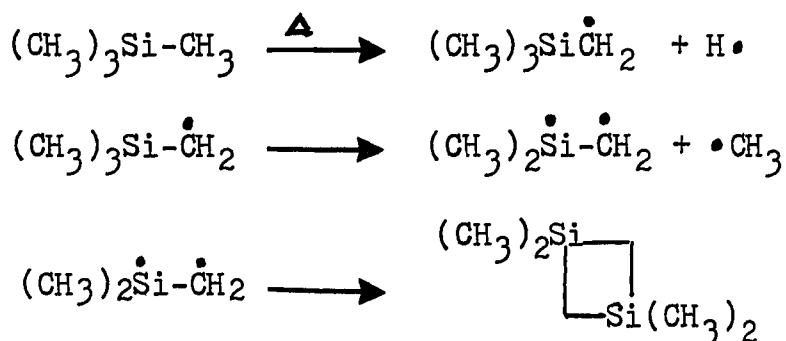
PART II. 2-METHYL-2-SILA-2-BUTENE

INTRODUCTION

Silicon and carbon belong to group IV elements and have same electronic configuration in their valence shells. Despite the fact that both elements can form sp^3 hybrid orbitals, there is no more striking example of discontinuity in properties between second and third row elements. One of the major differences is that carbon is capable of forming a variety of stable multiple-bond compounds and none are known for silicon.⁵⁰

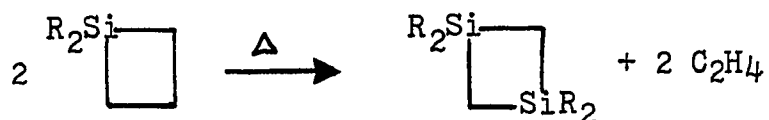
Until the last decade, unsaturated silicon compounds were believed to be nonexistent⁵¹ in spite of the many claims of the existence of stable compounds with silicon-carbon double bond in the early literature. These include the work by Gattermann in 1889,⁵² Schlenk and Renning⁵³ in 1912, and more recently Fritz and Grobe⁵⁴ in 1961. However, their assignments were later shown to be incorrect.⁵⁰ Even in recent years, compounds with unsaturated silicon have only been considered as short-lived, reactive intermediates.

Fritz et al.⁵⁵ were the first group to propose a silaolefin intermediate in the mechanism of the pyrolysis of tetramethylsilane to explain the formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. However, there



is no evidence to support intermediacy of the silaethylene.

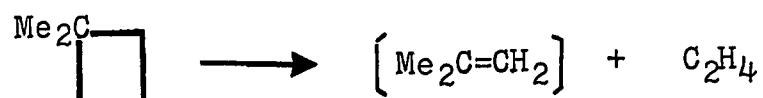
In 1966, Nametkin and his co-workers^{56,57} observed the elimination of ethylene and formation of 1,3-disilacyclobutanes during the study of pyrolysis of silacyclobutanes.



By comparing the kinetic data of thermal decomposition of silacyclobutane and of its carbon analogue, they also suggested the existence of a silaolefin in these reactions.⁵⁸

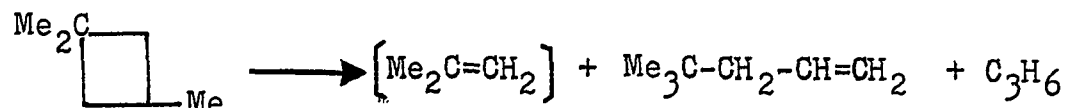
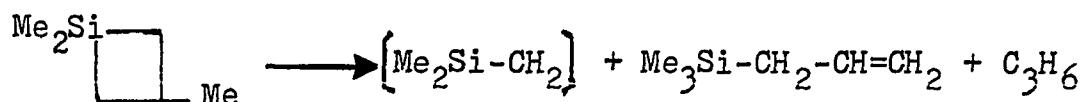


$$K(\text{sec}^{-1}) = 10^{15.6} \exp(-62300/\text{RT})$$



$$K(\text{sec}^{-1}) = 10^{15.62} \exp(-61000/\text{RT})$$

The analogy is also observed in pyrolysis of 1,1,3-trimethyl-1-silacyclobutane and 1,1,3-trimethylcyclobutane.⁵⁹



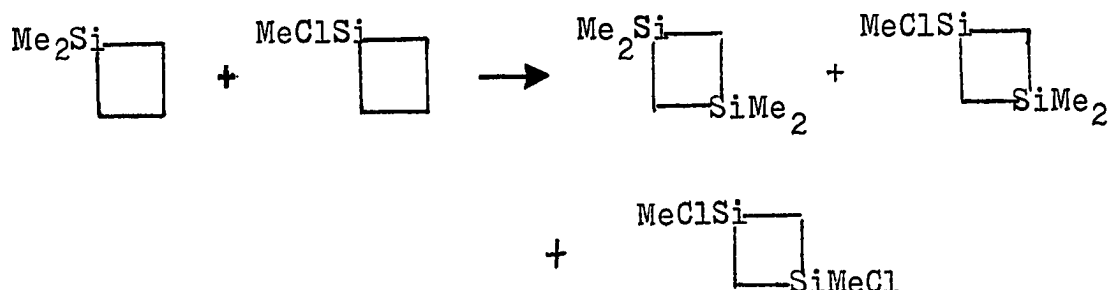
The analogy of the two reactions suggests an initial cleavage of either carbon-carbon or silicon-carbon bond of the silacyclobutane ring to the corresponding diradicals, followed by further rearrangement.

In 1974, Nametkin et al.⁶⁰ observed the formation of

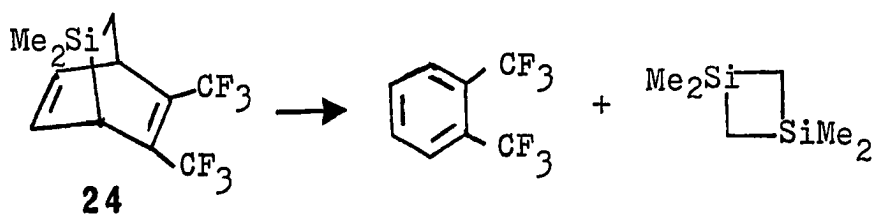
$(\text{Me}_2\text{SiCH}_2)_x$ polymer and the related decrease of 1,1,3,3-tetramethyl-1,3-disilacyclobutane among products by using a cold trap to collect the products when 1,1-dimethylsilacyclobutane was pyrolyzed at 600° . They also found that the ethylene/ $(\text{Me}_2\text{SiCH}_2)_2$ ratio depends not only on the flow rate of 1,1-dimethyl-1-silacyclobutane during the pyrolysis but also on the distance between oven and trap. They claimed that a shorter distance between hot zone and cold trap allowed more efficient collection of the intermediate and thus caused a higher ethylene/dimer ratio and more polymer formation.

Besides dimerization and polymerization, silaethylenes have been trapped by water, methanol, ammonia, alcohols, ethylene,^{58,61,62} acetonitrile,⁶³ propene,⁶⁴ ketones^{65,66} and butadienes.^{62,67}

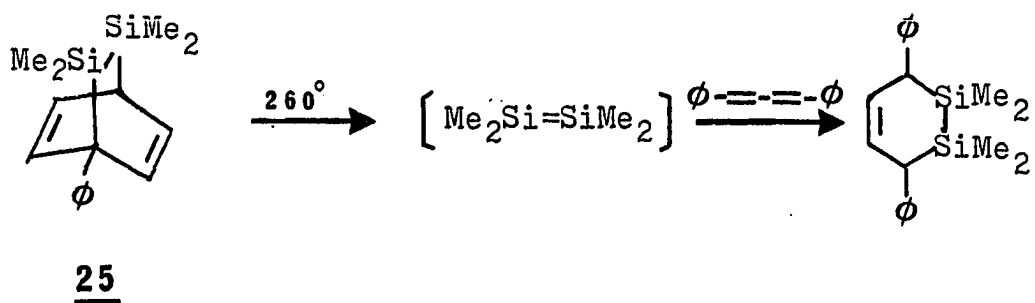
Grinberg reported⁶⁸ that if two different silacyclobutanes under copyrolysis, the products contain all possible direct and cross dimerizations.



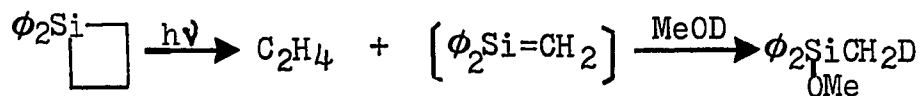
Barton and Kline⁶⁹ have found that thermal decomposition of 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2,2,2]octa-2,5-diene (24) at 400° gives 1,1,3,3-tetramethyldisilacyclobutane. In principal, aromatization is a good driving force for the formation of unstable species.



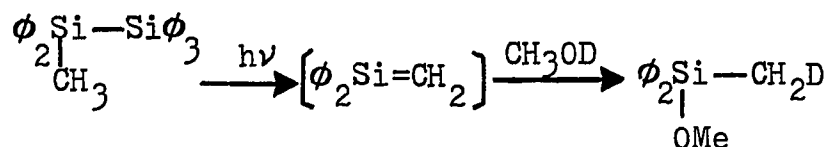
In similar work, reported by Peddle *et al.*⁷⁰ and Roark and Peddle⁷¹ pyrolysis of 1-phenyl-7,8-disilabicyclo[2,2,2]octa-2,5-diene (25) gave tetramethyldisilaethylene, which was trapped by variety of dienes.



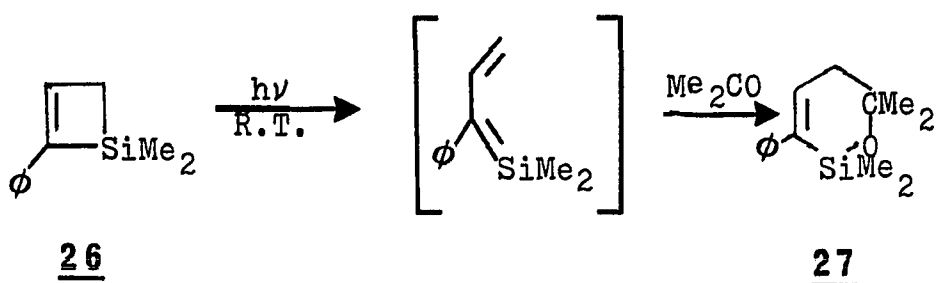
Photolysis has also been used in attempts to generate silaolefins. Diphenyl-silacyclobutane gave on photolysis in methanol-d, a product which can be derived from 1,1-diphenyl-silaethylene.⁷²



Photochemical dehydrosilation of pentaphenylmethyl-disilane possibly gives 1,1-diphenylsilaethylene.⁷³



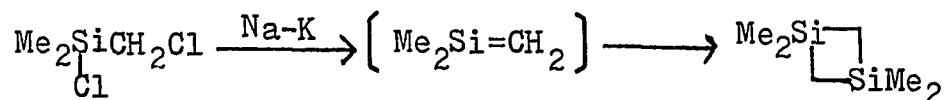
Valkovich and Weber⁷⁴ found photolysis in acetone solution of 1,1-dimethyl-2-phenyl-1-silacyclobut-2-ene (26) appears to involve 1,1-dimethyl-2-phenyl-1-sila-1,3-butadiene as a reactive intermediate. 2,2,6,6-Tetramethyl-1-oxa-3-phenyl-2-sila-3-cyclohexene (27) is formed in 82%



yield, showing that acetone is a very efficient trapping agent.

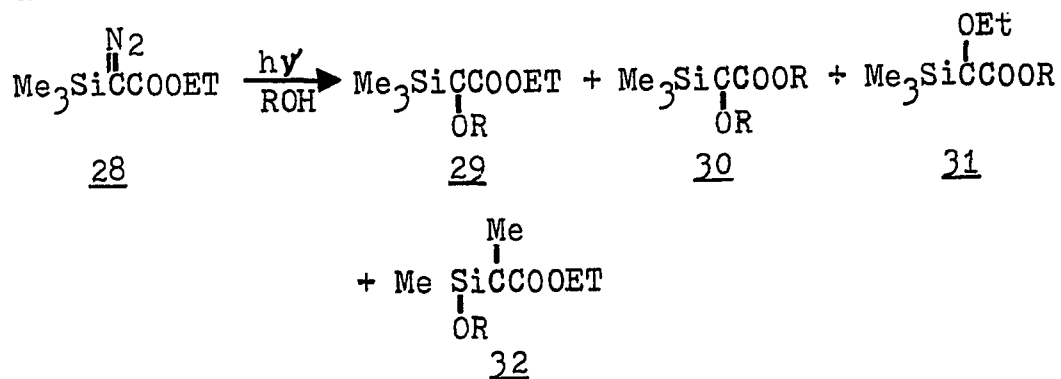
Interesting results have been observed in studies of

gas-phase dechlorination of chloro(chloromethyl)-dimethylsilane with sodium-potassium vapors.⁷⁵



Only one report, from Barton and McIntosh,⁷⁶ of an attempt to observe such a species spectroscopically is available. They reported that thermolysis of 1,1-dimethyl-1-silacyclobutane gives 1,1-dimethyl-1-silaethylene with one observed infrared band at 1407 cm^{-1} at 77° K . The assignment by these authors suffers from the fact that ethylene was not observed and that no other identification of the product was reported.

Finally, the result of photodecomposition of ethyl-trimethylsilyldiazoacetate (28), reported by Ando and co-workers⁷⁷ should be mentioned. Irradiation of 28 in alcohols, four products, 29-32, are obtained. Compound 32, in the authors opinion, is probably derived from a silaolefin.



From the above illustrated study, one can easily visualize that there has been a considerable amount of interest in the synthesis of molecules containing unsaturated silicon in the last decade. However, even after the tremendous effort that has been devoted to this area, only indirect evidence of the transient existence of silaolefins has yet been reported. The purpose of this research is to generate a silaolefin under conditions which would allow direct detection by spectroscopic means and study of the structure and bonding of the species.

RESULTS AND DISCUSSION

Trimethylsilyldiazomethane provides an attractive precursor for photochemical generation of 1,1,2-trimethylsilaethylene. Irradiation ($>3400 \text{ \AA}$) of trimethylsilyldiazomethane (33) matrix isolated in argon at 8° K gives trimethylsilyldiazirine (34) with bands at 3010, 2960, 2935, 2855, 1645, 1260, 1040, 975, 965, 865, 855, 770 and 760 cm^{-1} . Irradiation of trimethylsilyldiazomethane matrix isolated in argon at 8° K with shorter wavelength light ($>2000 \text{ \AA}$) produces a photostationary state (see Figure 10) involving trimethylsilyldiazirine (34). Trimethylsilyldiazirine is also formed on irradiation in variety of solvents at room temperature. The rearrangement between 33 and 34 quite similar to that reported by Fronich *et al.*⁷⁸ for 35 and 36. Continued irradiation of the photostationary mixture produced from either 33 or 34 matrix isolated in argon gives 1,1,2-trimethylsilaethylene (37) *via* the

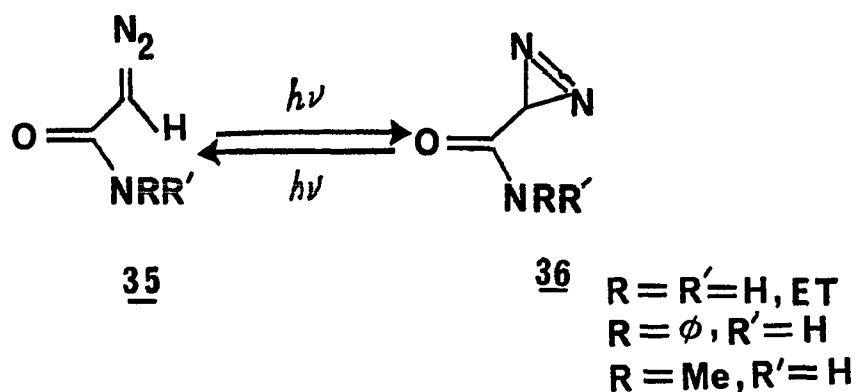
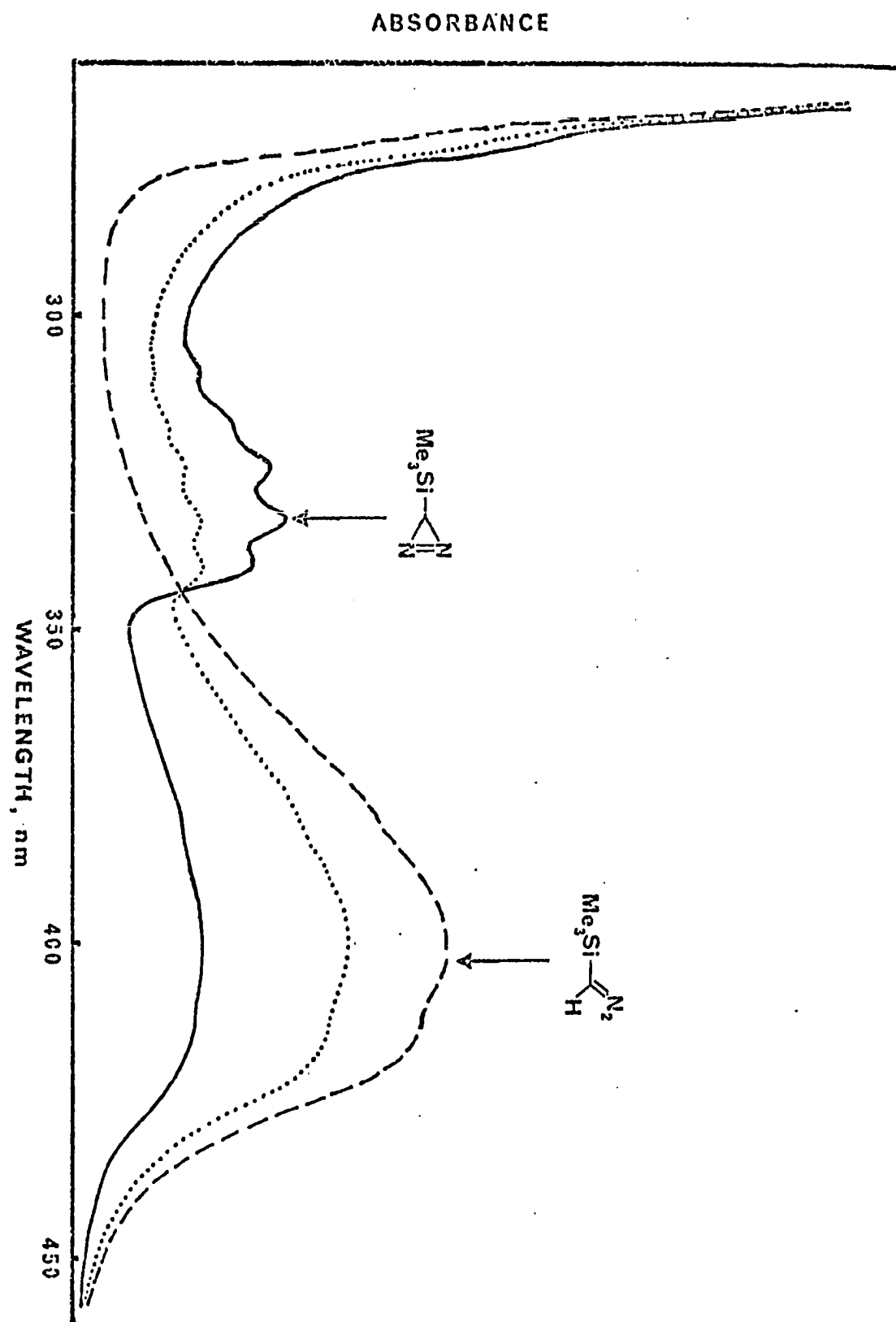
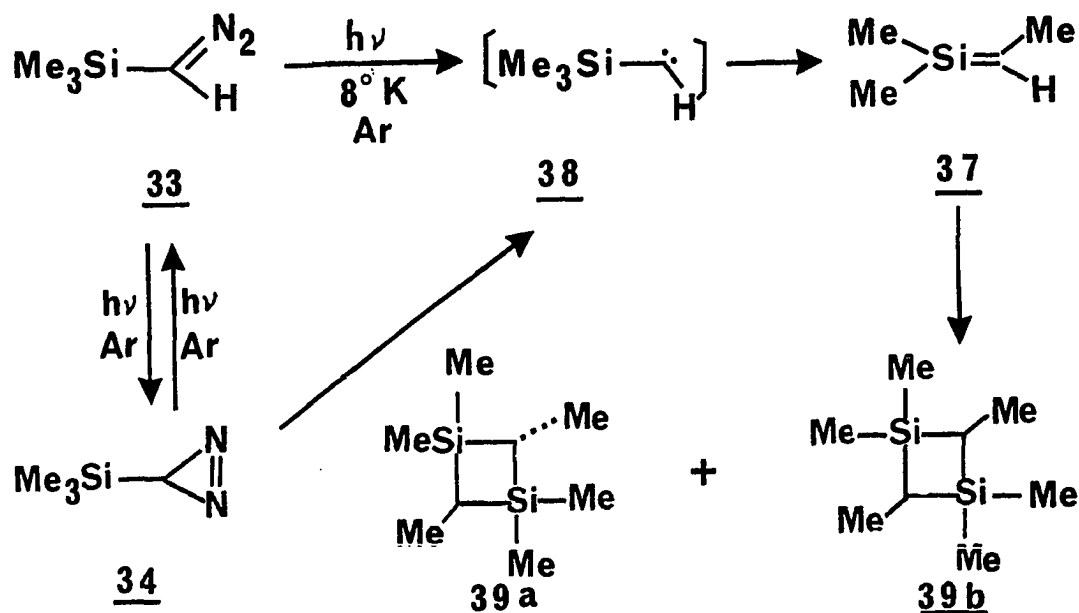


Figure 10 Irradiation of trimethylsilyldiazomethane at 77° K, uv spectrum

Ultraviolet spectrum of trimethylsilyldiazomethane (33) in 3-methylpentane at 77° K. Before irradiation (-), after 50 minutes irradiation (.....), and after 190 minutes irradiation ($\lambda > 355$ nm) (-----).



carbene 38. The infrared spectrum of 1,1,2-trimethylsilaethylene (37) matrix isolated in argon at 8° K has bands at 3020, 2980, 2965, 2940, 2900, 2870, 1450, 1410, 1370, 1315, 1255, 1120, 978, 883, 808, 795, 712, 708, 645, 608 and 358 cm⁻¹ (see Figure 11). The identity of 1,1,2-trimethylsilaethylene is established unambiguously by the thermal

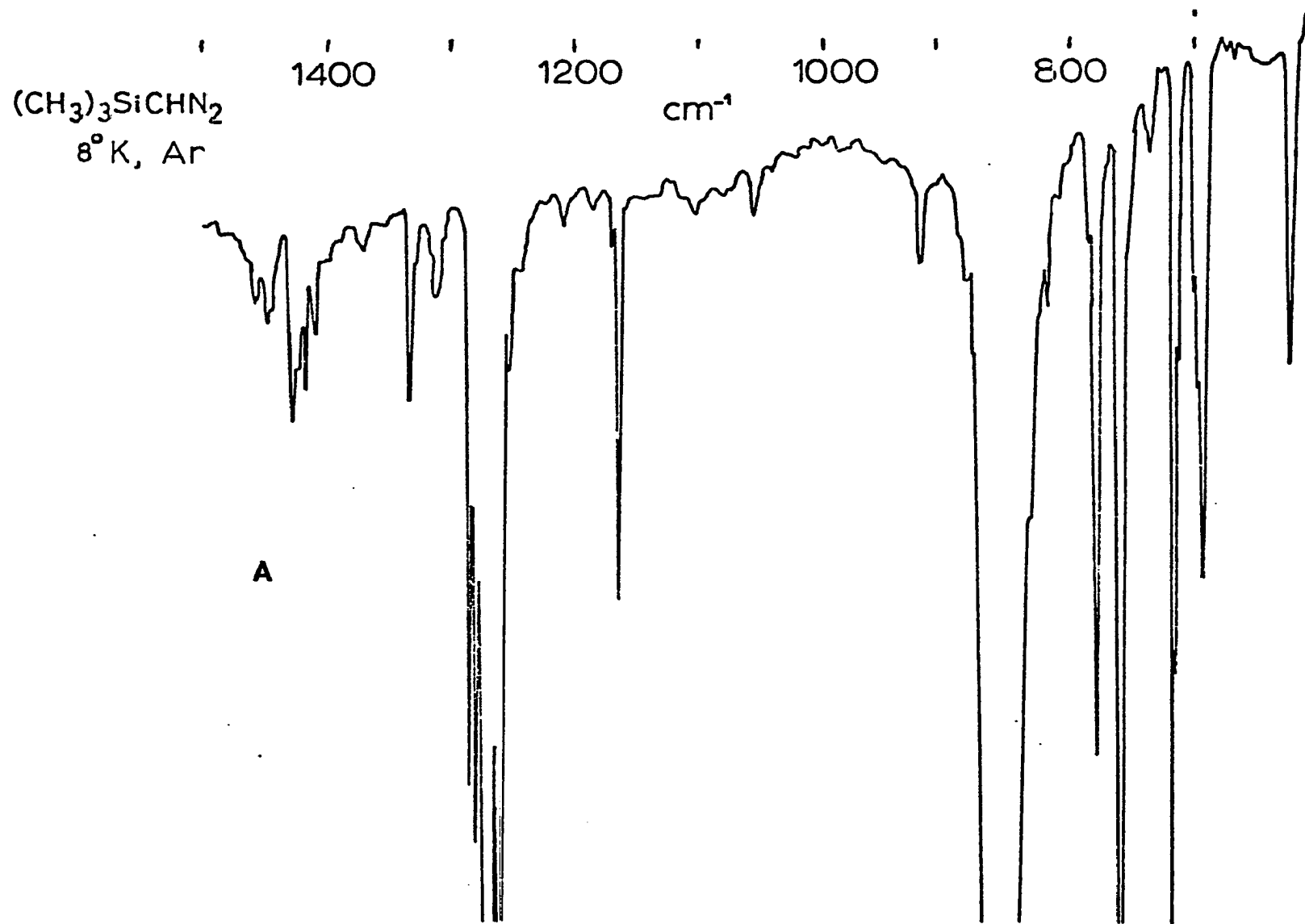


dimerization of 37 to the *cis* and *trans*-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes (39a and 39b) on warming above 45° K. In this transformation, the disappearance of the infrared bands of 1,1,2-trimethylsilaethylene is concurrent with the appearance of the bands of the dimers (39a,b). The dimers are compared with authentic samples which are kindly provided by professor T. J. Barton.

During the course of our experiment, Kreeger and

Figure 11 Irradiation of trimethylsilyldiazomethane at 77° K, ir spectrum

A. Infrared spectrum of trimethylsilyldiazomethane (33) matrix isolated in argon at 8° K before irradiation. B. Sample in A after irradiation for 1070 min. (quartz optics). The spectrum is that of 1,1,2-trimethylsilaethylene except for bands marked (-). C. Sample in B after warming to 45° K. The argon is lost in this process. Bands not present in the authentic dimers (5a,) are marked (+).



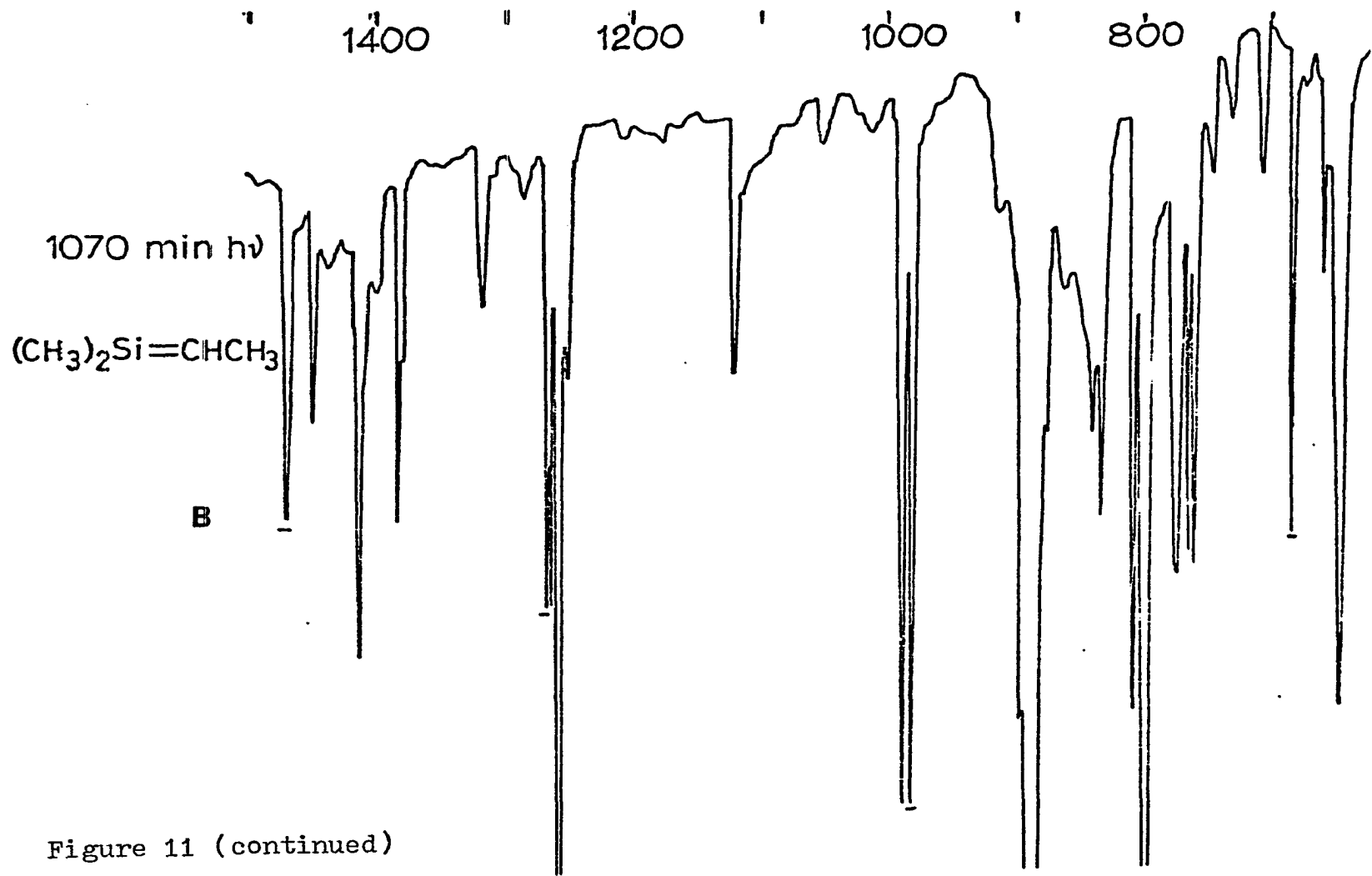


Figure 11 (continued)

