DICARBONIUM IONS FROM BIS-ARYL CARBINOLS

Thesis for the Degree of Ph. D.
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Theodore Sulzberg
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This is to certify that the

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DICARBONIUM IONS FROM BIS-ARYL CARBINOLS

presented by

Theodore Sulzberg

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Harold Hart
Major professor

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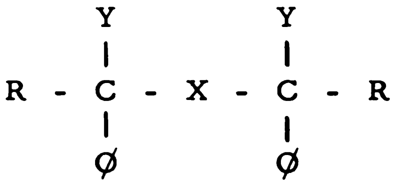
ABSTRACT

DICARBONIUM IONS FROM BIS-ARYL CARBINOLS

by Theodore Sulzberg

The main purpose of this thesis was to investigate compounds which could form stable dicarbonium ions by ionizations at separate sites in molecules (1). By use of the Friedel-Crafts benzoylation and Grignard reactions on the appropriate aromatic molecules the following types of compounds were prepared

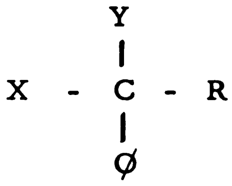


$$R - \overset{Y}{\underset{\phi}{C}} - X - \overset{Y}{\underset{\phi}{C}} - R$$

where R = phenyl or hydrogen, Y = hydroxyl or chlorine and X = benzene, biphenyl or fluorene.

All of the compounds studied dissolved in 98% sulfuric acid to form highly colored solutions ranging from yellow to blue. Investigation of the visible absorption spectra of solutions of these compounds in varying concentrations of sulfuric acid has shown that reversible ionization to dications can occur either stepwise or simultaneously and is, in general, a function of the moiety between the sites to be ionized. The pK_R's for these processes have also been determined and are given in Table 1 along with the λ_{max} and ϵ_{max} of the dications.

In order to interpret the visible spectra of these dications, a series of compounds were prepared which ionized to give monocations:



$$X - \overset{Y}{\underset{\phi}{C}} - R$$

Table 1. Spectral Data for the Bis-Aryl Carbinols in Sulfuric Acid

Compound	λ_{max}[a] (mμ)	ϵ_{max}[a]	pK_R 1	pK_R 2
α, α, α', α'-Tetraphenyl-p-xylene-α, α'-diol	455	59,000	-8.1	-10.5
α, α, α', α'-Tetraphenyl-m-xylene-α, α'-diol	440 419	70,000 73,000	-8.0	-10.1
α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol	455 373	44,000 30,500	∼-8.0[b]	-16.6
α, α'- Diphenyl-p-xylene--α, α'-diol	461	48,000	c	
α, α'-Diphenyl-m-xylene-α, α'-diol	447	35,000	c	
α, α, α', α'-Tetraphenyl p, p'-bitolyl-α, α'-diol	530 442 410_s	90,000 53,000 34,500	-8.2	d
α, α, α', α'-Tetraphenyl-m, m'-bitolyl-α, α-diol	430	67,500	-8.4	d
α, α, α', α'-Tetraphenyl-o, o'-bitolyl-α, α'-diol	428 390_s	35,500 24,000	∼ -8.3[e]	∼ -15.0
α, α'-Diphenyl-p, p'-bitolyl-α, α'-diol	563 420	134,000 13,000	c	
α, α'-Dichloro-α, α'-diphenyl-2, 7-dimethylfluorene	603 554	215,000 62,000	∼-12.0	-16.6
α, α, α', α'-Tetraphenyl-2, 7-dimethylfluorene-α, α'-diol	568 525 440	152,000 46,000 35,000	c	

[a] The λ_{max} and ϵ_{max} data were obtained in 98% sulfuric acid.

[b] The first pK_R was assumed to be the same as for the corresponding meta and para diols. The close proximity of the second -OH after mono-ionization permits cyclic protonated ether formation. This species, which was not detectable by visible spectrophotometry, required solutions of high acidity for further ionization.

[c] Not determined.

[d] In these diols, ionization occurred simultaneously at both sites.

[e] This compound ionizes similarly to the diol discussed in b. The first ionization was assumed to be the same as the corresponding meta and para derivatives.

Table 2. Spectral Data for the Aryl Carbinols in Sulfuric Acid

Compound	λ_{max}[a] (mμ)	ϵ_{max}[a]	pK_R
Triphenylmethanol	432 408	37,500 36,500	-7.4
Diphenylmethanol	442	47,000	-14.7
4-Biphenylyldiphenylmethanol[b]	510 420	43,000 21,500	-7.7
4-Biphenylylphenylmethanol	535	90,000	c
α-Phenyl-α-hydroxy-2-methylfluorene	547	66,000	$\sim$-12.0
α, α-Diphenyl-α-hydroxy-2-methylfluorene[b]	540 404	53,000 17,000	-6.5

[a] The λ_{max} and ϵ_{max} data were obtained in 98% sulfuric acid, except where noted.

[b] These spectra were taken in 80% sulfuric acid because sulfonation was shown to occur in concentrated acid.

[c] Not determined.

The spectral data for these compounds are given in Table 2. Comparison of the spectra of the mono- and dications has shown that the resonance interactions of the latter can be pictured as being composites of monocations.

In addition to spectral studies, the hydrolysis products of the dication solutions in concentrated sulfuric acid were also investigated. In all cases studied the starting diols (or cyclic ethers in the case of ortho substituted diols) were isolated in nearly quantitative yields. The hydrolysis of two carbinols (4-biphenylyldiphenylmethanol and α, α-diphenyl-α-hydroxy-2-methylfluorene) in 98% sulfuric acid showed that sulfonation occurred after carbonium ion formation. The alcoholysis of solutions of α, α, α', α'-tetraphenyl-o-xylene-α, α'-diol in concentrated sulfuric acid gave the corresponding ether of 9, 10, 10-triphenyl-9, 10-dihydro-9-anthrol.

The study of trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene in sulfuric acid was continued (1). It was demonstrated that in dilute sulfuric acid ionization of this diol gave the monocation which rearranged to the cis-diol. By increasing the acid strength the cis-diol rearranged to 9, 10-diphenylanthracene, which in more concentrated sulfuric acid gave 4-phenyl-2, 3-benzofluoranthene. At no time, however, was the presence of a dication noted.

REFERENCES

1. R. R. Rafos, Ph. D. Thesis, Michigan State University, 1961.

DICARBONIUM IONS FROM BIS-ARYL CARBINOLS

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TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

TABLE OF CONTENTS - Continued

LIST OF TABLES

LIST OF TABLES - Continued

LIST OF FIGURES

LIST OF FIGURES - Continued

FIGURE Page

LIST OF FIGURES - Continued

LIST OF FIGURES - Continued

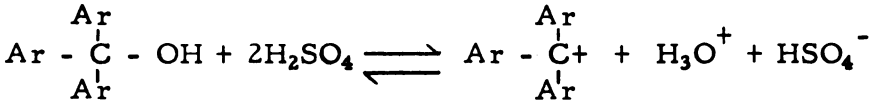
LIST OF FIGURES - Continued

INTRODUCTION

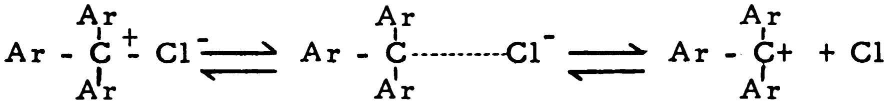
INTRODUCTION

Carbonium ions have long been recognized as one of the most important species in organic chemistry. Their existence both as transient intermediates and as stable species has been well documented (1, 2). The most thoroughly studied of the latter are the diaryl-and triarylmethyl cations. They can be formed in several ways:

1. Reversible Ionization

a.  (1)

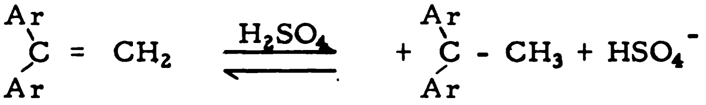
$$Ar - \underset{Ar}{\overset{Ar}{C}} - OH + 2H_2SO_4 \rightleftharpoons Ar - \underset{Ar}{\overset{Ar}{C}}+ \; + H_3O^+ + HSO_4^- \qquad (1)$$

b.  (2)

$$Ar - \underset{Ar}{\overset{Ar}{C}} \overset{+}{-} Cl^- \rightleftharpoons Ar - \underset{Ar}{\overset{Ar}{C}} \cdots\cdots Cl^- \rightleftharpoons Ar - \underset{Ar}{\overset{Ar}{C}}+ \; + Cl^- \qquad (2)$$

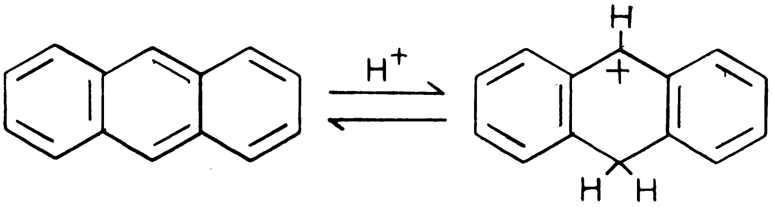
2. Protonation of Unsaturated Center

a. Olefins

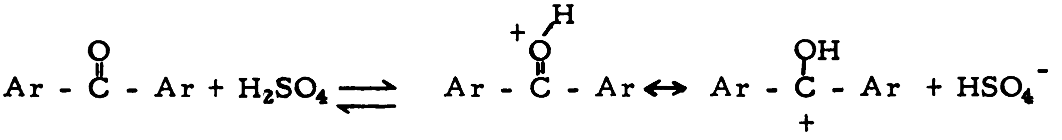
 (3)

$$\underset{Ar}{\overset{Ar}{C}} = CH_2 \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} + \underset{Ar}{\overset{Ar}{C}} - CH_3 + HSO_4^- \qquad (3)$$

b. Aromatic Hydrocarbons

 (4)

3. Protonation of Carbonyl Compounds

 (5)

$$Ar - \overset{O}{\overset{\|}{C}} - Ar + H_2SO_4 \rightleftharpoons Ar - \overset{\overset{+\;H}{O}}{\overset{\|}{C}} - Ar \leftrightarrow Ar - \underset{+}{\overset{OH}{C}} - Ar + HSO_4^- \qquad (5)$$

It is with carbonium ions formed by the reversible ionization of alcohols and halides that this thesis deals. In fact, the major part of this thesis concerns molecules which produce doubly charged ions by single ionizations at two separate sites, i.e., "ordinary" dipositive ions (3). Before discussing dipositive ions, it seems appropriate by use of selected examples to give a brief account of monopositive arylmethyl cations.

I. Monopositive Cations

The study of arylmethyl cations began at the turn of the twentieth century when interest in triphenylmethane dyes was high. The physical evidence for the existence of these stable species under equilibrium conditions came from several sources:

1. Conductivity Measurements

In 1902, Walden (4) and Gomberg (5) established that various triarylmethyl halides ionize in liquid sulfur dioxide in a manner similar to methylammonium chloride or potassium iodide (see equation 2). By using electrical conductivity, later workers showed that the relative effectiveness of various groups in promoting the ionization of triarylchloromethane is p-methoxy > p-methyl > p-phenyl > hydrogen > p-nitro (6). Recently Lichtin and Glazer (7) studied by conductance in liquid sulfur dioxide, the ionization of triphenylchloromethanes with phenyl, t-butyl and methyl groups in the meta and para positions. Their findings showed that ionization was enhanced by para substitution.

A number of possible sources of diarylmethyl cations have been studied in sulfur dioxide and benzhydryl chloride, m-chlorobenzhydryl chloride and p,p'-dimethylbenzhydryl chloride have been found not to conduct (8) but dimesitylmethyl chloride does (9).

2. Cryoscopy

The extent of ionization of a solute in a particular solvent (one capable of producing ions with the solute in a reversible way) can be found because the freezing point depression of the solvent is proportional to the number of particles produced. Perhaps the most useful solvent for such determinations is sulfuric acid, because most compounds behave as bases in it and it has a convenient melting point (10.371°) and a sizable molal freezing-point depression constant (6.12° $\text{mole}^{-1}\ \text{kg.}^{-1}$). A review on the behavior of organic compounds in sulfuric acid has recently been published (10).

Alcohols ionize in sulfuric acid in one of the following ways:

(i = van't Hoff factor = number of particles formed per molecule of solute)

$$ROH + H_2SO_4 \rightleftharpoons ROH_2^+ + HSO_4^- \quad (i = 2) \qquad (6)$$

$$ROH + 2H_2SO_4 \rightleftharpoons RHSO_4 + H_3O^+ + HSO_4^- \quad (i = 3) \qquad (7)$$

$$ROH + 2H_2SO_4 \rightleftharpoons R^+ + H_3O^+ + HSO_4^- \quad (i = 4) \qquad (8)$$

Since we are interested in the formation of arylmethyl cations, it is equation 8 that is important (see equation 1). This ionization may occur in a stepwise fashion:

$$ROH + H_2SO_4 \rightleftharpoons ROH_2^+ + HSO_4^- \qquad (9)$$

$$ROH_2^+ \rightleftharpoons R^+ + H_2O \qquad (10)$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \qquad (11)$$

$$ROH + 2H_2SO_4 \rightleftharpoons R^+ + H_3O^+ + 2HSO_4^- \qquad (12)$$

The first reported cryoscopic work on triarylmethanols was by Hantzsch in 1908 (11). He obtained values slightly greater than three.

Recently, Newman and Deno(12) studied the following methanols in 100% sulfuric acid and their results strongly indicate the formation of stable carbonium ions: tri-p-tolyl, tri-o-tolyl-, tri-p-aminophenyl-, tri-p-dimethylaminophenyl, di(p-dimethylaminophenyl) phenyl-, tri-p-chlorophenyl-, di-p-chlorophenylmethyl-.

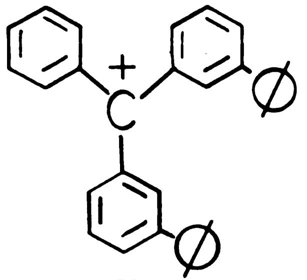
3. Absorption Spectra

In 1902, Walden (4) noted that the yellow solution formed by dissolving triphenylmethanol in concentrated sulfuric acid had an absorption spectrum identical with that of a solution of triphenylmethyl chloride in liquid sulfur dioxide. It is reasonable that if a certain spectrum always appears in conducting but not in non-conducting solutions of a compound, and if the absorption intensity parallels the electrical conductivity, then the spectrum can be assigned to one of the ions present. Walden who had observed both of these phenomena, assigned the absorption in the visible region to the triphenylmethyl cation, since it was common to both systems.

Recently, Newman, Deno and co-workers (12, 13, 14) studied the visible spectra of various diaryl- and triarylmethanols in concentrated sulfuric acid. In all cases the diarylmethyl cations absorbed at 16-25 mμ higher wavelength than the corresponding triarylmethyl cations. Newman and Deno explained this in either of two ways. First, there is steric inhibition to resonance so that the third ring contributes little to the electronic structure of the carbonium ion and resonance interactions are restricted to only one or two rings. Secondly, each of the three rings in the arylmethyl cations makes an equal contribution to the resonance but this contribution is lessened because of an increase in the angle of ring twist. This twist is greater with triarylmethyl cations than with diarylmethyl cations.

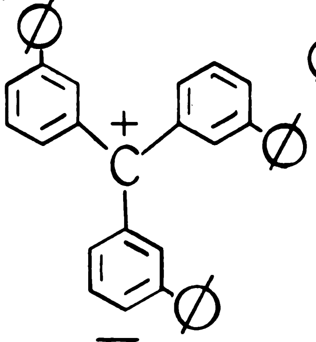
More recently, Deno and co-workers (15) have done LCAO-MO calculations (neglecting electron repulsion and overlap integrals) which predict that mono-, di-, and triphenylmethyl cations should possess nearly identical wavelength maxima in the 400-440 mμ region.

Grinter and Mason (16, 17) studied the steric and symmetry effects in the spectra of arylmethyl cations. Within the limitations imposed by neglecting ion-pairing, solvent effects, steric hindrance to conjugation in the arylmethyl ions, and the contribution of electron repulsion changes to the transition energy, it is to be expected that corresponding di- and triarylmethyl ions, independent of the position of substitution of the methyl group in the aromatic nucleus, and of whether the ion is positively or negatively charged, should absorb at a wavelength approximately twice that of the aromatic hydrocarbon from which the ion is derived. This can be stated since by use of the Hückel approximation, Grinter and Mason showed that the highest bonding and lowest antibonding levels have the same energy as the respective levels in the aromatic hydrocarbon from which the ion is derived. An example can be seen in the absorption bands of some biphenyl substituted carbonium ions (wavelengths in mμ):



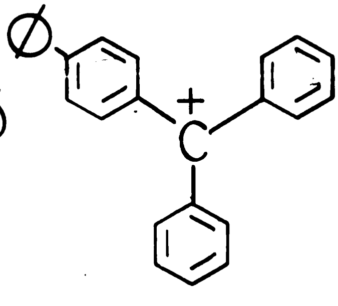
I

490



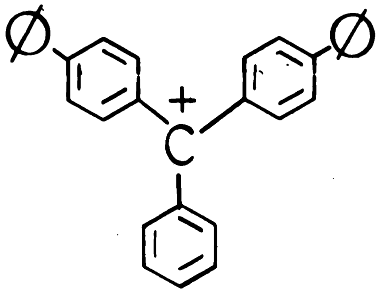
II

500



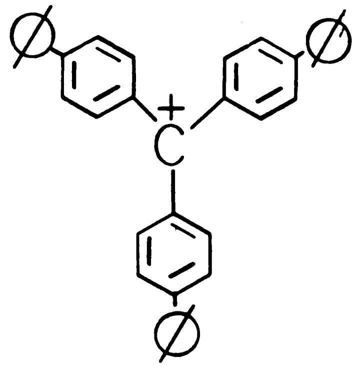
III

474



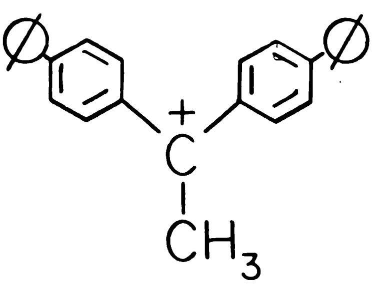
IV

500



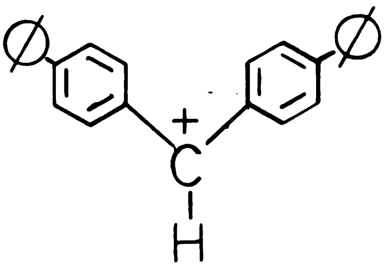
V

510



VI

512



VII

555

Since the position of the longest wavelength band of biphenyl lies at 250 mμ, it is expected that the maxima for the above cations should occur at 500 ± 10 mμ. Grinter and Mason state that compound III, as they expected, showed an absorption maximum at a wavelength lower than 500 ± 10 mμ. For a possible clarification of this point see page 45. The higher wavelength absorption of (VII) than (V) was explained by the better ground state stabilization of (VII). More will be said about the biphenylmethyl cation in the discussion of the results of this work.

4. Isolation of Stable Salts

In 1909, Hofmann and Reimsreuther (18) isolated triphenylmethyl perchlorate as a yellow solid by treating triphenylmethyl chloride with 71% perchloric acid in either nitrobenzene or acetic anhydride followed by evaporation of the solvent in a desiccator. Gomberg also succeeded in isolating the perchlorate (19, 20).

Treatment of triphenylmethyl chloride with acetyl tetrafluoroborate in acetic anhydride afforded triphenylmethyl tetrafluoroborate (21). The same salt was prepared by the addition of boron trifluoride to triphenylmethyl fluoride (22).

In 1957, as part of a study of complex fluorides, Sharp and Sheppard (23) allowed the appropriate silver salt to react in ether with triphenylmethyl chloride to form the following triphenylmethyl cation salts: hexafluorophosphate, hexafluoroarsenate, hexafluoroantimonate, hexafluoroniobate, hexafluorotantalate, fluorosulphonate and tetrafluoroborate. By condensing an excess of stannic chloride or antimony pentachloride into a benzene solution of triphenylmethyl chloride, the pentachlorostannate and hexachloroantimonate salts of triphenylmethyl cation were prepared. Since much discussion has appeared in the literature concerning the conformation of triphenylmethyl cation, these workers used infrared spectroscopy as a means of determining it.

The structures considered were the D_{3h} (all-planar), D_3 (propeller-like) and unsymmetrical conformations. By examining the infrared region between 1700 and 650 cm^{-1} of several crystalline salts of triphenylmethyl cation, toluene, triphenylmethane, and triphenylboron, Sharp and Sheppard concluded that D_3 symmetry best described the configuration of the triphenylmethyl cation. In the spectrum of toluene there is a strong band at 728 cm^{-1} which corresponds to the vibration in which all five aromatic C-H bonds bend out of the plane of the ring in unison. This band is quite sensitive to structural changes. In triphenylmethyl cation this band is split into components at 810 and 770 cm^{-1} (774 and 747 cm^{-1} for triphenylboron). This large splitting of 40 cm^{-1} is presumably caused by interaction of the aromatic rings with the cation. Karagounis (24) has considered the analogous problem with triphenylmethyl radical and has shown that D_{3h} structure would have only one such infrared band, the unsymmetrical configuration three such bands and the D_3 two bands. This and several other features of his observed infrared spectra can only be accounted for by propeller-like symmetry.

In 1958 Meerwein and co-workers (25) studied the preparation, complexing ability and use of silver and copper (I) tetrafluoroborates. They described the preparation of tri-anisylmethyl tetrafluoroborate by the treatment of trianisylmethane in ethylene dichloride with ethyl bromide and silver tetrafluoroborate. The red salt was obtained in 30% yield.

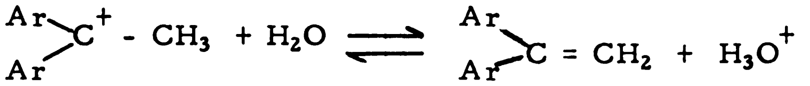
Dauben and co-workers have recently reported simple and convenient methods for obtaining the perchlorate and tetrafluoroborate of triphenylmethyl cation (26). Treatment of triphenylmethanol with acetic anhydride and 71% perchloric acid at room temperature gave the perchlorate in 85% yield. The corresponding tetrafluoroborate was produced almost quantitatively by allowing triphenylmethanol to react with fluoboric acid in propionic anhydride at 20°. The former salt was shown to be less stable since it turned dark and decomposed to 9-phenylfluorene

(6%) during two weeks in the dark while the tetrafluoroborate was completely stable.

In 1961 Harmon prepared and characterized the first carbonium tetrabromoborate (27). The reaction of equimolar amounts of triphenylmethyl bromide and boron tribromide in cyclohexane resulted in a nearly quantitative yield of triphenylmethyl tetrabromoborate. Unlike other triphenylmethyl cation salts, the tetriodoborate (28) was described as being so viciously hygroscopic and extremely light sensitive that a satisfactory analysis could not be obtained. The evidence for its existence was based on B^{11} n.m.r. spectra and on a rapid hydride exchange reaction with cycloheptatriene. The latter experiment gave a 57% yield of tropenium tetraiodoborate and a 95% yield of triphenylmethane.

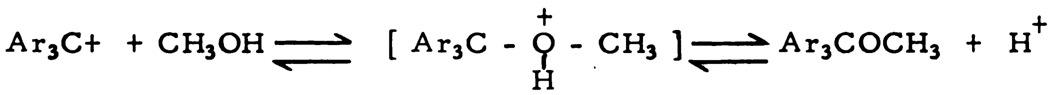
5. Quenching Experiments

Another important piece of evidence for the reversible formation of triarylmethyl cations in sulfuric acid is the quenching of such solutions with water and methanol. Newman and Deno (12) have shown that various triarylmethanols are recovered unchanged when their sulfuric acid solutions are poured onto ice. When a solution of a diarylcarbinol in concentrated sulfuric acid is poured onto ice, the corresponding bis-diarylmethyl ether is formed (29). When a solution of a diarylalkylmethanol in sulfuric acid is hydrolyzed, the corresponding olefin is obtained (30):



$$Ar_2C^+ - CH_3 + H_2O \rightleftharpoons Ar_2C = CH_2 + H_3O^+ \qquad (13)$$

The methyl ether corresponding to the diaryl- or triarylcarbonium ion can be formed by pouring the sulfuric acid solution into cold methanol:



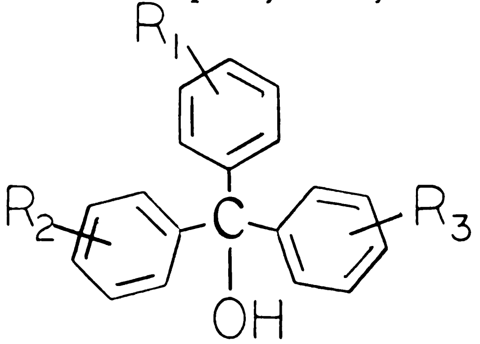
$$Ar_3C+ + CH_3OH \rightleftharpoons [\, Ar_3C - \underset{H}{\overset{+}{O}} - CH_3 \,] \rightleftharpoons Ar_3COCH_3 + H^+ \qquad (14)$$

6. Nuclear Magnetic Resonance (31)

Nuclear magnetic resonance has become a useful tool in determining the fine structure of molecules. One can ascertain the relative amount of positive charge on an atom in a given compound by studying the hydrogen bonded directly to that atom. By comparing the chemical shift of such hydrogens with various references, the degree of positive charge is discernable.

The first detailed study of the n.m.r. spectra of triarylmethyl cations was carried out by Stewart and his group (32). By dissolving arylmethanols in a mixture of trifluoroacetic acid-trifluoroacetic anhydride, the appropriate carbonium ions were obtained (as determined by visible spectrophotometry). The carbinols studied are shown in Table 1:

Table 1. N.M.R. Data of Triphenylmethyl Cations[a, b]

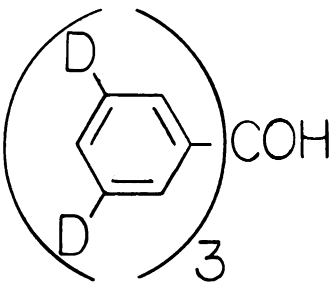


R_1	R_2	R_3	Aromatic Shift	Substituent Shift
H	H	H	-101.0	
p-Me	H	H	-98.0	+102.5
p-Me	p-Me	H	-94.75	+104.5
p-Me	p-Me	p-Me	-93.5	+105.5
p-OMe	H	H	-96.0	+42.0
p-OMe	p-OMe	p-OMe	-87.5	+47.0
m-Me	H	H	-95.5	+112.5
m-Me	m-Me	m-Me	-89.0	+112.5
Anisole			-68.0	+59.5
Toluene			-69.0	+124.0

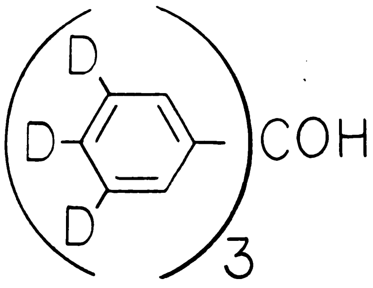
(a) All spectra run in trifluoroacetic acid-trifluoroacetic anhydride as solvent.
(b) Measured against water as external standard at 40 mc.

As can be seen in Table 1, successive substitution of methyl or methoxyl groups at the para positions increases the shielding on the methyl groups. Since the methyls appear as singlets in each compound, it is likely that the three rings are in the symmetrical propeller conformation. The meta methyls, as expected, carried a much smaller amount of positive charge. A study of the aromatic multiplet led Stewart to conclude that the para hydrogen is at lowest field with the meta next and the ortho at highest field.

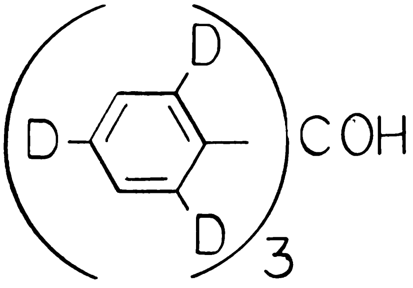
Vaughn and his co-workers (33) have also studied the question of charge distribution in triarylmethyl cations. They synthesized the following deuterated carbinols:



VIII



IX



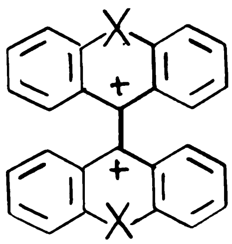
X

The n.m.r. spectra, which were run in liquid sulfur dioxide containing stannic chloride, showed conclusively that the greatest amount of positive charge is located at the para positions, since the para protons appeared at lowest field. The smallest share of the positive charge is at the ortho positions with the meta positions having slightly more. These findings are in excellent agreement with the prediction of self-consistent molecular orbital theory, as done by Pople (34), which gives the following negative charge densities: ortho, 0.95; meta 0.94; and para, 0.81.

These are the methods that have been used to study the stable arylmethyl cations containing but a single positive charge. They demonstrate with a high degree of certainty the structure of these species. These types of systematic studies, however, have not been extended to molecules containing more than one positive charge.

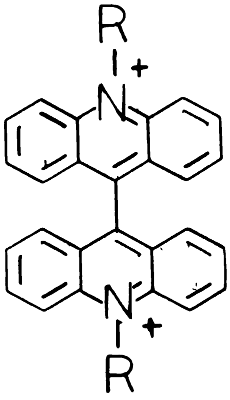
II. Dipositive Cations

A search of the literature has revealed that there is a limited amount of material on molecules that are polycarbonium ions. Representative examples of each group are:

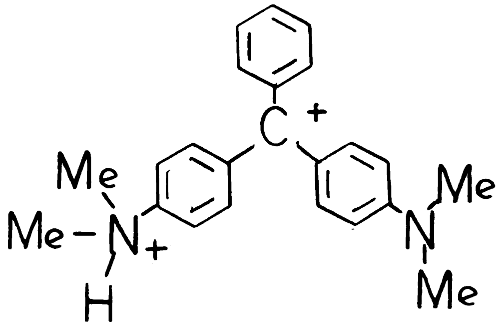


XI

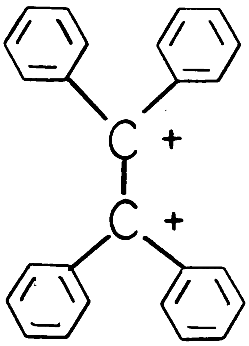
X=O or S



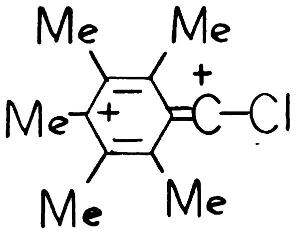
XII



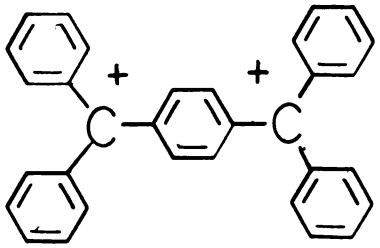
XIII



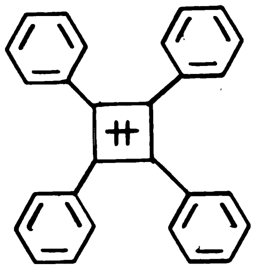
XIV



XV



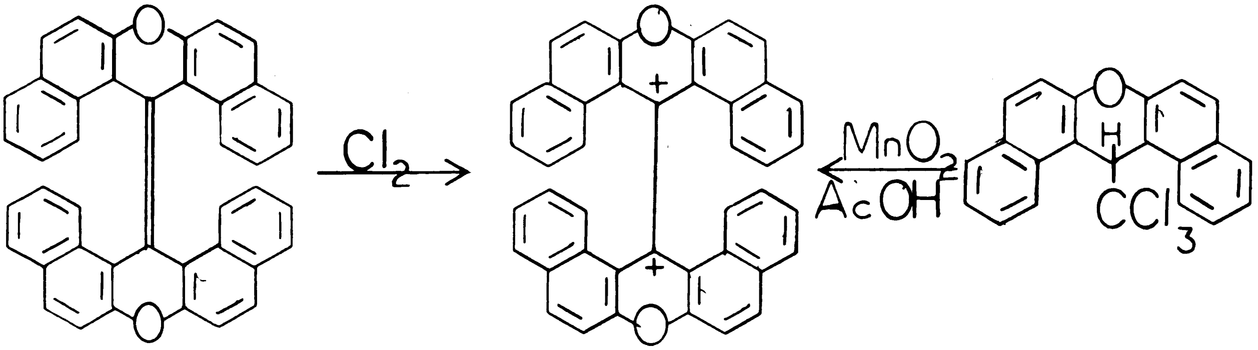
XVI



XVII

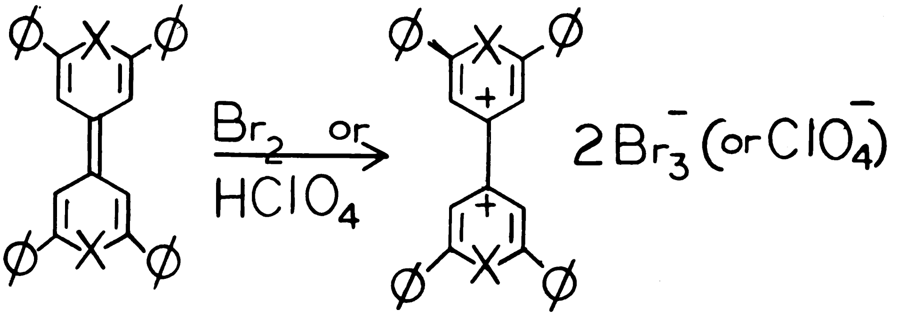
1. Dixanthylium Salts and Related Compounds

In 1901, Werner (35) reported that the reaction of xanthone with zinc and hydrobromic acid gave XI (X = 0) with the anion being the tribromide ion. A year later, Werner (36) showed that the following reactions each gave the same tetrabenzodixanthylium salt:



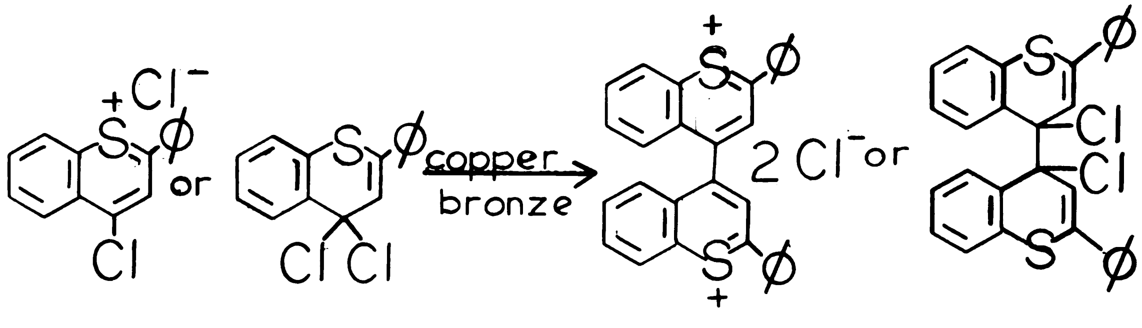
(15)

Similar types of dications were reported by Arndt and co-workers (37, 38):



(16)

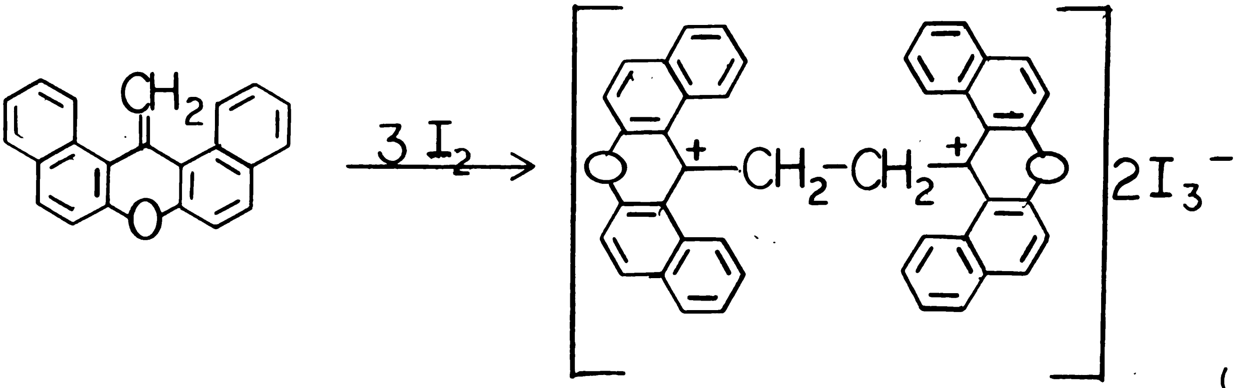
Schönberg (39) has done more extensive work on the preparation of the salts and has isolated the explosive dixanthylium diperchlorate (XI, X = 0) by treatment of xanthone with zinc, acetic acid and sodium perchlorate. He also reports the following reaction (40):



(17)

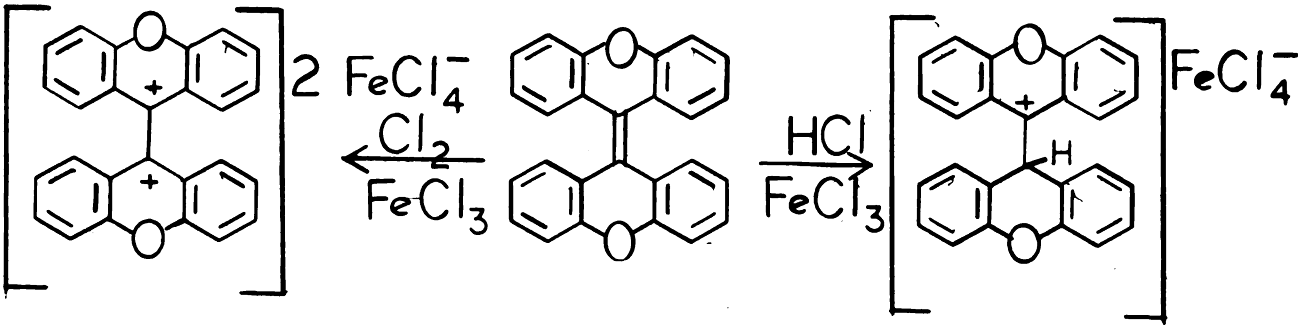
Sulfur and chlorine analyses that were each more than 1% low, were his only evidence for this product.

Wizinger and Al-Attar (41) reported the following dipositive carbonium ion in the xanthylium series:



(18)

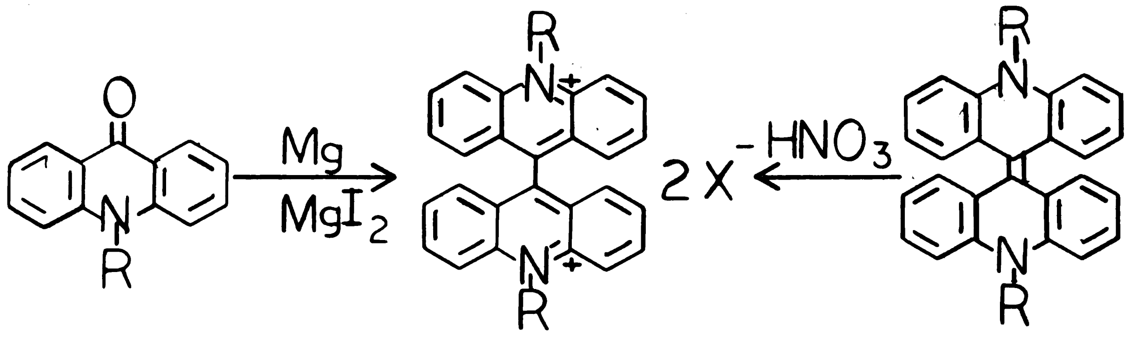
These workers found that by varying the conditions, either a mono- or dication could be formed from dixanthylene:



(19)

2. Bisacridinium Salts

By analogy, it would appear that by replacing the oxygen in the dixanthylium salts with nitrogen, a new type of dipositive carbonium ion should be formed (XII). These salts are known and two methods for their preparations are (42):



XVIII

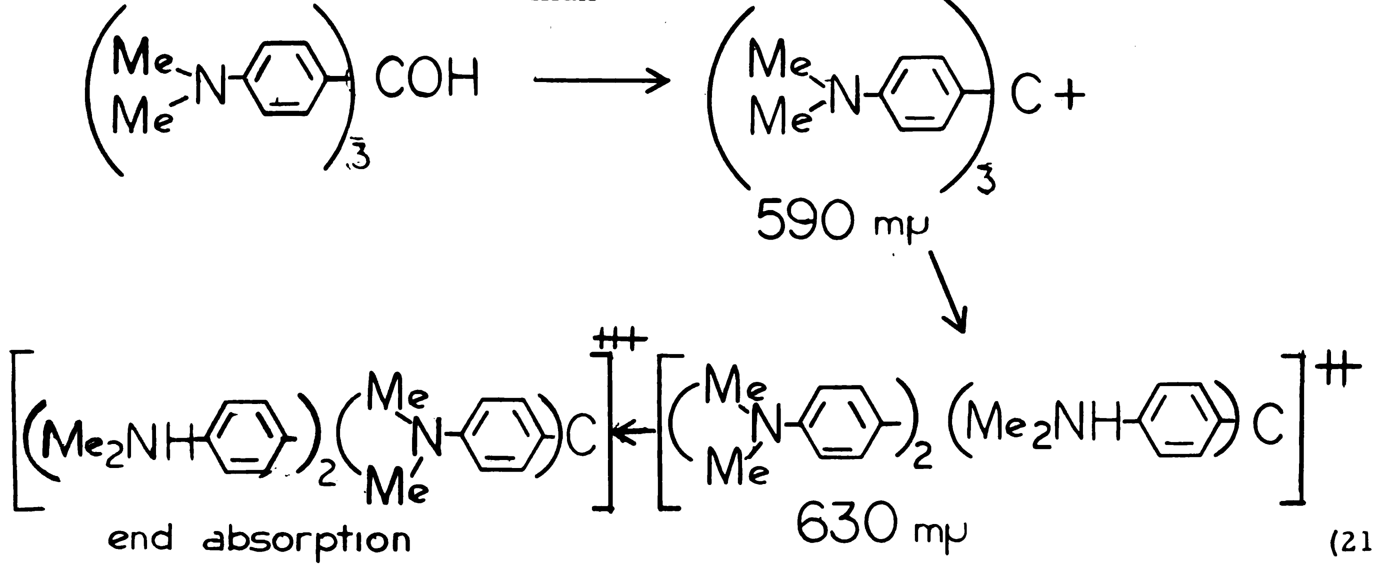
(20)

When a 0.05% solution of XVIII ($X = NO_3$) in aqueous alkali is treated with hydrogen peroxide, a light stronger than daylight results. The resulting species is the most powerful chemiluminescent substance known. For this reason, most studies of bisacridinium salts have been along these lines and crystalline materials have usually not been prepared.

3. Triphenylmethane Dyes

Of all the dications discussed, only in this category is there a cation formed by having a positive charge originating at a site other than a carbon atom.

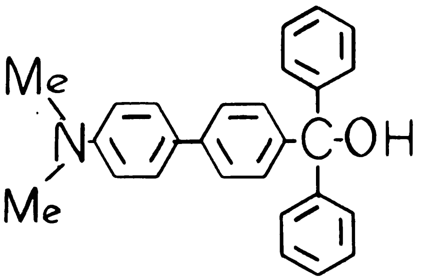
In 1939, Lewis and Calvin (43) showed that Crystal Violet could be ionized stepwise (λ_{max} in mμ):



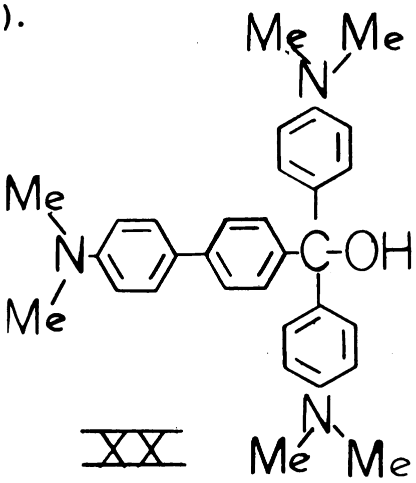
(21)

The absorption of the dication is very similar to that of XIII (Malachite Green) which has a λ_{max} at 623 mμ.

Similar effects were noted by Morton and Wood with XIX (44) and by Theilacker and Schmid with XX (45).

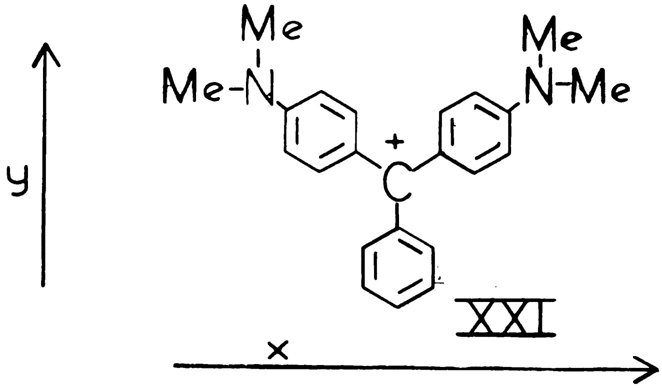


XIX



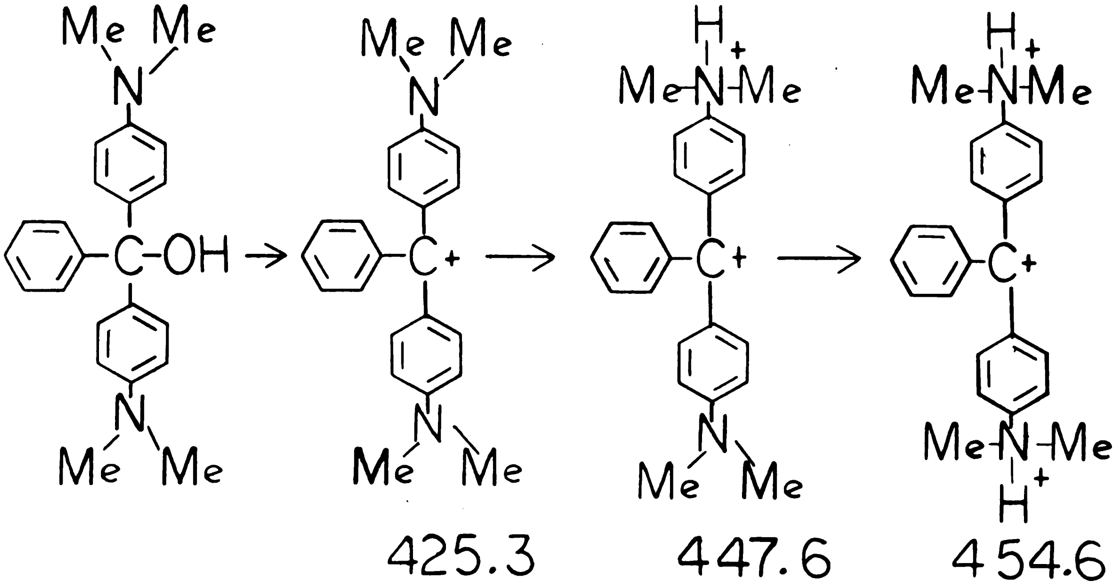
XX

In an attempt to explain the visible spectra of dyes, Lewis and his co-workers (46, 47, 48) formulated rules for predicting the position of the main absorption. They stated that an excited state produced by the absorption of light is characterized by an oscillation of the electronic cloud along the axes of the molecules. The main current is attributed to the x band in the horizontal direction with the second band in the y (vertical) direction



XXI

Since the x band has better resonance stabilization, it is of lower energy (higher wavelength) than the y band. Recently, it has been found by Anthony-Barbier and Rumpf (49) that the y band of Malachite Green (XXI) is actually three separate and distinct bands. The ionization of XXI occurs in a stepwise manner (λ_{max} in mμ):

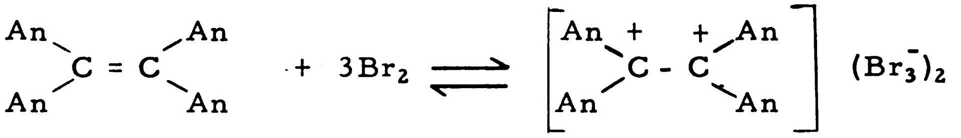


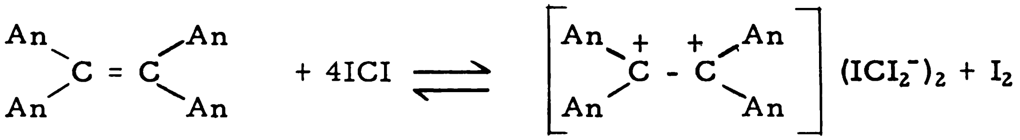
(22)

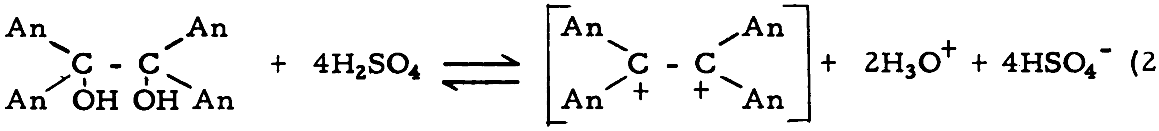
A review by Barker on steric effects in triphenylmethane dyes appeared recently (50).

4. Tetraarylethylene Compounds

It has been known for some time that the interaction of halogens with arylethylenes gives highly colored solutions (51). Buckles and Meinhart (52) studied the electrical conductivities of methylene chloride solutions containing bromine and various substituted tetraphenylethylenes. The tetraphenylethylenes with methoxyl and dimethylamino groups in at least two of the para positions gave highly colored solutions and had molar conductances of the same order of magnitude as tetrabutylammonium iodide. No attempt was made to interpret the data in terms of the composition of the complex or complexes. Buckles and Womer (53) reinvestigated the fact that when bromine in ethylene chloride was mixed with tetra bis-(p-methoxyphenyl)-ethylene a blue solution resulted immediately. This solution had an absorption peak at 575 mμ which was not characteristic of the starting materials. On standing a new absorbing species resulted (490 mμ). This latter species was shown to be the trianisylmethyl cation (53). More recently, the former species has been shown to be the tetraanisylethylene dication (54). It is postulated that this cation was produced in the following ways:


(23)


(24)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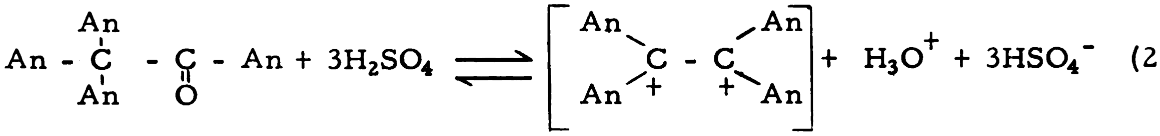
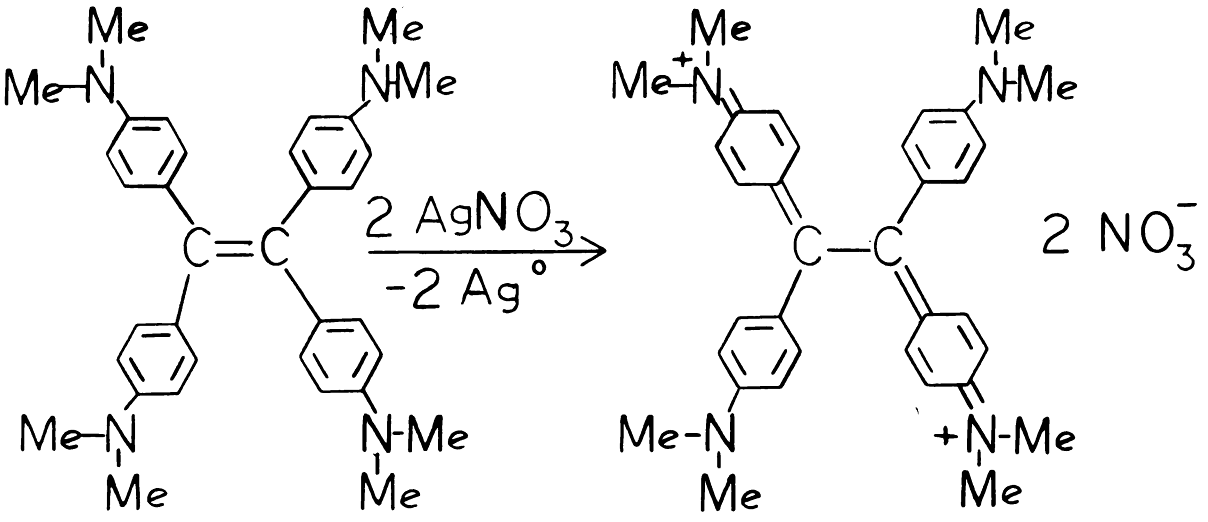

(26)

(where An = anisyl)

The dication was isolated as dark, blue-green trihalide salts and analyzed in the examples shown in equations (23) and (24). Attempts to study the formation of the tetraanisylethylene dication cryoscopically were not successful due to sulfonation of the anisyl rings (55).

In 1961, Anderson and co-workers (56) reported on the reaction of tetrakis-(p-dimethylaminophenyl)-ethylene with silver nitrate to form green crystals of the dinitrate. This in turn reacted with potassium iodide to give the green tetrakis-(p-dimethylaminophenyl)-ethylene diiodide-monohydrate. This lost water at 75° to give the black anhydrous diiodide.

