

In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institute shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or, in his absence, by the Dean of the Graduate Division when such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.

A handwritten signature in dark ink, consisting of a stylized first name and a surname, is written above a solid horizontal line.

7/25/68

THE PHOTOCHEMICAL REACTIONS OF
DIMETHYL 1-NAPHTHALENEMALEATE,
DIMETHYL 2,3-BENZOBICYCLO[2.2.2]OCTATRIENE -
5,6-DICARBOXYLATE, AND
DIMETHYL BENZOCYCLOOCTATETRAENE-5,6-DICARBOXYLATE

A THESIS

Presented to

The Faculty of the Graduate Division

by

Tomoo Shibata

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Chemistry

Georgia Institute of Technology

September, 1970

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. Erling Grovenstein, Jr., for his suggestion of the problem, for his advice and assistance, and, above all, for his valuable criticism and encouragement during the course of this research. The author also wishes to thank Dr. Drury S. Caine and Dr. Charles L. Liotta for serving as members of the reading committee.

The graduate assistantship provided by the Department of Chemistry, the support by the National Science Foundation, both of which were held by the author during the course of this research, are greatly appreciated.

The author is also grateful to Mr. and Mrs. John Bansley, Jr., and Mr. and Mrs. Enrico P. Domicone for encouragement while in the United States.

The author is most of all indebted to his family for their support and encouragement during this period.

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES	v
LIST OF ILLUSTRATIONS	v
SUMMARY	vi
Chapter	
I. INTRODUCTION	1
II. REAGENTS AND SOLVENTS	4
III. EQUIPMENT AND GENERAL EXPERIMENTAL PROCEDURES	8
Equipment	
General Experimental Procedures	
Analyses	
Vapor Phase Chromatography	
Liquid Chromatography	
Hydrogenations	
Photolysis Apparatus and Procedures	
IV. PHOTOCHEMICAL REACTIONS, SYNTHESSES, AND IDENTIFICATION OF PRODUCTS	12
Preparation of Dimethyl 1-Naphthalenemaleate	
Preparation of Dimethyl 2,3-Benzobicyclo[2.2.2]-octatriene-5,6-dicarboxylate	
Photolysis of Dimethyl 1-Naphthalenemaleate in Solution	
Dioxane	
Isopropyl Alcohol	
Methyl Alcohol	
Tetrahydrofuran	
Acetone	
Acetonitrile	
Cumene	
Benzene	
n-Hexane	
Cyclohexane	
Perdeuteroacetone	
Perdeuteroacetonitrile	
Methyl Alcohol-d ₁	

TABLE OF CONTENTS (Continued)

	Page
Dioxane with Deuterium Oxide	
Cyclohexane with Iodine	
Methyl Alcohol with Iodine	
Dioxane with Benzophenone	
Benzene with Benzophenone	
Photolysis of Dimethyl 2,3-Benzobicyclo[2.2.2]octa- triene-5,6-dicarboxylate in Solution	
Methyl Alcohol	
Benzene	
Benzene with Benzophenone	
Photolysis of Dimethyl Benzocyclooctatetraene-5,6-dicarboxy- late in Solution	
Dioxane	
Acetone	
Benzene	
Benzene with Benzophenone	
Methyl Alcohol	
V. DISCUSSION	42
Photolysis of Dimethyl 1-Naphthalenemaleate in Solution	
Photolysis of Dimethyl 1-Naphthalenemaleate in Deuterium- labeled Solvents	
Photolysis of Dimethyl 1-Naphthalenemaleate with Iodine	
Photolysis of Dimethyl 1-Naphthalenemaleate with Benzophenone	
Photolysis of Dimethyl 2, 3-Benzobicyclo[2.2.2]-octatriene-5, 6-dicarboxylate	
Photolysis of Dimethyl Benzocyclooctatetraene-5, 6-dicarboxylate	
Mechanistic Considerations	
Conclusions	
VI. RECOMMENDATIONS	58
APPENDICES	59
LITERATURE CITED	74

LIST OF TABLES

Table		Page
1.	Yield of Dimethyl Acenaphthene-1, 2-dicarboxylate.	42
2.	Incorporation of Deuterium into Dimethyl Acenaphthene-1, 2-dicarboxylate during Preparation by Irradiation of Dimethyl 1-Naphthalenemaleate.	44
3.	Reaction Products of Dimethyl 2,3-Benzobicyclo[2.2.2]-octatriene-5,6-dicarboxylate in Various Solvents	46
4.	Yield of Unknown II in Various Solvents.	48

LIST OF ILLUSTRATIONS

Figure		
1.	Mechanism of Cyclization of Dimethyl 1-Naphthalenemaleate. . .	49
2.	Possible Reaction Paths upon Photolysis of Dimethyl 1-Naphthalenemaleate in Benzene as Solvent	51
3.	Mechanism of Formation of Dimethyl Acenaphthene-1, 2-dicarboxylate.	52

SUMMARY

The purpose of this research was to study the photochemical reactions of dimethyl 1-naphthalenemaleate, dimethyl 2,3-benzobicyclo[2.2.2]-octatriene-5,6-dicarboxylate and dimethyl benzocyclooctatetraene-5,6-dicarboxylate.

The solutions of dimethyl 1-naphthalenemaleate were irradiated at room temperature in dioxane, isopropyl alcohol, methyl alcohol, tetrahydrofuran, acetone, acetonitrile, cumene, benzene, n-hexane, and cyclohexane. The major product isolated was dimethyl trans-acenaphthene-1,2-dicarboxylate, 3, containing variable but lesser amounts of the corresponding cis isomer. Another product, which was shown to be present by vpc analysis but not isolated from the reaction mixture, was dimethyl 1-naphthalene-fumarate, 2. In acetone, acetonitrile, and benzene, dimethyl acenaphthylene-1,2-dicarboxylate was found in 9.6, 13.9, and 6.0 percent, respectively. High yields of 3 were obtained when solutions of dimethyl 1-naphthalenemaleate were photolyzed in dioxane, isopropyl alcohol or methyl alcohol. Fair yields of 3 were obtained in tetrahydrofuran, acetone, acetonitrile, cumene or benzene. In n-hexane or cyclohexane, 3 was not formed. The photolysis of dimethyl 1-naphthalenemaleate in perdeuteroacetone or perdeuteroacetonitrile, gave dimethyl trans-acenaphthene-1,2-dicarboxylate-1-d₁, 4. In cyclohexane with iodine or methyl alcohol with iodine, the photochemical reaction gave a mixture of dimethyl 1-naphthalenefumarate, dimethyl 1-naphthalenemaleate,

dimethyl trans-acenaphthene-1,2-dicarboxylate and dimethyl acenaphthylene-1,2-dicarboxylate.

The photochemical reaction of dimethyl 2,3-benzobicyclo[2.2.2]-octatriene-5,6-dicarboxylate, 6, in benzene gave dimethyl benzocyclooctatetraene-5,6-dicarboxylate in good yield. The reactant, 6 with benzophenone in benzene gave 8 as the major isolated product in 69 percent yield. Compound 8 was identified as dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-1,8-dicarboxylate, from its spectral and chemical properties. The prolonged photolysis of 6 in methyl alcohol with a Pyrex filter gave an unknown compound II in 53 percent as a major product. The reaction with uranium glass filter in the same solvent gave compound 8 in 25 percent and unknown compound II in 12.3 percent yield.

The photochemical reaction of dimethyl benzobicyclooctatetraene-5,6-dicarboxylate in benzene with benzophenone gave unknown compound II as the major product in 70 percent. The unknown II was unstable and not isolated in pure state. The NMR spectrum of the crude product suggested the structure 9, dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene-1,7-dicarboxylate. The reaction without benzophenone gave a mixture of 0.5 percent of 6, 10 percent of 8, 18 percent of starting material, 26 percent of unknown II and 6.3 percent of unknown III. The photolysis of dimethyl benzobicyclooctatetraene-5,6-dicarboxylate in dioxane in a Pyrex cell gave no reaction, but in acetone solvent, 25 percent of unknown II was obtained.

The photochemical reaction of dimethyl 2,3-benzobicyclo[2.2.2]-octatriene-5,6-dicarboxylate in benzene follows the aryl-vinyl bridging path to give dimethyl benzocyclooctatetraene-5,6-dicarboxylate. The

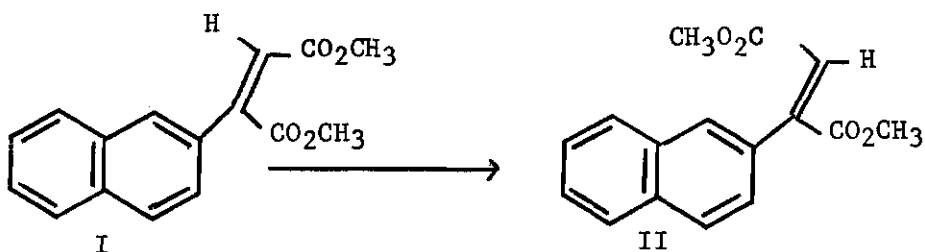
compound 8 isolated from the reaction with benzophenone was explained by a vinyl-vinyl bridging pathway.

CHAPTER I

INTRODUCTION

The purpose of this research was to study the reaction of dimethyl 1-naphthalenemaleate, dimethyl 2, 3-benzobicyclo[2.2.2]octatriene-5, 6-dicarboxylate, dimethyl benzocyclooctatetraene-5, 6-dicarboxylate activated by ultraviolet radiation. The influence of varying solvents upon the amounts and types of reaction products was studied. This work is a natural sequel to the study of the photochemical reactions of dimethyl 1-naphthalenemaleate in dioxane or methyl alcohol, and dimethyl 2, 3-benzobicyclo[2.2.2] octatriene-5, 6-dicarboxylate in methyl alcohol or acetone.¹

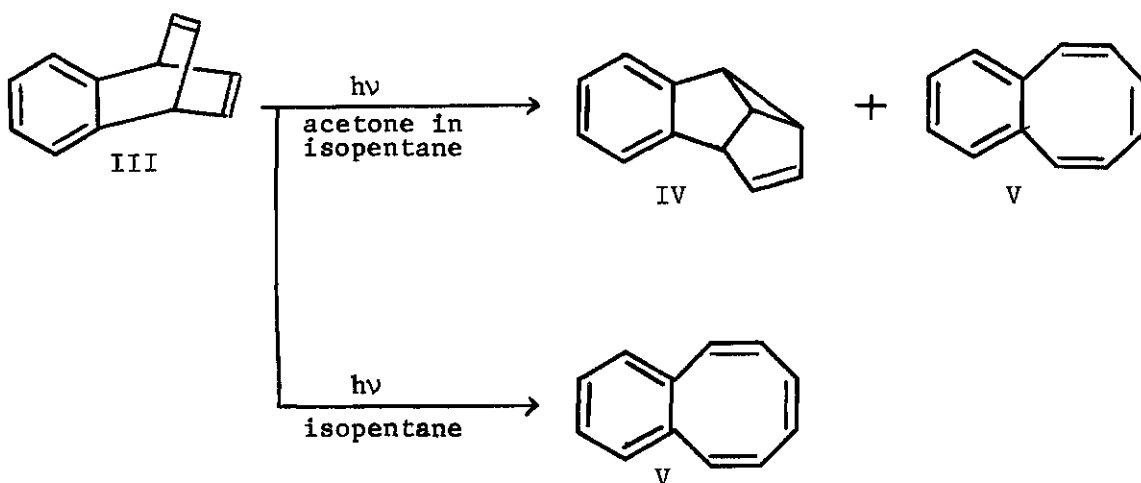
Dimethyl 2-naphthalenemaleate reacts photochemically in dioxane to give dimethyl 2-naphthalenefumarate.¹ There was no cyclization product.



¹E. Grovenstein, Jr., T. C. Campbell, and T. Shibata, *J. Org. Chem.*, **34**, 2418 (1969).

The photochemical reaction of dimethyl 1-naphthalenemaleate in dioxane or methyl alcohol gave dimethyl 1-naphthalenefumarate very rapidly and dimethyl trans-acenaphthene-1, 2-dicarboxylate somewhat more slowly. The yield of the dimethyl trans-acenaphthene-1, 2-dicarboxylate was 92.2 percent in dioxane and 74.4 percent in methyl alcohol.

Zimmerman, Givens and Pagni² recently reported that photoisomerization of benzobarrelene, III, with acetone sensitization afforded benzosemibullvalene, IV, and a small amount of benzocyclooctatetraene, V, while on direct irradiation, benzobarrelene in isopentane affords only benzocyclooctatetraene as shown below.

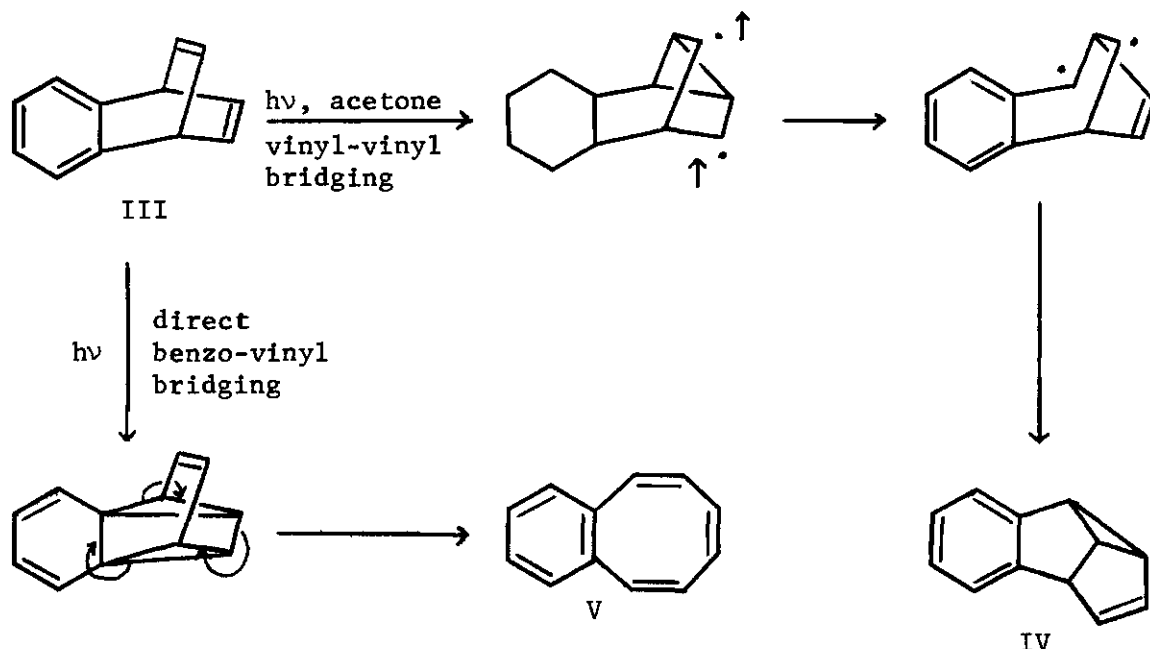


²H. E. Zimmerman, R. S. Givens, and R. M. Pagni, J. Am. Chem. Soc., 90, 4191 (1968).

Direct irradiation of III in cyclohexane leads to the exclusive formation of V (95 percent) while photosensitization (acetophenone or acetone in cyclohexane) produces IV (99 percent) with only a trace of V. Similarly, tetrafluorobenzobarrelene is converted to the tetrafluorosemibullvalene by sensitization while direct irradiation reaction gave tetrafluorobenzocyclooctatetraene.³

A similar type of photoisomerization was demonstrated by Rabideau, *et al.*³ who found that rearrangement of dibenzobicyclo[2.2.2]octatriene derivatives to cyclooctatetraenes occurs from the singlet, and to semibullvalenes from the excited triplet.