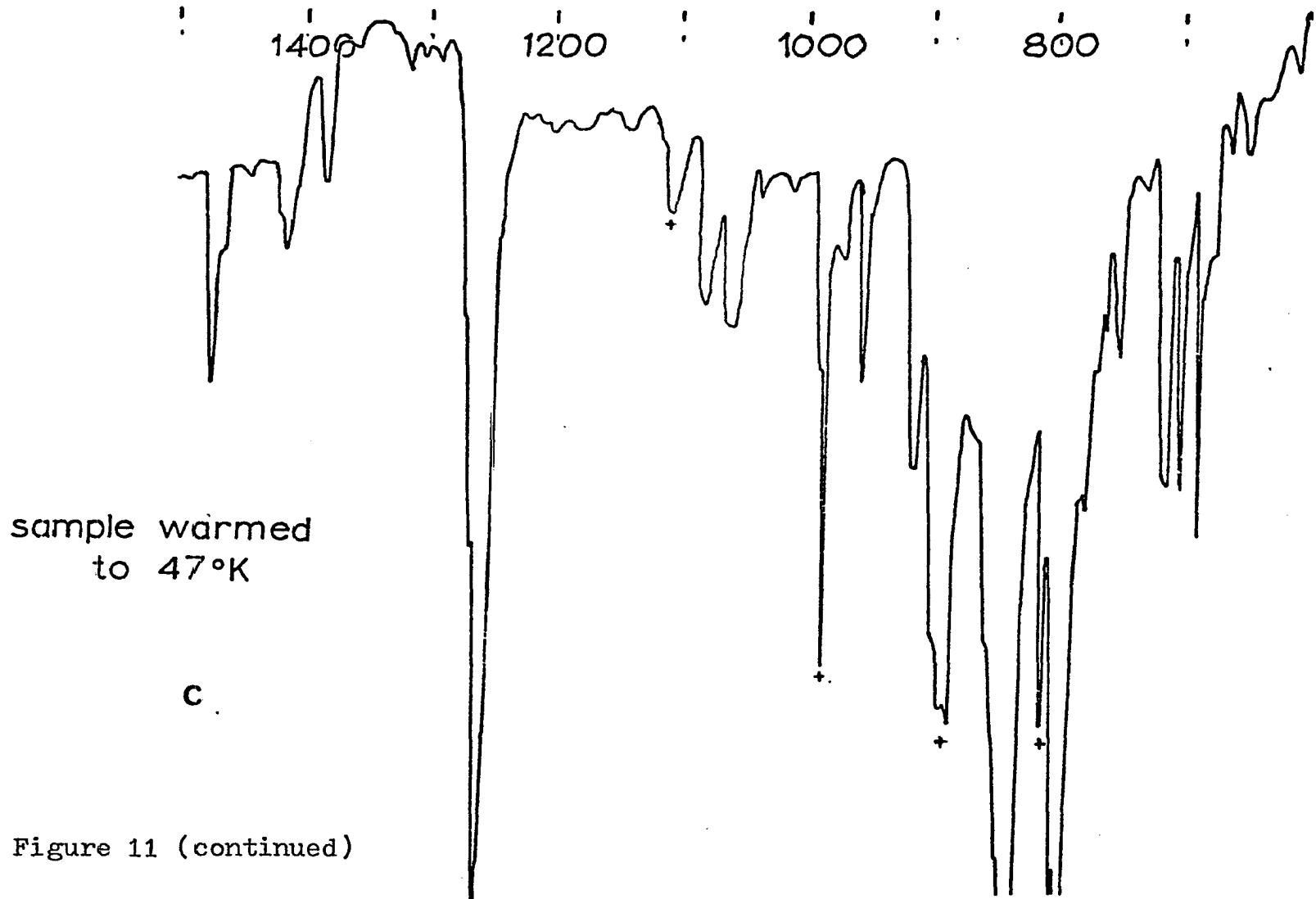
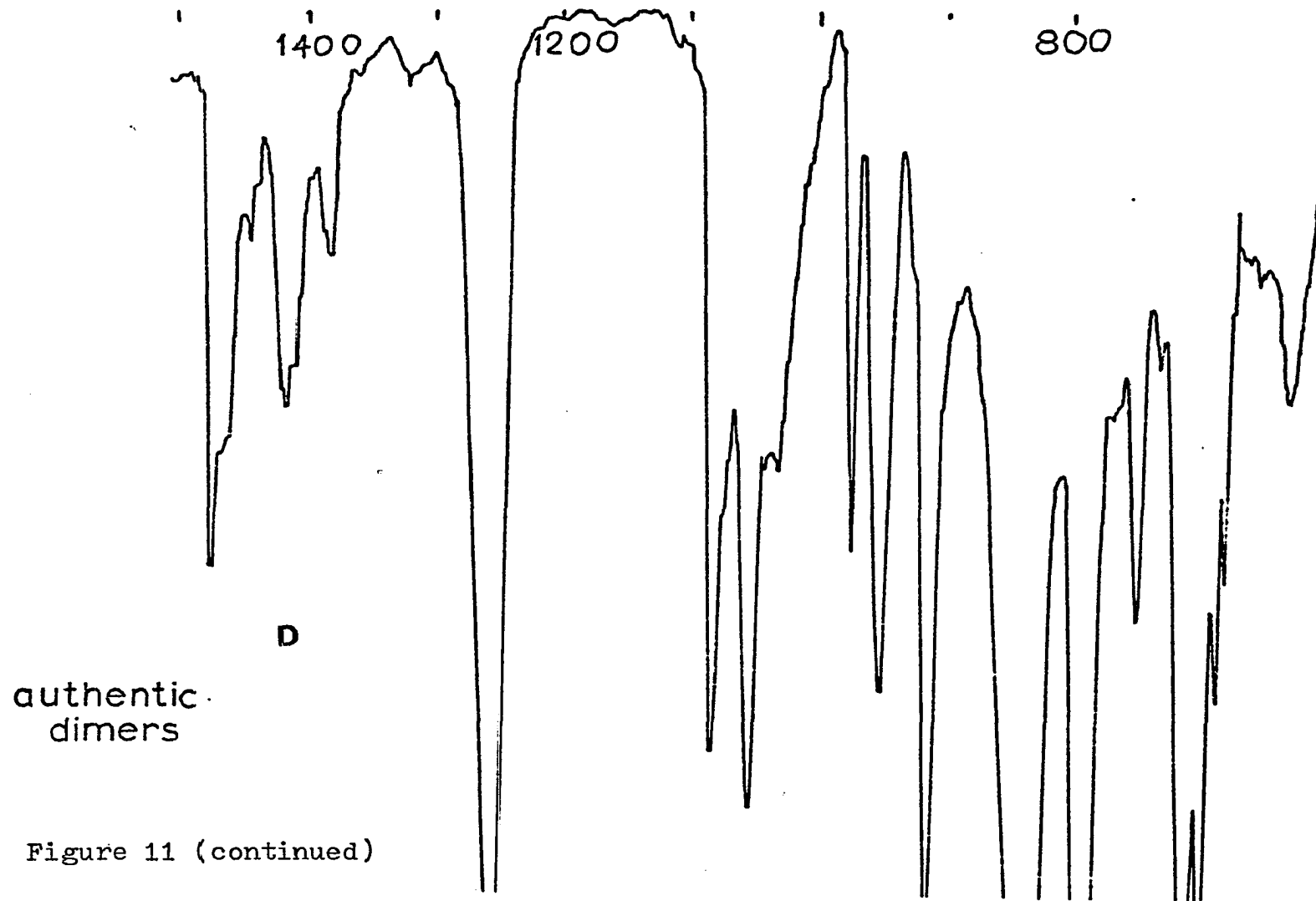


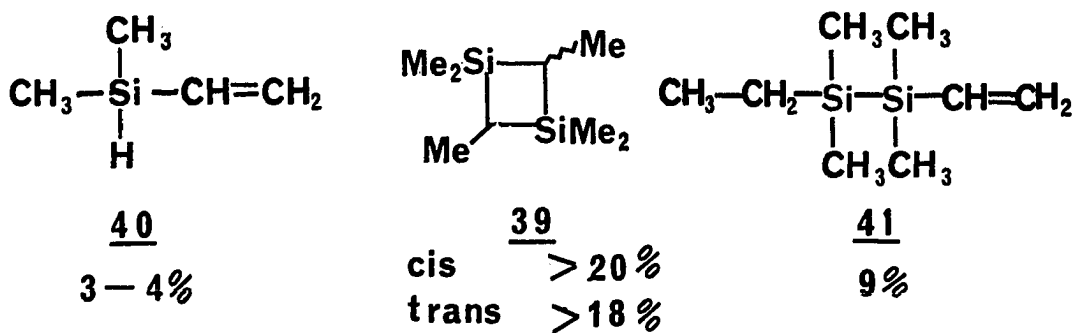
Figure 11 (continued)



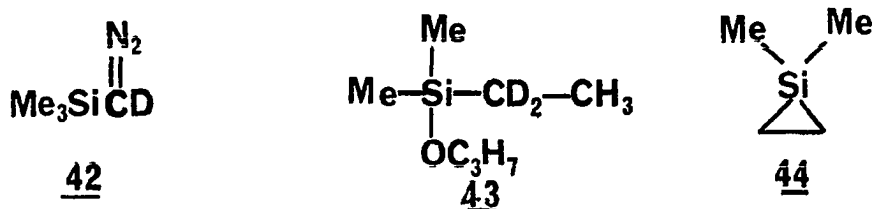
authentic
dimers

Figure 11 (continued)

Shechter⁷⁹ described the room temperature photochemistry and the thermolysis of trimethylsilyldiazomethane and provided evidence for the generation of 1,1,2-trimethylsilaethylene. They reported that decomposition of trimethylsilyldiazomethane at 440° to give vinyltrimethylsilane (40), cis- and trans-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes (39), 3,3,4,4-tetramethyl-3,4-disila-1-hexene (41) and other unidentified products.



Photolysis of α -deuteriotrimethylsilyldiazomethane (42) in 2-propanol-OD gives α,α -dideuterioethyldimethyl-2-propoxysilane (43) in which the methyl portion of the ethyl group does not contain deuterium. This excludes the possibility of intermediacy of 1,1-dimethylsilacyclopropane (44).



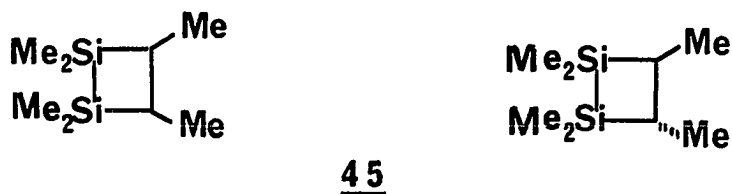
The infrared spectrum of 1,1,2-trimethylsilaethylene

shows several interesting features. The olefinic C-H stretch (3020 cm^{-1}) and the deformation modes ($795, 645\text{ cm}^{-1}$) are typical modes for a trisubstituted ethylene (trimethylethylene has bands at $3020, 800$ and 665 cm^{-1}). The similarities between the infrared spectra of trimethylethylene and 1,1,2-trimethylsilaethylene strongly suggest that the silaethylene is a planar molecule, i.e. that there is a significant barrier to rotation about the silicon-carbon double bond. Calculations at the STO-3G level also indicated that molecule was planar.⁸⁰ Geometry relaxation at the extended basis set level yielded an optimized structure of silaethylene (C_{2v} symmetry; Si = C, 1.693 \AA ; Si-H, 1.479 \AA ; C-H, 1.074 \AA ; \angle^{H-Si-C} , 122.9° ; \angle^{H-C-Si} , 122.7°). More recently, Strausz et al.⁸¹ carried out a calculation with s,p Gaussian-type function contracted to a minimal version of Gaussian 70 program. They predicted that the absolute minimum occurs at the skew position in the pyramidal triplet state lying about 1.4 kcal/mole below the minimum in the planar singlet surface. These results are in line with extreme reactivity of silaethylene suggesting a diradical character. However, if a large basic set for a fully correlated wave function is used, the computed order of stability of T_1 and S_0 state may be reversed.

At this time, it is impossible to assign a

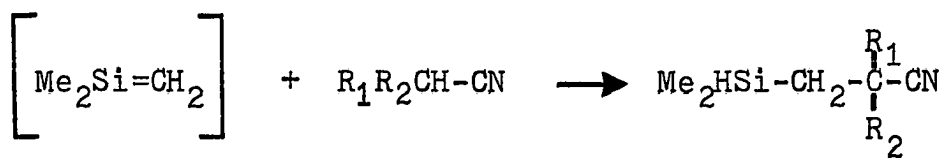
silicon-carbon double bond stretching vibration in the spectrum. A theoretical prediction of the infrared of silaethylene ($\text{H}_2\text{Si}=\text{CH}_2$) has been published by Schlegel *et al.* recently.⁸⁰ The bands at 1450 and 1120 cm^{-1} are quite close to those predicted for Si-C stretching modes (1490 and 1140 cm^{-1}).

It is interesting to note that the silaethylene dimerize to give disilacyclobutanes only in a "head-to-tail" fashion. The "head-to-head" dimers 45 have never been observed. This suggests that silicon-carbon double bond is



polarized. The dipole moment has been estimated⁸⁰ to be 1.1 D, which indicates a highly polarized bond.

From the results of pyrolysis of 1,1-dimethylsila-cyclobutane with acetonitrile, Bush and his co-workers⁶³ also suggested a polar double bond for silaethylene. Their



later work⁸² on reactions of silicon-carbon double bonds with silicon chlorides and fluorides provides better evidence for zwitterion character in the silicon-carbon double bond.



In sharp contrast to silicon-chlorine bonds, the silicon-hydrogen bond is well known to react via a radical mechanism. Thus any diradical character of silaethylene should lead to addition of silicon-hydrogen to silaethylene when the latter is generated in the presence of SiHCl_3 .

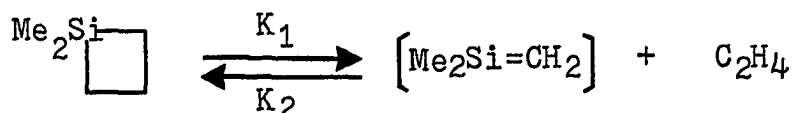
One can also rationalize the selective "head-to-tail" dimerization by a simple consideration of the bond energies⁸³ (Table 4-3). Formation of two silicon-carbon bonds (69×2 kcal).

Table

Bond	C-C	C-Si	Si-Si
Bond Energy kcal	83	69	42

formation of one silicon-silicon bond and one carbon-carbon carbon bond (42 kcal + 83 kcal).

Disagreeing with Fritz and Grobe's suggestion of a structure Si-CH_2 , Flowers and Gusel'nilov provide⁶¹ kinetic data which can be interpreted in terms of a reversible initial reaction to give an intermediate containing a silicon-carbon double bond.



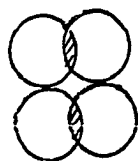
A biradical intermediate must be in a triplet electronic state (the singlet state is virtually equivalent to the assumption of a Si-C double bond). This requires a spin inversion in the primary step of decomposition. The measured Arrhenius factor is not in accord with a reaction involving spin inversion. The facts that the decomposition is very clean and that the addition of toluene⁶¹ does not affect the rate constant both suggest the diradical is not an appropriate structure for the intermediate.

Unlike ethylene, 1,1,2-trimethylsilaethylene readily undergoes dimerization at 45° K, the temperature at which argon is pumped out. This indicates that 1,1,2-trimethylsilaethylene may not exist in the neat form even at lower temperature. Indeed, the high reactivity of silaolefins is quite amazing and unexpected. Flowers and Gusel'nikov estimated the activation energy for dimerization of 1,1-dimethylsilaethylene to be about 11 kcal/mole.⁶¹ The value for dimerization of ethylene is 37.7 kcal/mole. Silaethylene is quite resistant to unimolecular decomposition.

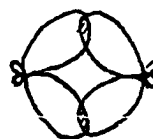
A number of attempts have been made to rationalize the high reactivity of the π -bond for the elements of the third and subsequent rows in group IV. Pitzer⁸⁴ suggested that the weak π -bond is due to the repulsion of bonding orbitals and filled inner cores of the heavier atom. Mulliken^{85,86} disagreed with this postulation. He concluded that this repulsion is no longer for the third-row element than for the second-row elements, and hence it is not likely that this is the reason for the high reactivity. He attributed the high reactivity to the fact that formation of a σ bond is more favorable than the double bond. This also explains the stronger tendency to form polymers and dimers rather than unsaturated monomers.

Levin *et al.*⁸⁷ estimated the amount of P π -P π interaction for carbon and silicon atoms from the heats of sublimation of diamond and silicon. They found that the Huckel parameter for silicon is approximately half that of carbon. Walsh⁸⁸ suggested a value of 30-42 kcal/mole for the π -bond energy in silaolefins.

Using Hoffman's extended Hückel MO theory, Curtis concluded⁸⁹ that the contribution of 3d orbitals to overlap is high. They also pointed out that the contribution of P π -d π (overlap population 0.197) to the overlap is larger than that of P π -P π (0.130). The C=Si π -bond overlap population is 0.327 and is composed of P π -P π



P-P



P-d hybrid

and P π -d π contributions:

$$\begin{array}{rcl}
 2P-3P & & 2P-3d \\
 0.130 & + & 0.197 = 0.327
 \end{array}$$

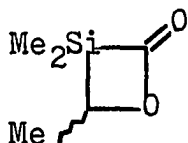
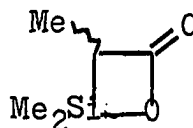
Since the EHMO method does not include Coulomb interactions, the charge separation is grossly over-estimated. The charges calculated by the CNDO method

indicate an exceedingly polar bond:

+0.061	-0.308	+0.422	-0.118
H	C	Si	H

Using CNDO/2 method. Damrauer and Williams calculated⁹⁰ a substantial π bond order and short silicon-carbon bond length (1.75 Å for silaethylene comparing with 1.89 Å for silicon-carbon single bond) strongly indicate the inherent stability of such bonds. In the author's opinion, the extremely high reactivity is due to the high polarity of silicon-carbon bond. However, the polarity seems not be the only reason for high reactivity of 1,1,2-trimethylsilaethylene since silaolefin reacts readily with ethylene and butadiene also. In any event, a planar molecule with low π -bond energy suggests, not that a molecular such as 1,1,2-trimethylsilaethylene would be unstable on its own, nor that it would be more stable in the biradical form, but that reaction with other molecules should be extremely facile. Therefore, it is clear that the remaining questions would be answered if one can synthesize the parent silaethylene, $H_2C=SiH_2$, and measure the required physical properties. By normal mode analysis, one can further understand the structure and bonding of an unsaturated silicon compound.

The irradiation of 33 matrix isolated in carbon dioxide at 8° K gave a product with 1780, 980, 890, 800 cm⁻¹ bands. This product may be a silyllactone (46 or 47). However, no further characterization was carried out on this species based on band at 1780 cm⁻¹.

4647

We have also tried to synthesize and characterize 1,1-dimethylsilaethylene from a variety of other precursors. Pyrolysis of 1,1-dimethylsilacyclobutane at 900° gave ethylene and a new product which are isolated in an argon matrix at 20° K. The bands due to the new species are 3110, 3025, 2150, 2140, 1900, 1450, 1425, 1305, 1190, 1085, 1080, 1035, 1025, 1005, 950, 940, 815 and 620 cm⁻¹. Identification of this species is very difficult since a large amount of 1,1-dimethylsilacyclobutane remains unpyrolyzed. If the pyrolysis tube is packed with quartz chips to increase the residence time in the oven, the bands due to silacyclobutane can almost be completely eliminated. However some bands not attributable to starting material are also missing (1450, 1415, 1190, 1085, 1080, 1005, 940 cm⁻¹). In addition, new bands are observed at 1260, 1035, 1020, 880 and 835 cm⁻¹.

It is clear that at least two products are involved besides the ethylene (3110, 1900, 1450 and 950 cm^{-1}).

The second precursor, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, was pyrolyzed under the same conditions at 1000°. Besides starting material, the infrared spectrum shows bands at 3230, 3020, 2150, 2140, 1305, 1035, 750 and 740 cm^{-1} . When the matrix was warmed to 60° K, all the bands decrease in intensity except the one at 3230 cm^{-1} . No increase in the starting material bands were observed due to large amount of starting material present under pyrolysis conditions.

Thermolysis of 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2,2,2] octa-2,5-diene (24; kindly provided by professor T, J, Barton) at 740° gave those bands of $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$ -hexa-fluoro-o-xylene, (48) and these additional bands at 2150, 2140, 1370, 1260, 935, 910, 895, 820, 815 and 650 cm^{-1} . The decomposition is complete under these conditions. The common product (see Table 2) of the

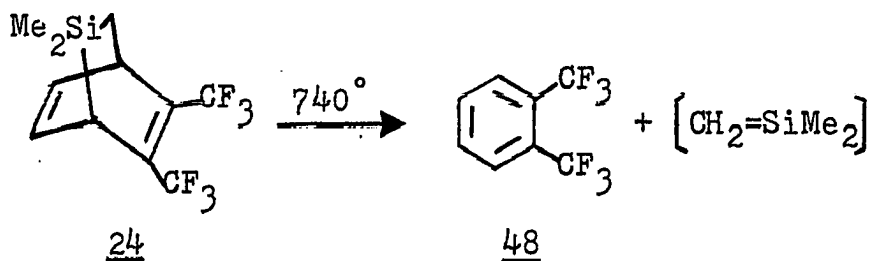
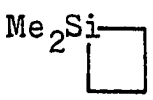
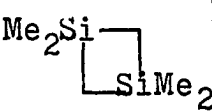
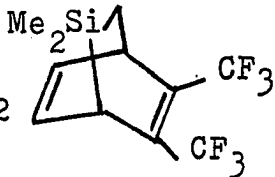


Table 2 The infrared bands of pyrolysis of 1,1-dimethylsilacyclobutane, 1,1,3,3-tetramethyl-1,3-disilacyclobutane, 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2,2,2]octa-2,5-diene

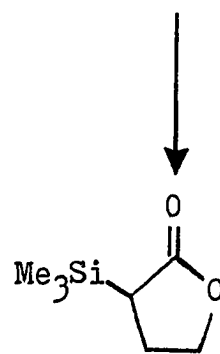
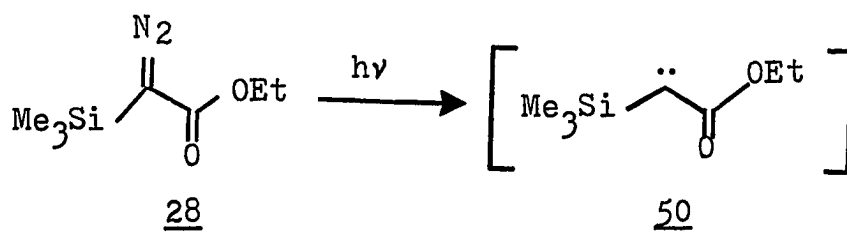
				
	900°	900° (packed with chips)	1000°	740°
	3110*	3110*	3230	
	3025	3025	3025	
	2150	2150	2150	2150
	2140	2140	2140	2140
	1900*	1900*		
	1450*	1450*		
	1425			
	1415			
				1370
				1315**
	1305	1305	1305	1280**
	1260	1260		1260
	1190			1192**
	1085			1185**
	1080			1170**
	1035	1035	1035	1110**
	1025			1095**
		1020		1145**
	1005			1137**
	950*	950*		
	940			
				935
				910
				895
		880		
		835		
	815			815
			750	770*
	740	740	740	
				650
	620			

* Bands of ethylene.

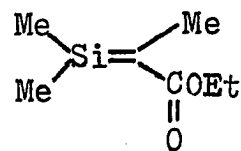
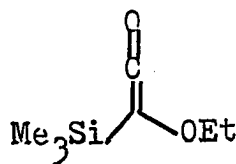
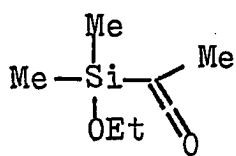
** Bands of $\alpha, \alpha, \alpha, \alpha', \alpha', \alpha'$ -hexafluoro-o-xylene (48).

pyrolysis of different precursors is probably 1,1-dimethyl-silaethylene. However, the extent of the conversions of the silacyclobutanes under pyrolysis are quite small even at very high temperature. Undoubtedly, there are many other new bands which are covered by those of the silacyclobutanes.

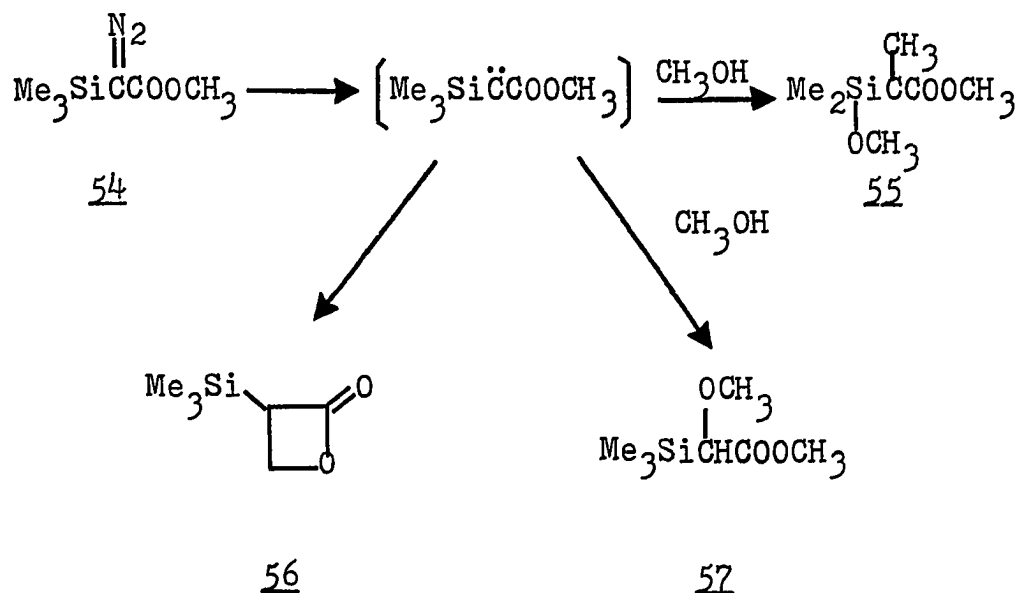
The photochemistry of ethyl trimethylsilyldiazoacetate (28) is not completely clear. Irradiation ($\lambda > 3400 \text{ \AA}$) of 28 matrix isolated in argon at 8° K give products with bands at 2220, 2080 (s), 1750, 1725, 1180, 1140, 880, 845, 755 cm^{-1} . Continued irradiation with shorter wavelength ($>2000 \text{ \AA}$) converts the primary products to new products with bands at 2120 (s), 1734, 1425, 1300, 1275 and 760 cm^{-1} . At this time it is not possible to assign structures of all the new bands, however, bands at 1725, 1750 cm^{-1} probably belong to a γ -lactone 49, which is formed by an insertion of carbene 50 into the carbon-hydrogen bond of the ethoxy group. Although 49 has not been isolated, a β -lactone (56) has been found in similar reaction.^{91,92} Bands at 2120 and 2080 cm^{-1} suggest that there are two ketenes involved. The new band at 1734 cm^{-1} may be an ester. Whether the structures 51, 52 and 53 are correct or not is difficult to know based on the observed data.



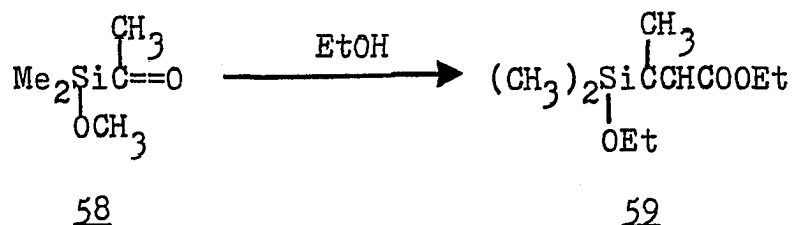
1725 cm⁻¹
1750 cm⁻¹



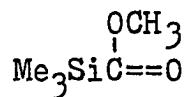
In the course of our experiment, Ando and his co-workers reported the thermolysis of methyl trimethylsilyldiazoacetate (54).⁹¹ When 54 was vaporized through a tube maintained at 360° and the products then treated with methanol, three compounds were observed (55, 56 and 57).



Pyrolysis of 54 at 360° followed by addition of benzene led to ketene 58 (2085 and 1088 cm⁻¹) in 12% yield without other products reported. They also found that treatment of 58 with ethanol at 60° C gives ester 59 quantitatively.



Therefore, 55 is not from silaethylene but ketene 58. The source of ketene 58 is not clear. The authors raised the possibility that ketene 60 may undergo rearrangement to ketene 58 of the dyotropic kind. If this is true, photochemistry of 48 may well be parallel to thermochemistry, since we have also observed two ketenes involved in a similar fashion.



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EXPERIMENTAL

Trimethylsilyldiazomethane was prepared followed the method reported in D. Seyferth, H. Menzel, A. W. Dow and T. C. Flood⁹³ by M. L. Tumey and J. A. Lowe. Trimethylsilyldiazirine was isolated by M. L. Tumey. Ethyl trimethylsilyldiazoacetate was prepared by J. A. Lowe. Cis and trans-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes, 1,1,3,3-tetramethyl-1,3-disilacyclobutanes and 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo [2,2,2]octa-2,5-diene were obtained from professor T. J. Barton. Commercially available dimethylsilacyclobutane was a kind gift from Dr. M. E. Jung.

Photolysis of matrix isolated trimethylsilyldiazomethane in Ar at 8° K with Pyrex filter

A trimethylsilyldiazomethane/argon (1/1500) mixture was deposited at a rate of 1 mm/min. for 180 minutes. Irradiation was accomplished using a 1000 Watt medium pressure mercury vapor lamp. Irradiation for 1200 minutes with a Pyrex filter (0%-3400 Å, 60%-3600 Å) resulted in complete destruction of the trimethylsilyldiazomethane with new bands at 3010, 2960, 2935, 2855, 1645, 1260, 1040, 975, 965, 865, 855, 770 and 760 cm^{-1} . Warm up to 30° K

showed no destruction of any of the new bands. The sample then was warmed up and pump into a liquid nitrogen trap. The collected sample when codeposited with argon showed a considerable amount of trimethyldiazomethane which was probably condensed on radiation shield.

Photolysis of trimethylsilyldiazomethane in 3-methyl-pentane at 77° K

Irradiation of trimethylsilyldiazomethane (degassed) in 3-methyl-pentane at 77° K was carried out using an 800 Watt high pressure mercury vapor lamp with a Pyrex filter (>355 nm). The reaction was followed by ultraviolet spectroscopy. Trimethylsilyldiazomethane was slowly converted to a new species with λ_{\max} 340, 332, 324, 317 and 309 nm. There is a isobestic point at 345 nm. The reaction was 60% completed in 190 minutes. Further irradiation caused little change of equilibrium. Warming up the glass to room temperature and recooling down to 77° K showed the new species unchanged.

Photolysis of matrix isolated trimethylsilyldiazomethane in argon at 8° K with quartz filter

Trimethylsilyldiazomethane (1 mm) in argon (750 mm) was pulse deposited at 20° K at a 2-3 mm interval for 162 mm. Complete destruction of starting material was

accomplished using a 1000 Watt mercury vapor lamp with a quartz filter in 1070 minutes. The reaction was monitored by infrared spectroscopy. New bands were formed at 3360, 3320, 3200, 2980, 2965, 2940, 2900, 2870, 2740, 1470, 1450, 1410, 1370, 1315, 1255, 1120, 983, 978, 883, 830, 808, 795, 730, 712, 708, 680, 660, 645, 608 and 358 cm^{-1} (Figure 11). The product is quite stable under irradiation.

The matrix was then warmed up gradually and the argon was pumped off from the cesium iodide window. Warming to 45°K caused destruction of bands at 3020, 2980, 2965, 2940, 2900, 2870, 1450, 1410, 1370, 1315, 1255, 1120, 978, 883, 808, 795, 712, 708, 645, 608 and 358 cm^{-1} with new bands growing at 2950, 2900, 2860, 2730, 1470, 1410, 1380, 1245, 1075, 1045, 965, 940, 905, 830, 785, 745, 705, 690 and 580 cm^{-1} .

The new bands formed upon warming are identical to those of the mixture of cis and trans-1,1,2,3,3,4-hexamethyl-1,3-disilacyclobutanes at same conditions.

Photolysis of matrix isolated trimethylsilyldiazomethane in carbon dioxide at 8°K

A mixture of trimethylsilyldiazomethane and CO_2 (1:400) was prepared in the gas handling system. The sample (80 mm) was deposited at 40°K at a rate of 1 mm/min. Photolysis was accomplished using 800 Watt high pressure mercury vapor lamp

with a quartz filter while being monitored by infrared. Irradiation for 1000 minutes caused complete destruction of starting material with new bands at 1780, 980, 890 and 800 cm^{-1} . Trapping the product of the mixture at 77° K followed by mass spectral analysis showed nothing.

Photolysis of trimethylsilyldiazirine in argon matrix at 8° K

A mixture of trimethylsilyldiazirine and argon (1:1000) was pulse deposited at 20° K at a 2-3 mm each time for 100 mm. Photolysis was carried out by using an 800 Watt high pressure mercury vapor lamp equipped with Pyrex filter ($>2740\text{ \AA}$) while being monitored by infrared. In first 10 minutes new bands grew at 2080, 2070, 1470, 1410, 1280, 1260, 985, 885 and 795 cm^{-1} . Further irradiation caused a gradual destruction of the new bands at 1280, 985 and 885 cm^{-1} . Continued irradiation with shorter wavelength ($>2000\text{ \AA}$) caused complete destruction of starting material with final bands at 1470, 1410, 1105, 1045, 895, 900, 845 and 795 cm^{-1} .

