# PART I
# DIPOSITIVE CARBONIUM IONS
# PART II
# AROMATIC ACYLIUM IONS

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
John S. Fleming
1964

# ABSTRACT

## PART I

## DIPOSITIVE CARBONIUM IONS

## PART II

## AROMATIC ACYLIUM IONS

by John S. Fleming

One intent of this work was to examine the possibility of isolating a stable salt of the reported pentamethylphenylchlorodicarbonium and 2,4,6-trimethylphenylchlorodicarbonium ions. Crystalline tetrafluoroborate and tetrachloroborate salts of these ions were prepared by reaction of the respective benzotrichloride with anhydrous fluoboric acid or boron trichloride in liquid sulfur dioxide; the salts were characterized by several physical and chemical methods. Attempts were made to prepare the dication of cyclooctatetraene by reaction of dibromocyclooctatetraene with silver tetrafluoroborate, without success. Similar efforts using boron tribromide were also unsuccessful.

The electron transfer from tetraphenyl-p-xylylene to tetraphenyl-p-xylylium diperchlorate to produce a radical-cation, examined some time ago by Weitz and Schmidt, was reinvestigated using spectroscopic methods. The rate of

reaction was measured and the electron spin resonance spectrum of the radical-cation in methylene chloride at $-90^{\circ}$ clearly shows the product to be a free radical.

Values for the $pK_R$ of ionization of some substituted benzoic acids were determined from their n.m.r. spectra in various concentrations of aqueous sulfuric acid. These values compared favorably with values determined from ultraviolet spectra of the same acids. The pK's for <u>para</u> substituted acids showed a linear correlation with $\sigma^+$ values and not with $\sigma$ values. Using these acids as hydroxyl-donating type bases (similar to triarylcarbinols) values of $H_R$ for 96 to 100 percent sulfuric acid solutions were estimated.

# PART I

# DIPOSITIVE CARBONIUM IONS

# PART II

# AROMATIC ACYLIUM IONS

By

John S. Fleming

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1964

## ACKNOWLEDGMENT

The author wishes to express his indebtedness to Dr. H. Hart for suggesting the problems undertaken and his perseverance during the course of investigation.

Acknowledgment is extended to the National Science Foundation whose funds provided financial assistance from June, 1962, through September, 1964.

TABLE OF CONTENTS

## LIST OF TABLES

## LIST OF FIGURES

# INTRODUCTION

This work is presented in two parts. The first deals with the preparation, isolation, and a few reactions of dipositive carbonium ions from polymethylbenzotrichlorides. Attempts to prepare the cycloöctatetraene dication are also described. Evidence is presented for a one-electron transfer to a dicarbonium ion from a neutral molecule which differs from it only by containing two additional electrons. The second part of this thesis describes the use of nuclear magnetic resonance (n.m.r.) to determine the $pK_R'$s for formation of acylium ions from various ortho-substituted benzoic acids.

* * * *

Carbonium ion salts have been prepared and isolated using several procedures; e.g., triphenylmethyl cation has been isolated as the respective salt from the reactants seen in Table 1. A limited number of molecular types of dicarbonium ions have been prepared. A literature search and discussion of the representative groups has been made by Sulzberg[10]. In general the preparation of dicarbonium ions is but an extention of procedures used for monocarbonium ions. Three types of molecular systems which could yield the dicarbonium ions are considered.

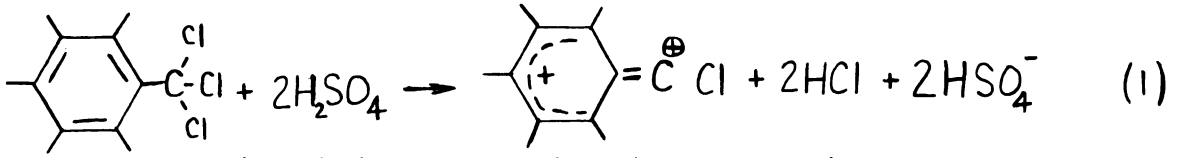
## 1. Polymethylbenzotrichlorides

Polymethylbenzotrichlorides, when dissolved in a strongly ionizing acid medium such as sulfuric acid, appear

Table 1. Some procedures used to prepare triphenylmethyl cation salts.

| Triphenylmethyl Halide | Solvent | Reagent |
|---|---|---|
| Chloride (1) | Nitrobenzene | Perchloric Acid (71%) |
| Chloride (2,3) | | Silver Perchlorate |
| Chloride (4) | Acetic Anhydride | Acetyl Tetrafluoroborate |
| Fluoride (5) | | Boron Trifluoride |
| Chloride (6) | Ether | Silver Hexafluorophosphate, Arsenate, Antimonate, Niobate, Tetrafluoroborate |
| Chloride | Benzene | Stannic Chloride |
| Chloride | Benzene | Antimony Pentachloride |
| Bromide (8,9) | Cyclohexane | Boron Tribromide |
| Triphenylmethanol (7) | Acetic Anhydride | Perchloric Acid (71%) |
| Triphenylmethanol (7) | Acetic Anhydride | Fluoboric Acid (48%) |

to lose two chloride ions from a single carbon atom. The

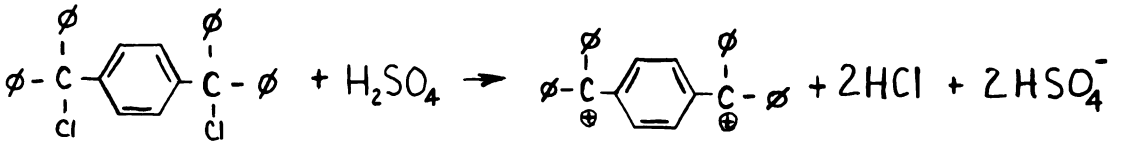


(1)

presence of dipositive carbonium ions of this type was deduced from a study of the extensive and chemical properties of these solutions.[11] Similar ions have been implicated in the hydrolysis of these trihalides in aqueous dioxane.[12] It was decided to attempt the isolation of crystalline salts of these dipositive carbonium ions, in order to confirm their existence and to study them further, free of sulfuric acid. Methods previously used for salts of the triphenylmethyl cation were used as a guide to prepare salts from pentamethylbenzotrichloride and 2,4,6-trimethylbenzotrichloride. The preparations were successful, and a few nucleophilic reactions were carried out on the salts.

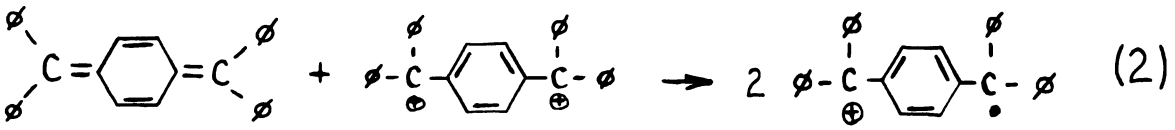
## 2. α,α'-Dichloro-α,α,α',α'-tetraphenyl-p-xylene

α,α,α',α'-Tetraphenyl-p-xylene-α,α'-diol and the corresponding dichloride produce red solutions when dissolved in sulfuric acid,[15] and it has been shown that the color is due to the corresponding dicarbonium ion.[16] By allowing α,α,α',α'-tetraphenyl-p-xylene-α,α'-dichloride and



silver perchlorate to react, the bis-perchlorate of the dication was prepared[19] and isolated as a stable salt.

It seems reasonable that Thiele's hydrocarbon (tetraphenylquinone dimethide), which differs from this dication only in the presence of two more electrons, might react to transfer one electron, forming two moles of radical-cation. Indeed, this reaction had been studied several

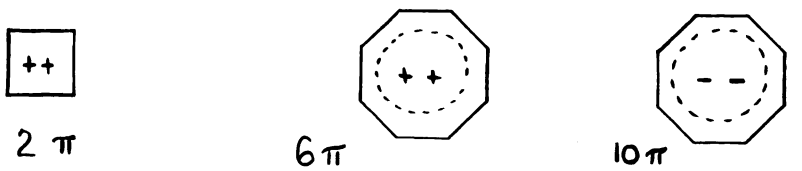


(2)

years ago by Weitz and Schmidt,[26] who found that intensely colored solutions were obtained when the dication and olefin were mixed. The reaction was reinvestigated using modern techniques (infrared and visible spectroscopy, as well as n.m.r. and electron spin resonance, e.s.r.). An estimate of the rate of the electron transfer process was made, and the general scope of the reaction has been extended by using <u>para</u>-chloro and <u>para</u>-methyl substituents in the reactants.

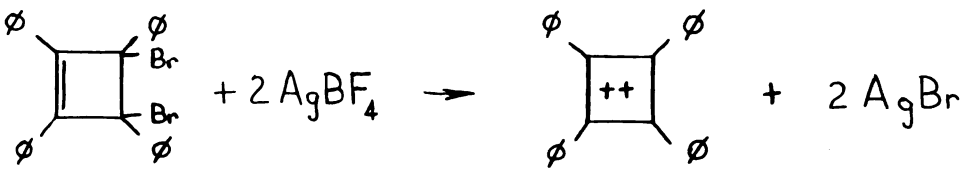
### 3. Cyclooctatetraene

It has been postulated[27] that the formation of an aromatic system might be a sufficient driving force to allow dication formation. A planar four-membered ring with two pi-electrons or eight-membered ring with six pi-electrons would constitute a Hückel aromatic system, although




in the latter case, two non-bonding orbitals would be empty. The energy gained by aromaticity would have to exceed the

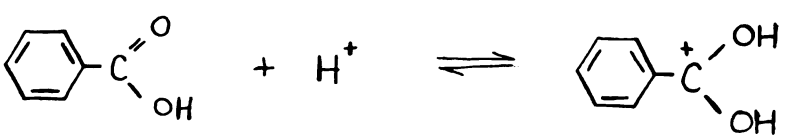
strain introduced by making the eight-membered ring planar. Freeman and Young[21] succeeded in preparing the tetraphenylcyclobutenyl dication from 3,4-dibromotetraphenylcyclobutene and silver tetrafluoroborate in methylene chloride. Katz[31] has prepared the cycloöctatetraene



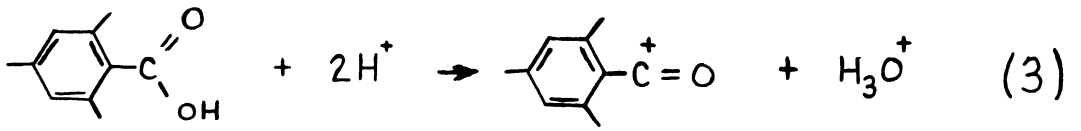
dianion by electron transfer from alkali metals to cycloöctatetraene. Despite electron repulsion and the increased strain demanded by the planar system, the dianion appears to be stable.

Numerous attempts were made to abstract the two bromines from cycloöctatetraene dibromide as bromide ions, using a variety of electrophiles. Although the bromines were removed, evidence could not be gathered for the formation of a dication in this system.

The second part of this thesis deals with the formation of acylium ions in sulfuric acid. Most aromatic acids, when dissolved in 100 percent sulfuric acid, behave as bases and are protonated on the carbonyl oxygen. But alkyl substituents in the <u>ortho</u> positions of benzoic acids



destabilize the protonated form (a dihydroxyarylcarbonium ion) by disallowing a planar carbonium ion. Such acids therefore form benzoyl cations (acylium ions), in which serious steric repulsions are removed. This second type



(3)

of ionization was found by Treffers and Hammett[32] for mesitoic acid and similarly substituted acids. Durenecarboxylic and pentamethylbenzoic acids show ionization similar to mesitoic acid[33]. Some acids appear to show intermediate behavior. These conclusions were based mainly on van't Hoff i-factor determinations.

It was decided to reinvestigate these equilibria using a more direct and more quantitative method. If the alkyl substituents, for example, showed different chemical shifts in the acids, the protonated acids, and the acylium ions, one might determine the ionization constants directly by studying the n.m.r. spectra in sulfuric acid solutions of varying strength.

This method, together with ultraviolet studies, was successful for a number of aromatic acids. Values for the $pK_R$'s were calculated. The effect of certain substituents in the aromatic ring, e.g. halides, on the $pK_R$ was also studied.

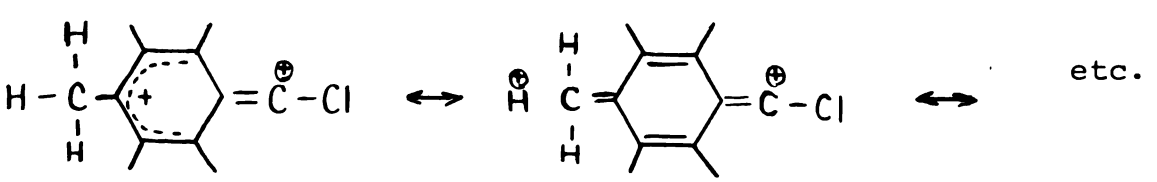
# RESULTS AND DISCUSSION

## Part I. Dicarbonium Ions

### 1. Preparation and Spectral Properties of Dicarbonium Ions

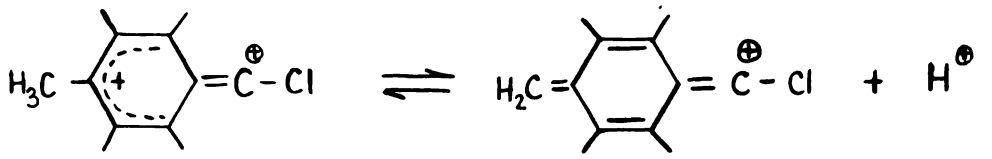
Evidence has been presented to establish the formation of dications[11,14,27] when polymethylbenzotrichlorides and polymethylhalobenzotrichlorides are dissolved in 90 to 100 percent aqueous sulfuric acid solutions. The steric effect of ortho substituents in the benzotrichlorides has been cited as one driving force for the reaction to form dications. Stabilization of the dication is provided by electron-releasing substituents on the aromatic ring. But at least one electron-withdrawing substituent, e.g., a halogen, on the ring can still be tolerated and support dication formation.[43,44] Without alkyl groups the dication has not been produced; for example, perchlorotoluene does not form a dication in concentrated sulfuric acid.[45]

One explanation for the stabilizing ability of alkyl groups on the benzene ring is hyperconjugation, as




Hyperconjugation has been suggested as a factor in stabilizing the mesityl acylium ion in sulfuric acid.[47] If hyperconjugation does occur, then the ortho and para alkyl

protons might be exchanged for deuterium if deuterated sulfuric acid were used. Furthermore, the dication might actually be in equilibrium with a monocation and a proton, as in

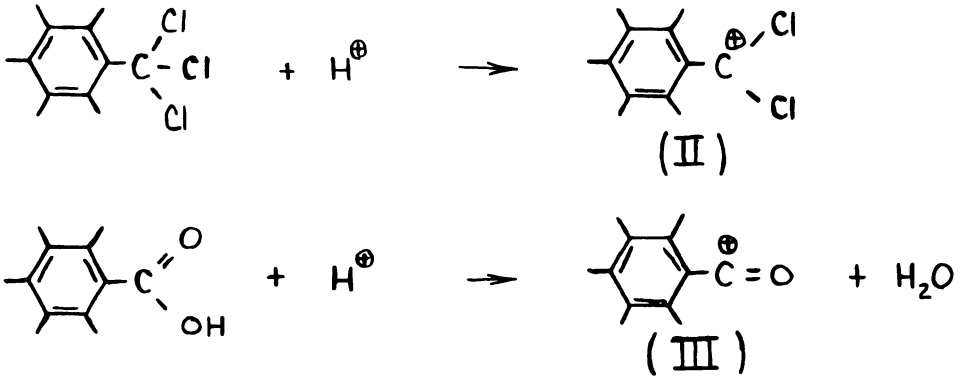


to eliminate having two charges.

With this possibility in mind, a sample of pentamethylbenzotrichloride was dissolved in deuterated sulfuric acid. Aliquots of the acid solution were taken at hourly intervals and poured into cold methanol. The resulting methyl ester was examined with n.m.r. and the spectrum electronically integrated, using the methyl ester protons as a reference. No change was observed in the hydrogen content of the aromatic methyl groups, even after the compound had been in the deuterated sulfuric acid for 24 hours. To verify this finding, samples of authentic methyl pentamethylbenzoate and the methyl ester from the pentamethylbenzotrichloride which had been in the deuterated sulfuric acid 24 hours were submitted for mass spectral analysis. The analysis showed less than 0.1 percent deuterium in the latter sample.

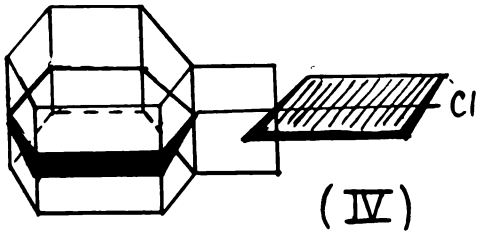
There may be some analogy between the formation of acylium ions from ortho substituted benzoic acids and the formation of dicarbonium ions from ortho substituted benzotrichlorides. Ionization of ortho-substituted benzoic

acids to acylium ions is accompanied by relief of steric strain, and the acylium ion is stabilized by electron-donating substituents. Formation of a mono-carbonium ion by the loss of one chloride ion, or, formation of an acylium ion by the loss of a molecule of water (or a hydroxyl ion), from an ionizable substituted aromatic system, results in a molecular structure where the positive charge can be stabilized by the substituents on the phenyl ring.




Any change in the aromatic ring should affect substituent electronic and magnetic environment (disturb the aromatic ring current) in the same way, to a first approximation, in the symetrical pentamethyl substituted carbonium and acylium ions. The alkyl proton n.m.r. spectra should appear identical if the structures have the same geometry. The dichloro structure II however, is sterically strained to such an extent that it is unstable. One of the chlorines is lost as chloride ion to form a more stable species. Loss of a second chloride ion from the carbonium ion would cause almost no change in the ring's

charge (using a simple pictorial representation of the ionization) since the vacated carbon orbitals would be perpendicular to the plane of the ring pi system, see IV, or perpendicular to the first ionization's vacated orbital on the benzylic carbon.




(IV)

The n.m.r. spectra of polymethyl substituted benzotrichlorides dissolved in 100 percent sulfuric acid are consistent with formation of the charged species which has been shown to be the dicarbonium ion. The corresponding substituted benzoic acids in sulfuric acid show n.m.r. absorptions at about the same field strength as the substituted benzotrichlorides. Volume susceptibility difference between solvent and reference and between reference and sample cause the chemical shifts to vary slightly as can be seen in the values given in Table 2 for the resonance positions.

The ultra-violet spectra of the substituted carbonium ions and substituted acylium ions would be expected to be different. Steric hindrance of the unionized polymethylbenzotrichlorides has been shown to produce bathochromic shifts in the benzenoid absorption band in their ultraviolet spectra. When the substituted benzotrichlorides are dissolved in sulfuric acid, the loss of a chloride ion

Table 2. Proton magnetic resonance spectra of pentamethyl and 2,4,6-trimethyl substituted benzotrichlorides and benzoic acids in various solvents.

| Compound/Solvent | Resonances | | | Reference |
|---|---|---|---|---|
| Pentamethylbenzotrichloride in: | o | p | m | |
| Sulfur Dioxide-Boron Trichloride | 7.16 | 7.39 | 7.68 | TMS |
| Sulfuric Acid | 7.10 | 7.25 | 7.42 | MSA |
| Sulfuric Acid | 7.20 | 7.43 | 7.71 | TMS |
| Sulfur Dioxide-Boron Fluoride | 7.40 | 7.63 | 7.90 | TMS |
| Pentamethylbenzoyl ion in: | o | p | m | |
| Sulfuric Acid | 7.62 | 7.76 | 7.95 | TMS |
| Trifluoroacetic Acid-Boron Fluoride | 7.68 | 7.70 | 7.77 | TMS |
| Sulfur Dioxide-Boron Chloride | 7.83 | 8.00 | 8.19 | TMS |
| Sulfur Dioxide-Boron Fluoride | 7.64 | 7.71 | 7.74 | TMS |
| Trichloromethylmesitylene in: | aryl | o | p | |
| Sulfuric Acid | 3.03 | 7.60 | 7.69 | TMS |
| Sulfur Dioxide-Boron Chloride | 2.58 | 7.03 | 7.42 | TMS |
| Trifluoroacetic Acid-Boron Fluoride | 3.03 | 7.57 | 7.67 | TMS |
| Sulfuric Acid | 2.53 | 7.27 | 7.57 | TMA |
| Mesitoyl ion in: | aryl | o | p | |
| Sulfuric Acid | 2.53 | 7.27 | 7.57 | TMA |
| Sulfuric Acid | 2.22 | 6.91 | 7.05 | TMS |

(internal TMS = Tetramethylsilane, $\tau$ = 10.00, MSA = internal Methane Sulfonic Acid, $\tau$ = 6.19, and internal TMA = Tetramethylammonium Tetrafluoroborate, $\tau$ = 6.90).

leaves a charge in the system. The introduction of this charge in the chromophoric system gives rise to the quite different (from the parent compound) charge-transfer resonance spectrum.[46] Ionization of the corresponding substituted benzoic acids to the respective acylium ions also leaves a positive charge in the molecular system. Again, the introduction of the charge gives rise to a quite different spectrum from the unionized parent compound. The monocation (II) can lose a second chloride ion leaving a vacant orbital on the carbon atom between the ring and remaining chlorine atom,, see structure (IV). This orbital would be parallel to the plane of the ring, but could be stabilized by resonance with the non-bonding electrons on the remaining chlorine, as

Sufficient information is not available to accurately assign the absorption bands of the dication, but it is predicted to absorb at wavelengths greater than 320 mμ (in the visible region) for excitation of the valence bond (charge-non-bonding system), and the charge resonating between the ring and carbon atom attached to the ring results in the bathochromic shift of the "ethylenic" bands in the ultra-violet spectrum.[46]

## 2. Isolation of Dicarbonium Ion Salts

It was decided to attempt preparation of crystalline salts of dicarbonium ions derived from benzotrichlorides.

Fish[42] tried to obtain a solid material from the reaction of pentamethylbenzotrichloride with boron trifluoride in trifluoroacetic acid-trifluoroacetic anhydride. The red semi-solid obtained after removing the solvent had an identical n.m.r. spectrum with that of pentamethylbenzotrichloride dissolved in 100 percent sulfuric acid (except that it was displaced to higher field strength due to solvent volume susceptibility difference--see Table 2). Roobol[43] attempted to obtain a solid from the reaction of 2,4,6-trimethylbenzotrichloride with silver tetrafluoroborate. A material was obtained which could not be purified, but had the dark red appearance similar to that produced when 2,4,6-trimethylbenzotrichloride is dissolved in 100 percent sulfuric acid.

A sulfur dioxide solution of fluoboric acid was prepared by mixing equimolar quantities of liquid boron trifluoride and hydrogen fluoride as sulfur dioxide solutions. Purity of the substituted benzotrichlorides was assured from an infrared spectrum of the material, which did not have any carbonyl absorption (from hydrolysis). The tetrafluoroborate salts of pentamethylphenylchlorodicarbonium and 2,4,6-trimethylphenylchlorodicarbonium ions were prepared by reaction of the respective substituted benzotrichlorides with fluoboric acid in liquid sulfur dioxide. Removal of the solvent gave crystalline solids, melting at 147-148° and 127-128° respectively, which were characterized by determination of chloride ion, tetrafluoroborate ion, and amount of acid produced when a sample of the salt was hydrolyzed. Analysis

for carbon and hydrogen content was not attempted due to the great ease of salt hydrolysis.

A weighed salt sample was hydrolyzed by placing it in ca. 33 percent aqueous acetone solution. Addition of a silver nitrate solution precipitated the chloride ion as 0.98 moles of silver chloride. The formation of the dication would require that one mole of chloride remain in the species and be liberated as chloride ion when the salt hydrolyzed, as

$$R\text{-}CCl_3 + 2\ HBF_4 \rightarrow R\text{-}C^{++}\text{-}Cl + 2\ HCl + 2\ BF_4^-$$

$$R\text{-}C^{++}\text{-}Cl + 2\ H_2O \rightarrow R\text{-}COOH + Cl^- + 3\ H^+$$

Another sample of the salt was hydrolyzed in ca. 50 percent aqueous acetone solution. Addition of a cold, 5 percent acetic acid solution of 4,5-dihydro-1,4-diphenyl-3,5-phenylimino-1,2,4-triazole (Nitron reagent)[48,49] precipitated the tetrafluoroborate ion. The resulting precipitate was 97 to 98 percent of theory for two moles of tetrafluoroborate ion per mole of salt. The nitron complex with tetrafluoroborate ion can be used for gravimetric determination of the tetrafluoroborate ion,[49] but the tetrafluoroborate ion does hydrolyze slowly to boric and hydrofluoric acids, as

$$BF_4^- + 3\ H_2O = H_3BO_3 + 4\ F^- + 3\ H^+ \quad K_{eq} = 2.5 \times 10^{-19} @ 18^\circ$$

The amount of acid produced from a salt sample hydrolyzed in ca. 50 percent aqueous acetone solution was determined by titrating to a phenolphthalein endpoint with standard sodium hydroxide solution. Hydrolysis of the polymethylphenylchlorodicarbonium tetrafluoroborates should yield an acidic solution consisting of the substituted carboxylic

acid, hydrochloric acid, and two moles of fluoboric acid.

$$R\text{-}C^{++}\text{-}Cl \cdot 2\ BF_4^- + 2\ H_2O \longrightarrow RCOOH + HCl + 2HBF_4$$

Four equivalents of titratable strong acid should be produced. If some of the tetrafluoroborate ion hydrolyzes further, the value for the acid content will be somewhat greater than four equivalents per mole of salt. The titrations showed 102 percent of four equivalents of acid per mole of hydrolyzed salt. This result indicates only slight hydrolysis of the tetrafluoroborate ion. Attempts to analyze for the amount of boric acid produced gave poor results (indicating an unreliable procedure).

N.m.r. spectra of the pentamethylphenylchlorodicarbonium and 2,4,6-trimethylphenylchlorodicarbonium tetrafluoroborates showed resonances relative to an internal reference of tetramethylsilane in liquid sulfur dioxide as shown in Table 2. It will be noticed that these resonance values are ca. 0.2 $\tau$ units higher than the resonances of the corresponding polymethylbenzotrichlorides in 100 percent sulfuric acid. This difference in field strength can be attributed to the solvent susceptibility. In sulfuric acid, the dicarbonium ions are probably associated with bisulfate anions, which being similar to the solvent will result in a lower resonance energy. The low field resonance in the pentamethylphenylchlorodicarbonium ion spectrum is assigned to the ortho methyl groups (relative to the site of ionization) in view of the adjacent electron-withdrawing group.[27] Symmetry of the molecule and the relative peak areas indicate the para

and meta methyl group resonances, respectively, appear next with increasing field strength. This order of appearance in the spectrum is consistant with the plausible resonance structures, where the para position bears more of the ring charge, on the average, than the meta position.

The ultraviolet-visible spectrum of the pentamethylphenylchlorodicarbonium ion in sulfur dioxide is similar to that of pentamethylbenzotrichloride in 100 percent sulfuric acid, showing bands at 545 mμ (log $\epsilon$ = 3.38), 393 mμ (log $\epsilon$ = 4.54), and 385 mμ (log $\epsilon$ = 4.51).

Tetrachloroborate salts of pentamethylphenylchlorodicarbonium and 2,4,6-trimethylphenylchlorodicarbonium ions were prepared using the methyl substituted benzotrichloride and boron trichloride in liquid sulfur dioxide. Details of the preparation are described in a later section. The tetrachloroborate salts were characterized by chloride analysis and by the amount of acid produced on hydrolysis of the salt.

A weighed sample of the tetrachloroborate was hydrolyzed in ca. 50 percent aqueous acetone solution. Addition of silver nitrate solution precipitated the chloride ion as silver chloride. This gravimetric determination showed 98 percent of the silver chloride expected for the hydrolysis of the dicarbonium tetrachloroborate into nine moles of chloride ion per mole of salt hydrolyzed.

$$R\text{-}C^{++}\text{-}Cl \cdot 2\ BCl_4^- + 8\ H_2O \rightarrow RCOOH + 9\ HCl + 2\ H_3BO_3$$

The amount of acid produced on hydrolyzing a sample

of the dication tetrachloroborate salt was determined by titrating the solution with standard sodium hydroxide to a phenolphthalein endpoint. The titration showed that 99 percent of the ten equivalents of strong acid expected per mole of hydrolyzed salt was obtained. An attempt to titrate the boric acid present, using the standard procedure of complexing the weak acid with mannitol, gave inconsistent results. Carbon and hydrogen content was not analyzed for, similar to the tetrafluoroborates, for the tetrachloroborates hydrolyze with such great ease.

N.m.r. spectra of the pentamethylphenylchlorodicarbonium tetrachloroborate and 2,4,6-trimethylphenylchlorodicarbonium tetrachloroborate show resonance values for the protons given in Table 2. As with the tetrafluoroborate salts, the n.m.r. spectra agree in number of resonances, relative position, and relative area of peaks, but not in absolute $\tau$ value for the resonances from the respective substituted benzotrichloride in 100 percent sulfuric acid. Although present in small quantity, any excess boron chloride present will influence the position of resonance in the n.m.r. spectrum.

Infrared spectra of pentamethylphenylchlorodicarbonium and 2,4,6-trimethylphenylchlorodicarbonium tetrachloroborates show a broad band at 13.1 to 13.5 $\mu$, characteristic of the tetrachloroborate ion, and absoprtions attributable to the carbon skeleton of the respective dication.

Visible-ultraviolet spectra of the dicarbonium tetrachloroborates were essentially identical to the respective

pentamethylphenylchlorodicarbonium and 2,4,6-trimethylphenylchlorodicarbonium tetrafluoroborates in sulfur dioxide ( see Figure I' ).

