PART I
THE SEARCH FOR BIS[CARBON MONOXIDE] AS A PHOTOELIMINATION PRODUCT FROM BRIDGED α-DIKETONES AT LIQUID NITROGEN TEMPERATURES

PART II
THE PHOTOCHEMISTRY OF 3-METHYLENEDIBENZOBICYCLO[2.2.2]-OCTADIENE-2-ONE AND SOME OF ITS DERIVATIVES

Thesis for the Degree of Ph. D.
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DAVID L. DEAN
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This is to certify that the

thesis entitled

PART I: THE SEARCH FOR BIS[CARBON MONOXIDE] AS A PHOTO-ELIMINATION PRODUCT FROM BRIDGED α-DIKETONES AT LIQUID NITROGEN TEMPERATURES.
PART II: THE PHOTOCHEMISTRY OF 3-METHYLENEDIBENZOBICYCLO[2.2.2]-OCTADIENE-2-ONE AND SOME OF ITS DERIVATIVES.

presented by

David L. Dean

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Harold Hart

Major professor

Date May 2, 1972

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ABSTRACT

PART I

THE SEARCH FOR BIS[CARBON MONOXIDE] AS A PHOTOELIMINATION PRODUCT FROM BRIDGED α-DIKETONES AT LIQUID NITROGEN TEMPERATURES

PART II

THE PHOTOCHEMISTRY OF 3-METHYLENEDIBENZOBICYCLO[2.2.2]-OCTADIENE-2-ONE AND SOME OF ITS DERIVATIVES

By

David L. Dean

In this thesis photochemically induced retro Diels-Alder reactions of bicyclic aromatic compounds were investigated as possible synthetic routes to compounds containing cumulated double bonds.

In Part I of this thesis diketones 5 and 10 were prepared and irradiated at liquid nitrogen temperatures in an effort to obtain bis[carbon monoxide], 1. However, the only nonaromatic product observed was carbon monoxide.

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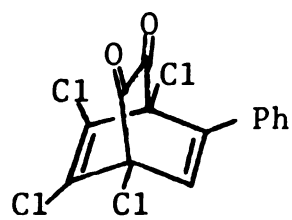

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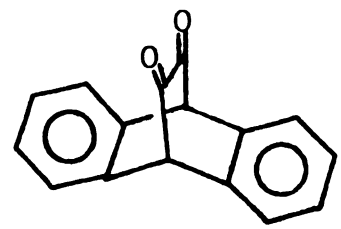

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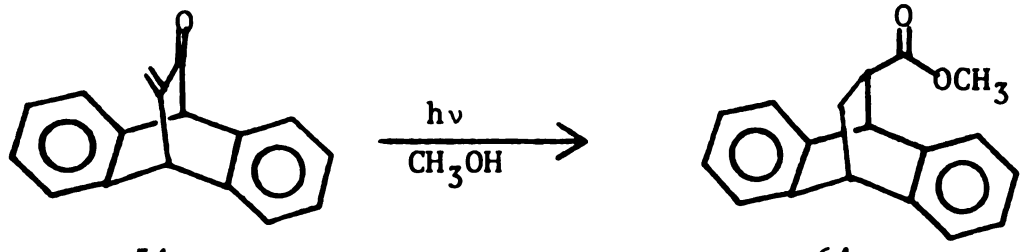
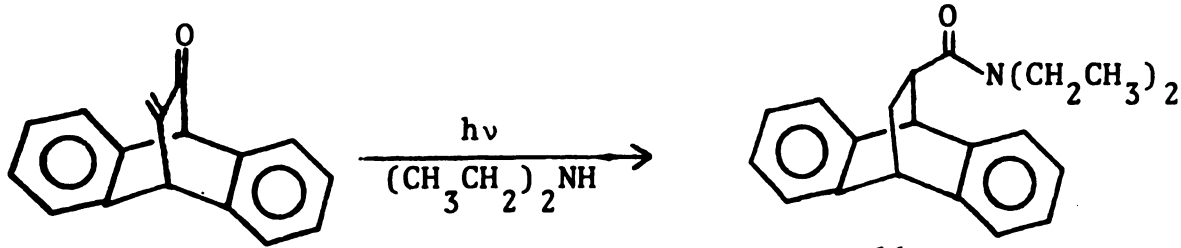
In Part II of this thesis methylene analogs of 10 were prepared and irradiated in an effort to obtain methylene ketenes. Some evidence for this type of cleavage was obtained, although in the examples studied this was never the major reaction that occurred. When enone 54 was irradiated in methanol in an effort to prepare methylene ketene and trap it as methyl acrylate, a new photo rearrangement was observed which gave ester 64 as the main product. Less than 1% of methyl acrylate was observed.



54 64

A ketene intermediate was postulated. It was confirmed when the irradiation of 54 in ether containing diethylamine



54 66

proceeded to give amide 66.

Phenyl substituents on the methylene group allowed the originally anticipated photoinitiated retro Diels-Alder reaction to occur. Irradiation of 69 in methanol gave a

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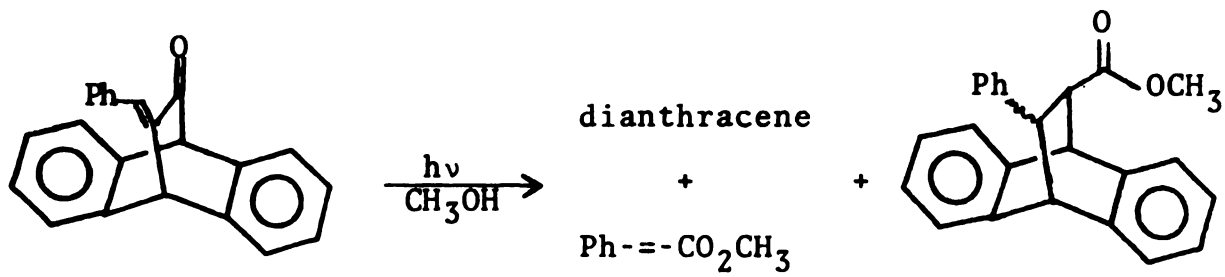
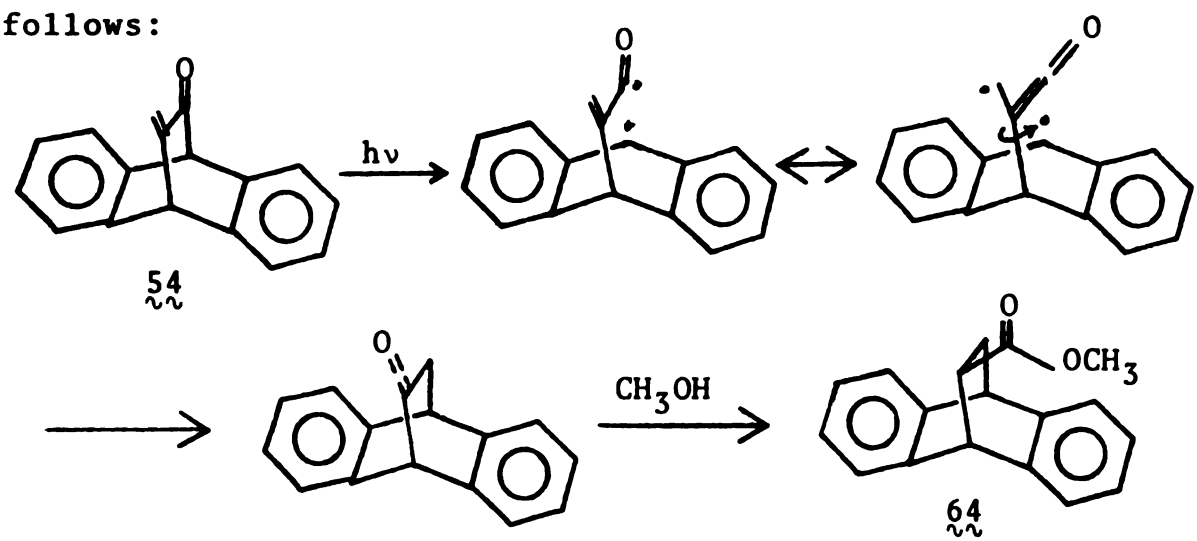


69 42% 58%

42% yield of methyl cinnamates with accompanying formation of dianthracene and a 58% yield of the previously observed rearrangement to give esters. p-Substituents of chloro-, methyl- or methoxy- on the phenyl ring in compound 69 had essentially no effect on the partition between these two reaction paths.

The proposed mechanism for the rearrangement was as follows:



The intermediacy of a ketene had already been established; the turn around was established when the irradiation of compounds 67 and 67a gave 68 and 68a. It was postulated

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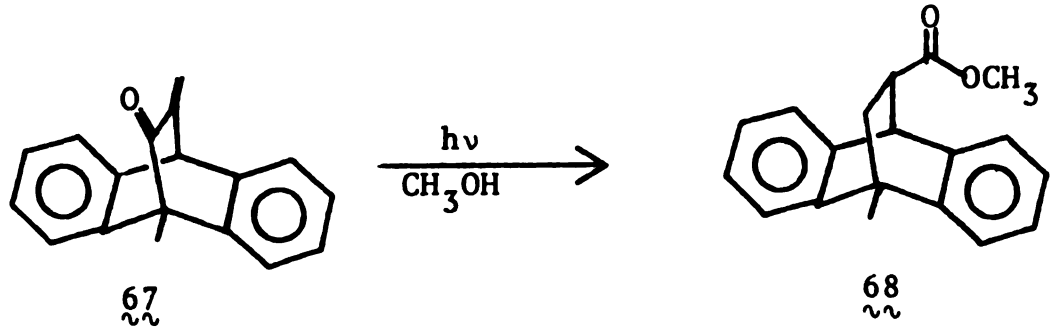

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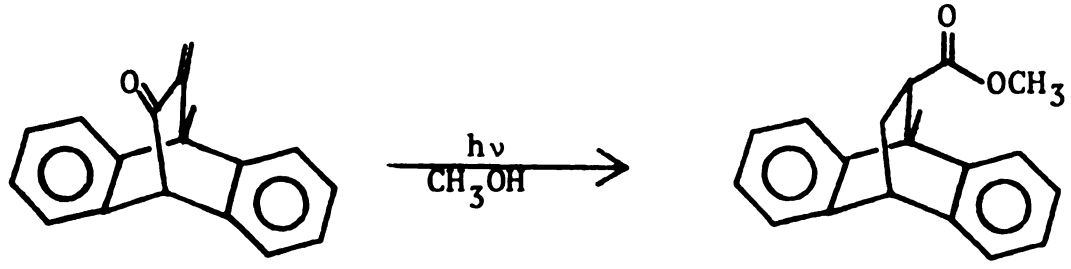

67a 68a

that the phenyl substitution in enone 69 lowered the energy of activation for the elimination reaction and allowed it to compete with the rearrangement.

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PART I

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By

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Department of Chemistry

1972

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PART I

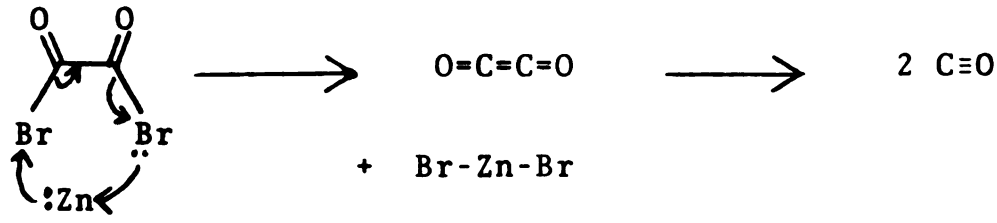
THE SEARCH FOR O=C=C=O AS A PHOTOELIMINATION PRODUCT FROM BRIDGED α-DIKETONES AT LIQUID NITROGEN TEMPERATURES

INTRODUCTION

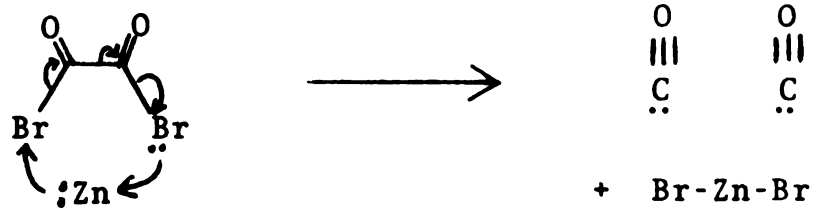
Since they are products of combustion, carbon monoxide and carbon dioxide were two of the earliest gases known to chemists, and accounts of them date from the 18th century. It was not until the 20th century, however, that another member was added to the group of carbon oxides. In 1906 O. Diels and B. Wolf reported the preparation of carbon suboxide by the dehydration of malonic acid with phosphorus pentoxide.[1]

Seven years later H. Staudinger and E. Anthes attempted to add yet another member.[2] Their first attempt to prepare O=C=C=O, $\underset{\sim}{1}$, or di(carbon oxide) as they termed it, was via the dechlorination of oxalyl chloride with zinc. There was no reaction when the two were refluxed in ether, but when the zinc was activated by allowing the metal to react with a little $Ph_2CClCOCl$ and then added to oxalyl chloride in ethyl acetate, the reaction proceeded to give carbon monoxide and zinc chloride. In their next attempt they used oxalyl bromide, which proved to be much more reactive than the chloride. It reacted with zinc shavings in ether to evolve carbon monoxide energetically and even reacted similarly when it was shaken with mercury. The authors concluded that $\underset{\sim}{1}$ must have been formed, but that it could not exist at room temperatures and spontaneously

decomposed into carbon monoxide. While it is possible that



1 was formed, it is just as likely that carbon monoxide was formed directly.



The largest member of this group of carbon oxides ever reported was C_5O_2. In 1937 Klemenc and Wagner reported that the pyrolysis of carbon suboxide at 200° gave a new compound which they concluded must be pentacarbondioxide.[3] However, in 1938 Diels carefully reviewed their methodology and came to the conclusion that their claim was unwarranted.[4]

Bis(dialkyl acetals) of 1 have been known since 1947 when McElvain and Clarke reported the preparation of diethoxy ketene diethyl acetal.[5] In 1964 Hoffmann and Häuser reported the preparation of tetramethoxyethylene.[6] It would appear that mild acid hydrolysis of this compound could produce 1, but instead it is reported that the reaction proceeds to give methyl dimethoxyacetate.[7] This is quite reasonable as the reaction sequence indicates.

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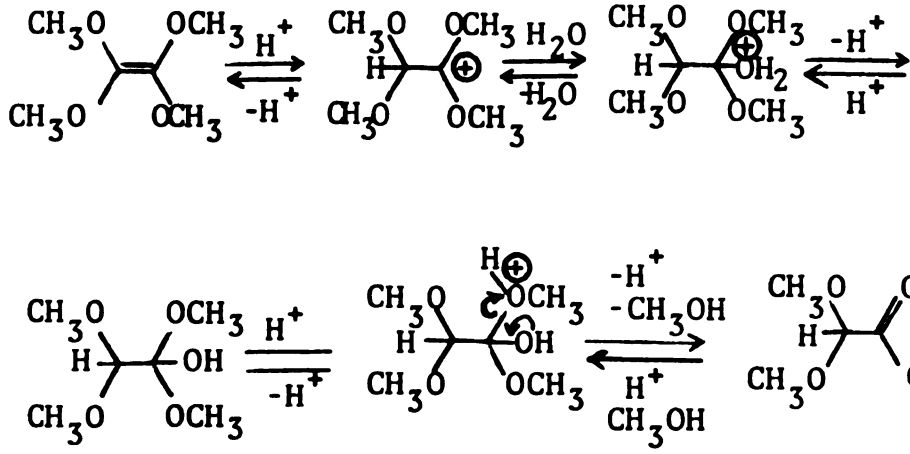
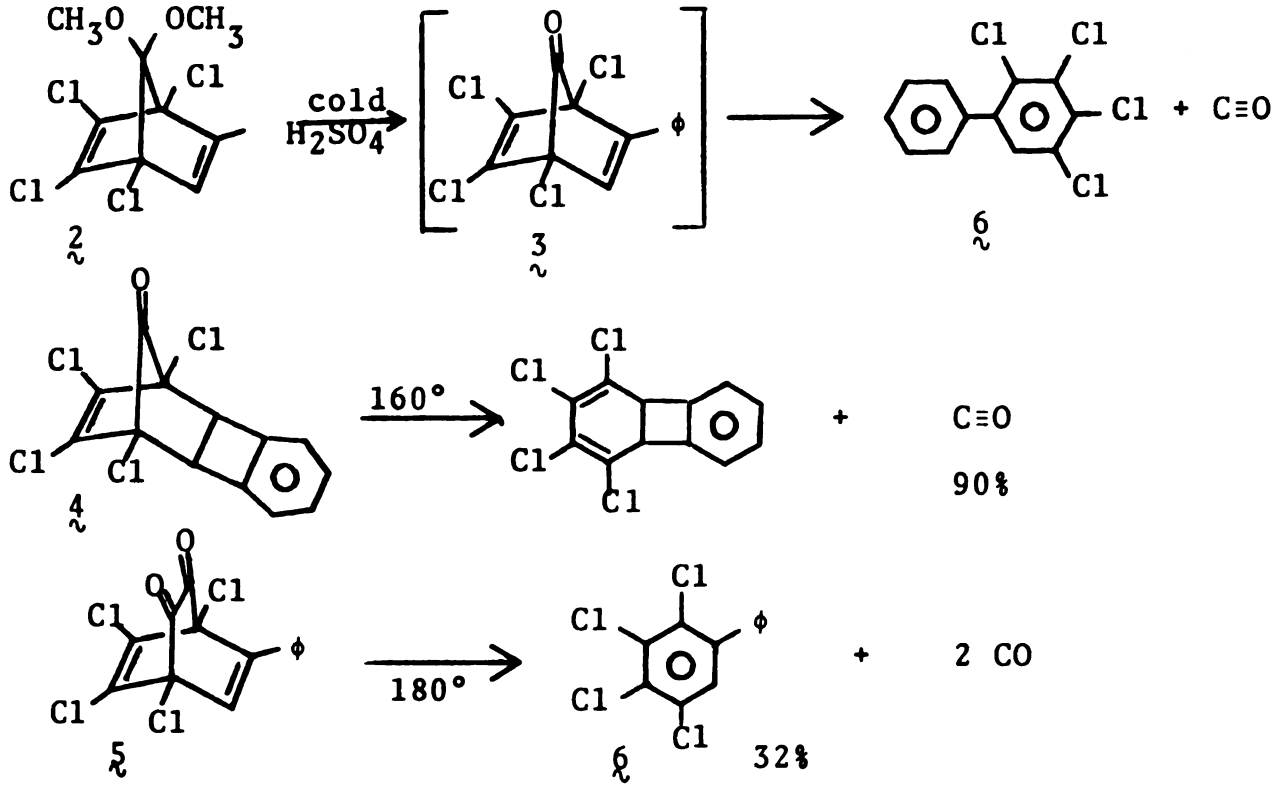


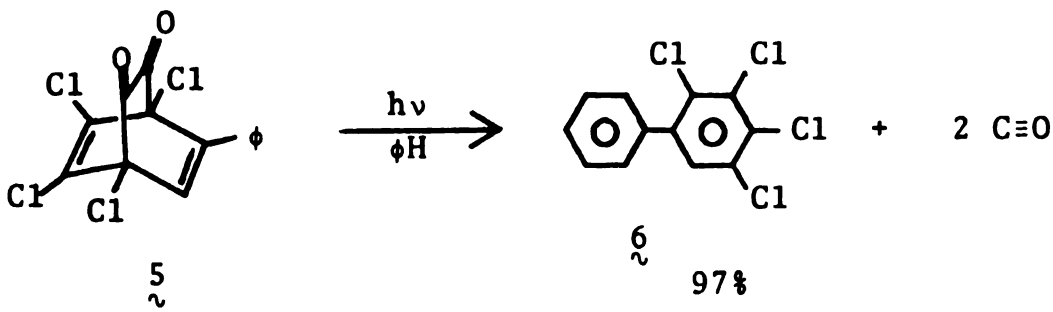
In 1969 Strating et al. attempted to obtain 1 by retro Diels-Alder reactions of compounds that contain a diketone bridge.[8] Since expulsion of the carbonyl bridge from norbornene-7-ones and norbornadiene-7-ones was well known,[9] they reasoned that expulsion of a diketone bridge might be expected from compounds with a similar double bond arrangement.

When several substituted bicyclo[2.2.2]octadiene-2,3-diones had been prepared and pyrolyzed, it was observed that the thermal decomposition of these compounds required much higher temperatures than the norbornene-7-ones and the norbornadiene-7-ones, and that the only volatile product observed was carbon monoxide. In the examples shown the norborn-adiene-7-one 3 was not stable at room temperature (the ketal 2



effervesced when cold sulfuric acid was added to it[7]), the norbornene-7-one 4 decomposed at its mp of 139° and was 90% decarbonylated in 15 min at 160°,[10] and the bicyclo[2.2.2]-octadiene-2,3-dione 5 gave only 32% of the tetrachlorobiphenyl 6 when pyrolyzed at 180°.[8]

In strong contrast irradiation of the diones in benzene at room temperature gave a smooth evolution of carbon monoxide.



This difference in reactivity toward photochemical and thermal eliminations appears to be general. Murray and Hart had previously observed that 1,3,3,4,7,8-hexamethylbenzobicyclo[2.2.2]octadiene-2-one readily eliminated dimethyl ketene on irradiation even at

temperatures as low as -100°, whereas temperatures of 450-550° were required for the thermal reaction.[11] In addition dibenzobicyclo[2.2.2]octadiene-2-one readily produces ketene on irradiation, although it melts at 153° without decomposition.[8]

Strating et al. were never able to observe any 1 or any derivatives of it as a result of their pyrolyses or their room temperature photolyses, although they tried to trap it with 2,3-dimethyl-1,3-butadiene, cyclopentadiene, and chlorine. However, several workers have made 1 the object of theoretical considerations, and all have concluded that 1 should be stable relative to two isolated carbon dioxide molecules.[6,12] However, since the two bicyclic aromatics mentioned above eliminate the bridge as a unit, it is possible that 1 is formed, and that it very rapidly falls apart into two carbon monoxide molecules as a result of the vibrational energy it would have at 298°K. Consequently, part I of this thesis explores the photochemical elimination reactions of two bicyclo[2.2.2]octadiene-2,3-diones at liquid nitrogen temperatures where, if 1 were formed, it might not fall apart immediately due to reduced vibrational energy and might be observable by infrared spectroscopy.