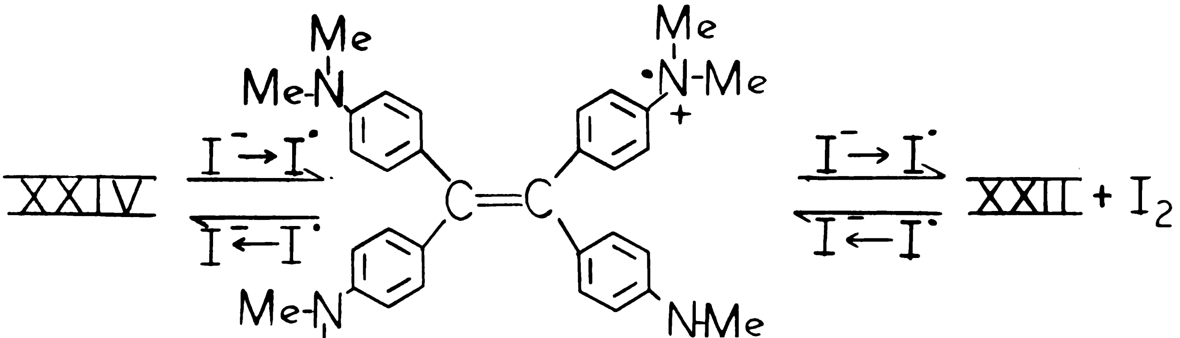


(27)

XXII XXIII

$$\underline{\text{XXIII}} \xrightarrow[2.\ 75^\circ]{1.\ \text{KI}} \text{diiodide } \underline{\text{XXIV}} \qquad (28)$$

(XXIII) and (XXIV) in water are purple and have identical visible and ultraviolet spectra. The same is true of the dinitrate in ethylene chloride. In ethylene chloride, however, the diiodide is green and is the only solution to show an e.p.r. spectrum (20% radical character). The following reaction shows the apparent fate of the dication:

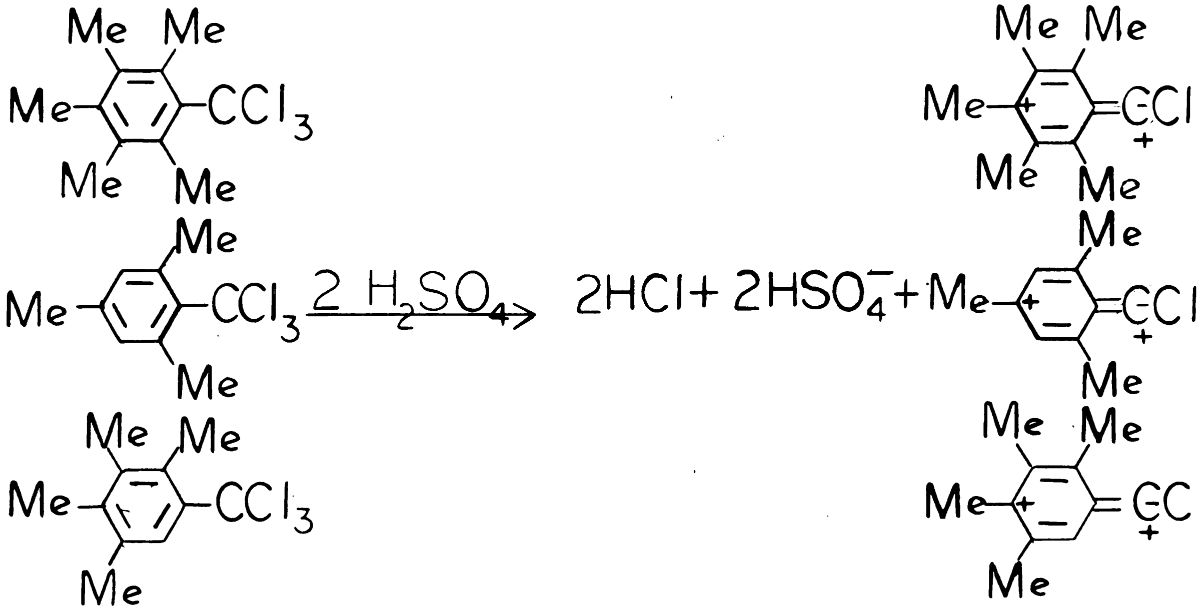


(29)

The reason that the diiodide undergoes the above reaction was attributed to the non-polar solvent (shift toward less charged species), the very good donor properties of the iodide ion as well as the good acceptor qualities of the quinoidal dication.

5. Trichloromethylbenzenes

Recently, Hart and Fish (57) observed that the following trichloromethylbenzenes ionize in 100% sulfuric acid to give red solutions with van't Hoff i-factors of five:



(30)

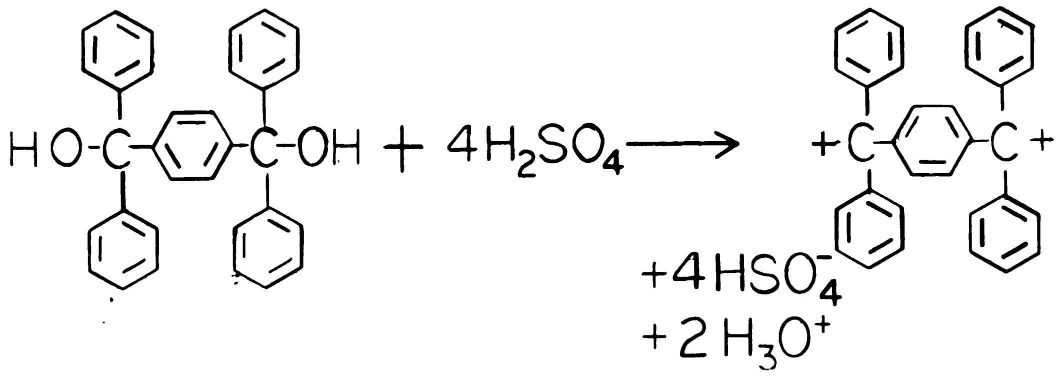
(31)

(32)

The evidence for these "extraordinary" dipositive carbonium ions (58a), which in a formal sense lost two anions from a single carbon atom, was based on cryoscopy, stoichiometry, electrical conductance, visible, ultraviolet and nuclear magnetic resonance spectroscopy. Confirmatory evidence for the existence of these "extraordinary" cations is the preparation of their crystalline bis-tetrachloroborate and tetrafluoroborate salts (59).

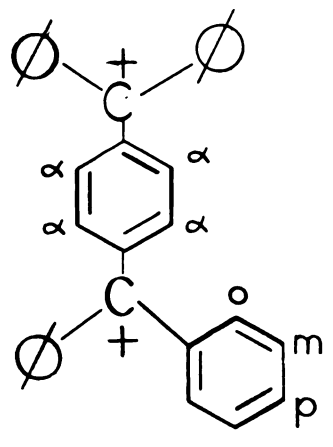
6. α, α, α', α'-Tetraphenyl-p-xylene Dication

The fact that α, α, α', α'-tetraphenyl-p-xylene-α, α'-diol gave a red color when dissolved in concentrated sulfuric acid has been known for a long time (60). It was only recently that a study of this reaction was undertaken by Rafos (61). With the use of several of the methods discussed earlier, he showed that the diol ionizes in the following way:

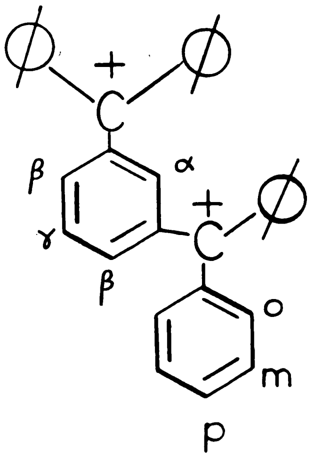


(33)

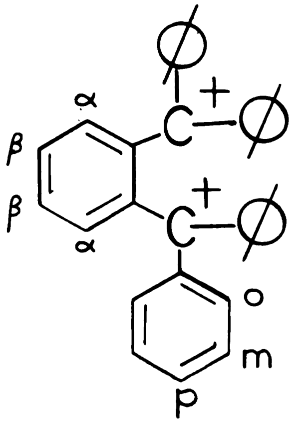
Hart and Wu (62) have studied the n.m.r. spectra of the following dications in order to determine the relative amounts of positive charge on the different carbon atoms.



XXV



XXVI



XXVII

The dications were generated by dissolving the corresponding diols in 100% deuterosulfuric acid and the spectra compared to methanesulfonic acid as an internal reference. The diols studied had deuterium placed in the appropriate positions so that the chemical shift of the different hydrogens could be determined. Their results indicate that:

1. The positive charge located in the outer rings of all three compounds are in the same ratio as in triphenylmethyl cation, i.e., $p > m > o$.

2. The percentages of total positive charge in the outer rings of XXVI and XXVII are about the same but in XXV the outer rings carry a larger share of the positive charge densities.

3. The following are the relative positive densities for the dications:

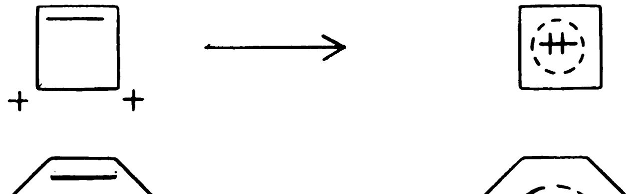
XXV - $p > m > \alpha \geq o$
XXVI - $\beta \geq \gamma \approx p > \alpha > m > o$
XXVII - $\beta > p > \alpha > m > o$

It should be noted that the β positions in XXVI and XXVII, which carry a large amount of charge, are located para to the position where the charge originates and would be expected to have a high positive charge density.

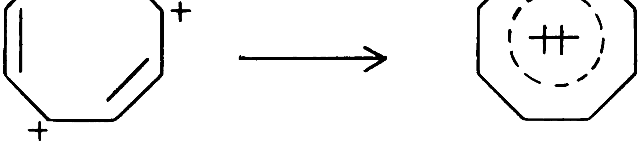
Sloan (63) measured the spectra of some homologues of XVI in concentrated sulfuric acid, but since the main purpose of his work was the study of aryl stabilized diradicals, no discussion of the various dications was included.

7. Tetraphenylcyclobutenyl Dication

In 1960, it was postulated that the formation of an aromatic system might be a sufficient driving force to allow dication formation (58b). The two examples proposed were the four- and the eight-membered "Hückel-aromatic" systems:

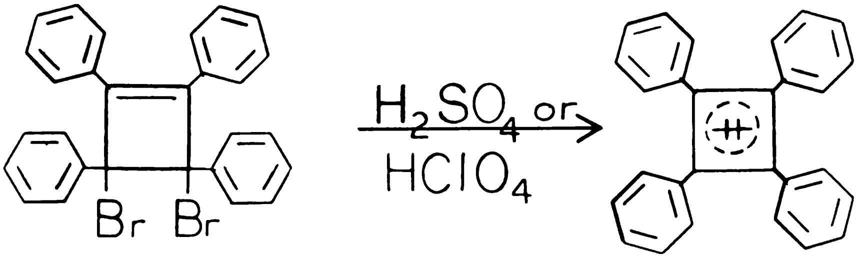


(34)



(35)

In fulfillment of this postulate, Freedman and Frantz (64) succeeded in preparing the tetraphenyl cyclobutenyl dication. Treatment of 3,4-dibromotetraphenylcyclobutene with either concentrated sulfuric or perchloric acid led to a deep red solution with simultaneous evolution of hydrogen bromide.



(36)

Hydrolysis of the red solution gave tetraphenylfuran. Other evidence for the dication included the formation of solid salts and the visible and n.m.r. spectra.

Work on the formation of an eight-membered "Hückel-aromatic" system is currently in progress (65).

III. Acidity Function Theory

Two extensive reviews on this subject have appeared recently, one by Paul and Long (66) and the other by Bushick (67). Since part of the present work involves the measurement of ionization constants of various carbinols and glycols by use of the H_R acidity function it is important to describe briefly the development of this function.

In the classical treatment of dilute aqueous solutions, the hydrogen or oxonium ion concentration expresses the acidity of the solution. In concentrated acids, however, the acid strength is not proportional to the oxonium ion concentration. Hammett and Deyrup (68) developed a method for expressing these acidities. This acidity function, H_0, is derived from the ionization equilibria of indicator bases such as the substituted anilines which behave as Brönsted-Lowry uncharged bases:

$$B + H^+ \rightleftharpoons BH^+ \tag{37}$$

The function H_0, is defined in the following equation.

$$H_0 = pK_{BH^+} - \log \frac{C_{BH^+}}{C_B} \tag{38}$$

where C_{BH^+}/C_B is the observed ratio of the indicator in its protonated and unprotonated forms and K_{BH^+} is the ionization constant of the indicator referred to dilute aqueous solution. Since the H_0 function measures the tendency for a given solution to transfer a proton to an uncharged base it has been quite useful for measuring the strengths of very weak bases and also for interpreting kinetics of various acid-catalyzed reactions.

Bases of different charge types should have related acidity functions. Work with the H_+ and H_- has not been extensive (69, 70), but the study of the carbinol-carbonium ion equilibrium has given rise to the H_R function which is particularly pertinent to the present work. This equilibrium,

$$H^+ + Ar_3COH \rightleftharpoons HOH + Ar_3C_+ \tag{39}$$

involves a charge type different than the one involved in H_0 studies and has water as a reactant; therefore, one would expect it to follow a different acidity function. Gold (71, 72) and Hawes (73) were the first to define such a function, which they called J_0:

$$J_0 = H_0 + \log a_{H_2O} \tag{40}$$

(where $\underline{a}$ denotes activity)

They assumed that the ionization of a carbinol would proceed via the following equilibria:

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{41}$$

$$ROH + H^+ \rightleftharpoons ROH_2^+ \tag{42}$$

$$ROH_2^+ \rightleftharpoons HOH + R^+ \tag{43}$$

J_0 would then be equal to:

$$J_0 = H_0 + \log a_{H_2O} = -pK_{ROH} - \log \frac{C_{R^+}}{C_{ROH}} - \log \frac{f_{R^+}}{f_{ROH_2^+}} \tag{44}$$

(where f refers to the molar-concentration activity coefficient). Gold and Hawes (73) suggested that the last term in equation 44 would be negligible since it is a ratio of activity coefficients of two similarly charged species. Williams and Bevan (74) and Deno and his group (13, 14), using arylcarbinols as indicators, showed that this approximation is unsatisfactory for sulfuric acid solutions between 60-80% even though it is valid for the 80 to 90% region. Their approach was on the basis of the equilibrium 39 represented quantitatively by pK_{R+}, the negative of pK_{ROH} and they defined the H_R acidity function (initially called Co by Deno and his group) as:

$$H_R = pK_{R+} + \log \frac{C_{R^+}}{C_{ROH}} \tag{45}$$

This function can be shown to differ from the J_0 function by the activity coefficient term $f_{R^+}/f_{ROH_2^+}$ which Gold and Hawes assumed to be negligible. The fact that this ratio is not unity is striking evidence that the activity coefficient behavior of carbonium ions and of other types of organic ions is quite different. It also indicated that the nature and amount of solvation might be quite different for various types of organic ions.

Recently, Bushick (67) studied the thermodynamics of the carbinol-carbonium ion equilibrium in aqueous sulfuric acid. He found that the difference between the Hammett and H_R indicators is due mainly to the difference in activity coefficients for the species involved and that the H_R scale, like H_0, is not very temperature dependent.

IV. Present Work

This thesis is concerned with the preparation and study of compounds that ionize in sulfuric acid to give dications of a type similar to (XVI). The previous work on $\alpha, \alpha, \alpha', \alpha'$-tetraphenyl-p-xylene dication was extended to the diphenyl derivatives as well as to the meta and ortho compounds in order to study the effect of amount and position of substitution on the visible absorption spectra. Work was also done on the effect of having additional benzene rings located between the two positive charges. This was done by using substituted biphenyl and fluorenes.

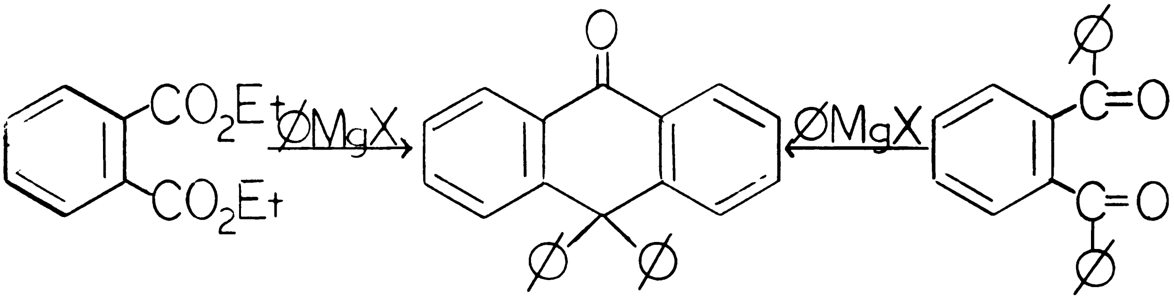
Since observation of the absorption spectra was sufficient in most cases to prove dication formation, the use of cryoscopy was limited. Another tool used to study dication formation was quenching experiments. With these three methods, it has been shown that it is possible to prepare various dications similar to (XVI). Their absorption spectra have been correlated with those of various monocations.

RESULTS AND DISCUSSION

I. Syntheses and Structure Proofs

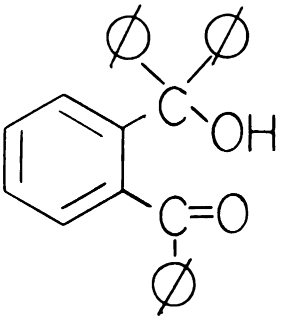
The majority of the diols and carbinols needed were known compounds and their syntheses were performed by the usual methods. There are several compounds, however, whose synthesis is of special interest. These compounds and the new compounds prepared in this thesis will be discussed in this section.

The reaction of phenylmagnesium bromide with methyl benzoate or with benzophenone has long been known to give triphenylmethanol (75, 76). The obvious way of preparing α, α, α', α'-tetraphenyl-o-xylene-α, α'-diol, therefore, was by the reaction of phenylmagnesium bromide with dimethyl phthalate. It has been shown, however, that when either o-dibenzoylbenzene (77) or diethyl phthalate (78) reacts with the phenyl Grignard reagent and is then heated to 300°, 10, 10-diphenyl-9-anthrone is obtained:



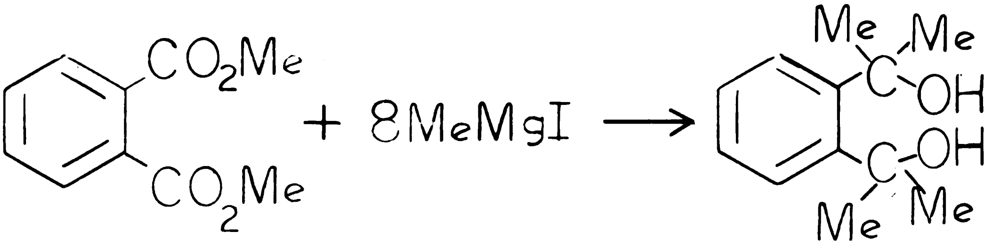
(46)

Since the oil that results from treatment of the carbonyl compounds with phenylmagnesium bromide is hydrolyzed first and then heated to 300°, it is probable that this oil is a mixture of starting material and o-benzoyltriphenylmethanol (XXVIII).



XXVIII

Indeed, Barnett, Cook and Nixon showed that when XXVIII was heated to 300° it gave 10, 10-diphenyl-9-anthrone even though concentrated sulfuric acid or hydrogen chloride in acetic acid did not catalyze this transformation (77). The bulkiness of the Grignard reagent and the steric hindrance at the carbonyl of XXVIII prevents further reaction with phenylmagnesium bromide. Alkylation of the aromatic ring is favored, however, because of the proximity of the reaction sites. Support for this steric effect is obtained from the work of Bennett and Wain (79) who prepared α, α, α', α'-tetramethyl-o-xylene-α, α'-diol without difficulty from dimethyl phthalate and methylmagnesium iodide.

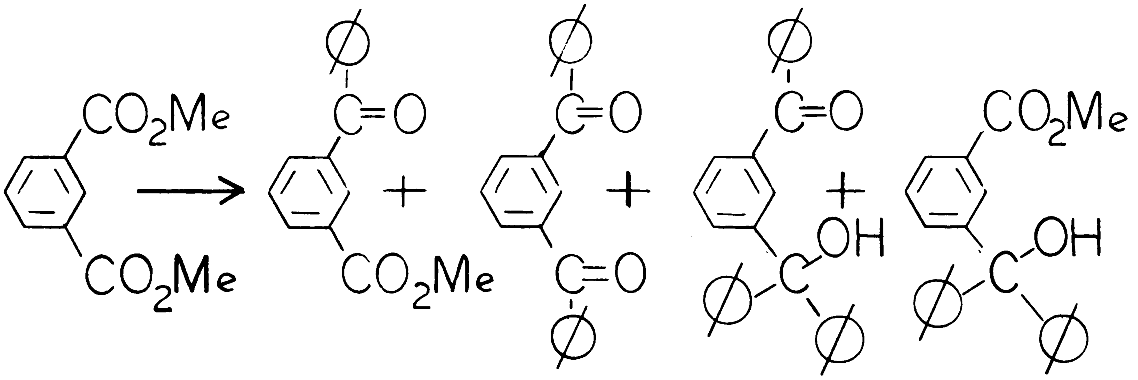


(47)

The formation of the anthrone, however, was of use later in this thesis in the synthesis of 9-chloro-10,10-diphenyl-9, 10-dihydroanthracene.

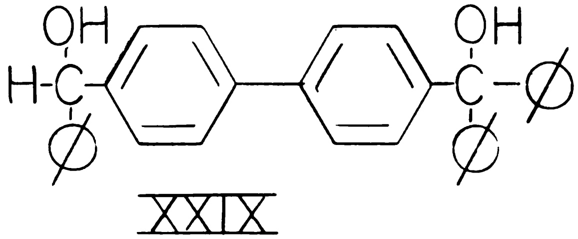
α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol was prepared in high yield from dimethyl phthalate and phenyl lithium. Being less bulky and more reactive, phenyl lithium allows the reaction to go to completion.

Sloan (63) has recently reported that the synthesis of some of the pure diols was quite difficult. The diols were obtained as oils, converted to the dichlorides in low yield, recrystallized, hydrolyzed back to the diols and recrystallized. This procedure was employed in this thesis for the preparation of α, α, α', α'-tetraphenyl-m-xylene-α, α'-diol, α, α, α', α'-tetraphenyl-p, p'-bitolyl-α, α'-diol and α, α, α', α'-tetraphenyl-m, m'-bitolyl-α, α'-diol. One dichloro compound, α, α'-dichloro-α, α'-diphenyl-2, 7-dimethylfluorene, was used without hydrolysis to the diol. The probable reason for the impurity of the diols is the inefficiency of the Grignard reaction. This results in the formation of a wide variety of possible products besides the diol:

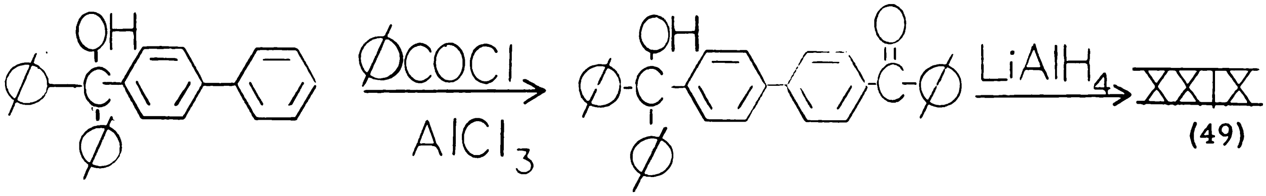

(48)

Evidence for the occurrence of these compounds were obtained from infrared spectra of the crude products.

Several paths to the synthesis of α, α, α'-triphenyl-p, p'-bitolyl-α, α'-diol were envisioned.

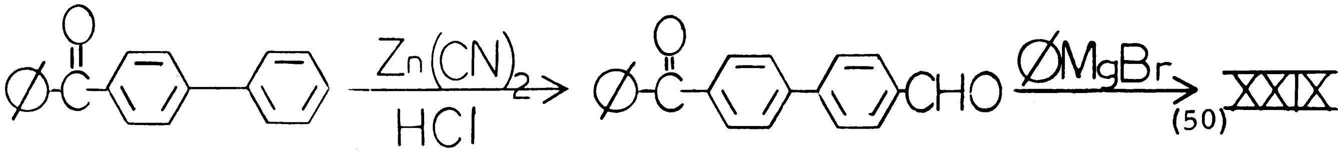

XXIX

The first method failed because the initial step in the following sequence did not produce any ketone.



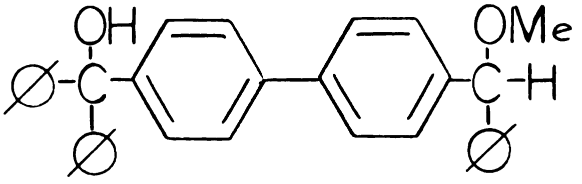
(49)

The second method also failed in the first step since the reaction of 4-benzoylbiphenyl with zinc cyanide and hydrochloric acid only produced an insoluble oil.



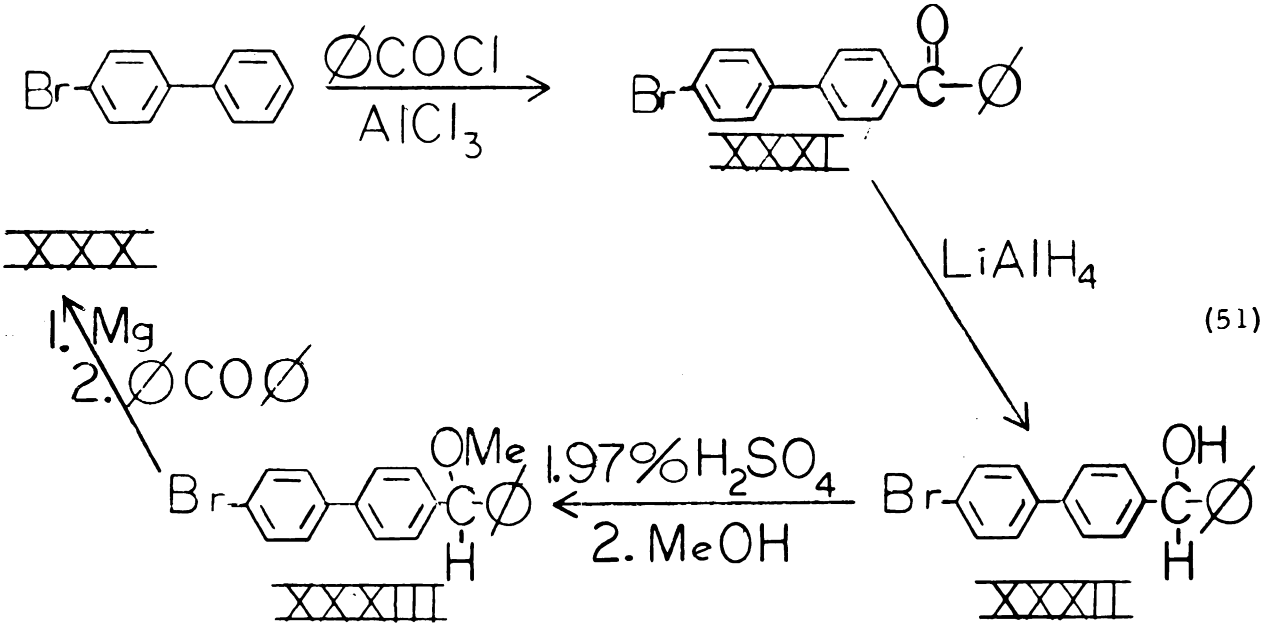
(50)

The third procedure involved four steps and was intended to form α, α, α'-triphenyl-α-hydroxy-α'-methoxy-p, p'-bitolyl as the end product.



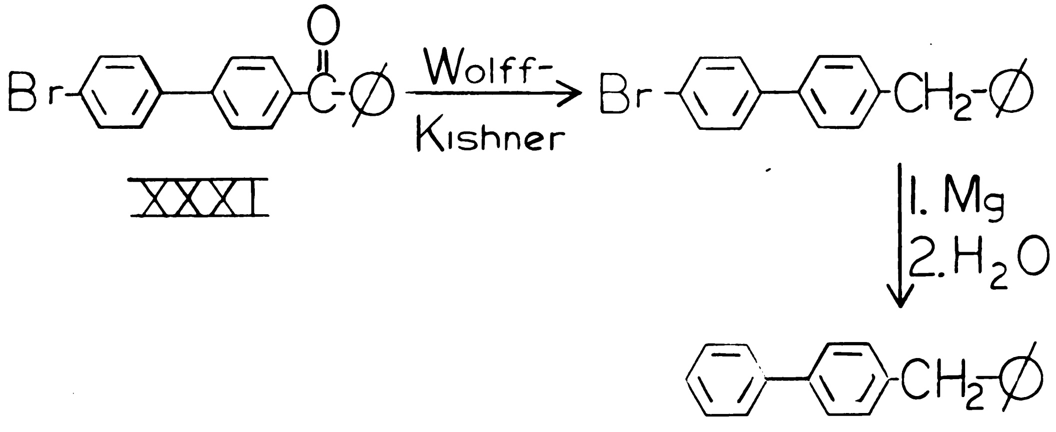
XXX

The procedure was as follows:



(51)

This sequence of reactions proved more successful since compounds XXXI, XXXII, and XXXIII were isolated. The final step, however, gave a compound whose analysis was not the same as XXX. In order to demonstrate that the benzoylation of 4-bromobiphenyl gave the 4,4'-derivative, XXXI was reduced to the bromohydrocarbon (by the Wolff-Kishner procedure) which was treated first with magnesium and then with water to give the known 4-benzylbiphenyl.



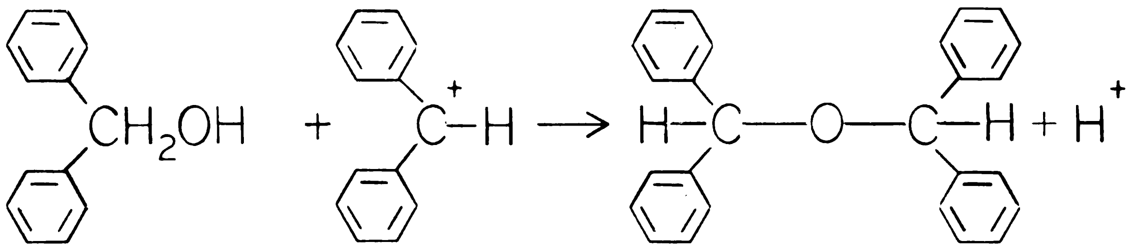
(52)

This demonstrates that the benzoyl group was in the 4-position in compound XXXI.

The structure of XXXII was shown by analysis, method of synthesis and its infrared spectrum. The structure of XXXIII was demonstrated by its n.m.r. spectrum. The reaction of XXXIII with magnesium followed by benzophenone gave a crystalline material which did not analyze correctly for XXX. Further work must be done to identify this product.

II. Visible Spectra in Sulfuric Acid and pK_R Studies

The visible spectra of the carbinols and diols prepared in this thesis were studied in sulfuric acid. By varying the concentration of sulfuric acid, the pK_R's of the triarylcarbinols were determined. It was not possible, however, to obtain accurate pK_R's of the diarylcarbinols since their solutions tended to fade rapidly near the region of the pK_R. This was presumed to be due to formation of bis-diarylmethyl ethers which tend to precipitate out of solution:



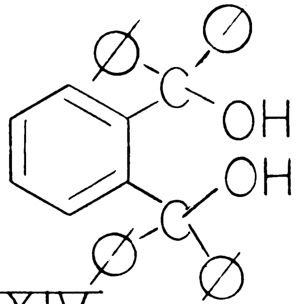
(53)

Burton and Cheeseman (80) have postulated a similar mechanism for the formation of dibenzhydryl ether from benzhydrol in acetic acid containing perchloric acid.

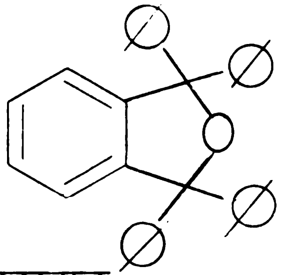
This section will present the results of the spectral studies and the following section will interpret them.

A. The Xylene Diols

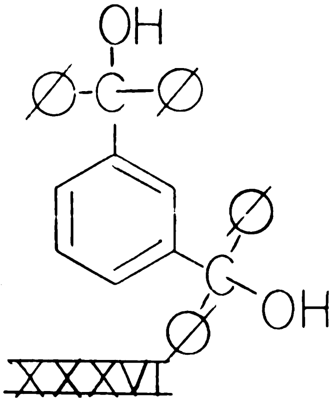
The compounds whose spectra are discussed in this section are:



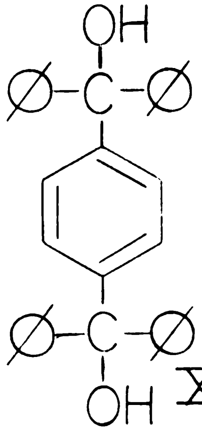
XXXIV



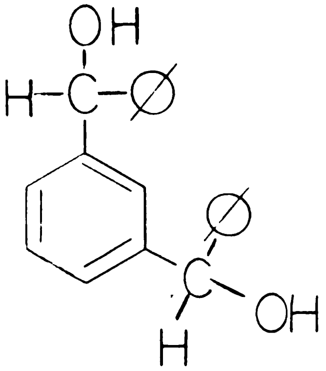
XXXV



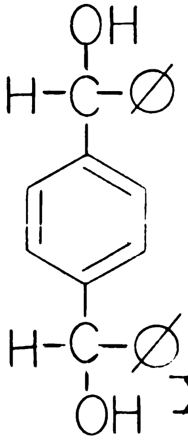
XXXVI



XXXVII



XXXVIII



XXXIX

It was shown previously (61) that XXXVII dissolved in concentrated sulfuric acid to form a red solution which gave a characteristic visible spectrum. It was of interest, therefore, to study the ortho and meta analogs of XXXVII as well as the corresponding diphenyl derivatives (XXXVIII and XXXIX).

The red solution formed by dissolving compound XXXIV in concentrated sulfuric acid gave a visible spectrum that had maxima at 455 mμ (ϵ = 44,000) and 373 mμ (ϵ =30,500). Solutions of XXXIV showed no visible absorbance in sulfuric acid whose concentration was less than 78%. Figure 1 shows the visible spectrum of α, α, α', α'-tetraphenyl-o-xylene-

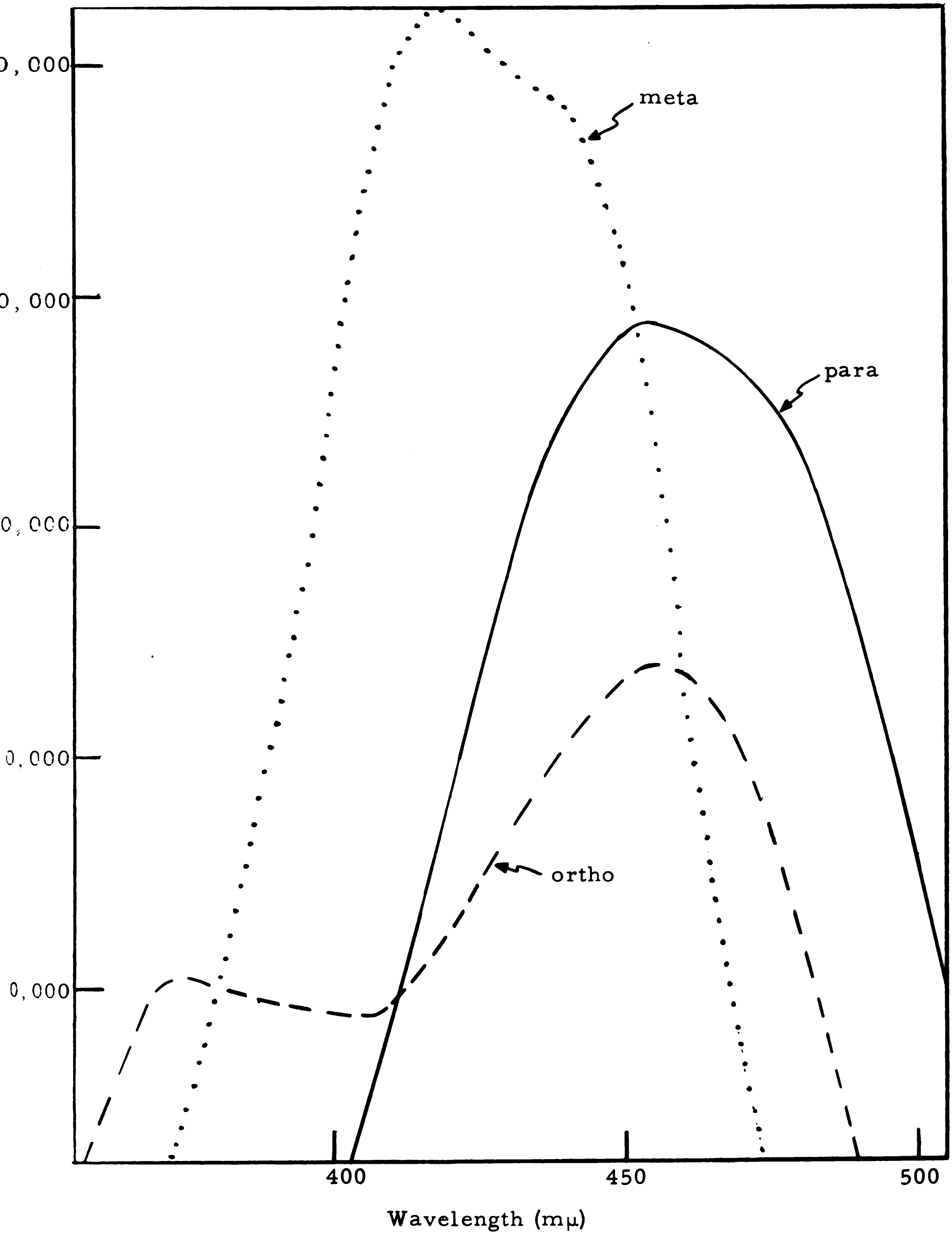


Figure 1. Visible spectra of the α, α, α', α'-tetraphenylxylene-α, α'-diols in concentrated sulfuric acid.

α, α'-diol in 98% sulfuric acid. A solution of tetraphenylphthalan (XXXV) in 98% sulfuric acid gave the identical visible spectrum as the diol.

Table 2 records the observed absorbances (A) at 455 mμ for solutions of XXXIV in varying concentrations of sulfuric acid (between 78 and 97%). A plot of A versus the H_{R+} of the solution is shown in Figure 2. A differential plot of $\Delta A/\Delta H_{R+}$ versus H_{R+} gives a value of -16.6 for the pK_R of α, α, α', α'-tetraphenyl-o-xylene-α, α'-diol. In agreement with this result, tetraphenylphthalan was found to have almost an identical pK_R, -16.4

The meta glycol XXXVI also gave a red solution when dissolved in 98% sulfuric acid. The visible spectrum of this dication also had two peaks: 440 mμ (ϵ = 70,000) and 419 mμ (ϵ = 73,000). It was necessary to use acid of greater than 50% in order to observe a visible spectrum. Figure 1 shows the visible spectrum of α, α, α', α'-tetraphenyl-m-xylene-α, α'-diol in 98% sulfuric acid, and, for comparison purposes, that of the para isomer. The latter compound absorbed at 455 mμ with an ϵ of 59,000.

The pK_R's of compounds XXXVI and XXXVII were determined as described above. Tables 3 and 4 give the appropriate data, Figures 3 and 4 the observed spectra, and Figure 2 shows the plot of A versus the H_{R+} of the solution. Figure 5 shows the plot of $\Delta A/\Delta H_{R+}$ versus H_{R+} used in determining the pK_R of compound XXXVII. This is typical of the differential plots employed in determining pK_R's in this thesis.

The meta diol has pK_R's at -8.0 and -10.1 and the para isomer at -8.1 and -10.5. This is in contrast to the ortho diol which has only one apparent pK_R. A more detailed discussion of this and other points concerning the visible spectra of the α, α, α', α'-tetraphenylxylene-α, α'-diols in sulfuric acid will be found in Section IIIA.

Table 2. Observed Visible Absorption Maxima at 455 mμ of α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol (6.2 x 10^{-5} moles/liter) in Varying Concentrations of Sulfuric Acid

Wt. Per Cent H_2SO_4	H_{R+}	Absorbance (A)
78.0	-14.60	0.10
78.4	-14.70	0.11
80.0	-15.28	0.22
81.0	-15.60	0.30
82.0	-15.94	0.47
83.0	-16.24	0.68
84.0	-16.58	1.00
85.0	-16.87	1.31
86.0	-17.21	1.58
87.0	-17.50	1.61
88.0	-17.82	1.63
89.0	-18.10	1.66
92.0	-18.99	1.67
97.0	-20.40	1.67

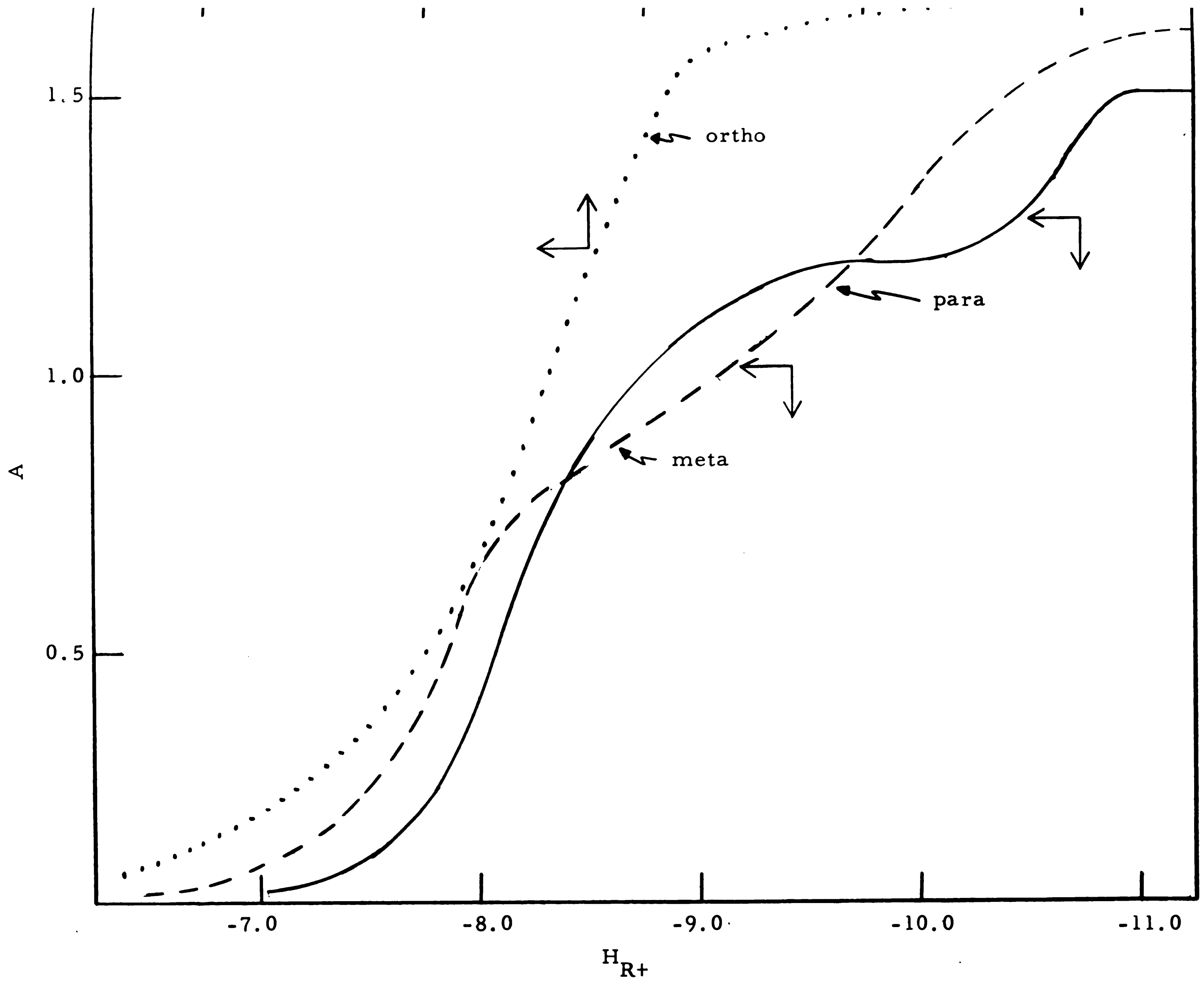


Figure 2. Plot of A versus H_{R+} for the α, α, α', α'-tetraphenylxylene-α, α'-diols.

Table 3. Observed Visible Absorption Maxima at 419 mμ of α, α, α', α'-Tetraphenyl-m-xylene-α, α'-diol (2.1 x 10^{-5} moles/liter) in Varying Concentrations of Sulfuric Acid

Wt. Per Cent H_2SO_4	H_{R+}	Absorbance (A)
50.0	-6.47	0.07
51.0	-6.62	0.08
52.0	-6.83	0.09
53.0	-7.02	0.12
54.0	-7.23	0.16
55.0	-7.46	0.23
56.0	-7.67	0.34
56.6	-7.80	0.44
57.0	-7.90	0.56
57.5	-8.00	0.67
58.0	-8.09	0.72
59.0	-8.37	0.80
60.0	-8.61	0.89
61.0	-8.90	0.95
62.0	-9.17	1.03
63.0	-9.45	1.11
64.0	-9.76	1.22
65.0	-10.06	1.37
66.0	-10.37	1.49
67.0	-10.70	1.56
68.0	-11.00	1.62
69.0	-11.33	1.63

Table 4. Observed Visible Absorption Maxima at 455 mμ of α, α, α', α'-Tetraphenyl-p-xylene-α, α'-diol (2.8 x 10^{-5} moles/liter) in Varying Concentrations of Sulfuric Acid

Wt. Per Cent H_2SO_4	H_{R+}	Absorbance (A)
53.0	-7.02	0.07
54.0	-7.23	0.08
55.0	-7.46	0.12
56.0	-7.67	0.18
57.0	-7.90	0.31
57.5	-8.00	0.41
58.0	-8.09	0.52
59.0	-8.37	0.83
60.0	-8.61	0.97
61.0	-8.90	1.01
62.0	-9.17	1.13
63.0	-9.45	1.18
64.0	-9.76	1.20
65.0	-10.06	1.20
66.0	-10.37	1.27
67.0	-10.70	1.41
68.0	-11.00	1.50
69.0	-11.33	1.50

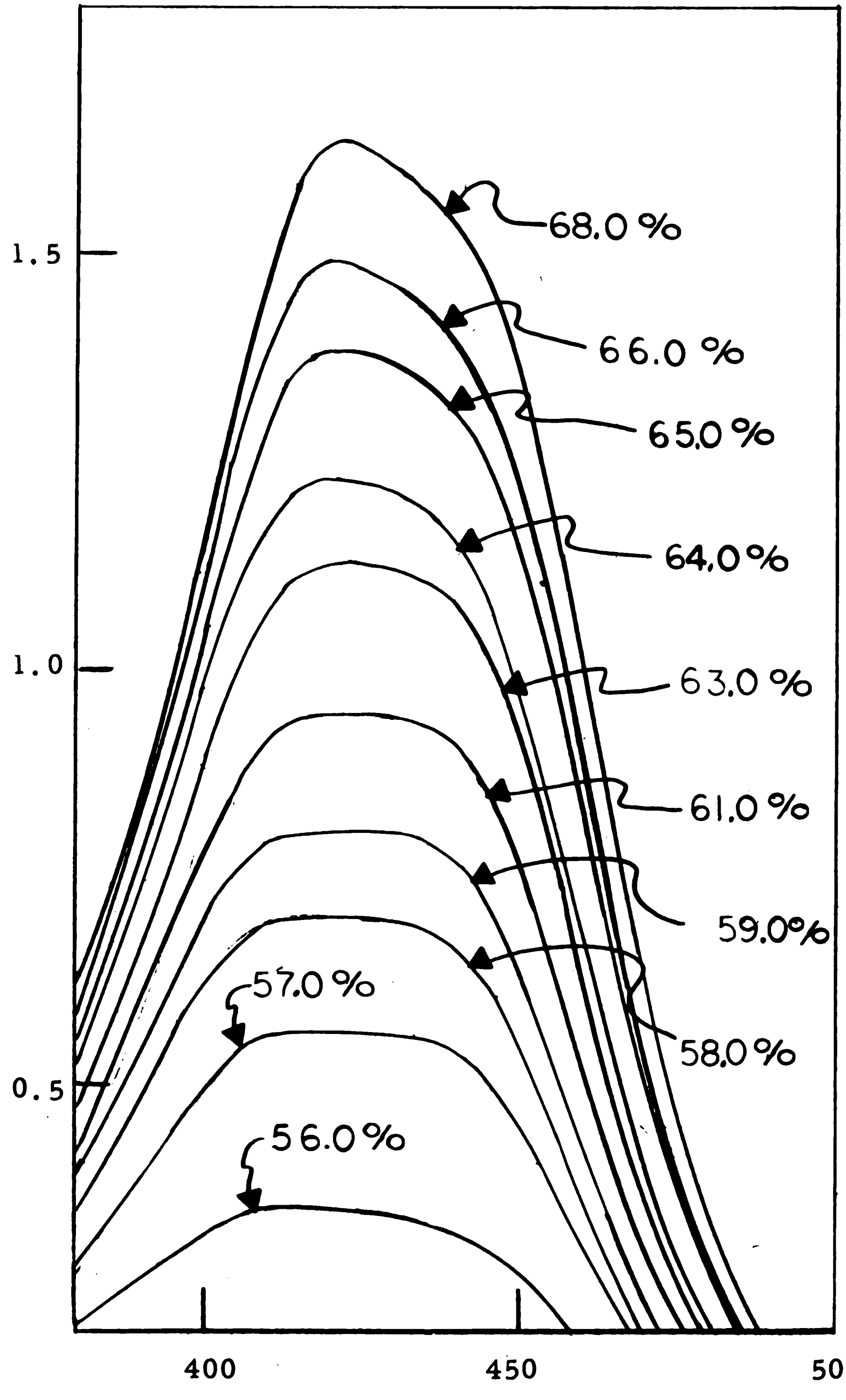


Figure 3. Visible spectra of α, α, α', α'-tetraphenyl-m-xylene-α, α'-diol in varying concentrations of sulfuric acid.

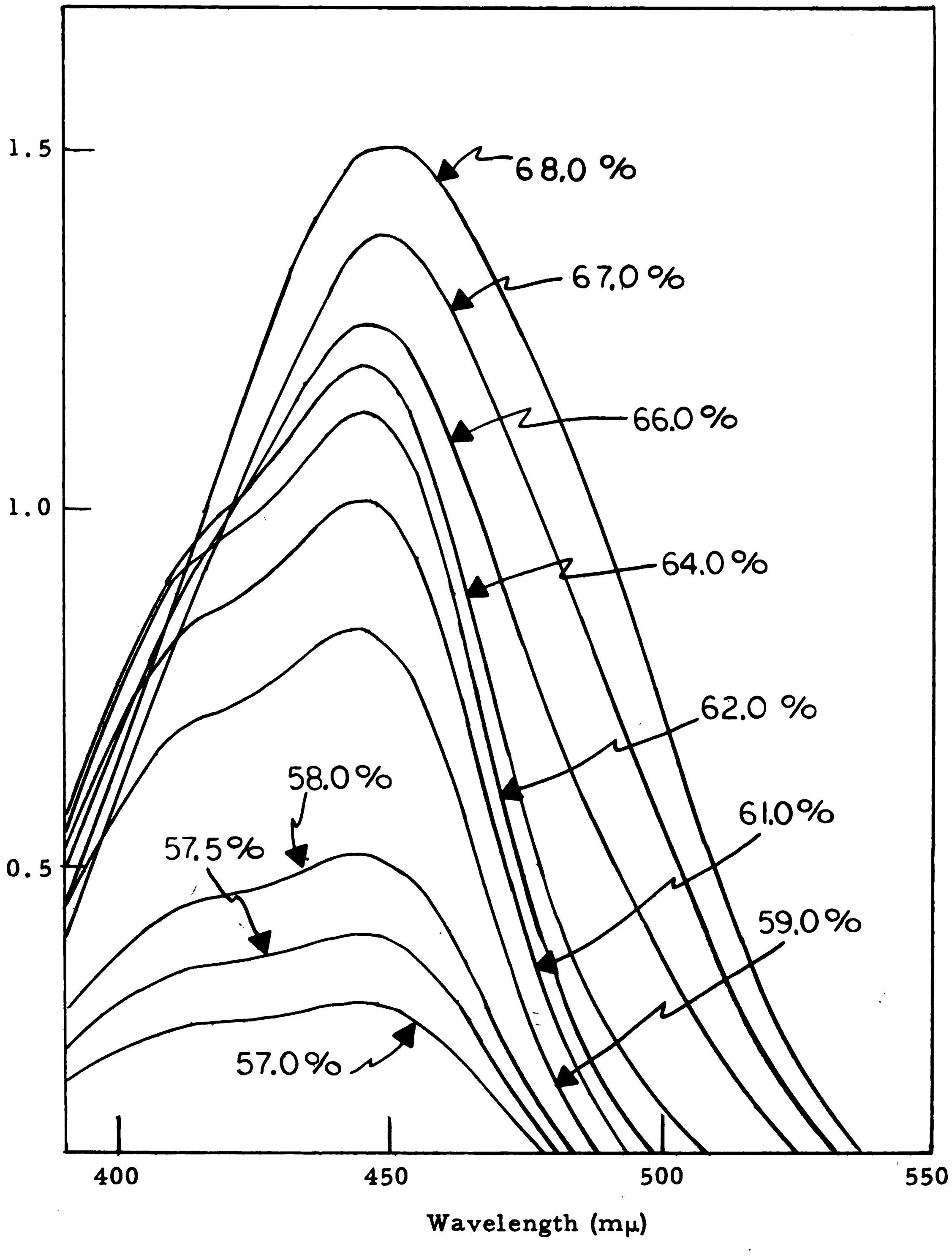


Figure 4. Visible spectra of α, α, α', α'-tetraphenyl-p-xylene-α, α'-diol in varying concentrations of sulfuric acid.

