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PART I

THE REACTION PRODUCT FROM 2,3-DIPHENYLQUINOXALINE
AND DIMETHYL ACETYLENEDICARBOXYLATE

PART II

PHOTOCHEMICALLY INDUCED REACTION
OF BENZENE WITH MALEIC ANHYDRIDE

A THESIS

Presented to
the Faculty of the Graduate Division

by
James Welch Taylor

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

Georgia Institute of Technology

June, 1958

62
127

PART I

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AND DIMETHYL ACETYLENEDICARBOXYLATE

PART II

PHOTOCHEMICALLY INDUCED REACTION
OF BENZENE WITH MALEIC ANHYDRIDE

Approved:

[Handwritten signature]

Date Approved by Chairman:

May 30, 1958

ACKNOWLEDGMENTS

The author wishes to thank Professor Erling Grovenstein, Jr., for his patient guidance and advice during this research; without his help and encouragement this work could never have been undertaken.

He is grateful to Dr. Ray L. Sweigert, Dean of the Graduate Division, and Dr. William M. Spicer, Director of the School of Chemistry for Graduate Assistantships and Grants-in-Aid during four quarters of graduate study.

In addition to the members of the Thesis Reading Committee, Dr. John R. Dyer and Dr. William Postman, the author wishes to express his appreciation to Dr. John W. Huffman, Dr. William H. Eberhardt and Dr. James A. Stanfield for their helpful suggestions in writing this thesis.

Most of all, he wishes to thank his wife for her patience and encouragement during the trying periods of graduate study.

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SUMMARY

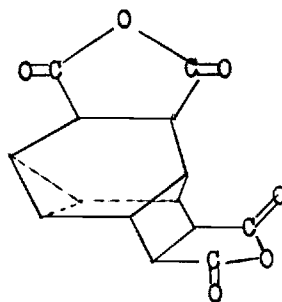
PART I

The product of the reaction between 2,3-diphenylquinoxaline and dimethyl acetylenedicarboxylate in methanol solution was examined to determine if there was 1,4-addition of the ester across the nitrogen-containing diene. The ease of replacement of one methoxyl group in acidic media suggested that a quinoxalinium ion might be involved; on the other hand, the substance could be sublimed and showed a normal molecular weight in triphenylmethane, as expected for a purely covalent compound.

The substance was shown to exist as N-(trans-1,2-dimethoxy-carbonylvinyl)-2,3-diphenyl-2-methoxy-1,2-dihydro-quinoxaline in neutral or basic methanolic solution but to exist as a N-(trans-1,2-dimethoxy-carbonylvinyl)-2,3-diphenylquinoxalinium salt in acidic media.

PART II

By the use of a 1000 watt mercury arc lamp, one mole of benzene has been found to react with two moles of maleic anhydride to produce a crystalline solid, m.p. 355-357°, whose structure is believed to be:



This product can be hydrolyzed to a tetracarboxylic acid and esterified with methanol to give a tetramethyl ester of m.p. 136.3-136.6°. Hydrogenation of the tetracarboxylic acid with platinum on charcoal in acetic acid at room temperature and atmospheric pressure produces a product which does not contain a cyclopropane ring.

The structure of the adduct between benzene and maleic anhydride was established on the basis of elementary analyses of the adduct, the corresponding tetracarboxylic acid, and the tetramethyl ester; molecular weight determinations upon the tetramethyl ester; infrared spectra of all of these substances as well as the hydrogenated tetracarboxylic acid after conversion to its anhydride; the ultraviolet absorption spectra of the tetramethyl ester and of the sodium salt of the tetracarboxylic acid; the nuclear magnetic resonance absorption of the tetramethyl ester. A reaction path for the formation of the adduct is suggested.

PART I

CHAPTER I

SUMMARY OF PREVIOUS WORK

While studying reactions of some 1,4-diaza-1,3-dienes with Diels-Alder dienophiles, Postman obtained a product from the reaction of equimolar quantities of dimethyl acetylenedicarboxylate with 2,3-diphenylquinoxaline in methanol.¹ The product melted between 152 and 154°. Microchemical analysis showed agreement for a product consisting of one mole of 2,3-diphenylquinoxaline, one mole of dimethyl acetylenedicarboxylate, and one mole of methanol.² Molecular weight determinations done on a semi-micro scale showed the molecular weight to be 465 ± 50 . The molecular weight for a product consisting of the above-mentioned three components is 456.50.³

The saponification equivalent was determined to be 196 on heating for two minutes in diethylene glycol and 167 on heating for five minutes. The calculated value for the compound of molecular weight 456 is 228.⁴ Acid hydrolysis yielded 70 per cent of the starting 2,3-diphenylquinoxaline, whereas alkaline hydrolysis yielded 45 per cent 2,3-diphenylquinoxaline,

¹W. Postman, Unpublished Ph.D Thesis, Georgia Institute of Technology, 1953, p. 88.

²Ibid., p. 92.

³Ibid., p. 95.

⁴Ibid., p. 96.

line, 16 per cent desoxybenzoin, 17 per cent quinoxaline-2-carboxylic acid, and 20 per cent carbon dioxide. Since one of the products expected was tolan, attempts were made to hydrate tolan to desoxybenzoin under the conditions of hydrolysis. These attempts were unsuccessful.⁵

Attempted oxidation with ferric chloride gave a yellow solid melting at 183-184° which contained iron and chlorine but was not further identified. Attempted oxidation with bromine gave inconclusive results, and with potassium permanganate gave no reaction. Oxidation with sodium dichromate in acetic acid yielded 59 per cent of the starting 2,3-diphenylquinoxaline.⁶ When the product was oxidized with hydrogen peroxide, Postman reported the formation of a white solid, m.p. 309-310°, which analyzed for a monohydrate of 2,3-diphenylquinoxaline monoxide. A lower melting (124-124.5°) yellow solid which analyzed for no simple whole number empirical formula was also found.⁷

Pyrolysis of the adduct at 210-255° yielded 36 per cent of the starting quinoxaline and a pale yellow liquid which had an index of refraction at 20° of 1.3991. Indications were that the yellow liquid was a mixture of methanol and the acetylenic ester. When heated briefly in a bath at 250-260° and between 0.05 to 0.10 mm. pressure, the adduct sublimed with little decomposition.⁸

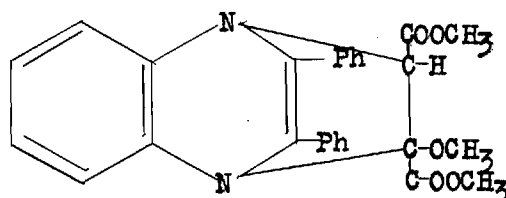
⁵Ibid., pp. 96 ff.

⁶Ibid., p. 102.

⁷Ibid., p. 104.

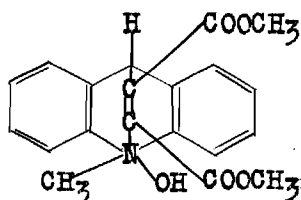
⁸Ibid., p. 105.

On the basis of these experimental facts, Postman formulated the following structure (I) for the yellow adduct.⁹

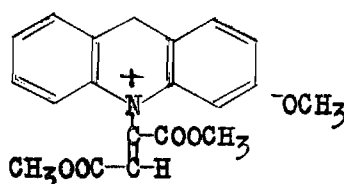


(I)

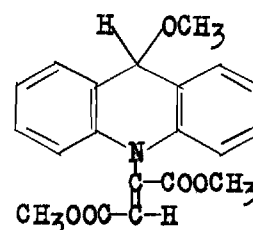
This structure was analogous to the structure of the product (II) of acridine and dimethyl acetylenedicarboxylate as proposed by Diels and Thiele in 1940.¹⁰ Acheson and Burstall, in 1954, showed that the addition of the dienophile was not across the 9,10 position but rather at the 10 position only. Structure (III) represents the adduct in neutral methanol and (IV) after addition of potassium hydroxide.¹¹



(II)



(III)



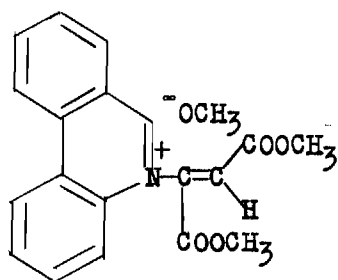
(IV)

⁹Ibid., p. 15

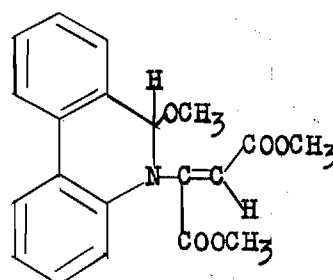
¹⁰Diels and W. E. Thiele, Justus Liebig's Annalen de Chemie, 543, 79 (1940).

¹¹R. M. Acheson and M. L. Burstall, Journal of the Chemical Society, 3240, (1954).

Acheson and Bond, in 1956, proved the structure of the product from phenanthridine and dimethyl acetylenedicarboxylate not to have the 9,10-dihydrophenanthridine structure of Diels and Thiele but instead structure (V) in acid conditions and (VI) when formed or under basic conditions.¹²

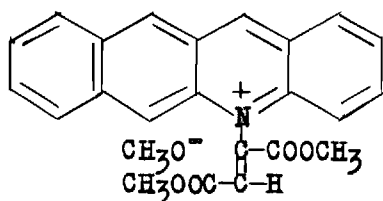


(V)

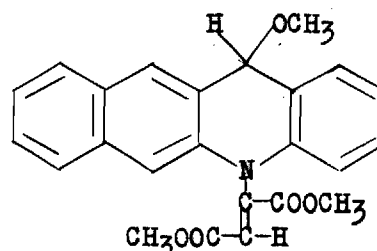


(VI)

Again with the product from 2,3-benzacridine and dimethyl acetylenedicarboxylate, Acheson and Jefford proved the structures (VII) and (VIII) and named compound (VII) N-(trans-1:2-dimethoxycarbonylvinyl)-2,3-benzacridinium methoxide in equilibrium with the conjugate benzacridan (VIII).¹³



(VII)



(VIII)

¹²R. M. Acheson and G. J. F. Bond, *ibid.*, 246 (1956).

¹³R. M. Acheson and C. W. Jefford, *ibid.*, 2676 (1956).

Clearly further investigation of the product from dimethyl acetylenedicarboxylate and 2,3-diphenylquinoxaline is warranted to determine if a system containing two nitrogens gives a structure comparable to that from compounds containing only one nitrogen. The present work will present additional facts learned about the molecule and conclusions concerning its structure.

CHAPTER II

DISCUSSION OF PRESENT WORK

It was found that one of the methoxyl groups of Postman's adduct (prepared from 2,3-diphenylquinoxaline, dimethyl acetylenedicarboxylate, and methanol) was labile. In ether solution, the methoxyl group could be replaced by perchlorate, picrate, chloride, and tetrachloroferrate(III). Microchemical analysis showed that in each case except the chloride, which was too unstable for analysis, only one methoxyl group was replaced by the various anions under the acidic conditions employed.

This ease of replacement would be a fairly strong argument for assigning to Postman's adduct a quinoxalinium type structure. By doing this, the explanation of the labile methoxyl group is apparent.

Postman has shown, however, that the adduct can easily be sublimed with little decomposition. His molecular weight determination, measured in triphenylmethane as solvent, is in good agreement with the calculated value. These two additional facts present an equally strong argument against the ionic structure.