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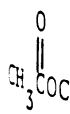

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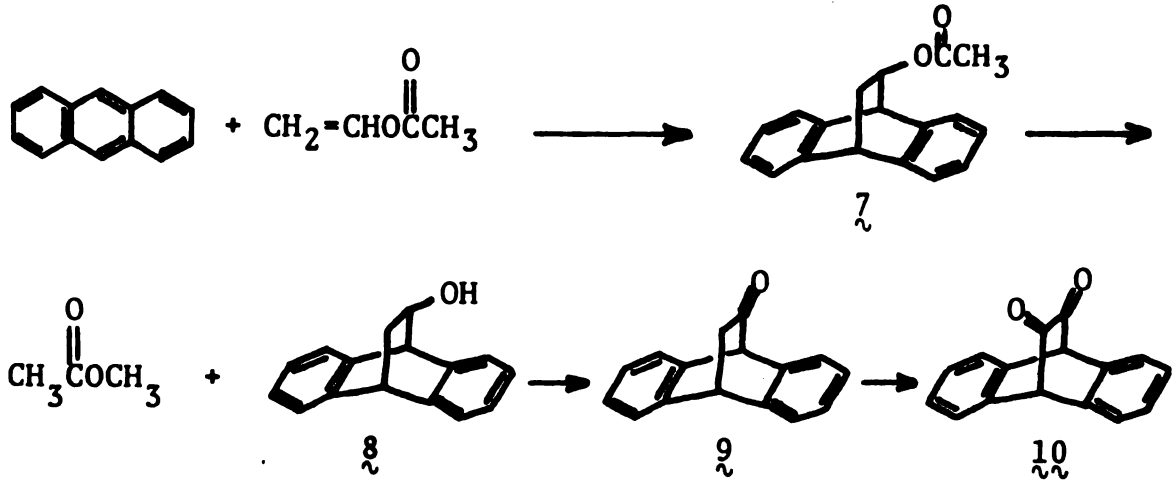
RESULTS AND DISCUSSION

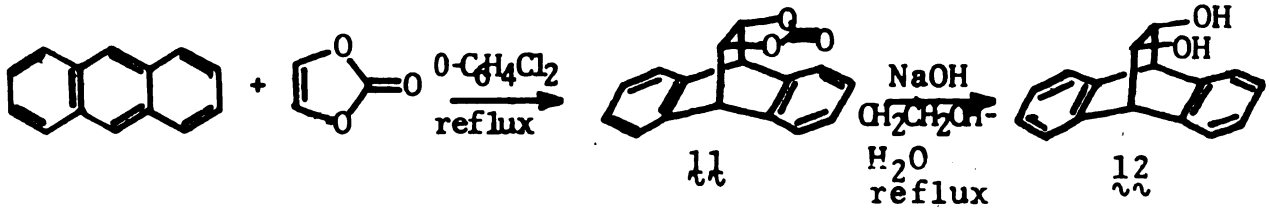
A. The Preparation of Dibenzobicyclo[2.2.2]octadiene-2,3-dione (10) and 1,4,5,6-tetrachloro-7-phenylbicyclo[2.2.2]octadiene-2,3-dione (5)

The known synthetic route for preparing 10 consisted of four steps.[13] They were (1) a Diels-Alder reaction between anthracene and vinyl acetate which gave the acetate 7, (2) an ester interchange which produced methyl acetate and freed the alcohol 8, (3) an Oppenaur Oxidation which gave the ketone 9, and (4) a selenium dioxide oxidation which produced the diketone 10. Reactions (1) and (4) required sealed vessels, and



reaction (4) required the handling of poisonous selenium compounds. The overall yield from anthracene was only 13%. Consequently, it was felt that a superior synthetic route could be found which would be safer, shorter, and have a better overall yield.

A survey of the literature revealed that the diol 12 could readily be prepared from anthracene in 84% yield.[14] The procedure required only two steps, and each could be performed



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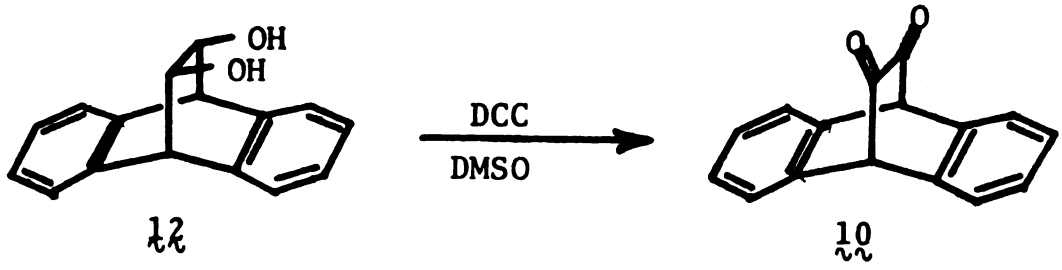
at atmospheric pressure. Oxidation of the diol 12 with the mild oxidizing system dimethyl sulfoxide-dicyclohexylcarbodiimide (DMSO-DCC) gave the diketone 10 in 71% yield. As a result

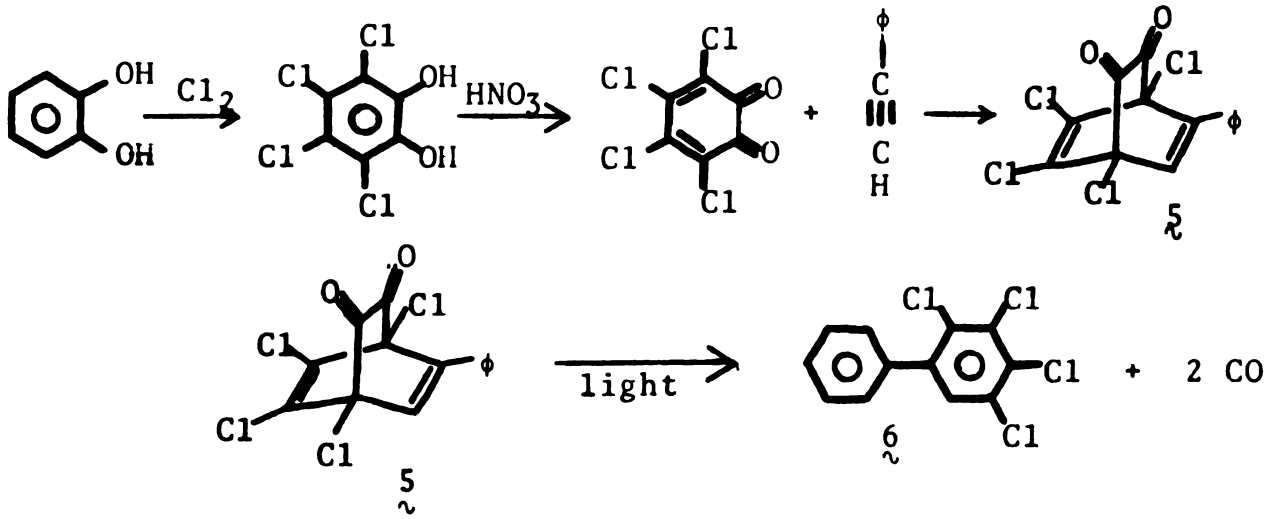


12 10

the synthesis of 10 has been improved from four steps to three, the time required for work-up has been substantially reduced, no poisonous selenium compounds are required, and the yield has been increased from 13 to 60%. A disadvantage of this procedure is the cost of the vinylene carbonate ($1.22/g in 25 g quantities at 1972 prices), but the value of the time saved (at 1972 wages) more than compensates for the cost difference.

The method of Horner and Merz was used to synthesize 5.[15] Phenylacetylene was added to o-chloranil (prepared from catechol via chlorination and oxidation) in a Diels-Alder reaction.

Although the original authors isolated only a quinoxaline derivative of 5 and never 5 itself, the crude product obtained from the Diels-Alder reaction can be dissolved in methylene chloride and the product 5 precipitated by the addition of low-boiling (30-60°) petroleum ether. It is obtained as a white solid which turns yellow when heated and dissolves to give yellow solutions. Its uv spectrum (cyclohexane) shows the characteristic diketone band at 435 nm, and its ir spectrum (KBr) shows a ketone absorption at 1758 cm^{-1}. Since visible



5 6

light provides enough energy to eliminate the diketone bridge photochemically, 5 usually contains some 2,3,4,5-tetrachlorobiphenyl as an impurity.

B. The Technology of Low Temperature Infrared Spectroscopy

Low temperature infrared spectroscopy is a useful technique for the study of molecules which are either unstable at higher temperatures or which would react with each other if not isolated in a matrix. For example, this technique has been used to study the NO_2 radical which usually dimerizes at

low temperatures. Matrix isolation for use in infrared spectroscopy appears to have been initiated in 1954 by Pimentel et al. whose communication in the Journal of Chemical Physics contained the following:

> "The intent of the method is to trap active molecules in a solid matrix of inert material, crystalline or glassy. If the temperature is sufficiently low, the matrix will inhibit diffusion of the trapped molecules, thus holding the active molecule immobile in a nonreactive environment."[16]

The concept was not a new one since Lewis et al. had used rigid solutions of hydrocarbons as matrices to obtain ultraviolet spectra in 1941.[17] However, infrared spectroscopy has different limitations, and different considerations must be applied.

In 1956 Becker and Pimentel listed the desirable properties of a matrix as (1) inertness, (2) rigidity, (3) transparency, and (4) volatility.[18] The matrix should be inert with respect to reactions with the active molecule, since a matrix material that would satisfactorily prevent hydrogen bonding might be quite reactive with radicals. Thus, a matrix material suitable for one study may not be suitable for a different one. The matrix must be sufficiently rigid to prevent diffusion of the active species. This property is usually temperature dependent, and a material that is not satisfactory at a given temperature is often acceptable at a significantly lower one. The matrix must be transparent in the spectral region of interest and must not scatter the incident light. Consequently, a glassy matrix is much better

than a crystalline one. For this reason Lewis et al. used EPA (ether, isopentane, and alcohol) which forms a rigid glass at low temperatures. However, these matrices usually absorb too strongly for infrared work. In the techniques employed by Becker and Pimentel, who studied small molecules, the active molecule was mixed with an inert gas, and the gaseous solution was sprayed on a cold window to form a matrix as it solidified. Thus, volatility was an important consideration in the selection of the matrix material.

The apparatus usually employed in matrix isolation consists of a Dewar with its evacuated area enlarged to hold a sample. The infrared radiation passes through an alkali halide window at the bottom of the Dewar, through the sample mounted in a holder connected to the inside of the Dewar and in thermal equilibrium with the coolant, and out another alkali halide window (see Figure 1).

Murray used 2-methyltetrahydrofuran as a matrix material for the low temperature detection of dimethyl ketene,[19] and Hart and Love reported the observation of a ketene in a pentane matrix at -196°.[20] Chapman et al. have reported the observation of ketenes at low temperatures in an ether-methanol glass and in an EPA glass.[21] These workers were able to observe ketenes in hydrocarbon matrices even though they were previously declared generally unsatisfactory because ketenes have very strong absorptions in the region of 2100 cm^{-1}, where the solvents only absorb weakly.

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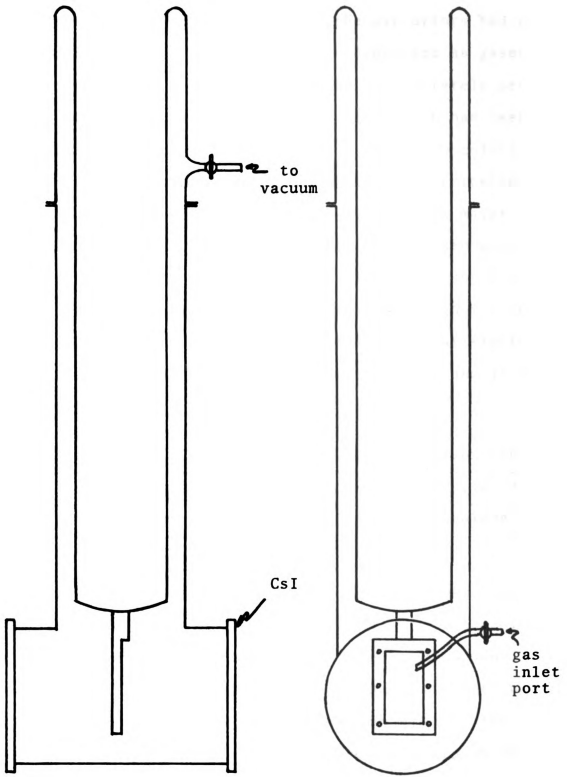
Figure 1. Low temperature ir cell: a modified Dewar



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Several factors were taken into account when various possible matrix materials were considered for use in the low temperature search for O=C=C=O, $\underset{\sim}{1}$: the precursors had very little vapor pressure and could not be deposited as gases, the strength and ν_{max} of $\underset{\sim}{1}$ could not be as accurately predicted as those of ketenes, and a KBr pellet of $\underset{\sim}{5}$ which had been in a desiccator for four days changed from yellow to colorless. Since it is inert, transparent, and allows the photoelimination to proceed, KBr was selected as a possible matrix material. In a trial run it was observed that KBr pellets are also rigid enough to prevent the diffusion and subsequent loss of carbon monoxide at liquid nitrogen temperatures, although the gas did escape on warming. Consequently, KBr was a satisfactory matrix material at liquid nitrogen temperatures, and it was used in this study.

C. The Search For O=C=C=O ($\underset{\sim}{1}$) as a Photoelimination Product from Dibenzobicyclo[2.2.2]octadiene-2,3-dione ($\underset{\sim}{10}$) and 1,4,5,6-Tetrachloro-7-phenylbicyclo[2.2.2]octadiene-2,3-dione ($\underset{\sim}{5}$) at Liquid Nitrogen Temperatures

A yellow KBr pellet of $\underset{\sim}{5}$ was placed in a recess between two brass plates with an opening for the infrared beam (see Fig. 2). The plates were bolted to the holder in the cell shown in Figure 1, the Dewar was evacuated, and liquid nitrogen was placed in the Dewar. After the system had equilibrated for 45 min, the ir spectrum of $\underset{\sim}{5}$ was scanned. The region between 2000 and 2500 cm^{-1} contained no significant absorptions.

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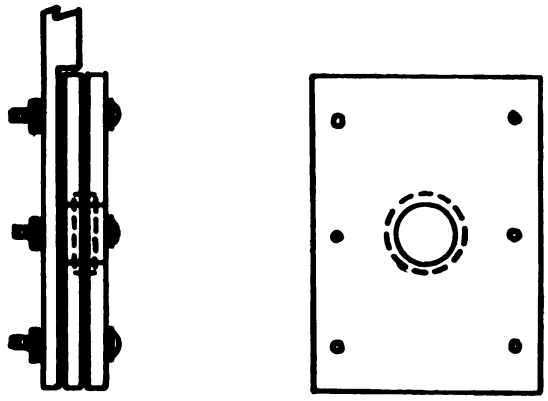

Figure 2. KBr pellet holder for low temperature ir cell.

The sample was irradiated through the CsI window with a Sylvania sun lamp for 30 min, and the 2000 to 2500 cm^{-1} region rescanned. A sharp peak was observed at 2132 cm^{-1}. There were no other new absorptions. A KBr pellet of 10 was treated similarly. This time a single new peak appeared at 2128 cm^{-1}, and a much longer irradiation time was required. In both cases the 2000 to 2500 cm^{-1} region was scanned periodically after all the liquid nitrogen had evaporated and the sample slowly warmed up. The absorption slowly disappeared and no new one took its place.

There are at least two possible carbonyl containing products from these irradiations: carbon monoxide, which had been previously observed at room temperature,[8] and/or its dimer 1. Since only one product is observed at low temperature, the question to be resolved is what it is. There is a substantial amount of data available on the ir spectrum of

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carbon monoxide at low temperatures for comparison. Leroi et al. studied carbon monoxide in an argon matrix at 20°K.[22] They report that it has two ν_{max} - one at 2148 cm^{-1} due to isolated molecules and one at 2138 cm^{-1} due to aggregates. When the sample was allowed to warm to 52°K and then was cooled back to 20°K, and its spectrum was recorded the aggregate peak had shifted to 2135 cm^{-1}. Charles and Lee studied carbon monoxide in krypton and xenon matrices at 20°K.[23] They reported that as the matrix material increases in size, the absorption assigned to aggregates shifts to lower frequencies. In Kr it is at 2135 cm^{-1}, and in Xe it is at 2133 cm^{-1}. In the KBr matrix used in this study, the Br^- is even larger than Xe. If carbon monoxide were present, it would be predicted to absorb at a somewhat lower frequency than it does in the Xe matrix. In addition, there are even larger organic molecules in the matrix which could affect the exact frequency. Since (1) the observed frequencies are very close to the known values for the carbon monoxide aggregates, (2) aggregates should be the species present as the carbon monoxide molecules would be formed in pairs, (3) the observed frequencies in KBr are different from the known values in Xe by only 1 and 5 cm^{-1}, and the matrix change is similar to the change in going from Ar to Xe which produced a comparable change of 5 cm^{-1}, and (4) the predicted decrease in frequency due to the larger matrix material has been observed, the absorptions recorded in the KBr matrix are probably due to carbon monoxide.

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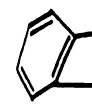
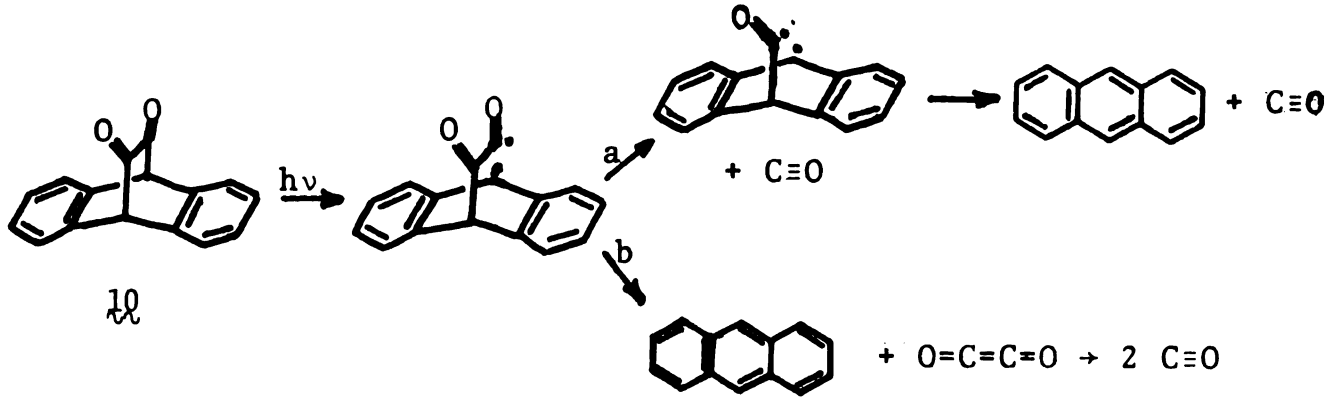


This is consistent with the observation that the absorption disappears on warming; the carbon monoxide simply diffuses out of the KBr matrix.

Two alternative pathways can be postulated to account for the formation of carbon monoxide: (a) stepwise loss of carbon monoxide molecules, or (b) loss of the diketone bridge as a unit which then undergoes either photochemical or thermal dissociation into two carbon monoxide molecules. From the



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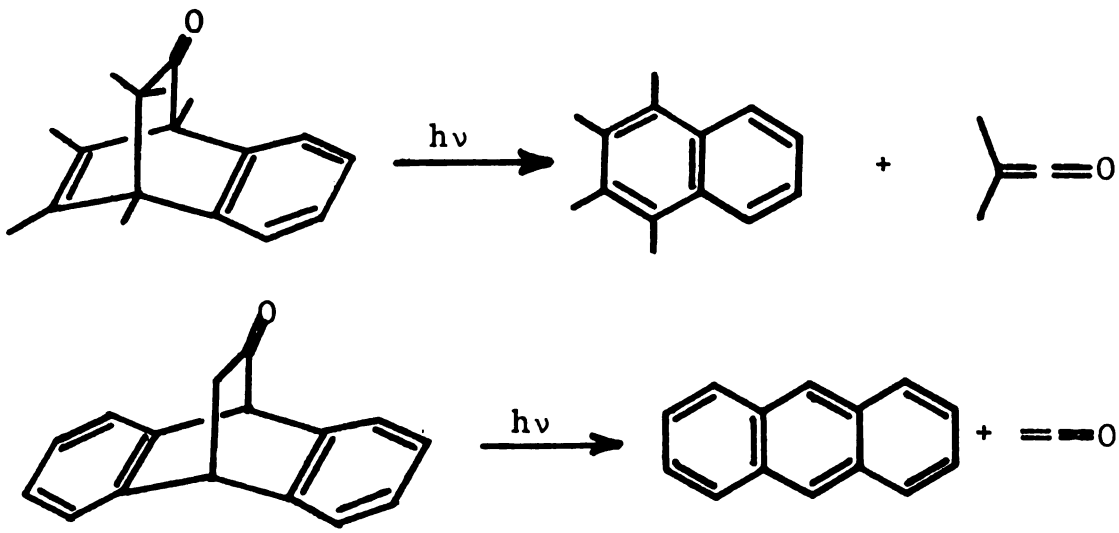
examples mentioned in the introduction it is clear that bridges can be expelled as units.[8,11] However, in each case the



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expelled fragment was a relatively stable molecule that was readily observed. In most reaction sequences which go through discrete intermediates, the intermediate builds up to an observable concentration and then is used up in a subsequent reaction. As nothing but carbon monoxide was observed here, it is unlikely that $\underset{\sim}{1}$ is formed and then dissociates. Thus the most probable reaction pathway is a. However, the data do not absolutely exclude the possibility that $\underset{\sim}{1}$ is formed, and that it very efficiently photochemically dissociates into two carbon monoxide molecules - a process which would keep its concentration sufficiently low as to be unobservable.

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EXPERIMENTAL

A. General Procedures

All nmr spectra were recorded on a Varian T-60 spectrometer in $CDCl_3$ with tetramethylsilane as an internal reference, given the value $\tau = 10.00$. Infrared spectra were obtained on a Unicam SP-200 spectrometer except for the low temperature study in which a Perkin-Elmer 225 spectrometer was used. All spectra of solids were obtained from KBr pellets, and spectra of oils were obtained from a neat smear between salt plates. Ultraviolet spectra were obtained with a Unicam SP-800 spectrometer in cyclohexane (unless specified otherwise). Mass spectra were obtained by Mrs. R. L. Guile on a Hitachi-Perkin-Elmer RMU-6 spectrometer. Melting points were determined on a Thomas Hoover Melting Point Apparatus and are uncorrected. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

B. Diels-Alder Reaction of Anthracene and Vinylene Carbonate: Synthesis of the Cyclic Carbonate of Dibenzobicyclo-[2.2.2]octadiene-cis-2,3-diol (11)

A solution of 55.2 g (0.31 mol) of anthracene and 26.6 g (0.31 mol) of vinylene carbonate in 155 ml of o-dichlorobenzene was refluxed for 46 hr. The crystals that formed as the solution

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was cooled were collected by suction filtration and were washed with hexane. The product 11 weighed 76 g (93%): mp 249-252.5° (lit.[14] 259-259.6°). It was saponified without further purification.

C. Saponification of the Diels-Alder Adduct of Anthracene and Vinylene Carbonate: Preparation of Dibenzobicyclo-[2.2.2]octadiene-cis-2,3-diol (12)

To a solution of 11.5 g (0.288 mol) of NaOH in 760 ml of ethanol and 760 ml of water was added 76 g (0.288 mol) of 11. The mixture was refluxed for 2 hr during which time the suspended material appeared to become finer. After the mixture had cooled overnight, the product 12 was collected by suction filtration and was washed with water. Water (200 ml) was added to the filtrate. The crystals that formed after the mixture had stood overnight were collected by suction filtration and were washed with water to give a combined yield of 62 g, (90%). Recrystallization from toluene-hexane gave colorless needles, mp 202-203° (lit.[14] 201.9-202.7°).