3. Solvolysis of Polymethylphenylchlorodicarbonium Salts

Hydrolysis of a sample of polymethylphenylchlorodicarbonium tetrafluoroborate, or tetrachloroborate, yields the corresponding polymethylbenzoic acid quantitatively. The same polymethylphenylchlorodicarbonium salt produces the corresponding methyl polymethylbenzoate quantitatively when placed in anhydrous methyl alcohol. These reactions proceed via a common acylium ion.[12,43]

When a sample of polymethylphenylchlorodicarbonium salt is dissolved in ether a solution results having a similar color to that of the salt; thus the pentamethylphenylchlorodicarbonium tetrafluoroborate forms a purple solution in ether. It was reported by Roobol[43] that the polymethyldicarbonium ions (in particular 2,4,6-trimethylphenylchlorodicarbonium ion) react with ether producing the corresponding ethyl polymethylbenzoate. He further reported the reaction to be general so that ethers as a class reacted with dicarbonium ions to produce the corresponding esters. In each case where Roobol prepared the dication, trifluoroacetic acid was used as the solvent, and the cationic species was generated by passing boron trifluoride through a solution of the substituted benzotrichloride. In several instances he reported that the ester was found, but in other attempts the product was the corresponding benzoic acid. Re-examination

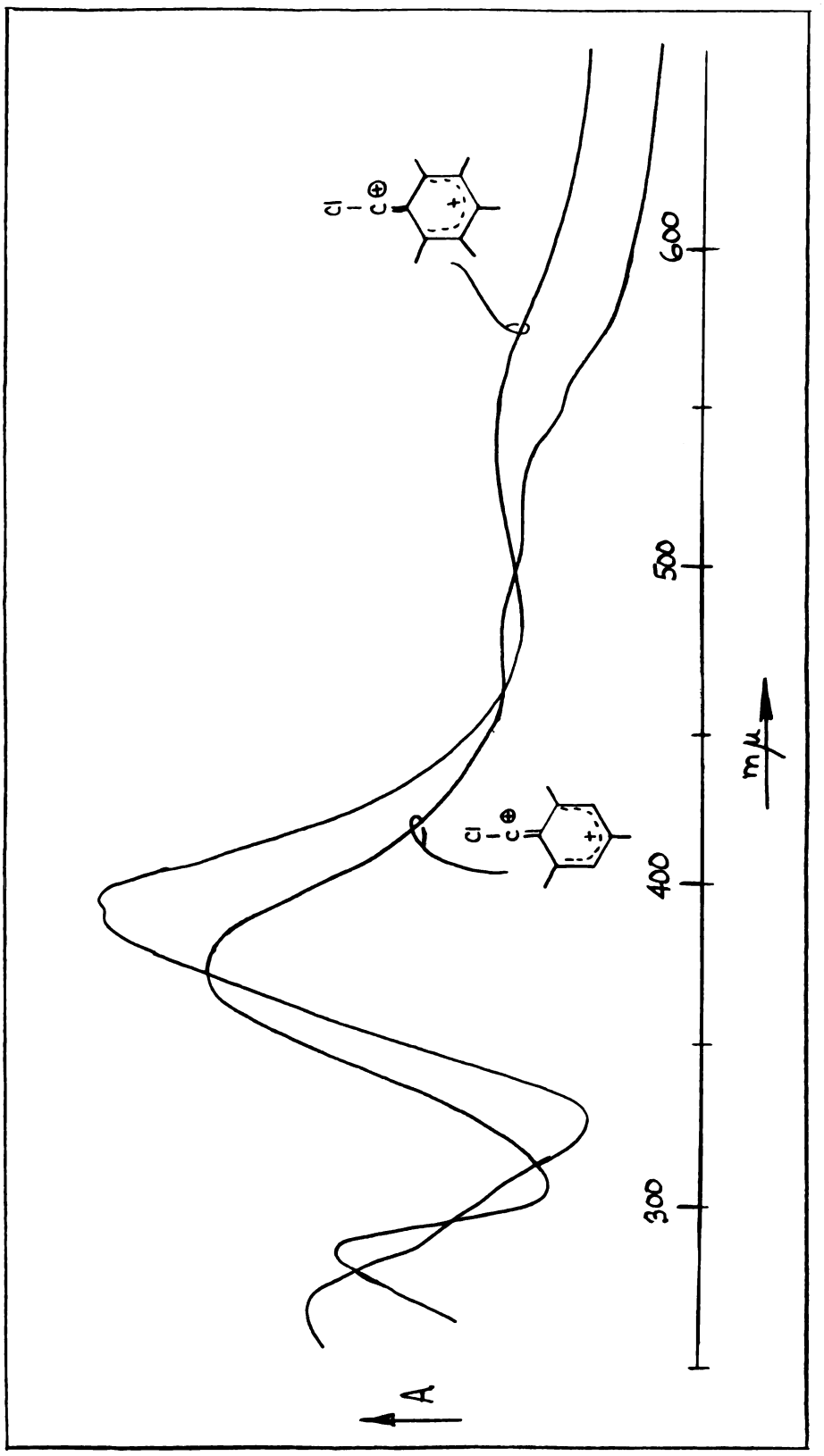
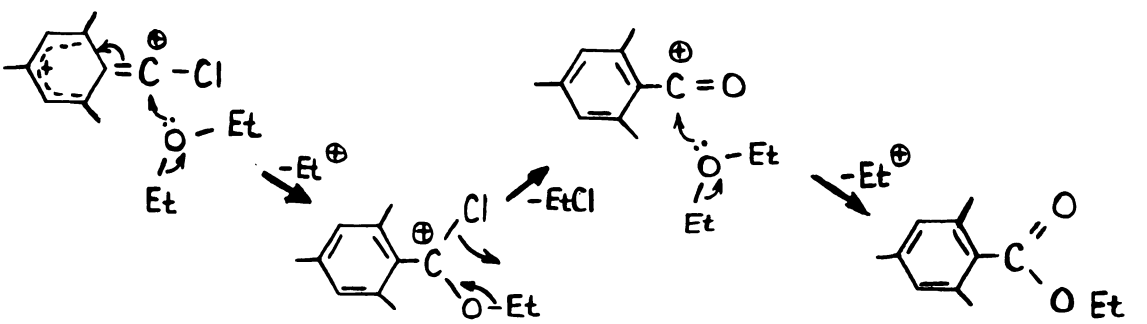



Figure I'. Ultraviolet-Visible Spectra of Pentamethylphenylchlorodicarbonium and 2,4,6-Trimethylphenylchlorodicarbonium Tetrafluoroborates and Tetrachloroborates in $SO_2$ Solution.

of the reactions reported by Roobol supports the conclusion that the particular experimental conditions determined which product was obtained. Roobol found that when a solution of ether and trifluoroacetic acid was treated with boron fluoride for four hours, no bands due to ethyl alcohol or ethyl trifluoroacetate were found in the infrared spectrum of the product. He concluded that ether was not cleaved by these reagents. The observed formation of ester or acid from the reaction of dicarbonium ions in ether solutions was explained by postulating formation of an anhydride and/or mixed anhydride, which then underwent reaction yielding the observed products.




In the present work 2,4,6-trimethylphenylchlorodicarbonium salt was dissolved in ether and agitated at room temperature for 24 hours. No change was observed in the appearance of the red solution, and when the ether solution was poured onto ice, mesitoic acid was recovered quantitatively. The same experiment was repeated using refluxing ether. After 24 hours the solution had turned black, but, on hydrolytic work up, only mesitoic acid was obtained. When a sample of the tetrachloroborate in ether was stirred at room temperature for 24 hours, followed by complete removal of the ether, the starting trichloromethylmesitylene was

obtained. Such reversion of the salt to its reactants had also been observed in the preparation of the tetrachloroborate salts, vide infra. The equilibrium obviously may be forced

to the left by removal of all the boron chloride. When preparing the tetrachloroborate salt, if the excess reactants are vaporized and removed under reduced pressure, care must be taken not to prolong the pumping operation lest the benzotrichloride be recovered. It is here concluded that reaction is not occurring between ether and the dicarbonium ion per se. Rather, in the presence of a strong electrophile the ether may react with the electrophile; the product reacts in turn with the dication.

4. Hydride Transfer to Dicarbonium Ions in Solution

A sample of 2,4,6-trimethylphenylchlorodicarbonium tetrachloroborate was prepared, in the manner described for the preparation of the salt, and dissolved in a small quantity of liquid sulfur dioxide. An n.m.r. spectrum of the solution showed the three resonances characteristic of the dication (see Table 2). To this solution was added, in two experiments, an equimolar and a twofold excess of triphenylmethane. A sample of triphenylmethane was used to obtain a reference n.m.r. spectrum in sulfur dioxide. N.m.r. spectra of the reaction solutions of triphenylmethane and 2,4,6-trimethylphenylchlorodicarbonium tetrachloroborate were run repeatedly

for four hours. No change was apparent in position or intensity of the resonance peaks for either reactant.

When cycloheptatriene was substituted for triphenylmethane in an attempt to transfer a hydride ion from the cycloheptatriene to 2,4,6-trimethylphenylchlorodicarbonium tetrachloroborate, in liquid sulfur dioxide as described above, the complex n.m.r. spectrum of the solution showed no change. The solution was hydrolyzed, and only mesitoic acid was isolated.

5. Attempted Reaction of 2,4,6-Trimethylphenylchlorodicarbonium Tetrachloroborate with Phenyl Lithium

Phenyl lithium was allowed to react with a sample of 2,4,6-trimethylphenylchlorodicarbonium tetrachloroborate in ether. There was an exothermic reaction as the brown and red (respectively) solutions were mixed. A white amorphous solid m.p. 205-207° was isolated from the reaction after hydrolysis and work up. An n.m.r. spectrum of the product, in deuterated acetone, showed two types of protons at low field (one aromatic and the other at a little higher field strength), and a small methyl resonance, with relative areas 16 to 2 respectively. An infrared spectrum (potassium bromide pellet) showed an O-H stretch and several sharp bands, but the identity of the solid has not been established.

6. Attempted Reaction of 2,4,6-Trimethylphenylchlorodicarbonium Tetrachloroborate with Methyl Magnesium Iodide

In a manner exactly analogous to that described before, 1.5 g of trichloromethylmesitylene was used to prepare

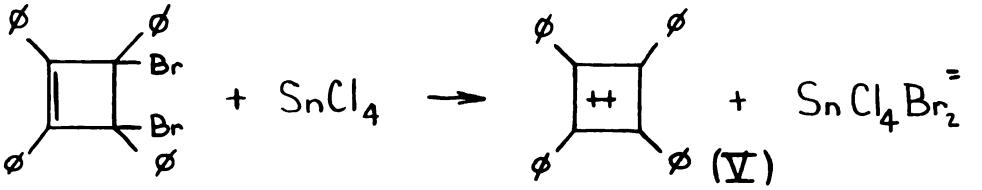
2,4,6-trimethylphenylchlorodicarbonium tetrachloroborate. The salt was dissolved in ether to form a bright red solution. Methyl magnesium iodide, in ether, was then allowed to drop into the stirred dication solution. A vigorous reaction occurred even though the dication solution was being cooled with an ice bath. A brown semi-solid formed during the addition. After an aqueous workup the gelatinous mass was extracted with ether, pentane, and carbon tetrachloride. The dark red organic layer was decolorized and attempts were made to crystallize any products. No solid was obtained. An infrared spectrum was taken on the syrup (freed of solvents under reduced pressure). The spectrum showed a few broad absorptions and several sharp bands. Identity of the syrup was not established, but it was noted that the syrup was not methyl 2,4,6-trimethylbenzoate for there was no carbonyl stretching frequency in the infrared spectrum.

## 7. Attempted Preparation of Cycloöctatetraene Dibromide Dication

The formation of an aromatic system might be accompanied by a sufficient decrease in internal energy to compensate for the charge repulsion involved in formation of a dicarbonium ion.[11] This decrease in energy also has to be greater than the energy increase caused by unfavorable geometric or steric conformations.

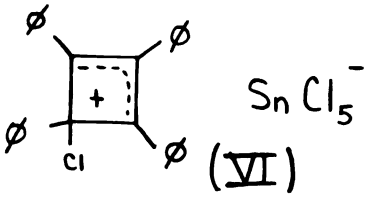
A planar, four-membered Hückel aromatic system with two pi electrons was claimed to be the product formed by abstracting two bromide ions from 3,4-dibromotetraphenylcyclobutene, using stannic chloride as the abstracting Lewis acid.[28]

X-ray examination by Bryan[22] showed that the crystalline




(V)

material was in fact the chloromonocation pentachlorostannate (VI) and not the dication (V). Freedman[21] thought that




(VI)

solvation forces, absent in the solid state, might be the decisive factor in the formation of the aromatic system (V), and investigated tetrafluoroborate as the stabilizing anion. He succeeded in preparing the dicarbonium tetrafluoroborate in methylene chloride.

A planar eight-membered ring with six or ten conjugated pi electrons should constitute a Hückel aromatic system. Katz[25] has prepared the ten electron system by adding two electrons (from sodium metal) to cycloöctatetraene, in an ether solvent. Apparently the increased strain required to make the eight-membered ring planar is not sufficiently large to prevent aromatization. An n.m.r. spectrum of the cycloöctatetraene dianion shows a single sharp line indicating that the protons are in equivalent, or an averaged equivalent, magnetic environment. Except for two non-bonding orbitals being empty (see Fig. 1), the six pi-electron, eight-membered cycloöctatetraene dication aromatic system should be as stable as the ten; indeed, it

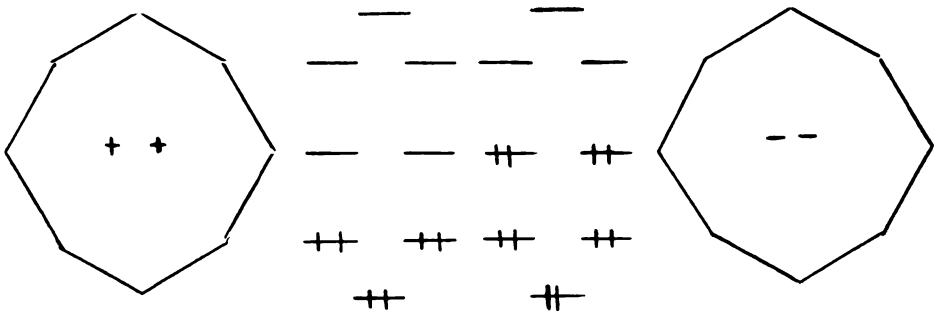
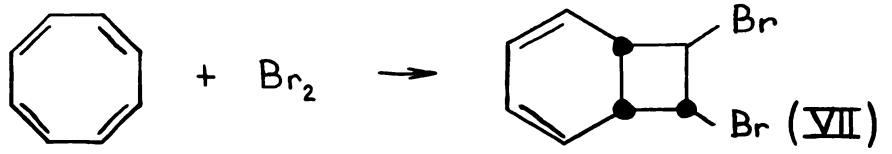


Figure 1. Molecular orbital energy level diagram of cycloöctatetraene dianion and dication.

might be the more stable because of less electron repulsion.

Cycloöctatetraene dibromide (7,8-dibromobicyclo-[4,2,0]-octa-2,4-diene) was prepared as a white crystalline solid, melting 32.5 to 33.5°, from reaction of bromine with cycloöctatetraene in methylene chloride. A maleic anhydride adduct of the dibromide had the same melting point (203-204°)




as reported;[13] and the n.m.r. spectrum shows an octet centered at 5.65 τ, which as a first order prediction, has led Allinger[23] to assign a trans arrangement to the bromines. Cycloöctatetraene dibromide is not thermally stable, for even at room temperature it rapidly darkens and melts to a syrup. After preparation, the dibromide was stored in dry ice either as the solid, or in nitromethane solution.

Attempts were made to remove the bromines as bromide ions from dibromocycloöctatetraene by reaction of the dibromide with silver tetrafluoroborate or silver perchlorate

in methylene chloride or nitromethane. Removal of the bromide ions could leave a dicarbonium ion which, if it were to become planar, would constitute a stable Hückel aromatic system. This reaction would require several rearrangements. First, the bromines in the dibromide molecule are trans to one another,[23] one of them undoubtedly being more hindered to attack by an electrophile than the other. The bromines may be removed individually or both at the same time. In either case, the reaction might require a rather high activation energy. Second, the molecular carbon skeleton of cycloöctatetraene dibromide has been shown to be that depicted as (VII).[23,13] The bonding of the molecule would have to rearrange before, during, or after the bromines were moved to form an eight-membered ring. Third, the dibromide molecule is not planar; so the structure would have to become planar. This would require overcoming any unfavorable geometric strain energy increase by the energy gained by aromatization of the molecule. Fourth, if two cations are produced, the repulsion between the like charges could be high enough to cause molecular rearrangement before both charges are produced on the ring.

Three observations could be used to determine whether or not the dication was found; the electronic spectrum, the n.m.r. spectrum, and the stoichiometry of the reaction. Both the Hückel theory and the self-consistant field molecular orbital theory indicate that the anion and cation of an alternant system, whether even or odd, should have the same

long wavelength absorption. The spectrum of the dianion is known.[25] If the dication were formed, one would expect it to have a simple (single line) n.m.r. spectrum analogous to that of the dianion, but shifted to lower field. Finally, two moles of silver bromide should be formed per mole of cycloöctatetraene dibromide used.

The quantity of silver bromide obtained from reaction between cycloöctratetraene and silver tetrafluoroborate in nitromethane was determined using standard gravimetric analytical techniques. These analyses showed that only 1.4 to 1.8 moles of silver bromide were produced per mole of dibromide. N.m.r. spectra of filtered solutions were complex, unlike the simple dicarbanion spectrum. It was thought that perhaps another electrophile than silver ion might serve to remove the bromide ion. Boron tribromide was allowed to react with either a liquid sulfur dioxide, or a methylene chloride solution of cycloöctatetraene dibromide (the sulfur dioxide solution was not homogeneous). A vigorous reaction ensued when the reagents were mixed, but on hydrolytic workup of the solution to obtain products, two materials were obtained. Repetition of the experiments did not yield the same products. Infrared, n.m.r., and visible-ultraviolet spectra were taken on the two major products, but were insufficient for product identification. It was thought that the heterogeneous system, and possibly a reaction of the boron tribromide with sulfur dioxide were the major causes for inconsistent results. Qualitative elemental analysis of

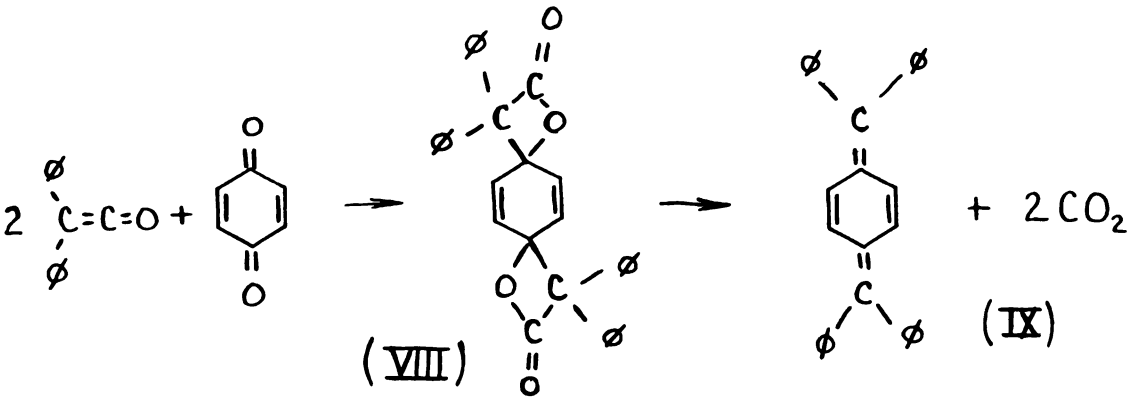
the product showed that sulfur and bromine were present in the reaction products. Mass spectral analysis showed bromine present in the reaction products in both solvent systems, as well as intermolecular reaction products.

The reactions tried for production of the eight-membered dicarbonium ion seem to produce an entity which is either too reactive for the reaction conditions being employed, or not sufficiently stable to remain once produced. It is thought however, that perhaps with a larger anion (e.g., hexafluoroantimonate) the dication of the eight-membered Hückel aromatic system might be prepared.

## 8. Electron Transfer from Tetraphenyl-p-xylylene to Tetraphenyl-p-xylylium Dicarbonium Ion

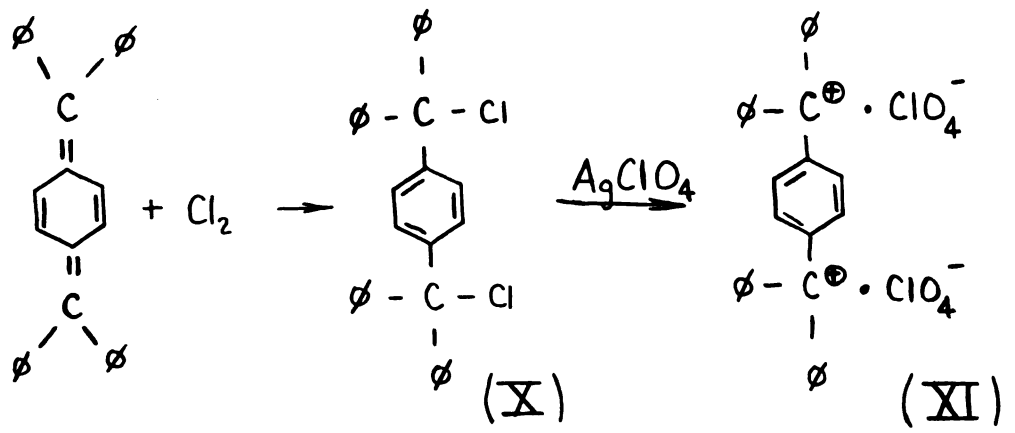
Rapid electron transfer between α,α,α',α'-tetraphenyl-p-xylylene and the corresponding dichloride in liquid sulfur dioxide was observed some time ago.[26] The originally yellow solutions became intensely reddish-brown upon mixing, presumably due to the formation of radical-ion, then called "a meriquinoid salt." In the present work, reaction (2) on page 5 was investigated in more detail.

Tetraphenyl-p-xylylene was prepared as a yellow-orange solid, melting at 248°, from the thermal decomposition of the bis-β-lactone (VIII) which in turn was obtained by reaction of diphenylketene with quinone (the stereochemistry of VIII is not known).



The visible spectrum of tetraphenyl-p-xylylene (IX) in dioxane showed an absorption band at 424 mμ (log ε = 4.68). Its n.m.r. spectrum showed a broad aromatic proton resonance at 2.82 τ and a resonance at 3.09 τ, which was assigned to the quinoid hydrogens. Electronic integration of the n.m.r. spectrum showed the resonances to have an area ratio of five to one respectively.

Reaction of tetraphenyl-p-xylylene with chlorine gave a quantitative yield of the white crystalline bis-tetraphenyldichloro-p-xylene (X), m.p. 240-241°.



Bis-tetraphenyl-p-xylylium diperchlorate was prepared in 90 percent yield from the reaction of silver perchlorate with bis-tetraphenyldichloro-p-xylene in liquid

sulfur dioxide. The red-brown crystalline solid (XI), m.p. 143-145(d), was decolorized when dissolved in aqueous acetone and a quantitative yield of tetraphenyl-p-xylene diol, m.p. 169-170°, was obtained. The visible spectrum of bis-tetraphenyl-p-xylylium diperchlorate in methylene chloride showed absorptions at 424 mμ (log $\epsilon$ = 4.50) and 463 mμ (log $\epsilon$ = 4.57).

Equimolar methylene chloride solutions of bis-tetraphenyl-p-xylylene and bis-tetraphenyl-p-xylylium diperchlorate were prepared in separate vessels. After carefully degassing the solutions, they were placed into a stopped-flow apparatus. The pale yellow and orange solutions respectively were mixed; at the point of juncture of the two arms of the apparatus, no color change was observed until the flow was stopped. After flow was stopped, three seconds elapsed before the mixed solutions became deep red. Thus the half life of the reaction is approximately three seconds and if the reaction is first order in each reactant, and bimolecular, the rate constant is about $10^2$ liter moles$^{-1}$ sec$^{-1}$.

Most organic electron-transfer reactions are extremely fast. The relatively slow rate at which radical-cation (I) is formed may be the result of at least two steps, the electron-transfer and any molecular orientation required for the transfer. The electron-transfer itself probably occurs very rapidly; the slow apparent rate of reaction may be a result of the necessity for proper spacial orientation of the

reactants. Reaction between the olefin and dication may require that the two molecules come into juxtaposition, unless of course the solvent acts as a bridge for the electron transfer. The molecules need not be completely superpositioned on one another but should be aligned well enough to permit electron transfer. The dication exerts an attraction for two rather bulky perchlorate anions. Depending on the tightness of this ion-pair, transfer from the olefin may be fast or slow. In a tight ion-pair the bulky anions prevent close approach of the olefin to the dication. The tightness of the ion-pair is affected by the distribution of positive charge in the cation (thus substituents on the phenyl rings which would tend to alleviate the positive charge would weaken the ion-pair bonding), and also by the distribution of charge in and size of the anion. With greater distribution of the positive charge over the cation, the anion will not be held as tightly and in a polar solvent may be more easily separated (making molecular orientation easier and reaction more readily possible). In a similar way, closeness of approach during transfer would affect any attraction of the cation for the olefin's electron.

Thus, the rate of reaction may depend upon the high entropy of activation for the orientation step. Under favorable circumstances this entropy would be lowered to the point where the observed rate would approach that for the electron transfer.

Only one product is expected from the reaction between tetraphenyl-p-xylylene and bis-tetraphenyl-p-xylylium

diperchlorate. If the radical-ion is more stable than the reactants, none of the latter (if equimolar at the start of reaction) should remain. A visible spectrum of the dark red methylene chloride-product solution showed an absorption band at 580 mμ. Since this absorption did not appear in the visible spectrum of either reactant, it can be assumed that this absorption is due only to the product. By means of a simple concentration and extinction coefficient relationship with the reactants, it can be shown that the product must be present at least to the extent of 64 percent. This value is based on the assumption of zero absorption by the radical-ion in a region where the reactants have an absorption maximum; since this is highly unlikely, it is probable that the equilibrium lies very far toward the product side. Weitz and Schmidt[26] thought the product was a radical by noting that if the darkly colored product solution was exposed to the atmosphere (or oxygen) the solution lost its color in ca. ten seconds. This observation was confirmed. Additional evidence for the radical was obtained in the present work from an electron spin resonance (e.s.r.) spectrum of the darkly colored reaction solution. The e.s.r. spectrum was rather poorly resolved at room temperature (see Fig. 24), but by lowering the temperature to ca. $-90^{\circ}$ resolution was improved to where 23 equally spaced lines, having a splitting of 0.69 gauss (possibly hyperfine interactions), could be seen (Fig. 25). The e.s.r. spectrum cannot as yet be analyzed completely. Equivalent interaction

of the odd electron with all hydrogens in the molecule would not be expected, because of the non-equivalence of the hydrogens in plausible resonance structures. The relative areas of the e.s.r. peaks eliminate this possibility. It is surprising that the observed spacing is so regular where the splitting constants for the four types of protons present are quite likely to be different. If the four phenyl groups had substituents, e.g., para methyl groups, interpretation of the e.s.r. spectrum might be simplified.

An n.m.r. spectrum of the radical-ion in methylene chloride (Fig. 26) showed multiplet resonances at 2.40, 2.55, and 2.87 $\tau$. The dication showed n.m.r. peaks at 2.62 and 2.81 $\tau$, and tetraphenyl-p-xylylene showed resonances at 2.82 and 3.09 $\tau$ (all multiplets). These spectra indicate that the protons in the radical-ion are influenced by the carbonium ion deshielding, but, surprisingly show little signal broadening due to the unpaired electron.

To examine the behavior of the radical-ion more closely, the solvent, methylene chloride, was removed under reduced pressure from the darkly colored solution resulting from reaction of equimolar amounts of tetraphenyl-p-xylylene and tetraphenyl-p-xylylium dication. A yellow-orange solid remained in the flask. This solid became lighter when the solid was cooled (becoming very pale yellow at liquid nitrogen temperature, ca. -200°) and darker when the solid was warmed (becoming red-orange at ca. 100°). This color change was perhaps due to a shift in the equilibrium of the radical-ion

with the olefin and dication (to the left in (2)), or to the free electron becoming more mobile as the energy barriers to rotation (and vibration) are overcome. An e.s.r. spectrum showed a very broad signal for the yellow-orange solid (ambient temperature). Neither the olefin nor the dication showed an e.s.r. signal, even when heated to ca. 100°, as the solid. When methylene chloride was added to the yellow-orange solid the solution once again had the same deep red appearance as the solution prepared from the reactants. A visible spectrum of the dissolved solid showed an absorption band at 580 mμ. The absorption of dissolved solid was less than for a freshly prepared (equal concentration) solution, but probably this was due to a trace of oxygen in the solvent reacting with the radical. An infrared spectrum taken on the solid (potassium bromide pellet and methylene chloride solution) showed the same absorptions as the originally prepared solution, but was rather poorly resolved. Thus it seems the radical-cation of the tetraphenyl-p-xylyl skeleton is isolable as a solid material (although little was done to crystallize or purify this material). In view of the stability of the triphenylmethyl radical this seems plausible however. By varying substituents on the four phenyl groups, it should be possible to alter the stability of the radical-cation, and to affect the rate of electron transfer.

## Part II. Acylium Ions

### 1. The $pK_R$'s of Some Acylium Ions

The behavior of benzoic acids in concentrated sulfuric acid may be used to determine their base strength. A quantitative measure of the proton-donating ability of a solvent to a Hammett base is the acidity function $H_o$, defined[34] as

$$H_o = pK_{BH^+} - \log \frac{C_{BH^+}}{C_B}$$

where $C_{BH^+}/C_B$ is the observed ratio of the concentration of base in its protonated and unprotonated forms, and $K_{BH^+}$ is the ionization constant of the base (referred to dilute aqueous solution). Starting with a base for which the pK is known, $H_o$ has been evaluated for mixtures of water-sulfuric acid.[35] From the value of $H_o$ for a given medium and the ratio of protonated to unprotonated base, pK may then be calculated for a base of unknown strength.

When equilibria of the type

$$ROH + H^+ = R^+ + H_2O$$

are studied, a number of cases follow another acidity function $H_R$, where the activity coefficient of water is not unity, and the function is defined[36] by the equation

$$H_R = H_o + \log a_{H_2O}$$

Williams and Bevan[37] and Deno,[38] using arylcarbinols, showed that the acidity function $H_R$ can be expressed by the relation

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

Arnett and Bushick[40] studied the thermodynamics of the carbinol-carbonium ion equilibrium in aqueous sulfuric acid, and found that the $H_R$ scale, like $H_o$, is not very temperature dependent.

The similarity between the carbinol-carbonium ion equilibrium and the hindered aromatic acid, or ester-acylium ion equilibrium suggested that a study of the ionization of hindered aromatic acids, or

$$ArCOOH + H^+ = ArC^+O + H_2O$$

esters in varying strengths of aqueous sulfuric acid might be fruitful.[39]

The equilibrium between a hindered aromatic acid and the corresponding acylium ion can be studied spectrophotometrically because the acid (free or protonated) and the acylium ion usually have different electronic spectra. One might also use n.m.r. spectroscopy to determine the relative concentrations of acid and acylium ion provided the chemical shifts for some or all of the protons on the aromatic ring or on substituents differ for the two types of species. The pK values of pentamethylbenzoic acid, 2,4,6-trimethylbenzoic acid, 2,3,4,5-tetramethylbenzoic acid, 2,3,5,6-tetramethylbenzoic acid, 4-bromo-2,3,5,6-tetramethylbenzoic acid, and 2,6-dimethylbenzoic acid were obtained spectrophotometrically (by C. Y. Wu[18]) using ultraviolet spectra, taking advantage of the fact that most acylium ions have a strong absorption band in the 280-310 mμ region. These values are compared in Table 3, with values obtained using n.m.r.

Table 3. pK values for some substituted benzoic acids from ultraviolet and n.m.r. spectra.

| Substituted Acid | pK from U.V. Spectra | pK from NMR Spectra |
|---|---|---|
| Pentamethyl | -18.81 | -19.14 |
| 2,3,4,5-Tetramethyl | -22.07 | -22.05 |
| 2,3,5,6-Tetramethyl | -20.38 | -20.40 |
| 4-Bromo-2,3,5,6-tetramethyl | -20.68 | -20.93 |
| 2,4,6-Trimethyl | -20.43 | -20.49 |
| 2,6-Dimethyl | -21.70 | -21.76 |

Values for pK of the substituted benzoic acids using n.m.r. were obtained in an analogous manner to that used for 2,4,6-trimethylbenzoic acid which follows as an example: In sulfuric acid media which were thought to be of sufficient strength that the protonated and unprotonated (ionized and unionized) substituted acid was present n.m.r. spectra of the acid were taken using tetramethylammonium tetrafluoroborate as an internal reference. The n.m.r. spectrum of the substituted acid in sulfuric acid solutions of intermediate strength to those used for the completely ionized and unionized acid were then taken, see Figure 23. Electronic integration of the spectrum of partially ionized acid allowed the ratio of ionized to unionized acid to be calculated for each sulfuric acid strength used. These ratios are shown in Table 4 for 2,4,6-trimethylbenzoic acid. Using the known values of $H_R$ for each sulfuric acid strength and the ratio of ionized to unionized acid, a value for pK can be calculated, as in Table 4, using the relationship

$$pK = H_R - \log \frac{[\text{ionized acid}]}{[\text{unionized acid}]}$$

Table 4. Determination of pK for 2,4,6-trimethylbenzoic acid using n.m.r. data in sulfuric acid.

| % $H_2SO_4$ | % ionized/% unionized(Q) | log Q | $H_R$ | $pK_R$ |
|---|---|---|---|---|
| 95.85 | $\frac{.250}{.750}$ = .334 | .476 | -20.02 | -20.49 |
| 96.10 | $\frac{.253}{.747}$ = .339 | .469 | -20.10 | -20.57 |
| 96.72 | $\frac{.406}{.594}$ = 1.03 | -.013 | -20.22 | -20.23 |
| 97.14 | $\frac{.566}{.434}$ = 1.31 | -.117 | -20.33 | -20.44 |
| | | | av. = | -20.41 |

The agreement between values obtained by both methods is reasonably good, and evidently warrants the use of n.m.r. as a new technique to study the ionization of weak bases. The pK's of 4-fluoro-2,3,5,6-tetramethylbenzoic acid, 4-chloro-2,3,5,6-tetramethylbenzoic acid, 4-bromo-2,3,5,6-tetramethylbenzoic acid, 4-iodo-2,3,5,6-tetramethylbenzoic acid, 4,4'- dicarbomethoxybiduryl, and 4,4'-dicarbomethoxy-2,2',6,6'-tetramethylbiphenyl were obtained only by the n.m.r. method (Table 6).