These results support the mechanism proposed by Zimmerman,² wherein the major singlet process from benzobarrelene derivatives to benzocyclooctatetraenes involves benzo-vinyl interaction, while the triplet process to semibullvalenes involves vinyl-vinyl interaction.



³ P. W. Rabideau, J. B. Hamilton, and L. Friedman, *J. Am. Chem. Soc.*, **90**, 4465 (1968).

CHAPTER II

REAGENTS AND SOLVENTS

Acetic Anhydride

Fisher certified A.G.S. acetic anhydride was used without further purification.

Acetone

Commercial grade acetone was distilled through a 30 cm Vigreux column.

Acetonitrile

Fisher certified grade acetonitrile was distilled through a 30 cm Vigreux column.

1-Aminonaphthalene

Aldrich reagent grade 1-aminonaphthalene (m.p. 48° - 51°) was used without further purification.

Benzene

Matheson, Coleman & Bell, Inc., industrial grade (thiophene-free) benzene was distilled through a 30 cm column packed with glass helices.

Carbon Tetrachloride

Baker spectroscopic grade carbon tetrachloride was used without further purification.

Chloroform

Baker reagent grade chloroform was used without further purification.

Cumene

Eastman Organic Chemicals white label cumene was distilled through a 30 cm Vigreux column.

Cyclohexane

Phillips 99.5 percent cyclohexane was used without further purification.

Deuteroacetone

Stohler Isotope Chemicals acetone-d₆ 99.5 atom percent deuterium was used without further purification.

Deuteroacetonitrile

Stohler Isotope Chemicals acetonitrile-d₃ 99.0 atom percent deuterium was used without further purification.

Diethyl Ether

Baker reagent grade diethyl ether was used without further purification.

Dimethyl Acetylenedicarboxylate

Aldrich reagent grade dimethyl acetylenedicarboxylate was redistilled at 92°-93° at 15 mm pressure through a 15 cm Vigreux column.

1,4-Dioxane

Fisher certified grade 1,4-dioxane was distilled over sodium metal through a 15 cm Vigreux column.

Ethanol

Commercial 95 percent ethanol was used without further purification.

Ethyl Acetate

Commercial ethyl acetate was distilled through a 30 cm column packed with glass helices.

n-Hexane

Phillips 99 percent n-hexane was used without further purification.

Isopropyl Alcohol

Commercial isopropyl alcohol was shaken with 50 percent of sodium hydroxide solution and dried over barium oxide for two days. Then isopropyl alcohol was distilled through a 30 cm column packed with glass helices.

Maleic Acid

Aldrich maleic acid m.p. 135^o-137^o was used without further purification.

Methanol

Fisher certified grade methyl alcohol was refluxed over magnesium turnings overnight and then distilled through a 30 cm column packed with glass helices.

Methanol-d₁

Diaprep Incorporated CH₃OD 99 atom percent deuterium was used without further purification.

Naphthalene

Baker reagent grade naphthalene was used without further purification.

Petroleum Ether

Commercial petroleum ether (b.p. 30° -60° C) was used without further purification.

Silica Gel

Brinkman Instruments Company No. 7734 Silica gel (0.05 to 0.20 mm) was used without further treatment.

Tetrahydrofuran

Fisher certified grade tetrahydrofuran was used without further purification.

CHAPTER III

EQUIPMENT AND GENERAL EXPERIMENTAL PROCEDURES

Equipment

Melting points were determined in capillary tubes on a Mel-Temp apparatus. Proton magnetic resonance spectra were obtained at 60 MHz using a Varian Associates Model A-60A spectrometer equipped with a spin decoupler and variable temperature probe. Ultraviolet and visible spectra were determined on a Cary Model 14 recording spectrophotometer. Infrared spectra were measured on a Perkin-Elmer Model 237 Infracord.

General Experimental Procedures

Analyses

Elemental analyses and molecular weight determinations were performed by Galbraith Laboratories, Knoxville, Tennessee.

Vapor Phase Chromatography

An F & M Scientific Company Model 810 research chromatograph and a Perkin-Elmer Corporation Model 880 Gas Chromatograph, both equipped with dual flame ionization detectors, were used for all vapor phase chromatographic analysis.

For the F & M gas chromatograph machine, a pair of five foot, one-fourth inch o.d. stainless steel columns packed with 10 percent Apiezon L on 60-80 mesh Chromosorb P, which had been acid-washed and treated with dichlorodimethylsilane, and a pair of 6 foot, one-fourth inch o.d. stainless steel columns packed with 10 percent SE-30 silicone

gum rubber on 80-100 mesh Diatoport S, which had been acid-washed and treated with dichlorodimethylsilane, were used. Typical operating conditions for these columns for analysis of the photoproducts of dimethyl 1-naphthylmaleate included holding the temperature of the oven constant at 220°. In most cases, the flow rate was set at a scale reading of 20 mm at 50 psig, which corresponded to a flow rate of about 40 ml per minute, according to the calibration curve supplied with the instrument. The injector temperature was 280°.

For a Perkin-Elmer Model 880 gas chromatograph, a pair of six foot, one-eighth inch o.d., stainless steel columns packed with 10 percent Apiezon L on 80-100 mesh Chromosorb W and a pair of six foot, one-eighth inch o.d., stainless steel columns packed with 5 percent SE-30 silicone gum rubber on 100-120 mesh Chromosorb G were used. Typical operating conditions for these columns with the flame detector for analysis of the photoproducts of dimethyl 1-naphthalenemaleate and dimethyl 2,3-benzobicyclo[2.2.2]octatriene-5, 6-dicarboxylate included holding the temperature of the oven at 200°. The flow rate was set at a scale reading of 20 mm at 60 psig. The injector port temperature was 235° and the detector temperature was 210°.

The progress of the reaction was followed by removing a tiny sample (generally by using a Hamilton 10 μ l syringe) from the cell and injecting a 0.2 μ l sample into the vpc. The disappearance of the starting material was followed as was the appearance of the products. The reactions were generally stopped when the peak height of the starting material was reduced to 5 percent of the peak height of the original sample. The yield of the products was generally determined by comparing

the peak area of the starting material, which was taken as 100 percent, with the peak area of the products. This vpc analysis of the isomers is accurate within about 5 percent.

Liquid Chromatography

The liquid chromatographs were run according to the procedure given in T. C. Campbell's thesis.*

Hydrogenations

All hydrogenations were carried out in an atmospheric pressure apparatus using 5 percent palladium on charcoal as the catalyst. The catalyst and solvent were pre-reduced for one to three hours to equilibrate the system. The amount of hydrogen taken up was measured versus time. The temperature and atmospheric pressure were recorded for conversion of the volume of hydrogen to standard conditions.

Photolysis Apparatus and Procedures

The photolysis were carried out, unless otherwise specified, in a cylindrical quartz or Pyrex cell which had an inner jacket for temperature control and an outer sample jacket of 220 ml capacity (quartz cell) or 350 ml capacity (Pyrex cell). The temperature of the cell was kept near 23^o by passing tap water through the jacket. Nitrogen was bubbled through the solution for all of the photolyses unless otherwise specified. The irradiation apparatus was made by the Hanovia Chemical and

* T. C. Campbell, Ph.D. Thesis, Georgia Institute of Technology, 1967, p. 16.

Manufacturing Company of Newark, New Jersey, and contained a high pressure mercury lamp (type LL) of 30 cm arc length. The lamp operated on about 1000 watts at a current of 3.8 to 4.2 amperes. A Pyrex filter could be inserted between the lamp and the cell to eliminate nearly all of the radiation below 3000 Å, if so desired. A uranium glass filter could be used to eliminate nearly all of the radiation below 3400 Å. This 1000-watt lamp was used unless otherwise specified; in other experiments, 450-watt or 200-watt Hanovia high pressure lamps were used.

CHAPTER IV

PHOTOCHEMICAL REACTIONS, SYNTHESSES AND IDENTIFICATION OF PRODUCTS

Preparation of Dimethyl 1-Naphthalenemaleate

1-Naphthalenemaleic anhydride was prepared by the following procedure of Denivell and Razavi:⁸ 28.6 g of crude 1-aminonaphthalene (0.200 mole) was added to 80 ml of concentrated hydrochloric acid in a 400 ml beaker. The mixture was heated on the hot plate to 100° with vigorous stirring. The amine hydrochloride never did go into solution appreciably, but remained a fine precipitate. The mixture was set aside to cool. In a separate 600 ml beaker, 23.0 g of maleic acid (0.200 mole) was added to 9.0 g of cupric chloride dihydrate (0.050 mole) and the solution was cooled to 0°C. The amine hydrochloride suspension was cooled in an ice-salt bath to -5°C and 20 more milliliters of concentrated hydrochloric acid was added, along with 25 ml of water. A solution of 15 g of sodium nitrite in 25 ml of water was cooled to 0°C and placed in a small separatory funnel with the stem of the funnel kept under the surface of the liquid. The addition of sodium nitrite solution was controlled so that the temperature of the solution did not exceed 5°C. As soon as an excess of nitrous acid was

⁸L. Denivell and D. Razavi, Compt. rend., 237, 570 (1953)

shown to be present (by a test with starch-iodide paper), the foam was skimmed off and diazonium solution was poured immediately into the cold solution of maleic acid and catalyst. The temperature of the solution increased to 10°-15°. The mixture was allowed to stand overnight with occasional stirring the first hour. The solution in the beaker was washed into a round-bottomed flask with acetone and the acetone was removed on the roto-vac. The aqueous solid mixture was taken up in ether and poured into a one-liter separatory funnel. The ether layer and undissolved solids were washed three times with dilute hydrochloric acid to remove any unreacted amine and copper salts. Three 250 ml portions of saturated sodium bicarbonate solution were then used to wash the ether solution. The ether layer was then discarded and the sodium bicarbonate solution was extracted with three 150 ml portions of ether to remove the highly colored diazonium coupling products. The sodium bicarbonate solution was carefully acidified to a pH of two with 50 percent hydrochloric acid. The acid solution was extracted with three 300 ml portions of ether. The ether solutions were combined, washed twice with 150 ml of water, and dried over anhydrous sodium sulfate. The solvent was removed on the rotating evaporator to give 6.51 g of crude 2-(1-naphthyl)-3-chlorosuccinic acid. The yield of the acid was 11.7 percent. The crude acid was dissolved in 30 ml of acetic anhydride and the solution was refluxed overnight. The solvent was removed in vacuo to give 6.5 g of crude 1-naphthalenemaleic anhydride, corresponding to a yield of 14.5%. The crude anhydride was recrystallized from ethyl acetate to give 5.0 g of yellow crystals. The crystals were vacuum sublimed at 125° and 500 μ

pressure to give 4.7 g of bright yellow crystals melting at 115.0° - 116.0° (reported:⁴ 116°).

1-Naphthalenemaleic anhydride (2.0 g) was dissolved in 100 ml of anhydrous methyl alcohol, and 2 ml of concentrated sulfuric acid was added. The mixture was refluxed for 24 hours on a steam bath with drying tube filled with Drierite attached to the top of the condenser. The methyl alcohol was removed down to about 30 ml in vacuo and neutralized with aqueous sodium bicarbonate solution. The solution was extracted with three 50 ml portions of ether and ether solution was dried over anhydrous sodium sulfate. The ether was removed in vacuo to give 1.7 g of a very pale yellow oil. The oil would not crystallize from methyl alcohol.

Preparation of Dimethyl 2,

3-Benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate

This compound was synthesized by the thermal reaction of naphthalene with dimethyl acetylene dicarboxylate. A mixture of 35 g of naphthalene (0.273 mole), 20.0 ml of dimethyl acetylene-dicarboxylate (0.160 mole), and 0.25 g of hydroquinone was placed in a 100 ml of round-bottomed flask which was sealed with a glass stopper. The flask was placed in a hot oil bath at a temperature of 170° - 180° C for four days.

Removal of the starting materials in vacuo at 200μ on the steam bath gave 32.03 g of residue. The residue was dissolved in 60 ml of chloroform and poured slowly into two liters of 30° - 60° petroleum ether. The insoluble residue weighed 19.08 g. The solvent was removed from the filtrate in vacuo on the rotating

evaporator to give 13.80 g of residue. The residue was dissolved in 50 ml of chloroform and chromatographed on 400 g of Brinkman No. 7734 silica gel using 2000 ml of benzene as an eluent. The first fraction containing all of the 1:1 adduct, dimethyl 2,3-benzobicyclo[2.2.2]-octatriene-5,6-dicarboxylate, weighed 5.10 g, which was a 11.8 percent yield based on the dimethyl acetylenedicarboxylate used. The m.p. was 105° - 105.5° after recrystallization from methyl alcohol. The reported melting point¹ was 76° - 77° . T. Campbell's sample was rechecked and showed m.p. 104° - 105° . NMR spectra indicated that both compounds were identical.

Photolysis of Dimethyl 1-Naphthalenemaleate in Solution

Dioxane

A solution of 0.4557 g of dimethyl 1-naphthalenemaleate (1.69 mmol) in 150 ml anhydrous dioxane was irradiated in a quartz cell with a Pyrex filter under nitrogen for 8 hours. The reaction was followed throughout the irradiation by withdrawal of 1 ml portion of the sample for vpc analysis. The yield of the products was as follows.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1, 2-dicarboxylate
10 min	41.8%	15.3%	39.1%
20 min	34.9	4.9	52.8
1 hr	10.0	1.2	75.3
8 hr	0	0	92.5

The reaction mixture was washed into a 300 ml round-bottomed flask with dioxane and the solvent was removed in vacuo for 2 hours on the rotating evaporator at 700 μ , while the temperature was kept below 24°C to give 0.5214 g of photo product. Analysis of the photo product by vpc using the Apiezon L column at 240° with a flow rate 60 ml per minute showed that it consisted of four products with retention times of 7.5 minutes, 11.4 minutes, 18.8 minutes and 20.2 minutes. The starting material had a retention time of 6.8 minutes under the same conditions. Analysis of the photo product by vpc simultaneously with known compounds showed that the product which had retention times of 7.5 minutes corresponded to dimethyl-acenaphthene-1, 2-dicarboxylate in 92.5 percent yield based on the amount of starting material used. The percent yield of unknown compounds with retention times of 11.4, 18.8 and 20.2 minutes were 0.6 percent, 1.84 percent and 1.84 percent, respectively. These unknowns were not investigated further. The crude photo product was recrystallized from 10 ml of n-hexane to give 0.0982 g of white crystal melting at 82° - 83°.

Isopropyl Alcohol

A 0.2463 g sample of dimethyl 1-naphthalenemaleate (0.912 μ mol) was dissolved in 65 ml of dry isopropyl alcohol. The solution was irradiated in a Pyrex cell under a nitrogen atmosphere for 3.5 hours. The yield of the photo products as function of time was as follows.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1, 2-dicarboxylate
30 min	15.9%	44.6%	39.5%
1 hr	3.0	47.8	49.3
2 hr	1.0	20.6	68.5
3.5 hr	0	0	89.0

The solvent was removed in vacuo on the rotating evaporator to give 0.262 g of oily compound. The NMR spectrum of the crude photo product showed 85 percent of dimethyl trans-acenaphthene-1, 2-dicarboxylate and 15 percent of cis isomer by comparing peak area ratio at 4.88 τ (trans) and 5.18 τ (cis) in deuteriochloroform solvent.

Methyl Alcohol

A solution of 0.900 g of dimethyl 1-naphthalenemaleate (3.33 mmol) in 250 ml of dry methyl alcohol was poured into a 350 ml cylindrical quartz cell with a Pyrex filter. The mixture was irradiated for 13 hours under nitrogen. The temperature of the mixture was 18.5° to 26.5° according to the thermocouples. The irradiation mixture was transferred to a 500 ml of round-bottomed flask and the solvent was removed in vacuo to give 0.813 g of brown oil which crystallized at room temperature after 5 days. Its melting point was 68° - 78°. Quantitative vpc analysis for dimethyl acenaphthene-1, 2-dicarboxylate showed 74.4 percent yield in the crude photo product.