D. Oxidation of Dibenzobicyclo[2.2.2]octadiene-cis-2,3-diol (12): Synthesis of Dibenzobicyclo[2.2.2]octadiene-2,3-dione (10)

To a mechanically stirred, dry nitrogen flushed mixture of 47.2 g (0.23 mol) of dicyclohexylcarbodiimide, 145 ml of benzene (previously dried over 4A molecular sieve), 145 ml of dimethyl sulfoxide (freshly distilled from CaH_2), 18.3 g

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(0.077 mol) of 12, and 6.35 ml (0.079 mol) of pyridine (dried over KOH) was added 3.4 ml of trifluoroacetic acid. The solution immediately began to turn yellow, and soon a precipitate began to form.

After the reaction mixture had been stirred for 24 hr, 24.6 g (0.195 mol) of oxalic acid dihydrate was added slowly; this caused the solution to foam extensively. After it had been stirred for another 30 min, the yellow-orange solution was poured into a mixture of water (600 ml) and chloroform (400 ml). The mixture was agitated, and the solid was removed by suction filtration. The solid was washed with chloroform; all the chloroform filtrates were combined and washed twice with 1N $NaHCO_3$, twice with water, dried ($MgSO_4$), and rotatory evaporated to give 22.6 g of a solid. This was taken up in hot benzene, and the undissolved dicyclohexyl urea was removed by suction filtration. Crystallization afforded 9.15 g (50%) of 10: mp 199-202° (lit.[10] 199-201.5°); nmr τ 2.37-2.78 (m, 8, aryl), and 5.0 (s, 2, bridgeheads); ir 1742 and 1728 cm^{-1} (C=O). The residue can be chromatographed on silica gel with 1:9 hexane-chloroform to improve the yield to 71%.

E. Preparation of Tetrachlorocatechol (13)

Chlorine gas was bubbled into a solution of 40 g (0.364 mol) of catechol in 200 ml of glacial acetic acid until the solution solidified. The white product 13 was collected by suction filtration, and more chlorine gas was bubbled into the filtrate. The process was repeated until no more precipitate formed.

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The yield of the crude product 13 was 83 g (89%). After two recrystallizations from acetic acid, the product 13 had a mp 193-194° (lit.[18] 194°).

F. Preparation of o-Chloranil (14)

A solution of 6.0 g (0.0242 mol) of 13 in 40 ml of glacial acetic acid was cooled until crystals began to form. A solution of 2.2 g (0.0349 mol) of nitric acid in 12 ml of acetic acid was added slowly as the solution was stirred. Ice and water (100 g) were stirred into the mixture 90 sec after the addition of the nitric acid was complete. The red quinone began to precipitate and 10 min later was collected by suction filtration. After the product 14 had been washed with water until it no longer contained acetic acid and had been dried, it weighed 3.57 g (60%): mp 127-129° (lit.[24] 133°).

G. Diels-Alder Reaction of Phenylacetylene and o-Chloranil (14): Preparation of 1,4,5,6-Tetrachloro-7-phenylbicyclo-[2.2.2]octadiene-2,3-dione (5)

A solution of 1.0 g (0.00413 mol) of 14 and 0.42 g (0.00413 mol) of phenylacetylene in 3 ml of benzene was heated on a steam bath for 30 min. The solution was evaporated to dryness, and the residue was dissolved in methylene chloride. The addition of low boiling (30-60°) petroleum ether produced a precipitate. The white solid 5 was collected by suction filtration and melted at 95-97° (lit.[8] 120°) with a change in color to yellow as it was heated. The low mp was probably

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due to the presence of some 2,3,4,5-tetrachlorobiphenyl (mp 92-92.5°), which is produced photochemically by visible light. Spectral data: uv 435 and 255 (sh) nm; ir 1758 cm^{-1}.

H. The Low Temperature Irradiation of 1,4,5,6-Tetrachloro-7-phenylbicyclo[2.2.2]octadiene-2,3-dione (5)

A KBr pellet was prepared containing 1 mg of 5 and 200 mg of KBr. The yellow pellet was placed in the apparatus shown in Fig 1 and Fig 2. The apparatus was evacuated and liquid nitrogen was placed in the well. After the system had equilibrated for 45 min, the ir spectrum was recorded. It contained no significant peaks between 2000 and 2500 cm^{-1}. The apparatus was removed from the spectrophotometer, and the KBr pellet was irradiated for 30 min (Sylvania sun lamp) through the CsI window. After the light was removed, the KBr pellet was observed to have been decolorized. The ir spectrum of the 2000 to 2500 cm^{-1} region contained a sharp new absorption at 2132 cm^{-1} which was assigned to carbon monoxide. No other new absorption was observed in this region.

The temperature of the sample was allowed to rise after the liquid nitrogen was all gone, and the 2000 to 2500 cm^{-1} region recorded periodically. The photochemically produced peak disappeared as the temperature rose, and no other new peak appeared. A room temperature scan of the 5000 to 800 cm^{-1} region gave a spectrum identical to an authentic sample of 2,3,4,5-tetrachlorobiphenyl.

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I. The Low Temperature Irradiation of Dibenzobicyclo[2.2.2]octadiene-2,3-dione (10)

The same procedure was followed with 10 as had been followed with 5. It also formed a yellow pellet. The first difference occurred when it was observed that the pellet was not completely decolorized after 30 min of irradiation. The new absorption, which appeared at 2128 cm^{-1} and was assigned to carbon monoxide, was not as strong as the absorption obtained from 5 had been. Irradiation was continued for a total time of 90 min. The pellet still did not appear to be completely decolorized although the strength of the new absorption had increased. As previously, only one new absorption was observed, and it disappeared when the sample was warmed.

PART II

THE PHOTOCHEMISTRY OF 3-METHYLENEDIBENZO-BICYCLO[2.2.2]OCTADIENE-2-ONE AND SOME OF ITS DERIVATIVES

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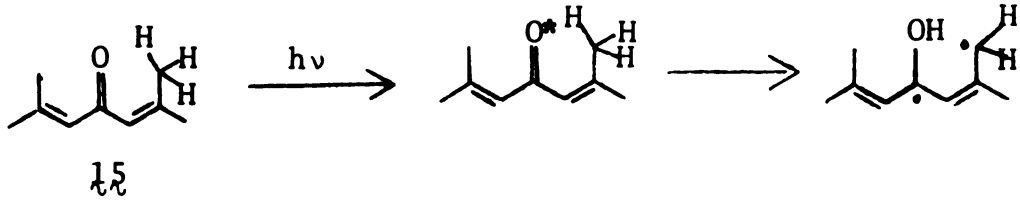
INTRODUCTION

In part II of this thesis the photochemistry of certain bicyclic α,β-unsaturated ketones was investigated and related to the previously known photochemistry of similar compounds. A brief review of the known photochemistry of α,β-unsaturated ketones is presented here.

α,β-Unsaturated ketones undergo a diversity of intra- and intermolecular photochemical transformations, most of which have only been discovered and studied within the last decade. Although the excitation energy always goes into the same moiety, the course of the reaction depends on (1) the entire structure of the molecule, (2) whether the enone reacts from a singlet or a triplet manifold, (3) the polarity of the solvent and whether it has readily abstractable hydrogen atoms, and (4) whether there is another component present, such as an olefin, with which the enone can react.

One of the most common reactions that an α,β-unsaturated ketone can undergo is a deconjugation reaction such as that observed by Meinwald *et al.* with phorone, 15.[25] The reaction appears to be initiated in a manner similar to a Norrish Type II photoprocess, in that the excited carbonyl oxygen abstracts a hydrogen atom from the γ-carbon. Unlike the Norrish Type II process, however, no bond cleavage is necessary to get to a stable state; instead a valence

isomerization gives a β,γ-double bond and the enol form of the ketone 16a which subsequently tautomerizes to the observed product 16b. In the polar solvent system 1:2 methanol:water



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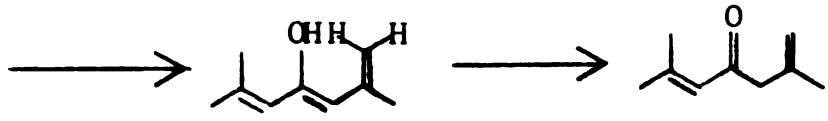
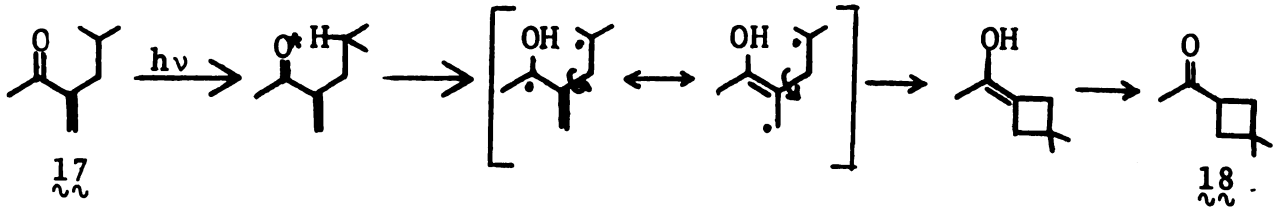


16a 16b

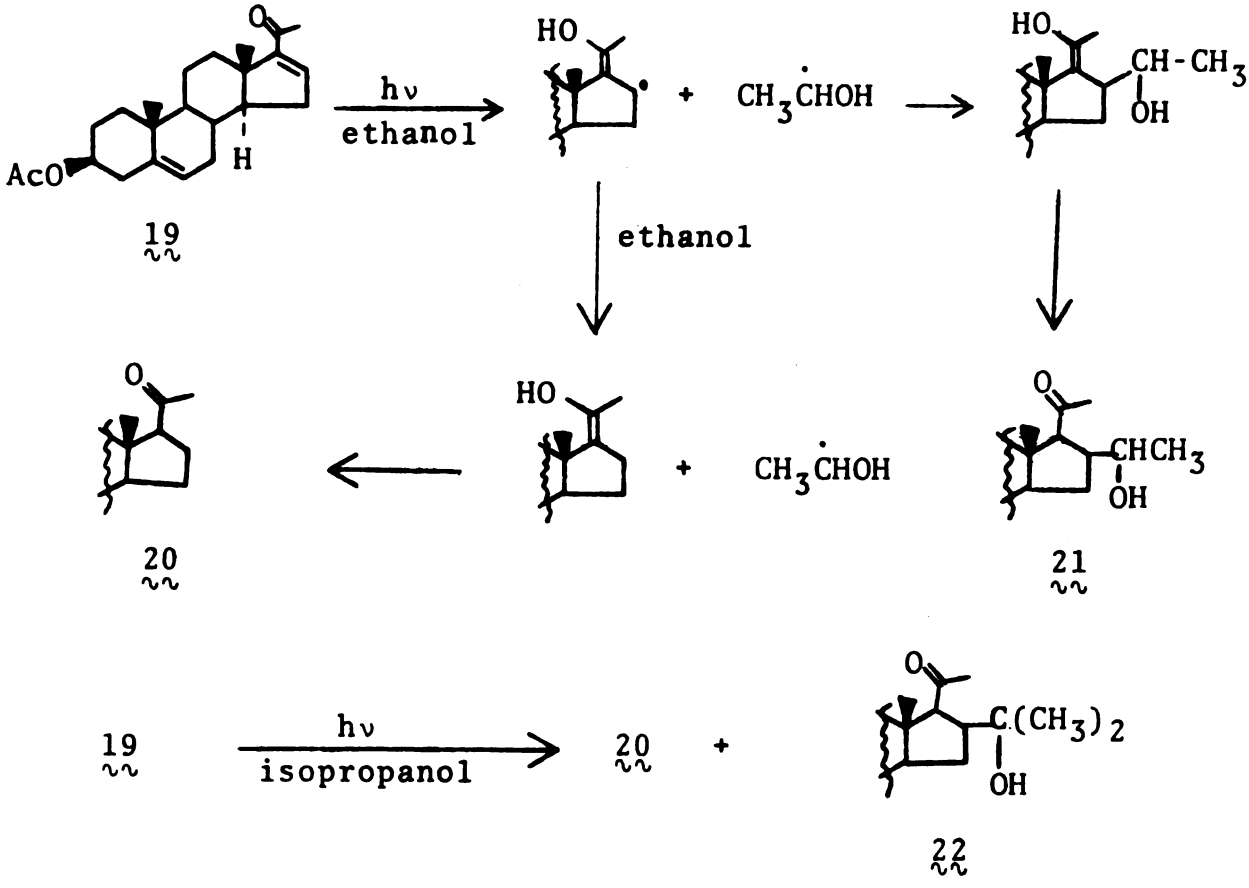
the product 16b was obtained in a 59% yield, whereas in the nonpolar solvent hexane 16b was obtained in only about a 10% yield with the concomitant formation of greater amounts of polymeric substances. Recently Schreiber and Agosta reported a similar reaction which they used to synthesize acyl cyclobutanes from α-methylene ketones.[26] For example, irradiation of 17 in pentane gave 18 in 68% yield.



17 18

Bladon and Williams have shown that when there are no γ-hydrogens available for an intramolecular abstraction, the excited chromophore can abstract a hydrogen atom from the solvent.[27] The resultant allylic radical either abstracts

another hydrogen atom from the solvent to give a net addition of H_2 and reduction, or it couples with a radical in the solution. If it couples with a solvent radical the net result is addition of a solvent molecule to the substrate. Thus the steroid 19 gave 20 (40%) and 21 (also 40%) on irradiation in ethanol. Similarly 20 and 22 were obtained in isopropanol.



When the double bond of the α,β-unsaturated ketone is contained in a five or six member ring and no γ-hydrogens are available, the most frequently observed photochemical reaction is dimerization. Hammond et al. have found that 2-cyclohexenone dimerizes in high yield in a variety of solvents to give head-to-tail and head-to-head dimers, 24 and 25, in ratios

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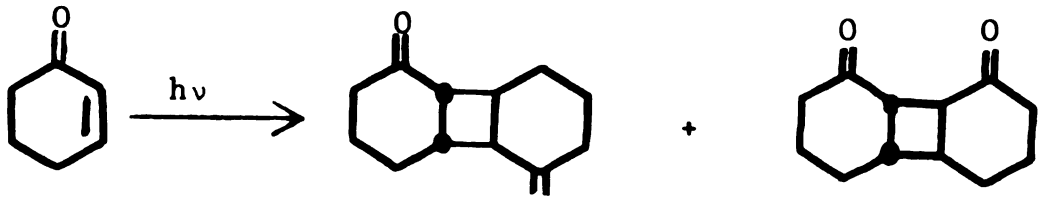

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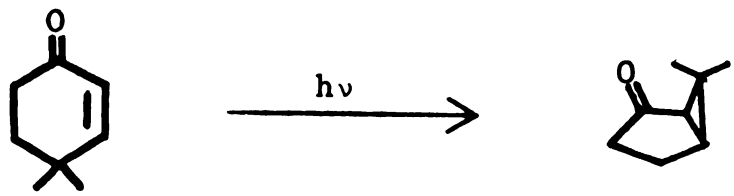
which has only a small dipole moment, is the major product. However, in polar solvents, 25, which has a larger dipole moment, becomes the major product. The reaction occurs between a ground state molecule and a triplet state excited molecule; E_T is 61 kcal/mol.[28]

Dauben et al. have reported that most substituents do not appreciably affect the photodimerization reaction of 2-cyclohexenones,[29] but, as Chapman et al. have shown, when the enone is disubstituted in the 4 position a different reaction can occur. For example, 26 gave 27 in 60% yield on irradiation in t-butanol. This reaction is very solvent dependent; it proceeds



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well in t-butanol, but does not go at all in benzene or cyclohexane. In acetic acid a photoinduced rearrangement occurs, but in this case the bicyclic compound 27 is only a minor product. A mixture was obtained which consisted of

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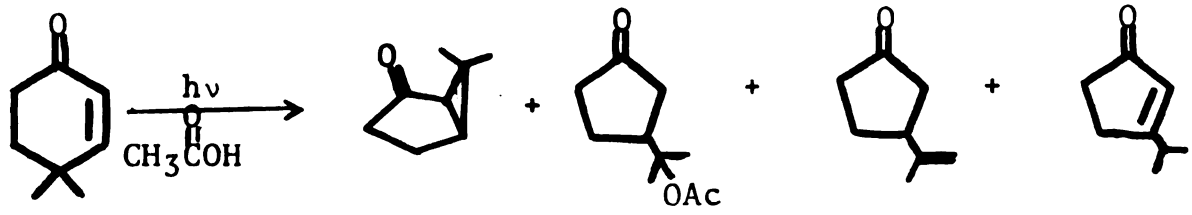
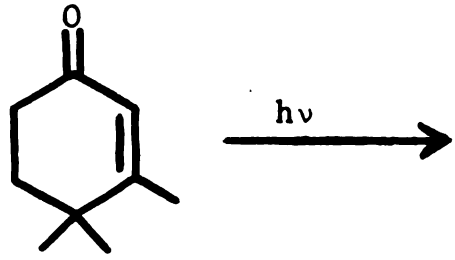
27 (5%), 28 (30-40%), 29 (20-25%), and 30 (5-10%). From the



26 27 28 29 30

nature of these products, which are similar to the types of compounds usually obtained in acid rearrangements (26 is stable in acetic acid in the dark), the authors concluded that the intermediate in the photoinduced rearrangement must have a substantial amount of carbonium ion-like character.[30]

Disubstitution at the 4-position appears to be a necessary condition for rearrangement to bicyclic structures like 27 (so-called lumi products, because of the similar rearrangement of santonin to lumisantonin which was discovered earlier), but it is not a sufficient condition. The presence of an additional methyl group in the 2 or 3 position is enough to suppress this photorearrangement. Thus, 31 gave only dimers and polymers on irradiation.[29]



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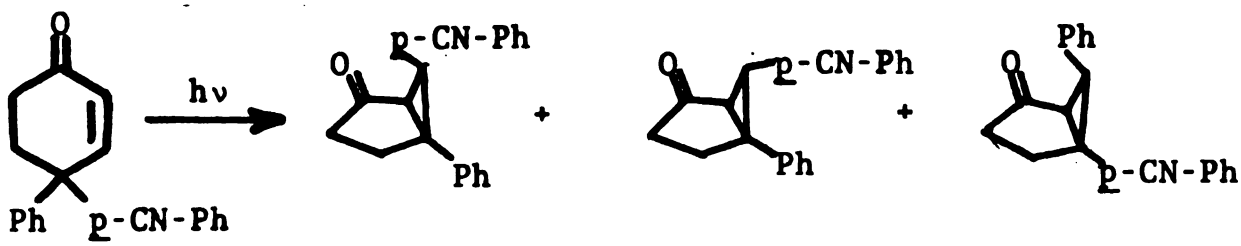
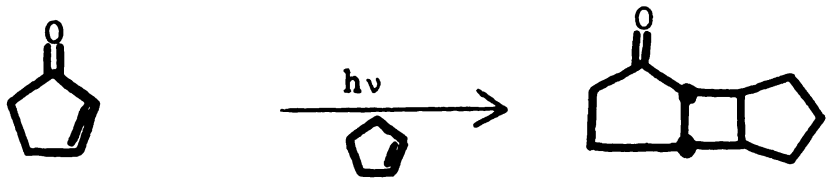
Zimmerman and Lewin reported that the irradiation of 32 gave 33, 34, and 35 in the ratio of 166:1:15. Thus, lumi



32 33 34 35

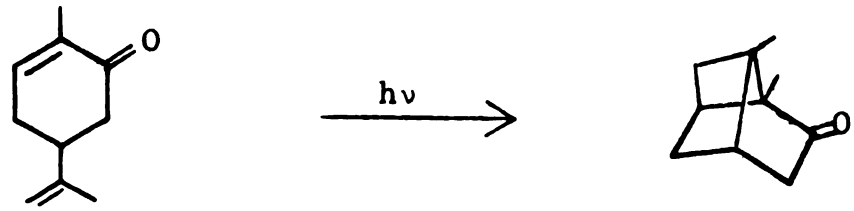
products are formed when the 4-position of 2-cyclohexenone is disubstituted with aryl groups, but the aryl substituents are on different carbons in the products than their alkyl counterparts were. The reaction can be sensitized by propiophenone and quenched by dienes; thus, it proceeds from the triplet state. From quantum mechanical considerations and the fact that the p-cyanophenyl group migrates preferentially, the authors concluded that the intermediate cannot be electron deficient as was suggested for the dimethyl case, but must proceed through an odd electron center.[31]

Eaton has shown that when 2-cyclopentenone, 36, is irradiated in the presence of olefins, an intermolecular cyclo-addition occurs at the carbon-carbon double bond to give products such as 37.[32] de Mayo et al. have found this



36 37

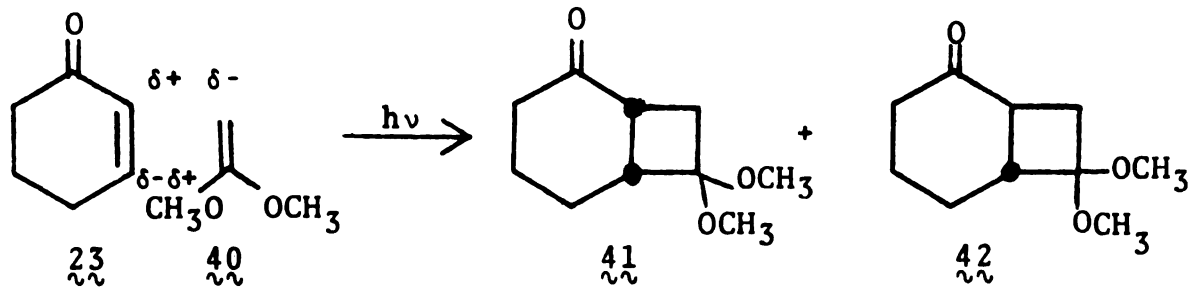
to be a triplet state reaction.[33] Büchi and Goldman had previously demonstrated that similar intramolecular cycloadditions were possible by the photochemical conversion of carvone, 38, to carvone camphor, 39,[34] but Eaton was the first



38 39

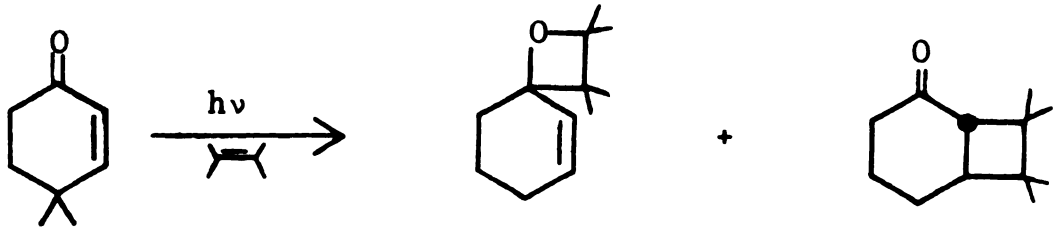
to realize the generality of cycloaddition reactions between α,β-unsaturated ketones and compounds containing multiple bonds.[35]

Corey et al. studied the cycloaddition reaction of 2-cyclohexenone with several olefins and concluded that the cyclobutane ring is formed in a two-step process with a 1,4-diradical intermediate, and that the orientation of addition could be explained by an initial oriented π-complex. A typical example is the reaction between 23 and 40, which produces 41 (21%), and 42 (49%).[36]



23 40 41 42

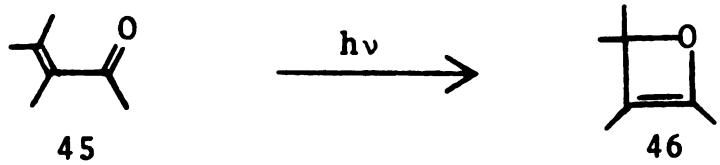
Yet another reaction type is the formation of oxetanes by addition of olefins to the carbon-oxygen double bond. Chapman et al. have reported that when 4,4-dimethyl-2-cyclohexenone, 26, was irradiated in tetramethylethylene, the major products were the oxetane 43 (47%) and the trans-cyclobutane 44 (42%).[37] Turro et al. have found that for



26 43 44

saturated ketones (1) oxetane formation proceeds from the singlet state, (2) olefins quench fluorescence, and (3) the energy transfer interaction proceeds most effectively when the olefin can lie above or below the carbonyl faces.[38] Consequently, perhaps the reason that this is the only reported case of intermolecular oxetane formation from an α,β-unsaturated ketone is because other enone-olefin pairs studied were too sterically hindered to approach close enough to achieve the necessary orbital overlap before intersystem crossing to the triplet occurred.