The ultraviolet spectra of the following compounds, measured in methanol, are presented in Fig. 1: the adduct, the adduct in 0.1 N perchloric acid, the adduct perchlorate, the adduct in 0.1 N sodium methoxide, and 2,3-diphenylquinoxaline. In 0.1 N methanolic hydrochloric acid 2,3-diphenylquinoxaline (not shown) is essentially the same as 2,3-diphenylquinoxaline in methanol. The adduct in 0.1 N

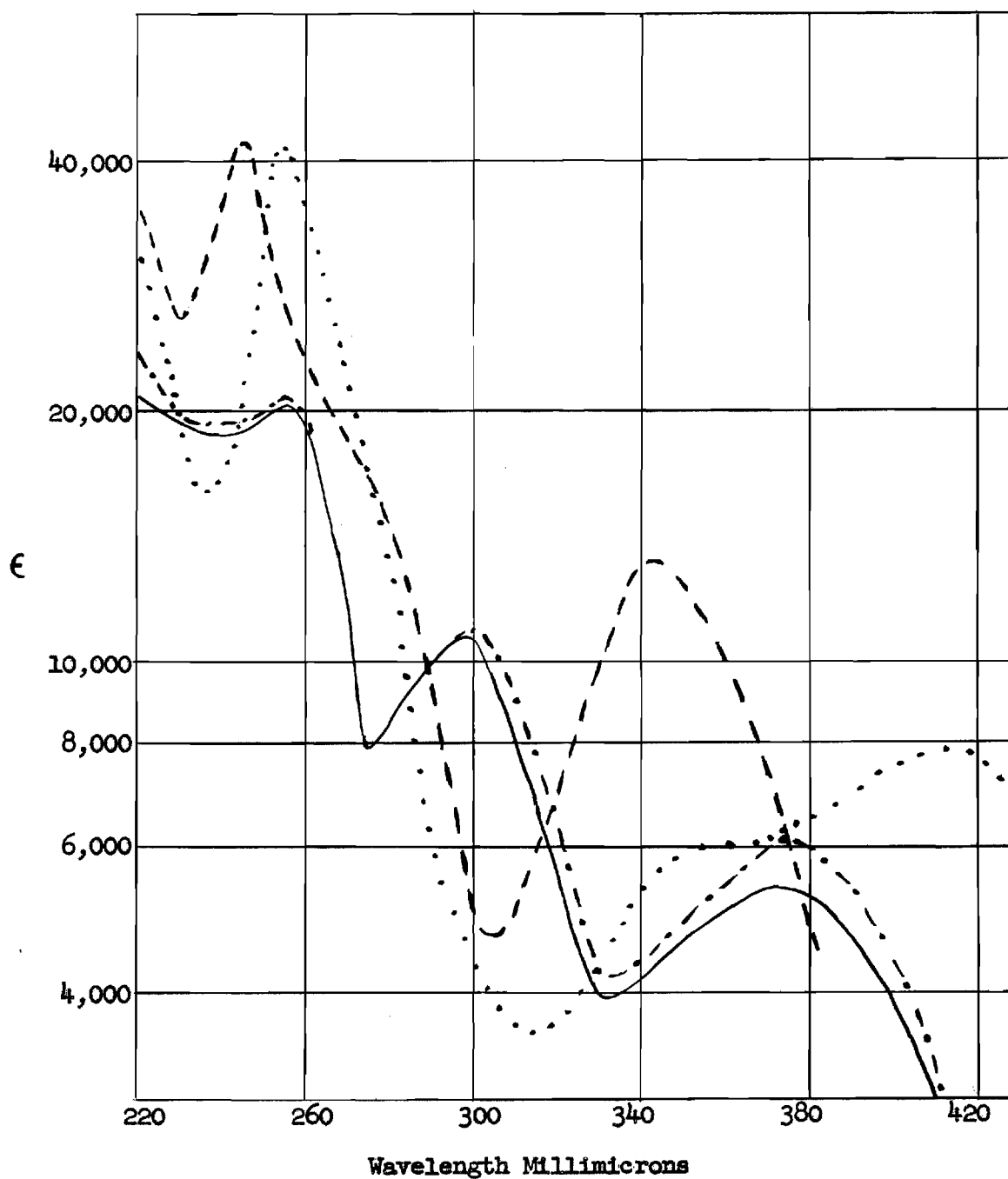
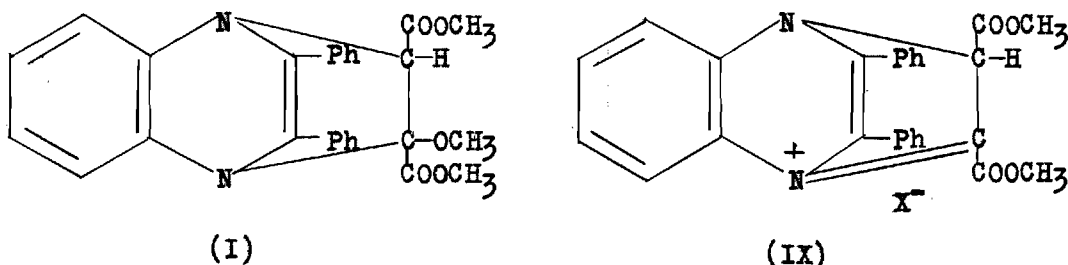


Figure 1. The Adduct ———
 Adduct in Perchloric Acid.....
 Adduct Perchlorate —.—
 2,3-Diphenylquinoxaline - - -
 (All measured in methanol)
 (The Adduct in Sodium Methoxide gives the same curve
 as the Adduct.)

hydrochloric acid (not shown) gives the same spectrum as the adduct in 0.1 N perchloric acid.

It is interesting to note that the spectrum of the adduct in neutral or basic media is not the same as the spectrum measured in acidic media. Clearly the adduct may exist in two forms. In acidic media it is best represented by an ionic structure, but in neutral or basic media by a covalent structure.

Structure (I) as given by Postman does not lend itself easily

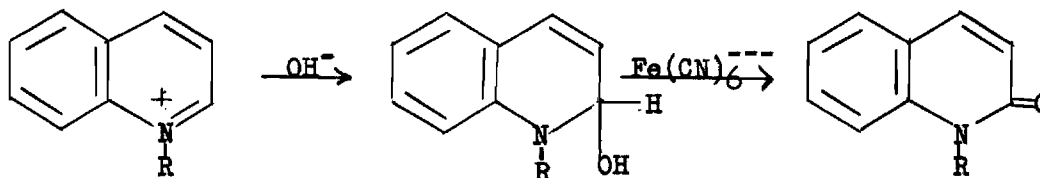


to explanation of this equilibrium between ionic and covalent structures. While (I) appears to be a possible covalent structure, the corresponding ionic structure (IX) has a double bond at a bridgehead and, therefore, is in violation of Bredt's rule; on the other hand, unless the hetero-nitrogen atom stabilizes the cation, then no ready equilibrium between covalent and ionic structures would appear feasible.

Structure (I) cannot explain the ultraviolet absorption spectra or the bright yellow color of the adduct. There are but two isolated chromophores in this structure, the ortho disubstituted benzene ring and cis stilbene (λ_{max} 280 millimicrons, $\epsilon = 10,500$; see Fig. 1 for spectrum of adduct). If the nitrogens are bridged as shown in (I), the

indicates that structure (XI) is a better representative of the structure of the adduct.

The equilibrium between (X) and (XI) is analogous to the tautomeric change first recognized by Hantzsch.¹⁶ One of his leading examples was provided by salts of N-alkylquinolinium derivatives. The salts of this cation on basification yield alkaline solutions, which in course of time lose alkalinity with the production of non-ionic carbinols which Hantzsch termed "pseudo-bases." The latter can be oxidized by ferricyanide to α -quinolones,¹⁷ and are, therefore, regarded as 2-carbinols:



This analogy provides additional evidence in favor of (XI) over (XII) for the covalent form of the present adduct.

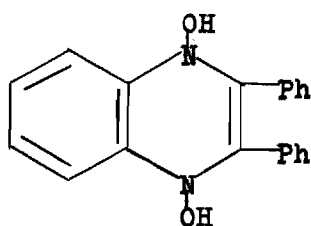
Acid hydrolysis to give 70 per cent of 2,3-diphenylquinoxaline is easily explained by these structures, but alkaline hydrolysis to give 45 per cent 2,3-diphenylquinoxaline, 16 per cent desoxybenzoin, 17 per cent quinoxaline-2-carboxylic acid, and 20 per cent carbon dioxide is a

¹⁶A. Hantzsch, Berichte der Deutschen Chemischen Gesellschaft, 32, 575 (1899); A Hantzsch and M. Kalb, ibid., 32, 3109 (1899). For a summary see C. K. Ingold, Structure and Mechanism in Organic Chemistry, Ithaca, N. Y.: Cornell University Press, 1953, pp. 575-586.

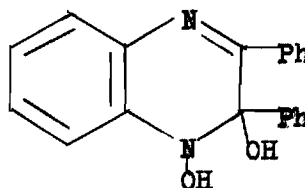
¹⁷H. Decker, Berichte der Deutschen Chemischen Gesellschaft, 25, 443 (1892); J. Prakt, Journal für praktische Chemie, 47, 28 (1893).

rather complicated reaction. There is a possibility that the reaction proceeds through structure (I) as a reactive intermediate, although other reaction paths can be envisioned as well.

Postman's white 2,3-diphenylquinoxaline "hydrated monoxide," m.p. 309-310°, which was originally obtained from oxidation of the adduct by hydrogen peroxide in acetic acid has now been obtained also from the oxidation of 2,3-diphenylquinoxaline. In addition, a bright yellow solid, m.p. 202-202.5°, was also isolated. The dioxide of 2,3-diphenylquinoxaline is reported to be canary yellow and to melt at 208-209°. ¹⁸ Since the "hydrated monoxide" sublimes unchanged at 270° and 0.06 mm. pressure, doubt is cast on the assumption that the substance is a true hydrate. It was found that the "hydrated monoxide" could be oxidized with fresh refluxing acetic acid-hydrogen peroxide solution to give the dioxide of m.p. 202-202.5°. The product must have been an intermediate in the complete oxidation. One possible structure might be (XIII), although the tautomeric structure (XIV) would be expected to be more stable for the same reasons for which (XI) is favored over (XII).



(XIII)



(XIV)

¹⁸Silvio Maffei, Gazzetta chimica Italiana, 76, 239 (1946).

The stereochemistry of the adduct was not rigorously established, but its structure suggests that the reaction of formation is analogous to Michael additions. These additions are well known to take place with acetylenic esters, and to give mainly trans adducts.¹⁹

¹⁹A. W. Johnson, Acetylenic Acids, London: Edwards Arnold & Co., 1950.

CHAPTER III

EXPERIMENTAL DETAILS

Sources and Purification of Starting Materials

Benzil.--Eastman's white label grade was used without further purification.

Dimethyl Acetylenedicarboxylate.--This material was prepared from the monopotassium salt of acetylenedicarboxylic acid and methanol using the method of Organic Syntheses.²⁰ Yields were obtained on the order of 50 per cent of material with index of refraction 1.4444 at 25° (reported, 1.4444-1.4452).

2,3-Diphenylquinoxaline.--Samples of this material which had been earlier prepared by Postman were recrystallized from purified methanol before use. Subsequent samples were prepared in 80 per cent yield by condensing equimolar quantities of *o*-phenylenediamine and benzil in refluxing glacial acetic acid by the method of Bost and Towell.²¹

Anhydrous Diethyl Ester.--Matheson, Coleman and Bell anhydrous diethyl ether was distilled from concentrated sulfuric acid and then stored over sodium wire.

Anhydrous Methanol.--The alcohol was prepared by refluxing commercial

²⁰E. H. Huntress, T. E. Leslie, and J. Bornstein, Organic Syntheses, New York: John Wiley and Sons, 32, 1952, p. 55.

²¹R. W. Bost and E. E. Towell, Journal of the American Chemical Society, 70, 904 (1948).

alcohol with magnesium turnings and then distilled.²²

Mono Potassium Salt of Acetylenedicarboxylic Acid.--Eastman's white label grade was used without further purification.

o-Phenylenediamine.--Eastman's white label grade was used without further purification.