Photolysis of ethyl trimethylsilyldiazoacetate matrix isolated in argon at 8° K

A mixture of ethyl trimethyldiazoacetate and argon (1:1600) was deposited at 20° K at a rate of 0.5 mm/min

for 270 minutes. Irradiation using Pyrex filter ($>3400 \text{ \AA}$) for 1054 minutes caused complete destruction of starting material with new bands arising at 2220, 2080, 1750, 1725, 1180, 1140, 1000, 880, 845 and 755 cm^{-1} . Further irradiation with shorter wavelength light ($>2000 \text{ \AA}$) caused complete destruction of previously mentioned bands with new bands arising at 2120, 1740, 1425, 1300, 1275 and 760 cm^{-1} .

Photolysis of ethyl trimethylsilyldiazomethane in cyclohexane glass at 77° K

Irradiation of ethyl trimethylsilyldiazomethane in cyclohexane glass at 77° K was carried out using an 800 Watt high pressure mercury vapor lamp with two corning CS 0-52 filters ($>350 \text{ nm}$). The starting material was gradually converted to a product with an isobestic point at 320 nm. The product absorbs at shorter wavelengths (below 300 nm). This absorption overlaps the starting material absorption. The conversion is about 25% in 100 minutes irradiation.

Pyrolysis of dimethylsilacyclobutane

A sample of dimethylsilacyclobutane maintained at -78° at 10^{-6} mm is slowly vaporized through a 2 inch quartz tube

at 900°. The apparatus is shown in Figure 7. The inner diameter is 25 mm. The pyrolysis products are codeposited with argon on a cesium iodide window at 20° K. The argon is deposited at a rate of 1 mm/min (from a 3 liter flask). The matrix isolated mixture showed new bands at 3110, 3025, 2150, 2140, 1900, 1450, 1425, 1415, 1305, 1190, 1085, 1080, 1035, 1025, 1005, 950, 950, 815, 740 and 620 cm⁻¹ as well as those of starting material. A reference spectrum of ethylene, matrix isolated in argon, shows bands at 3100, 1900, 1450 and 950 cm⁻¹.

In a different run with quartz chips packed in the hot zone, all the starting material was destroyed with new bands growing at 3110, 3030, 2150, 2140, 1900, 1450, 1305, 1260, 1035, 1025, 1020, 950, 880, 835, 815 and 740 cm⁻¹. If the quartz chips are more tightly packed, nothing passes through the oven. Therefore an attempt to pyrolyze a sample through more heavily packed quartz tube at lower temperature was not successful.

Pyrolysis of 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo 2,2,2 octa-2,5-diene

A sample of 2,3-bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2,2,2]octa-2,5-diene at -45° (chlorobenzene/liquid nitrogen slush) is slowly vaporized through an oven

maintained at 740° (see Figure 7). The pressure of pyrolysis chamber is 10^{-6} mm. The products, isolated in argon at 20° K, show new bands at 2150, 2140, 1370, 1315, 1280, 1260, 1190, 1185, 1165, 1105, 1092, 1035, 958, 935, 910, 895, 820, 815, 770 and 650 cm^{-1} . 2,3-Bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2,2,2]octa-2,5-diene is stable up to 700° in this apparatus. The bands at 1315, 1280, 1190, 1185, 1165, 1105, 1092, 1035, 958 and 770 cm^{-1} are attributed to $\alpha, \alpha, \alpha, \alpha', \alpha', \alpha'$ -hexafluoro-o-xylene by comparison of matrix isolated spectrum of an authentic sample.

Pyrolysis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane

1,1,3,3-Trimethyl-1,3-disilacyclobutane, maintained at -45° (Chlorobenzene/liquid N_2 slush), is slowly vaporized through a quartz tube which is heated to 1000° . The pressure of the system is 10^{-6} mm. The pyrolysis products in argon matrix at 20° K have bands at 3230, 3020, 2150, 2140, 1305, 1035, 750 and 740 cm^{-1} and those bands of unchanged starting material. Attempts at pyrolysis at higher temperature are not successful because of the difficulty of matrix isolation. Argon is evaporated due to the heat radiated from the oven.

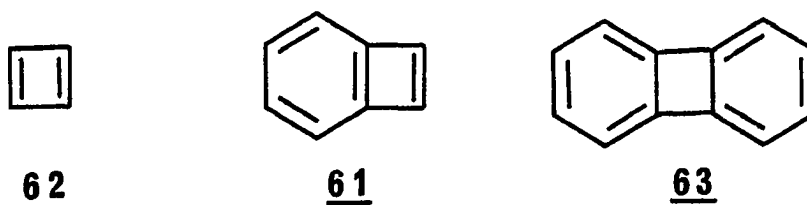
Warming up the matrix to 60° K caused all bands

mentioned previously to decrease in intensity except the band at 3230 cm^{-1} which becomes even more intense and sharper.

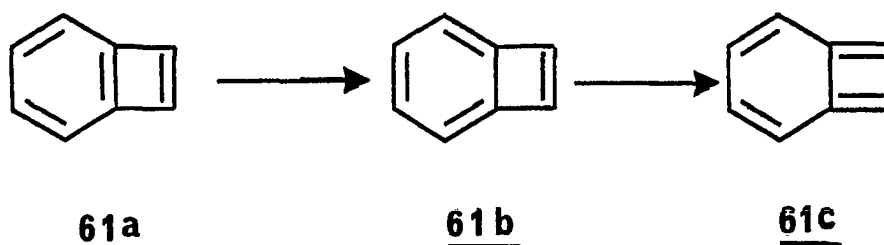
PART III. BENZOCYCLOBUTADIENE

INTRODUCTION

Benzocyclobutadiene (61), the monobenzo derivative of cyclobutadiene, has been a subject of extensive studies⁹⁴ In that, they have been known only as transient reaction intermediates, benzocyclobutadiene and its derivatives resemble cyclobutadiene (62) rather than the stable dibenzo analog, biphenylene (63). There are three

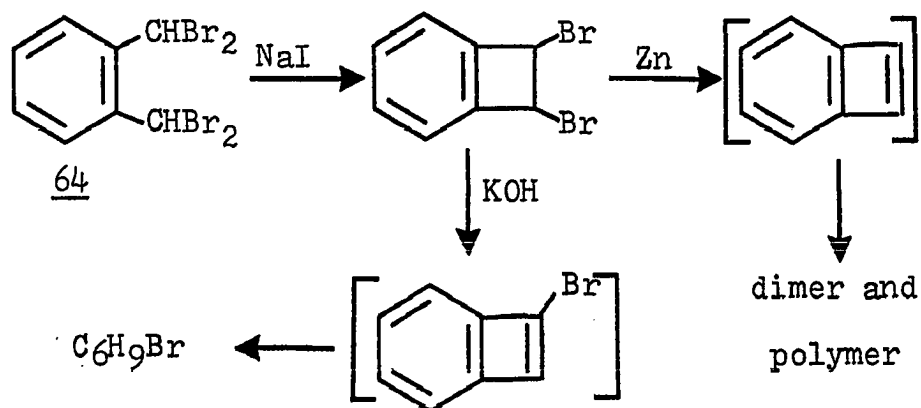


resonance forms for benzocyclobutadiene, 61a, 61b and 61c. Among them, 61b is expected to have more important contribution since both 61a and 61c contained a cyclobutadiene moiety and also have more strain at the fused carbons.

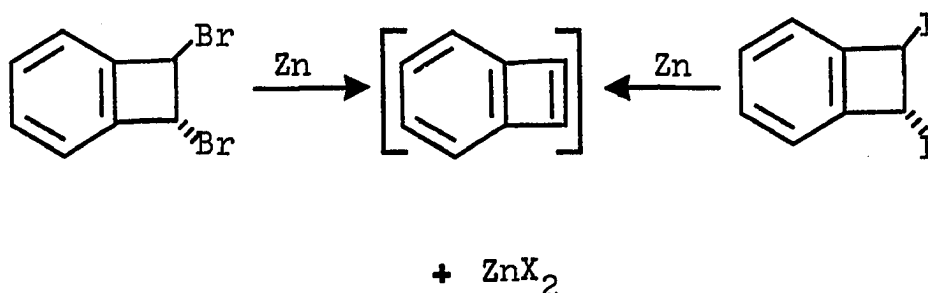


The first attempt to synthesize benzocyclobutadiene was reported in 1907 by Willstatter and Veraguth, who heated α, α' -dibromo-o-xylene with solid potassium hydroxide

and quinoline. The only products isolated were naphthalene and 1,3-dihydroisobenzofuran respectively.⁹⁵ Malachowski made several unsuccessful attempts to prepare benzocyclobutene derivatives suitable for conversion into benzocyclobutadiene.⁹⁶ A few years later, Griffin and Weber carried out what is now believed to be the first reaction involving a genuine benzocyclobutadiene intermediate.^{97,98} They reported that 1,2-dibromobenzocyclobutene, obtained from the reaction of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-*o*-xylene (64) with sodium iodide, could be dehalogenated with zinc suspended in acetone or acetic acid. However, they were unable to isolate benzocyclobutadiene. They also reported the reaction of the dibromide with ethanolic potassium hydroxide to yield a yellow crystalline compound of undetermined structure and with empirical formula C_6H_9Br , rather than 1-bromobenzocyclobutadiene (see following scheme). Thiele and Finkelstein's attempts to synthesize

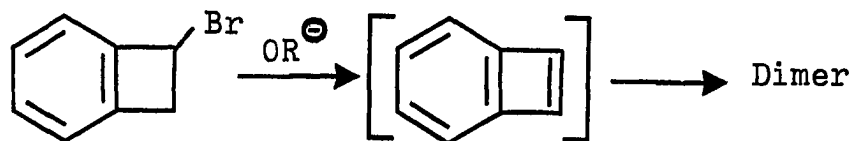


benzocyclobutadiene were only recorded in latter's dissertation.⁹⁹ Their work lay unnoticed for more than four decades until Cava reinvestigated it in detail beginning in 1956. Cava et al. reported^{100,101,102,103} that benzocyclobutadiene is readily generated by the action of zinc dust on either trans-1,2-dibromo or trans-1,2-diiodobenzocyclobutene. Lithium amalgam,¹⁰⁴ sodium

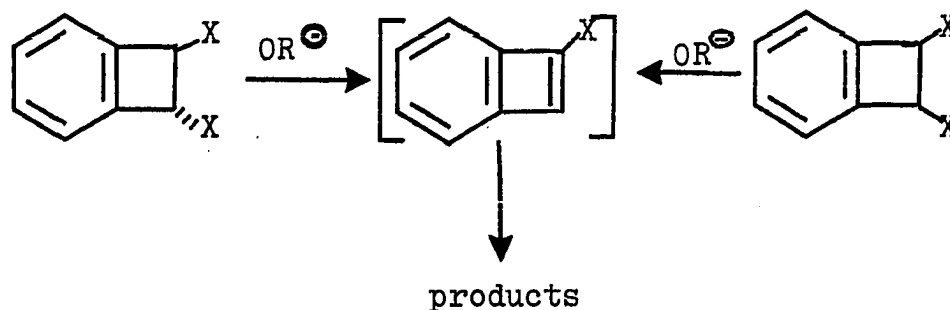


amalgam,¹⁰⁵ sodium iodide,¹⁰¹ and nickel tetracarbonyl¹⁰⁵ were also used as the dehalogenating agents. Among these reagents, zinc dust is the most convenient to use, but it has one pronounced disadvantage. The zinc halides which form in the reaction appear to act as Lewis acids and may promote the polymerization of benzocyclobutadiene. Benzocyclobutadienes have also been generated in good yield by the dehydrohalogenation of appropriate 1-halobenzocyclobutene with potassium tert-butoxide in tert-butyl alcohol. Cava and Napier reported¹⁰² that benzocyclobutadiene was generated by the dehydrobromination of bromobenzocyclo-

butene. A dimer was isolated in 84% yield. Polymer formation is negligible in dehydrohalogenation reaction and

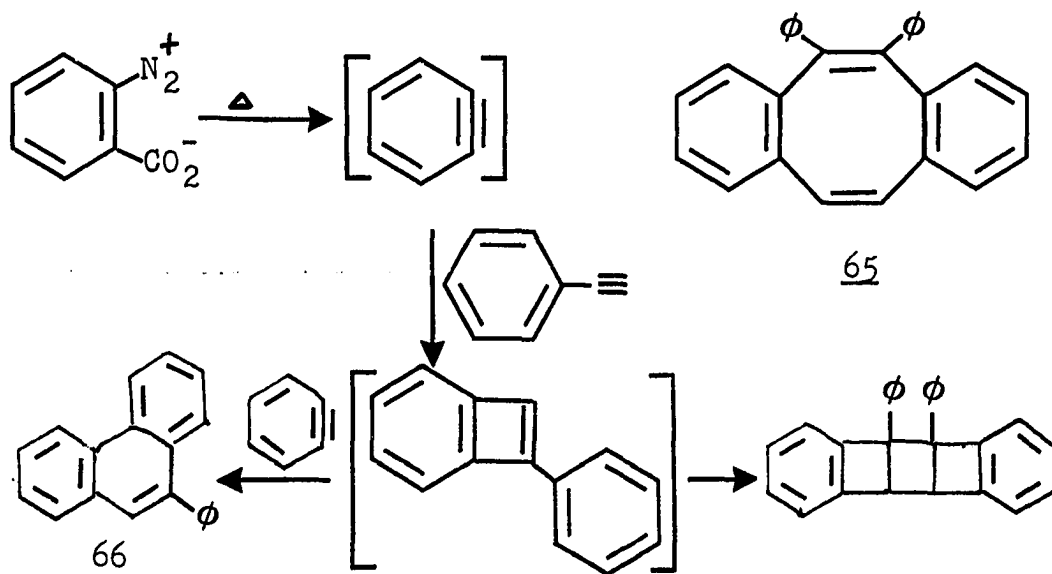


high dilution conditions are not required since there is no zinc halide produced which promotes the polymerization of benzocyclobutadiene. The dehydrohalogenation of both trans and cis-1,2-dihalobenzocyclobutene by potassium tert-butoxide gives the same products, suggesting a common intermediate, halobenzocyclobutadiene.



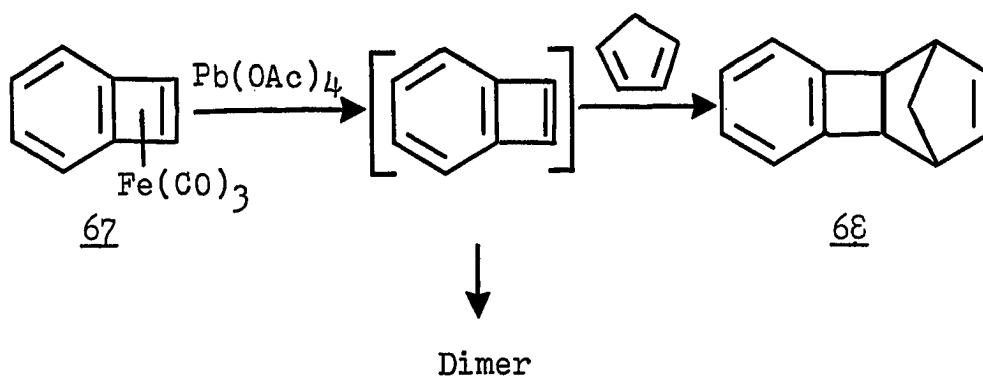
Benzocyclobutadiene can also be generated by the reaction of benzyne and substituted acetylenes in low yield.¹⁰⁶ Sisido found that benzyne, generated by the thermolysis of benzenediazonium-2-carboxylate, reacts with phenylacetylene to give 5,6-diphenyldibenzo a,e cyclo-octatetraene (65) in 29% yield and phenanthrene (66) in

8% yield.¹⁰⁶ This novel method is probably applicable in

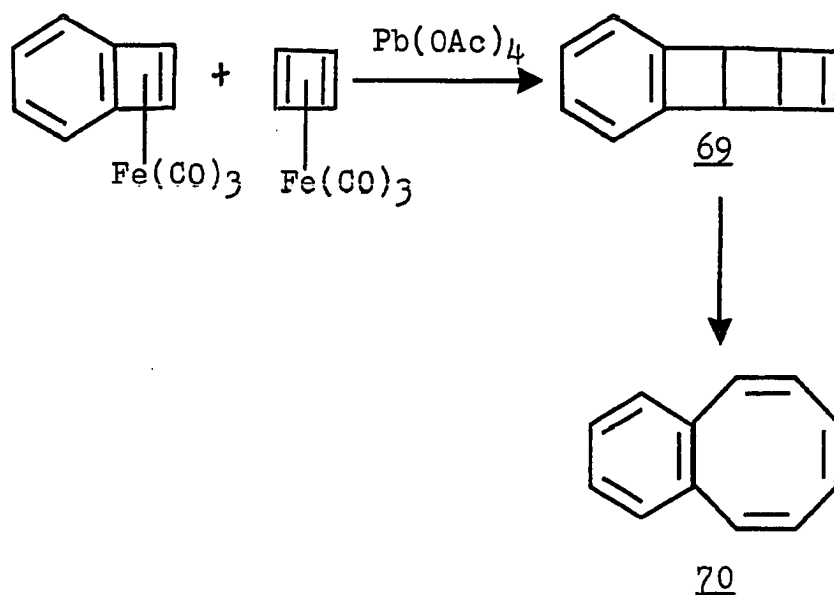


only a few special cases, but is nevertheless of great interest from a theoretical point view. The N-bromo-succinimide bromination of benzocyclobutene and of its derivative is always accompanied by polymer formation. This may be the result of generation of benzocyclobutadienes.

Merk and Pettit¹⁰⁷ have indicated that oxidative degradation of the benzocyclobutadieneiron tricarbonyl complex (67) in the presence of cyclopentadiene, using lead tetraacetate in pyridine, produces the Diels-Alder adduct 68. In the absence of cyclopentadiene, the oxidation gave dimer in good yield. The rate of oxidation of the complex 67 is fast and appears to be comparable to that of the oxidation of cyclobutadieneiron tricarbonyl with $\text{Pb}(\text{OAc})_4$. They also found that the addition of a mixture

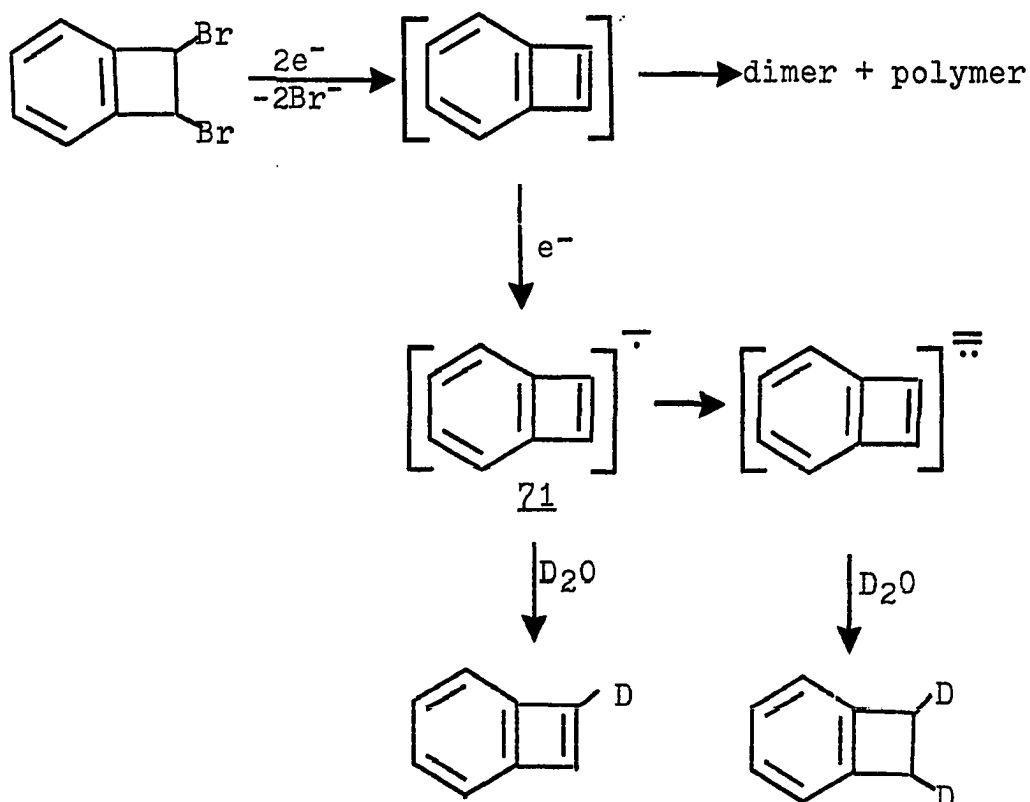


of cyclobutadieneiron tricarbonyl and complex 67 to $\text{Pb}(\text{OAc})_4$ afforded the adduct 69 in 75% yield. Compound 69 undergoes thermal rearrangement to benzocyclooctatetraene (70) in almost quantitative yield.



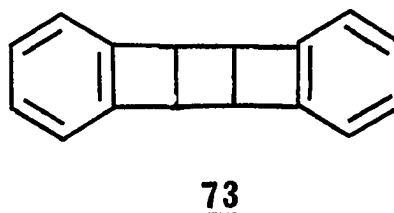
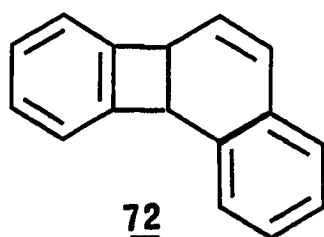
Rieke and Hudnall¹⁰⁸ has attempted to trap the benzocyclobutadiene as its radical anion. The method

involves the addition of trans-1,2-dibromobenzocyclobutene to an excess of solvated electrons in a mixture of glyme and diglyme at -60° . The two bromide atoms are first reduced off. Further reduction gave a paramagnetic species, which exhibited a 27 line spectrum in the esr and which was interpreted to be benzocyclobutadiene radical anion (71). In their later paper,¹⁰⁹ they stated that considerable amount of benzocyclobutene was formed during the reduction. By quenching with D_2O , they conclude that both mono and dianion are present in the solution. However, they have never explained the esr spectral temperature

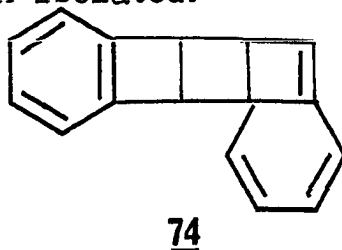


dependence of the radical anion of benzocyclobutadiene which varied from 65 lines to 27 lines then to 45 lines upon warming.

Benzocyclobutadiene and its derivatives can form two kinds of dimer, the so-called "angular" dimer (72) and "linear" dimer (73). The angular dimers have been rationalized as the products formed through a Diels-Alder

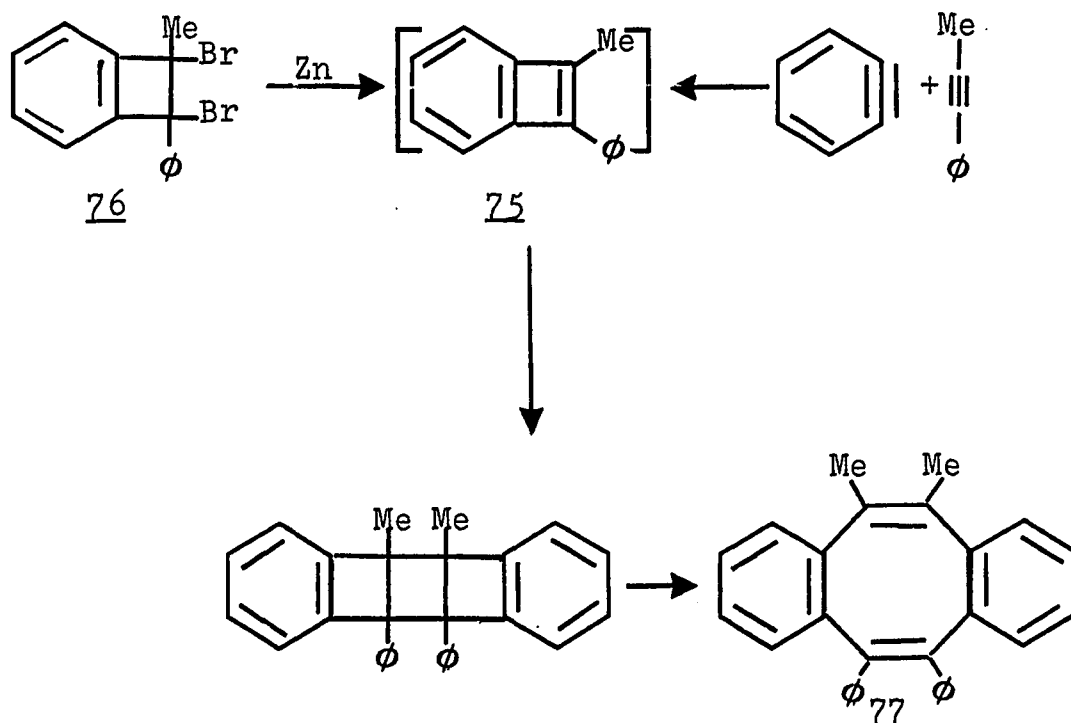


reaction in which one molecule of benzocyclobutadiene, acting as a diene, adds to another molecule of the same species, acting as a dienophile. However, the initial adduct (74) has never been isolated.

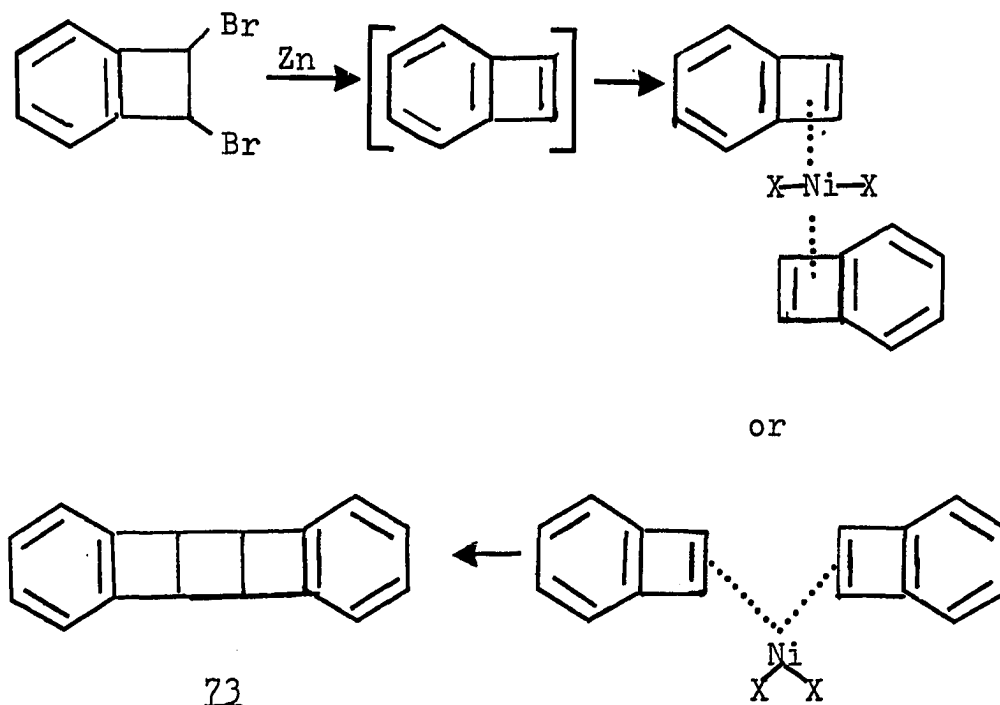


More substituted benzocyclobutadiene frequently do not give the usual angular dimer but rather a linear dimer. For example, 1-methyl-2-phenylbenzocyclobutadiene (75), generated by either the reaction of benzyne with methylphenylacetylene¹⁰⁶ or by the reaction of 1,2-dibromo-1-methyl-2-phenylbenzocyclobutene (76) with zinc dust,¹⁰⁵

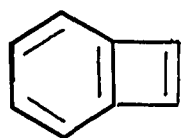
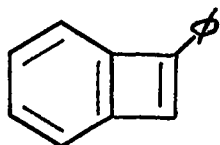
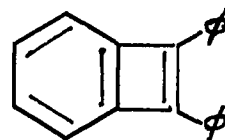
forms the linear dimer, dibenzocyclooctatetraene (77).



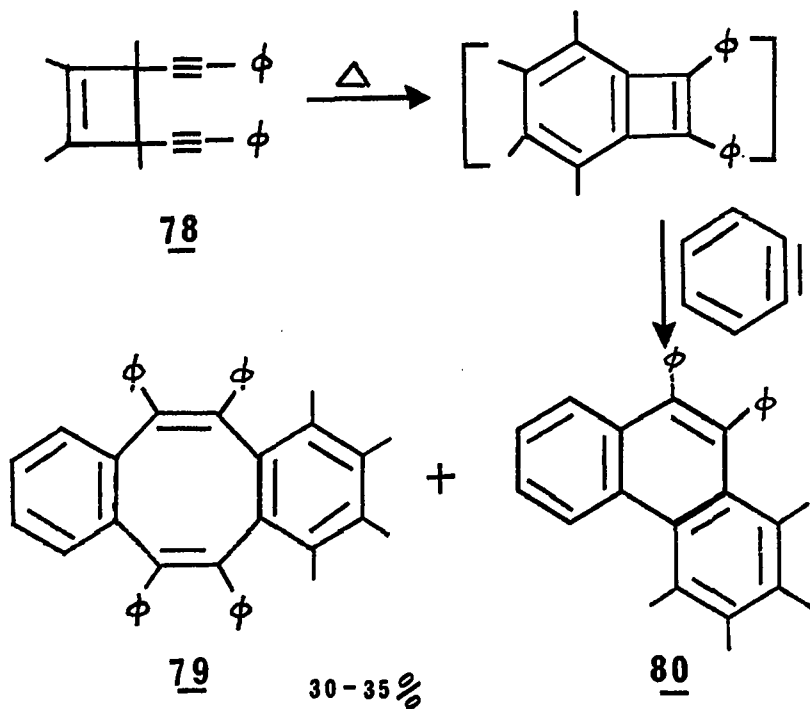
When benzocyclobutadiene is generated from 1,2-dibromobenzocyclobutene by debromination in the presence of nickel tetracarbonyl, the usual angular dimer is not formed. Instead, a linear dimer, 3,4,7,8-dibenzotricyclo[4,2,0,0^{2,5}]octadiene (73) is obtained.^{110,111,112} It is interesting to note that the two types of dimers have never been detected in the same reaction. Besides self-trapping, benzocyclobutadiene has been trapped by cyclopentadienes,¹⁰³ furans,¹¹³ fuvalene,¹¹⁴ anthracene^{115,116} and N-phenylmaleimide.¹⁰³



Molecular orbital calculations^{117,118} predict that benzocyclobutadiene should have a substantial delocalization energy (2.38β , approx. 48 kcal/mole). Phenyl substitution at the 1- and 2- positions should have a substantial stabilizing effect on the system. The calculated values for the delocalization energies of 1-phenylbenzocyclobutadiene and of 1,2-diphenylbenzocyclobutadiene are 4.84β and 7.32β , respectively, which indicates that the diphenylbenzocyclobutadiene may be isolated. However, Muller *et al.*¹¹⁹ were unable to detect diphenylbenzocyclobutadiene in

DE = 2.38 β 4.84 β 7.32 β

the thermolysis of diacetylene 78. In that study, diphenylbenzocyclobutadiene dimer (79) and an adduct of



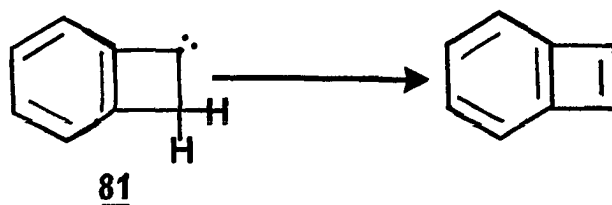
diphenylbenzocyclobutadiene and benzyne (80) were isolated.