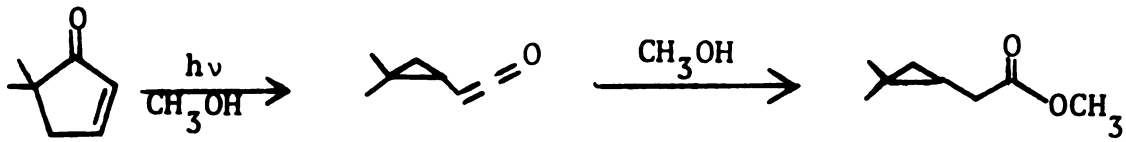
Intramolecular oxetane formation has been observed by Friedrich and Schuster. Irradiation of 45 gave 46 which is



45 46

actually an oxetene rather than an oxetane.[39] The olefinic part of this enone is structurally very similar to tetramethylethylene and the high degree of methyl substitution on the olefin may have been an essential factor contributing to the success of this reaction.

When an α,β-unsaturated ketone is sufficiently substituted with radical-stabilizing groups in the α'-position, it can formally undergo a Norrish Type I cleavage. The diradical thus formed has been observed to either valence isomerize to a ketene or rearrange through an acyl migration. Thus Agosta et al. have observed that on irradiation enone 47 produces ketene 48 which reacts with the solvent to give ester 49.[40]



47 48 49

With enone 50 both ketene formation and acyl migration are possible because of the presence of β,γ- as well as α,β-unsaturation. The solvent system determines which product is formed. Irradiation of the neat film of 50 at -190° gave the ketene 51 as did the irradiation of a solution of 50 in methanol.[41] However, the irradiation of a solution of 50 in acetonitrile gave 53 as the product of an acyl migration.[42]

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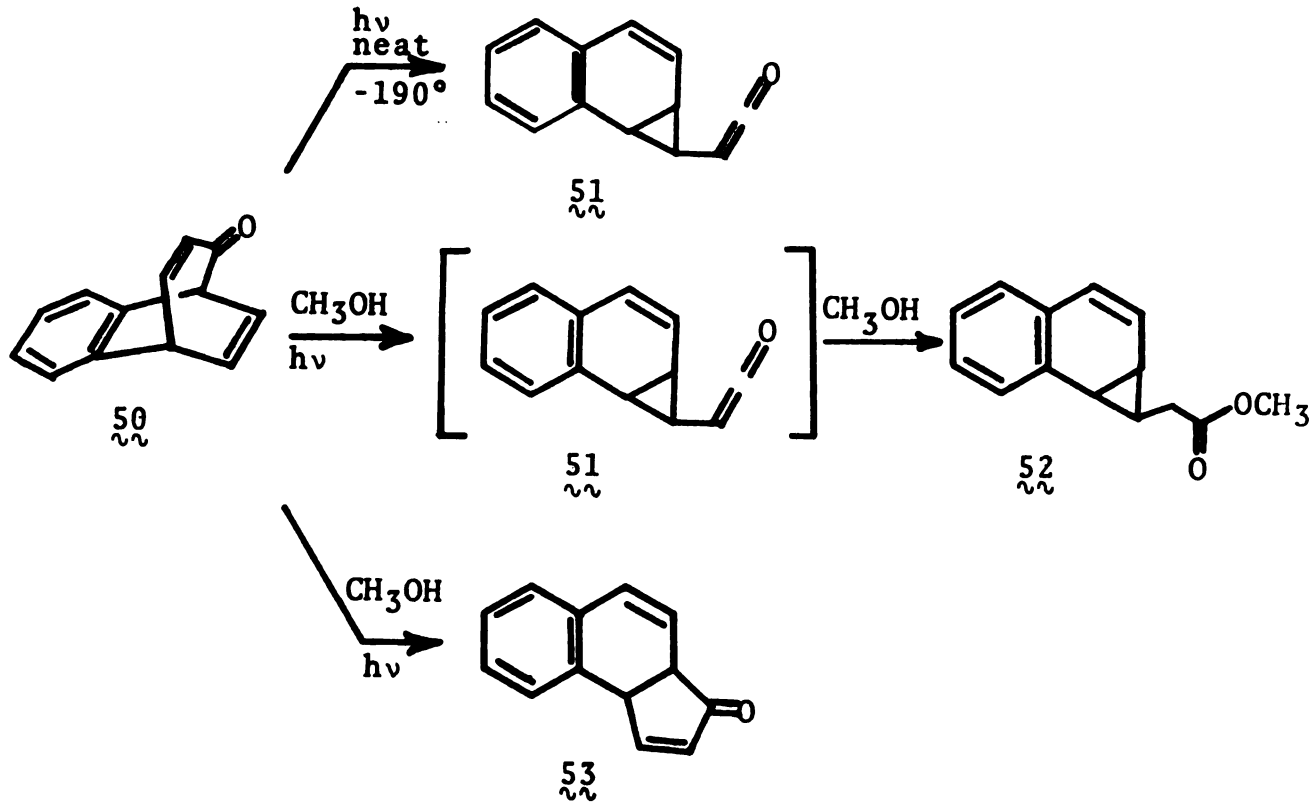
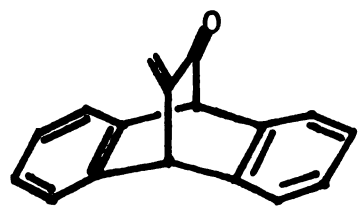


Loss of the bridge with formation of naphthalene (and cyclopropenone) was not observed from the photolysis of 50, although several examples of photochemical bridge expulsions from bicyclic aromatics to give polynuclear aromatic products have been reported (see page 16).[8,11] In part II of this thesis the photochemistry of 3-methylenedibenzobicyclo-[2.2.2]octadiene-2-one, 54, and its vinyl substituted analogs



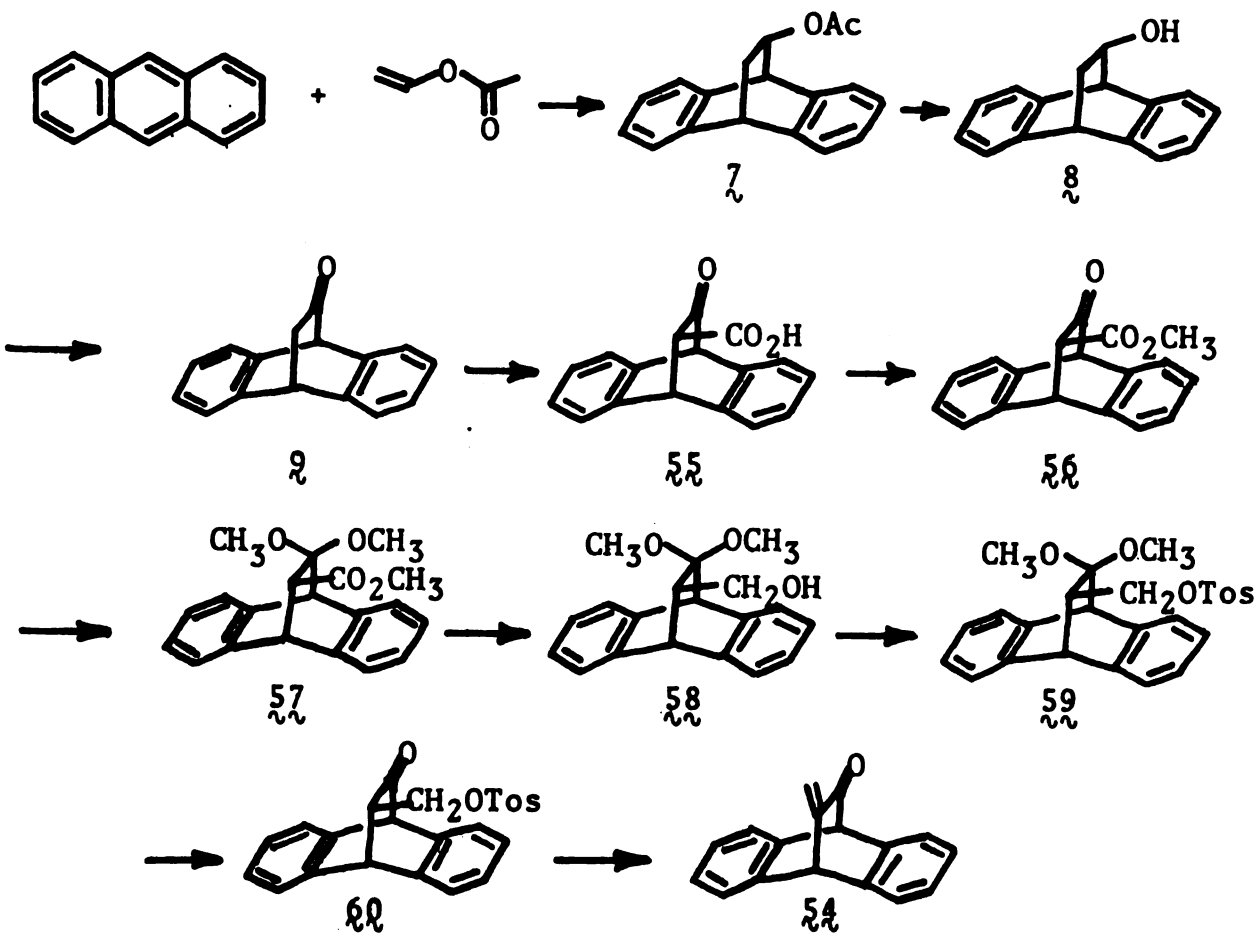
54

was investigated to determine whether (1) they would eliminate the bridge and thus provide a new synthetic route to methylene ketenes, (2) they would react in a manner similar to some of the other reactions described in this introduction, or (3) they would react in new and different ways.

RESULTS AND DISCUSSION

A. The Synthesis of 3-Methylenedibenzobicyclo[2.2.2]octadiene-2-one (54)

The parent enone 54 was already a known compound when the decision was made to study this α,β-unsaturated bridged bicyclic system. In 1960 Snyder and Clement reported its synthesis using the ten-step sequence shown below.[43] This sequence can be divided into two basic parts: the preparation of ketone 9 from anthracene, and the preparation of enone 54 from ketone 9.



7 8 9 55 56 57 58 59 60 54

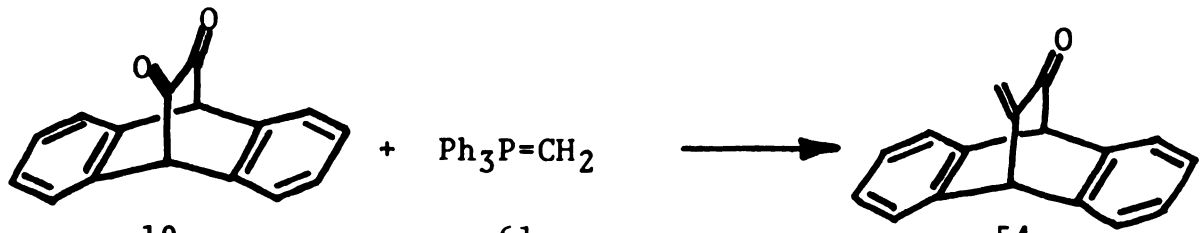
The preparation of ketone 9 used by these authors was very similar to that of Wawzonek and Hallum who obtained acetate 7 by a Diels-Alder reaction of anthracene and vinyl acetate, freed alcohol 8 by a trans-esterification of acetate 7 with methanol, and prepared ketone 9 by an Oppenaur Oxidation of alcohol 8.[44] Snyder and Clement varied this procedure by using lithium aluminum hydride to convert acetate 7 to alcohol 8, and obtained the ketone in an overall yield of 45% from anthracene.

The preparation of enone 54 from ketone 9 reported by these authors required seven steps. Ketone 9 was converted to acid 55 by successive treatments with sodium triphenylmethide, carbon dioxide, and aqueous hydrochloric acid. Esterification of 55 with diazomethane gave keto-ester 56, and ketalization with methanol, ethyl orthoformate, and p-toluenesulfonic acid gave the ketal-ester 57. Reduction of 57 with lithium aluminum hydride afforded alcohol 58, which, when reacted with p-toluenesulfonyl chloride in pyridine, yielded the tosylate 59. Trans-ketalization of 59 with p-toluenesulfonic acid in acetone gave keto-tosylate 60, which was eliminated to the desired enone 54 with sodium hydroxide in aqueous dioxane. The overall yield of 54 based on ketone 9 was 25%; based on anthracene it was 11%.

The synthetic route to enone 54 chosen by Snyder and Clement was determined in a large part by their desire to study elimination reactions of its immediate precursor, compound 60, and was not chosen simply because they had determined it to

be the most efficient synthesis of 54. As the object of the current investigation was simply to study enone 54, a shorter and more efficient method for its preparation was desired.

The first route tried was a mono-Wittig reaction on diketone 10 since it had been prepared for part I of this thesis and was available. The reaction was run with various ratios of

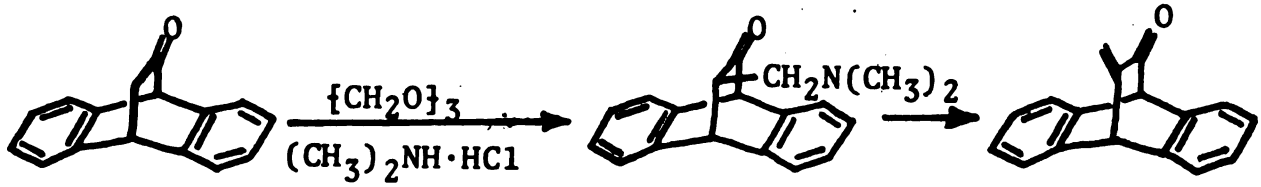


10 61 54

diketone 10 and Wittig ylid 61 (prepared by the method of Corey et al.[45]). It always gave the desired monomethylene derivative, enone 54, although the yield did vary. The best yield (50%), which was depressed by the use of either more or less ylid, was obtained with a 10:61 ratio of 1:2.5. The overall yield of 54 from anthracene by this procedure was 30%, an improvement over the method used by Snyder and Clement with an accompanying reduction in the number of steps required from ten to four. However, since as noted previously the vinylene carbonate required in this sequence is expensive, and since the last step proceeded in only 50% yield, it was anticipated that an even better synthetic route could be devised.

If enone 54 could be obtained from ketone 9 in one or two short steps in good yield, a substantial improvement over Snyder and Clement's procedure should result through the elimination of five or six steps. From a review of the

literature it was learned that (1) compound 62 was known,[46] and that (2) Mannich bases of this type readily eliminate an amine to produce an enone.[47] When ketone 9, dimethylamine hydrochloride, and paraformaldehyde were refluxed in isoamyl alcohol under conditions similar to literature procedures,[48] it was observed that the intermediate Mannich base 62 underwent elimination to give the desired enone 54. Under optimal



9 62 54

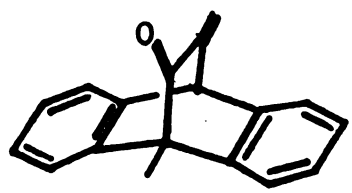
conditions for the production of enone 54, a sevenfold excess of paraformaldehyde and dimethylamine hydrochloride refluxed with ketone 9 in isoamyl alcohol for 24 hr resulted in a two layer reaction mixture and the formation of 54 in 80% yield.

When it was subsequently discovered that the mild oxidizing system DMSO-DCC raised the yield for the conversion of alcohol 8 to ketone 9 to 89% from the 78% reported by Wawzonek and Hallum for the Oppenaur Oxidation, a new more efficient procedure for the preparation of enone 54 had been achieved. It can now be synthesized in four steps from anthracene in 41% overall yield, almost four times better than Snyder and Clement's overall yield, and about one and a third better than the route via diketone 10.

The nmr spectrum of 54 had singlet absorptions at τ 4.03, 4.58, 4.93, and 5.05, which were shifted by $Eu(fod)_3$ in the

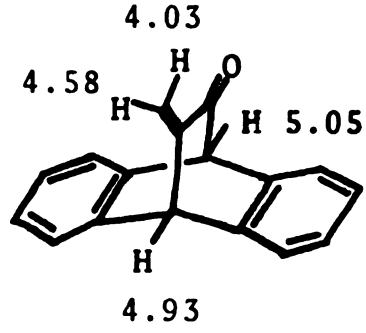
respective ratios of 2.5, 1.0, 1.0, and 2.6. In general, the amount of shift is dependent on the dihedral angle between the proton shifted and the carbonyl, and is inversely proportional to the distance between the proton shifted and the carbonyl.[49] Since all the protons in question are in the same plane as the carbonyl group, the shift is dependent only on the distance from the carbonyl oxygen.

The proton that absorbs at τ 5.05 is adjacent to the carbonyl since it is shifted the most by $Eu(fod)_3$ and has a chemical shift similar to that of the bridgehead protons in diketone 10, which absorb at τ 5.00. Since the proton at τ 4.03 is shifted a similar amount by $Eu(fod)_3$), it must be the vinyl proton cis to the carbonyl. Assignments for the protons with degenerate $Eu(fod)_3$ shifts rest on a comparison with the similar compound 67 for which the proton nmr



67

assignments are known. In 67 the bridgehead proton absorbs at τ 5.05, and the methylene proton trans to the carbonyl absorbs at τ 4.67.[50] Thus it seems reasonable to conclude that the τ 4.58 absorption in 54 is due to the methylene proton trans to the carbonyl, and the τ 4.93 absorption is due to the remaining bridgehead proton. The nmr assignments are summarized in the following structure:

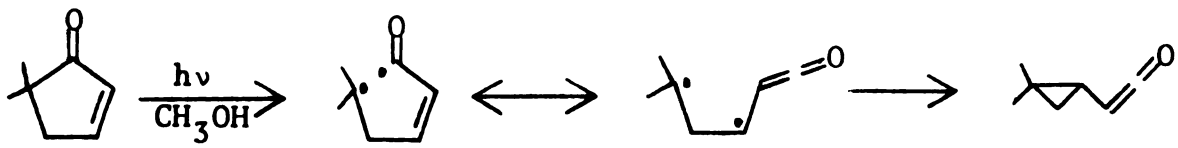


B. The Photochemistry of 3-Methylenedibenzobicyclo[2.2.2]octadiene-2-one (54)

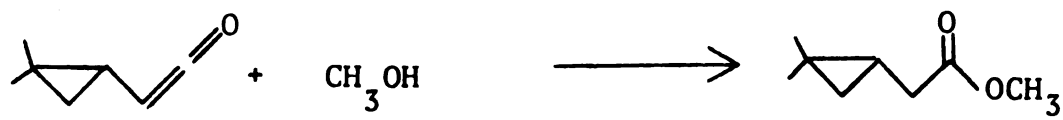
Irradiation of a 5 X 10^{-3} M solution of 54 in methanol through a Pyrex filter proceeded efficiently to give a 93.6% yield of 2-carbomethoxydibenzobicyclo[2.2.2]octadiene, 64, which was identified by comparison (mp, ir, and nmr spectra) with an authentically prepared sample.[44] Also produced was a 0.6% yield of dianthracene, which was identified by its insolubility at these low concentrations, its mp, and by comparison of its ir spectrum with that of authentic dianthracene.[51]

Two competing mechanisms occur: a minor bridge expulsion which produces anthracene that is photodimerized, and a major rearrangement which results in ester 64. In the introduction to this part of the thesis, the question of whether the bridge would be eliminated was posed. The answer is that it is, but only to a minor extent.

The major reaction involves the incorporation of a solvent molecule to form an ester, and rearrangement of the entire bridged framework with relocation of the carbonyl from the bridge to a substituent position. The incorporation of methanol is a well known reaction in α,β-unsaturated ketones. It normally proceeds through an α-cleavage of the ketone to form a diradical, followed by a valence isomerization to a ketene and the formation of a new bond from the β-carbon of the enone to some other part of the molecule, as for example the place where the carbonyl was originally bonded. A good example is the photoreaction of 5,5-dimethyl-2-cyclopentenone, 47.

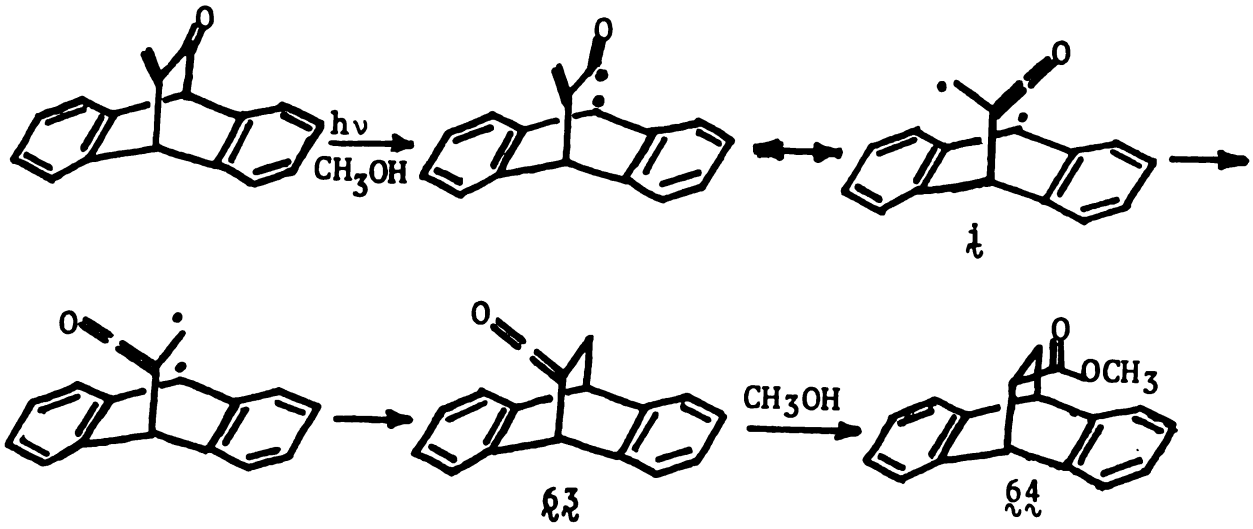


47 48



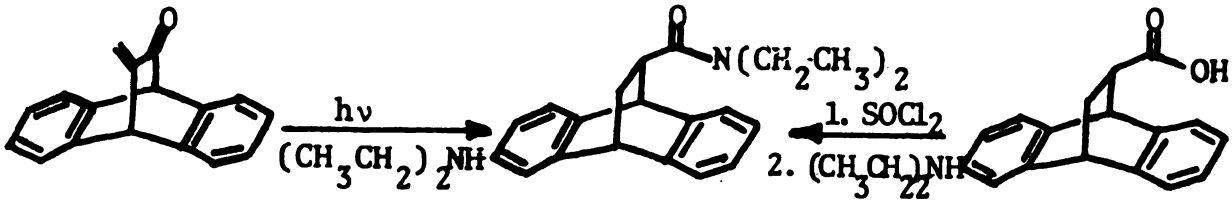
48 49

Like enone 47, enone 54 has good radical-stabilizing substituents in the α'-position, and undoubtedly reacts in an analogous manner as shown. The only difference of note is that bond rotation must occur in diradical i before radical recombination can take place.