Postman's Adduct.--The procedure of Postman²³ which produced the highest yields of product was used. In a typical experiment two moles of dimethyl acetylenedicarboxylate (47.00 g.; 0.33. moles) per mole of 2,3-diphenylquinoxaline (46.60 g.; 0.165 moles) were mixed in methanol (300 cc.) and left in a stoppered flask for two days. The yellow material which separated was filtered with a suction funnel and yielded 37.24 g. Recrystallization from acetonitrile gave 34.08 g., m.p. 156-157°. By concentrating the reaction solution an additional 12.01 g. separated which, when recrystallized twice from acetonitrile, yielded 9.42 g., m.p. 156-157°. By combining and concentrating the acetonitrile solutions more adduct could be obtained which, when recrystallized from acetonitrile, gave 2.78 g. The total yield was 46.29 g. or 61.5 per cent based on a molecular weight of 456. Postman's maximum yield was 76 per cent. The infrared spectrum is shown in Fig. 2.

Solvents for Recrystallization.--All the solvents used for recrystallization purposes were distilled through a fractionating column and only the portion boiling at the reported boiling point was used. Glacial acetic acid was purified by fractional freezing in addition to distillation.

²²H. Lund and J. Bjerrum, Berichte der Deutschen Chemischen Gesellschaft, 64, 210 (1931).

²³W. Postman, op. cit., p. 88.

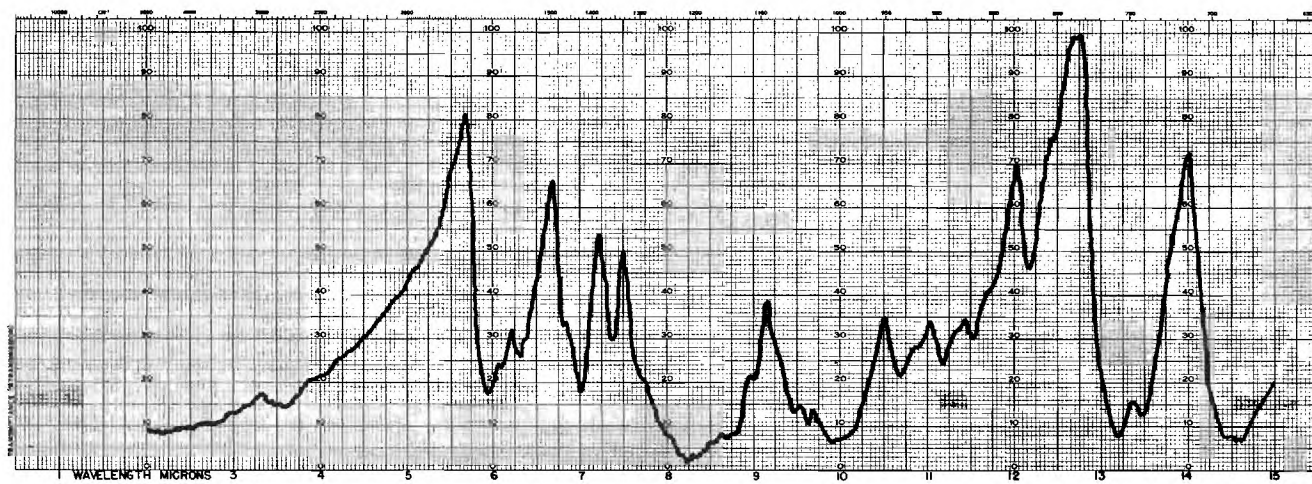


Figure 2. The Infrared Spectrum of Postman's Adduct.

Derivatives of Postman's Adduct

Adduct Chloride.--To 50 cc. of 0.6 M hydrogen chloride in diethyl ether, made by bubbling anhydrous hydrogen chloride through ether, was added 25 cc. of diethyl ether in which 1.5 g. of Postman's adduct had been dissolved. A yellow solid immediately precipitated. Suction filtration removed the ether, but on momentary contact with the air, the solid was converted to an oil. No attempt was made to identify this oil, but Postman reported that acid hydrolysis gives 70 per cent of the starting 2,3-diphenylquinoxaline.²⁴

Adduct Tetrachloroferrate(III).--A solution of 45 cc. of anhydrous diethyl ether and 1.35 g. of ferric chloride hexahydrate was filtered to remove undissolved ferric chloride and then mixed with 25 cc. of a diethyl ether solution containing 1.5 g. of Postman's adduct. Yellow crystalline needles were precipitated with m.p. 184-190°. No suitable solvent for recrystallization was found, but further purification was effected by dissolving the product in 20 cc. of distilled acetonitrile and diluting with 35 cc. of ether. The needles which settled out melted between 182-183°. Additional dissolving and precipitation steps did not increase the melting point.

Anal. Calcd. for $C_{26}H_{21}O_4N_2Cl_4Fe$: C, 50.19; H, 3.40; N, 4.50; Cl, 22.80; ash (Fe_2O_3), 12.84. Found C, 50.31; H, 3.34; N, 4.61; Cl, 22.69; ash 12.81.^a

Adduct Perchlorate.--In 25 cc. of anhydrous diethyl ether 1.5 g. of Postman's adduct was dissolved and the solution was added to an ethereal

²⁴W. Postman, op. cit., p. 96.

^aAnalysis by Clark Microchemical Laboratory, Urbana, Illinois

solution of perchloric acid, prepared by mixing 20 cc. of 70 per cent perchloric acid and 25 cc. of anhydrous diethyl ether in a small separatory funnel and separating the lower acid layer. The yellow product, 1.02 g., which precipitated melted at 222.5-223° (dec.). On dissolving the product in 20 cc. of freshly distilled methyl ethyl ketone and diluting with 35 cc. of anhydrous diethyl ether, 0.89 g. precipitated with a m.p. of 228-229° (dec.). The infrared spectrum is shown in Fig. 3.

Anal. Calcd. for $C_{26}H_{21}O_8N_2Cl$; C, 59.49; H, 4.03; N, 5.34; Cl, 6.76. Found; C, 59.84; H, 4.05; N, 5.35; Cl, 6.81.^a

Use of the same procedure with 1.5 g. of 2,3-diphenylquinoxaline resulted in the formation of 0.92 g. of a yellow perchlorate of m.p. 254-255.5°. A mixed melting point of a fifty-fifty mixture of this solid with the adduct perchlorate gave a m.p. of 205-216°.

Adduct Picrate.--When 1.3 g. of Postman's adduct was dissolved in 20 cc. of an ethereal solution of picric acid, prepared by dissolving 2.3 g. of picric acid in 50 cc. of anhydrous diethyl ether and filtering to remove any undissolved picric acid, minute yellow crystals formed. On dissolving in distilled acetonitrile followed by addition of ether, a yellow solid precipitated with m.p. 167-170°. On repeating the recrystallization technique, the m.p. rose to 169.3-170.5° and could not be increased by further recrystallization.

Anal. Calcd. for $C_{32}H_{23}O_{11}N_5$: C, 58.80; H, 3.55; N, 10.72. Found; C, 58.33; H, 3.60; N, 10.72.^a

Hydrogen Peroxide Oxidation of 2,3-Diphenylquinoxaline.--In a typical experiment 3.0 g. of the quinoxaline was dissolved in 25 cc. of 95 per cent ethanol and added to a mixture of 25 cc. of glacial acetic acid and

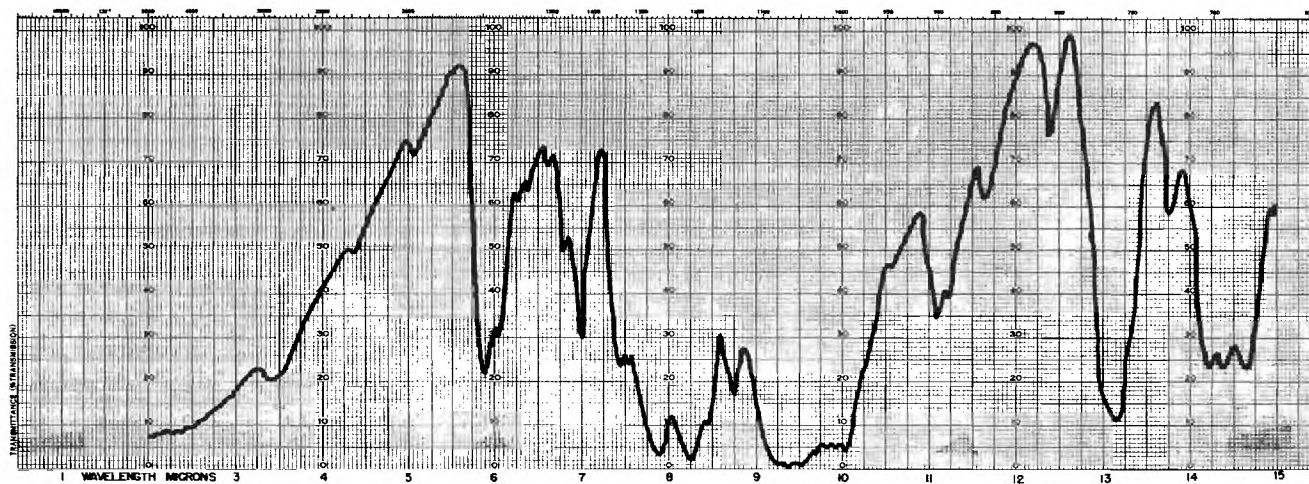


Figure 3. The Infrared Spectrum of the Adduct Perchlorate.

50 cc. of 30 per cent hydrogen peroxide. This mixture, boiled under reflux for forty hours, was allowed to cool slowly and then allowed to stand undisturbed for twenty-four hours. Two differently-colored crystals settled out of the reaction mixture. The dark orange crystals were soluble in hot methanol and the light orange crystals were rendered white by this treatment. The weight of the white product was 1.33 g.

The dark orange crystals were recrystallized from methanol to give 1.58 g. of crystals of m.p. 193-195°. Recrystallization from ethanol gave a product of m.p. 199-200°. Finally sublimation at 220° and 0.05 mm. pressure gave a substance of m.p. 202-202.5°. The final color was canary yellow. The dioxide of 2,3-diphenylquinoxaline melts 208-209° and is canary yellow in color.

The melting point of the white crystals, initially yellow from contamination by the orange material, was 309-310°. No melting point depression was observed with a fifty-fifty mixture of it and the original sample of Postman's "hydrated 2,3-diphenylquinoxaline monoxide,"²⁵ $C_{20}H_{16}O_3N_2$, which he prepared by oxidation of his adduct with hydrogen peroxide. The infrared spectra of the two compounds, made by using the potassium bromide pellet technique, were identical and are shown in Fig. 4. The "hydrated monoxide" (1.02 g.) could be converted quantitatively into the 202-202.5° compound by further treatment with a freshly prepared solution of 25 cc. of acetic acid and 50 cc. of fresh 30 per cent hydrogen peroxide and then by boiling under reflux for one hour. A fifty-fifty mixture of the two yellow compounds had a m.p. of 202-202.5°. The

²⁵W. Postman, op. cit., p. 104.