Tetrahydrofuran

A solution of dimethyl 1-naphthalenemaleate (0.473 mmol) in 100 ml of tetrahydrofuran was irradiated for 8 hours in a quartz cell with a Pyrex filter under nitrogen gas. The solvent was removed in vacuo on the rotating evaporator using the water aspirator to give 0.1939 g of crude oily photo product.

Quantitative analysis of the residue by vpc showed 50.8 percent of dimethyl acenaphthene-1, 2-dicarboxylate, and 1.2 percent of dimethyl acenaphthylene-1, 2-dicarboxylate. The crude photo product

was recrystallized from 2 ml of n-hexane to give 0.0124 g of white crystal melted at 81° - 82°.

Acetone

A 1.7467 g sample of dimethyl 1-naphthalenemaleate (6.469 mmol) was dissolved in 60 ml of acetone. A 0.5 ml portion of this solution was taken up and kept in the refrigerator for vpc comparisons. The solution was irradiated for 24 hours in a quartz cell with a Pyrex filter under nitrogen gas. The composition of the volatile material in the reaction mixture by vpc analysis was 47.7 percent of dimethyl acenaphthene-1, 2-dicarboxylate, 6.8 percent of dimethyl acenaphthylene-1, 2-dicarboxylate, 2.3 percent of starting material and 3.2 percent of dimethyl 1-naphthalenefumarate by comparison with the peak area of dimethyl 1-naphthalenemaleate in the starting solution. The solvent was removed in vacuo to give 1.80 g of non-volatile residue. The NMR spectrum of the crude dimethyl acenaphthene-1, 2-dicarboxylate showed that it was a mixture of 80 percent of dimethyl trans-acenaphthene-1, 2-dicarboxylate and 20 percent of the cis isomer by comparing the peak area ratio at 4.88 τ and 5.18 τ , respectively, in deuteriochloroform solvent. The crude photo product was dissolved in 5 ml of chloroform and placed on a column packed with 150 g of Brinkman No. 7734 silica gel. The chloroform was eluted with 100 ml of 30°-60° petroleum ether. Elution with six liters of benzene gave 0.20 g of dimethyl trans-acenaphthene-1, 2-dicarboxylate melting at 81° - 82°.

Acetonitrile

A solution of 0.2825 g of dimethyl 1-naphthalenemaleate (1.046 mmol) in 60 ml of acetonitrile was irradiated in a quartz cell with a

Pyrex filter under nitrogen gas atmosphere for 6 hours. The yield of volatile materials in the photo-product as a function of time was as follows.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1, 2-dicarboxylate
0 hr	0 %	100%	0 %
1 hr	16.9	41.9	10.3
3 hr	14.0	1.0	39.0
6 hr	1.0	0	38.2*

* Dimethyl acenaphthylene-1, 2-dicarboxylate (13.8%) was also formed.

Cumene

A solution of 0.2500 g of dimethyl 1-naphthalenemaleate (0.926 mmol) in 60 ml of dry cumene was irradiated in a quartz cell with a Pyrex filter under nitrogen gas for 19 hours. A steel wire gauze was inserted between the lamp and the cell to cut down the intensity of light. The reaction was followed throughout the irradiation by withdrawal of small samples for vpc analysis.

The solvent was removed in vacuo on the rotating evaporatory to give 0.2550 g of residue. The NMR spectrum of the crude photo-product showed that it was a mixture of 81.8 percent of dimethyl trans-acenaphthene-1, 2-dicarboxylate and 18.2 percent of cis isomer by comparing the peak area ratio at 4.88 τ and 5.18 τ , respectively, in deuteriochloroform solvent.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1, 2-dicarboxylate
0 hr	0.6%	99.4%	0 %
20 min	10.9	80.3	1.0
40 min	16.7	57.8	6.1
1 hr 10 min	18.8	45.0	7.9
2 hr 10 min	15.6	32.2	12.2
3 hr	9.7	17.6	16.4
5 hr	8.7	11.3	20.0
7 hr	3.4	4.1	20.7
9 hr	1.5	1.5	24.9
14 hr	0	0	26.1*
19 hr	0	0	23.1

* Dimethyl acenaphthylene-1, 2-dicarboxylate (3.6%) was also formed.

Benzene

A solution of 0.8450 g of dimethyl 1-naphthalenemaleate (3.130 mmol) in 250 ml of distilled benzene was irradiated for 14 hours in a quartz cell with a Pyrex filter under a nitrogen atmosphere. The solvent was removed in vacuo to give 0.870 g of brown crystals which melted at 168° - 207°. The vpc analysis of this crude photo-product showed that the volatile material consisted of two products with retention times of 15.4 and 23.6 minutes, using Apiezon L column at 220° and the flow rate set at a scale reading of 20 mm at 40 psig (F & M machine). The peak area at 15.4 minutes corresponded to 20.6 percent absolute yield of

dimethyl acenaphthene-1, 2-dicarboxylate. The other product, dimethyl acenaphthylene-1, 2-dicarboxylate, was formed in 6.0 percent absolute yield. The dimethyl acenaphthylene-1, 2-dicarboxylate had retention times of 5.3 minutes on 10 percent silicone gum rubber at oven temperature 210°, and 11.3 minutes on 10 percent Apiezon L column at 225° using Perkin-Elmer VPC machine. This dimethyl acenaphthylene-1, 2-dicarboxylate had exactly the same retention times on both columns as the product isolated from irradiation of dimethyl 1-naphthalene-maleate in cyclohexane with iodine.

n-Hexane

A solution of dimethyl 1-naphthalenemaleate (1.181 mmol) in 60 ml of n-hexane was irradiated in a quartz cell with a Pyrex filter under a nitrogen atmosphere for 18 hours. The reaction was followed by VPC. The formation of dimethyl acenaphthylene-1, 2-dicarboxylate was not observed.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1, 2-dicarboxylate
0 hr	0 %	100 %	0 %
1 hr	9.1	69.7	0
3 hr	10.3	48.6	0
7 hr	10.3	29.1	0
18 hr	5.3	10.6	0

Cyclohexane

A solution of 0.310 g of dimethyl 1-naphthalenemaleate (1.148 mmol) in 60 ml of cyclohexane was irradiated in a quartz cell with a

Pyrex filter under a nitrogen atmosphere for 23 hours. The reaction was followed by vpc.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1, 2-dicarboxylate
0 hr	0 %	100 %	0 %
1 hr	10.3	50.8	0
2 hr	14.6	44.3	0
3 hr	20.0	36.8	0
6 hr	15.2	23.2	0
11 hr	14.1	19.2	1.0
23 hr	10.1	14.1	1.0

An insoluble polymer formed in the cell during the photolysis. The polymer was removed by filtration and dried. It weighed 0.062 g and melted at 120° - 125°. The polymer was recrystallized from methyl alcohol to give 0.0042 g of crystal melting at 175° to 180°. The crystals were not investigated further.

Acetone-d₆

A solution of 1.447 g of dimethyl 1-naphthalenemaleate (5.359 mmol) in 25 g of per-deuteroacetone was irradiated for 40 hours in a quartz cell with a Pyrex filter under a nitrogen atmosphere. The vpc analysis of the solution showed that 50.9 percent of dimethyl acenaphthene-1, 2-dicarboxylate, 7.3 percent of dimethyl 1-naphthalene-fumarate, a trace of starting material and 9 percent of dimethyl acenaphthylene-1, 2-dicarboxylate had been formed. The solvent was

removed by simple distillation to recover 18.54 g of deuterioacetone. The residue was washed with 200 ml of n-hexane and the solution was evaporated down to 5 ml to give an oily compound which did not crystallize. The whole residue was dissolved in 5 ml of chloroform and chromatographed on 20 g of silica gel, using 200 ml of benzene to elute 0.0648 g of the product. The product was recrystallized from n-hexane to give a white unknown crystal melting at 109° - 110° (Cf. m.p. 84.5° - 85.0° for dimethyl trans-acenaphthene-1, 2-dicarboxylate). The unknown compound had the same vpc retention time as dimethyl trans-acenaphthene-1, 2-dicarboxylate on Apiezon L column. The NMR spectrum of the unknown compound in deuteriochloroform showed that 5.8 protons at between 2.18τ and 2.67τ , 0.88 protons at 5.18τ and 6.00 protons at 6.30τ . In carbon tetrachloride solvent, NMR spectrum showed 6.00 protons between 2.20τ and 2.70τ , 0.86 protons at 5.32τ and 6.00 protons at 6.37τ . The unknown product was dissolved with 10 ml of dry methyl alcohol and the solution was refluxed for 40 hours on the steam bath. The solvent was removed in vacuo. The NMR spectrum in carbon tetrachloride showed three peaks at 2.34τ to 2.86τ , 4.95τ and 6.33τ . These were at the same locations as for dimethyl trans-acenaphthene-1, 2-dicarboxylate. Because of the crude nature of the product, the accurate number of protons could not be calculated, but original peaks at 5.32τ and 6.37τ had disappeared. The unknown compound is assumed to be dimethyl cis-acenaphthene-1, 2-dicarboxylate.

In a separate reaction, a solution of 1.0977 g of dimethyl 1-naphthalenemaleate (4.066 mmol) was irradiated in 12.5 g of per-deuterioacetone under the same conditions as before. Forty hours

of irradiation gave 51.2 percent of dimethyl acenaphthene-1, 2-dicarboxylate, 4.4 percent of dimethyl 1-naphthalenefumarate, and a trace of starting material. The solvent was removed by simple distillation. The NMR spectrum of the crude photo product in DCCl_3 showed that 1.10 protons at 4.88 τ and 6.00 protons at 6.32 τ for the trans isomer and 0.69 protons at 5.18 τ and 6.00 protons at 6.30 τ for the cis isomer. The ratio of trans to cis was 78:22. The crude photo-product was liquid-chromatographed on 15 g of silica gel using 600 ml of benzene as the eluent to give 0.30 g of an oily compound. The NMR spectrum showed 1.32 protons at 4.88 τ and 6.00 protons at 6.32 τ for the trans isomer and 0.857 protons at 5.18 τ and 6.00 protons at 6.30 τ for the cis isomer. The oily compound was recrystallized from 3 ml of methyl alcohol to give 0.0457 g of white compound melting at 80° - 81°.

For a blank test, 0.200 g of dimethyl trans-acenaphthene-1, 2-dicarboxylate was dissolved in 18 g of perdeuteroacetone. The solution was irradiated in a quartz cell with a Pyrex filter under nitrogen for 40 hours. The yield of acenaphthene decreased to 67.7 percent. The solvent was removed by distillation to give 0.255 g of residue. The NMR spectrum of the residue showed 2.03 protons at 4.88 τ and 6.00 protons at 6.32 τ in deuteriochloroform solvent; therefore, neither deuterium exchange nor cis-trans-isomerism occurred appreciably under these conditions.

Perdeutero-acetonitrile

A solution of 1.1945 g of dimethyl 1-naphthalenemaleate (4.424 mmol) in 25 ml of perdeuteroacetonitrile was irradiated in a quartz cell with a Pyrex filter under nitrogen for 18 hours. The reaction was

followed by vpc as a function of time.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1, 2-dicarboxylate
0 hr	0.4%	99.6%	0 %
5.5 hr	21.8	0.8	29.4
10.5	9.7	0.4	42.4
18.0	0.4	0	38.2*

*Dimethyl acenaphthylene-1, 2-dicarboxylate (13.9%) was also formed.

The solvent was removed by simple distillation to recover 22 ml of solvent. The NMR spectrum of the crude photo-product in DCCl_3 showed 1.0 protons at 4.88τ and 6.0 protons at 6.32τ for dimethyl trans-acenaphthene-1, 2-dicarboxylate and 1.0 protons at 5.18τ and 6.0 protons at 5.30τ for the cis isomer. The ratio of the trans and cis isomers was 64 to 36 by comparing the two peak area at 4.88τ and 5.18τ . The crude photo product was dissolved in 5 ml of chloroform and chromatographed on 15 g of Brinkman No. 7734 silica gel, using benzene as the eluent. The first fraction, weighing 0.18 g, was eluted with 150 ml of solvent. The NMR spectrum showed that 1.68 protons at 4.88τ and 6.00 protons at 6.32τ for the trans isomer and 1.57 protons at 5.18τ and 6.00 protons at 6.30 for the cis isomer. The ratio of trans to cis isomer was 78:22. The second 150 ml elution gave 0.16 g of product and the NMR spectrum showed 1.31 protons at 4.88τ and 6.00 protons at 6.32τ for the trans and 1.36 protons at 5.18τ and 6.00 protons at 6.30 for the cis isomer. The ratio of trans to cis was 30:70.

As a blank test, a solution of 0.1929 g of dimethyl trans-acenaphthene-1, 2-dicarboxylate (0.71 mmol) in 15 ml of perdeutero-acetonitrile was irradiated in a quartz cell with a Pyrex filter under nitrogen for 20 hours. The solvent was removed by distillation. The NMR spectrum of the residue showed 1.86 protons at 4.88 τ and 6.00 protons at 6.32 τ .

Methyl Alcohol-d₁ (CH₃OD)

A solution of 0.5515 g of dimethyl 1-naphthalenemaleate (2.043 mmol) in 26.5 ml of methyl alcohol-d₁ was irradiated in a 160 ml of Pyrex cell under nitrogen for 20 hours. Analysis of the solution by vpc showed 3.4 percent of dimethyl 1-naphthalenefumarate and 81.4 percent of dimethyl acenaphthene-1, 2-dicarboxylate. The solvent was removed in vacuo at room temperature and at 100 μ , using a dry ice-acetone trap. The residue weighed 0.560 g. The NMR spectrum indicated that 0.96 protons at 4.88 τ and 6.00 protons at 6.32 τ for the trans isomer and 1.00 protons at 5.18 τ and 6.00 protons at 6.30 τ for cis isomer. The ratio of trans to cis was 79:21 comparing the peak area at 6.32 τ and 6.30 τ . After correction for C¹³, this mass spectrum gives for the dimethyl acenaphthene-1, 2-dicarboxylate a ratio of d₀:d₁:d₂ of 1.00:2.03:1.02, as expected for random deuteration at the two positions alpha to the carbomethoxyl groups.

As a blank test, a sample of 0.3451 g of dimethyl trans-acenaphthene-1, 2-dicarboxylate (1.278 mmol) (isolated from the photolysis of dimethyl 1-naphthalenemaleate in dioxane) was dissolved

in 16.6 ml of methyl alcohol- d_1 , CH_3OD . The solution was irradiated for 20 hours under the same conditions as used previously for this solvent. The vpc analysis showed the dimethyl trans-acenaphthene-1, 2-dicarboxylate decreased to 62.3 percent after 20 hours irradiation. The solvent was removed in vacuo for 3 hours at room temperature and at 100μ . The residue weighed 0.354 g. The NMR spectrum of the residue showed 1.07 protons at 4.88τ and 6.00 protons at 6.32τ .

As another blank test, a 0.1514 g sample of dimethyl trans-acenaphthene-1, 2-dicarboxylate (0.561 mmol) was dissolved in 9.0 ml of CH_3OD . The solution was poured into a 160 ml Pyrex cell which was wrapped with aluminum foil to keep out light. The solution was allowed to stand for 20 hours. The solvent was removed under the same conditions to give 0.1530 g of crystal. The NMR spectrum showed 6.85 protons at 2.18 to 2.67τ , 1.85 protons at 4.88τ and 6.00 protons at 6.32τ .