63 64

If this is indeed the reaction mechanism, the intermediate ketene that is produced should react with any good nucleophile present in the solution to form an acid derivative. Consequently, further support for this mechanism was established when the irradiation of a 10^{-2} M solution of 54 in anhydrous diethyl ether containing 4% diethylamine proceeded efficiently to give a 92% yield of 2-diethylcarbamidodibenzobicyclo[2.2.2]-octadiene, 66, which was identified by comparison (ir and nmr spectra) with a sample prepared from the known acid 65.[52]

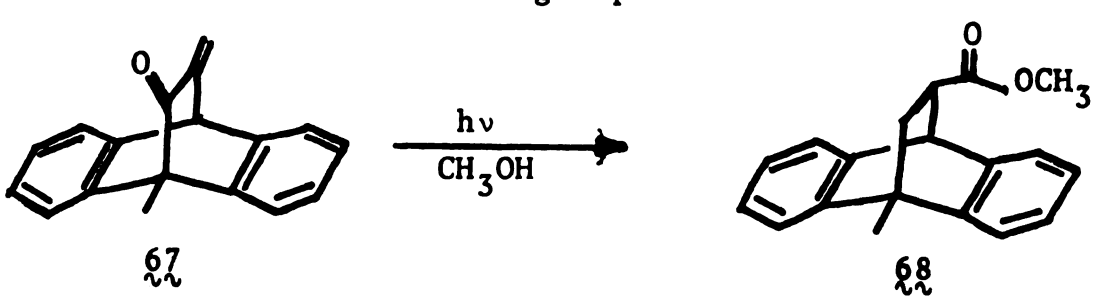


54 66 65

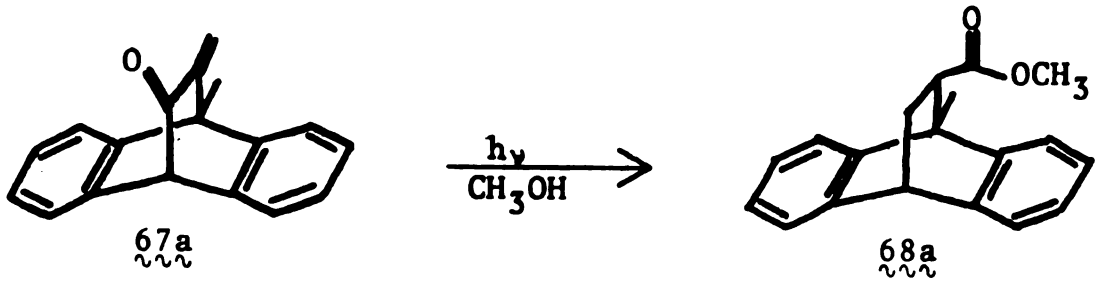
The ir spectrum of amide 66 contained a broad carbonyl peak at 1643 cm^{-1} which is characteristic of an amide. The nmr spectrum contained an aromatic multiplet of 8 protons at τ 2.54-2.99, a doublet at τ 5.59 for the bridgehead proton

adjacent to the carbamido group, a triplet at τ 5.61 for the bridgehead proton adjacent to the methylene protons, a complex multiplet of five protons at τ 6.17-7.26 due to the protons of two non-equivalent overlapping methylene groups from the two amide ethyl groups and the bridge proton adjacent to the carbonyl, a doublet of doublets at τ 8.00 for the two methylene protons on the bridge, and two overlapping triplets of three protons each at τ 8.93 and 8.98 for the two non-equivalent terminal methyls in the two amide ethyl groups. The use of $Eu(fod)_3$ was necessary to interpret the bridgehead region in order to make assignments for the bridgehead protons which overlap in the uncomplexed spectrum. However $Eu(fod)_3$ did not simplify the spectra in any of the other regions.

That the proposed mechanism in which the bridge rotates 180° is correct as opposed to the possible alternative that the bridge was lost and re-added in a photochemical Diels-Alder reaction was finally unequivocally established by the work of D. N. Buchanan in this laboratory. He prepared enones 67 and and 67a and found that on irradiation each gave only one ester, 68 and 68a respectively. If the mechanism had involved elimination and re-addition of the bridge, it is unlikely that the reaction would be so regiospecific.



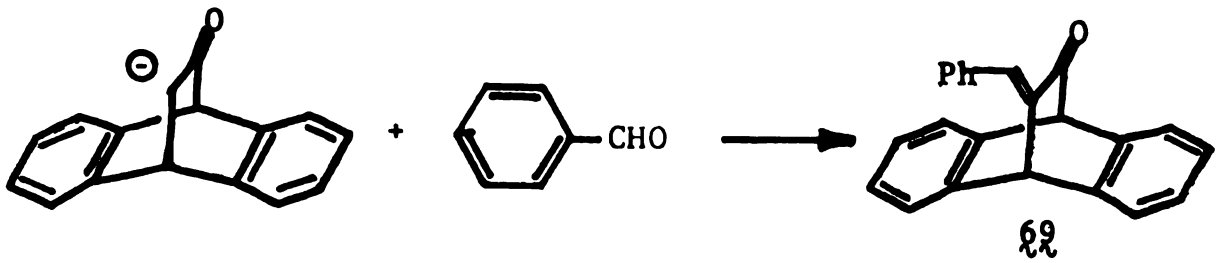
67 68



67a 68a

C. The Preparation of 3-Benzylidenedibenzobicyclo[2.2.2]octadiene-2-ones

The weakly nucleophilic base derived from hexamethyldisilizane and n-butyllithium was used to convert ketone 9 to its anion, which was then condensed with benzaldehyde to give enone 69 in 52% yield. An oily yellow semi-solid was



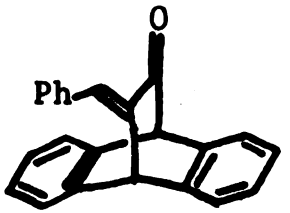
69

formed in the workup which, when washed with ether, gave almost pure white crystals of a single isomer. It had only a 2-degree mp range, characteristic enone infrared absorptions at 1701 and 1625 cm^{-1}, and nmr singlets at τ 2.62 (obtained by extrapolation of data obtained with the shift reagent), 4.30, and 4.97. $Eu(fod)_3$ readily shifted the low field signal out of the aromatic absorption region for this compound, and subsequent additions showed the low field signal to shift the same amount as the high field signal while the middle signal

was shifted significantly less. Consequently the τ 2.62 signal must be the vinyl proton cis to the carbonyl, the τ 4.30 signal must be the bridgehead proton adjacent to the benzylidene, and the τ 4.97 signal must be the bridgehead proton adjacent to the carbonyl. Thus the isomer obtained is that shown as enone 69; the other stereoisomer was not observed.

Similarly, the anion obtained from ketone 9 was condensed with p-tolualdehyde to give enone 70 in 45% yield, with p-anisaldehyde to give enone 71 in 49% yield, and with p-chlorobenzaldehyde to give enone 72 in 7% yield. Only one stereoisomer was observed in each case. From the similarity of the spectral data, especially the chemical shift of the bridgehead proton, which is quite sensitive to differences in substitution on the double bond, they were all assigned the configuration of the parent enone 69. That is, all are considered to have the vinyl proton cis to the carbonyl group.

The spectral characteristics of these new compounds are listed in Table I. All have strong infrared absorptions at about 1700 and 1626 cm^{-1} which are characteristic of an α,β-unsaturated ketone. All have the expected number of aromatic protons plus the vinyl proton in the aromatic envelope, and two bridgehead protons, the positions of which vary very little from compound to compound in this series. The ultraviolet spectra are more interesting. Enone 54 had two distinct groups of absorptions - a π-π* band in the 280 nm region with extinction coefficients of about 4000-5000, and an n-π* band



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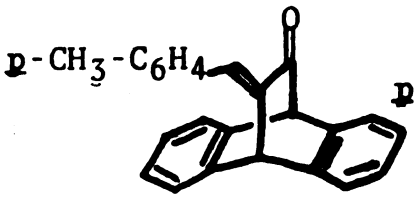

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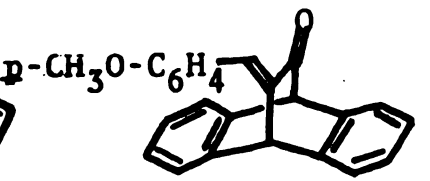

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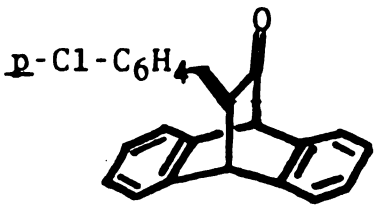


72

	69	70	71	72
ir in cm^{-1}	1701, 1625	1698, 1624	1699, 1628	1701, 1628
nmr in τ(H)	2.47-3.00(14) 4.30(1) & 4.97(1)	2.47-2.90(13) 4.31(1) & 5.00(1) 7.60(3)	2.42-2.90(13) 4.28(1) & 5.00(1) 6.12(3)	2.46-2.90(13) 4.40(1) & 4.97(1)
uv in nm(ε)	271(13,400) 298(16,000) 343(sh, 660) 363(sh, 499) 380(sh, 211)	273(13,200) 303(19,600) 344(sh, 769) 361(sh, 515) 382(sh, 185)	279(sh,10,200) 315(23,000) 364(sh, 702) 382(sh, 236)	273(14,000) 302(16,900) 341(sh, 839) 362(sh, 524) 384(sh, 205)

Table I

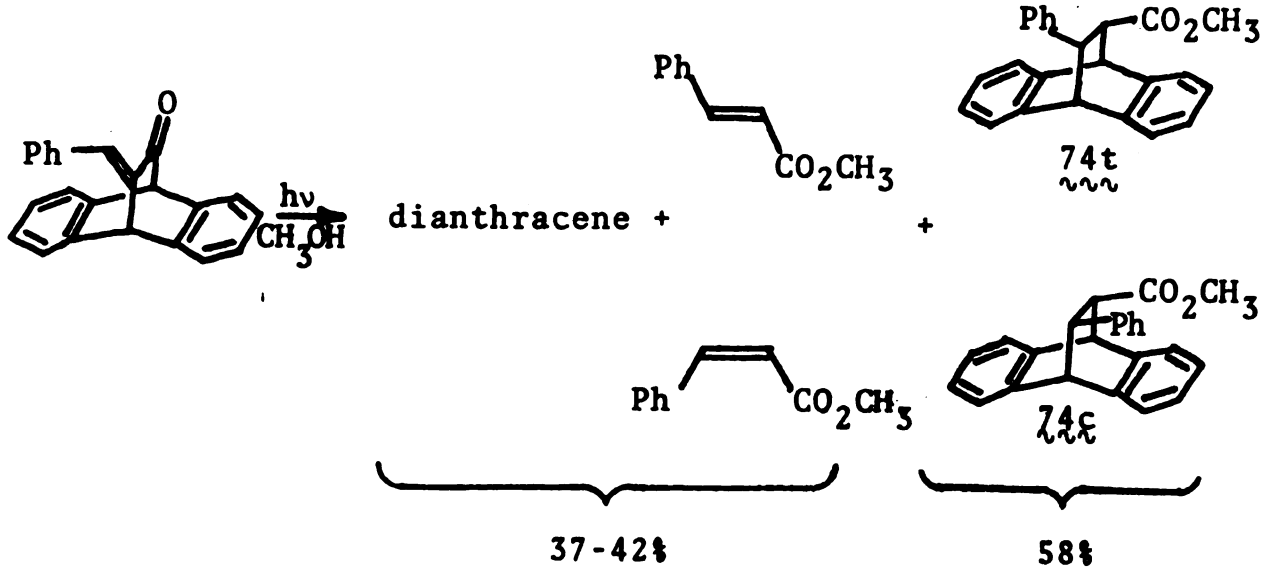
Spectral data of four new 3-benzylidenedibenzobicyclo[2.2.2]octadiene-2-ones

in the 309-384 nm region with extinction coefficients of about 400-500. In enone 54 the π-π^* and n-π^* absorptions are distinct groupings, and the long wavelength n-π^* band has fine structure. However, when a phenyl group is placed in conjugation with the enone (Table I) the π-π^* band is shifted to longer wavelengths, becomes broader, and has an enhanced extinction coefficient. The n-π^* band becomes swamped by the π-π^* band, its fine structure becomes partially indistinguishable, and the remainder is seen only as shoulders on the π-π^* band. However, the λ_{max} of the n-π^* absorptions are unaffected by this substitution. In the extreme case of enone 71, the π-π^* band has become so strong and broad, and has moved so far to the red that the only remnants of the n-π^* band that can be seen are two small shoulders.

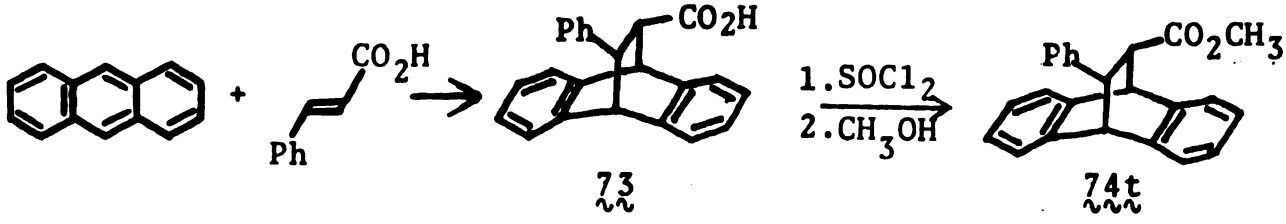
D. The Photochemistry of 3-Benzylidenedibenzobicyclo[2.2.2] octadiene-2-ones

The irradiation of a 2.17 X 10^{-3} M solution of enone 69 in methanol through a Pyrex filter proceeded cleanly and efficiently to give (1) a precipitate of dianthracene (37-42%) which was identified by its low solubility and by a comparison of its ir spectrum with that of an authentic sample,[51] (2) an equimolar mixture of methyl cis- and trans-cinnamates (37-42%)[53] which were identified by comparison of their nmr spectra with those of authentic material,[54] and (3) a 68:32 mixture of trans-:cis-2-carbomethoxy-3-phenyl-dibenzobicyclo[2.2.2]octadienes, 74t and 74c, which were

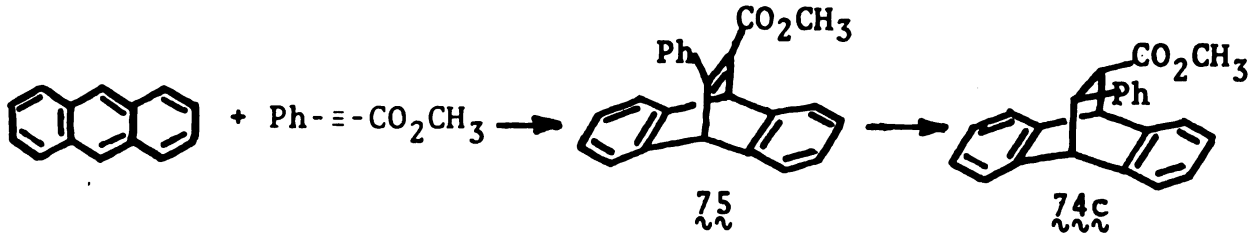
identified by a comparison of their nmr spectra with those of the independently prepared pure compounds and mixtures of known ratios of the two. The nmr spectrum of the crude photolysis mixture after the dianthracene and solvent had been removed showed no significant signals which could not be assigned to one of these compounds.



The previously unknown esters 74t and 74c were independently synthesized for confirmation of their structures by the following procedures. The known acid 73[55] was prepared by the Diels-Alder addition of trans-cinnamic acid to anthracene, and was esterified with thionyl chloride and methanol to give 74t,



the major ester obtained from the irradiation of 69. A Diels-Alder reaction of anthracene and methyl phenylpropynoate gave 2-carbomethoxy-3-phenyldibenzobicyclo[2.2.2]octatriene, 75, as a colorless crystalline adduct which on catalytic hydrogenation with palladium on carbon in ethanol was converted to 74c, the minor ester obtained from the irradiation of 69.

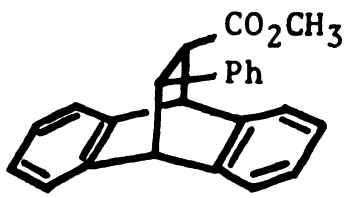


75 74c

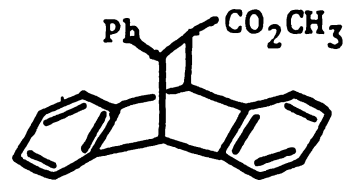
The spectral data of esters 74c and 74t are shown in Table II. The uv spectra were essentially identical to each other and were very similar to that of ester 64. The ir spectra clearly showed the presence of a carbonyl group and otherwise differed from each other only slightly. The nmr spectra, however, were significantly different. The methoxyl peak in the cis ester 74c was shifted upfield about 0.6 ppm to τ 7.02 from the position occupied in both ester 64 which absorbs at τ 6.42, and ester 74t which absorbs at τ 6.40. Apparently the methoxy protons experience a net shielding from the adjacent phenyl ring in the cis ester. Another significant difference appears in the coupling constants between the vicinal bridge protons. In the cis ester 74c the dihedral angle is about zero degrees and the vicinal coupling constant is predicted to be large, whereas in the trans ester 74t the dihedral angle is about 120° and the vicinal coupling

Table II

Spectral data for esters 74c and 74t



74c



74t

uv:	nm(ε)	252(sh, 743) 258(989) 265(1,310) 272(1,360)	252(sh, 759) 258(953) 265(1,250) 272(1,330)
ir:	cm^{-1}	1725(ester C=O)	1727(ester C=O)
nmr:	τ	2.28-2.48(m, 1, aryl) 2.58-3.18(m, 10, aryl) 3.52-3.82(m, 2, aryl) 5.36(d, 1, J=1.8 Hz, bridgehead adjacent to carbomethoxy) 5.75(d, 1, J=2.4 Hz, bridgehead adjacent to phenyl) 6.29(d of d, 1, J=11.8, 2.4 Hz, bridge proton adjacent to phenyl) 6.72(d of d, 1, J=11.8, 1.8 Hz, bridge proton adjacent to carbomethoxy) 7.02(s, 3, methoxy)	2.45-3.06(m, 11, aryl) 3.30-3.48(m, 2, aryl) 5.23(d, 1, J=2.4 Hz, bridgehead adjacent to carbomethoxy) 5.80(d, 1, J=2.4 Hz, bridgehead adjacent to phenyl) 6.39(d of d, 1, J=6.0, 2.4 Hz, bridge proton adjacent to phenyl) 6.42(s, 3, methoxy) 7.02(d of d, 1, J=6.0, 2.4 Hz, bridge proton adjacent to carbomethoxy)

constant is predicted to be small.[56] The observed values agree with the predictions: the J value for the bridge protons in 74c is 11.8 Hz while in 74t it is only 6.0 Hz. Thus the physical data support the structural assignments for these compounds.

In contrast to the photochemical behavior of enone 54 where bridge expulsion (hereafter known as pathway a) accounted for less than 1% of the observed products, with enone 69 the anticipated bridge photoelimination reaction occurred to a significant extent (37-42%) even though photorearrangement to esters 74c and 74t (hereafter known as pathway b) was still the major reaction. Apparently pathway a has a lower activation energy when benzylidene ketene is formed than when methylene ketene is formed, and is able to compete with pathway b in this case.

The mechanism for pathway b is undoubtedly the same for benzylidene enone 69 as it was for unsubstituted enone 54. Due to the formation of two isomeric esters (74c and 74t) in this case, it is possible to learn more about the addition of methanol to the ketene. It must be a kinetically controlled process, since, under conditions favoring thermodynamic control, only the trans isomer is formed. When a solution of cis ester, 74c, and sodium methoxide in methanol was refluxed for 6 hr, trans ester 74t was the only product.

Enones 70, 71, and 72 were prepared to study the effects of para electron-donating substituents (-CH_3 and -OCH_3) and para electron-withdrawing substituents (-Cl) on the phenyl

ring. It was anticipated that they might have an influence on the amount of products formed from pathway a versus those formed from pathway b. However, none of the substituents had a significant effect. Essentially the same amount of products derived from pathway a was observed from the p-substituted benzylidene enones as had been observed from the parent enone 69. The yields of products (dianthracene) derived from pathway a on irradiation of enones 70, 71, and 72 through Pyrex were 42%, 38%, and 37% respectively.

In retrospect this is not surprising. The intermediates involved in this reaction such as the biradical must be very similar to the intermediates involved in Norrish Type II photoprocesses, and as Wagner has reported for this type of reaction, "These inductive effects are noteworthy primarily for their smallness."[57]

The amount of products derived from pathway a and pathway b is somewhat wavelength dependent. Irradiation of enone 69 with 350 and 300 nm wavelength light gave 18 and 32% yields respectively of products (dianthracene) derived from pathway a. A possible explanation for this behavior is that pathway b proceeds exclusively from an n-π^* triplet state, and that pathway a proceeds exclusively from a π-π^* triplet state. Since ketones with aromatic rings are known to have n-π^* and π-π^* triplet states of similar energies,[54] it is possible that there is some sort of an exchange between them. It can be postulated that in this case the n-π^* triplet is of lower energy, and that the π-π^* triplet normally decays

to it, while in some instances the exchange proceeds in the opposite direction. Thus, no matter which triplet was initially populated, some reaction would occur from each, and the greater amount would occur from the n-π^* triplet.