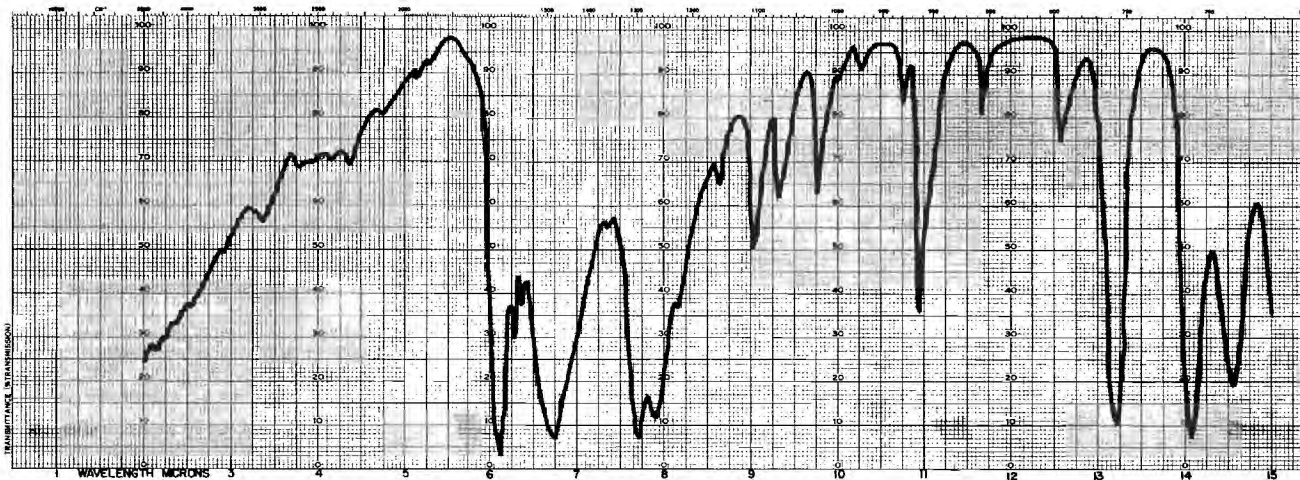
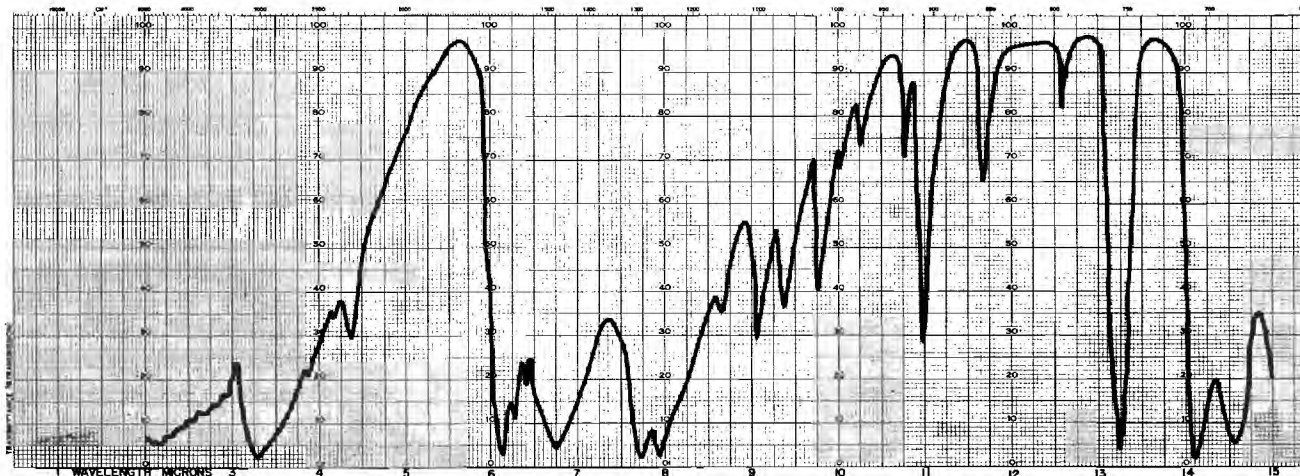


Figure 4. Postman's 2,3-Diphenylquinoxaline "Hydrated Monoxide."



The Product from the Hydrogen Peroxide Oxidation of 2,3-Diphenylquinoxaline.

"hydrated monoxide" must have been an intermediate in the formation of the dioxide. It is possible that the hydrogen peroxide initially was not at full strength and that the "monoxide" was not completely oxidized.

Experimental Procedures and Instrumentation

Melting Points.--All melting points reported were determined with a set of Anschultz thermometers. All glass capillary tubes (1.5 mm.) sealed at one end were filled to a height of 5 mm. with packed sample. From 25-225° a mechanically stirred oil bath was used, and from 225-350° a metal block was employed. Sample heating rate was one degree per minute in the vicinity of the melting point.

Infrared Spectra.--All spectra were obtained using a Perkin-Elmer Model 21 Infrared Spectrophotometer set up as follows: resolution, 927; response, 2-2; gain, 6; speed, 4; automatic suppression, 5; scale, 1:1; light source intensity, 0.34. Unless specifically stated otherwise, the spectra were obtained through the potassium bromide pellet technique using one hundred milligrams of finely powdered potassium bromide to one milligram of sample.

Ultraviolet Spectra.--All spectra were obtained using a Beckman DK-1 Spectrophotometer with automatic recorder set up as follows: slit servo, automatic with slit reading at least 1.88 at 220 millimicrons; time constant, 0.1; sensitivity, 0.80; absorbance scale, 0-1; detector, photomultiplier 20 X position; scanning time, 10 minutes; source, hydrogen lamp; chart speed, 3 inches per minute. Although the instrument was a double beam spectrophotometer, a zero line was run with the solvent and adjustments were made to compensate for instrument lag. The molecular extinction coefficients, ϵ , were calculated by the following formula

$$\epsilon = A/cl$$

where c is the concentration of the solution expressed in moles per liter, l is the width of the cell, and A refers to the optical density with values from 0.00 to 1.00. The cells used were a matched set of 1.003 cm. width.

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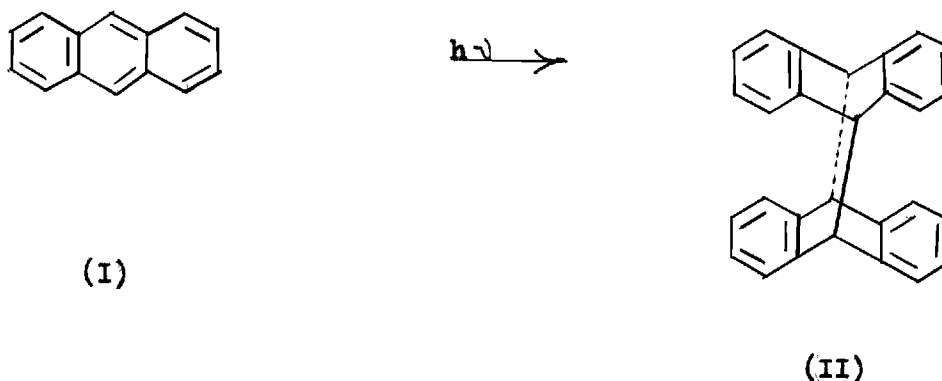
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24. Ibid., p. 96.
25. Ibid., p. 104

PART II

CHAPTER I

INTRODUCTION

There appear to be no well authenticated cases of photochemically induced Diels-Alder reactions. There are, however, a number of reactions which are more or less related and have been summarized by Walling¹ under the general topic of photochemical non-chain processes. An example of these is the dimerization of anthracene (I), when exposed to sunlight, to give structure (II):²

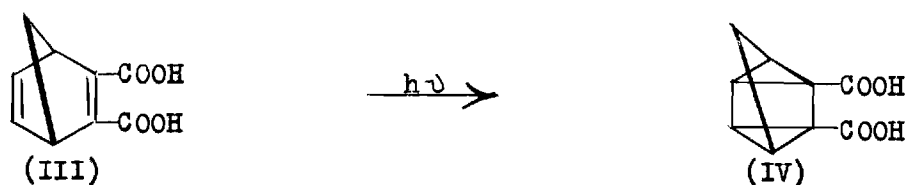


An interesting intramolecular example is the conversion of bicyclo-(2.2.1)-heptadiene-2,3-dicarboxylic acid (III) to its tetracyclic

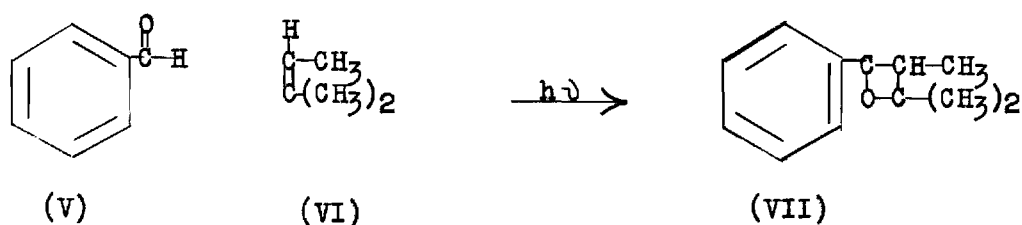
¹C. Walling, Free Radicals in Solution, New York: John Wiley and Sons, 1957, pp. 539-558; see also A. Mustafa, Chemical Reviews, 51, 1 (1952).

²C. A. Coulson and coworkers, Journal of the Chemical Society, 2961 (1955); see also F. D. Green and coworkers, Journal of the American Chemical Society, 77, 3852 (1955).

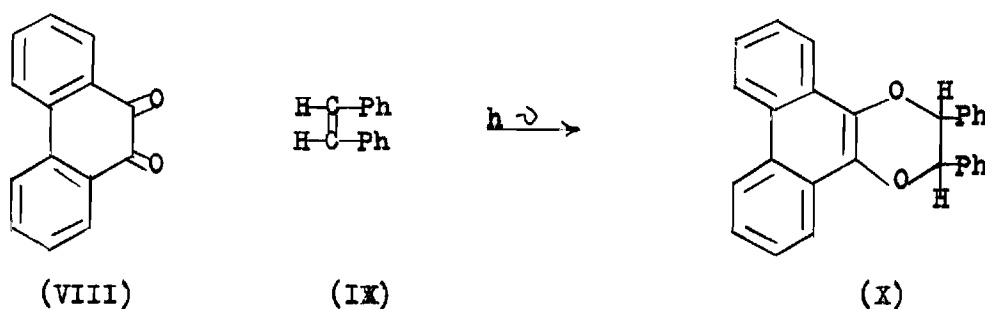
isomer (IV):³



Reactions which involve the addition of carbonyl compounds to multiple bonds are known. Examples are benzaldehyde (V) and 1,1,2-trimethyl ethylene (VI) to give structure (VII);⁴



and the reaction of phenanthraquinone (VIII) with 1,2-diphenyl ethylene (IX) to give structure (X):⁵



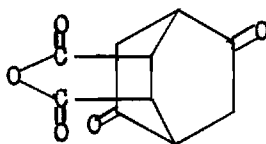
³J. Cristol and R. L. Snell, *ibid.*, 80, 1950 (1958).

⁴G. Buchi, C. G. Inman and E. S. Lipinsky, *ibid.*, 76, 4327 (1954); see also G. Buchi, J. T. Kefron, E. Keller, and D. Rosenthal, *ibid.*, 78, 876 (1956).

⁵A. Schonberg, W. E. Awad, G. A. Mousa, *ibid.*, 77, 3850 (1955).

Calculations based on thermodynamic data indicate that benzene and maleic anhydride will not react spontaneously to give a one to one adduct and that naphthalene and maleic anhydride will react but not to any great extent.⁶ Naphthalene has been reported to give one per cent yield of a Diels-Alder adduct with a thirty molar excess of maleic anhydride.⁷

Recently the Diels-Alder reaction has been extended to hydroquinone and maleic anhydride to give structure (XI);⁸ here the reaction is favored by the conversion of an enol to a more stable keto form.



(XI)

The possibility that benzene and maleic anhydride might react was suggested by the reported intramolecular complex formed when solutions of benzene are mixed with maleic anhydride (λ_{\max} 280 millimicrons, $\epsilon = \sim 1300$, nearest absorption maxima of benzene is at 270 millimicrons, $\epsilon = 10$).⁹ Several reactions which are thermodynamically unfavored can sometimes be promoted by light (cf. photosynthesis).

⁶G. W. Wheland, Resonance in Organic Chemistry, New York: John Wiley and Sons, 1955, pp. 377-381.

⁷M. C. Kloetzel and H. L. Herzog, Journal of the American Chemical Society, 72, 1991 (1950).

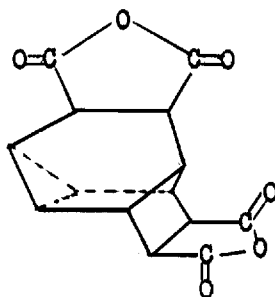
⁸R. C. Cookson and N. S. Wariyar, Journal of the Chemical Society, 327 (1957).

