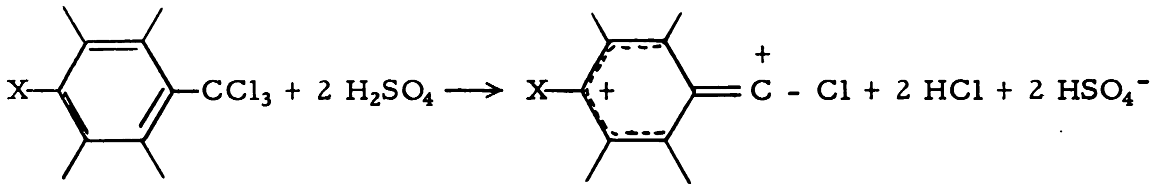
ABSTRACT

DIPOSITIVE CARBONIUM IONS

by Robert Roland Rafos

The primary purpose of this thesis was to further investigate the scope of dipositive carbonium ion chemistry. The aluminum chloride-catalyzed reaction of carbon tetrachloride with pentamethylbenzene, which gave high yields of trichloromethylpentamethylbenzene (1), was extended to the preparation of 4-bromo-, 4-chloro-, and 4-fluoro-2, 3, 5, 6-tetramethylbenzotrichlorides.

Each of these 4-halo derivatives dissolved in 100% sulfuric acid to form intensely red solutions. Two moles of hydrogen chloride were quantitatively swept from these solutions, using dry nitrogen. Cryoscopic measurements showed that five particles were produced in the reaction. Hydrolysis of the colored solutions gave nearly quantitative yields of the corresponding 4-halodurenecarboxylic acids, which were synthesized by independent routes. By analogy with earlier work, the best explanation for these data is the formation of stable dipositively charged carbonium ions.



The structures of these dipositive ions were investigated by ultraviolet, visible and proton magnetic resonance spectroscopy.

Dipositive carbonium ions formed from single ionizations at two different sites in a molecule were also investigated. The three compounds studied, which were in a sense analogs of triphenylcarbinol, were tetraphenyl-p-xylyleneglycol, tetra-p-anisyl-p-xylyleneglycol and 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene. The first two dissolved in 100% sulfuric acid to form intensely red solutions. Hydrolysis gave nearly quantitative yields of the starting glycols. A study of the visible spectra in solutions of varying acidity showed that both glycols undergo reversible stepwise ionizations to monopositive and dipositive carbonium ions.

9, 10-Dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene dissolved in 100% sulfuric acid to form a deep-blue solution. Hydrolysis did not yield the starting glycol, but rather a mixture containing 9, 10-diphenylanthracene (36%), 4-phenyl-2, 3-benzofluoranthene (19%) and some products which remain unidentified.

In much less acidic solutions 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene undergoes the normal stepwise ionization to a yellow monopositive and a red dipositive carbonium ion, as shown by hydrolysis experiments.

The pK's for the process:

$$(ROH)^{+} + H^{+} \rightleftharpoons R^{++} + H_2O$$

were determined spectroscopically for the three glycols and were found to be -8.7 for tetraphenyl-p-xylyleneglycol and 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene and -3.4 for tetra-p-anisyl-p-xylyleneglycol.

REFERENCES

1) H. Hart and R. W. Fish, J. Am. Chem. Soc., 82, 5419 (1960).

DIPOSITIVE CARBONIUM IONS

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TABLE OF CONTENTS

PART B

TABLE OF CONTENTS - Continued

Page

TABLE OF CONTENTS - Continued

LIST OF TABLES

LIST OF TABLES - Continued

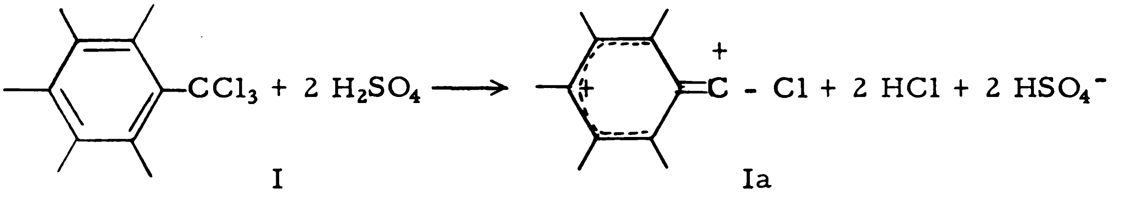
LIST OF FIGURES

LIST OF FIGURES - Continued

LIST OF FIGURES - Continued

INTRODUCTION

It was recently observed (1) that trichloromethylpentamethylbenzene (I) dissolved in 100% sulfuric acid to give a deep red stable solution. The color was attributed to the dipositively charged pentamethylphenylchlorodicarbonium ion (Ia), formed by ionization of I according to the equation:

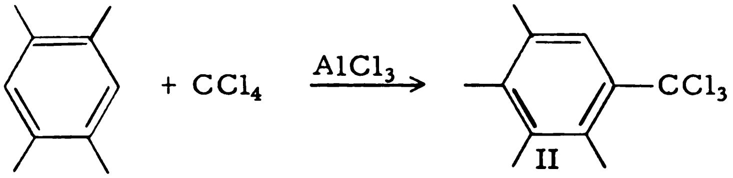


I Ia (1)

The cogent evidence included cryoscopic measurements, which established the production of five particles in solution per mole of solute. Two of these were hydrogen chloride, which could be rapidly and quantitatively swept from the solution. After sweeping, the remaining solution showed as expected a three-fold molal freezing point depression. Conductance measurements supported the formation of two bisulfate ions. Hydrolysis of the red solutions produced pentamethylbenzoic acid quantitatively. The visible, ultraviolet, and nuclear magnetic resonance spectra of these solutions also support the structure Ia. The ionization of trichloromethylpentamethylbenzene to the dipositive carbonium ion was rapid and the ion itself was quite stable.

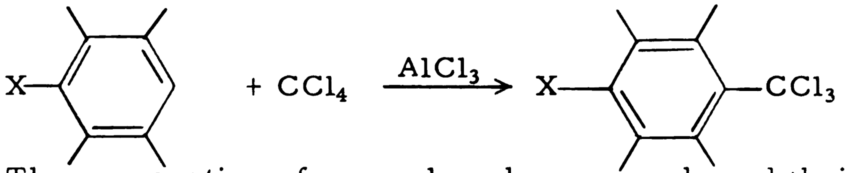
It was one intent of the present work to examine the scope of dipositive carbonium ion formation from trichloromethylbenzenes.

Trichloromethylpentamethylbenzene had been prepared by the reaction of pentamethylbenzene with carbon tetrachloride and aluminum chloride (1). Under similar conditions rearrangement occurred with durene and the product formed was trichloromethylprehnitene II (2).



II (2)

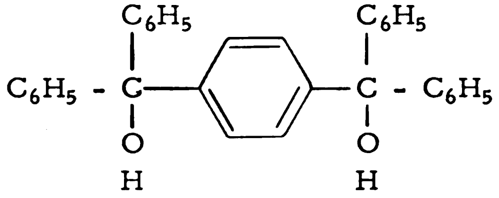
It was thought that one might avoid the rearrangement and at the same time examine structural influences on dicarbonium ion formation by first preparing monosubstituted durenes and then carrying out the trichloromethylation reaction.



(3)

The preparation of several such compounds and their reaction with 100% sulfuric acid is reported in the first part of this thesis.

Previous work on dicarbonium ion chemistry (1, 2) centered about the formation of a dication by multiple ionization at a single carbon atom. One can also conceive of dipositive carbonium ions derived from single ionizations at two separate sites in a molecule. One example might be the ionization of tetraphenyl-p-xylylene glycol,



which by analogy with the well-known ionization of triphenylcarbinol in sulfuric acid to triphenylcarbonium ion might be expected to produce the analogous dication. If as would seem likely the ionization of such a glycol were a stepwise process, going first to a monocarbonium ion and then to the dicarbonium ion, one might perhaps measure the separate pK's and determine how much energy is required to introduce the second charge. One can visualize other interesting problems posed by systems of this type, and some work on their chemistry will be presented here.

This thesis will be presented in two separate sections, Part A dealing with experiments on the monosubstituted trichloromethyldurenes and Part B on the glycol systems.

PART A

DIPOSITIVE CARBONIUM IONS ARISING FROM MULTIPLE IONIZATIONS AT A SINGLE SITE IN A MOLECULE

RESULTS AND DISCUSSION

The Trichloromethylation Reaction

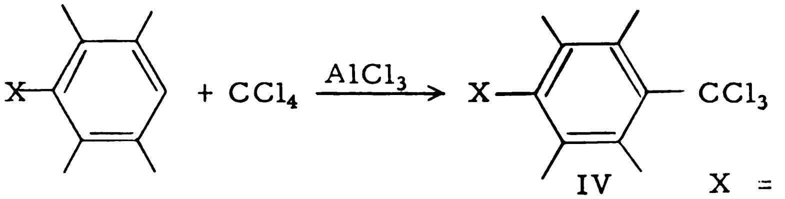
The reaction of benzene with carbon tetrachloride in the presence of aluminum chloride has been known since 1877 (3). The main products from this reaction are diphenyldichloromethane and triphenylchloromethane or the corresponding hydrocarbons, depending on the reaction conditions (4, 5). Toluene and the xylenes behave similarly (6, 7, 8, 9).

Application of this reaction to mesitylene, durene or pentamethylbenzene (see references 1 and 2) gave trichloromethyl derivatives without the formation of condensation products. But in the case of durene rearrangement occurred and the only product isolated was trichloromethylprehnitene. Isodurene when treated in a similar manner also gave trichloromethylprehnitene (10).

There is precedent for such rearrangements in the work of Baddely and Pendleton (11) who have shown that acetyldurene when heated to 100° with an excess of aluminum chloride yielded a mixture of products, 80% of which was acetylprehnitene. There was no reaction between acetylprehnitene and excess aluminum chloride when refluxed at 150° for three hours. Therefore acetylprehnitene was assumed to be the most thermodynamically stable product.

The Jacobsen rearrangement (12) is an analogous reaction. When durene was treated with sulfuric acid a 70% yield of prehnitenesulfonic acid was obtained. Isodurene gave a 50% yield of the same acid and in the case of prehnitene itself only sulfonation occurred without rearrangement. This again implies that the most stable product is formed. In each case the methyls migrate in order to have only one methyl group ortho to the bulky substituent, whether it be trichloromethyl, acetyl or sulfonic acid. This is strong evidence for steric strain which can be relieved by migration of one of the methyl groups.

In the reaction of monosubstituted durene derivatives with carbon tetrachloride no rearrangement occurred. 4-Bromo-, 4-chloro-, and 4-fluoro-2, 3, 5, 6-tetramethylbenzotrichlorides were prepared.



IV

(4)

X = Br IVa
= Cl IVb
= F IVc

Since these compounds were new, it was necessary to unequivocally establish their structure. The infrared spectra of the three compounds differed only in their carbon-halogen frequencies and the ultraviolet spectra were quite similar (Figure II). They were readily hydrolyzed to the corresponding monosubstituted durenecarboxylic acids by refluxing with aqueous acetone. The infrared spectra of the acids differed only in their carbon-halogen frequencies and lead one to conclude that the trichloromethyl and acid derivatives had the same structural features.

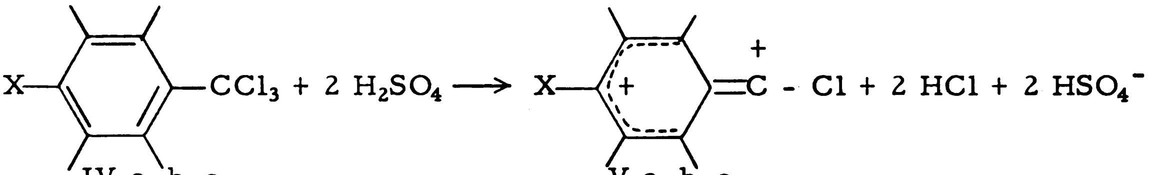
p-Bromodurenecarboxylic acid was prepared by an independent synthesis. Dibromodurene was converted to the mono Grignard reagent and then carbonated. The acid obtained by this method was identical in all respects (neutralization equivalent, m.p., m.m.p., and infrared spectrum) to the acid obtained from the hydrolysis of IVa. This conclusively proves there was no rearrangement during the trichloromethylation reaction of bromodurene. By analogy IVb and c were assumed to have the structures indicated.

Attempts were also made to synthesize 4-iodo- and 4-nitro-2, 3, 5, 6-tetramethylbenzotrichloride. In the former case iodine was obviously liberated and only a brown solid that remains unidentified was isolated. Apparently the carbon iodine bond is too labile to resist attack by the aluminum chloride catalyst. In the case of nitrodurene only starting material was recovered and it appears the compound is too deactivated for the Friedel-Crafts reaction to take place.

Reaction of 4-Halo-2, 3, 5, 6-tetramethylbenzotrichlorides with 100% Sulfuric Acid

Each of the 4-halo-2, 3, 5, 6-tetramethylbenzotrichlorides, when added to 100% sulfuric acid, dissolved with the formation of a deep red solution. Hydrogen chloride was evolved and the red color persisted for long periods of time if the solutions were kept anhydrous. When the red solutions were hydrolyzed on ice a better than 90% yield of the corresponding 4-halodurenecarboxylic acids was obtained. The acids were identical (m.p. and infrared spectra) with those obtained when the corresponding trichloromethyldurenes were hydrolyzed by refluxing with aqueous acetone.

In the light of previous work, it is reasonable that the species responsible for the red color observed when IVa, b, or c is dissolved in 100% sulfuric acid are the corresponding dicarbonium ions (V).



IV a, b, c

V a, b, c

(5)

Because of the available analogy, the evidence for V need not be as rigorous as that presented in earlier work (1, 2). Nevertheless, the cryoscopic, stoichiometric and spectroscopic measurements to be described seem sufficient to firmly establish the ionization depicted in equation 5.

Cryoscopic Measurements

The results from freezing point measurements are given in Table I. Following Gillespie's conventions (12), ν is the number of moles of particles (molecules or ions) produced in solution by one mole of solute, and i is the observed multiple of the molal freezing point depression. To become familiar with the technique, preliminary measurements were made on triphenylcarbinol, trichloromethylprehnitene, and trichloromethylpentamethylbenzene where the ν -values were already known. Slightly aqueous sulfuric acid with freezing point range 9.82° to 10.125° was used in order to suppress the self-dissociation of the sulfuric acid. The data in Table I show that 4-bromo-2, 3, 5, 6-tetramethylbenzotrichloride (IVa) produces 5 particles when it dissolves in 100% sulfuric acid. It did not seem necessary, in view of this and subsequent results, to also run the 4-chloro and 4-fluoro compounds.

Stoichiometry

One obvious product of the reaction of trichloromethyl compounds with 100% sulfuric acid is hydrogen chloride. Using a suitable apparatus, this gas can readily be swept from the red solutions and trapped in aqueous sodium hydroxide. The latter was then acidified and titrated for chloride ion by the Fajans' method. The results from these experiments are presented in Table II. It is clear that in each case two moles of hydrogen chloride were produced per mole of trichloromethyl compound. In each case prolonged (12-24 hours) sweeping produced only small additional amounts of hydrogen chloride which may be attributed to the slow hydrolysis of the dicarbonium ion due to trace amounts of moisture.

In one experiment 4-fluoro-2, 3, 5, 6-tetramethylbenzotrichloride was dissolved in sulfuric acid that contained an excess (approximately 0.5 molar) of sulfur trioxide. After sweeping for 26 hours only 26.59% of

Table I. Freezing Point Data

Compound	Wt., g.	g. H_2SO_4	T_1, °C	ΔT, °C	i[a]	ν
$(C_6H_5)_3COH$	0.9462	90.9	10.001	1.038	4.21	4
Triphenylcarbinol	1.0007[c]			2.108	4.11	
$(CH_3)_5C_6CCl_3$	0.2369	95.3	9.95	0.302	5.27	5
Trichloromethylpenta-	0.2384[c]			0.613	5.33	
methyl benzene	0.2377[c]			0.882	5.10	
	0.2510	95.1	9.99	0.299	4.91	
	0.2409[c]			0.591	4.95	
	0.2106[c]			0.819	4.80[b]	
$(CH_3)_4C_6HCCl_3$	0.2718	114.3	10.098	0.300	5.18	5
2,3,4,5-Tetramethyl	0.2868[c]			0.615	5.16	
Benzotrichloride	0.3095	94.2	9.904	0.402	5.04	
	0.3100[c]			0.798	5.00	
$Br(CH_3)_4C_6CCl_3$	0.3108	100.67	9.982	0.298	5.22	5
4-Bromo-2,3,5,6-	0.3093[c]			0.593	5.19	
tetramethyl	0.3062	94.82	9.982	0.311	5.20	
benzotrichloride	0.3081	81.03	10.125	0.345	4.90	
	0.5623			1.015	5.10	

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

[b] After 2,4 and 9 hours, this value increased to 4.85, 4.89 and 5.00 respectively.

[c] These are successive additions of solute to a single sulfuric acid sample; the ΔT values are additive and the i-values cumulative.

Table II. Stoichiometry with Respect to Hydrogen Chloride

Compound	Wt. (g)	Time (hrs.)[a]	Ml. of $AgNO_3$[b]	Moles Cl^-/mole of trichloromethyl compound
p-Bromotrichloromethyldurene	0.5122	4[c]	36.40	2.010
	0.5055	7	36.45	2.022
p-Chlorotrichloromethyldurene	0.4944	6[d]	40.65	2.010
	0.5036	5[e]	42.35	2.056
p-Fluorotrichloromethyldurene	0.5022	4[f]	43.40	1.994
	0.5005	24[g]	11.55	0.532

[a] Length of time that nitrogen swept through the solution; the rates of flow varied.

[b] Cl^- titer = 3.034 mg.Cl^-/ml. of $AgNO_3$.

[c] Sweeping for 17 more hours produced an additional 14.0 mg. of Cl^-. This corresponds to a total of 2.26 moles of Cl^- at 21 hours.

[d] 2 additional hours of sweeping gave no detectible Cl^-.

[e] 5 additional hours of sweeping produced 7.3 mg. of Cl^- giving a total of 2.172 moles of Cl^- at 10 hours.

[f] An additional 8 hours of sweeping produced no detectible Cl^-. After sweeping for another 12 hours 27.3 mg. of Cl^- obtained corresponding to a total of 2.29 moles of Cl^-.

[g] Sulfuric acid approximately 0.5 molar in sulfur trioxide.

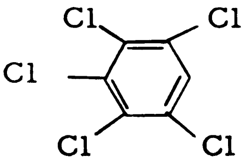
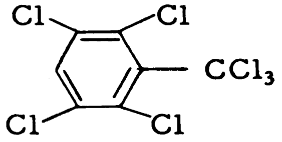
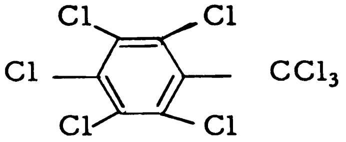
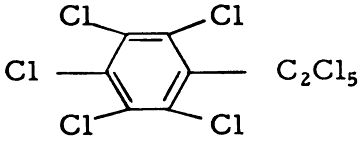
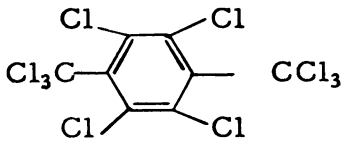
the theoretical amount of hydrogen chloride had been obtained. This was significant since in the previous experiments the hydrogen chloride was rather rapidly liberated. Evidently the free sulfur trioxide reacts rapidly with the hydrogen chloride to form chlorosulfonic acid. Reversal of this equilibrium and recovery of the hydrogen chloride is obviously very slow. Whereas the reaction of hydrogen chloride with sulfur trioxide is apparently rapid, reaction with sulfuric acid molecules which could also lead to chlorosulfonic acid, must be slow and incomplete.

Ultraviolet and Visible Spectra

Benzene absorbs in two main regions of the ultraviolet, one of high intensity near 198 mμ (ϵ ca. 8,000) and called the K-band and the other of much lower intensity between 230 mμ and 270 mμ (ϵ ca. 230) called the B-band. These bands are characteristic of all benzene derivatives. The K- band arises from conjugation in the aromatic ring whereas the B-bands are ascribed to changes in the symmetry properties of the pi-electron system (13). Substitution on the aromatic nucleus causes these bands to shift and vary in intensity due to conjugation and steric effects.

Recently Ballester and Castañer (14) reported the ultraviolet spectra of some polychlorinated alkylbenzenes. In Table III the molar absorbancy indices and the maxima for some of these compounds are reported. The spectrum of A is referred to as normal since it has the essential features found in other benzene derivatives. The spectra of B, C, D, and E are abnormal compared with A because they exhibit large bathochromic shifts. In each "abnormal" compound at least one trichloromethyl group is flanked by two ortho chlorine atoms. Presumably substances having such structures are sterically strained. (Note that a trichloromethyl is nearly as large as a t-butyl group.) This strain raises the energy of both the ground and excited states of the

Table III. Ultraviolet Absorption Maxima of Some Polychloro Alkylbenzenes in Cyclohexane

Compound	Wavelength $(m\mu)$	Molar Absorbancy Index (ϵ)
 Pentachlorobenzene (A)	298	390
	289	370
	219	21,500
 2, 3, 5, 6-tetrachloro-1-trichloromethylbenzene (B)	316	2,100
	221	30,000
 Perchlorotoluene (C)	319	1,420
	223	35,000
 Perchloroethylbenzene (D)	319	2,050
	224	41,000
 Perchloro-p-xylene (E)	365	3,000
	280	6,600
	236	25,500
	219	27,000

molecule. However, due to the greater anti-bonding character of the excited states their energies are less effected by distortion. Consequently, it can be expected that the ultraviolet spectra would show bathochromic shifts.

Since the sizes of a chlorine atom and a methyl group are about the same one would expect the ultraviolet spectra of monosubstituted trichloromethyldurene derivatives to be quite similar to those of the "abnormal" polychlorinated alkylbenzenes. Figure I shows a comparison between the spectra of benzotrichloride, perchlorotoluene and 4-chloro-2, 3, 5, 6-tetramethylbenzotrichloride. One can easily see the displacement from a normal benzene derivative in the spectra of the latter two compounds. Similar steric strain is also suggested for these compounds.

Figure II shows a comparison of the ultraviolet spectra of trichloromethylpentamethylbenzene and the 4-halo-2, 3, 5, 6-tetramethylbenzotrichlorides. The curves are almost identical and suggest very common structural features. The maxima for the 4-bromo, 4-chloro, and 4-methyl derivatives occur at almost identical wavelength with almost equal intensity. This is expected due to very similar resonance and steric contributions of these substituents. However, in the case of the 4-fluoro group both maxima undergo a hypsochromic shift with a decrease in intensity. This can be attributed to release of steric strain in the ground state since the fluorine atom is considerably smaller than the other 4-position substituents.

Figure III shows a comparison of the ultraviolet and visible spectra of some trichloromethyl derivatives in 100% sulfuric acid. The great difference between the spectra of the parent compounds and the corresponding dicarbonium ions is due to the effect of introducing a permanent charge into the chromophoric system giving rise to charge-resonance spectra (15). Sufficient information is not available to discuss the shifts in wavelength and increased intensity of the maxima. Since the spectra

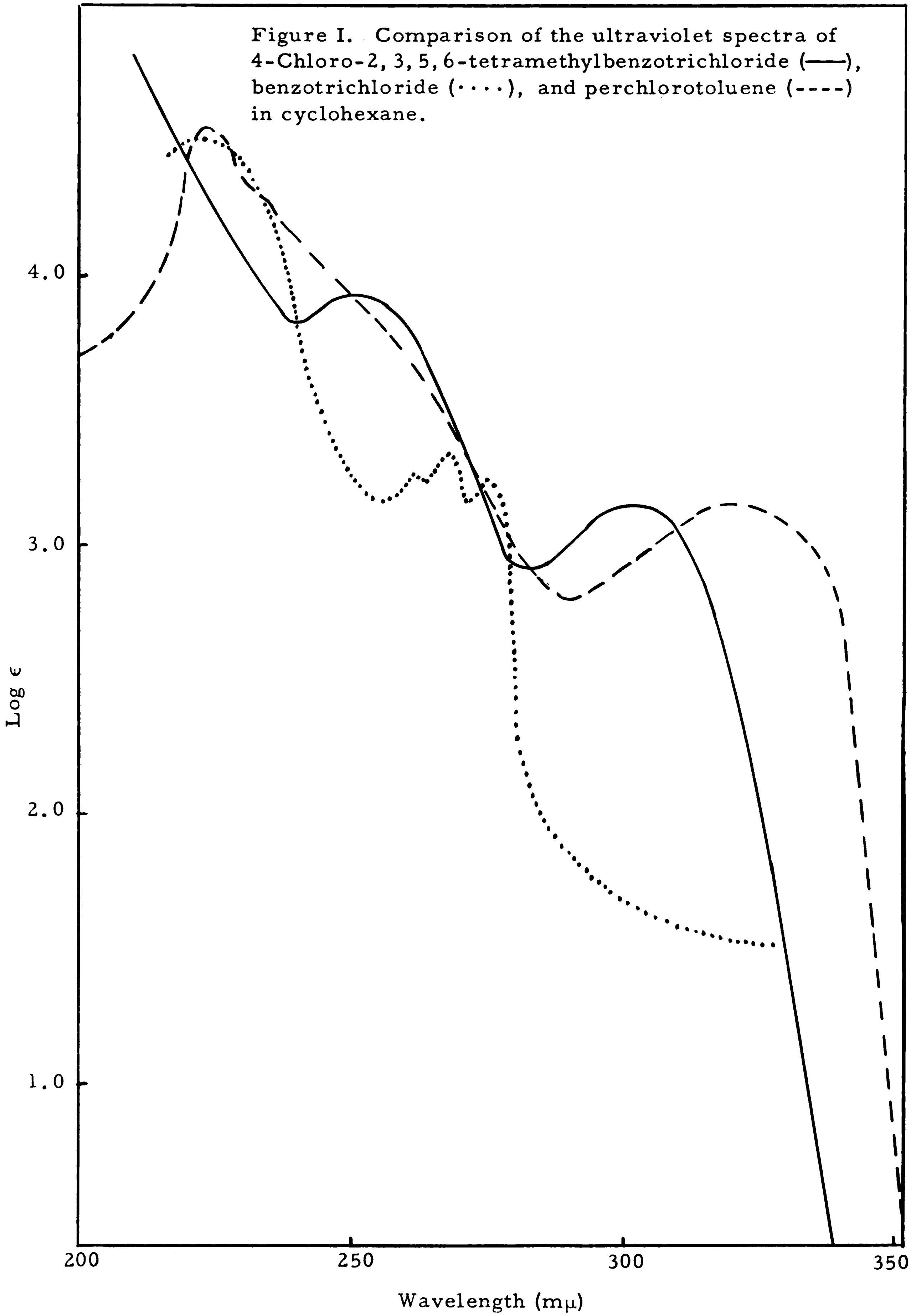


Figure I. Comparison of the ultraviolet spectra of 4-Chloro-2, 3, 5, 6-tetramethylbenzotrichloride (——), benzotrichloride (····), and perchlorotoluene (----) in cyclohexane.

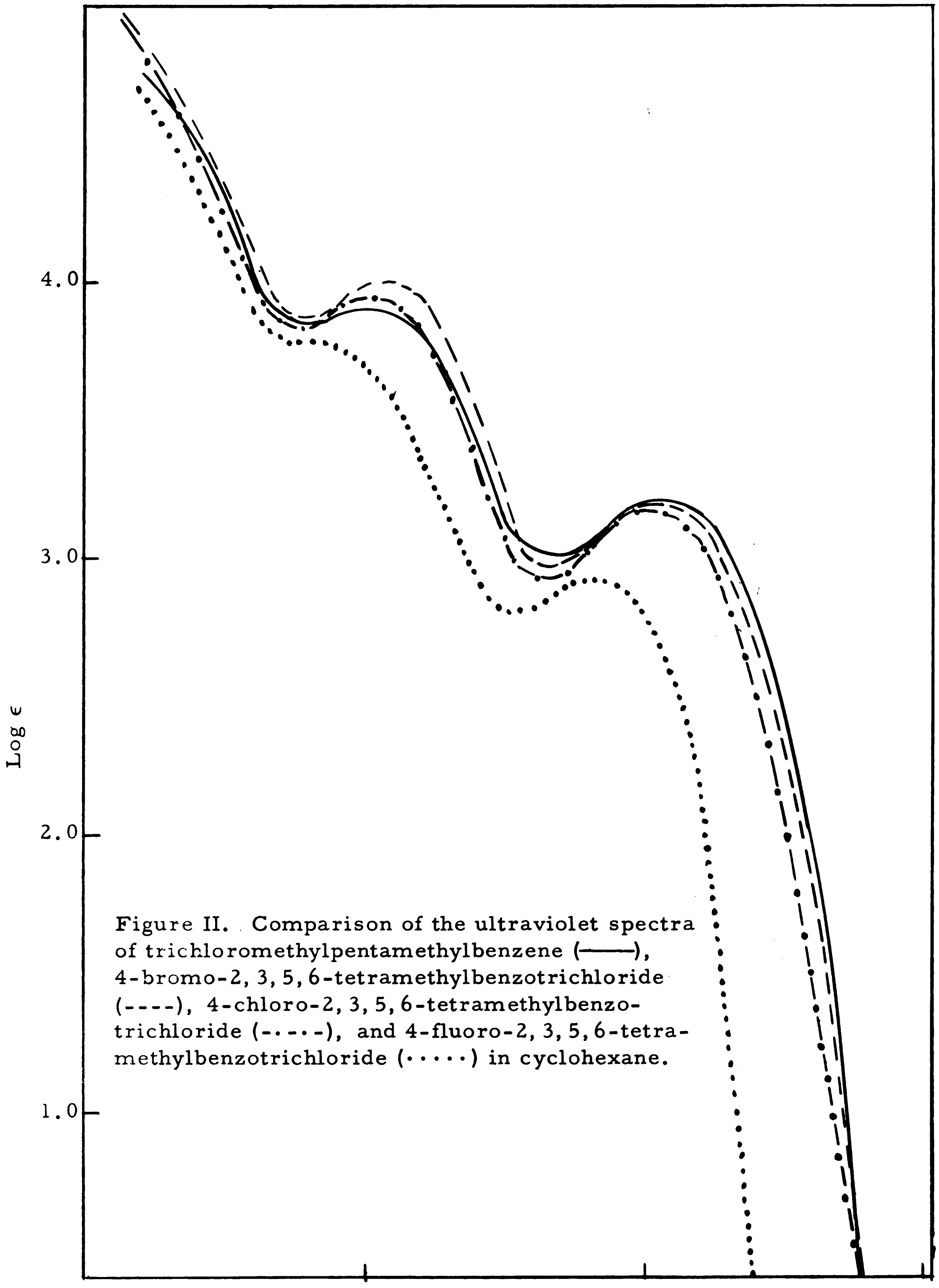


Figure II. Comparison of the ultraviolet spectra of trichloromethylpentamethylbenzene (———), 4-bromo-2, 3, 5, 6-tetramethylbenzotrichloride (----), 4-chloro-2, 3, 5, 6-tetramethylbenzotrichloride (-·-·-), and 4-fluoro-2, 3, 5, 6-tetramethylbenzotrichloride (·····) in cyclohexane.