Dioxane with Deuterium Oxide

A 0.3437 g sample of dimethyl 1-naphthalenemaleate (1.27 mmol) was dissolved in 120 ml of dioxane along with 1.2 ml of deuterium oxide (66.6 mmol). The reaction mixture was irradiated for 4 hours in a quartz cell with a Pyrex filter under nitrogen. The yield of dimethyl acenaphthene-1, 2-dicarboxylate was 61.4 percent. The solvent was removed at room temperature by using a vacuum pump for 3 hours to give 0.4218 g of crude photo-product. The NMR spectrum showed that 6.00 protons in the region of 2.34τ to 2.86τ , 1.50 protons in a singlet at 4.95τ and 6.00 protons in a singlet at 6.33τ .

The crude photo-product was recrystallized from 30 ml of n-hexane to give 0.0305 g of dimethyl trans-acenaphthene-1, 2-dicarboxylate, melting at 82.0° - 82.5° . The NMR spectrum of the purified crystals indicated 6.00 protons in the region of 2.34τ to 2.86τ , 1.69 protons in a singlet at 4.95τ and 6.00 protons in a singlet at 6.33τ .

As a blank test, a solution of 0.0794 g of dimethyl trans-acenaphthene-1, 2-dicarboxylate (0.29 mmol) in 120 ml of dioxane with 1.2 ml of deuterium oxide was irradiated under the same conditions for 4 hours as the previous reaction. The solvent was removed at room temperature at 700μ to give 0.1889 g of photo-product. The NMR spectrum of the crude photo-product showed 5.89 protons in a region of 2.34τ to 2.86τ , 1.80 protons in a singlet at 4.95τ and 6.00 protons in a singlet at 6.33τ .

As another blank test, a 0.1092 g sample of dimethyl 1-naphthalenemaleate (0.40 mmol) was dissolved in 120 ml of dioxane and to this was added 1.2 ml of deuterium oxide. The solution was poured into a quartz cell which was wrapped with aluminum foil. The cell was allowed to stand for 4 hours. The solvent was removed at room temperature and 700μ pressure to give 0.2391 g of residue. The NMR spectrum of the residue showed 7.10 protons in the region of 1.72τ to 2.82τ , 0.96 protons in a singlet at 3.91τ and 6.00 protons at 6.28τ .

As a further blank test, a 0.0775 g sample of dimethyl trans-acenaphthene-1, 2-dicarboxylate (0.29 mmol) was dissolved with 120 ml of dioxane, and 1.2 ml of deuterium oxide was added to this solution. The solution was poured into a quartz cell which was wrapped with

aluminum foil. The cell was allowed to stand for 4 hours. The solvent was removed under the same conditions to give 0.1840 g of the product. The NMR spectrum showed 6.00 protons in the region of 2.34 τ to 2.86 τ , 1.96 protons in a singlet at 4.95 τ and 6.00 protons in a singlet at 6.33 τ .

Cyclohexane with Iodine

A mixture of 0.6482 g of dimethyl 1-naphthalenemaleate (2.401 mmol) and 0.0789 g of iodine (0.311 mmol) in 280 ml of cyclohexane was irradiated for 20 hours in a quartz cell with a Pyrex filter under nitrogen. The yield of the products as a function of time was followed by vpc.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1,2-dicarboxylate	Dimethyl Acenaphthylene-1,2-dicarboxylate
0 hr	0 %	100 %	0 %	0 %
1 hr	8.3	32.0	15.5	6.8
2 hr	7.3	21.4	15.5	10.2
6 hr	7.3	13.6	15.5	10.7
12 hr	4.4	2.9	8.7	10.7
20 hr	4.4	2.9	8.7	10.7

During the photolysis, insoluble polymer formed. The reaction mixture was washed with acetone into a 500 ml of round bottomed flask. The solvents were removed on the rotating evaporator on the steam bath to give 0.701 g of residue. The residue was dissolved in 10 ml of chloroform and chromatographed on 15 g of Brinkman No. 7734 silica

gel, using benzene as the eluent. The first fraction of 80 ml of benzene gave dimethyl acenaphthene-1, 2-dicarboxylate, and this solution was discarded. The second 160 ml of benzene elution gave 0.23 g of orange-colored residue. The residue was dissolved in 30 ml of ether and the ether solution was washed with 30 ml of thio-sulfate solution. The ether solution was dried over anhydrous magnesium sulfate for three hours. The ether was removed in vacuo to give an orange crystal which melted at 84° - 87° . The compound was recrystallized twice from methyl alcohol to give yellow crystals, melting at 103.0° - 103.5° , and weighing 0.0712 g. The ultraviolet spectrum showed maxima at $230\text{ m}\mu$ ($\epsilon = 20,300$), $260\text{ m}\mu$ ($\epsilon = 4,162$), $355\text{ m}\mu$ ($\epsilon = 8,120$). The NMR spectrum showed 6.05 protons between 1.90τ and 2.71τ and 6.00 protons at 6.06τ in deuteriochloroform solvent. The infrared spectrum had the following bands: 3.39 (m), 5.81 (s), 5.83 (s), 6.20 (m), 6.30 (w), 6.58 (s), 6.76 (m), 6.92 (s), 7.02 (s), 7.37 (s), 7.78 (s), 8.10 (s), 8.46 (s), 8.63 (s), 8.80 (s), 9.30 (s), 9.67 (m), 10.3 (m), 10.6 (w), 11.8 (m), 12.1 (s), 13.0 (s) and 13.8 (m). These results (m.p., IR and UV spectra) are identical with those for dimethyl acenaphthylene-1, 2-dicarboxylate as reported by R. W. Hoffmann et al.⁴

In a separate reaction, 1.000 g of dimethyl 1-naphthalene-maleate (3.740 mmol) and 0.941 g of iodine (3.708 mmol) (1:1 mole ratio) were dissolved with 280 ml of cyclohexane. The solution was irradiated in a Pyrex cell under nitrogen for 18 hours. Analysis

4

R. W. Hoffmann, G. Guhn, M. Preiss, and B. Dittirich, J. Chem. Soc. C 1969 (5), 769

of the reaction mixture by vpc showed 4.5 percent of dimethyl naphthalenefumarate, and 14.9 percent of dimethyl acenaphthene-1, 2-dicarboxylate. There was no peak for dimethyl acenaphthylene-1, 2-dicarboxylate. The solution was transferred to a flask. A thick dark purple film on the wall of the cell was not dissolved in cyclohexane. The solution and polymer were not investigated further.

As a blank test, methyl trans-acenaphthene-1, 2-dicarboxylate (0.3138 g, 1.162 mmol) and a 0.0341 g of iodine (0.134 mmol) were dissolved in 140 ml of cyclohexane. The solution poured into a quartz cell with a Pyrex filter, and the cell was then wrapped with aluminum foil and allowed to stand at room temperature for 20 hours under nitrogen. The iodine color did not disappear. Analysis of the solution by vpc showed no reaction. This solution was then irradiated for 20 hours under nitrogen. At the end of this time, the iodine color still was present. No precipitate formed. The vpc analysis showed that dimethyl trans-acenaphthene-1, 2-dicarboxylate decreased to 76.3 percent after 11 hours, and 63.8 percent after 20 hours, but dimethyl acenaphthylene-1, 2-dicarboxylate did not form.

Methyl Alcohol with Iodine

A solution of 0.2256 g of dimethyl 1-naphthalenemaleate (0.836 mmol) with 0.0218 g of iodine (0.086 mmol) in 80 ml of methyl alcohol was irradiated in a Pyrex cell under nitrogen. The reaction was followed by vpc as a function of time.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1 2-dicarboxylate	Dimethyl Acenaphthylene-1 2-dicarboxylate
0 hr	0 %	100 %	0 %	0 %
30 min	17.4	75.0	4.0	2.9
1.5 hr	35.3	43.9	12.7	8.1
3 hr	46.2	9.8	25.4	15.0
5 hr	49.1	1.2	28.9	15.0
22 hr	23.7	0	24.2	15.6

As a blank test, a solution of 0.1753 g of dimethyl trans-acenaphthene-1, 2-dicarboxylate, with 0.0454 g of iodine in 50 ml of methyl alcohol, was irradiated in a Pyrex cell under nitrogen for 19 hours to give 70.0 percent of dimethyl acenaphthene-1, 2-dicarboxylate and 4.8 percent of dimethyl acenaphthylene-1, 2-dicarboxylate.

Dioxane with Benzophenone

A solution of 0.1269 g of dimethyl 1-naphthalenemaleate (0.470 mmol) dissolved in 50 ml of dioxane containing 0.0145 g of benzophenone (0.080 mmol) was irradiated under a nitrogen atmosphere in a Pyrex cell with a uranium glass filter, using a 200 watt mercury lamp. The reaction was followed by vpc.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1, 2-dicarboxylate
0 hr	2.7%	97.3%	0 %
1 hr	28.6	20.5	30.4
2 hr	14.3	3.6	34.8
3 hr	0.9	0	44.6

A solution of 0.1317 g of dimethyl 1-naphthalenemaleate (0.49 mmol), in 55 ml of dioxane, was irradiated under the same conditions as in the previous experiment, but without the presence of benzophenone.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1, 2-dicarboxylate
0 hr	2.7%	97.3%	0 %
1 hr	24.1	29.9	26.3
2 hr	26.3	21.2	37.2
3 hr	20.4	14.6	43.8
5 hr	9.5	1.5	51.1
7 hr	0.7	0	58.4

Benzene with Benzophenone

A solution of 0.4917 g of dimethyl 1-naphthalenemaleate (1.821 mmol) with 0.2587 g of benzophenone (1.421 mmol) in 200 ml of benzene was irradiated in a Pyrex cell with a uranium glass filter under nitrogen.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1, 2-dicarboxylate
0 hr	2.5%	97.5%	0 %
15 min	36.7	38.3	0
30 min	28.3	30.0	0
1.5 hr	18.3	14.9	3.3
2.5 hr	12.5	5.8	5.0

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1, 2-dicarboxylate
(Continued)			
3.5 hr	4.2%	1.7%	5.8%
4.5 hr	1.0	0	7.5
5.5	0	0	7.5

A solution of 0.3797 g of dimethyl 1-naphthalenemaleate (1.406 mmol) in 150 ml of benzene was irradiated in a Pyrex cell with a uranium glass filter under nitrogen, in the absence of benzophenone.

Irradiation Time	Dimethyl 1-Naphthalene-fumarate	Starting Material	Dimethyl Acenaphthene-1, 2-dicarboxylate
0 hr	2.5%	97.5%	0 %
15 min	16.0	42.4	0
1 hr	8.5	13.2	5.7
2 hr	1.9	2.8	5.7
5 hr	0	1.9	4.7

Photolysis of Dimethyl 2, 3-Benzobicyclo-
[2.2.2]octatriene-5, 6-dicarboxylate in Solution

Methyl Alcohol

A solution of 1.1560 g of dimethyl 2, 3-benzobicyclo [2.2.2]-octatriene-5, 6-dicarboxylate (4.28 mmol), in 300 ml of methyl alcohol, was irradiated in a Pyrex cell under nitrogen for 4 hours. The reaction

was followed by vpc.

Irradiation Time	Starting Material	Dimethyl Benzocyclooctatetraene-5, 6-dicarboxylate	Unknown II
0 hr	100 %	0 %	0 %
1 hr	38.6%	57.9	3.6
2 hr	7.2	64.5	13.5
3 hr	1.6	56.2	23.4
4 hr	1.6	33.9	36.9

Removing the solvent on the rotating evaporator gave 1.349 g of residue. The residue was dissolved in 10 ml of methyl alcohol. A polymer (0.06 g) was obtained upon filtration; this became brown at 310° - 325°.

A solution of 0.25 g of dimethyl 2, 3-benzobicyclo[2.2.2] - octatriene-5, 6-dicarboxylate (0.926 mmol) in 65 ml of methyl alcohol was irradiated under nitrogen for 50 hours in a Pyrex cell with a uranium glass filter. Analysis of the product by vpc indicated 17.8 percent of starting material, 24.7 percent of dimethyl 3, 4-benzobicyclo[3.3.0.0^{2,8}]octa-3, 6-diene-1, 8-dicarboxylate, 4.8 percent of dimethyl benzocyclooctatetraene-5, 6-dicarboxylate and 12.3 percent of unknown II.

Benzene

A solution of 2.230 g of dimethyl 2, 3-benzobicyclo[2.2.2] - octatriene-5, 6-dicarboxylate (8.259 mmol) in 300 ml of benzene was irradiated for six hours in a Pyrex cell under nitrogen. Analysis

of the product by vpc showed 89.4 percent of dimethyl benzocyclooctatetraene-5, 6-dicarboxylate and 2.9 percent of unknown II. The solvent was removed on the rotating evaporator to give 2.33 g of brown oil. The brown oil was dissolved in 10 ml of chloroform and chromatographed on 15 g of Brinkman No. 7734 silica gel, using 500 ml of benzene as the eluent, to give 1.45 g of crude dimethyl benzocyclooctatetraene-5, 6-dicarboxylate. The crude product was recrystallized from 15 ml of methyl alcohol to give 0.585 g of white crystal melting at $74^{\circ} - 75^{\circ}$.

Dimethyl 2, 3-benzobicyclo[2.2.2]octatriene-5, 6-dicarboxylate (0.996 g, 3.69 mmol) and benzophenone (1.027 g, 5.64 mmol) in 340 ml of benzene were irradiated for one hour in a Pyrex cell with a uranium glass filter under nitrogen, using a 450 watt mercury lamp. The vpc analysis showed only a single peak which corresponded to the dimethyl 3, 4-benzotricyclo[3.3.0.0^{2,8}]octa-3, 6-diene-1, 8-dicarboxylate in 42 percent yield. The solvent was removed on the rotating evaporator to give 2.29 g of yellow residue. The residue was then dissolved in 10 ml of chloroform and chromatographed on 50 g of Brinkman No. 7734 silica gel using 375 ml of benzene as the eluent to give 0.985 g of benzophenone. Further elution of the column with 250 ml of ten percent ethyl ether in benzene gave 1.105 g of dimethyl 3, 4-benzotricyclo[3.3.0.0^{2,8}]octa-3, 6-diene-1, 8-dicarboxylate. The vpc analysis showed that there were traces of benzophenone and some impurities. The residue was rechromatographed on 30 g of silica gel, using 300 ml of benzene to give 0.32 g of the product, m.p. $58.0^{\circ} - 59.0^{\circ}$.

A 1.00 g sample of dimethyl 2, 3-benzobicyclo[2.2.2]octatriene-5, 6-dicarboxylate (3.70 mmol) and 2.53 g of benzophenone

(13.9 mmol) were dissolved in 300 ml of benzene. The solution was irradiated for 2 hours and 5 minutes in a Pyrex cell with a uranium glass filter, under nitrogen using a 200 watt mercury lamp, to give 68.7 percent of dimethyl 3, 4-benzotricyclo[3.3.0.0^{2,8}]octa-3, 6-diene-1, 8-dicarboxylate. The solvent was removed on the rotating evaporator to give 3.72 g of residue. The residue was chromatographed as before to give 1.18 g of crude dimethyl 3, 4-benzotricyclo[3.3.0.0^{2,8}]octa-3, 6-diene-1, 8-dicarboxylate. The crude product was combined with the product of the previous photolysis (total 1.50 g) and vacuum distilled at 85° and at 20 μ pressure to give 0.708 g of colorless viscous oil. Half of the distilled compound was crystallized from 10 ml of n-pentane (m.p. 56° - 57°). The remainder was crystallized after seeding. The crystals were combined and recrystallized from 8 ml of methyl alcohol to give 0.30 g of white crystals, melting at 58.1° - 59.0°. The NMR spectrum showed 4.02 protons in a multiplet in the range of 2.50 τ to 3.10 τ , a quartet centered at 4.30 τ with coupling constants of 5.0 cps and 2.5 cps containing 0.99 protons, a doublet centered at 4.75 τ with coupling constant of 5.0 cps containing 0.99 protons, a doublet centered at 5.60 τ with coupling constant of 2.5 cps and a superimposed singlet at 5.63 τ containing a total of 2.01 protons, a singlet at 6.28 τ containing 3.00 protons, a singlet at 6.40 τ containing 3.00 protons. The ultraviolet spectrum of the compound showed maxima at 212 m μ (ϵ = 20,961), 245 m μ (ϵ = 3,553), 270 m μ (ϵ = 855) and 277 m μ (ϵ = 654). The infrared spectrum of the compound showed the following bands: 3.32 (w), 3.39 (w), 3.46 (w), 5.90 (s), 6.38 (m), 6.89 (m), 6.94 (m), 7.04 (s), 7.36 (s), 7.55 (w), 7.70 (m), 7.78 (m),

7.96 (s), 8.10 (s), 8.20 (s), 8.33 (s), 8.45 (m), 8.80 (s),
8.90 (s), 9.08 (m), 9.24 (m), 9.42 (s), 9.80 (m), 10.0 (w), 10.4 (m),
10.6 (m), 10.9 (m), 11.4 (m), 11.8 (w), 12.0 (w), 12.5 (s), 13.0 (s),
13.3 (s), 13.7 (s), 14.3 (s).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22.