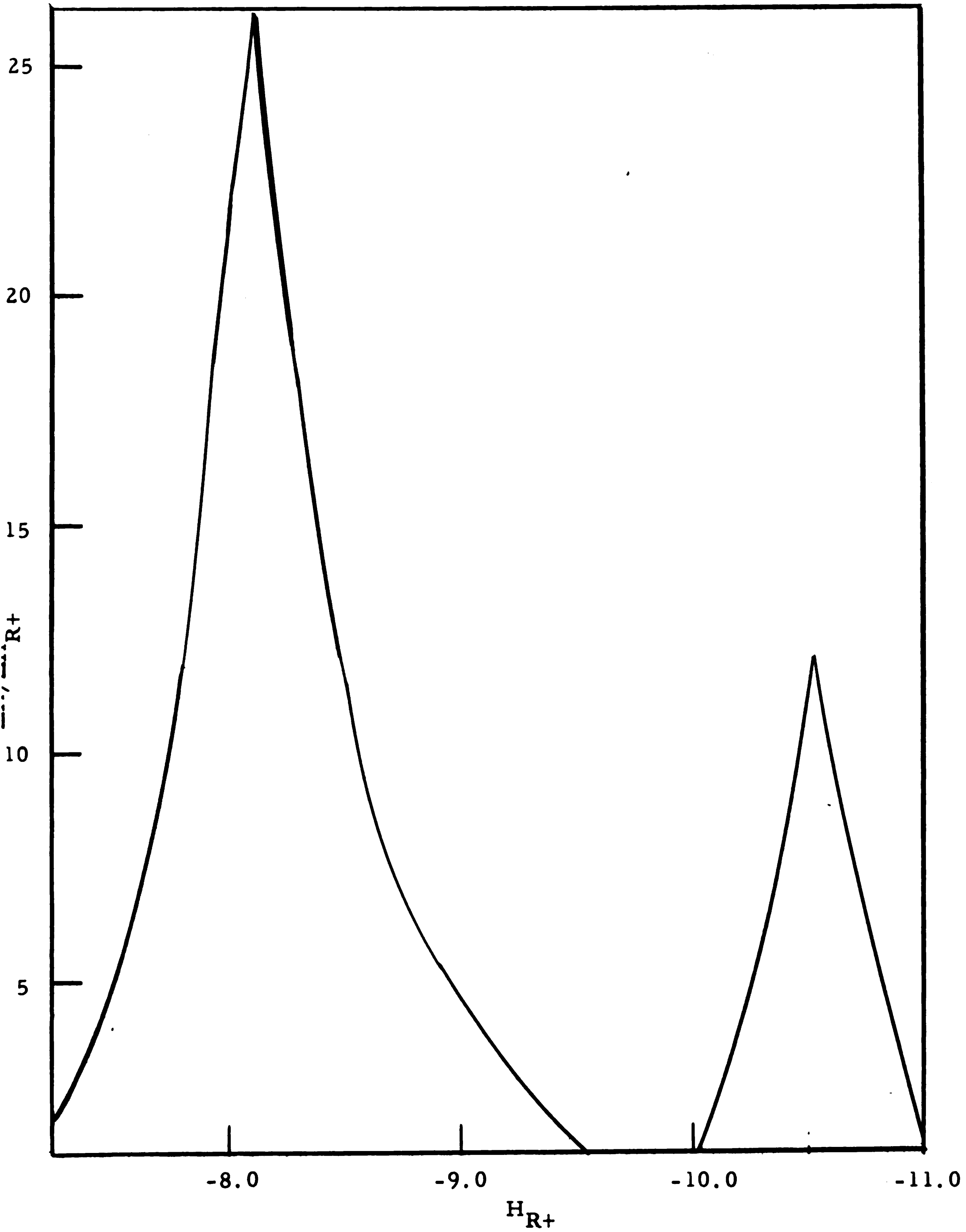
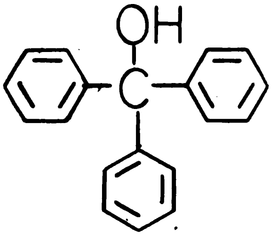


Figure 5. Plot of $\Delta A/\Delta H_{R+}$ versus H_{R+} for a, a, a', a'-tetraphenyl-p-xylene-a, a'-diol.

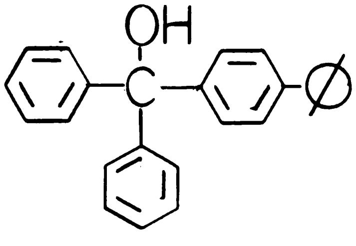
Compounds XXXVIII and XXXIX in concentrated sulfuric acid gave characteristic absorption spectra in the visible region. The former absorbed at 447 mμ (ϵ = 35,000) and the latter at 461 mμ (ϵ = 48,000). Figure 6 shows the visible spectra of these dications in 98% sulfuric acid. As explained above, no pK_R studies were done on these compounds.

B. The Biphenyl Diols and Carbinols

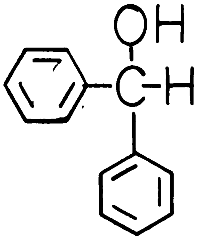
The compounds whose spectra are discussed in this section are:



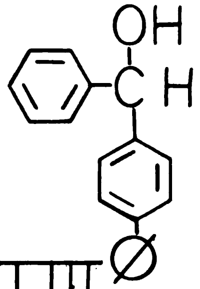
XL



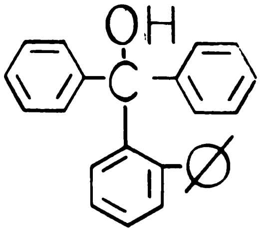
XLI



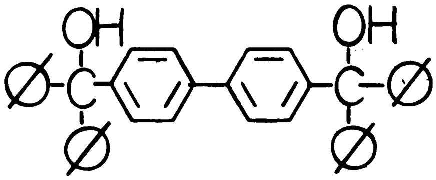
XLII



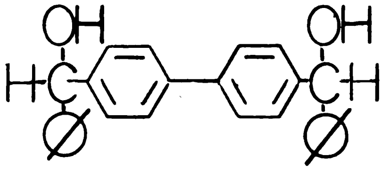
XLIII



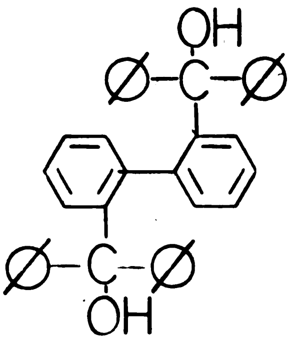
XLIV



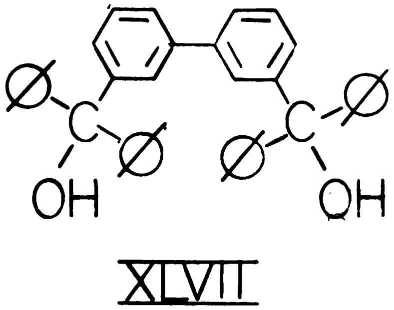
XLV



XLVI



XLVIII



XLVII

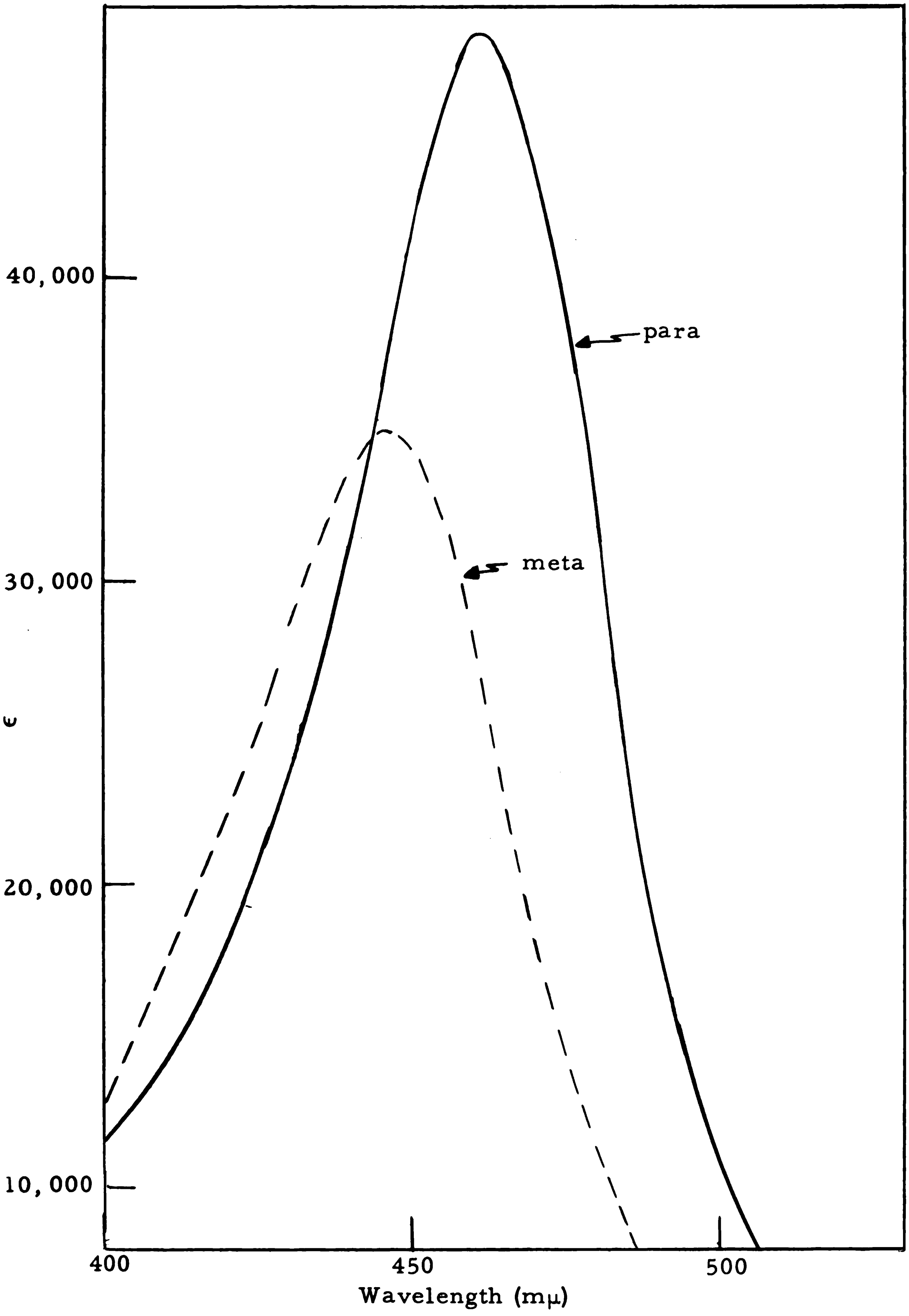


Figure 6. Visible spectra of meta and para α, α'-diphenylxylene-α, α'-diols in concentrated sulfuric acid.

Triphenylmethanol (XL) dissolved in concentrated sulfuric acid to give a yellow solution. The visible spectrum showed two maxima: 432 mμ (ϵ = 37,500) and 408 mμ (ϵ = 36,500). These values are the same as those reported by Deno *et al.* (14). Figure 7 shows the visible spectrum of XL in 98% sulfuric acid. Table 5 records the observed absorbances (A) at 432 mμ for solutions of XL in varying concentrations of sulfuric acid between 51 and 68%. A plot of A versus the H_{R+} of the solution is shown in Figure 8. The pK_R of triphenylmethanol as obtained from a differential plot of $\Delta A/\Delta H_{R+}$ versus H_{R+} is -7.4. The literature values are -6.4 (67) and -6.7 (14).

When XLI was dissolved in concentrated sulfuric acid a red solution resulted. In less than a minute, however, the solution became orange. The visible spectrum of the orange solution (98% sulfuric acid) showed maxima at 476 mμ (ϵ = 49,000) and 432 mμ (ϵ = 34,000). Mason reported a λ_{max} of 474 mμ and an ϵ_{max} of 51,000 (see page 6). In 78% sulfuric acid, where the solution was red, maxima were observed at 510 mμ (ϵ = 43,000) and 420 mμ (ϵ = 21,500). Anderson and Fisher reported a visible spectrum for XLI that showed a maximum at 508 mμ (ϵ = 39,000) (81). The solvent used was 5 ml. of concentrated sulfuric acid in 95 ml. of glacial acetic acid. This spectrum, which is due to the carbonium ion, is depicted in Figure 9. Table 6 gives the A at 510 mμ for solutions of XLI in sulfuric acid between 52 and 78%. Figure 8 shows the plot of A versus H_{R+}. The pK_R was -7.7. Since in 93.9% sulfuric acid the change from the red to the orange solution was slow, it was followed as a function of time. Figure 10 shows this change at 93.9% sulfuric acid. The time for completion of one-half of the reaction was 135 minutes ($k = 5.1 \times 10^{-3}$ min.$^{-1}$).

Benzhydrol (XLII) dissolved in concentrated sulfuric acid to form a yellow solution. Figure 9 shows the visible spectrum of compound XLII in 98% sulfuric acid. Table 7 records the observed absorbances at the

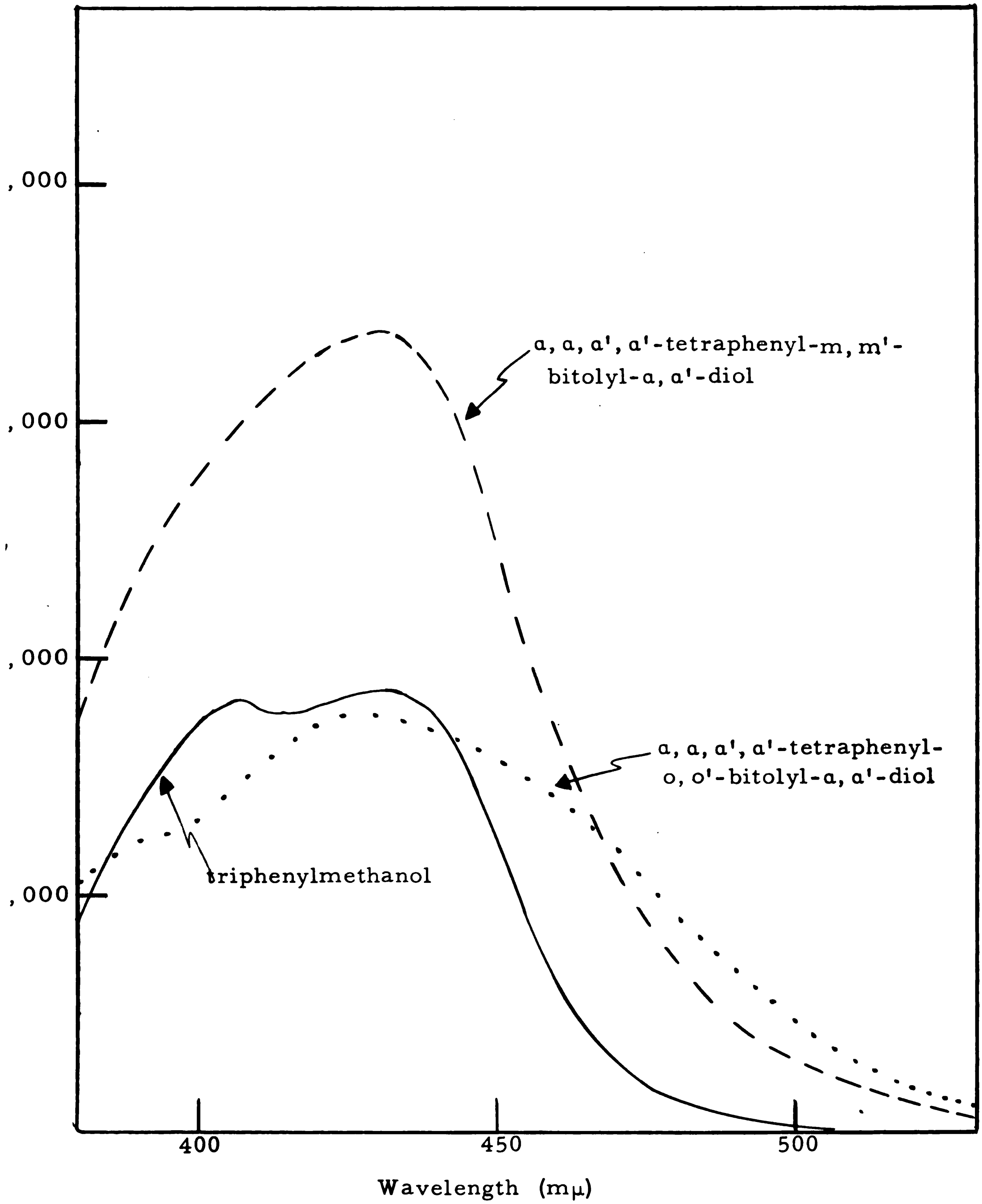


Figure 7. Visible spectra of triphenylmethanol, a, a, a', a'-tetraphenyl-m, m'-bitolyl-a, a'-diol and a, a, a', a'-tetraphenyl-o-o'-bitolyl-a, a'-diol in concentrated sulfuric acid.

Table 5. Observed Visible Absorption Maxima at 432 mμ of Triphenylmethanol (5.0×10^{-5} moles/liter) in Varying Concentrations of Sulfuric Acid

Wt. Per Cent H_2SO_4	H_{R+}	Absorbance (A)
51.0	-6.62	0.22
53.0	-7.02	0.49
54.0	-7.23	0.62
55.0	-7.46	1.19
56.0	-7.67	1.56
56.3	-7.73	1.64
58.5	-8.23	1.83
70.0	-11.64	1.91
97.0	-20.40	1.91

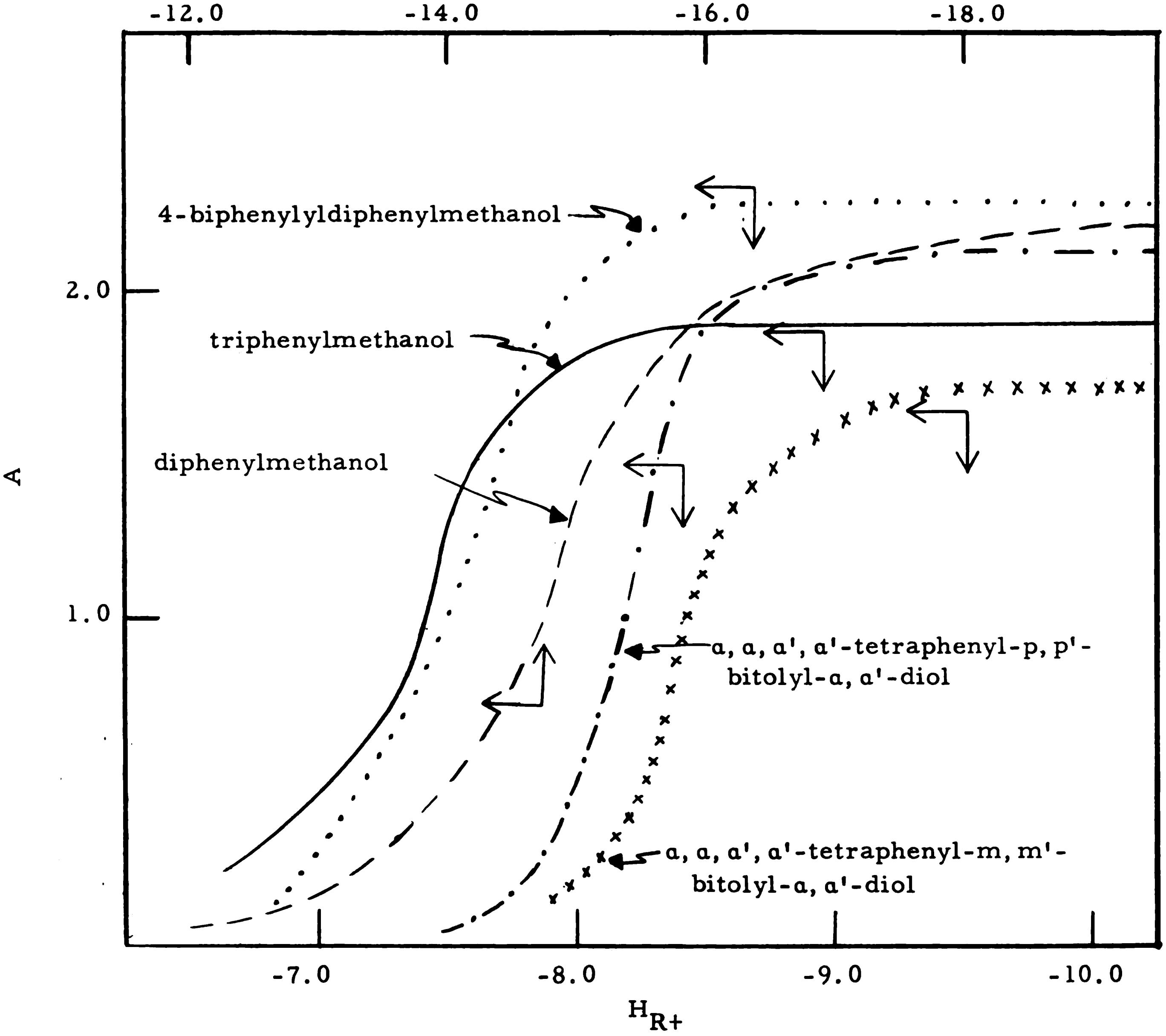


Figure 8. Plot of A versus H_{R+} for triphenylmethanol, diphenylmethanol, 4-biphenylyldiphenylmethanol, α, α, α', α'-tetraphenyl-p, p'-bitolyl-α, α'-diol and α, α, α', α'-tetraphenyl-m, m'-bitolyl-α, α'-diol.

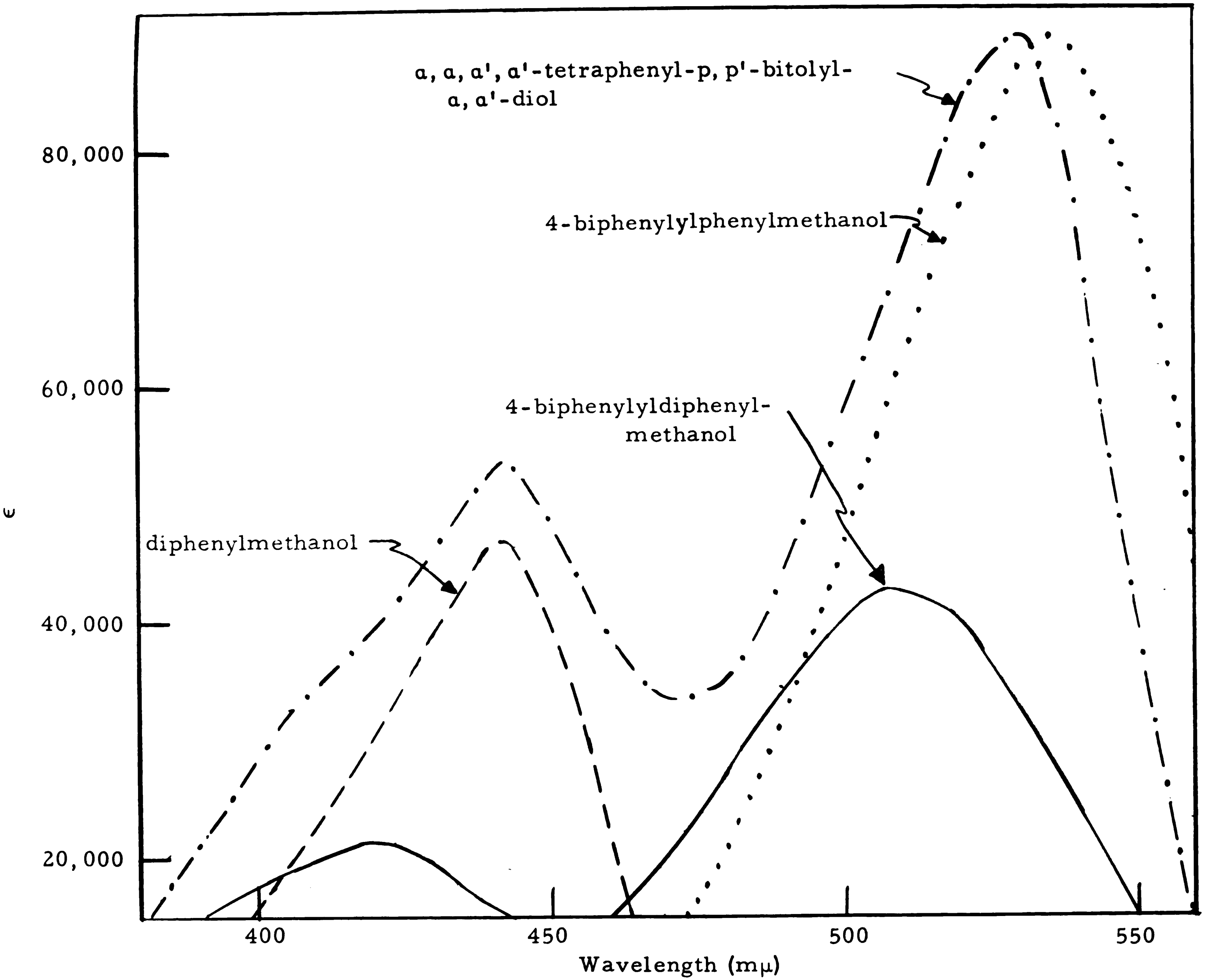


Figure 9. Visible spectra of 4-biphenylyldiphenylmethanol in 78% sulfuric acid and diphenylmethanol, 4-biphenylylphenylmethanol and a, a, a', a'-tetraphenyl-p-p'-bitolyl-a, a'-diol in concentrated sulfuric acid.

Table 6. Observed Visible Absorption Maxima at 510 mμ of 4-Biphenylyldiphenylmethanol (5.4 x 10^{-5} moles/liter) in Varying Concentrations of Sulfuric Acid

Wt. Per Cent H_2SO_4	H_{R+}	Absorbance (A)
52.0	-6.83	0.12
53.0	-7.02	0.32
54.0	-7.23	0.56
55.0	-7.46	0.94
56.0	-7.67	1.45
56.3	-7.73	1.62
56.6	-7.80	1.76
57.0	-7.90	1.92
58.0	-8.09	2.09
59.0	-8.37	2.22
60.0	-8.61	2.27
78.0	-14.60	2.27

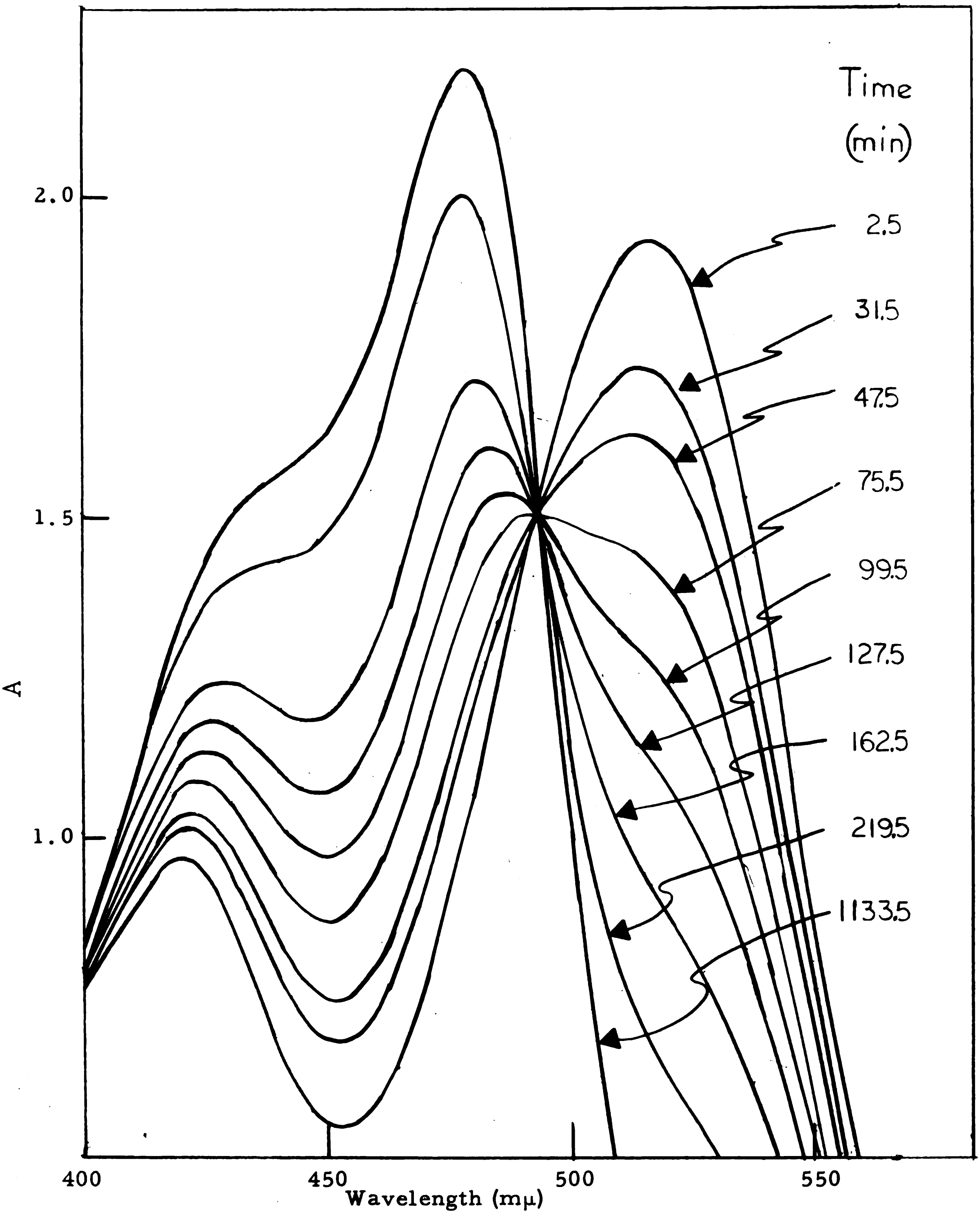


Figure 10. Change in the visible spectrum of 4-biphenylyldiphenylmethanol in 93.9% sulfuric acid with time.

Table 7. Observed Visible Absorption Spectra at 442 mμ of Diphenylmethanol (4.7 x 10^{-5} moles/liter) in Varying Concentrations of Sulfuric Acid

Wt. Per Cent H_2SO_4	H_{R+}	Absorbance (A)
71.0	-12.01	0.04
72.0	-12.40	0.06
73.0	-12.74	0.10
74.0	-13.11	0.14
75.0	-13.50	0.28
76.0	-13.82	0.48
77.0	-14.21	0.68
78.0	-14.60	0.88
78.4	-14.70	0.99
80.0	-15.28	1.62
81.0	-15.60	1.76
87.0	-17.50	2.06
88.0	-17.82	2.08
93.9	-19.50	2.20
97.0	-20.30	2.20

maximum absorbance (442 mμ; ϵ = 47,000) in varying concentrations of sulfuric acid. The previously reported values are 441 mμ (ϵ = 43,000) (82). A plot A versus H_{R+} is given in Figure 8. The pK_R of this carbinol was determined to be -14.7. The literature value is -13.3 (14).

4-Phenylbenzhydrol (XLIII) dissolved in concentrated sulfuric acid with formation of a red solution. Figures 9 and 11 depict its visible spectrum which showed a single maximum at 535 mμ (ϵ = 90,000). The pK_R of this compound was not determined because its solution in dilute sulfuric acid were unstable.

The spectrum of the cation from compound XLIV was not obtained because on treatment of a solution of XLIV in either acetic acid or methanol with sulfuric acid, a reaction occurred and the solutions were colorless. The sulfuric acid used was between 50 and 97%.

The 4,4'-biphenyl derivative XLV dissolved in concentrated sulfuric acid to form a deep red solution. Solutions of XLV were colorless in sulfuric acid whose concentration was less than 54%. In Figure 9, which shows the visible spectrum of compound XLV in 98% sulfuric acid, it can be seen that three spectral maxima occur: 530 mμ (ϵ = 90,000), 442 mμ (ϵ = 53,500) and a shoulder at 410 mμ (ϵ = 34,500). Theilacker and Ozegowski reported maxima at 525 and 440 mμ and a shoulder at 412 mμ (ϵ's were 89,000, 50,000 and 32,000 respectively) (83). Table 8 records the A at 530 mμ and 442 mμ for solutions of XLV in sulfuric acid whose concentration varied between 55 and 67%. A plot of A versus H_{R+} is seen in Figure 8. The pK_R of the diol was determined to be -8.2.

The corresponding diphenylcarbinol XLVI, which dissolved in concentrated sulfuric to form a violet solution, showed two absorption maxima: 563 mμ (ϵ = 134,000) and 420 mμ (ϵ = 13,000). This spectrum is shown in Figure 11. Even though the pK_R of this bis-secondary alcohol was not determined, it was observed that the position of the absorption

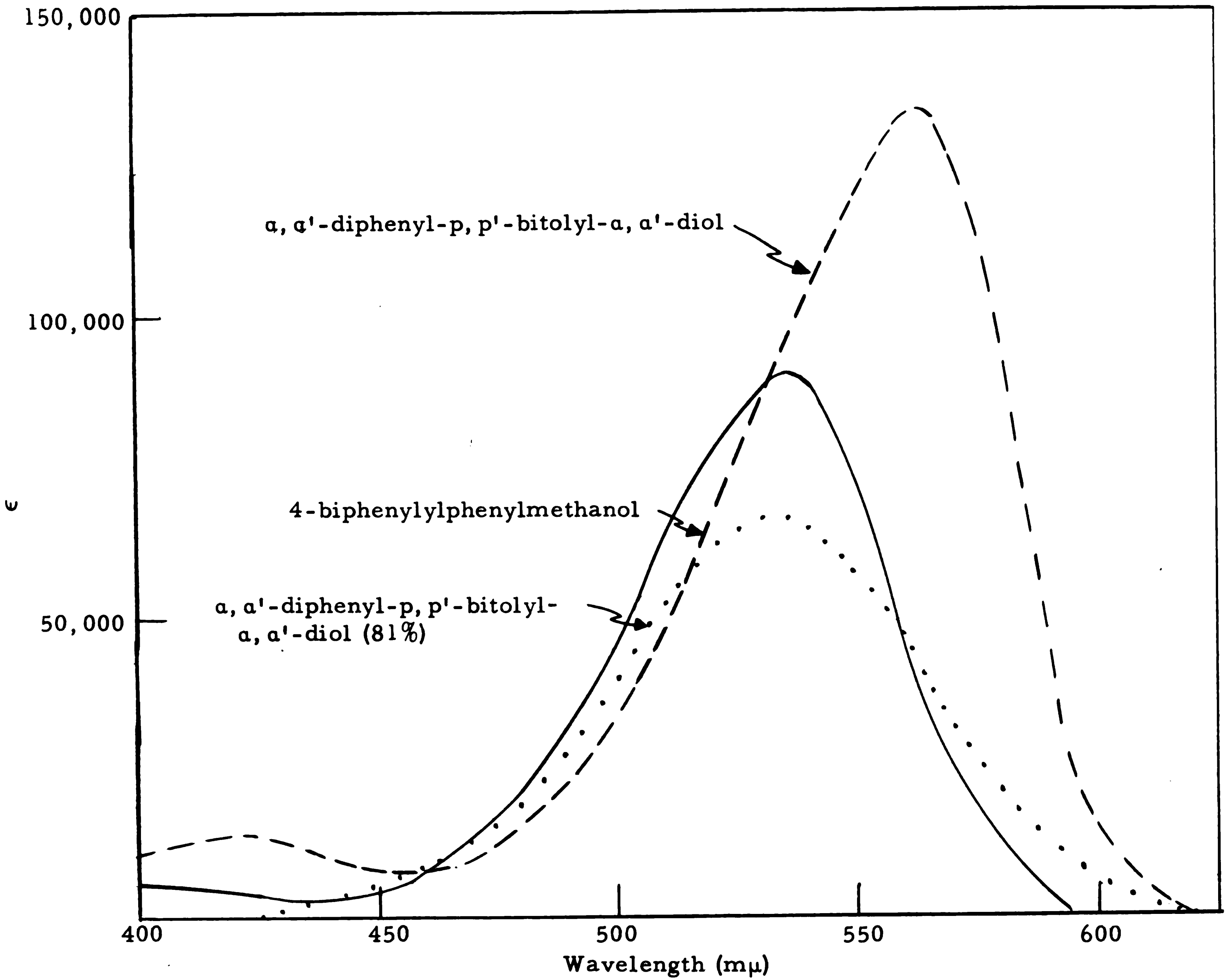


Figure 11. Visible spectra of 4-biphenylylphenylmethanol in concentrated sulfuric acid and a, a'-diphenyl-p, p'-bitolyl-a, a'-diol in concentrated and 81% sulfuric acid.

Table 8. Observed Visible Absorption Maxima at 530 and 442 mμ of α, α, α', α'-Tetraphenyl-p, p'-bitolyl-α, α'-diol (2.4 x 10^{-5} moles/liter) in Varying Concentrations of Sulfuric Acid

Wt. Per Cent H_2SO_4	H_{R+}	Absorbance (A)	
		442 mμ	530 mμ
55.0	-7.46	0.03	0.04
56.0	-7.67	0.08	0.10
57.0	-7.90	0.18	0.29
57.5	-8.00	0.28	0.50
58.0	-8.09	0.44	0.80
58.5	-8.23	0.64	1.20
59.0	-8.37	0.88	1.65
60.0	-8.61	1.07	1.96
61.0	-8.96	1.11	2.05
63.0	-9.45	1.15	2.12
67.0	-10.70	1.15	2.12
80.0	-15.28	1.16	2.12

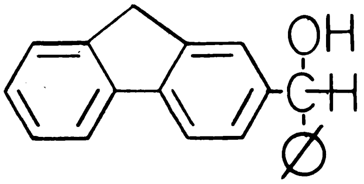
maximum shifts with decreasing acidity and in 83% sulfuric acid appears at 535 mμ (ϵ = 66,000). This is also shown in Figure 11.

The meta diol XLVII gave a yellow solution when dissolved in concentrated sulfuric acid. Its solutions were colorless below 55% acid. In 98% sulfuric acid, compound XLVII showed one maximum at 430 mu (ϵ = 67,500). This is depicted in Figure 7. Table 9 records the A at 430 mμ for solutions of XLVII in varying concentrations of sulfuric acid (between 57 and 72%). A plot of A versus H_{R+} is shown in Figure 8. The pK_R was -8.4.

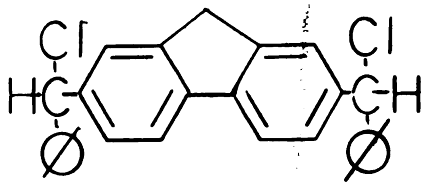
Solutions of the analogous ortho diol XLVIII in concentrated sulfuric acid were yellow. Its visible spectrum in 98% sulfuric acid, which is shown in Figure 7, had a maximum at 428 mμ (ϵ = 35,500) and shoulder at 390 mμ (ϵ = 24,000). Solutions of XLVIII in sulfuric acid were colorless below 75%. The pK_R of this diol was approximately -15.

C. The Fluorene Diols and Carbinols

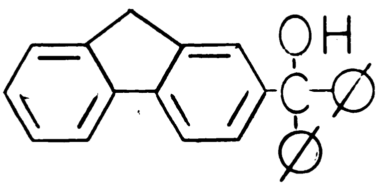
The compounds whose spectra are discussed in this section are:



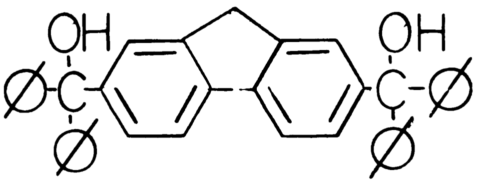
XLIX



L



LI



LII

Table 9. Observed Visible Absorption Maxima at 430 mμ of α, α, α', α'-Tetraphenyl-m, m'-bitolyl-α, α'-diol (2.5 x 10^{-5} moles/liter) in Varying Concentrations of Sulfuric Acid

Wt. Per Cent H_2SO_4	H_{R+}	Absorbance (A)
57.0	-7.90	0.13
58.0	-8.09	0.26
59.0	-8.37	0.70
60.0	-8.61	1.34
61.0	-8.96	1.58
70.0	-11.64	1.70
71.0	-11.95	1.70

The violet solution formed when compound XLIX was dissolved in concentrated sulfuric acid gave a visible spectrum that had a maximum at 547 mμ ($\epsilon = 66,000$). As the acid strength was decreased, the position of the maximum shifted to 542 mμ. Figure 12 shows the visible spectrum of XLIX in 98% sulfuric acid. An exact determination of the pK_R of this carbinol was not possible because of rapid fading of the solutions in dilute acid (see page 32) but an approximate value of -12.0 was found.

Compound L dissolved in concentrated sulfuric acid to form a blue solution. Its visible spectrum showed maxima at 603 mμ ($\epsilon = 215,000$) and 554 mμ ($\epsilon = 62,000$) and is depicted in Figure 12. As the acid strength was decreased, the intensity of the peak at 603 mμ also decreased and eventually it disappeared at 76% sulfuric acid. The peak at 554 mμ, however, did not change in intensity until 80% sulfuric acid where the intensity increased slightly, reaching a maximum at 78% acid, and the λ_{max} shifted to 547 mμ. Below 78%, the absorption intensity decreased. The solutions were colorless below 65% sulfuric acid. Table 10 records the observed absorbances at 603 and 554 mμ for solutions of L in varying concentrations of sulfuric acid and Figure 13 shows the plot of A versus the H_{R+} of the solutions. The pK_R's of the two ions are -16.6 and -12.0. The latter pK_R, like the pK_R of compound XLIX, was approximate.

The visible spectrum of compound LI in sulfuric acid behaved similar to that of XLI in sulfuric acid (see page 45), i.e., the spectrum in 80% sulfuric acid was different from that in 98% acid. In 98% sulfuric acid there were two absorption maxima at 505 mμ ($\epsilon = 53,000$) and at 425 mμ ($\epsilon = 18,000$). In 80% sulfuric acid the peaks were at 540 mμ ($\epsilon = 53,000$) and 404 mμ ($\epsilon = 17,000$). Since the former spectrum is shown later to be due to sulfonation, the latter represents the spectrum of the genuine carbonium ion (see Figure 14). Figure 15 shows the change

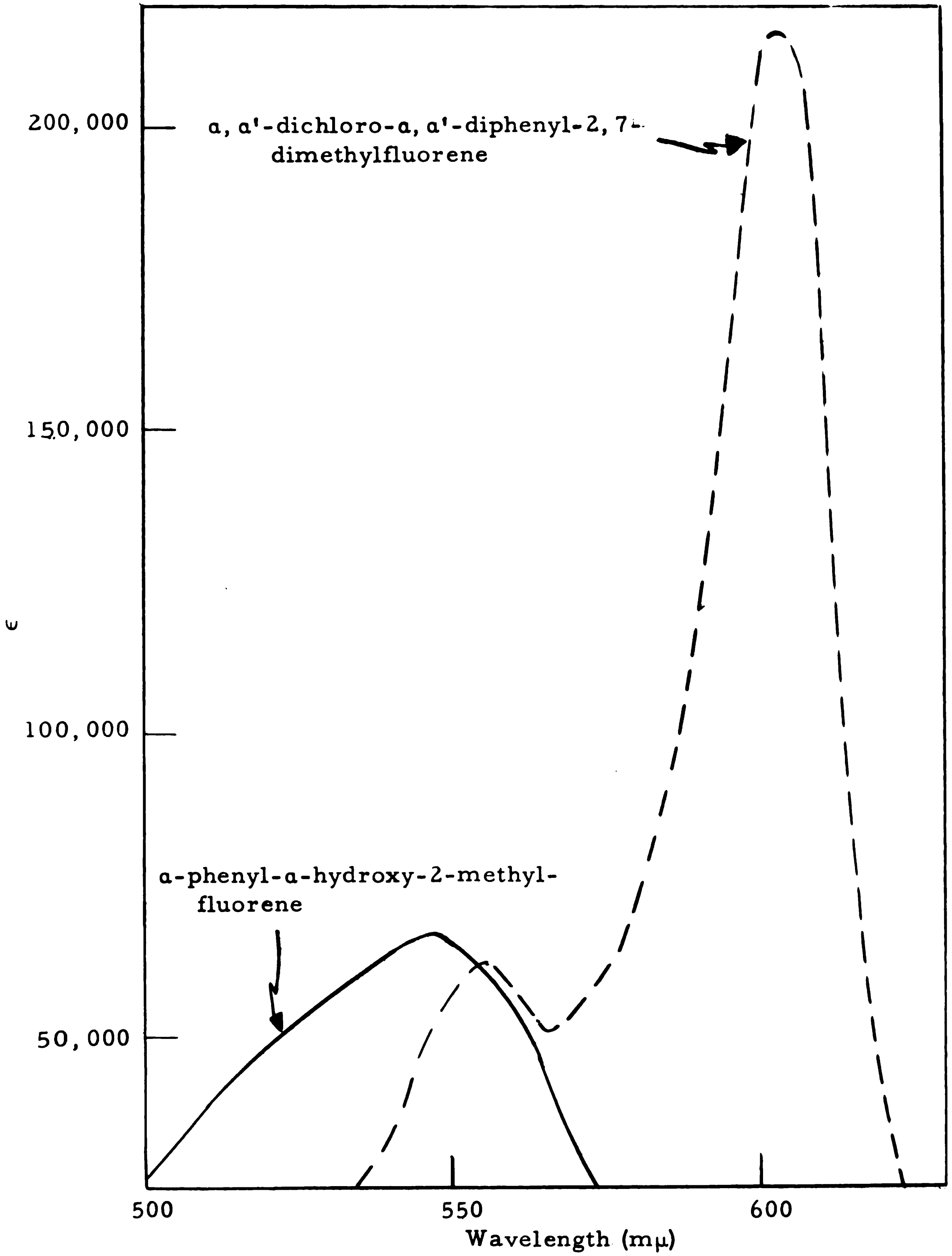


Figure 12. Visible spectra of a-phenyl-a-hydroxy-2-methylfluorene and a, a'-dichloro-a, a'-diphenyl-2, 7-dimethylfluorene in concentrated sulfuric acid.

Table 10. Observed Visible Absorption Maxima at 554 and 603 mμ of α, α'-Dichloro-α, α'-diphenyl-2, 7-dimethylfluorene (1.2 x 10^{-5} moles/liter) in Varying Concentrations of Sulfuric Acid

Wt. Per Cent H_2SO_4	H_{R+}	Absorbance (A) 554 mμ	Absorbance (A) 603 mμ
70.0	-11.68	0.39[a]	0.00
71.0	-12.02	0.48[a]	0.00
72.0	-12.40	0.55[a]	0.02
73.0	-12.75	0.68[a]	0.03
74.0	-13.10	0.74[a]	0.03
75.0	-13.50	0.80[a]	0.03
78.0	-14.60	0.88[a]	0.10
79.0	-14.91	0.83[a]	0.15
80.0	-15.28	0.77[a]	0.23
81.0	-15.60	0.77[b]	0.40
82.0	-15.94	0.70[c]	0.60
83.0	-16.24	0.74[d]	0.82
84.0	-16.58	0.73	1.18
85.0	-16.87	0.69	1.62
92.0	-18.99	0.69	2.38
96.0	-20.08	0.75	2.60

a. 547 mμ; b. 549 mμ; c. 550 mμ; d. 552 mu.

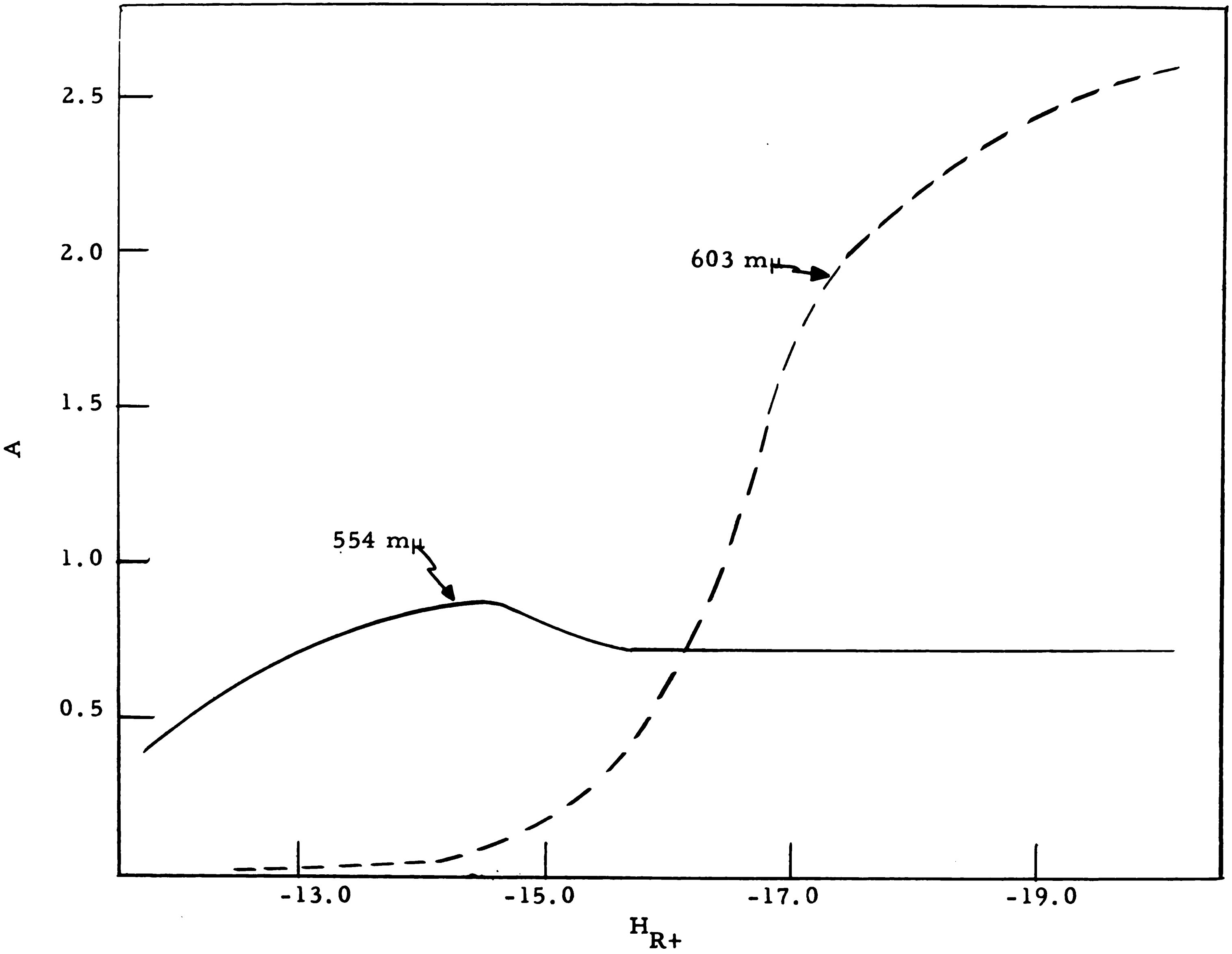


Figure 13. Plot of A versus H_{R+} for α,α'-dichloro-α,α'-diphenyl-2,7-dimethylfluorene.

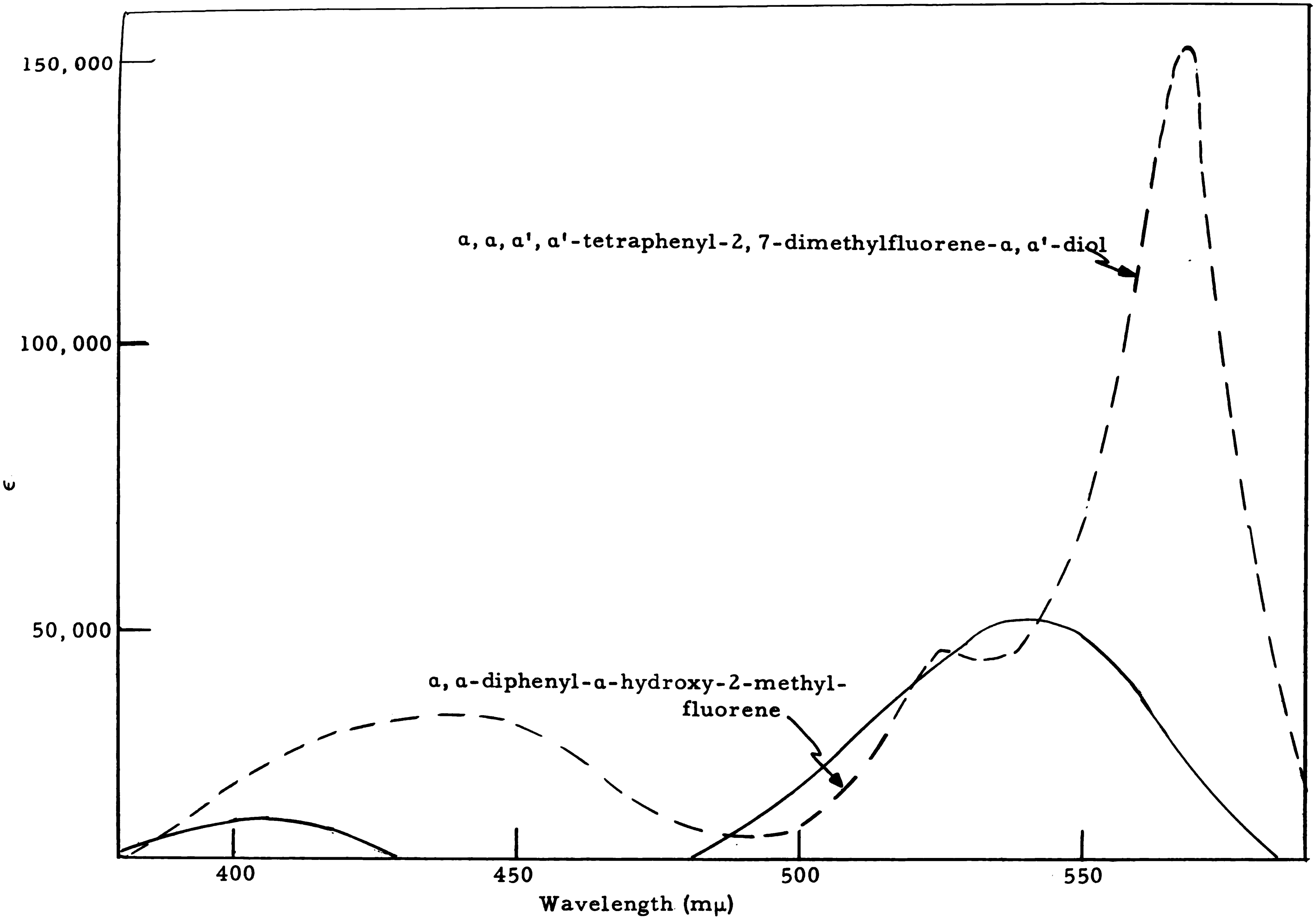


Figure 14. Visible spectra of a, a-diphenyl-a-hydroxy-2-methylfluorene in 78% sulfuric acid and a, a, a', a'-tetraphenyl-2, 7-dimethylfluorene-a, a'-diol in concentrated sulfuric acid.