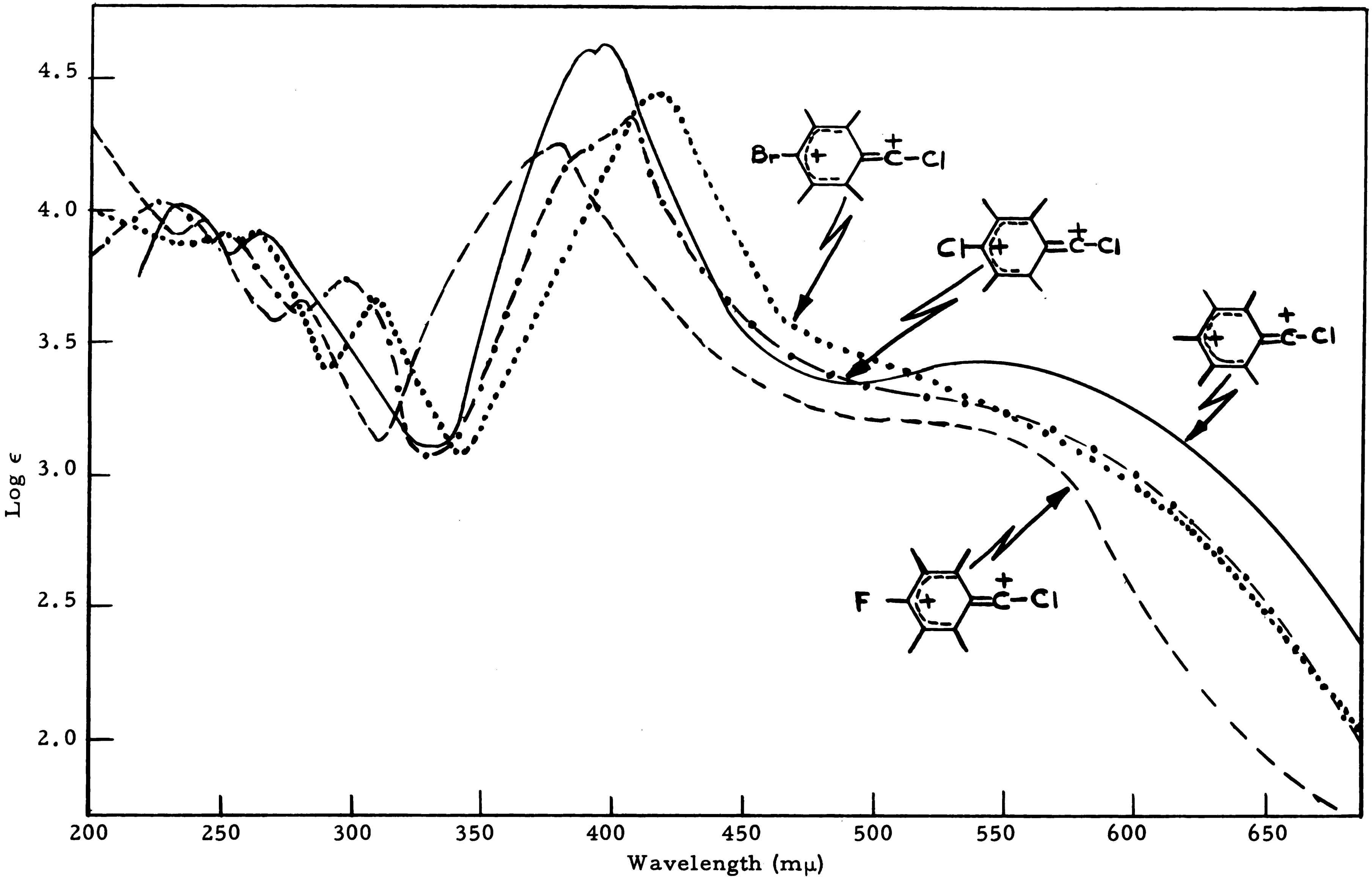


Figure III. Comparison of the ultraviolet-visible spectra of some trichloromethyl compounds in 100% sulfuric acid.

of the monosubstituted trichloromethyldurene derivatives in 100% sulfuric acid are quite similar to the spectrum of trichloromethylpentamethylbenzene it can be concluded that the dipositive ions arising from these species have nearly identical charge distribution and structural features.

The molar absorbancy indices of the maxima and minima absorption peaks are given in Tables IV and V.

Proton Magnetic Resonance Spectra

Figure IV shows a comparison of the proton magnetic resonance spectra of the 4-bromo-, 4-chloro-, and 4-fluoro-2, 3, 5, 6-tetramethylbenzotrichlorides in carbon tetrachloride. Figure V shows a comparison of the corresponding dipositive carbonium ions in 100% sulfuric acid. All peaks have been assigned τ - values (16) relative to tetramethylsilane (τ value = 10.00) as an internal standard. The spectra were determined at 60 Mc.

The spectra in carbon tetrachloride are very similar. All show two peaks with relative areas 1:1. The low field peaks are assigned to the methyl groups ortho to the trichloromethyl group. The high field peaks are assigned to the methyls meta to the trichloromethyl group because of the shift in τ -values observed for the different halogen substituents. Whereas the low field resonance remains constant at about 7.43 τ, successive replacement of the bromine atom with chlorine and fluorine causes the higher field resonance to shift from 7.59 τ to 7.64 τ to a split peak at 7.81 τ and 7.86 τ respectively. The largest shift was observed for the methyls ortho to the fluorine atom and is probably due to the higher electronegativity of this atom. The high field peak of the 4-fluoro substituent has been split due to coupling with the fluorine atom.

Table IV. Ultraviolet Absorption of Some Trichloromethyl Compounds in Cyclohexane

Compound	Wavelength (mμ)	Molar Absorbancy Index (ε)
Trichloromethylpentamethyl benzene	302 (max.)	1,560
	283 (min.)	920
	250 (max.)	7,680
	239 (min.)	6,440
4-Bromo-2,3,5,6-tetramethylbenzotrichloride	303 (max.)	1,611
	284 (min.)	940
	254 (max.)	10,320
	239 (min.)	7,390
4-Chloro-2,3,5,6-tetramethylbenzotrichloride	301 (max.)	1,503
	282 (min.)	831
	251 (max.)	8,980
	238 (min.)	6,730
4-Fluoro-2,3,5,6-tetramethylbenzotrichloride	291 (max.)	853
	276 (min.)	650
	246 (max.)	6,150
4-Chloro-2,3,5,6-tetramethylbenzotrichloride	700 (min.)	41
	520 (shoulder)	2,095
	406 (max.)	24,550
	399 (shoulder)	22,100
	330 (min.)	1,270
	299 (max.)	5,730
	283 (min.)	4,170
	260 (max.)	7,500
	253 (min.)	7,220
	226 (max.)	11,000
4-Fluoro-2,3,5,6-tetramethylbenzotrichloride	670 (min.)	44
	500 (shoulder)	1,775
	380 (max.)	18,250
	313 (min.)	1,370
	282 (max.)	4,950
	270 (min.)	4,000
	244 (max.)	9,200
	236 (min.)	8,800

Table V. Ultraviolet and Visible Spectra of Trichloromethyl Compounds in 100% Sulfuric Acid

Compound	Wavelength (mμ)	Molar Absorbancy Index (ε
Trichloromethylpentamethylbenzene	710 (min.)	260
	545 (max.)	2, 370
	485 (min.)	1, 550
	393 (max.)	34, 600
	387 (min.)	32, 200
	385 (max.)	32, 600
	327 (min.)	1, 000
	265 (max.)	7, 300
	250 (min.)	5, 820
	235 (max.)	9, 160
4-Bromo-2, 3, 5-6-tetramethylbenzotrichloride	699 (min.)	123
	530 (shoulder)	2, 130
	419 (max.)	27, 150
	405 (shoulder)	21, 300
	340 (min.)	1, 305
	310 (max.)	4, 800
	289 (min.)	2, 630
	262 (max.)	7, 820
	255 (min.)	7, 615
	243 (max.)	8, 150
	232 (min.)	7, 720
4-Chloro-2, 3, 5, 6-tetramethylbenzotrichloride	700 (min.)	41
	520 (shoulder)	2, 095
	406 (max.)	24, 550
	399 (shoulder)	22, 100
	330 (min.)	1, 270
	299 (max.)	5, 730
	283 (min.)	4, 170
	260 (max.)	7, 500
	253 (min.)	7, 220
	226 (max.)	11, 000
4-Fluoro-2, 3, 5, 6-tetramethylbenzotrichloride	670 (min.)	44
	500 (shoulder)	1, 775
	380 (max.)	18, 250
	313 (min.)	1, 370
	282 (max.)	4, 950
	270 (min.)	4, 000
	244 (max.)	9, 200
	236 (min.)	8, 800

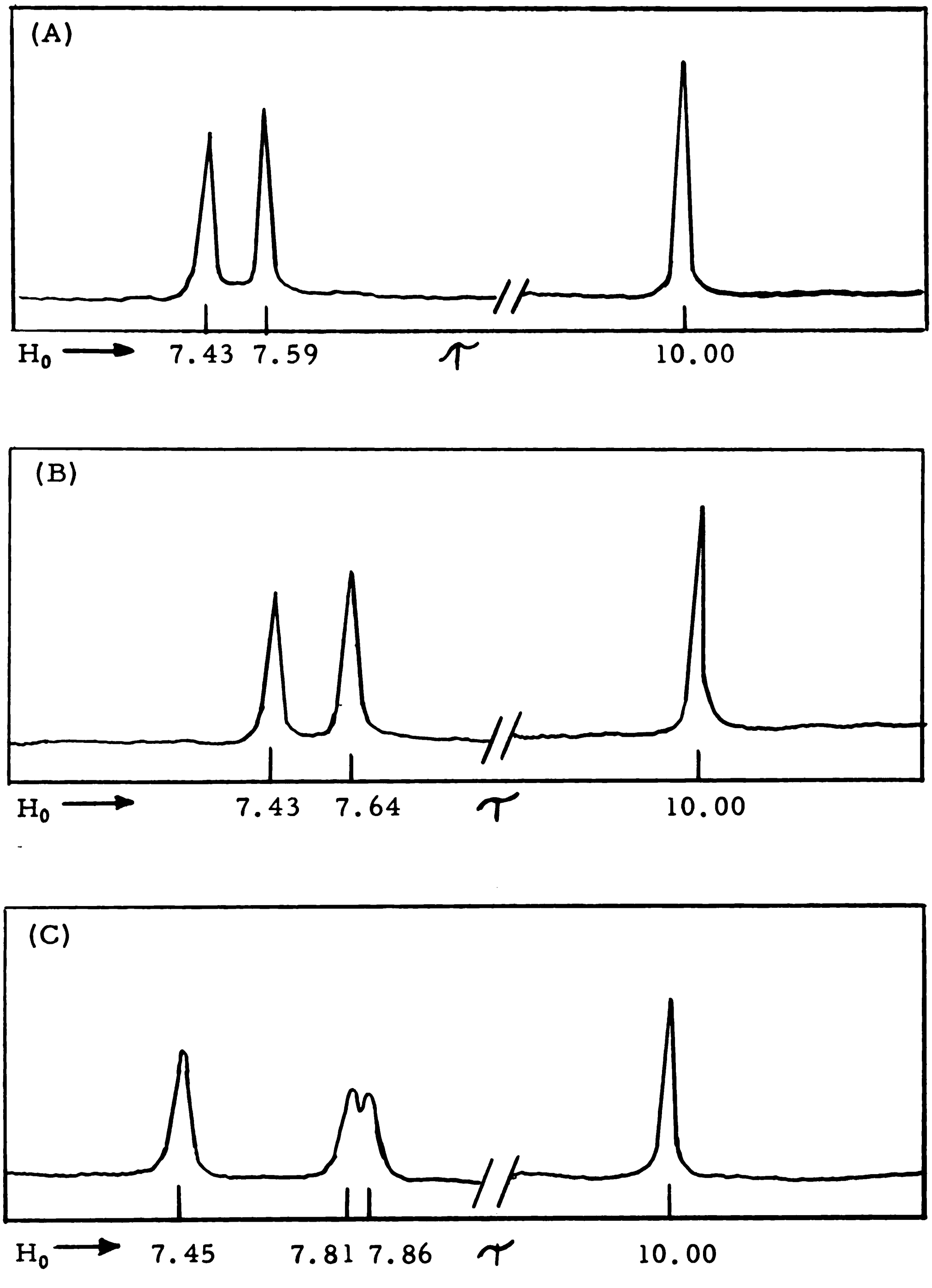


Figure IV. Proton magnetic resonance spectra in CCl_4.
(A) 4-Bromo-2, 3, 5, 6-tetramethylbenzotrichloride.
(B) 4-Chloro-2, 3, 5, 6-tetramethylbenzotrichloride.
(C) 4-Fluoro-2, 3, 5, 6-tetramethylbenzotrichloride.

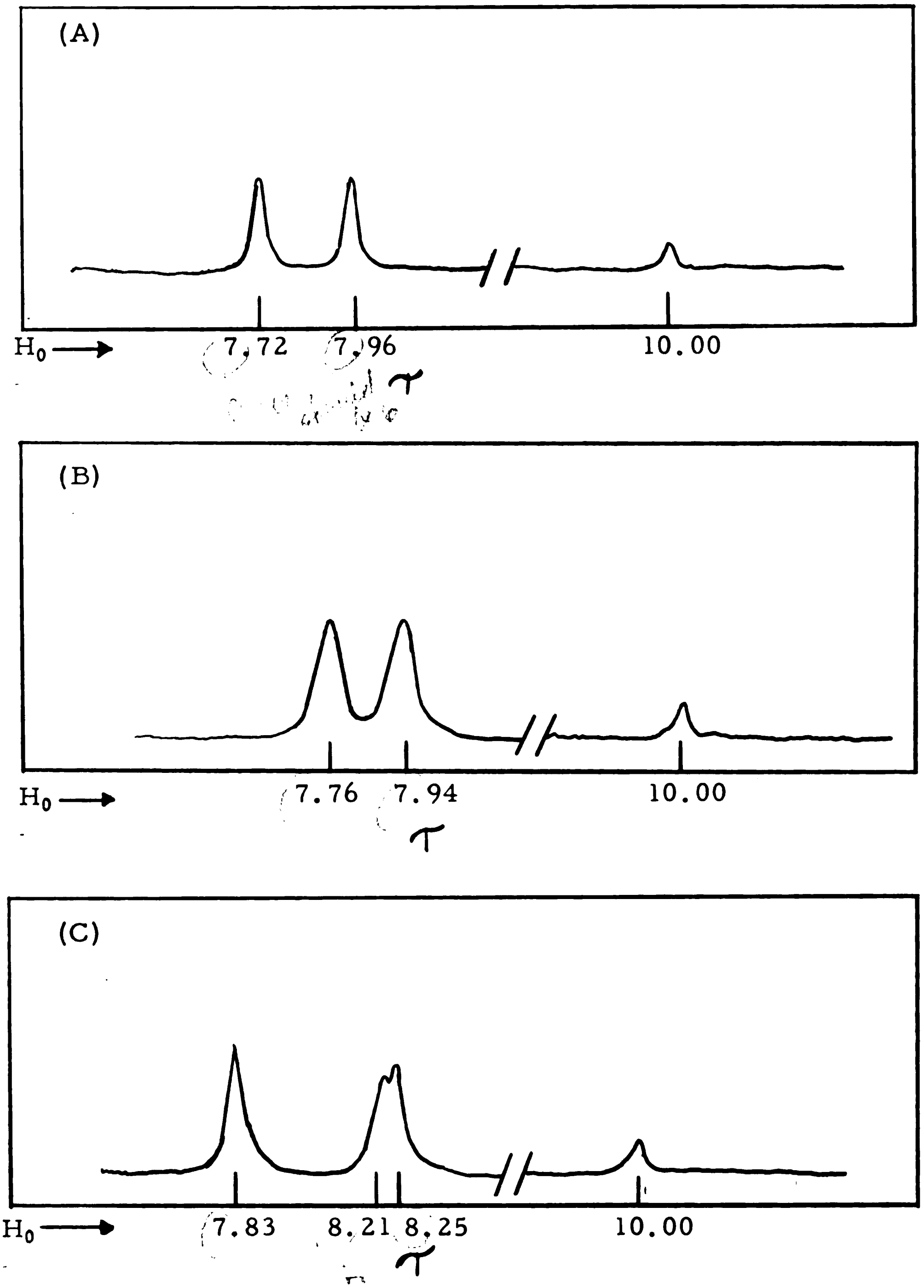


Figure V. Proton magnetic resonance spectra in 100% sulfuric acid.
(A) 4-Chloro-2, 3, 5, 6-tetramethylbenzotrichloride.
(B) 4-Bromo-2, 3, 5, 6-tetramethylbenzotrichloride.
(C) 4-Fluoro-2, 3, 5, 6-tetramethylbenzotrichloride.

The spectra of the three ions V a, b, and c are consistent with their structures. Again only two peaks appear in each spectrum with relative areas of 1:1 and the high field peak of V c has been split by the fluorine atom. As was observed in the parent compounds the down field methyl groups of the three ions have very similar τ -values, whereas the τ -values for the high field methyl groups shift depending on the halogen substituent.

EXPERIMENTAL

A. Syntheses and Reactions in 100% Sulfuric Acid

Preparation of Bromodurene

Bromodurene was prepared by the method of Smith and Moyle (17). In a 1-l. 3-necked round-bottomed flask provided with a dropping funnel, stirrer, and exit tube was placed 100 g. (0.746 mole) of durene and 200 g. of carbon tetrachloride. A crystal of iodine was added and the flask was cooled in an ice bath. A solution of 124 g. (0.775 mole) of bromine in 120 ml. of carbon tetrachloride was added dropwise over a 3 hour period, after which the mixture was stirred at room temperature for an additional hour. The organic layer was separated and washed with 100 ml. of 5% sodium hydroxide solution, then with 100 ml. of water. The solvent was removed on a Rinco rotary evaporator and the solid was refluxed for one hour with a solution of 8 g. of sodium in 200 ml. of ethanol and then allowed to stand overnight. Water (1800 ml.) was added and the solid filtered and subjected to a 7 hour steam distillation. The solid in the distillate was filtered and recrystallized once from 95% ethanol to yield 105 g. (66%) of white needles of bromodurene, m.p. 57-60°.

Preparation of 4-bromo-2, 3, 5, 6-tetramethylbenzotrichloride (1)

In a 1-l. 3-necked flask equipped with a Trubore stirrer, thermometer, reflux condenser and dropping funnel was placed 27 g. (0.2 mole) of powdered anhydrous aluminum chloride and 100 ml. of carbon tetrachloride previously dried over calcium chloride and distilled. The slurry was stirred and heated between 37-42° while a solution of 20 g. (0.094 mole) of bromodurene in 100 ml. of carbon tetrachloride was added dropwise (two hours). After the addition, heating and stirring were continued for another two hours.

The deep purple complex was slowly added with vigorous stirring to a mixture of 100 g. of ice, 10 ml. of concentrated hydrochloric acid and

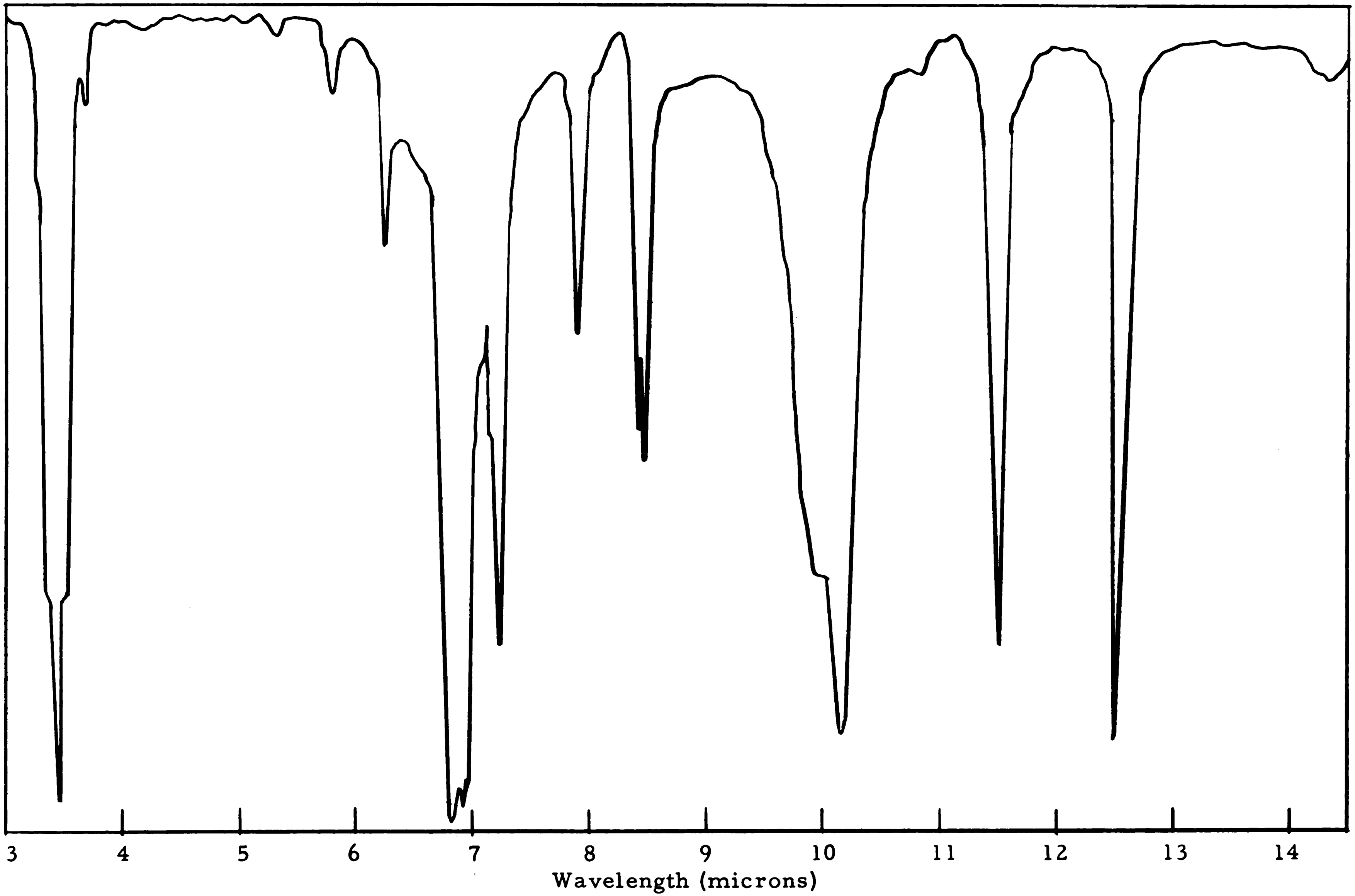


Figure VI. Infrared spectrum of bromodurene.

150 ml. of carbon tetrachloride. (The hydrolysis of the aluminum chloride complex proceeds slowly.) The carbon tetrachloride layer was separated and the aqueous layer extracted with two 100-ml. portions of carbon tetrachloride. The combined organic layers were washed with 150 ml. of water, two 200-ml. portions of 5% sodium carbonate solution, and finally with another 100 ml. of water. The solution was dried overnight with calcium chloride and the solvent removed on a Rinco rotary evaporator. The brown residue was dissolved in anhydrous n-pentane and treated with Norite. This procedure was repeated until 23 g. (75%) of pure 4-bromo-2, 3, 5, 6-tetramethylbenzotrichloride, m.p. 83.5-84.5°, was obtained.

Anal.* Calcd. for $C_{11}H_{12}BrCl_3$: C, 39.98; H, 3.66; Br, 24.18; Cl, 32.18,

Found: C, 40.09; H, 3.78; Br, 24.37; Cl, 32.02.

Preparation of 4-bromo-2, 3, 5, 6-tetramethylbenzoic acid

The acid was prepared by a modification of the method described by Newman and Lloyd (18) for the preparation of durenecarboxylic acid. In a 1-l. 3-necked flask fitted with a dropping funnel, Trubore stirrer and a reflux condenser with a drying tube was placed 2.5 g. (0.10 g.-atom) of magnesium. A solution of 4.6 g. of dibromodurene (17) and 1.45 g. of ethyl bromide in 180 ml. of ether was added to the flask and the reaction started immediately. It was maintained for three hours by the slow addition of 10.0 g. (0.05 mole total) of dibromodurene and 4.0 g. (0.05 mole total) of ethyl bromide in 250 ml. of ether. After the addition was completed the reaction flask was warmed gently and most of the ether was removed. Three hundred ml. of anhydrous benzene was

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*All analyses by Spang Microanalytical Laboratory, Ann Arbor, Michigan. Melting points are uncorrected unless otherwise indicated.

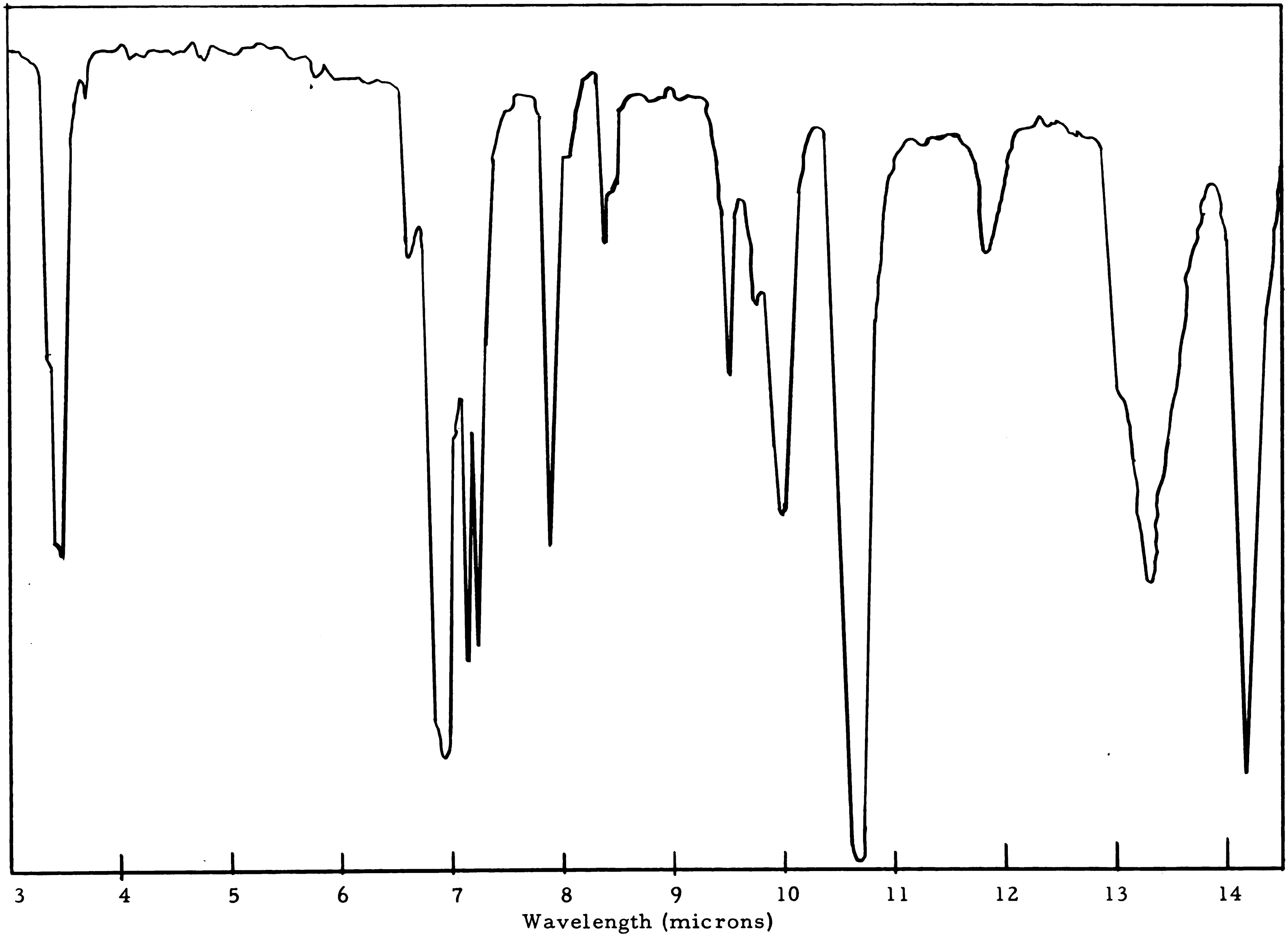


Figure VII. Infrared spectrum of 4-bromo-2, 3, 5, 6-tetramethylbenzotrichloride.

added and the solution refluxed for another hour. The reaction mixture was cooled in an ice bath and carbon dioxide gas (from the evaporation of dry ice in a suction flask) was bubbled into the mixture for 20 minutes. Water (200 ml.) was added and the aqueous layer separated, extracted with 100 ml. of ether to remove any organic material, and acidified with dilute hydrochloric acid. The white precipitate was filtered, washed with water and recrystallized twice from aqueous acetone to yield 4 g. (47.3% based on 5.0 g. of recovered durene) of 4-bromo-2, 3, 5, 6-tetramethylbenzoic acid, m.p. 224-225°.

Anal. Calcd. for $C_{11}H_{13}BrO_2$: C, 51.38; H, 5.10; Br, 31.08.
Neutralization Equivalent: 257.14.
Found: C, 51.63; H, 5.20; Br, 30.89.
Neutralization Equivalent: 257.1.

Reaction of a Solution of 4-Bromo-2, 3, 5, 6-tetramethylbenzotrichloride in 100% Sulfuric Acid with Water

A sample of 0.9318 g. of 4-bromo-2, 3, 5, 6-tetramethylbenzotrichloride was dissolved in 5 ml. of 100% sulfuric acid. The deep red solution was slowly poured onto 50 g. of ice and a fluffy white precipitate was collected. The solid was washed with water and recrystallized twice from aqueous acetone. The yield was 0.6690 g. (91.7%) of 4-bromo-2, 3, 5, 6-tetramethylbenzoic acid, m.p. 224-225°.

Hydrolysis of 4-Bromo-2, 3, 5, 6-tetramethylbenzotrichloride

A sample of 2 g. of 4-bromo-2, 3, 5, 6-tetramethylbenzotrichloride dissolved in 50 ml. of 75% aqueous acetone was refluxed overnight. The solvent was removed on a Rinco rotary evaporation and the solid recrystallized once from aqueous acetone to yield 1.33 g. (85%) of 4-bromo-2, 3, 5, 6-tetramethylbenzoic acid, m.p. 223.5-225°.

The melting points and infrared spectra of the acids from all three experiments were identical.

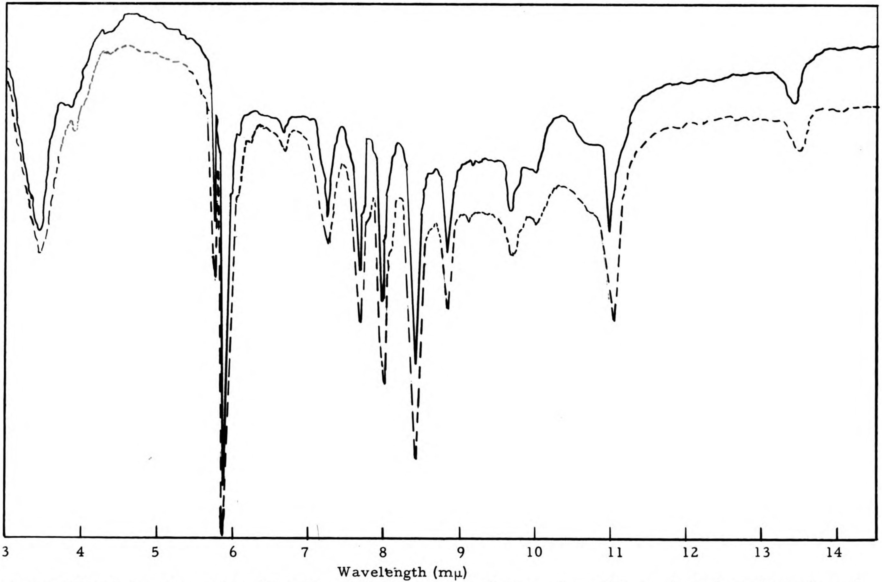


Figure VIII. Infrared spectra of 4-bromo-2, 3, 5, 6-tetramethylbenzoic acid from the Grignard reaction of dibromodurene (——) and from the reaction of 4-bromo-2, 3, 5, 6-tetramethylbenzotrichloride-sulfuric acid with water (----).