Found: C, 70.96, 71.08; H, 5.32, 5.38.

Photolysis of Dimethyl Benzocyclooctatetraene-5,

6-dicarboxylate in Solution

Dimethyl benzocyclooctatetraene-5, 6-dicarboxylate was synthesized by the photolysis of dimethyl 2, 3-benzobicyclo[2.2.2]-octatriene-5, 6-dicarboxylate in benzene as shown previously.

Dioxane

A solution of 0.15 g of the ester (0.556 mmol) in 70 ml of dioxane was irradiated for 5 hours in a Pyrex cell under nitrogen, using a 450 watt mercury lamp. The vpc analysis showed only starting material (95 percent recovery). The solution was transferred into a quartz cell and irradiated one hour. The vpc analysis indicated that there was no volatile material left.

Acetone

A solution of 0.15 g of the ester (0.556 mmol) was dissolved in 65 ml of acetone. The solution was irradiated in a Pyrex cell under nitrogen using the 1000 watt lamp. Two hours irradiation gave 50.0 percent of starting material and 30.8 percent of unknown II. Five hours of irradiation gave no starting material and 25.3 percent

of unknown II according to the vpc analysis. The solution was not investigated further.

Benzene

A solution of 0.2546 g of dimethyl benzocyclooctatetraene-5, 6-dicarboxylate (0.94 mmol) in 80 ml of benzene was irradiated in a Pyrex cell with a uranium glass filter for 16 hours. The vpc analysis of the solution indicated no reaction. The uranium glass filter was taken away and the solution was irradiated in a Pyrex cell. After 23 hours of irradiation, 0.5 percent of dimethyl 2, 3-benzobicyclo-[2.2.2]octatriene-5, 6-dicarboxylate, 9.7 percent of dimethyl 3, 4-benzotricyclo [3.3.0.0^{2,8}]octa-3, 6-diene-1, 8-dicarboxylate, 18 percent of starting material, 26.3 percent of unknown II, and 6.3 percent of unknown III were indicated.

Benzene with Benzophenone

A 0.746 g sample of dimethyl benzocyclooctatetraene-5, 6-dicarboxylate (2.76 mmol) and a 0.070 g of benzophenone (0.385 mmol) were dissolved in 350 ml of benzene. The solution was irradiated for six hours in a Pyrex cell with a uranium glass filter. Analysis of the reaction mixture by vpc showed 70 percent of unknown II was formed. The solvent was removed on the rotating evaporator at 20° to give 0.832 g of residue. The residue was dissolved in 60 ml of methyl alcohol and the resulting polymer was filtered off. It weighed 0.32 g. The filtrate was evaporated on the rotating evaporator to give 0.50 g of the product. A 0.25 g portion of the product was dissolved with 2 ml of chloroform and chromatographed on 5 g of Brinkman No. 7734 silica gel

using 100 ml of benzene as the eluent to give 0.19 g of product. Analysis of the product by vpc showed only dimethyl benzocyclooctatetraene-7, 8-dicarboxylate. The remainder (0.25 g) of crude product was dissolved with 10 ml of methyl alcohol and the resulting white polymer (0.01 g) was filtered off. The solvent was removed in vacuo. The residue did not crystallize from carbon tetrachloride.

In a separate reaction, a 1.0315 g portion of ester (3.82 mmol) was dissolved in 320 ml of benzene and 0.10 g of the benzophenone (0.549 mmol) was added. The solution was irradiated for six hours under the same conditions as the previous run to give 2.2 percent of starting material and 71.9 percent of unknown II. The solvent was removed in vacuo to give 1.230 g of residue. The residue was dissolved in 8 ml of benzene and poured slowly into 250 ml of pentane to remove polymer. It weighed 0.21 g. The pentane was removed in vacuo to give 1.01 g of residue. The NMR spectrum of the residue showed 5.9 protons in the region of 2.10τ to 3.18τ , 0.94 protons in a doublet centered at 3.15τ ($J = 2.9$ cps), 1.00 protons in a doublet centered at 5.58τ ($J = 2.9$ cps), 2.00 protons in a singlet at 6.31τ , 3.00 protons in a singlet at 6.42τ and 3.00 protons in a singlet at 6.51τ . The numbers of protons in the aromatic region (2.10τ to 3.18τ) could not be determined accurately because of the presence of benzophenone. The 100 MC NMR spectrum (Japan Electron Optics Lab.) showed that the singlet peak at 6.31τ was split into a doublet, each of which was a complex multiplet. The unknown II would not distill in a vacuum sublimation apparatus (up to 200° at 20μ).

Methyl Alcohol

A solution of 0.1371 g of dimethyl benzocyclooctatetraene-5, 6-dicarboxylate (0.508 mmol) in 50 ml of methyl alcohol was irradiated in a quartz cell with a Pyrex filter. The photo-products were followed by vpc.

Irradiation Time	Starting Material	Unknown II
0 hr	100 %	0 %
5 hr	72.8	5.8
10 hr	42.1	16.9
12 hr	32.8	27.2
17 hr	4.5	36.9

The unknown peak had the same retention times on both columns, Silicon gum rubber (SE-30) (7.4 min., starting material, 6.4 min.) at oven temperature of 210°, and Apiezon L column (9.4 min., starting material, 6.8 min.) at oven temperature of 200°, as unknown II which had been prepared by the irradiation of dimethyl benzocyclooctatetraene-5, 6-dicarboxylate with benzophenone in benzene solution.

CHAPTER V

DISCUSSION

Photolysis of Dimethyl 1-Naphthalenemaleate in Solution

The yield of the dimethyl acenaphthene-1, 2-dicarboxylate and the proportions of cis and trans isomers are summarized in Table 1 for the preparations via irradiation of dimethyl 1-naphthalenemaleate in various solvents.

Table 1. Yield of Dimethyl Acenaphthene-1, 2-dicarboxylate and Dimethyl Acenaphthylene-1,2-dicarboxylate

	Yield of Dimethyl Acenaphthene-1, 2-dicarboxylate	Percent		Yield of Dimethyl Acenaphthylene-1, 2-dicarboxylate
		<u>cis</u>	<u>trans</u>	
Dioxane	92.5%	8%	92%	0%
Isopropyl Alcohol	89.0	--	--	0
Methyl Alcohol	74.4	21 [*]	79 [*]	0.1
THF	50.8	--	--	1.2
Acetone-d ₆	51.2	22	78	9.6
Acetonitrile	44.0	36 ^{**}	64 ^{**}	13.9 ^{**}
Cumene	26.1	18	81	3.6
Benzene	20.6	--	--	6.0
<u>n</u> -Hexane	0	--	--	0
Cyclohexane	1.0	--	--	0

* Based on work in CH₃OD as solvent

** Based on work in CD₃CN as solvent

Obviously there is a great influence by solvents upon the yield of dimethyl acenaphthene-1, 2-dicarboxylate. Dioxane was the best solvent studied for the cyclization, while cyclohexane and n-hexane gave practically no acenaphthene derivative. With the latter solvents, about 80 percent of the dimethyl 1-naphthalenemaleate went to non-volatile material; only starting material and dimethyl 1-naphthalenefumarate were found upon vpc analysis. From these results it may be suggested that active hydrogen from the solvent participated in the cyclization. In benzene, unlike cyclohexane, the acenaphthene derivative was formed in 20.6 percent, along with 6.0 percent of dimethyl acenaphthylene-1, 2-dicarboxylate. Dimethyl acenaphthylene-1, 2-dicarboxylate was also formed in fairly good yield in acetone or acetonitrile. The reaction in these solvents may proceed through processes like those in benzene (Figure 2).

Photolysis of Dimethyl 1-Naphthalenemaleate
in Deuterium-Labeled Solvents

The photolysis of dimethyl 1-naphthalenemaleate in perdeutero-acetone, perdeuteroacetonitrile, methyl alcohol- d_1 and dioxane containing deuterium oxide are summarized in Table 2. The results clearly showed that the irradiation of dimethyl 1-naphthalenemaleate in deuterium-labeled solvents gave much incorporation of deuterium in the product dimethyl acenaphthene-1, 2-dicarboxylate. In perdeutero-acetone and perdeutero-acetonitrile, essentially one deuterium atom was taken up on the average per molecule of product; the product itself was shown not to undergo incorporation of deuterium under the reaction conditions--hence

deuterium was taken up during the photoisomerization process. On the other hand, in CH_3OD and in dioxane- D_2O , while deuterium incorporation occurred, this was shown to be wholly (CH_3OD) or largely (dioxane- D_2O) due to deuterium exchange upon the product dimethyl acenaphthene-1, 2-dicarboxylate during the irradiation. This interpretation was confirmed by showing via mass spectral analysis that the product from CH_3OD was as expected for random exchange, *i.e.*, d_0 , d_1 , and d_2 compounds, were in the statistical ratio of 1.0:2.0:1.0.

Table 2. Incorporation of Deuterium into Dimethyl Acenaphthene-1,2-dicarboxylate during Preparation by Irradiation of Dimethyl 1-Naphthalenemaleate

Solvent	Yield of Dimethyl Acenaphthene-1, 2-dicarboxylate	Average Number of Deuterium Atoms per Molecule for Mixture of Isomers	Percent	
			<u>cis</u>	<u>trans</u>
CD_3COCD_3	51 %	0.99	22	78
CD_3CN	38	1.00	36	64
CH_3OD	81	1.03	21	79
D_2O in Dioxane (1 vol. %)	61.4	0.50*	--	--

* On 0.31 atoms of D in the isolated trans isomer.

Photolysis of Dimethyl 1-Naphthalenemaleate with Iodine

Irradiation of dimethyl 1-naphthalenemaleate in cyclohexane and methyl alcohol with iodine gave fair yield of dimethyl acenaphthylene-1, 2-dicarboxylate which was isolated and had the same m.p., IR and UV spectral properties as previously reported.⁴ The yield of dimethyl

acenaphthylene-1, 2-dicarboxylate was 10.7 percent in cyclohexane and 15.6 percent in methyl alcohol. Blank tests showed that dimethyl acenaphthene-1, 2-dicarboxylate was not detectably oxidized to dimethyl acenaphthylene-1, 2-dicarboxylate by iodine under the reaction conditions.

Photolysis of Dimethyl 1-Naphthalenemaleate
with Benzophenone

A solution of dimethyl 1-naphthalenemaleate with benzophenone in dioxane and benzene were irradiated in a Pyrex cell with a uranium glass filter to compare the reaction rate with the reaction without benzophenone. The reaction in dioxane with 17% mole of benzophenone took 3 hours to yield 0.9 percent of dimethyl 1-naphthalenefumarate and 44.6 percent of dimethyl acenaphthene-1, 2-dicarboxylate. The same solution without benzophenone took 7 hours to yield 0.7 percent of dimethyl 1-naphthalenefumarate and 58.4 percent of dimethyl acenaphthene-1, 2-dicarboxylate. A uranium glass filter seems to cut down the yield of dimethyl acenaphthene-1, 2-dicarboxylate. In benzene, there is no significant difference in reaction rate with or without benzophenone, but the yield of dimethyl acenaphthene-1, 2-dicarboxylate is poor. These results also indicate that while the reaction may go via a triplet, still the reaction is complex in that active hydrogen in the solvents has an important role and possibly an intermediate can react with benzophenone to give a non-volatile product.

Photolysis of Dimethyl 2,

3-Benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate

The results of the photolysis of dimethyl 2,3-benzobicyclo-[2.2.2]octatriene-5, 6-dicarboxylate in methyl alcohol, benzene and

benzene with benzophenone are as follows.

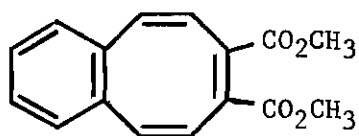
Table 3. Reaction Products of Dimethyl 2, 3-Benzobicyclo[2.2.2]octatriene-5, 6-dicarboxylate in Various Solvents

Solvent	Products*			
	A	B	C	Unk. II
CH ₃ OH** (Pyrex)	7.2%	0%	64.5%	13.5%
C ₆ H ₆ (U-glass)	0	0	89.0	2.9
C ₆ H ₆ /Ph ₂ CO (U-glass)	0	69.0	0	0

* A = Dimethyl 2, 3-Benzobicyclo[2.2.2]octatriene-5,6-dicarboxylate

B = Dimethyl 3, 4-Benzotricyclo[3.3.0.0^{2,8}]octa-3, 6-diene-1, 8-dicarboxylate

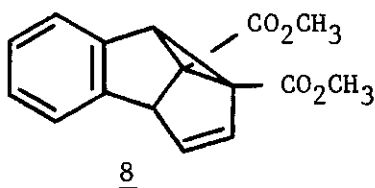
** C = Dimethyl Benzocyclooctatetraene-5, 6-dicarboxylate
2 hours irradiation



7

Apparently the reaction via a singlet state gives initially dimethyl benzocyclooctatetraene-5, 6-dicarboxylate, 7, while the sensitized

reaction yields a new compound, dimethyl 3,4-benzotricyclo[3.3.0.0^{2,8}]-octa-3, 6-diene-1, 8-dicarboxylate, 8. The structure of the new compound was confirmed by C,H-analysis which agreed with the formula, C₁₆H₁₄O₄. Moreover, the NMR spectrum showed four aromatic protons in the region of 2.50τ to 3.10τ, one vinyl proton in a quartet centered at 4.30τ (J = 5.0, 2.5 cps), one vinyl proton in a doublet centered at 4.75τ (J = 5.0 cps), two benzylic protons of which one is in a doublet centered at 5.63τ (J = 2.5 cps), and the others a superimposed singlet at 5.63τ, with two methoxy groups in a singlets at 6.28τ and 6.40τ. These data agree well with the structure below:



Photolysis of Dimethyl Benzocyclooctatetraene-5,6-dicarboxylate

Dimethyl benzocyclooctatetraene-5, 6-dicarboxylate was irradiated in various solvents. The results are summarized in Table 4.

Table 4. Yield of Unknown II in Various Solvents

Solvent	Irrad. Time	Unk. II	Comment
Dioxane (Pyrex)	5 hr	none	No reaction
CH ₃ OH (Pyrex)	17 hr	36.9%	
CH ₃ COCH ₃ (Pyrex)	5 hr	25.3%	
C ₆ H ₆ (U-glass)	16 hr	none	No reaction
C ₆ H ₆ (Pyrex)	23 hr	26.3%	Three other Products
C ₆ H ₆ /Ph ₂ CO (U-glass)	6 hr	71.9%	

The formation of Unknown II clearly takes place most readily by photosensitization by benzophenone and, therefore, likely occurs in a triplet state. The formation of Unknown II in methyl alcohol likely also occurs via a triplet state since the initial rate of the reaction in methyl alcohol is slow but gets faster with increasing concentration of Unknown II; this result indicates that a self-sensitized reaction by Unknown II is involved, or else the concurrently formed polymer acts as a sensitizer.