Despite the favorable character predicted for benzocyclobutadiene, previous experience has shown that it is

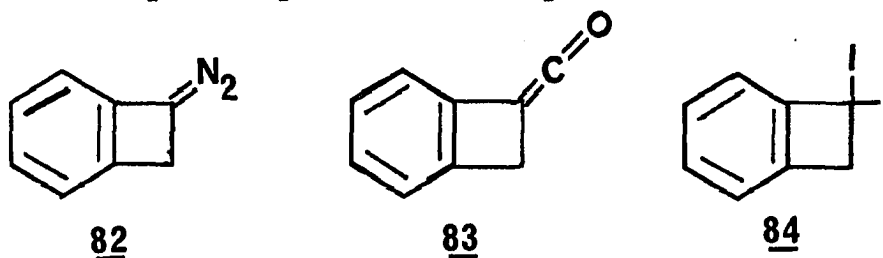
extremely reactive. A variety of methods for generating benzocyclobutadiene as a reactive intermediate are known, but direct observation of this species has not been possible. This study is concerned with the synthesis and characterization of this intermediate under conditions which allow direct spectroscopic observation of it and which may therefore provide more information on the nature of the bonding and geometry of this fascinating species.

RESULTS AND DISCUSSION

Due to its high reactivity, benzocyclobutadiene was expected to be observable by direct spectroscopic techniques only if it were trapped in a rigid, inert medium. This problem, therefore, seemed particularly suited for the low temperature matrix isolation technique. In this study, several approaches to the synthesis of benzocyclobutadiene were explored. Carbene 81 may rearrange to the desired benzocyclobutadiene by undergoing carbon-hydrogen insertion. Possible precursors to carbene 81 are diazocompound 82,

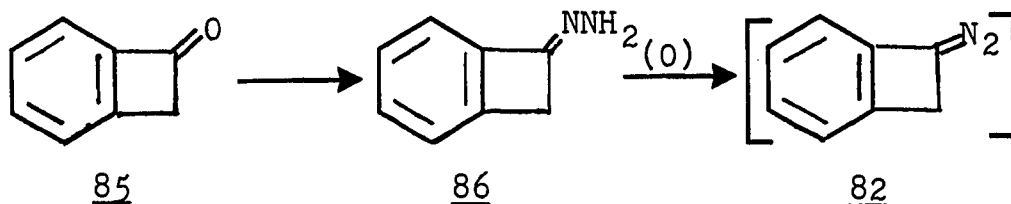


ketene 83 and 1,1-diodobenzocyclobutene 84. The synthesis of these species posed serious problems.



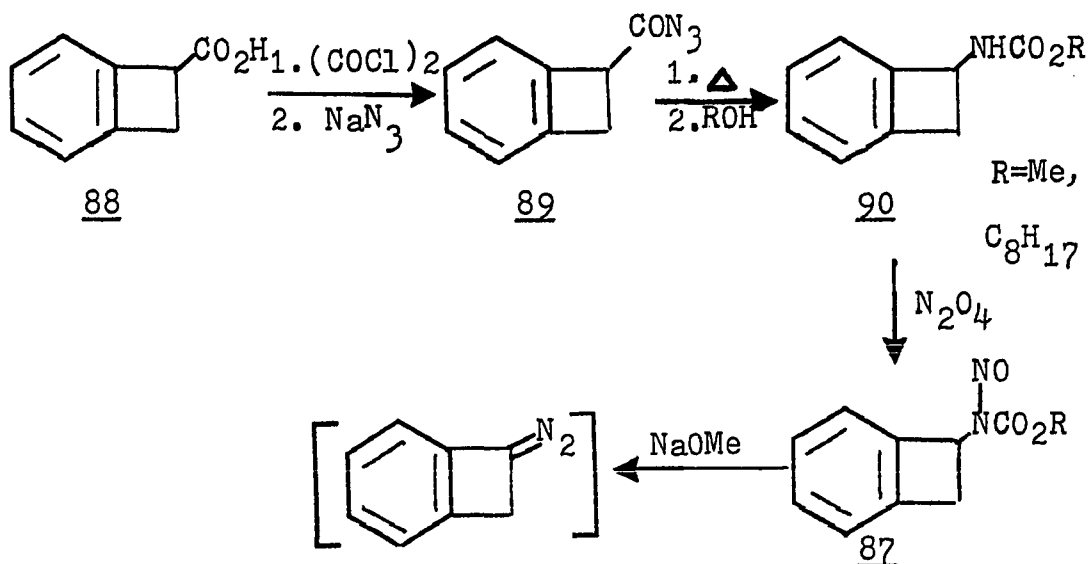
Our approach of benzocyclobutadiene started with attempts to prepare diazobenzocyclobutene, possibly the most promising of the precursors. Dr. N. Rosenquist converted the benzocyclobutenone 85 to corresponding

hydrazone 86, which in turn was oxidized using lead tetraacetate¹²⁰ to give no isolable diazo product. As soon as the reaction solution warmed up to -30° , the red



color disappeared. The diazobenzocyclobutene 82 appears to be too reactive to isolate.

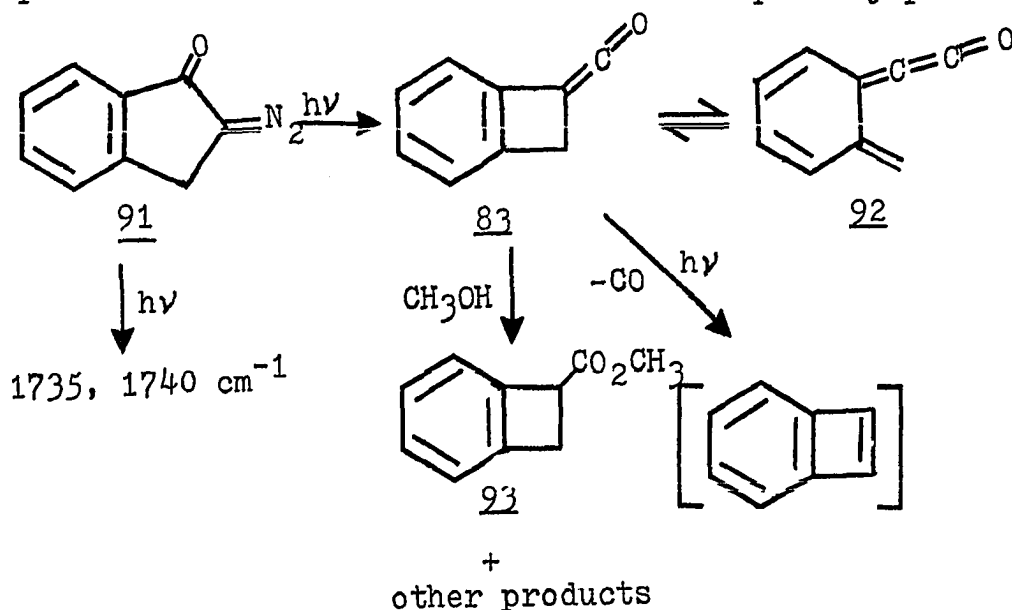
Our second approach to diazocyclobutene was to prepare nitrosocarbamate 87 and to react with a base. Benzocyclobutene-1-carboxylic acid 88 was converted to corresponding acyl azide 89 by treating it first with oxalyl chloride then with azodium azide. The acyl azide 89 undergoes a



Curtius rearrangement to give the isocyanate which was then trapped with either methanol or octanol to give the corresponding carbamates 90. Nitrosation of the carbamates 90 gave the desired nitrosocarbamates 87. Diazocyclobutene was not trapped on the cold window, however, when 87 was decomposed with dry sodium methoxide in the high vacuum system near the cold window.

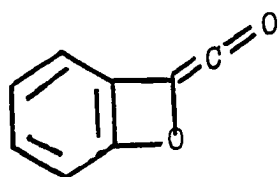
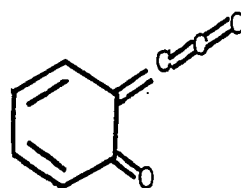
2-Diazo-1-indanone 91 is a precursor of ketene 83, which may in turn decarbonylate photochemically to benzocyclobutadiene.

Irradiation of 91 at low temperature gives ketene 93 as a primary product as expected on the basis of room temperature irradiations.^{121,122} A second primary product



has infrared absorption bands at $1735, 1740 \text{ cm}^{-1}$. This product has not been identified, but it could be indenone ($\nu_{\text{max}}^{300^\circ \text{K}} 1737, 1713 \text{ cm}^{-1}$).¹²³ Irradiation of 83 gives 92

as the major secondary product. A photostationary state is established between 83 and 92. The ketene 83 has been trapped by warming in an argon matrix containing methanol. The product is identified as the known ester (93) by infrared and mass spectrometry (ν_{CO} 1730 cm^{-1} ; m/e 162). The spectra of 83 (2132 cm^{-1} ; $\lambda_{\text{max}}^{2\text{MeTHF}}$ 251, 289, 295 nm; Figure 12) and 92 (2040 cm^{-1} ; $\lambda_{\text{max}}^{2\text{MeTHF}}$ 520 nm; Figure 12) are quite similar to those of 94 and 95 (Part I), respectively.

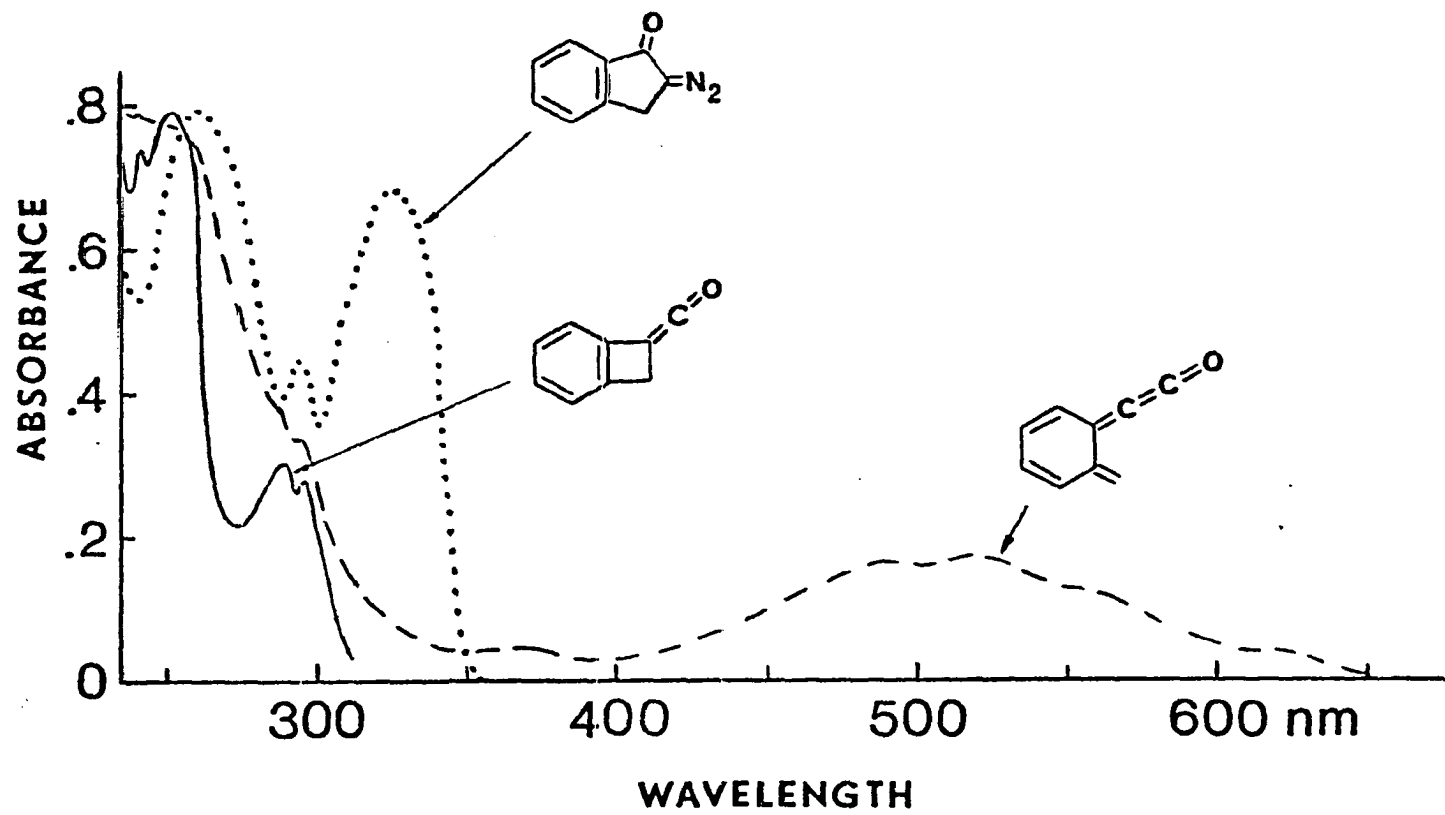
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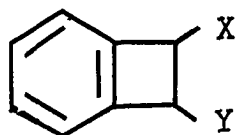
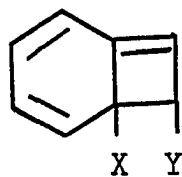
Continued irradiation with shorter wavelength light ($>2000 \text{ \AA}$) decarbonylates the ketene 83 very slowly to give CO and weak bands at 1387, 1340, 1285, 1244, 1188, 1174, 1147, 1078, 1040, 1029, 903, 827, 768, 743, 737 (s), 715, 706, 532 and 524 cm^{-1} . No triplet carbene intermediate was observed when this process was followed by esr spectroscopy. No further characterization of the decarbonylation product was possible.

Alternate precursors to benzocyclobutadiene are molecules of the general structures 96 and 97.

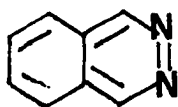
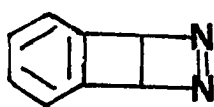
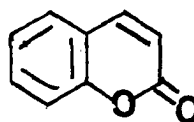
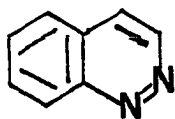
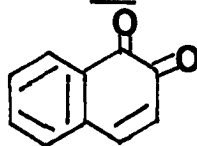
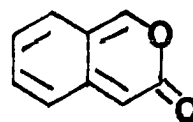
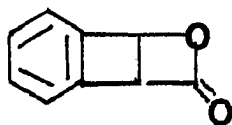
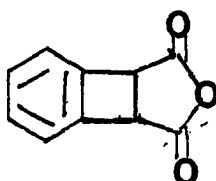
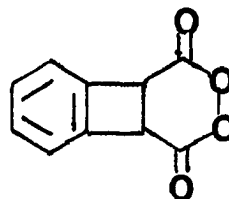
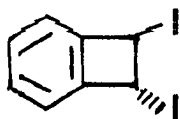
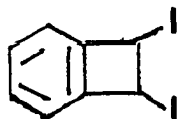
Figure 12 Irradiation of 2-diazo-1-indanone at 77° K,
uv spectrum

Dotted line 91 in 2-MeTHF; dashed line 92
(with some 83) generated by photodecomposition
of 83 with ultraviolet light (254 nm); solid
line 83, after bleaching of 92 away with
visible light. All spectra and photochemistry
at 77° K.



9697

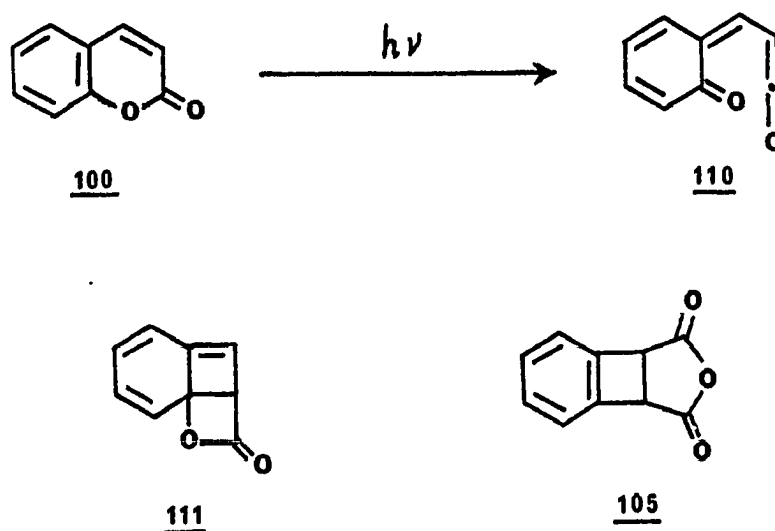
The following molecules are either example of such a structure or are potential photochemical precursors to such structures:

9899100101102103104105106107108109

Among all of these 98, 100, 101, 102, 107, 108 and 109 are known compounds.

Photolysis of 98, 101 and 102 matrix isolated in argon at 8° K showed no reaction. No reaction was observed on thermolysis of either 98 or 101. The results are not surprising since 98 and 101 have very strong aromatic character.

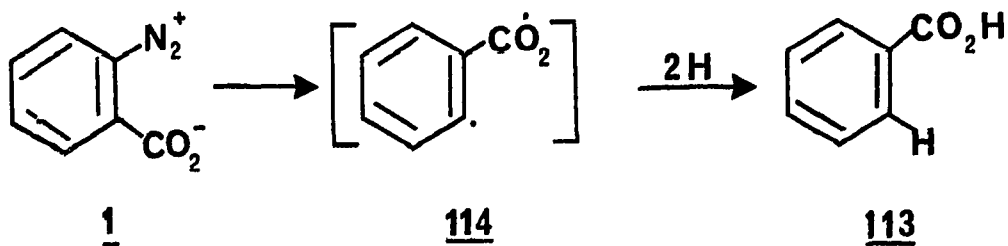
Irradiation of coumarin (100) matrix isolated in argon at 8° K gave a small amount of ketene (2132, 2120, 1710, 1250 and 1030 cm^{-1}), presumably 110. However, when the reaction was carried out in a glass matrix at 77° K, no quinone methide moiety was detectable by ultraviolet spectroscopy. There is no evidence for the formation of β -lactone 111.



Pyrolysis of 3,4:benzotricyclo [4,2,1,0^{2,5}]nona-3,7-diene (109) at 800° gives species with infrared bands at 3070, 3035, 2940, 2917, 2862, 1645, 1632, 1610, 1520, 1502, 1464, 1357, 1267, 1184, 1145, 997, 922, 855, 796, 780, 770, 758, 743 and 696 cm⁻¹. This species may be 112. Benzyne, cyclopentadiene, norbornadiene and 3,4:benzo-5,6-dihydro-biphenylene (dimer of benzocyclobutadiene) were not observed.

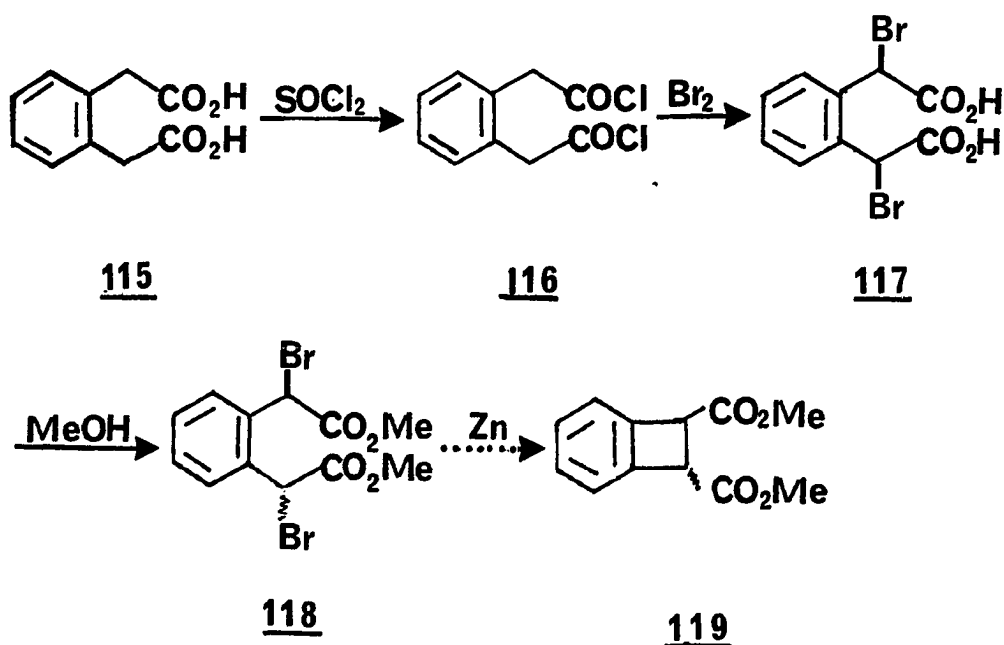
112

In a different approach, an attempt to synthesize benzocyclobutene-1,2-dicarboxylic acid anhydride (105) was made by decomposition of benzene-diazonium-2-dicarboxylate 1 in dioxane containing excess maleic anhydride. Benzoic acid 113 was isolated in 50% yield. None of the desired anhydride 105 was isolated. It is surprising that the intermediate 114 abstracts two hydrogens to form benzoic acid



acid before further decomposition or addition to maleic anhydride.

One also could prepare the anhydride 105 from benzocyclobutene-1,2-dicarboxylic acid. Thus, *o*-phenylene-diacetic acid (115) was converted to the corresponding diacylchloride 116 by thionyl chloride. The diacyl chloride then brominated to the α, α' -dibromodiacid 117 which subsequently was converted to the dibromodimethyl ester 118. The total yield based on starting diacid is 79%.



Attempts to debrominate 118 with zinc dust under various temperature and solvents conditions were unsuccessful.

Using *cis*-1,2-diiodobenzocyclobutene, 108, as precursor, a clean sample of benzocyclobutadiene was successfully isolated in an argon matrix at 8° K.¹²⁴ Infrared and ultraviolet spectra were obtained. For this work, a new method was developed for the generation and

matrix isolation of highly reactive species, the dehalogenation of a vicinal dihalo compound in the high vacuum system near the cold window.

The apparatus is shown in Figure 13. cis-1,2-Diiodobenzocyclobutene is heated to 65° at 10⁻⁶ mm by the first heater to provide a sufficient rate of sublimation. The diiodide vapor is passed over zinc powder heated to 230° by the second heater. The vapor is then passed through a zone cooled by acetone evaporation. Small quantities of two products, benzocyclobutadiene dimer and trans-diiodide, deposit in the cooled region. The matrix deposited on the cesium iodide plate is free of both dimer and trans-diiodide. After deposition, the vacuum shroud is rotated 90° for infrared spectroscopic observation. The same procedure is used for ultraviolet spectroscopic observation except that a sapphire plate is used. The infrared spectrum of benzocyclobutadiene is shown in Figure 14 and the ultraviolet spectrum in Figure 15. The species in the matrix is identified as benzocyclobutadiene by the thermal dimerization above 75° K to the known benzocyclobutadiene dimer. The disappearance of the infrared and ultraviolet absorption bands due to benzocyclobutadiene and the concurrent appearance of the absorption bands due to the dimer establish the identity of the matrix isolated species as benzocyclobutadiene. In the infrared experiment, the

Figure 13 Apparatus for thermal generation of
benzocyclobutadiene

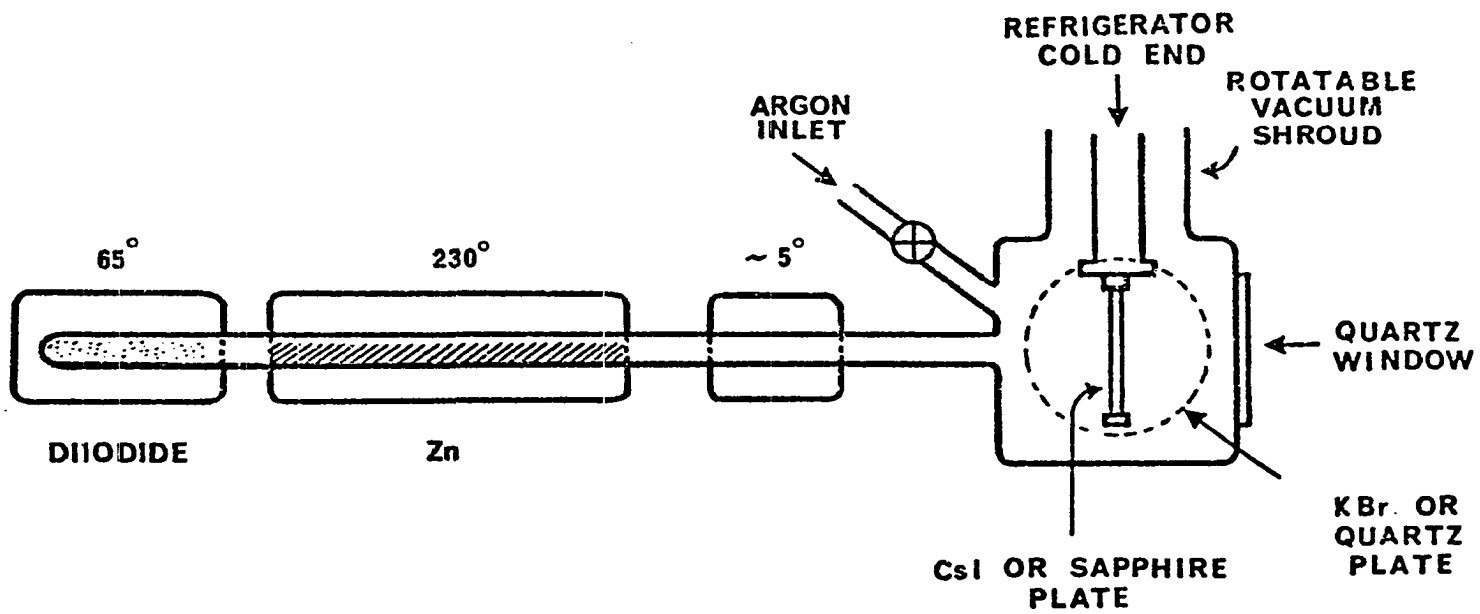


Figure 14 Infrared spectrum of benzocyclobutadiene

Bands marked x were in the spectrum of the cesium iodide plate before deposition.

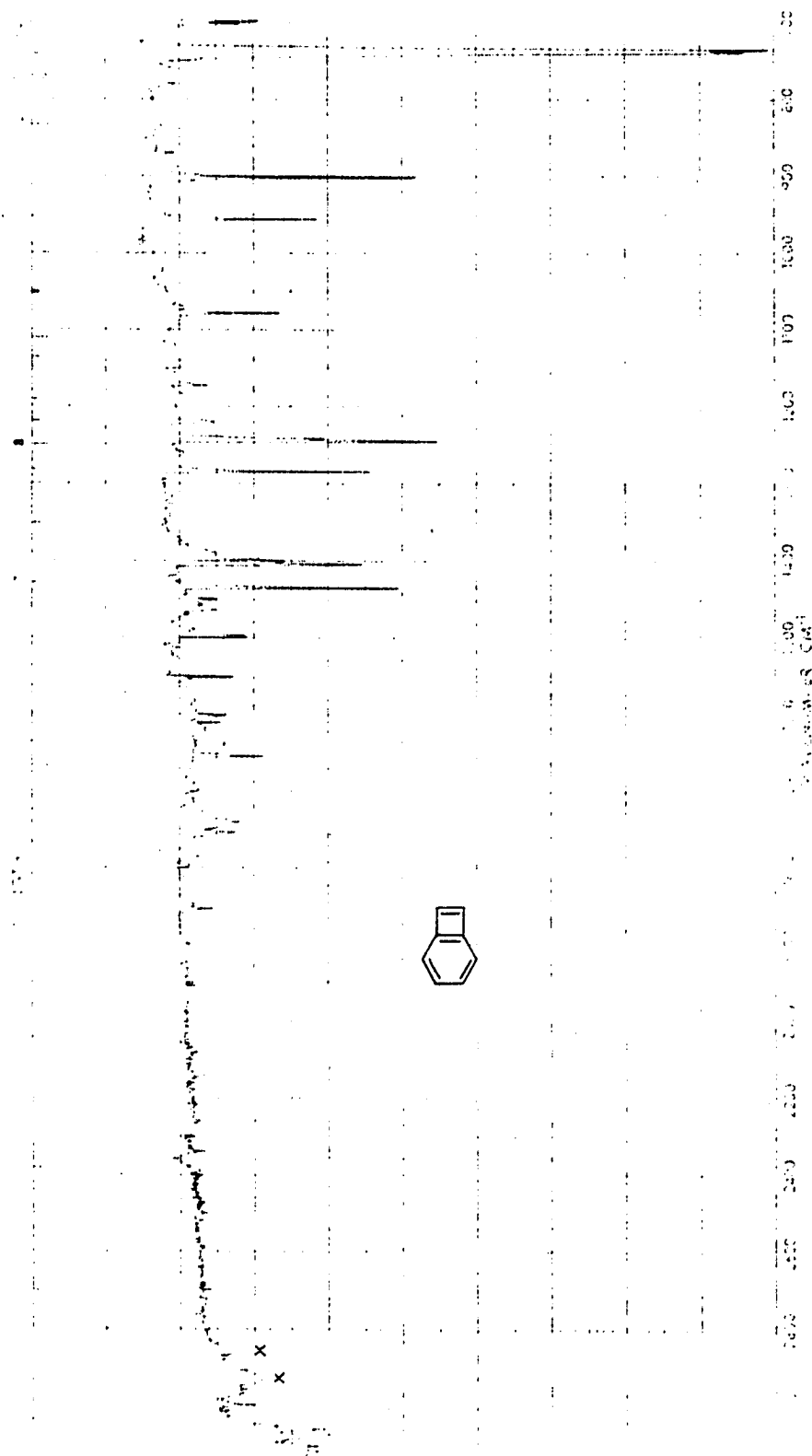
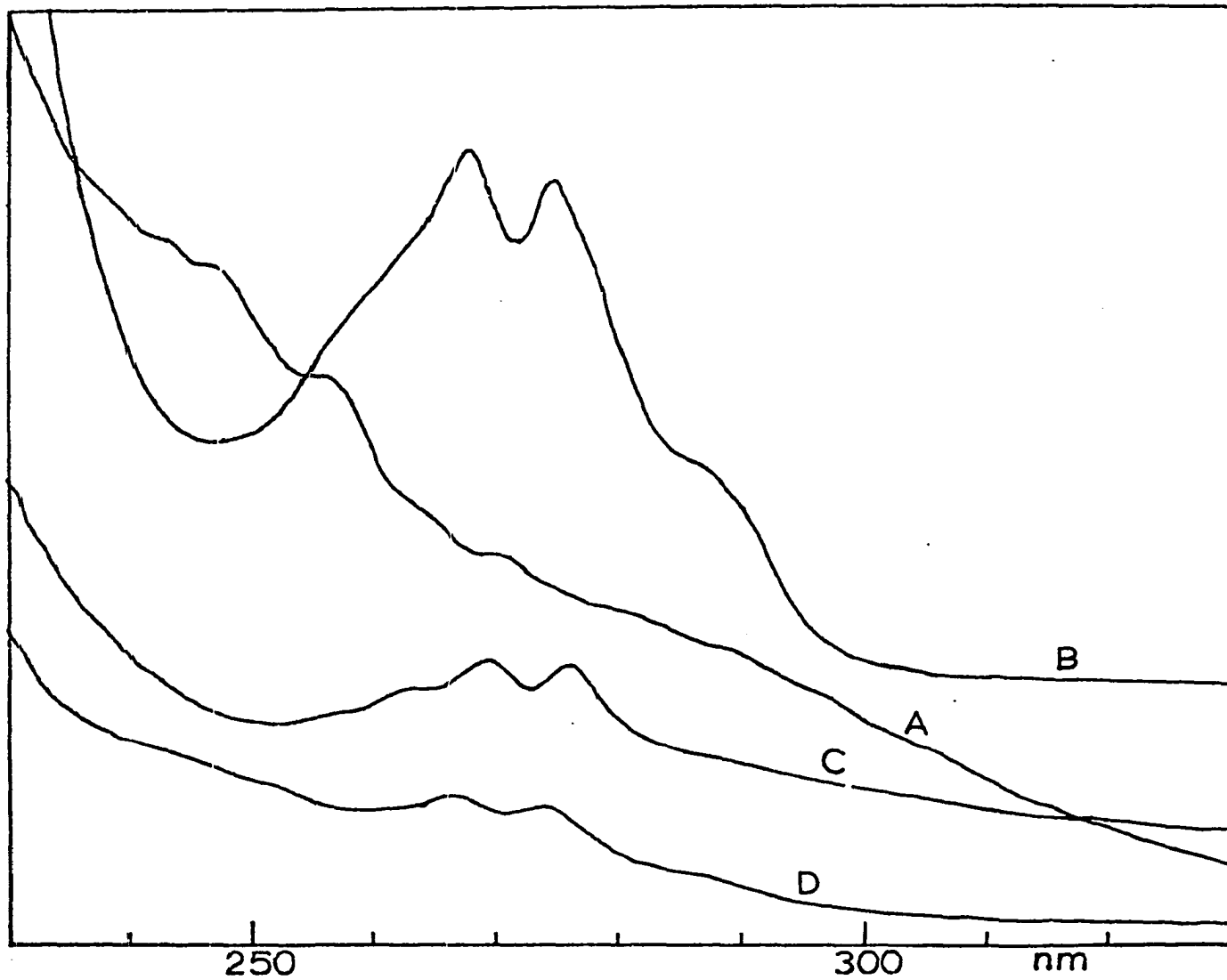
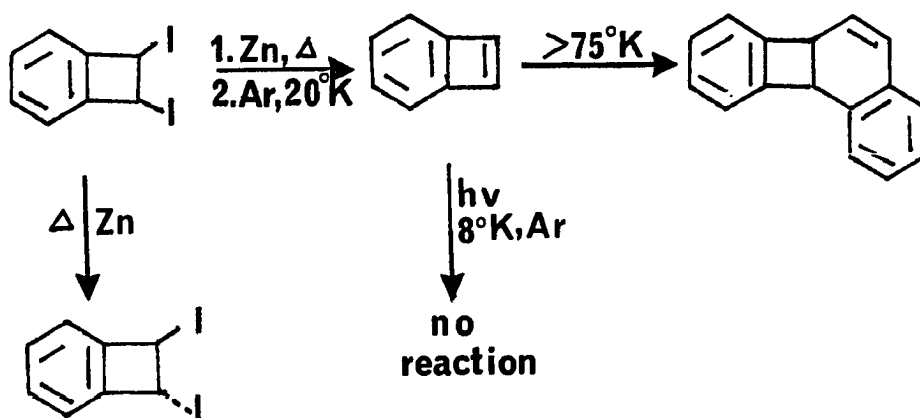


Figure 15 Ultraviolet spectrum of benzocyclobutadiene

(A) Ultraviolet spectrum of benzocyclobutadiene (62) matrix isolated in argon at 8° K. (B) Ultraviolet spectrum of authentic benzocyclobutadiene dimer in 95% ethanol solution. (C) Ultraviolet spectrum of sample A after warming above 75° K. (D) Ultraviolet spectrum of the product recovered from the cesium iodide window after warming the sample shown in Figure 14 to room temperature. Vertical axis is optical density. The relative position; of A, B, C and D are arbitrary and do not show relative optical densities.