Preparation of Chlorodurene

Chlorodurene was prepared by the method of Smith and Moyle (19). A solution of 72 g. (0.5 mole) of durene in 200 g. of chloroform was chlorinated at 0°C. by addition of 39 g. (0.55 mole) of chlorine in 210 g. of chloroform during a 15 minute period. The product was steam distilled and the oil in the distillate was separated. The aqueous layer was extracted with 200 ml. of chloroform and the combined organic layers were dried over calcium chloride for 12 hours. The solvent was removed and the remaining oil distilled at reduced pressure (20 mm). A small amount of durene (7 g.) came over first followed by the main fraction of chlorodurene, b.p. 120-128°. The residue was mainly dichlorodurene. The crude product was recrystallized once from 95% ethanol and yielded 41 g. (50.3% corrected for recovered durene) of white plates of chlorodurene, m.p. 46-48°.

Preparation of 4-Chloro-2, 3, 5, 6-tetramethylbenzotrichloride

In a 1-l. 3-necked flask provided with a Trubore stirrer, thermometer, reflux condenser, and dropping funnel was placed 37.2 g. (0.28 mole) of powdered anhydrous aluminum chloride and 100 ml. of carbon tetrachloride (previously dried with calcium chloride and distilled). The slurry was stirred and warmed from 37-42° while a solution of 23.6 g. (0.14 mole) of chlorodurene in 100 ml. of carbon tetrachloride was added dropwise over a two hour period. After the addition heating and stirring were continued for two more hours.

The deep purple complex was hydrolyzed by slowly adding it with vigorous stirring to a mixture of 100 g. of ice, 10 ml. of concentrated hydrochloric acid and 150 ml. of carbon tetrachloride. The carbon tetrachloride layer was separated and the aqueous layer extracted with two 50-ml. portions of carbon tetrachloride. The combined organic layers were washed with 100 ml. of water, two 100-ml. portions of 5% sodium

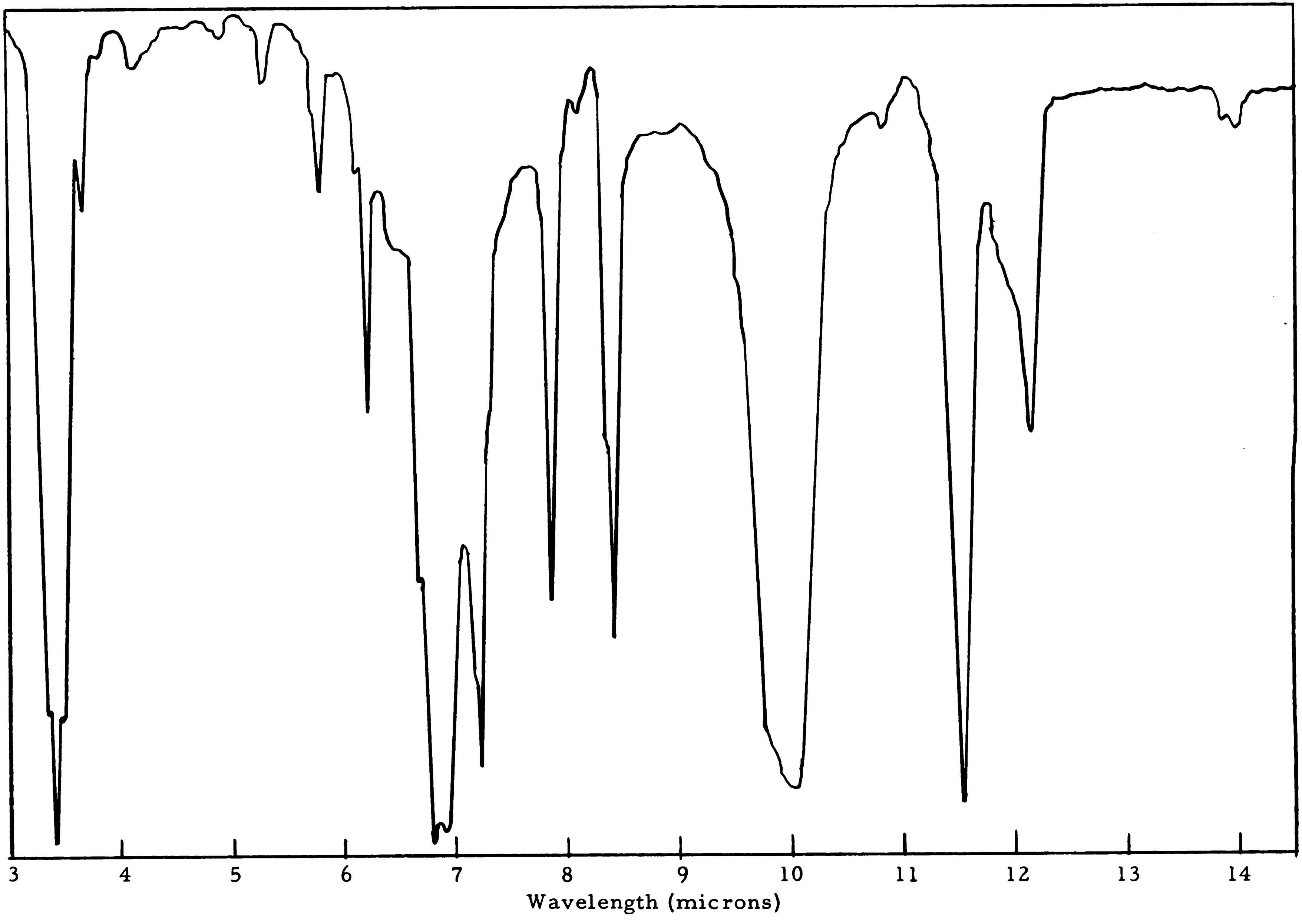


Figure IX. Infrared spectrum of chlorodurene.

carbonate solution, and finally with another 100 ml. of water. The solution was dried overnight with calcium chloride and the solvent removed on a Rinco rotary evaporator.

The dark brown oily residue was dissolved in anhydrous n-pentane and treated with Norite. The pentane solution was filtered, cooled in dry ice and the brown precipitate filtered under a nitrogen atmosphere. After four recrystallizations from pentane 22 g. (56.5%) of white plates of 4-chloro-2, 3, 5, 6-tetramethylbenzotrichloride was obtained, m.p. 72-73°.

Anal. Calcd. for $C_{11}H_{12}Cl_4$: C, 46.18; H, 4.23; Cl, 49.58.
Found: C, 46.49; H, 4.35; Cl, 49.58.

Reaction of 4-Chloro-2, 3, 5, 6-tetramethylbenzotrichloride in 100% Sulfuric Acid with Water

A sample of 1.008 g. (0.0035 mole) of 4-chloro-2, 3, 5, 6-tetramethylbenzotrichloride was dissolved in 20 g. of 100% sulfuric acid cooled to 10°. The sample was stirred (magnetically) and maintained at 10° until it had completely dissolved (ca. 5 min). The red solution was slowly added to 100 g. of ice and the white precipitate filtered, washed with water and recrystallized twice from aqueous acetone. The yield was 0.6904 g. (92%) of white needles of 4-chloro-2, 3, 5, 6-tetramethylbenzoic acid, m.p. 206-207°.

Anal. Calcd. for $C_{11}H_{13}O_2Cl$: C, 62.12; H, 6.16; Cl, 16.67.
Neutralization Equivalent: 212.68.
Found: C, 62.16; H, 6.34; Cl, 16.56.
Neutralization Equivalent: 209.8.

Hydrolysis of 4-Chloro-2, 3, 5, 6-tetramethylbenzotrichloride

A sample of 2.00 g. (0.007 mole) of 4-chloro2, 3, 5, 6-tetramethylbenzotrichloride was dissolved in 50 ml. of 80% aqueous acetone.

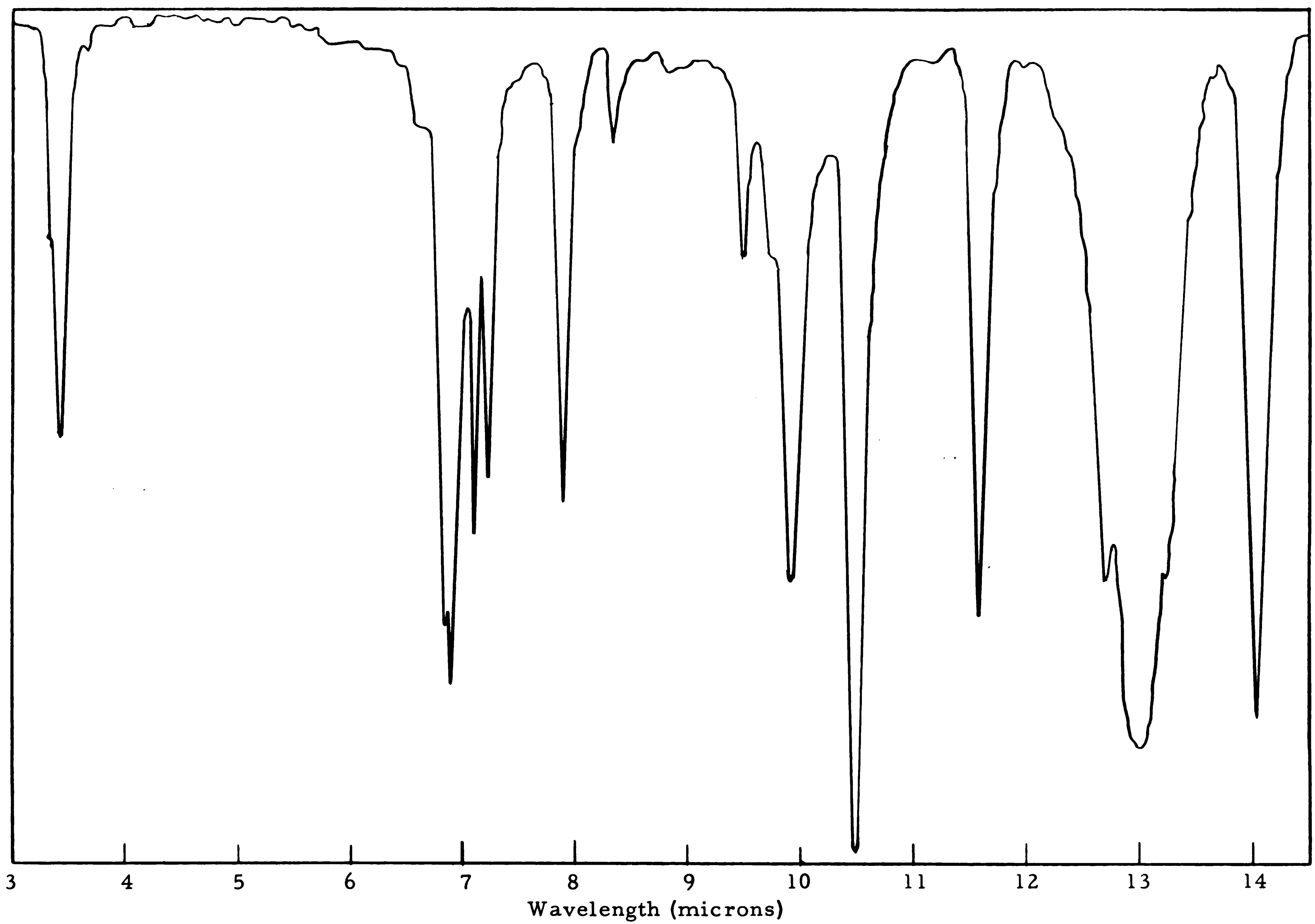


Figure X. Infrared spectrum of 4-chloro-2, 3, 5, 6-tetramethylbenzotrichloride.

The solution was refluxed for 12 hours and the solvent removed on a Rinco rotary evaporator. The white solid was recrystallized from aqueous acetone to yield 1.34 g. (90%) of 4-chloro-2, 3, 5, 6-tetramethylbenzoic acid, m.p. 206-207°. A mixed melting point with the acid from method I gave no depression. The infrared spectra of both acids were identical.

Preparation of Dinitrodurene

Dinitrodurene was prepared by the method of L. I. Smith (20). A solution of 13.4 g. (0.1 mole) of durene in 100 ml. of chloroform was added to 75 ml. of concentrated sulfuric acid in an 800-ml. beaker provided with a stirrer and thermometer. The mixture was cooled to 10° and 16 g. of fuming nitric acid was added dropwise at such a rate that the temperature did not go over 50° (approximately 15 minutes). As soon as all of the acid had been added the mixture was poured into a separatory funnel, the sulfuric acid layer was removed, and the organic layer immediately run into 500 ml. of 10% sodium carbonate solution. Six portions were nitrated and the combined chloroform solutions were washed twice with 500 ml. of 2.5% sodium carbonate solution, dried overnight with calcium chloride, and the chloroform distilled until crystals appeared. At this point four times the volume of 95% ethanol (2 l.) was added and the solution cooled to 10°. The solid was filtered and washed twice with 100 ml. of cold (10°) 95% ethanol. The pale yellow crystals of dinitrodurene were not recrystallized, m.p. 205-208°. The yield was 118 g. (88%).

Preparation of Aminonitrodurene (21)

A typical experiment is described. Forty grams (0.178 mole) of dinitrodurene and 1 l. of 95% ethanol were heated to reflux, and a solution

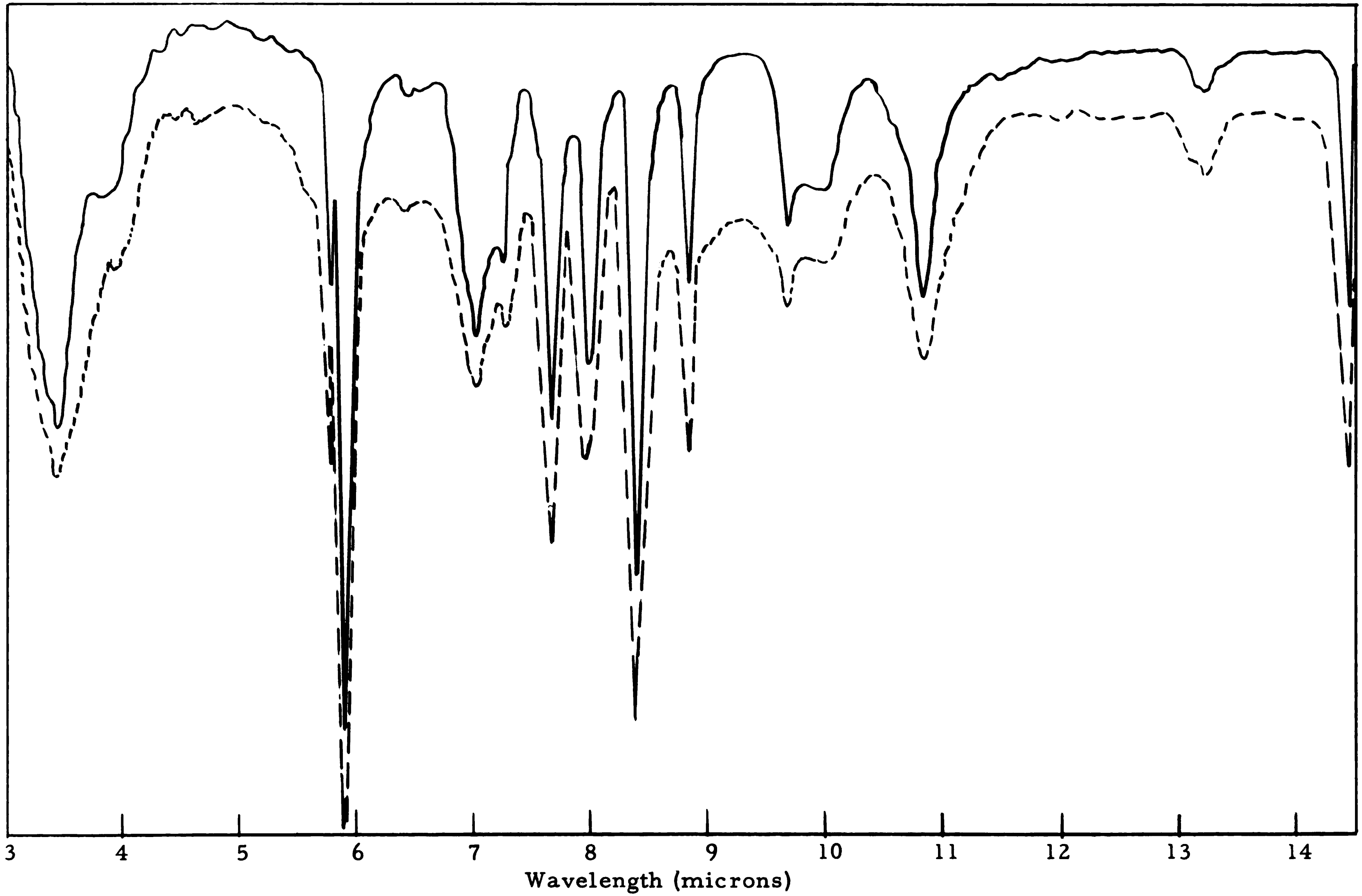


Figure XI. Infrared spectra of 4-chloro-2, 3, 5, 6-tetramethylbenzoic acid from the hydrolysis of 4-chloro-2, 3, 5, 6-tetramethylbenzotrichloride (——) and from the reaction of 4-chloro-2, 3, 5, 6-tetramethylbenzotrichloride-sulfuric acid with water (----).

of sodium disulfide (prepared by warming 140 g. [0.583 mole] of $Na_2S \cdot 9\ H_2O$ in 400 ml. of water with 18 g. [0.563 g.-atom] of flowers of sulfur) was added slowly with stirring. After addition, the mixture was refluxed and stirred for 9-10 hours. The excess alcohol (about 700 ml.) was removed by distillation and the remaining solution poured into 2 l. of cold water. The yellow precipitate was filtered, washed with water, and heated with 1500 ml. of 2 N hydrochloric acid. The solution was filtered hot to remove any unreacted dinitrodurene or sulfur and the filtrate made basic with ammonium hydroxide. The orange solid was filtered, washed with water and dried. The experiment was repeated until 170 g. (0.76 mole) of dinitrodurene had been reduced. The over-all yield was 133.4 g. (90.5%) of aminonitrodurene, m.p. 158.5-160°. The reported m.p. after recrystallization from 95% ethanol was 161-162°. The material was used without further purification.

Preparation of 4-Fluoronitrodurene (22)

A total of 130 g. (0.671 mole) of aminonitrodurene was diazotized in small batches. Aminonitrodurene (10 g.) was added to 100 ml. of 6 M sulfuric acid. The mixture was cooled to 0° in an ice-salt bath and a saturated solution of sodium nitrite was added dropwise while maintaining the temperature between 0-5°. The diazotization was complete when a positive test for nitrous acid was observed with starch-potassium iodide paper. Approximately 55 ml. of 40% tetrafluoroboric acid was added to the clear solution and a pale yellow solid immediately precipitated. Three batches were run simultaneously. The diazonium fluoroborate salt was filtered, washed with 30 ml. of cold water, 50 ml. of 95% ethanol, and 200 ml. of ether. The solid (188 g., 96.4% based on 130 g. of aminonitrodurene) was dried at room temperature in a dessicator for 48 hours.

The diazonium fluoroborate was decomposed by heating (Bunsen burner) 30 g. portions in a 1-l. flask under reduced pressure. After 60 g. of material had been decomposed in this manner the remaining solid which was in a large crystallizing dish decomposed spontaneously with a voluminous evolution of boron trifluoride. The brown oily residue was dissolved in 1500 ml. of ether, washed with three 200-ml. portions of 5% sodium hydroxide solution and 200 ml. of water. The ether layer was separated and dried with Drierite for 24 hours. The solvent was evaporated and the brownish-yellow solid dissolved in 95% ethanol, treated with Norite, filtered, and recrystallized. The yield was 65 g. (49.3%) of 4-fluoronitrodurene, m.p. 93.5-95.5° (Literature value 96-97°).

Preparation of 4-Fluoroaminodurene (22)

Fluoronitrodurene (60 g., 0.305 mole) dissolved in 600 ml. of boiling acetic acid was reduced with 120 g. (1.01 g.-atoms) of tin and 600 ml. of concentrated hydrochloric acid. The solution was refluxed and stirred for 4 hours, made alkaline with concentrated sodium hydroxide solution, and steam distilled for 7 hours. The precipitate in the distillate was filtered, washed with water and dried. The yield was 34 g. (66.5%) of light fluffy needles of 4-fluoroaminodurene, m.p. 98-99°. Reported m.p. 101-102° after recrystallization from 85% aqueous ethanol.

Preparation of Fluorodurene (22, 23)

To a 1-l. Erlenmeyer flask containing 450 ml. of water and 18 ml. of concentrated hydrochloric acid heated to boiling was added 22.5 g. (0.135 mole) of 4-fluoroaminodurene with magnetic stirring. After two minutes the hot mixture was rapidly cooled to 10° and 22.5 ml. of concentrated hydrochloric acid was added. The mixture was cooled to

0-5° and diazotized with a saturated sodium nitrite solution until an excess of nitrous acid was present (indicated by potassium iodide-starch indicator paper). The reaction mixture was maintained at 0-5° for another thirty minutes and then 214 ml. (2.025 moles) of ice-cold 50% hypophosphorous acid was added. The flask was loosely stoppered and stored in a refrigerator at or near 0° for three days. The pale yellow solid was filtered dissolved in 100 ml. of ether, washed with two 50-ml. portions of 10% sodium hydroxide solution, once with 50 ml. of water and dried over magnesium sulfate for 24 hours. The ether was evaporated and the solid residue (about 17 g.) was dissolved in 20 ml. of petroleum ether and adsorbed on 80 g. of Fisher Adsorption alumina (80-200 mesh). The column was eluted with 1200 ml. of petroleum ether and on evaporation of the solvent there remained 15 g. (73.3%) of fluorodurene, m.p. 53.5-55.0°.

Preparation of 4-Fluoro-2, 3, 5, 6-tetramethylbenzotrichloride

In a 500-ml. 3-necked flask fitted with a Trubore stirrer, thermometer, reflux condenser, and dropping funnel was placed 26.6 g. (0.2 mole) of powdered anhydrous aluminum chloride and 100 ml. of carbon tetrachloride previously dried over calcium chloride and distilled. The slurry was stirred and heated at 37-42° while a solution of 15.2 g. (0.10 mole) of fluorodurene in 100 ml. of carbon tetrachloride was added dropwise (two hours). After the addition heating and stirring were continued for an additional two hours.

The purple complex was slowly added with mechanical stirring to a mixture of 100 g. of ice, 10 ml. of concentrated hydrochloric acid and 150 ml. of carbon tetrachloride. The aqueous layer was separated and extracted with two 100-ml. portions of carbon tetrachloride. The combined organic layers were washed with two 150-ml. portions of 5% sodium carbonate solution and dried over magnesium sulfate. The solvent

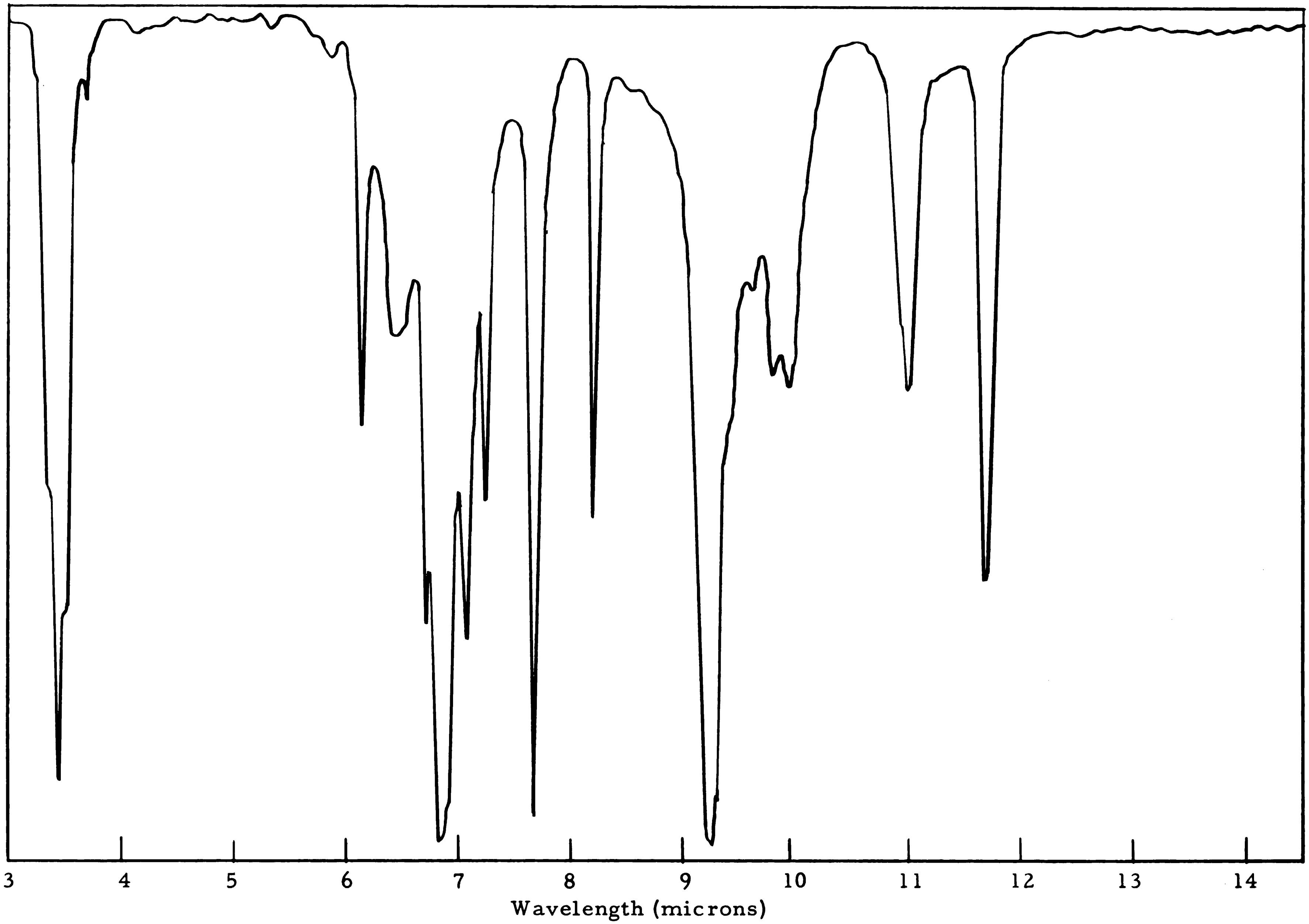


Figure XII. Infrared spectrum of fluorodurene.

was removed on the Rinco rotary evaporator and the brown oil was dissolved in anhydrous n-pentane and treated with Norite. This procedure was repeated until 20 g. (74.4%) of white plates of 4-fluoro-2, 3, 5, 6-tetramethylbenzotrichloride were obtained, m.p. 56-57.5°. A mixed melting of the product with fluorodurene (m.p. 54.5-55.5°) gave a definite depression.

Anal. Calcd. for $C_{11}H_{12}Cl_3F$: C, 49.01; H, 4.49; Cl, 39.46; F, 7.05.

Found: C, 49.08; H, 4.64; Cl, 39.55; F, 7.04.

Hydrolysis of 4-Fluoro-2, 3, 5, 6-tetramethylbenzotrichloride

A sample of 2.00 g. (0.0075 mole) of 4-fluoro-2, 3, 5, 6-tetramethylbenzotrichloride was dissolved in 50 ml. of 75% aqueous acetone. The solution was refluxed for 6 hours and the solvent evaporated. The white solid was recrystallized once from aqueous acetone to yield 1.40 g. (96%) of white needles of 4-fluoro-2, 3, 5, 6-tetramethylbenzoic acid, m.p. 168-169.5°.

Anal. Calcd. for $C_{11}H_{13}FO_2$: C, 67.33; H, 6.68; F, 9.68.
Neutralization equivalent: 196.2
Found: C, 67.49; H, 6.77; F, 9.60.
Neutralization equivalent: 198.1

Reaction of 4-Fluoro-2, 3, 5, 6-tetramethylbenzotrichloride in 100% Sulfuric Acid with Water

A sample of 1.0159 g. (0.00376 mole) of 4-fluoro-2, 3, 5, 6-tetramethylbenzotrichloride was dissolved in 10 ml. of 100% sulfuric acid. The red solution was slowly added to 100 g. of ice and a white precipitate was collected. The solid was recrystallized twice from aqueous acetone to yield 0.7300 g. (99%) of white needles of 4-fluoro-2, 3, 5, 6-tetramethylbenzoic acid, m.p. 168-169.5°. A m.m.p. with the acid from the

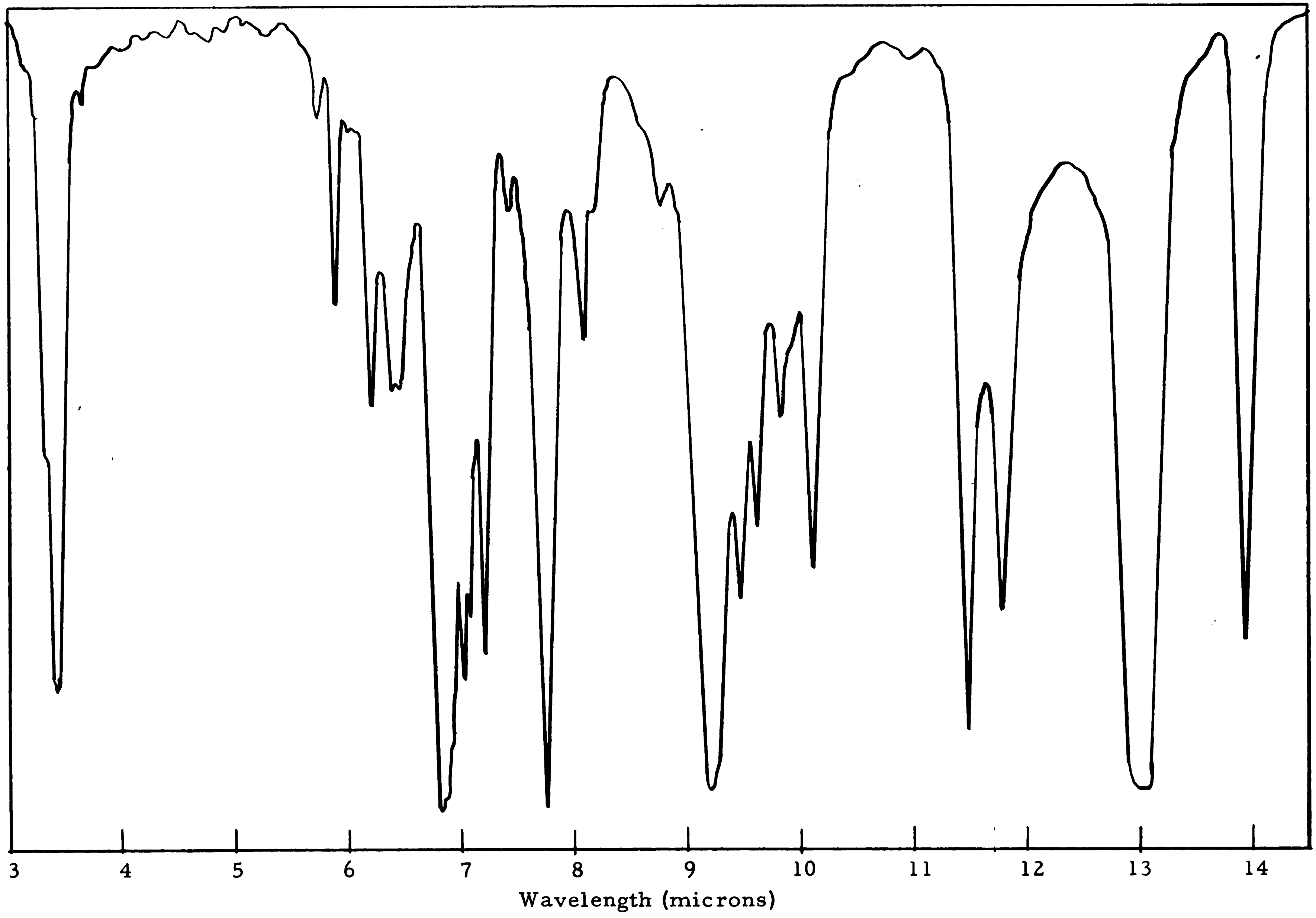


Figure XIII. Infrared spectrum of 4-fluoro-2, 3, 5, 6-tetramethylbenzotrichloride.