Mechanistic Considerations

Dimethyl 1-naphthalenemaleate, 1, was converted into dimethyl 1-naphthalenefumarate, 2, very rapidly, and both materials were converted into dimethyl trans-acenaphthene-1, 2-dicarboxylate, 3, by irradiation in suitable solvents. However, the reaction did not give

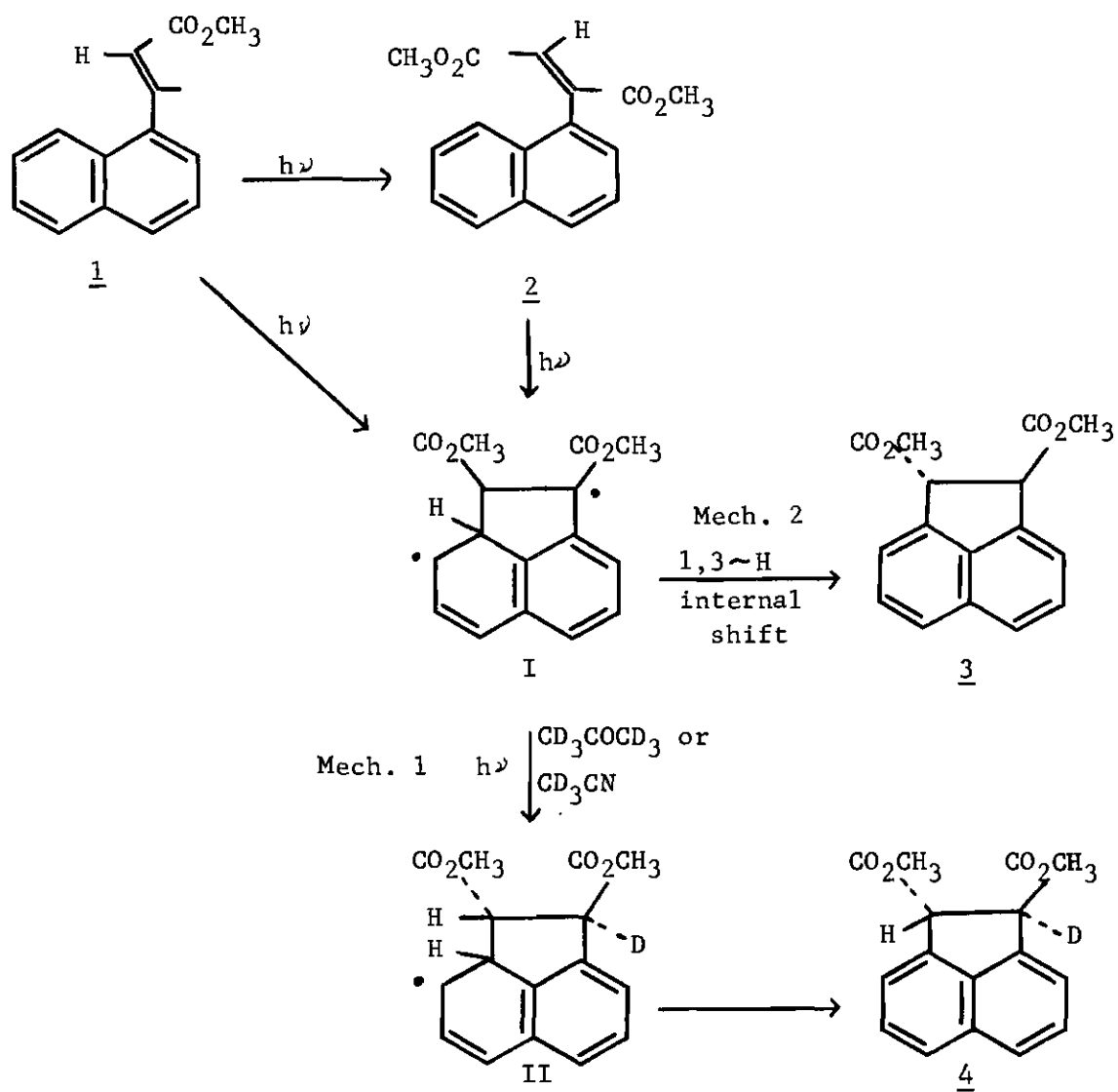


Figure 1. Mechanism of Cyclization of Dimethyl 1-Naphthalenemaleate

appreciable dimethyl trans-acenaphthene-1, 2-dicarboxylate in n-hexane or cyclohexane. Furthermore, the reaction in per-deuteroacetone and per-deuteroacetonitrile gave dimethyl trans-acenaphthene-1, 2-dicarboxylate-1-d, 4. In CH₃OD, dimethyl trans-acenaphthene-1, 2-dicarboxylate itself was deuterated by irradiation and hence, appreciable deuterium uptake probably did not occur during the cyclization step itself. Dimethyl 1-naphthalenemaleate in dioxane with one percent of deuterium oxide gave 50 percent deuterated compound, 4, apparently by a process like that for CH₃OD. These results support the mechanism, 1, wherein active hydrogen from the solvent takes part in the proton transfer. Only solvents which have hydrogens which are easily attacked by free radicals are effective.

The reaction in benzene may proceed through processes such as those shown in Figure 2. Presumably, I, II, III, and IV can all act as hydrogen atom donors or acceptors; also, all of these intermediates should be capable of dimerizing with themselves as the other radicals to give ultimately dimers or polymers.

In cyclohexane or methyl alcohol with iodine, once the initial attack had formed a carbon-to-carbon bond, the diradical would be free to react in at least two ways. The radical at the 1-position could attack an iodine molecule or the hydrogen on the aromatic ring might be extracted by an iodine atom. Related steps would then give rise to the acenaphthylene derivative, compound 5.

The reaction of dimethyl 1-naphthalenemaleate with benzophenone in dioxane proceeded faster than the reaction without benzophenone. This result suggests that the reaction goes via a triplet, but the

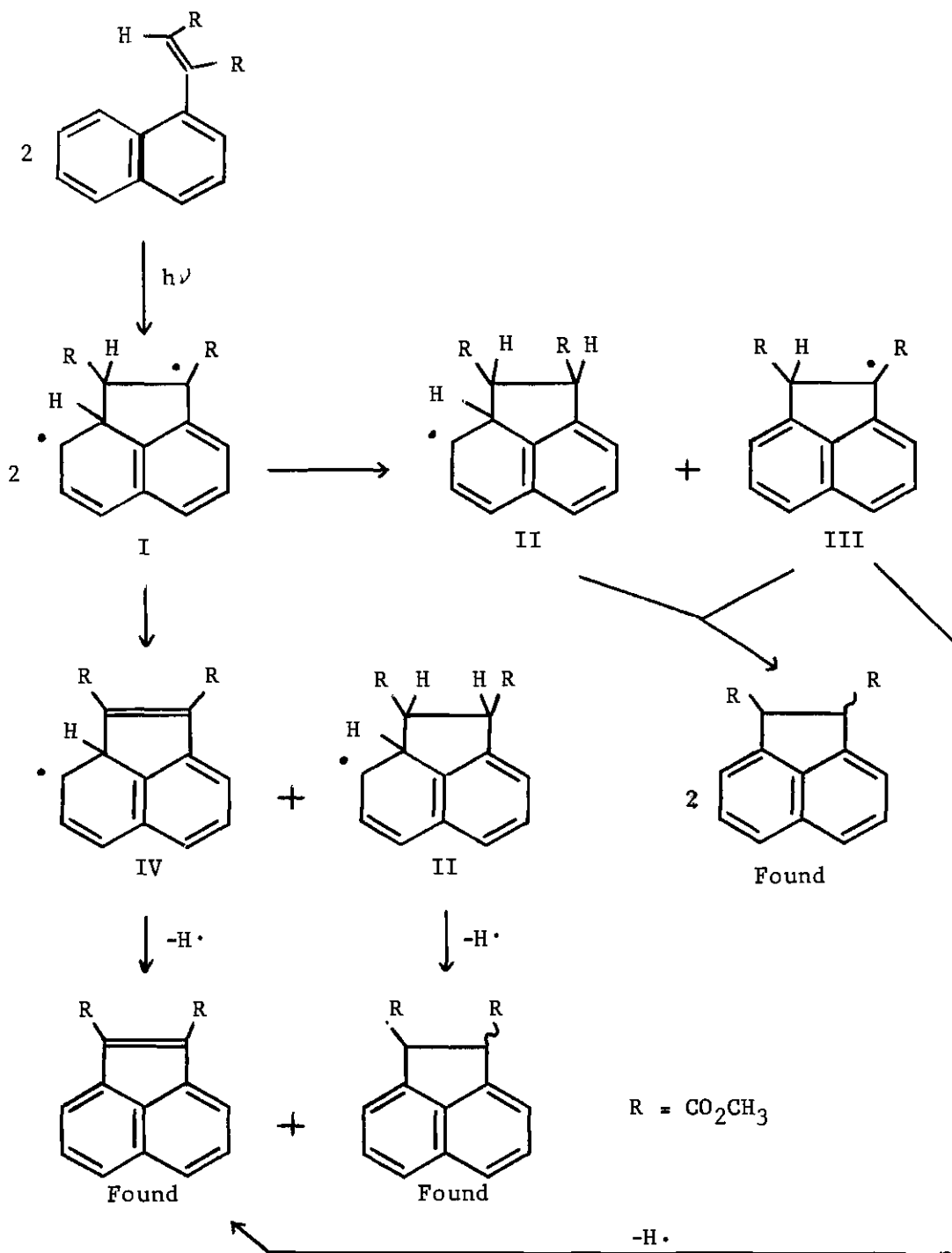


Figure 2. Possible Reaction Paths upon Photolysis of Dimethyl 1-Naphthalenemaleate in Benzene as Solvent.

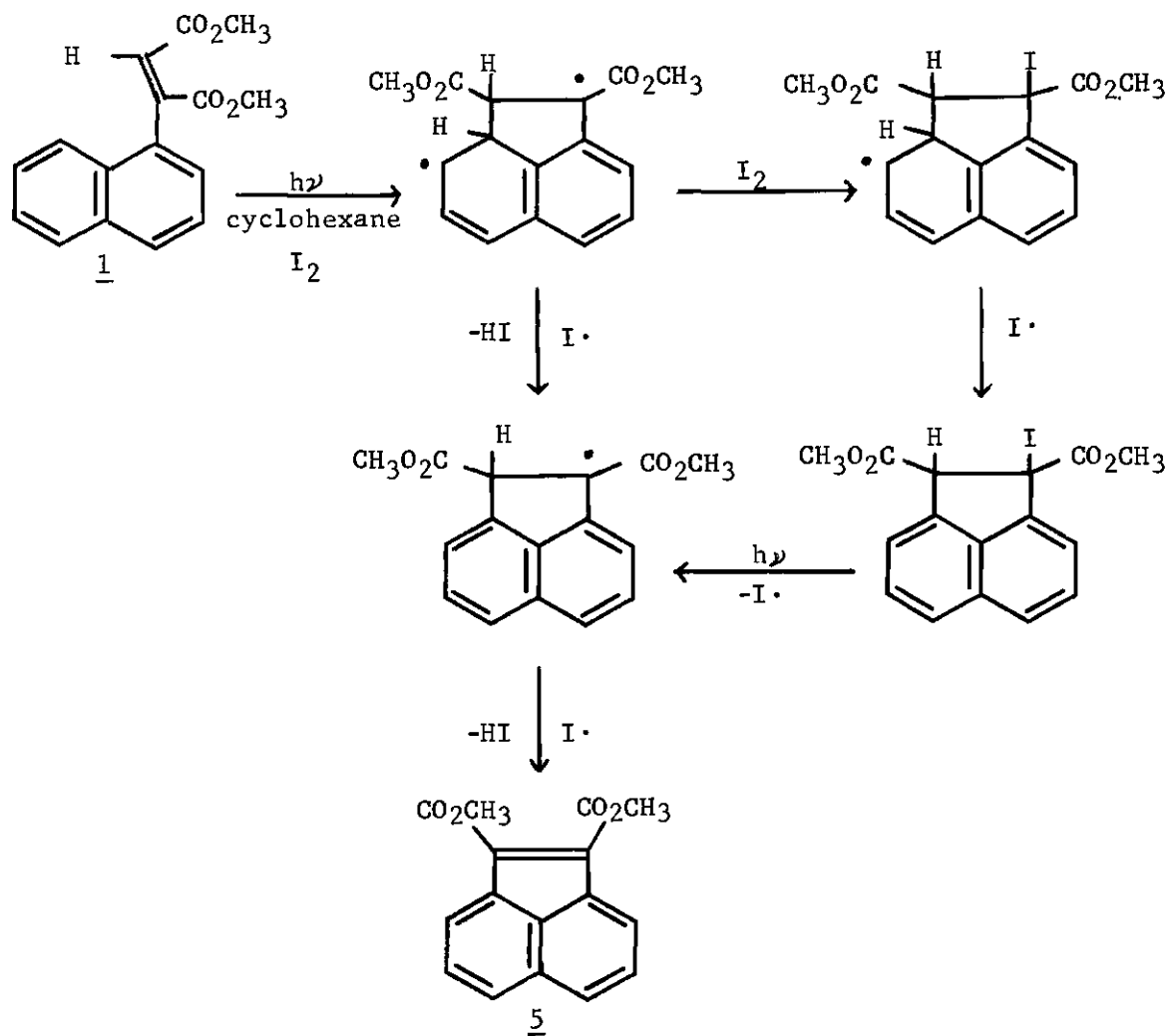
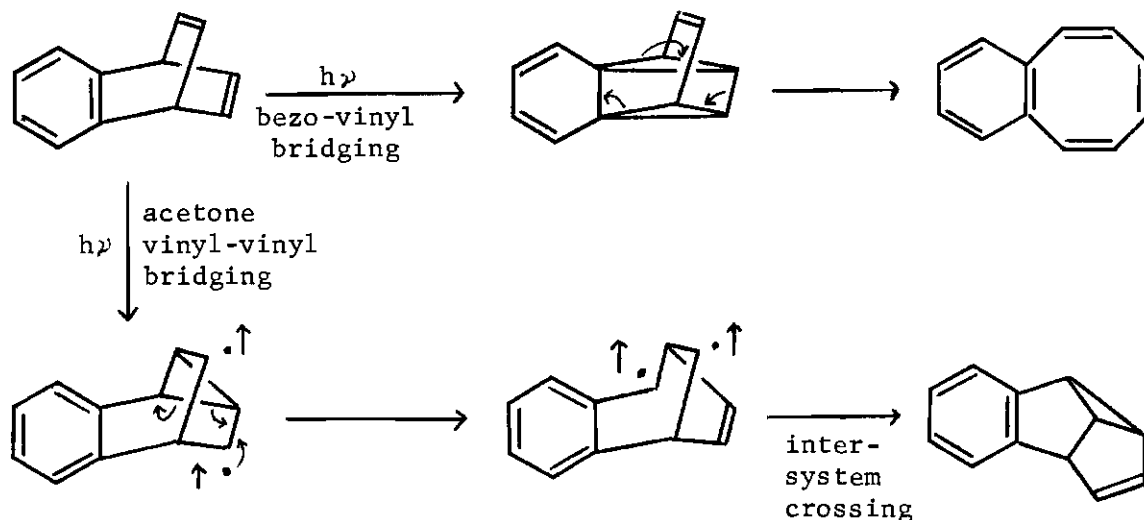


Figure 3. Mechanism of Formation of Dimethyl Acenaphthene-1, 2-dicarboxylate

absolute yield of the dimethyl trans-acenaphthene-1, 2-dicarboxylate was decreased and hence the result is not entirely clean.