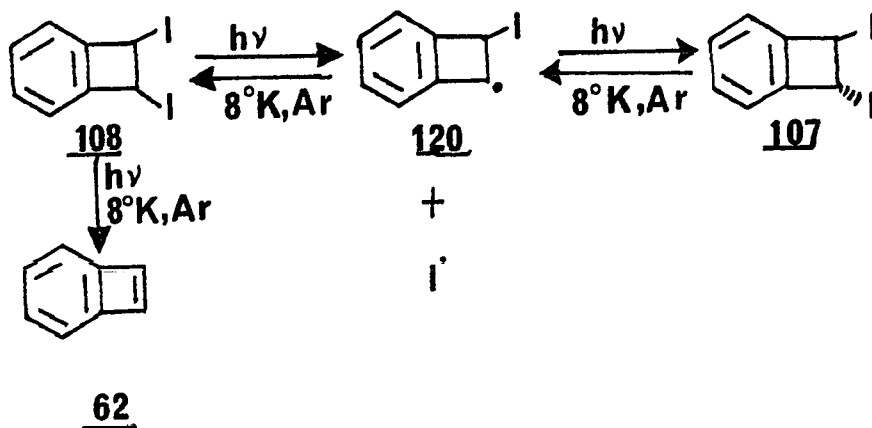
dimer was washed from the window and further characterized by comparison of mass spectra, ultraviolet spectra and thin layer chromatographic behavior in five solvent systems with authentic benzocyclobutadiene dimer. Attempts to degrade benzocyclobutadiene to benzyne and acetylene by ultraviolet irradiation were unsuccessful. Benzocyclobutadiene is quite stable to irradiation in an argon matrix. The comparison of this result with the photolysis of ketene 83 is extremely interesting. The common bands at 705, 737 (S), 901, 1078, 1244 and 1285 cm^{-1} suggest that benzocyclobutadiene is a product of photolysis of ketene 83.



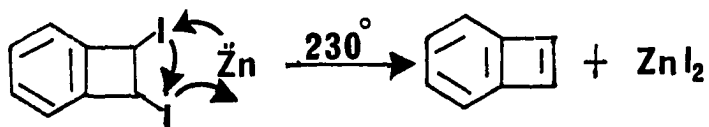
The most intense band (737 cm^{-1}) in the infrared spectrum of benzocyclobutadiene is the deformation mode due to the four carbon-hydrogen bonds in a 1,2-disubstituted

benzene. The band at 700 cm^{-1} is probably also a deformation mode of the olefinic carbon-hydrogen bonds (cf. 650 and 570 cm^{-1} for the in-plane and out-of-plane modes for cyclobutadiene^{11, 12}). The ultraviolet spectrum of benzocyclobutadiene ($\lambda_{\text{max}}^{\text{Ar}}$ 243, 246.5, 256, 264, 270, 281.5 and 289 nm) shows considerable structure over a broad range. The rapidly rising baseline in the ultraviolet spectrum is due to light scattering by the argon. On warming, the benzocyclobutadiene dimer absorption appears (Figure 15). In this process, the argon is pumped off, and light scattering is less serious.

Irradiation of the cis-diiodide (108) matrix isolated in argon at 8°K gives two primary products, trans-diiodide (major) and benzocyclobutadiene (minor). Similar irradiation of the trans-diiodide (107) gives only cis-diiodide as a photoproduct. When the irradiations are



monitored by esr a free radical (presumably the 2-iodo-benzocyclobutyl radical, 120) signal.



It is instructive to note that the zinc-induced elimination is much more facile with the cis- than with the trans-diiodide. This observation suggests the possibility of a cyclic elimination.

Considering its high reactivity at 75° K, it is likely that benzocyclobutadiene has considerable antiaromatic character. It would thus be of interest in further work in this area to obtain the nuclear magnetic resonance spectrum of benzocyclobutadiene in order to observe the magnitude of the paramagnetic effect.

EXPERIMENTAL

Preparation of β -naphthoquinone

β -Naphthoquinone is prepared following the procedure of Fieser.¹²⁵ To 3.9 g. of Orange II in 50 ml of water, was added 4.5 g. of sodium hydrosulfite dihydrate. The resulting mixture was boiled for few minutes and add 10 ml of concentrated hydrochloric acid and 50 mg of stannous chloride to give aminonaphthol hydrochloride. After treated with a solution contained 5.5 g. of ferric chloride in 2 ml of concentrated hydrochloric acid and 10 ml of water, β -naphthoquinone was isolated in 75% yield.

Photolysis of β -naphthoquinone matrix isolated in argon at 8° K

β -Naphthoquinone and argon were codeposited on a cesium iodide window at 20° K by direct deposition. Irradiation (>2000 Å, 1000 Watt mercury medium pressure lamp) caused no destruction of starting material.

Preparation of benzenediazonium-2-carboxylate

Benzenediazonium-2-carboxylate was prepared following the procedure of Stiles et al.¹²⁶ A solution of 5.48 g. (0.040 mole) of anthranilic acid in 60 ml of absolute alcohol was cooled to 0° and treated

with 4 ml of concentrated hydrochloric acid. Cold isoamyl nitrite (10 ml, 0.076 mole) was added dropwise to the stirred solution at 0° during approximate 30 minutes. Addition of 60 ml of ether caused precipitation of diazonium salt, which was collected and washed with more ether. Then small amount of cold water (ca. 10 ml) was added to dissolve the diazonium salt. The aqueous solution was then stirred at 0° with 6 g. of powdered silver oxide for 2 hours. After filtration, the salt was dissolved in a mixture of 200 ml of absolute ethanol and 100 ml of ether, previously cooled to 0°. Additional ether was added until the diazonium carboxylate began to crystallize. The yield of nearly colorless needles was 50% (3.0 g.).

Attempt of preparation of benzocyclobutene-1,2-dicarboxylic acid anhydride

To a solution of 9.2 g. of maleic anhydride in 100 ml of dioxane (freshly distilled from sodium) was added 2.74 g. of benzenediazonium-2-carboxylate. The resultant slurry was magnetically stirred at 50° under nitrogen atmosphere for overnight. The solution was dark brown at end of reaction. The dioxane was removed under reduced pressure. Maleic anhydride was sublimed at 50° C (1 mm). When the temperature was increased to 75°, a fraction of white crystal was

collected (1.5 g.). The nmr, ir and m.p. (122°) were identical to those of benzoic acid.¹²⁷ None of the desired anhydride was obtained.

Photolysis of phthalazine matrix isolated in argon at 8° K

An argon matrix of phthalazine was made by using direct deposition technique. The phthalazine was heated to 40° to provide enough vapor and argon was codeposited at a rate 0.5 mm per minute from a 3 liter flask. Irradiation using a 1000 Watt medium pressure Hg arc caused no destruction of phthalazine.

Photolysis of cinnoline matrix isolated in argon at 8° K

An argon matrix of cinnoline was deposited by the same method used for phthalazine. Prolonged irradiation ($>2000 \text{ \AA}$) caused no change in the sample.

Preparation of 3,4:benzotricyclo[4,2,1,0^{2,5}]nona-3,7-diene

Benzocyclobutadiene was generated in a reaction mixture by adding a solution of 1.78 g. (0.005 mole) of trans-1,2-diodobenzocyclobutene in 30 ml of ethanol to a stirred suspension of 5 g. of zinc dust in 50 ml of ethanol containing 5 ml of cyclopentadiene. The zinc dust was activated by 10% aqueous ammonium chloride and was

subsequently washed six times each with water and ethanol. The temperature was held at 30° with the reaction mixture under nitrogen. When half of the diiodide solution had been added, an additional 2.5 ml of cyclopentadiene was poured into the flask. After the addition was finished (2 hrs.), the reaction mixture was filtered, the filtrate was concentrated. Then it was poured into 15 ml of water, extracted by petroleum ether and washed with water. After drying over sodium sulfate, distillation gave 0.56 g. 3,4:benzotricyclo[4,2,1,0^{2,5}]nona-3,7-diene. (65%). b.p. 80-81.5° (2 mm). reported b.p. 68-70° (1-2 mm).¹⁰³

Pyrolysis of 3,4:benzotricyclo[4,2,1,0^{2,5}]nona-3,7-diene

Pyrolysis apparatus is similar to that used for pyrolysis of silabutanes. (Part 3). 3,4:Benzo-tricyclo-[4,2,1,0^{2,5}]nona-3,7-diene was maintained at -15° (CCl₄/liquid nitrogen) to provide enough vapor to pass through a quartz tube which was heated to 800°. The pyrolysis product and argon were codeposited on a cesium iodide at 20° K. The products isolated in argon matrix has infrared bands at 3070, 3035, 2940, 2917, 2862, 1645, 1632, 1610, 1520, 1502, 1464, 1351, 1267, 1184, 1145, 997, 922, 855, 796, 780, 770, 758, 743 and 696 cm⁻¹. Benzyne, cyclopentadiene and norbonadiene were not observed.

Cis and trans-diiodobenzocyclobutene

Cis and trans-diiodobenzocyclobutene were prepared followed the procedure of F. R. Jenson and W. E. Coleman¹²⁸ by Dr. N. Rosenquist. These two isomers were separated mechanically and have m.p. at 150° and 62° respectively (lit. 150.1-150.8° and 62-63° respectively).

Photolysis of cis-diiodobenzocyclobutene matrix isolated in argon at 8° K

An argon matrix of cis-diiodobenzocyclobutene was made by using direct deposition technique. The diiodide was slowly evaporated at 60° onto the cesium iodide window during deposition. Irradiation ($>2000 \text{ \AA}$) using a 1000 Watt mercury vapor lamp caused new bands at 1165, 1135, 1100, 1080, 1080, 895, 780, 753, 739, 658, 650, 565 and 545 cm^{-1} . The matrix turned brown after irradiation. With exception of the bands at 739 cm^{-1} , all other bands were identified as trans-diiodobenzocyclobutene by comparison of authentic spectrum.

Photolysis of trans-diiodobenzocyclobutene matrix isolated in argon at 8° K

An argon matrix of trans-diiodobenzocyclobutene was made similarly as that of the cis isomer except that the diiodide was evaporated at 68°. Irradiation ($>2000 \text{ \AA}$)

using same light source as in the previous experiment, caused new bands at 1350, 1160, 1113, 910, 890, 879, 785, 750, 670, 650, 565, 495 and 485 cm^{-1} . This product was identified as cis-diiodobenzocyclobutene by comparison of infrared spectra with an authentic sample.

Photolysis of cis-diiodobenzocyclobutene in 2-methyltetrahydrofuran glass at 77° K

Photolysis of cis-diiodobenzocyclobutene was carried out in a 2 mm Suprasil cell at 77° K. An 800 Watt high-pressure mercury arc was used throughout. Irradiation of the glass ($>2000 \text{ \AA}$) gave products with an absorption maximum at 414 nm and an isosbestic point at 278 nm. Warmed up to room temperature and recooled to 77° K the glass showed a new absorption maximum at 365 nm. The yellow color formed upon irradiation disappeared on warming.

Preparation of 1,2-dibromobenzocyclobutene

1,2-Dibromobenzocyclobutene was prepared from $\alpha, \alpha, \alpha', \alpha'$ -tetrabromo-o-xylene and sodium iodide following the procedure of M. P. Cava and D. R. Napier.¹⁰¹ The dibromide has m.p. 51.5-52.5° (lit. 52.4-52.8°)

Photolysis of cis-dibromobenzocyclobutene in 2-methyl-tetrahydrofuran at 77° K

Irradiation of cis-dibromobenzocyclobutene in 2-methyl-tetrahydrofuran by high-pressure Hg arc ($>2000 \text{ \AA}$) caused no reaction. Irradiation by Penlite (254 nm) gave a trace amount of product with broad absorption at 330-350 nm.

Preparation of 1,2:benzo-11,12-dihydro-biphenylene

1,2-Dibromo-benzocyclobutene (3 g.) in 500 ml of anhydrous ether was added to 100 g (0.5%) of LiHg amalgam. The reaction mixture was cooled at 0° for 10 minutes and then was stirred at room temperature for 16 hr. under nitrogen atmosphere. Evaporated ether to give a white solid. The 1,2:benzo-11,12-dihydro-biphenylene was sublimed at 100° at 0.01 mm give white solid. The product has same m.p. at 74° as reported.¹⁰⁴

Photolysis of 1,2:benzo-11,12-dihydro-biphenylene matrix isolated in argon at 8° K

1,2:Benzo-11,12-dihydro-biphenylene (heated at 80°) and argon were codeposited on a cesium iodide window at 20° K by direct deposition. Irradiation using 1000 Watt Hg arc caused no destruction of the material.

Photolysis of matrix isolated 2-diazo-1-indanone in argon at 8° K

2-Diazo-1-indanone and argon were codeposited on a cesium iodide window at 20° K by direct deposition. Irradiation was accomplished using a 1000 Watt medium pressure mercury vapor lamp with a Pyrex filter ($>3400 \text{ \AA}$). The reaction was monitored by infrared spectroscopy. New bands were formed at 2132, 2040, 1605, 1455, 1170, 1145, 995, 770, 740, 704, and 470 cm^{-1} . Further irradiation caused slight destruction of starting material and a new band at 2040 cm^{-1} . Further irradiation with shorter wavelength light ($>2740 \text{ \AA}$ or $>2000 \text{ \AA}$) caused slow destruction of all the new bands with final bands arising at 2140, 1387, 1340, 1285, 1244, 1188, 1174, 1147, 1078, 1040, 1029, 903, 827, 768, 743, 737, 715, 706, 532 and 524 cm^{-1} .

Photolysis of 2-diazo-1-indanone in 2-methyltetrahydrofuran at 77° K

Photolysis of 2-diazo-1-indanone in 2-methyltetrahydrofuran was carried out in 2 mm Suprasil at 77° K. A 800 Watt high pressure Hg arc equipped with a CS 7-37 Corning filter ($320 < \lambda < 385 \text{ nm}$) was used. Irradiation caused gradual destruction of starting material giving product with absorption maxima at 295, 289 and 251 nm. An isobestic point at 250 nm was observed. Further irradiation with Penlite

(254 nm) caused destruction of the previously mentioned product(s) with the final absorption maximum at 520 nm. The glass was purple at this point. Further irradiation with the high pressure Hg arc lamp with a CS-052 filter ($\lambda > 350$ nm) caused destruction the absorption maximum at 520 nm giving a shorter wavelength absorbing species. (see Figure 12)

Photolysis of 2-diazo-1-indanone in a glass containing methanol at 77° K

A glass sample of 2-diazo-1-indanone in 2-methyltetrahydrofuran containing 10% of absolute methanol at 77° K was irradiated using a high pressure Hg arc with a CS 7-54 Corning filter ($250 < \lambda < 400$ nm) as previously described for 25 minutes. The glass turned pink at this moment. The sample was warmed up and recooled to 77° K giving new absorption maxima at 298, 271 and 264 nm.

Photolysis of 2-diazo-1-indanone matrix isolated in argon containing methanol at 8° K

The sample of 2-diazo-1-indanone was prepared as in the previously experiment except 5 mm of methanol in 500 mm of argon was used instead of the pure argon. Irradiation for 50 minutes ($> 2740 \text{ \AA}$) resulted in complete

destruction of 2-diazo-1-indanone. The sample was warmed, collected in a trap at 77° K and sent for mass spectra. Mass spectral analysis at both 16 e.v. and 70 e.v. showed parent ion of methyl benzocyclobutene-1-carboxylate at 162 as well as high molecular weight ions.

Preparation of dimethyl- α, α' -dibromo-o-phenylenediacetate

Thionyl chloride (10.71 g., 0.09 mole) was added to 5.826 g (0.03 mole) of o-phenylenediacetic acid and was stirred for 10 hours at room temperature. The reaction flask was equipped with dry tube and hydrogen chloride was collected in sodium hydroxide trap. Additional 10 drops of thionyl chloride was added and allowed to stir for two more hours. Then 11 g. of dry bromine (dried over concentrated sulfuric acid) was added slowly over 2 hours. A sunlamp was used to accelerate the bromination. After the reaction was irradiated and stirred for 4 hours, 25 ml of absolute methanol was added into the solution slowly. A vigorous reaction was slowed down by external cooling. The solution was left at room temperature for one hour and then poured into 30 ml of distilled water. The top methanolic aqueous layer was decanted and extracted by 30 ml of ether twice. The oil bottom layer was dissolved in the extract and washed first with 30 ml of 2% of sodium bisulfite

solution and then with two portions of 3% sodium carbonate solution. When 30 ml of water and salt were added, the solution became turbid and failed to give two layers. Two grams of anhydrous potassium carbonate was added. Filtration and evaporation of solvent gave 9.1 g. of dibromo diester (78.5%). The nmr (CDCl_3 , TMS) exhibits resonances at: 7.45 δ (AABB 4H), 5.70 δ (S, 2H) and 3.70 δ (S, 2H).

Attempt of debromination of dimethyl- α,α' -dibromo-o-phenylenediacetate by zinc dust

Dibromo diester (1.90 g.) prepared from previous experiment in 30 ml of tetrahydrofuran was added into 250 ml of boiling tetrahydrofuran contained 10 g. of activated zinc powder. The reaction was stirred and refluxed for 20 hours under nitrogen atmosphere. No reaction was detected by nmr spectroscopy. A small particle of I_2 was added in order to initiate the reaction and showed no effect.

Attempt of debromination of dimethyl- α,α' -dibromo-o-phenylenediacetate by zinc-copper couple

Zinc-copper couple was prepared following the procedure in "Organic synthesis" Coll. V, P. 330. 13.1 g. of zinc powder washed by 10 ml of 3% hydrochloric acid twice, 10 ml of distilled water twice, 20 ml of 2% CaSO_4 twice, 10 ml of

acetone twice and then 10 ml of DMF for 3 times. Dibromo diester (1.9 g.) prepared from previous experiment in 5 ml of DMF was added into a mixture solution of 30 ml of DMF contained zinc-copper couple prepared above. The reaction mixture was stirred for 24 hours at room temperature and then at 150° for 25 minutes. No desired benzocyclobutene-1,2-dimethylester was detectable.

Attempt of preparation diazobenzocyclobutene from methyl benzocyclobutene-nitroso-1-carbamate and sodium methoxide

Methyl benzocyclobutenenitroso-1-carbamate was maintained at -20° to provide enough vapor under a pressure at 10⁻⁶ mm. The apparatus is similar to that of the reaction of diiodobenzocyclobutene with zinc dust. The carbamate vapor was passed through a zone packed with dry sodium methoxide. Product and argon were codeposited on a cesium iodide window at 20° K. No diazobenzocyclobutene was detected by infrared spectroscopy. Control of the temperature of the region of sodium methoxide down to -30° by circulating methanol-Dry Ice solution outside the tube showed no positive effect.

Attempt of preparation of diazobenzocyclobutene from Octyl-benzocyclobutenenitroso-1-carbamate and sodium methoxide

The apparatus was same as previous experiment. Octyl nitrosocarbamate was used instead of methyl nitrosocarbamate. No diazobenzocyclobutene could be detected on the cesium iodide window. Variation of the amount of sodium methoxide showed no positive effect.

Preparation of benzocyclobutadiene in argon matrix

The apparatus is shown in Figure 13. cis-1,2-Diiodobenzocyclobutene is heated to 65° C at 10⁻⁶ mm by the first heater to provide a sufficient rate of sublimation. The diiodide vapor is passed over zinc powder heated to 230° by the second heater. The vapor is then passed through a zone cooled by acetone evaporation. Small quantities of two products deposit in the cooled region. Ultraviolet spectrum showed one component has same absorption with that of 1,2-benzo-11,12-dihydrobiphenylene. Thin layer chromatographic analysis showed same behavior in five solvent systems with authentic 1,2-benzo-11,12-dihydrobiphenylene and trans-diiodobenzocyclobutene. The infrared spectrum of the species isolated in argon has bands at 3080, 3060, 1650, 1550, 1500, 1430, 1405, 1285, 1245, 1225, 1170, 1080, 955, 905, 735 and 700 cm⁻¹ (see Figure 14). An attempt to degrade this species by ultraviolet

irradiation was unsuccessful. Warming the matrix above 75° K caused disappearance of the species and new bands of 1,2-benzo-11,12-dihydrobiphenylene appeared. The dimer was washed from the window and further characterized by comparison with authentic sample.¹⁰⁴

Attempt to trap benzocyclobutadiene by cyclopentadiene at low temperature

Benzocyclobutadiene sample was prepared as in the previous experiment except the argon contained cyclopentadiene (argon/cyclobutadiene = 500/1). Cyclopentadiene evaporated before the temperature reached 75° K. Dimer was formed instead of 3,4:benzotricyclo[4,2,1,0²,5]nona-3,7-diene. The dimer was identified as 1,2:benzo-11,12-dihydrobiphenylene by comparison with authentic sample.¹⁰⁴

Ultraviolet spectrum of benzocyclobutadiene

Benzocyclobutadiene matrix isolated in argon was prepared by the same procedure used for infrared spectrum observation except that a sapphire plate is used. The external windows for vacuum shroud were quartz for this experiment. The ultraviolet spectrum of benzocyclobutadiene has absorption maxima at 243, 246.5, 256, 264, 270, 281.5 and 289 nm (see Figure 14). Warming the matrix above 75° K caused the disappearance of the bands of benzocyclo-

butadiene and the concurrent appearance of the absorption at λ_{\max} 262, 267.5, 275 and 287 nm. This species was identified as 1,2:benzo-11,12-dihydrobiphenylene by comparison with authentic sample.¹⁰⁴

Attempt of preparation of benzocyclobutadiene from trans-diiodobenzocyclobutene and zinc dust

The procedure used here was same as that for cis-diiodobenzocyclobutene except the trans-diiodide was heated to 68° by the first heater. The product isolated in argon matrix has infrared bands at 1350, 1160, 910, 890, 879, 785, 750, 670, 650, 565, 495 and 485 cm^{-1} . The species was identified as cis-diiodobenzocyclobutene by comparison with authentic sample.

Attempt of preparation of benzocyclobutadiene from phthalazine and cinnoline

The apparatus was similar to that used for the pyrolysis of silacyclobutanes (Part 4). Passing phthalazine and cinnoline through a quartz tube at 550° under a pressure at 10^{-6} mm showed only starting material by infrared spectral analysis.

PART IV. 9,10-DEHYDROANTHRACENE (DIBENZO-1,4-DEHYDRO-
BENZENE)

INTRODUCTION

Dehydrobenzenes have fascinated chemists since the suggestion of 1,2-dehydrobenzene (benzyne or o-benzyne) as a reactive intermediate.²¹ Benzyne is now a well-characterized molecule^{23,26,34,43} with a clearly-defined triple bond⁴³ and a singlet ground state.⁴² The isomeric 1,4-dehydrobenzene (121) has not yet been isolated and has been reported only as a transient intermediate.¹²⁹⁻¹³¹

This species has been indexed in Chemical Abstracts under the names para-benzyne, p-didehydrobenzene, bicyclo[2,2,0]hexa-1,3,5-triene, butalene and 1,4-phenylene. There are many possible structures which are pictured in Figure 16. A planar bisallenic structure is equivalent to biradical 121d,e or a bis-carbene 121g,h due to impossibility of overlap represented in structure 121c. Structure 121e is a triplet benzenoid σ biradical and 121d is the corresponding singlet. Structure 121b, 121f, 121a can be resonance forms. Only if they possess different geometries, will they be distinct species. Structure 121g represents a bis-singlet-carbene which sacrifices benzene resonance energy, while structure 121h is a quintet with four unpaired spins. The name butalene most clearly applies to structure 121a,b, while the term p-benzyne correlates mostly clearly with the structures 121c-g. The only

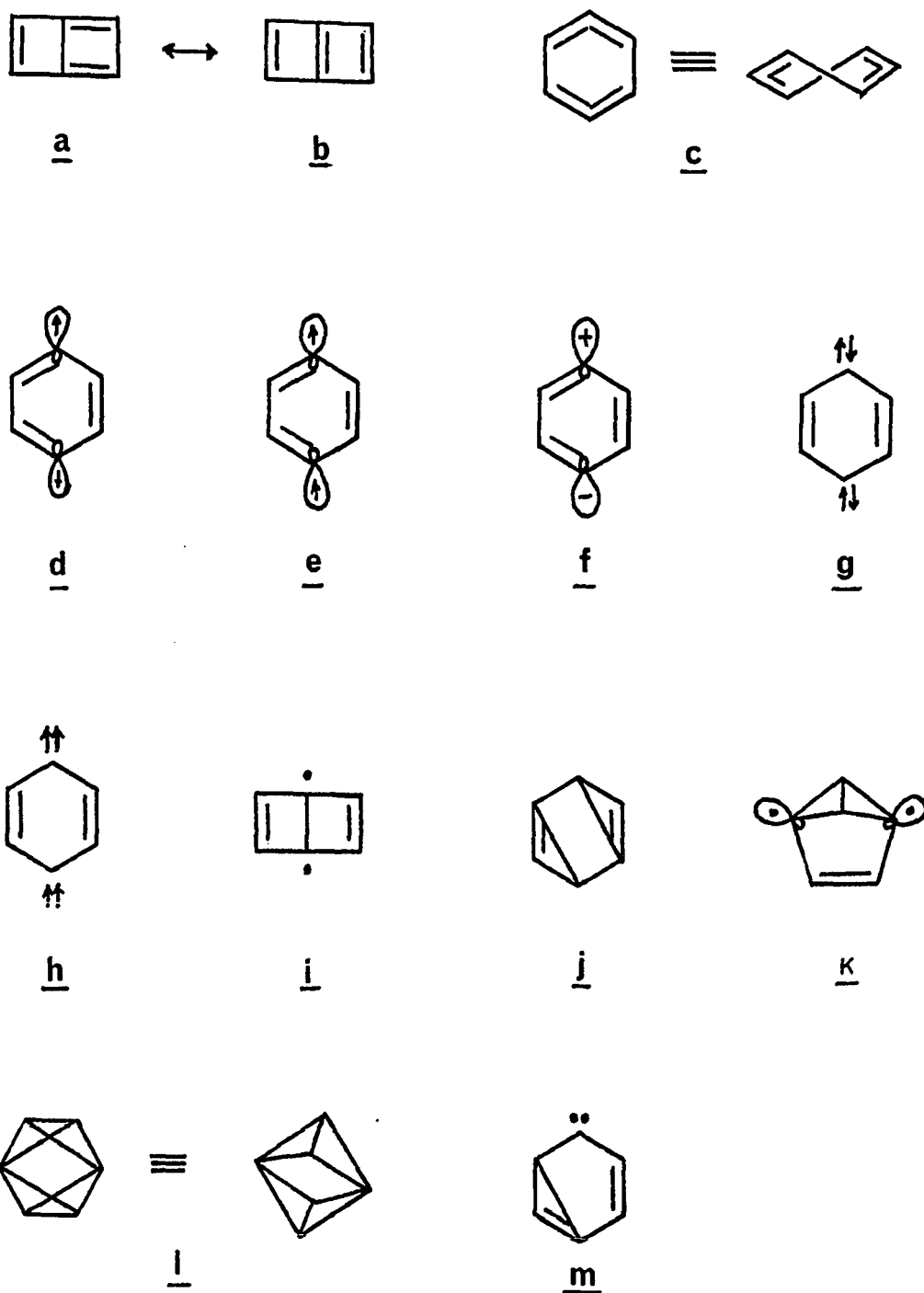


Figure 16 Possible structure of 1,4-dehydrobenzene

structural features 121i-m possess in common with 121a-h is that the dehydro centers are 1,4-disposed. In this thesis I shall use the more systematic name 1,4-dehydrobenzene to refer to all species 121.

The first reference to the 1,4-dehydrobenzene system was by Roberts, et al., who predicted the delocalization energy (1.66β), bond orders, and low free valence for bicyclo[2,2,0]hexatriene¹³² (Figure 17). The first order treatment predicts a zero order for the bond between carbons 1 and 4 thus favoring 121a over 121b. The Hückel treatment also gives a closed shell and hence a prediction of aromatic stabilization for 121a. However, Hess and Schaad¹³³ using a more realistic standard state, arrived at an HMO π electron energy (resonance energy per electron) of -0.067β , making 121a as antiaromatic as planar cyclooctatetraene (-0.060β), but still far more aromatic than cyclobutadiene (-0.268β). Dewar's semiempirical SCF-MO method¹³⁴ support Hess's Huckel numbers predicting a resonance energy of -6.5 kcal/mole for 121a and -18 kcal/mole for cyclobutadiene compared to 20 kcal/mole for benzene.