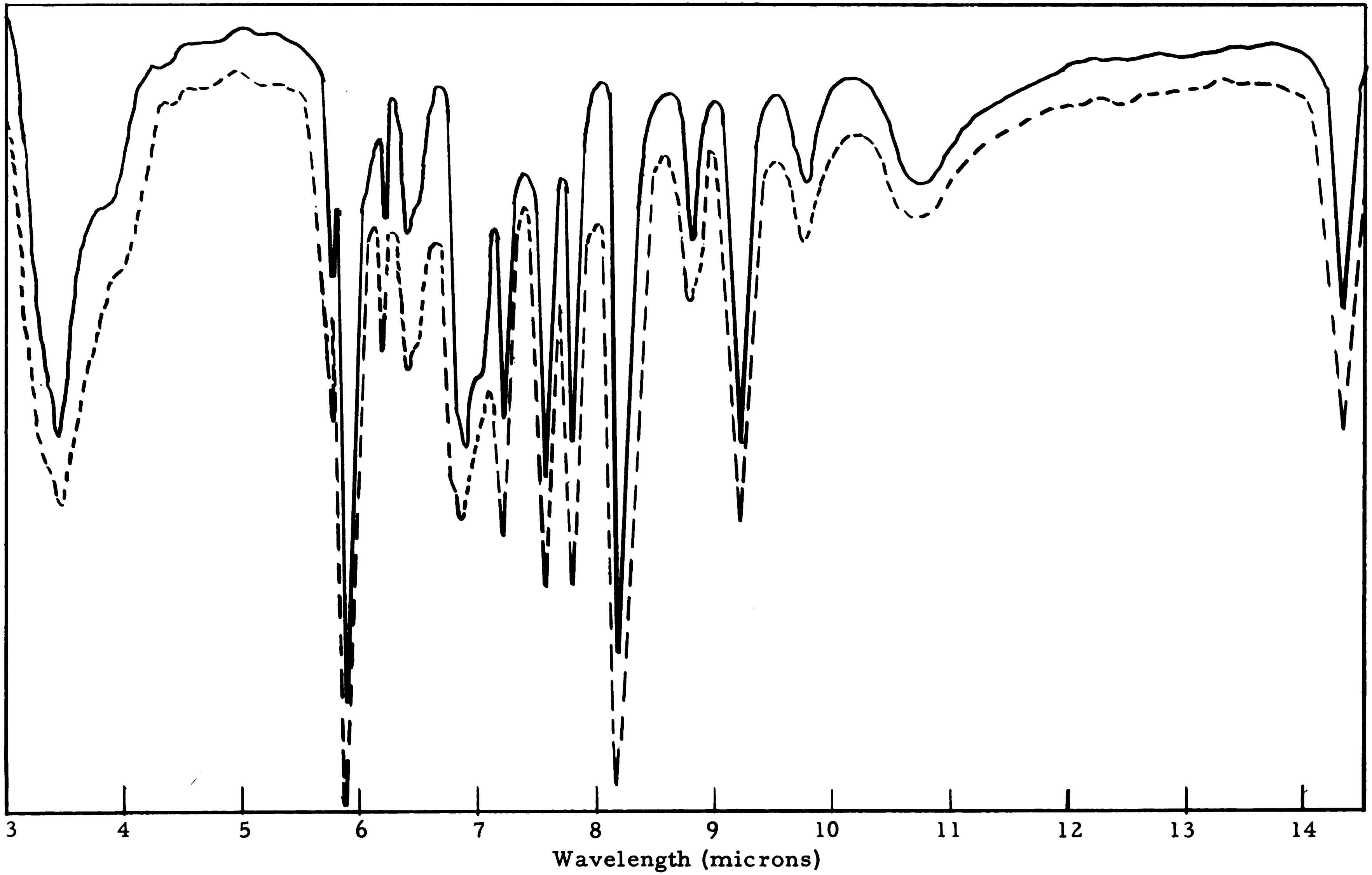


Figure XIV. Infrared spectra of 4-fluoro-2, 3, 5, 6-tetramethylbenzoic acid from the hydrolysis of 4-fluoro-2, 3, 5, 6-tetramethylbenzotrichloride (———) and from the reaction of 4-fluoro-2, 3, 5, 6-tetramethylbenzotrichloride-sulfuric acid with water (- - - -).

previous hydrolysis of 4-fluoro-2,3,5,6-tetramethylbenzotrichloride gave no depression. The infrared spectra of both acids were identical.

Neutralization equivalent calcd. for $C_{11}H_{13}FO_2$: 196.2.
Found: 195.6.

Preparation of Acetoxymercuridurene (24)

To a 1-liter round-bottomed flask was added 72 g. (0.537 mole) of durene, 360 ml. of methanol, 171 g. (0.537 mole) of mercuric acetate and 50 ml. of glacial acetic acid. The solution was refluxed for 5 days and then filtered hot to remove any diacetoxydurene formed. The filtrate was cooled and the white precipitate collected. The crude product was recrystallized from methanol to yield 87.5 g. (41.5%) of acetoxymercuridurene, m.p. 158-159°.

Preparation of Nitrodurene (25)

Seventy-five grams (0.191 mole) of acetoxymercuridurene was heated and shaken with 800 ml. of nitric acid (sp. gr. 1.26). The substance was converted to a material which floated (presumably nitrosodurene) and nitrogen oxides were evolved. At 70°, all of the nitrosodurene had dissolved within 10 minutes. The solution was kept warm 2 minutes longer, and then it was poured into 200 g. of ice and 200 ml. of water, and filtered. The yellow precipitate was triturated and washed with water and dried. The crude product was recrystallized from absolute ethanol and yielded 32.5 g. (95%) of pale yellow prisms of nitrodurene, m.p. 111-112.5°.

Attempted Preparation of 4-Nitro-2,3,5,6-tetramethylbenzotrichloride

In a 1-l. 3-necked flask equipped with a Trubore stirrer, thermometer, reflux condenser, and dropping funnel was placed 39.90 g.

(0.30 mole) of powdered anhydrous aluminum chloride and 150 ml. of carbon tetrachloride. The slurry was stirred and heated between 37-42° while a solution of 26.85 g. (0.15 mole) of nitrodurene in 150 ml. of carbon tetrachloride was added dropwise (two hours). After the addition, heating and stirring were continued for another two hours.

The light purple complex was slowly added with vigorous stirring to a mixture of 150 g. of ice, 20 ml. of concentrated hydrochloric acid and 200 ml. of carbon tetrachloride. The carbon tetrachloride layer was separated and washed with 150 ml. of water, two 200-ml. portions of 5% sodium carbonate solution, and finally with another 100 ml. of water. The solution was dried overnight with calcium chloride and the solvent removed on a Rinco rotary evaporator. The yellow solid was recrystallized from absolute ethanol and yielded 23 g. (86%) of nitrodurene. The m.p., m.m.p., and infrared spectrum of the product was identical with that of the starting material.

Preparation of iododurene (26)

Into a round-bottomed flask fitted with a mechanical stirrer and condenser was placed 26.8 g. (0.2 mole) of durene, 100 ml. of acetic acid, 20 ml. of water, 3.0 ml. of concentrated sulfuric acid, 20.4 g. (0.16 g.-atom) of iodine, 8.2 g. (0.04 mole) of iodic acid, and 10 ml. of carbon tetrachloride. The mixture was heated and stirred for two hours at 85°.

The reaction product was separated by addition of 600 ml. of water and then extracted with 100 ml. of chloroform. The chloroform layer was separated and washed with 100 ml. of 5% sodium hydroxide solution, 100 ml. of 5% sodium thiosulfate solution, and 100 ml. of water. It was dried for twelve hours over anhydrous sodium carbonate. The solvent was evaporated and the white residue was recrystallized once from 95% ethanol to yield 44 g. (85%) of white needles of iododurene, m.p. 78.5-80°. A m.m.p. with durene gave a definite depression.

Attempted Preparation of 4-Iodo-2, 3, 5, 6-tetramethylbenzotrichloride

To a 1-l. 3-necked round-bottomed flask equipped with a stirrer, thermometer, reflux condenser, and dropping funnel was added 26.7 g. (0.20 mole) of powdered anhydrous aluminum chloride and 125 ml. of carbon tetrachloride previously dried over calcium chloride and distilled. The slurry was stirred and heated to 37-42°. A solution of 26.0 g. (0.1 mole) of iododurene in 100 ml. of carbon tetrachloride was added dropwise over a two hour period, and the solution was then heated and stirred for an additional three hours. Iodine appeared to be liberated during this 5 hour period.

The colored complex was hydrolyzed by slowly adding it with vigorous stirring to a mixture of 100 g. of ice, 15 ml. of hydrochloric acid and 150 ml. of carbon tetrachloride. The complex hydrolyzed with some difficulty. The organic layer was separated, washed with 100 ml. of water, two 50-ml. portions of 5% sodium carbonate solution, again with 100 ml. of water and finally dried over calcium chloride. The solvent was removed on a Rinco rotary evaporator. A brown viscous oil (12 g.) that could not be purified and was not identified remained after evaporation of the solvent.

B. Cryoscopic Measurements

Apparatus

The apparatus was the same as that described by Fish (27).

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.

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°.

After the sample had completely dissolved the new freezing point was determined. Two to four weighed portions of solute were added and the freezing point determined after each addition.

Two techniques were used to add the sample. One method was to weigh the sample on glazed paper and then pour it into the cell by means of a long funnel made of glazed paper. This method was not satisfactory since the cell had to be opened for each addition and undoubtedly the sulfuric acid picked up some atmospheric moisture.

A better method for adding the sample was by means of a solid dropping funnel with a long stem extending almost to the surface of the sulfuric acid. The sample and dropping funnel were weighed and then placed in the cell. A small sample was introduced into the cell the freezing point determined, the dropping funnel removed, and reweighed. This procedure was repeated until all of the sample had been added.

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.

C. Quantitative Determination of Hydrogen Chloride From the Reaction of the Trichloromethyl Compounds with Sulfuric Acid

Apparatus

The apparatus consisted of three drying towers and two traps arranged in series. The traps and towers had ground glass joints and were connected by Tygon tubing. Each trap had a long inlet tube with a fritted glass tip protruding below the surface of the solution, and an exit tube connecting it to the next trap. The first tower contained reagent grade concentrated sulfuric acid, the second and third towers contained slightly greater than 100% (maximum 0.001 molar sulfur trioxide) sulfuric acid. The first trap contained a solution of trichloromethyl compound in 100% sulfuric acid and the last trap contained a 2 to 5% sodium hydroxide solution for collecting the hydrogen chloride.

Procedure

The apparatus was assembled as described. A known weight of trichloromethyl compound was added to the first trap, followed by approximately 50 ml. of 100% sulfuric acid. The solution was stirred magnetically and a stream of oil-pumped nitrogen was bubbled through the system. At various time intervals the aqueous sodium hydroxide trap was changed, the solution acidified with dilute nitric acid to pH 7-8 (pH was determined by a Beckman pH meter), and the chloride ion determined by the Fajans' method (28).

D. Spectra

The ultraviolet-visible spectra were obtained with the Beckman DK-2 Recording Spectrophotometer and Beckman DU-Spectrophotometer using 1 cm. glass-stoppered quartz cells.

The proton magnetic resonance spectra were obtained with a high-resolution nuclear-induction type N.M.R. spectrometer, Varian Associates (VA) Model V-4300-2.

The infrared spectra were scanned using a Perkin-Elmer (Model 21) Recording Infrared Spectrophotometer with 0.5 mm. thickness solution cells. All of the infrared spectra were run in carbon disulfide except for the region of 6.2 mμ to 7.1 mμ which was run in carbon tetrachloride.

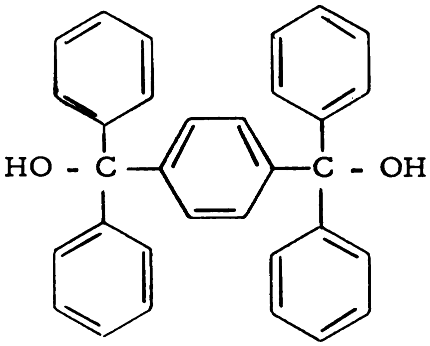
PART B

DIPOSITIVE CARBONIUM IONS ARISING FROM SINGLE IONIZATIONS AT TWO SEPARATE SITES IN A MOLECULE

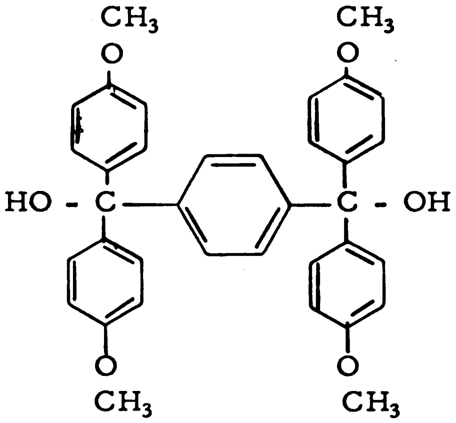
RESULTS AND DISCUSSION

This part of the thesis deals with the mode of ionization of three glycols related structurally to the triarylcarbinols. Each is in principle capable of ionization to a mono or dicarbonium ion. The ionization was studied by examining the spectra in solutions of varying acidity and by characterizing the hydrolysis products of acidic solutions of the glycols.

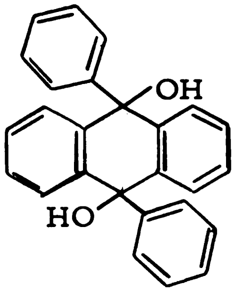
The three compounds studied were tetraphenyl-p-xylyleneglycol (I), tetra-p-anisyl-p-xylyleneglycol (II), and 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene (III).



I



II



III

Spectra

Each of the compounds dissolved readily in 100% sulfuric acid producing intensely colored stable solutions.

Compound I gave a deep red solution in 100% sulfuric acid. The visible spectrum of this solution had a single maximum at 455 mμ (ϵ = 58,700). Solutions of I in acetic acid showed no absorbance in the visible region. Addition of sulfuric acid to an acetic acid solution of I produced a yellow color which persisted to approximately 28% sulfuric acid. Above this concentration the solutions were red. The maximum absorbance occurs between 40 and 46% sulfuric acid in acetic acid, and the spectrum was identical to that of I in 100% sulfuric acid. Figure XV shows the visible spectra of tetraphenyl-p-xylyleneglycol in varying concentrations of sulfuric acid in acetic acid. The molar absorbancy indices of the maxima are given in Table VI. At approximately 3.5% sulfuric acid in acetic acid ϵ at 455 mμ (dipositive ion) is one-half of its maximum value.

In the solvent system sulfuric acid-water I gave similar color changes. At 5.9% sulfuric acid ϵ for the 455 mμ band was half of its maximum value and the extinction coefficient did not change above 70% sulfuric acid. (Actually, the position of $\lambda_{max.}$ shifts slightly, from 445 mμ in 56-64% acid to 455 mμ in 70-100% acid.) Figures XVI and XVII show the visible spectra of tetraphenyl-p-xylyleneglycol in varying concentrations of sulfuric acid in water and Table VII records the molar absorbancy indices of the maxima.

Compound II dissolved in 100% sulfuric acid forming a cherry-red solution. The visible spectrum of this solution had two peaks at 525 mμ (ϵ = 88,500) and 445 mμ (ϵ = 52,500).

When II was dissolved in acetic acid the solution was yellow and the visible spectrum had two peaks at 500 mμ (ϵ = 11,900) and 430 mμ (ϵ = 4,160). Addition of very small amounts of sulfuric acid to II in

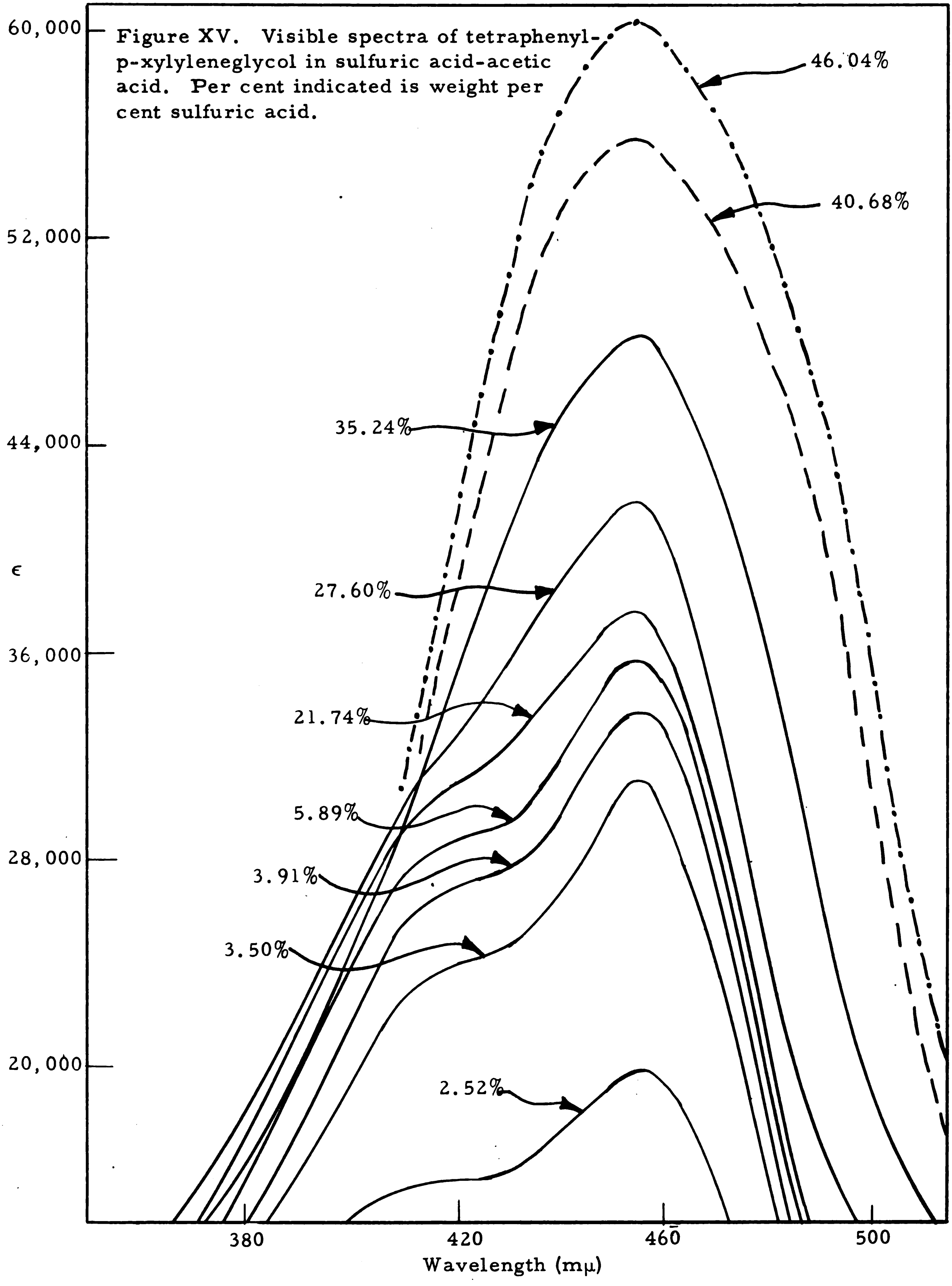


Figure XV. Visible spectra of tetraphenyl-p-xylyleneglycol in sulfuric acid-acetic acid. Per cent indicated is weight per cent sulfuric acid.

Table VI. Visible Absorption Maxima of Tetraphenyl-p-xylyleneglycol in Varying Concentrations of Sulfuric Acid-Acetic Acid

Wt. Per Cent H_2SO_4	Molar Absorbancy Index (ϵ) at 425 mμ	Molar Absorbancy Index (ϵ) at 455 mμ
2.52	15,740	19,700
3.50	24,100	31,000
3.91	27,100	33,700
5.89	29,000	35,700
13.96	30,700	37,000
21.74	31,400	38,200
27.60	---	41,800
35.24	---	48,200
40.68	---	55,800
46.04	---	59,900

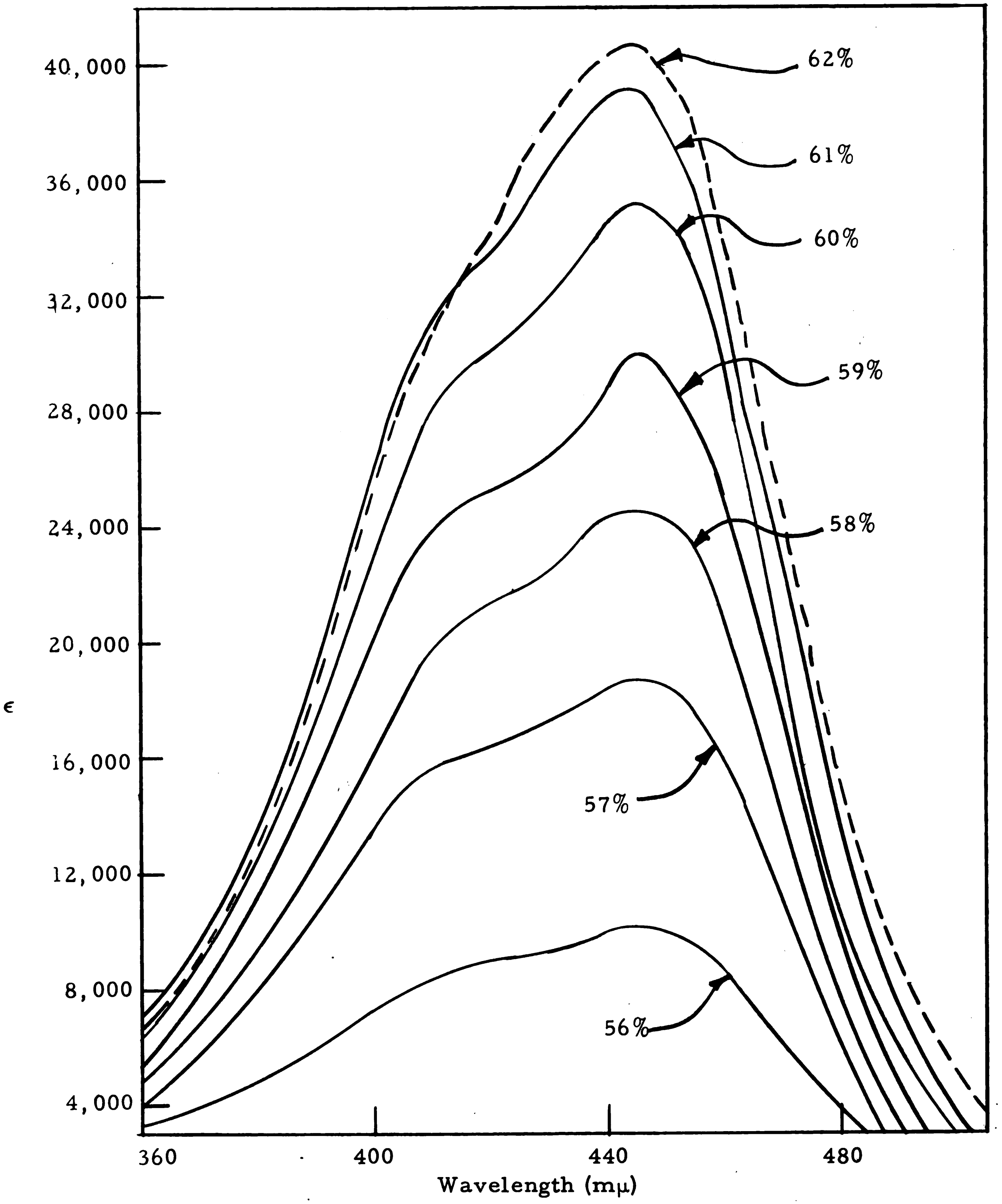


Figure XVI. Visible spectra of tetraphenyl-p-xylyleneglycol in varying concentrations of sulfuric acid-water. Per cent indicated is weight per cent sulfuric acid.

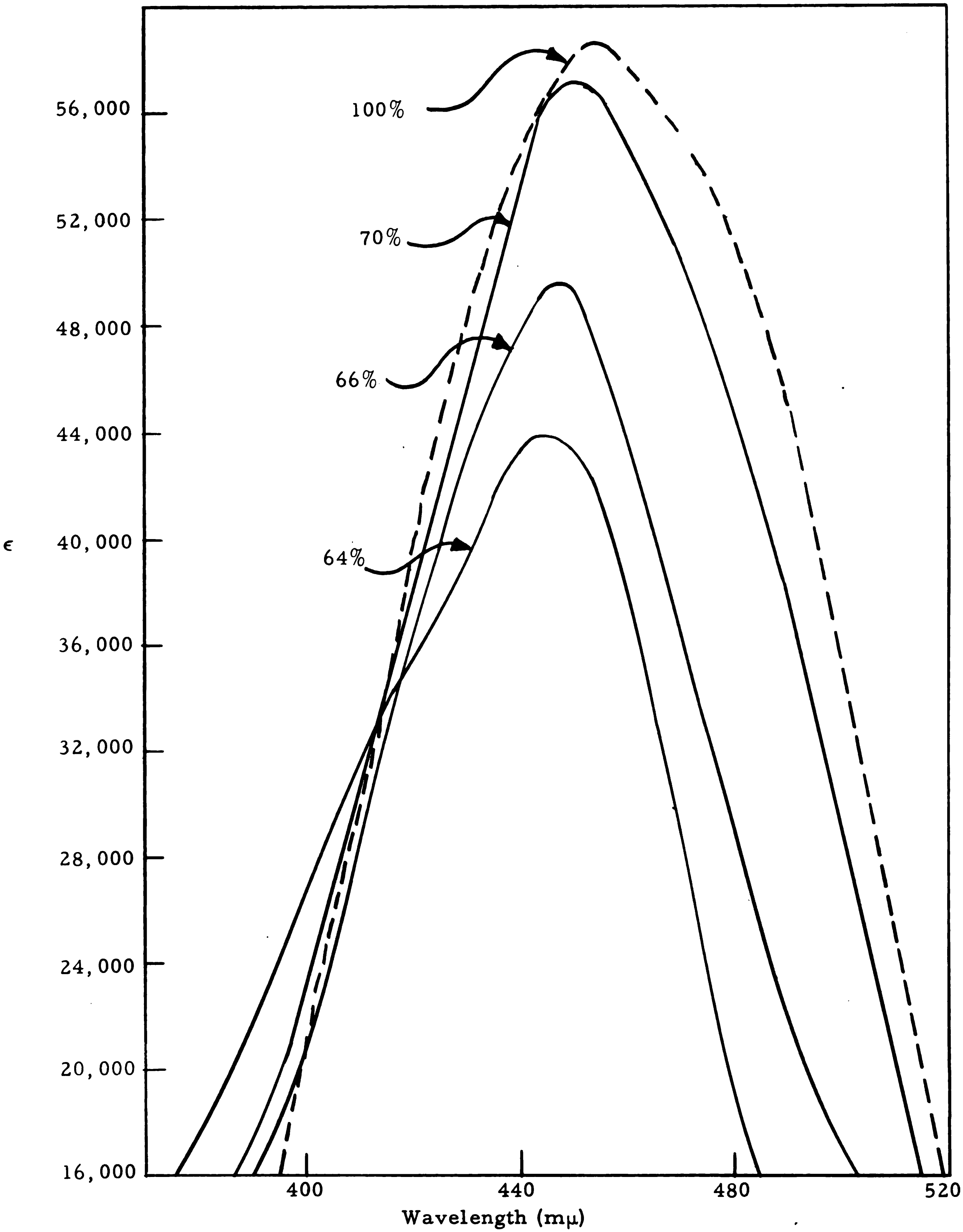


Figure XVII. Visible spectra of tetraphenyl-p-xylyleneglycol in varying concentrations of sulfuric acid-water. Per cent indicated is weight per cent sulfuric acid.

Table VII. Visible Absorption Maxima of Tetraphenyl-p-xylyleneglycol in Varying Concentrations of Sulfuric Acid-Water

Wt. Per Cent H_2SO_4	Molar Absorbancy Index (ϵ) at 420 mμ	Molar Absorbancy Index (ϵ) at 445 mμ
56	9,000	10,150
57	16,600	18,750
58	21,400	24,700
59	25,200	30,000
60	30,100	35,200
61	33,500	39,100
62	34,100	40,600
66	----	47,600[a]
68	----	57,200[b]
70	----	58,500[c]
100	----	58,700[c]

[a] Maximum has shifted to 447 mμ.
[b] Maximum has shifted to 450 mμ.
[c] Maximum has shifted to 455 mμ.

acetic acid caused the solution to become red and produced a bathochromic shift and a large increase in intensity of the maxima. Figure XVIII shows the visible spectra and Table VIII records the molar absorbancy indices for tetra-p-anisyl-p-xylyleneglycol in varying concentrations of sulfuric acid in acetic acid. The maximum absorbance occurs between 0.2 and 0.4% sulfuric acid, and half of ϵ maximum occurred between 0.0 and 0.02% sulfuric acid in acetic acid.

Figures XIX and XX show the visible spectra of II in varying concentrations of sulfuric acid and water. The spectrum and shifts in the maxima by varying the sulfuric acid concentration were analogous to those observed in sulfuric acid-acetic acid. At 60% sulfuric acid in water II showed two peaks at 520 mμ and 455 mμ with ϵ = 96,000 and 51,800 respectively. In 31% sulfuric acid the bands were displaced to 505 mμ and 450 mμ with ϵ equal to 50,500 and 26,200.

The colors produced by I and II in acid media can be reversed by appropriately varying the sulfuric acid concentration. Beer's law was obeyed by both compounds.

Compound III dissolves in 100% sulfuric acid forming a deep blue solution. If III is dissolved in acetic acid the solution is colorless. Addition of a small amount of sulfuric acid causes the solution to become yellow. Increasing the sulfuric acid concentration changes the color progressively from yellow to red to blue. Once the blue color has been formed it cannot be reversed by the addition of acetic acid, whereas the red solution can be converted back to a yellow solution by dilution with acetic acid. Figure XXI shows the visible spectrum and Table X reports the molar absorbancy index for 9,10-dihydro-9,10-dihydroxy-9,10-diphenylanthracene (III) in varying amounts of sulfuric acid in acetic acid. Figure XXII and Table XI record the comparable data for III in varying concentrations of sulfuric acid in water.