The photochemical reaction of benzobarrelene 10, with and without sensitizer had been reported.² The mechanism of this reaction which has been suggested is that the singlet process involves benzo-vinyl interaction to give benzocyclooctatetraene, while vinyl-vinyl interaction is favored in the triplet for the formation of benzosemi-bullvalene.

These mechanisms are supported by similar reactions of tetra-fluorobenzobarrelene,³ 1, 4-epoxy-1, 4-dihydronaphthalene,⁵ and dibenzobicyclo[2.2.2]octatriene derivatives, and recently by the reaction of triptycene.⁶

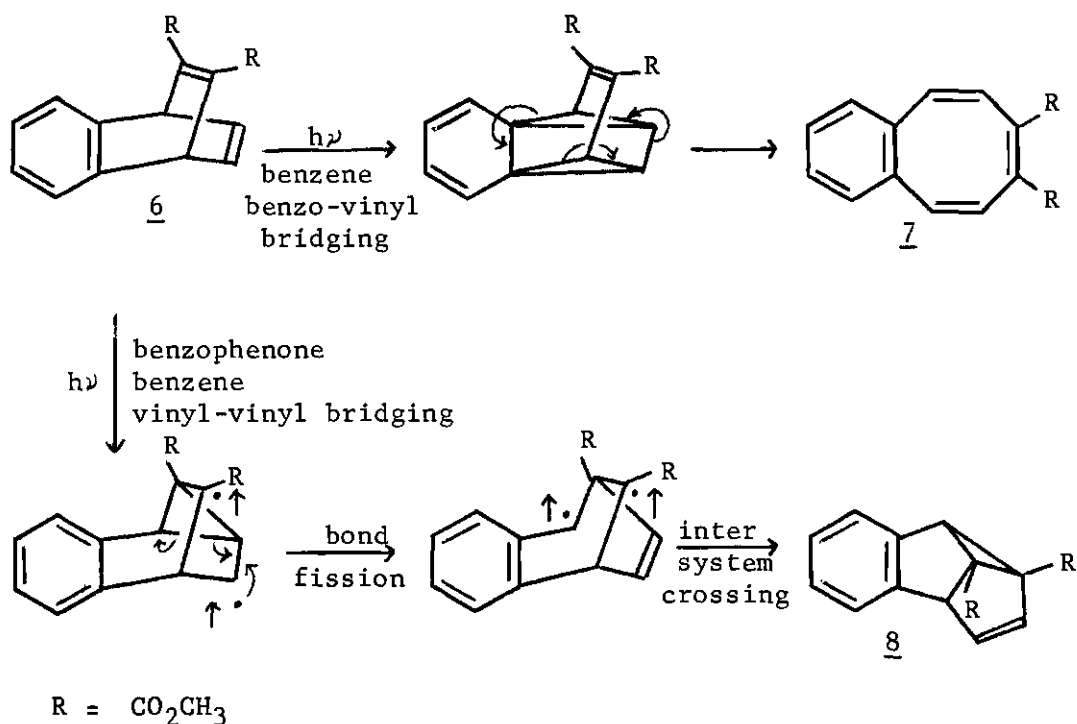


⁵G. R. Ziegler and G. S. Hammond, J. Am. Chem. Soc., 90, 513 (1968)

⁶(a) T. D. Walsh, ibid., 91, 515 (1969)

(b) N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, ibid., 91, 516 (1969)

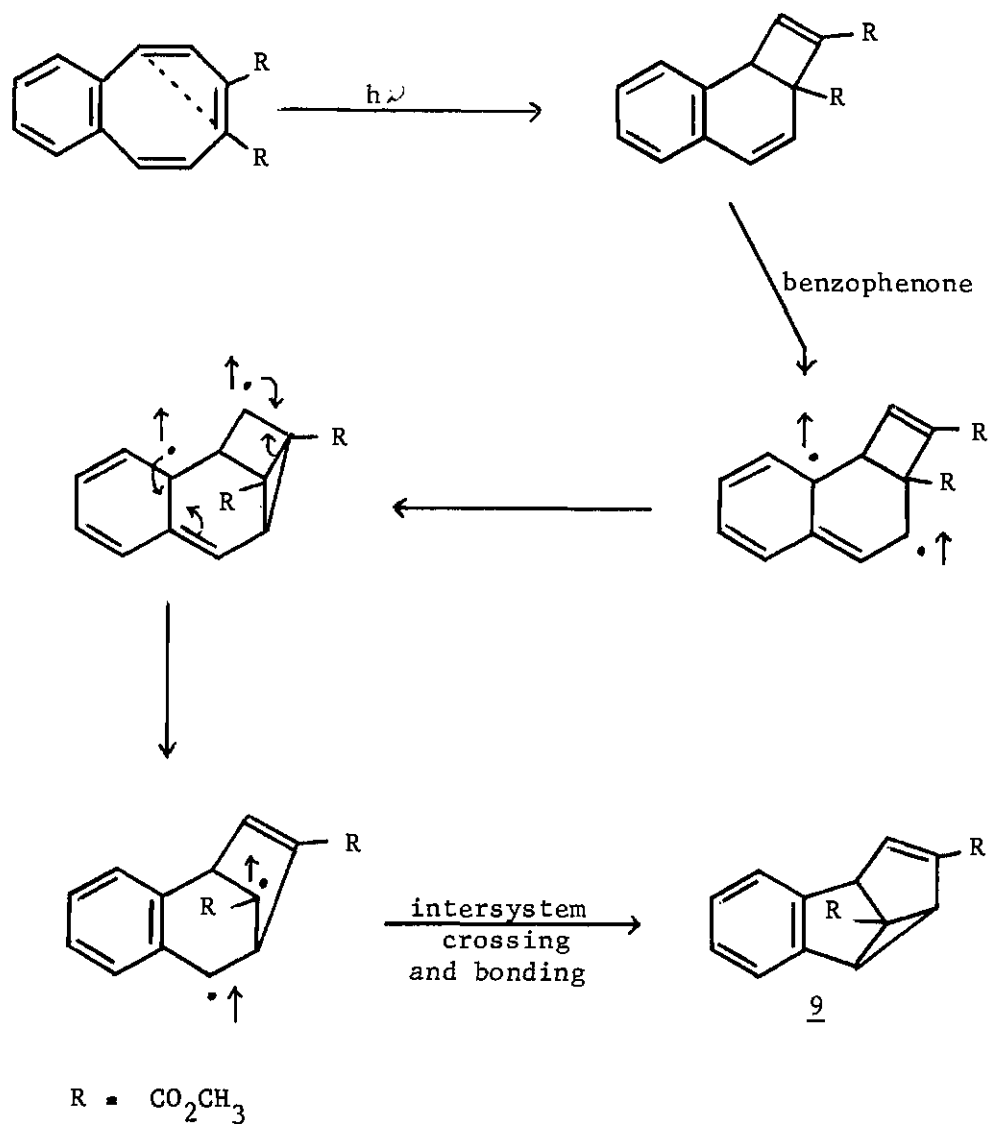
Similarly, the formation of dimethyl benzocyclooctatetraene-5, 6-dicarboxylate, 7, by irradiation of dimethyl 2, 3-benzobicyclo-[2.2.2]octatriene-5, 6-dicarboxylate, 6, in benzene and the formation of dimethyl 3, 4-tricyclo[3.3.0.0^{2,8}]octa-3, 6-diene-1, 8-dicarboxylate, 8, by irradiation of 6 with sensitizer may be explained as shown below.



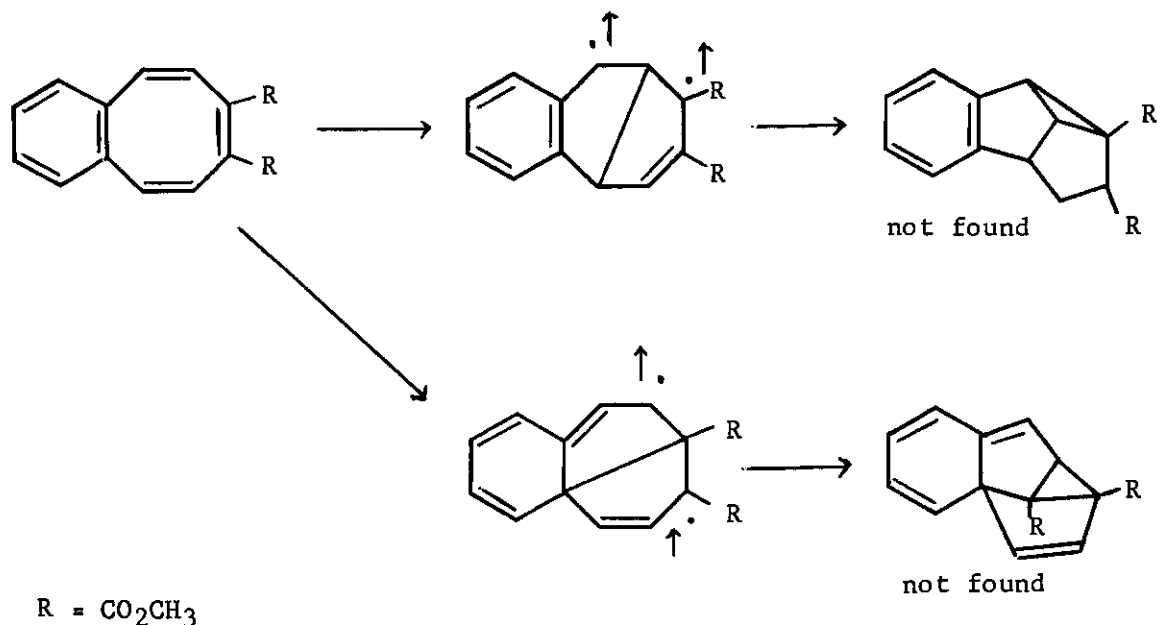
In contrast, the photolysis of dimethyl benzocyclooctatetraene-5, 6-dicarboxylate with benzophenone gave Unknown II whose structure is suggested by NMR spectrum as dimethyl 3, 4-benzotricyclo[3.3.0.0^{2,8}]-octa-3, 6-diene-1, 7-dicarboxylate, 9. If so, the mechanism of this reaction is explained below by one of the mechanisms proposed⁷ for the

⁷H. E. Zimmerman, and H. Iwamura, J. Am. Chem. Soc., 90, 4763 (1968)

sensitized photolysis of cyclooctatetraene into semibullvalene.



Zimmermann's alternate mechanism of 1,5-bridging seems to be ruled out by the present results:



Conclusions

It has been found that the photochemical conversions of dimethyl 1-naphthalenemaleate, 1, into dimethyl trans-acenaphthene-1, 2-dicarboxylate, 3, are influenced by solvents. The yield of 3 was higher when 1 was irradiated in solvents with hydrogen active toward attack by free radicals. The photolysis of 1 in deuterio solvents, per-deuteroacetone, and per-deuteroacetonitrile gave dimethyl acenaphthene-1, 2-dicarboxylate-1-d (4). In CH₃OD, dimethyl trans-acenaphthene-1, 2-dicarboxylate underwent a facile photo "enolization" to give 4 (as well as d₀ and d₂ derivatives). The photochemical reaction of dimethyl 1-naphthalenemaleate appears to proceed primarily through a two step intramolecular process involving initial attack of the electronically excited dimethyl 1-naphthalenemaleate to form a carbon-to-carbon bond at the 8-position. This initial step was followed by hydrogen atom transfer from solvent

to give an intermediate which in turn is converted into dimethyl trans-acenaphthene-1, 8-dicarboxylate, 4, by loss of a proton from the aromatic ring.

The photochemical reaction of dimethyl 1-naphthalenemaleate with iodine in cyclohexane or methyl alcohol gave some dimethyl acenaphthylene-1, 2-dicarboxylate, 5, apparently by reaction of iodine or iodine atoms with an intermediate diradical.

The photochemical reaction of dimethyl 2, 3-benzobicyclo[2.2.2]-octatriene-5, 6-dicarboxylate, 6, in benzene gave dimethyl benzocyclooctatetraene-5, 6-dicarboxylate, 7, in good yield via a singlet state. This product was probably formed by an aryl-vinyl bridging pathway. The product from the photochemical reaction of 6 with benzophenone in benzene was dimethyl 3, 4-benzotricyclo[3.3.0.0^{2,8}]octa-3, 6-diene-1, 8-dicarboxylate, 8, which was probably formed by a vinyl-vinyl bridging pathway via a triplet state.

The unknown product II formed in the photochemical reactions of dimethyl benzocyclooctatetraene-5, 6-dicarboxylate, 7, in presence of benzophenone is likely dimethyl 3, 4-benzotricyclo[3.3.0.0^{2,8}]octa-3, 6-diene-1, 9-dicarboxylate.

CHAPTER VI

RECOMMENDATIONS

The photolysis of dimethyl phenylmaleate with or without sensitizer should be attempted to see if the molecule would cyclize to form four-membered ring derivatives. Also, the photolysis of dimethyl 2-naphthalenemaleate should be further attempted to see if four-membered ring derivatives could be formed.

The photolysis of dimethyl benzocyclooctatetraene-5, 6-dicarboxylate with sensitizer should be investigated further since this reaction gave an unstable compound and it was not isolated in a pure state.

APPENDICES

APPENDIX A

SOLVENTS USED IN OBTAINING SPECTRA

All ultraviolet spectra were determined in 95 percent ethanol using a one-cm cell. All infrared spectra were determined in potassium bromide pellets. All NMR spectra were determined using deuteriochloroform or carbon tetrachloride as solvents with tetramethylsilane added as an internal standard.