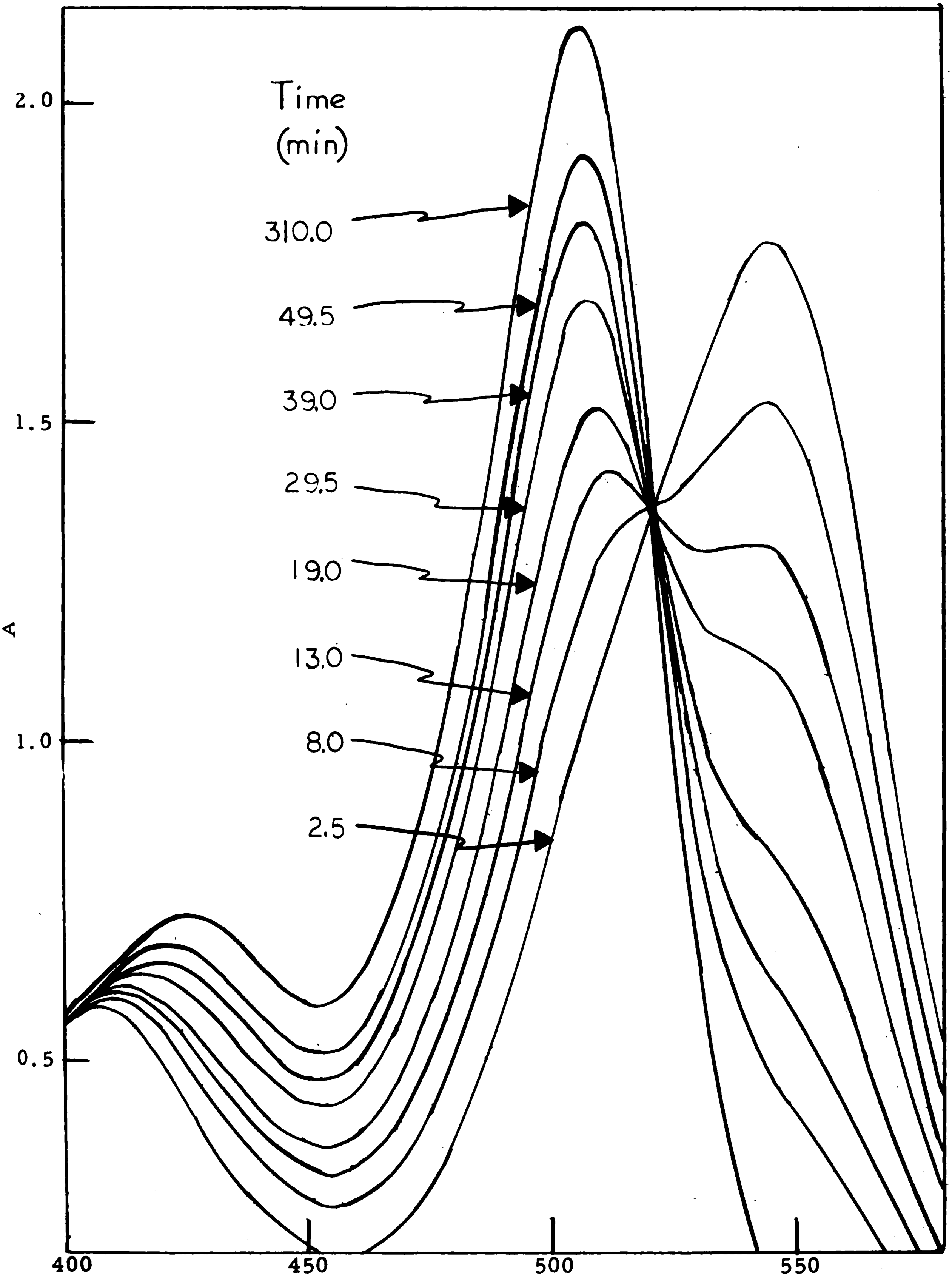


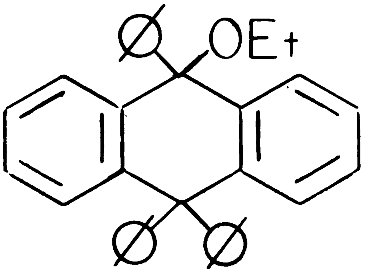
Figure 15. Change in the visible spectrum of α, α-diphenyl-α-hydroxy-2-methylfluorene in 93.9% sulfuric acid with time.

of the spectrum in 93.9% sulfuric acid (note that the initial maxima, those attributed to the cation, occur at 545 and 408 mμ in this more concentrated acid). The time for completion of one-half of the reaction was 22 minutes (34.6×10^{-3} min.$^{-1}$). Table 11 gives the observed absorbance at 535 mμ and 404 mμ for solutions of LI in sulfuric acid between 45 and 65%. A plot of H_{R+} versus A is shown in Figure 16. The pK_R is -6.5.

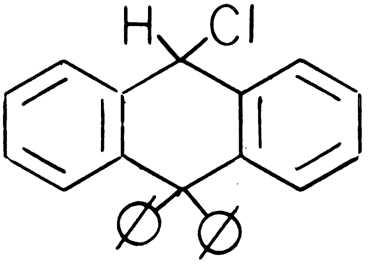
The spectrum of the corresponding bis-diol LII in concentrated sulfuric acid is shown in Figure 14. The purple solution has maxima at 568 mμ (ϵ = 152,000), 525 mμ (ϵ = 46,000) and 440 mμ (ϵ = 35,000).

D. The Anthracene Diols and Carbinols

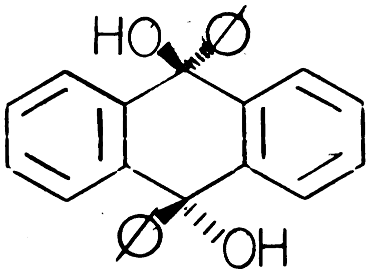
The compounds whose spectra are discussed in this section are:



LIII



LIV



LV

The assignment of the trans configuration for LV is based on infrared studies (115).

Compound LIII dissolved in concentrated sulfuric acid to form a yellow solution. Its visible spectrum showed a maximum at 438 mμ (ϵ = 22,000). Solutions of LIII showed no visible absorbance in sulfuric acid whose concentration was less than 59%. Figure 17 shows the visible spectrum of LIII in 98% sulfuric acid. Table 12 records the observed absorbances (A) at 438 mμ for solution of LIII in varying concentrations

Table 11. Observed Visible Absorption Maxima at 404 and 535 mμ of α, α -Diphenyl-α-hydroxy-2-methylfluorene (4.0 x 10^{-5} moles/liter) in Varying Concentrations of Sulfuric Acid

Wt. Per Cent H_2SO_4	H_{R+}	Absorbance (A) 404 mμ	Absorbance (A) 535 mμ
45.0	-5.40	0.04	0.06
46.0	-5.61	0.06	0.10
47.0	-5.80	0.16[a]	0.17
48.0	-6.00	0.18[a]	0.26
49.0	-6.20	0.25[a]	0.48
50.0	-6.47	0.30[a]	0.70
51.0	-6.62	0.46	1.34
52.0	-6.83	0.56	1.75
53.0	-7.10	0.64	2.00
54.0	-7.23	0.68	2.10
61.0	-8.90	0.70	2.14[b]
64.0	-9.76	0.70	2.15[b]

a. 400 mμ; b. 538 mμ.

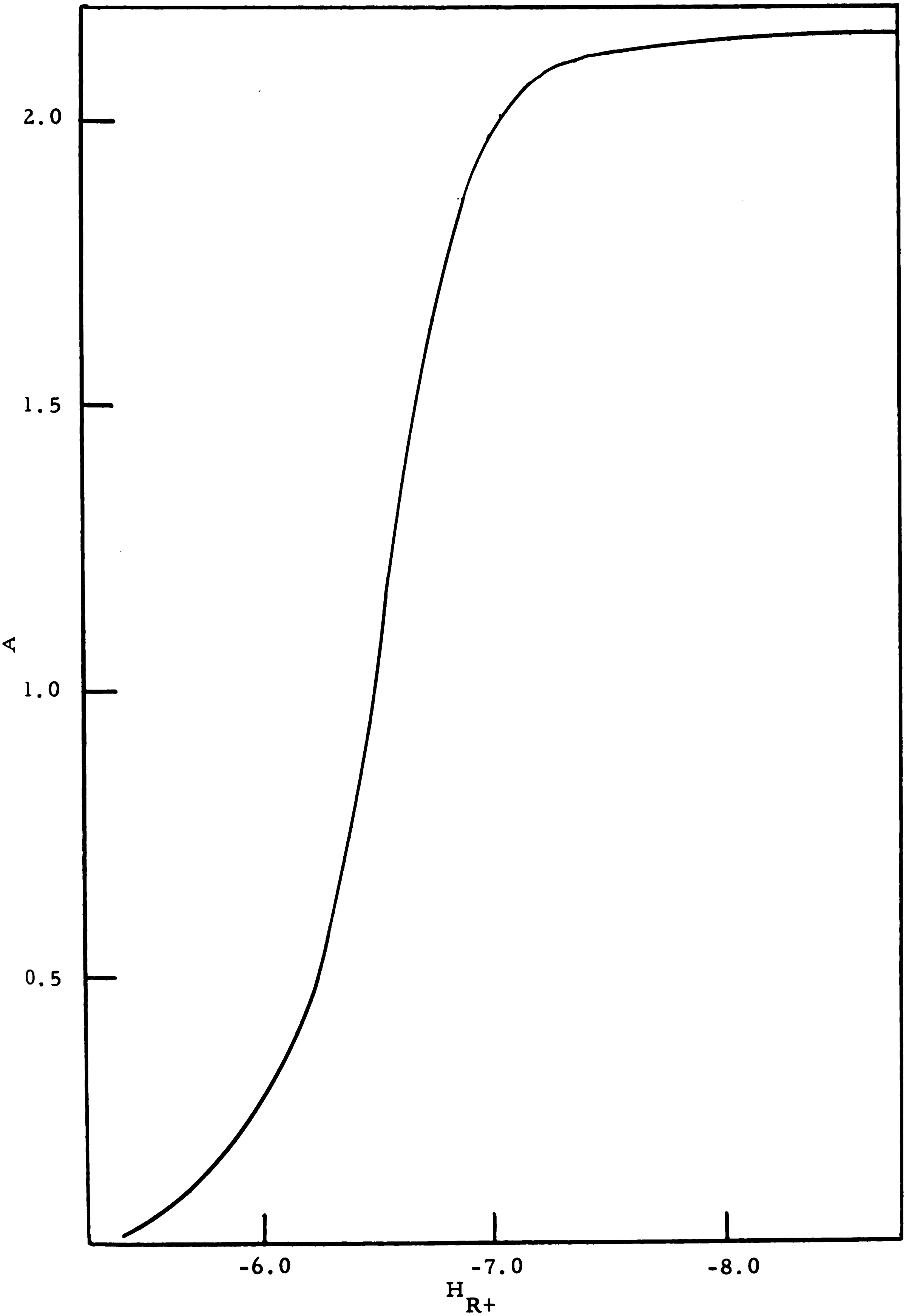


Figure 16. Plot of A versus H_{R+} for α, α-diphenyl-α-hydroxy-2-methylfluorene.

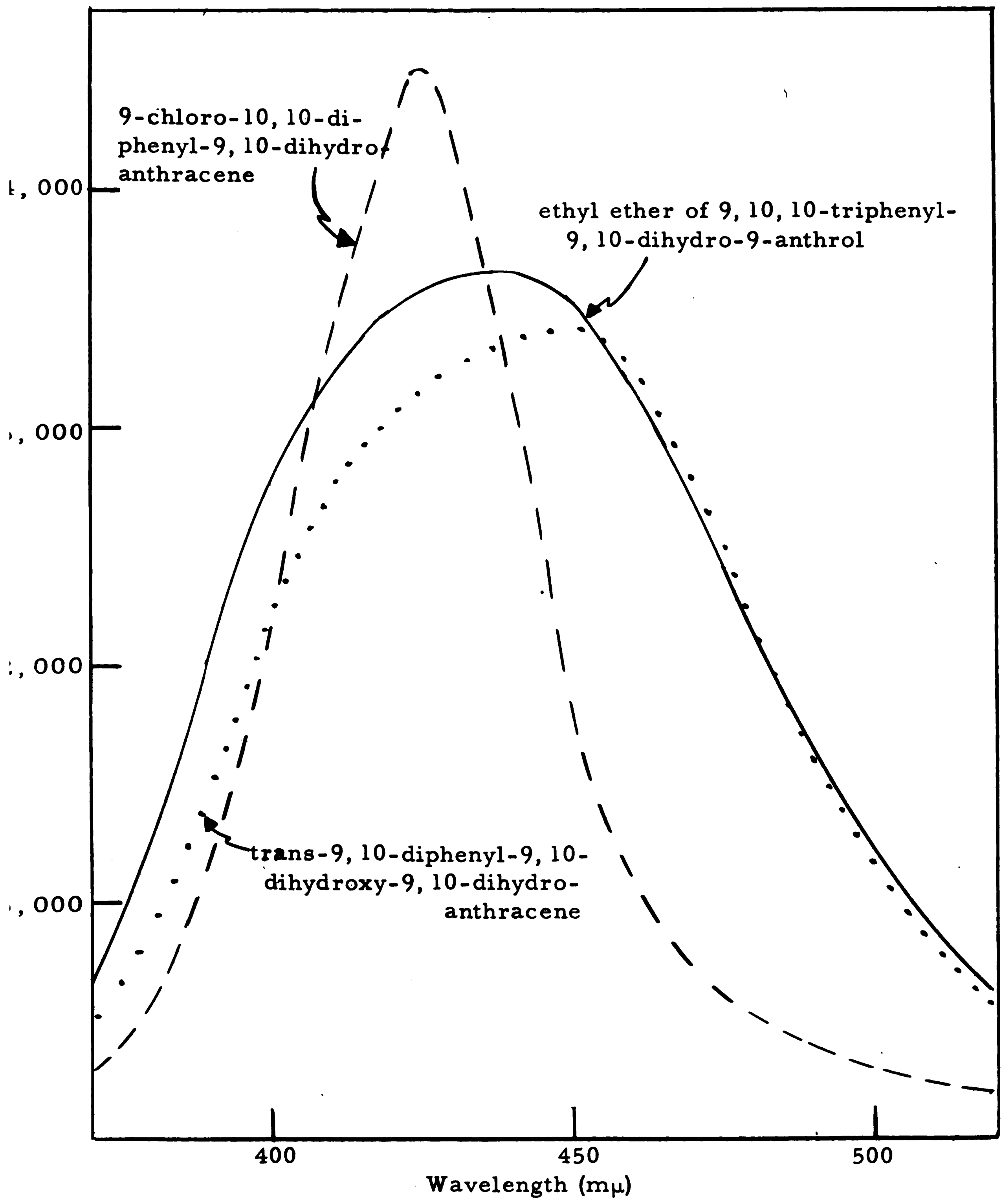


Figure 17. Visible spectra of the ethyl ether of 9, 10, 10-triphenyl-9, 10-dihydro-9-anthrol and 9-chloro-10, 10-diphenyl-9, 10-dihydroanthracene in concentrated sulfuric acid and trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene in 62% sulfuric acid.

Table 12. Observed Visible Absorption Maxima at 438 mμ of the Ethyl Ether of 9, 10, 10-Triphenyl-9, 10-dihydro-9-anthrol (2.6 x 10^{-5} moles/liter) in Varying Concentrations of Sulfuric Acid.

Wt. Per Cent H_2SO_4	H_{R+}	Absorbance (A)
60.0	-8.67	0.05
61.0	-8.90	0.08
62.0	-9.17	0.14
63.0	-9.45	0.22
64.0	-9.76	0.33
66.0	-10.37	0.53
70.0	-11.67	0.57
75.0	-13.49	0.57

of sulfuric acid (between 60 and 75%). A plot of A versus the H_{R+} of the solution is shown in Figure 18. The pK_R was found to be -9.6.

Compound LIV also gave a yellow solution when dissolved in concentrated sulfuric acid. The visible spectrum of this cation, which is shown in Figure 17, had a peak of 425 mμ (ϵ = 27,000). No pK_R studies were done on this compound.

Compound LV dissolved in concentrated sulfuric acid with formation of a deep blue color. This color was formed with sulfuric acid 76% and stronger. In sulfuric acid below 70%, compound LV dissolved with formation of a yellow to orange color. Figure 17 shows the visible spectrum of LV in 62% sulfuric acid. Table 13 gives the observed absorbances at 450 mμ for solutions of LV in sulfuric acid between 51 and 65%. A plot of H_{R+} versus A is shown in Figure 18. The pK_R was -8.4.

In sulfuric acid between 60 and 74%, solutions of LV tended to fade. The rate of change was very rapid at 74%. In 62% acid this change was followed with time. The maximum at 450 mμ (ϵ = 20,500) decreased and was replaced by maxima at 340, 360, 380 and 402 mμ (ϵ's of 8,300, 7,000, 8,300 and 8,300 respectively) (see Figure 19).

The visible spectrum of the blue solution formed when LV was dissolved in 78% sulfuric acid is shown in Figure 20. Also shown in Figure 20 is the spectrum of 9,10-diphenylanthracene in 97% sulfuric acid. The latter compound was isolated upon hydrolysis of a solution of LV in 97% sulfuric acid (61).

Figure 21 depicts the visible spectrum of LV in 97% sulfuric acid. This spectrum was taken within five minutes of the time that the solution was prepared. Figure 21 also shows the visible spectra of 9,10-diphenylanthracene and 4-phenyl-2,3-benzofluoranthene in 97% sulfuric acid. The latter compound was formed with 9,10-diphenylanthracene in the hydrolysis experiment mentioned above.

Table 13. Observed Visible Maxima a 450 mμ of 9, 10-Diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene (7.3 x 10^{-5} moles/liter) in Varying Concentrations of Sulfuric Acid

Wt. Per Cent H_2SO_4	H_{R+}	Absorbance (A)
51.0	-6.62	0.05
53.0	-7.02	0.10
55.0	-7.46	0.20
56.6	-7.80	0.44
57.5	-8.00	0.55
58.0	-8.09	0.73
59.0	-8.37	0.95
60.0	-8.61	1.10
61.0	-8.96	1.30
62.0	-9.20	1.48
63.0	-9.45	1.46
64.0	-9.74	1.50

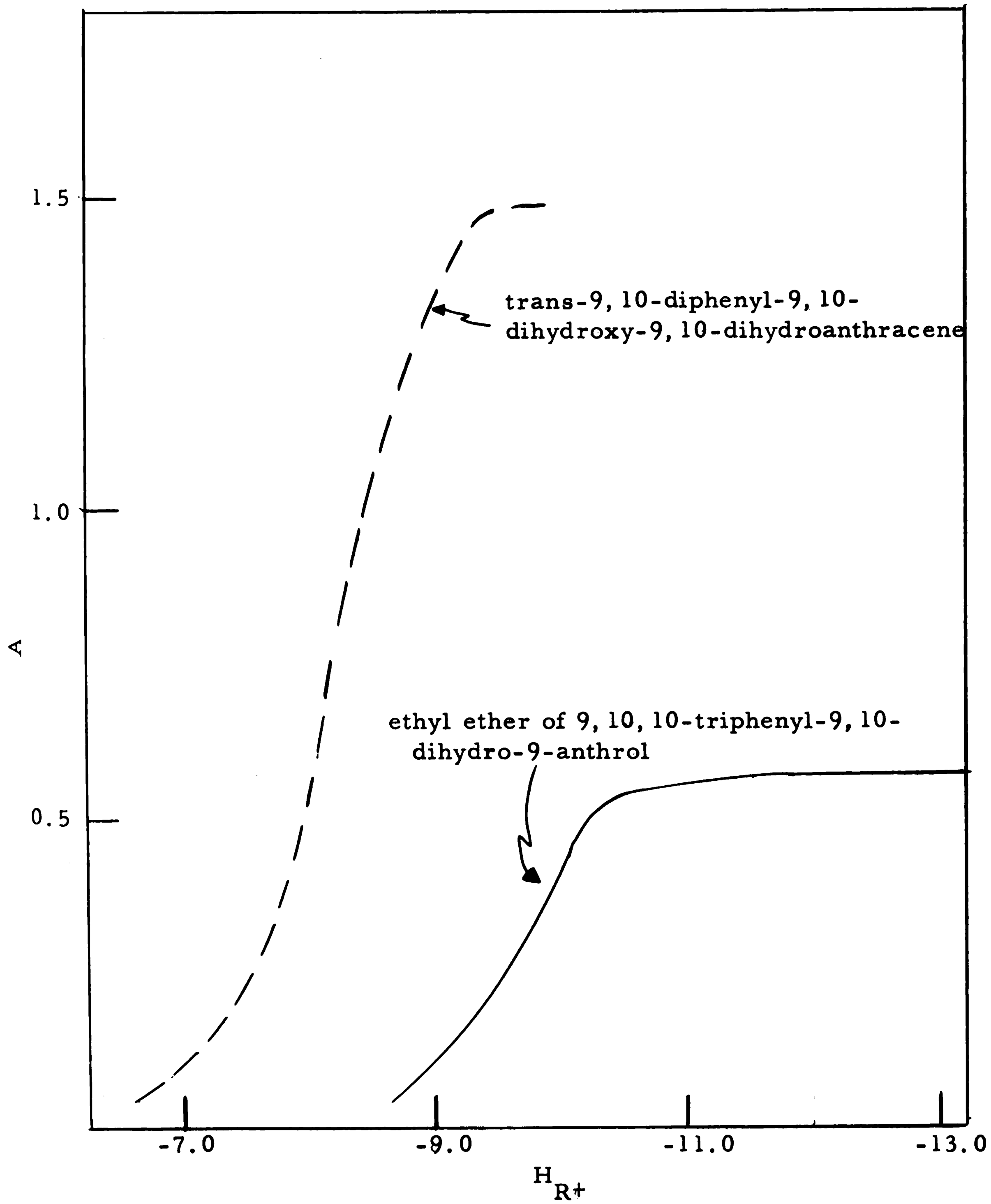


Figure 18. Plot of A versus H_{R+} for the ethyl ether of 9, 10, 10-triphenyl-9, 10-dihydro-9-anthrol and trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene.

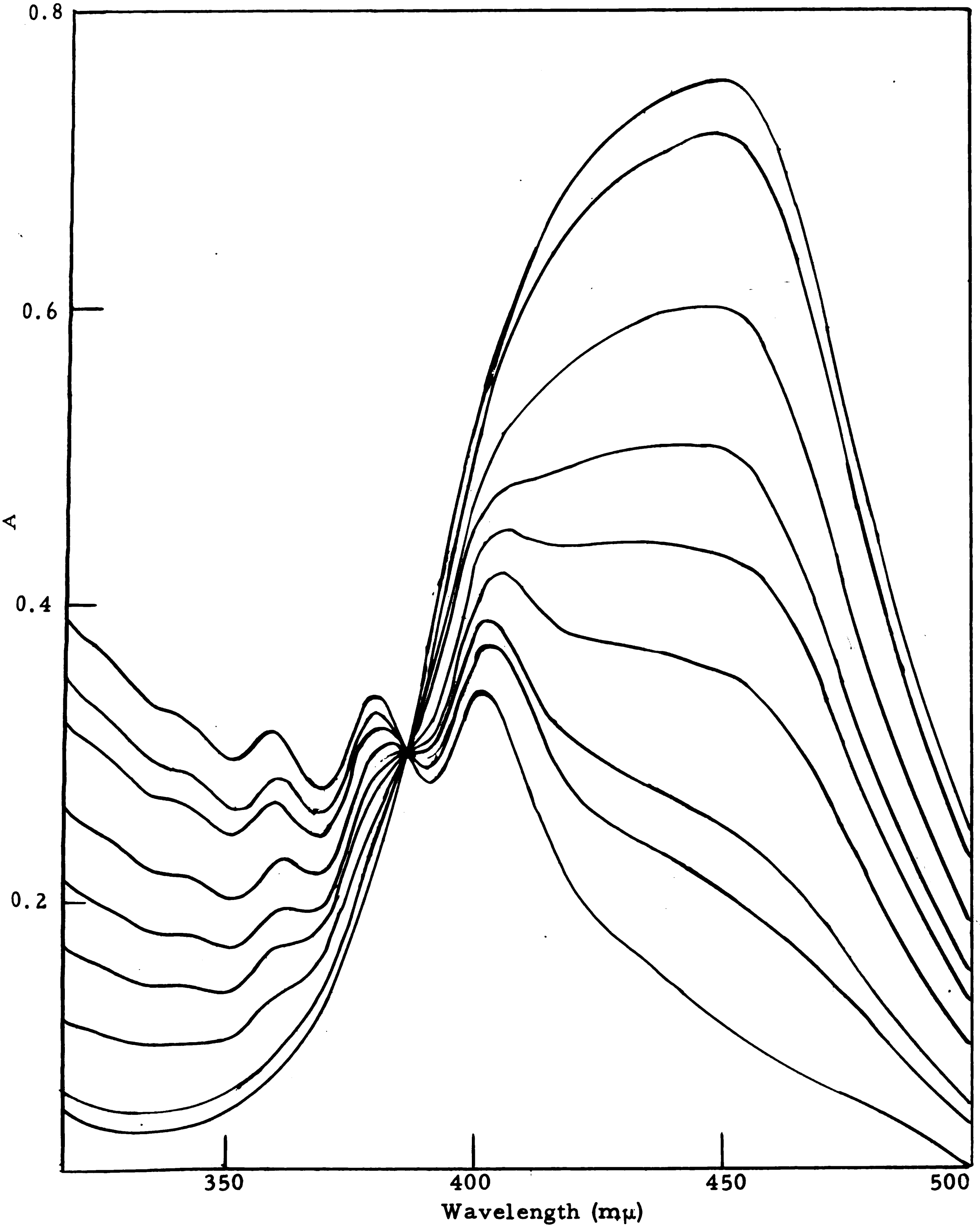


Figure 19. Change in the visible spectrum of trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene in 62% sulfuric acid with time.

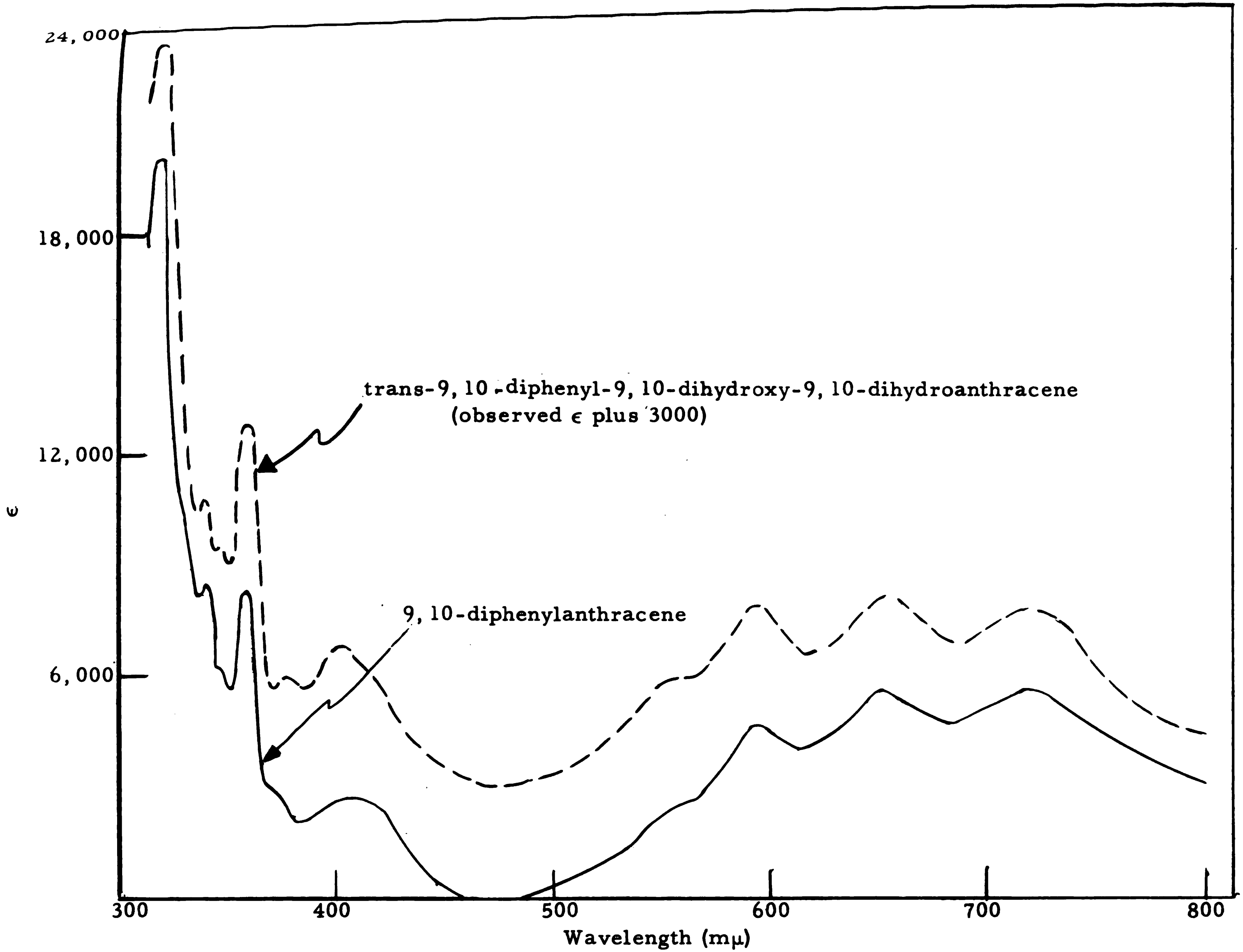


Figure 20. Visible spectra of 9, 10-diphenylanthracene in concentrated sulfuric acid and trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene in 78% sulfuric acid.

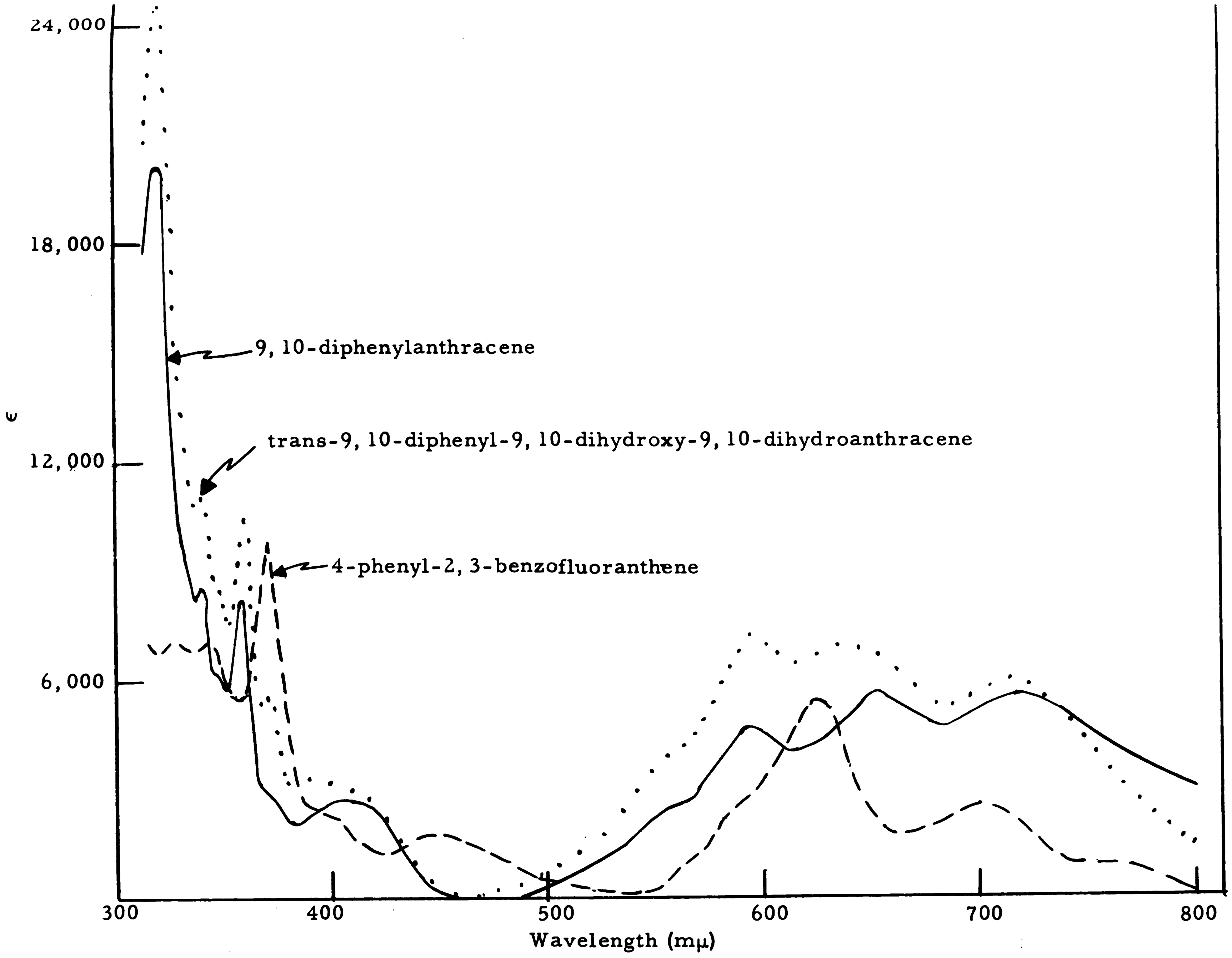
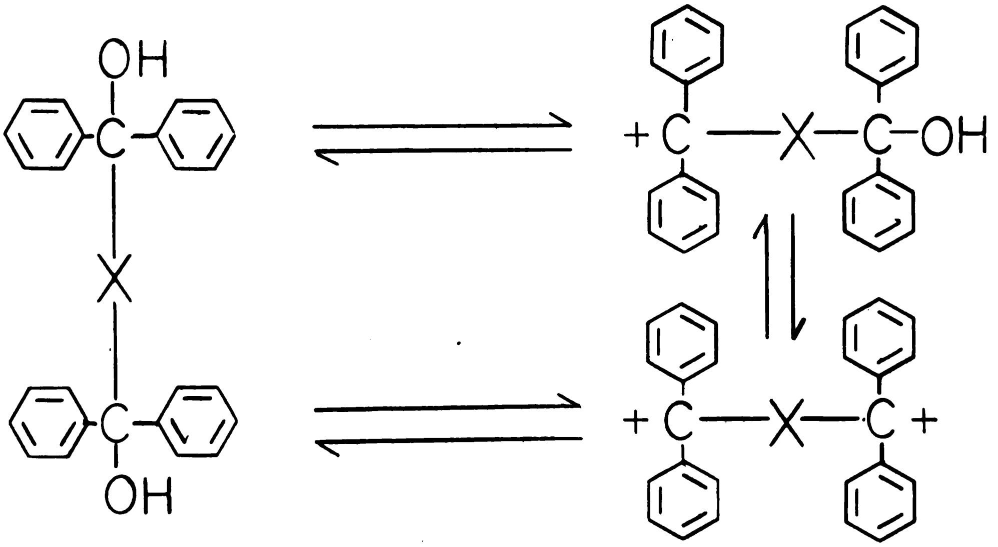


Figure 21. Visible spectra of 9, 10-diphenylanthracene, 4-phenyl-2,3-benzofluoranthene and trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene in concentrated sulfuric acid

When a solution of LV in 97% sulfuric acid was allowed to stand for 16 hours, the visible spectrum underwent a change. This is seen in Figure 22. Also shown in Figure 22 is the spectrum of 4-phenyl-2, 3-benzofluoranthene in 97% sulfuric acid.

III. Interpretation of the Spectra

It has been shown that in sulfuric acid, aryl carbinols and diols undergo reversible color formation. Ionization of carbinols was discussed on page 2 (see equation 1). With diols, however, ionization can either occur stepwise or all at once:



(54)

(55)

In all examples studied in this thesis, X was aromatic. Evidence, mainly in the form of ionization constants, will be presented to show that the reactions represented by equations 54 and 55 can occur and that it is a function of the type of aromatic placed between the two sites to be ionized.

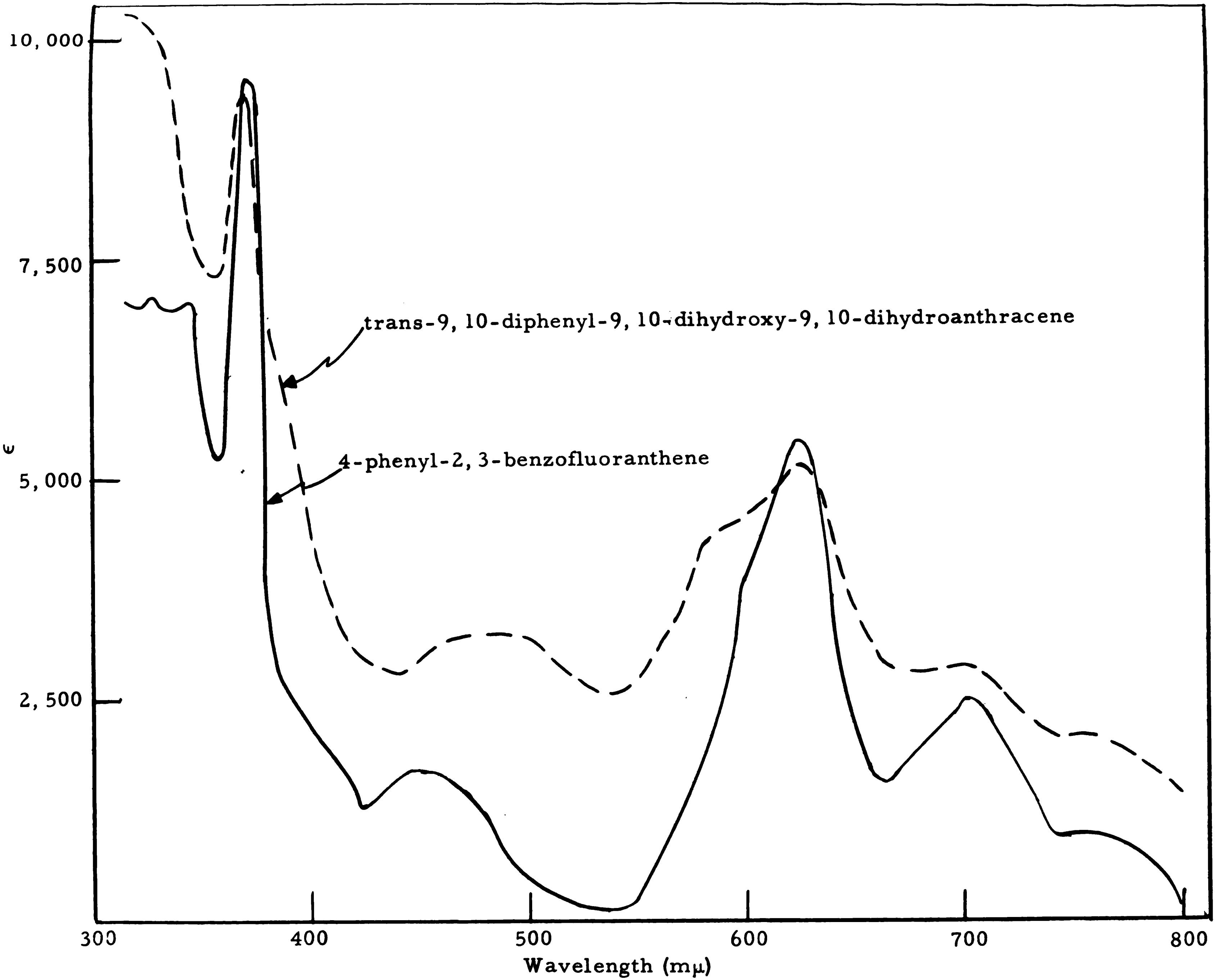


Figure 22. Visible spectra of 4-phenyl-2,3-benzofluoranthene in concentrated sulfuric acid and trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene in concentrated sulfuric acid after 16 hours.

A. The Xylene Diols

At first glance, it would appear that the xylene diols are ionized all at once (see equation 55) since the position of the absorption maximum does not shift with changing sulfuric acid concentration. This could indicate the formation of only one species on ionization and not the two required by the stepwise process. The meta and para derivatives, however, each showed two breaks in the plot of A versus H_{R+} (Figure 2). If one makes the assumption that either the spectra of the monocation and the dication are indistinguishable or that the maximum of one masks the maximum of the other then it appears that ionization does occur in a stepwise manner.

If the xylene diols ionize in a stepwise fashion (see equation 54) and if it is assumed that the dication is not formed until monocation formation is complete (this is reasonable since the cation is an electron withdrawing group and would make the second -OH more difficult to protonate) then several possibilities arise. The ϵ_{max} of the dication may be less than, greater than or equal to that of the monocation. The first two are depicted in Figures 23 and 24, respectively. When the two are equal, there is only one break in the curve and only one apparent pK_R. The experimentally observed pK_R plots for the para and meta diols (see Figure 2) are very similar to Figure 24. It can be seen that the ϵ_{max} of both monocations are identical whereas the intensity of the absorption of the meta dication is greater than that of the para dication. This is in agreement with the n.m.r. data discussed on page 20 which showed that the central ring in the meta dication carried an appreciable portion of the positive charge, whereas in the para dication this was not the case. In other words, the ground state is more stabilized in the meta than in the para dication, i.e., it is of lower energy.

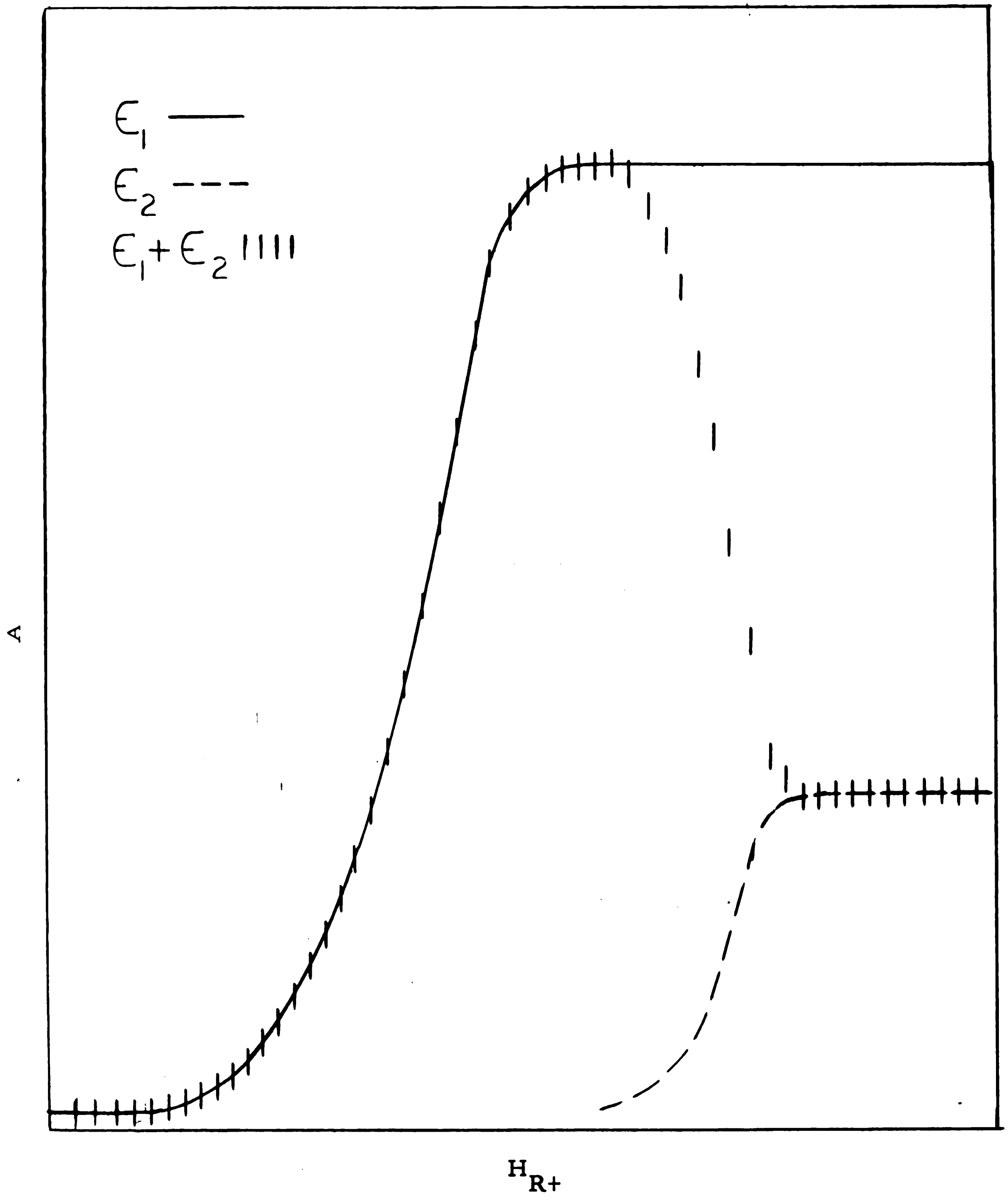
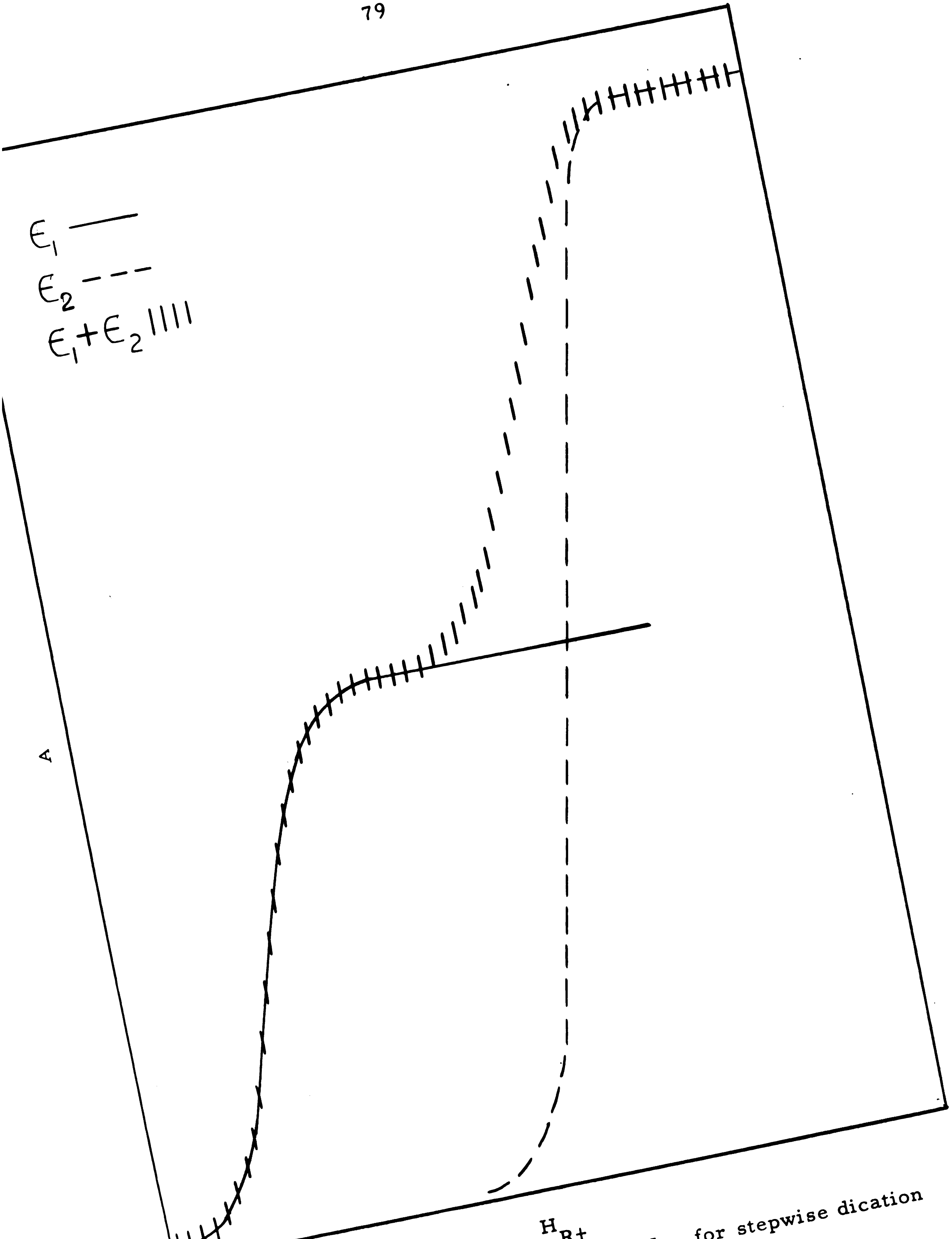


Figure 23. Theoretical plot of A versus H_{R+} for stepwise dication formation where $\epsilon_1 > \epsilon_2$.



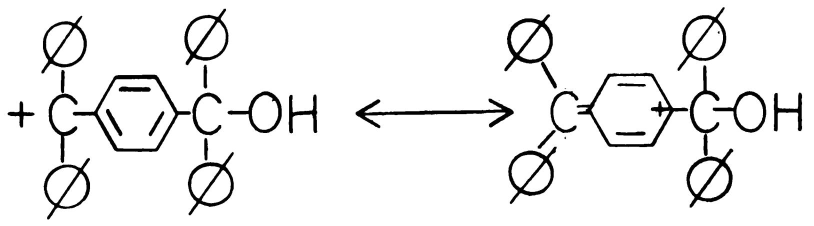
Theoretical plot of A versus H_{R+} for stepwise dication where $\epsilon_2 > \epsilon_1$.

It was assumed above that in order to explain the two pK_R's, either the monocation and dication had similar absorption maxima or that one masked the other. By careful examination of the spectra of the meta and para diols in the region between the pK_R's it can be concluded that the latter effect occurs. In the para diol, the absorption spectrum is constant between H_{R+} of -8.00 and -10.00, i.e., a peak at 445 mμ and a shoulder at 405 mμ (see Figure 4). Since this is the region assumed to contain only monocation then these peaks are attributed to this species. At acidities higher than -10.00, the shoulder disappears and there is one peak at 450 mμ. It appears, therefore, that the dication absorbs at 450 mμ.

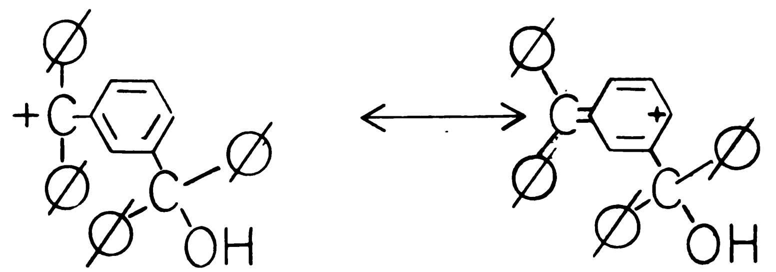
In the meta diol, this is reversed since two peaks appear at higher acidity where only one existed at lower acidity. The monocation, therefore, has a peak at 420 mμ and the dication has a peak at 420 mμ and a shoulder at 440 mμ (see Figure 3).

The fact that the para dication absorbs at a higher wavelength (lower energy) than the meta dication is readily explained (Figure 1). When the dications absorb light their π electrons are elevated from the ground state to the first excited state. It is this energy absorption that produces the observed visible spectrum. If it is assumed that the energy of the excited states of the meta and para dications are similar, then, since the meta derivative has a lower ground state energy, it must take less energy for the para dication to go to the excited state, i.e., it absorbs at a longer wavelength..