There are certain advantages and disadvantages in using the n.m.r. method. Since the n.m.r. peak areas can be integrated accurately, provided all the peaks are well separated, the indicator ratio Q, ($C_{RCO^+}/C_{RCOOH}$), can be measured directly. In this way so-called medium effects, which may cause $\lambda_{max}$ for the acid and its conjugate base to vary with acid strength are eliminated. Each indicator ratio can be measured independently, thus not requiring a series of

Table 5. N.m.r. data for protonated and unprotonated substituted benzoic acids in sulfuric acid solutions.

| Compound | % $H_2SO_4$ | Resonances (τ) |
|---|---|---|
| 2,6-Dimethylbenzoic Acid | 97 | 2.22, 7.05 |
| | 102 | 1.29(t), 1.92(d), 6.69 |
| 4-Bromo-2,6-dimethylbenzoic Acid | 97 | 2.09, 7.05 |
| | 100.4 | 1.77, 6.78 |
| 4-Iodo-2,6-dimethylbenzoic Acid | 97 | 1.90, 7.10 |
| | 100.4 | 1.50, 6.82 |
| 2,4,6-Trimethylbenzoic Acid | 95.0 | 2,48, 7.09, 7.17 |
| | 100.2 | 2.22, 6.91, 7.05 |
| 2,3,5,6-Tetramethylbenzoic Acid | 95 | 3.09, 8.03 |
| | 100.9 | 2.41, 7.65, 7.93 |
| 4-Fluoro-2,3,5,6-tetramethylbenzoic Acid | 90.9 | 7.27, 7.32 |
| | 104 | 6.95, 7.32 |
| 4-Chloro-2,3,5,6-tetramethylbenzoic Acid | 94.0 | 7.21, 7.22 |
| | 104 | 6.91, 7.14 |
| 4-Bromo-2,3,5,6-tetramethylbenzoic Acid | 90 | 7.15, 7.25 |
| | 102 | 6.75, 6.73 |
| 4-Iodo-2,3,5,6-tetramethylbenzoic Acid | 90 | 1.90, 7.10 |
| | 103 | 1.50, 6.82 |
| Pentamethylbenzoic Acid | 89 | 7.26 |
| | 98 | 6.82(o), 6.96(p), 7.14(m) |

solutions with equal indicator concentrations as is necessary with the spectrometric method. Usually four to six measurements are sufficient to obtain a good pK value, if the measurements are made in acid solution in which the indicator is nearly 50 percent ionized.

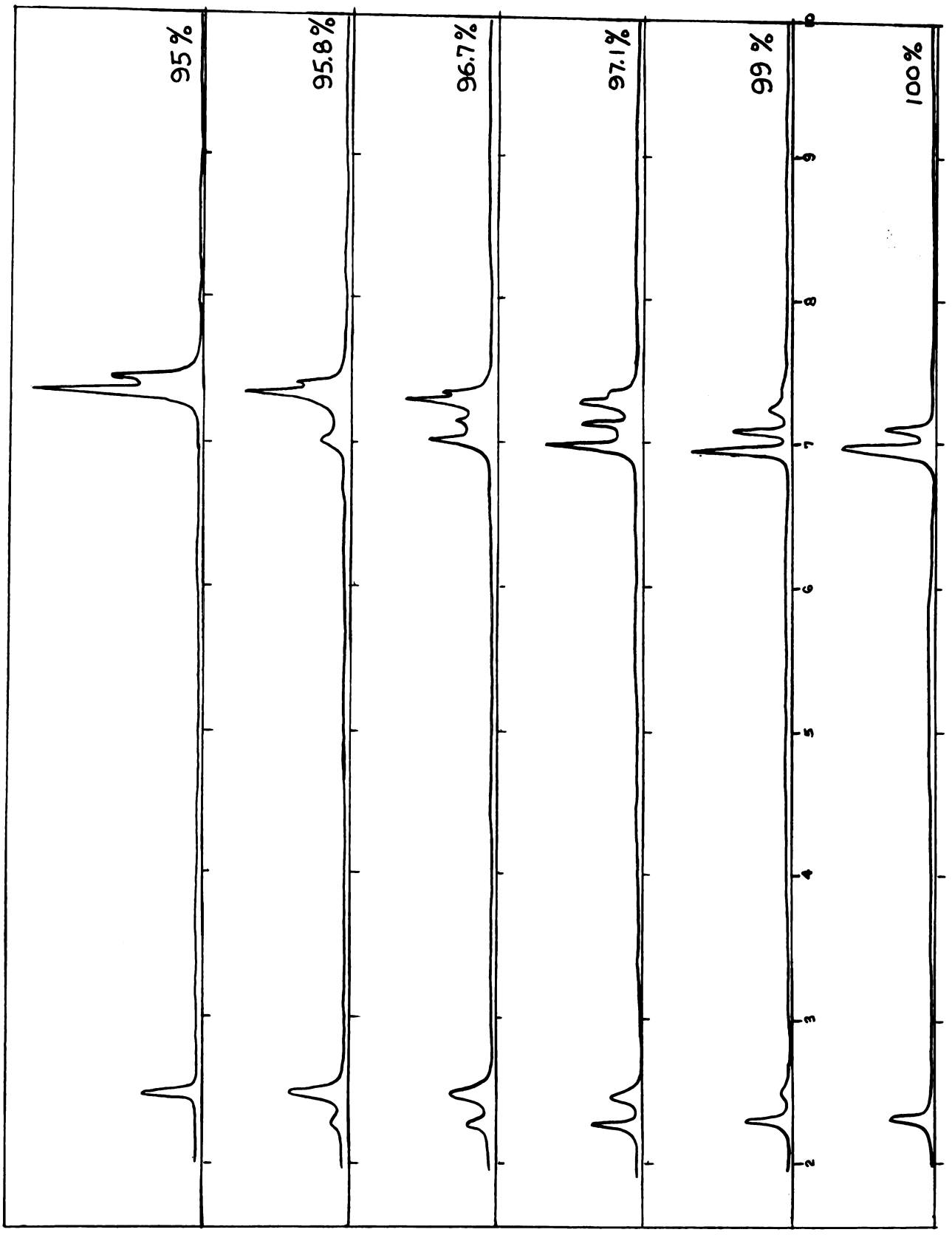


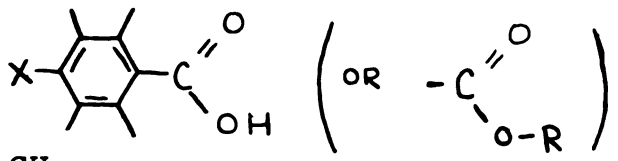
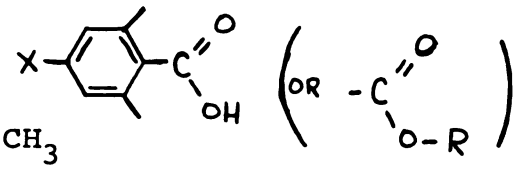
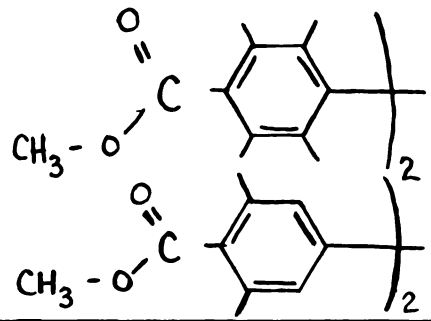

Figure 3. Nuclear Magnetic Resonance Spectra of Mesitoic Acid in Sulfuric Acid of Different Strengths.

In addition to the larger sample required for the n.m.r. measurements, this method has two other limitations; peaks in the n.m.r. spectrum must not overlap, and perhaps more serious, the use of more concentrated solutions of aromatic acid necessary to get a satisfactory n.m.r. signal (vis-à-vis an ultraviolet absorption spectrum) requires that allowance be made for changes in the acid concentration due to the relatively large quantity of water produced (e.g., if the most unfavorable circumstances are taken, viz. benzoic acid dissolved in fuming sulfuric acid, the water produced by ionization could be sufficient to lower the acid concentration by 0.6 percent). The difference in pK values for pentamethylbenzoic acid and 4-bromo-2,3,5,6-tetramethylbenzoic acid as determined by the two techniques may be due to difficulty with the integration of the n.m.r. peaks of the methyl protons, which overlap in the ionized and unionized acid.

The pK values for the ionization of certain hindered aromatic acids are summarized in Table 6. Since the acylium ions carry a full positive charge, they are more likely to be stabilized by electron-donating para substituents than are the unionized acids. Thus a negative value for rho is expected, as is a correlation with $\sigma^+$ constants rather than $\sigma$ constants. This relationship can be seen in Figure 2.

In their study on the protonation of the carbonyl group, Stewart and Yates[50-52] found that the basicities of benzaldehydes, acetophenones, and benzoic acids are correlated

Table 6. Equilibrium constants for substituted benzoic acids in $RCO^+ + H_2O = RCOOH + H^+$.

| Acid or Ester | $pK_{RCO^+}$ |
|---|---|
|  | |
| X = $CH_3$ | -18.81 |
| F | -20.22 |
| H | -20.38 |
| Cl | -20.57 |
| Br | -20.68 |
|  | |
| X = $CH_3$ | -20.43 |
| H | -21.76 |
| I | -22.46 |
| Br | -22.49 |
| Prehnitenecarboxylic acid | -22.07 |
| 3,5-Dibromo-2,4,6-trimethylbenzoic acid | -22.44 |
|  | -22.01 |
|  | -22.72 |

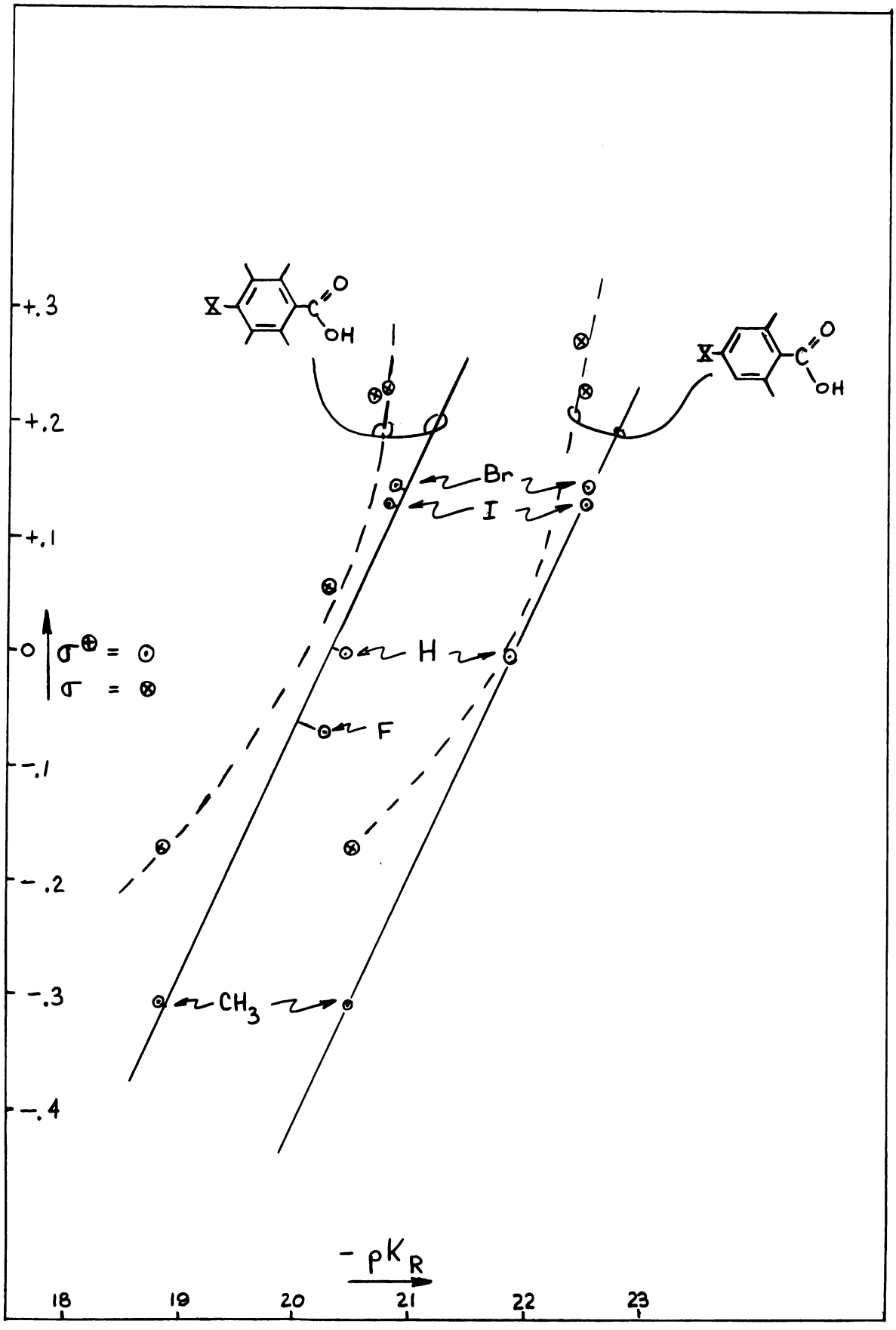



Figure 2. $pK_R$ <u>versus</u> $\sigma$ and $\sigma^+$ for Some Hindered Aromatic Acids in Sulfuric Acid Solution.

better by $\sigma^+$ than by $\sigma$. Bender and Chen[47] studied the hydrolysis of methyl 4-substituted 2,6-dimethylbenzoates. In proposing the formation of acylium ion intermediates in the rate-determining step, they have shown that the reaction rates can be correlated with $\sigma^+$, and estimate the rho of the rate-determining step to be between -3.22 and -2.3. The present result that the equilibrium between a hindered aromatic acid and the corresponding acylium ion has a rho value of -2.4 seems to be in agreement with these other observations.

The formation of an acylium ion from prehnitene carboxylic acid shows that two ortho substituents are not required for that type of ionization. However $\Delta$ pK between pentamethylbenzoic acid and durenecarboxylic acid is only 1.57, whereas the $\Delta$ pK between pentamethylbenzoic acid and prehnitenecarboxylic acid is 3.26. It can be concluded that steric hinderance of the second ortho methyl, although not necessary, greatly enhances acylium ion formation. The difference in pK's between seemingly equal ortho methyl steric hinderance in pentamethylbenzoic acid and durene-carboxylic acid might be attributed to the meta methyl groups in pentamethylbenzoic acid forcing the methyl groups to be non-planar in a buttressing effect.

Another method of determining the pK using extinction values at one wavelength from spectroscopic measurements has been reported.[53] Mesitoic acid was shown to have a value of 9.1 for $H_o$, which this work supports ($H_o$ of 9.1 corresponds to a pK of -20.35).

The pK of 3,5-dibromo-2,4,6-trimethylbenzoic acid is given in Table 6 as -22.44. This value was determined from spectroscopic measurements although earlier workers reported[54] the acid did not ionize to the acylium ion. A sample of 3,5-dibromo-2,4,6-trimethylbenzoic acid was dissolved in 100.2 percent sulfuric acid and then solvolyzed by pouring the sulfuric acid solution into cold anhydrous methanol. Needles of methyl 3,5-dibromo-2,4,6-trimethylbenzoate were obtained, melting point 110-111°. An n.m.r. spectrum of the needles in carbon tetrachloride (Fig. 32) showed resonances at 6.00, 7.21 and 7.61 $\tau$ with relative areas 1:1:2 respectively. The infrared spectrum of methyl 3,5-dibromo-2,4,6-trimethylbenzoate (Figure 31)

## 2. $H_R$ Values for 96 to 100 Percent Sulfuric Acid Solutions

If the ionization of an aromatic acid to form an acylium ion follows the $H_R$ acidity function, an estimate of the pK of ionization can be made from the equation

$$pK_{RC^+O} = H_R + \log \frac{C_{RC^+O}}{C_{RCOOH}}$$

Using the pK of an indicator, the $H_R$ acidity function in any sulfuric acid solution can be calculated, provided its indicator ratio in the solution, log $C_{RC^+O}/C_{RCOOH}$ (log Q), can be accurately measured. By studying the ionization of triphenylcarbinol type indicators, Bushick[40] determined $H_R$ values of sulfuric acid solutions at 30°. Wu,[18] using Bushick's values of $H_R$ for 90 to 96 percent sulfuric acid,

determined the pK of pentamethylbenzoic acid. The average value of 0.30 for $\frac{d \log Q}{d \% H_2SO_4}$ was in good agreement with the value of 0.32 which Bushick had obtained using 4,4',4"-trinitrotriphenylcarbinol as the indicator. This can be taken as evidence for the assumption that the ionization of an aromatic acid to form an acylium ion follows the $H_R$ acidity function.

Using the same technique which was used to construct both the $H_o$ and the $H_R$ scales, an estimate of the $H_R$ values of 96 to 100 percent sulfuric acid solutions has been made. Since in highly concentrated acid solutions, both Hammett indicator and triphenylcarbinol indicators do not give parallel lines when log Q is plotted against percent sulfuric acid, maximum overlapping data were used to establish the $H_R$ acidity scale in this region. In Figures 4 and 5 are shown plots of log Q *versus* percent sulfuric acid from ultraviolet and n.m.r. data. In Figures 6 and 7 are shown the plots of $H_R$ *versus* percent sulfuric acid. A sharp increase in $H_R$ was observed in 98 to 100 percent sulfuric acid solutions. A similar increase in $H_o$ values in this region has been reported by Paul and Long.[35] (The observation that the pK of ionization for *para*-substituted aromatic acids can be correlated with Brown's $\sigma^+$, can be taken as supporting the accuracy of the $H_R$ values, for if ionization of the *para* substituted aromatic acid in various sulfuric acid solutions shows a linear relationship when $\sigma^+$ is compared with pK, then the error or irregularity in $H_R$ would appear as an irregularity in pK.

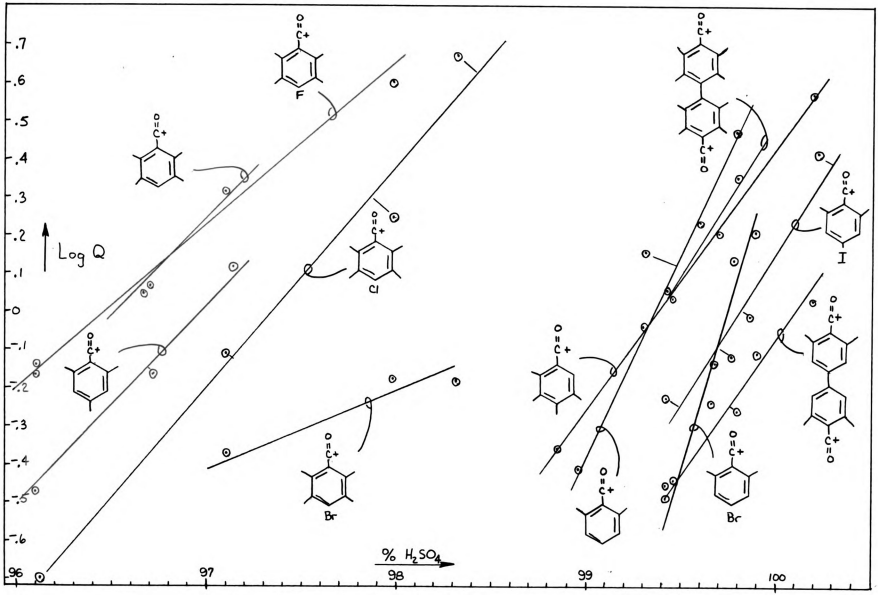



Figure 4. Plot of Log Q versus % Sulfuric Acid for Some Substituted Benzoic Acids and Esters from N.M.R. data.

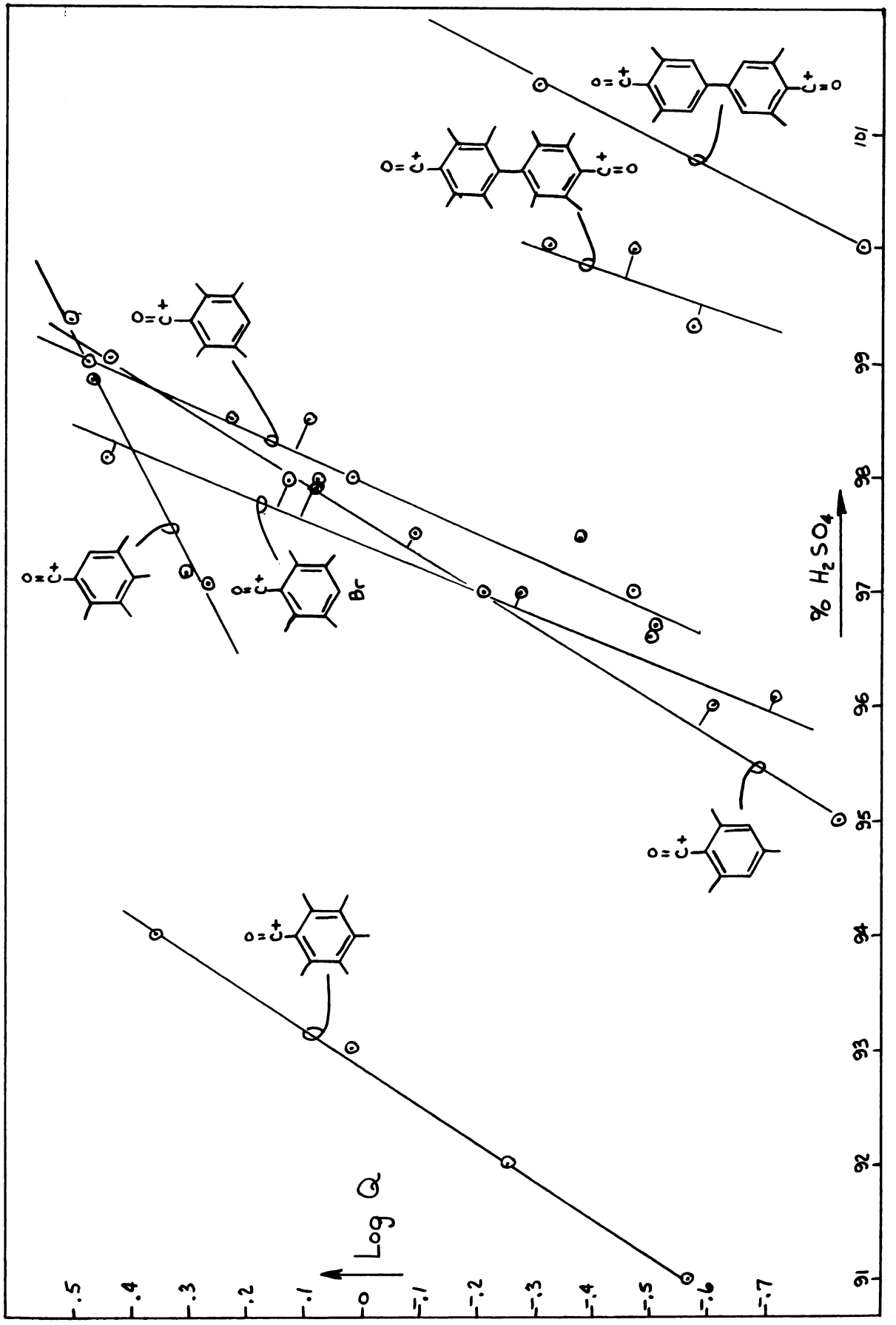



Figure 5. Plot of Log Q versus % Sulfuric Acid for Some Substituted Benzoic Acids and Esters from U.V. data.

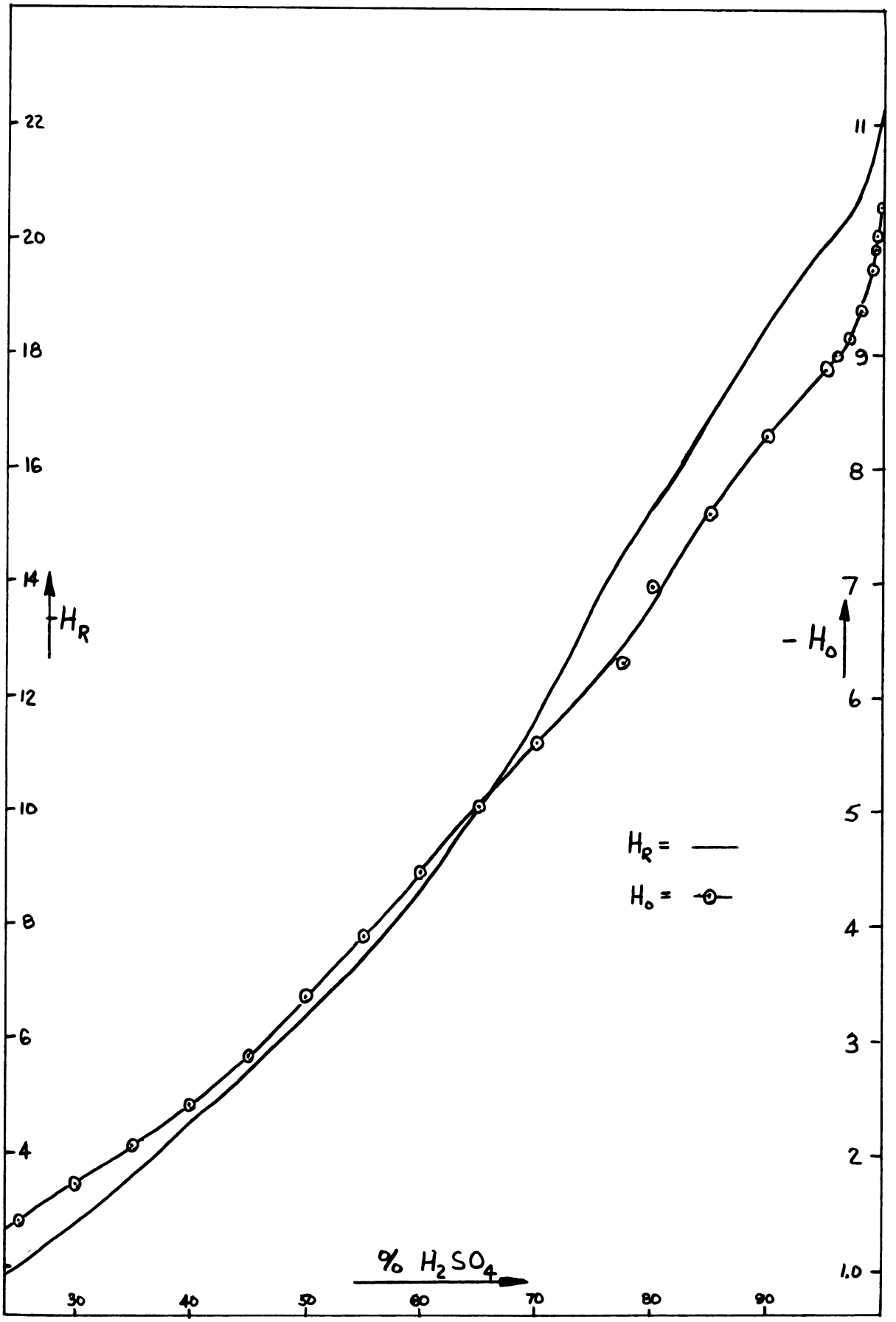



Figure 6. Plot of $H_R$ and $H_o$ <u>versus</u> % Sulfuric Acid (10 to 100%).

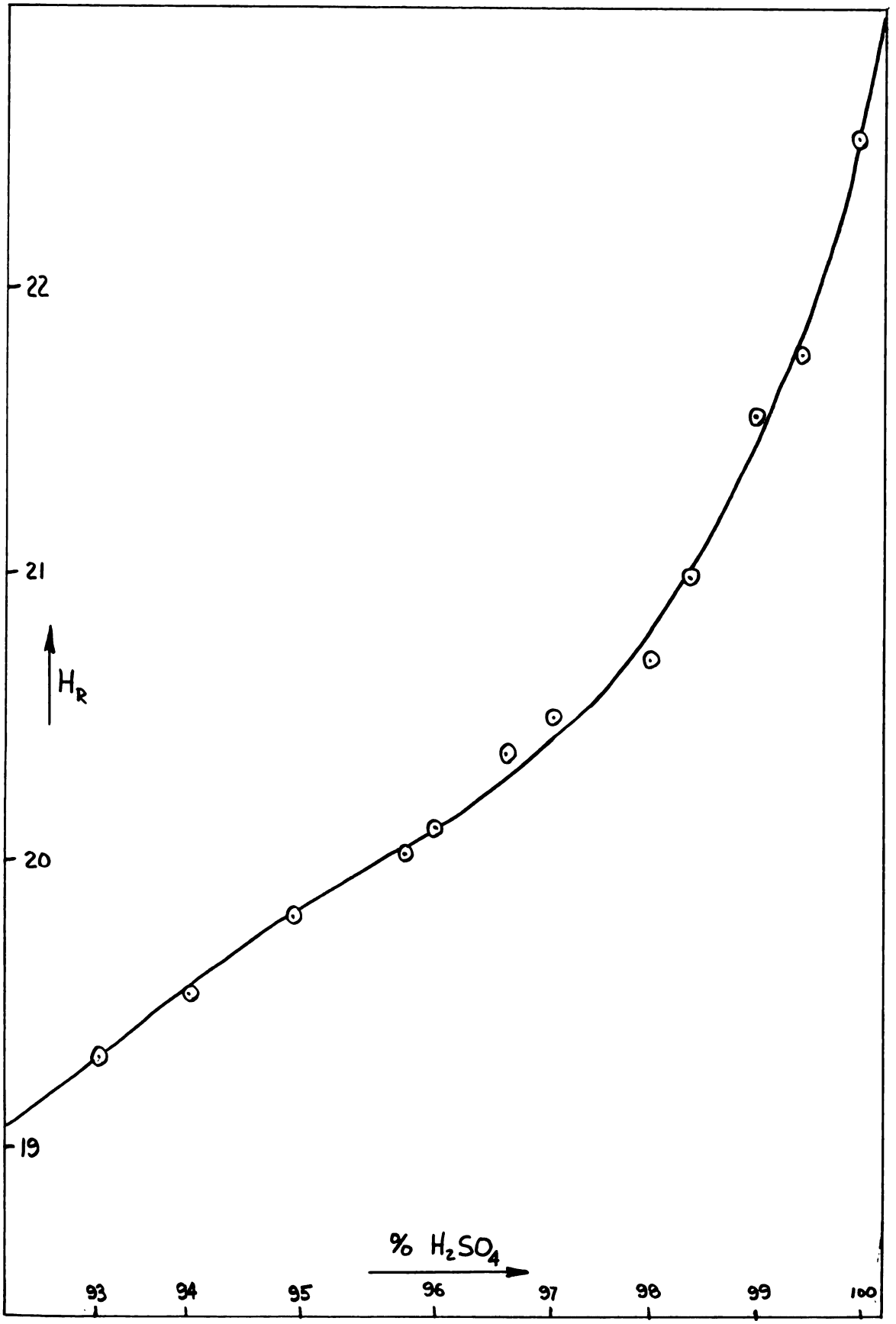



Figure 7. Plot of $H_R$ <u>versus</u> % Sulfuric Acid (90 to 100%).