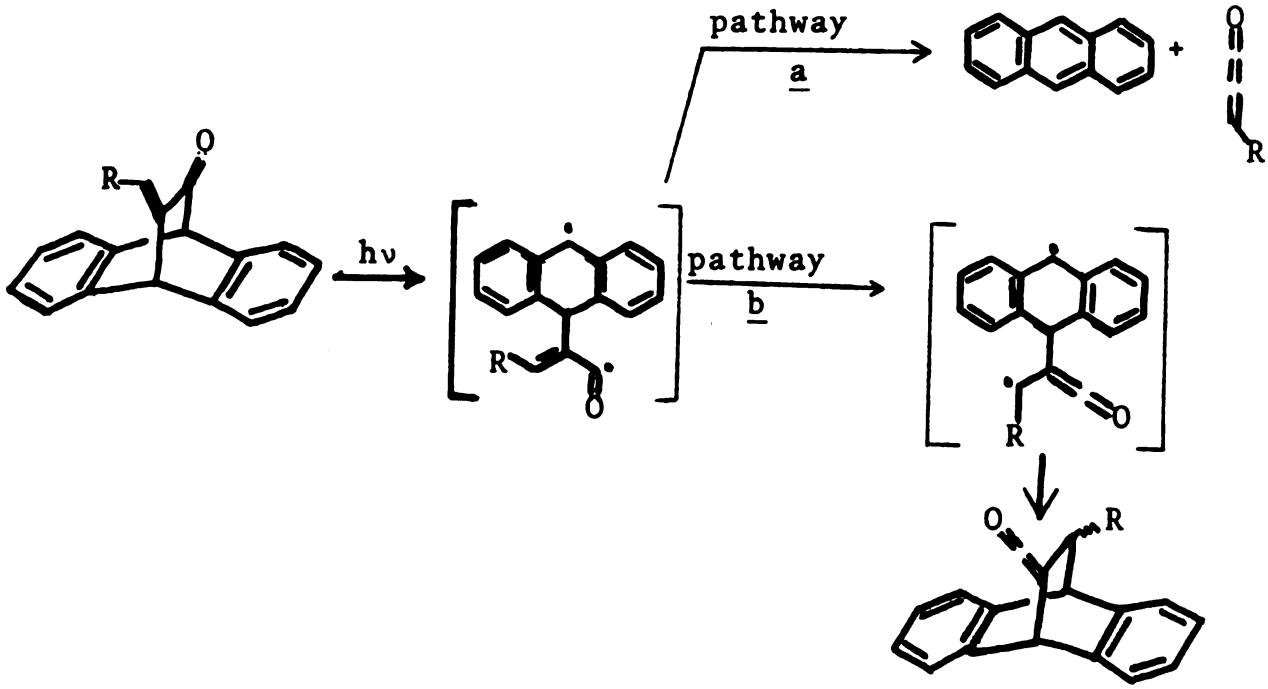
The n-π^* triplet would be populated directly as a result of intersystem crossing from the excited singlet (a very efficient process in phenyl ketones[57]) when 350 nm wavelength light was used, and one would expect to obtain primarily products from pathway b if the above theory is valid. The theory correctly predicts the observation that products of pathway b are observed in circa 82% yield, while products of pathway a are observed in only an 18% yield.

Similarly one would expect to obtain primarily π-π^* triplets from excitation with a 300 nm wavelength light, although there are some weak n-π^* absorptions that would be excited (vide supra). Consequently, the above theory would predict a substantial increase in the amount of product obtained via pathway a when the light source is changed from 350 to 300 nm. The experimental results show that the amount of product obtained from pathway a about doubles when this change is made.

E. Conclusion

Clearly more work must be done before everything is known about this reaction. Although it was not possible to study it in exhaustive detail here, it is apparent that some conclusions can be drawn, and that several areas can be singled out which merit consideration for further investigation.

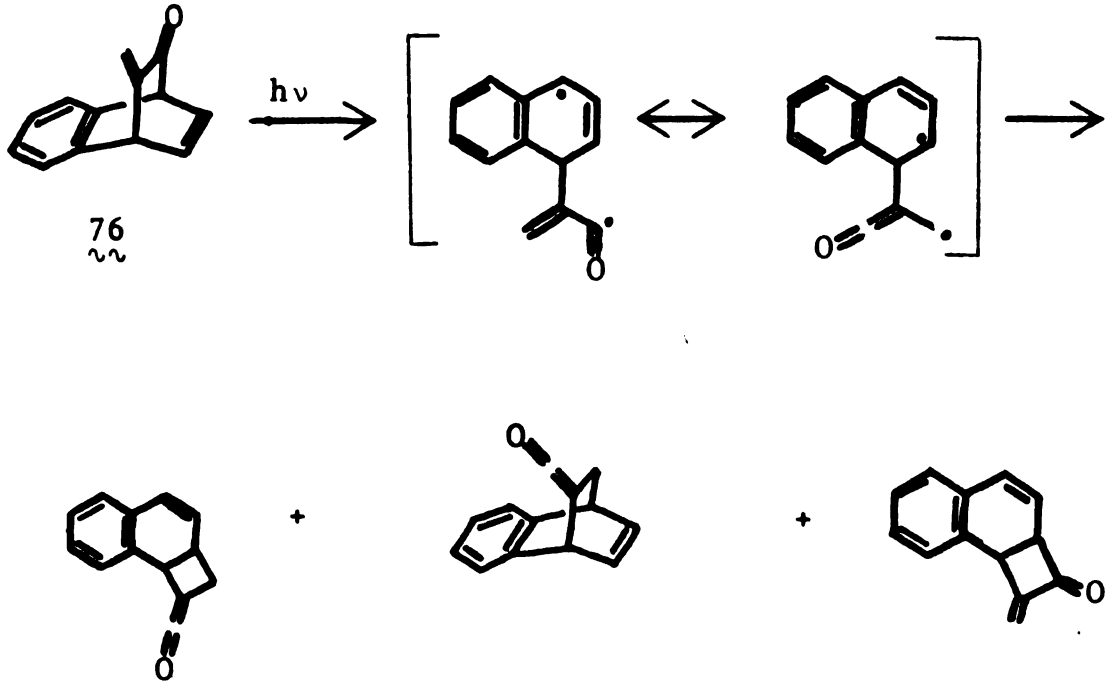
In general terms the photoreaction studied in part II of this thesis initially proceeds to form a diradical by an α'-cleavage of the enone. This diradical then partitions itself between two pathways. Pathway a proceeds through bridge cleavage to form a methylene ketene and an aromatic molecule. Pathway b proceeds through valence isomerization and intramolecular rebonding to form a ketene. Areas for further study can be defined in terms of factors affecting these three processes.



The first area for study would be an investigation into the question of what factors are necessary to insure the initial α'-cleavage. It occurs readily with the enones studied here where a radical on the α' carbon would be stabilized by two phenyl substituents, as well as with enones 47 and 50. However, 2-cyclohexenones and 2-cyclopentenones do not react this way. Clearly radical stabilizing groups favor formation

of the intermediate diradical, but the minimal amount of stabilization required for this type of photoprocess to occur should be determined.

The second area that could use some study is the question of what the diradical prefers to do when there are other places in the molecule where rebonding to form a stable ketene or another stable enone can occur. Enone 76 provides a good test of this question. The intermediate diradical can close



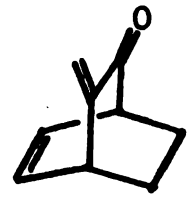
to give any or all of the three products shown. Which ones will be favored? This compound has been prepared, but its photochemistry has not yet been investigated.

The amount of partitioning between pathways a and b provides a third area for investigation. This study has shown that phenyl substitution on the methylene greatly increases the percent of bridge elimination compared to the unsubstituted case. Either the benzylidene ketene or its immediate precursor must

be stabilized by the presence of the phenyl. Other substituents should be tried in this position to determine whether this stabilization results from inductive or resonance effects.

In this study the substrate moiety remained constant. However, it is quite likely that a change in the substrate will produce a change in the amount of partitioning between pathways a and b. This concept can begin to be tested on enone 76 as the eliminated substrate molecule would be naphthalene instead of anthracene which was obtained in the current study. If the amount of bridge elimination is directly related to the increased amount of aromaticity in the product, one would predict more bridge elimination from enone 76 than from enone 54. Indeed, were this a major driving force, one would predict a substantial amount of bridge elimination from enone 77. In fact, the previously mentioned synthetic route to methylene ketenes might lie with this type of molecule.

77



78

In contrast is the question of whether enone 78 would eliminate at all since the substrate moiety cannot go to an aromatic molecule.

Some theses solve neat, well defined problems. This one has provided the answers to some questions and posed many others. Such is often the nature of research.

EXPERIMENTAL

A. $Eu(fod)_3$ Shift Numbers Procedure

An nmr spectrum of the pure compound was recorded. Then $Eu(fod)_3$* was added to the nmr tube in small increments. After each addition the nmr spectrum was scanned, and the new frequency of each absorption was recorded. The shift for each absorption was obtained by subtracting the original absorption from the shifted one. The $Eu(fod)_3$ shift numbers are ratios which were obtained by dividing each shift in the group by the smallest in that group. The numbers reported are averages from the several additions.

B. General Photolysis Procedures

Irradiations were carried out with a 450 watt Hanovia Type L medium pressure mercury lamp. The solutions were not degassed as this appeared to have no effect on the reaction studied. Large volumes were irradiated in an open well through an appropriate filter and the immersion well. The temperature was maintained at 12-17° by tap water running through the immersion well. Smaller volumes were placed in capped Pyrex test tubes and hung near the outside of the immersion well in a water bath which kept the temperature at 15-20°.

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*Europium(III) tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione)

The extent of the reaction was monitored by withdrawing samples of the solution and recording their uv spectra. In all cases the products absorbed at lower wavelengths than the reactants or had substantially smaller extinction coefficients in the area of interest, thus enabling the approximate extent of reaction to be determined. In the cases where anthracene and its photodimer were products, the reaction was considered complete when the concentration of anthracene, calculated from its absorbance and extinction coefficient at 252 nm, was less than 10^{-5} M.

Since the solvent (methanol) used for most of the photolyses was one in which the starting materials could be purified by recrystallization, no dark reactions were deemed necessary. In cases where other solvents were used, dark reactions were run and are described in the specific sections.

C. Wittig Reaction of Dibenzobicyclo[2.2.2]octadiene-2,3-dione (10): Preparation of 3-Methylenedibenzobicyclo-[2.2.2]octadiene-2-one (54)

Into a reaction flask equipped with a magnetic stirrer and flushed with dry nitrogen were placed 0.77 g (0.032 mol) of pulverized NaH and 8 ml of dimethyl sulfoxide (freshly distilled from CaH_2). The flask was placed in an oil bath at room temperature and was heated to 70° for 1 hr and 15 min. After the mixture had cooled to room temperature, a solution of 11.4 g (0.032 mol) of methyltriphenylphosphonium bromide in 30 ml of dry dimethyl sulfoxide was added via a syringe;

a yellow-green color was produced. The solution of ylid was transferred to an addition funnel that had been flushed with dry nitrogen and was added dropwise to a magnetically stirred orange solution of 3.74 g (0.16 mol) of 10 over a period of 50 min. The addition produced a deep red color which darkened as the reaction proceeded.

After 22 hr the solution was poured into 175 ml of water and was extracted three times with benzene. The dark benzene solution was evaporated to give an oil which solidified on standing. The gray-green solid was titrated with 15 ml of ethanol and was suction filtered to give 1.82 g (50%) of the product 54: mp 221-224° (lit.[40] 223.0-223.4°); uv max 246 nm (ε 5,470), 280(sh, 3,480), 286 (4,160), 309(sh, 149), 322 (274), 335 (460), 348 (564), 367 (503), and 384 (192); ir 1708 cm^{-1} (conjugated C=O) and 1633 (C=C); nmr τ 2.48-2.88 (m, 8, aryl), 4.03 (s, 1, vinyl adjacent to carbonyl), 4.58 (s, 1, vinyl adjacent to bridgehead), 4.93 (s, 1, bridgehead adjacent to vinyl), 5.05 (s, 1, bridgehead adjacent to carbonyl). The $Eu(fod)_3$ shift numbers for the nmr singlets in order of increasing τ are 2.5, 1.0, 1.0, and 2.6. The use of 1.5 or 2.5 equivalents of the ylid along with a similar workup resulted in a decreased yield.

D. Diels-Alder Reaction of Anthracene and Vinyl Acetate: The Preparation of 2-Acetoxydibenzobicyclo[2.2.2]octadiene (7)

A solution of 10 g (0.056 mol) of anthracene and 10 g (0.117 mol) of vinyl acetate in 40 ml of xylene was heated to 220° in a stainless steel bomb. After 12 hr at 210-220° the bomb was cooled, and the yellow solution was decanted. The solvent was evaporated, the product was taken up in methanol, and the undissolved anthracene was removed by suction filtration. Evaporation of the methanol and recrystallization from ethanol gave 9.0 g (60%) of the product 7: mp 98-99.5° (lit.[58] 100-101°).

E. Preparation of Dibenzobicyclo[2.2.2]octadiene-2-ol (8) from 2-Acetoxydibenzobicyclo[2.2.2]octadiene (7)

A solution of 3.5 g (0.0133 mol) of 7 and 0.117 g (0.0217 mol) of $NaOCH_3$ in 29 ml of methanol was refluxed for 19 hr. The volatile material was evaporated, and the product 8 was taken up in ether. The insoluble sodium salts were removed by filtration, and the solvent was evaporated to give 2.82 g (95%) of the product 8: mp 139-141° (lit.[44] 142-143°). It was not further purified prior to oxidation.

F. Oxidation of Dibenzobicyclo[2.2.2]octadiene-2-ol (8): Preparation of Dibenzobicyclo[2.2.2]octadiene-2-one (9)

Into a mechanically stirred, dry nitrogen flushed reaction flask were placed 62.5 g (0.303 mol) of dicyclohexylcarbodiimide,

300 ml of benzene (previously dried over 4A molecular sieve), 296 ml of dimethyl sulfoxide (freshly distilled from CaH_2), 22.5 g (0.101 mol) of 8, and 8.2 ml of pyridine (previously dried over KOH). The addition of 4.2 ml of trifluoroacetic acid initiated the formation of a precipitate.

After 24 hr the nitrogen flush was stopped, and 30 g (0.273 mol) of oxalic acid dihydrate was added slowly; this caused the solution to foam extensively. After the mixture had stirred for 30 min, it was poured into a mixture of water (800 ml) and chloroform (200 ml). The mixture was agitated, and the solid was removed by suction filtration. The solid was washed with chloroform; all the chloroform filtrates were combined and washed twice with 1N $NaHCO_3$, twice with water, and then dried ($MgSO_4$). Evaporation of the solvent gave a tan solid. It was dissolved in benzene with heating, and the insoluble dicyclohexyl urea was removed by suction filtration. Crystallization proceeded to give 10.7 g of the product 9: mp 152-153° (lit.[44] 152.5-153°); nmr 2.47-2.90 (m, 8, aryl), 5.16 (s, 1), 5.47 (t, 1, J=3.0), and 7.67 (d, 2, J=3.0). Further crystallization from the mother liquor gave product 9 of lower purity which weighed 9.1 g for a total yield of 89%.

G. Mannich Reaction of Dibenzobicyclo[2.2.2]octadiene-2-one (9): Alternate Preparation of 3-Methylenedibenzobicyclo-[2.2.2]octadiene-2-one (54)

A solution of 0.88 g (0.004 mol) of 9, 0.84 g (0.028 mol) of paraformaldehyde, and 2.3 g (0.028 mol) of dimethylamine

hydrochloride in 10 ml of isoamyl alcohol was refluxed for 24 hr. Shortly after everything dissolved, two layers were observed to form. The lower layer was dark, and the upper layer was colorless. When the solution was cooled, crystals formed in two distinct layers. The upper layer was separated, and the product 54 was collected by suction filtration. After it was washed with ethanol, it weighed 0.569 g; mp 222-224° (lit.[43] 223.0-223.4°). The lower layer was titrated with ethanol and the insoluble material was collected by suction filtration. It was washed with aqueous Na_2CO_3 and water, and was dried to give 0.009 g of product 54. The combined yield of 54 weighed 0.578 g (62%). Chromatography of the residue (obtained after removal of the amine salts and isoamyl alcohol) using benzene or chloroform on silica gel can increase the yield to 80%.

H. Photolysis of 3-Methylenedibenzodicyclo[2.2.2]octadiene-2-one (54) in Methanol: Photosynthesis of 2-Carbomethoxydibenzobicyclo[2.2.2]octadiene (64)

A 5.0 X 10^{-3} M solution of 54 was prepared by dissolving 0.464 g of 54 in 400 ml of methanol. It was placed in a photolysis well and was irradiated through a Pyrex filter for 1 hr. A uv spectrum contained new peaks at 264 nm and 271 nm. After 2 hr of irradiation the original maximum at 286 nm had essentially vanished, and the reaction was considered complete. A small amount of white solid had precipitated out of solution.

Suction filtration gave 2.1 mg of dianthracene (0.6%). Its ir spectrum matched that of an authentic sample of dianthracene.[51]

Evaporation of the solution gave off-white 64 weighing 0.494 g (93.6%). An nmr spectrum showed no significant impurities. Recrystallization from methanol gave pure white crystals mp 117-118° (lit.[44] 117-118°): uv 249 nm (sh, ε489), 258 (sh, 728), 264 (1,140), and 271 (1,420); nmr τ 2.54-3.00 (m, 8, aryl), 5.31 (d, 1, J=5.0, bridgehead adjacent to carbomethoxy), 5.67 (t, 1, J=5.0, bridgehead adjacent to methylene protons), 6.42 (s, 3, methoxy), 6.96-7.30 (m, 1, bridge proton adjacent to carbomethoxy), 7.77-8.10 (m, 2, methylene protons); ir 1721 cm^{-1} (ester C=O).

I. Diels-Alder Reaction of Methyl Acrylate and Anthracene: Synthesis of 2-Carbomethoxydibenzobicyclo[2.2.2]octadiene (64)

A solution of 8.9 g (0.05 mol) of anthracene and 5.15 g (0.06 mol) of methyl acrylate in 50 ml of xylene was heated to 205-215° for 12 hr in a 75 ml stainless steel bomb. After it was cooled, the solution was decanted, the volatile materials were evaporated, and the product was taken up in methanol. The unreacted anthracene was removed by suction filtration, and the 6.15 g (47%) of 64 was crystallized from methanol to give fine white needles mp 117-118° (lit.[44] 117-118°).

J. Photolysis of 3-Methylenedibenzobicyclo[2.2.2]octadiene-2-one (54) in Diethyl Ether Containing Diethylamine: Photosynthesis of 2-Diethylcarbamidodibenzobicyclo[2.2.2]-octadiene (66)

A 10^{-2} M solution of 54 was prepared by dissolving 0.116 g (5.0×10^{-4} mol) of 54 in 50 ml of a solution containing 48 ml of diethyl ether and 2 ml of diethylamine. Two ml were removed: one was for an initial uv spectrum, and one was for monitoring a dark reaction by uv. The bulk of the solution was placed in a Pyrex test tube, was clamped next to an immersion well in a beaker of cold water, and was irradiated for 1 hr and 40 min. A uv spectrum of the dark reaction indicated that about 4% of the starting material had reacted. A uv spectrum of the irradiated solution showed: essentially no λ_{max} at 206 nm (starting material), a λ_{max} at 307 nm (the product of the dark reaction), and λ_{max} at 266 and 273 nm (the main product 66).

Evaporation of the solution gave 0.152 g of residue. A tlc using $CHCl_3$ on silica gel showed three spots. Chromatography was performed on a 19 X 2 cm silica gel column. The first component was eluted using CCl_4. It was not the desired product and was discarded as it weighed only 16 mg. The eluant was changed to 9:1 $CHCl_3$:CCl_4 and the product 66 came off as a yellow-brown band. Evaporation gave an oil. The 66 weighed 0.135 g (92%). Its spectral data were the same as those of independently prepared material.

K. Saponification of 2-Carbomethoxydibenzobicyclo[2.2.2]octadiene (64): Synthesis of Dibenzobicyclo[2.2.2]octadiene-2-carboxylic Acid (65)

A mixture of 2.64 g (0.01 mol) of 64, 4.4 g (0.11 mol) of NaOH, and 45 ml of water was refluxed for 4 hr. The solution was suction filtered, and the residue was extracted with water. The combined filtrates were acidified with dilute HCl, and the precipitate was collected by suction filtration to give 2.4 g (96%) of 65 mp 187-189° (lit.[52] 189°).

L. Preparation of 2-Diethylcarbamidodibenzobicyclo[2.2.2]octadiene (66)

After the initial reaction had subsided, a mixture of 0.4 g (0.8 mmol) of 65 and 2 ml of thionyl chloride was heated and agitated until the 65 had all dissolved. The excess thionyl chloride was removed by rotatory evaporation, and the acid chloride was taken up in 6 ml of benzene. To this solution was added 0.5 ml (5.0 mmol) of diethylamine; this caused a precipitate to form and the flask to become warm. The mixture was stirred, heated briefly to reflux, and then cooled. The reaction mixture was washed with 2N Na_2CO_3 until the washes were clear, was washed similarily with dilute HCl, and then was washed with water. The benzene was removed by rotatory evaporation to give the 66 as a yellow oil which weighed 0.336 g (69%).

Spectral data: nmr τ 2.54-2.99 (m, 8, aryl), 5.59 (d, 1, J=2.0, bridgehead adjacent to carbamido group),5.61 (t, 1, J=2.7, bridgehead adjacent to methylenes), 6.17-7.26 (m, 5, non-equivalent amide methylenes and bridge proton adjacent to carbonyl), 8.0 (d of d, 2, J=8, 2.7), 8.93 (t, 3, J=7.0), 8.98 (t, 3, J=7.0), these are methyls from the two non-equivalent ethyl groups of the amide (see Figure 3); ir 1643 cm^{-1} (broad, amide C=O).

M. Preparation of the α-Lithio Salt of Dibenzobicyclo[2.2.2]-octadiene-2-one (9)

Into a reaction flask equipped with a magnetic stirrer and flushed with dry nitrogen was placed 15 ml of tetrahydrofuran (THF) (previously dried over 4A molecular sieve). It was cooled in an ice bath, and 8.25 ml (0.0132 mol) of 1.6N n-butyllithium in hexane was added. The addition of 2.85 ml (0.0132 mol) of hexamethyldisilizane (Dow Corning Z-6079 silane) discharged the yellow color. The dropwise addition of a THF solution of 2.64 g (0.012 mol) of 9 produced a white precipitate which was presumably the desired salt.