It was observed that the ionization of the second -OH was more difficult for the para than the meta diol, i.e., it occurred at higher acidity (see Figure 2). This is consistent with the fact that the monocation can inhibit the ionization of the second -OH to a greater extent in the para diol than in the meta diol.

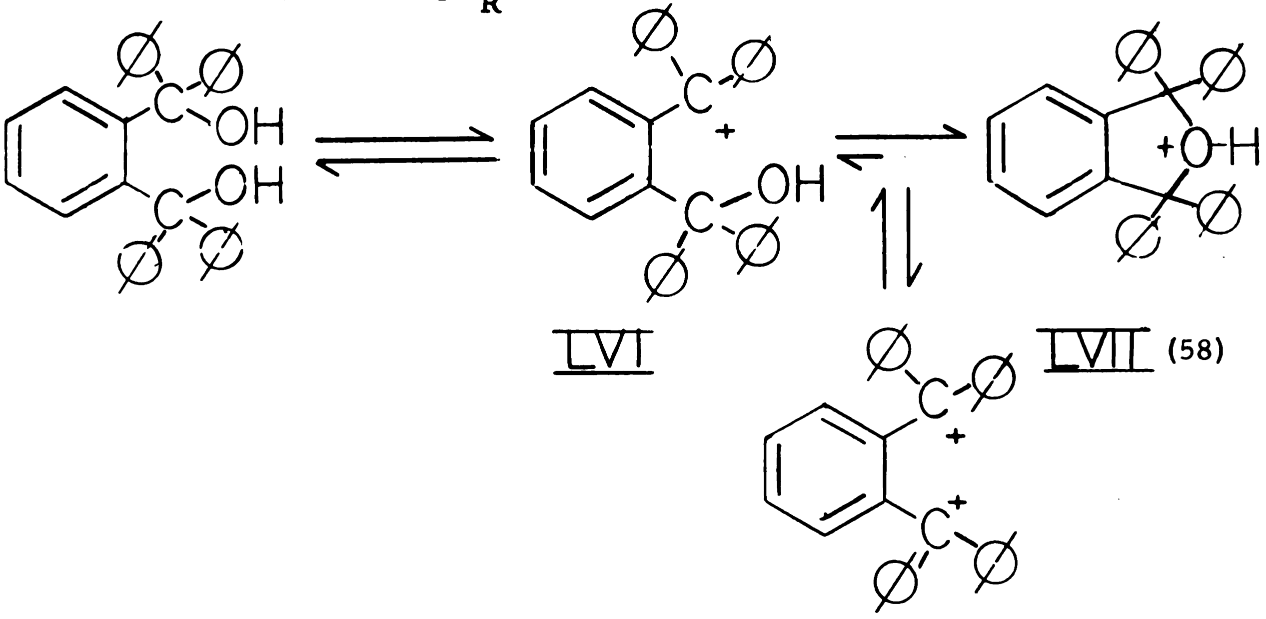


(56)



(57)

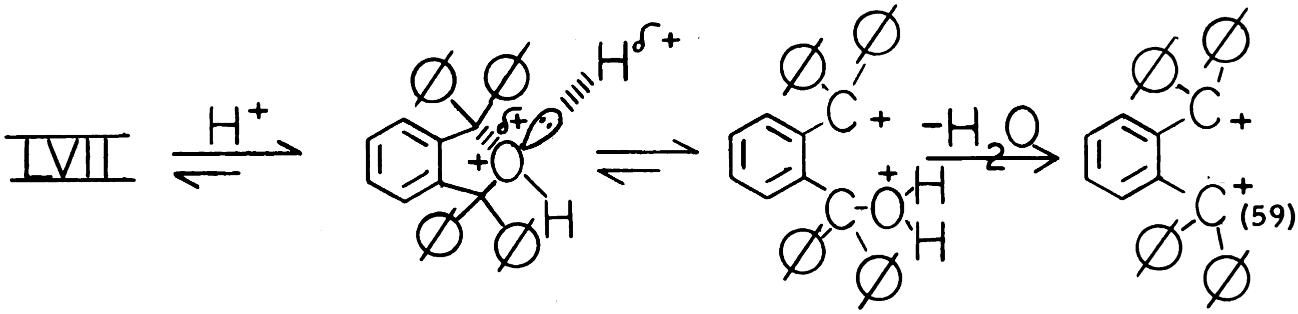
The discussion thus far has not included the ortho diol. It is a special case, because of the proximity of the positive charges in the dication. It has only one ionization point that is detectable by means of visible spectrophotometry (Figure 2). One can envision the ortho diol ionizing to the monocation which is in rapid equilibrium with the colorless protonated phthalan. This first ionization presumably occurs in the same region of acidity as the meta and para diols, i.e., at a pK_R of about -8.0. The great stability of the protonated phthalan (LVII) makes the second ionization more difficult, therefore requiring more acidic conditions, i.e., a pK_R of -16.6.



LVI

LVII (58)

The dication can either be formed from the monocation (LVI) by protonation and subsequent loss of water or by further protonation of (LVII):



(59)

From the spectral data it is clear that the tetraphenyl xylene diols ionize in a stepwise fashion to give their respective dications.

Since the spectra of the diphenyl xylene diols (compounds XXXVIII and XXXIX) were only studied in concentrated sulfuric acid the interpretations can be drawn only from the λ_{max} and ϵ_{max} of the dications. Compound XXXIX had a higher absorption intensity as well as a higher position of maximum absorption. The conclusions, therefore, are the same as with the tetraphenyl dications, i.e., the meta derivative must have a lower ground state energy than the para compound.

B. The Biphenyl Diols and Carbinols

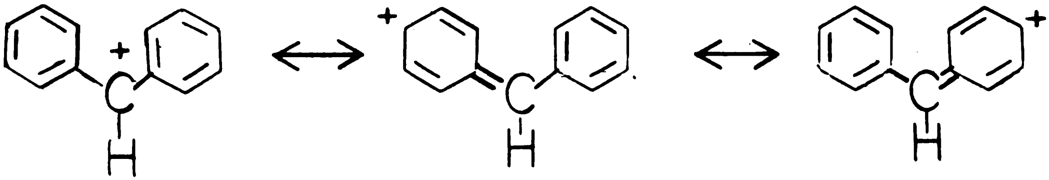
The pK_R's and spectra of the carbinols XL-XLIV were studied in order to interpret those of diols XLV-XLVIII.

In section III-A it was shown that if X was phenyl (see page 75) the diols ionized in a stepwise manner. In this section it will be demonstrated that when X is a biphenyl moiety only one pK_R is observed, i.e., ionization occurs simultaneously at both sites.

It was observed that the p, p'-and m, m'-biphenyl diols (XLV) and (XLVII) had one pK_R whereas the corresponding xylene diols had two. This is reasonable since after mono-ionization of the latter compounds, a different type of carbinol remained, i.e., one with an electron withdrawing group on the ring containing this carbinol (see equation 54).

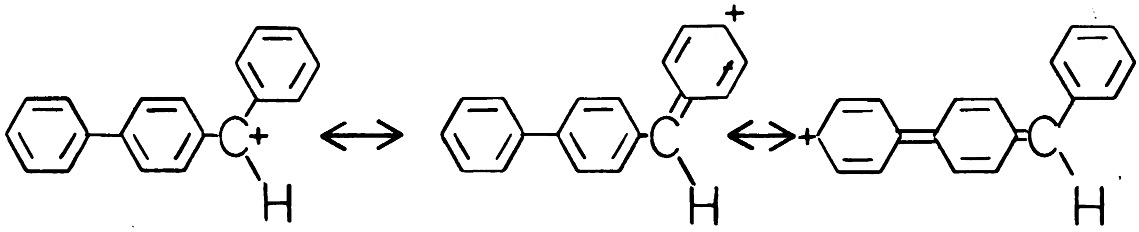
With the biphenyl diols, however, mono-ionization would leave a carbinol identical with the initial alcohol. It will therefore behave like two independent triphenylmethanols and ionize with the same pK_R (see equation 55). The o, o'-biphenyl diol (XLVIII) appeared to ionize in a stepwise manner (see below).

Compound XLV in 98% sulfuric acid had absorption maxima at 530, 442 and 410 mμ (ϵ_{max} of 90, 000, 53, 500 and 36, 000 respectively). In order to identify the types of resonance interactions occurring in this dication, the visible spectra of the cations from XLI, XLII, and XLIII were taken (see Figure 9). Compound XLI absorbed at 510 mμ (ϵ = 43, 000) and 420 mμ (ϵ = 22, 000), compound XLII at 442 mμ (ϵ = 53, 000) and compound XLIII at 536 mμ (ϵ = 90, 000). The spectra of XLII and XLIII are due to the following resonance interactions, respectively:



LVIII

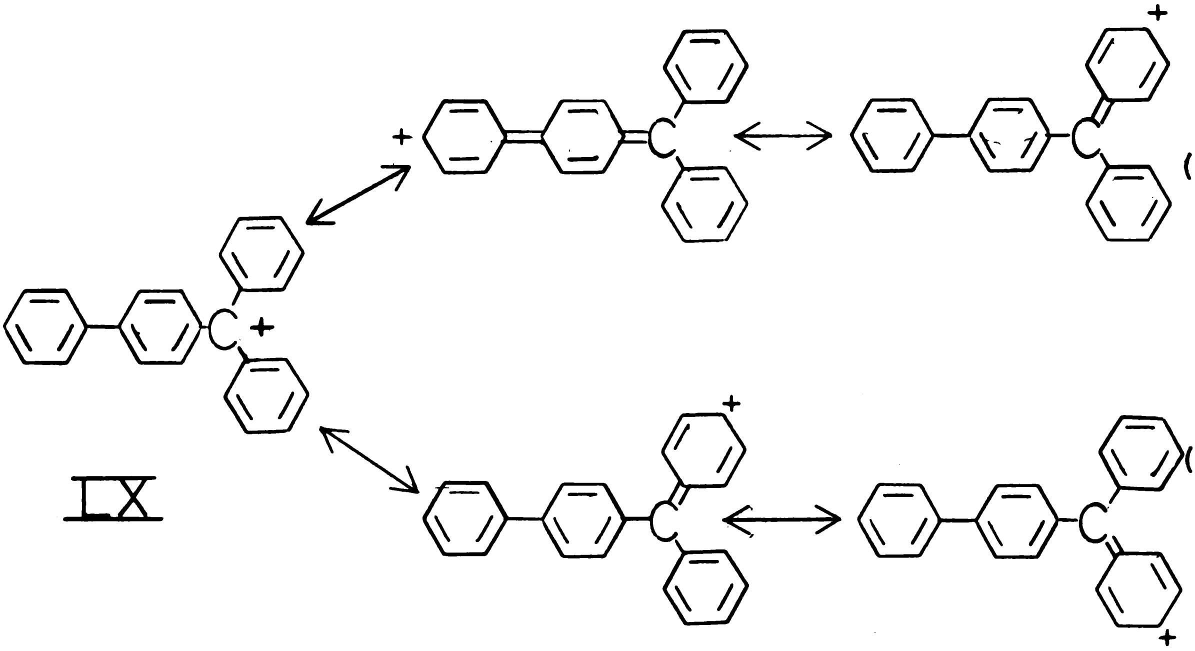
(60)



LIX

(61)

The electronic interactions of compound XLI can be explained as Lewis explained the spectrum of malachite green, i. e., with an x and a y band (47):



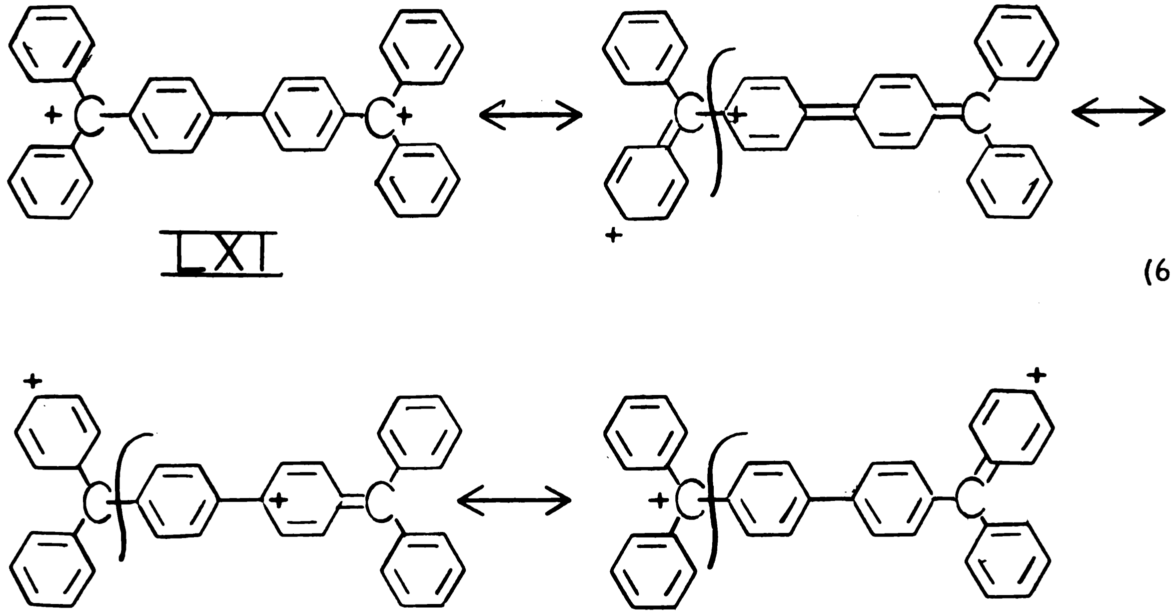
LX

(62)

(63)

The resonance shown in equation 62 is similar to that depicted in equation 61 for compound XLIII whose λ_{max} is 536 mμ. The low energy absorption in compound XLI is located at 510 mμ. This difference of 28 mμ can be attributed to the decrease in conjugation caused by the increase in steric hindrance in going from a diphenyl cation (LIX) to a triphenyl cation (LX). The absorption at 420 mμ for compound XLI can be attributed to a diphenylmethyl cation-like species (see equation 63).

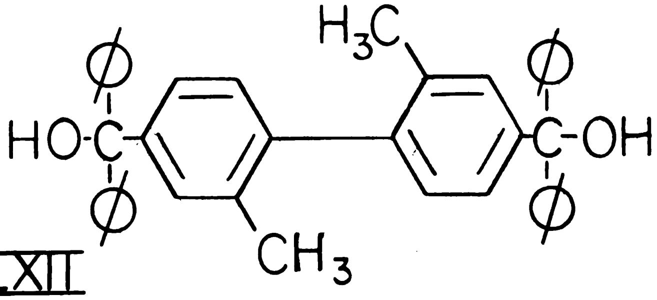
With this information, we can better understand the spectrum of XLV in concentrated sulfuric acid (see Figure 9). This dication which has absorption maxima at 530, 442 and 410 mμ, can have resonance interactions very similar to those attributable to species like LVIII and LIX.



LXI

(64)

Evidence supporting the type of resonance as depicted in 64 is obtained from the visible spectrum of LXII in concentrated sulfuric acid (83).

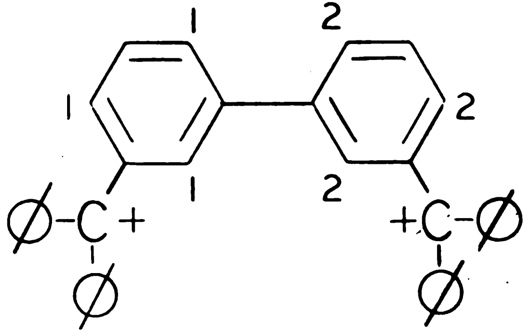


LXII

The increase in steric hindrance has decreased the possibility for the center rings becoming coplanar. This is clearly shown since the dication from LXII had maxima at 470 mμ ($\epsilon = 71,000$) and 420 mμ ($\epsilon = 56,000$).

It was shown on page 45 that compound XLI gave a different visible spectrum in concentrated sulfuric acid than in 80% acid. In acid of intermediate strength it was possible to follow this change and to observe an isosbestic point (Figure 10). The time for completion of one-half of the change was found to be 135 minutes. A further discussion of this phenomenon appears on page 91 where evidence is presented which indicates that the observed change is due to sulfonation.

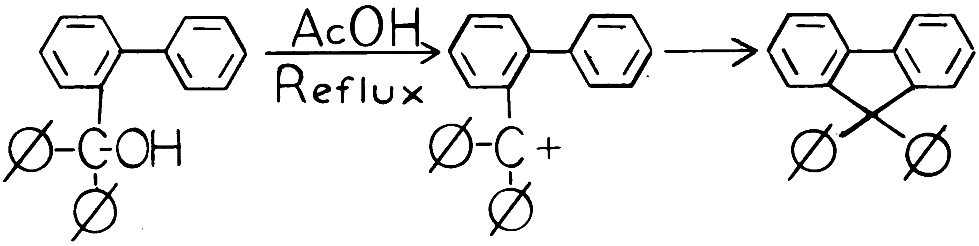
Compound XLVII like XLV, was found to have a single pK_R (Figure 8). Unlike XLV, however, the dication from XLVII had only one visible absorption maximum, which occurred at 430 mμ (see the comparison to triphenylmethyl cation's maxima in Figure 7). It is reasonable to picture this dication as two separate monocations. This view is supported by looking at the possible resonance interactions of this dication in which the middle rings are substituted meta.



Carbon atoms 1 represent the possible sites in the middle rings on which the positive charge on the left can reside and 2 is the same for the charge on the right. The dication therefore, contains two triphenylmethyl cations per molecule and should have an ϵ_{max} about twice that of triphenylmethyl cation. The ϵ_{max} for compound XLVII in sulfuric acid is 67,500 and for XL is 37,500.

The reason that the pK_R of XL is greater than that of XLVII (-7.4 and -8.4, respectively) can be due to a - I inductive effect of the middle phenyl rings which are meta to the site of ionization.

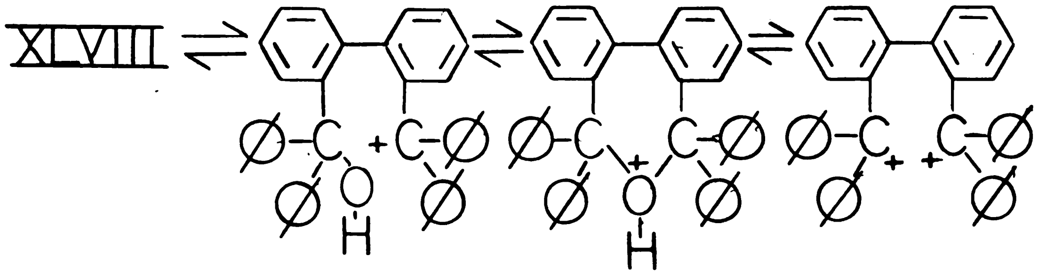
At first glance, the visible spectrum of compound LXVIII in concentrated sulfuric acid might be expected to be similar to that of XLV. The type of resonance interactions that occur in LXI can not occur in the ortho dication because of steric hindrance. It was hoped that by comparing the spectra in sulfuric acid of XLIV and XLVIII the spectrum of the latter could be interpreted. It turns out, however, that when XLIV was dissolved in sulfuric acid it turned yellow but faded within seconds. This was true of acid between 50 and 95%. This is reasonable since it is known that when XLIV is refluxed in acetic acid, 9, 9-diphenylfluorene is formed (84).



(65)

Inspection of molecular models shows that the benzene rings in the dication from XLVIII should be less coplanar than the rings in triphenylmethyl cation. This is manifested in the ϵ_{max} of the single maximum at 428 mμ which is 35, 500 or 17, 750 per triphenylmethyl cation. This indicates a decrease in resonance stabilization.

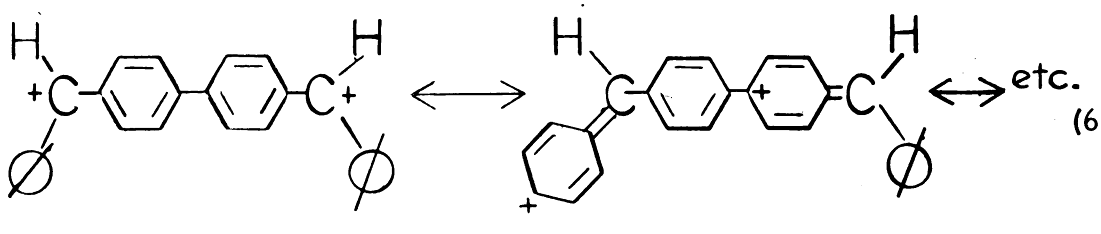
The pK_R of XLVIII was about -15. This value is similar to the pK_R of XXXIV (-16.6) which apparently ionized in a stepwise manner (see page 81). The analogous ionization of XLVIII would also give a protonated ether:



(66)

The first pK_R of this diol should be similar to that of the meta and para derivatives, i.e., about -8.3. Hydrolysis of this dication was shown to give the cyclic ether.

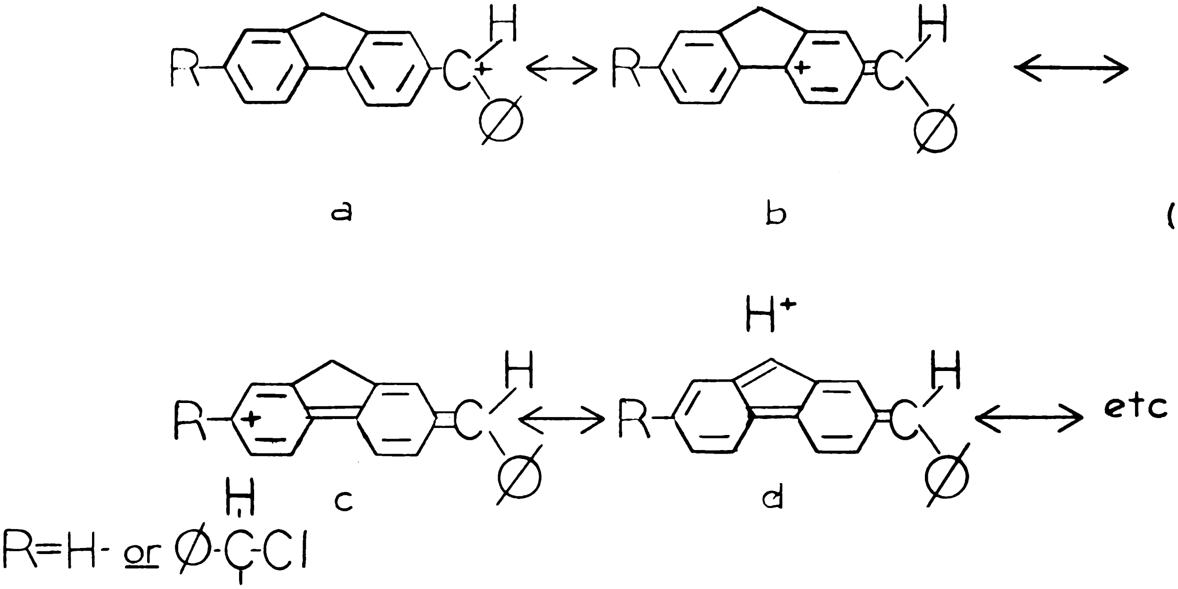
Compound XLVI, unlike XLV, appeared to have two pK_R's. Since it was not possible to determine the pK_R's of XLVI, it is from the visible spectra of this diol at several acidities that evidence is obtained for the occurrence of two ionization points. In concentrated sulfuric acid there are maxima at 563 and 420 mμ (ε = 134,000 and 13,000). Decreasing the acid strength shifts the position of the maximum as well as decreasing the absorption intensity. In sulfuric acid between 80 and 83% the peak is at 535 mμ (ε = 66,000) (see Figure 11). Compound XLIII in concentrated sulfuric acid was observed to have a maximum at 535 mμ (ε = 90,000). The tentative conclusion is that XLVI first ionizes to a monocation which resembles the ion from XLIII in its resonance interactions. The second ionization produces the dication in which the charges can resonate throughout the whole molecule:



(67)

C. The Fluorene Diols and Carbinols

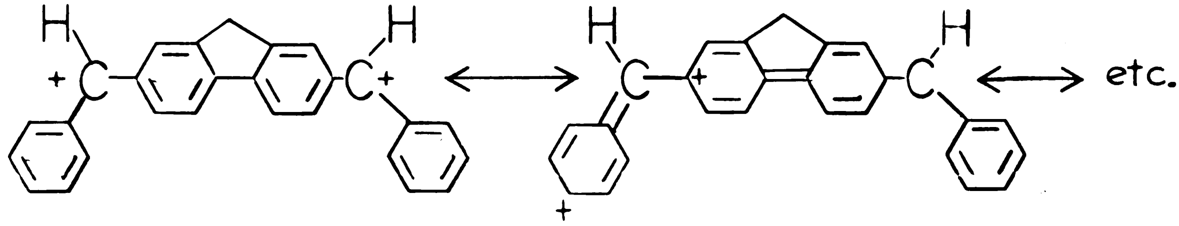
Examination of the visible spectra of XLIX and L (see page 58) in varying concentrations of sulfuric acid has clearly shown that L ionizes in a stepwise manner to the dication (Figure 13). Compound XLIX was shown to have a pK_R of about -12.0, a λ_{max} of 542 mμ (shifts to 547 mμ in concentrated acid) and an ϵ_{max} of 66,000. These data are almost identical with those for the first ionization of L which has a pK_R of -12.0, a λ_{max} of 547 mμ and an ϵ_{max} of 66,000 (at acid concentration of 75%, i.e., just prior to the onset of the second ionization). From this it appears that the monocation of compound L has the same electronic interactions as the cation from XLIX:



(68)

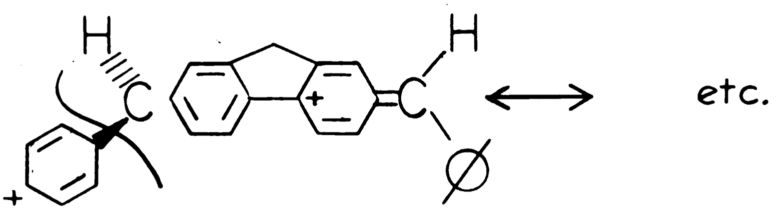
Since the positions of the absorption maxima of these two ions are similar to those for the cation derived from compound XLIII (536 mμ), they are best described by structures a-c.

The dication formed from L showed absorption maxima at 554 mμ (ϵ = 62,000) and 603 mμ (ϵ = 215,000). The latter absorption can be pictured as being due to the following type of electronic interactions:

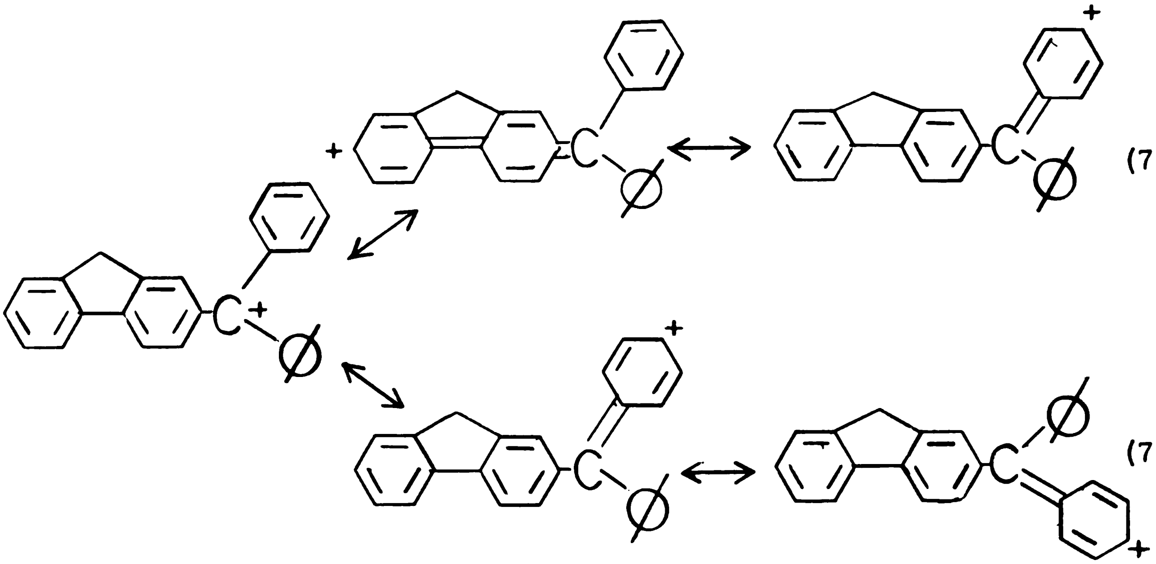


(69)

The maximum at 554 mμ can be assigned to a species similar to the one attributed to the monocation with the second charge localized on the side chain phenyl ring.



The visible spectrum of the cation derived from compound LI (Figure 14) can be interpreted in the same way as Lewis explained the spectrum of malachite green (47). There are two modes of electronic interactions that this carbonium ion can undergo:

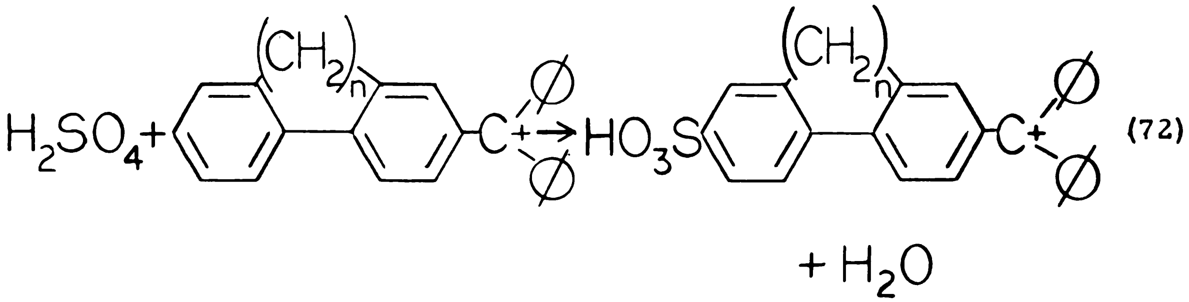

(70)

(71)

The resonance depicted in equation 70 is similar to that described above for the cation of compound XLIX. Compound LI has an absorption maximum (540 mμ) and an absorption intensity (53, 000) that is in close agreement with compound XLIX. The absorption at 405 mμ is attributed to a diphenylcation-like species, i.e., resonance as depicted in equation 71.

The pK_R of compound LI is -6.5, as compared to -7.7 for compound XLI. This is further evidence that the fluorene molecule with its planar structure is better than biphenyl as a stabilizer of positive charge (85).

It was also shown that compound LI in sulfuric acid can undergo further reaction after carbonium ion formation. This reaction is instantaneous in 97% sulfuric acid and non-existent (or very slow) in 80% acid. The rate of the reaction was followed in 93.9% sulfuric acid (see Figure 15). The time for completion of one-half of the reaction was 22 minutes. On page 45 it was shown that the time necessary for compound XLI to undergo one-half reaction was 135 minutes. Since this reaction occurred more readily in concentrated sulfuric acid and was much faster with the fluorene than with the biphenyl derivative (the former being more susceptible to electrophilic attack) it appears that the observed reaction was one of sulfonation:

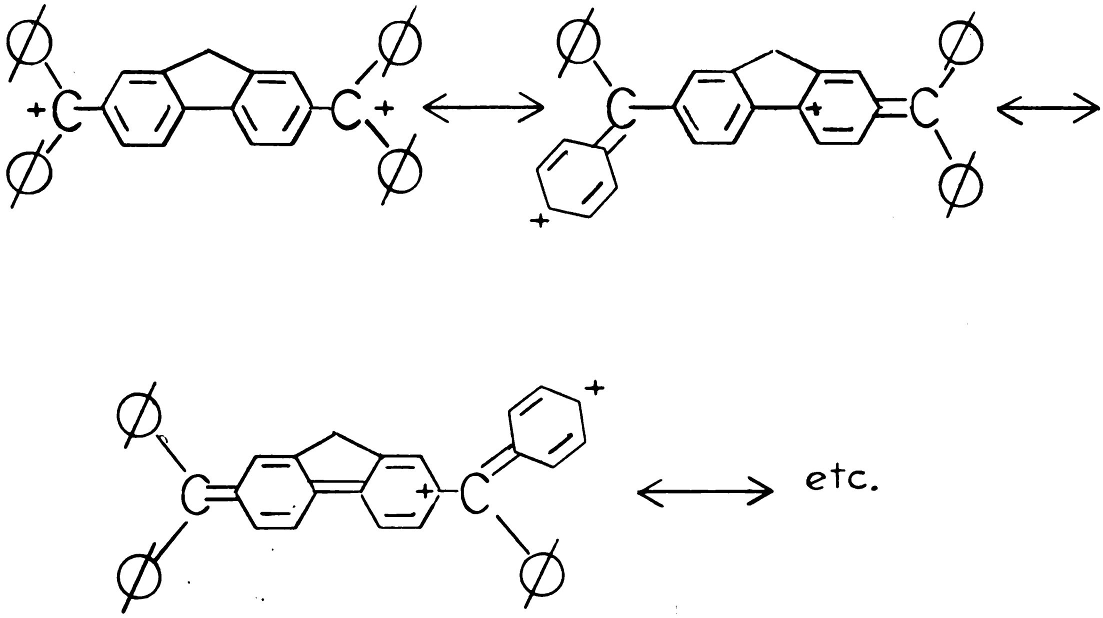


(72)

where n = 0 or 1

Further evidence for sulfonation is presented on page 102.

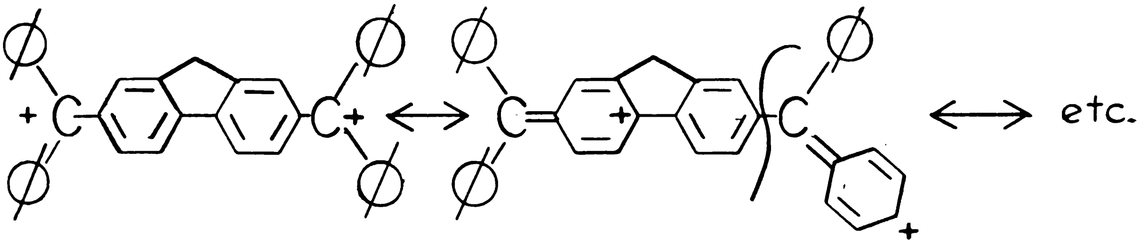
By comparing the spectrum of LII in concentrated sulfuric acid with the spectra of the other cations studied, spectral assignments can be made (Figure 14). The major absorption at 568 mμ is due to resonance throughout the entire molecule:



(73)

The reason that this absorption occurs at a lower wave length (higher energy) than that of compound L (568 mμ bs. 603 mμ) is attributed to the increase in steric hindrance relative to resonance stabilization when four instead of two phenyl groups are placed on the carbons in the 2 and 7 positions.

The absorptions at 525 and 440 mμ can be assigned to resonance structures resembling LI and diphenyl methanol in sulfuric acid, respectively:



(74)

At this point it is of interest to compare the spectra of the mono- and dications in the biphenyl and fluorene series (see Table 14). Correlations can be made between the major absorptions in the spectra of the dications. Compound F absorbs at 563 mμ. The addition of two phenyls (compound H) lowers the maximum absorption by 33 mμ or -16.5 mμ per phenyl. The same effect is noted in going from E (603 mμ) to G (568 mμ). Here there is a 35 mμ shift or -17.5 mμ per phenyl. The effect of adding a methylene bridge to go from a biphenyl to a fluorene dication also has a constant effect on the spectra. This change to a planar molecule causes a bathochromic shift. From E to F there is a change of + 40 mμ and from G to H a change of + 38 mμ is noted.

The absorption intensities of the dications also fit a general pattern. The removal of 2 phenyl rings increases the intensities by a constant factor since E/G and F/H both are equal to 1.4. The methylene bridge enhances the intensity by 1.6 (E/F) and 1.7 (G/H).

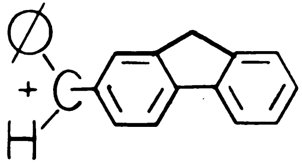
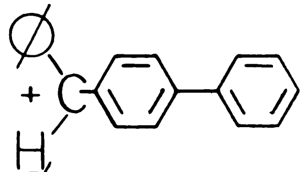
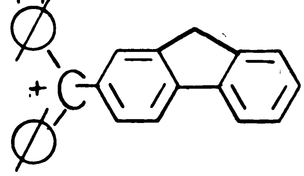
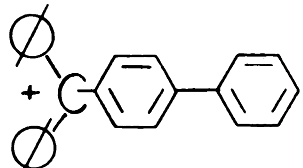
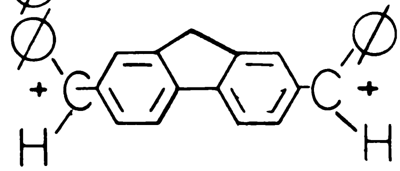
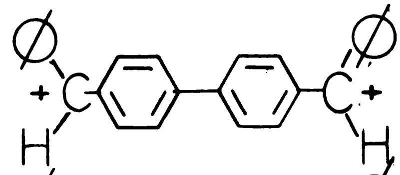
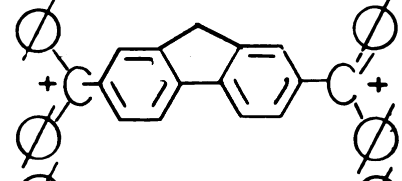
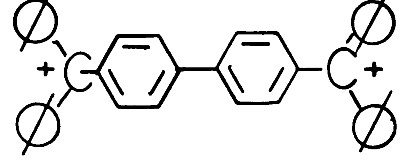
When one compares compounds A-D, no correlations are forthcoming. The cause of this might be attributed to the symmetry in the dication molecules and the lack of it in the monocations.

D. The Anthracene Diols and Carbinols

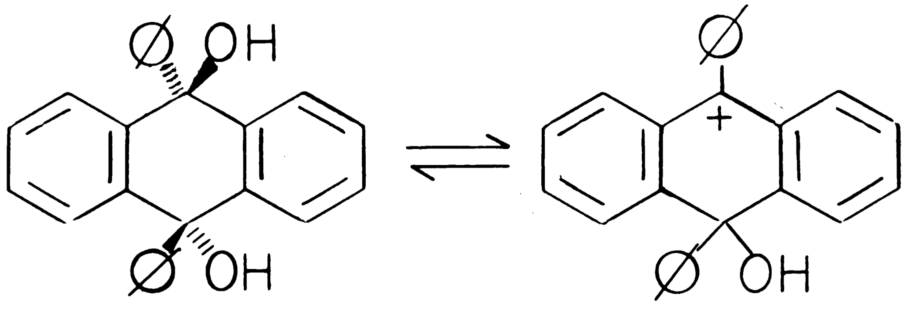
The position of the spectral maxima for LIII and LIV in concentrated sulfuric acid are typical of triphenylmethyl and diphenylmethyl-like cations (see Figure 17). The low ϵ_{max} for these compounds is due to the extra energy needed to stretch the tetrahedral angle ($109^{o}28'$) in the 9 positions of LIII and LIV to 120^{o}. This occurs because the two phenyls in the 10 position also move when this transformation occurs.

The expected similarity between the visible spectrum of LIV in sulfuric acid and the monocation from LV is seen in Figure 17.

Table 14. Visible Spectra of Some Mono- and Dications in The Biphenyl and Fluorene Series.

Compound		Wavelength (mμ)	Molar Absorbance (ε)
	A	547	66,000
	B	536	90,000
	C	540	53,000
		404	17,000
	D	510	43,000
		420	22,000
	E	603	215,000
		554	62,000
	F	563	134,000
		420	13,000
	G	568	152,000
		525	46,000
		420	35,000
	H	530	90,000
		442	53,500
		410 sh	36,000

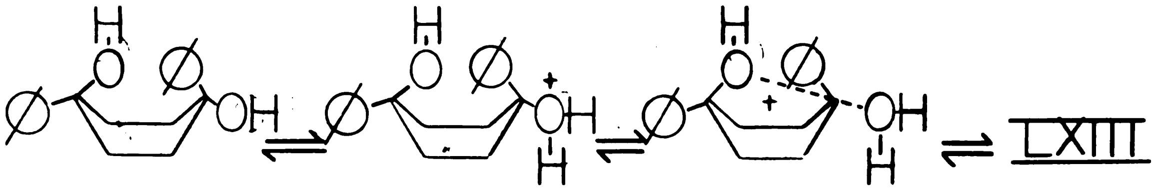
The spectrum of compound LV in sulfuric acid varied with the concentration of acid. In dilute acid (between 55 and 62%) it was possible to determine the pK_R for ionization to the monocation.



LV LXIII

(75)

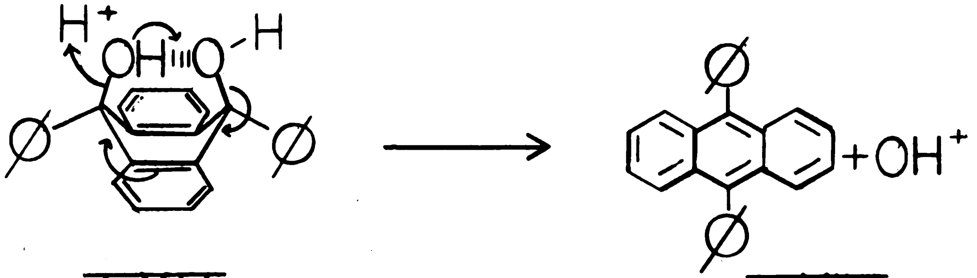
This pK_R was higher than the one for LIV (-8.4 and -9.6) (Figure 18). The difference in ease of ionization can be attributed to the second hydroxyl group in the molecule. Since the -OH groups are trans, one can assist in ionization of the other and even stabilize the carbonium ion. Looking along the side of the molecule will help in seeing this.



(76)

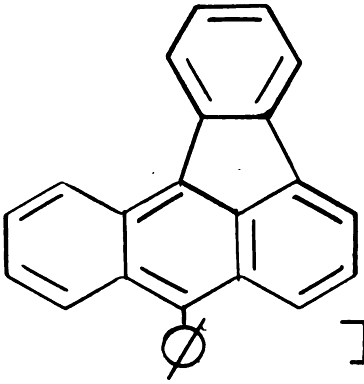
Between 62 and 75% acid, the cis analog of LV is formed (see section IV and equation 85). Figure 19 shows the change from the monocation to the cis diol in 62% acid.

In 78% sulfuric acid LV forms a blue solution. Inspection of Figure 20 shows the striking similarity between the spectrum of this solution and that of 9,10-diphenylanthracene (LXIV) in 97% sulfuric acid. LXIV is one of the hydrolysis products of LV in 97% sulfuric acid (see page 69). It is proposed that the cis-diol (LXV) does not undergo ordinary ionization but, due to the proximity of the hydroxyl groups, is involved in an intramolecular hydride transfer reaction forming LXIV. It can be seen, therefore that dication formation does not occur.



LXV LXIV (77)

The visible spectrum of LV in 97% sulfuric acid after standing for 16 hours is very similar to that of a sulfuric acid solution of 4-phenyl-2, 3-benzofluoranthene (LXVI), another hydrolysis product (61) (see Figure 12).



LXVI

The visible spectrum of LV in 97% sulfuric acid when taken immediately after mixing looks like a combination of LXIV and LXVI (Figure 21). It appears, therefore, that LXIV is formed first and this in turn reacts further to give LXVI. Since there are unidentified products obtained from the hydrolysis experiment (61), no attempt will be made to propose a mechanism for the formation of LXVI from LXIV.

E. Molecular Orbital Approach

In recent years, the use of quantum mechanics has entered the field of organic chemistry (86, 87). It is now used to explain the absorption spectra of complex molecules, including those of carbonium ions (17). Simply, if one compares the relative energies of the highest bonding, non-bonding and lowest antibonding π orbitals of an aromatic compound and the arylmethyl ions derived from it, they appear as pictured in Figure 25 (17).

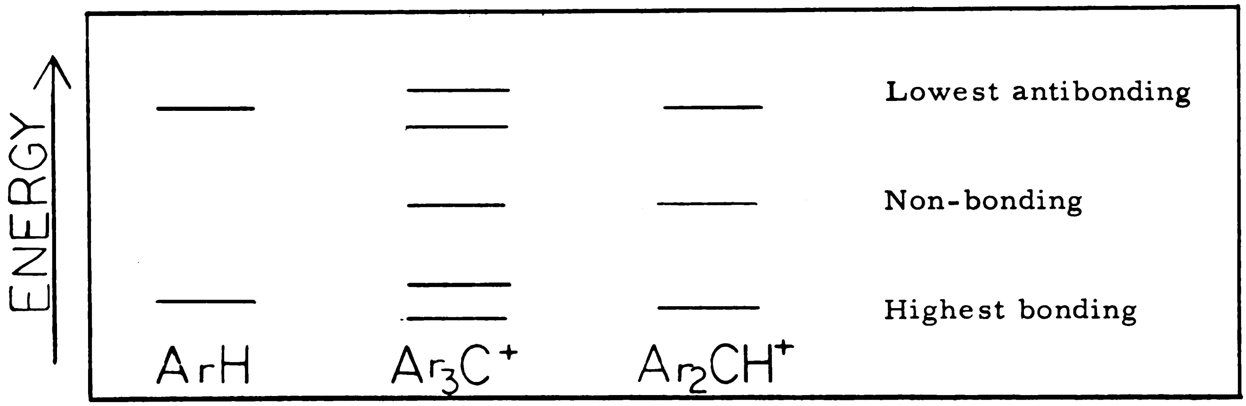


Figure 25. The relative energies of the lowest antibonding, non-bonding, and highest bonding π-orbitals of an aromatic hydrocarbon (ArH), and of the symmetrical diarylmethyl (Ar_2CH) and triarylmethyl (Ar_3C) systems.

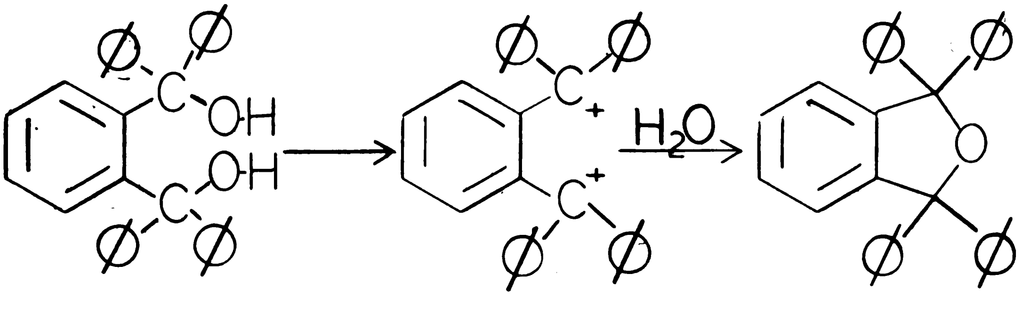
It can be demonstrated that the antibonding and bonding π orbitals in aromatic compounds and in the derived arylmethyl ions are paired. In the ions there is an extra orbital which is non-bonding that bisects the other orbitals at the center of gravity of their energies (88). In the Huckel approximation, the highest bonding and lowest antibonding levels of the arylmethyl ions have the same energies as the respective levels in the aromatic hydrocarbon from which they are derived. On page 5 it was stated that by neglecting various factors, the ion should absorb at a wavelength twice that of the hydrocarbon from which it is derived. This is true since the Δ E needed for the excitation of an electron in a hydrocarbon is twice that of the ion and Δ E is inversely proportional to the wavelength.

Molecular orbital theory would predict, therefore, that the cations and dications studied in this thesis should absorb at a wavelength twice that of the hydrocarbon's principal absorption band. The hydrocarbons involved are benzene, biphenyl and fluorene. They absorb at 207, 250 and 300 mμ respectively. If a cation is derived from two different hydrocarbons, the spectrum should have absorptions due to electronic transitions from both of them. Table 15 gives the predicted and observed values for several of the cations and dications studied in this work. The reason that it was not predicted that the second compound in Table 15 had an electronic transition due to biphenyl is caused by the position of the charges on the biphenyl molecule. At the point of juncture of the two rings making up biphenyl, the molecular orbitals cancel. This is the same as saying in valence band terms that there are no resonance interactions between the rings.

It is seen from Table 15 that at times molecular orbital theory predicts the spectra of the cations quite well. At other times it is in error. It is possible that with more refined theories one will be able to predict these spectra more closely.

IV. Hydrolysis and Methanolysis Products

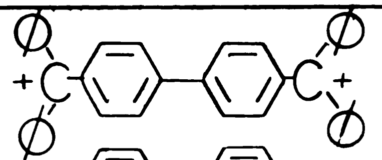
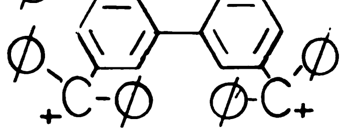
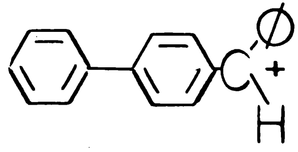
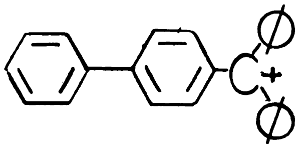
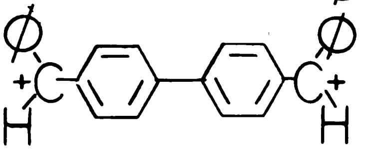
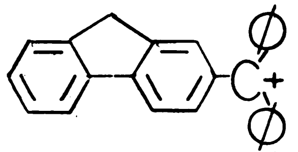
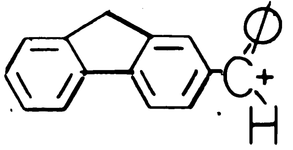
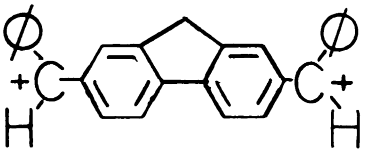
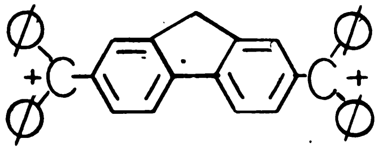
On page 8, the importance of quenching experiments was discussed. In this connection, when a solution of α, α, α', α'-tetraphenyl-o-xylene-α, α'-diol in 98 % sulfuric acid was poured onto ice, tetraphenylphthalan (XXXV) resulted:



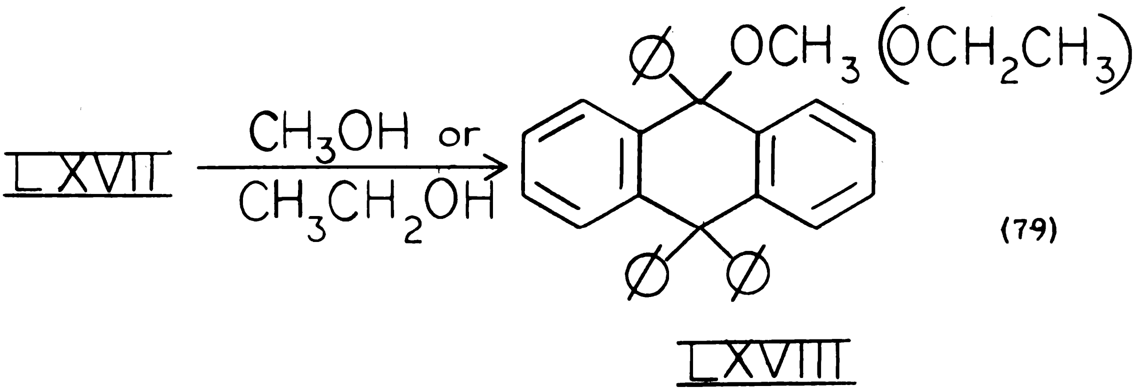
(78)

XXXIV LXVII XXXV

Table 15. Observed and Predicted (by the Huckel Approximation) Absorption Maxima for Several Cations and Dications

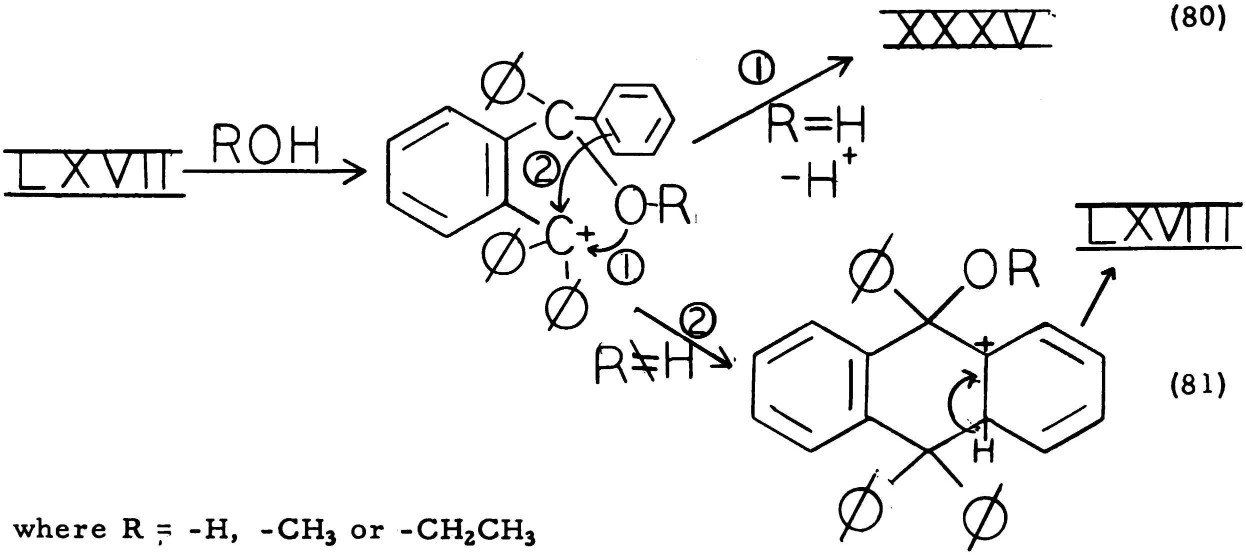
Compounds	λ_{max} Predicted	λ_{max} Observed
	410 500	440 525
	410	430
	410 500	- 535
	410 500	420 510
	410 500	420 563
	410 600	404 540
	410 600	- 547
	410 600	554 603
	410 600	440 525 568

This is consistent with the fact that efforts to prepare the corresponding dichloro compound with reagents such as thionyl chloride, acetyl chloride or hydrogen chloride also resulted in the phthalan (89). When LXVII was poured onto ice-cold methanol or ethanol, an interesting product was formed:



(79)

Possible mechanisms, via the same intermediate, for the formation of XXXV and LXVIII are:



(80)

(81)

where R = -H, -CH₃ or -CH₂CH₃

When R = H, a proton can readily be lost but when R ≠ H, an unstable methyl or ethyl cation would have to be eliminated. When R ≠ H, therefore, it is reasonable, since the dication in sulfuric acid reacts instantaneously when added dropwise to excess alcohol (immediate disappearance of the red color), that the dication reacts with alcohol and not with another nucleophile. The alkylation step is reasonable because of the close proximity of the benzene ring to the cation. An analogous type of intramolecular alkylation was shown on page 27 in the formation of 10, 10-diphenyl-9-anthrone from o-benzoyltriphenylmethanol.