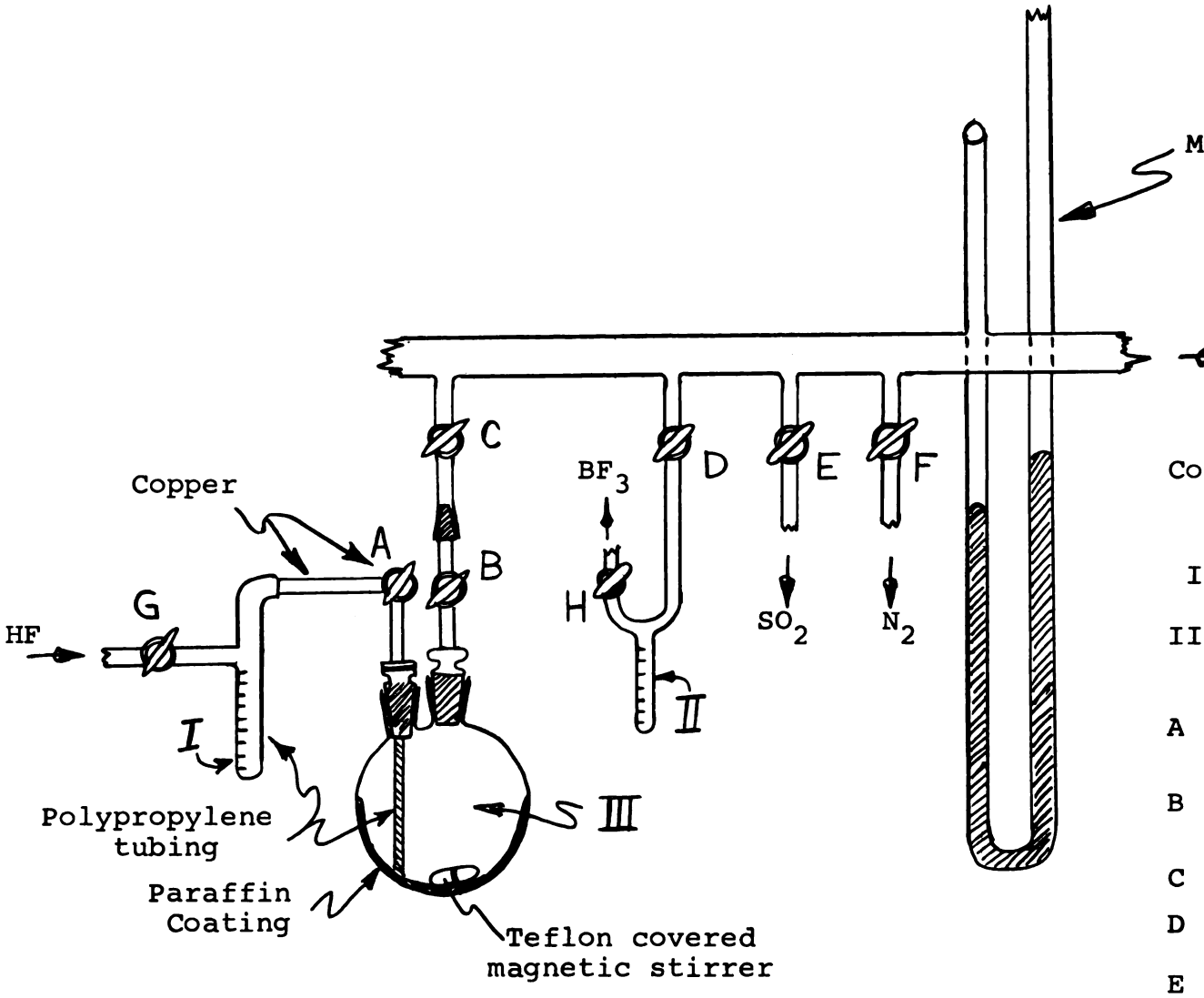
# EXPERIMENTAL

## Part I. Dicarbonium Ions

### 1. Preparation of Fluoboric Acid-Sulfur Dioxide Solution

A 100 ml., two-necked, round-bottomed glass flask was used for the preparation of fluoboric acid-sulfur dioxide solutions. The flask was a part of the system shown in Figure 8 and described below. (This arrangement, with slight modification, was also used for other vacuum-line preparations).

The flask was fitted with a polypropylene gas admission tube extending below a standard tapered teflon bushing and a copper tube with stopcock above the bushing; a glass stopcock, B, was fitted to the second neck, a teflon coated magnetic stirring bar placed inside, and a paraffin coating put on the walls of the lower half of the flask. The copper tubing was attached to a graduated polypropylene tube, I, which was connected to a cylinder of anhydrous hydrogen fluoride by teflon tubing. The manifold of a vacuum line to which the flask was attached was also connected to cylinders of dry nitrogen, sulfur dioxide, and boron trifluoride. Flow of gases was regulated at each cylinder and monitored on the manifold's open-ended manometer. Boron trifluoride was measured by condensing the gas in a graduated tube, II, cooled by liquid nitrogen. Allowing the liquid to slowly warm, vaporize and recondense in the reaction flask almost quantitatively transferred the reagent.




Containers

I (polypropylene) graduated HF measure
II (glass) graduated $BF_3$ measure
III (glass) reaction flask
Stopcocks

A (copper) Admit HF to flask III

B (glass) Close reaction flask (III)

C (glass) Close manifold

D (teflon) Admit $BF_3$

E (glass) Admit $SO_2$

F (glass) Admit $N_2$

G (copper) Admit HF to I

H (teflon) Admit $BF_3$ to II

Figure 8. Apparatus for Preparing Hydrogen Fluoride - Boron Fluoride - Sulfur Dioxide Solutions.

A typical half mole preparation was made as follows: The flask III was attached to the manifold, evacuated and warmed with a cool flame to remove any adsorbed water in the flask and fittings. During the warming the stirring bar was used to swirl the liquid paraffin up the sides of the flask and thus maintain a coating on the walls of the flask. After allowing the flask to cool until the paraffin solidified but left the stirring bar free, the flask was cooled in a dry ice-isopropyl alcohol bath and ca. 30 ml of sulfur dioxide was condensed in the flask. The stopcock B was closed and the flask was allowed to stand until the sulfur dioxide began to solidify. A dry ice-isopropyl alcohol bath was then used to cool the polypropylene tube I. The copper stopcock A was closed and the hydrogen fluoride cylinder G opened slowly to allow 10.1 ml (0.5 mole) of hydrogen fluoride to condense in tube I. Then by allowing I to warm to room temperature, the liquid vaporized and was allowed to transfer into III by opening A and closing G. Boron trifluoride (23.7 ml; 0.5 mole) was condensed in II by cooling II with liquid nitrogen (stopcocks C, E and F closed; stopcocks H and D open). Transfer of the boron trifluoride was then made by allowing the liquid to warm, vaporize, and pass through D, C and B to flask III. In the flask the boron trifluoride was allowed to react with the hydrogen fluoride and/or sulfur dioxide which was kept at $-78^{\circ}$ with a dry ice-isopropyl alcohol bath. (Earlier preparations were made by passing the hydrogen fluoride and

boron trifluoride directly into the flask and weighing the flask to determine the stoichiometry, but this was cumbersome and rather inaccurate.) The solution was then agitated for half an hour with the stirring bar, the pressure brought to one atmosphere with dry nitrogen, (F), the stopcocks A, B and C closed, and then the flask stored in a dry-ice isopropyl alcohol bath until the solution was needed. When needed the fluoboric acid solution was poured through B.

2. Preparation of Pentamethylphenylchlorodicarbonium Tetrafluoroborate

A 100 ml, two-necked, round-bottomed flask equipped with a teflon-covered magnetic stirring bar, a polypropylene gas admission tube with copper fittings and stopcock, and a standard tapered bushing and glass stopcock was attached to the manifold of a vacuum line and while being evacuated was heated with a cool flame. After allowing the flask to cool to room temperature dry nitrogen was admitted through the manifold and allowed to escape through the flask fittings. With the nitrogen still flowing through the flask in a gentle stream, 4.3 g (0.16 moles) of pentamethylbenzotrichloride was placed in the flask. The nitrogen flow was stopped, the flask closed and re-evacuated. About 20 ml of anhydrous sulfur dioxide was then condensed in the flask which was cooled in a dry-ice isopropyl alcohol bath while the slightly soluble solid was agitated with the stirring bar. The flask was then attached to the previously described flask for the preparation of fluoboric acid-sulfur dioxide solution.

A solution of 0.25 moles of hydrogen fluoride and 0.25 moles of boron trifluoride in 50 ml of liquid sulfur dioxide was added to the pentamethylbenzotrichloride-sulfur dioxide mixture. The resulting solution immediately became deep red-purple as the pentamethylbenzotrichloride reacted and dissolved. The solution was kept at ca. -78° and stirred for two hours. By removing the cooling bath, the solution was allowed to warm to room temperature so that the sulfur dioxide and excess boron trifluoride and hydrogen fluoride evaporated through a vent, via a Gilman sulfuric acid trap. When all of the volatile materials had escaped, the flask was attached to the manifold and evacuated for two hours. A dark purple semi-crystalline material remained in the flask. The flask was cooled in a dry ice-isopropyl alcohol bath and ca. 20 ml of sulfur dioxide was condensed onto the purple solid. The deep purple solution which resulted was agitated for 10 minutes before being allowed to warm to room temperature. By agitating rapidly during the warming period, the solution which washed the sides of the flask deposited a purple crystalline solid. These crystals were continually being washed by the solvent until the liquid level dropped to where it could not be swirled over the solid. The last portion of solvent to be vaporized left residual material containing most of the impurities on the bottom of the flask. Analyses and other properties were measured on the solid which had crystallized in the upper and middle portions of the flask. The slower the solvent was removed and the

greater the agitation, the larger the quantity of solid "purified." When all of the solvent had evaporated the flask was evacuated for an hour. Dry nitrogen was then admitted to a pressure of one atmosphere and the flask again evacuated. The flask was then stored in a dry box and samples taken for analysis.

The crystalline material was too sensitive to hydrolysis to permit elemental analysis, but chloride ion, tetrafluoroborate, and equivalents of acid were determined to verify the structure.

The chloride ion was gravimetrically determined as silver chloride. A 0.8355 g sample of pentamethylphenylchlorodicarbonium tetrafluoroborate was placed in a small flask and 10 ml of a 50 percent aqueous acetone solution added. The mixture was stirred vigorously for ten minutes. During the stirring the purple crystalline solid dissolved and the solution almost instantly lost its color. The colorless solution was extracted with ten ml of ethyl ether and then five ml of a ten percent silver nitrate-one percent nitric acid aqueous solution added. A dense white precipitate of silver chloride was immediately observed and was allowed to digest for five minutes while the mixture was warmed on a steam bath. The silver chloride was filtered (with a fine fritted glass funnel), washed with 20 ml of one percent nitric acid solution, dried at 105$^{o}$ in an oven to constant weight of 0.3190 g.

The tetrafluoroborate ion was determined gravimentrically as its nitron complex. A 0.1731 g sample of crystalline

pentamethylphenylchlorodicarbonium tetrafluoroborate was dissolved in 15 ml of a 50 percent aqueous-acetone solution. The solution was cooled with an ice bath to $0^{\circ}$. Fifteen ml of a 1.5 percent Nitron reagent in five percent acetic acid solution (cooled to $0^{\circ}$) was added to the colorless acetone solution. A tan precipitate formed when the solutions were mixed. The precipitate was allowed to digest for 30 minutes. The solid was then filtered with a sintered glass funnel, washed twice with 10 ml of five percent acetic acid (at $0^{\circ}$) and once with 10 ml of distilled water, dried in the oven at $105^{\circ}$ for four hours, to a constant weight of 0.3709 g. This weight is 98.2 percent of theoretical of the expected nitron complex.

The neutralization equivalent of acid produced on hydrolysis of the crystalline dicarbonium ion was determined from the following: A 0.2790 g sample of pentamethylphenylchlorodicarbonium tetrafluoroborate was dissolved in 15 ml of a 50 percent aqueous-acetone solution in a 125 ml Erlenmeyer flask. Three drops of phenolphthalein indicator solution were added to the solution and then the acid solution titrated with standard sodium hydroxide. The solution required 3.08 milliequivalents of base.

Anal: Calculated for pentamethylphenylchlorodicarbonium tetrafluoroborate: $BF_4^-$, 47.1; $Cl^-$, 9.64; Neutralization Equivalent, 92.1. Found: $BF_4^-$, 46.6, 46.4; $Cl^-$, 9.42, 9.45; Neut. Equivalents, 90.5, 90.8. A sealed capillary melting point was $147\text{-}148^{\circ}$ (with darkening above $130^{\circ}$). The

n.m.r. spectrum of pentamethylphenylchlorodicarbonium tetrafluoroborate in liquid sulfur dioxide showed peaks at 7.40, 7.63 and 7.90 $\tau$ (relative to an internal tetramethylsilane reference) with relative areas 2:1:2. The visible spectrum in the same solvent showed bands at 542 m$\mu$ ($\epsilon$ 2500), 393 m$\mu$ ($\epsilon$ 26,050), and 382 m$\mu$ ($\epsilon$ 25,390). The infrared spectrum (see Figure 9; potassium bromide pellet) showed an intense broad brand at 8.9-9.7 $\mu$ characteristic of the tetrafluoroborate anion.

3. Preparation of Pentamethylphenylchlorodicarbonium Tetrachloroborate

A 50 ml, two-necked, round-bottomed flask equipped with a teflon covered magnetic stirring bar, a polypropylene gas admission tube, and a standard taper glass bushing and stopcock was attached to the manifold and the flask evacuated. The flask and its fittings were heated with a cool flame to remove any adsorbed water on the glass surface. Dry nitrogen was then admitted to the flask and allowed to flow out the fittings. While the gas was still gently flowing, 0.98 g (0.0034 moles) of pentamethylbenzotrichloride was placed in the flask. The nitrogen flow was stopped, and the flask re-evacuated. About 20 ml of sulfur dioxide was condensed into the flask which was cooled in a dry ice-isopropyl alcohol bath to ca. -78°. The magnetic stirrer was used to agitate the solution during the entire addition of reagents and all warming and cooling steps. Boron trichloride (0.83 ml; 0.013 moles) measured by volume in a graduated tube (II in Figure 8) was condensed into the reaction flask. Immediately

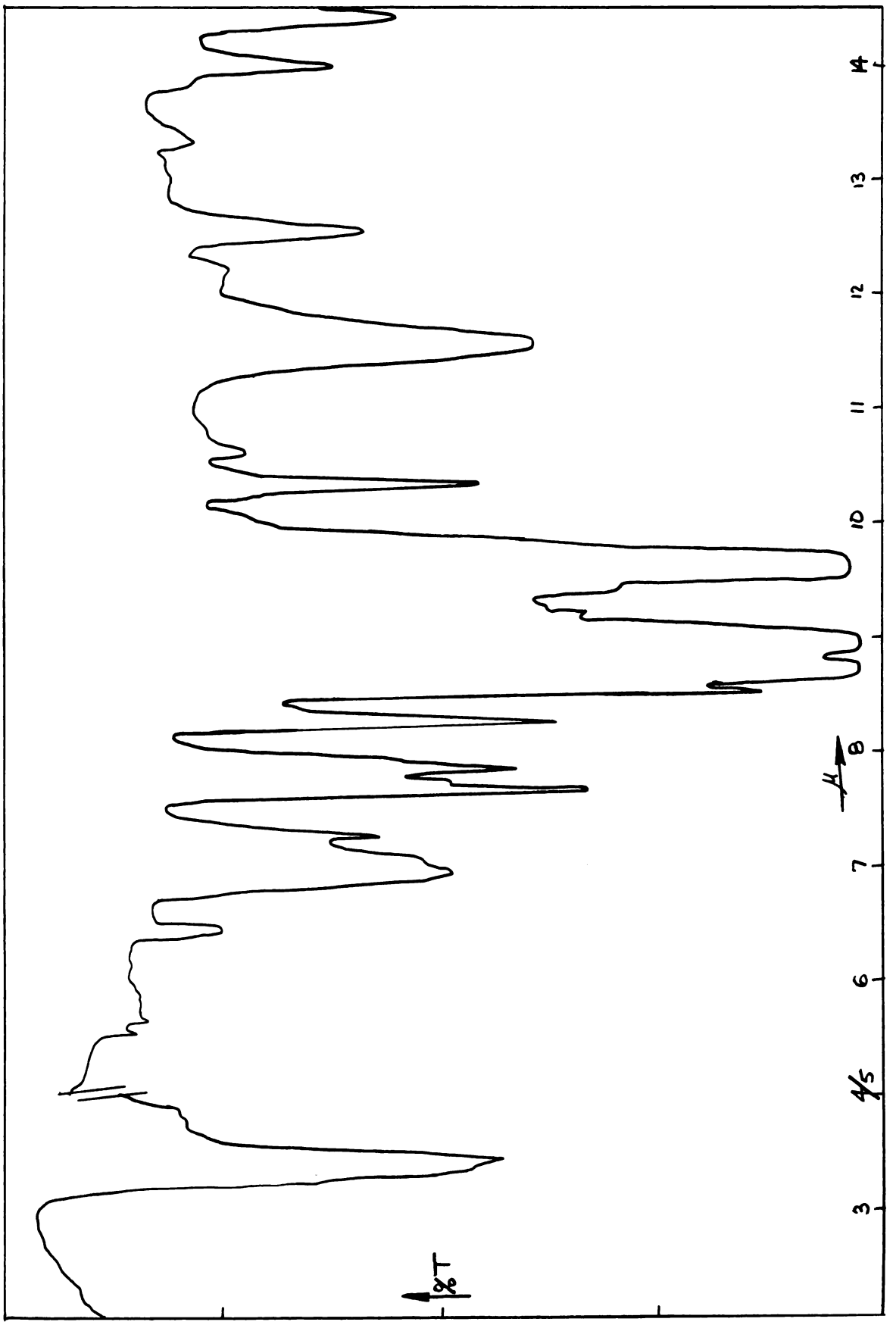



Figure 9. Infrared Spectrum of Pentamethylphenylchlorodicarbonium Tetrafluoroborate ( as KBr Pellet ).

upon addition of the boron trichloride, the mixture turned a dark red-purple and remained so as the solid reacted and dissolved. The solution was kept cold and agitated for an hour, then allowed to warm to room temperature by removing the cooling bath. A purple crystalline material remained in the flask as the last of the excess reagent and solvent evaporated. Recrystallization of this purple salt was effected by dissolution in ca. 10 ml of sulfur dioxide and allowing the sulfur dioxide to vaporize slowly with rapid stirring as described above for the tetrafluoroborate. When all of the solvent had vaporized, the flask was evacuated for half an hour. The flask was then filled with dry nitrogen to a pressure of one atmosphere, re-evacuated and stored in a dry box. The melting point of the salt (sealed tube) was 152-153° (dec.). The n.m.r., visible, and ultraviolet spectra were nearly identical to those of pentamethylphenylchlorodicarbonium tetrafluoroborate. The infrared spectrum in liquid sulfur dioxide showed a broad band at 13.1-13.55 μ (see Figure 10) due to the tetrachloroborate ion. Hydrolized samples were analyzed for chloride gravimetrically.

Anal. Calculated for pentamethylphenylchlorodicarbonium tetrachloroborate: $Cl^-$, 63.82. Found: $Cl^-$, 61.12.

4. Preparation of 2,4,6 -Trimethylphenylchlorodicarbonium Tetrafluoroborate

The procedure was similar to that described previously for pentamethylphenylchlorodicarbonium tetrafluoroborate. From 2 g (0.0084 moles) of trichloromethylmesitylene there

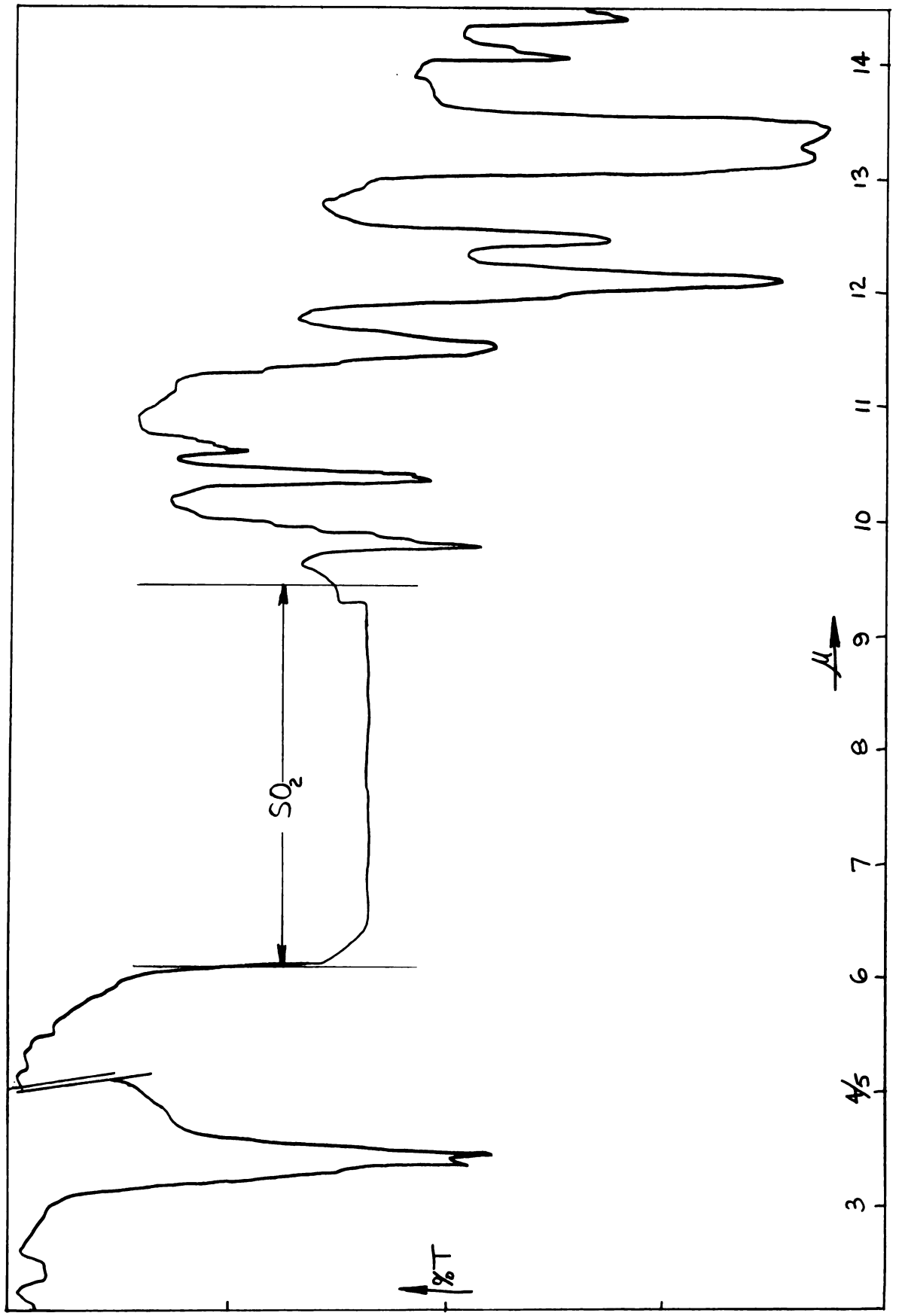



Figure 10. Infrared Spectrum of Pentamethylphenylchlorodicarbonium Tetrachloroborate ( in $SO_2$ Solution ).

was isolated 3.9 g of a dark red crystalline material, melting point (sealed tube) 127-128°, dec. The n.m.r. spectrum in liquid sulfur dioxide showed peaks at 3.04, 7.70, and 7.78 τ (relative to tetramethylsilane as an internal reference) with relative areas 2:6:3. The visible spectrum in sulfur dioxide showed bands at 485 mμ (ε 2110), 372 mμ (ε 20,650), and 281 mμ (ε 5670). Again because the material was too sensitive to hydrolysis to permit elemental analysis, the chloride ion, tetrafluoroborate, and equivalents of acid were determined to verify the structure.

Anal. Calculated for 2,4,6-trimethylphenylchlorodicarbonium tetrafluoroborate: $BF_4^-$, 51.0; $Cl^-$, 10.4; Neut. Equiv., 85.1. Found: $BF_4^-$, 50.0, 49.9; $Cl^-$, 10.6, 10.7; Neut. Equiv. 86.5, 86.6.

## 5. Preparation of 2,4,6-Trimethylphenylchlorodicarbonium Tetrachloroborate

In a manner similar to pentamethylbenzotrichloride, 2,4,6-trimethylbenzotrichloride was allowed to react with boron trichloride in liquid sulfur dioxide and a red crystalline salt isolated having a melting point (sealed tube) 134-135°, dec. The n.m.r., visible, and ultraviolet spectra were nearly identical to those of 2,4,6-trimethylphenylchlorodicarbonium tetrafluoroborate. The infrared spectrum in liquid sulfur dioxide showed a broad band 13.1-13.5 μ due to the tetrachloroborate ion (see Fig. 11). Hydrolyzed samples were analyzed for chloride gravimetrically.

Anal. Calculated for 2,4,6-trimethylphenylchlorodicarbonium tetrachloroborate: $Cl^-$, 67.6. Found: $Cl^-$, 66.8.

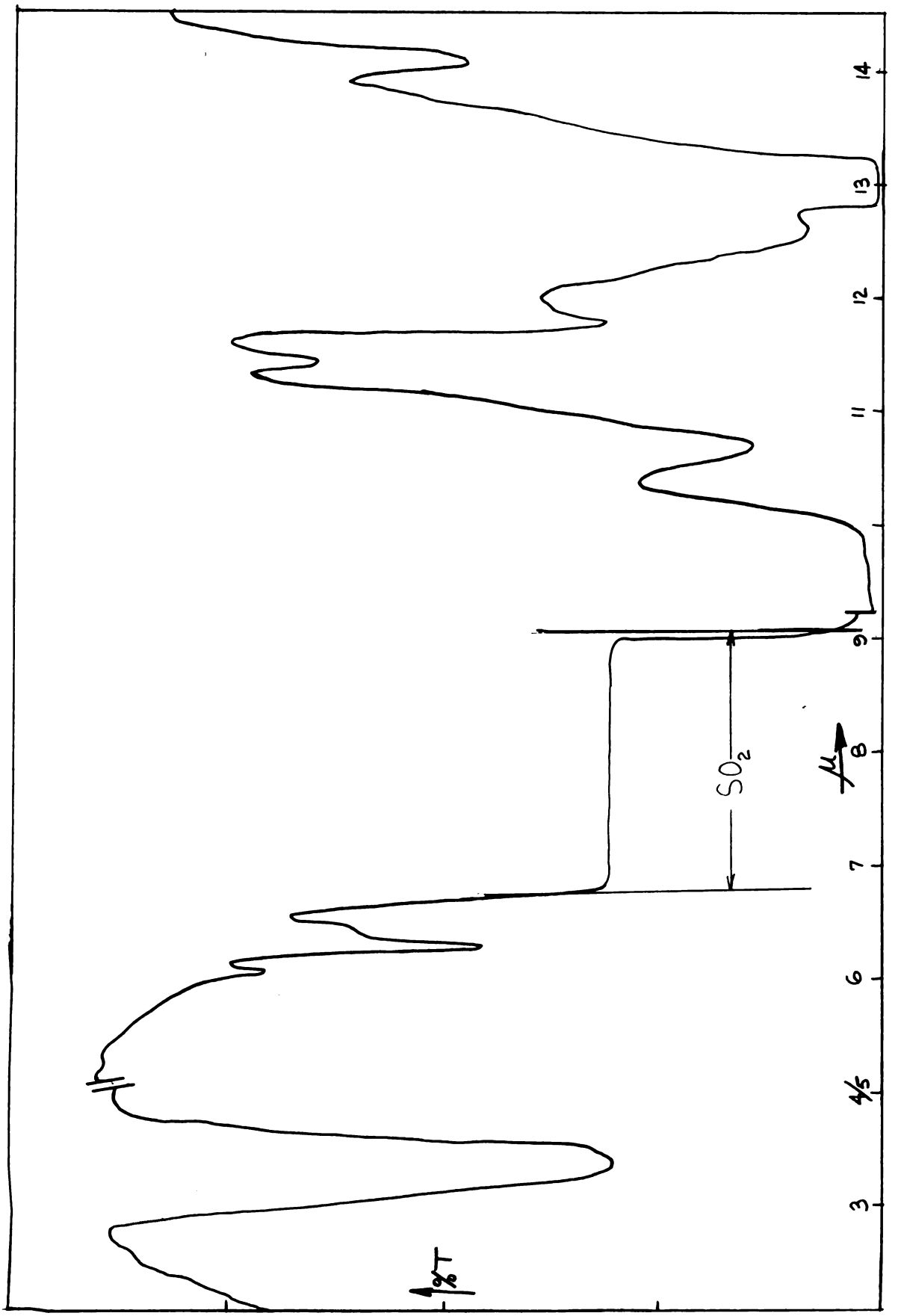



Figure 11. Infrared Spectrum of 2,4,6- Trimethylphenylchlorodicarbonium Tetrachloroborate ( in $SO_2$ Solution ).

6. Preparation of Pentamethylbenzoyl chloride

In a 100 ml, round-bottomed flask equipped with a reflux condenser and a magnetic stirring bar (the system being isolated from the atmosphere through a sulfuric acid trap) was placed 3.3 g (0.016 moles) of white crystalline (m.p. 207-208°) pentamethylbenzoic acid. The system was flushed with a stream of dry nitrogen and then 15 ml (0.208 moles) of thionyl chloride (b.p. 75-76°) was added to the flask. The flask was heated and the solution stirred for 5 hours (at reflux). After stripping off the excess thionyl chloride and other volatiles a cream-colored needle-like material remained. Recrystallization from ether-petroleum ether gave a 95% yield of needles melting 83.2-83.6°. The infrared spectrum in carbon disulfide showed a carbonyl stretching band absorption at 5.62 μ (see Fig. 12).

7. Preparation of Pentamethylbenzoyl Tetrafluoroborate

A 2.5 g sample of pentamethylbenzoyl chloride was placed in a 50 ml flask arranged as previously described for the preparation of the tetrafluoroborate salts (see Fig. 8). In a manner similar to that described previously an almost quantitative yield of a colorless crystalline solid melting at 120° was obtained. The n.m.r. spectrum in liquid sulfur dioxide showed bands at 7.64, 7.71, and 7.74 τ (relative to tetramethylsilane as an internal reference) with relative areas 2:1:2 for the solid. The infrared spectrum showed the tetrafluoroborate ion (see Fig. 13).