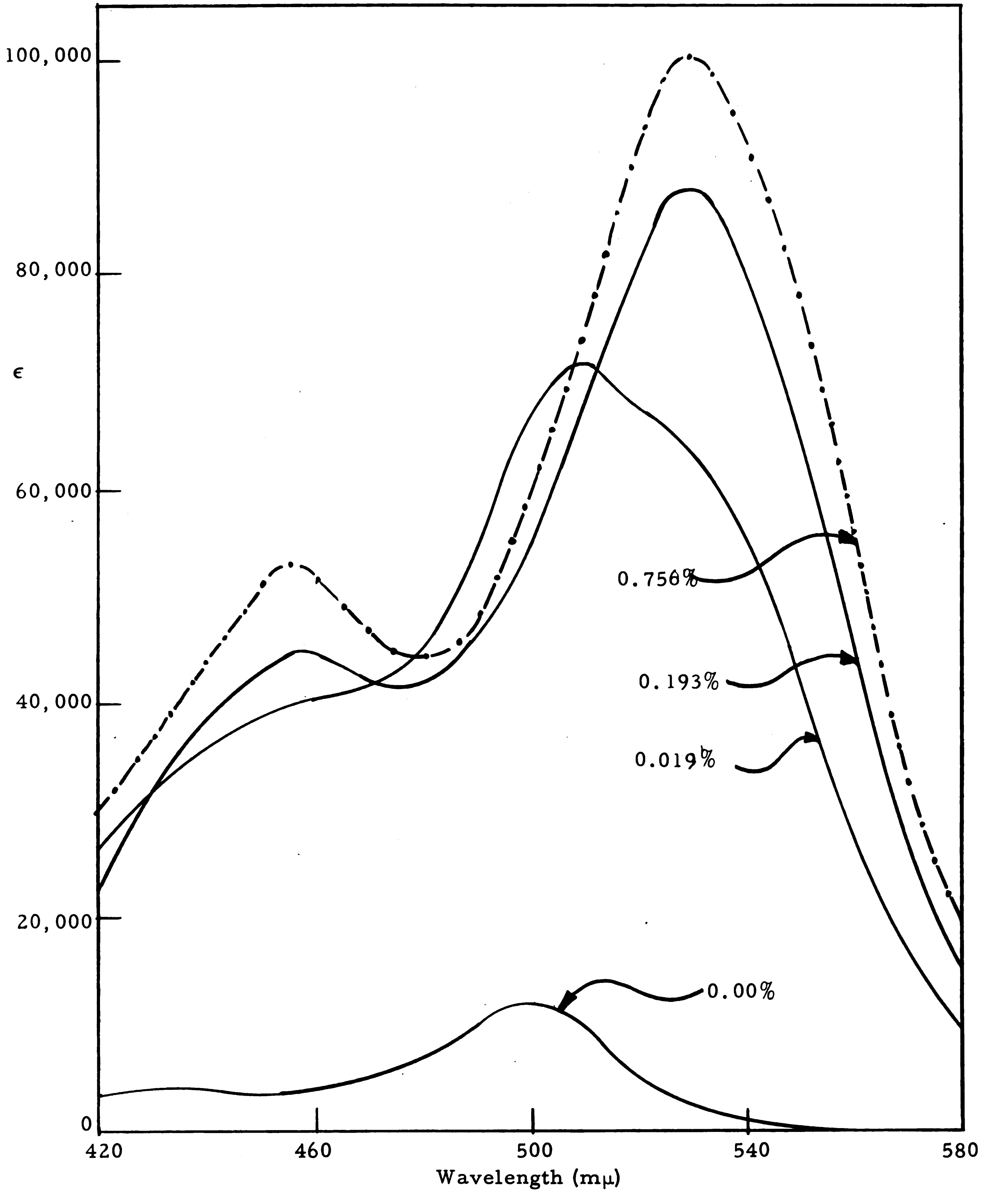


Figure XVIII. Visible spectra of tetra-p-anisyl-p-xylyleneglycol in varying concentrations of sulfuric acid-acetic acid. Per cent indicated is weight per cent sulfuric acid.

Table VIII. Visible Absorption Maxima of Tetra-p-anisyl-p-xylyleneglycol in Varying Concentrations of Sulfuric Acid-Acetic Acid

Wt. Per Cent H_2SO_4	Molar Absorbancy Index (ε) of the 400 mμ Region Band		Molar Absorbancy Index (ε) of the 500 mμ Region Band	
	λ(mμ)	ε	λ(mμ)	ε
0.00	430	4,160	500	11,950
0.019	470 (shoulder)	40,600	510	71,800
0.193	456	45,000	530	88,300
0.756	458	53,000	530	101,500
1.50	459	53,000	530	101,300
6.01	457	53,000	530	101,500
9.33	457	53,000	530	101,300
100.0	445	52,500	525	88,500

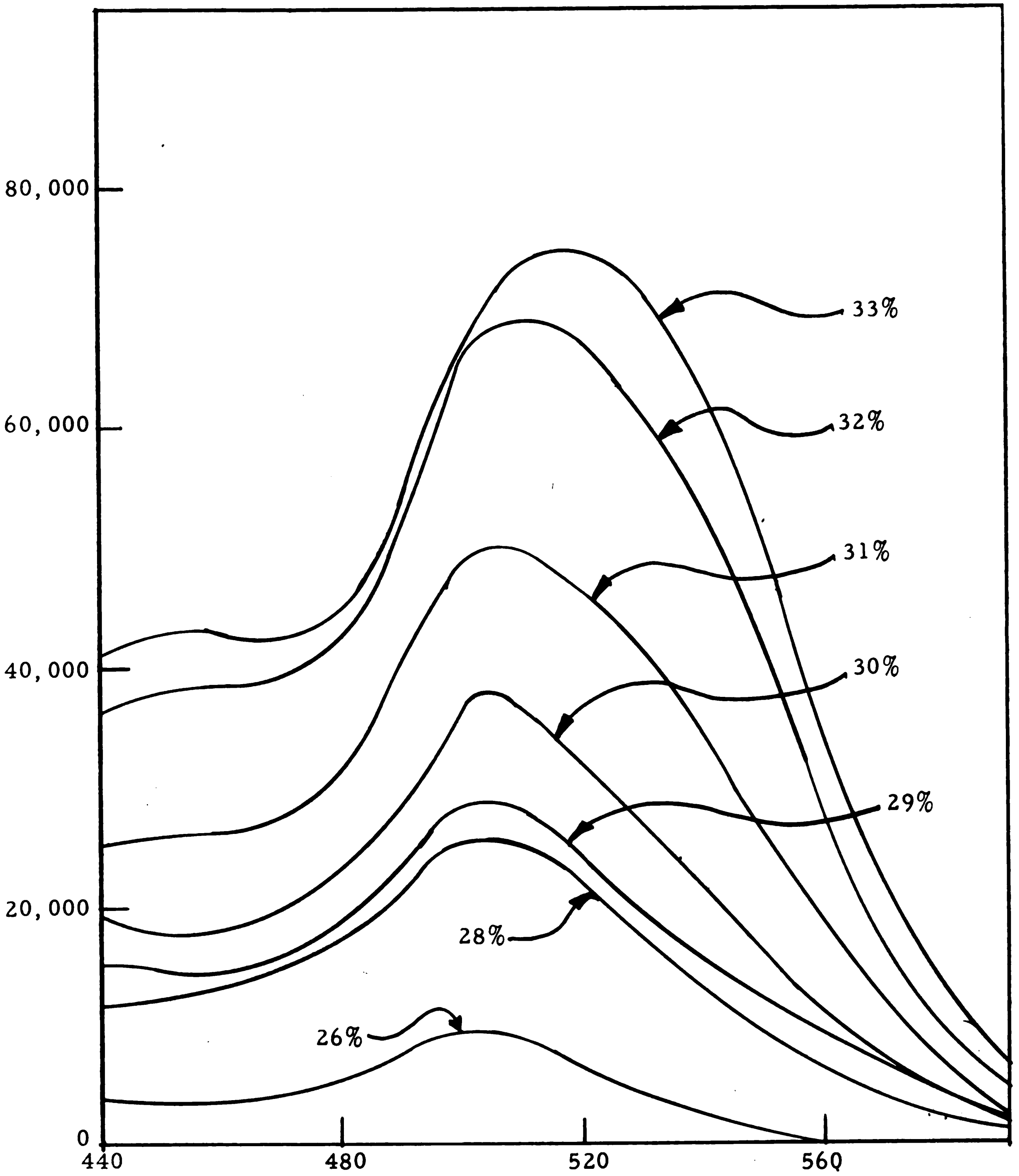


Figure XIX. Visible spectra of tetra-p-anisyl-p-xylyleneglycol in varying concentrations of sulfuric acid-water. Per cent indicated is weight per cent sulfuric acid.

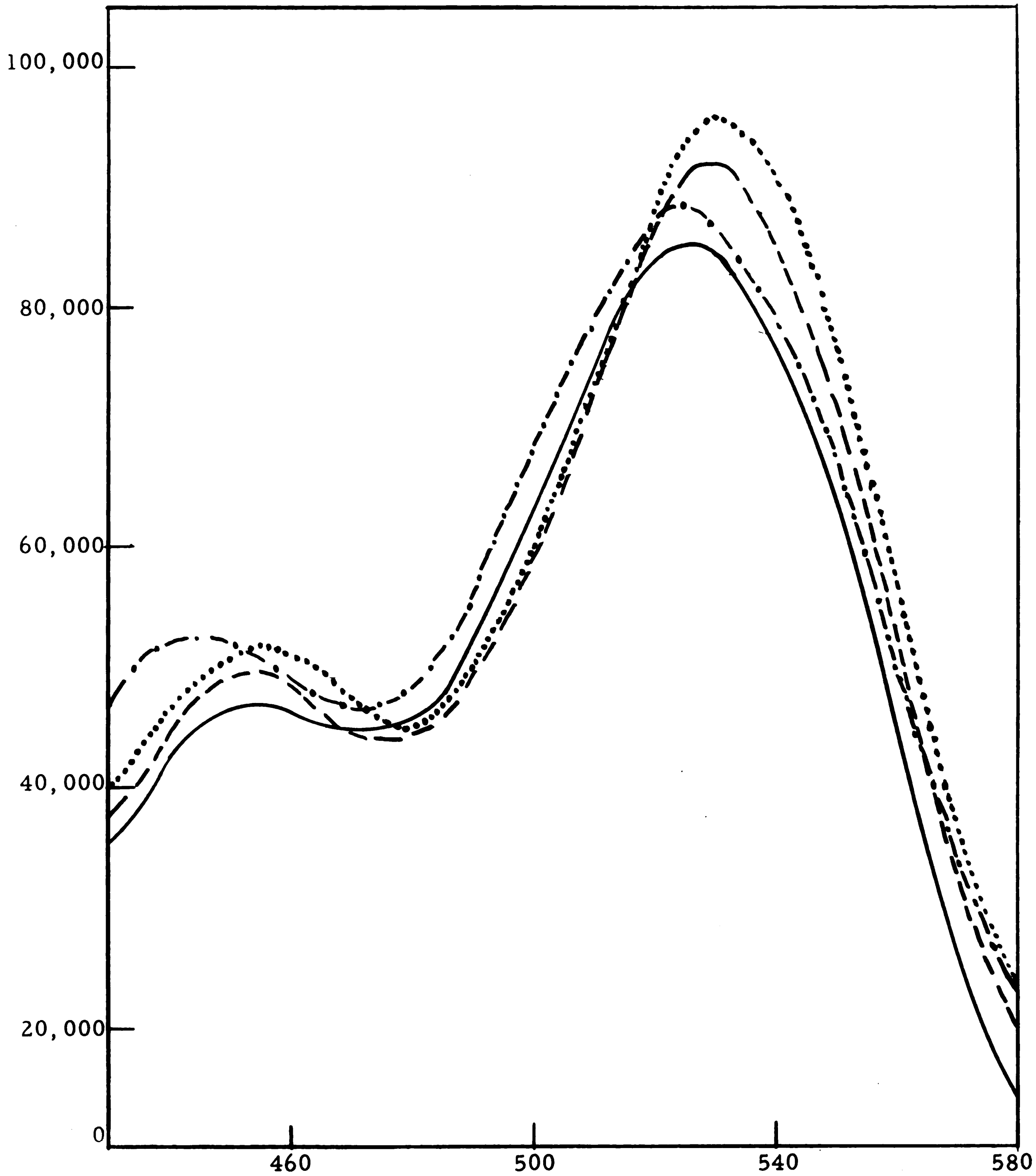


Figure XX. Visible spectra of tetra-p-anisyl-p-xylyleneglycol in varying concentrations of sulfuric acid-water. Weight per cent sulfuric acid: 35% (———), 40% (----), 60% (····), 100% (-·-·-).

Table IX. Visible Absorption Maxima of Tetra-p-anisyl-p-xylyleneglycol in Varying Concentrations of Sulfuric Acid-Water

Wt. Per Cent H_2SO_4	Molar Absorbancy Index (ε) of the 400 mμ Region Band		Molar Absorbancy Index (ε) of the 500 mμ Region Band	
	λ(mμ)	ε	λ(mμ)	ε
26	425	5,000	500	10,000
28	427	12,500	502	26,000
29	430	14,200	504	28,900
30	450 (shoulder)	18,300	505	38,000
31	450 (shoulder)	26,200	505	50,500
32	460 (shoulder)	38,000	510	69,100
33	455	42,300	515	75,000
45	455	47,600	526	85,600
40	455	49,800	530	92,150
60	455	51,800	530	96,000
100	445	52,500	525	88,500

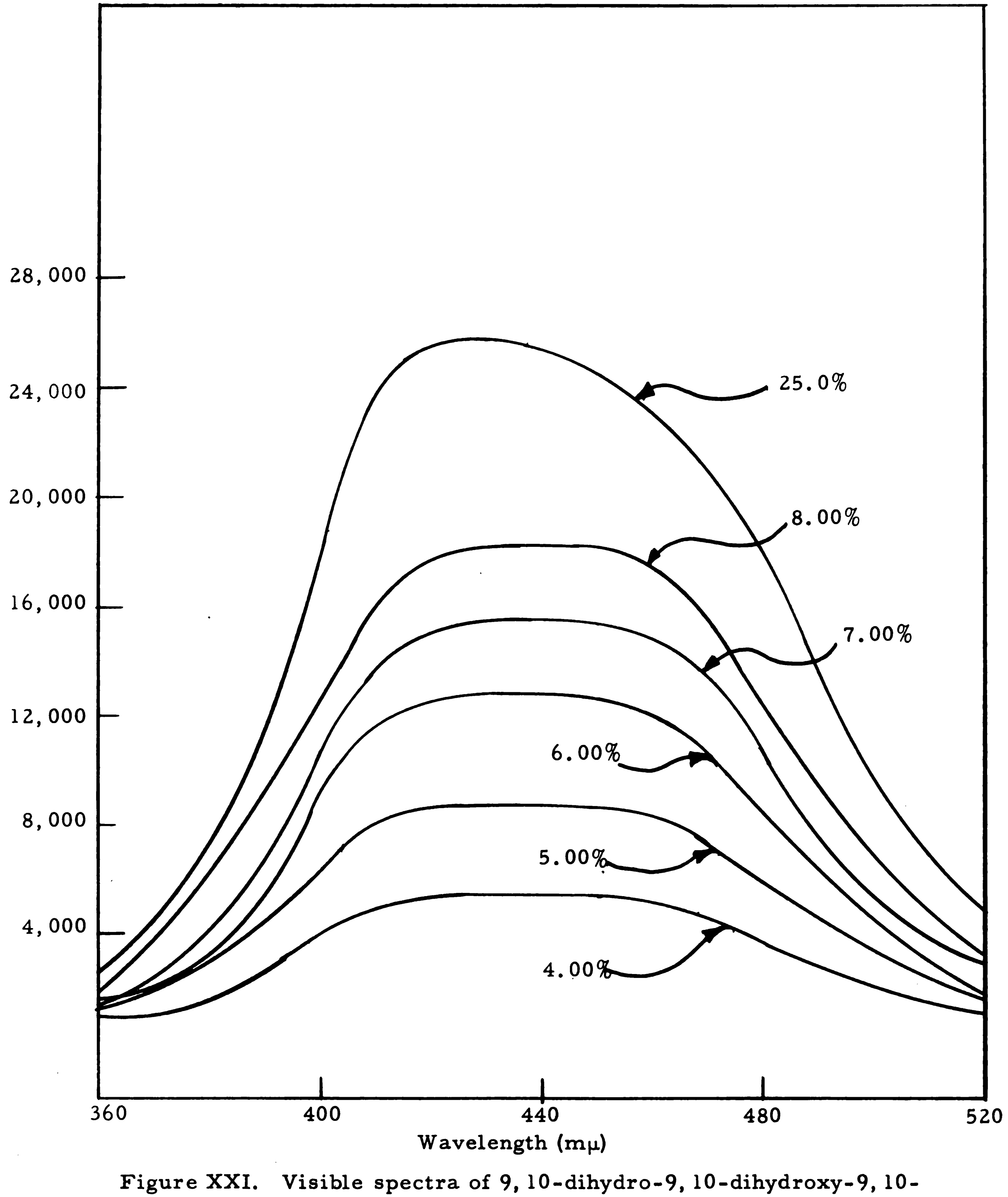


Figure XXI. Visible spectra of 9,10-dihydro-9,10-dihydroxy-9,10-diphenylanthracene in varying concentrations of sulfuric acid-acetic acid. Per cent indicated is weight per cent sulfuric acid.

Table X. Visible Absorption Maxima of 9, 10-Dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene in Varying Concentrations of Sulfuric Acid-Acetic Acid

Wt. Per Cent H_2SO_4	Wavelength (mμ)	Molar Absorbancy Index (ε)
4.0	420 to 455	5, 350
5.0	420 to 455	8, 560
6.0	420 to 450	12, 800
7.0	425 to 450	15, 500
8.0	426 to 449	18, 150
9.0	427 to 448	18, 750
20.0	425 to 435	25, 200
25.0	425 to 433	25, 800

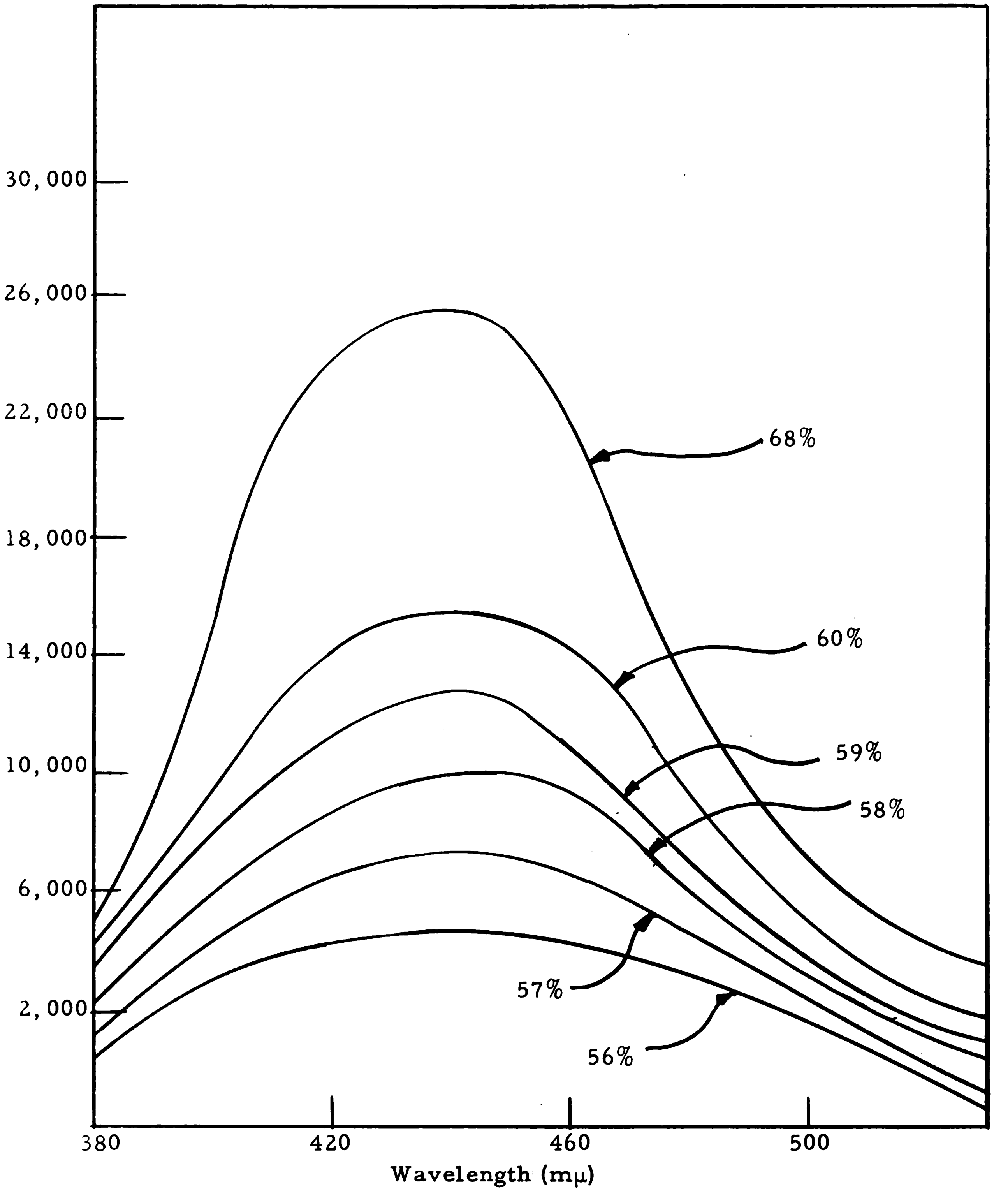


Figure XXII. Visible spectra of 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene in varying concentrations of sulfuric acid-water. Per cent indicated is weight per cent sulfuric acid.

Table XI. Visible Absorption Maxima of 9, 10-Dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene in Varying Concentrations of Sulfuric Acid-Water

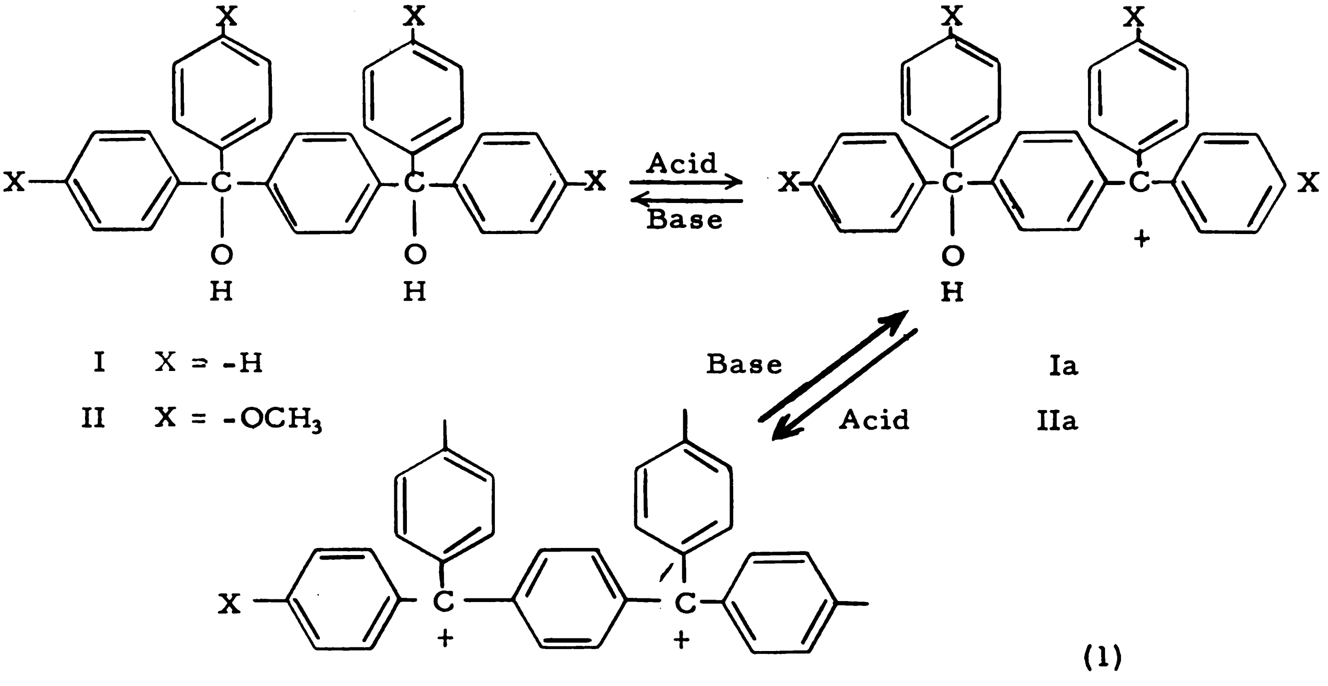
Wt. Per Cent H_2SO_4	Wavelength (mμ)	Molar Absorbancy Index (ϵ)
56	445	4,800
57	447	7,330
58	447	10,000
59	447	12,800
60	445	15,500
61	445	18,450
65	445	23,000
68	445	26,000

The yellow and red solutions of III are stable and obey Beer's Law. However, the blue solutions when diluted for spectral studies (concentration of the order of 2×10^{-5} M) fade rapidly and do not give absorbance in the visible region. The maximum stable absorbance of III in acetic acid is reached at 25% sulfuric acid and the blue color appears at approximately 32% sulfuric acid in acetic acid. One-half of ϵ maximum is attained at 6% sulfuric acid.

In sulfuric acid-water the maximum absorbance occurs at 67% sulfuric acid, one-half of λ maximum occurs at 59% sulfuric acid and the blue color arises at 70% sulfuric acid in water.

Interpretation of the Visible Spectra

Because of the reversible color formation observed for compounds I and II in acid media it is proposed that they ionize and establish an equilibrium in accordance with equation 1.



I X = -H

II X = $-OCH_3$

Ia

IIa

Ib

IIb

(1)

In 1955 Deno, et al. (29) defined an acidity function (C_0) which provided an acidity scale for secondary bases that ionize according to the equation:

$$ROH + H^+ = R^+ + H_2O \qquad (2)$$

where R^+ is a carbonium ion. C_0 was defined as:

$$C_0 = pK_{R^+} - \log (C_{R^+}/C_{ROH}) \qquad (3)$$

When half the alcohol is ionized the concentration of R^+ would be equal to the concentration of ROH and the pK_{R^+} would then be equal to the acidity function C_0. This acidity function was applied only to the sulfuric acid-water solvent system, but it was valid throughout the entire range of sulfuric acid concentrations. Using this acidity function Deno, et al. were able to determine the pK_{R^+}'s of some substituted triarylcarbinols, which ionized according to equation 2.

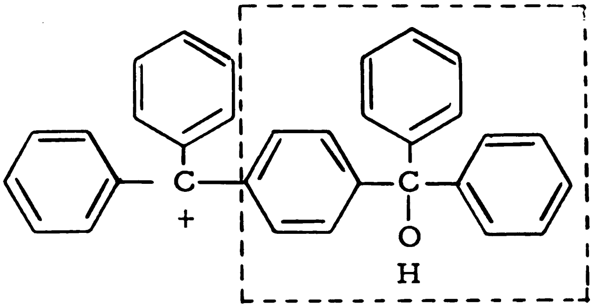
The red color of solutions of I in sulfuric acid, and more particularly the band at 455 mμ, is attributed to the dipositive carbonium ion (Ib), whereas the yellow color and the shoulder at 420 mμ probably are due to the monopositive carbonium ion (Ia). This reasonable assignment is consistent with the principal absorption of the triphenylmethyl cation (30) at 431 mμ (ϵ = 39,800; secondary band at 404 mμ) and is substantiated by methanolysis studies discussed in a later part of the thesis.

Unfortunately, the absorption peaks for the mono and dications from I and II are not sufficiently separated, nor are the first and second pK's sufficiently far apart to allow their determination from the spectra without certain assumptions.

The first is that the only species present where ϵ was one-half of ϵ_{max} are the mono- and dipositive carbonium ions Ia and Ib. There is considerable basis for this assumption in solvolysis studies described in detail in a later part of this thesis. When compound I was dissolved in acetic acid containing 2.5% sulfuric acid (H_0 = -2.17) (31), and the resulting solution poured into cold absolute methanol, a maximum of 17% of unionized glycol was recovered. One-half $\epsilon_{max.}$ was attained in 59% aqueous sulfuric acid, a solution appreciably more acidic (H_0 = -4.46) (32) than used in the methanolysis experiment. It is therefore eminently reasonable to conclude that no unionized glycol remains in 59% aqueous sulfuric acid. C_0 is -8.7, and in solutions where ϵ is 50% of its maximum this value can then be given to $pK_{R^{++}}$ for I. $pK_{R^{++}}$ is defined as the pK of the reaction described in equation 4.

$$(ROH)^{+} + H^{+} \rightleftharpoons R^{++} + H_2O \qquad (4)$$

The second assumption is that pK_{R^+} for I is approximately the same as that of triphenylcarbinol. The monopositive ion Ia has two unsubstituted phenyls and the third phenyl has a para substituent. This substituent, however, cannot conjugate with the developing positive charge, and therefore should not seriously affect the first ionization. A comparison of the pK_{R^+}'s of 4-t-butyltriphenylchloromethane (-6.1) and triphenylcarbinol (-6.63) shows little effect on the pK_{R^+} by a 4-t-butyl substituent (29). It is therefore reasonable to assume that pK_{R^+} for compound I is approximately -6.63, the value for triphenylcarbinol.

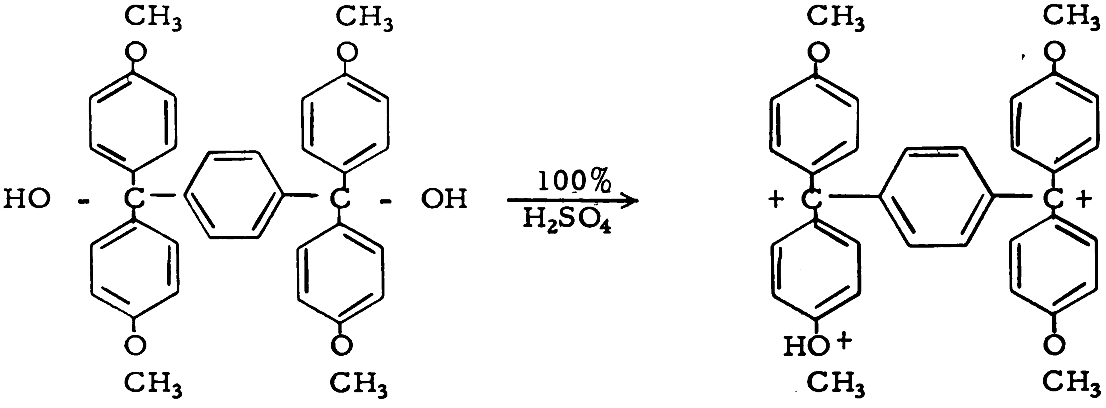


Ia

The same analogies were applied to compound II. This case was not as clear-cut as compound I, because the bands in the spectrum shifted slightly in wavelength with varying sulfuric acid concentration. Also no particular peak could be attributed to the monopositive carbonium ion (IIa), whereas the dipositive carbonium ion (IIb) was assumed (reasonably) to give rise to the longer wavelength band. The $pK'_{R^{++}}$ of compound II was found to be -3.4. The pK_{R^+} for II was assumed to be approximately -1.24, the value for 4,4-dimethoxytriphenylcarbinol (29).

The $\Delta pK'_R$, the difference between the first and second ionization constants, was 2.16 for compound II and 2.07 for compound I. Also the ΔpK_{R^+} between the estimated first ionization constants of I and II was 5.39 and the $\Delta pK'_{R^{++}}$ between the experimentally determined second ionization constants of compounds I and II was 5.3. That these ΔpK_R's are of the same order lead one to conclude that the original assumptions were quite valid.