⁹L. J. Andrews and R. M. Keefer, Journal of the American Chemical Society, 75, 3777 (1953).

CHAPTER II

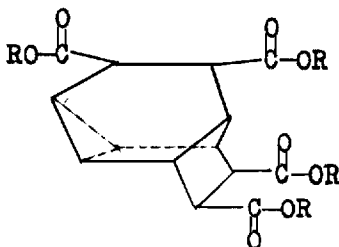
RESULTS AND DISCUSSION

When a thiophene free benzene solution which was 0.03 molar in maleic anhydride was irradiated for six hours with a 1000 watt mercury arc lamp, a white crystalline material, m.p. 355-357° (dec.), settled out of the reaction mixture. The structure of the product is believed to be (XII).



(XII)

Hydrolysis of the anhydride gives an acid the structure of which is believed to be (XIII) and esterification by methanol gives a structure which is believed to be (XIV).



(XIII), R=H
(XIV), R=CH₃

The evidence supporting these structures is summarized below:

1. Microchemical analysis and the neutralization equivalent of the anhydride agree with a product containing one mole of benzene and two moles of maleic anhydride.

2. The anhydride could be esterified by methanol to give a tetramethyl ester; the microchemical analysis and molecular weight of which are in agreement with the proposed structure.

3. The tetracarboxylic acid could be obtained and had a neutral equivalent and microchemical analysis in agreement with the proposed structure.

4. Only one mole of hydrogen was slowly absorbed upon catalytic hydrogenation of the tetracarboxylic acid.

5. There is no unsaturation in the molecule as evidenced by chemical tests for unsaturation. The anhydride gave no reaction with potassium permanganate in acetone and no reaction with bromine in boiling glacial acetic acid; the methyl ester did not absorb bromine from anhydrous methanol solution and gave no reaction with tetranitromethane. The infrared spectra of all these compounds show no bands which are indicative of an unsaturated molecule.

6. The infrared spectra of the anhydride, the corresponding acid, and the methyl ester all show absorption in the 9.8-10.0 micron region which could be assigned to the presence of a cyclopropane ring. The methyl ester also has a cyclopropane correlation band in the 1.64 micron region.

7. The hydrogenated tetracarboxylic acid shows an absence of a band in the 9.8-10.0 micron region but does show a band in the 6.8 region

which is attributed to $-\text{CH}_2-$ absorption. Neither the adduct, the adduct ester, nor the original tetracarboxylic acid show absorption in the $-\text{CH}_2-$ region.

8. The nuclear magnetic resonance absorption spectrum of the methyl ester shows at least three different types of proton environment, the bands of which can be assigned to the hydrogens of carbomethoxyl groups, methine hydrogen, and hydrogens on a cyclopropane ring.

9. The ultraviolet spectra of the methyl ester and of the sodium salt of the tetracarboxylic acid show absorption at greater intensity than sodium succinate. In part, this could be due to the presence of a cyclopropane ring.

10. The possibility that the adduct is formed from fulvene is made unlikely by the absence of a band in the infrared spectra which could be attributed to a $-\text{CH}_2-$ group.

11. Bicyclo(2.2.1)hepta-2,5-diene was shown to react with maleic anhydride, under the same conditions as benzene and maleic anhydride, to form a high melting solid.

A more complete discussion of each one of these statements is presented in the following pages.

The product (XII) could be obtained in yields of approximately one per cent from a saturated solution of maleic anhydride in benzene by irradiation for six hours. Yields of product on the order of ten per cent were obtained by irradiating a mixture of benzene and a saturated solution of maleic anhydride in methyl ethyl ketone or acetone. For best yields the time of irradiation, when methyl ethyl ketone was used, was ten hours.

The adduct was found to be insoluble in methanol, benzene, ethanol, carbon tetrachloride, ether, and acetonitrile. It was slightly soluble in methyl ethyl ketone and soluble in acetone. Molecular weight determinations tried in camphor, triphenylethane, β -naphthol, biphenyl, and 2,4,6-tribromophenol were unsuccessful because of the extreme insolubility of the material. Microchemical analysis showed the adduct to be composed of one mole of benzene and two moles of maleic anhydride in agreement with the empirical formula $C_{14}H_{10}O_6$. The neutralization equivalent was found to be 68.4. A value of 68.5 is calculated for the dianhydride of a tetracarboxylic acid of composition $C_{14}H_{10}O_6$.

Esterification to the tetramethyl ester (XIV), m.p. 136.3-136.6°, was accomplished by heating the adduct in anhydrous methanol which was 0.1 M in dry hydrogen chloride. The molecular weight of the tetramethyl ester could be determined by the melting point depression of a mixture of the ester and camphor. The value obtained was 366. The calculated value is 366.36 for $C_{18}H_{22}O_8$; this formula corresponds to that of the tetramethyl ester of an adduct composed of one mole of benzene combined with two moles of maleic anhydride.

The acid (XIII) was obtained by boiling the adduct with sodium hydroxide and neutralizing with hydrochloric acid. The microchemical analysis of the acid after correction for a 7.4 per cent ash content gave agreement for $C_{14}H_{14}O_8$, which is the formula for the hydrolyzed anhydride. The neutral equivalent found was 77.35 (no correction for ash), and that calculated is 77.55.

Hydrogenation of the acid (XIII) was effected by using five per cent platinum on charcoal in glacial acetic acid at room temperature and

atmospheric pressure. The initial hydrogen absorption rate was approximately two milliliters per hour but slowly diminished over a period of twenty-four hours. The hydrogenation was continued for an additional forty-eight hours, but no further hydrogen absorption was observed. The total absorption by one mole of acid was 0.925 moles of hydrogen. If correction is made for the 7.4 per cent ash found on microchemical analysis, one mole of acid absorbed one mole of hydrogen. The hydrogenated material, m.p. 295-297° (dec.), was extremely soluble in acetic acid in contrast to the moderate solubility of the adduct acid.

All the chemical tests for unsaturation were negative. Maleic anhydride, even in small concentrations, rapidly decolorizes potassium permanganate-acetone solutions. This test is so sensitive that it can be used to test for small amounts of maleic anhydride impurity in the sample. A sample of the adduct, which had been washed with boiling benzene to remove all traces of maleic anhydride, did not decolorize even dilute solutions of potassium permanganate in acetone. Bromine was not absorbed by the adduct in boiling glacial acetic acid. No yellow color was evidenced when the tetranitromethane test was run on the methyl ester in carbon tetrachloride solutions. This test could not be performed on the adduct itself because of its insolubility. Bromination of the methyl ester was not effected in methanol solutions even after a period of six days.

The infrared spectra of the anhydride (Fig. 5), the tetracarboxylic acid (Fig. 6), the tetramethyl ester (Fig. 7), and the hydrogenation product of the acid after conversion to its anhydride by acetic anhydride (Fig. 8) are shown on the following pages. Assignments for some of the bands are listed in Table 1.

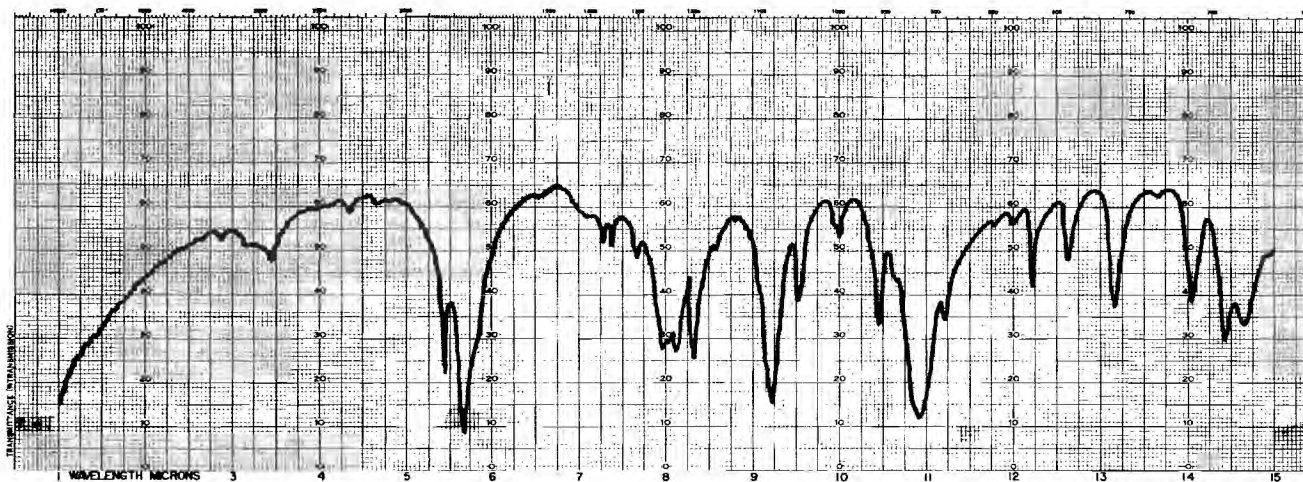


Figure 5. The Anhydride.

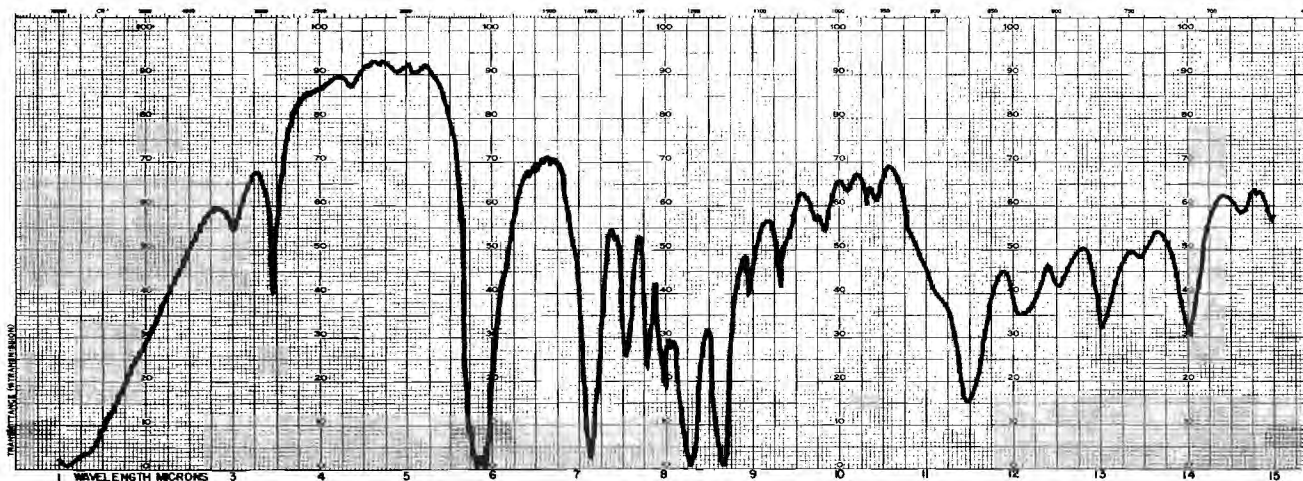


Figure 6. The Tetracarboxylic Acid.