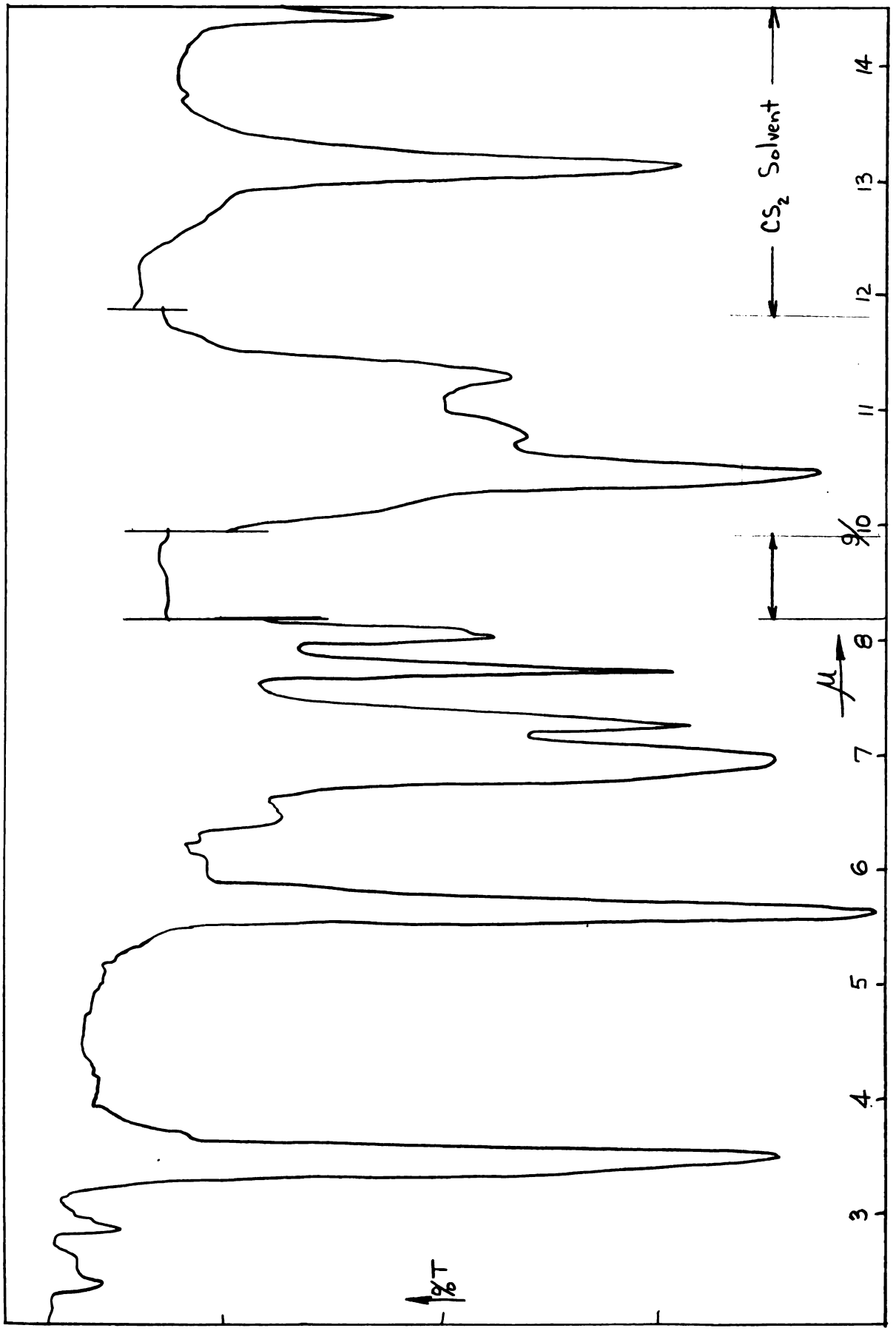



Figure 12. Infrared Spectrum of Pentamethylbenzoyl chloride ( in $CCl_4$ and $CS_2$ Solutions ).

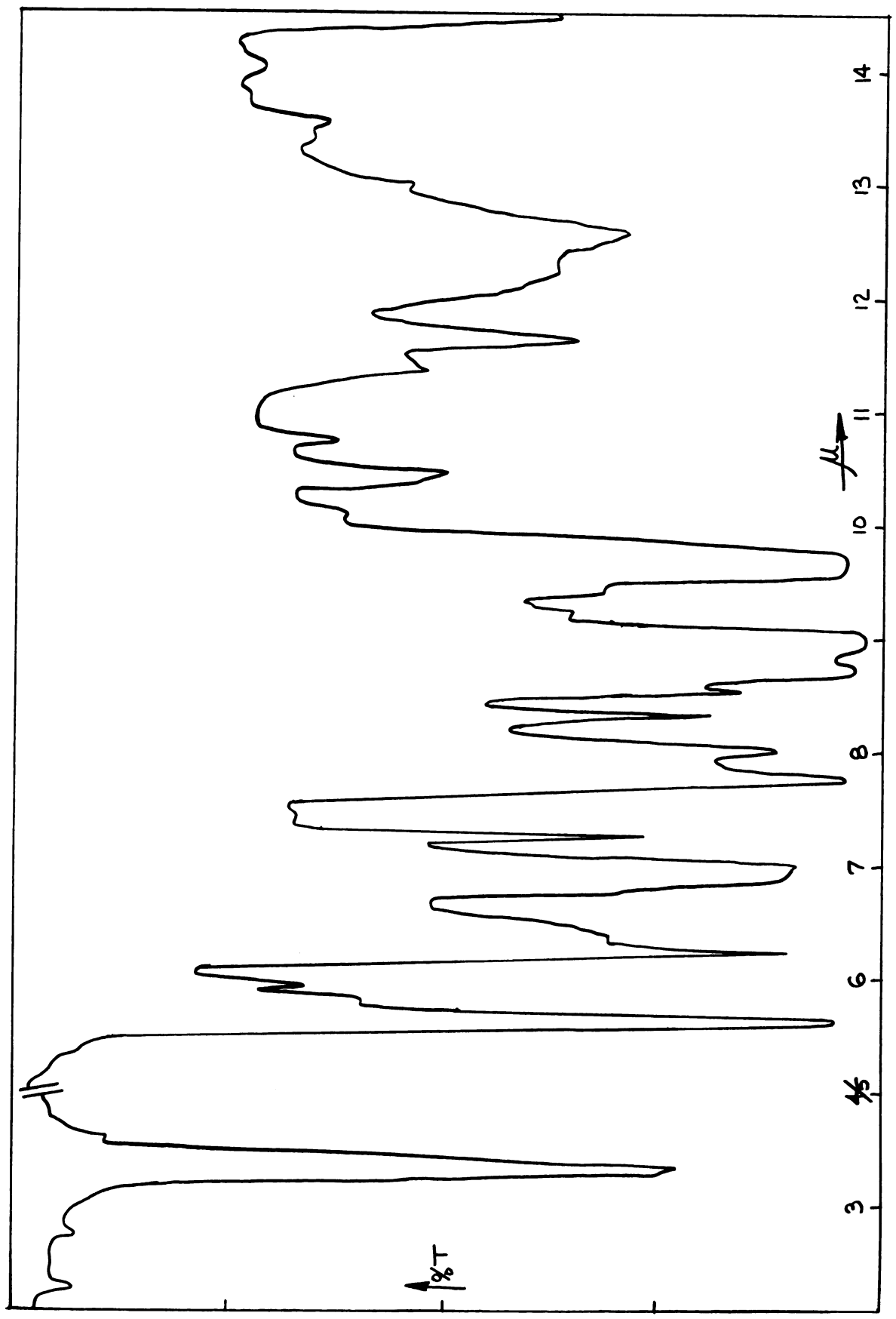



Figure 13. Infrared Spectrum of Pentamethylbenzoylium Tetrafluoroborate (as KBr Pellet ).

Anal. Calculated for pentamethylbenzoylium tetrafluoroborate: $BF_4^-$, 33.1; Neut. Equiv., 131.0. Found: $BF_4^-$, 32.6, 32.7; Neut. Equiv., 132.1, 130.6.

8. Hydrolysis of Pentamethylphenylchlorodicarbonium Tetrafluoroborate

A sample of pentamethylphenylchlorodicarbonium tetrafluoroborate, 0.1g, (m.p. 147-148°) was added to ca. 20 ml of an ice-water mixture. The solid lost its deep red-purple appearance as hydrolysis occurred, and a white solid precipitated from solution. The mixture was stirred for ten minutes. The white solid was filtered and recrystallized from aqueous ethanol. A quantitative yield of pentamethylbenzoic acid, m.p. 208-209° (literature[41] 208-210°) was obtained.

9. Possible Deuterium-Hydrogen Exchange of Pentamethylbenzotrichloride in Deuterated Sulfuric Acid

Pentamethylbenzotrichloride, 1.55 g, (m.p. 95.5-96°) was placed in an Erlenmeyer flask and ca. 25 ml of 100 percent deuterated sulfuric acid was added. After the deuterium chloride evolution ceased, the flask was stoppered and allowed to stand in the dark for 24 hours. The solution was sampled (4 ml of solution was pipetted from the major portion of the solution) every hour, for five hours. The last sample of solution was taken after 24 hours. Each 4 ml aliquot was poured slowly into 30 ml of anhydrous methanol at 0°, washed with 20 ml of a 10 percent sodium bicarbonate solution, twice with 20 ml ether and then 20 ml of water. The organic layer

was dried over anhydrous magnesium sulfate and the ether removed under reduced pressure. Recrystallization from methanol yielded 63 percent of methyl pentamethylbenzoate (84 percent crude) total. An infrared spectrum of the ester showed no carbon-deuterium stretching frequency band in any of the six samples. The n.m.r. spectrum of each sample was identical to that of a known sample; the area of the ring methyl protons was 99 percent of that of the authentic sample. A mass spectrum on the 24 hour sample of methyl pentamethylbenzoate and an authentic sample showed less than 0.1 percent difference, or, 0.1 percent deuterated ester.

10. Hydrolysis of Pentamethylbenzotrichloride in Deuterated Sulfuric Acid Solution

Pentamethylbenzotrichloride, 2.45 g, was placed in a flask which was cooled in an ice-water bath and 10 ml of deuterated sulfuric acid was added to the flask. Deuterium chloride was evolved as soon as the sample was added to the acid. When the evolution of gas slowed to where samples could be taken (about 5 minutes), two one-ml aliquots were hydrolized one in deuterium oxide and the other in water. The aqueous solutions were each allowed to react with dilute sodium hydroxide (a small quantity of the solid being added to the aqueous solution) until the pentamethylbenzoic acid had dissolved, and then were reacidified to precipitate the acid from solution. The solid was filtered, dried, and an infrared spectrum taken. Samples were taken and worked up in an analogous manner after the pentamethylbenzotrichloride

had been in the deuterated sulfuric acid one hour, 12 hours, and 24 hours. The infrared spectra showed no carbon-deuterium stretching frequency absorption band for any of the samples.

11. Hydrolysis of 2,4,6-Trimethylphenylchlorodicarbonium Tetrafluoroborate

In a manner analogous to that used with pentamethylphenylchlorodicarbonium tetrafluoroborate, a sample of 2,4,6-trimethylphenylchlorodicarbonium tetrafluoroborate was dissolved in an aqueous acetone solution. A 93 percent yield of the corresponding 2,4,6-trimethylbenzoic acid, m.p. 152-153, was obtained.

12. Attempted Hydride Exchange between 2,4,6-Trimethylphenylchlorodicarbonium Tetrachloroborate and Triphenylmethane

To an n.m.r. sample tube was added 0.024 g of triphenylmethane, 0.024 g of trichloromethylmesitylene, ca. 0.25 ml of boron trichloride, and two ml of sulfur dioxide. The mixture formed a deep red solution. Control samples were also prepared. An n.m.r. tube was charged with 0.024 g triphenylmethane, ca. 0.25 ml of boron trichloride, and two ml of sulfur dioxide. Another tube was charged with 0.024 g of trichloromethylmesitylene, ca. 0.25 ml of boron trichloride, and two ml of sulfur dioxide. The n.m.r. spectrum of each sample was taken to observe the possibility of hydride exchange from the triphenylmethane to the dication which would be generated. Spectra were taken again after two and four hours in the solution. No change was observed in the

n.m.r. peak positions or intensities; thus no hydride exchange was observed.

The solutions were hydrolized by reaction of the sulfur dioxide solution with ca. 10 ml of 50 percent aqueous acetone. The corresponding 2,4,6-trimethylbenzoic acid was quantitatively obtained.

13. Attempted Hydride Exchange between 2,4,6-Trimethylphenylchlorodicarbonium Tetrachloroborate and Cycloheptatriene

N.m.r. spectra were taken on two control samples (the two reactants) and the reaction solution, similar to the case of triphenylmethane. An n.m.r. tube was charged with 0.009 g of cycloheptatriene, ca. 0.25 ml boron trichloride, and two ml of sulfur dioxide. Another tube was charged with 0.024 g trichloromethylmesitylene, ca. 0.25 ml of boron trichloride, and two ml of sulfur dioxide. A third tube was charged with 0.009 g cycloheptatriene,, 0.024 g trichloromethylmesitylene, ca. 0.25 ml boron trichloride, and two ml of sulfur dioxide. A spectrum was taken for each sample. The spectrum of cycloheptatriene with boron trichloride was so complex however that it was considered almost impossible to determine whether or not the spectrum had changed because of a hydride shift. The sample with the mixture of reactants was then hydrolized by dissolving it in ca. 10 ml of 50 percent aqueous acetone solution. Loss of the bright red color was almost instantaneous. An essentially quantitative yield of the corresponding 2,4,6-trimethylbenzoic acid was obtained from the aqueous acetone solution.

## 14. Attempted Hydride Exchange between 2,4,6-Trimethylbenzotrichloride and Triphenylmethane in Sulfuric Acid

An n.m.r. sample tube was charged with 0.024 g triphenylmethane, 0.024 g trichloromethylmesitylene, and two ml of 100 percent sulfuric acid. A spectrum was taken and found to show five resonance peaks which are those due to the sum of the spectra for each of the reactants. The solution was allowed to stand for six hours. After that time there had been no change in the n.m.r. spectrum.

## 15. Attempted Reaction of 2,4,6-Trimethylphenylchlorodicarbonium Tetrachloroborate with Ether

A small sample (ca. 0.1 g) of 2,4,6-trimethyltrichloromethylbenzene was placed in a reaction flask and an excess of sulfur dioxide and boron trichloride condensed in the flask and allowed to react with the trichloromethylmesitylene. The red crystalline dicarbonium tetrachloroborate salt was prepared as previously described. About ten ml of anhydrous ether was added to the flask through a dropping funnel. The mixture became black immediately upon the ether addition, the reaction being exothermic. As the last portions of ether were added the solution became red-brown. This solution was poured into an ice-water mixture, the layers separated, each layer washed with the other solvent, and then the combined organic layers were dried over anhydrous magnesium sulfate and evaporated to dryness. The residue was slightly colored but an aliquot was used to obtain an infrared and n.m.r. spectrum.

The spectra indicated that the solid (m.p. 147-149°) was impure 2,4,6-trimethyltrichloromethylbenzene.

When caution was taken to purify the dicarbonium salt and completely remove the excess reagents, no darkening occurred on ether addition to the salt (and the residual material after ether evaporation was 2,4,6-trimethyltrichloromethylbenzene).

Another sample (ca. 0.1 g) of 2,4,6-trimethyltrichloromethylbenzene was converted to the tetrachloroborate salt as described above. About ten ml of ether was added to the salt but the solution remained red-brown. An aliquot of the red-brown solution was poured into an aqueous-acetone solution with rapid stirring. When the exothermic hydrolysis was complete a white solid remained. The white solid was filtered, dried and identified as mesitoic acid from its melting point, 209-210°, and infrared spectrum (in carbon disulfide). The major portion of the red-brown solution was equally divided into two portions. One of the samples was stoppered and allowed to stand at room temperature while the other sample was heated to reflux, both for 24 hours. Each sample was then poured into an aqueous-acetone solution. The red-brown solution was changed to a cream-colored mixture as the exothermic hydrolysis occurred. The solid was filtered, dried, and from its melting point and infrared spectrum identified as mesitoic acid. Evaporation of the ether from the organic filtrates left only a small quantity of solid residue. An infrared spectrum of this solid residue showed

no ester absorption bands, only the spectrum of mesitoic acid.

16. Reaction between 2,4,6-Trimethylphenylchlorodicarbonium Tetrachloroborate and Phenyl Lithium

A 0.1 mole sample of the red crystalline 2,4,6-trimethlyphenylchlorodicarbonium tetrachloroborate was prepared following the previously described method. A 0.1 mole phenyl lithium solution was prepared in 100 ml ether. The phenyl lithium solution was then added dropwise to the solid dication which was in an ice cooled flask. An exothermic reaction occurred as the brown solution dropped onto the red solid. After the addition was complete the dark brown solution was stirred 10 minutes. Then 25 ml of water was added dropwise to the flask. A vigorous exothermic reaction occurred but the mixture remained brown. An equal quantity (25 ml each) of ether and chloroform was used to extract the organic material from the aqueous layer. The layers were separated, the organic layer washed with 10 ml of water, dried over anhydrous magnesium sulfate, and evaporated to dryness. A white amorphous solid melting at 205-207$^{o}$ remained. An n.m.r. spectrum, in deuterated acetone, showed (Figure 14) two low field resonances (at 3.67 and 4.13 $\tau$), and one small methyl resonance with relative areas of 16 to 2 respectively. An infrared spectrum was taken, as a potassium bromide pellet on the solid (see Figure 15). A Beilstein test showed no halogen present in the solid. The material is soluble in aromatic hydrocarbons, but recrystallization

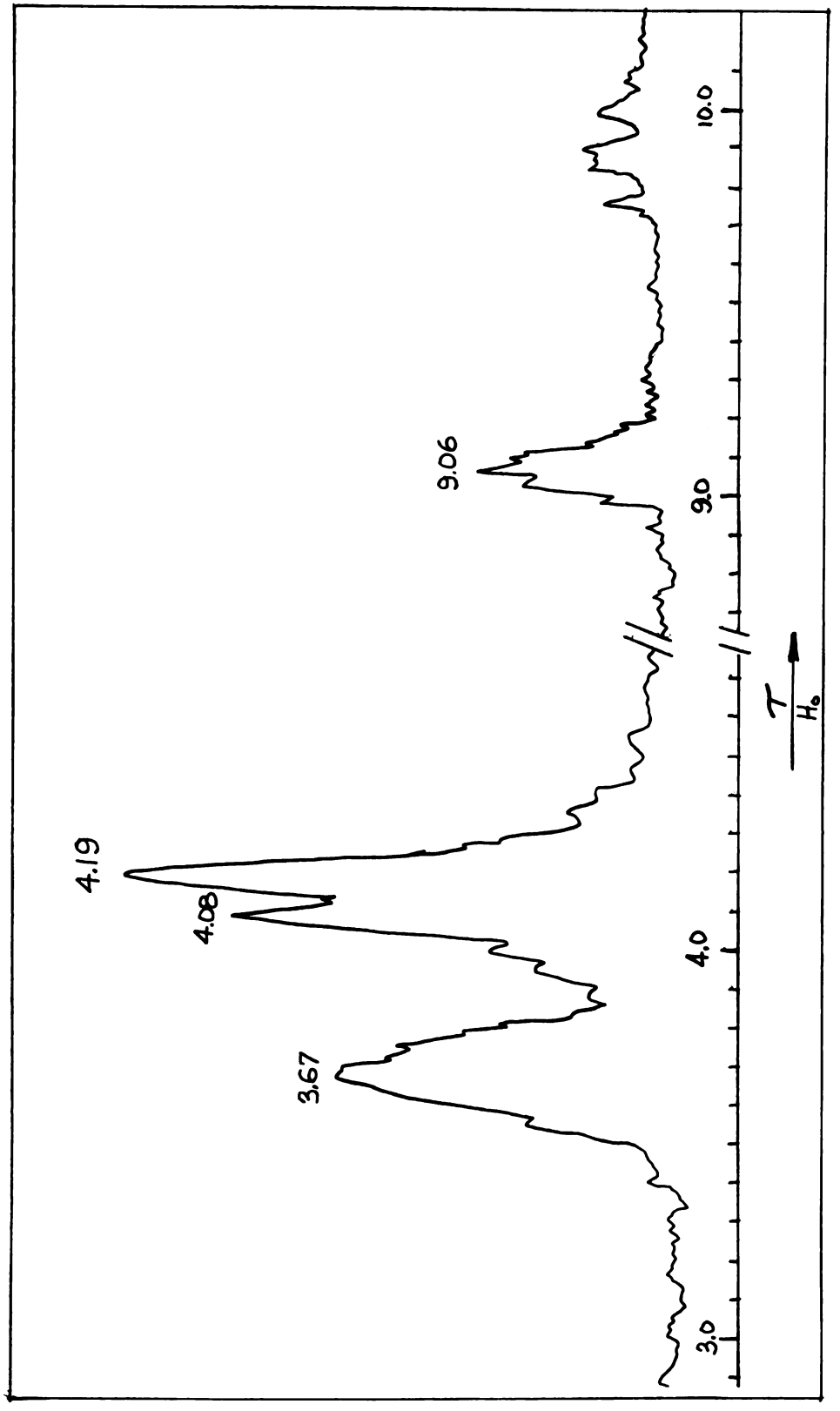



Figure 14. N.M.R. Spectrum of Product from Reaction between Phenyl Lithium and 2,4,6- Trimethylphenylchlorodicarbonium Tetrachloroborate (in deuterated acetone).

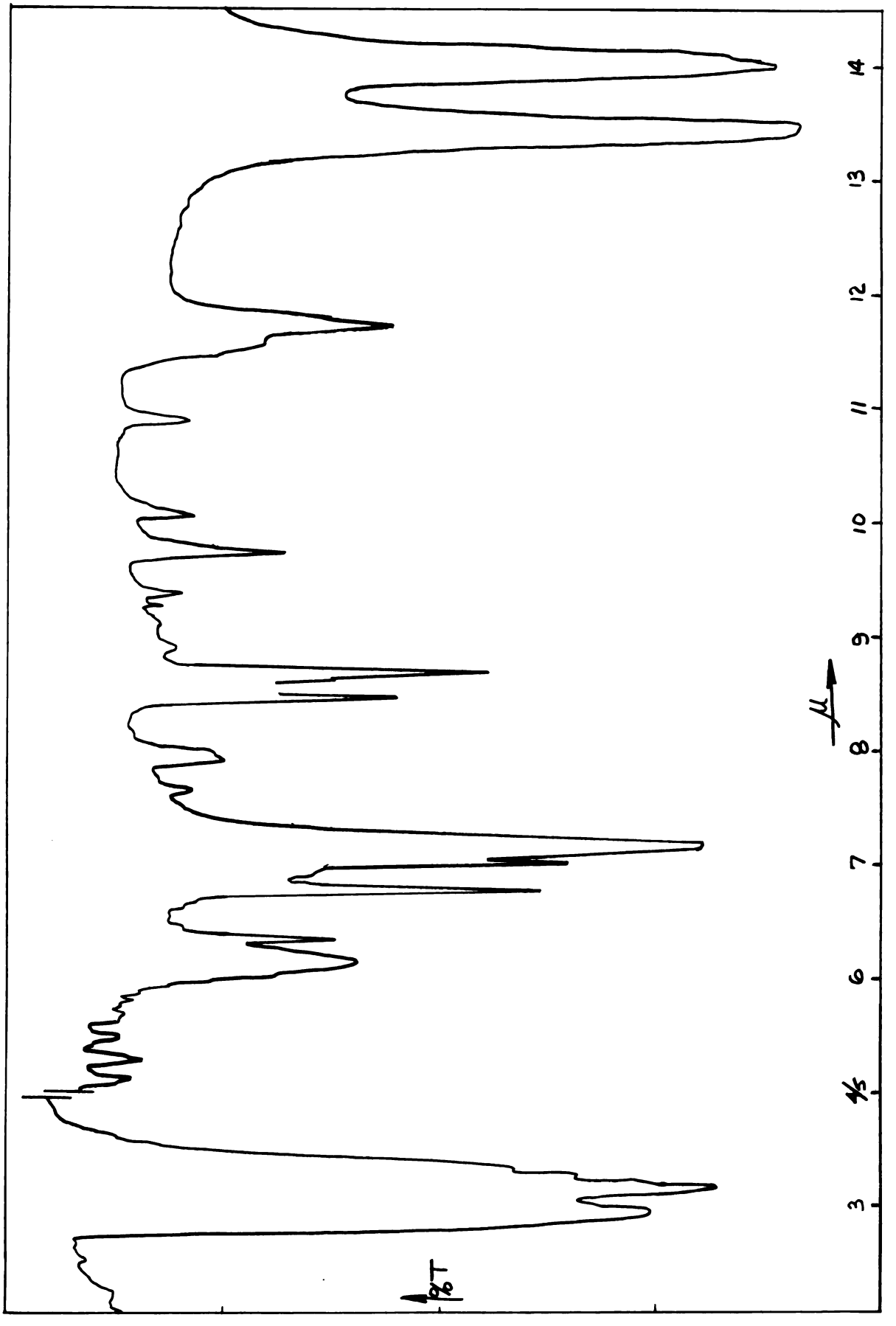



Figure 15. Infrared Spectrum of Solid obtained from Reaction between Phenyl Lithium and 2,4,6- Trimethylphenylchlorodicarbonium Tetrachloroborate (as $KBr$ pellet).

from benzene did not change the melting point.

17. Reaction of 2,4,6-Trimethylphenylchlorodicarbonium Tetrachloroborate with Methyl Magnesium Iodide

In a manner analogous to that used before, 1.5 g of trichloromethylmesitylene was converted to the tetrachloroborate salt using liquid sulfur dioxide and boron trichloride. In another flask (equipped with a standard taper attachment so that the filtered solution could be transferred to another flask) an ether solution of 0.1 mole methyl magnesium iodide was prepared. The ether solution was transferred dropwise into the flask which contained the dication salt (and 10 ml of ether). The latter flask was cooled in an ice bath, but the reaction was very exothermic as the gray solution was dropped into the bright red solution. A brown semi-solid formed during the addition, so the mixture was allowed to stir for an hour after the addition was complete. Distilled water (ca. 25 ml) was then added to the still cooled flask, and again there was an exothermic reaction, accompanied by the formation of a gelatinous mass. This mass was extracted twice with ether, pentane, and carbon tetrachloride. The layers were separated, the dark red organic layer was decolorized with charcoal, and attempts were made to crystallize a product from solution by cooling and concentrating the solution. None could be crystallized. The solvent was removed under reduced pressure and an infrared spectrum taken on the residual syrup (Figure 16). Qualitative flame tests showed no halogen in the syrup.

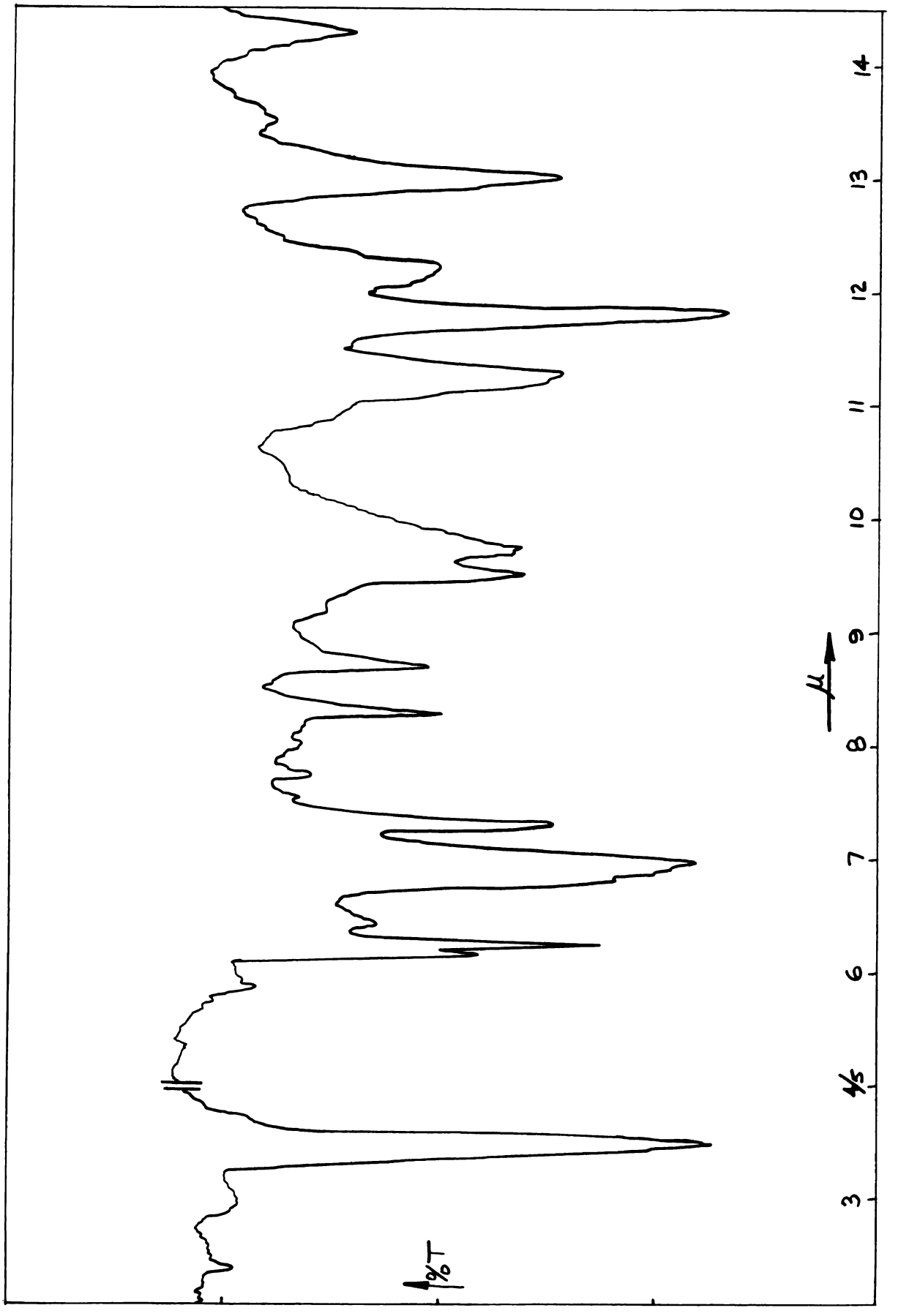



Figure 16. Infrared Spectrum of Syrup from Reaction between Methyl Magnesium Iodide and 2,4,6- Trimethylphenylchlorodicarbonium Tetrachloroborate ( smear ).

18. Preparation of Silver Tetrafluoroborate

A 500 ml, three-necked, round-bottomed flask was modified with a sintered glass frit sealed into the flask as a fourth neck to which was attached a standard tapered cylindrical tube with side arm so that liquid could be filtered from the main flask under reduced pressure. The flask which was equipped with thermometer, two gas addition tubes (one extending to the bottom of the flask) and a teflon-covered magnetic stirring bar was purged with a stream of dry nitrogen as the flask and attachments were heated with a cool flame to drive out any adsorbed water. Silver fluoride (34 g; 0.268 moles) was added under a nitrogen purge so the flask was left with a nitrogen atmosphere. About 100 ml of nitromethane was added to cover the silver fluoride, the bulb of the thermometer and end of the longer addition tube. Boron trifluoride was then bubbled through the liquid, which was agitated with the magnetic stirring bar. The slow passage of boron fluoride was continued until the gas was detected coming out of the sulfuric acid vent, the temperature being kept below ca. $50^{\circ}$ by cooling the flask with a water bath. Stirring was continued for half an hour and then nitrogen was passed through the flask to sweep out the excess boron fluoride. The apparatus was then rotated and the solution filtered through the frit, the nitromethane removed under reduced pressure, and nitrogen admitted to leave a pressure of one atmosphere in the tube. White crystalline silver tetrafluoroborate remained in the tube and was stored under dry pentane until used.