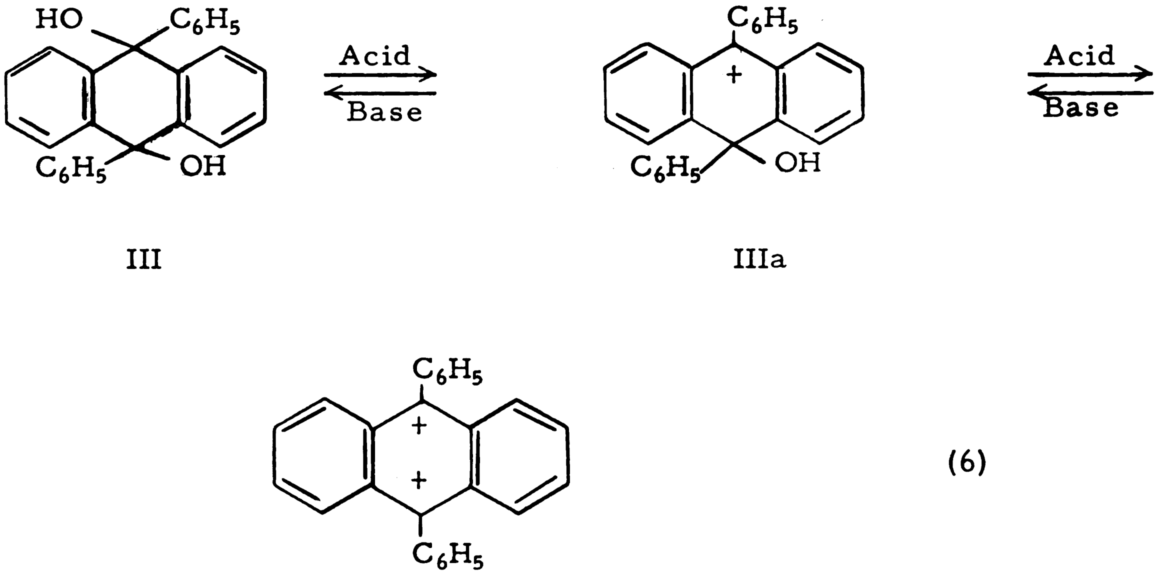
The decrease in intensity and hypsochromic shift of the maxima observed in the visible spectrum of II in 100% sulfuric acid was unusual. A possible explanation for this is the protonation of one or more of the methoxyl groups according to equation 5.



(5)

This would eliminate the methoxyl group(s) from participating in resonance stabilization of the ions and should decrease the wavelength of maximum absorption.

It is proposed that 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene (III) also ionizes to give mono and dipositive carbonium ions, as depicted in equation 6.



III

IIIa

IIIb

(6)

But, when a certain acidity is reached the dipositive carbonium ion IIIb undergoes further irreversible reactions to be discussed more fully later.

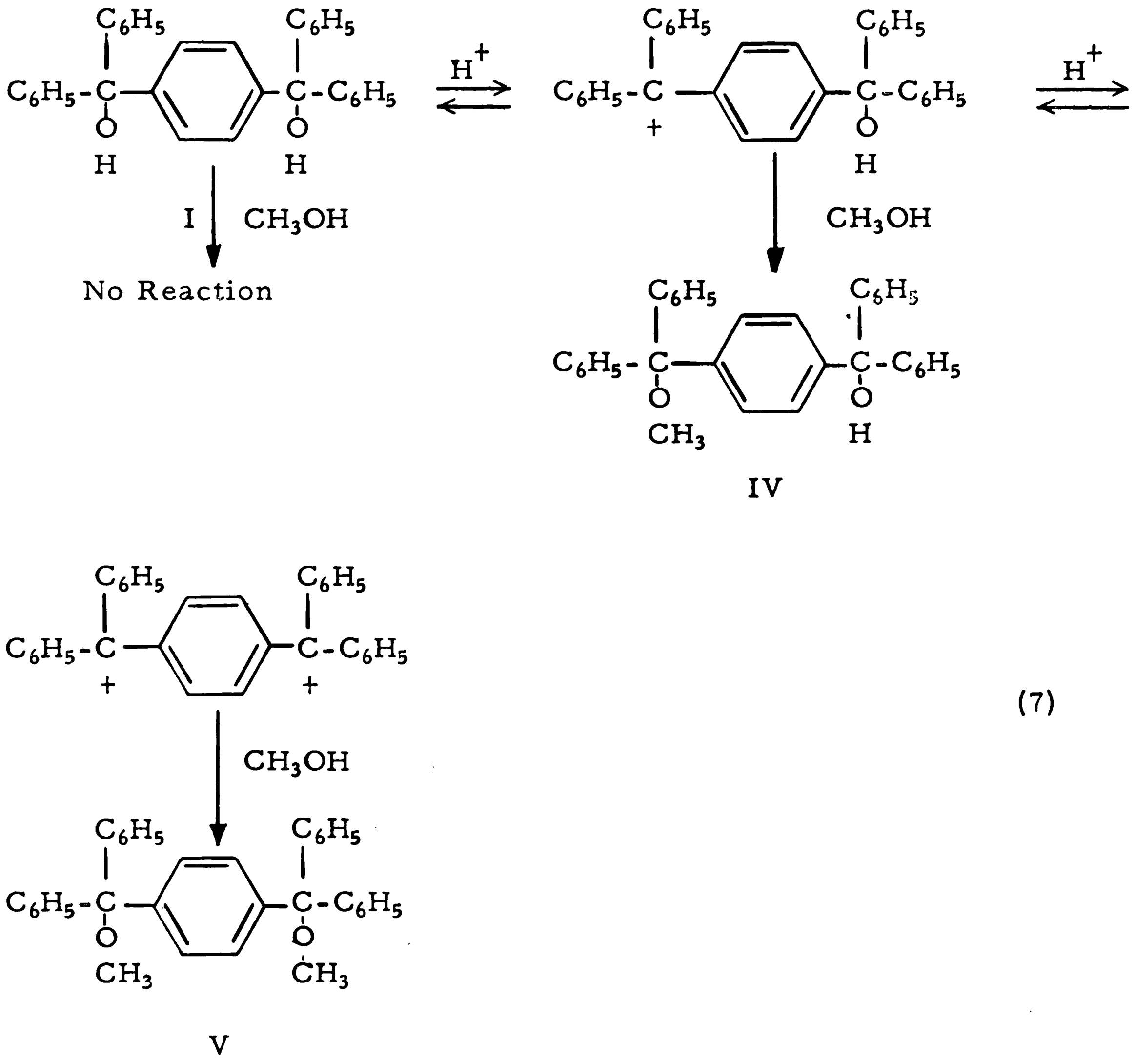
The yellow color of III in acidic solutions is attributed to the monopositive ion IIIa and the red color is attributed to the dipositive carbonium ion IIIb. The value of pK'_R++ for III was found to be -8.7, identical to that for compound I. This is perhaps not too surprising since the substituents are the same for both compounds, although one would have perhaps thought that the time-average closer proximity of the positive charges in IIIb would decrease its stability when compared with Ib. It is assumed that the pK'_R+ for III is approximately the same as that for triphenylcarbinol.

Hydrolysis Products

When solutions of compounds I or II in 100% sulfuric acid were hydrolyzed by pouring them on ice the corresponding glycols were recovered in better than 90% yields. Solutions of the dichloride of I in 100% sulfuric acid gave a visible spectrum identical to that of the glycol in 100% sulfuric acid. Hydrolysis of this red solution also gave a nearly quantitative yield of glycol.

In 1942 Weitz and Schmidt (33) reported the isolation of a brownish-red perchlorate salt from tetraphenyl-p-xylylenedichloride. They proposed that this was the salt of the dipositive carbonium ion, but no further work was done on it. Recently in this laboratory a red perchlorate salt was isolated (34) from the dichloride of I. Solutions of this salt in chloroform were red and conducted an electric current. A quantitative yield of the glycol I was obtained when the salt was hydrolyzed. Obviously the red species isolated as a crystalline salt as well as that formed by the ionization of I in sulfuric acid-water or sulfuric acid-acetic acid was the dipositive carbonium ion Ib.

In an attempt to more accurately determine the amounts of glycol, monopositive carbonium ion and dipositive carbonium ion formed in varying concentrations of sulfuric acid-acitic acid, methanolysis studies were undertaken. The general procedure was to dissolve a sample of the glycol I in dilute solutions of sulfuric acid (approximately 2.5%) in acetic acid. These solutions were then added under anhydrous conditions to cold absolute methanol. The methanol would be expected to react with the different species to give the corresponding products in accordance with equation 7.



(7)

Some preliminary experiments were run to prepare compound IV (previously unknown) and to work out a suitable separation for I, IV, and V using column chromatography. Addition of a solution of the glycol in concentrated sulfuric acid to a cold solution of methanol and water in the molar ratio of 2 to 3 yielded a mixture of the three products.
A suitable chromatographic scheme of separation was devised and the amounts of products obtained were 12% of the glycol, 36% of the dimethylether (V) and 46% of the monomethylether-monoalcohol (IV), m.p. 130.5-131°. The structure of the latter was proved by analysis and by

the fact that dissolution in 100% sulfuric acid followed by hydrolysis gave the glycol (I) in quantitative yield. A change in the molar ratio of methanol to water varied the relative amounts of products obtained.

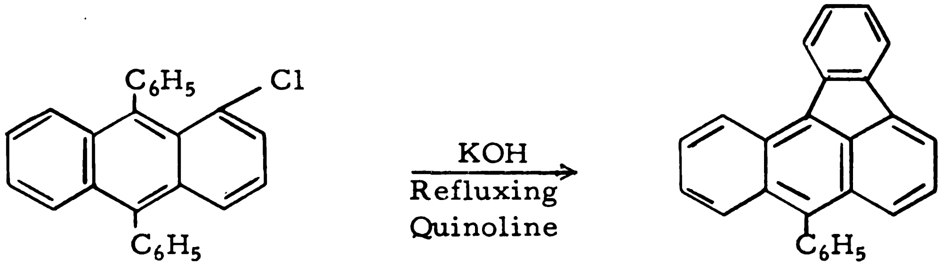
Three samples, each of the same concentration of glycol in 2.52% sulfuric acid-acetic acid were added to cold absolute methanol and worked up in the same manner. Chromatography of the products did not give consistent results, different relative amounts of I, IV and V being obtained for each sample. This indicated that the products were either exchanging hydroxyl and methoxyl groups on the column or that the alcohol groups were reacting with the methanol under the acid conditions of methanolysis. The latter undoubtedly did occur to some extent, because when the glycol was dissolved in cold methanol and the sulfuric acid-acetic acid was added to it, no color was formed, but after purification and chromatography a 10% yield of V and a 6% yield of IV was obtained. Although this observation precluded further quantitative methanolysis studies, some valuable information was obtained from the work already completed. First, the amount of compound IV obtained from the methanolysis of I in 2.52% sulfuric acid-acetic acid, even though it varied from sample to sample (21 to 40%), was much greater than can be attributed to reaction of the glycol with methanol in acid medium. This leads one to conclude that the majority of compound IV was formed from the reaction of the ion Ia with methanol. The second conclusion was that at very low acidity (H_0 = -2.17) there was very little unreacted diol (12-17%) and that at higher acidities there should be negligible amounts of unionized glycol.

The hydrolysis products of compound II in sulfuric acid were not studied as extensively as I, because of the convenient analogy with compound I. When the red solution of II in 100% sulfuric acid was hydrolyzed on ice a better than 90% yield of the starting glycol was obtained. Hydrolysis of the solution of II in acetic acid also gave very high yields of the glycol.

In 1904 Haller and Guyot (35) first reported the preparation of 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene (III). They observed an indigo color when III was added to concentrated sulfuric acid. Since that time a number of workers (36, 37, 38) have prepared this compound and observed the same color. However, no one had attempted either to explain the blue color or to isolate any hydrolysis products from sulfuric acid solutions of III.

In the present work the blue color was originally attributed to the dipositive carbonium ion IIIb. By analogy to compound I and II, hydrolysis should produce the starting glycol. However, when the blue solution of III in 100% sulfuric acid was added to ice only a brownish-green solid could be isolated. The material could not be purified by recrystallization and was chromatographed on alumina. Elution with 1:1 pentane-benzene yielded a light yellow solid, m.p. 247-248°, which fluoresced blue in solution; these properties correspond to those of 9, 10-diphenylanthracene. 9, 10-Diphenylanthracene was prepared independently by the reduction of III in acetic acid with sodium iodide (39). The pale yellow solid isolated from the hydrolysis of the blue solution of III in sulfuric acid was identical (m.p., m.m.p. and infrared spectrum) to 9, 10-diphenylanthracene. The yield of 9, 10-diphenylanthracene (VI) from hydrolysis of the blue solution was 36%.

Further elution of the column with benzene yielded an orange solid, m.p. 191.2-192.4°, which fluoresced greenish-yellow in solution. The infrared spectrum indicated the compound was an aromatic hydrocarbon; it analyzed correctly for $C_{26}H_{16}$. Recently Clar and Willicks (40) reported the preparation of 4-phenyl-2, 3-benzofluoranthene (VII), m.p. 185-186°, by the method depicted in equation 8. A comparison of its ultraviolet and visible spectra (reported by Clar) with that of the material isolated from hydrolysis of the blue solution showed the same

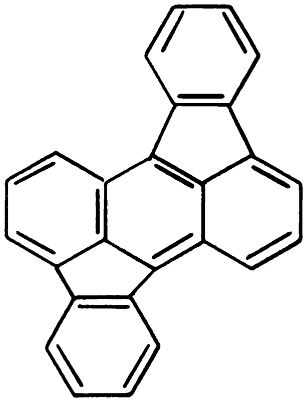


(8)

VII

maxima with almost identical extinction coefficients. Table XII shows this comparison. The compounds are apparently identical and the small difference in melting points may be due to the different solvents used for recrystallization. Clar and Willicks reported using alcohol (presumably ethanol) for the solvent. When this author tried ethanol the orange solid appeared to be insoluble, whereas this material readily dissolved in benzene-pentane. The yield of 4-phenyl-2, 3-benzofluoranthene (VII) from the hydrolysis of the blue solution of III in sulfuric acid was 19%.

Continued elution of the column with 1:1 benzene-ether gave a very small amount of red solid which melted at approximately 385°. It was at first believed to be rubicene, but the carbon-hydrogen analysis was not correct. The material remains unidentified.



Rubicene

Finally the remainder of the material on the column was removed with methanol. A dark brown solid was obtained which did not melt sharply (110-170°) and appeared to be a mixture. Attempts to purify it by recrystallization failed. The infrared spectrum of the crude material

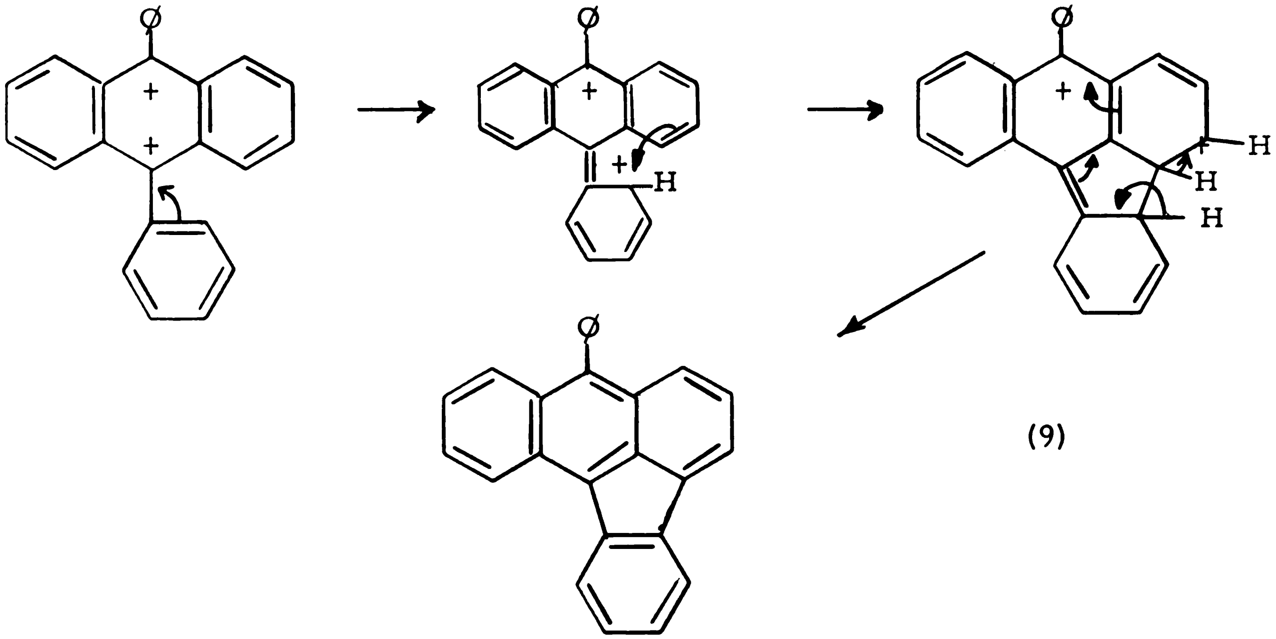
Table XII. Ultraviolet-Visible Absorption Maxima of 4-Phenyl-2, 3-benzofluoranthene in Absolute Ethanol

Clar and Willicks (40)		This Work	
Wavelength (mμ)	Molar Absorbancy Index (ε)	Wavelength (mμ)	Molar Absorbancy Index (ε)
430	13,500	430	12,600
366	6,300	366	5,830
310	11,500	310	12,000
270	100,000	270	94,500

indicated that it contained both hydroxyl and carbonyl functions. None of the constituents of the mixture have been identified.

Hydrolysis of the yellow solutions of III in sulfuric acid-acetic acid gave between 90 and 95% yield of the starting material along with traces of VI and VII.

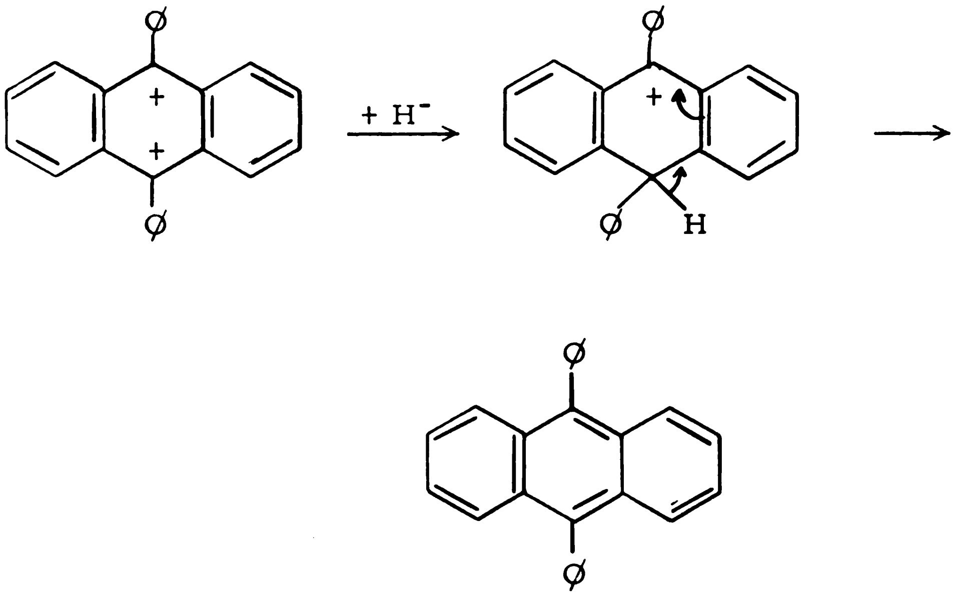
It seems that in low sulfuric acid concentrations the glycol undergoes normal stepwise ionization to the dipositive carbonium ion IIIb. In more concentrated acid (32% sulfuric acid and above) further reactions occur, presumably including internal alkylation and hydride transfer. 4-Phenyl-2, 3-benzofluoranthene may arise from the mechanism suggested in equation 9.



VII

(9)

The formation of 9, 10-diphenylanthracene is more difficult to explain, because it requires the transfer of a hydride ion as shown in equation 10.



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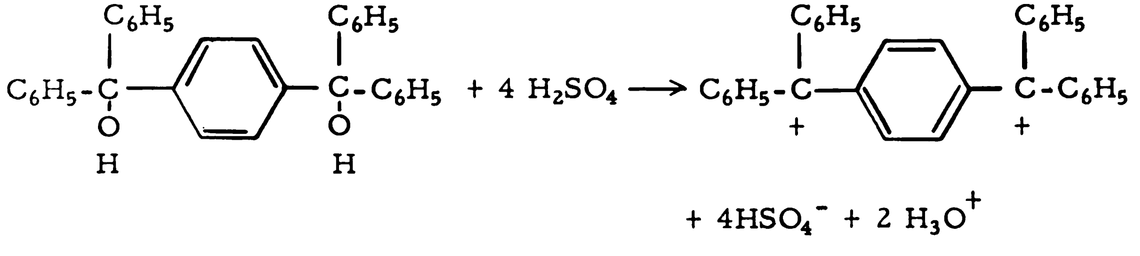
(10)

Until all of the hydrolysis products have been isolated and identified the nature of the hydride donor remains unknown, except that it presumably ends up as the polar residue which is last to be eluted from alumina, and which contains hydroxyl and carbonyl functions. The species responsible for the blue color is as yet not known.

Cryoscopic Measurements

Cryscopic measurements were run on solutions of tetraphenyl-p-xylyleneglycol (I) in 100% sulfuric acid. When I ionizes in 100% sulfuric acid 7 particles should be produced in accordance with equation 11.



$$(C_6H_5)_2C(OH)-C_6H_4-C(OH)(C_6H_5)_2 + 4\,H_2SO_4 \longrightarrow (C_6H_5)_2\overset{+}{C}-C_6H_4-\overset{+}{C}(C_6H_5)_2 + 4HSO_4^- + 2\,H_3O^+ \qquad (11)$$

The results are reported in Table XIII. The data in general support a molal freezing point depression of 7, although the _i_-value is a bit high. It should be pointed out that the first cryoscopic measurements determined by the author were done on compound I and the experimental technique had not yet been mastered. Also compounds that exhibit large molal freezing point depressions can not be determined as accurately as compounds that have lower _i_ factors.

Further cryoscopic measurements should be run on I before making a conclusive decision on the results.

Table XIII. Freezing Point Data on Tetraphenyl-p-xylyleneglycol

Sample Wt., g.	g. H_2SO_4	T_1, °C.	ΔT, °C.	Time (hrs.)[a]	i[b]
1.5257	97.10	9.941	1.728	X[c]	7.67
			1.717	4	7.62
1.7174	80.00	9.929	2.333	X	7.55
1.7204	85.12	9.889	2.143	X	7.39
			2.093	13	7.22

[a] Indicates time elapsed between addition of the sample to sulfuric acid and determination of the i-factor.

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

[c] i-Factor determined immediately after addition of the sample to sulfuric acid.

EXPERIMENTAL

A. Synthesis

Preparation of Tetraphenyl-p-xylyleneglycol (41)

To a 1-l. three-necked flask fitted with a Trubore stirrer, dropping funnel, and reflux condenser with a calcium chloride drying tube was added 8 g. (0.33 g.-atom) of magnesium and 50 ml. of ether. A solution of 50 g. (0.318 mole) of bromobenzene in 150 ml. of anhydrous ether was added slowly. When the initial vigorous reaction had subsided the remainder of the solution was added at such a rate as to maintain refluxing. After the Grignard reagent had been prepared a solution of 15 g. (0.077 mole) of dimethyl terephthalate in 350 ml. of benzene (previously dried over sodium and redistilled) was added dropwise to the refluxing liquid during a three hour period. The reaction mixture became orange and a solid precipitated. After three hours of further reflux, the mixture was poured onto 200 g. of ice, acidified with dilute sulfuric acid, and the organic layer separated. The aqueous phase was extracted with two 100-ml. portions of benzene and the combined organic layers were dried for 12 hours with magnesium sulfate. The benzene was distilled and the pale-yellow, oily crystal mass was filtered and washed with benzene and petroleum ether. There was approximately 25 g. of crude product, m.p. 165-169°. The solid was recrystallized from benzene-petroleum ether to yield 22 g. (64.5%) of tetraphenyl-p-xylyleneglycol, m.p. 169-170°. (Literature value 168-169°.) Its infrared spectrum is shown in Figure XXIII.

Preparation of Tetraphenyl-p-xylylenedichloride (41)

Tetraphenyl-p-xylyleneglycol (5 g., 0.0113 mole) was dissolved in 100 ml. of hot anhydrous benzene. Dry hydrogen chloride was bubbled

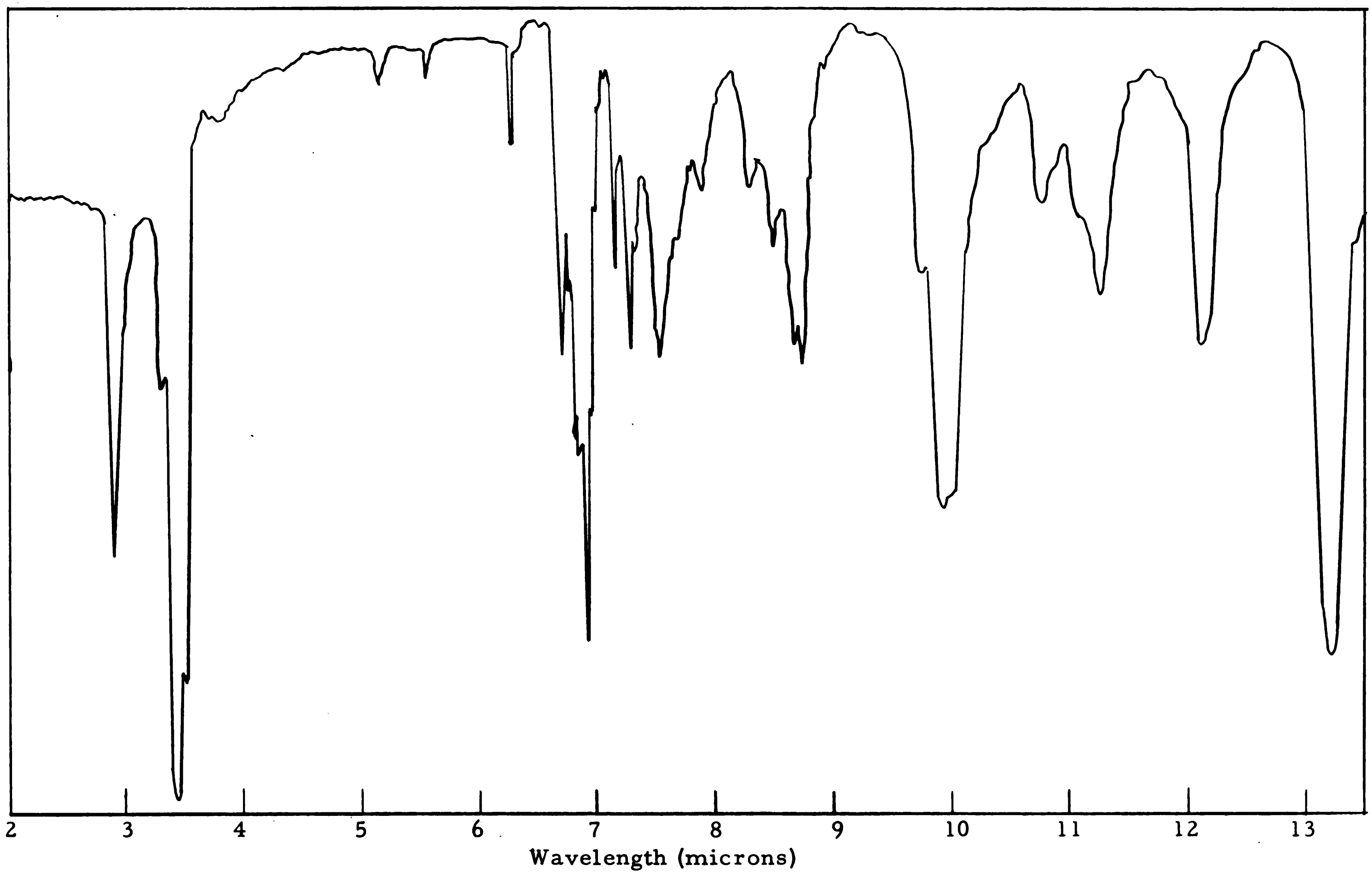


Figure XXIII. Infrared spectrum of tetraphenyl-p-xylyleneglycol (mull).

into the refluxing solution and after approximately five minutes white crystals began to precipitate. The gas was bubbled into the solution for another five minutes and then the contents were cooled to 10°. The white crystals were filtered and recrystallized from benzene to yield 4 g. (72%) of tetraphenyl-p-xylylenedichloride, m.p. 247-248°. (Literature value 240-241°.)

Reaction of a Solution of Tetraphenyl-p-xylyleneglycol in 100% Sulfuric Acid with Water

Tetraphenyl-p-xylyleneglycol (1.5 g.) was dissolved in 15 g. of 100% sulfuric acid. The deep red solution was slowly added to 100 g. of ice. The white precipitate was collected, washed with water, and dissolved in 50 ml. of ether. The ether layer was washed with two 50 ml.-portions of 5% sodium bicarbonate solution and then dried with magnesium sulfate. The ether was evaporated, to yield 1.38 g. (92%) of tetraphenyl-p-xylyleneglycol m.p. 166-168°. One recrystallization from benzene-petroleum ether raised the melting point to 169-170°. A m.m.p. with an authentic sample gave no depression.

Reaction of a Solution of Tetraphenyl-p-xylylenedichloride in 100% Sulfuric Acid with Water

Tetraphenyl-p-xylylenedichloride (1.0 g.) was dissolved in 15 g. of 100% sulfuric acid. The red solution was slowly added to 100 g. of ice and the white precipitate was filtered, washed with water and dissolved in 50 ml. of ether. The ether layer was washed with two 40 ml.-portions of 5% sodium bicarbonate solution and then dried over magnesium sulfate. The ether was evaporated to yield 0.83 g. (90.3%) of a white solid, m.p. 166-169°. Recrystallization from benzene-petroleum ether raised the melting point to 169-170°. The product had a m.p., m.m.p., and infrared spectrum identical to tetraphenyl-p-xylyleneglycol.

Preparation of the Dimethylether of Tetraphenyl-p-xylyleneglycol

This compound was prepared by two different methods.

Method A

Tetraphenyl-p-xylylenedichloride (3 g., 0.0063 mole) was dissolved in a solution of 50 ml. of absolute methanol containing 0.625 g. (0.0126 mole) of sodium methylate. The mixture was refluxed for 12 hours and the precipitate filtered, washed with water and dried. The solid was recrystallized from benzene-petroleum ether to yield 2.6 g. (87%) of white crystals of the dimethylether of tetraphenyl-p-xylyleneglycol, m.p. (sinters 182-183°) 185°. (Literature value 181-183°.) (41).

Method B

Tetraphenyl-p-xylyleneglycol (2.0 g.) was refluxed with 50 ml. of absolute methanol and two drops of concentrated sulfuric acid for two hours. (A white solid formed almost immediately.) The crystals were filtered and recrystallized from benzene-petroleum ether to yield 1.8 g. (87%) of the dimethylether of tetraphenyl-p-xylyleneglycol, m.p. (sinters 182-183°) 185°. The m.p., m.m.p., and infrared spectra of the product isolated from both reactions were identical. The infrared spectrum of the dimethylether is shown in Figure XXIV.