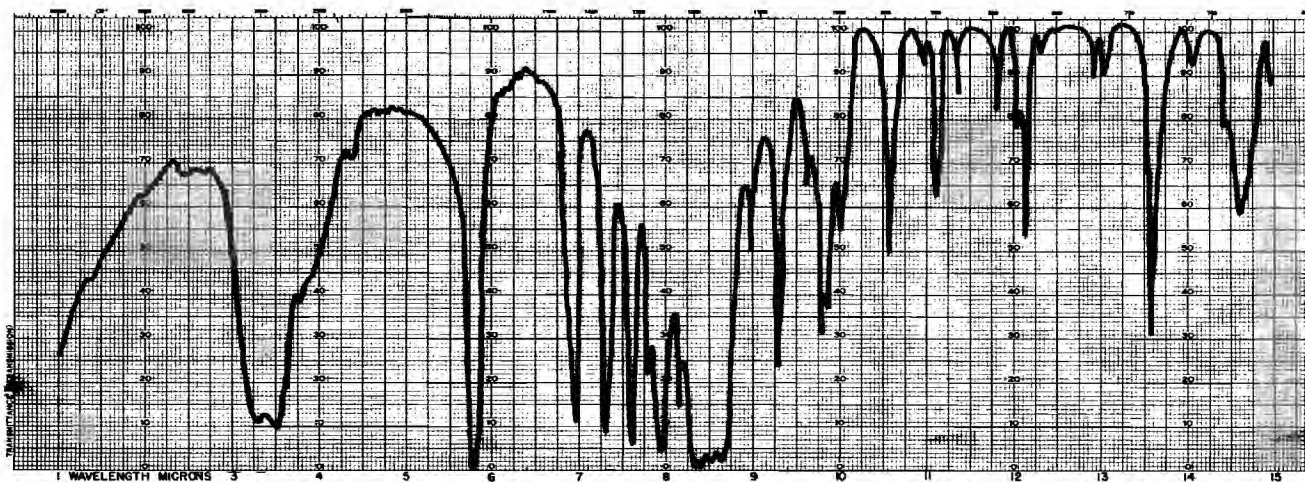


Figure 7. The Tetramethyl Ester.

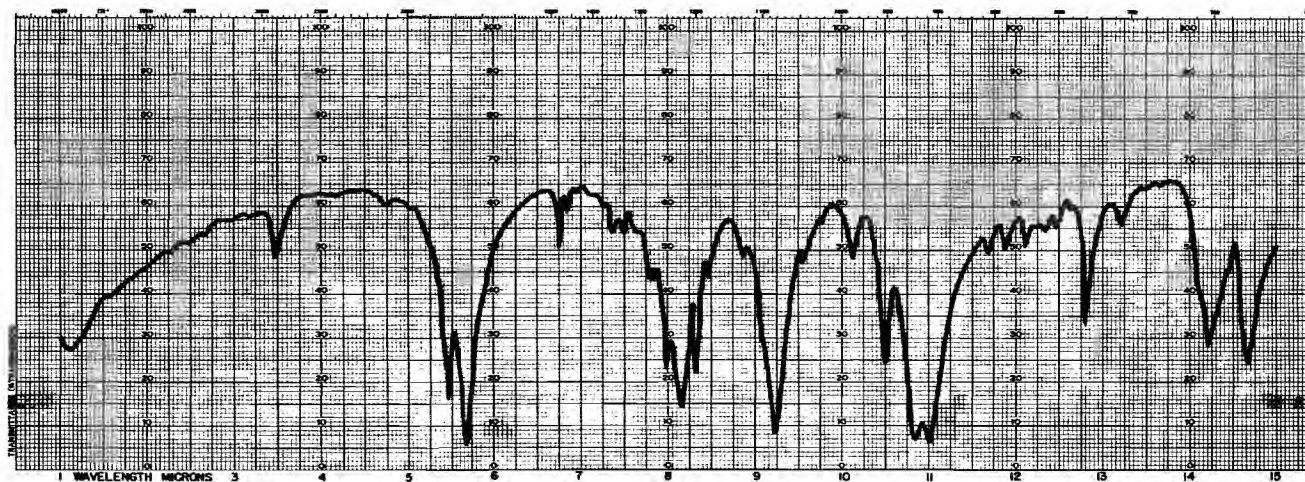


Figure 8. The Hydrogenated Acid Converted to its Anhydride.

Table 1. Assignments of the Infrared Absorption Bands.¹⁰

| Product | Band | Assignment |
|---------------------------|---|--|
| The Anhydride | 3.45 | C-H Stretching Vibrations |
| | 5.45 } 5.67 } | C-O of a Five Membered Anhydride Ring |
| | 7.67-8.32 | C-O Stretching Vibrations |
| | 10.01 | Cyclopropane Ring |
| The Tetra-carboxylic Acid | 3.45 | C-H Stretching Vibrations |
| | 5.82 } 5.92 } | C=O and O-H of an Acid |
| | 7.15 } 7.55 } | C-O and O-H Stretching and Deformation Vibrations |
| | 7.80-8.03 | C-O Stretching Vibrations |
| | 9.85 | Cyclopropane Ring |
| The Tetra-methyl Ester | 3.30 } 3.50 } | CH ₃ Stretching Vibrations |
| | 5.80 | C=O of an Ester |
| | 6.90 } 7.30 } | C-CH ₃ Deformation Vibrations, Asymmetrical and Symmetrical |
| | 7.80-8.15 | C-O Stretching Vibrations |
| | 8.55 | C-O-C Stretching Vibrations |
| | 9.87 | Cyclopropane Ring |
| | The Hydrogen-ation Product of the Acid Converted to its Anhydride | 3.47 |
| 5.45 } 5.67 } | | C-O of a Five Membered Anhydride Ring |
| 6.76 | | CH ₂ Stretching Vibrations |
| 7.98-8.32 | | C-O Stretching Vibrations |

¹⁰L. J. Bellamy, Infrared Spectra of Complex Molecules, New York: John Wiley and Sons, 1954.

The methyl ester has an absorption band at 1.69 microns measured in carbon tetrachloride using the Beckman spectrophotometer (Fig. 9). A recent correlation for the cyclopropane ring is 1.64 microns.¹¹

In the infrared spectra of the adduct, acid, and the ester there is no absorption in the 5.95-6.17 micron region (assignment $-C = C-$ stretching) and in the 6.73-6.92 micron region (assignment $-CH_2-$ deformation). The hydrogenated product clearly shows a band at 6.80 microns indicating the presence of $-CH_2-$, and in the region 9.8-10.0 microns it shows no absorption which indicates the absence of a cyclopropane ring. On the other hand, the adduct, the acid and the ester absorb at 9.8-10.0 microns.

A nuclear magnetic resonance absorption spectrum of the methyl ester in deuterated chloroform using protonated chloroform as the reference is shown in Fig. 10. Assignments for the bands and the integrated intensity for each one is given in Table 2.

The spectrum is not inconsistent with twelve hydrogens on the methyl groups of the ester, seven methine hydrogens on a five or six membered ring and three on a cyclopropane ring.

The ultraviolet spectra of the adduct in sodium hydroxide, the ester in methanol, succinic anhydride in sodium hydroxide, and maleic anhydride in sodium hydroxide are presented in Fig. 11. From the relatively low extinction coefficient of the adduct compared to maleic anhydride, one can say with reasonable assurance that there is no conjugation between the carboxyl groups and an olefinic bond. The absorption,

¹¹W. H. Washburn and M. J. Mahoney, Journal of the American Chemical Society, 80, 504 (1958).

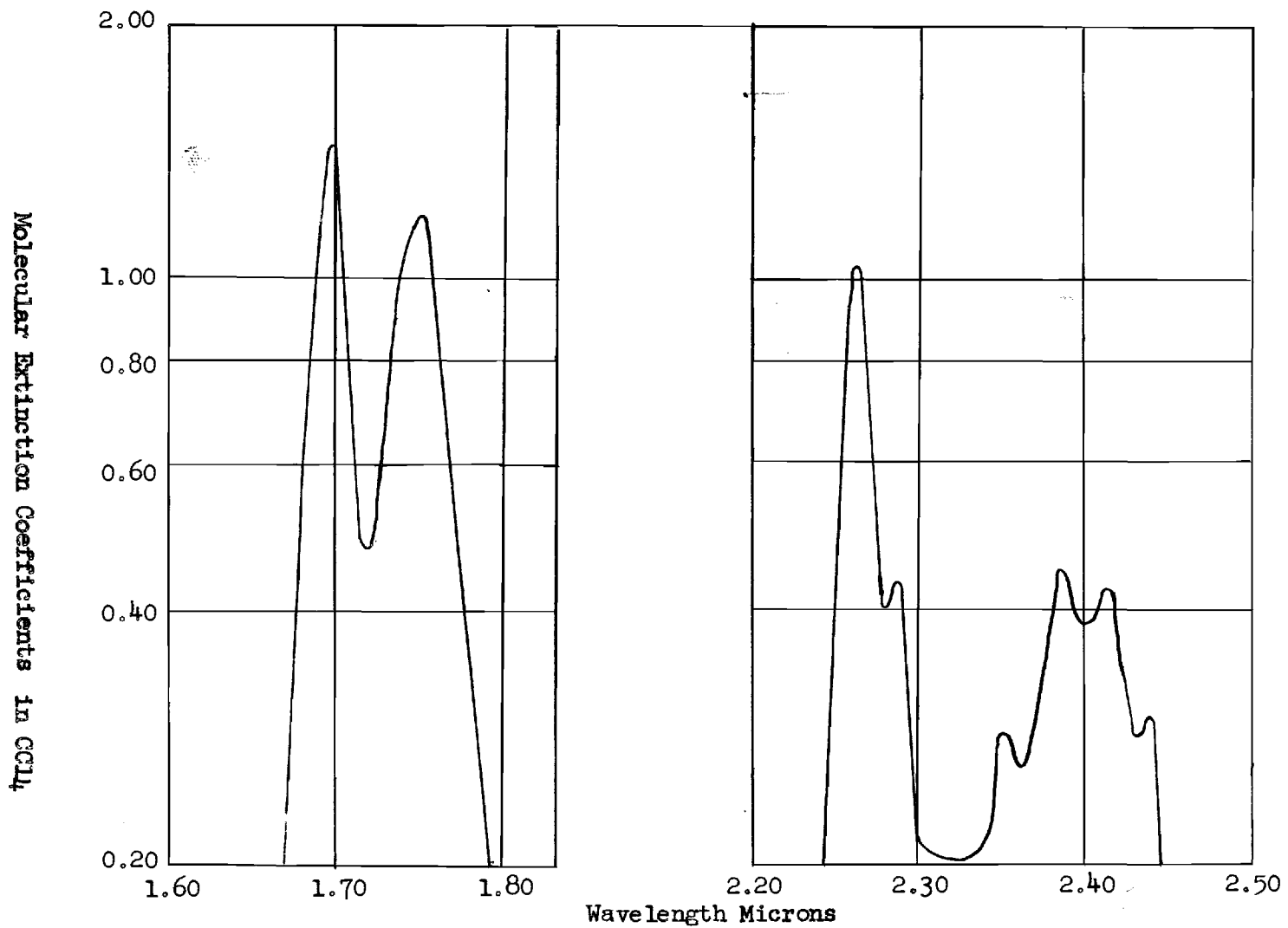


Figure 9. The Near Infrared Spectrum of the Tetramethyl Ester.
 (There are no absorption bands from 1.80-2.20.)