19. Preparation of Cycloöctatetraene Dibromide

A 50 ml, three-necked, round-bottomed flask equipped with a teflon covered magnetic stirring bar, dropping funnel, and two gas tubes was flushed with a stream of dry nitrogen while being heated with a cool flame. About 10 ml of dry methylene chloride was placed in the flask with 0.93 g (0.0089 moles) of freshly distilled cycloöctatetraene. The flask was immersed in an ice-salt bath at -10°. A solution of 0.487 ml (0.0089 moles) bromine and 10 ml of methylene chloride was added dropwise to the rapidly stirred yellow solution. As the bromine reacted the red solution faded to bright yellow. Stirring was continued for 10 minutes after addition was complete. The cooling bath was then removed and solvent stripped under reduced pressure. Dry nitromethane (10 ml) was added to dissolve the remaining syrup and crystallize the bicyclo [4,2,0] octa-7,8-dibromo-1,3,5-triene, melting 32.5-33.5°; literature[55] 33° for the cycloöctatetraene dibromide. A maleic anhydride adduct melted at 203-204° and the literature[13] reports 205° for 3,6-endo-(3',4'-dibromo) cyclobutylene cyclohexene-4,5-dicarboxylic acid-1,2-anhydride.

20. Reaction between Cycloöctatetraene Dibromide and Silver Tetrafluoroborate

In a small flask was placed 2.3 g (0.0089 moles) of cycloöctatetraene dibromide with 10 ml of nitromethane. In a dropping funnel connected to the flask by a standard taper was placed 3.46 g (0.0178 moles) of silver

tetrafluoroborate and 10 ml of nitromethane. The system was isolated from the atmosphere and then partially evacuated. The flask was cooled in an ice-water bath, and then the system was evacuated. Dry nitrogen was allowed into the flask to provide an inert atmosphere for the reaction. A magnetic stirring bar was used to stir the solution in the flask as that in the dropping funnel was added slowly. The solution became a muddy brown until about half of the silver tetrafluoroborate solution had been added when a blue-purple cast was observed. This purple appearance remained throughout the remainder of the addition period. Addition was complete in about 10 minutes. The mixture was then filtered through a glass frit attached to the flask, the filtrate being collected in an n.m.r. sample tube and a second glass bulb. The solid silver bromide was collected on the glass frit, which was then removed, dried, and the amount of silver bromide determined by difference in weight (the frit was tared at start of reaction). The silver bromide weighed 2.6 g, more than one but less than two moles per mole of cyclooctatetraene dibromide used in the reaction. An n.m.r. spectrum was taken on the filtrate and showed a very complex spectrum over most of the field (between 3 and 9 $\tau$). The solvent was removed from remaining filtrate, but only an intractable tar remained.

## 21. Reaction between Cycloöctatetraene Dibromide and Boron Bromide

In a flask was placed 0.69 g (0.0026 moles) of cycloöctatetraene dibromide. The flask was then cooled

and about 15 ml of sulfur dioxide condensed onto the dibromide. Through a dropping funnel connected to the flask 0.49 ml of boron bromide was added dropwise to the mixture in the flask. As each drop mixed there was an increase in pressure (slight) as observed on a manometer also attached to the flask, due to the exothermic reaction vaporizing some of the sulfur dioxide. The mixture was stirred for half an hour after the addition was complete. About ten ml of water was then slowly added to the brown-red mass in the flask. When the exothermic reaction had ceased, the mass was extracted with 50 ml of ether. Removal of the ether under reduced pressure left a white solid. Crystallization of the solid from carbon tetrachloride gave 0.23 g of a crystalline material melting 142-144°. An infrared spectrum (Figure 17) of the solid was very well resolved, but could not be identified. Qualitative analysis of the solid showed the presence of bromine and sulfur.

A parallel experiment was run using methylene chloride in place of sulfur dioxide. Again the product was brown-red and was hydrolized with ca. 10 ml of water. Extraction of the resulting mass with 50 ml of ether and vaporization of the ether left 0.2 g of solid which when recrystallized from carbon tetrachloride melted 90-91°. An infrared spectrum (Figure 18) of the solid was again well resolved but not at all similar to that of the product from reaction in sulfur dioxide. Qualitative analysis of the solid showed the presence of bromine. Micro analysis of the two samples were made.

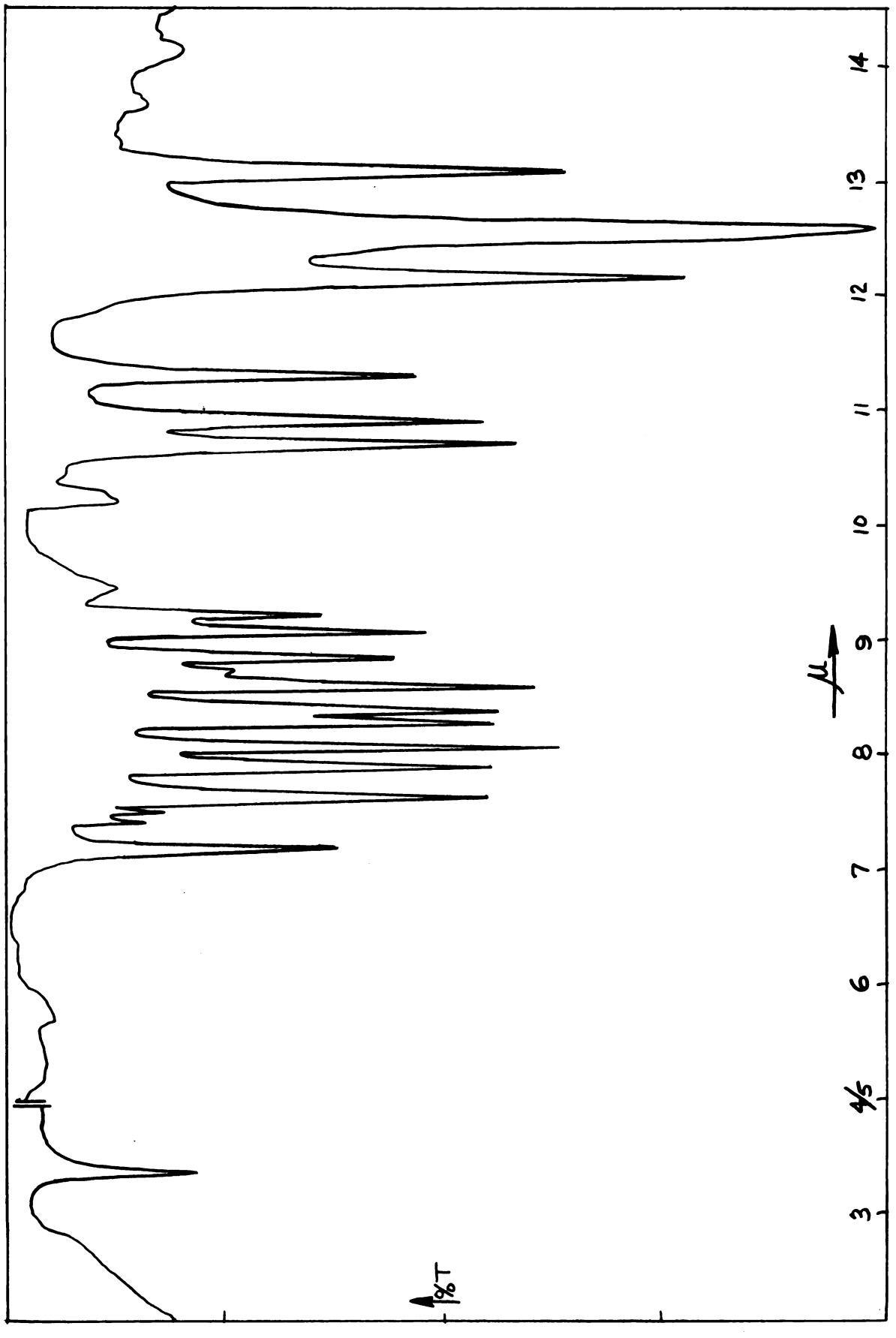



Figure 17. Infrared Spectrum of Solid from Reaction between Cycloöctatetraene Dibromide and Boron Bromide in Sulfur Dioxide ( as KBr Pellet ).

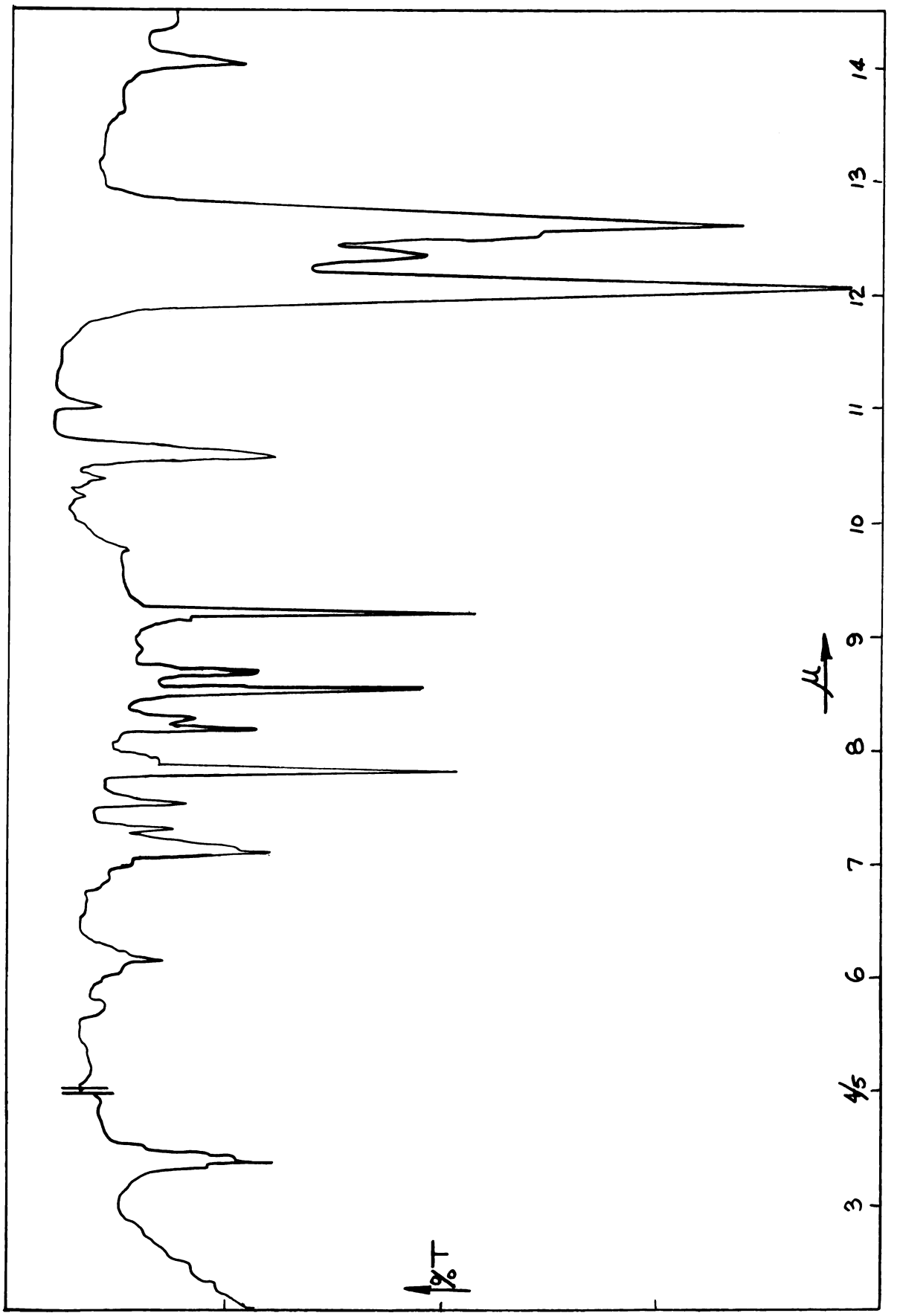



Figure 18. Infrared Spectrum of Solid from Reaction between Cycloöctatetraene and Boron Bromide in Methylene Chloride ( as KBr Pellet ).

Anal: Found for solid melting 142-144°; C: 22.49, 22.41; H: 2.04, 1.91.

Anal: Found for solid melting 90-92°; C: 15.33, 15.13; H: 1.27; 1.18.

These analyses serve to indicate a mixture, but a mass spectrum was taken on each sample. The spectra were uninterpretable, being so complex. N.m.r. spectra were taken (Figures 19 and 20) but were unexplicable.

Silver nitrate solution was added to the aqueous layer from the reaction workup, in excess. The resulting silver bromide precipitate was filtered, washed, dried, and weighed. The mole ratio of bromines precipitated to moles of starting bromide was 7 to one.

## 22. Preparation of Azibenzil (Phenylbenzoyldiazomethane)[19]

In a one-liter, three-necked, round-bottomed flask equipped with mechanical stirrer, reflux condenser, and dropping funnel 176 g (0.838 moles) of benzil was dissolved in 500 ml of refluxing 95 percent ethanol. To the ethanol solution 100 g (1.25 moles) of 40 percent hydrazine was added dropwise over a period of half an hour. When about two-thirds of the hydrazine solution had been added the monohydrazone precipitated suddenly from the solution. After complete addition the mixture was stirred and refluxed for two hours. The mixture was then cooled with an ice bath and the white crystals of monohydrazone filtered and air dried.

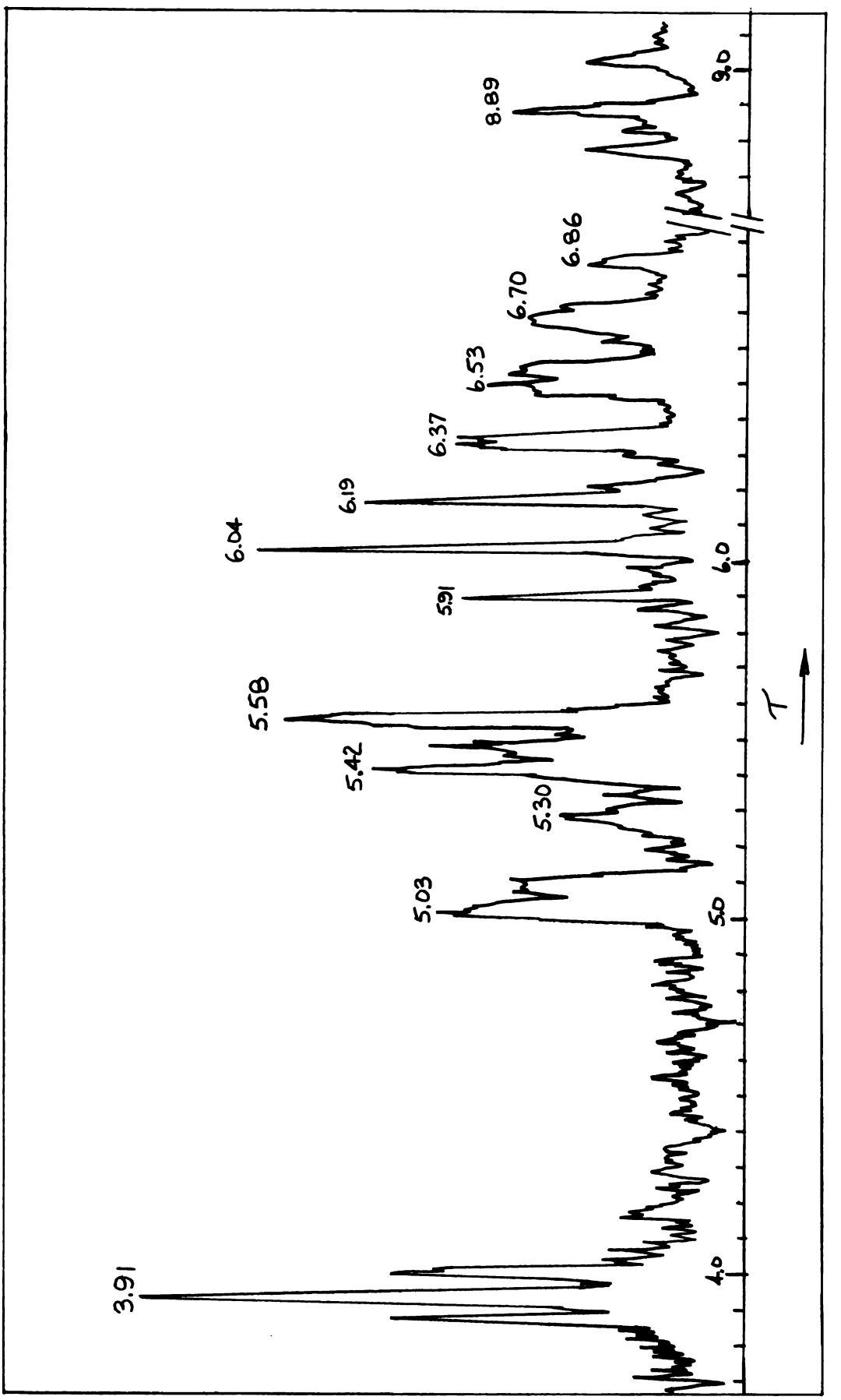



Figure 19. N.M.R. Spectrum of Solid from Reaction between Cycloöctatetraene Dibromide and Boron Bromide in Sulfur Dioxide ( in $CCl_4$ Solution ).

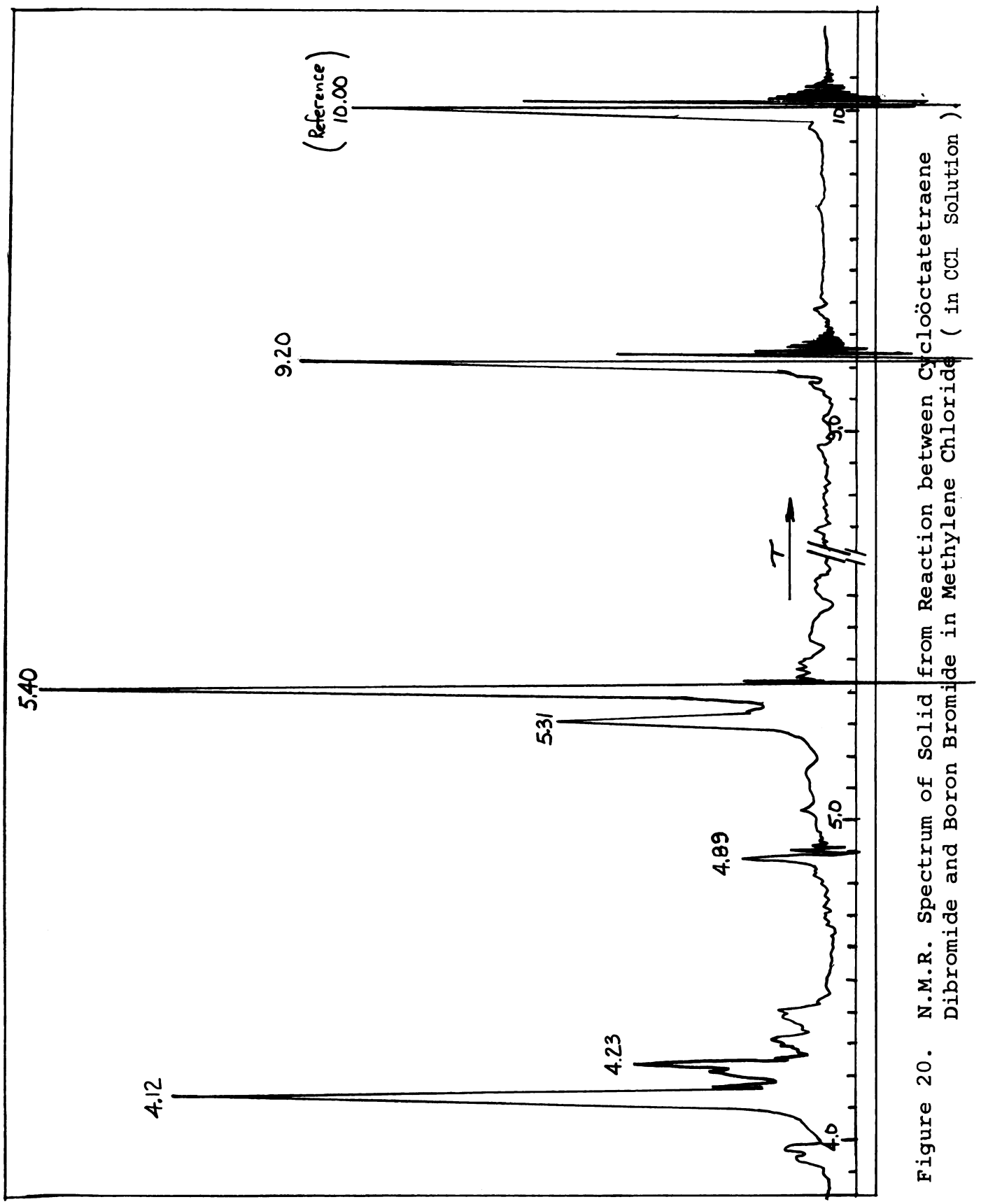



Figure 20. N.M.R. Spectrum of Solid from Reaction between Cycloöctatetraene Dibromide and Boron Bromide in Methylene Chloride ( in CCl Solution )

In a three-liter, three-necked, round-bottomed flask equipped with mechanical stirrer and two reflux condensers was placed 150 g (0.67 moles) of benzil monohydrazone, 152 g (0.704 moles) of yellow mercuric oxide (commercially available material was dried at 150° in an oven and used), and 750 ml of anhydrous ether. The mixture was agitated and refluxed four hours (until the orange color had become a muddy brown and did not seem to deepen further). Benzene, 500 ml, was then used to extract the mixture (the solid material was triturated with small portions, ca. 25 ml, until no further coloration was obtained). The decanted organic and wash benzene solutions were combined and ether added until precipitation started. Cooling the solution crystallized orange needles of azibenzil in 64 percent yield. A visible-ultraviolet spectrum in dioxane showed absorption bands at 236 mμ (log $\epsilon$ = 4.16) and 424 mμ (log $\epsilon$ = 4.63) for the orange needles. The literature[57] reports absorption bands in the visible-ultraviolet spectrum of azibenzil at 272-274 mμ (log $\epsilon$ = 4.19) and 424-428 mμ (log $\epsilon$ = 4.63) in several solvents.

23. Preparation of Diphenylketene and Reaction with Quinone

A 100 ml, two-necked, round-bottomed flask was arranged to be heated in a bath maintained at 110° while a solution was being dropped into the flask and an argon purge flowed through the flask. About a 50 percent solution of azibenzil in benzene was allowed to drop into the flask while a stream of argon passing through the flask carried

the vaporizing benzene to a second vessel to be condensed. As the solution dropped into the hot flask and the benzene flashed, the azibenzil decomposed with the evolution of nitrogen and a red-orange liquid, diphenylketene, was left in the flask. The liquid was then distilled at reduced pressure (bp 123/2 mm) and collected in ca. 350 ml of petroleum ether (30-60°).

Diphenylketene, 50 ml, in 250 ml of petroleum ether and 11 g of quinone in 200 ml anhydrous ether were placed in a one-liter, round-bottomed flask and allowed to stand under an inert atmosphere of argon until a yellow-orange material crystallized in 80 percent yield. This solid, the bis-β-lactone (VIII), liquified above its melting point, 142-143°, with the evolution of carbon dioxide. A visible spectrum showed an absorption band at 424 mμ in methylene chloride and an n.m.r. spectrum in deuterated chloroform showed a large multiplet at 2.56, 2.60, 2.70 and four smaller triplets at 3.21, 3.42, 3.60, and 3.79 τ (using tetramethylsilane as an internal reference).

## 24. Preparation of bis-Tetraphenyl-p-xylylene

The bis-β-lactone (VIII), 2 g, was placed in a flask with 25 ml of xylene and the xylene heated to reflux for 30 minutes. The solution on cooling went from red-brown to orange and a yellow-orange solid, melting point 248°, crystallized in ca. 30 percent yield. A visible spectrum in dioxane showed an absorption band at 273 mμ (14,300) and at 424 mμ (42,600). An n.m.r. spectrum showed

a rather broad aromatic proton resonance at 2.82 τ and a smaller multiplet at 3.09 τ (see Fig. 21). Infrared spectra (solution and solid) were taken (see Fig. 22).

25. Preparation of bis-Tetraphenyldichloro-p-xylene

Using the procedure of Rafos[16] bis-tetraphenyl-p-xylylene (ca. 0.1 g) was dissolved in 10 ml methylene chloride and chlorine (gas) allowed to bubble through the solution for ten minutes. The solvent was stripped using an aspirator and the resulting 0.11 g of white crystalline solid recrystallized from methylene chloride-benzene, m.p. 240-241° (literature[58] 248; Rafos[16] 242-243°).

Later preparations of the dichloride were made using benzene instead of methylene chloride, for the bis-tetraphenyl-dichloro-p-xylene precipitates from solution and can be filtered and dried pure.

26. Preparation of bis-Tetraphenyl-p-xylylium Diperchlorate

In a dry flask was placed 0.2 g (0.00042 moles) of bis-tetraphenyl- dichloro-p-xylene and ca. 25 ml of sulfur dioxide was condensed on the solid, which dissolved to a clear light yellow solution. Silver perchlorate, 0.174 g (0.00084 moles), was added to the sulfur dioxide solution. The first few pieces of solid that hit the liquid turned the solution orange, further addition of silver perchlorate only darkened the solution to deep orange-red. Agitation of the solution was continued for about 10 minutes. Then the solution was allowed to warm to room temperature to

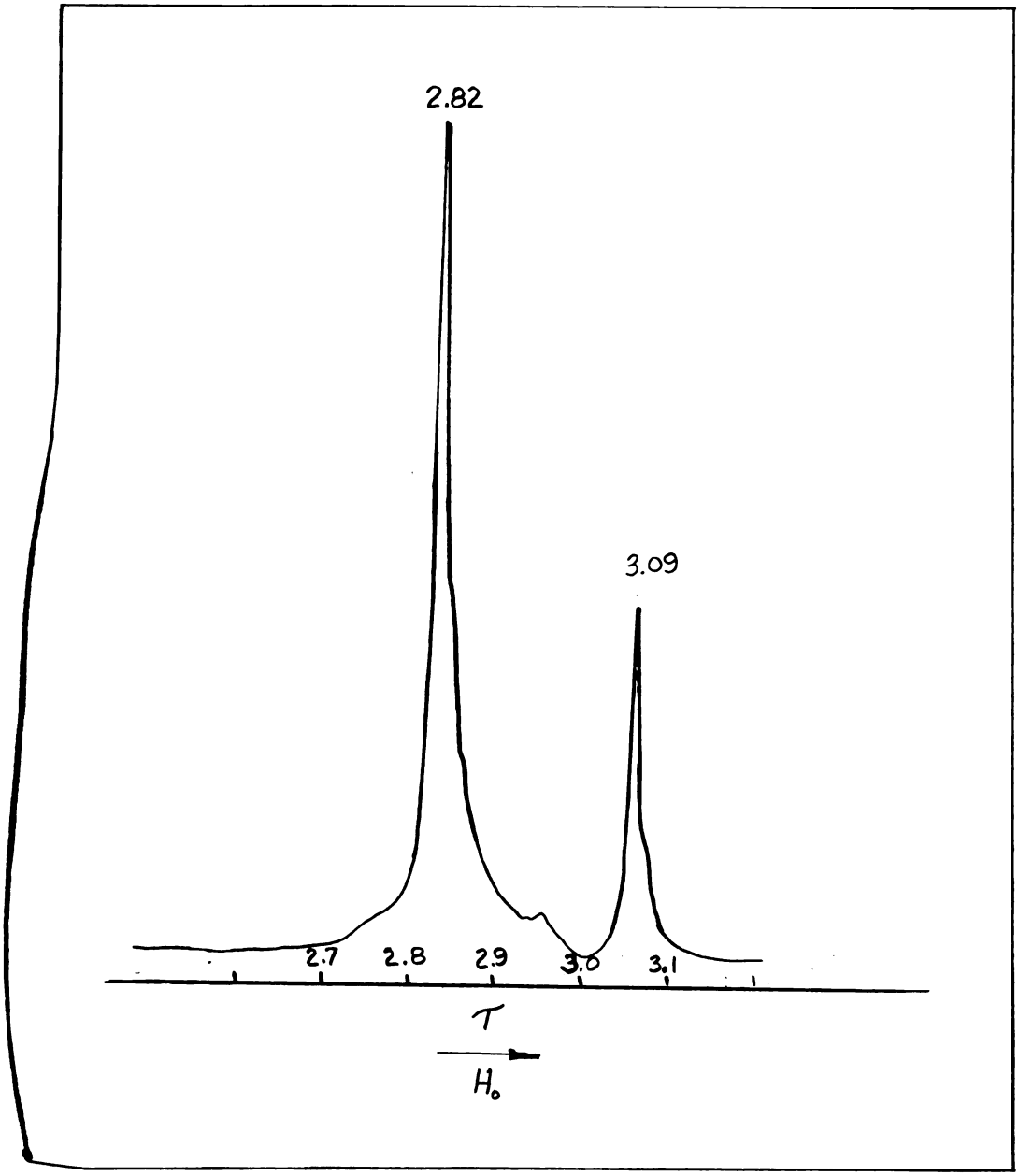



Figure 21. N.M.R. Spectrum of bis Tetraphenyl-p-xylylene ( in $CH_2Cl_2$ Solution ).

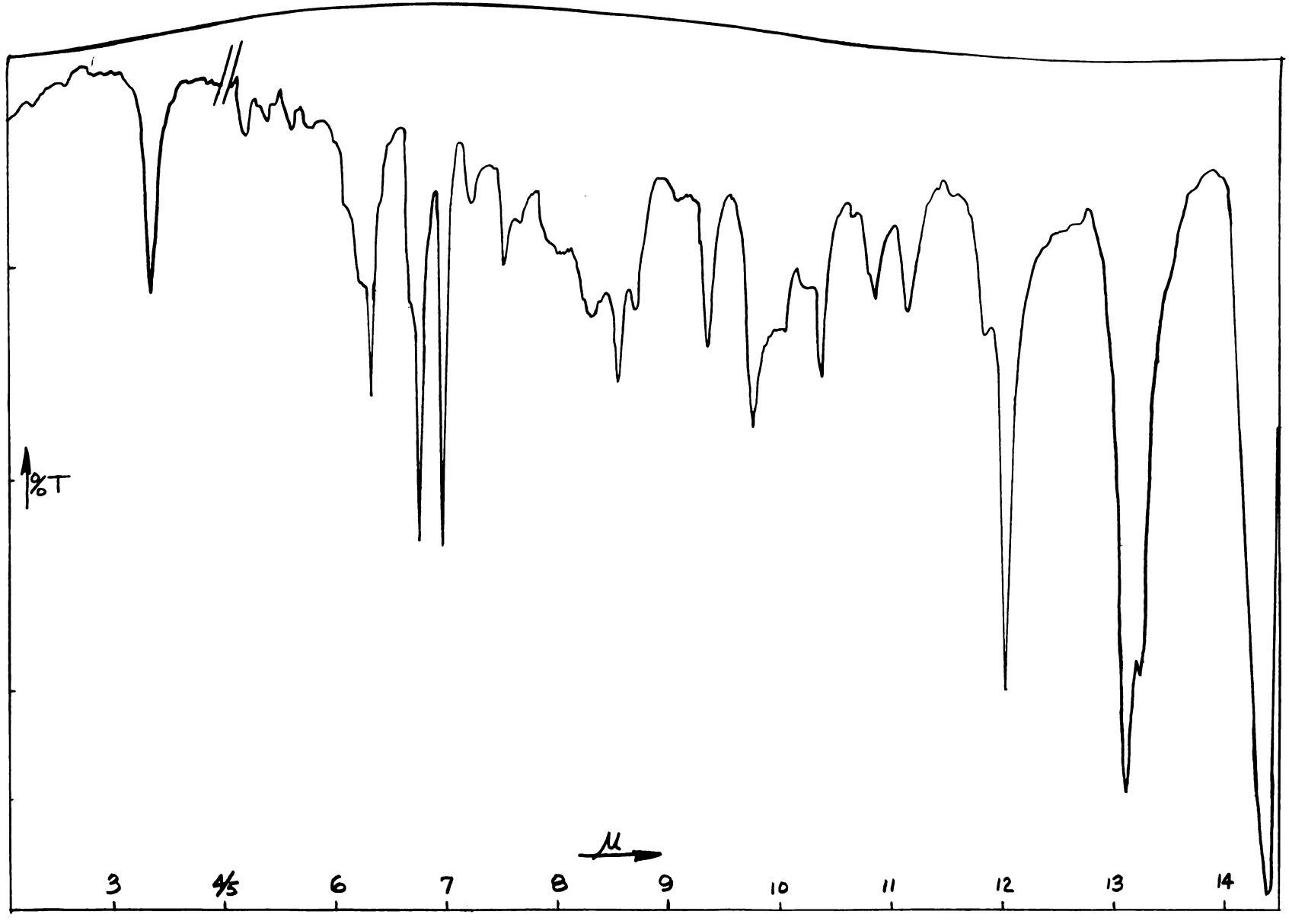



Figure 22. Infrared Spectrum of bis-Tetraphenyl-p-xylylene ( as KBr Pellet ).

permit the sulfur dioxide to evaporate; a white-orange residue remained in the flask. About 10 ml of benzene and 5 ml of chloroform was used to triturate the solid. Separation of the liquid and solid, and removal of the solvents at the aspirator left a red-brown semi-crystalline solid. Recrystallization from benzene yielded 0.251 g of the crystalline bis-tetraphenyl-p-xylylium diperchlorate, m.p. 143-145(d). The white solid from the preparation was reprecipitated from ammoniacal solution, filtered, dried, and weighed. A 90 + % yield (0.119 g) of the silver chloride for complete ionization of the bis-tetraphenyldichloro-p-xylene was obtained.