N. Condensation of Benzaldehyde with the α-Lithio Salt of Dibenzobicyclo[2.2.2]octadiene-2-one (9): Preparation of 3-Benzylidenedibenzobicyclo[2.2.2]octadiene-2-one (69)

To a solution of the α-lithio salt of 9 prepared as in part M was added 1.27 g (0.012 mol) of benzaldehyde in 5 ml of THF. There was no immediate change. The ice bath was

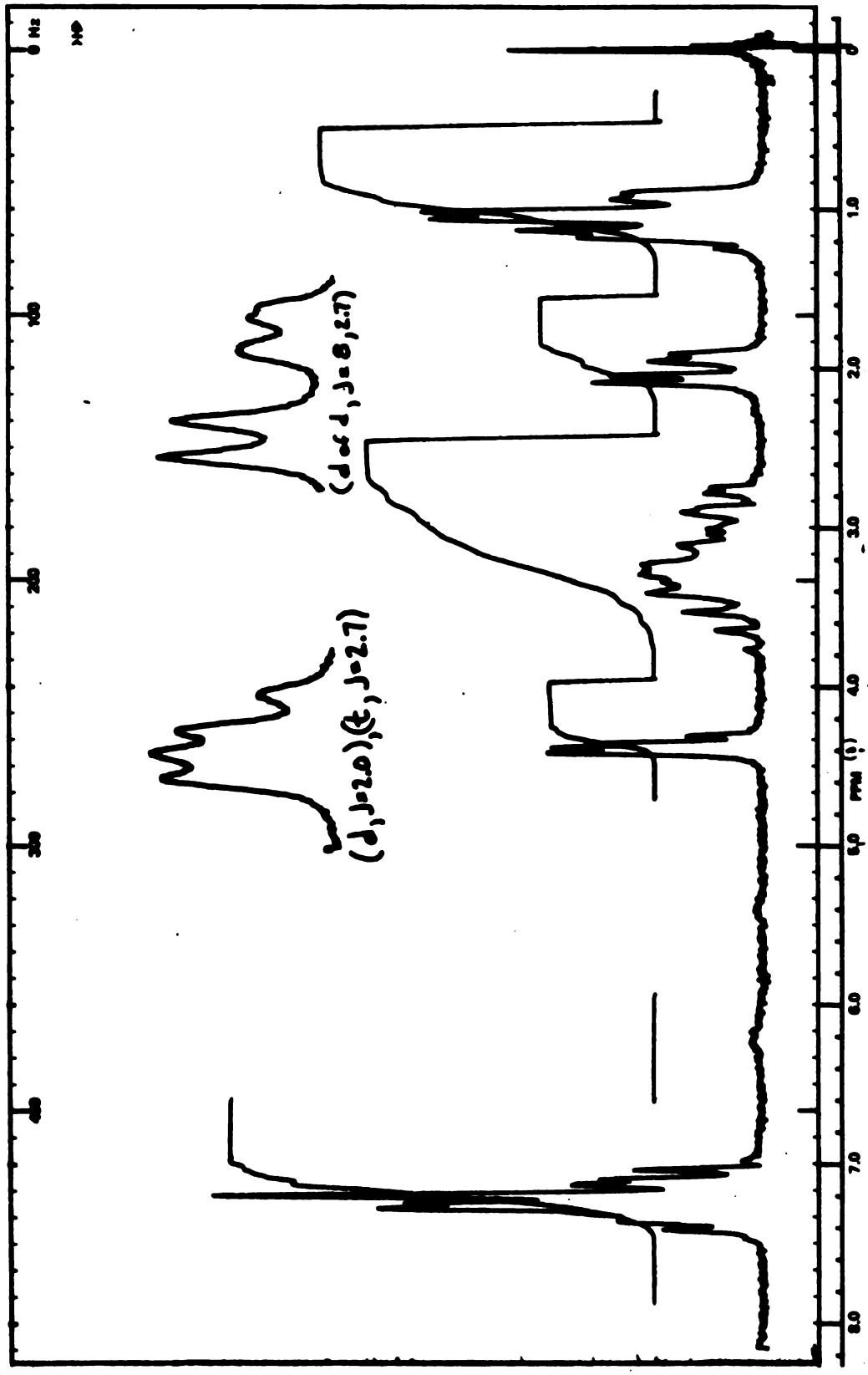

Figure 3. Nmr spectrum of 2-diethylcarbamidodibenzobicyclo[2.2.2]octadiene (66)

removed and the solution was heated to reflux, which caused a yellow color to appear. After an hour the precipitate had dissolved, and the solution had turned orange.

After the solution had been cooled, it was diluted with ether, washed four times with 25% HCl, once with water, dried ($MgSO_4$), and concentrated on a rotary evaporator to give 1.65 g (45%) of the product 69 as an off-white solid: mp 214-215. After recrystallization from ethanol the 69 melted at 216.5-217.5.

Anal. Calcd. for $C_{23}H_{16}O$: C, 89.58; H, 5.23

Found: C, 89.64; H. 5.26

Spectral data: ir 1701 cm^{-1} (conjugated C=O) and 1625 (C=C); uv max 271 nm (ε13,400), 298 (16,000), 343 (sh, 660), 363 (sh, 499), 380 (sh, 211); mass spectrum m/e (rel intensity) 308 (1) and 178 (100); nmr τ 2.47-3.00 (m, 14, aryl and vinyl), 4.30 (s, 1, bridgehead adjacent to vinyl), 4.97 (s, 1, other bridgehead). $Eu(fod)_3$ shift numbers for the vinyl and bridgehead protons in order of increasing τ are 2.8, 1.0, and 2.8. Thus the vinyl proton is cis to the carbonyl. The stereoisomer of this compound was not observed.

O. Photolysis of 3-Benzylidenedibenzobicyclo[2.2.2]octadiene-2-one (69)

A 2.17 X 10^{-3} M solution of 69 was prepared by dissolving 0.100 g in 150 ml of methanol. After the solution had been irradiated for an hour, its uv spectrum contained only a weak absorption at 252 nm which indicated that the intermediate

photoproduct anthracene was present in less than 10^{-5} M concentration. The solution contained a precipitate of dianthracene which when collected by suction filtration weighed 24 mg (42%). Its ir spectrum matched that of an authentic sample of dianthracene.[51]

The filtrate was evaporated, and an nmr spectrum (Fig. 4) was taken of the residue. The strong singlets of equal area at τ 6.32 and 6.20 correspond respectively to the $-OCH_3$ protons in cis and trans methyl cinnamate.[54] With the exclusion of all the cinnamate peaks, the remaining peaks could all be assigned to either cis-2-carbomethoxy-3-phenyldibenzobicyclo-[2.2.2]octadiene, 74c, or trans-2-carbomethoxy-3-phenyldibenzo-bicyclo[2.2.2]octadiene, 74t. From a comparison of the peak heights of the bridgehead protons at 5.23 (74t) and 5.36 (74c) with mixtures of known ratios it was concluded that 74t and 74c were present in a 68:32 ratio. In this instance a comparison of peak heights was observed to be much more reliable than integration ratios, i.e. the integration ratios were not reproducible whereas the peak heights were.

P. Diels-Alder Reactions of trans-Cinnamic Acid and Anthracene: Preparation of trans-3-Phenyldibenzobicyclo[2.2.2]octadiene-2-carboxylic Acid (73)

A solution of 2.0 g (0.0112 mol) of anthracene and 1.5 g (0.0101 mol) of trans-cinnamic acid in 4 ml of o-dichlorobenzene was refluxed for 17 hr. The solvent was removed by steam distillation and the residue was taken up in ether. The

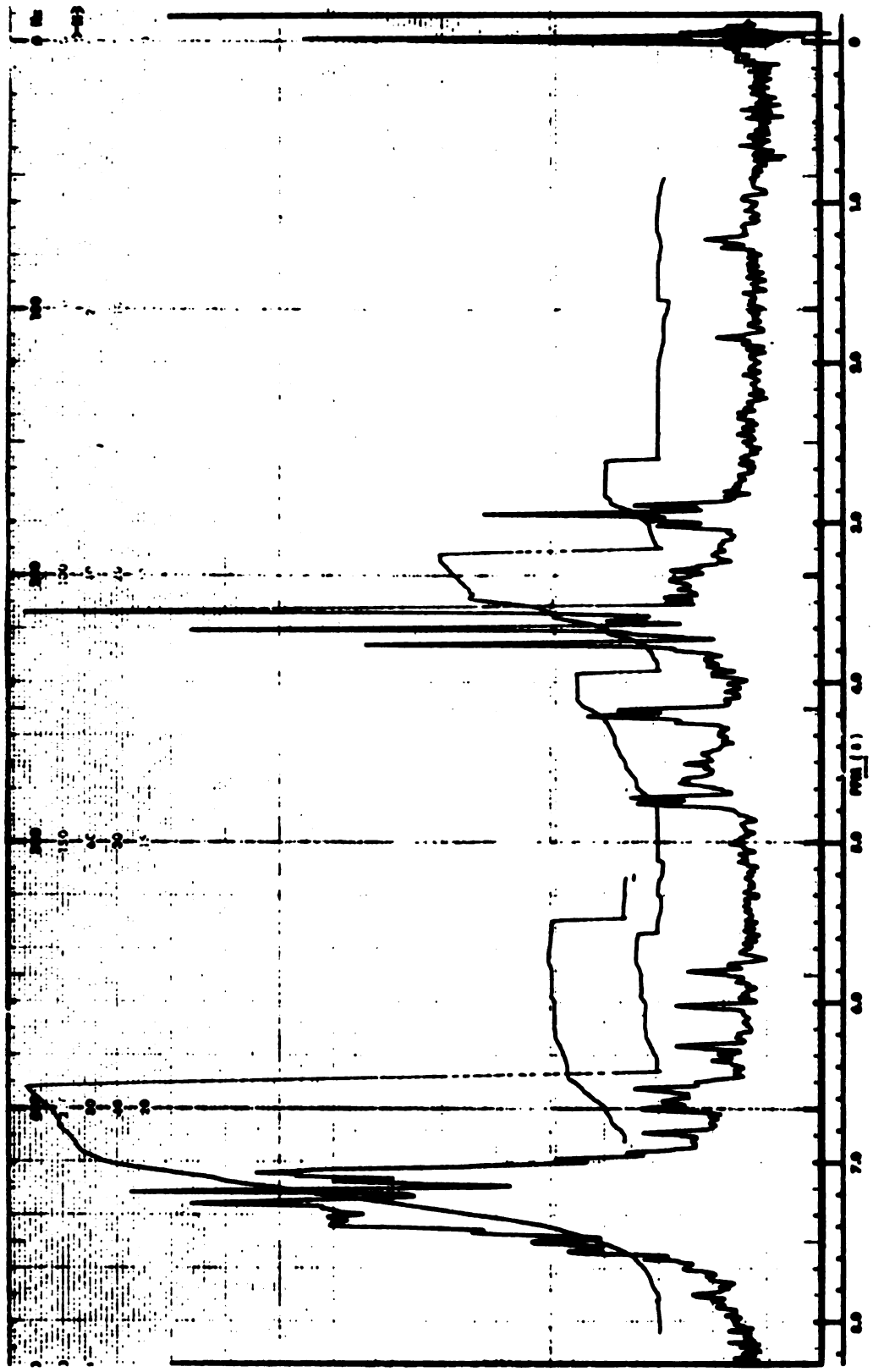

Figure 4. Nmr spectrum of the crude photolysis mixture after irradiation of 3-benzylidenedibenzobicyclo[2.2.2]octadiene-2-one (69) in methanol and removal of the insoluble dianthracene

undissolved anthracene was removed by suction filtration, and the filtrate was extracted with aqueous NaOH. The basic extract was acidified, and the white solid was collected by suction filtration. The residual cinnamic acid dissolved when the product was refluxed in 50% acetic acid. The undissolved product was collected by suction filtration and washed with 50% acetic acid and then with water to give 0.7 g (21%) of 73: mp 240-240.5 (lit.[55] 248°)

Q. Esterification of trans-3-Phenyldibenzobicyclo[2.2.2]octadiene-2-carboxylic Acid (73): Preparation of trans-2-Carbomethoxy-3-phenyldibenzobicyclo[2.2.2]octadiene (74t)

After the initial reaction had subsided, a mixture of 0.100 g (0.00424 mol) of 73 and 2 ml of thionyl chloride was heated until the acid dissolved. The excess $SOCl_2$ was removed by rotatory evaporation, and the acid chloride was dissolved in 2 ml of benzene. The addition of 0.35 ml of methanol with agitation was exothermic. The solvents were removed by rotatory evaporation. The yield of 74t was essentially quantitative. After recrystallization from methanol the fine white crystals of 74t melted at 116-116.5.

Anal. Calcd. for $C_{24}H_{20}O_0$: C, 84.58; H, 5.92

Found: C, 84.65; H, 6.04

Spectral data: ir 1727 cm^{-1} (ester C=O); uv max 259 nm (sh, ε759), 258 (953), 265 (1,250), and 272 (1,330); nmr τ 2.45-3.06 (m, 11, aryl), 3.30-3.48 (m, 2, aryl), 5.23 (d, 1, J=2.4 Hz, bridgehead adjacent to carbomethoxy), 5.80 (d, 1, J=2.4 Hz,

bridgehead adjacent to phenyl), 6.39 (d of d, 1, J=6.0, 2.4 Hz, bridge proton adjacent to phenyl), 6.42 (s, 3, methoxy), and 7.02 (d of d, 1, J=6.0, 2.4 Hz, bridge proton adjacent to carbomethoxy) (see Figure 5). The $Eu(fod)_3$ shift numbers for the non aryl absorptions in order of increasing τ are 3.1, 1.0, 3.2, 2.5, and 3.6.

R. Diels-Alder Reaction of Methyl Phenylpropynoate and Anthracene: Preparation of 2-Carbomethoxy-3-phenyldibenzobicyclo[2.2.2]octatriene (75)

A solution of 3.5 g (0.0219 mol) of methyl phenylpropynoate and 7.8 g (0.0438 mol of anthracene in 8 ml of o-dichlorobenzene was refluxed for 4 hr. After removal of the solvent by steam distillation, the solid was collected by suction filtration and was extracted with methanol. Removal of the undissolved anthracene by suction filtration, and concentration of the methanol solution produced crystals. The solution was cooled to promote further crystallization, and the product 75 was collected by suction filtration. It weighed 2.95 g (40%). After recrystallization from methanol the colorless 75 melted at 153.5-154.5°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36
Found: C, 85.25; H, 5.29

Spectral data: ir 1688 cm^{-1} (conjugated ester C=O); nmr τ 2.45-3.08 (m, 13, aryl), 4.22 (s, 1, bridgehead adjacent to phenyl), 4.70 (s, 1, bridgehead adjacent to carbomethoxy), 6.43 (s, 3, methoxy).

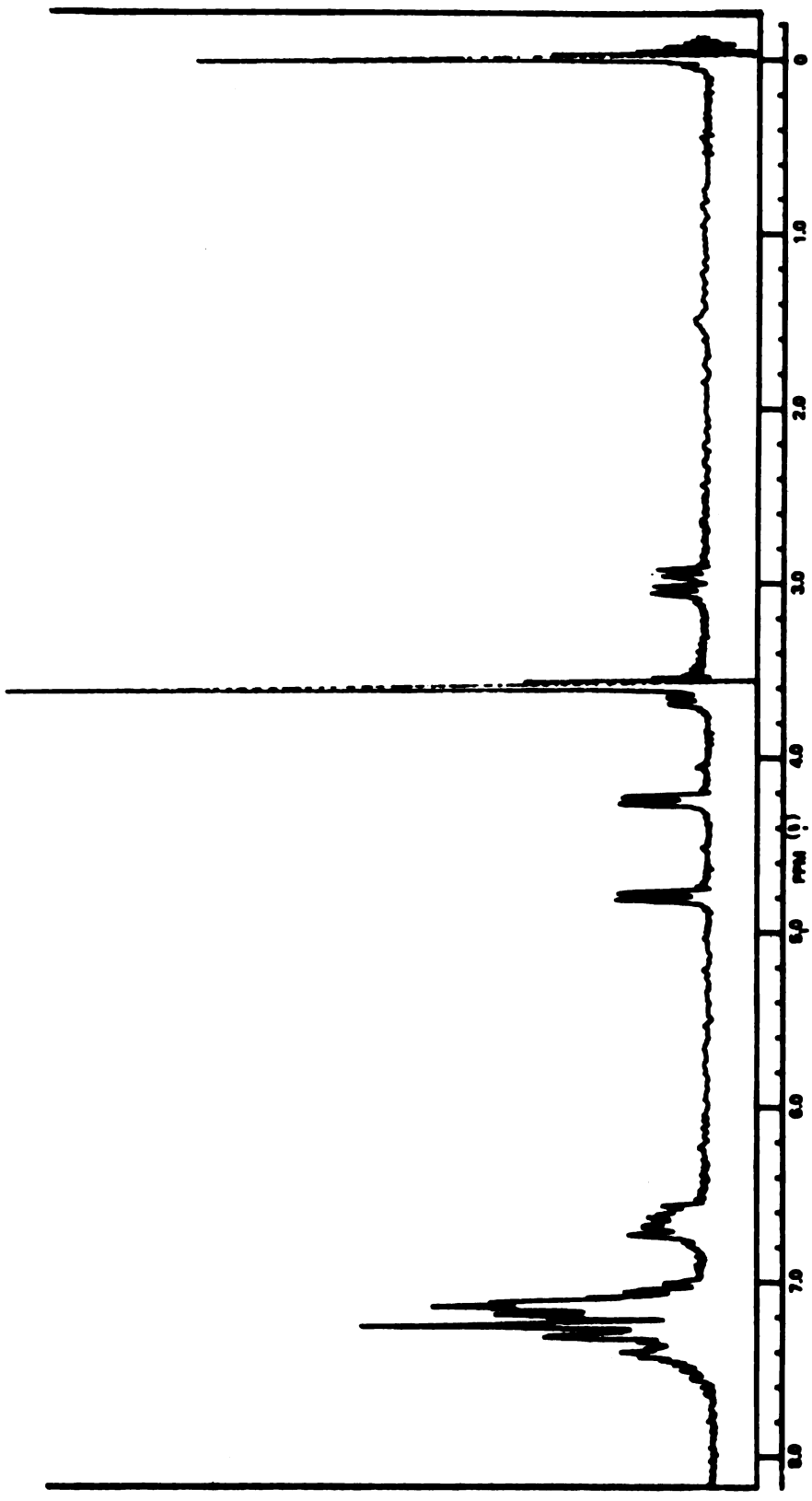

Figure 5. Nmr spectrum of trans-2-carbomethoxy-3-phenyldibenzobicyclo[2.2.2.]-octadiene (74t)

S. Reduction of 2-Carbomethoxy-3-phenyldibenzobicyclo[2.2.2]-octatriene (75) with H_2 over Palladium on Carbon: Preparation of cis-2-Carbomethoxy-3-phenyldibenzobicyclo-[2.2.2]octadiene (74c)

A solution of 0.6 g (1.77 mmol) of 75 in 60 ml of ethanol containing 40 mg of 5% Pd/C was placed in the Brown[2] hydrogenation apparatus. The apparatus was flushed with hydrogen, and the reaction mixture was vigorously stirred for 3 days during which there was no decrease in the volume of the 1.0 M BH_4 solution in the burette. The catalyst was removed by suction filtration, and the solvent was evaporated to give a quantitative yield of the product 74c. After recrystallization from methanol the fine white crystals of 74c melted at 104-105°.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.58; H, 5.92
Found: C, 84.84; H, 5.91

Spectral data: ir 1726 cm^{-1} (ester C=O); uv max 252 nm (sh, 743), 258 (989), 265 (1,310), and 272 (1,360); nmr τ 2.28-2.48 (m, 1, aryl), 2.58-3.18 (m, 10, aryl), 3.52-3.82 (m, 2, aryl), 5.36 (d, 1, J=1.8 Hz, bridgehead adjacent to carbomethoxy), 5.75 (d, 1, J=2.4 Hz, bridgehead adjacent to phenyl), 6.29 (d of d, 1, J=11.8, 2.4 Hz, bridge proton adjacent to phenyl), 6.72 (d of d, 1, J=11.8, 1.8 Hz, bridge proton adjacent to carbomethoxy), and 7.02 (s, 3, methoxy) (see Fig. 6). The $Eu(fod)_3$ shifts for the non aryl protons in order of increasing τ are 2.1, 1.0, 1.4, 2.1, and 1.9.

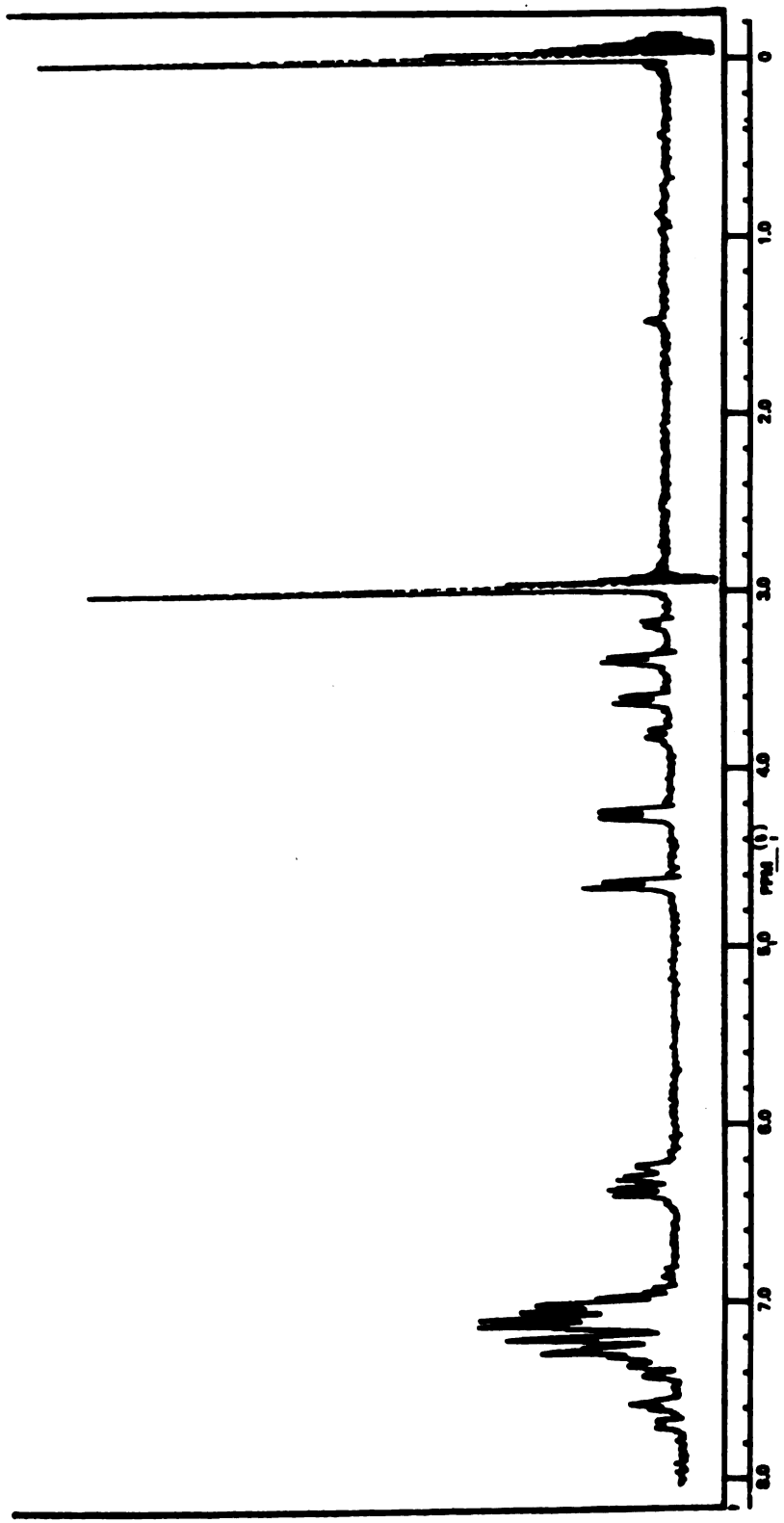

Figure 6. Nmr spectrum of cis-2-carbomethoxy-3-phenyldibenzobicyclo[2.2.2]-octadiene (74c)

T. Equilibration of cis- and trans-2-Carbomethoxy-3-phenyl-dibenzobicyclo[2.2.2]octadienes (74c) and (74t) with Sodium Methoxide

A solution of 34 mg of the cis isomer 74c and 2 mg of sodium methoxide were refluxed for 6 hr. The solvent was evaporated, and the product (34 mg) was taken up in deuterochloroform. The nmr spectrum was that of pure trans isomer 74t; there was no methoxyl signal observable at τ 7.02 where the cis isomer 74c is known to absorb.