Preparation of the Monomethylether of Tetraphenyl-p-xylyleneglycol

Tetraphenyl-p-xylyleneglycol (2.0 g.) was dissolved in 15 g. of 100% sulfuric acid. The red solution was added dropwise to a cold and well-stirred solution of 43.2 g. (2.4 moles) of water and 51.2 g. (1.6 moles) of methanol. The white solid was collected, dissolved in 75 ml. of ether, and washed with two 50-ml. portions of 5% sodium carbonate solution, and dried over magnesium sulfate. The ether was evaporated

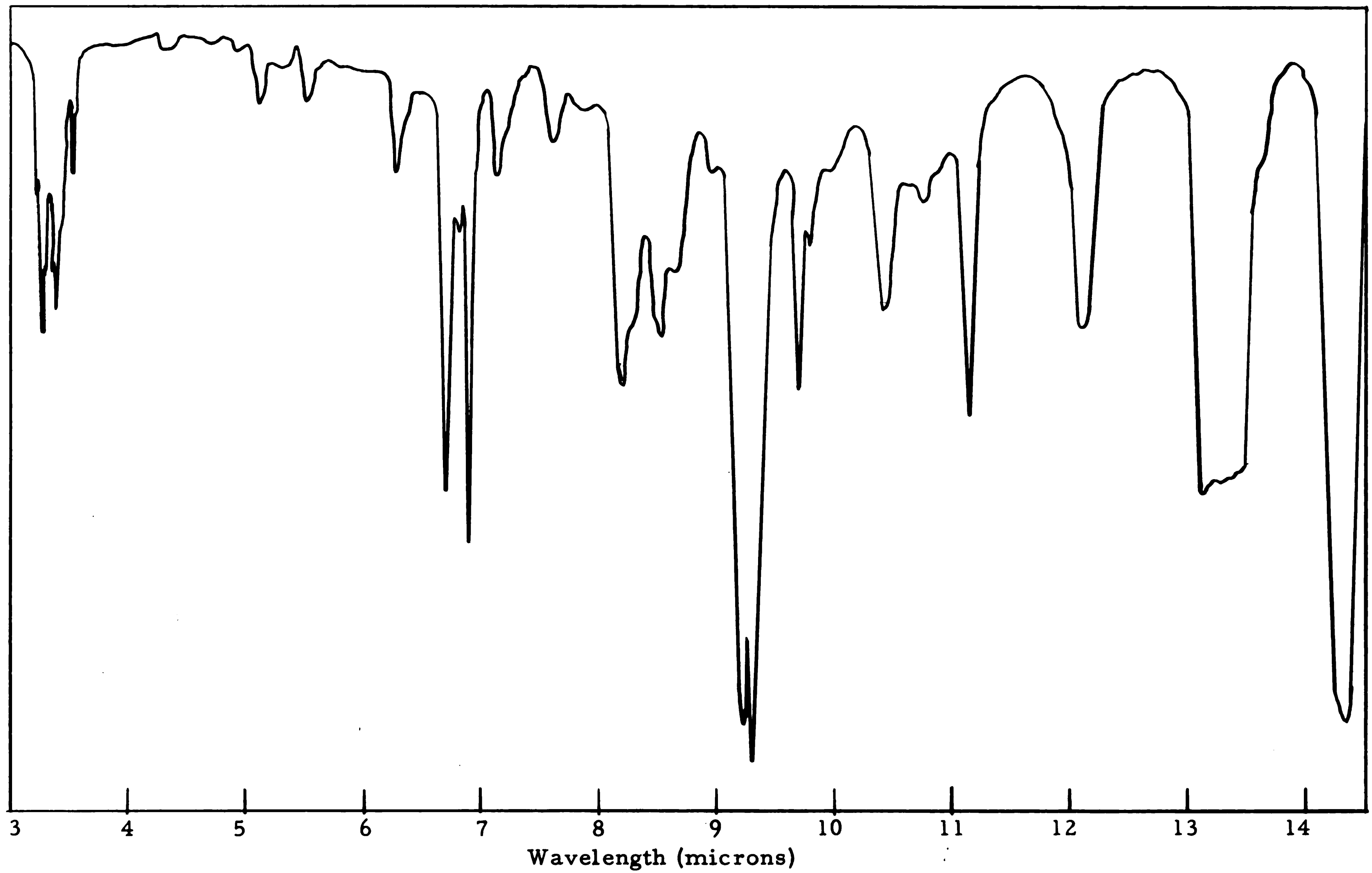


Figure XXIV. Infrared spectrum of the dimethylether of tetraphenyl-p-xylyleneglycol.

and the solid was dissolved in 10 ml. of benzene and adsorbed on 70 g. of Fisher's Adsorption alumina (80-200 mesh). The column was eluted with 300 ml. of benzene and yielded 0.77 g. (36.45%) of the dimethylether of tetraphenyl-p-xylyleneglycol, m.p. 185°. Further elution of the column with 500 ml. of tetrahydrofuran yielded 0.946 g. (45.83%) of white crystals of the monomethylether of tetraphenyl-p-xylyleneglycol, m.p. 130.0-130.5°. Its infrared spectrum is shown in Figure XXV.

Anal. Calcd. for $C_{33}H_{28}O_2$: C, 86.81; H, 6.18.
Found: C, 86.84; H, 6.21.

The glycol was removed by eluting with 200 ml. of absolute methanol and yielded 0.24 g. (12%) of tetraphenyl-p-xylyleneglycol, m.p. 168-170°. The total yield of recovered material was 94.2%.

Reaction of a Solution of Tetraphenyl-p-xylyleneglycol in Sulfuric Acid (2.52%)-Acetic Acid with Absolute Methanol

A sample of 0.2500 g. of tetraphenyl-p-xylyleneglycol was dissolved in 25 ml. of 2.52% sulfuric acid in acetic acid. The red solution was added dropwise to 100 ml. of cold (-10°) absolute methanol. Cold water (100 ml.) was then added to the colorless alcohol solution to precipitate all of the products. The solid was filtered, dissolved in 100 ml. of ether and washed with two 50-ml. portions of 5% sodium bicarbonate solution. The basic washings were separated and extracted with 100 ml. of ether. The combined organic layers were dried with magnesium sulfate for twelve hours and the ether was evaporated on a Rinco rotary evaporator. The solid residue was dissolved in 10 ml. of benzene and adsorbed on 80 g. of Fisher's Adsorption alumina (80-200 mesh). The column was eluted successively with 200 ml. of benzene, 600 ml. of tetrahydrofuran, and 200 ml. of absolute methanol. The experiment was run in triplicate using identical conditions and the same amount of sample for each run. The results are recorded in Table XIV.

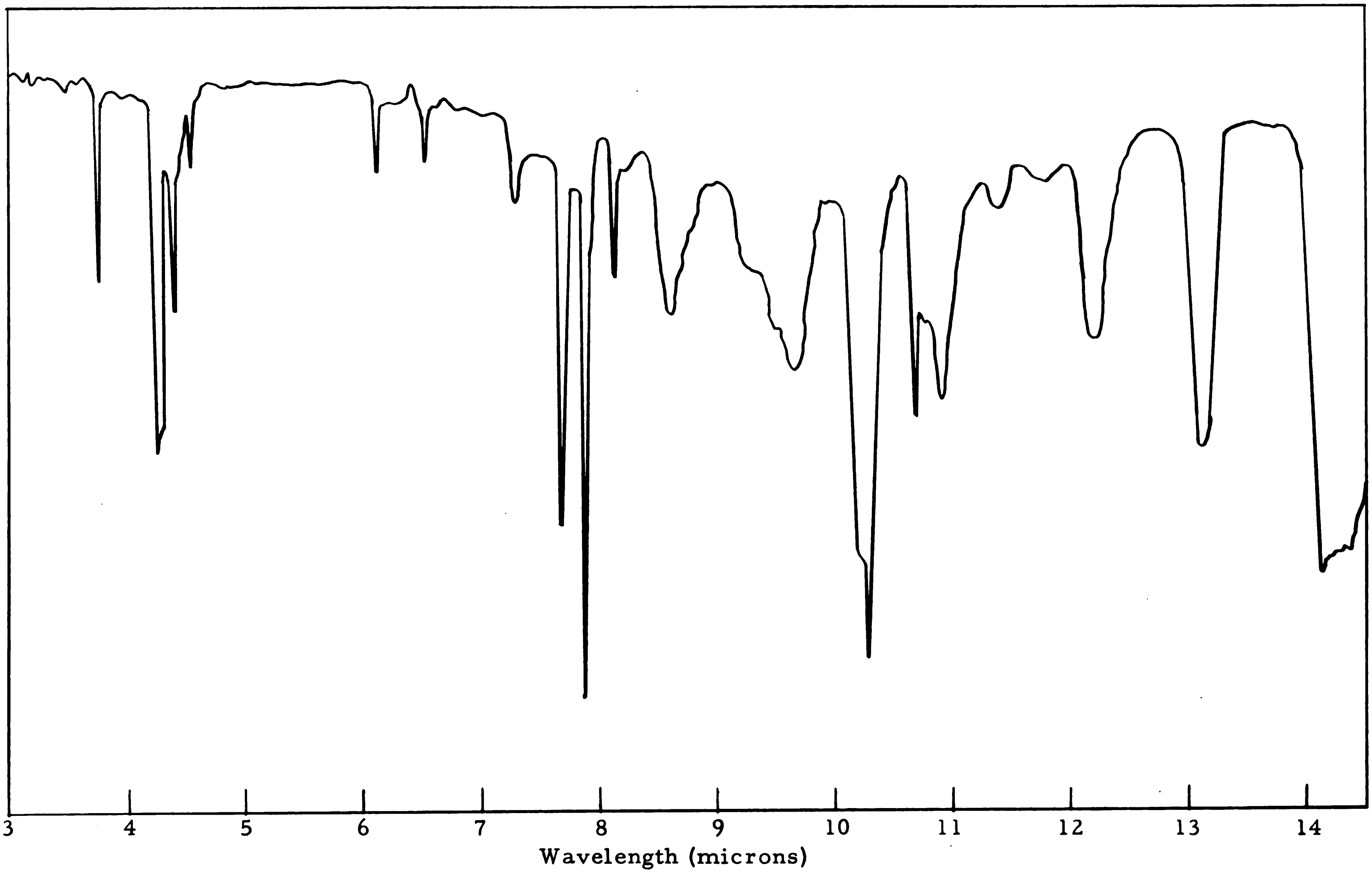


Figure XXV. Infrared spectrum of the monomethylether of tetraphenyl-p-xylyleneglycol.

Table XIV. Relative Amounts of Products Formed from the Reaction of a Solution of Tetraphenyl-p-xylyleneglycol in 2.52 Weight Per Cent Sulfuric Acid in Acetic Acid with Absolute Methanol

Sample	Compound					
	I		IV		V	
	Wt. (g.)	Per Cent Yield	Wt. (g.)	Per Cent Yield	Wt. (g.)	Per Cent Yield
I	0.149	55.8	0.119	44.57	0.198	74.50
II	0.084	32.4	0.103	40.76	0.055	21.20
III	0.038	14.95	0.032	12.76	0.04	16.45

Reaction of a solution of tetraphenyl-p-xylyleneglycol in Absolute Methanol with Sulfuric Acid (2.52%)-Acetic Acid

A sample of 0.100 g. of tetraphenyl-p-xylyleneglycol was dissolved in 40 ml. of absolute methanol. The solution was cooled to -10° and a solution of 10 ml. of 2.5% sulfuric acid in acetic acid was added dropwise while maintaining the temperature between -10 and 0°. After the addition the acid was neutralized with 10% sodium carbonate solution. The solid was filtered, dissolved in 50 ml. of ether, and dried with magnesium sulfate. The solvent was evaporated and the solid residue was dissolved in 5 ml. of benzene and adsorbed on 35 g. of Fisher's Adsorption alumina (80-200 mesh). The column was eluted successively with 100 ml. of benzene, 300 ml. of tetrahydrofuran and 100 ml. of absolute methanol. The amount of products obtained was 0.010 g. (9%) of the dimethylether of tetraphenyl-p-xylyleneglycol, 0.0072 g. (6%) of the monomethylether of tetraphenyl-p-xylyleneglycol, and 0.0833 g. (83.3%) of tetraphenyl-p-xylyleneglycol.

Reaction of a Solution of the Monomethylether of Tetraphenyl-p-xylyleneglycol in 100% Sulfuric Acid with Water

The monomethylether of tetraphenyl-p-xylyleneglycol (0.50 g.) was dissolved in 5 ml. of 100% sulfuric acid. The red solution was slowly added to 50 g. of ice and the white precipitate was filtered, washed with water and dried. The crude product (0.47 g., 95%) was recrystallized from benzene-petroleum ether to yield white crystals of tetraphenyl-p-xylyleneglycol, m.p. 167-169°.

Preparation of Tetra-p-anisyl-p-xylyleneglycol (42)

To a 1-l. 3-necked round-bottomed flask equipped with a Trubore stirrer, dropping funnel and a reflux condenser with a calcium chloride drying tube was added 14.58 g. (0.6 g.-atom) of magnesium and 150 ml.

of anhydrous ether. Approximately 25 ml. of a solution of 112.2 g. (0.6 mole) of 4-bromoanisole in 200 ml. of ether was added to the flask and the mixture was refluxed until the Grignard reagent began to form. After the initial vigorous reaction had subsided the remainder of the 4-bromoanisole solution was added at such a rate as to maintain reflux (2 hours). After the formation of the Grignard reagent a solution of 19.4 g. (0.10 mole) of dimethyl terephthalate in 200 ml. of anhydrous benzene was added slowly (2 hours). When the addition was complete the reaction mixture was refluxed for an additional 8 hours after which the solution was hydrolyzed by adding it to 300 ml. of saturated ammonium chloride solution. The organic layer was separated and steam distilled until the distillate was clear. The residue was filtered and recrystallized from benzene and then acetone to yield 20 g. of a pale yellow solid, m.p. 163-166°, which was taken up in 250 ml. of benzene and chromatographically absorbed on 100 g. of Fisher's Adsorption alumina (80-200 mesh). Elution with 3 l. of benzene containing 15 ml. of absolute ethanol yielded 18 g. (32%) of cream-colored powder, m.p. 165-167°. Recrystallization from acetone raised the melting point of the tetra-p-anisyl-p-xylyleneglycol to 167-168°. (Literature value 170-171°.) Its infrared spectrum is shown in Figure XVI.

Reaction of a Solution of Tetra-p-anisyl-p-xylyleneglycol in 100% Sulfuric Acid with Water

Tetra-p-anisyl-p-xylyleneglycol (2.0 g.) was dissolved in 15 g. of 100% sulfuric acid. The cherry-red solution was slowly added to 100 g. of ice. The white precipitate was collected, washed with water, and dissolved in 50 ml. of ether. The ether layer was washed with two 50-ml. portions of 10% sodium carbonate solution and then dried with magnesium sulfate. The ether was evaporated and yielded 1.79 g. (90%) of tetra-p-anisyl-p-xylyleneglycol, m.p. 166.5-168°. The m.p., m.m.p., and infrared spectrum were identical to those of the starting glycol.

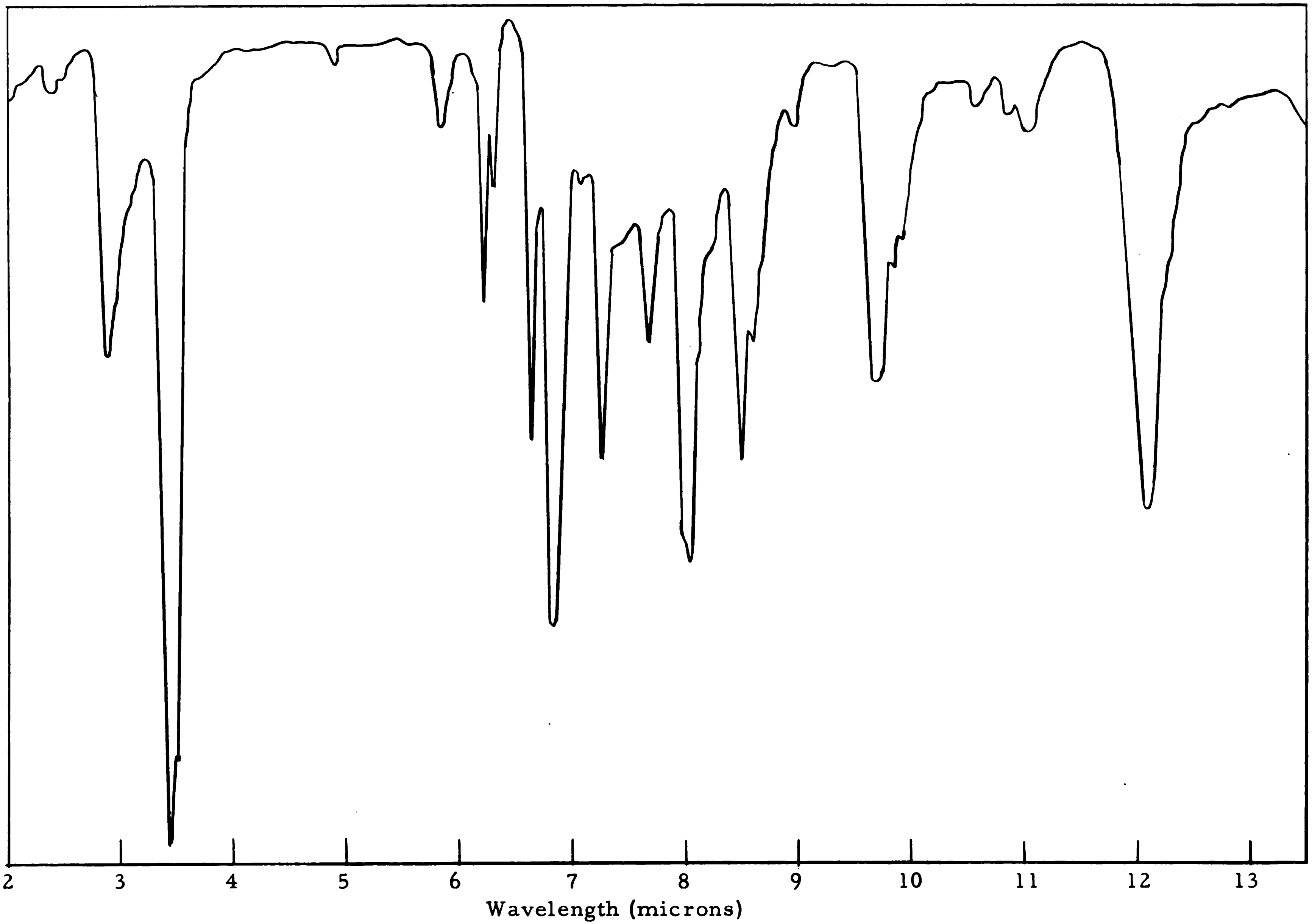


Figure XXVI. Infrared spectrum of tetra-p-anisyl-p-xylyleneglycol (mull).

Preparation of 9, 10-Dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene (35, 38)

To a 1-l. 3-necked round-bottomed flask equipped with a Trubore stirrer, reflux condenser and a dropping funnel was added 32.9 g. (1.35 g.-atoms) of magnesium, 100 ml. of anhydrous ether, and 30 g. of bromobenzene. After the initial vigorous reaction had subsided a solution of 185 g. (a total of 1.37 moles) of bromobenzene in 200 ml. of anhydrous ether was added dropwise during a 3 hour period. In a second 1-l. 3-necked round-bottomed flask equipped with a stirrer and reflux condenser with a calcium chloride drying tube was placed 57.3 g. (0.274 mole) of anthraquinone in 250 ml. of ether. The previously prepared Grignard solution was transferred under a nitrogen atmosphere to a 500 ml. dropping funnel and was then slowly added (1 hr.) to the refluxing and stirred slurry of anthraquinone in ether. After the addition, the reaction mixture was refluxed for an additional three hours and then hydrolyzed on 400 g. of ice, 100 ml. of water and 20 ml. of concentrated sulfuric acid. The solution was filtered to remove unreacted anthraquinone and the layers were separated. The aqueous phase was extracted with two 100-ml. portions of ether. The organic layer and the ether extracts were combined and the solvent was removed on a Rinco Rotary evaporater. The solid residue was combined with the previously filtered solid and added to 500 ml. of boiling ethyl acetate. The mixture was cooled and filtered and the solid residue was again added to 500 ml. of boiling ethyl acetate. The mixture was cooled and filtered and the filtrate was combined with the previously filtered ethyl acetate. The solution was concentrated until a solid began to precipitate. The solution was cooled to 0°, filtered and the solid was washed with ligroin. It was recrystallized from acetone and then benzene to yield 35 g. (35.1%) of white needles of 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene, m.p. 258-259°. Because of the wide deviation between the melting points reported in the literature for this compound a sample was sent for analysis.

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

Found: C, 85.54; H. 5.66.

Its infrared spectrum is shown in Figure XXVII.

Preparation of 9, 10-Diphenylanthracene (39)

9, 10-Dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene (2.0 g.) and 2.48 g. (0.0165 mole) of sodium iodide were dissolved in 50 ml. of acetic acid. The solution was warmed on a steam bath for three hours. At the end of this time the solution was added to 50 g. of ice and 50 g. of 10% sodium thiosulfate solution. The pink solid was filtered, dissolved in 50 ml. of benzene, washed with two 50-ml. portions of 10% sodium thiosulfate solution, and dried with magnesium sulfate. The benzene was removed on a Rinco Rotary evaporator and the pale yellow solid was recrystallized from benzene-pentane to yield 1.42 g. (85%) of 9, 10-diphenylanthracene, m.p. 247-248°. (Literature value 248°.) Its infrared spectrum is shown in Figure XXVIII.

Reaction of a Solution of 9, 10-Dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene in Concentrated Sulfuric Acid with 15% Sodium Hydroxide Solution

A sample of 3.573 g. of 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene was dissolved in 35 ml. of 98% sulfuric acid. The solution was stirred and maintained at 0° for 15 minutes. The deep blue solution was slowly added to 150 ml. of 15% sodium hydroxide solution at -5 to 0°. The greenish-brown solid was filtered, washed with water and dried. The solid (3.334 g.) was dissolved in 15 ml. of benzene and adsorbed on 100 g. of Fisher's Adsorption alumina (80-200 mesh). The column was eluted with 200 ml. of 1:1 benzene-pentane and yielded 1.171 g. (36.6%) of a pale-yellow solid, m.p. 247-248°. The m.p., m.m.p., and infrared spectrum of this material were identical to those of an authentic sample of 9, 10-diphenylanthracene.

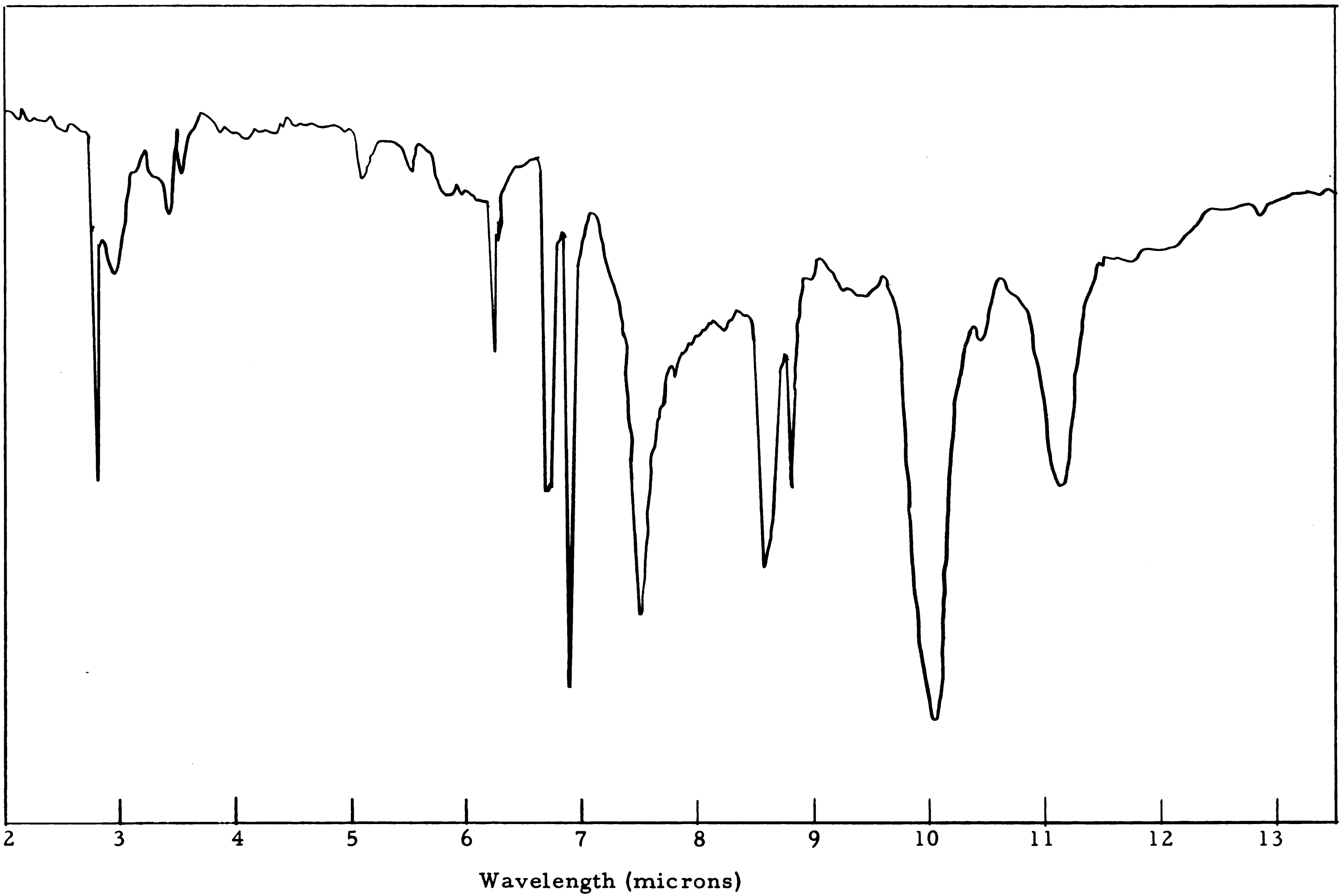


Figure XXVII. Infrared spectrum of 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene ($CHCl_3$ solution).

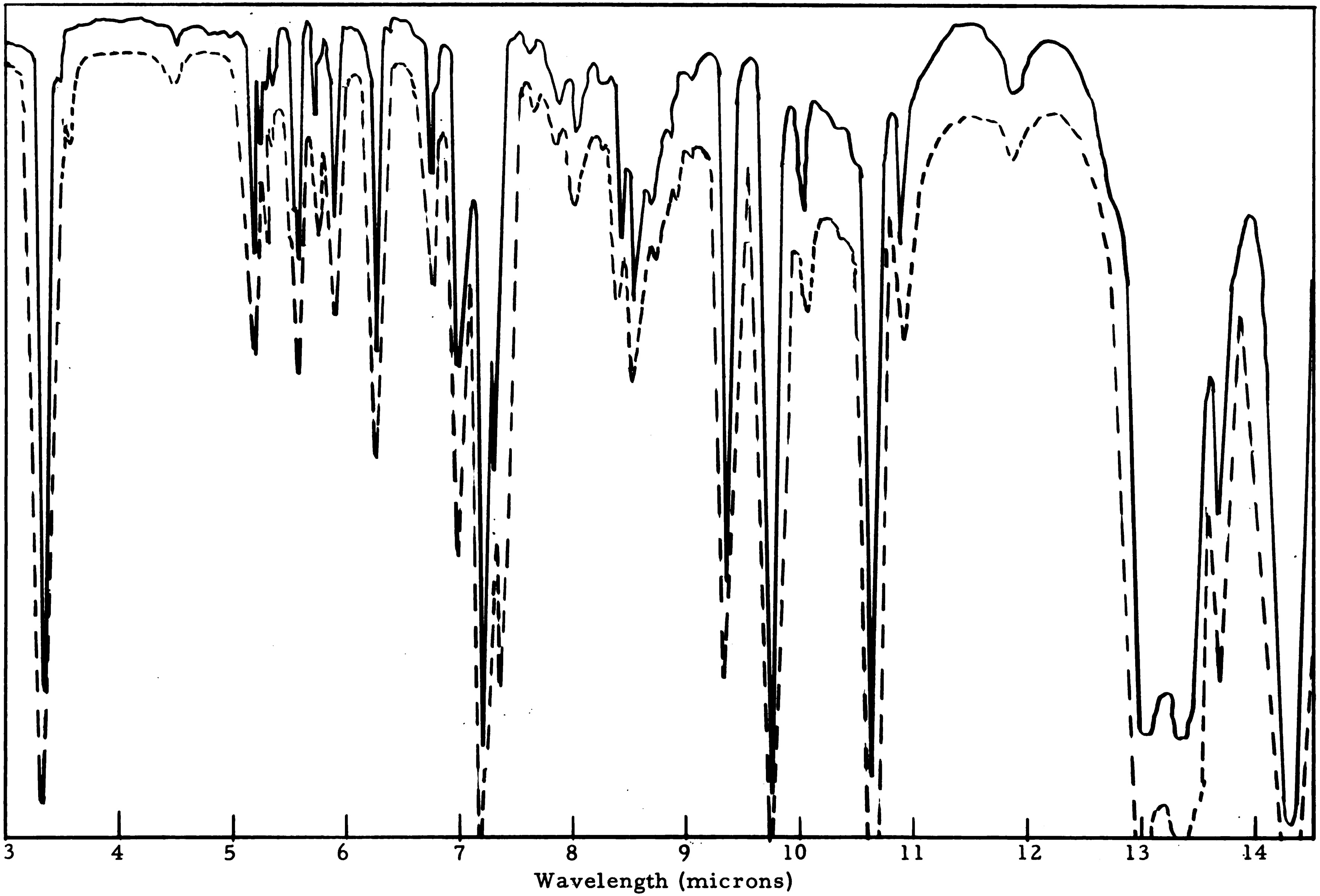


Figure XXVIII. Infrared spectrum of 9, 10-diphenylanthracene from the reduction of 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene (——), and from hydrolysis of the blue sulfuric acid solution (----).

Continued elution of the column with 300 ml. of benzene yielded 0.6016 g. (19%) of an orange solid, m.p. 188-190°. Recrystallization from benzene-pentane raised the m.p. to 191.2-192.4° (corrected). The compound has an ultraviolet-visible spectrum (Figure XXIX) that is almost identical to that of 4-phenyl-2, 3-benzofluoranthene reported by Clar and Willicks (40). Because of the difference between the observed melting point (191.2-192.4°) and that reported (185-186°) for this compound a sample was sent for analysis.

Anal. Calcd. for $C_{26}H_{16}$: C, 95.09; H, 4.91.

Found: C, 95.14; H, 5.05.

Its infrared spectrum is shown in Figure XXX.