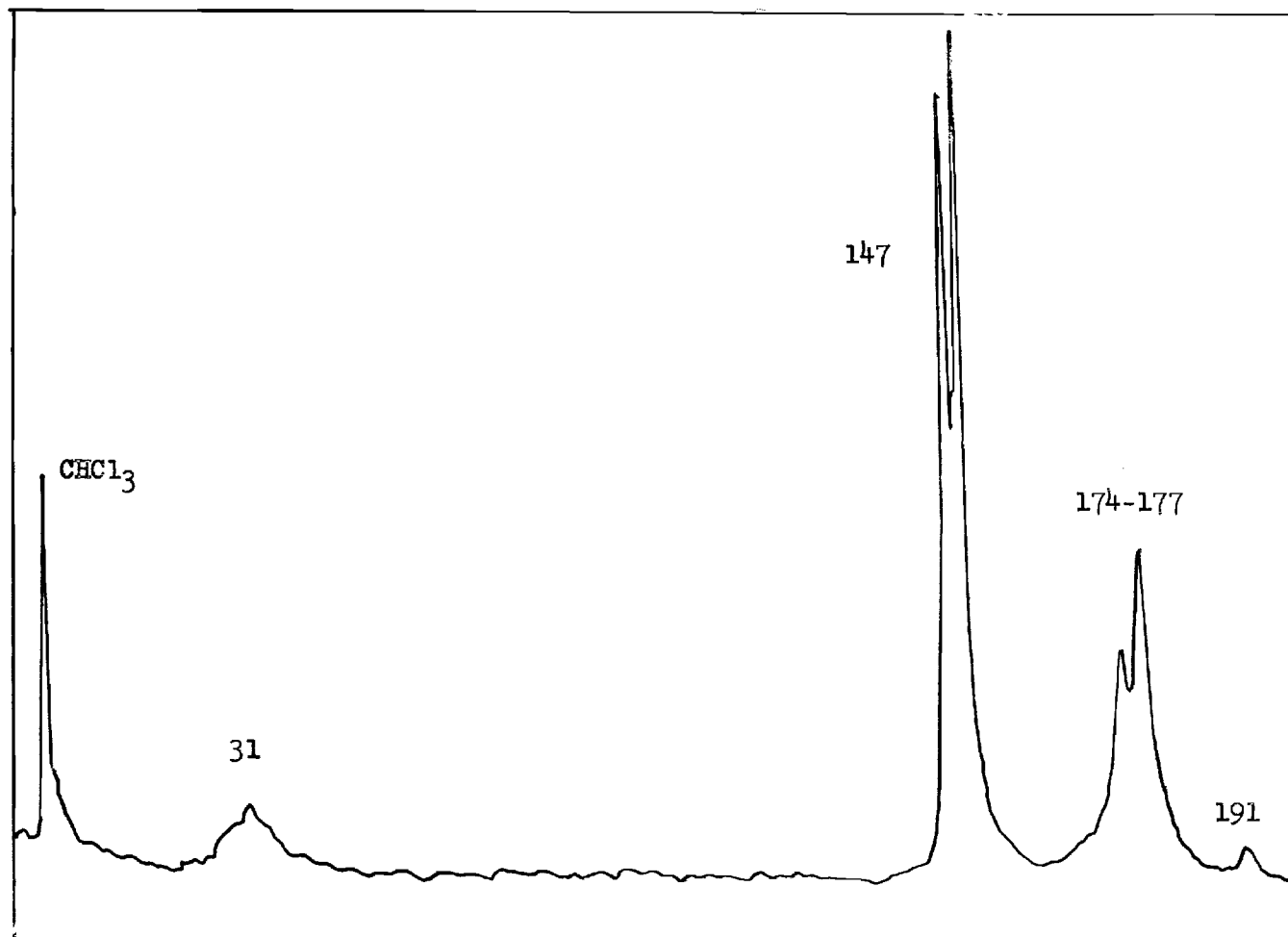


Figure 10. The Nuclear Magnetic Resonance Absorption Spectrum of the Tetramethyl Ester in Deuteriochloroform with Chloroform as Reference.

Table 2. Assignments and the Integrated Intensity of the Bands in the Nuclear Magnetic Resonance Absorption Spectrum of the Tetramethyl Ester.

| Proton Shift | | Intensity | Assignment |
|---------------------|----------------------------------|-----------|--|
| Cycles ^a | δ -values ^{12,b} | | |
| 31 | +0.16 | 3.00 | C-H of Cyclopropane ^c |
| 147 | -0.138 | 10.65 | CH-O ₃ of an Ester ¹² |
| 174-177 | -0.185 | 7.67 | C-H of Methine on Cyclic Ring ^{13,14} |
| 191 | -0.24 | 0.678 | C-H of Methine on Cyclic Ring ^{15,d} |
| | +0.07 | Missing | -C = CH-C ¹² |
| | -0.35 | Missing | -CH ₂ - ¹² |
| | +0.05 | Missing | CH ₂ = C ¹² |

^aShifts are on sample dissolved in deuteriochloroform without correction for concentration effects and are based on chloroform as reference standard. The shifts are given in cycles at 40 Mc/sec.

^bThe δ -values are based on water as the reference standard, taking chloroform to have a shift of -96 cycles relative to water. (See L. E. Meyer, E. S. Gutowsky, Journal of Physical Chemistry, **53**, 481 (1953).)

^cThis absorption is in the absorption region of a C-H on an aromatic ring.

^dThis peak is considered to be a part of the larger peak near it.

¹²L. E. Meyer, A. Aoika, E. S. Gutowsky, Journal of the American Chemical Society, **75**, 4567 (1953).

¹³L. Goodman, R. M. Silverstein, A. Benitez, ibid., **79**, 3075 (1957).

¹⁴E. E. Van Tamlen and coworkers, ibid., **80**, 501 (1958).

¹⁵R. C. Pearson, R. Munson, R. Basolo, ibid., **80**, 503 (1958).

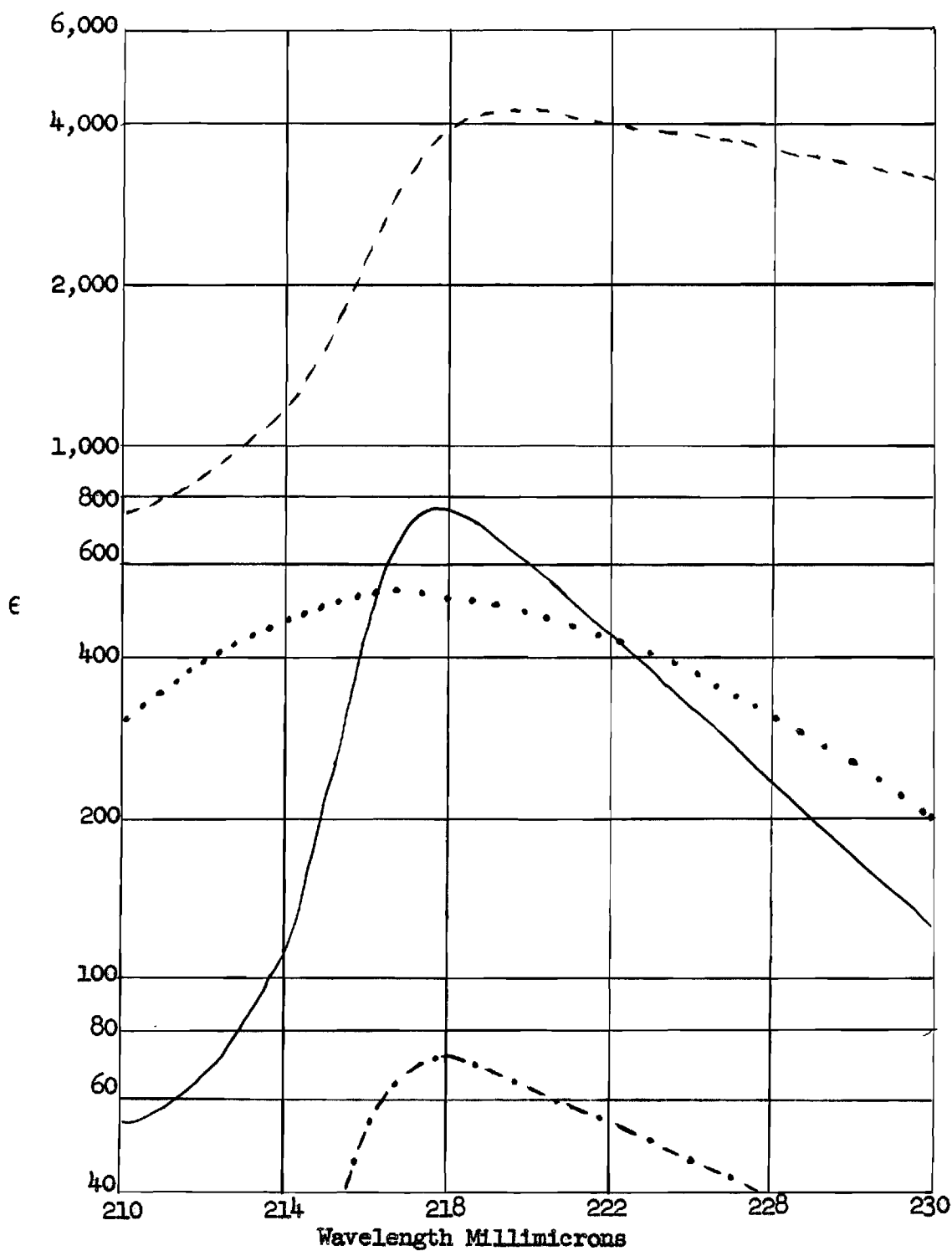


Figure 11. The Anhydride in Sodium Hydroxide ———
 Succinic Anhydride in Sodium Hydroxide - · - · -
 Maleic Anhydride in Sodium Hydroxide - - - -
 The Tetramethyl Ester in Methanol · · · · ·

however, appears too intense for a saturated acid. This unusual absorption can be explained, in part, by the fact that, although the cyclopropyl group is not conjugated with the carbonyl of the acid, the end absorption of the cyclopropyl group may well increase the carbonyl absorption.¹⁶ Of course, isolated olefinic bonds also have this same effect, but their presence can be excluded by the infrared spectra and unsaturation tests which were mentioned earlier.

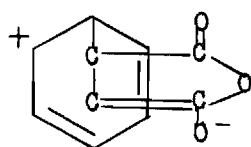
It has been reported recently that irradiation of benzene solutions with ultraviolet light gives rise to fulvene.¹⁷ Mono adducts of maleic anhydride are known and the exo isomer has a m.p. of 86-87°, while the endo has a m.p. of 80-82°.¹⁸ If it were fulvene which formed the adduct and if no rearrangement of carbon skeleton occurred during the reaction, the -CH₂- group would show up in the infrared as well as in the nuclear magnetic resonance spectrum. Since this was not observed, the possibility of fulvene being the precursor of the adduct seems unlikely.

Andrews and Keefer⁹ postulated, on the basis of the ultraviolet absorption of solutions of maleic anhydride and benzene, that these substances formed a one to one complex for which they suggested structures (XVI) and (XVII) as contributors to the hybrid structure of the complex.

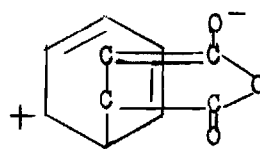
¹⁶Louis Dorfman, Chemical Reviews, 53, 53 (1953).

¹⁷J. McDonald Blair and D. Bryce-Smith, Proceedings of the Chemical Society, 287 (1957).

¹⁸J. Thiel and J. Wiemann, Bulletin de la Societe chimique de France, 177 (1956).

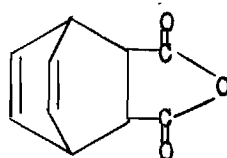


(XVI)



(XVII)

If we assume that addition of the maleic anhydride portion can occur across the para position of benzene, we would have a derivative of bicyclo(2.2.2)octadiene (XVIII):

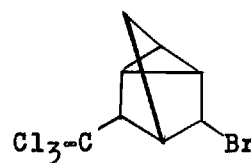
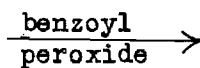
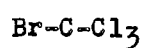


(XVIII)

which might be expected to react with a second mole of maleic anhydride in an analogous manner to the addition of bromochloroform to bicyclo(2.2.1)hepta-2,5-diene (XIX) in the presence of benzoyl peroxide to give structure (XX).¹⁹



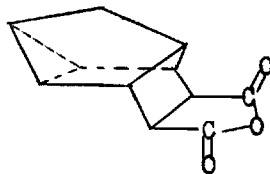
(XIX)



(XX)

¹⁹Shell Oil Company Information Circular, MD-101, "Bicyclo(2.2.1)hepta-2,5-diene," p. 2.

Striking evidence for this reaction path for the benzene and maleic anhydride adduct was obtained when bicyclo(2.2.1)hepta-2,5-diene was found to undergo reaction with maleic anhydride under the same conditions that benzene does. The reaction products are not as yet completely identified but appear to be high melting and very insoluble. If the bicycloheptadiene-maleic anhydride adduct could be shown to exhibit structure (XXI), even more strength could be added to the proof already amassed to support structure (XII) for the benzene and maleic anhydride adduct.