27. Reaction of Bis-tetraphenyl-p-xylene dication with Bis-tetraphenyl-p-xylylene

Bis-tetraphenyl-p-xylylene (0.0125 g) and bis-tetraphenyl-p-xylene diperchlorate (0.0145 g) were each put in an arm of a reaction vessel arranged to hold two solutions separately unless the vessel is rotated. When rotated the solutions are mixed and contained in a third portion of the vessel (once attached to the vacuum manifold, aliquots could be taken from this container without having to open it to the atmosphere). A total of 7.5 ml of degassed methylene chloride was distilled into the vessel's separate chambers. When the solids had dissolved to clear orange and red solutions respectively, the vessel was rotated, allowing the solutions to mix. An immediate deepening of the red color was observed. A visible spectrum on an aliquot showed

an absorption band, not present in either reactant, at 580 mμ (5420), as well as the bands of the reactants 467 mμ (17,050) and 424 mμ (14,700). An electron spin resonance spectrum was taken with another aliquot of the deep red solution. A signal was observed, and by lowering the temperature to ca. $-90^{\circ}$ the resolution was improved to where the spectrum clearly showed 23 equally spaced lines (see Figures 24 and 25). An n.m.r. spectrum (Figure 26) taken on an aliquot of the red solution showed multiplet resonances at 2.40, 2.55, and 2.87 τ (referred to tetramethylsilane as an internal reference). The n.m.r. spectrum of the dication showed resonances at 2.62 and 2.81 τ and the tetraphenyl-p-xylylene showed resonances at 2.82 and 3.09 τ. With reduced pressure the solvent was removed from the remainder of the deep red solution leaving a yellow-brown residue. A portion of the residue was redissolved in methylene chloride. The resulting solution had the same appearance as the solution before solvent removal. A visible spectrum (Figure 27) taken on the solution showed an absorption band at 580 mμ but the value of the extinction coefficient was low and decreasing (due probably to oxygen in the solvent reacting with the radical). An infrared spectrum (Figure 28) was taken on the residue as a potassium bromide pellet and methylene chloride solution. The spectrum in solution (Figure 29) was poorly resolved and the solid showed one strong band at 1259 $cm^{-1}$, but the rest of the spectrum showed

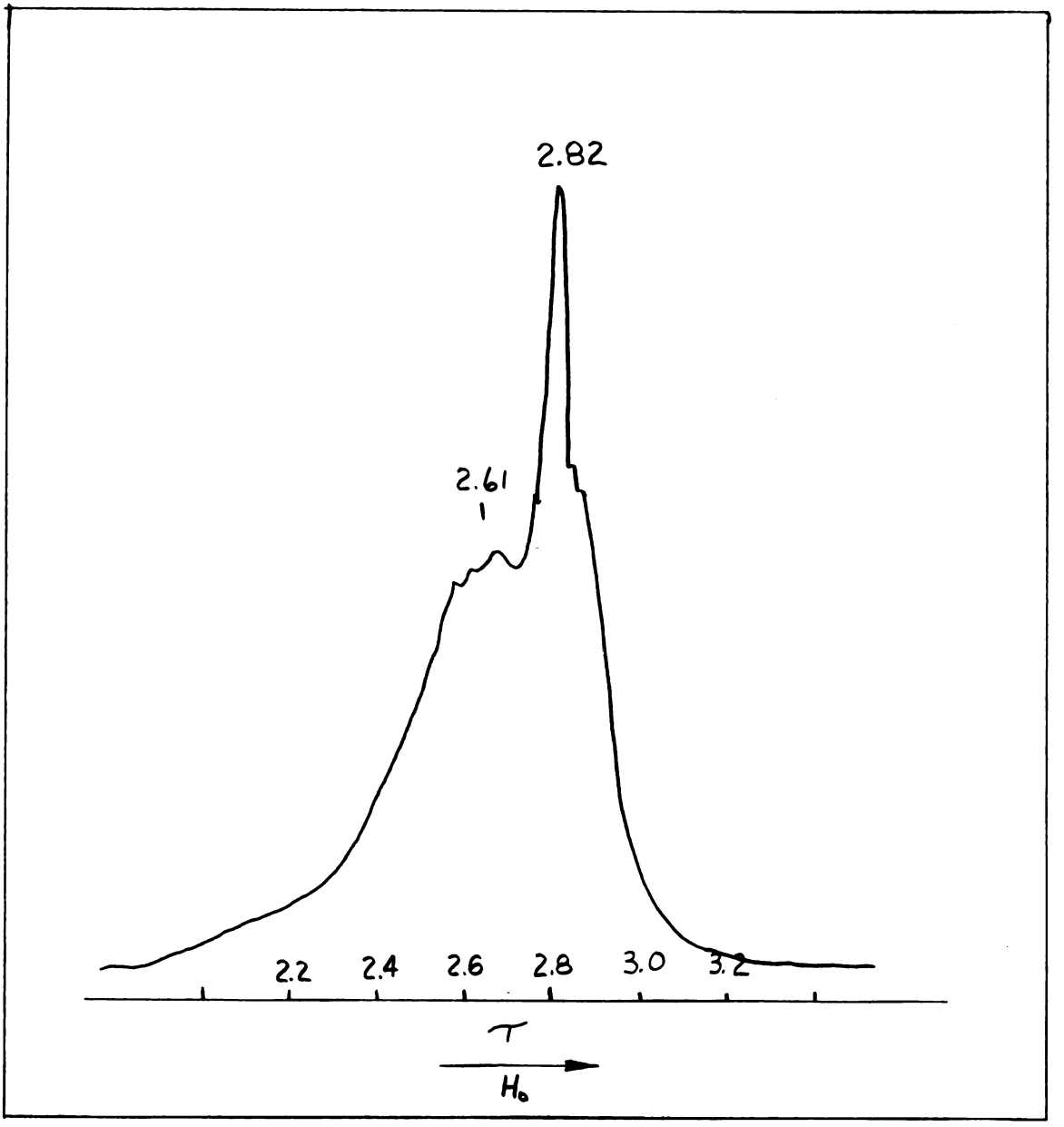



Figure 23. N.M.R. Spectrum of bis Tetraphenyl-p-xylylium Diperchlorate ( in $CH_2Cl_2$ Solution ).

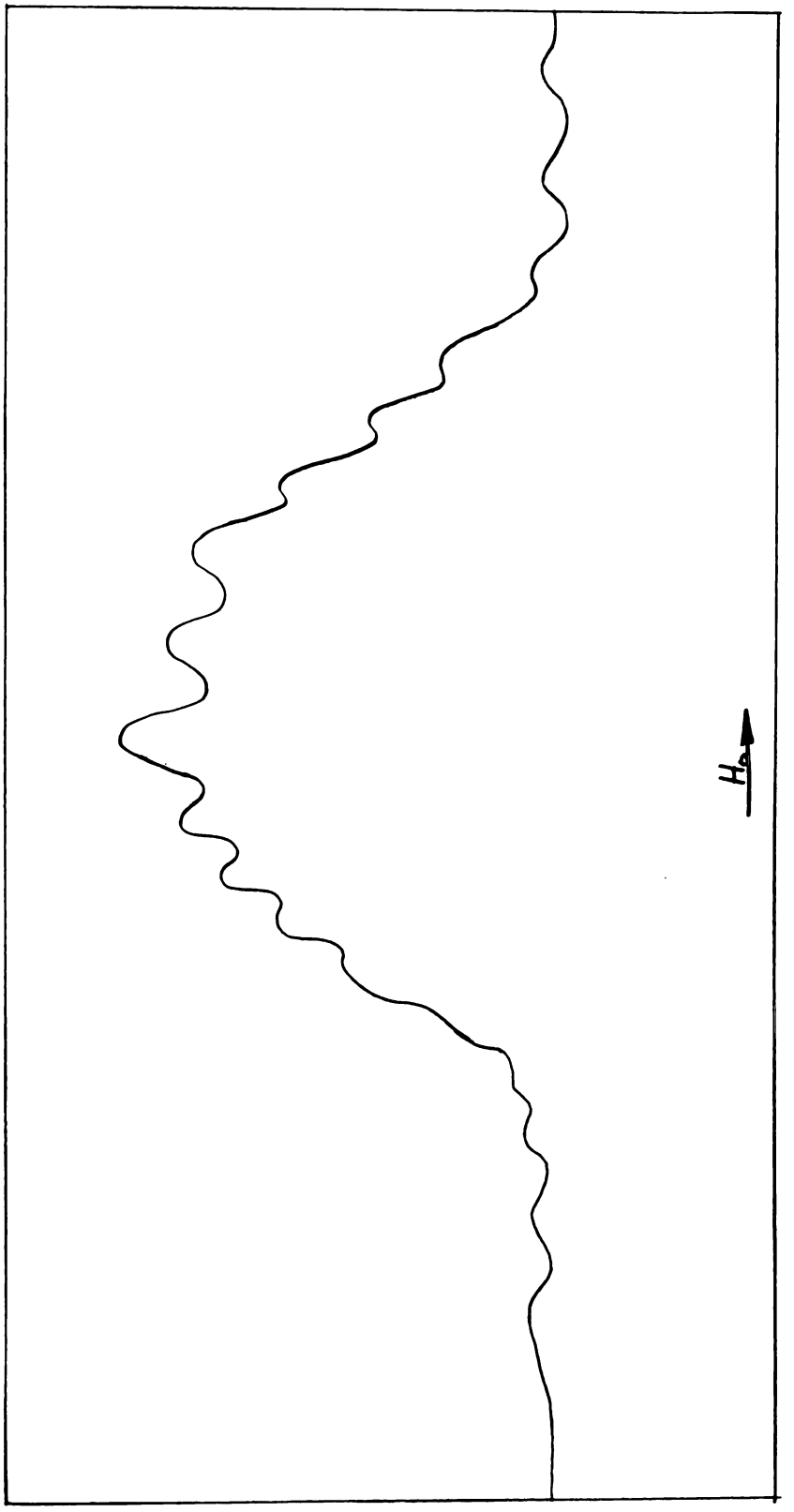



Figure 24. E.S.R. Spectrum of Radical-Cation at Ambient Temperature ( in $CH_2Cl_2$ ).

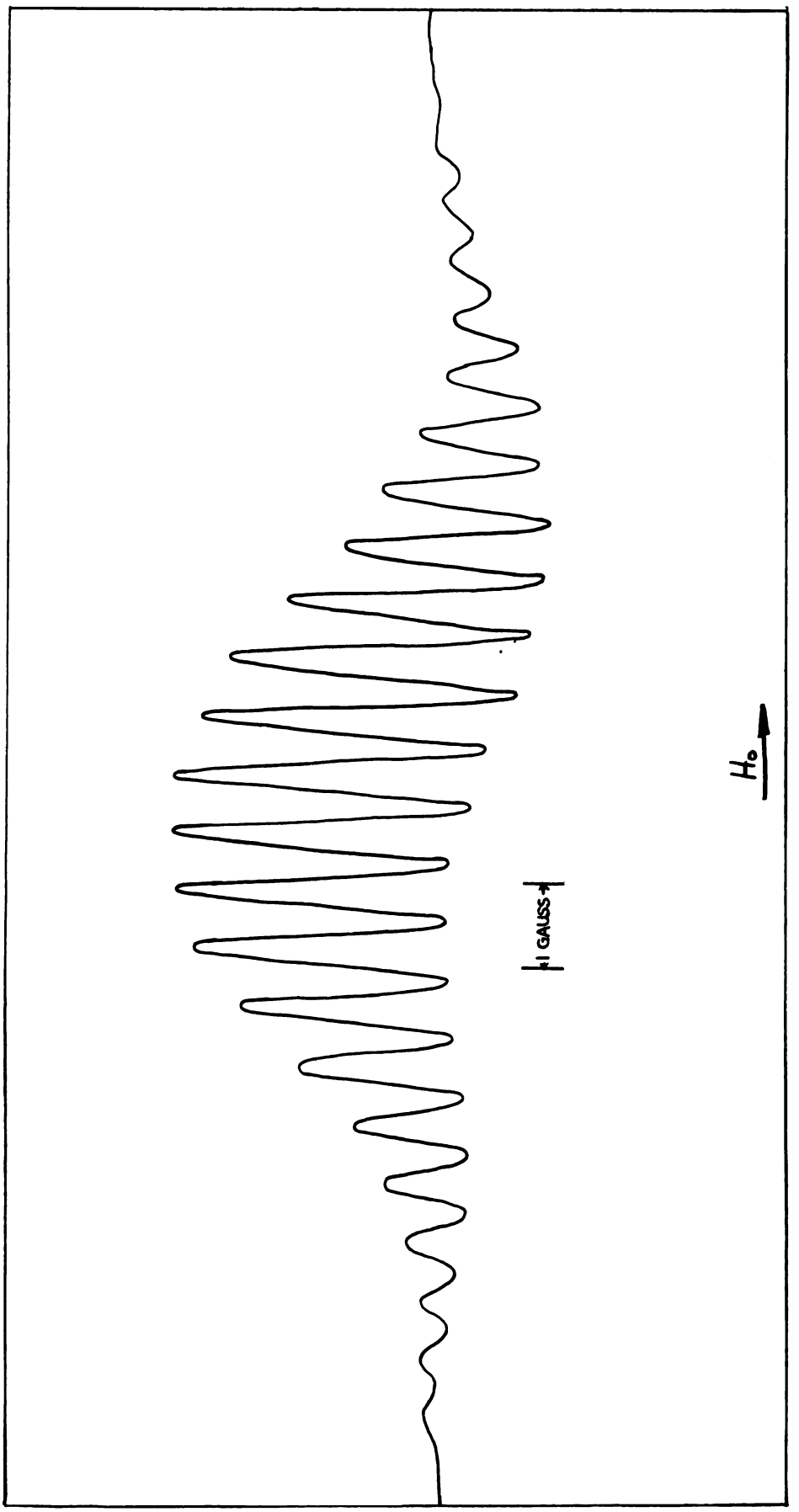



Figure 25. E.S.R. Spectrum of Radical-Cation at -90° ( in $CH_2Cl_2$ ).

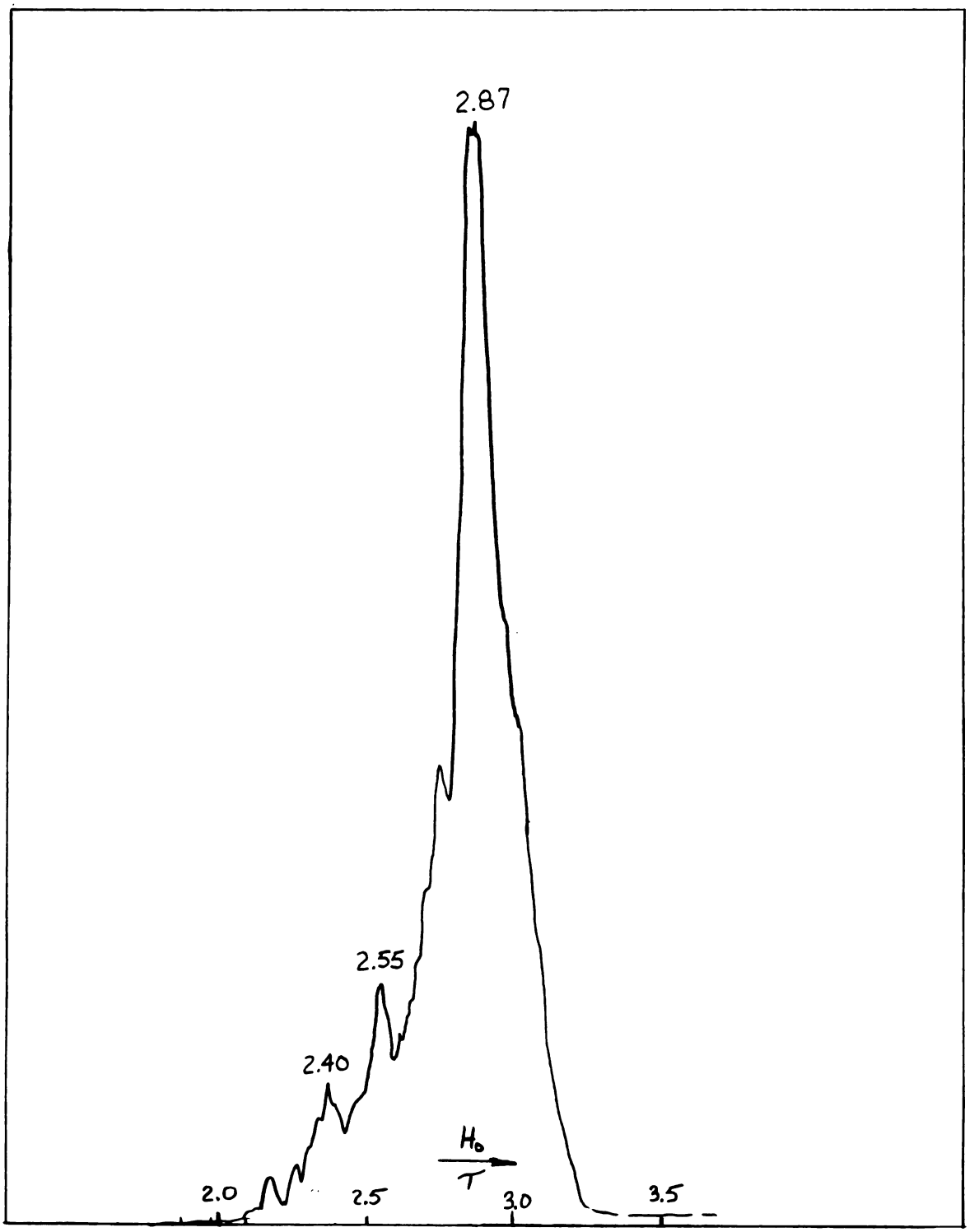



Figure 26. N.M.R. Spectrum of Radical-Cation ( in $CH_2Cl_2$ ).

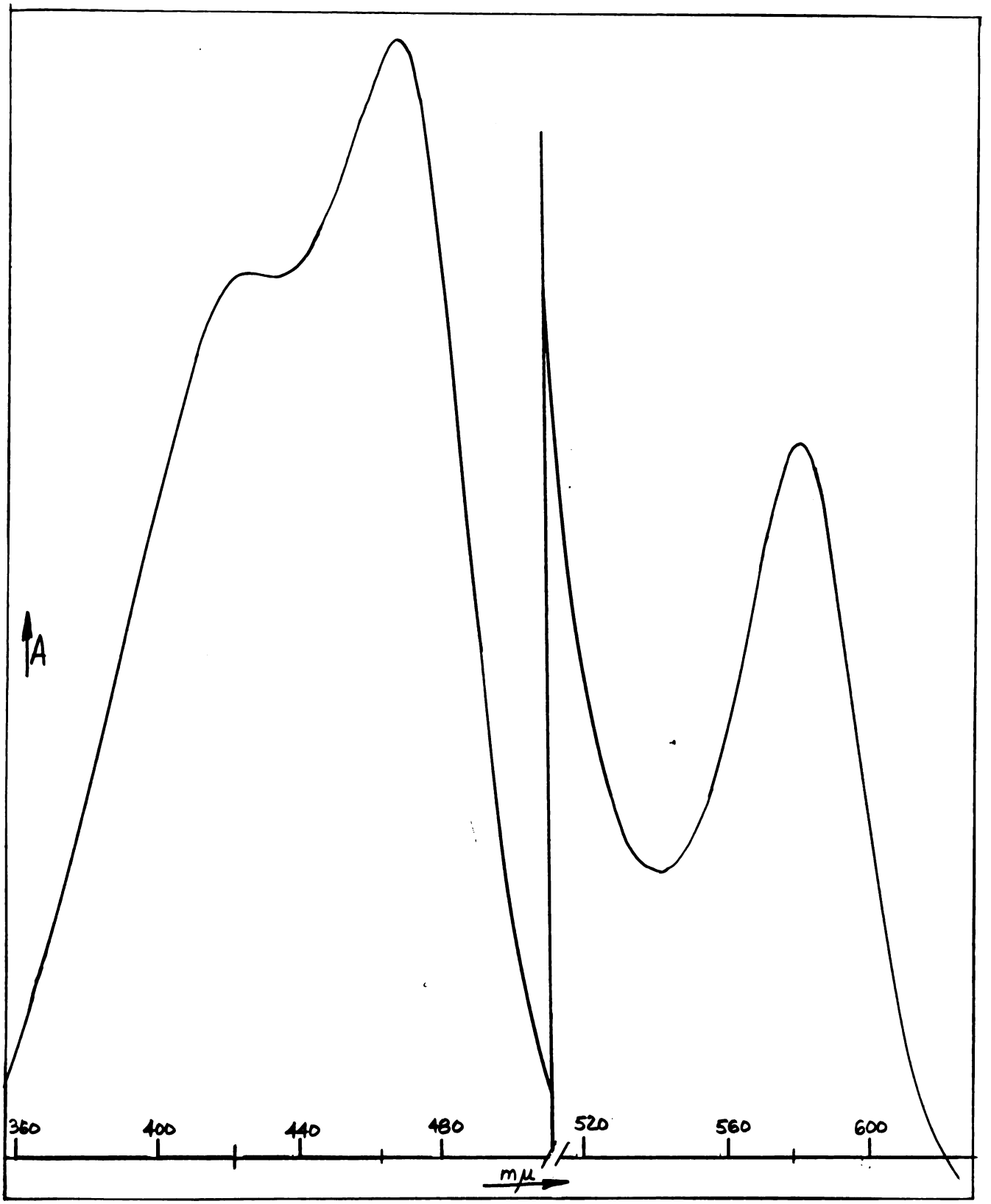



Figure 27. Visible Spectrum of Radical-Cation in Methylene Chloride.

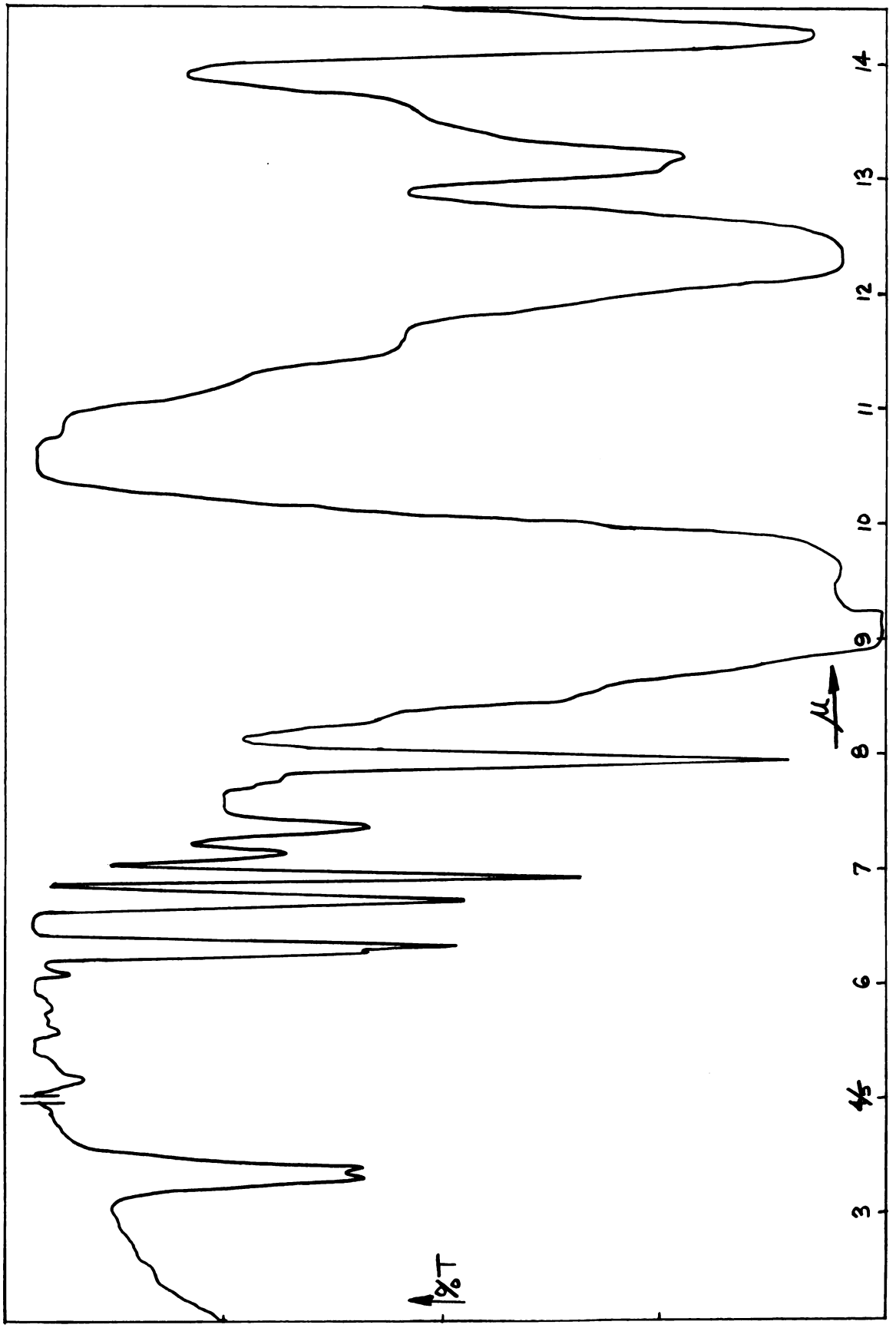



Figure 28. Infrared Spectrum of Radical-Cation (as KBr pellet).

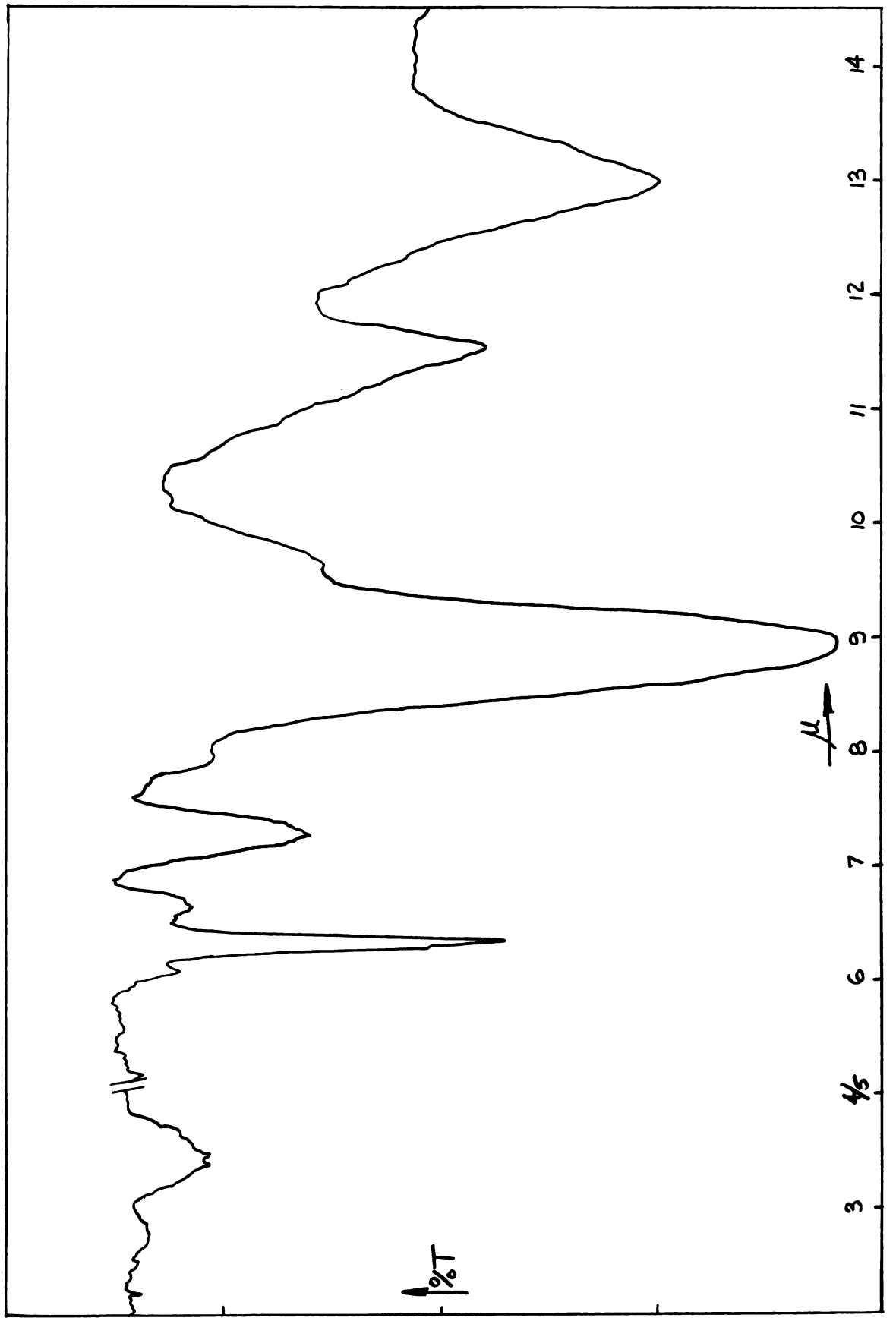



Figure 29. Infrared Spectrum of Radical-Cation ($CH_2Cl_2$).

bands observed in the original deep red solution. An e.s.r. spectrum taken on a solution of the residual solid showed the same spectral pattern, although not as well resolved, 23 lines of equal spacing. Calibration of the e.s.r. spectra was made from a spectrum of $[Cr(NO)(CN)_5]^{-3}$ ion.[41] The observed lines for the radical-cation were found to have a $\Delta$ H of 0.69 gauss.

## 28. Rate of Reaction between Bis-tetraphenyl-p-xylylene and Bis-tetraphenyl-p-xylene Dication

Bis-tetraphenyl-p-xylylene (0.1134 g; 0.000276 moles) was placed in a dried flask which was then attached to the vacuum manifold for several hours evacuation. Bis-tetraphenyl-p-xylylium diperchlorate (0.1323 g; 0.000218 moles) was similarly placed in another dry flask which was evacuated on the manifold. These flasks were then alternately filled with argon and evacuated several times to insure removal of all oxygen from the flasks. Dry, distilled methylene chloride was degassed on the same manifold (by alternate cooling with liquid nitrogen, evacuating the frozen methylene chloride, and warming to room temperature).