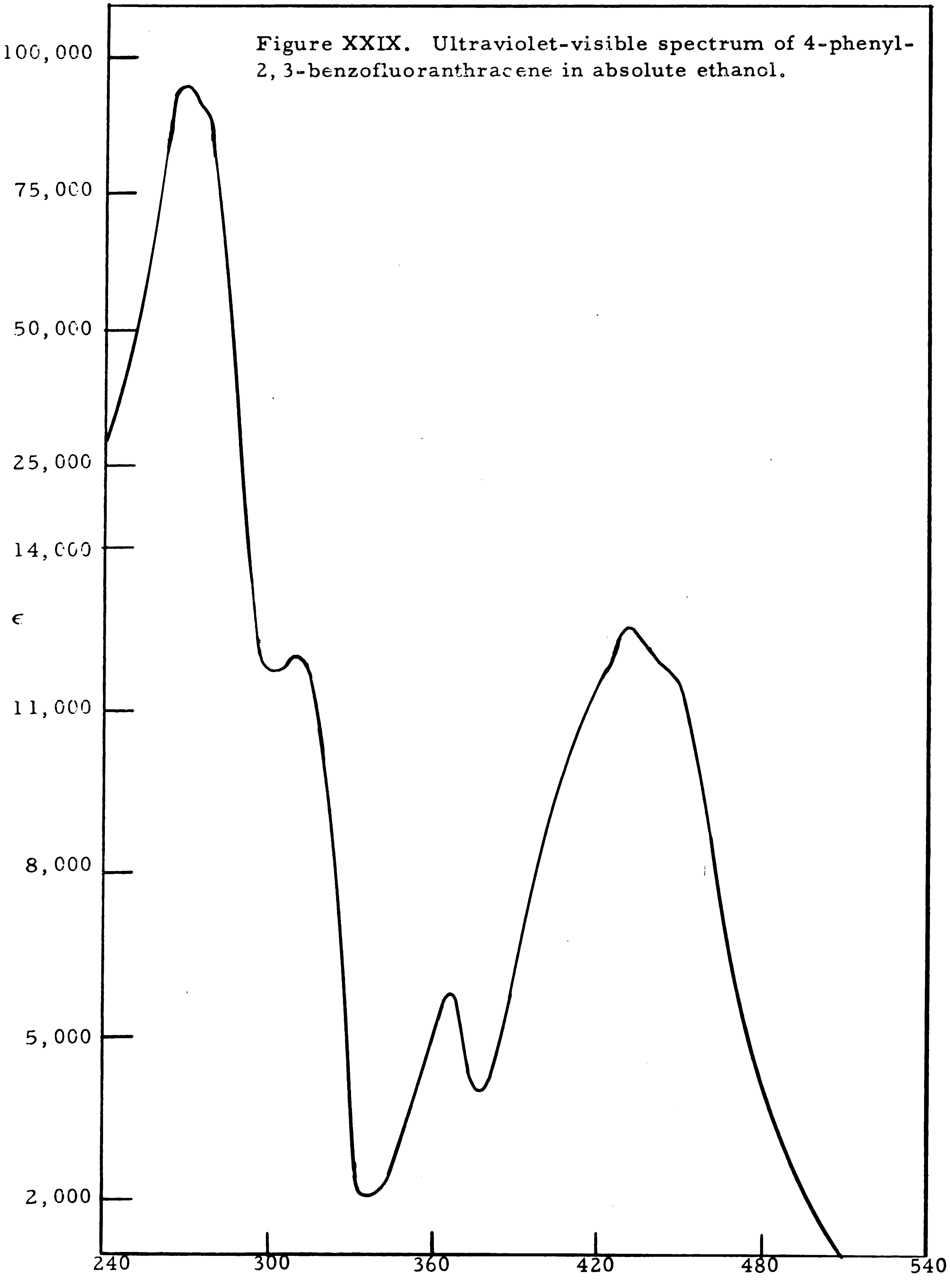
Continued elution of the column with 1:1 benzene-ether yielded 0.040 g. of a red solid. The material was recrystallized from xylene-petroleum ether and had a m.p. of approximately 385°. There was only enough material for one carbon-hydrogen analysis and the compound was found to contain some ash and possibly an element(s) other than carbon or hydrogen.

Anal. Found: C, 91.81; H, 4.89; Ash, 1.24.

The material was not identified.

Finally elution of the column with ether, ether-methanol mixtures or methanol yielded only a dark brown residue. Attempts to purify it by recrystallization from methanol were unsuccessful. The material melted over a very wide range (110-170°) and the infrared spectrum, shown in Figure XXXI, of the crude material showed hydroxyl and carbonyl bonds. The identity and composition of this material was not determined.

Figure XXIX. Ultraviolet-visible spectrum of 4-phenyl-2, 3-benzofluoranthracene in absolute ethanol.



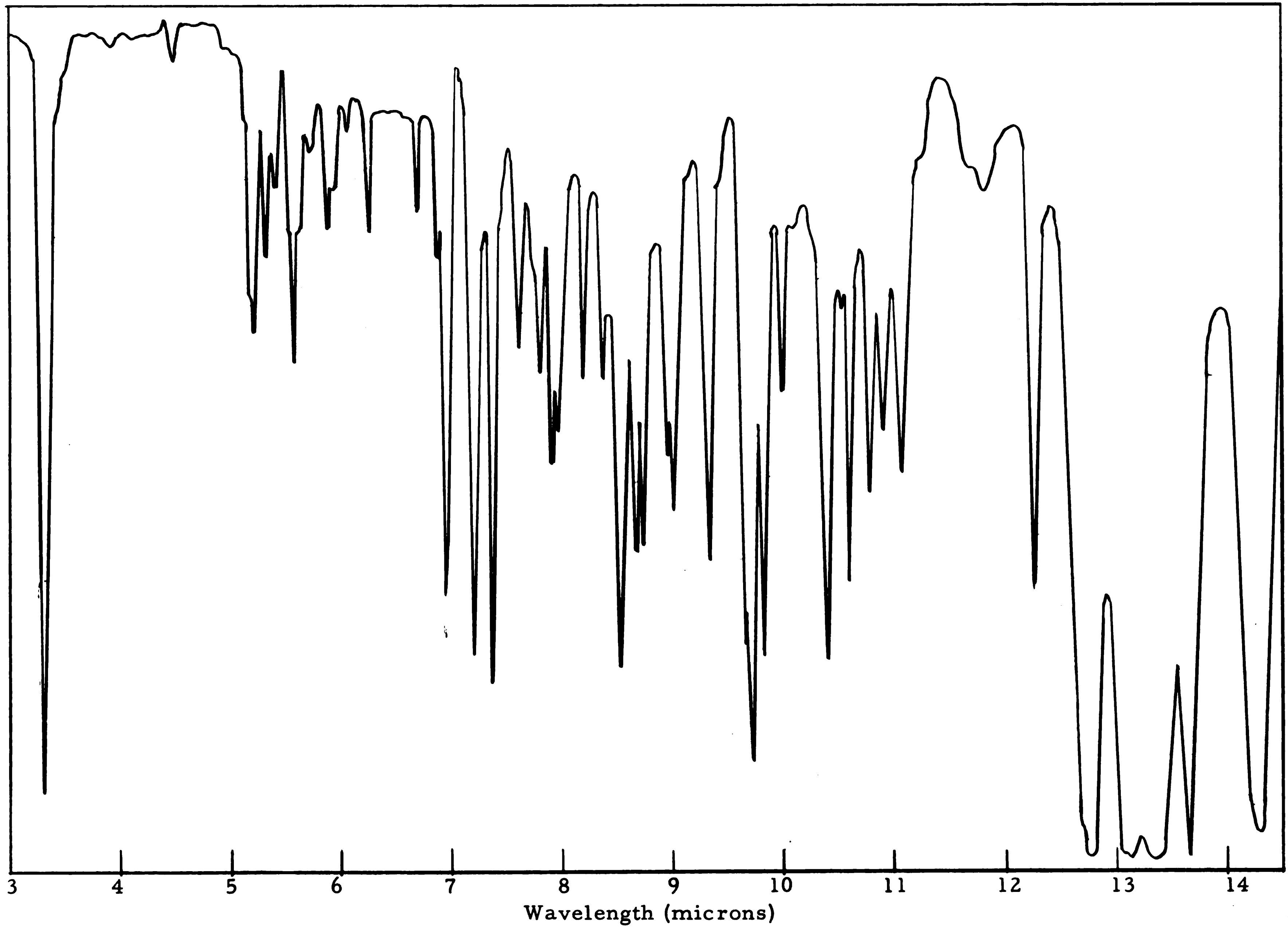


Figure XXX. Infrared spectrum of 4-phenyl-2, 3-benzofluoranthracene.

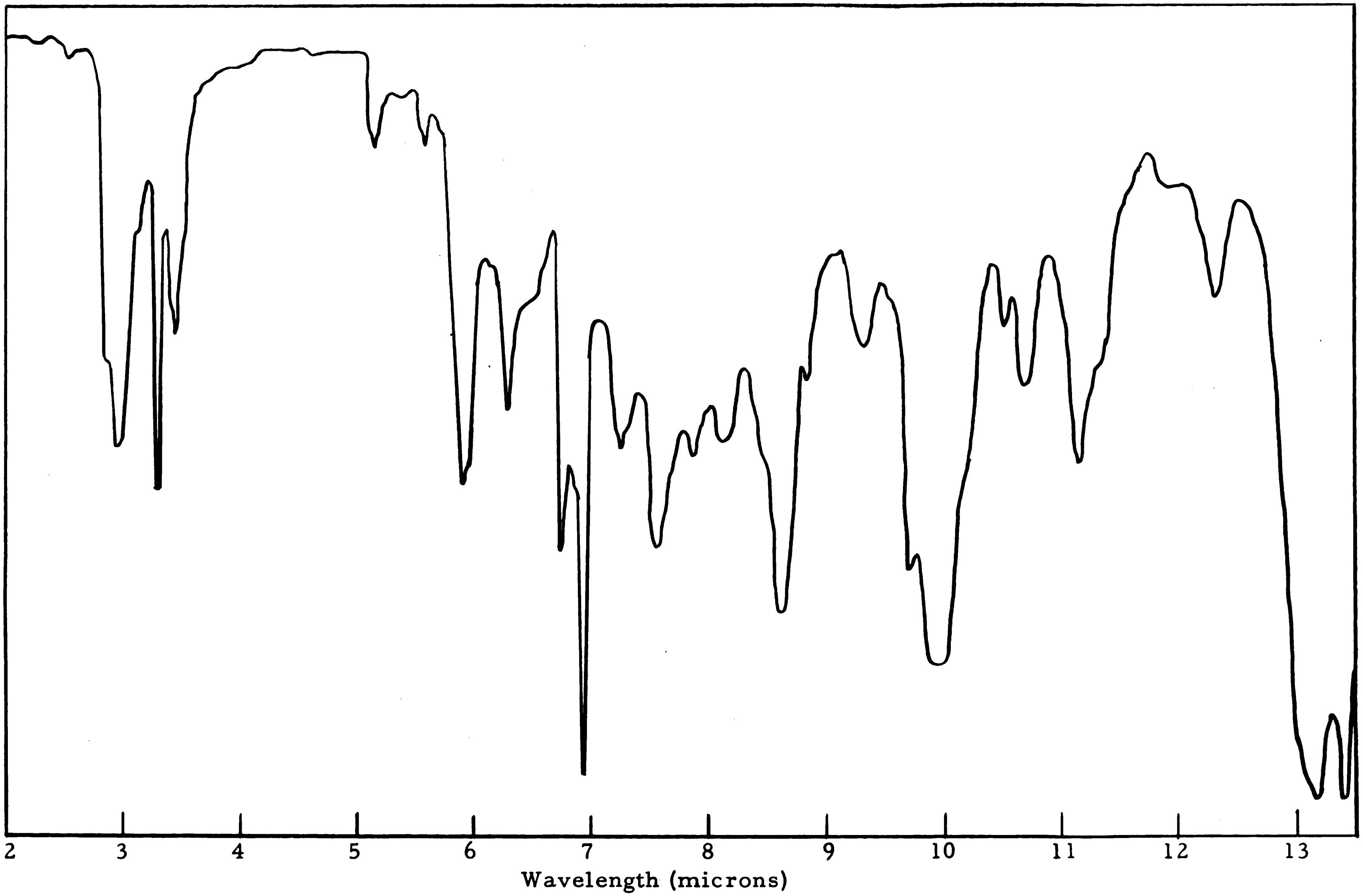


Figure XXXI. Infrared spectrum of the polar residue from the hydrolysis of the blue sulfuric acid solution.

Reaction of a Solution of 9, 10-Dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene in 6% Sulfuric Acid in Acetic Acid with Water

9, 10-Dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene (0.8705 g.) was dissolved in 15 ml. of 6% sulfuric acid in acetic acid. The yellow solution was slowly added to 100 g. of ice and the light yellow precipitate collected. The solid was dissolved in 50 ml. of ether, washed with two 30-ml. portions of 5% sodium carbonate solution and dried with magnesium sulfate. The ether was evaporated and the solid residue dissolved in 15 ml. of benzene and adsorbed on 60 g. of Fisher's Adsorption alumina (80-200 mesh). Elution with 200 ml. of 1:1 benzene-ether yielded a small amount of yellow solid (0.023 g.) presumably a mixture of 9, 10-diphenylanthracene and 4-phenyl-2, 3-benzofluoranthene. Elution with 250 ml. of absolute methanol gave 0.8071 g. (92.5%) of 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene, m.p. 257-258.5°. A mixed m.p. with an authentic sample of glycol gave no depression.

B. Solutions for Spectral Measurements

Preparation of Weight Per Cent Sulfuric Acid-Water Solutions for the Visible Spectra

Stock solutions consisted of "Baker Analyzed" Reagent grade concentrated sulfuric acid. The per cent composition of the stock solution was determined by titrating a weighed volume of sulfuric acid with standardized sodium hydroxide solution to the phenolphthalein end point. Calculated weights of water were then added to known weights of stock solution to give the desired weight per cent of sulfuric acid-water for the spectral measurements.

Preparation of Weight Per Cent Sulfuric Acid-Acetic Acid Solutions for the Visible Spectra

Reagent grade glacial acetic acid was fractionally distilled in an all glass still protected from atmospheric moisture. Only acid boiling at 118°/atm. press. was used. Clear 100% sulfuric acid was prepared as previously described in the experimental section in Part A of this thesis. The sulfuric acid-acetic acid solutions were prepared by the method of Hall and Spengeman (6) at $25^{\circ} \pm 2^{\circ}$. Standard sulfuric acid solutions were prepared by directly weighing 100% sulfuric acid and diluting to a known volume with acetic acid. The solutions were then made up by mixing known volumes of acetic acid with known volumes of stock solution. For solutions 3 M or less the stock solutions could be measured from a buret. For more concentrated solutions, however, it was necessary to weigh out the stock solution because of its viscosity.

C. Spectra

The ultraviolet-visible spectra were obtained with the Beckman DK-2 Recording Spectrophotometer using 1 cm. glass-stoppered quartz cells.

The infrared spectra were scanned using a Perkin-Elmer (Model 21) Recording Infrared Spectrophotometer with a 0.5 mm. thickness solution cell.

All of the infrared spectra were run in carbon disulfide except for the region 6.2-7.1 mμ which was run in carbon tetrachloride. This region was incorporated into the carbon disulfide spectrum to give one continuous spectrum. For solubility purposes some compounds were run in chloroform or as mulls, as indicated on the spectra.

Test of Beer's Law

Each of the three glycols studied was observed to obey Beer's Law. The results were obtained with the Beckman DU-Spectrophotometer using 1 cm. glass-stoppered quartz cells. A set of sample data is given for tetraphenyl-p-xylyleneglycol in 2.52% sulfuric acid-acetic acid in Table XV.

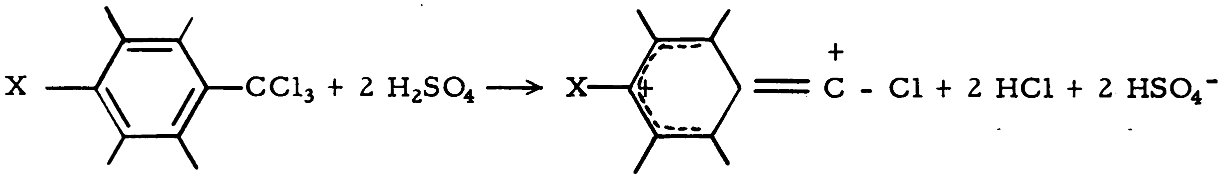
Table XV. Test of Beer's Law for Tetraphenyl-p-xylyleneglycol in 2.52% Sulfuric Acid-Acetic Acid

Conc. (moles)	Optical Density at 455 mμ	Molar Absorbancy Index (ε)
7.03×10^{-6}	0.138	19,650
1.406×10^{-5}	0.274	19,450
2.109×10^{-5}	0.405	19,200

SUMMARY

1. The aluminum chloride-catalyzed reaction of carbon tetrachloride with polymethylbenzene derivatives was extended to monosubstituted durene derivatives to yield 4-bromo-, 4-chloro-, and 4-fluoro-2, 3, 5, 6-tetramethylbenzotrichlorides. The structures of the latter were established by hydrolysis to the corresponding acids and comparison with independently synthesized authentic specimens.

2. Each of the 4-halo-2, 3, 5, 6-tetramethylbenzotrichlorides dissolved in 100% sulfuric acid to form a deep red solution. In each case two moles of hydrogen chloride were quantitatively swept from these solutions. Hydrolysis of the colored solutions gave better than 90% yield of the corresponding 4-halodurenecarboxylic acids. Cryoscopic measurements showed that five particles were produced when 4-bromo-2, 3, 5, 6-tetramethylbenzotrichloride dissolved in 100% sulfuric acid. By analogy to the reaction of trichloromethylpentamethylbenzene with 100% sulfuric acid it was found that the 4-halo-2, 3, 5, 6-tetramethylbenzotrichlorides ionize in 100% sulfuric acid to form the corresponding dipositively charged carbonium ions.



IV a = Br
b = Cl
c = F

V a, b, c

The ultraviolet, visible and proton magnetic resonance spectra supported the structure assignments for the dipositive carbonium ions.

3. The formation of dipositive carbonium ions arising from single ionizations at two separate sites in a molecule was observed for three glycols. Tetraphenyl-p-xylyleneglycol and tetra-p-anisyl-p-xylyleneglycol dissolved in 100% sulfuric acid to form intensely red solutions. Hydrolysis gave better than a 90% yield of the corresponding glycols.

A study of the visible spectra in solutions of varying acidity showed that both glycols undergo reversible stepwise ionizations to monopositive and dipositive carbonium ions.

9, 10-Dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene dissolved in 100% sulfuric acid to form an intense blue solution. Hydrolysis did not yield the starting material, but rather a mixture containing 9, 10-diphenylanthracene (36%), 4-phenyl-2, 3-benzofluoranthene (19%) and some products which remain unidentified.

In much less acidic solutions 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene undergoes the normal stepwise ionization to monopositive and dipositive carbonium ions, as shown by hydrolysis experiments.

4. The $pK_{R^{++}}$'s, the pK's for the process:

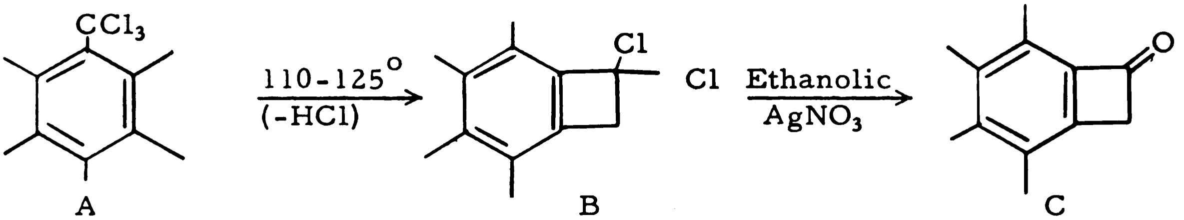
$$(ROH)^+ + H^+ \rightleftharpoons R^{++} + H_2O$$

were determined spectroscopically for the three glycols, and were found to be -8.7 for tetraphenyl-p-xylyleneglycol and 9, 10-dihydro-9, 10-dihydroxy-9, 10-diphenylanthracene and -3.4 for tetra-p-anisyl-p-xylyleneglycol.

MISCELLANEOUS

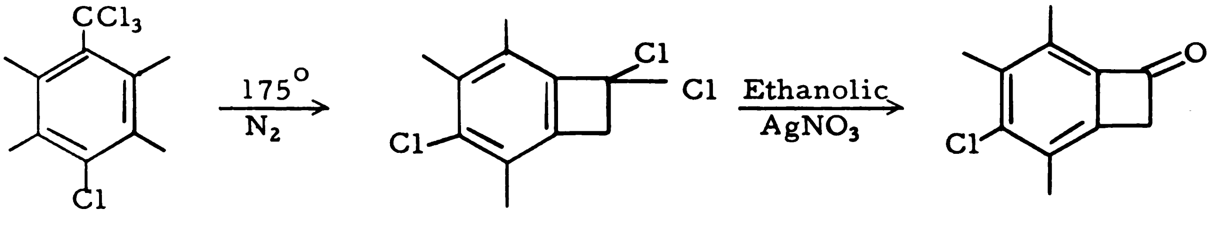
Results and Discussion

Recently Hart and Fish (1) reported an unusual thermal reaction for trichloromethylpentamethylbenzene (A). When A was heated slightly above its melting point (94.5-95.0°), hydrogen chloride was evolved and a new compound 7,7-dichloro-1,2,3,4-tetramethyl-bicyclo[4,2,0] octa-1,3,5-triene was formed. Hydrolysis of B with ethanolic silver nitrate solution gave the ketone (C)



A B C (1)

In order to ascertain the applicability of this reaction to analogous systems 4-chloro-2,3,5,6-tetramethylbenzotrichloride (D) was heated to 175° for 4 hours. A new compound was isolated which analyzed correctly for 3,7,7-trichloro-1,2,4-trimethyl-bicyclo[4,2,0]octa-1,3,5-triene (E). Compound (E) was then hydrolyzed with ethanolic silver nitrate to the corresponding ketone (F).



D E F (2)

The structural assignments of E and F rest only on their microanalysis, infrared spectra, ready hydrolysis of E to F, and analogy with previous work (43). The unusual elimination of hydrogen chloride seems to be capable of further extension.

Experimental

Preparation of 3, 7, 7-Trichloro-1, 2, 4-trimethyl-bicyclo-[4, 2, 0]octa-1, 3, 5-triene

To a 100-ml. round-bottomed flask equipped with a side arm for nitrogen inlet and a take-off for gaseous outlet, there was placed 5.0 g. of 4-chloro-2, 3, 5, 6-tetramethylbenzotrichloride. The outlet tube was connected to a trap containing a 3% sodium hydroxide solution. The reaction vessel was immersed in an oil bath heated to 175° and nitrogen was passed through the system. After heating for 3 hours 0.75 equivalents of hydrogen chloride had been liberated. (Chloride ion determined by the Fajans' method at pH 8.) The flask was heated for another hour at 175° and then cooled to room temperature. The brown oily residue, 4.0 g., was dissolved in anhydrous n-pentane and distilled under reduced pressure. Three fractions were collected:

I B.P. 94-100°/0.5 mm, n_D^{25} 1.5730, 1.68 g.;
II B.P. 102-104°/0.5 mm, n_D^{25} 1.5709, 1.58 g.;
III B.P. 104-114°/0.5 mm, n_D^{25} 1.5746, 0.6 g.

On standing fractions I and II solidified and had m.p.'s of 37-39° and 40.0-40.5° respectively. The infrared spectra of both fractions were identical. Fractions I and II were combined and recrystallized from anhydrous n-pentane to yield 3.10 g. (69%) of 3, 7, 7-trichloro-1, 2, 4-trimethylbicyclo[4, 2, 0]octa-1, 3, 5-triene, m.p. 40.0-40.5°.

Anal. Calcd. for $C_{11}H_{11}Cl_3$: C, 52.94; H, 4.44; Cl, 42.62.
Found: C, 53.07; H, 4.46; Cl, 42.40.

Its infrared spectrum is shown in Figure XXXII.

Preparation of 3-Chloro-1, 2, 4-trimethyl-bicyclo-[4, 2, 0]octa-1, 3, 5-triene-7-one

A sample of 0.50 g. of 3, 7, 7-trichloro-1, 2, 4-trimethyl-bicyclo-[4, 2, 0]octa-1, 3, 5-triene and 0.71 g. of silver nitrate were dissolved in

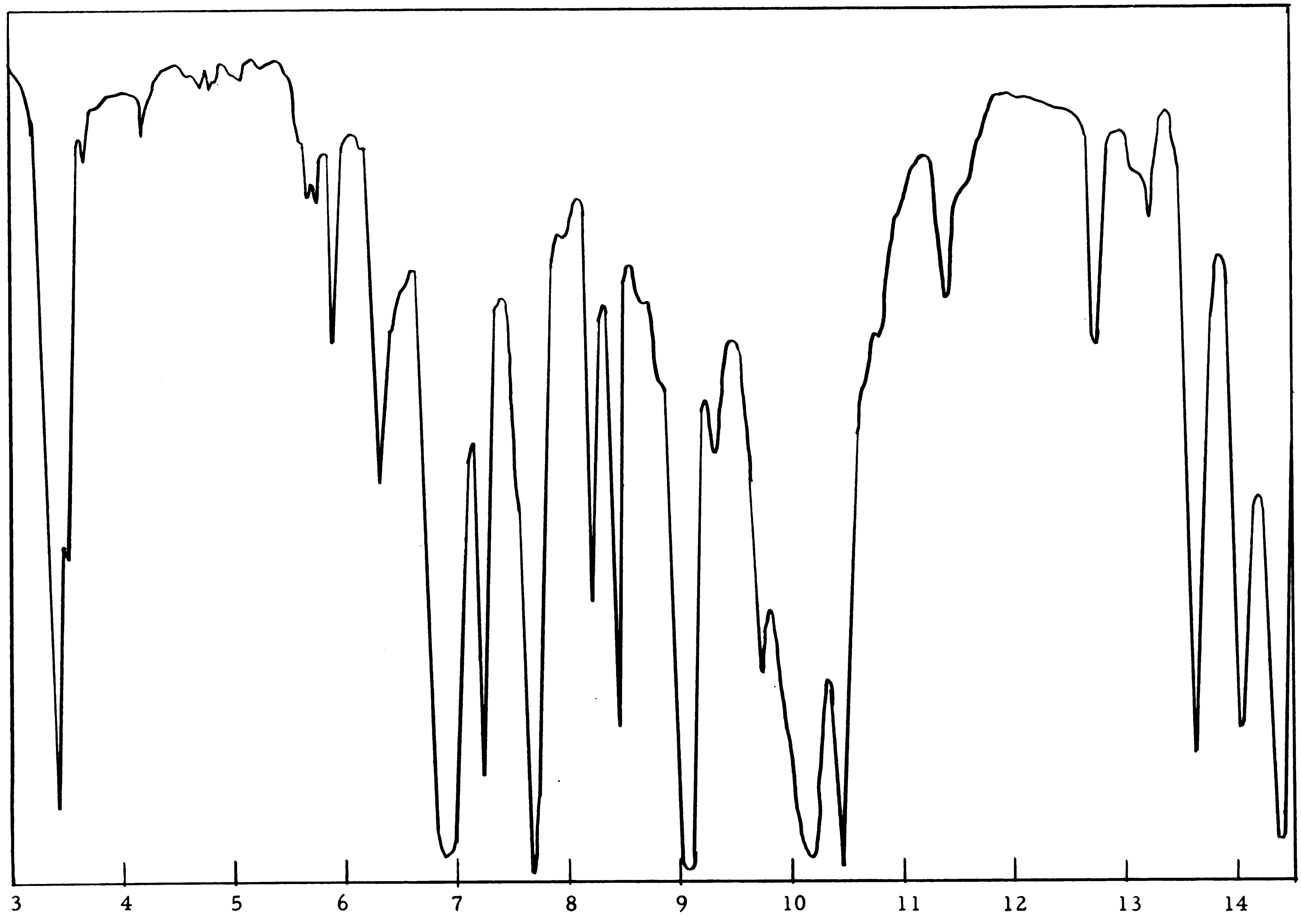


Figure XXXII. Infrared spectrum of 3, 7, 7-trichloro-1, 2, 4-trimethylbicyclo[4, 2, 0]octa-1, 3, 5-triene.

20 ml. of 80% aqueous ethanol. A precipitate of silver chloride formed immediately. After stirring the solution for one hour at room temperature the silver chloride was filtered. The filtrate was evaporated to dryness, the residue dissolved in anhydrous ether and filtered again. The ether was evaporated and yielded 0.35 g. (89%) of crude product. The material was recrystallized from aqueous-ethanol and then sublimed to give white needles of 3-chloro-1, 2, 4-trimethyl-bicyclo[4, 2, 0]-octa-1, 3, 5-triene-7-one, m.p. 182.5-184°.

Anal. Calcd. for $C_{11}H_{11}ClO$: C, 67.87; H, 5.70; Cl, 18.21.
Found: C, 67.81; H, 5.79; Cl, 18.23.

Its infrared spectrum is shown in Figure XXXIII.

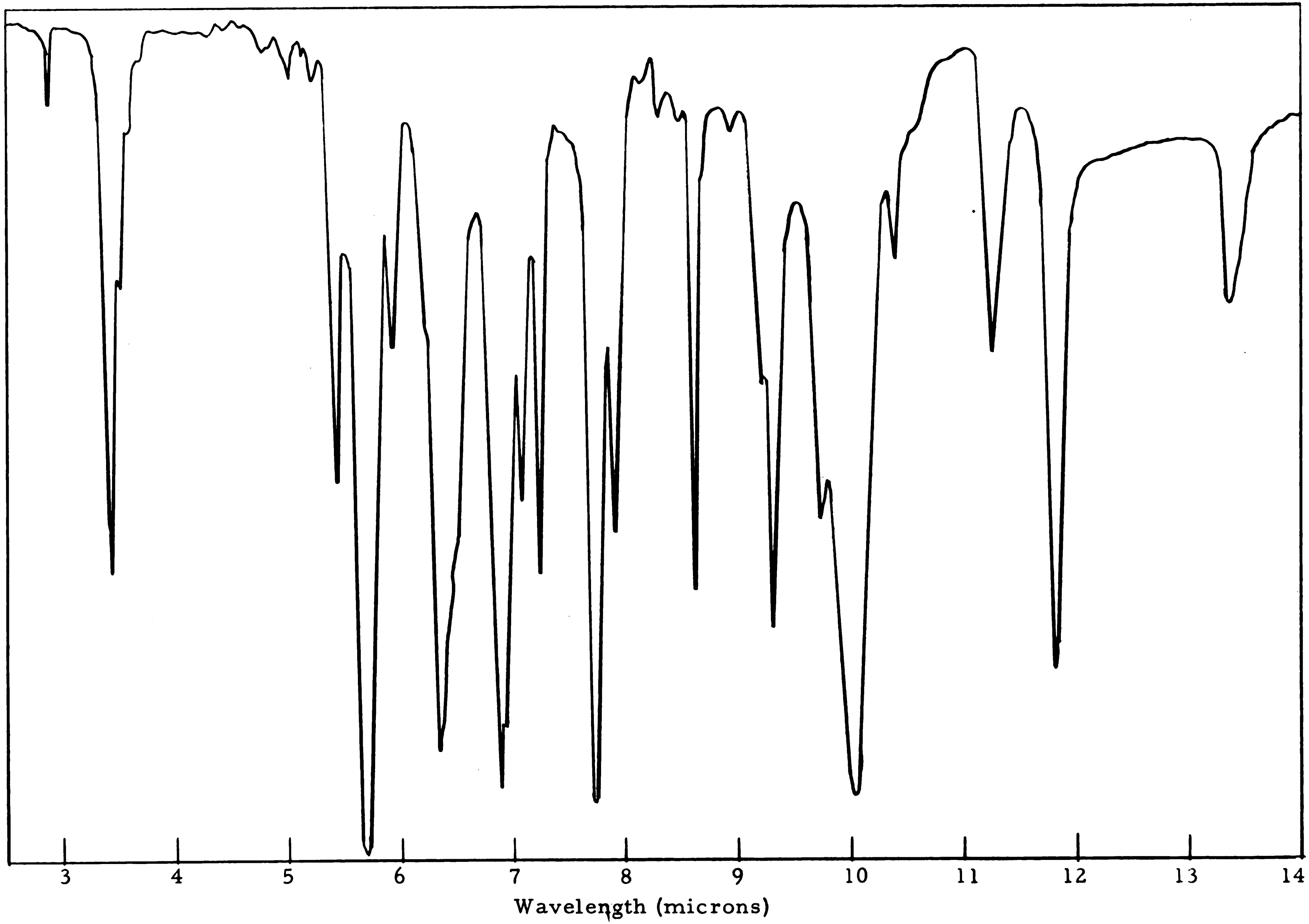


Figure XXXIII. Infrared spectrum of 3-chloro-1, 2, 4-trimethylbicyclo[4, 2, 0]octa-1, 3, 5-triene-7-one.

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