(XXI)

CHAPTER III

EXPERIMENTAL DETAILS

Sources and Purification of Starting Materials

Benzene.--Matheson, Coleman, and Bell special thiophene-free benzene was distilled and used for all the reactions with the exception of the test reaction (see adduct preparation). For the test reaction 400 cc. of the thiophene-free benzene was washed with four 50 cc. portions of concentrated sulfuric acid, three 50 cc. portions of distilled water, two 25 cc. portions of two per cent sodium bicarbonate solution, and three more 25 cc. portions of distilled water.²⁰ The benzene was dried over magnesium sulfate, decanted, then filtered and distilled.

Maleic Anhydride.--Matheson white label grade was ground to a powder and used without further purification in all reactions except the test reaction. Freshly distilled maleic anhydride was used for the test run.

Solvents

Acetone.--Commercial grade was dried over potassium carbonate and distilled.

Methyl Ethyl Ketone.--Commercial grade was distilled before use.

Preparations

Benzene and Maleic Anhydride Adduct.--An example of the first series of experiments follows: Benzene (300 cc. thiophene free) and powdered maleic anhydride (10.30 g., 0.105 moles) were mixed until solution was effected.

²⁰L. F. Fieser, Experiments in Organic Chemistry, Boston: D. C. Heath and Co., 1955, p.282.

This solution was then irradiated for six hours with a 1000 watt Hanovia mercury arc lamp in a water cooled quartz cell. The white crystals which precipitated were filtered by suction on a fritted glass funnel and washed with three 25 cc. portions of boiling benzene. The m.p. of the product was 355-357° (dec.). The ultraviolet cell was also washed with three 25 cc. portions of boiling benzene and the undissolved material added to that originally filtered. The total yield was 1.404 g. or 0.97 per cent based on maleic anhydride and molecular weight of 274.22 for the adduct anhydride.

The test experiment, mentioned in the purification of benzene and maleic anhydride, was next conducted to insure that no impurity in the benzene, such as traces of thiophene, or impurity in the maleic anhydride was giving rise to the high melting product. The maleic anhydride and benzene were, therefore, subjected to the purification procedure indicated earlier. When the same proportions of purified starting materials and the same reaction conditions were used in this test run as were used for the first experiment, the yield, calculated on the same basis, was 0.97 per cent of product of m.p. 355-357° (dec.). Clearly then, no impurity in either the benzene or the maleic anhydride was likely as a source leading to the high melting solid.

In the second series of experiments the same proportions of benzene and maleic anhydride were used as mentioned in the first experiments, but the time of irradiation was increased to sixteen hours. The yield of product was 1.36 per cent in a typical run. In a similar reaction for which the time of irradiation was ten hours, the yield of product was 1.10 per cent. The yield is thus seen to be dependent upon the time of irradiation.

In the third series, an attempt was made to increase the concentration of maleic anhydride in the solution. In a typical example 87.45 g. (0.892 moles) of maleic anhydride was dissolved in 150 cc. of distilled methyl ethyl ketone, and then this solution was added to 100 cc. (1.126 moles) of benzene. After irradiation for eleven hours, 7.20 g. of product with m.p. of 355-357° (dec.) precipitated in the cell and an additional 5.93 g. was recovered from the reaction solution by adding water and filtering off the precipitated product. This 5.93 g. sample was heated with 25 cc. of acetic anhydride and the solution allowed to cool. The product which precipitated on cooling weighed 5.12 grams. The total yield was 10 per cent, and the average yield for four runs was 8.5 per cent. On the inner walls of the cell a hard brown film was formed which was difficult to remove. Acqua regia removed the major portion of the film after the acid was allowed to stand in the cell for two days. (The coating on the inner walls appeared to decrease the amount of product isolated because the ultraviolet light was filtered before it reached the solution.)

Reactions run in acetone as the solvent for maleic anhydride gave better yields than the methyl ethyl ketone reactions. The yield of a typical reaction was 15 per cent.

The reaction product (.9540 g.) could be sublimed at 175° and 0.05 mm. pressure over a period of four hours to give 0.740 g. of a material of m.p. 355-357° (dec.). The material at the bottom of the sublimation apparatus turned brown when higher temperatures were employed.

The neutral equivalent was determined as follows: The anhydride, 0.114267 g., was dissolved in 50 cc. of 0.1008 N sodium hydroxide and boiled under reflux for an hour. Protection from atmospheric carbon dioxide was effected by the use of a soda-lime tube connected by a bent

tube to the top of the condenser. Back titration with 0.1007 N hydrochloric acid showed 16.72 cc. of base was required to titrate the anhydride. The titration was followed with the aid of a Beckman pH meter Zeromatic Model. The value found was 68.4, and the value calculated for an adduct containing one mole of benzene and two moles of maleic anhydride is 68.55.

The adduct did not decolorize dilute solutions of potassium permanganate in acetone, although this test is very sensitive in testing for the presence of maleic anhydride. Bromination of the anhydride was not effected by boiling an acetic acid-bromine solution of the anhydride.

Molecular weight determinations attempted by the freezing point lowering method were not successful. The anhydride did not appear to be soluble in the solvents tried. The solvents tried were camphor, triphenylethane, β -naphthol, biphenyl, and 2,4,6-tribromophenol.

Anal. Calcd. for $C_{14}H_{10}O_6$ (two moles of maleic anhydride and one mole of benzene): C, 61.32; H, 3.65; Found C, 61.24, 61.37; H, 3.64, 3.74.^a

The Acid.--A 1.05 g. sample of the anhydride was boiled under reflux for one hour in 200 cc. of 0.1 N sodium hydroxide. Then 200 cc. of 0.1 N hydrochloric acid was added, and the solution concentrated to 40 cc. The precipitated product was filtered and dissolved in 100 cc. of boiling 0.1 N hydrochloric acid and the solution concentrated to 25 cc. Repetition for seven more times of this purification technique gave a product which expelled a liquid between 125-200° on determining the melting point. The material finally melted at 355-357° (dec.). Presumably the liquid expelled was water.

^aAnalysis by Clark Microchemical Laboratory, Urbana, Illinois.

Anal. Calcd. for $C_{14}H_{14}O_8$: C, 54.20; H, 4.55; Found: C, 49.99; H, 4.38; ash, 7.4.^b Correcting for the ash (assuming the ash to be sodium chloride or other such inorganic material), these results became C, 54.02; H, 4.70.

Hydrogenation of 0.553205 g. of the acid took twenty-four hours at room temperature and atmospheric pressure using 80 cc. of glacial acetic acid and 0.491500 g. of 5 per cent platinum on charcoal. The hydrogenation was continued an additional seventy-two hours, but no further hydrogen was absorbed. Total absorption was 36.92 cc. of hydrogen (corrected to STP) or 0.925 moles per mole of the acid. If correction is made for the 7.4 per cent impurity (found on microchemical analysis), one mole of hydrogen is absorbed per mole of acid.

The neutral equivalent of the acid was determined by mixing 0.119134 g. of the acid in 25 cc. of water and then titrating with 0.0275 N sodium hydroxide. The titration was followed with the aid of a Beckman Zeromatic Model pH meter. A volume of 56.0 cc. of the sodium hydroxide was required to neutralize the acid. This gave a neutralization equivalent of 77.4. The value calculated for the acid is 77.5. If correction is made for the 7.4 per cent impurity, the calculated value is then 83.6, assuming the impurity to be some inorganic salt.

The Methyl Ester.--The anhydride (1.80 g.) was esterified by boiling under reflux with anhydrous methanol (100 cc.), which was 0.078 N in dry hydrogen chloride, for six hours. The solution was concentrated to 20 cc. on a steam bath and, on cooling, 1.58 g. of white crystals precipitated, m.p. 130-132°. Recrystallization three times from anhydrous

^bAnalysis by Galbraith Microchemical Laboratory, Knoxville, Tenn.

methanol gave the methyl ester, m.p. 136.3-136.6°.

To determine the molecular weight of the ester, 0.006557 g. of ester was dissolved in 0.128661 g. camphor (m.p. 175.6°), and the average of three melting points was 171.2°. A sample (0.011432 g.) of triphenylmethane was mixed with 1.120392 g. of camphor, and the average of three melting points was 163.3°. The freezing point constant calculated for camphor is 31.65. The molecular weight of the ester is then 366.

Anal. Calcd. for $C_{18}H_{22}O_8$: C, 59.01; H, 6.05; Found: C, 58.82, 58.91; H, 5.88, 5.89.^b

To 0.023340 g. of the ester dissolved in 10 cc. of anhydrous methanol was added .01 cc. of a bromine solution containing approximately one cc. of bromine per liter of methanol. A test blank containing only 10 cc. of methanol was used for comparison. At the end of six days in the dark, no visible difference in color was noted between the two solutions.

The tetranitromethane test produced no bright yellow color on addition of a carbon tetrachloride solution of tetranitromethane to a concentrated carbon tetrachloride solution of the ester. There was no difference in color between the tetranitromethane-ester solution and a blank run for comparison.

When 0.01 g. of the ester dissolved in 2 cc. of carbon tetrachloride was added to 5 cc. of a carbon tetrachloride solution containing 0.01 cc. of a 5 per cent bromine in carbon tetrachloride, no reaction was observed. On leaving the sample on a white paper out on the desk top for fifteen minutes, the bromine color was discharged. Over a period of twenty-four hours a total of 0.15 cc. of the bromine solution was

absorbed. No more bromine was taken up in the next twelve hours after addition of the last 0.01 cc. bromine sample. Rough calculations indicated 4.2×10^{-5} moles of bromine were absorbed by 3.2×10^{-5} moles of ester.

Experimental Procedures and Instrumentation

Melting Points.--All melting points reported were determined with a set of Anschultz thermometers. All glass capillary tubes (1.5 mm.) sealed at one end were filled to a height of 5 mm. with packed sample. From 25-225° a mechanically stirred oil bath was used, and from 225-350° a metal block was employed. Sample heating rate was one degree per minute in the vicinity of the melting point.

Infrared Spectra.--All spectra were obtained using a Perkin-Elmer Model 21 Infrared Spectrophotometer set up as follows: resolution, 927; response, 2-2; gain, 6; speed, 4; automatic suppression, 5; scale, 1:1; light source intensity, 0.34. Unless specifically stated otherwise, the spectra were obtained through the potassium bromide pellet technique using one hundred milligrams of finely powdered potassium bromide to one milligram of sample.

Ultraviolet Spectra.--All spectra were obtained using a Beckman DK-1 Spectrophotometer with automatic recorder set up as follows: slit servo, automatic with slit reading at least 1.88 at 220 millimicrons; time constant, 0.1; sensitivity, 0.80; absorbance scale, 0-1; detector, photomultiplier 20 X position; scanning time, 10 minutes; source hydrogen lamp; chart speed, 3 inches per minute. Although the instrument was a double beam spectrophotometer, a zero line was run with the solvent and adjustments were made to compensate for instrument lag. The molecular

extinction coefficients, ϵ , were calculated by the following formula:

$$\epsilon = A/cl$$

where c is the concentration of the solution expressed in moles per liter, l is the width of the cell, and A refers to the optical density with values from 0.00 to 1.00. The cells used were a matched set of 1.003 cm. width.

Nuclear Magnetic Resonance Absorption Data.--A Varian fixed frequency R-F Unit Model V4310C was used with frequency of 40 megacycles and a field of 10,000 gauss. The ester (0.10 g.) was dissolved in 0.3 cc. of deuterated chloroform and protonated chloroform was used as the reference. The author is indebted to Dr. Leon Mandell, Department of Chemistry, Emory University for obtaining this spectrum.

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BIOGRAPHICAL SKETCH

The author was born September 17, 1935 at Newton, Mississippi. He attended public schools in Carthage and Jackson, Mississippi, and Memphis, Tennessee, where he graduated from Whitehaven High School in 1952. From Vanderbilt University in Nashville, Tennessee, he received his Bachelor of Arts degree in mathematics and chemistry on June 6, 1956.

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