Since butalene may contain approximately 30 kcal/mole less resonance energy than benzene and 76 kcal/mole more strain¹³⁵ (see Table 3), 121a and 121d (e) may be comparable in energy despite the fact that 121d (e) contains one fewer σ -bond. The thermochemical prediction by Benson¹³⁶ allows

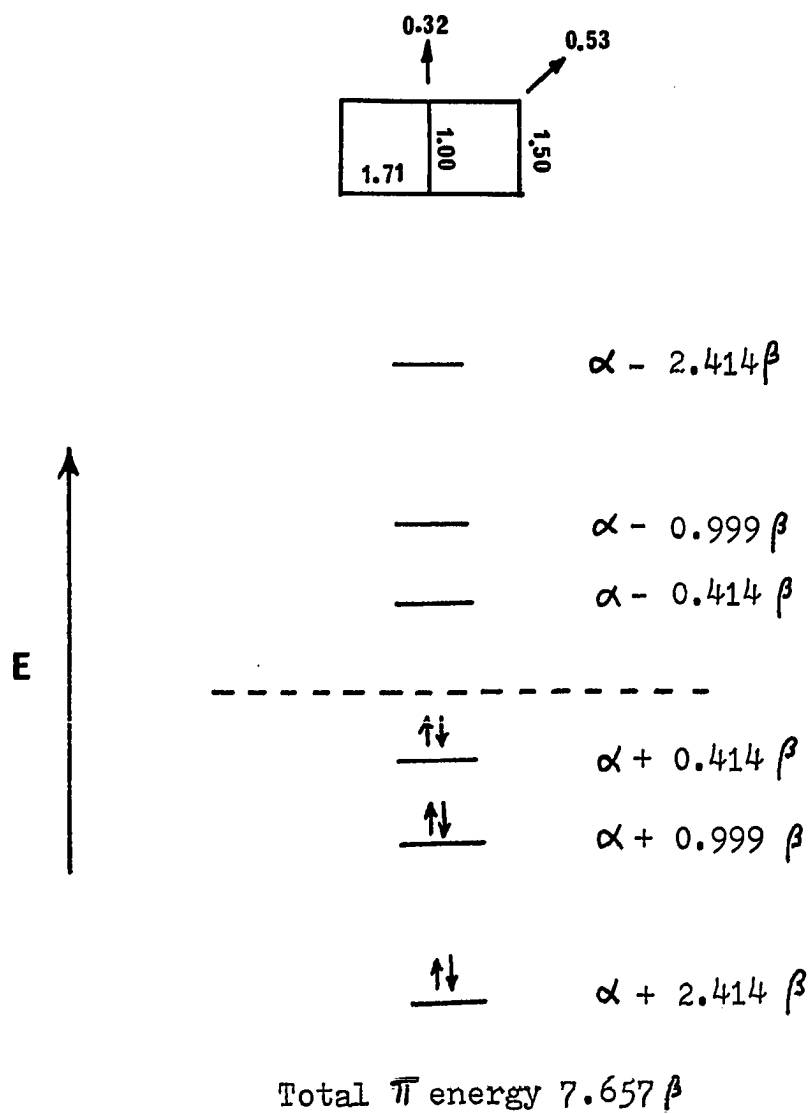






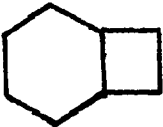
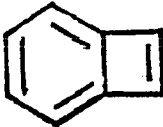


Figure 17 HMO(LCAO) calculation of butalene

Table 3 Strain energies for some four member ring compounds

Compound	Strain (kcal/mole)	Ref.
	26.5	137
	30.0	137
	(50.0)	135
	53.0	138
	60	139
	(76)	135
	26.6	137
	(50)	135

a resonance approximation of the heats of formation of these species. A similar calculation for 121a using a 6.5 kcal/mole resonance destabilization and 80 kcal/mole strain energy predicts a heat of formation of 130 kcal/mole for butalene. For the 1,4-benzenediyl structure 121d,e, a heat of formation may be estimated by addition of two phenyl C-H bond energies to the heat of formation of benzene and subtraction of bond energy of H₂. This gives a ΔH_f of +140 kcal/mole¹²⁹ for 121d,e assuming that there is no appreciable interaction of the two radical centers. To test the validity of this assumption, Hoffmann and co-workers³⁵ have carried out extended Hückel calculations on the 1,4-benzenediyl 121d,e and found important through-bond coupling which places the antisymmetric nonbonding combination orbital below the symmetric (Figure 18). If this picture is correct, it provides for some degree of 2,3-6-bond stabilization making the heat of formation of 121d and 121e somewhat lower than +140 kcal/mole, assuming that the benzene π system remains undisturbed. The same type of interaction has been supported by Rees and Storr in 1965 for a 1,8-dehydronaphthalene (122).¹⁴⁰ They reported that 122 reacts with olefins stereospecifically in cycloadditions. If one accepts the existence of 1,8-dehydronaphthalene and its apparently concerted 1,2 addition, the antisymmetric combination of two nonbonding orbitals

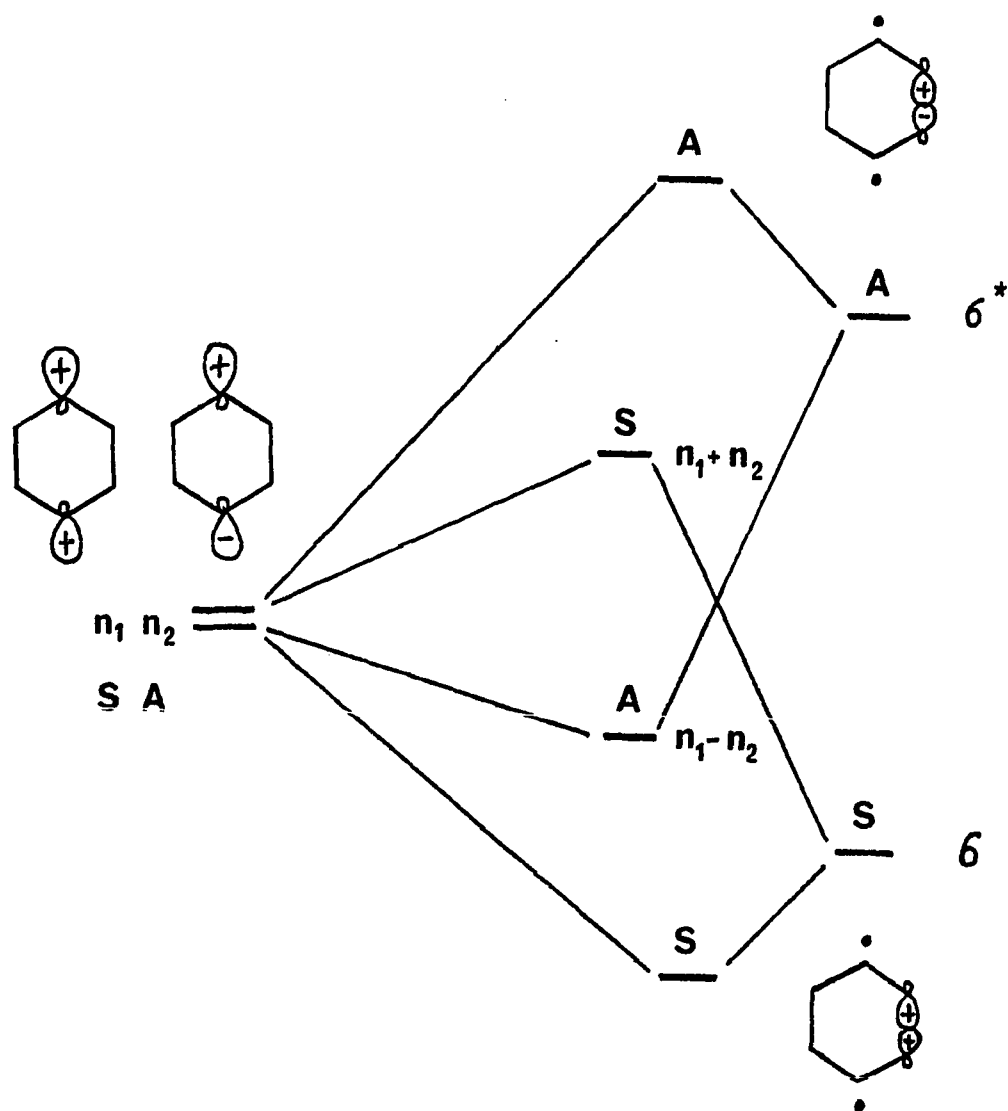
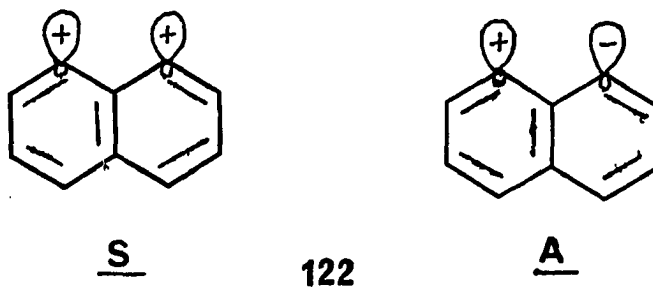


Figure 18 Interaction diagram for the nonbonding orbitals in p -benzyne

has to be lower than the symmetric. That an A below S



ordering would give allowed 1,2 addition while S below A would be forbidden as shown in the energy correlation diagram (Figure 19). Wilhite and Whitten used the same argument in an ab initio SCF and configuration interaction (mixing of wavefunction of the excited states with that of the ground state) calculation which predicted that triplet p-benzyne is more stable than the singlet.¹⁴¹ However, all these calculations were made essentially at the equilibrium geometry of benzene, and since the splitting between these levels is small, a slight variation in geometry might reorder the symmetric and antisymmetric combination orbitals. More recently Dewar and Li⁴⁰ reported the complete geometry-optimized MINDO/3 calculations for all the benzynes based on the half-electron approximation (see Figure 20). The result for 1,4-dehydrobenzene can be summarized in Figure 21. Without configuration interaction he predicts that triplet 121e will be 10.8 kcal/mole more stable than the singlet 121d, in agreement with Hoffman's and Wilhite's predictions. However, when the configuration

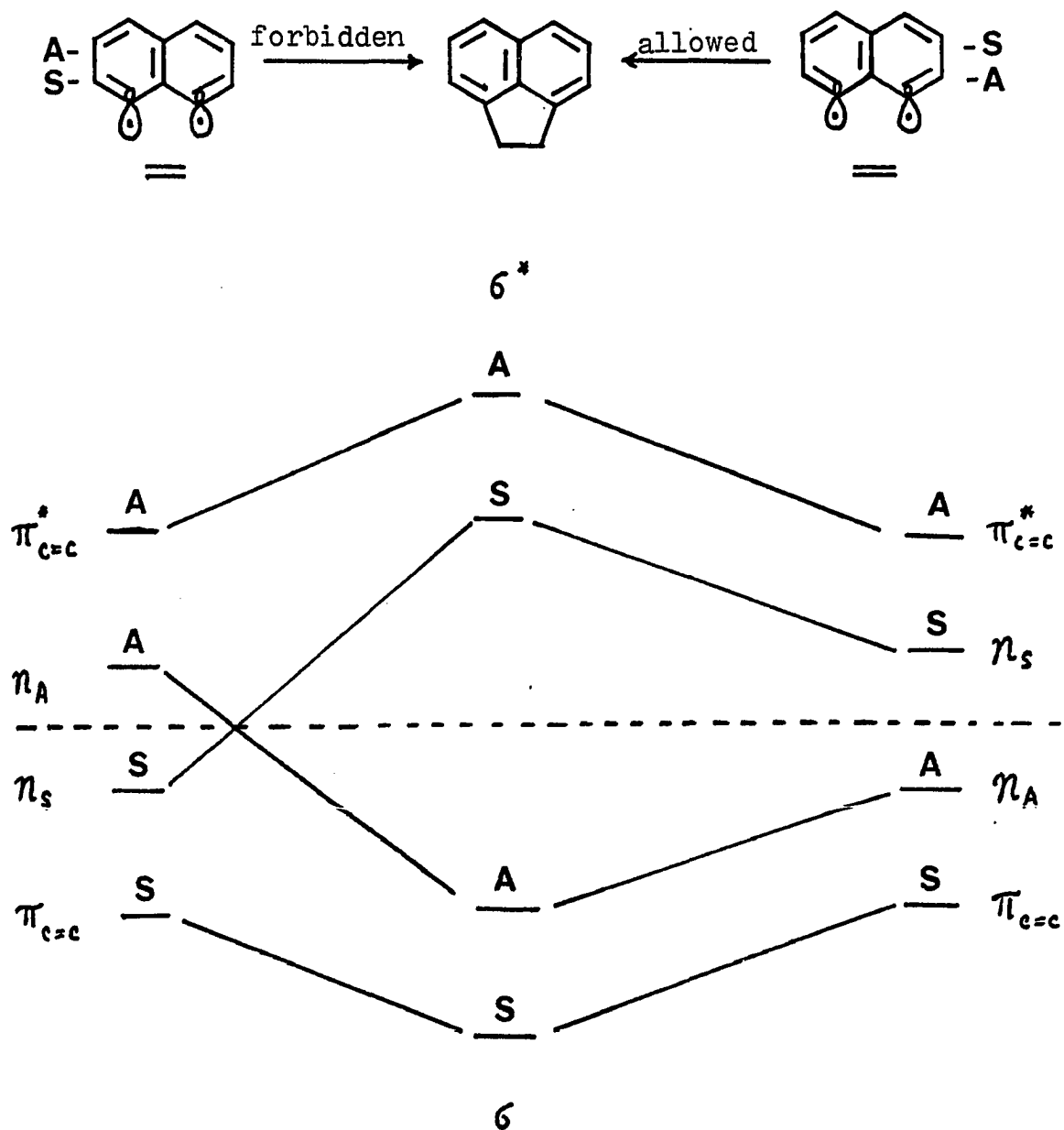
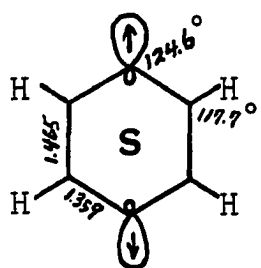
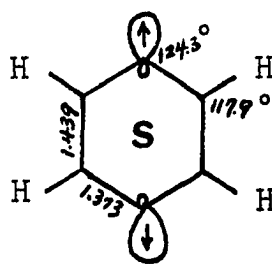


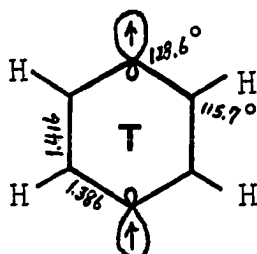
Figure 19 Energy correlation diagram for the addition¹⁴⁰ of two possible kinds of 1,8-dehydronaphthalenes to ethylene



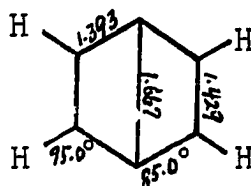
133.9 (7.80)

121d (w/o CI)

116.9 (7.72)

121d (CI)

123.1

121e

152.8

121a

Figure 20 Calculated structure for 1,4-dehydrobenzene

Calculated⁴⁰ bond lengths (Å), bond angles, heats of formation (ΔH_f , kcal/mole at 25°), and ionization potentials for singlet p-benzyne (121d) without CI; for singlet p-benzyne (121d) with CI; for triplet p-benzyne (121e); and for butalene (121a). The transition state for conversion of 121a to 121d and e has $\Delta H_f = 157.5$ kcal/mole

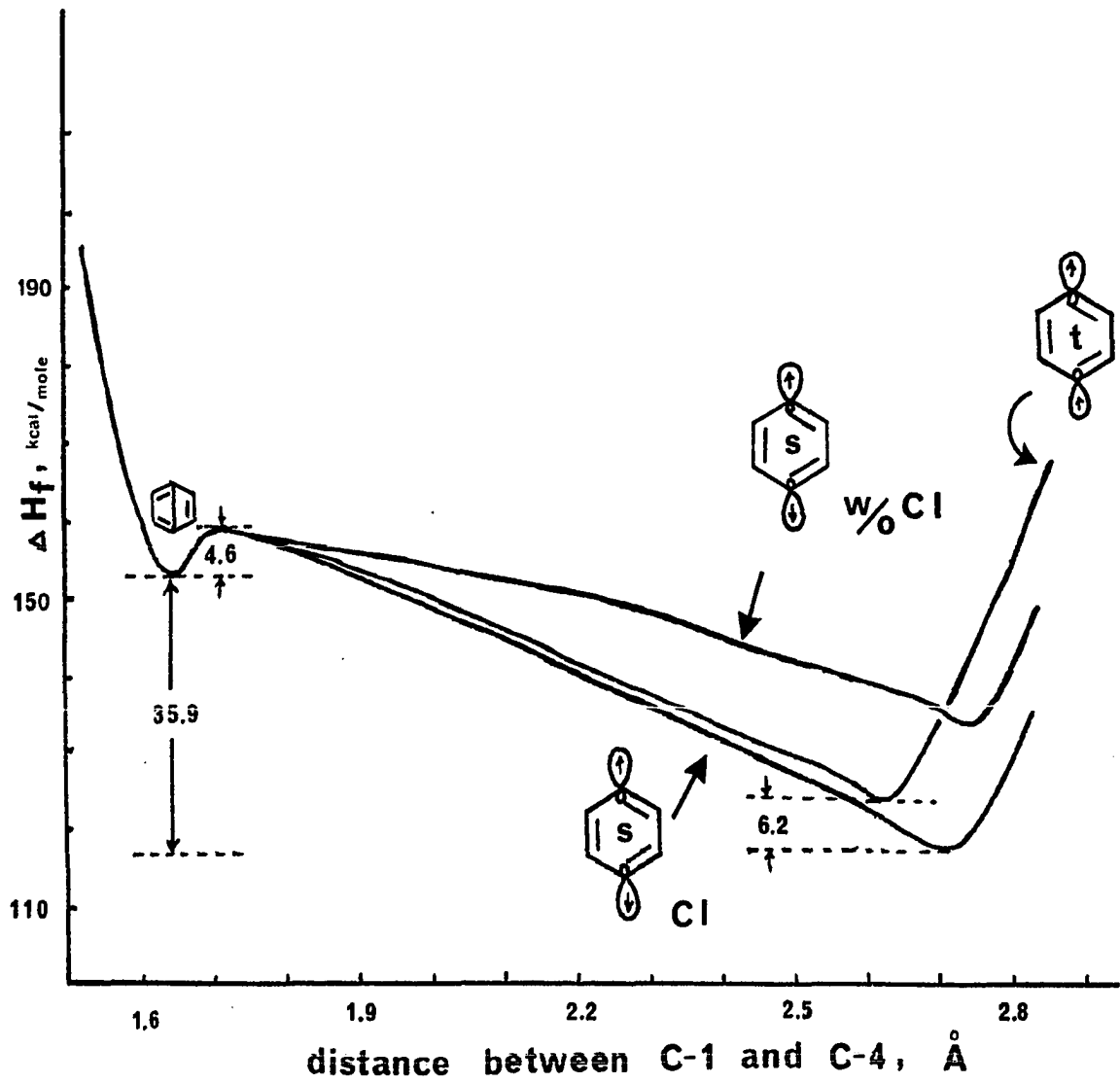
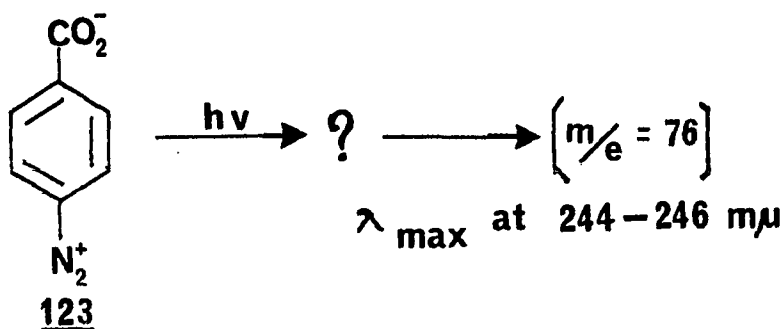


Figure 21 Predicted heat of formation of 1,4-dehydrobenzene

interaction is considered, the singlet is predicted to be the more stable state by 6.2 kcal/mole. The most interesting thing about these latest estimations is that both 121a and 121e are predicted to be energy minima differing by approximately 36 kcal/mole with as little as a 4.6 kcal/mole activation barrier for conversion of butalene into the much more stable p-benzyne.

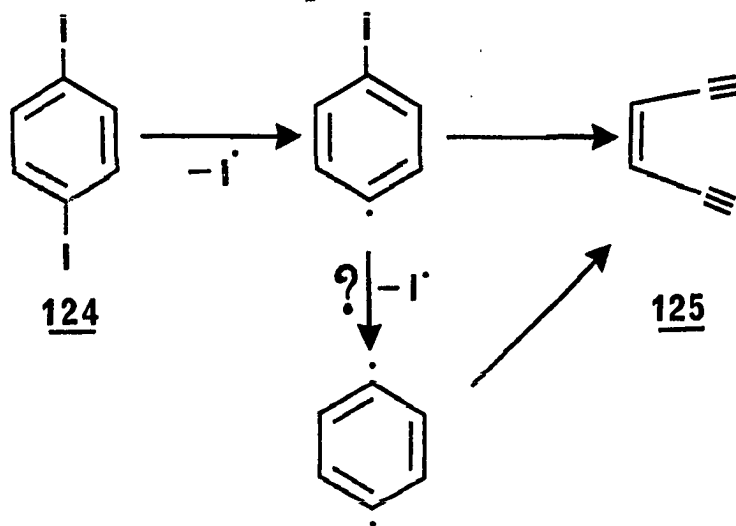
The first attempt to generate a 1,4-dehydrobenzene reported in the literature is by Berry and coworkers^{23,24} who reported the flash photolytic decomposition of benzenediazonium-4-carboxylate (123). They found that photo-decomposition of 123 gave a mixture of products which showed broad absorption up to 290 m μ and a possible flat maximum at 244-246 m μ . This absorbing intermediate appeared from 50 μ sec to at least a half second after flashing. Time resolved mass spectrometry shows a strong peak at m/e 76 which arose from a species having an even longer lifetime than that reported for 1,2-dehydrobenzene, for it persisted



for up to two minutes in the vacuum system applied. In the

author's opinions, the species giving rise to this peak is 1,4-dehydrobenzene. However, it is still an open question whether the ion at 76 is a parent ion with a molecular weight 76 or a fragment of molecule with high molecular weight.

Fisher and Lossing have examined the pyrolysis of *p*-diiodobenzene (124) at 960° in a reactor coupled to a mass spectrometer.¹⁴² They identified a product which gives a mass peak at *m/e* 76 and has an apparent ionization potential of 9.46 e.v. On the basis of this value, they assigned the structure of the ionizing species as 3-hexene-1,5-diyne,¹²⁵ which they estimated should have an ionization potential close to that observed. Amusingly, 1,3-diiodobenzene gave rise to at *m/e* 76 species with an identical ionization potential.



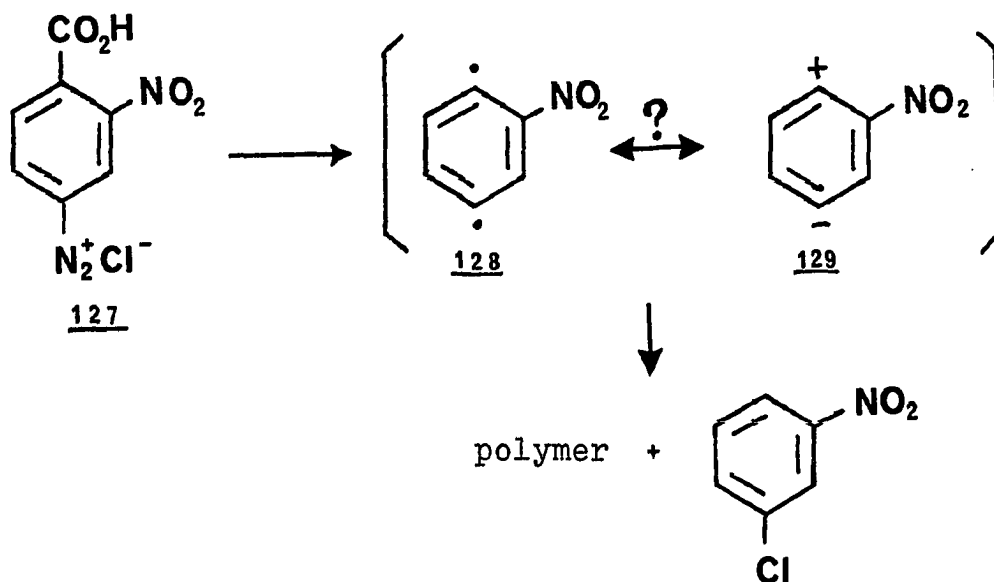
Kampmeier and Hoffmeister¹⁴³ have shown that the

photolysis of p-diiodobenzene gives p-terphenyl when benzene is used as solvent.

Rossi and his co-workers¹⁴⁴ have examined the thermal decomposition of 1,4-benzenediazoniumcarboxylate hydrochloride salt 126 and its 2-nitro analog 127. With 126 the major products were p-chlorobenzoic acid and carboxylated polymer with only a very small amount of chlorobenzene. On

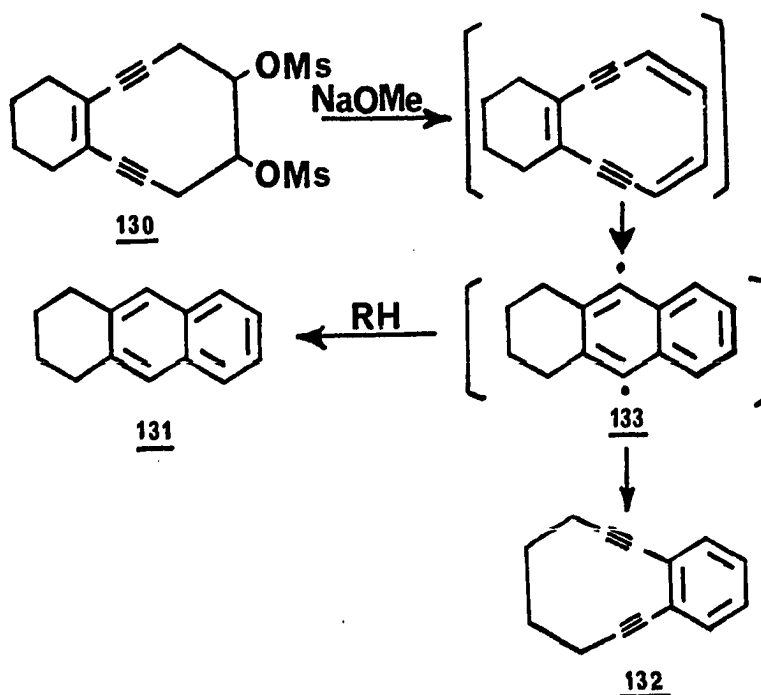


the other hand, when 127 was pyrolyzed, m-chloronitrobenzene was the major product together with a large amount of polymer. The authors suggest that the intermediate in this



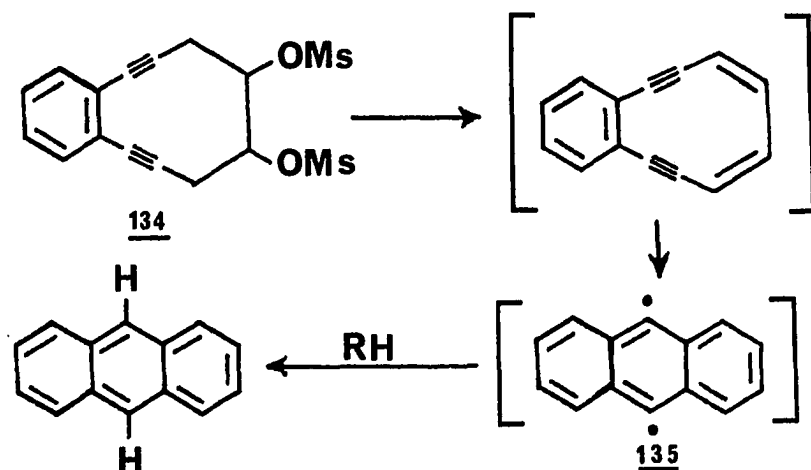
reaction could be either 128 or 129. Clearly, this work lacks strong evidence for the production of 1,4-dehydrobenzenes.

Darby and his co-workers¹⁴⁵ reported a striking transformation of 130. Treatment of dimethylate 130 with sodium methoxide gave both tetrahydroanthracene 131 and substituted diethynylbenzene 132.



They also reported that the dimesylate 134 invariably provided anthracene under various elimination conditions and two hydrogen atoms (also two deuterium atoms) have been added at the 9 and 10 positions. Although the authors did not suggest any intermediate, it seems likely that 9,10-dehydroanthracene 135 and a substituted 5,6-dehydro-

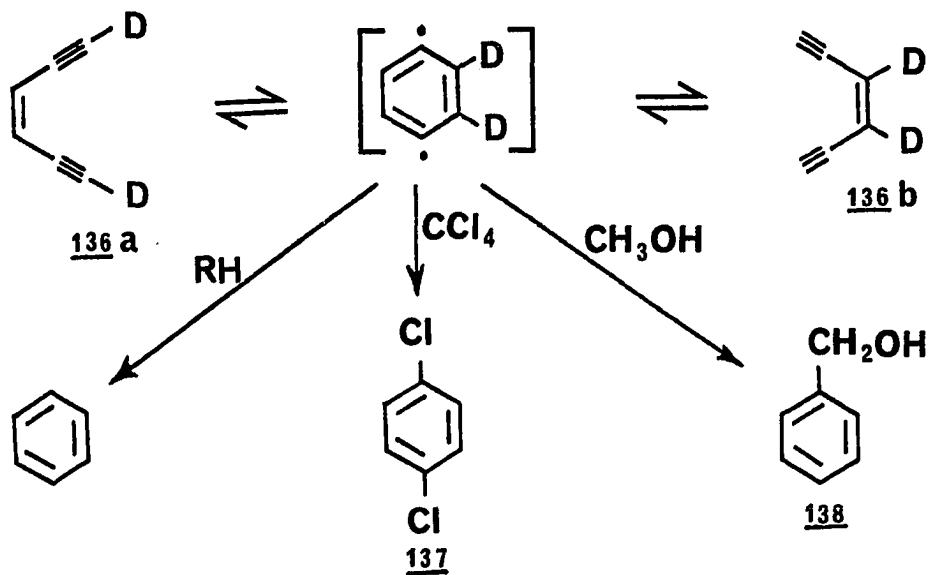
naphthalene 133 were probably involved in the reactions.



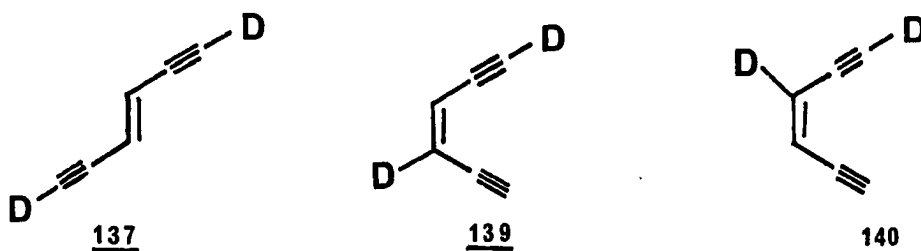
Richardson *et al.*¹⁴⁶ argued that the ease of substitution of halogen in 9-haloanthracene by piperidine may possibly involve a transient formation of 9,10-dehydroanthracene. It should be noted that it is improper to compare the rate of 9-haloanthracene with that of 1 or 2-haloanthracene in the substitution reactions. The dehalogenation at 9,10 positions seems quite improbable since 9-lithio-10-chloroanthracene is stable in refluxing ether¹⁴⁷ and does not afford any products indicative of 9,10-dehydroanthracene when refluxed in tetrahydrofuran.¹⁴⁸ Attempt to generate 135 from 9,10-dibromoanthracene and lithium in ether also remained fruitless.¹⁴⁹

Jones and Bergman¹²⁹ reported a rearrangement of 136a to 136b which is related to Masamune's work. Gas-phase

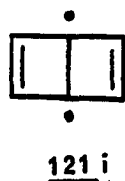
pyrolysis in a flow system at 300° (atmospheric pressure) caused complete scrambling of deuterium between the acetylenic and vinyl positions of 136 and no such rearrangement in the trans isomer 137. When the thermal



isomerization is carried out in presence of 2,6,10,14-tetramethylpentadecane, carbon tetrachloride or methanol, starting material was destroyed, with formation of benzene, p-dichlorobenzene (137) and benzyl alcohol (138) respectively. The capabilities of removing hydrogen and chloride atoms from solvent suggested that a radical intermediate may be involved. No deuterium scrambling products 139 and 140 were detectable. All these results strongly suggested a new species with a C₂ axis. An intermediate such as p-benzyne will readily account for all



the data. An alternate structure would be the bicyclo [2,2,0]hexadiene-1,4-diyl (121i) which may have higher energy than *p*-benzyne. From the contact time required to carry the reaction to ~50% completion at 200°,



they estimated the activation energy of the reaction at 32 kcal/mole. They concluded that *p*-benzyne lies only 14 kcal/mole above the starting material (136) and in a very substantial energy well (18 kcal/mole, see Figure 22).