APPENDIX B

ULTRAVIOLET SPECTRAL COMPARISONS OF:

- DIMETHYL 1-NAPHTHALENEMALEATE (A),
 DIMETHYL 1-NAPHTHALENEFUMARATE (B),
 DIMETHYL ACENAPHTHYLENE-1, 2-DICARBOXYLATE (C),
 DIMETHYL 3, 4-BENZOTRICYCLO[3.3.0.0.^{2,8}]OCTA-3,
 6-DIENE-1, 8-DICARBOXYLATE (D)
 DIMETHYL 3, 4-BENZOTRICYCLO[3.3.0.0.^{2,8}]OCTA-3,
 6-DIENE-6, 7-DICARBOXYLATE (E)

Wavelength m	ϵ				
	A	B	C	D	E
200					42,500
212				20,961	
220					19,650
221	63,316				
223		63,000			
230			20,300		
245				3,553	
260	3,741		4,162		
264		4,400			
265					4,770
270				850	
272		5,430			
274	3,741				
277				654	
281	4,475	5,780			
288		4,760			
295	4,915				
315	4,255				
320	3,742		7,308		
335			12,586		
362			8,120		

APPENDIX C

VPC RETENTION TIMES OF ALL COMPOUNDS SUBJECTED TO VPC ANALYSIS*

Compound	Retention Time (min)	
	SE-30(225°)	Apiezon L(210°)
Dimethyl 1-Naphthalene fumarate	2.8	2.1
Dimethyl 1-Naphthalenemaleate	3.8	2.9
Dimethyl <u>trans</u> -Acenaphthene-1, 2-dicarboxylate	5.4	3.3
Dimethyl Acenaphthylene-1, 2-dicarboxylate	11.3	5.3

Compound	Retention Time (min)	
	SE-30(205°)	Apiezon L(190°)
Dimethyl 2, 3-Benzobicyclo[2.2.2]- octatriene-5, 6-dicarboxylate	4.2	3.6
Dimethyl 3, 4-tricyclo[3.3.0.0 ^{2,8}]- octa-3, 6-diene-1, 8-dicarboxylate	5.0	4.1
Dimethyl Benzocyclooctatetraene-5, 6-dicarboxylate	5.8	4.6
Dimethyl 3, 4-tricyclo[3.3.0.0 ^{2,8}]- octa-3, 6-diene-6, 7-dicarboxylate	6.4	4.9
Unknown II	8.1	5.4

* Determined at the flow rate of 25 mm at 60 psig using Perkin-Elmer Model 880 Gas Chromatograph described in Chapter III

APPENDIX D

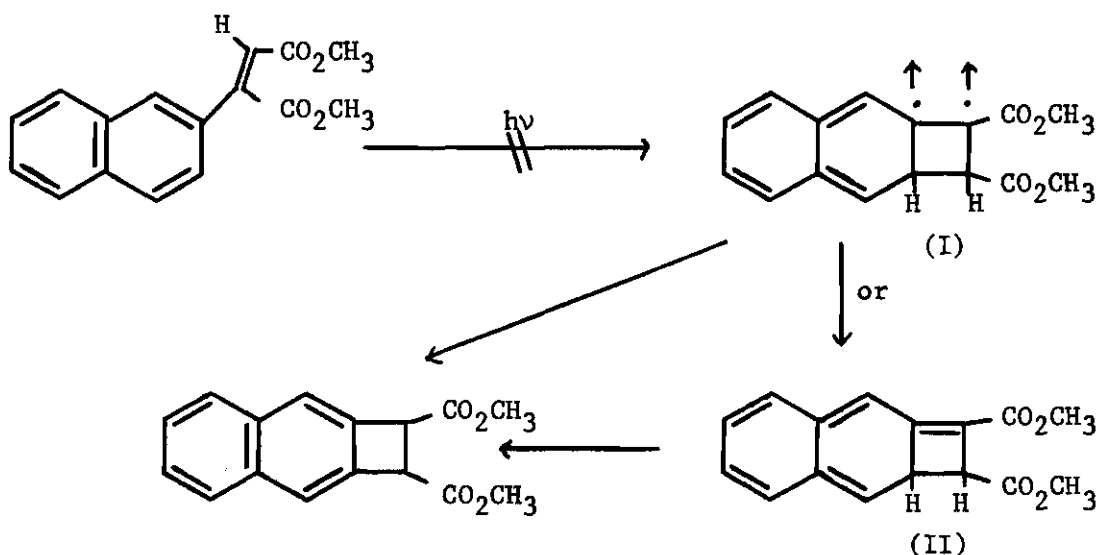
PHOTOLYSIS OF DIMETHYL 2-NAPHTHALENEMALEATE

A solution of 1.50 g of dimethyl 2-naphthalenemaleate (5.55 mmol) was dissolved in 400 ml of dioxane. The solution was irradiated in a Pyrex cell under nitrogen. The vpc analysis of the solution after one hour irradiation showed 90 percent of unknown at 8.2 minutes retention time and 10 percent of starting material at 11.4 minutes on Apiezon L column at 250° using the F & M machine. Longer periods of irradiation, up to 8 hours, did not alter the yield of the photo product. The solvent was removed on the rotating evaporator to give 1.8785 g of yellow liquid. Recrystallization from 10 ml of methyl alcohol gave 1.2416 g of crystals. These were combined with 0.5 g of crystals from a similar reaction. The mixture was liquid-chromatographed on 100 g of Brinkman No. 7734 silica gel, using 3000 ml of benzene as eluent to give 1.2574 g of crystals. The crystals were recrystallized from 10 ml of methyl alcohol to give 1.0 g of pale yellow crystal with a melting point 51.8° - 52.5°. This product has the expected spectral properties for dimethyl 2-naphthalenefumarate: $\lambda_{\text{max}}^{\text{EtOH}}$ 223 m μ ($\epsilon = 82,700$), 267.5 m μ ($\epsilon = 13,300$), 305 m μ (shoulder, $\epsilon = 5,200$), 338 m μ (shoulder, $\epsilon = 1,700$); NMR (CCL) τ 2.1-2.8 (6.7 H, multiplet), 3.01 (1.0 H, singlet), 6.26 (3.0 H, singlet), 6.53 (3.0 H, singlet). A 0.49 g portion of the product (1.8 mmol) was hydrogenated in 50 ml of ethyl acetate over 1.80 g of 5 percent palladium on charcoal

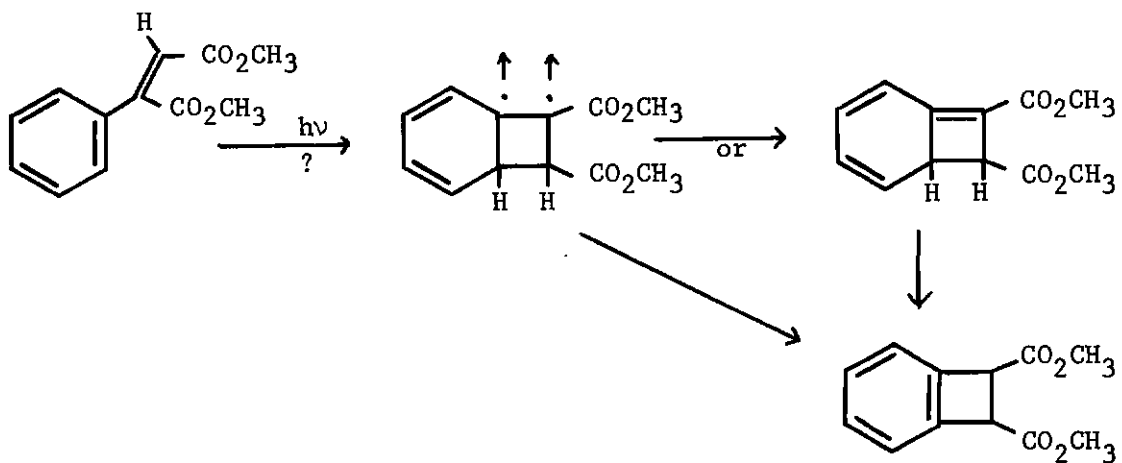
catalyst. The product absorbed 1.8 mmol of hydrogen. The charcoal was filtered off and the solvent was removed on the rotating evaporator to give 0.364 g of crude product. The product was recrystallized from methyl alcohol to yield white needles of m.p. 63.0° - 63.5° . NMR (CCl_4) τ 2.2-2.8 (7.1 H, complex multiplet), 5.83 (1.0 H, quartet, $J = 6$ and 10 Hz), 6.39 (6.0 H, singlet), 6.78 (1.0 H, quartet, $J = 10$ and 16 Hz), 7.38 (1.0 H, quartet, $J = 6$ and 16 Hz). The hydrogenated photo product has identical melting points and IR, NMR, and vpc properties with those of the sample of dimethyl 2-naphthalene-succinate prepared by hydrogenation of dimethyl 2-naphthalenemaleate. The photo product from dimethyl 2-naphthalenemaleate is accordingly dimethyl 2-naphthalenefumarate.

Discussion

The inability to effect ring closure here may be because the intermediate (I) or initial product (II) has too high an energy content.



Work with the following phenyl compound may be more promising:



APPENDIX E

PHOTOLYSIS OF 1-NAPHTHALENEMALEIC ANHYDRIDE IN VARIOUS SOLVENTS

Benzene

A solution of 1.004 g of 1-naphthalenemaleic anhydride (4.48 mmol) in 250 ml of benzene was irradiated in a quartz cell with a Pyrex filter under a nitrogen atmosphere for 13 hours. The solvent was removed on the rotating evaporator to give 1.042 g of residue. Quantitative analysis by vpc showed no reaction.

A solution of 1.000 g of 1-naphthalenemaleic anhydride (4.46 mmol) in 250 ml of benzene was irradiated in a quartz cell for 13 hours under nitrogen. The solvent was removed in vacuo to give 1.059 g of residue. The vpc analysis showed 61.4 percent of starting material and 1.1 percent of unknown with the remainder non-volatile material.

Ethyl Ether

A solution of 1.000 g of 1-naphthalenemaleic anhydride (4.46 mmol) in 250 ml of ether was irradiated in a quartz cell with a Pyrex filter for 13 hours. The relative yield of the starting material (retention time, 1.00 min.) in the solution by vpc was 70.6 percent and there also were seven unknowns in relative percentage yields of 1.7, 0.7, 0.1, 4.6, 0.1, 0.1, and 22.1 and with retention times of 0.55, 1.19, 1.26, 1.61, 2.0, 2.16 and 2.69 min., respectively.

A solution of 1.000 g of 1-naphthalenemaleic anhydride (4.46 mmol) in 250 ml of ether was irradiated without a Pyrex filter under the same

conditions. The relative yield of the starting material (retention time, 1.00 min.) was 6.0 percent. The relative percentage yield of the six unknowns was 40.0, 6.7, 0.8, 0.8, 21.5, and 25.2, and the retention times were 1.20, 1.40, 1.63, 1.72, 2.04, and 2.20 min., respectively.

Acetonitrile

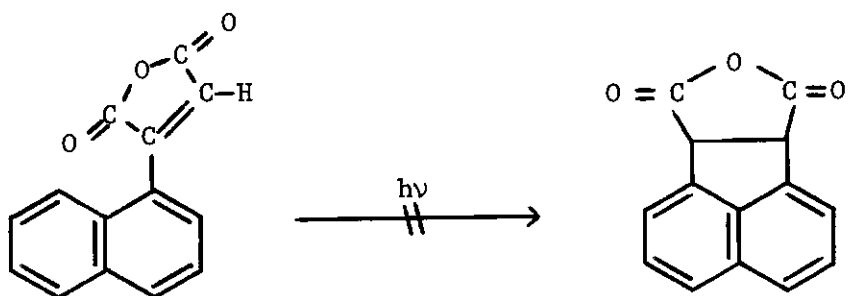
A 0.500 g sample of 1-naphthalenemaleic anhydride (2.23 mmol) was dissolved in 250 ml of acetonitrile. The solution was irradiated in a quartz cell with a Pyrex filter under nitrogen for 14 hours. The relative yields of the products in solution by vpc were 90.3 percent of starting material, 9.6 percent and 0.1 percent of two unknowns, and retention times were 1.00, 1.18, and 1.68 min., respectively.

Acetone

A solution of 0.005 g of 1-naphthalenemaleic anhydride (2.32 mmol) in 250 ml of acetone was irradiated in a quartz cell under nitrogen for 5 hours. The quantitative vpc analysis of the product showed only a trace of volatile material.

Discussion

The failure to effect cyclization of 1-naphthalenemaleic anhydride in appreciable yield in solvents in which dimethyl 1-naphthalenemaleate cyclizes in reasonable yield is surprising.



It would be of interest to attempt a photosensitized cyclization of the above anhydride using benzophenone as sensitizer in benzene as the solvent.

APPENDIX F

PHOTOLYSIS OF 1,2-DIMETHYLNAPHTHALENE

n-Hexane

A 0.5916 g sample of 1,2-dimethylnaphthalene (3.79 mmol) was dissolved in 150 ml of n-heptane. The solution was irradiated in a quartz cell nitrogen. The reaction was followed by vpc as a function of time up to 72 hours. The starting material gradually decreased to 44.8 percent but no other volatile peak was found by vpc analysis which was shown to be capable of separating 1,2- from 1,3-dimethylnaphthalene.

Methyl Alcohol

A solution of 0.6707 g of 1,2-dimethylnaphthalene (4.30 mmol) in 150 ml of dry methyl alcohol was irradiated in a quartz cell under nitrogen for 74 hours. The analysis of the solution by vpc showed only starting material peak which corresponded to 56.8 percent recovery.

APPENDIX G

PHOTOLYSIS OF NAPHTHALENE WITH DIMETHYL MALEATE

A mixture of 12.8 g of naphthalene (0.1 mol) and 2.936 g of dimethyl maleate (0.0204 mol) in 250 ml of methyl alcohol was irradiated in a quartz cell under nitrogen for 50 hours. The vpc analysis showed no reaction. Benzophenone (4.93 g, 0.027 mol) was added to the above solution and the solution was irradiated with a Pyrex filter under nitrogen for 48 hours. The vpc analysis showed only starting material.

APPENDIX H

PHOTOLYSIS OF NAPHTHALENE
WITH MALEIC ANHYDRIDE AND ISOBUTYLENE

A 30 g quantity of naphthalene (0.23 mol) was dissolved in 100 ml of dioxane and 5 g of maleic anhydride (0.05 mol) was added. A 42 g portion of isobutylene (0.75 mol) in 100 ml of dioxane was mixed with the above solution. The solution was poured into a quartz cell and 50 ml more dioxane was added. The solution was irradiated with a Pyrex filter (no nitrogen) for 6 hours. An insoluble white precipitate formed. The precipitate was filtered off. It weighted 9.69 g and melted at 305° - 310° . The vpc showed that this was not a volatile material. No product was formed in the dioxane solution.

APPENDIX I

PHOTOLYSIS OF DIPHENYLMETHANE

A solution fo 3.08 g of diphenylmethane (18.36 mmol) in 300 ml of n-pentane was irradiated in a Pyrex cell for 45 hours (no nitrogen). The vpc analysis showed 91 percent of starting material, 8 percent of unknown and one percent of another unknown. The solution was not investigated further.

A solution of 4.61 g of diphenylmethane (27.44 mmol) in 350 ml of n-pentane was irradiated in an immersed type quartz cell using a 200 watt mercury lamp (no nitrogen) for 48 hours. Polymer (0.0207 g) was formed during irradiation. The analysis of the solution by vpc showed only starting material.

APPENDIX J

PHOTOLYSIS OF 1,1,1-TRIPHENYLETHANE

n-Pentane

A solution of 1.28 g of 1,1,1-triphenylethane (4.98 mmol) in 350 ml of n-pentane was irradiated by an immersed type quartz cell under oxygen atmosphere using a 200 watt mercury lamp for 20 hours. The vpc analysis showed only starting material. The irradiation of the above solution was continued under nitrogen gas for 42 hours. A white precipitate (0.0121 g) formed. The analysis of the solution by vpc showed no volatile material.

Benzene with Benzophenone

A mixture of 0.779 g of 1,1,1-triphenylethane (3.02 mmol) and 0.8077 g of benzophenone (4.44 mmol) were dissolved in 300 ml of benzene and the solution was irradiated in a Pyrex cell using a 200 watt mercury lamp for 81 hours. A trace of precipitate was formed. The vpc analysis of the solution showed only starting material.

Cyclohexane with Iodine

A 0.965 g portion of 1,1,1-triphenylethane (3.74 mmol) was dissolved in 250 ml of cyclohexane. A 0.05 g quantity of iodine (0.20 mmol) was added to this solution. The solution was irradiated in a quartz cell using a 200 watt mercury lamp for 20.5 hours. The vpc analysis of the solution showed only starting material.

LITERATURE CITED*

1. E. Grovenstein, Jr., T. C. Campbell, and T. Shibata, J. Org. Chem., 34, 2418 (1969).
2. H. E. Zimmerman, R. S. Givens, and R. M. Pagni, J. Am. Chem. Soc., 90, 4191 (1968).
3. P. W. Rabideau, J. B. Hamilton, and L. Friedman, J. Am. Chem. Soc., 90, 4465 (1968).
4. R. W. Hoffman, G. Guhn, M. Preiss, and B. Dittirich, J. Chem.Soc., C 1969 (5), 789.
5. G. R. Ziegler and G. S. Hammond, J. Am. Chem. Soc., 90, 513 (1968).
6. (a) T. D. Walsh, J. Am. Chem. Soc., 91, 515 (1969).
(b) N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, J. Am. Chem. Soc., 91, 516 (1969).
7. H. E. Zimmerman and H. Iwamura, J. Am. Chem. Soc., 90, 4763 (1968).
8. L. Denivell and D. Razavi, Compt. rend., 237, 570 (1953).