If the mode of addition were reversed, sulfuric acid would be in excess and it should react with the alcohol as it was added:

$$ROH + H_2SO_4 \longrightarrow ROSO_3H + H_2O \qquad (82)$$

$$H_2O + H_2SO_4 \longrightarrow HSO_4^- + H_3O^+ \qquad (83)$$

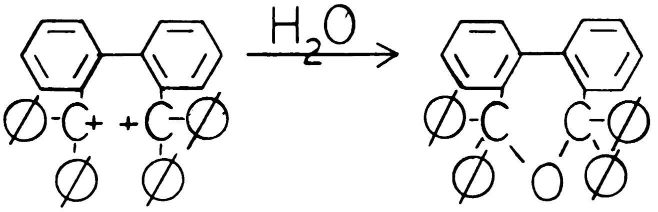
Reaction between the dication and either water or hydronium ion should result in the formation of tetraphenylphthalan. This was demonstrated by addition of methanol to the dication, which resulted in formation of tetraphenylphthalan.

An interesting but as yet unclarified reaction is the formation of tetraphenylphthalan in 90% yield when LXVII is poured onto anhydrous tetrahydrofuran.

9, 10, 10-Triphenyl-9, 10-dihydro-9-anthrol (83%) resulted from the hydrolysis of a sulfuric acid solution of LXVIII.

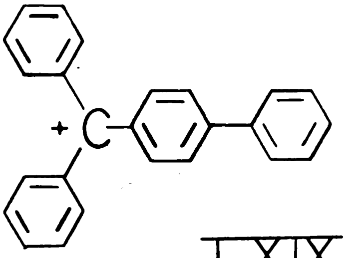
When the red solution of α, α'-dichloro-α, α, α',α'-tetraphenyl-m-xylene in 98% sulfuric acid was poured onto water and methanol, the corresponding diol and di-ether were formed respectively. The respective diols were also obtained when sulfuric acid solutions of α, α, α', α'-tetraphenyl-p, p'-bitolyl-α, α'-diol and α, α'-dichloro-α, α, α', α'-tetraphenyl-m, m'-bitolyl were hydrolyzed.

In a manner analogous to the formation of tetraphenylphthalan from LXVII, a sulfuric acid solution of α, α, α', α'-tetraphenyl-o, o'-bitolyl-α, α'-diol formed the anhydro derivative (98):

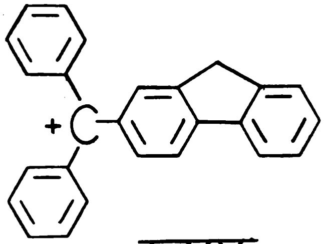


(84)

The other dications were not subjected to quenching experiments but two monocation were:



LXIX

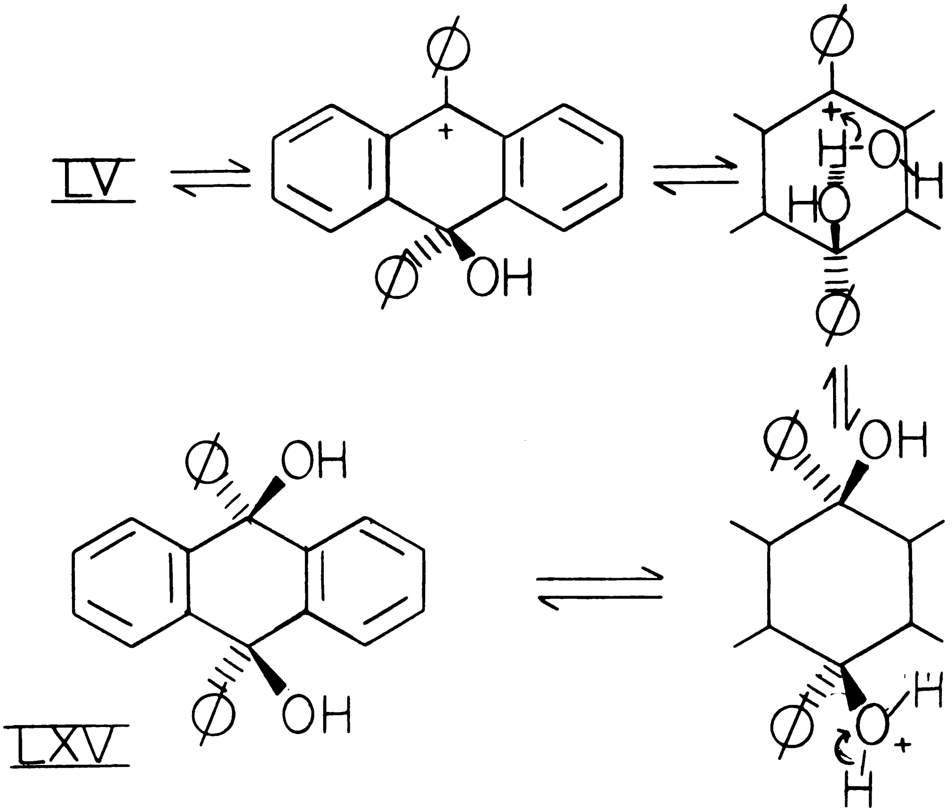


LXX

When a solution of either LXIX or LXV in concentrated sulfuric acid was poured onto water, no precipitate resulted. If dilute sulfuric acid was used, the respective carbinols were obtained in high yield. This is further evidence that sulfonation is occurring in concentrated acid (see page 91). Additional proof that sulfonation occurred was obtained by examination of the infrared spectrum of a carbon tetrachloride extract of the hydrolysis solution of LXX.. The presence of sulfonic acid bands were indicated (see Figure 45) (90). After refluxing this hydrolysis solution for several hours, the carbinol was isolated. The spectral (page 58) and hydrolysis studies, therefore, indicate that in concentrated sulfuric acid LXIX and LXX are sulfonated.

It was shown in 1923 that hydrolysis of the blue solution of trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene (LV) in concentrated sulfuric acid gave 9, 10-diphenylanthracene and an unidentified red-yellow compound (91). This work was recently repeated and 4-phenyl-2, 3-benzofluoranthene was isolated in addition to 9, 10-diphenylanthracene (61). Rafos also found that hydrolysis of a solution of the diol in 6% sulfuric acid in acetic acid (at this acidity the diol was found to be half ionized to the monocation) afforded nearly quantitative yields of the starting diol.

Spectral studies of LV in dilute sulfuric acid indicated that the monocation (yellow solutions), once completely formed, reacts further to give an almost colorless species. Since the monocation is completely formed in 62% sulfuric acid, and the species giving the blue solution is formed in 75%, it was decided to prepare a solution of LV in 65% sulfuric acid and study its hydrolysis products. The results of this experiment were a mixture of LV and its cis analog (LXV). The reaction sequence going from the trans to the cis diol can be illustrated as follows:

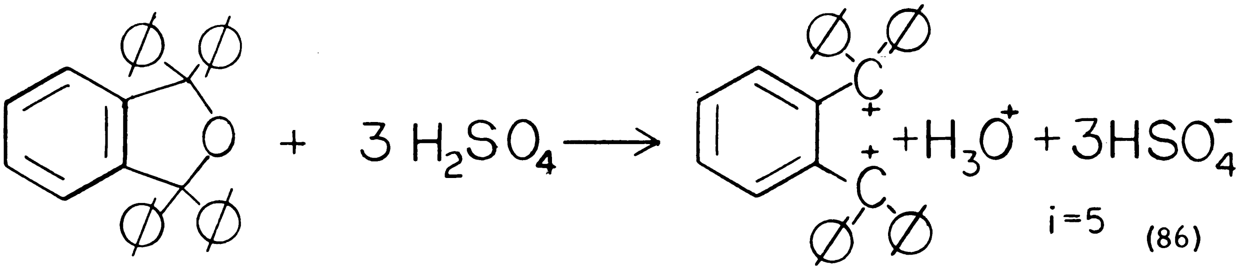


(85)

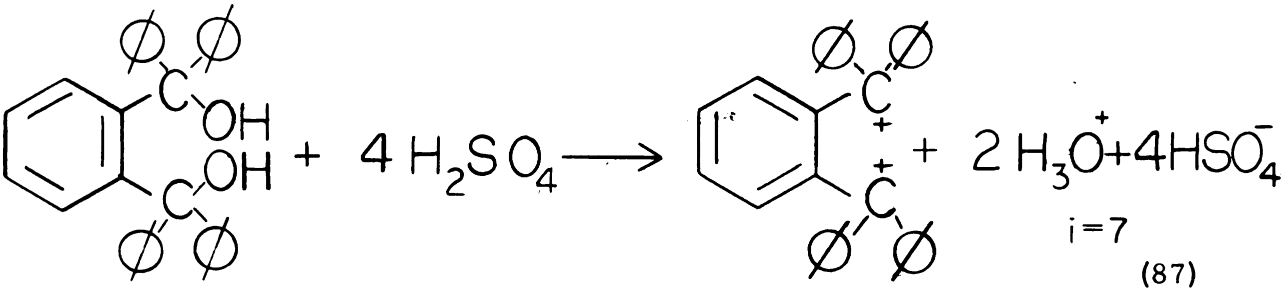
In section III-D a further discussion of the reactions of LV in sulfuric acid was presented.

V. Cryoscopic Measurements

Cryoscopic measurements in this thesis were made only on tetraphenylphthalan in 100% sulfuric acid since there was a possibility that the resulting dication would not form because of the proximity of the two positive charges. Since the same species was formed in concentrated sulfuric acid from either tetraphenylphthalan or α, α, α', α'-tetraphenyl-o-xylene-α, α'-diol (see page 35) only one was studied cryoscopically. The former was chosen because it should ionize to give 5 particles while the latter should form 7. A smaller number of particles results in more accurate i factors.



(86)



(87)

The data, which are given in Table 16, support the formation of a dication from tetraphenylphthalan.

Table 16. Cryoscopic Data on Tetraphenylphthalan

Sample Wt., g.[a]	g. H_2SO_4	T_1, °C.	T, °C	i[b, c]
0.0		9.262	0.0	
0.460	107.4	8.969	0.308	4.99
0.490	107.4	8.637	0.332	5.05
0.450	107.4	8.301	0.326	5.39
0.950	106.8	8.637	0.640	4.99
0.94	106.7	8.301	0.658	5.05
1.41	106.3	8.301	0.966	5.18

[a] The first three values are the actual weights of the samples. The other weights incorporate two or three samples.

[b] Calculated from $i = \Delta T/6.12 \cdot m_s$, where m_s is the molality of the solute.

[c] The average value for i is 5.11.

EXPERIMENTAL

I. Syntheses and Reactions

A. The Xylene Diols

Preparation of α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol (89)

To a mechanically stirred solution of 84 ml. (126 g., 0.8 mole) of bromobenzene in 300 ml. of anhydrous ether was added 9 g. (1.3 g. atoms) of lithium slices, all at once. Stirring was continued at room temperature for one hour under a dry nitrogen atmosphere. The reaction mixture was then placed in an ice bath and 38.8 g. (0.2 mole, 37.5 ml.) of dimethyl phthalate was added dropwise. After 3 hours the stirring was stopped and the reaction mixture was allowed to stand overnight under a nitrogen atmosphere. The free glycol was obtained by pouring the ether solution onto 300 ml. of an ice-water mixture and collecting the resulting solid by filtration. The crude glycol was taken up in 100 ml. of benzene, dried over magnesium sulfate, treated with Norite and filtered. The glycol was precipitated by adding petroleum ether (35-60°) and cooling in a dry ice-isopropyl alcohol bath. The yield was 70 g. (78%) of α, α, α', α'-tetraphenyl-o-xylene-α, α'-diol, m.p. 203-204° (literature value, 203.5°). Its infrared spectrum is shown in Figure 26.

Preparation of α, α, α', α'-Tetraphenylphthalan (89)

α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol (1.8 g., 4.1 mmoles) was dissolved in 70 ml. of glacial acetic acid and 5 ml. of water. The solution was refluxed for one hour. As the solution cooled, white crystals began to precipitate. After standing overnight, 1.1 g. of solid was collected. Addition of water to the mother liquor afforded an additional 0.2 g. of solid (total yield, 75%). The melting point of the tetraphenylphthalan was 174-176° (literature value, 174-175°). Its infrared spectrum is shown in Figure 27.

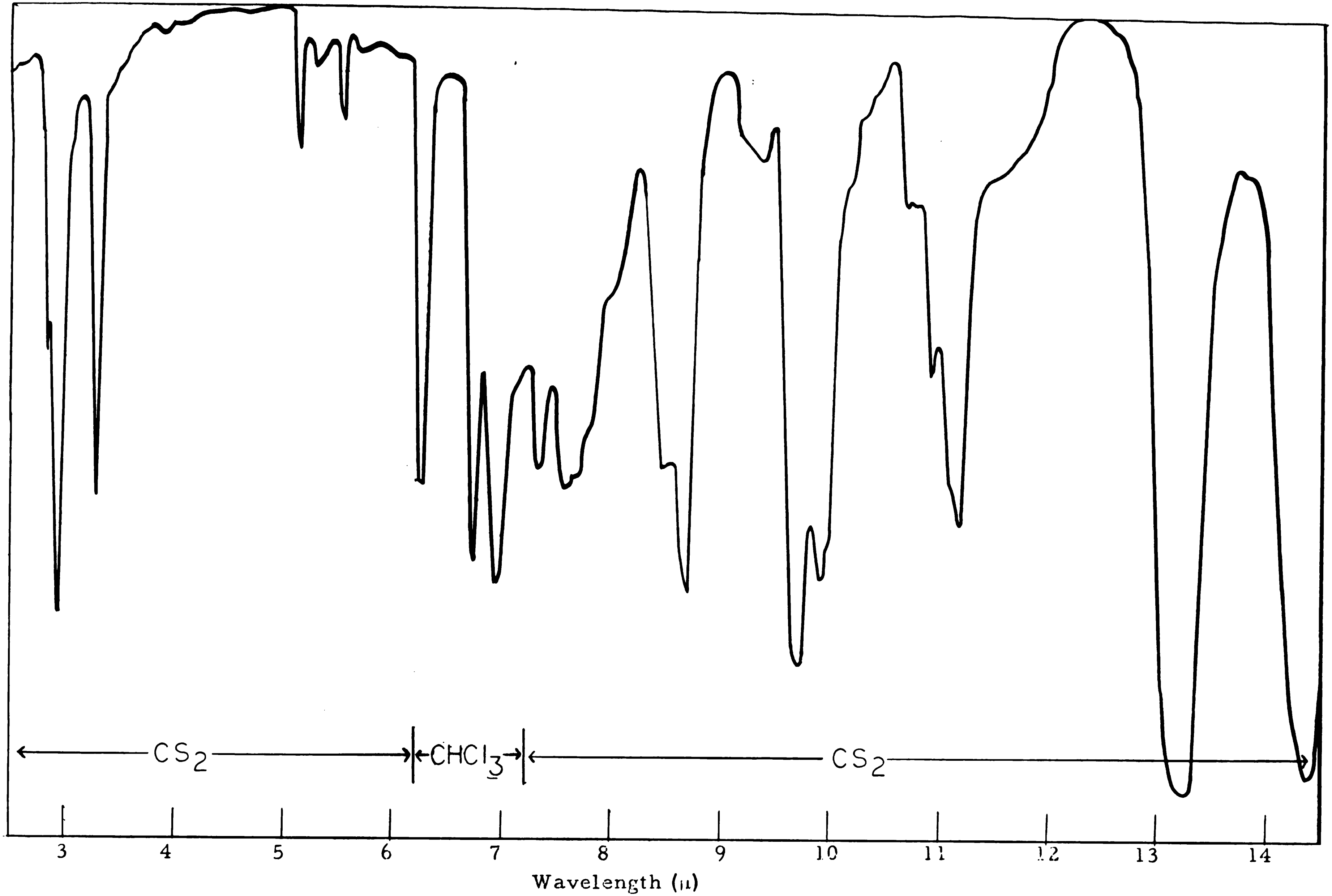


Figure 26. Infrared spectrum of α, α, α', α'-tetraphenyl-o-xylene-α, α'-diol.

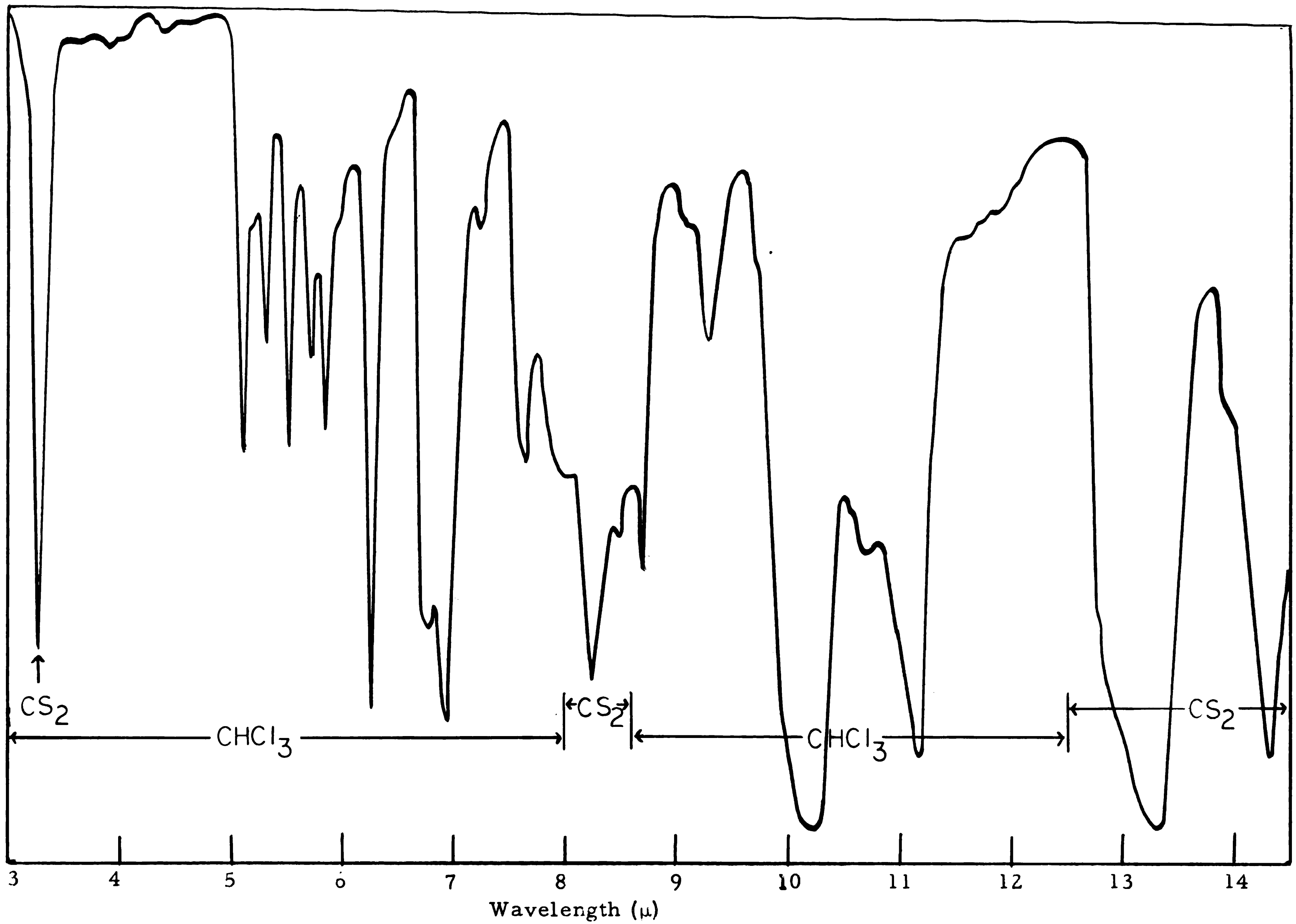


Figure 27. Infrared spectrum of α, α, α'α'-tetraphenylphthalan.

Reaction of α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol in 98% Sulfuric Acid with Water

α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol (0.119 g., 0.27 mmoles) was dissolved in 10 ml. of 98% sulfuric acid. The resulting orange-red solution was poured onto 50 ml. of ice-water. The white solid was collected, dissolved in 15 ml. of benzene, washed three times with 10-ml. portions of 5% sodium carbonate solution and then dried over calcium chloride. The solution was filtered and the benzene was distilled in vacuo to give 0.960 g. (84%) of tetraphenylphthalan, m.p. 164-169°. Two recrystallizations from benzene raised the melting point to 173-174° (literature value, 174-175°). A m.m.p. with an authentic sample gave no depression.

Reaction of α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol in 98% Sulfuric Acid with Absolute Methanol

α, α, α', α'-Tetraphenyl-o-xylene-α,α'-diol (1.00 g., 2.25 mmoles) was dissolved in 10 ml. of 98% sulfuric acid. The orange-red solution was poured onto 75 ml. of ice-cold absolute methanol with magnetic stirring. The resulting white precipitate was washed with 5% sodium carbonate solution, with water and dried to give 0.885 g. of a compound melting at 208-211°. Two recrystallizations raised the melting point to 220.5-221°. The compound had a melting point almost identical with that of the methyl ether of 9, 10, 10-triphenyl-9, 10-dihydro-9-anthrol (92).

Anal. Calcd. for $C_{33}H_{26}O$: C, 90.37; H, 5.97

Found: C, 89.86, 89.80; H, 6.21, 6.16.

The yield of substituted anthrol was 89%. The infrared spectrum is shown in Figure 28.

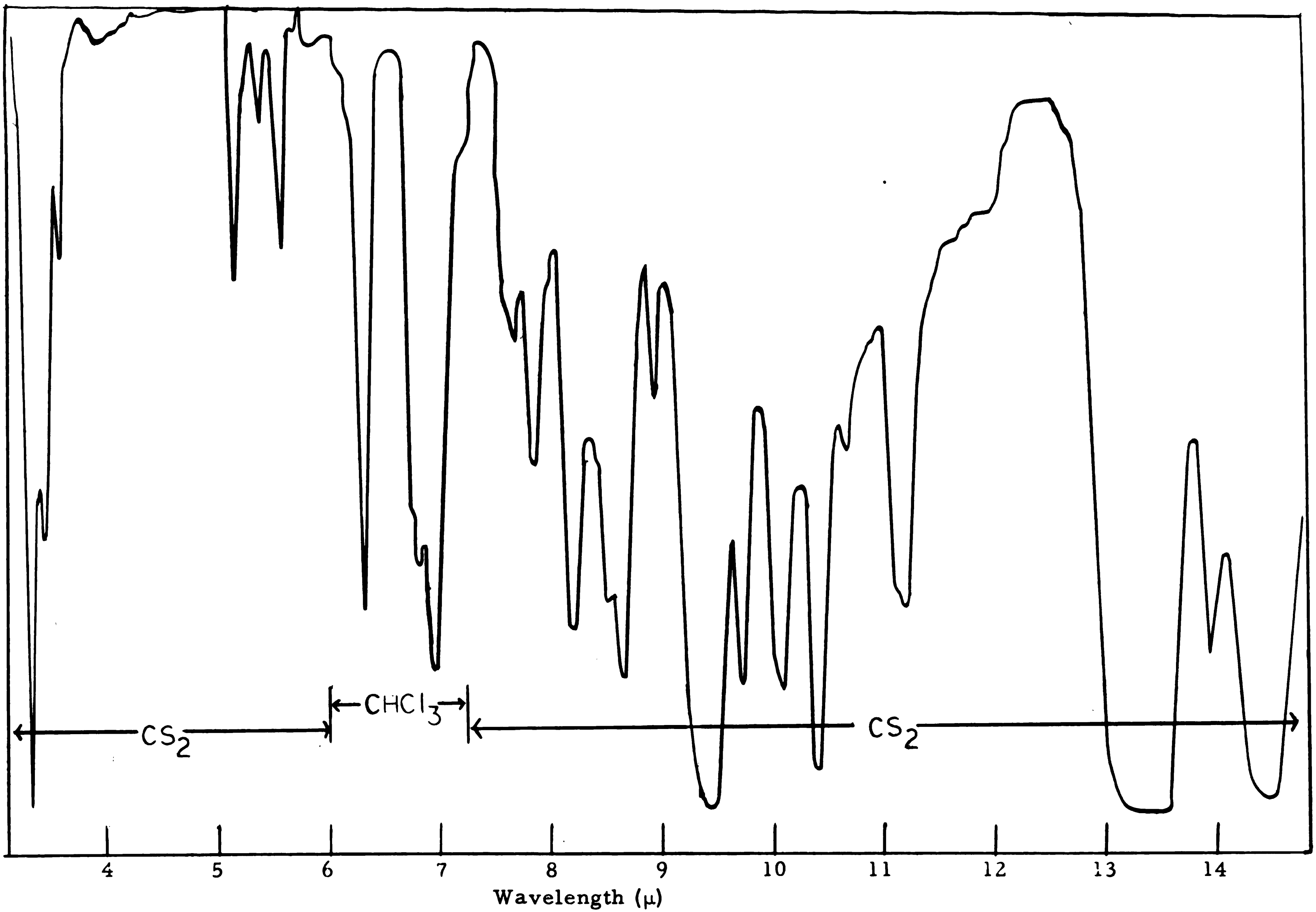


Figure 28. Infrared spectrum of the methyl ether of 9, 10, 10-triphenyl-9, 10-dihydro-9 -anthrol.

Reaction of Absolute Methanol with α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol in 98% Sulfuric Acid

To the magnetically stirred orange-red solution of α, α, α', α'-tetraphenyl-o-xylene-α, α'-diol (0.150 g., 0.34 mmole) in 50 ml. of 98% sulfuric acid, 50 ml. of absolute methanol was added dropwise. The color lightened slowly with the formation of a white solid. When addition was complete, the white solid was filtered, washed with 5% sodium carbonate solution, with water and dried at 100°. The m.p. was 175-176° and a m.m.p. with tetraphenylphthalan was also 175-176°. The yield was 0.120 g. (80%).

Reaction of α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol in 98% Sulfuric Acid with Absolute Ethanol

The procedure and amounts used were identical with those for the reaction with absolute methanol (page 10), except that absolute ethanol was used. The yield was 0.850 g. (84%) of the ethyl ether of 9, 10, 10-triphenyl-9, 10-dihydro-9-anthrol, m.p. after recrystallization from toluene-ligroin (90-120°) was 254-255° (literature value, 250°) (92). Its infrared spectrum is shown in Figure 29.

Reaction of α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol in 98% Sulfuric Acid with Anhydrous Tetrahydrofuran

α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol (0.200 g., 0.45 mmoles) was dissolved in 3 ml. of 98% sulfuric acid. The red solution was poured into 50 ml. of anhydrous tetrahydrofuran with stirring. The resulting clear solution was neutralized with solid sodium carbonate, filtered and the tetrahydrofuran distilled to give 0.180 g. (90%) of a white solid residue. After one recrystallization from ligroin (90-120°) it melted at 174-175° and gave no depression in melting point with an authentic sample of tetraphenylphthalan.

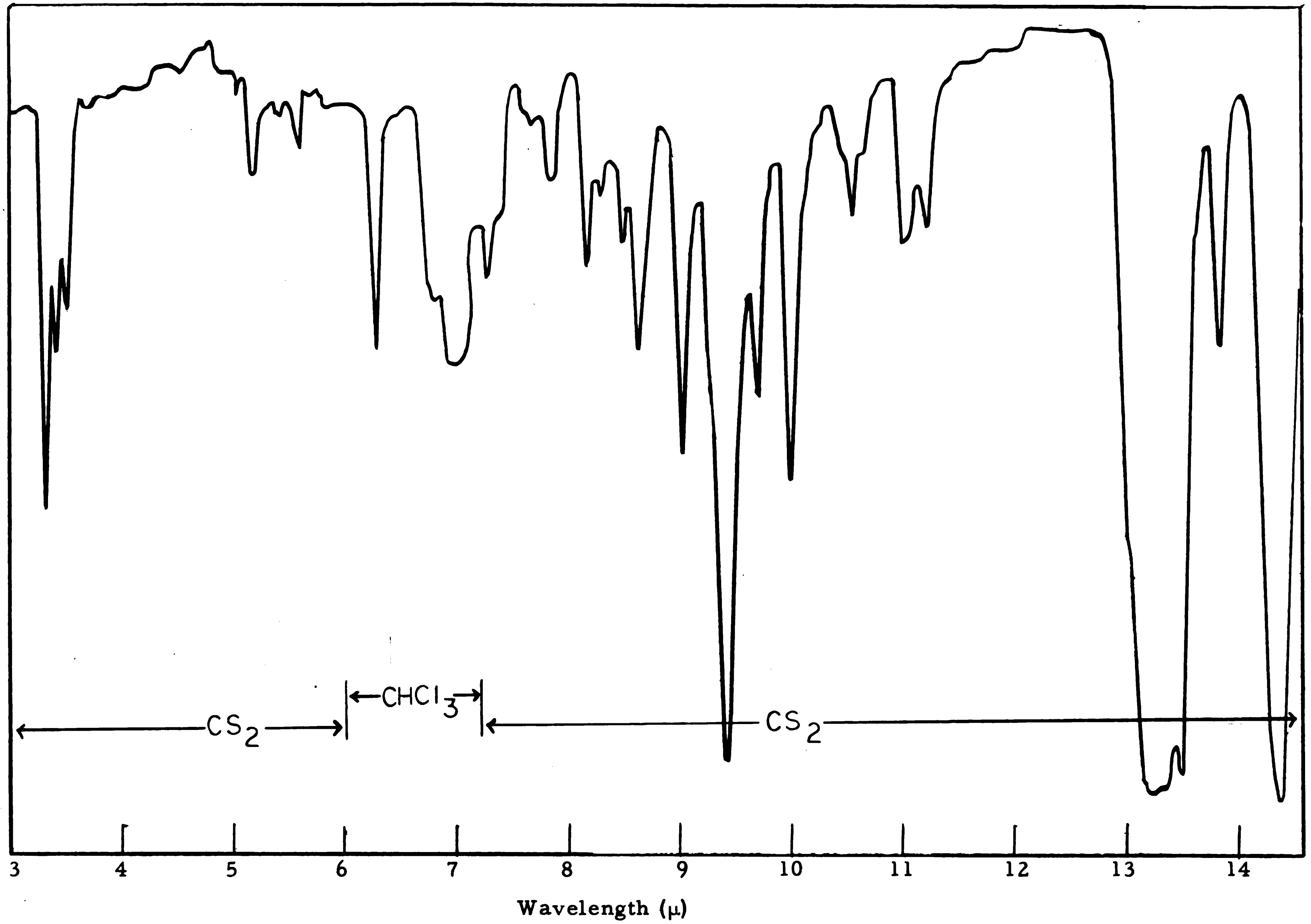


Figure 29. Infrared spectrum of the ethyl ether of 9, 10, 10-triphenyl-9, 10-dihydro-9-anthrol.

Preparation of m-Dibenzoylbenzene

To a stirred mixture of 26.8 g. (0.20 mole) of anhydrous aluminum chloride in 100 ml. of dry benzene, 20.3 g. (0.10 mole) of isophthaloyl chloride in 100 ml. of dry benzene was added dropwise. The temperature was maintained between 0-10° during the addition. The reaction mixture was refluxed for 5 hours, poured onto 300 ml. of ice-water and the organic layer separated. After washing twice with 50-ml. portions of 2N sodium hydroxide and water, the benzene solution was dried over calcium chloride. Distillation of the benzene left 25.5 g. (89%) of m-dibenzoylbenzene, which melted at 108° after three recrystallizations from 95% ethanol (literature value, 101-102°) (93).

Reaction of m-Dibenzoylbenzene with Phenylmagnesium bromide

To a stirred solution of phenylmagnesium bromide (0.25 moles) prepared in the usual way from 39.3 g. (26.2 ml.) of bromobenzene and 6 g. of magnesium in 100 ml. of anhydrous ether, 25 g. (0.087 moles) of m-dibenzoylbenzene in 250 ml. of dry benzene was added dropwise. After being stirred for 4.5 hours, the reaction mixture was decomposed by pouring onto 300 ml. of an ice-water mixture. The organic layer was separated, dried over calcium chloride and the benzene distilled. An infrared spectrum of the resulting oil showed strong absorption in the carbonyl and hydroxyl regions. Attempts to recrystallize the product from various solvents were unsuccessful.

Preparation of α, α'-Dichloro-α, α, α', α'-tetraphenyl-m-xylene

Phehylmagnesium bromide (0.90 mole) was prepared in the usual way from 141 g. (94 ml.) of bromobenzene and 21.6 g. of magnesium in 200 ml. of anhydrous ether. Dimethyl isophthalate (30 g., 0.15 mole) in 200 ml. of benzene was added dropwise to a stirred solution of the Grignard reagent. After refluxing for 8 days with stirring, the reaction mixture was decomposed by pouring onto ice-hydrochloric acid, the benzene separated and dried over magnesium sulfate. After distilling the benzene, the resulting oil was triturated with ligroin (90-120°) to remove any biphenyl and bromobenzene. The oil was then dissolved in 50 ml. of acetic acid-acetyl chloride (3:1) and treated with anhydrous hydrogen chloride for 3 hours. After standing in the refrigerator for one week a brown solid was formed. One recrystallization from acetyl chloride gave 8 g. (11%) of a tan solid, m.p. 125-130°. Further recrystallization from acetyl chloride raised the melting point to 138-140° (literature value, 140.5°). The infrared spectrum is shown in Figure 30.

Preparation of α, α, α', α'-Tetraphenyl-m-xylene-α, α'-diol (94)

α, α'-Dichloro-α, α, α', α'-tetraphenyl-m-xylene (0.2 g., 0.42 mmole) was dissolved in 6 ml. of 98% sulfuric acid. After the evolution of hydrogen chloride had stopped, the red solution was poured onto 50 ml. of ice-water. The white solid was filtered, washed with 5% sodium carbonate solution, with water, dried at 40° and recrystallized from ligroin (90-120°) to give a white crystalline solid which melted sharply at 87°. This was apparently a complex between the glycol and the solvent because if the melt was resolidified or if the compound was dried overnight in a drying pistol, the melting point was 112-113° (literature value, 112-113°). The yield of α, α, α', α'-tetraphenyl-m-xylene-α, α'-diol was 0.175 g. (94%). Its infrared spectrum is shown in Figure 31.

Reaction of α, α'-Dichloro-α, α, α', α'-tetraphenyl-m-xylene in 98% Sulfuric Acid with Absolute Methanol (95)

α, α'-Dichloro-α, α', α', α'-tetraphenyl-m-xylene (0.1 g., 0.21 mmole) in 5 ml. of 98% sulfuric acid was added to 50 ml. of ice-cold methanol.

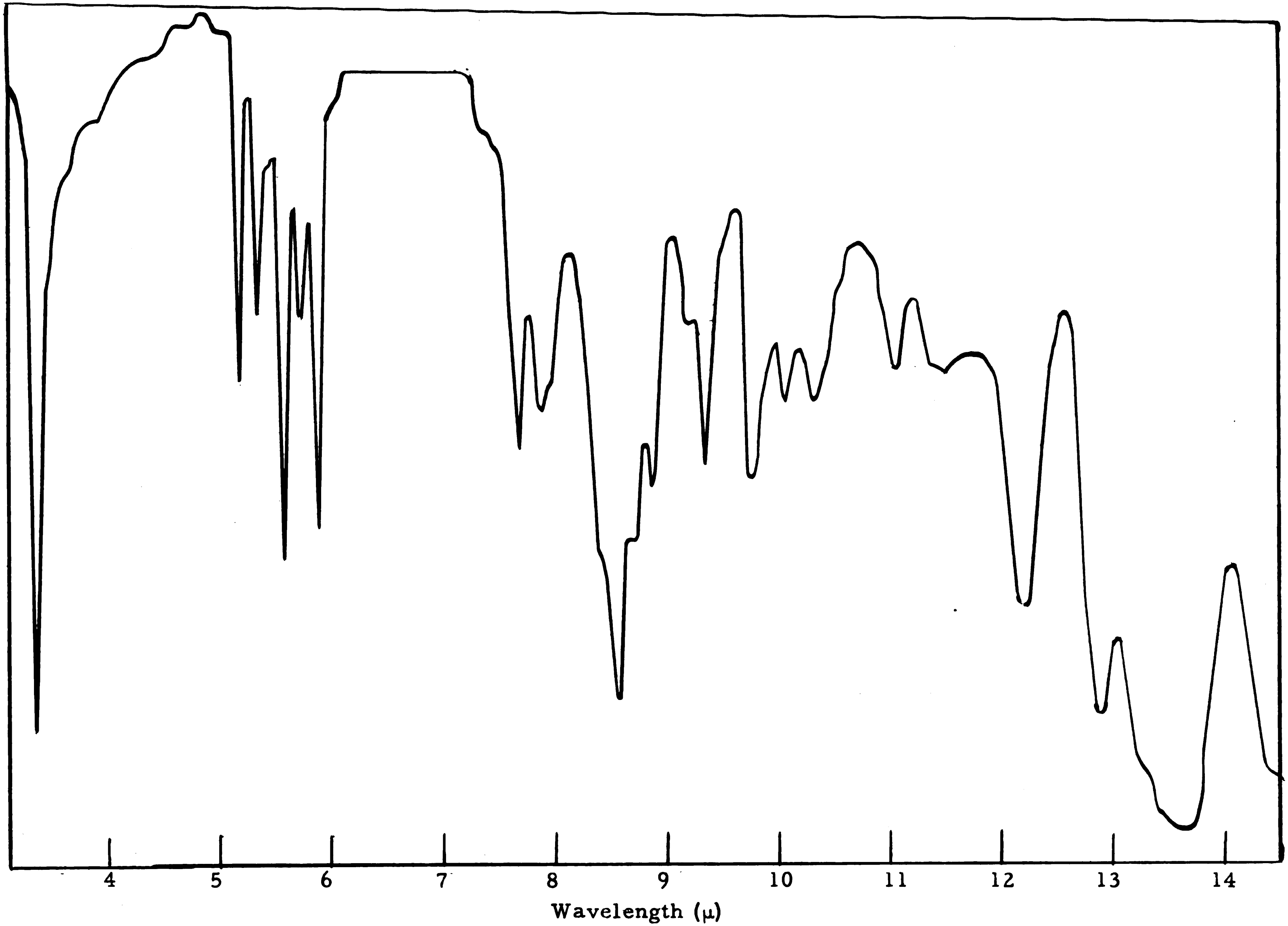


Figure 30. Infrared spectrum of α, α'-dichloro-α, α, α', α'-tetraphenyl-m-xylene (CS$_2$ solution).

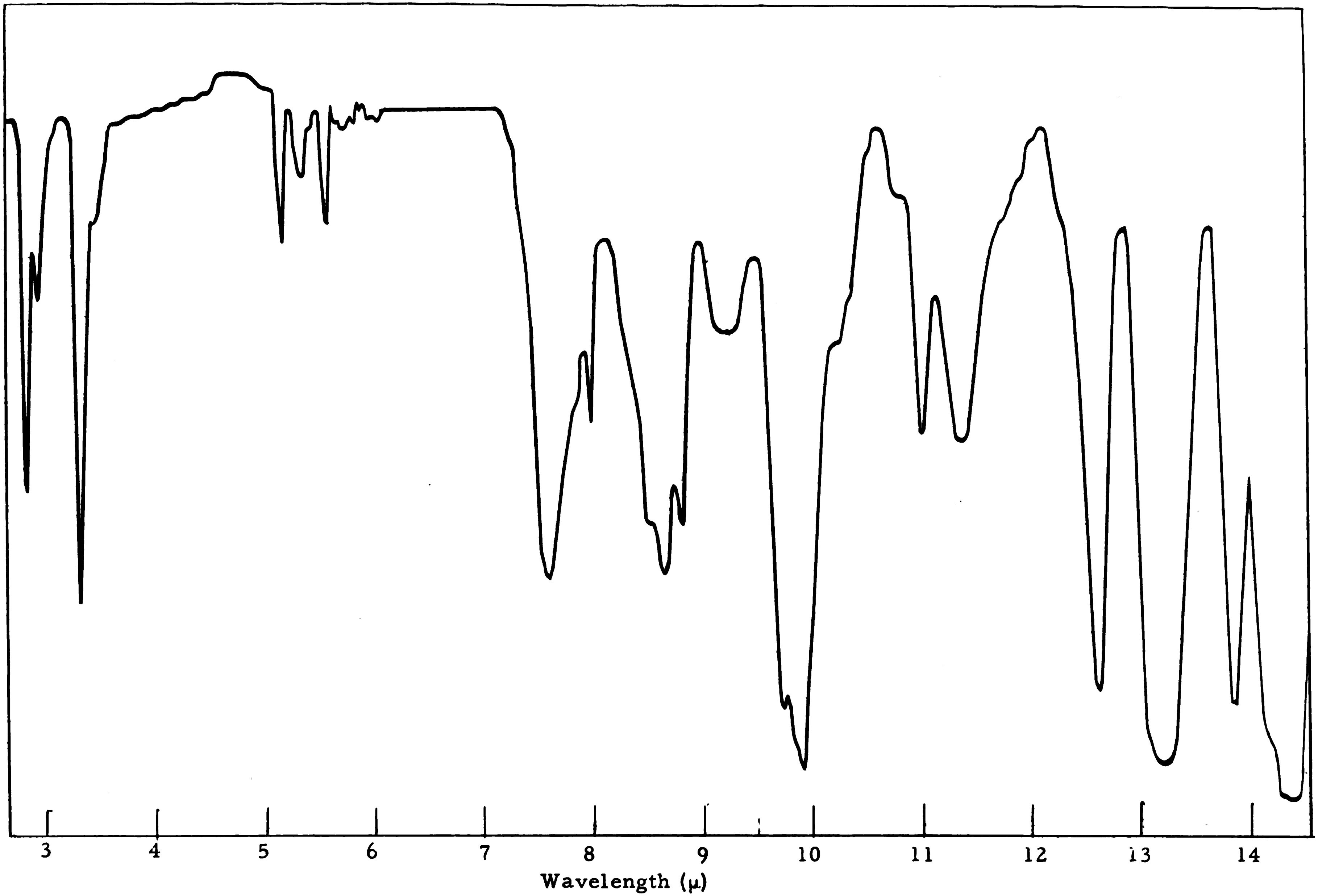


Figure 31. Infrared spectrum of α, α, α', α'-tetraphenyl-m-xylene-α, α'-diol (CS$_2$ solution).

The resulting clear solution was treated with 50 ml. of 5% sodium carbonate solution and the white solid that formed was filtered, washed with water and recrystallized from aqueous methanol. The dimethyl ether of α, α, α', α'-tetraphenyl-m-xylene-α, α'-diol (0.08 g., 82%) melted at 103° (literature value, 103-104°). Its infrared spectrum is shown in Figure 32.

Preparation of α, α'-Diphenyl-m-xylene-α, α'-diol (96)

To a magnetically stirred slurry of 0.05 g. (1.2 mmoles) of lithium aluminum hydride in 30 ml. of anhydrous ether, 0.11 g. (0.38 mmole) of m-dibenzoylbenzene in 25 ml. of dry benzene was added dropwise. After refluxing for 12 hours the reaction mixture was decomposed by pouring onto an ice-sulfuric acid mixture. The benzene layer was separated, dried over magnesium sulfate and the benzene distilled to give 0.08 g. (70%) of α, α'-diphenyl-m-xylene-α, α'-diol. After one recrystallization from toluene-ligroin (90-120°) its melting point was 153-155° (literature value, 157°).

Preparation of α, α'-Diphenyl-p-xylene-α, α'-diol (96)

Terephthalaldehyde (13.4 g., 0.1 mole) in 300 ml. of an anhydrous benzene-ether mixture (5:1) was added to 0.2 mole of phenylmagnesium bromide (from 47.1 g. of bromobenzene and 7.2 g. of magnesium) in 100 ml. of dry ether. After being stirred for 1.5 hours, the reaction mixture was poured onto 300 ml. of an ice-hydrochloric acid mixture. The resulting solid was filtered to give 5.1 g. (18%) of α, α'-diphenyl-p-xylene-α, α'-diol. After two recrystallizations from ethanol it melted at 173° (literature value, 171°).

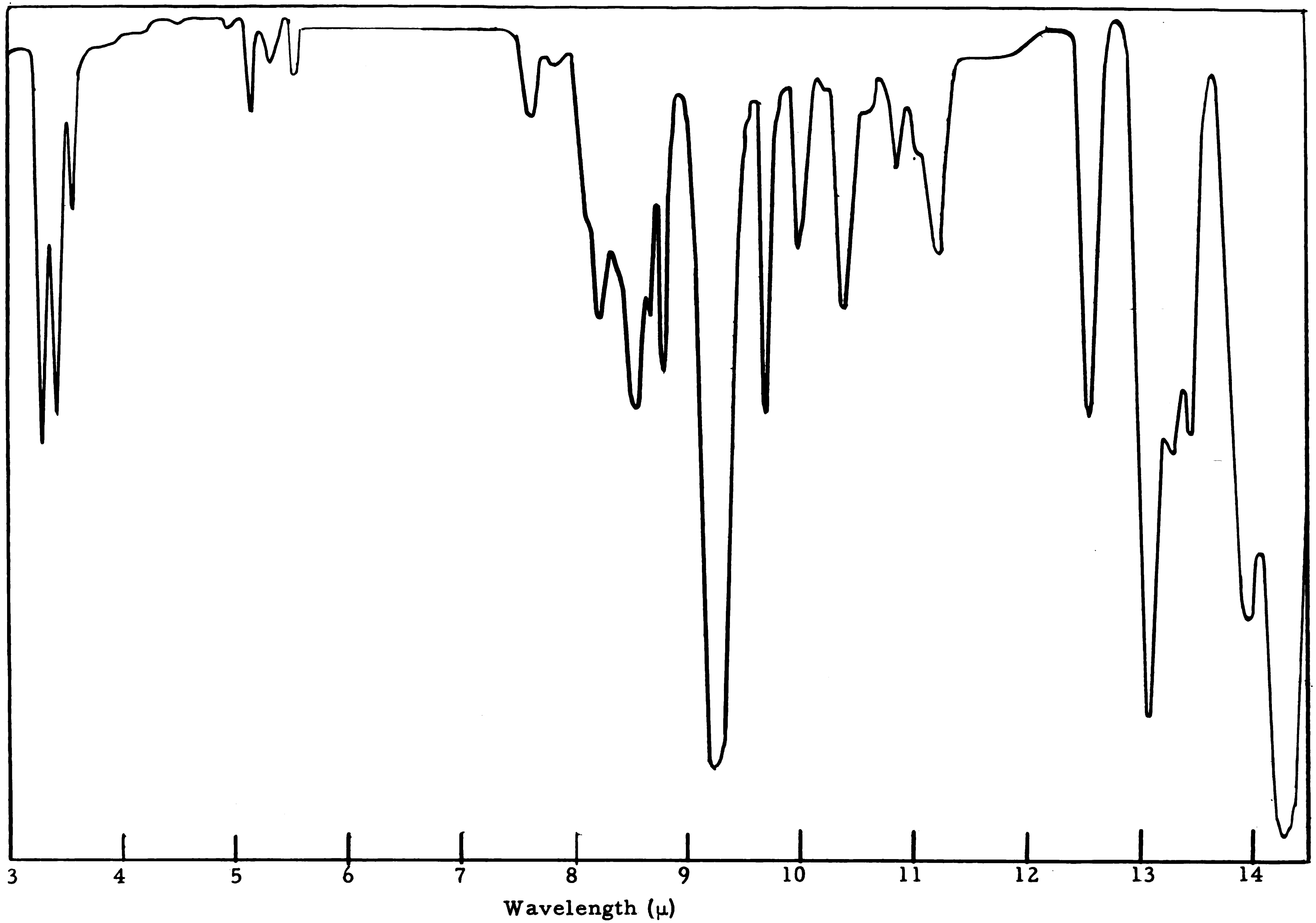


Figure 32. Infrared spectrum of the dimethyl ether of α, α, α', α'-tetraphenyl-m-xylene-α, α'-diol (CS$_2$ solution).

B. The Diols and Carbinols in the Biphenyl Series

Preparation of 4,4'-Dibromobiphenyl (97)

An evaporating dish containing 15.4 g. (0.1 mole) of biphenyl was set on a porcelain rack in a desiccator. Below the rack was placed an evaporating dish with 39 g. (12 ml., 0.24 mole) of bromine. The desiccator was closed but a small opening was left for hydrogen bromide evolution. After 12 hours, the top dish was removed and placed in the hood for 4 hours so that bromine and hydrogen bromide could escape from the crystals. Recrystallization from benzene gave 19.3 g. (62%) of 4,4'-dibromobiphenyl, m.p. 163-164° (literature value, 162-163°).

Attempted Preparation of α, α, α', α'-Tetraphenyl-p, p'-bitolyl-α, α'-diol

To 1 g. (0.14 g.-atoms) of lithium in 25 ml. of anhydrous ether, 15.6 g. (0.05 mole) of 4,4'-dibromobiphenyl in 50 ml. of anhydrous ether was added dropwise. After stirring for 3 hours, 18.2 g. (0.1 mole) of benzophenone in 50 ml. of dry ether was added dropwise and the reaction was refluxed for 24 hours. The reaction mixture was poured onto ice, extracted with toluene and dried over magnesium sulfate. Most of the toluene was distilled and the residue was placed in the freezer for 2 days. The resulting viscous orange solid could not be recrystallized.

Benzoylation of Biphenyl

To a stirred slurry of 79.8 g. (0.6 mole) aluminum chloride in 75 ml. of carbon disulfide, 84 g. (0.6 mole) of benzoyl chloride and 31 g. (0.2 mole) of biphenyl in 75 ml. of carbon disulfide were added dropwise. After being refluxed for 25 hours, the reaction mixture was poured onto 500 ml. of ice-water and the resulting solid collected by filtration. The filtrate was set aside for further work-up.

The solid was recrystallized from isopropyl alcohol to give 6.8 g. (9%) of 4, 4'-dibenzoylbiphenyl, m.p. 218° (literature value, 216°) (98).

After the organic layer was separated in the filtrate, it was dried over magnesium sulfate, filtered and the benzene distilled. Recrystallization of the residue from benzene-petroleum ether (35-60°) gave 23.0 g. (45%) of 4-benzoylbiphenyl, m.p. 101° (literature value, 104°) (99).

Preparation of α, α'-Dichloro-α, α, α', α'- tetraphenyl-p, p'-bitolyl

To a stirred solution of phenylmagnesium bromide (0.055 mole) prepared in the usual way from 8.64 g. (5.8 ml.) of bromobenzene and 1.35 g. of magnesium in 100 ml. of dry ether, 9.1 g. (0.025 mole) of 4, 4'-dibenzoylbiphenyl in 100 ml. of dry benzene was added dropwise. After being refluxed for 3 hours, the reaction mixture was decomposed by pouring onto 200 ml. of an ice-sulfuric acid mixture. The organic layer was separated, washed with 5% sodium carbonate and the benzene was distilled. The residue was steam distilled to remove side products and starting materials. It was then taken up in 50 ml. of ether, dried over calcium sulfate and filtered. Acetyl chloride (10 ml.) was added and the solution was treated with anhydrous hydrogen chloride for 3 hours. The α, α'-dichloro-α, α, α', α'-tetraphenyl-p, p'-bitolyl (4.1 g., 32%) was collected. After one recrystallization from acetyl chloride-benzene it melted at 223-224° (literature value, 223°) (100). The infrared spectrum is shown in Figure 33.