U. Condensation of p-Tolualdehyde with the α-Lithio Salt of Dibenzobicyclo[2.2.2]octadiene-2-one (9): Preparation of 3-(p-Methylbenzylidene)-dibenzobicyclo[2.2.2]octadiene-2-one (70)

To a solution of the α-lithio salt of 9, prepared as in part M, was added dropwise 1.44 g (0.12 mol) of p-tolualdehyde in 5 ml of THF, which caused the solution to turn yellow. The ice bath was removed, and about 25 min after the addition was complete the solution was refluxed for 30 min. This caused the solution to turn orange. An ir spectrum of the crude reaction mixture showed a strong double bond absorption at 1624 cm^{-1}.

The solution was diluted with ether, washed five times with 25% HCl, once with water, and dried ($MgSO_4$). A crystalline solid formed as the solvents were evaporated. It weighed 3.9 g. Recrystallization from ethanol gave 1.75 g

(45%) of the desired enone 70: mp 203.5-204°. An nmr spectrum of the residue in the mother liquor did not have any absorptions in the bridgehead region.

Anal. Calcd. for $C_{24}H_{18}O$: C, 89.41; H, 5.63
Found: C, 89.53; H, 5.59

Spectral data: ir 1698 cm^{-1} (conjugated C=O) and 1624 (C=C); uv max 273 nm (ε13,200), 303 (19,600), 344 (sh, 769), 361 (sh, 515), and 382 (sh, 185); mass spectrum m/e (rel intensity) 322 (1.98) and 178 (100); nmr τ 2.47-2.90 (m, 13, aryl and vinyl), 4.31 (s, 1, bridgehead adjacent to vinyl), 5.00 (s, 1, bridgehead adjacent to carbonyl), and 7.60 (s, 3, methyl). Only one stereoisomer was observed.

V. Condensation of p-Anisaldehyde with the α-Lithio Salt of Dibenzobicyclo[2.2.2]octadiene-2-one (9): Preparation of 3-(p-Methoxybenzylidene)-dibenzobicyclo[2.2.2]octadiene-2-one (71).

To a solution of the α-lithio salt of 9, prepared as in part M, was added dropwise 1.63 g (0.12 mol) of p-anisaldehyde in 5 ml of THF. The reaction proceeded and was worked up as in the previous section. After the solvents had been evaporated, a viscous oil was obtained which would not crystallize. Tlc on silica gel with benzene showed several spots.

The oil was chromatographed on a 2 cm column using 70 g of silica gel finer than 200 mesh (Brinkmann) with chromato-quality benzene. The first material off was discarded. The second band which was yellow contained the desired enone.

It weighed 2.00 g (49%). After recrystallization from ethanol 71 melted at 161.8-162.3°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36

Found: C, 85.05; H, 5.33

Spectral data: ir 1699 cm^{-1} (conjugated C=O) and 1628 (C=C); uv max 279 nm (sh, ε10,200), 315 (23,000), 364 (sh, 702), and 382 (sh, 236); mass spectrum m/e (rel intensity) 338 (3.7) and 176 (100); nmr τ 2.42-2.90 (m, 13, aryl and vinyl), 4.28 (bridgehead adjacent to vinyl), 5.00 (s, 1, bridgehead adjacent to carbonyl), and 6.12 (s, 3, methoxy). Only one stereoisomer was isolated.

W. Condensation of p-Chlorobenzaldehyde with the α-Lithio Salt of Dibenzobicyclo[2.2.2]octadiene-2-one (9): Preparation of 3-(p-Chlorobenzylidene)-dibenzobycyclo[2.2.2]octadiene-2-one (72)

To a solution of the α-lithio salt of 9, prepared as in part M, was added dropwise over a period of 3 min 1.68 g (0.12 mol) of p-chlorobenzaldehyde dissolved in 4 ml of THF. Shortly after the addition was complete the solution turned yellow. The reaction vessel was removed from the ice bath, and the solution was refluxed for 2 hr. Ether was added to the cooled solution; it was washed five times with 25% HCl, once with water, dried ($MgSO_4$), and evaporated to give a viscous yellow oil.

After three days the oil, which contained crystals, was diluted with chloroform and 60 mg of a colorless crystalline

product was collected by suction filtration. An ir spectrum of these crystals which sublimed at 237-239° contained a strong absorption at 1680 cm^{-1}, but had no double bond absorption around 1630 cm^{-1}. As this was not the desired product, it was set aside.

The chloroform was evaporated from the viscous oil, and 95% ethanol was added. A precipitate formed which was collected by suction filtration and weighed 1.1 g. An nmr spectrum of the precipitate contained bridgehead peaks at τ 4.40 and 4.97, although tlc indicated that several compounds were present. This material was chromatographed on a 2 cm column of 25 g of silica gel finer than 200 mesh (Brinkmann) with chromatoquality benzene as the eluant. The first material off the column contained no carbonyl absorption in its ir spectrum. The second band, which was yellow, contained the desired enone. After recrystallization from ethanol the colorless needles of 72 weighed 0.227 g (7%): mp 191.5-192.5°.

Anal. Calcd. for $C_{23}H_{15}ClO$: C, 80.58; H, 4.41
Found: C, 80.47; H, 4.51

Spectral data: ir 1701 cm^{-1} (conjugated C=O) and 1628 (C=C); uv max 273 nm (ε14,000), 302 (16,900), 341 (sh, 839), 362 (sh, 524), and 384 (sh, 205); mass spectrum m/e 344 (0.23), 3.42 (0.68, and 178 (100); nmr τ 2.46-2.90 (m, 13, aryl and vinyl), 4.40 (s, 1, bridgehead adjacent to vinyl), and 4.97 (s, 1, bridgehead adjacent to carbonyl). Only one stereoisomer was isolated.

X. Photolysis of 3-(p-Substituted benzylidene)-dibenzobicyclo-[2.2.2]octadiene-2-ones 70, 71, and 72

Approximately 100 mg ± 1 of the enone to be photolyzed was dissolved in 190 ml of methanol and irradiated through a Pyrex filter with a medium pressure mercury lamp until the uv absorption for anthracene at 252 nm was very small. This meant that anthracene was no longer being formed, and that virtually all that had been formed had been photodimerized. The insoluble dianthracene was collected by suction filtration and weighed to determine the percent of reaction that went by this pathway. Enone 70 yielded 20.3 and 23.0 mg of dianthracene in two different runs which correspond to yields of 37 and 42%. Enone 71 afforded 22.3 mg (38%) of dianthracene, and enone 72 gave 18.9 mg for a 37% yield.

The solvent was then evaporated and an nmr taken of the crude reaction mixture. In all cases the reactions were clean; only cinnamates and ethanoanthracene esters analogous to 74c and 74t were formed as shown in Fig. 7 and Fig. 8. Consequently the percent of the reaction which proceeded to form the ethanoanthracene esters was calculated as 100 minus the percent of dianthracene obtained.

Y. Photolysis of 3-Benzylidenedibenzobicyclo[2.2.2]octadiene-2-one (69) in the Rayonet Reactor with 300 and 350 nm Lamps

Approximately 100 mg ± 1 of enone 69 was dissolved in 190 ml of methanol and placed in a photolysis well. An immersion

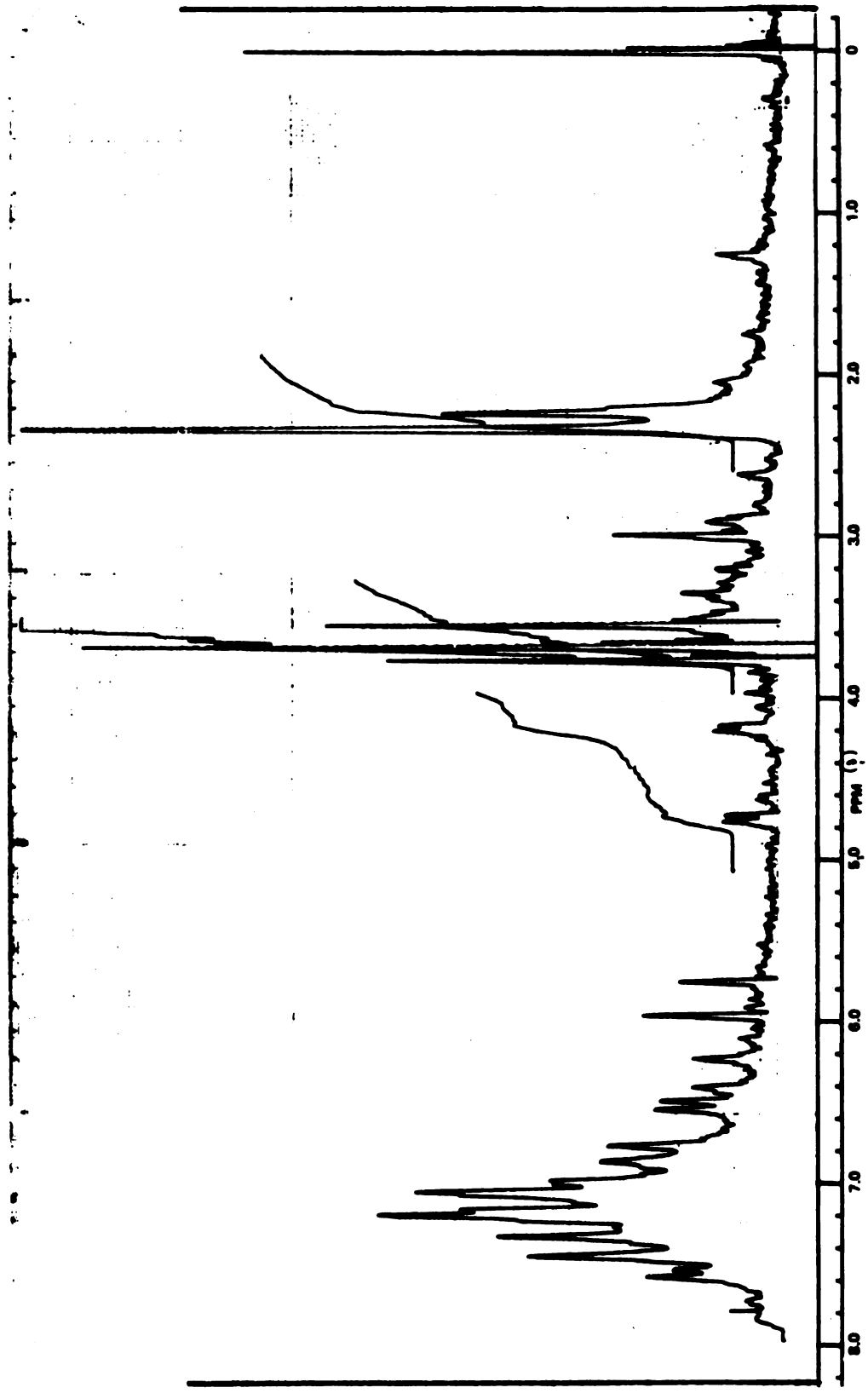

Figure 7. Nmr spectrum of the crude photolysis mixture after irradiation of 3-(p-methylbenzylidene)dibenzobicyclo[2.2.2]octadiene-2-one (7ℓ) in methanol and removal of the insoluble dianthracene

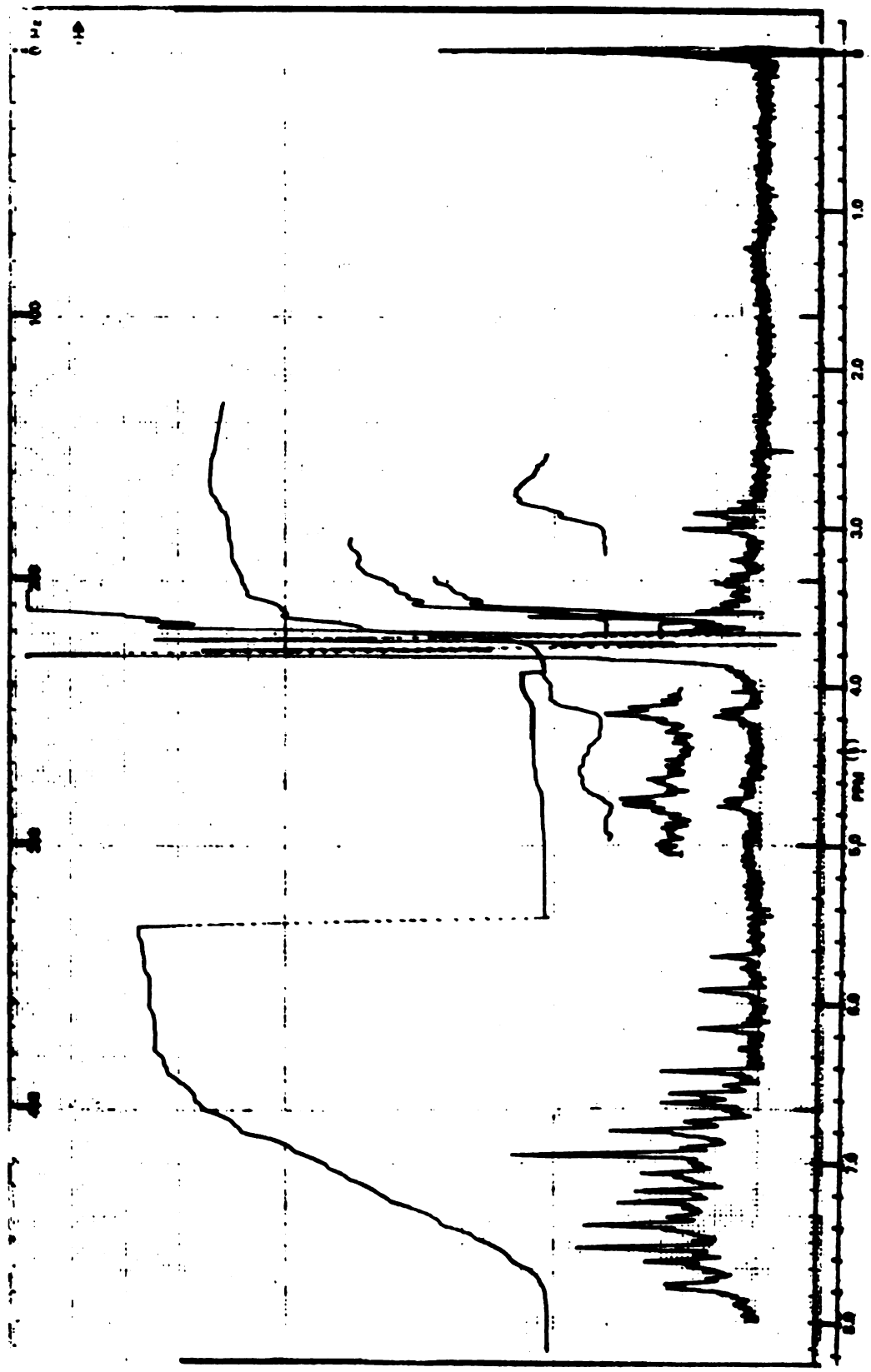

Figure 8. Nmr spectrum of the crude photolysis mixture after irradiation of 3-(p-methoxybenzylidene)dibenzobicyclo[2.2.2]octadiene-2-one (71) in methanol and removal of the insoluble dianthracene

well with cooling water flowing through it was inserted in the photolysis well and the whole apparatus was placed in the Rayonet.

When the effect of 300 nm wavelength irradiation was to be studied, the solution was irradiated until the peak at 298 nm due to enone 69 had essentially vanished. The lamps were then changed to ~350 nm ones, and the solution further irradiated to dimerize the anthracene which does not absorb much at 300 nm. When the anthracene peak was small, the dianthracene was collected by suction filtration. It weighed 18.8 mg (32%).

When the effect of 350 nm wavelength irradiation was to be studied, the solution was simply irradiated until the size of the anthracene peak at 252 nm had become small. The yield of dianthracene obtained was 10.6 mg (18%).

LITERATURE CITED

LITERATURE CITED

1. O. Diels and B. Wolf, Ber., 39, 689 (1906).
2. H. Staudinger and E. Anthes, Ber., 46, 1426 (1913).
3. A. Klemenc and G. Wagner, Ber., 70, 1880 (1937).
4. O. Diels, Ber., 71, 1197 (1938).
5. S. M. McElvain and R. L. Clarke, J. Amer. Chem. Soc., 69, 2661 (1947).
6. R. W. Hoffmann and H. Häuser, Tetrahedron Lett., 197 (1964).
7. D. M. Lemal, E. P. Gosselink, and A. Ault, Tetrahedron Lett., 579 (1964).
8. J. Strating, B. Zwanenburg, A. Wagenaar, and A. C. Udding, Tetrahedron Lett., 125 (1969).
9. B. P. Stark and A. J. Duke, Extrusion Reactions, Pergamon Press, 1967; C. F. H. Allen, Chem. Rev., 37, 209 (1945); ibid., 62, 653 (1962); M. A. Ogliaruso, M. G. Romanelli and E. I. Becker, ibid., 65, 261 (1965).
10. A. J. Boulton and J. F. W. McOmie, J. Chem. Soc., 2549 (1965).
11. R. K. Murray, Jr. and H. Hart, Tetrahedron Lett., 4995 (1968).
12. N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, J. Amer. Chem. Soc., 92, 3854 (1970).
13. W. R. Vaughn and M. Yoshimine, J. Org. Chem., 22, 528 (1957).
14. M. S. Newman and R. W. Addor, J. Amer. Chem. Soc., 77, 3789 (1955).

15. L. Horner and H. Merz, Ann., 570, 89 (1950).

16. E. Whittle, D. A. Dows, and G. Pimentel, J. Chem. Phys., 22, 1943 (1954).

17. G. N. Lewis, E. Lipkin, and T. T. Magel, J. Amer. Chem. Soc., 63, 3005 (1941).

18. E. D. Becker and G. C. Pimentel, J. Chem. Phys., 25, 225 (1956).

19. R. K. Murray, Jr., Ph.D. Thesis, Michigan State University, 1968.

20. H. Hart and G. M. Love, J. Amer. Chem. Soc., 93, 6266 (1971).

21. L. Barber, O. L. Chapman, and J. D. Lassila, J. Amer. Chem. Soc., 90, 5933 (1968).

22. G. E. Leroi, G. E. Ewing, and G. C. Pimentel, J. Chem. Phys., 40, 2298 (1964).

23. S. W. Charles and K. O. Lee, Trans. Faraday Soc., 61, 614 (1965).

24. C. L. Jackson and R. D. MacLaurin, Amer. Chem. J., 37, 7 (1907).

25. K. J. Crowley, R. A. Schneider, and J. Meinwald, J. Chem. Soc. (C), 571 (1966).

26. W. L. Schreiber and W. C. Agosta, J. Amer. Chem. Soc., 93, 6292 (1971).

27. P. Bladon and I. A. Williams, J. Chem. Soc. (C), 2032 (1967).

28. D. Y. Y. Lam, D. Valentine, and G. S. Hammond, J. Amer. Chem. Soc., 89, 3482 (1967).

29. W. G. Dauben, G. W. Schaffer, and N. D. Vietmeyer, J. Org. Chem., 33, 4060 (1968).

30. O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, Tetrahedron Lett., 2049 (1963).

31. H. E. Zimmerman and N. Lewin, J. Amer. Chem. Soc., 91, 879 (1969).

32. P. E. Eaton, J. Amer. Chem. Soc., 84, 2454 (1962).

33. P. de Mayo, J. P. Pete, and M. Tchir, Canad. J. Chem., 46, 2535 (1968).

34. G. Buchi and I. M. Goldman, J. Amer. Chem. Soc., 79, 4741 (1957).

35. P. E. Eaton, Tetrahedron Lett., 3695 (1964).

36. E. J. Corey, J. D. Bass, R. LeMahiew, and R. B. Mitra, J. Amer. Chem. Soc., 86, 5570 (1964).

37. P. J. Nelson, D. Ostreem, J. D. Lassila, and O. L. Chapman, J. Org. Chem., 34, 811 (1969).

38. N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, Accounts. Chem. Res. 5, 96 (1972).

39. L. E. Friedrich and G. B. Schuster, J. Amer. Chem. Soc., 91, 7204 (1969).

40. W. C. Agosta, A. B. Smith, A. S. Kende, R. G. Eilerman, and J. Benham, Tetrahedron Lett., 4517 (1969).

41. O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, J. Amer. Chem. Soc., 91, 6856 (1969).

42. J. Ciabattoni, J. E. Crowley, and A. S. Kende, J. Amer. Chem. Soc., 89, 2778 (1967).

43. E. I. Snyder and R. A. Clement, J. Amer. Chem. Soc., 82, 1424 (1960).

44. S. Wawzonek and J. V. Hallum, J. Org. Chem., 18, 288 (1953).

45. R. Greenwald, M. Chaykovsky, and E. J. Corey, J. Org. Chem., 28, 1128 (1963).

46. Serge Lecolier, Chim. Ther., 3, 34 (1969).

47. F. Newmann, O. Mancera, G. Rosenkranz, and F. Sondheimer, J. Amer. Chem. Soc., 77, 5676 (1955).

48. A. Burger and W. B. Bennet, J. Amer. Chem. Soc., 72, 5414 (1950), and P. L. Julian, W. W. Meyer, and H. C. Printy, J. Amer. Chem. Soc., 70, 3872 (1948).

49. D. R. Kelsey, J. Amer. Chem. Soc., 94, 1764 (1972).

50. Unpublished work of D. N. Buchanan of this laboratory.

51. Sadtler Standard Infrared Spectrum #20684.

52. H. Scheibler and U. Scheibler, Ber., 87, 379 (1954).

53. This is the expected photostationary state ratio under the reaction conditions; cf. D. R. Arnold, L. B. Gillis, and E. B. Whipple, Chem. Commun., 918 (1969).

54. J. S. Walia and L. C. Vishwakarma, Chem. Commun., 396 (1969).

55. E. de B. Barnett, N. F. Goodway, and E. V. Weekes, J. Chem. Soc., 1102 (1935).

56. J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1965, pp 116-118.

57. P. J. Wagner, Accounts. Chem. Res., 4, 168 (1971).

58. K. Alder and H. F. Rickert, Ann., 543, 1 (1940).