Recently, Breslow *et al.* reported evidence of generation and trapping of butalene 121a (b).¹³⁰ Photolytic cyclization of 3-chloro-1,2-dihydrophthalic anhydride 141 followed by anodic decarboxylation of the bicyclic diacid gave a chlorodewarbenzene 142 together with chlorobenzene 143 (9:1). When this mixture was treated with lithium dimethylamide in deuteriodimethylamine and (tetramethyl-ethylenediamine) at -35°, 142 was quantitatively converted

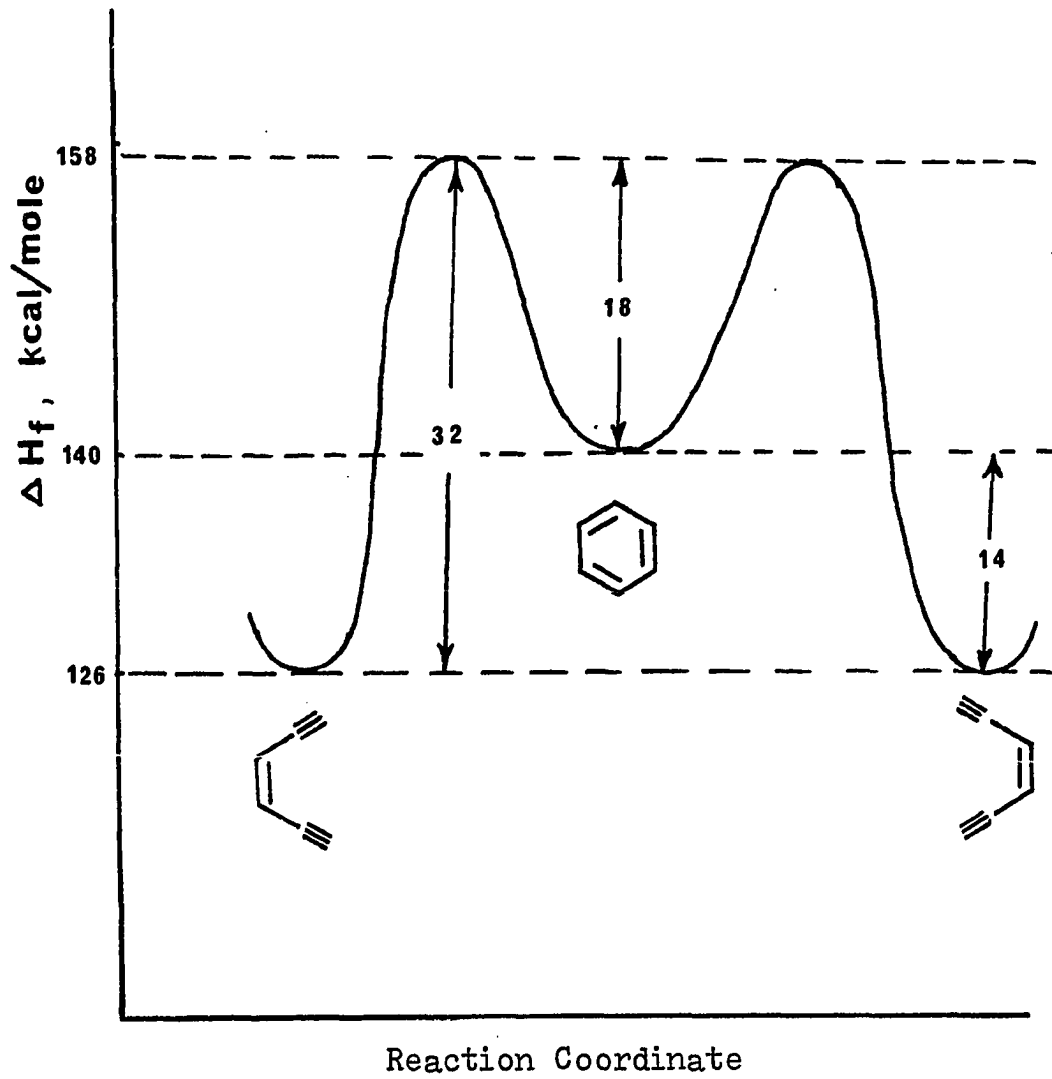
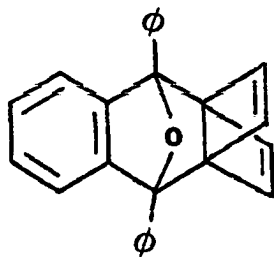
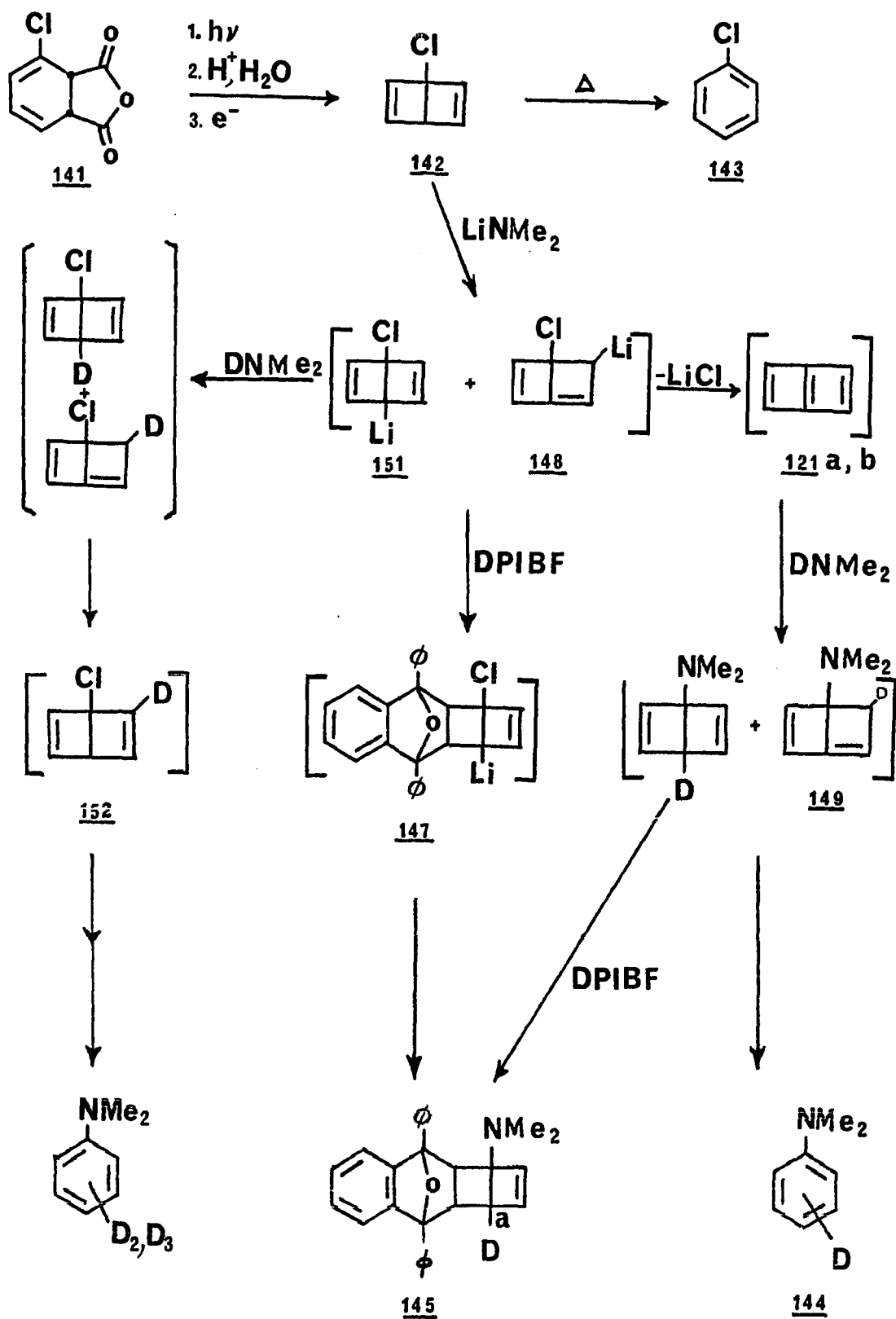


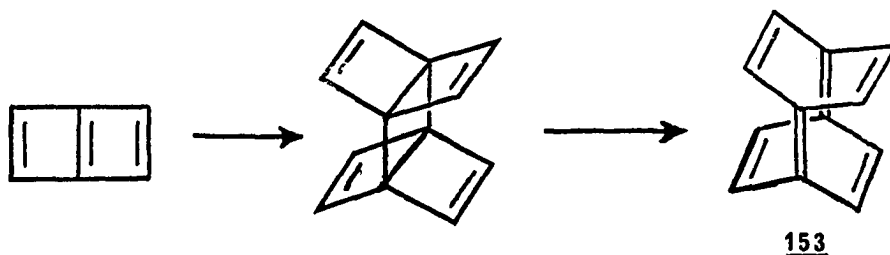
Figure 22 Energy diagram for degenerate rearrangement¹²⁹ of *cis*-3-hexene-1,5-diyne

to deuteriodimethylaniline,¹⁴⁴ 25% d₁, 38% d₂, 22% d₃ and 6.3% d₀. Nmr shows 76%, 5% and 25% of the deuteration to the para, meta and ortho positions of 144 respectively. Under the same conditions in presence of a five fold excess of diphenylisobenzofuran (DPIBF), the adduct 145 was isolated in 10-15% yield, 90% d₁ and 90% deuterated at position a. The mechanism favored by Breslow to account for these results begins with elimination of HCl from 142 to form 121a (b) followed by addition of dimethylamine. The adduct 145 seems quite unlikely arise from reaction of DPIBF with butalene since one would expect the 1,4-bond be trapped by DPIBF to give adduct 146. It is unlikely, though not impossible, that adduct 145 arises from 147 without involving butalene. It is somewhat surprising that DPIBF does not trap 148 or 149 which both have very strained double bonds. The observation of large amounts of N,N-dimethylaniline-d₂,d₃ implies that the organo-lithium compounds 148 and 151 (or the anions) have life times

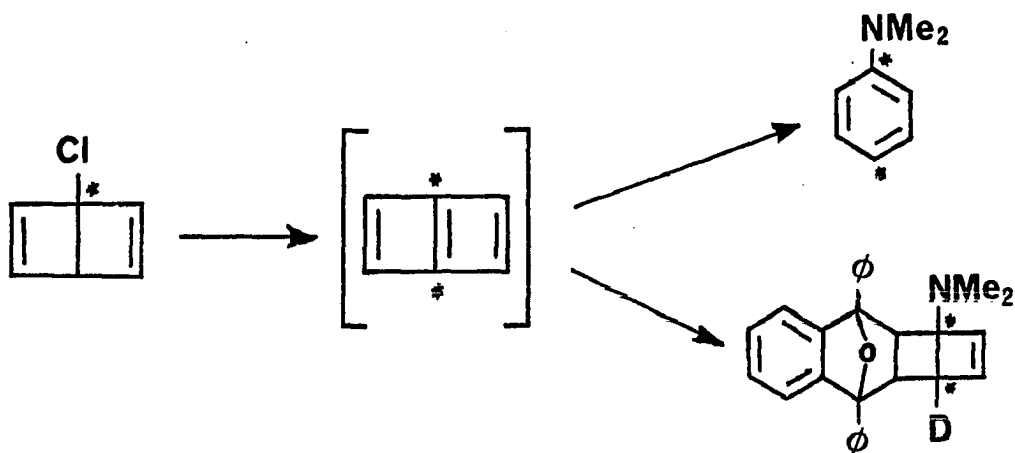
146



sufficiently long to reprotonate at the C-2 and C-4 positions. One also would expect some 2-deuteriochlorobenzene to be formed from the 1-chloro-2-deuterio-dewarbenzene (152), however, no information was provided. It is also surprising that butalene does not rearrange to *p*-benzyne (the calculated activation energy is only 4.6 kcal/mole¹³⁶) nor dimerize to 153 whose benzo analog is



known to be stable.¹⁵⁰ As a further check on the reaction, one could label the C-1 or C-4 with carbon-13. If butalene indeed is intermediate, the final products should have



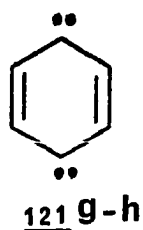
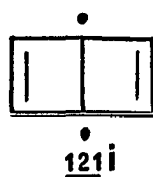
C-13 even at the C-1 and C-4 positions.

Despite the fact that intermediacy of 121 is a reasonable mechanism for some of the above reactions, none of the attempts to observe 1,4-dehydrobenzene so far have provided unambiguous evidence of its existence. The major problem with all of the above routes to 1,4-dehydrobenzene is that the reactions were carried out under conditions not allowing the spectroscopic observation of 1,4-dehydrobenzene. 1,4-Dehydrobenzene would be too reactive (intramolecularly) and unstable (intramolecularly) to isolate at their conditions. It is clear that a complete different approach is needed. First, 1,4-dehydrobenzene has to be generated unimolecularly and free from species which will react with it. Second, it should be generated without vibronic excitation), so that intramolecular rearrangements or decompositions are excluded. Low temperature matrix isolation satisfies these two requirements.

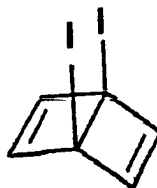
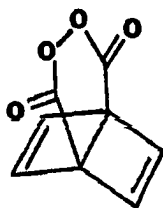
Thus, I began my work on 1,4-dehydrobenzene in the hope that I might be able to obtain more direct evidence such as infrared or esr spectral data for the existence of 1,4-dehydrobenzene or a derivative of this elusive system.

RESULTS AND DISCUSSION

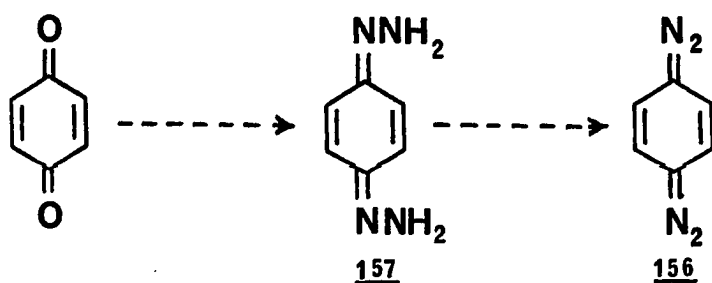
After an intensive review of the literature on 1,4-dehydrobenzene, it occurred to me that a particularly clean synthesis of 121 might be obtained if the molecule could be generated from an unimolecular decomposition or isomerization of a high energy substrate, making the 1,4-dehydrobenzene energetically accessible. However, the precursor had to be kinetically unreactive enough to allow one to isolate and handle it in a matrix procedure. Compounds which can lead to diradical 121i or bis-carbene 121g-h would be most promising precursors. Peroxide 154 and diiodide 155 are good candidates, however, each



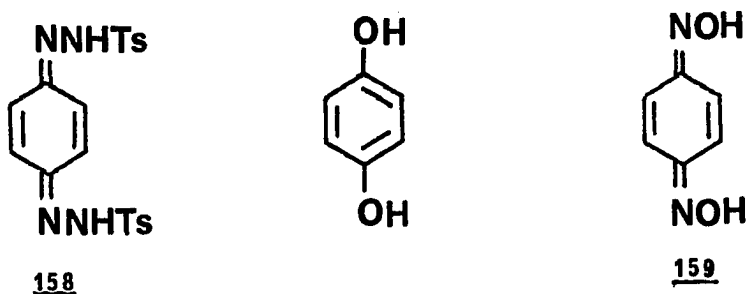
represents a great synthetic challenge.



Few examples of Dewar benzene with electron withdrawing groups at the 1,4-positions are known. It has been reported that chlorodewar-benzene readily isomerizes to chlorobenzene in solution.¹³⁰ The most promising precursor for the bis-carbene 121g-h is the bis-diazocompound 156 which also posed serious problems since no diazocycloalkane with a six membered ring has been isolated. My approach to bis-carbene 121g-h started with attempts to prepare bis-hydrozone 157 and bis-tosylhydrazide 158 from benzoquinone. However, treatment of benzoquinone with



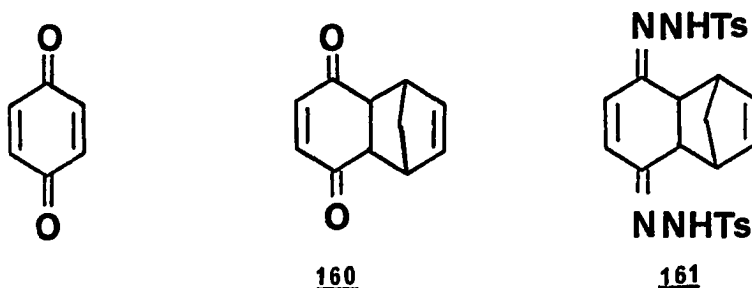
hydrazine did not give bis-hydrazide 157, hydroquinone was



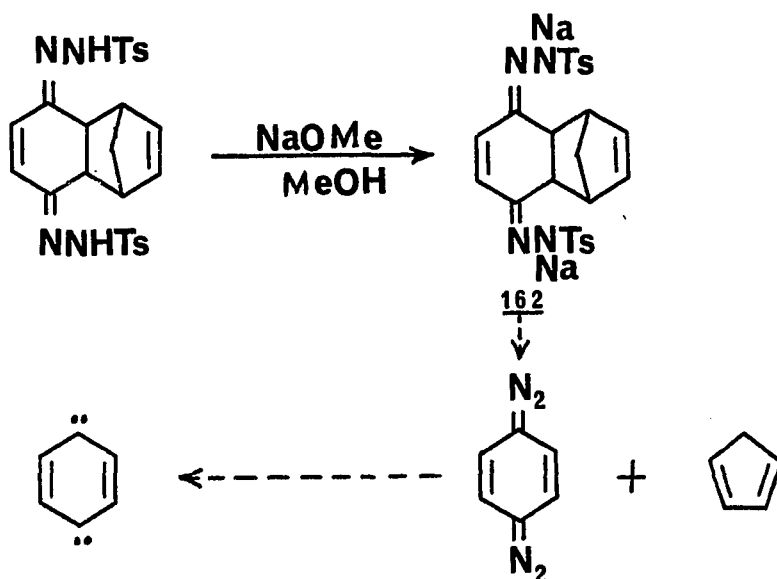
obtained instead. Benzoquinone does not react with tosylhydrazide to give 158 either. An alternative approach to 156 was to react dioxime 159 with chloroamine. However, no desired diazocompound was obtained when one treats dioxime

159 with sodium hypochlorite in sodium hydroxide solution.

To prevent aromatization on the way to 156, it seemed necessary to protect one double bond of benzoquinone. Cyclopentadiene was chosen for this purpose. Benzoquinone reacts with cyclopentadiene readily to give the Diels-Alder adduct 160.¹⁵¹ Treatment of 160 with two equivalents of tosylhydrazide in methanol containing small amounts of hydrochloric acid at room temperature gave bis-tosylhydrazone 161 in 70% yield. The bis-tosylhydrazone 161 was

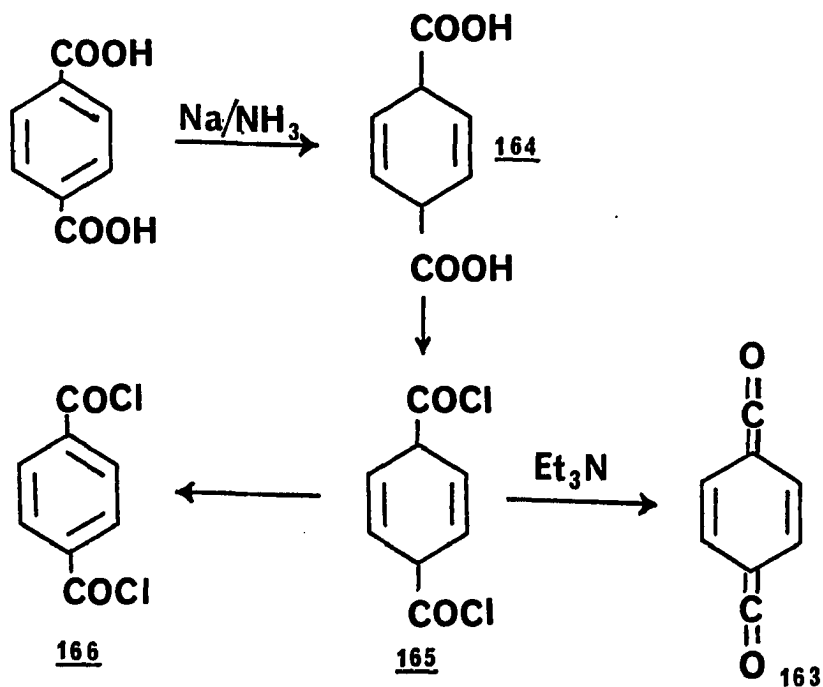


quite insoluble in common solvents and only slightly soluble in DMSO. Attempts to degrade 161 to 158 were unsuccessful. Compound 161 was destroyed in 40 minutes at 85°. However, no cyclopentadiene or 158 were observed. Therefore, 161 was converted to its disodium salt 162 by sodium methoxide in methanol with the hope that the retro-Diels-Alder reaction and the decomposition of two tosylhydrazone sodium salt groups would occur in the thermolysis.



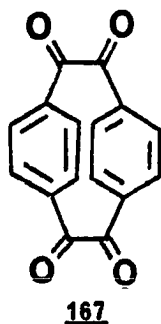
Pyrolysis of 162 at 370° by dropping the salt into a flask (in Wood's metal) under vacuum (0.01 mm) gave only cyclopentadiene as a volatile product. No deazocompound, benzene, or cis-3-hexene-1,5-diyne was detected by infrared. An intractable polymer was left in the hot zone.

The next precursor investigated was the bis-ketene 163. Terephthalic acid after Birch reduction gave the dihydrodiacid 164 in 55% yield.¹⁵² Treatment of 164 with oxalylchloride in benzene gave the diacylchloride 165 which was unstable at room temperature. It undergoes oxidation to terephthaloyl chloride 166 slowly in an nmr tube on standing. Attempts to convert diacyl chloride 165 to bis-ketene 163 by immediate treatment of 165 with

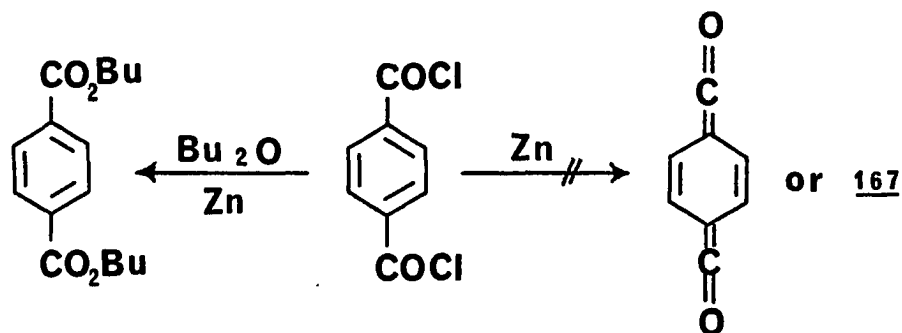


triethylamine were unsuccessful. Neither bis-ketene nor the possible dimer **167** were observed.

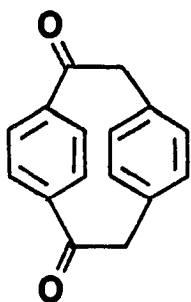
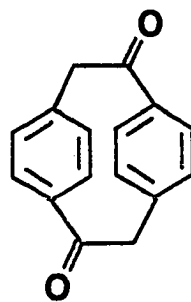
Terephthaloyl chloride is also a possible precursor of diketene **163**. Treating **166** with an excess amount of zinc dust in refluxing *n*-butylether gave a yellow oil. After chromatography di-*n*-butyl terephthalate was the only product



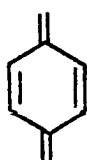
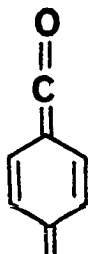
isolated (42%). A variety of other solvents such as *m*-xylene and decalin were also used but were unsuccessful.



The next precursors examined were diketo-paracyclophanes 168 and 169. Prolonged photolysis of 168 and 169 in 2-methyltetrahydrofuran glass at 77°K showed little

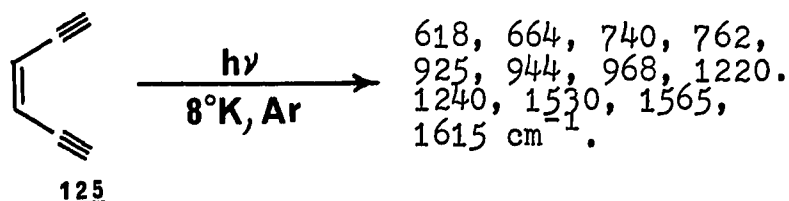
168169

destruction. If trace amounts of p-xylylene (170), ketene 171 or bis-ketene 163 were formed, one would be able to detect them by UV.

170171163

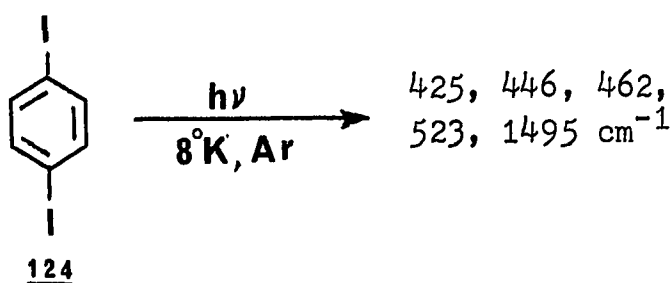
Irradiation ($\lambda > 2000 \text{ \AA}$) of an argon matrix containing

cis-3-hexene-1,5-diyne 125 at 8° K caused new bands to appear at 618 (s), 664 (s), 740, 762, 925, 944, 968, 1220, 1240, 1530, 1565 and 1615 cm^{-1} . However, the conversion was quite small. Although 1,4-dehydrobenzene was a possible



product, other products are also possible. The mass spectral analysis of the photolysis products showed only the starting material.

Since 1,2-dehydrobenzene is the photoproduct of o-diiodobenzene (see Part I), one would expect that 1,4-dehydrobenzene would be generated from irradiation of 1,4-diiodobenzene 124. Prolonged irradiation (>200 nm) of 124 caused new bands to arise at 425, 446, 462, 523 and



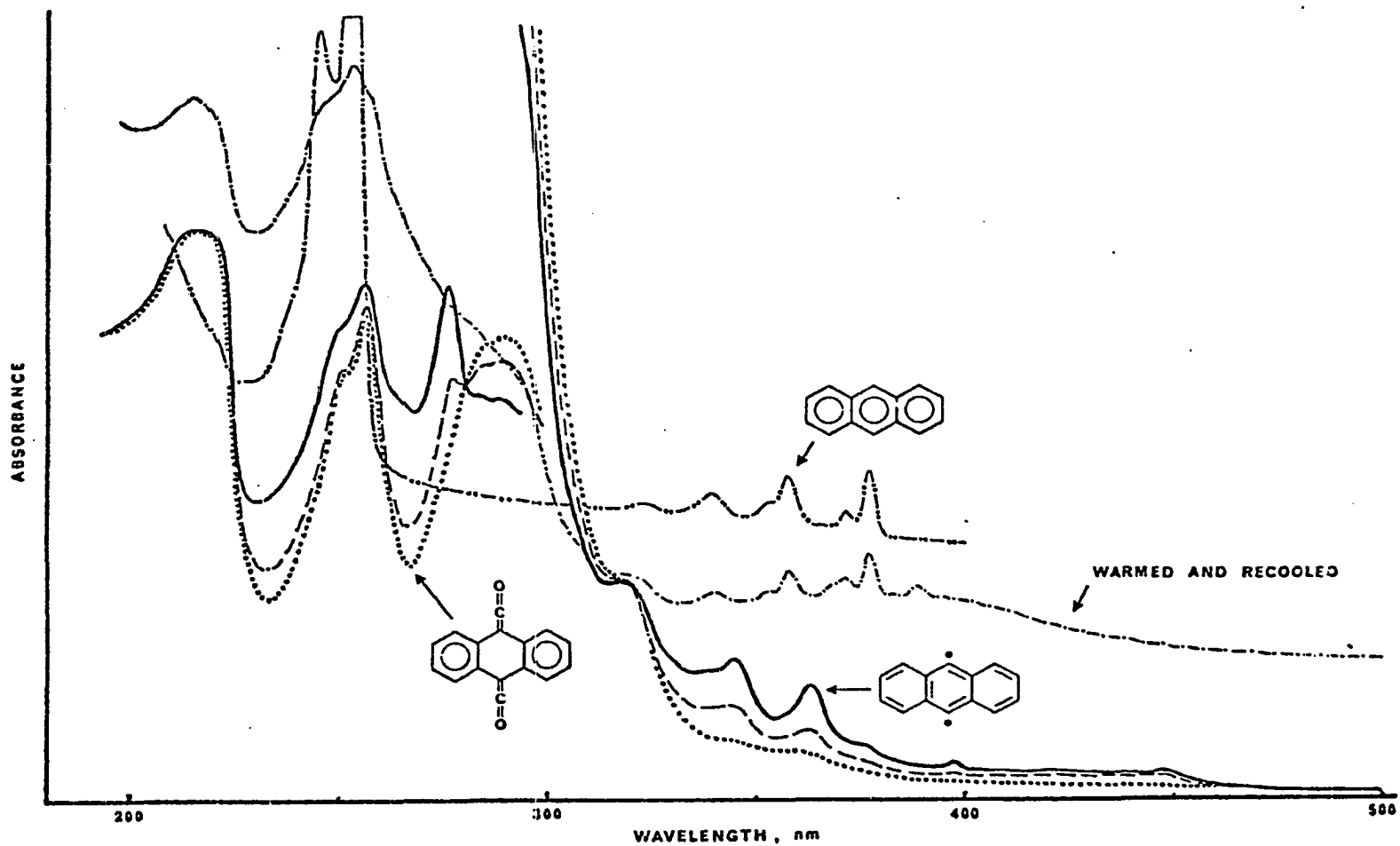
1495 cm^{-1} . The reaction had reached a photosteady state. The conversion of 124 was quite small over 30 hours. The

photolysis products were trapped at 77° K and submitted for mass spectral analysis. There were very weak peaks at m/e 76, 78.

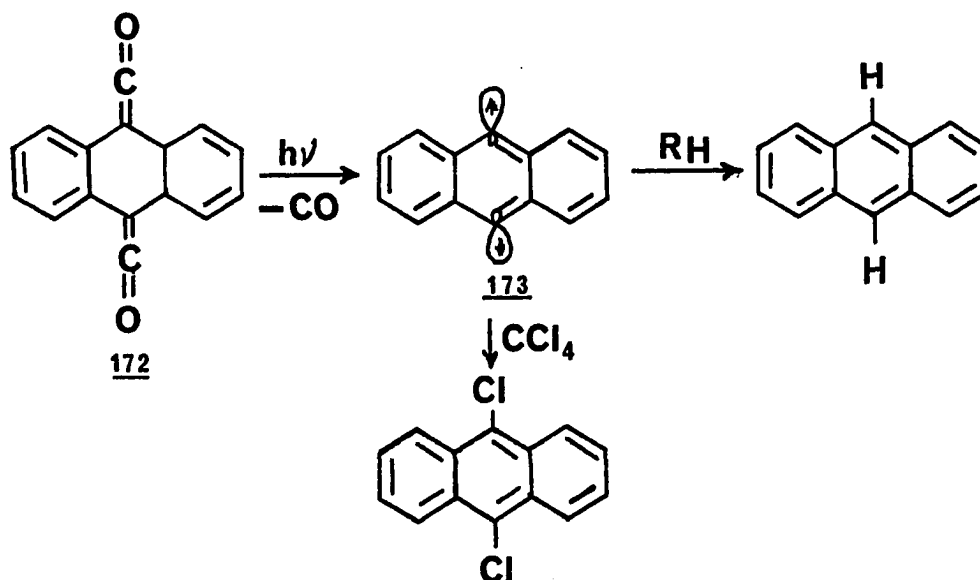
In this work, 9,10-dehydroanthracene 172, a derivative of 1,4-dehydrobenzene, was also studied. The bis-ketene 172 was irradiated ($\lambda > 2000 \text{ \AA}$) in a 3-methylpentane glass at 77° K. The progress of the reaction was monitored by ultraviolet spectroscopy (see Figure 23). A new species was produced which gave anthracene on warming. Similar photolysis in a 3-methylpentane glass containing 5% carbon tetrachloride gave the same reactive intermediate which on warming gave anthracene and 9,10-dichloroanthracene (identified by ultraviolet spectrum and thin layer chromatographic behavior). Significantly higher concentrations of carbon tetrachloride in the 3-methylpentane gave problems in generation of the intermediate. In this case, 9,10-dichloroanthracene was generated by photolysis. Irradiation ($\lambda > 2000 \text{ \AA}$) of 172 matrix-isolated in argon at 8° K gave carbon monoxide (2139 cm^{-1}) and a new species with intense bands at 710 and 760 cm^{-1} . When this matrix was warmed to room temperature, the product isolated from the cesium iodide window was anthracene (identified by comparison of the ultraviolet spectrum, mass spectrum and thin layer chromatographic behavior)

Figure 23 Irradiation of anthraquinone-bis-ketene,
uv spectrum

Ultraviolet spectra in a 3-methylpentane glass at 77° K of 172 (.....), 172 after 60 min. irradiation through quartz (---), 173 (—), 173 after warming to room temperature and recooling to 77° K (----) and authentic anthracene (-..-..-).