Preparation of α, α, α', α'-Tetraphenyl-p, p'-bitolyl-α, α'-diol

Method A: n-Butyllithium (0.16 mole) (from 2.9 g. of lithium slices and 22.8 g. of n-butyl bromide) in 75 ml. of dry ether was added all at once to a mechanically stirred solution of 13 g. (0.041 mole) of

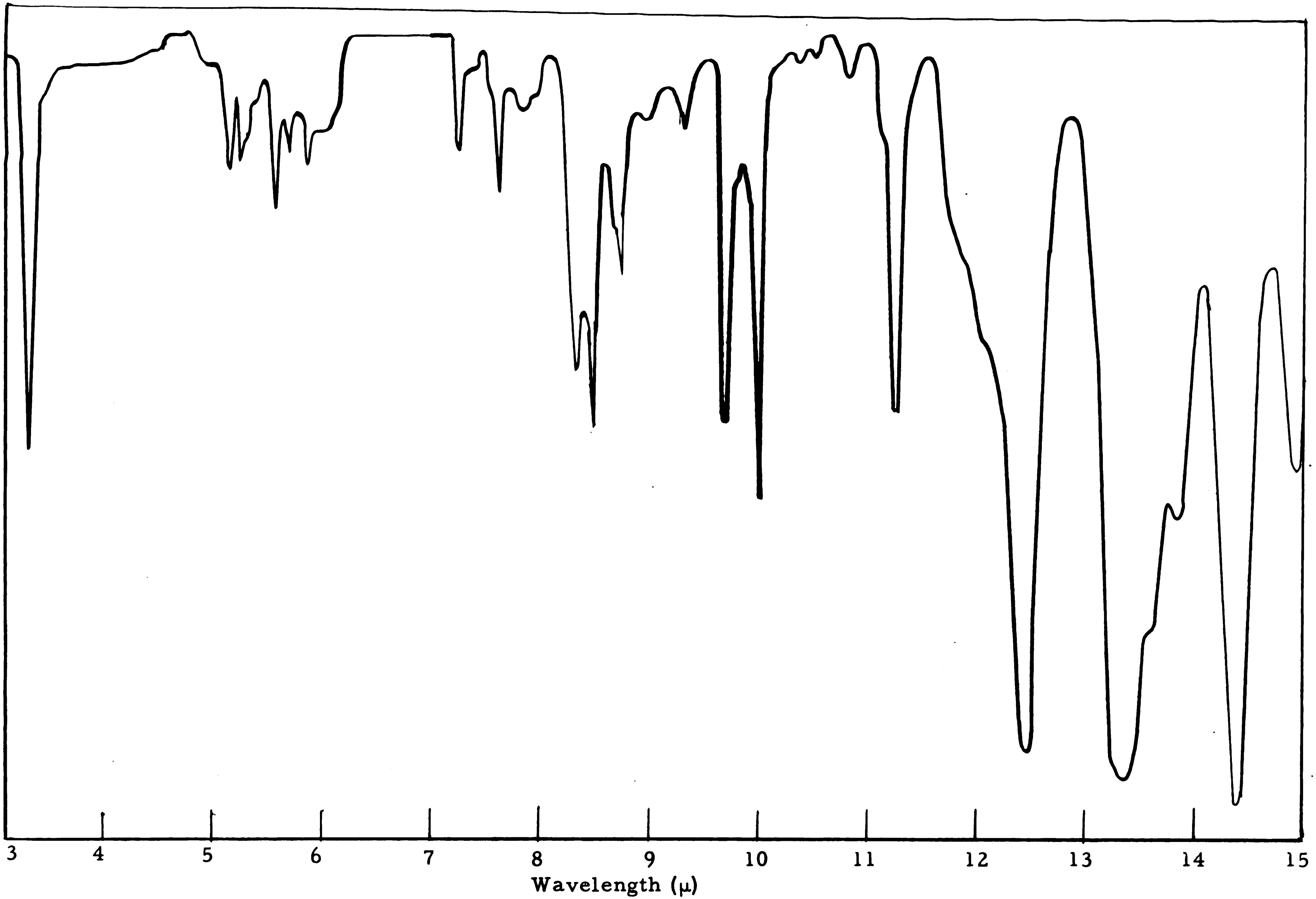


Figure 33. Infrared spectrum of α, α'-dichloro-α, α, α', α'-tetraphenyl-p, p'-bitolyl (CS_2 solution).

4,4'-dibromobiphenyl in 125 ml. of anhydrous ether. After 12 hours, 15.2 g. (0.083 mole) of benzophenone in 150 ml. of dry ether was added dropwise and stirring was continued for another two hours. The reaction mixture was poured onto ice-water to give an oily solid which was collected by filtration. Recrystallization from ethyl acetate-ligroin (90-120°) gave a very small amount of a solid, m.p. 177-178°. The literature value for α, α, α', α'-tetraphenyl-p, p'-bitolyl-α, α'-diol is 177-178° (63).

Method B: α, α'-Dichloro-α, α, α', α'-tetraphenyl-p, p'-bitolyl (0.110 g., 0.19 mmole) in 75 ml. of 25% aqueous acetone was refluxed for 15 minutes. After cooling to room temperature, the reaction mixture was poured onto 150 ml. of ice-water and extracted with ether. After drying over calcium sulfate, the ether was distilled to leave a white residue which was recrystallized to give 0.07 g. (70%) of α, α, α', α'-tetraphenyl-p, p'-bitolyl-α, α'-diol, m.p. 177-178° (literature value, 177-178°) (63). Its infrared spectrum is shown in Figure 34.

Reaction of α, α, α', α'-Tetraphenyl-p, p'-bitolyl-α, α'-diol in 98% Sulfuric Acid with Water

α, α, α', α'-Tetraphenyl-p, p'-bitolyl-α, α'-diol (0.06 g., 0.12 mmole) was dissolved in 10 ml. of 98% sulfuric acid. The red solution was poured onto 75 ml. of ice-water and the resulting solid was collected. After being washed with 5% sodium carbonate, with water and dried, the crude α, α, α', α'-tetraphenyl-p, p'-bitolyl-α, α'-diol (0.05 g., 84%) was recrystallized from toluene-ligroin (90-120°). The m.p. and m.m.p. were identical with that of an authentic sample of the glycol.

Preparation of 4-Biphenylyldiphenylmethanol (101)

To 3.1 g. (0.13 g.-atoms) of magnesium was added 30 g. (0.13 mole) of 4-bromobiphenyl in 175 ml. of anhydrous ether dropwise with stirring.

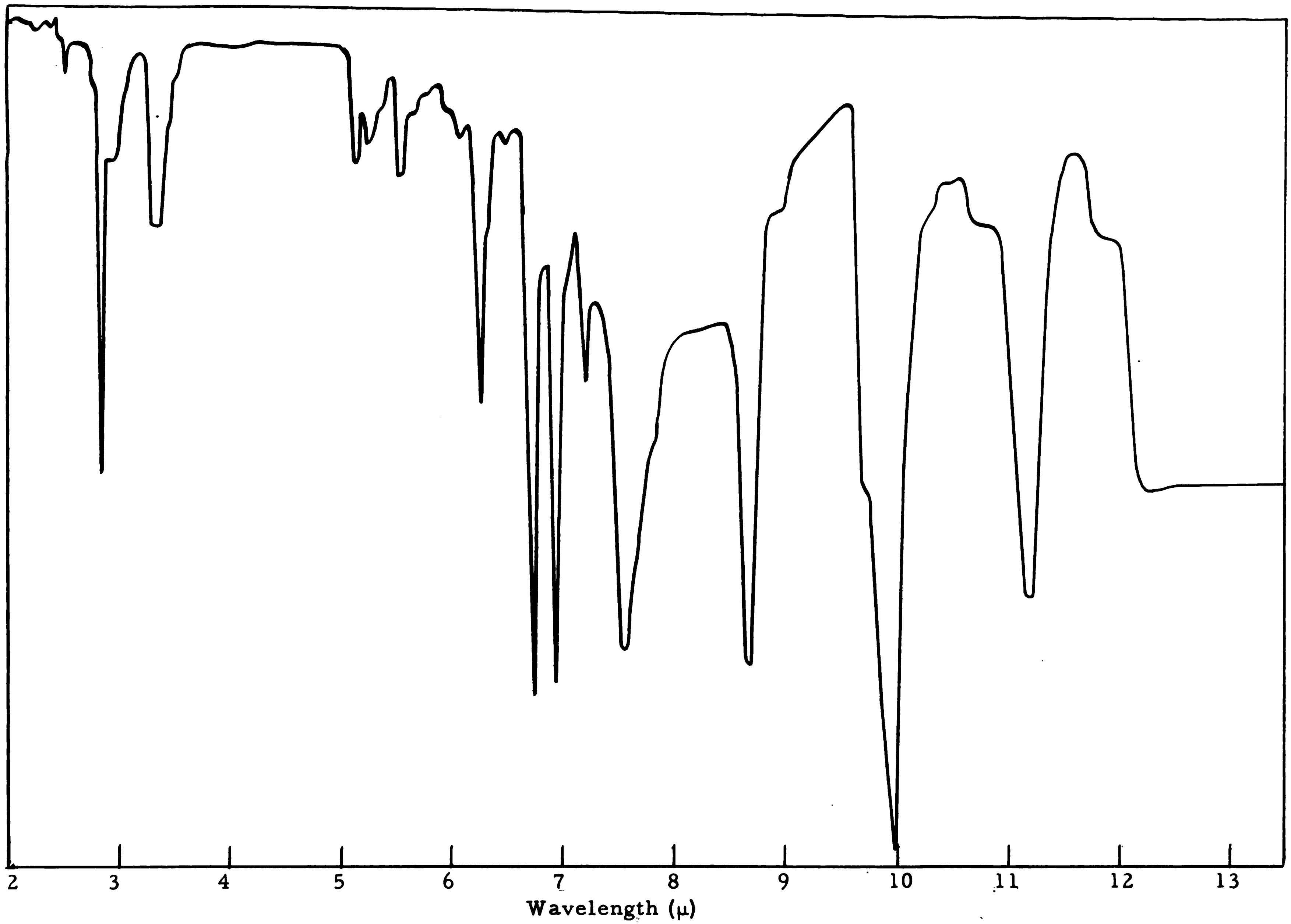


Figure 34. Infrared spectrum of α, α, α', α'-tetraphenyl-p, p'-bitolyl-α, α'-diol ($CHCl_3$ Solution).

After 5 hours, 18.2 g. (0.10 mole) of benzophenone in 100 ml. of dry ether was added dropwise. The stirring was continued for 12 hours, at which time the reaction mixture was poured onto 500 ml. of an ice-sulfuric acid mixture. The ether layer was separated, washed with 5% sodium carbonate solution, with water and the ether distilled. The residue was steam distilled for two hours, taken up in benzene, dried over magnesium sulfate and the benzene distilled. Recrystallization of the residue from cyclohexane gave 11.2 g. (33%) of 4-biphenylyldiphenyl methanol, m.p. 134-135° (literature value, 136°). Its infrared spectrum is shown in Figure 35.

Reaction of 4-Biphenylyldiphenylmethanol in 98% Sulfuric Acid with Water

4-Biphenylyldiphenylmethanol (0.08 g., 0.24 mmole) was dissolved in 10 ml. of 98% sulfuric acid. After being magnetically stirred for 10 hours, the red solution was poured onto 100 ml. of an ice-water mixture to give a clear solution. The aqueous solution was refluxed for 5 hours, cooled and extracted 3 times with 25-ml. portions of ether. The ether layer was washed 2 times with 15 ml. portions of 5% sodium carbonate, dried over magnesium sulfate and the ether layer distilled to give 0.06 g. (75%) of 4-biphenylyldiphenylmethanol, m.p. 135°. A m.m.p. with an authentic sample gave no depression.

Reaction of 4-Biphenylyldiphenylmethanol in Dilute Sulfuric Acid-Acetic Acid with Water

To 4-biphenylyldiphenylmethanol (0.01 g., 0.3 mmole) in 5 ml. glacial acetic acid, 2 drops of 98% sulfuric acid was added. The red solution was cooled in an ice bath for 15 minutes and then poured onto 150 ml. of an ice-water mixture. The resulting white precipitate was collected to give a quantitative recovery of 4-biphenylyldiphenylmethanol. It was identical in all respects with an authentic sample.

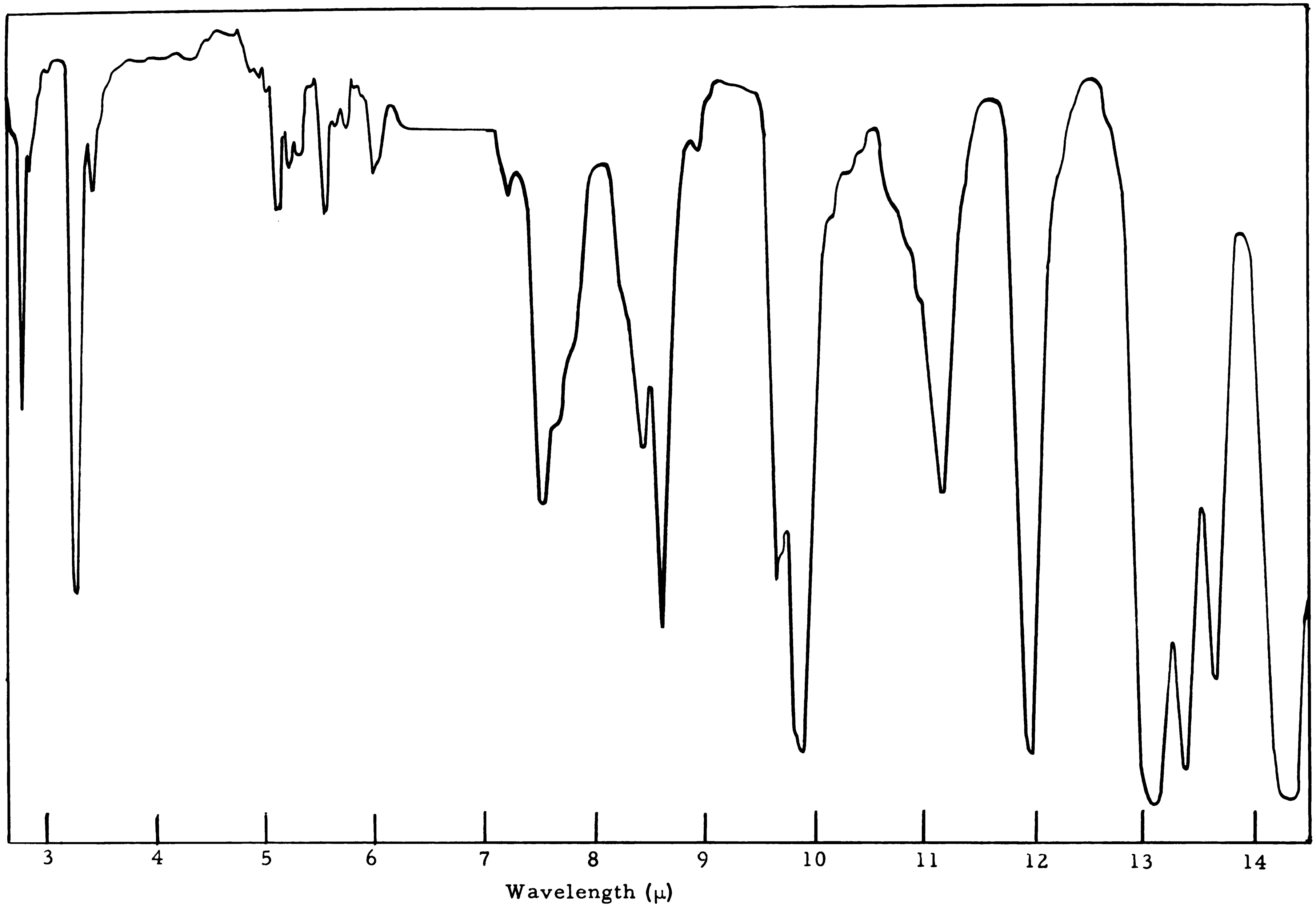


Figure 35. Infrared spectrum of 4-biphenylyldiphenylmethanol (CS_2 solution).

Preparation of 2-Biphenylyldiphenylmethanol

2-Bromobiphenyl (10 g., 0.043 mole) in 50 ml. of dry ether was treated with lithium (0.6 g., 0.086 g.-atoms) to form 2-lithiobiphenyl. Benzophenone (7.8 g., 0.043 mole) was added with stirring and the reaction was refluxed for two hours. The reaction mixture was poured onto 200 ml. of an ice-water mixture, extracted with benzene, steam distilled in the presence of sodium carbonate and the residue extracted with benzene. After being dried over magnesium sulfate, the benzene was distilled and the residue recrystallized from petroleum ether (35-60°) to give 6.2 g. (43%) of 2-biphenylyldiphenylmethanol, m.p. 91-92° (literature value, 87-88°) (84). Its infrared spectrum is shown in Figure 36.

Preparation of 4-Biphenylylphenylmethanol (102)

The procedure and amounts used were identical with that for the preparation of 4-biphenylyldiphenylmethanol (see page 123)except that 10.6 g. (0.1 mole) of benzaldehyde was used in place of the benzophenone. The yield was 23.0 g. (88%) of 4-biphenylylphenylmethanol which, after one recrystallization from cyclohexane, melted at 93-94° (literature value, 96°). The infrared spectrum is shown in Figure 37.

Preparation of α, α'-Diphenyl-p, p'-bitolyl-α, α'-diol

Lithium aluminum hydride (0.5 g., 12 mmoles) was added all at once to a magnetically stirred solution of 1.0 g. (2.8 mmoles) of 4,4'dibenzoylbiphenyl in 40 ml. of pyridine. After being heated at 70° for 2 hours, water was added dropwise to decompose the excess lithium aluminum hydride. When the reaction mixture was poured onto ice-hydrochloric acid a white solid precipitated and was collected by filtration. Recrystallization twice from ethanol gave 0.36 g. (35%) of α, α'-diphenyl-p, p'-bitolyl-α, α'-diol, m.p. 183°.

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05.
Found: C, 85.01; H, 6.17.

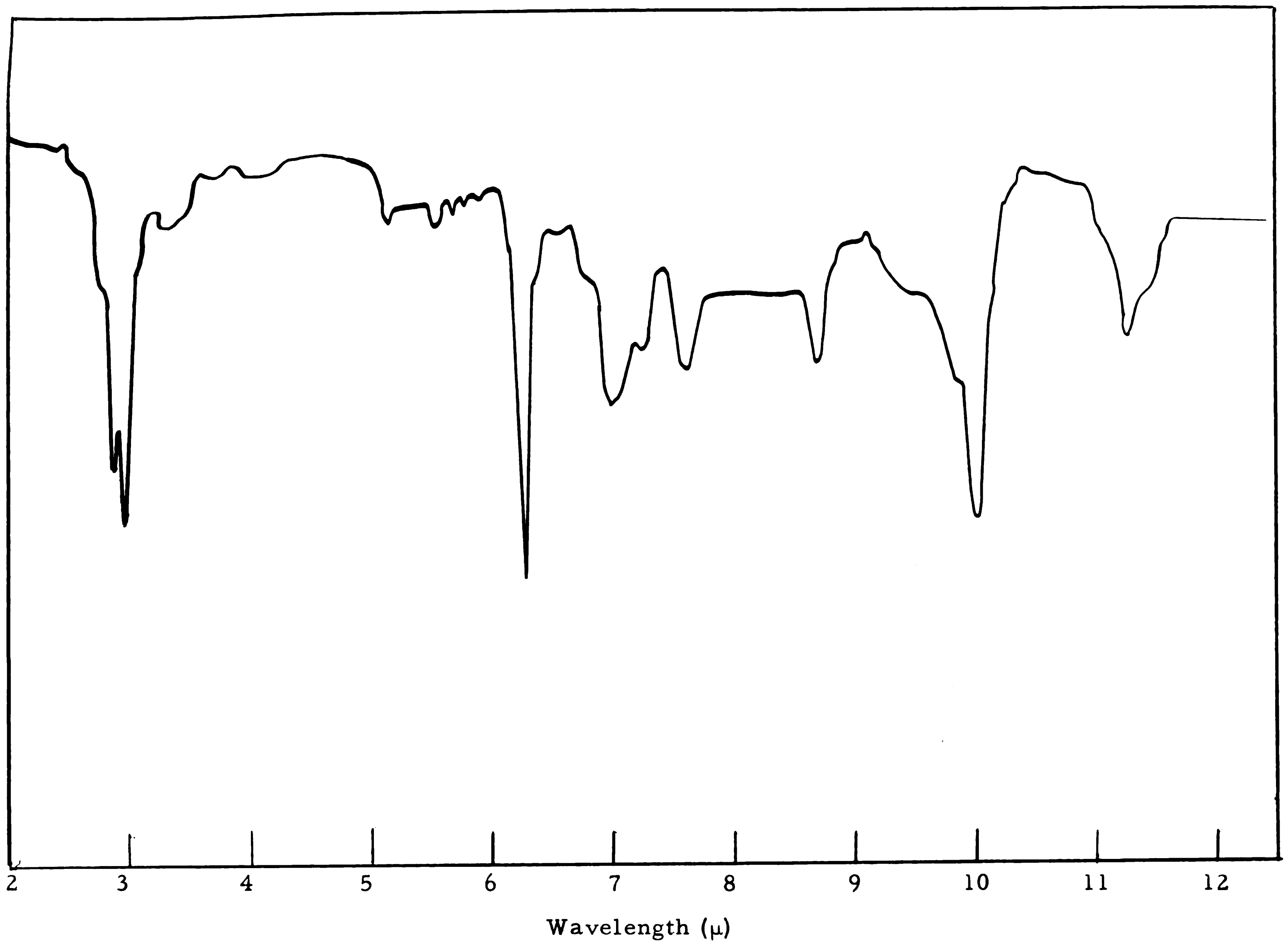


Figure 36. Infrared spectrum of 2-biphenylyldiphenylmethanol ($CHCl_3$ solution).

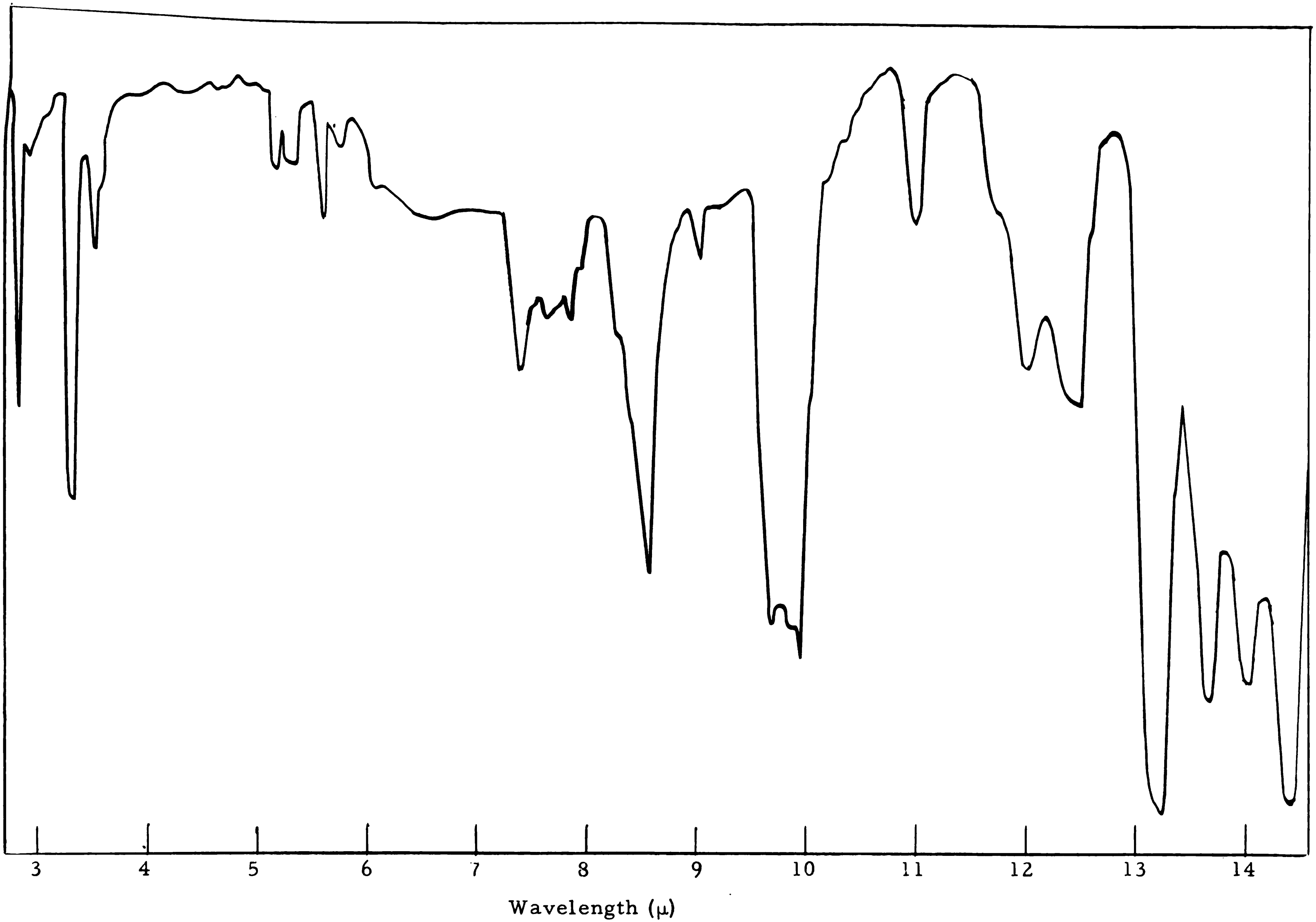


Figure 37. Infrared spectrum of 4-biphenylylphenylmethanol (CS_2 solution).

Reaction of 4-Biphenylyldiphenylmethanol with Benzoyl chloride and Aluminum chloride

To a mechanically stirred solution of 4-biphenylyldiphenylmethanol (6.3 g., 0.018 mole) in 75 ml. of methylene chloride was added 5.3 g. (0.04 mole) of aluminum chloride. To this red solution (presumably due to carbonium ion formation) 2.6 g. (0.018 mole, 2.2 ml.) of benzoyl chloride in 50 ml. of methylene chloride was added dropwise. The reaction was refluxed for 3 hours, the organic layer separated and the methylene chloride evaporated in a stream of air. The residue was treated with 50 ml. of 5% sodium carbonate, extracted with benzene, dried over magnesium sulfate and the solvent distilled. Since an infrared spectrum of the residue showed only a small amount of carbonyl present, the reaction was repeated under more vigorous conditions. The procedure was the same as above with the following exceptions: 8.0 g. (0.06 moles) of aluminum chloride, 75 ml. of chloroform (in place of methylene chloride) and 8 hour reflux were used. After the same work-up, an infrared spectrum on the crude product still showed only a trace of carbonyl present.

Reaction of 4-Benzoylbiphenyl with Zinc Cyanide and Hydrochloric Acid

Hydrogen chloride was bubbled into a stirred solution of 10 g. (0.04 mole) of 4-benzoylbiphenyl and 7 g. (0.06 mole) of zinc cyanide in 150 ml. of tetrachloroethane for 1.5 hours. After aluminum chloride (23.2 g., 0.18 mole) was added portionwise with ice-bath cooling, hydrogen chloride was bubbled in for 2 hours at 30° and 3 hours at 50°. The reaction mixture was poured onto an ice-hydrochloric acid mixture, stirred for 3.5 hours and heated to boiling for 2 hours. The organic layer was separated, washed with 100 ml. of a 5% sodium carbonate solution and steam distilled. The product was a dark oil which was insoluble in organic solvents.

Preparation of 4-Bromo-4'-benzoylbiphenyl

To a stirred mixture of 14 g. (0.06 mole) of 4-bromobiphenyl and 9.8 g. (0.07 mole, 8.1 ml.) of benzoyl chloride in 150 ml. of carbon disulfide, 9.3 g. (0.07 mole) of aluminum chloride was added portionwise. After being refluxed for 28 hours, the reaction mixture was poured onto 500 ml. of ice-water, the organic layer separated and the carbon disulfide removed by distillation. The residue was treated with 250 ml. of a boiling 5% sodium carbonate solution and the solid filtered. Recrystallization twice from benzene-petroleum ether (35-60°) gave 14.1 g. (70%) of 4-bromo-4'-benzoylbiphenyl, m.p. 156.5-157.5°.

Anal. Calcd. for $C_{19}H_{13}BrO$: C, 67.67; H, 3.89; Br, 23.69.
Found: C, 67.51; H, 3.89; Br, 23.95.

The infrared spectrum is shown in Figure 38.

Wolff-Kishner Reduction of 4-Bromo-4'-benzoylbiphenyl

A mixture of 9.5 g. (0.027 mole) of 4-bromo-4'-benzoylbiphenyl, 2.3 g. (0.057 mole) of sodium hydroxide and 4.5 ml. of 99% hydrazine hydrate in 70 ml. of triethylene glycol was refluxed for 1 hour. The condenser was removed and the water was driven off (flask temperature was 210-220°). After an additional hour of refluxing, the reaction mixture was cooled, poured onto 200 ml. of an ice-water mixture and extracted with ether. The ether solution was dried over magnesium sulfate, filtered and the ether distilled. Since all attempts to recrystallize the residue were fruitless, the compound was used without further characterization.

Preparation of 4-Benzylbiphenyl

This compound was prepared by two different methods.

Method A: A mixture of 6.5 g. (0.025 mole) of 4-benzoylbiphenyl, 1.75 g. (0.045 mole) of sodium hydroxide and 3 ml. of 99% hydrazine

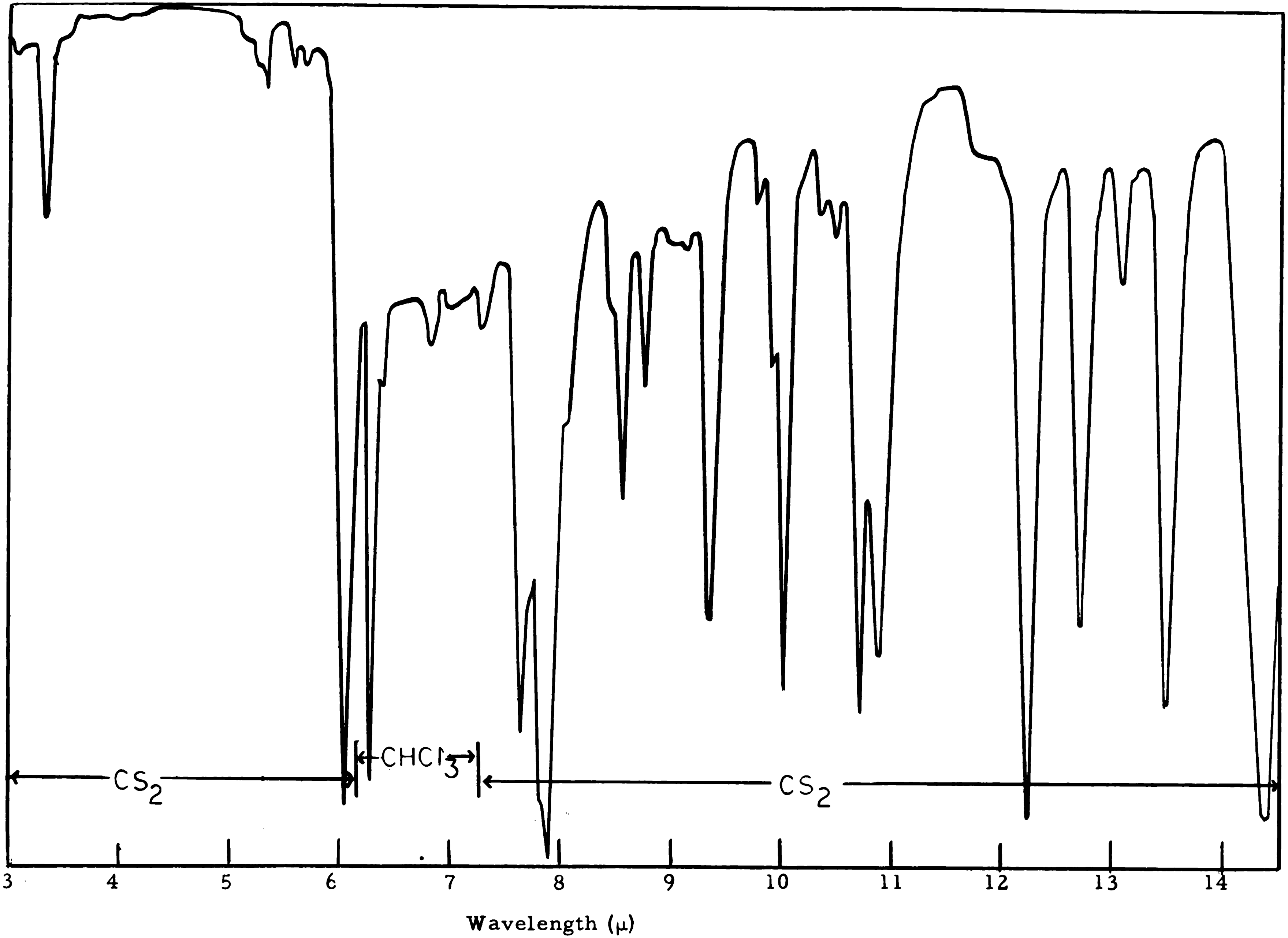


Figure 38. Infrared spectrum of 4-bromo-4'-benzoylbiphenyl.

hydrate in 50 ml. of triethylene glycol was treated in the same way as was 4-bromo-4'-benzoylbiphenyl (see above). After the ether was distilled, 4.25 g. (70%) of crude 4-benzylbiphenyl resulted, m.p. 79-81°. One recrystallization from isopropyl alcohol raised the melting point to 84-85° (literature value, 85°) (103).

Method B: To a stirred solution of 0.65 g.(0.027 g.-atoms) of magnesium in 30 ml. of dry ether was added dropwise the residue from the Wolff-Kishner reduction of 4-bromo-4'-benzoylbiphenyl in 30 ml. of ether. After being refluxed for 0.5 hour, water was added dropwise and the resulting solid was collected by filtration. Recrystallization from isopropyl alcohol gave 3.0 g. (45%) of 4-benzoylbiphenyl. The m.p. and m.m.p. of the products from method A and method B were identical.

Preparation of 4-(p-Bromophenyl)diphenylmethanol

To a stirred solution of 9.4 g. (0.027 mole) of 4-bromo-4'-benzoylbiphenyl in 100 ml. of pyridine, 0.5 g. (0.013 mole) of lithium aluminum hydride was added all at once. After refluxing for 2 hours, water was added dropwise to decompose the excess lithium aluminum hydride. The reaction mixture was poured onto an ice-hydrochloric acid mixture and the resulting white solid was collected. Recrystallization from isopropyl alcohol gave 7.1 g. (77%) of 4-(p-bromophenyl)diphenylmethanol, m.p. 120-121°.

Anal. Calcd. for $C_{19}H_{15}BrO$: C, 67.27; H, 4.46; Br, 23.56.
Found: C, 67.40, 67.27; H, 4.66, 4.66; Br, 23.44.

The infrared spectrum is shown in Figure 39 and the n.m.r. spectrum is shown in Figure 40. The n.m.r. spectrum is of interest since the apparent quartet at 4.17τ is due to spin-spin splitting between the hydrogens on the tertiary carbon and on the hydroxy group. The fact that they appear as a quartet and not two doublets is caused by the solvent, dimethyl sulfoxide (116).

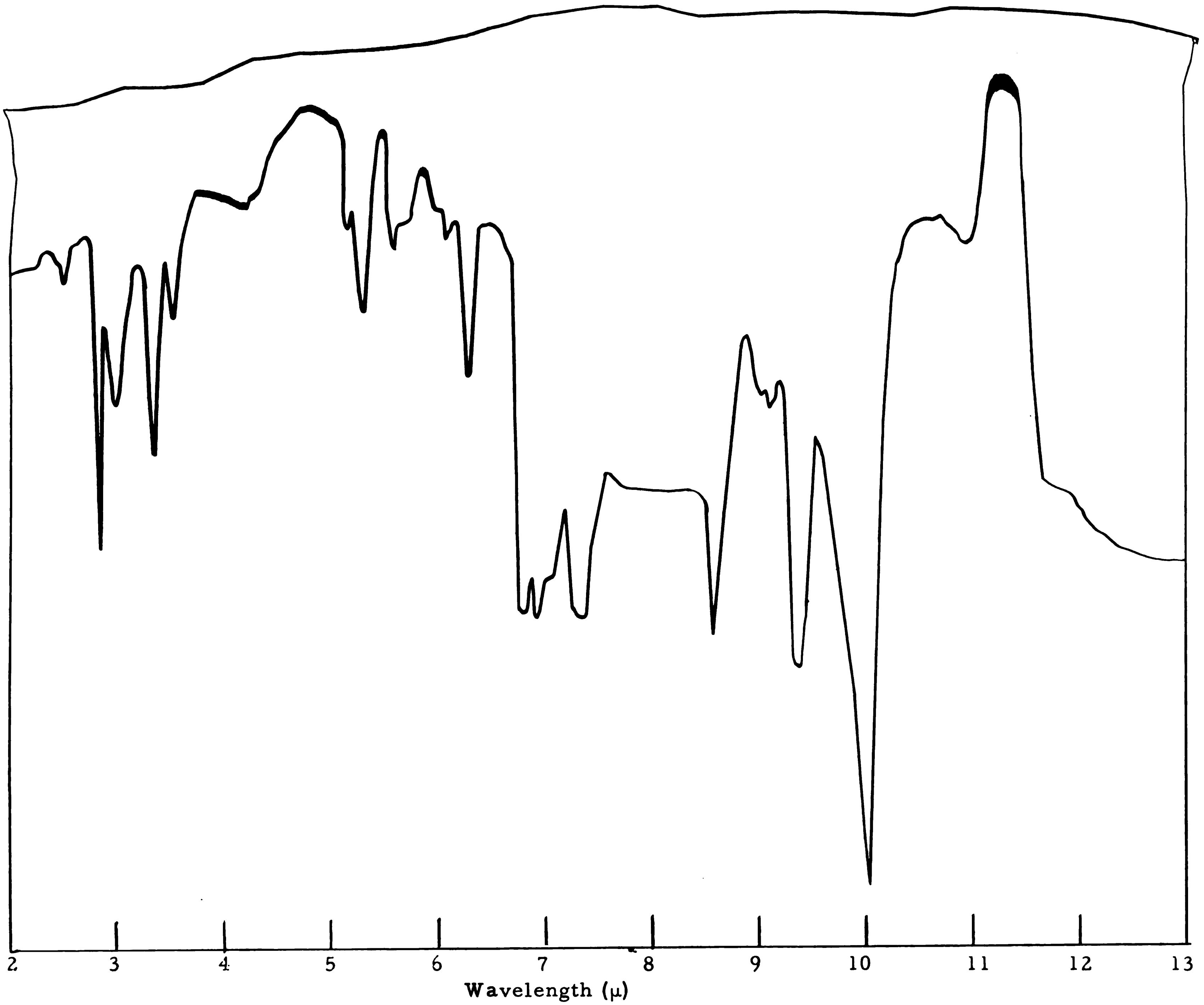


Figure 39. Infrared spectrum of 4-(p-bromophenyl)diphenylmethanol ($CHCl_3$ solution).

Figure 40. Nuclear magnetic resonance spectrum of 4-(p-bromophenyl)-diphenylmethanol. ($CH_3-\overset{O}{\overset{\|}{S}}-CH_3$ solution)

Preparation of the Methyl ether of 4-(p-Bromophenyl)-diphenylmethanol

To 4-(p-bromophenyl)diphenylmethanol (4.0 g., 12 mmoles) dissolved in 200 ml. of carbon tetrachloride, 50 ml. of 99% sulfuric acid was added all at once. The violet mixture was poured onto 200 ml. of ice-cold absolute methanol with stirring. The clear solution was poured onto ice, extracted with ether, dried over magnesium sulfate, filtered and the solvent distilled. The residue was recrystallized from isopropanol to give 3.1 g. (74%) of the methyl ether of 4-(p-bromophenyl)diphenylmethanol, m.p. 93-94°. The n.m.r. spectrum is shown in Figure 41.

Attempted Preparation of α, α, α'-Triphenyl-α-hydroxy-α'-methoxy-p, p'-bitolyl

To a stirred solution of 0.29 g. (12 mg.-atoms) of magnesium in 25 ml. of anhydrous ether, 3.1 g. (8.7 mmoles) of the methyl ether of 4-(bromophenyl)diphenylmethanol and 0.2 g. (1 mmole) of ethylene bromide in 30 ml. of dry benzene were added. After reaction of the magnesium appeared to be complete, 1.6 g. (8.7 mmoles) of benzophenone in 30 ml. of dry ether was added. The reaction mixture was refluxed for 3 hours, poured onto an ice-hydrochloric acid mixture, extracted with benzene, and dried over magnesium sulfate-sodium carbonate. The benzene was distilled and the residue was recrystallized from benzene-ligroin (90-120°) to give 1.4 g. of solid material, m.p. 178-179°.

Anal. Calcd. for $C_{33}H_{28}O_2$: C, 86.81, H, 6.18.

Found: C. 84.86, 84.92; H, 6.11, 6.16.

The infrared spectrum is shown in Figure 42.

Preparation of Methyl 3-Iodobenzoate

3-Iodobenzoic acid (24.8 g., 0.1 mole) in 125 ml. of anhydrous methanol saturated with dry hydrogen chloride was refluxed for 5 hours

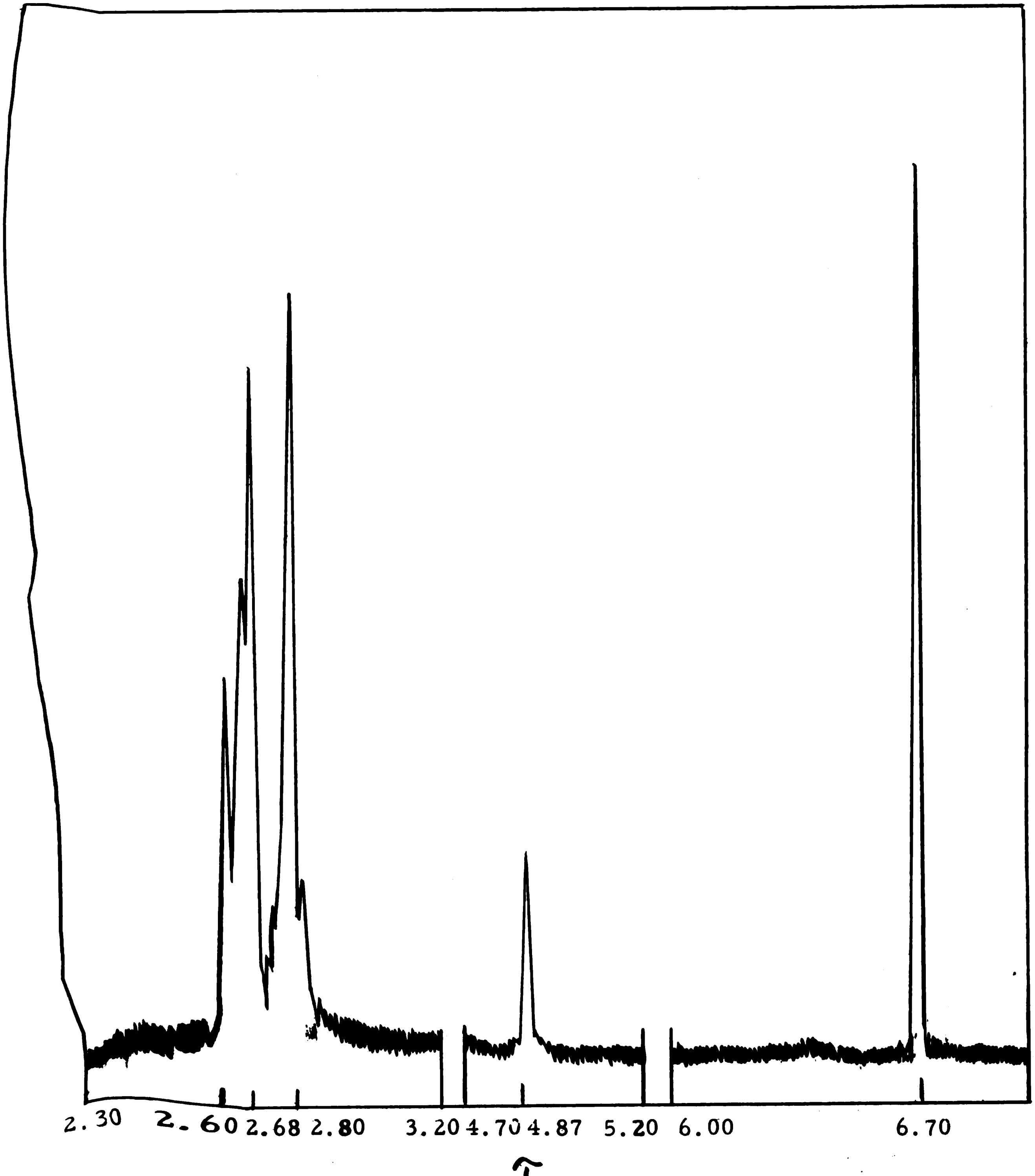


Figure 41. Nuclear magnetic resonance spectrum of the methyl ether of 4-(p-bromophenyl)diphenylmethanol.(CCl_4 solution).

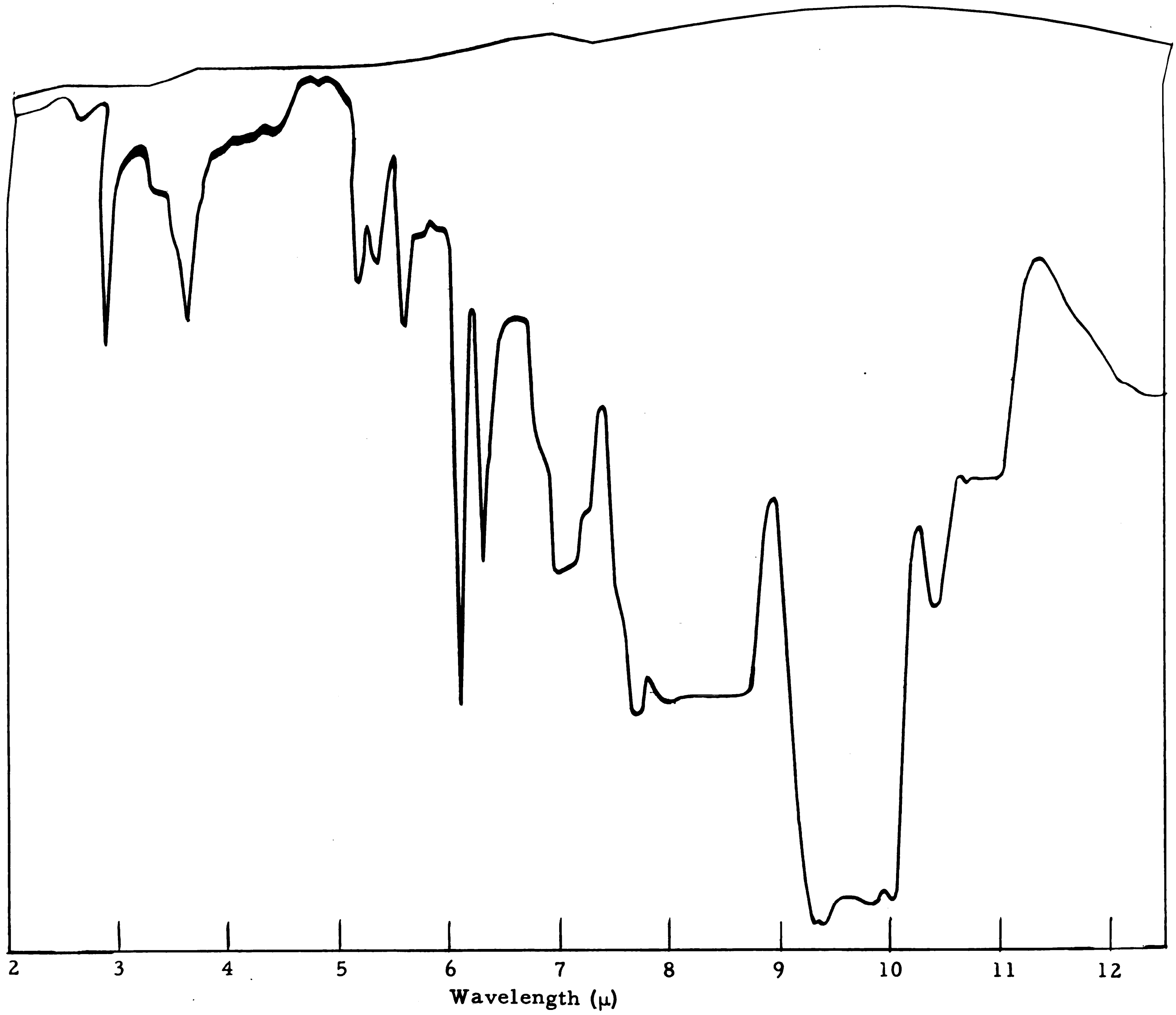


Figure 42. Infrared spectrum of the solid isolated from the reaction of 4-(p-bromophenyl)diphenylmethanol and magnesium with benzophenone (CHCl$_3$ solution)

with stirring. After the methanol was distilled, the resulting oil solidified and was dissolved in 100 ml. of ether. The ether solution was washed twice with 50-ml. portions of 5% sodium carbonate solution, once with 50 ml. of water and dried over calcium sulfate. Distillation of the ether resulted in 25.5 g. (98%) of methyl 3-iodobenzoate. After one recrystallization from ether, the ester melted at 48-50° (literature value, 54°) (104).

Preparation of 3, 3'-Dicarbomethoxybiphenyl

A. Activation of Copper Bronze (105)

Copper bronze (70 g.) was treated with 1 l. of a 2% solution of iodine in acetone for 10 minutes, filtered and treated for 15 minutes with 300 ml. of a hydrochloric acid - acetone mixture (1:1). After being filtered, the copper bronze was washed with acetone, dried and stored in a vacuum desiccator.

B. Preparation of 3, 3'-Dicarbomethoxybiphenyl

This is a modification of Kornblum's procedure (106). To a stirred solution of 22.1 g. (0.084 mole) of methyl 3-iodobenzoate in 100 ml. of dry dimethylformamide heated to reflux, 20 g. of copper bronze was added. After 5 hours, 25 g. of copper bronze was added and the refluxing was continued for an additional 48 hours. The reaction mixture was filtered hot, the filtrate poured onto 500 ml. of ice-water and the resulting precipitate filtered. The solid was dissolved in benzene, dried over magnesium sulfate and the benzene distilled to give 8.0 g. (70%) of 3, 3'-dicarbomethoxybiphenyl, m.p. 96-97° (literature value, 104°).

Preparation of α, α'-Dichloro-α, α, α', α'-tetraphenyl-m, m'-bitolyl

To a stirred solution of 0.15 moles of phenylmagnesium bromide (from 23.5 g. of bromobenzene and 3.6 g. of magnesium) in 50 ml. of dry ether, 8.0 g. (0.029 mole) of 3,3'-dicarbomethoxybiphenyl in 150 ml. of dry benzene was added dropwise. After being refluxed for 24 hours, the reaction mixture was poured onto 700 ml. of an ice-sulfuric acid mixture, the organic layer was separated and dried over magnesium sulfate. The benzene was distilled to a volume of 25 ml. and addition of petroleum ether (35-60°) resulted in the formation of a solid. On heating, the precipitate dissolved, but on cooling an oil resulted. The solvent was distilled, the residue was dissolved in 60 ml. of an acetic acid-acetyl chloride mixture (1:2) and anhydrous hydrogen chloride was bubbled into the solution for 1 hour. The α,α'-dichloro-α,α,α',α'-tetraphenyl-m,m'-bitolyl (5.6 g., 35%) was collected. After one recrystallization from toluene-acetyl chloride it melted at 176-177° (literature value, 175-176°) (98).

Preparation of α,α,α',α'-Tetraphenyl-m,m'-bitolyl-α,α'-diol

α,α'-Dichloro-α,α,α',α'-tetraphenyl-m,m'-bitolyl (1.0 g., 1.8 mmoles) was dissolved in 97% sulfuric acid. The red solution was poured onto 100 ml. of ice-water with formation of a colorless precipitate. The solid was filtered, washed with 5% sodium carbonate, with water and dried. Recrystallization from toluene-ligroin (90-120°) gave 0.65 g. (70%) of α,α,α',α'-tetraphenyl-m,m'-bitolyl-α,α'-diol, m.p. 186-187° (literature value, 183-184°) (98).

Preparation of 2,2'-Dicarbomethoxybiphenyl (107)

Diphenic acid (15.0 g., 0.062 mole) in 100 ml. of anhydrous methanol saturated with dry hydrogen chloride was refluxed for 12 hours with stirring. After one-half of the methanol was removed by distillation, a solid was deposited. It was collected, washed twice with 30-ml. portions of 5% sodium carbonate, twice with 50-ml. portions of water and recrystallized from methanol to give 11.2 g. (67%) of 2, 2'-dicarbomethoxybiphenyl, m.p. 70-71° (literature value, 73-74°).

Preparation of α, α, α', α'-Tetraphenyl-o, o'-bitolyl-α, α'-diol (89)

2, 2'-Dicarbomethoxybiphenyl (11.2 g., 0.041 mole) in 100 ml. of anhydrous ether was added dropwise with stirring to 0.33 mole of phenyllithium (from 51.8 g. of bromobenzene and 4.6 g. of lithium) in 150 ml. of anhydrous ether under a dry nitrogen atmosphere. After being stirred overnight, the reaction mixture was poured onto 700 ml. of ice-hydrochloric acid, the ether was evaporated in a stream of dry air and the solid was filtered. The yield of crude tetraphenyl-o, o'-bitolylyl glycol was 20.0 g. (94%). After one recrystallization from toluene, it melted at 247-250° (literature value, 252-253°).

Preparation of the Anhydro Derivative of α, α, α', α'-Tetraphenyl-o, o'-bitolyl-α, α'-diol

α, α, α', α'-Tetraphenyl-o, o'-bitolyl-α, α'-diol (1.0 g., 1.8 mmoles) in 60 ml. of acetic acid-water (5:1) was refluxed for 2 hours. The reaction mixture was poured onto 400 ml. of ice-water and the resulting solid was collected, washed twice with 20 ml.-portions of 5% sodium carbonate solution, once with 30 ml. of water and then dried. There resulted 0.85 g. (88%) of the anhydro derivative of α, α, α', α'-tetraphenyl-o, o'-bitolyl-α, α'-diol, m.p. 290-292° (literature value, 290-292°) (98).