About 250 ml of methylene chloride was distilled into each flask containing the solid reactants to form a $1 \times 10^{-3}$ molar solution. The solutions were covered with an atmosphere of argon and the flasks were transferred to an apparatus in which each flask was connected to an arm of a "Y" tube through a glass syringe (see Fig. 30 for a schematic drawing of this "stop-flow apparatus"). Depressing the

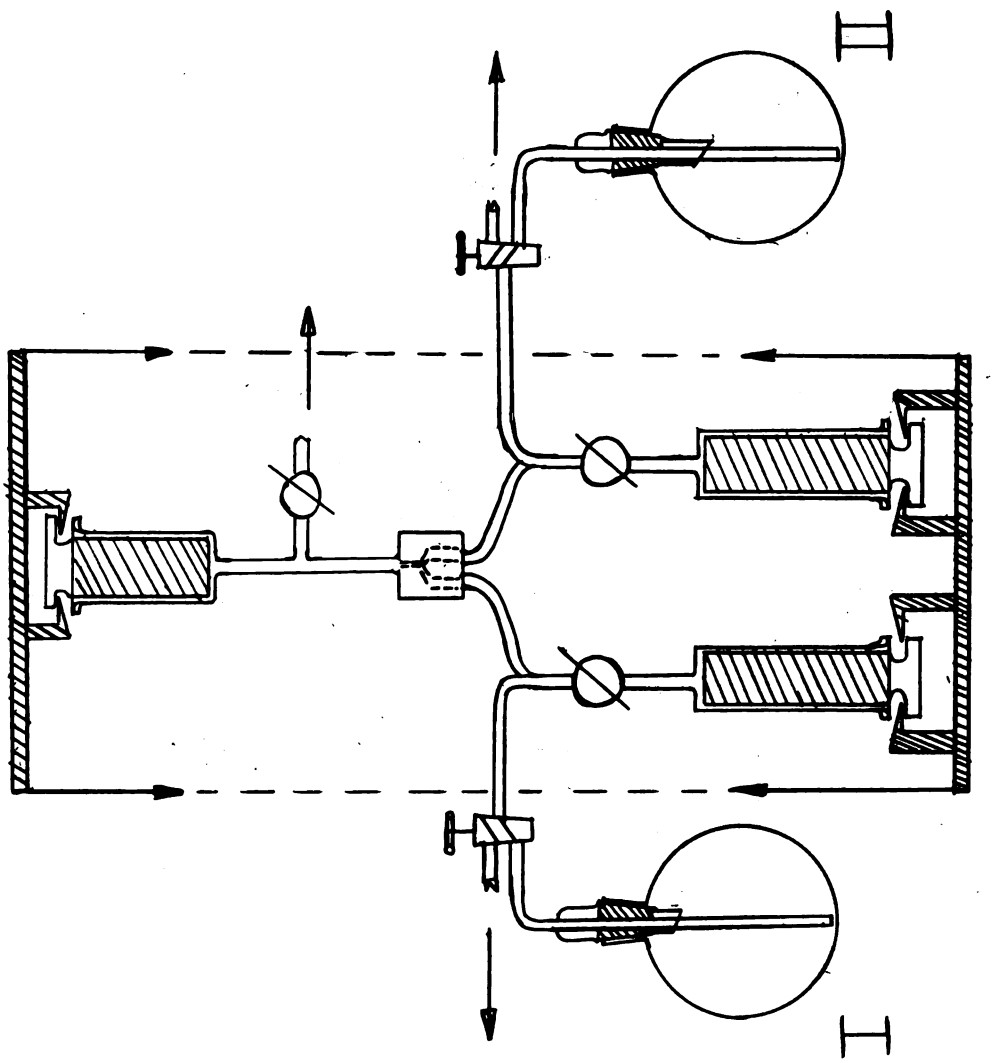



Figure 30. Stopped-Flow Apparatus for Measuring Rates of Rapid Reactions.

syringe plungers simultaneously forced equal volumes into the third leg of the "Y" tube. The solutions mix in this tube, react, and are forced into a receiving container. When the flow of liquid is stopped, the mixed reagents at the Y of the tube react; the time elapsed between the stopped flow and the change in appearance gives an estimate of the half-life of the reaction. Thus, when the flow was stopped, the yellow bis-tetraphenyl-p-xylylene and red bis-tetraphenyl-p-xylylium diperchlorate solutions which were so dilute, and in such a small diameter tube that they were almost colorless, became an easily observable deep red three seconds after the flow was stopped. (As reported,[26] when this red solution was accidentally exposed to the air once, the solution lost its red color in a very short time as the radical reacted with molecular oxygen.)

29. Preparation of 4,4'-Dimethylbenzoin[59]

p-Tolualdehyde (b.p. 43°/0.5 mm), 50 g (0.416 moles), about 200 ml of fifty percent aqueous ethanol, and 10 g (0.204 moles) of sodium cyanide were placed in a one-liter, one-necked, round-bottomed flask. The flask was fitted with a reflux condenser and teflon coated magnetic stirring bar. The solution was heated to reflux and stirred four hours. Allowing the solution to cool to room temperature crystallized a yellow material. The 4,4'-dimethybenzoin crystals were filtered, recrystallized from ethanol, and dried; m.p. 87-88°; the yield was 34 percent.

30. Preparation of 4,4'-Dimethylbenzil[60]

A 200 ml, two-necked, round-bottomed flask equipped with mechanical stirrer and reflux condenser was charged with ca. 0.1 g of cupric acetate, 5 g of ammonium nitrate, 7 g (0.029 moles) of p,p'-dimethylbenzoin, and 50 ml of an 80 percent (by volume) aqueous acetic acid solution. The mixture was mechanically stirred and heated to reflux (while the solution became pale green, dark green, black, brown, yellow and then suddenly emerald green) until nitrogen was evolved; the solution finally remained clear pale green. Heating was continued to reflux the solution an additional 1-1/2 hours. The solution was then allowed to cool and stand one hour. The crystalline mass which formed in the flask was filtered, washed with water, and dried to yield 19.2 g (95 percent) of the 4,4'-dimethylbenzil,[64] m.p. 100-101°.

31. Preparation of bis-Tetra(p-tolyl)-p-xylylene

Crystalline 4,4'-dimethylbenzil (19.2 g; 0.08 moles) was dissolved in 50 ml of absolute ethanol by refluxing in a one-necked, round-bottomed flask. An aqueous solution of hydrazine (3 g of 85 percent) was added slowly to the ethanol solution and heating continued for twenty minutes. The monohydrazone was crystallized by cooling the solution to 0°, was filtered and dried, melting point 146-147° (for the p-toluoin monohydrazone).[61] The yield was 86 percent.

Yellow mercuric oxide (13 g), 11 g (0.69 moles) of p-toluoin monohydrazone, and 70 ml of ether were placed in a

one-necked, round-bottomed flask with a reflux condenser, and the mixture allowed to reflux (heating) ten hours. The olive solution was then stripped of its solvent under reduced pressure. Benzene, 100 ml, was used to extract the little solid remaining in the flask. An orange solution was formed and decanted from the residue in the flask. The orange solution was dried over anhydrous magnesium sulfate and then allowed to drop into a flask which was heated to 150° and swept with a stream of argon. The benzene flash vaporized as it hit the flask. When all of the benzene solution had been added a red-liquid (ditolylketene) was all that remained in the flask. After cooling to room temperature, the red liquid was dissolved in ca. 25 ml of ether and 3 g (0.0028 moles) of quinone dissolved in ca. 25 ml ether added, and the solution allowed to stand overnight. The ether was removed under reduced pressure leaving a red-orange residue in the flask.

Heating a small sample of the β-lactone to ca. 140° caused a darkening and evolution of carbon dioxide. The red-orange β-lactone, ca. 5 g, was dissolved in about 15 ml of xylene and the solution heated to reflux for two hours, allowed to cool, when a dark orange solid precipitated from the solution. Recrystallization of the solid α,α,α',α'-tetra-p-tolyl-p-xylylene from benzene-ether[60] gave orange crystals (2.8 g) melting at 293-294°.

32. Hydrolysis of bis-Tetraphenyl-p-xylylium Diperchlorate

A 0.1 g sample of bis-tetraphenyl-p-xylylium diperchlorate was added to 33 percent aqueous acetone. The color was immediately lost and on addition of benzene (ca. 10 ml) the cloudiness and small quantity of white solid disappeared. Separation of the layers, drying the organic layer, and then addition of petroleum-ether precipitated a white solid. The solid was filtered, dried, recrystallized from benzene-petroleum ether to give 0.85 g of a white powder, m.p. 169-170°, which agrees with the reported[16] m.p. 170°, for tetraphenyl-p-xylene-diol.

## Part II. Acylium Ions

1. Preparation of 2,6-Dimethylbenzoic Acid

A one-liter, three-necked, round-bottomed flask was charged with 20 g (0.165 moles) of 2,6-dimethylaniline, 100 ml of concentrated hydrochloric acid, and crushed ice, added when necessary to maintain the mixture at 0 to -5°. Sodium nitrite, 11.4 g, in 75 ml of water was added dropwise (to keep the temperature of the mixture below 5°) until the presence of excess nitrous acid was observed with a starch-iodide test. The solution was then warmed to 45° and a mixture of 15 g of cuprous cyanide, 20 g of sodium cyanide, 100 ml of benzene, and 150 ml of water was added in 10 minutes with vigorous stirring. After standing 5 hours, the mixture was warmed on the steam bath and steam distilled. The solid material obtained was recrystallized from petroleum

ether to give a 35 percent yield of crystalline 2,6-dimethylbenzonitrile, m.p. 88-89°.[62]

About 2 g of 2,6-dimethylbenzonitrile was dissolved in 10 ml of 100 percent sulfuric acid. Two drops of water were added and the solution heated on the steam bath for one hour. The solution was then poured on ice and a white solid formed. The solid (1.8 g) was filtered, dried and a melting point, 136-138°, showed the solid was 2,6-dimethylbenzamide, reported[62] melting at 139°.

About 70 g of orthophosphoric acid and 30 g phosphorus pentoxide were mixed to form ca. 100 percent phosphoric acid.[63] The 100 percent phosphoric acid (10 ml) was used to dissolve 1.8 g of 2,6-dimethylbenzamide, and the resulting solution heated to 150° for half an hour. The solution was poured on ice, the resulting solid filtered, dried and recrystallized from benzene to give a 60 percent yield (calculated from 2,6-dimethylbenzonitrile) of crystalline 2,6-dimethylbenzoic acid, melting[63] 115-116°.

## 2. Methanolysis of 2,6-Dimethylbenzoic Acid-Sulfuric Acid Solutions

A 0.084 g sample of 2,6-dimethylbenzoic acid was dissolved in 2 ml of 100.2 percent sulfuric acid, the yellow solution stirred well, and then poured into ca. 10 ml of methanol at 0°. A solid could not be crystallized or precipitated from solution. The solvent was removed under reduced pressure and an n.m.r. spectrum taken on the residual syrup. The n.m.r. spectrum showed that the material

was neither 2,6-dimethylbenzoic acid nor its methyl ester, but had rearranged to a mixture of products.

3. Preparation of 3,5-Dibromomesitoic Acid

Mesitoic acid (5.5 g; 0.033 moles) was placed in a 100 ml, three-necked, round-bottomed flask equipped with mechanical stirrer and reflux condenser. About 50 ml of chloroform was added, a few granules of powdered iron, and then 10.5 g (0.66 moles) of bromine in ca. 10 ml of chloroform were added dropwise to the rapidly agitated mixture, which was cooled to $0^{\circ}$. When all of the bromine solution had been added, the mixture was heated to reflux for ten hours and then the condenser removed to allow any excess bromine to escape. The solution was allowed to cool and poured into 100 ml of a 10 percent aqueous sodium bisulfite solution. Separation of the layers and stripping the solvent left a white solid from the chloroform portion. The solid was dissolved in dilute base, the solution acidified and the precipitated material filtered. Recrystallization from 50 percent aqueous ethanol gave a 42 percent yield of 3,5-dibromomesitoic acid, melting 121-121$^{\circ}$ (literature reports[56] 121$^{\circ}$).

4. Methanolysis of 3,5-Dibromomesitoic Acid in Sulfuric Acid

A 0.2 g sample of 3,5-dibromomesitoic acid (m.p. 121-122$^{\circ}$) was placed in ten ml of 100.2 percent sulfuric acid, and the solution stirred for 15 minutes. The solution was then slowly poured into cold anhydrous methanol. White

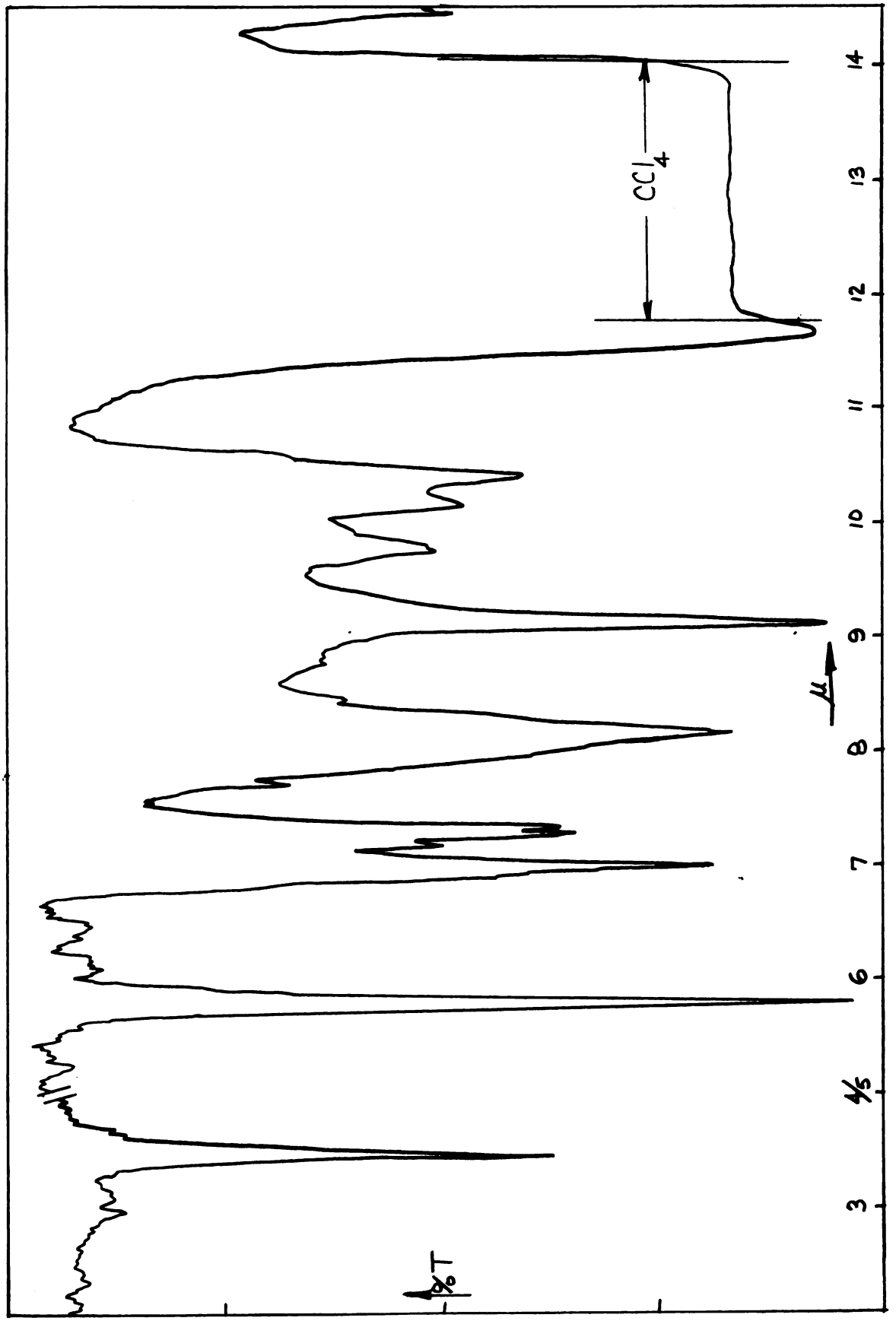



Figure 31. Infrared Spectrum of Methyl 3,5-Dibromo-2,4,6- Trimethylbenzoate ( in $CCl_4$).

needles formed as the solution cooled. These crystals were filtered with a sintered glass disk, dried, and a melting point and n.m.r. spectrum taken (in carbon tetrachloride). The needles, melting 110-111°, had n.m.r. peaks at 6.00, 7.21, and 7.61 τ with relative areas of 1:1:2 which is consistent with methyl 3,5-dibromomesitoate (see Figure 32).

5. Methanolysis of Prehnitene Carboxylic Acid-Sulfuric Acid Solution

A sample of prehnitene carboxylic acid was dissolved in 2 ml of 100.2 percent sulfuric acid. The yellow solution was stirred well, and then poured into ca. 10 ml of methanol at 0°.

A solid could not be crystallized by cooling the solution, but when a little water was added the solution became cloudy. Cooling the cloudy solution yielded a precipitate which, on recrystallization from ethanol gave a solid, melting 35-35.5°, that had an infrared spectrum (carbon disulfide) which showed the same absorptions as a known sample[42] of methyl prehnitene carboxylate.

6. Preparation of Sulfuric Acid Solutions

Sulfuric acid solutions of desired concentration above commercial concentrated sulfuric acid were prepared by diluting commercial 30-33 percent fuming sulfuric acid (30-33 percent free sulfur trioxide) with concentrated sulfuric acid. The quantities of each solution were gravimetrically measured and slowly poured together with

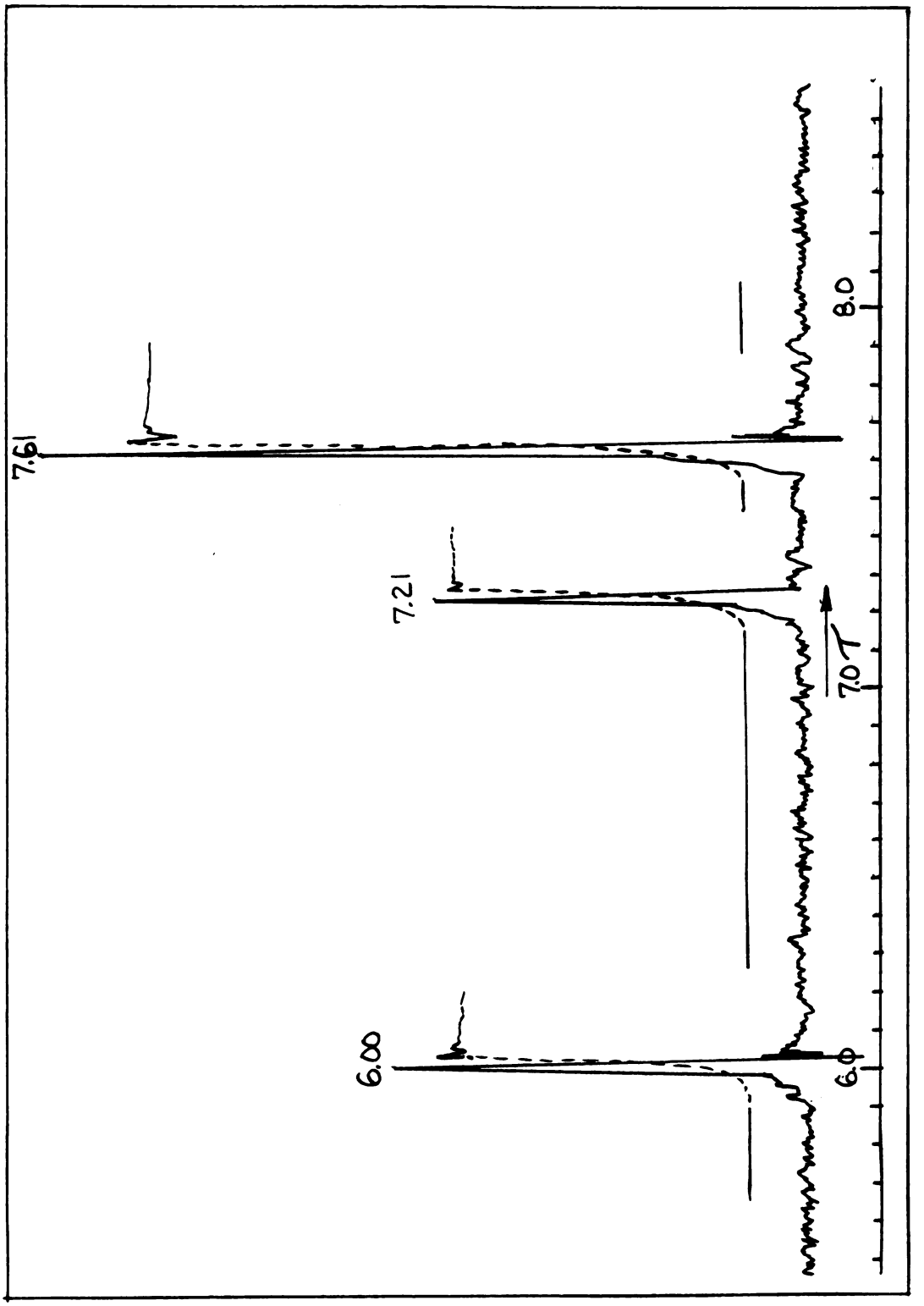



Figure 32. N.M.R. Spectrum of Methyl 3,5-Dibromo-2,4,6- Trimethylbenzoate ( in $CCl_4$).

rapid stirring. Each solution was agitated for half an hour after addition was complete, and the aliquots titrated with standard sodium hydroxide solution to a phenolphthalein endpoint. Agreement among three successive determinations to a precision of 0.1 percent was necessary for each solution prepared. Acid concentrations over 100 percent, viz. fuming sulfuric acid solutions, were determined by pipetting an aliquot into a thin walled, tared, glass bubble which was immediately sealed and weighed. The bubble was broken under ca. 10 ml of distilled water in a flask and then titrated with standard sodium hydroxide solution to a phenolphthalein endpoint. In the manner described solutions of sulfuric acid were prepared up to 104 percent (calculated as 100 percent sulfuric acid).

Sulfuric acid solutions below commercial acid concentration were prepared by diluting the commercial acid with the appropriate weight of distilled water and titrating with standard base to the same precision.

## 7. Determination of the $pK_R$ by N.M.R. Spectroscopy

The $pK_R$'s of substituted benzoic acids and esters using n.m.r. were determined by the following procedure:

About 0.1 g sample of acid which had been recrystallized and dried (in an oven) before use was dissolved in 2 ml of sulfuric acid solution in an n.m.r. sample tube. As soon as the solid seemed to be dissolved a spectrum was recorded. If it was thought that the sample might sulfonate, spectra were taken at ca. 5 minute intervals and the change

in resonance intensities plotted versus time, and extrapolated back to the time of dissolution of the compound. The sulfuric acid solutions were used randomly rather than in order of increasing or decreasing strength to minimize any bias.

Integration of spectral areas allowed comparison between the ionized and unionized samples. The ratio of areas, for example, of a methyl group plotted against acid strength allows the value for 50 percent ionization to be found from three or four measurements.

## 8. Determination of the $pK_R$ by Ultraviolet Spectroscopy

Determination of the $pK_R$'s of substituted benzoic acids and esters for comparison with the n.m.r. values was accomplished by the following procedure:

A weighed sample of the recrystallized and oven dried compound was dissolved in 10 ml of absolute methanol in a volumetric flask. A 0.01 ml aliquot of the methanol solution was put into a 10 ml volumetric flask from a buret (graduated to 0.01 ml). Sulfuric acid of the desired concentration was then pipetted into the flask to a volume of 10 ml. After thoroughly stirring the solution it was put into glass-stoppered 1 cm silica cells and the spectrum (ultraviolet) taken. Ten or twelve such sulfuric acid solutions were prepared and run. Comparison of completely ionized and unionized samples with partially ionized samples allowed the respective ratios to be calculated. The ratio of

the two ratios, ionized/partially ionized and partially ionized/ unionized, allowed the calculation of the $pK_R$ for the sulfuric acid solutions used. An average $pK_R$ was then calculated for each compound from ten to twelve such determinations.

9. Instruments

The instruments used in this work were as follows:

Infrared - Perkin-Elmer, Model 21.
Beckman, Model IR-7.

Visible-Ultraviolet - Cary, Model 11.
Beckman, Model DB.
Beckman, Model DU.

Nuclear Magnetic Resonance - Varian, Model V-4311
Varian, Model A-60

Electron Spin Resonance - Varian, Model 4100-10A

## SUMMARY

1. Pentamethylphenylchlorodicarbonium tetrafluoroborate and tetrachloroborate have been prepared and isolated. Similarly, 2,4,6-trimethylphenylchlorodicarbonium tetrafluoroborate and tetrachloroborate have been prepared and isolated. These salts hydrolyze to produce the corresponding benzoic acids, undergo alcoholysis to produce the corresponding benzoates, do not take up hydride ion from triphenylmethane or cycloheptatriene under conditions tried.

2. Attempts to produce a planar Hückel aromatic dicarbonium ion by removal of two bromines as bromide ions from cyclooctatetraene dibromide with silver tetrafluoroborate or boron tribromide were unsuccessful.

3. The production of a radical-cation by reaction of tetraphenyl-p-xylylene and tetraphenyl-p-xylylium perchlorate in methylene chloride has been reinvestigated. An electron spin resonance spectrum of the radical-ion has been taken and an estimate of the rate of reaction has been measured as $10^2$ liter moles$^{-1}$ sec$^{-1}$.

4. The $pK_R'$s of some substituted hindered benzoic acids have been measured from their nuclear magnetic resonance spectra in various concentrations of sulfuric acid. This method is proposed as a supplement to other methods of determining weak base strengths. A linear relationship

of substituents $pK_R$'s with $\sigma^+$ rather than $\sigma$ for the substituent was found. The $H_R$ acidity function scale was extended to 100 percent sulfuric acid solution.

# BIBLIOGRAPHY

1. K. A. Hofmann and H. Reimsreuther, Ber., 42, 4856, (1909).

2. M. Gomberg, Ber., 40, 1847 (1907).

3. M. Gomberg and L. H. Cone, Ann., 370, 142 (1910).

4. F. Seel, Z. anorg. Chem., 250, 331 (1943).

5. C. R. Witschonke and C. A. Kraus, J. Am. Chem. Soc., 69, 2472 (1947).

6. D. W. A. Sharp and N. Sheppard, J. Chem. Soc., 674 (1957).

7. H. J. Dauben, L. R. Honnen, and K. M. Harmon, J. Org. Chem., 25, 1442 (1960).

8. K. M. Harmon and A. B. Harmon, J. Am. Chem. Soc., 83, 865 (1961).

9. K. M. Harmon and F. E. Cummings, J. Am. Chem. Soc., 84, 1751 (1962).

10. T. Sulzberg, Ph.D. Thesis, Michigan State University, 1962.

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

12. W. P. Giddings and R. F. Buchholy, J. Am. Chem. Soc., 86, 1261 (1964).

13. J. Copenhaven and M. Bigelow, Acetylene and Carbon Monoxide Chemistry, Reinhold Publishers, New York, New York, 1949 (p. 235).

14. H. Hart and R. W. Fish, J. Am. Chem. Soc., 83, 4460 (1961).

15. J. Thiele and H. Balhorn, Ber., 37, 1468 (1904).

16. R. Rafos, Ph.D. Thesis, Michigan State University, 1962.

17. H. Hart, R. Rafos, and T. Sulzberg, J. Am. Chem. Soc., 85, 1800 (1963).

18. H. Hart and C. Y. Wu, unpublished results.

19. T. Curtius and J. Thun, J. Prakt. Chem., 44, 176, 182 (1891).

20. D. G. Farnum and B. Webster, J. Am. Chem. Soc., 85, 3502 (1963).

21. H. H. Freedman and A. E. Young, J. Am. Chem. Soc., 86, 734 (1964).

22. R. F. Bryan, J. Am. Chem. Soc., 86, 733 (1964).

23. N. Allinger, M. Miller, and L. Tuschaus, J. Org. Chem., 28, 2555 (1963).

24. H. L. Strauss, T. J. Katz, and G. K. Fraenkel, J. Am. Chem. Soc., 85, 2360 (1963).

25. T. J. Katz and H. L. Strauss, J. Chem. Phys., 32, 1873 (1960).

26. E. Weitz and F. Schmidt, Ber., 75, 1921 (1942).

27. H. Hart and R. W. Fish, J. Am. Chem. Soc., 82, 5419 (1960), footnote 24.

28. H. Freedman and A. Frantz, J. Am. Chem. Soc., 84, 4165 (1962).

29. E. Hückel, Z. Physik., 70, 204 (1931); 76, 628 (1932).

30. A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Son, Inc., New York, 1961.

31. T. J. Katz, J. Am. Chem. Soc., 59, 1758 (1937).

33. M. S. Newman and N. C. Deno, J. Am. Chem. Soc., 73, 3651 (1951).

34. L. P. Hammett and A. J. Deyrup, J. Am. Chem. Soc., 54, 2721 (1932).

35. M. A. Paul and F. A. Long, Chem. Revs., 57, 1 (1957).

36. A. M. Lowen, M. A. Murray, and G. Williams, J. Chem. Soc., 3318 (1950).

37. G. Williams and M. A. Bevan, Chem. and Ind., 171 (1955).

38. N. Deno, J. Jaruzelski, and A. Schriesheim, J. Am. Chem. Soc., 77, 3044 (1955).

39. N. Deno, J. Jaruzelski, and A. Schriesheim, J. Org. Chem., 19, 155 (1954).

40. E. M. Arnett and R. D. Bushick, J. Am. Chem. Soc., 86, 1564 (1964).

41. M. Rogers and H. Kuska, J. Chem. Phys., 40, 910 (1964).

42. R. W. Fish, Ph.D. Thesis, Michigan State University, 1960.

43. N. R. Roobol, Ph.D. Thesis, Michigan State University, 1961.

44. C. A. Beuhler, Ph.D. Thesis, Michigan State University, 1963.

45. M. Ballester, C. Molinet, and J. Castaner, J. Am. Chem. Soc., 82, 4254, 4259 (1960).

46. R. Silverstein and G. Bassler, "Spectrometric Identification of Organic Compounds," J. Wiley and Sons, Inc., New York, New York, 1963.

47. M. L. Bender, H. Ladenheim, and M. C. Chen, J. Am. Chem. Soc., 83, 126 (1961).

48. W. Lange, Ber. Dtsch, 59, 2107 (1926).

49. W. C. Cope and J. Barab, J. Am. Chem. Soc., 39, 504 (1917).

50. R. Stewart and K. Yates, J. Am. Chem. Soc., 80, 6355 (1958).

51. R. Stewart and K. Yates, Can. J. Chem., 37, 664 (1959).

52. R. Stewart and K. Yates, J. Am. Chem. Soc., 82, 4059 (1960).

53. H. Hosoya and S. Nagakura, Spec. Chim. Acta, 17, 324 (1961).

54. L. Hammett, J. Am. Chem. Soc., 59, 1708 (1937).

55. A. Cope and M. Burg, J. Am. Chem. Soc., 74, 168 (1952).

56. P. Shildneck and R. Adams, J. Am. Chem. Soc., 53, 351 (1931).

57. A. Pullman and B. Pullman, Bull. Soc. Chim., 18, 707 (1951).

58. J. Thiele and H. Balhorn, Ber., 37, 1469 (1904).

59. L. Gattermann, Ann., 347, 364.

60. B. Klein, J. Am. Chem. Soc., 63, 1474 (1941).

61. T. Curtius and R. Kastner, J. Prak. Chim, 83, 230.

62. A. Noyes, J. Am. Chem. Soc., 20, 790 (1898).

63. R. Fraser, Can. J. Chem., 38, 2226 (1960).