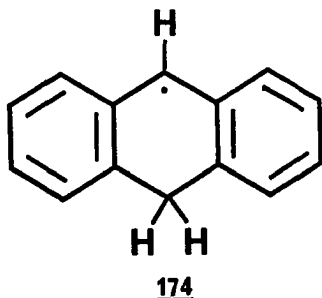


and an intractable polymer. These experiments are sensibly interpreted in terms of 9,10-dehydroanthracene as the intermediate 173. When the results were submitted for



publication, a referee has raised the question whether the species observed in the ultraviolet spectroscopic experiments might be the radical 174. In an effort to exclude 174 on a rigorous basis, 9,10-dehydroanthracene was irradiated ($\lambda = 2537 \text{ \AA}$) in 3-methylpentane at 77° K to generate 174 by a similar technique reported by Migirdicyan and Bandet¹⁵³. In this experiment anthracene and a reactive species believed to be the radical 174 were generated. The reactive species was converted to anthracene on warming to room temperature. The reactive intermediate had a sharp ultraviolet maximum at 352 nm (which corresponds to a minimum in the ultraviolet spectrum of 9,10-dehydro-

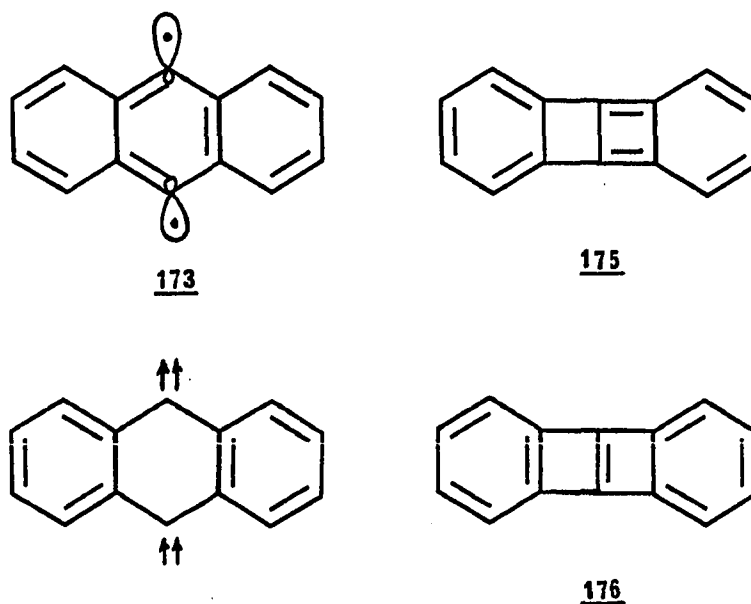
anthracene). The position of this band was in the wave-



length range expected for the radical 174. Diphenylmethyl radical, for example, is reported to have λ_{\max} 338 nm¹⁵⁴ and λ_{\max} 335 nm.¹⁵⁵ Irradiation of diphenylmethane in our apparatus under the same conditions used for 9,10-dihydroanthracene gave diphenylmethyl radical (λ_{\max} 335 nm).

The structure of 9,10-dehydroanthracene is of considerable interest. We have been unable to observe a triplet esr signal from either 9,10-dehydroanthracene or 9,10-diiodoanthracene (matrix isolated in argon at 10° K) and tentatively conclude that it has a singlet ground state. The choice is then between a singlet diradical structure 173 and a dibenzobutalene structure 175, 176. The radical-like abstraction reactions of 9,10-dehydroanthracene suggest that it react as the diradical. This could, however, be due to ring opening of a dibenzobutalene structure during the warming process. The general similarity of the ultraviolet spectrum of 9,10-dehydroanthracene (λ_{\max} ^{3-MePentane} 256, 276, 320, 345, 363, 378,

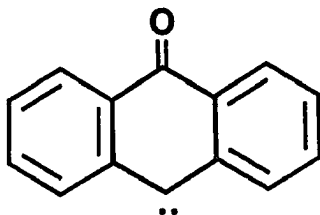
397 and 449 nm) to that of anthracene strongly suggests that the singlet diradical 173 was, in fact, the species we have observed. It remains an open question whether or not dibenzobutalene also represents a potential minimum on this energy surface. The characterization of 173 strongly supports Bergman's evidence on the existence of 1,4-dehydrobenzene. The chemistry of 9,10-dehydroanthracene also suggests that it may be an intermediate in the conversion



of 1,5-didehydro-3,4-benz[10]annulene to anthracene¹⁴⁵
(see page 150).

A final point of interest deserves comment. The isosbestic points (280, 320 nm) observed in the ultraviolet spectra during photolysis of 172 and the absence of carbene intermediates which should have been detected in the

ultraviolet and esr experiment, for example, 9-oxo-10-anthracenyldiene (177) was observed in an ultraviolet experiment in this work, suggests that either the loss of both molecules of carbon monoxide is operationally concerted or the intermediate ketene-carbene is destroyed photo-



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chemically at a much faster rate than that of the bis-ketene.

EXPERIMENTAL

Propioaldehyde

This compound was prepared according to the procedure by Sauer.¹⁵⁶ A 3-l. three-necked round-bottomed flask was fitted with a thermometer, a graduated dropping funnel; a stirrer, a capillary tube for introducing nitrogen, and an exit tube attached to three traps set in series. In the flask were placed propargyl alcohol (112.1 g., 2.0 mole and a cooled solution of 135 ml. of sulfuric acid and 200 ml. of water. The flask was cooled in an ice-salt mixture. The first trap was cooled to about -15° . The last two traps in the series are cooled to -78° . The pressure in the system was reduced to 40-60 mm., nitrogen was introduced through the capillary, and the mixture was stirred vigorously. A solution of 210 g. of chromium trioxide (2.1 moles) in 400 ml. of water and 135 ml of sulfuric acid was added dropwise in about 5 hours while maintaining a reaction temperature of $3-10^{\circ}$. After the addition of the chromium trioxide, the ice bath was removed, and the flask was permitted to warm to room temperature while the pressure is gradually lowered to 14-20 mm. to remove the last of the aldehyde. The condensates of the three traps were combined and dried over anhydrous magnesium sulfate. The propioaldehyde was distilled through an 8-in. packed column.

The fraction distilling at 53-56° weighed 42 g., 37% yield (lit.¹⁵⁶ is 54-57°). nmr (neat, TMS) 3.75δ (singlet, 2H) and 9.0δ (singlet, 1H) i.r. (CCl₄) 3280 (s), 3030 (w), 2860 (s), 2740 (w), 2330 (w), 2105 (m), 1890 (w) and 1695 cm⁻¹.

meso-1,5-Hexadiyne-3,4-diol

The compound was prepared according to the procedure of Figeys and Gelbcke.¹⁵⁷ The zinc-copper couple was prepared from 47 g. of zinc and 31 g. of anhydrous copper sulfate using the procedure of Gladstone and Tribe.¹⁵⁸ Propioaldehyde (38 g., 0.7 mole) and the zinc-copper were mixed in 200 ml of THF and 42 g. (0.7 mole) of acetic acid and the resultant suspension stirred for 4 hours at room temperature under nitrogen. A brown solid was obtained after filtration and evaporation of solvents. After sublimation (80-83°/0.1 mm), 16 g. of meso-1,5-hexadiyne-3,4-diol (40%), m.p. 101-102° (lit. 101°¹⁵⁷) was obtained.

meso-1,5-Hexadiyne-3,4-ditosylate

This compound was prepared by the procedure of Figeys and Gelbcke.¹⁵⁷ 1,5-Hexadiyne-3,4-diol (11g., 0.1 mole) was treated with 42 g. (0.22 mole) of p-toluene-sulfonyl chloride for 4 days in 27 ml (0.33 mole) of pyridine at

0-5°. Excess pyridine was removed by washing with 10 ml of cold 10% aqueous HCl. The product was extracted into chloroform. Evaporation of the chloroform yielded a powder which was recrystallized (CHCl₃/Petroleum ether, 60-70°) to give 37 g. (88%) of meso-1,5-hexadiyne-3,4-ditosylate, m.p. 156-158° (lit.¹⁵⁷ 157-158°); mass spectrum m/e 418 (p+), 247, 173, 108 and 91.

cis-3-Hexene-1,5-diyne

This compound was synthesized by a modification of the method by Figeys and Gelbeke.¹⁵⁷ 2-(2-Ethoxy-ethoxy) ethanol (EEE) was dried over molecular sieves (4 Å), then distilled. Sodium iodide was powdered and dried under reduced pressure (0.01 mm) in desiccator for 12 hours. The ditosylate was dried in a similar way. A 25 ml three-necked round-bottomed flask was fitted with an addition funnel, a magnetic stirrer and a condenser. The exit of the condenser was attached to four traps in series. The first two traps were cooled to about -5°. The third trap was cooled to -78°. The fourth trap, which could be connected to a glass handling system for low temperature studies was cooled to -196°. The system was evacuated to 0.3 mm. To a solution of 4.95 g. of sodium iodide in 15 ml of EEE maintained at 65-75°, 1.57 g. of 1,5-hexadiyne-3,4-

ditosylate in 15 ml of EEE was added over 9 hours. After 60 hours, the third trap was warmed to -5° . The cis-3-hexene-1,5-diyne, a colorless liquid, was distilled into the fourth trap. Upon exposure to air, the compound rapidly turns green. nmr (CCl_4 , TMS) 3.21 δ (singlet, 2H), 5.81 δ (singlet, 2H), (lit.¹⁵⁹ 5.89 δ , 2H; 3.28 δ , 2H), ir $\nu_{\text{Ar}}^{8^{\circ}\text{K}}$ 622 (s), 639 (s), 727, 752, 755, 1200, 1245 (m), 1630, 1700, 2120, 2145, 2300 and 3320 cm^{-1} (m). (lit.¹⁵⁹ $\nu^{300^{\circ}}$ 723 (m), 752 (m), 2085, 2105, 3295 (s).

Photolysis of cis-3-hexene-1,5-diyne matrix isolated in argon at 8°K

An argon matrix of cis-3-hexene-1,5-diyne was prepared using indirect deposition (ratio 700/1). The reaction was monitored by infrared spectroscopy. Prolonged irradiation using a 200 Watt medium pressure lamp cause slight destruction of starting material and produced new bands at 618 (s), 664 (s), 740, 762, 925, 944, 968, 1220, 1240, 1530, 1565 and 1615 cm^{-1} . The photolysis products were trapped at 77°K and submitted for mass spectral analysis. The only prominent peaks observable at 70 e.v. are: m/e 76, 50, 44, 28 and 18.

Attempted preparation of bis-hydrazone of benzo-1,4-quinone

Hydrazine (6.4 g., 0.2 mole) was added dropwise to of benzoquinone (2.16 g., 0.1 mole) in 100 ml of methanol at 0°. The solution was stirred at room temperature overnight. The gray precipitate which formed was filtered and washed with cold methanol to give 1.92 g. of a solid, m.p. 172° (dec.); nmr (CDCl₃, TMS) 6.5 δ . mass spectrum, m/e 110 (p+), 83, 44; ir (nujol mull) 755, 825, 1200 (s), 1450 (s), 2950, 3000 and 3250 cm⁻¹.

Attempted preparation of cyclohexa-1,4-diene-3,6-ditosylhydrazone

Benzoquinone (2.75 g.) and tosylhydrazide (9.66 g.) were dissolved in 160 ml. of methanol and the solution stirred at 50° overnight. Removal of two-thirds of the solvent yielded no precipitate. On standing for 2 hours at 0°, a white powder (0.67 g.) formed which was collected by filtration, m.p. 89-90°; mass spectrum m/e 258, 246, 215, 139, 123 and 91.

Tricyclo[6,2,1,0^{2,7}]undeca-4,8-diene-3,6-dione

To a slurry of benzoquinone (10.0 g., 0.093 mole) in 60 ml of absolute ethanol at 0°, cyclopentadiene (6.0 g., 0.0924 mole) was added dropwise over 20 minutes. The

reaction mixture was stirred at room temperature for one hour, then heated to 55° for 20 minutes. After the ethanol was removed under vacuum, the yellow solid was recrystallized from Skelly B to give 13.5 g. of tricyclo[6,2,1,0^{2,7}]undeca-4,8-diene-3,6-dione, m.p. 71-73° (lit.¹⁵¹ 71-73°); nmr (CDCl₃, TMS) 1.49δ (multiplet, 2H), 6.48δ (singlet, 2H).

Preparation of bis-tosylhydrozone of tricyclo[6,2,1,0^{2,7}]undeca-4,8-diene-3,6-dione

Tricyclo[6,2,1,0^{2,7}]undeca-4,8-diene-3,6-dione (0.348 g. 0.002 mole) and tosylhydrazide (0.744 g., 0.004 mole) were dissolved in 100 ml of methanol which contained 1 ml of concentrated hydrochloric acid. On standing at room temperature for 20 hours, bright yellow needles precipitated from the solution. Filtration and washing with 80 ml of methanol gave 0.70 g. of bis-tosylhydrazone of tricyclo[6,2,1,0^{2,7}]undeca-4,8-diene-3,6-dione in 70% yield, m.p. 148-149° (dec.) nmr (DMSO-d₆, TMS) 7.22δ (AA'BB' 8H), 6.15δ (singlet, 2H), 5.75δ (singlet, 2H), 3.50δ (broad, 4H), 3.25δ (singlet, 2H), 2.54δ (multiplet, 2H), 2.20δ (singlet, 2H), ir 665 (m), 745, 790 (m), 812, 830, 910, 925, 1052 (m), 1162 (s), 1338 (m), 1600, 1650, 2960 and 3200 cm⁻¹.

Attempted synthesis of bis-tosylhydrazone of benzoquinone from bis-tosylhydrazone of tricyclo[6,2,1,0^{2,7}]undeca-4,8-diene-3,6-dione

A nmr tube contained the bis-tosylhydrazone of tricyclo[6,2,1,0^{2,7}]undeca-4,8-diene-3,6-dione dissolved in DMSO-d₆ was heated to 85°. The reaction was followed by nmr spectroscopy. The starting material was completely destroyed in 30 minutes, and new broad peaks appeared at 6.2δ, 4.1δ, 2.1δ and 1.1δ. Peaks from cyclopentadiene and its dimer were not observed. In a different run, a stream of dry nitrogen gas was passed through the solution and volatile products were collected in a trap cooled to -78°. Analysis of the products collected by infrared spectroscopy showed no cyclopentadiene or its dimer.

An attempt to carry out the reaction in presence of excess tetracyanoethylene, in order to trap the cyclopentadiene, was also unsuccessful.

Disodium salt of bis-tosylhydrazone of tricyclo[6,2,1,0^{2,7}]undeca-4,8-diene-3,6-dione

To a suspension of bis-tosylhydrazone (0.026 g., 0.00005 mole) in 3 ml of absolute methanol, a solution of sodium methoxide (0.0054 g., 0.0001 mole) in 3 ml. of absolute methanol was added. The resulting yellow solution

was stirred for 20 minutes at room temperature.

Evaporation of methanol gave 0.028 g. of title compound (100%), m.p. 243° (dec.); ir 585, 668 (m), 710, 750, 810, 840, 860, 928 (m), 1042 (s), 1080 (s), 1130 (s), 1240 (m) and 1635 cm^{-1} . Acidification of the salt with hydrochloric acid yield a yellow solid which had an identical m.p., ir and nmr spectra of bis-tosylhydrazone of tricyclo[6,2,1,0^{2,7}]undeca-4,8-diene-3,6-dione.

Pyrolysis of the disodium salt of bis-tosylhydrazone of tricyclo[6,2,1,0^{2,7}]undeca-4,8-diene-3,6-dione

A 100 ml three-necked round-bottomed flask was fitted with an addition funnel containing the title salt and an exit tube connected to a trap cooled to 77° K. The cold trap was fitted with two stop cocks so that it could be closed off and later connected to a low temperature ir cell. The flask was heated in a Wood's metal bath to 370° and evacuated to 0.01 mm. The disalt of bis-tosylhydrazone of tricyclo[6,2,1,0^{2,7}]undeca-4,8-diene-3,6-dione was added slowly by trapping the addition funnel. The pressure of the system increased rapidly during the addition. After about 1 g. of the disalt was added, the volatile product which had collected in the trap was transferred on to the window of a 77° K ir cell. The infrared spectrum had

identical bands with those of cyclopentadiene. Benzyne, benzenorbonadiene and 3-hexene-1,5-diyne were not observed. An intractable polymer was left in the flask, which was not further characterized due to its low solubility in common solvents.

1,4-Dihydroterephthalic acid

This compound was prepared in 55% yield following the procedure for synthesis of 1,4-dihydrobenzoic acid.¹⁶⁰

1,4-Dihydro-terephthalic acid had m.p. 330° (lit.¹⁵² 300°), nmr 11.55 δ (broad, 2H) 5.80 δ (broad, 2H), 5.80 δ (singlet, 4H) and 3.65 δ (singlet, 2H).

Preparation of 1,4-dihydroterephthalic acid chloride

Dihydroterephthalic acid (0.58 g., 0.0035 mole) and oxalyl chloride (4.4 g., 0.035 mole) in 25 ml of dry benzene was refluxed for 6 hours under nitrogen. The excess oxalyl chloride was removed under vacuum to give 0.5 g. Of yellow oil. nmr 6.20 δ (singlet, 4H) and 4.3 δ (singlet, 2H). Upon standing a new peak appeared at 8.15 δ . Acidification gave a white solid which has identical infrared spectrum with that of terephthalic acid.

Attempted synthesis of benzo-1,4-quinone-bis-ketene from terephthalic acid chloride and zinc

Terephthalic acid chloride (1.01 g., 0.005 mole) and zinc dust (2.8 g., 0.05 mole) in 150 ml of dry *n*-butylether was refluxed for 4 hours. Filtration and evaporating the solvent gave 1.35 g. of yellow oil. After chromatography on silica gel, 0.58 g. of liquid was obtained, nmr (CDCl₃, TMS), 7.91 δ (singlet, 4H), 4.20 δ (triplet, 4H), 1.21-1.72 δ (multiplet, 8H), 1.01 δ (broad, 6H); ir 730, 1020, 1100, 1120, 1275 (s), 1723 (s) and 2960 cm⁻¹; mass m/e 278 (p+), 223, 206, 167 and 55.

Attempted synthesis of benzo-1,4-quinone-diketene from dihydroterephthalic acid chloride

Dihydro terephthalic acid (0.84 g., 0.01 mole) and oxalyl chloride (9 ml., 0.05 mole) were kept in a flask under nitrogen for 6 hours. After the excess amount of oxalyl chloride was removed, triethylamine (1.01 g., 0.01 mole) was added. The solution was kept in a dry nitrogen box for 12 hours. The reaction mixture was filtered and benzene was evaporated to give yellow solid. Infrared spectral analysis showed no carbonyl or ketene groups. It was not further characterized due to its low solubility in common solvents.

Preparation of 1,9-diketo[2,2]paracyclophane and 1,10-diketo[2,2]paracyclophane

These two compounds were prepared by the procedure published by Dewhirst and Cram.¹⁶¹ 1,9-diketo[2,2]paracyclophane, m.p. 265° (lit.¹⁶¹ ca. 270°); 1,10-diketo[2,2]-paracyclophane, m.p. 218° (lit.¹⁶¹ 222-226°)

Photolysis of 1,9-diketo[2,2]paracyclophane in 2-methyltetrahydrofuran glass at 77° K

Photolysis ($>2000 \text{ \AA}$ or 2537 \AA) of the title compound in 2-methyltetrahydrofuran at 77° K using an 800 Watt mercury vapor lamp or a Penlite caused new absorption to appear at 320 nm (shoulder).

Photolysis of 1,10-diketo[2,2]paracyclophane in 2-methyltetrahydrofuran glass at 77° K

Photolysis of the title compound under the same conditions as the 1,9-isomer caused new absorption to appear at 302 nm (shoulder). Warming the glass to room temperature and recooling to 77° K resulted in the disappearance of the absorption at 302 nm.

Photolysis of 1,4-diiodobenzene matrix isolated in argon at 8° K

An argon matrix of 1,4-diiodobenzene was prepared using direct deposition (diiodide warmed at 50°) photolysis

was carried out under the same conditions used for 1,2-diodobenzene. Irradiation for 3000 minutes caused new bands to appear at 425, 446, 462, 523 and 1495 cm^{-1} . The photolysis products were trapped at 77° K and submitted for mass spectral analysis, m/e 350, 203, 165, 122, 108, 94, 78 (m), 76 (m) and 44.

9,10-Dihydroanthracene-9,10-dicarboxylic acid

This compound was prepared by a modification of the procedure of Mathieu.¹⁶² A 3-l. three-necked round-bottomed flask was fitted with a mechanical stirrer and a tube for introducing carbon dioxide and nitrogen gas near the paddle. Sodium (13.8 g., 0.60 mole) was added in pieces into a mixture of anthracene (50.0 g., 0.28 mole) and 1500 ml of anhydrous ether. Glass beads were added to help breaking the sodium into smaller pieces. The reaction mixture was stirred under a nitrogen atmosphere for 4 hours at room temperature. The nitrogen gas was then disconnected and replaced by carbon dioxide gas. The violet color of disodium dihydroanthracene faded when the reaction was complete (it took about one hour). Ethanol (100 ml) was added to destroy the excess amount of sodium, then 500 ml

of water was added. The organic layer was extracted three times with 600 ml of 10% dilute sodium hydroxide. After acidification of the alkaline layer, it was extracted three times with 300 ml of ethyl acetate. Removal of solvent yielded a slightly yellow solid, m.p. 259-280° (lit.¹⁶³ cis-diacid 265-268° trans-diacid 306-308°), ir (KBr pellet, 700 (m), 758, 940, 1170, 1224 (s), 1245, 1292 (s), 1350 (s), 1440, 1490, 1650 (s), 1715 (s), 2500-3200 cm⁻¹ (broad) nmr (acetone-d₆, TMS) 7.30δ (AA'BB', 8H), 5.10δ (singlet, 2H).

9,10-Dihydroanthracene-9,10-cis-dicarboxylic anhydride

The crude diacid (21 g.) obtained from previous step was refluxed with 50 ml of acetic anhydride for 30 minutes. Chloroform (250 ml) was added. The unchanged diacid was extracted with 0.1 N sodium hydroxide. The organic solution was dried over magnesium sulfate. After evaporation of chloroform, the solid was recrystallized from dioxane to give 6.9 g. of fine colorless needles, m.p. 193° (lit.¹⁶⁴ 194-195°).

9,10-Dihydroanthracene-cis-9,10-dicarboxylic acid

This compound was synthesized by following Beckett and Walker's procedure.¹⁶³ The anhydride (2.0 g.) obtained

from previous step was added to a boiling solution of 0.5 N sodium hydroxide (35 ml) diluted to 120 ml with water. When most of the anhydride had dissolved (10 min.), the solution was rapidly cooled (0°), filtered, and acidified with 0.1 N hydrochloric acid. The precipitated 9,10-dihydroanthracene-cis-9,10-dicarboxylic acid (1.95 g., 91%), m.p. 265-269° resolidified and melted at 306-308° (lit.¹⁶³ 265-268°, 306-308°).

9,10-Dihydroanthracene-9,10-dicarboxylic acid chloride

This compound was prepared using the procedure published by Blomquist.¹⁶⁵ The title compound was obtained as colorless needles, m.p. 156-159° (lit.¹⁶³ 156-158°). nmr 5.70δ (singlet, 2H), 7.51δ (AA'BB', 8H).

Anthraquinone-bis-ketene

Anthraquinone-bis-ketene was prepared using the procedure published by Blomquist and Meinwald.¹⁶⁶ The diacyl chloride (1.5 g., 0.01 mole) was dissolved in dry deoxygenated benzene (10 ml) under a nitrogen atmosphere. The solution was added to triethylamine (2.02 g., 0.02 mole) in 10 ml of benzene. The mixture was allowed to stand for 5 hours. The intense red solution was warmed

to 60°. After filtration and concentration, a red crystal were obtained, m.p. 150° (dec.) (lit.¹⁶⁶ 150°). The infrared spectrum was identical with that published.¹⁶⁴

Photolysis of anthraquinone-bis-ketene matrix isolated in argon at 8° K

An argon matrix of the title compound was prepared using direct deposition. The compound was heated to 45° and the argon was deposited at a rate of 0.2 mm/min. The reaction was monitored by infrared spectroscopy. Irradiation ($\lambda > 2000 \text{ \AA}$) was accomplished using a 1000 Watt medium pressure mercury lamp. New bands rose at 710, 760 and 2140 cm^{-1} . The bis-ketene was only partially destroyed. The photolysis products were trapped at 77° K and submitted for mass spectral analysis, mass spectrum at 70 e.v. : m/e 44, 28 and 18. The residue left on cesium iodide windows was also analyzed, mass spectrum at 70 e.v. 18, 28, 44, 63, 76, 89, 134, 176, 178, 256 and other higher ions. Thin layer chromatographic analysis showed that there was a component which had the same behavior when eluted with chloroform, carbon tetrachloride, hexane, benzene and ethyl acetate as authentic anthracene.

In a different experiment, the reaction progress was monitored by esr spectroscopy. A $g = 2$ signal was observed

(Figure 24) but no triplet signal.

Photolysis of anthraquinone-bis-ketene in 3-methylpentane glass at 77° K

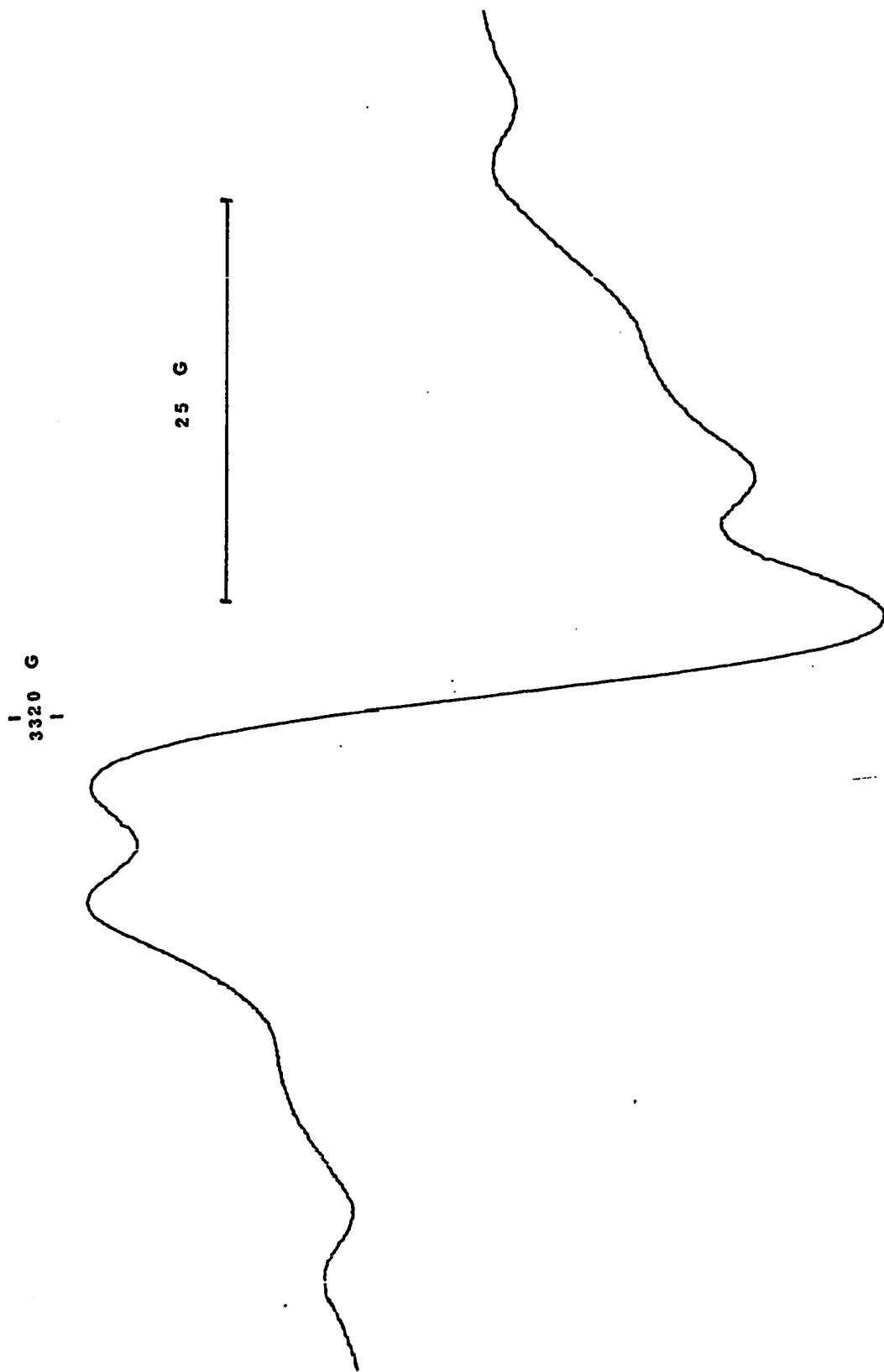
Photolysis ($\lambda > 2000 \text{ \AA}$) of the title compound in 3-methylpentane at 77° K using an 800 Watt mercury vapor lamp caused destruction of starting material to give product with absorption maxima at 256, 276, 320, 345, 363, 378, 397 and 449 nm. (Figure 23). The glass was warmed up to room temperature and recooled to 77° K to caused new absorption maxima at 334, 350, 368 and 388 nm.

Photolysis of anthraquinone-bis-ketene in 3-methylpentane glass containing carbon tetrachloride at 77° K

The photolysis was carried out as previous experiment except the glass containing 5% of carbon tetrachloride. After the species with the absorption maxima at 256, 276, 320, 345, 363, 378, 397 and 449 nm was generated, the glass was warmed up and recooled as previously. New absorption maxima appeared at 351, 358, 362, 370, 376, 381, 390 and 420 nm. Thin layer chromatography analysis showed that there were two compounds which showed the same behavior in chloroform and carbon tetrachloride with authentic anthracene and 9,10-dichloroanthracene.

Figure 24 Irradiation of anthraquinone-bis-ketene,
esr spectrum

After irradiation through quartz filter for
113 minutes in an argon matrix .



Photolysis of dihydroanthracene in 3-methylpentane glass at 77° K

Irradiation (2537 Å) of dihydroanthracene in 3-methylpentane at 77° K using an 800 Watt lamp caused new absorption maxima to appear at 377, 372, 364, 358, 352, 340, 330, 320, 278, 266, 265, 248 and 246 nm. Warming the glass to room temperature and recooling to 77° K resulted in the disappearance of the absorption maxima at 352 nm and slight increase the other previously mentioned absorption maxima.

Photolysis of diphenylmethane in 3-methylpentane glass at 77° K

Irradiation (2537 Å) of diphenylmethane under the same conditions as in the previous experiment with dihydroanthracene produced a new absorption maximum at 335 nm. Warming the glass and recooling to 77° K as previously resulted in the disappearance of the new absorption.

9-Diazo-anthrone

This compound was prepared by the procedure of Regitz¹⁶⁷ from anthrone and tosylazide. 9-diazoanthrone: m.p. 150° (dec.) (lit.¹⁶⁷ 150°), nmr (CDCl₃, TMS) 7.3-7.7δ (multiplet).

Photolysis of 9-diazo-anthrone in 2-methyltetrahydrofuran glass at 77° K

Photolysis ($\lambda > 3500 \text{ \AA}$) of 9-diazoanthrone in 3-methyltetrahydrofuran glass at 77° K using an 800 Watt mercury arc produced new absorption maxima at 354, 522, 550 and 566 nm. Warming the glass to room temperature and recooling to 77° K resulted in the disappearance of all the previous absorption and gave new absorption maxima at 358, 374 and 397 nm. Two isosbestic points were observed (340 and 360 nm).

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