Reaction of α, α, α', α'-Tetraphenyl-o, o'-bitolyl-α, α'-diol in 98% Sulfuric Acid with Water.

α, α, α', α'-Tetraphenyl-o, o'-bitolyl-α, α'-diol (0.150 g., 0.29 mmole) was dissolved in 10 ml. of 98% sulfuric acid. The resulting yellow solution was poured onto 150 ml. of ice-water. The white solid was collected, washed with 5% sodium carbonate solution, with water and dried to give 0.125 g. (86%) of the anhydro derivative of α, α, α', α'-tetraphenyl-o, o'-bitolyl-α, α'-diol. The m.p. and m.m.p. were identical to that of a known sample.

C. The Diols and Carbinols in the Fluorene Series

Preparation of 2-Benzoylfluorene (108)

To a stirred solution of 33.3 g. (0.2 mole) of fluorene and 28.2 g. (0.2 mole) of benzoyl chloride in 250 ml. of carbon disulfide, 20.0 g. (0.15 mole) of aluminum chloride was added in small portions. After being stirred for 4 hours at room temperature, the reaction was heated at reflux for 0.5 hour to expel hydrogen chloride. The reaction mixture was poured onto ice-water, the carbon disulfide layer was separated and dried over calcium sulfate. The carbon disulfide was distilled and a white solid resulted. Recrystallization from ethanol gave 34.2 g. (85%) of 2-benzoylfluorene, m.p. 123-124° (literature value, 124-125°).

Preparation of α-Chloro-α-phenyl-2-methylfluorene

To a stirred solution of 2-benzoylfluorene (1.9 g., 7 mmoles) in 25 ml. of pyridine, 0.27 g. (7 mmoles) of lithium aluminum hydride was added all at once. After heating for 2 hours at 40°, the reaction mixture was poured onto 150 ml. of an ice-hydrochloric acid mixture, extracted with ether and dried over magnesium sulfate. The ether was distilled and an attempt was made to recrystallize the resulting residue. Since all recrystallization efforts were fruitless, the oily residue was dissolved in 20 ml. of toluene-ligroin (90-120°) and anhydrous hydrogen chloride was bubbled through for 20 minutes. The brown solid was collected and recrystallized from toluene-petroleum ether (35-60°) to give 0.67 g. (35%) of α-chloro-α-phenyl-2-methylfluorene, m.p. 115-118°

(literature value, 122.5-123.5°) (109). Its infrared spectrum is shown in Figure 43.

Preparation of α-Phenyl-α-hydroxy-2-methylfluorene

α-Chloro-α-phenyl-2-methylfluorene (0.67 g., 2.5 moles) was dissolved in 50 ml. of aqueous acetic acid (80%) and the mixture was heated to reflux for 1 hour. The acetic acid solution was poured onto an ice-water mixture, extracted with ether, dried over magnesium sulfate and the ether distilled. The residue was recrystallized from aqueous ethanol to give 0.50 g. (74%) of α-phenyl-α-hydroxy-2-methylfluorene, m.p. 105-107° (literature value, 113-114°) (109).

Preparation of α, α-Diphenyl-α-hydroxy-2-methylfluorene

To 0.090 mole of phenylmagnesium bromide (from 14.1 g. of bromobenzene and 2.2 g. of magnesium) in 50 ml. of anhydrous ether, was added dropwise 12.3 g. (0.0455 mole) of 1-benzoylfluorene in 245 ml. of benzene-ether (2.5:1). After 4 hours of reflux, the reaction mixture was poured onto 500 ml. of an ice-hydrochloric acid mixture, extracted with benzene and dried over calcium sulfate. The benzene was distilled to a small volume and placed on a neutral alumina column. Elution was done with cyclohexane, benzene, ether and methanol. In all, 44 fractions were collected and fractions 19-35 (benzene and benzene-ether (1:1)) were used. The solvents were distilled and the combined residues were recrystallized from acetone-petroleum ether (35-60°) to give 6.5 g. (41%) of α, α-diphenyl-α-hydroxy-2-methylfluorene, m.p. 145-146° (literature value, 143-144°) (110). Its infrared spectrum is shown in Figure 44.

Reaction of α, α-Diphenyl-α-hydroxy-2-methylfluorene in 97% Sulfuric Acid with Water

α, α-Diphenyl-α-hydroxy-2-methylfluorene (0.067 g., 0.19 mmole)

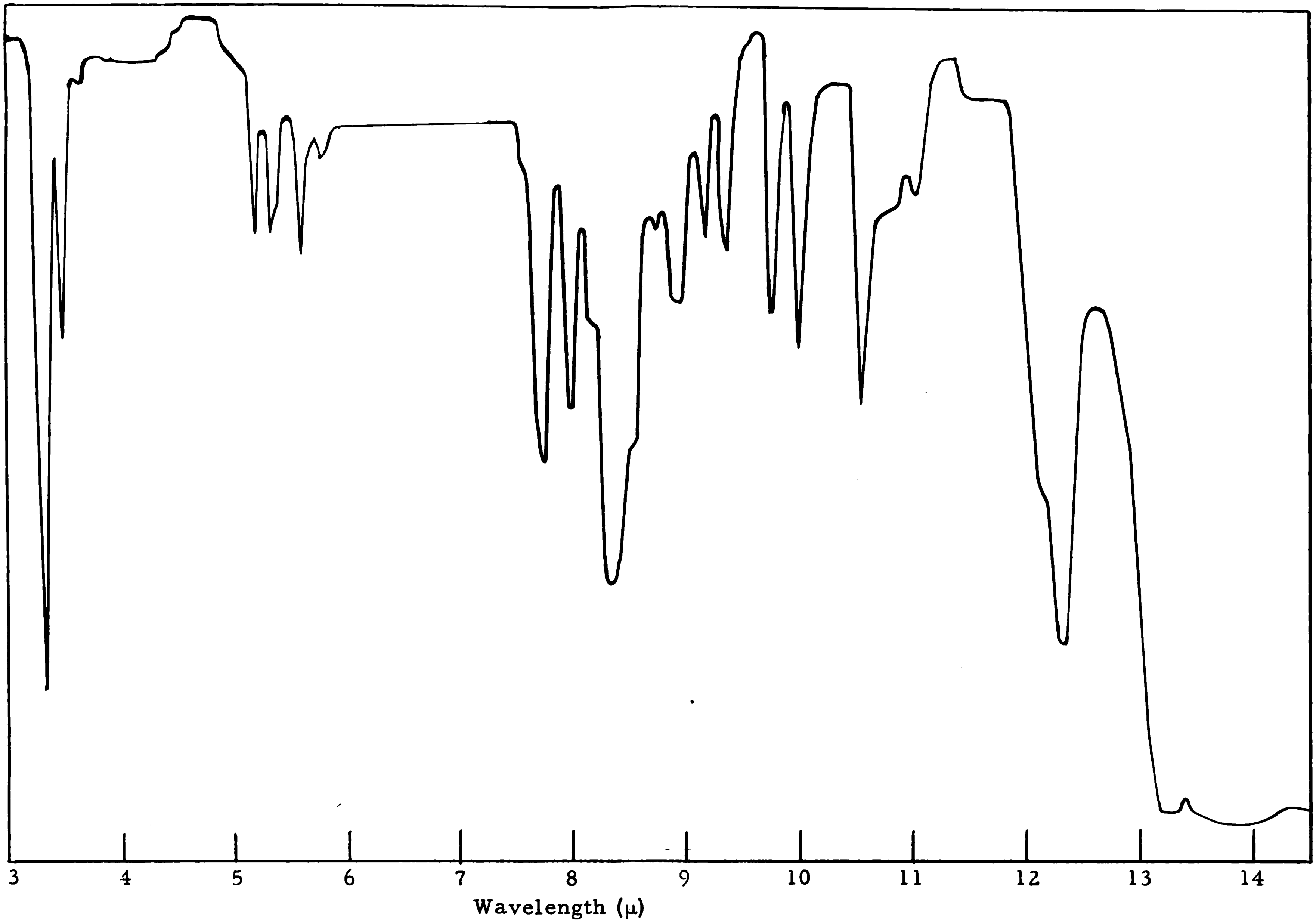


Figure 43. Infrared spectrum of α-chloro-α-phenyl-2-methylfluorene (CS_2 solution).

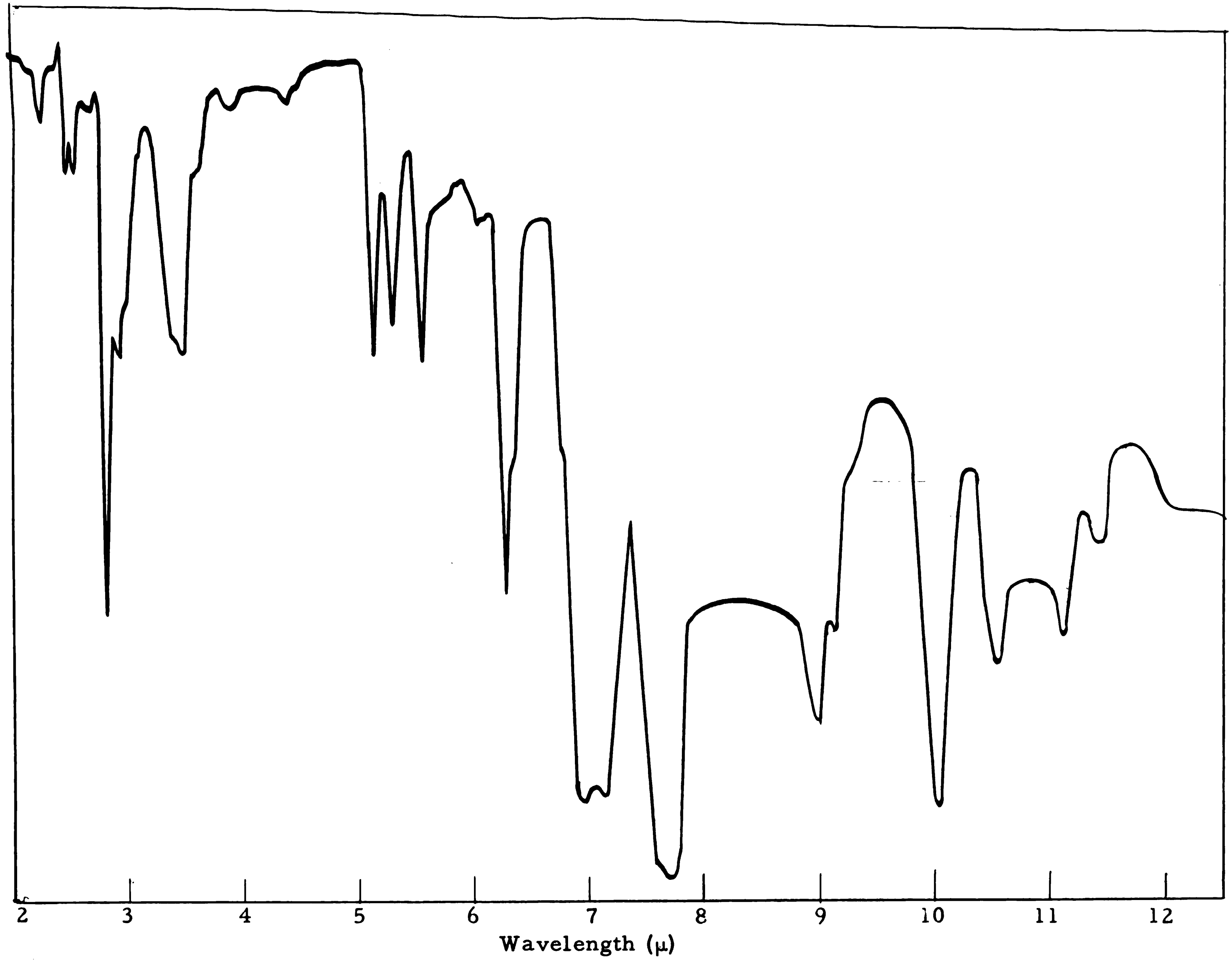


Figure 44. Infrared spectrum of α, α-diphenyl-α-hydroxy-2-methylfluorene ($CHCl_3$ solution).

was dissolved in 25 ml. of 97% sulfuric acid. The purple solution rapidly became orange-red. After stirring for several minutes, the solution was poured onto 300 ml. of an ice-water mixture. No precipitate resulted but the solution was extracted twice with 25 ml.-portions of ether, dried over calcium chloride and the ether distilled. An infrared spectrum of the residue (see Figure 45) showed the presence of strong bands between 9 and 10 μ, indicative of sulfonic acids.

Reaction of α, α-Diphenyl-α-hydroxy-2-methylfluorene in 85% Sulfuric Acid with Water

α, α-Diphenyl-α-hydroxy-2-methylfluorene (0.07 g., 0.20 mmole) was dissolved in 25 ml. of 85% sulfuric acid. The purple solution was stirred for one minute, poured onto 300 ml. of an ice-water mixture and the resulting white precipitate collected by filtration. The solid was washed with 5% sodium carbonate, taken up in ether and dried over magnesium sulfate. Distillation of the ether gave 0.060 g. (85%) recovery of α, α-diphenyl-α-hydroxy-2-methylfluorene. It was identical in all respects with an authentic sample.

Preparation of 2, 7-Dibenzoylfluorene (111)

To a stirred solution of 15.0 g. (0.056 mole) of 2-benzoylfluorene and 8.0 g. (0.056 mole) of benzoyl chloride in 100 ml. of carbon disulfide, 20.0 g. (0.15 mole) of aluminum chloride was added in small portions. After refluxing for 5 hours, 200 ml. of water was added and the resulting solid was filtered. Recrystallization from isopropyl alcohol gave 14.1 g. (67%) of 2, 7-dibenzoylfluorene, m.p. 193-194^{o} (literature value, 193-194^{o}).

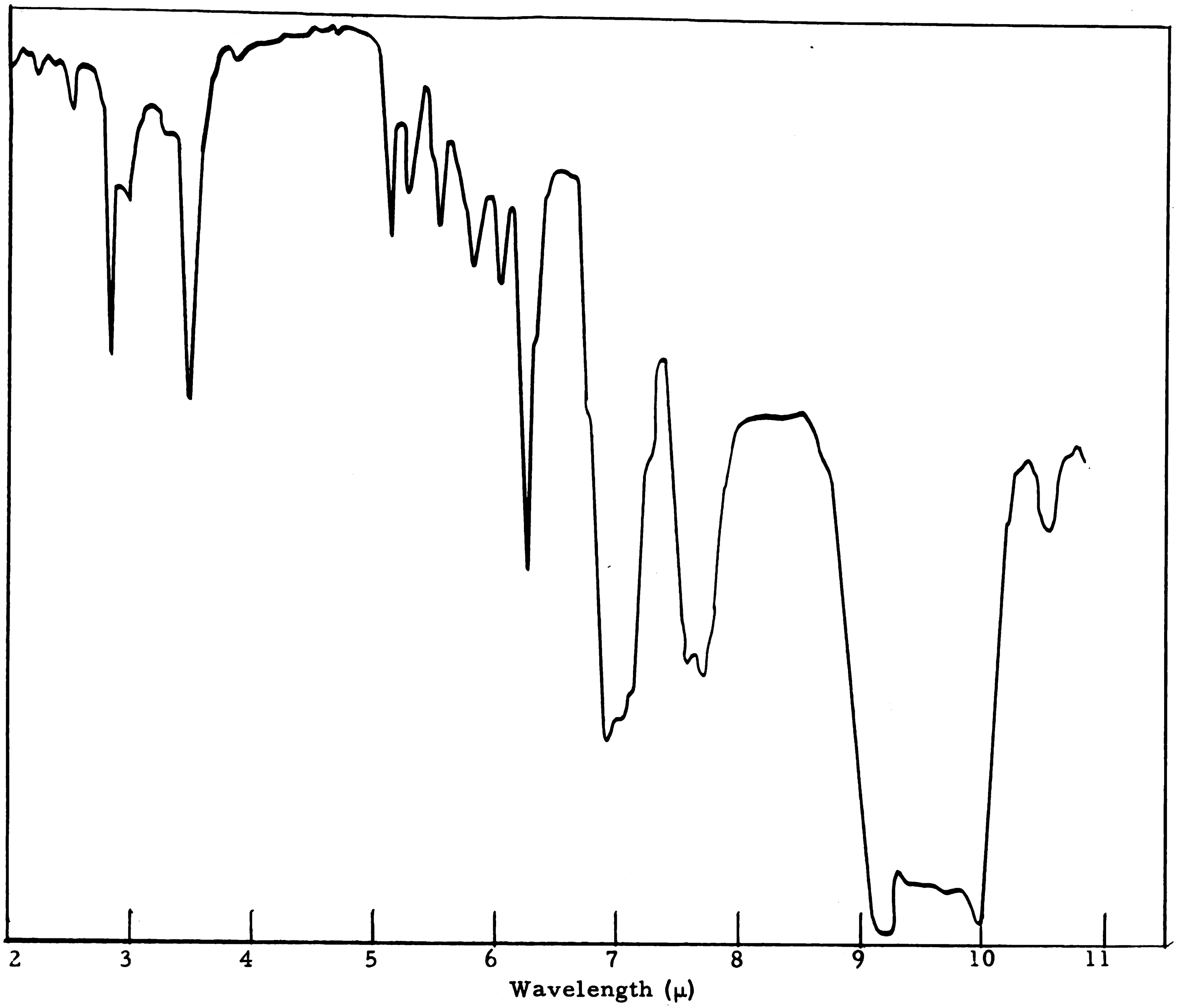


Figure 45. Infrared spectrum of the hydrolysis product of α, α-diphenyl-α-hydroxy-2-methylfluorene in 97% sulfuric acid. ($CHCl_3$ solution).

Preparation of α, α'-Dichloro-α, α'-diphenyl-2, 7-dimethylfluorene

To a stirred solution of 1.30 g. (3.5 mmoles) of 2, 7-dibenzoylfluorene in 60 ml. of pyridine, 0.14 g. (3.5 mmoles) of lithium aluminum hydride was added all at once. After 1 hour, water was added to decompose the excess lithium aluminum hydride and the reaction mixture was poured onto an ice-hydrochloric acid mixture, extracted with ether and dried over magnesium sulfate. After the ether was distilled, the residue was dissolved in 50 ml. of acetic acid-acetyl chloride (2:1) and anhydrous hydrogen chloride was bubbled in for 1 hour. The brown solid was collected and recrystallized from ligroin (90-120°) to give 0.42 g. (35%) of α, α'-dichloro-α, α'-diphenyl-2, 7-dimethylfluorene, m.p. 119-121°. After a second recrystallization (from ligroin-acetyl chloride) it melted at 121-122°.

Anal. Calcd. for $C_{27}H_{20}Cl_2$: C, 78.07; H, 4.85; Cl, 17.07

Found: C, 77.88, 77.92; H, 5.03, 4.87; Cl, 16.84, 16.91.

Preparation of α, α, α', α'-Tetraphenyl-2, 7-dimethylfluorene-α, α'-diol

2, 7-Dibenzoylfluorene (1.84 g., 4.9 mmoles) in 100 ml. of benzene-ether (3:1) was added dropwise to a stirred solution of 19.6 mmoles phenylmagnesium bromide (prepared in the usual way from 0.47 g. of magnesium and 3.08 g. of bromobenzene) in 30 ml. of anhydrous ether. The reaction mixture was refluxed for 2 hours, poured onto ice, extracted with benzene, dried over magnesium sulfate and the benzene distilled. The residue was recrystallized three times from toluene-ligroin (60-90°) to give 1.6 g. of α, α, α', α'-tetraphenyl-2, 7-dimethylfluorene-α, α'-diol, m.p. 218-219°.

Anal. Calcd. for $C_{39}H_{30}O_2$: C, 88.27; H, 5.70.

Found: C, 87.04, 86.86; H, 6.03, 6.17.

The infrared spectrum is shown in Figure 46.

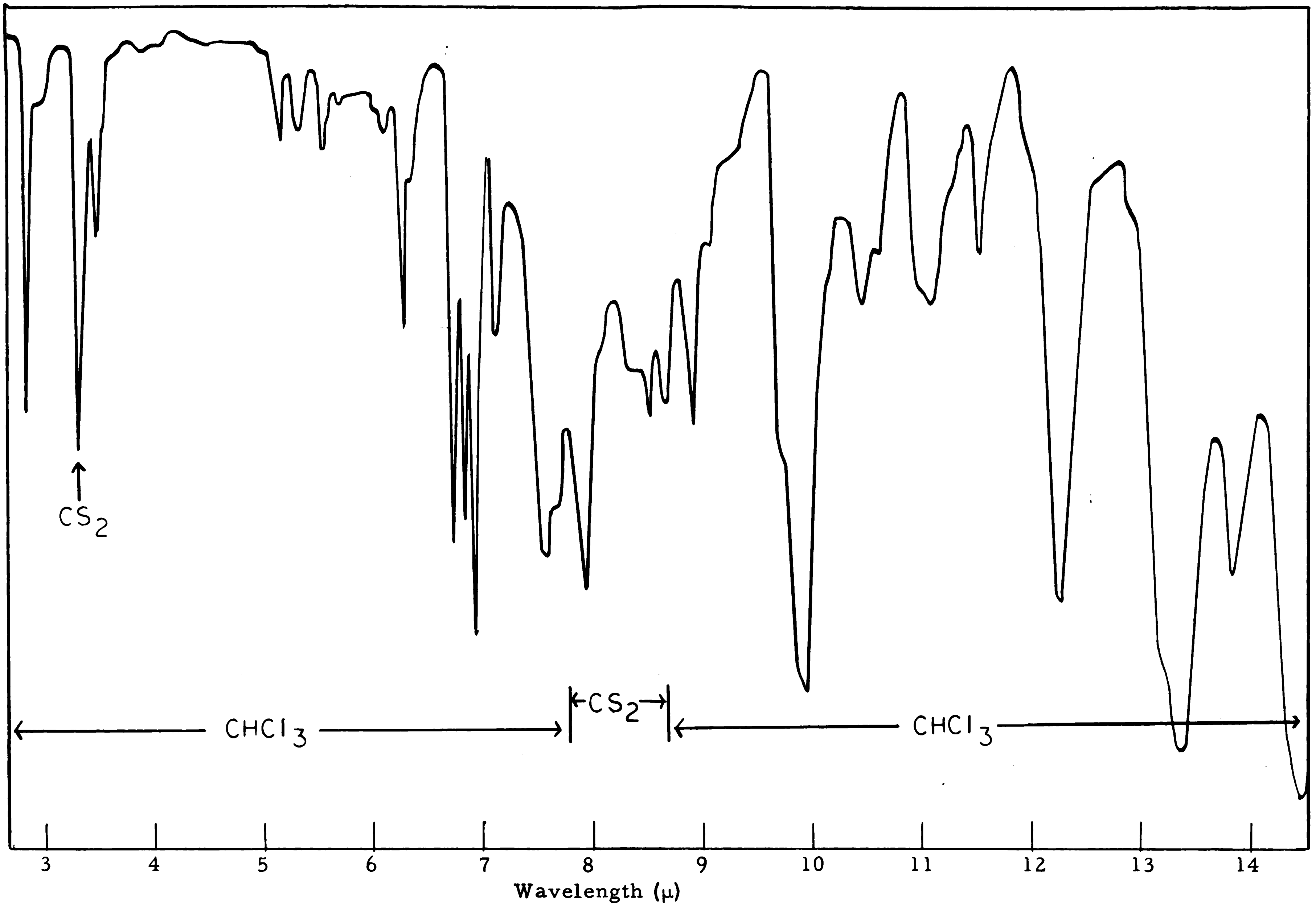


Figure 46. Infrared spectrum of α, α, α', α'-tetraphenyl-2, 7-dimethylfluorene-α,α'-diol.

D. The Diols and Carbinols in the Anthracene Series

Preparation of the Methyl Ether of 9, 10, 10-Triphenyl-9, 10-dihydro-9-anthrol

See page 110.

Preparation of the Ethyl Ether of 9, 10, 10-Triphenyl-9, 10-dihydro-9-anthrol

See page 112.

Preparation of 9, 10, 10-Triphenyl-9, 10-dihydro-9-anthrol

The methyl ether of 9, 10, 10-triphenyl-9, 10-dihydro-9-anthrol (0.100 g., 0.23 mmole) was dissolved in 10 ml. of 98% sulfuric acid. The red solution was poured onto 50 ml. of an ice-water mixture with stirring. The resulting white solid was filtered, washed with 5% sodium carbonate solution, with water and dried to give 0.80 g. (83%) of 9, 10, 10-triphenyl-9, 10-dihydro-9-anthrol. After one recrystallization from ligroin (90-120^{o}) it melted at 204-204.5^{o} (literature value, 204^{o}) (77). The infrared spectrum is shown in Figure 47.

Preparation of 10, 10-Diphenyl-9-anthrone (77, 78)

Dimethyl phthalate (14.4 g., 0.1 mole) in 40 ml. of anhydrous ether was added with mechanical stirring to 0.4 moles of phenylmagnesium bromide (from 62.8 g. of bromobenzene and 9.7 g. of magnesium) in 70 ml. of anhydrous ether. After the addition was complete, 100 ml. of dry benzene was added all at once and the reaction mixture was refluxed for 30 hours with stirring. It was then poured onto 300 ml. of ice-hydrochloric acid, extracted with benzene and the organic layer separated. The benzene was distilled and the residue steam distilled to remove side

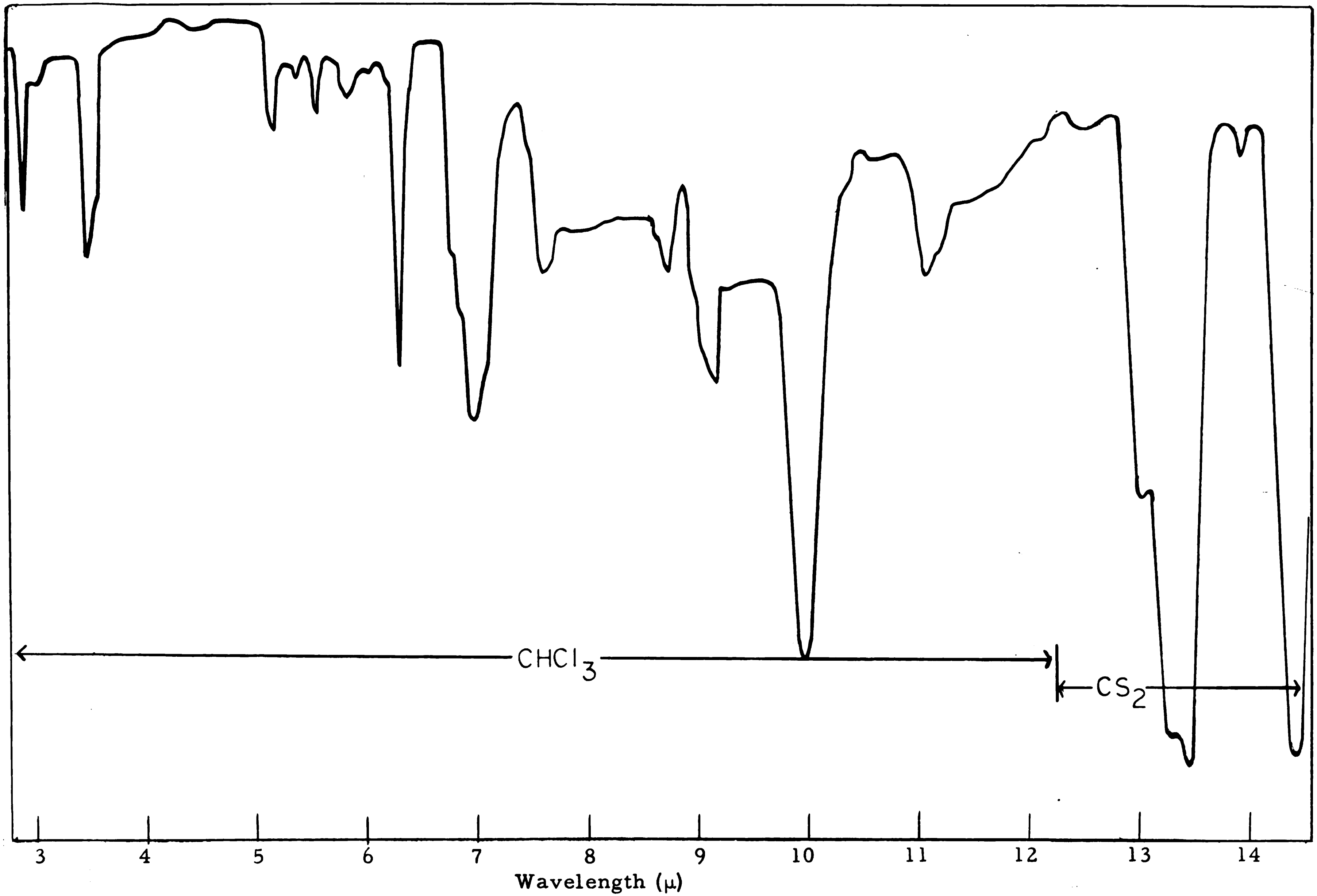


Figure 47. Infrared spectrum of 9, 10, 10-triphenyl-9, 10-dihydro-9-anthrol.

products and unreacted starting materials. The residue was again taken up in benzene and the mixture was distilled. The portion boiling between 100-200° at 1 mm. was collected and recrystallized from acetone to give 11 g. (32%) of an impure yellow solid, m.p. 175-190° (literature value, 194-195°). An infrared spectrum of the crude product showed strong carbonyl absorption at 6.08 microns. The 10, 10-diphenyl-9-anthrone was used without further purification.

Preparation of 9-Chloro-10, 10-diphenyl-9, 10-dihydroanthracene (112)

Crude 10, 10-diphenyl-9-anthrone (11 g., 0.03 mole) was dissolved in 50 ml. of anhydrous benzene and added dropwise to 0.95 g. (0.025 mole) of lithium aluminum hydride in 25 ml. of anhydrous ether. The reaction mixture was refluxed for 3 hours with magnetic stirring. After decomposition with water and with dilute sulfuric acid, the benzene-ether layer was separated and dried over magnesium sulfate. The solvents were distilled and the residue was dissolved in 15 ml. of benzene, 15 ml. of acetic acid and 25 ml. of acetyl chloride. Hydrogen chloride gas was passed through the solution for 3 hours and 5 g. (50%) of 9-chloro-10, 10-diphenyl-9, 10-dihydroanthracene was collected, m.p. 220°. One recrystallization from benzene raised the melting point to 224° (literature value, 226°). Its infrared spectrum is shown in Figure 48.

Preparation of trans-9, 10-Diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene

To 0.25 mole of phenylmagnesium bromide (from 40.0 g. of bromobenzene and 6.0 g. of magnesium) in 150 ml. of dry ether, a slurry of 15.2 g. (0.075 mole) of anthraquinone in 250 ml. of toluene was added with stirring. After addition was complete, the reaction mixture was stirred for one hour and refluxed for six. After the mixture was poured onto ice, the anthraquinone was collected, the organic layer separated,

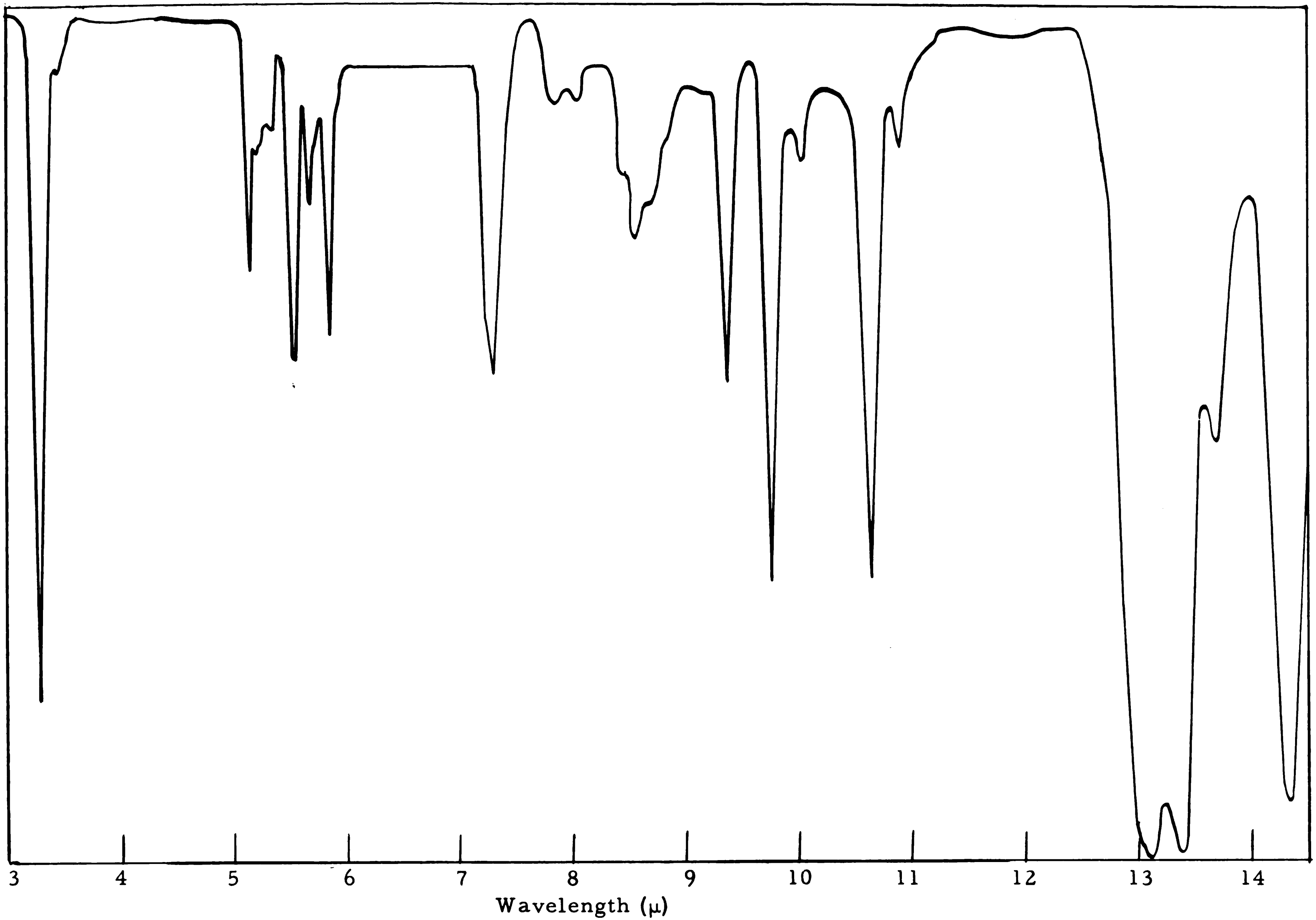


Figure 48. Infrared spectrum of 9-chloro-10, 10-diphenyl-9, 10-dihydroanthracene (CS_2 solution).

dried over magnesium sulfate and evaporated almost to dryness. The residue was extracted twice with boiling ethyl acetate and the filtrate evaporated to dryness. Recrystallization three times from toluene-ligroin gave 7.6 g. (28%) of trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene, m.p. 260-261° (literature value, 258-260°) (61). Its infrared spectrum is shown in Figure 49.

Reaction of trans-9, 10-Diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene in 65% Sulfuric Acid with Water

The red solution formed when trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene (0.280 g., 0.77 mmole) in 10 ml. of glacial acetic acid was reacted with 150 ml. of approximately 65% sulfuric acid, stirred for 10 minutes and then poured onto 200 ml. of an ice-water mixture. The resulting solid was collected, dried and recrystallized twice from toluene-ligroin (60-90°). The two types of crystals collected on the filter disk were separated by hand.

The needle-like solid melted at 258-260° and was found to be identical in all respects with the starting material.

The cube-like solid melted at 188-190° and had an infrared spectrum similar to that of trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene (see Figure 50).

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.71; H, 5.57.

Found: C, 89.24; H, 5.47.

This analysis is similar to that calculated for 9, 10-diphenyl-9, 10-epoxy-9, 10-dihydroanthracene (C, 90.17; H, 5.20). The melting point was identical to that reported for the epoxide (117) and for the cis-diol (118). Since the solid shows the presence of intramolecular hydrogen bonding in its infrared spectrum, it is proposed that it is cis-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene. When one attempts to take its melting point, it dehydrates to the oxide. The same is true for its analysis since it was first heated at 100° for one hour.

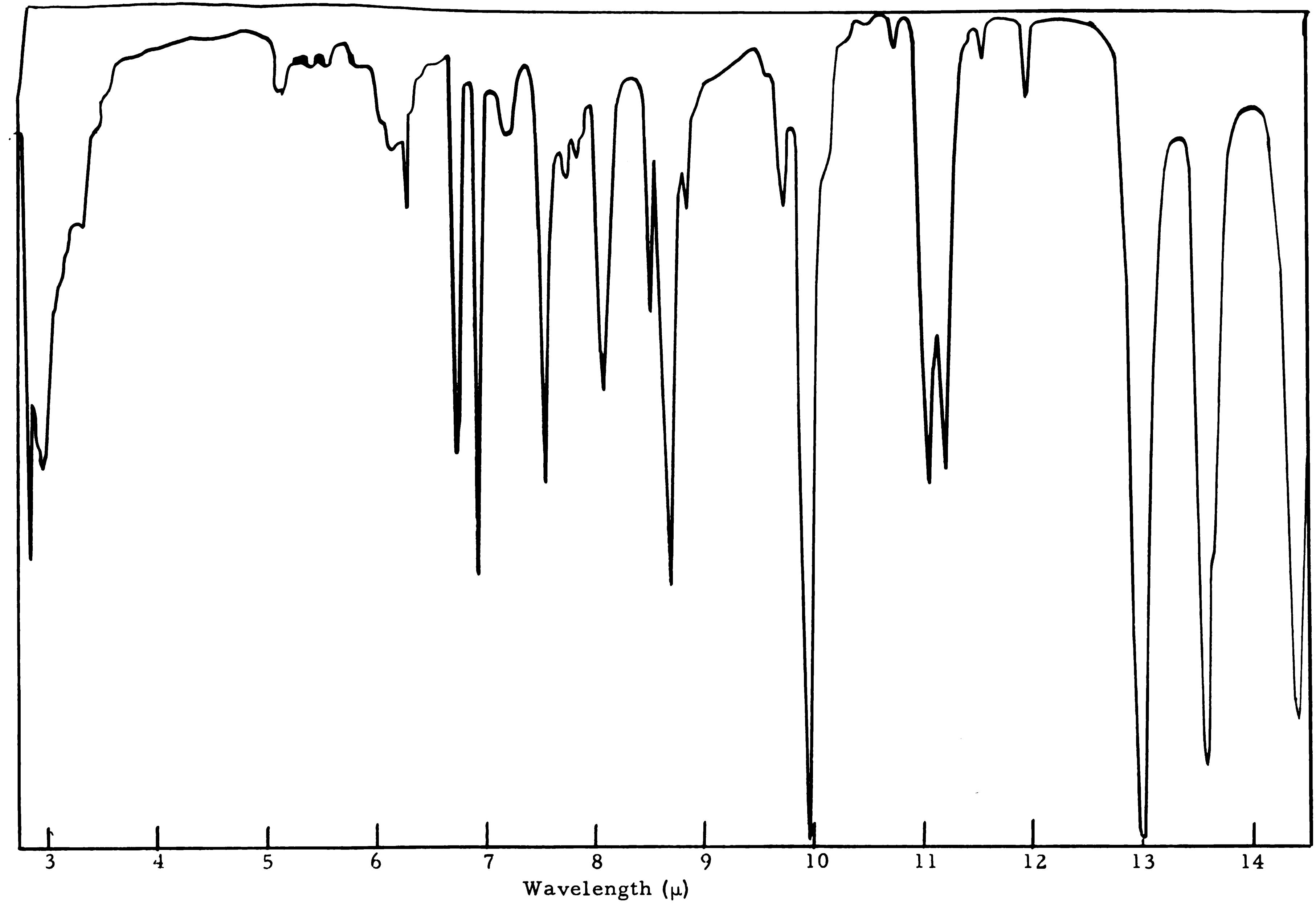


Figure 49. Infrared spectrum of trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene (KBr pellet).

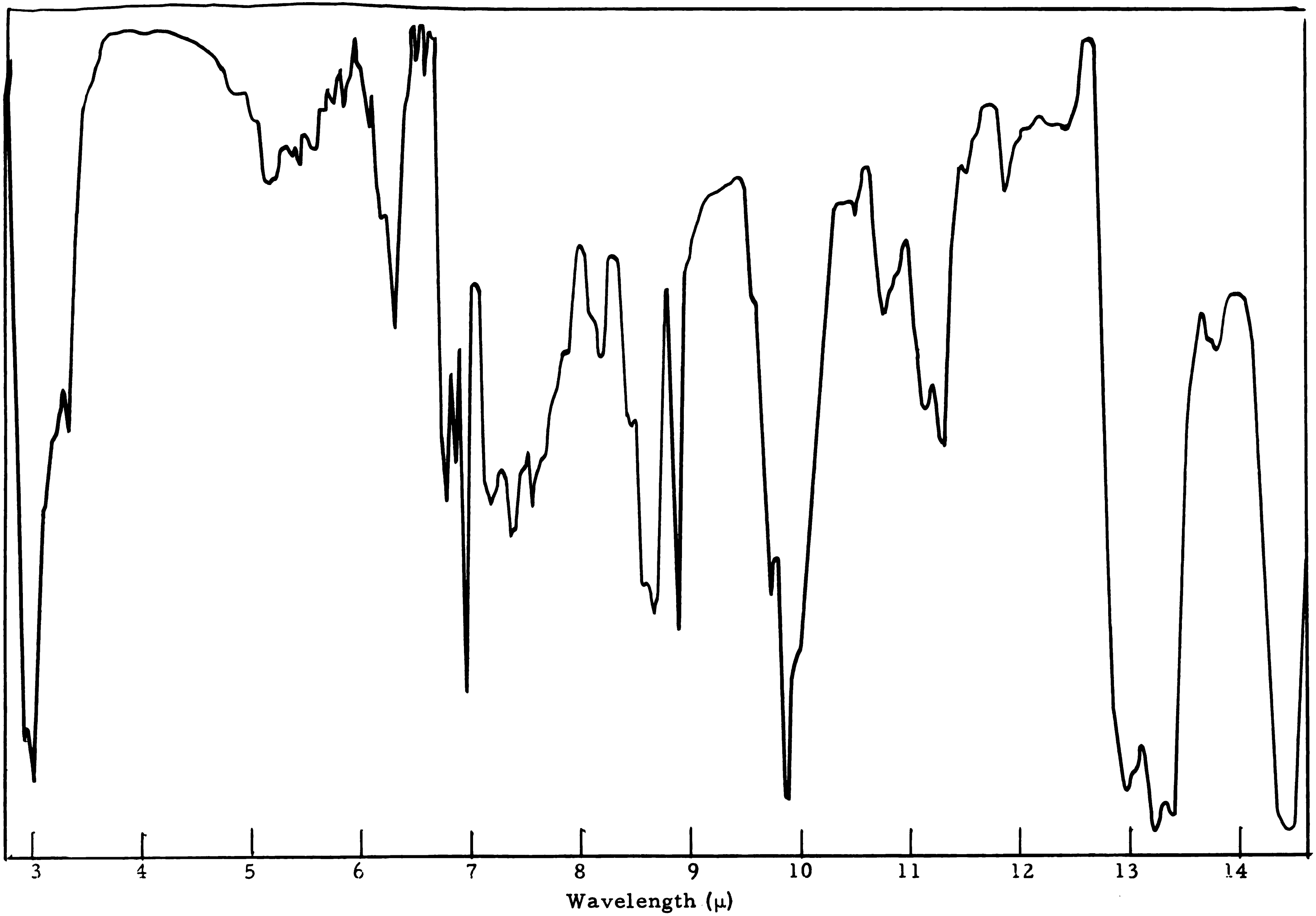


Figure 50. Infrared spectrum of cis-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene (KBr pellet).

II. Cryoscopic Measurements

A. Apparatus

The apparatus was the same as that described by Fish (113).

The thermistor consisted of a bead of metallic oxides, with lead wires sealed in a glass envelope, designed by Fenwal Electronics Inc. The glass envelope was sealed to a piece of lead glass tubing extending from the cap of the freezing point cell to within a half inch of the bottom of the cell. The thermistor was calibrated from 0° to 20° against a U. S. Bureau of Standards platinum resistance thermometer (No. 1016073). A Leeds and Northrup 5-decade Wheatstone bridge and a Rubicon lamp-scale galvanometer with a sensitivity of 0.0015 μa/mm. were used to measure resistance.

The freezing point cell was equipped with ground-glass joints which were lubricated with silicone grease. The cell cap was equipped with three standard ground joints, one accommodating the stirrer, another the thermistor and the third was fitted with a stopper and used to add solutes.

The cell was surrounded by a Styrofoam insulated air-jacket provided with an upward sloping side arm through which a piece of Dry-ice could be inserted to touch the cell wall and induce crystallization.

B. Procedure

The apparatus was always cleaned in hot sulfuric acid, rinsed with distilled water and dried in an oven. The cell was assembled and approximately 90 g. of stock sulfuric acid was added. After placing the cell in the insulated air-jacket, the entire apparatus was surrounded by a cooling bath of crushed ice and the solution stirred. The temperature of the sulfuric acid was reduced to about one to two degrees below its freezing point, and crystallization was induced by touching the side of the cell with a piece of Dry-ice. The steady maximum of temperature, obtained by one-minute temperature reading intervals, reached after crystallization was taken as the freezing point. Since the stock solution was maintained on the sulfur trioxide side, a small amount of concentrated sulfuric acid was added and the freezing point determined. The addition of concentrated sulfuric acid was repeated until the desired freezing point was obtained. The final freezing point was rechecked after two hours to see that it had remained constant. Sufficient solute was then added to depress the freezing point approximately 0.3°. The sample was added by means of a solid dropping funnel which had a long stem reaching close to the sulfuric acid surface. The sample and funnel were weighed before and after the sample was added. The difference constituted the weight of sample. After the sample was dissolved, the freezing point was redetermined. In order to eliminate such errors as freezing too rapidly or too slowly and improper stirring, the frozen mixture was allowed to melt and the freezing point determined again. This was repeated four to five times and the average of the closest three to four values were used. This was done until all of the samples were used.

C. Stock Sulfuric Acid

Stock sulfuric acid was always slightly on the sulfur trioxide side. It was prepared by suitably diluting J. T. Baker's reagent grade fuming (30-33% sulfur trioxide) sulfuric acid with reagent grade concentrated (96-98%) sulfuric acid.

III. Preparation of Solutions for Spectral Measurements

A. Aqueous Sulfuric Acid

The stock solutions of sulfuric acid were obtained by the titration of "Baker Analized" Reagent grade with sodium hydroxide to a phenolphthalein end point. To obtain the aqueous solutions, calculated weights of distilled water were added to known weights of stock sulfuric acid. The water was added dropwise and the sulfuric acid was kept in an ice-bath during addition. This was done to prevent loss of water by evaporation since the reaction between water and sulfuric acid is highly exothermic.

B. Spectral Solutions

The solutions for the spectral studies were made up by dissolving a known amount of sample in 25 ml. of anhydrous glacial acetic acid (114) and taking 0.1 ml. (measured with a LaPine needle valve precision bore microburette which has a total capacity of 0.50 ml. and which can be estimated to 0.001 ml.) of this solution and diluting it to 10 ml. with the appropriate sulfuric acid. The stock solutions of sample were made up so that the final solution had an absorbance of approximately 2.0 in a 1 cm. light path.

IV. Spectra

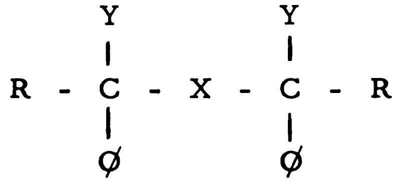
The visible spectra were obtained mainly with the Cary 11 Recording Spectrophotometer, with much of the early work being done on the Beckman DK-2 Recording Spectrophotometer. All of the spectra were run using 1 cm. glass-stoppered quartz cells.

The proton magnetic resonance spectra were obtained with a High-Resolution Analytical N.M.R. Spectrometer System, Varian Associates A-60.

The infrared spectra were obtained with a Perkin-Elmer (Model 21) Recording Infrared Spectrophotometer with 0.5 mm. solution cells and 1.0 mm. cavity cells.

SUMMARY

1. By use of the Friedel-Crafts benzoylation and Grignard reactions on the appropriate aromatic molecules the following types of compounds were prepared

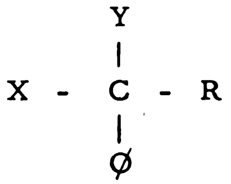


$$R - \underset{\phi}{\overset{Y}{C}} - X - \underset{\phi}{\overset{Y}{C}} - R$$

where R = phenyl or hydrogen, Y = hydroxyl or chlorine and X = benzene, biphenyl or fluorene.

2. All of the compounds studied dissolved in 98% sulfuric acid to form highly colored solutions ranging from yellow to blue. Investigation of the visible absorption spectra of solutions of these compounds in varying concentrations of sulfuric acid has shown that reversible ionization to dications can occur either stepwise or simultaneously and is, in general, a function of the moiety between the sites to be ionized. The pK_R's for these processes have also been determined and are given in Table 17 along with the λ_{max} and ϵ_{max} of the dications.

In order to interpret the visible spectra of these dications, a series of compounds were prepared which ionized to give monocations:



$$X - \underset{\phi}{\overset{Y}{C}} - R$$

The spectral data for these compounds are given in Table 18. Comparison of the spectra of the mono- and dications has shown that the resonance interactions of the latter can be pictured as being composites of monocations.

3. In addition to spectral studies, the hydrolysis products of the dication solutions in concentrated sulfuric acid were also investigated.

In all cases studied the starting diols (or cyclic ethers in the case of ortho substituted diols) were isolated in nearly quantitative yields. The hydrolysis of two carbinols (4-biphenylyldiphenylmethanol and α, α-diphenyl-α-hydroxy-2-methylfluorene) in 98% sulfuric acid showed that sulfonation occurred after carbonium ion formation. The alcoholysis of solutions of α, α, α', α'-tetraphenyl-o-xylene-α, α'-diol in concentrated sulfuric acid gave the corresponding ether of 9, 10, 10-triphenyl-9, 10-dihydro-9-anthrol.

4. The study of trans-9, 10-diphenyl-9, 10-dihydroxy-9, 10-dihydroanthracene in sulfuric acid was continued. It was demonstrated that in dilute sulfuric acid ionization of this diol gave the monocation which rearranged to the cis-diol. By increasing the acid strength the cis-diol rearranged to 9, 10-diphenylanthracene, which in more concentrated sulfuric acid gave 4-phenyl-2, 3-benzofluoranthene. At no time, however, was the presence of a dication noted.

Table 17. Spectral Data for the Bis-Aryl Carbinols in Sulfuric Acid

Compound	λ_{max}[a] (mμ)	ϵ_{max}[a]	pK_R 1	pK_R 2
α, α, α', α'-Tetraphenyl-p-xylene-α, α'-diol	455	59,000	-8.1	-10.5
α, α, α', α'-Tetraphenyl-m-xylene-α, α'-diol	440 419	70,000 73,000	-8.0	-10.1
α, α, α', α'-Tetraphenyl-o-xylene-α, α'-diol	455 373	44,000 30,500	∼-8.0[b]	-16.6
α, α'- Diphenyl-p-xylene--α, α'-diol	461	48,000	c	
α, α'-Diphenyl-m-xylene-α, α'-diol	447	35,000	c	
α, α, α', α'-Tetraphenyl p, p'-bitolyl-α, α'-diol	530 442 410_s	90,000 53,000 34,500	-8.2	d
α, α, α', α'-Tetraphenyl-m, m'-bitolyl-α, α-diol	430	67,500	-8.4	d
α, α, α', α'-Tetraphenyl-o, o'-bitolyl-α, α'-diol	428 390_s	35,500 24,000	∼ -8.3[e]	∼ -15.0
α, α'-Diphenyl-p, p'-bitolyl-α, α'-diol	563 420	134,000 13,000	c	
α, α'-Dichloro-α, α'-diphenyl-2, 7-dimethylfluorene	603 554	215,000 62,000	∼ -12.0	-16.6
α, α, α', α'-Tetraphenyl-2, 7-dimethylfluorene-α, α'-diol	568 525 440	152,000 46,000 35,000	c	

[a] The λ_{max} and ϵ_{max} data were obtained in 98% sulfuric acid.

[b] The first pK_R was assumed to be the same as for the corresponding meta and para diols. The close proximity of the second -OH after mono-ionization permits cyclic protonated ether formation. This species, which was not detectable by visible spectrophotometry, required solutions of high acidity for further ionization.

[c] Not determined.

[d] In these diols, ionization occurred simultaneously at both sites.

[e] This compound ionizes similarly to the diol discussed in b. The first ionization was assumed to be the same as the corresponding meta and para derivatives.

Table 18. Spectral Data for the Aryl Carbinols in Sulfuric Acid

Compound	λ_{max}[a] (mμ)	ϵ_{max}[a]	pK_R
Triphenylmethanol	432 408	37,500 36,500	-7.4
Diphenylmethanol	442	47,000	-14.7
4-Biphenylyldiphenylmethanol[b]	510 420	43,000 21,500	-7.7
4-Biphenylylphenylmethanol	535	90,000	c
α-Phenyl-α-hydroxy-2-methylfluorene	547	66,000	∼-12.0
α, α-Diphenyl-α-hydroxy-2-methylfluorene[b]	540 404	53,000 17,000	-6.5

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[a] The λ_{max} and ϵ_{max} data were obtained in 98% sulfuric acid, except where noted.

[b] These spectra were taken in 80% sulfuric acid because sulfonation was shown to occur in concentrated acid.

[c] Not determined.

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