### RATES AND MECHANISM OF DIPOSITIVE CARBONIUM ION HYDROLYSIS

Thesis for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY Norman Richard Roobol 1962 THESIS

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### RATES AND MECHANISM OF DIPOSITIVE

CARBONIUM ION HYDROLYSIS

By

Norman Richard Roobol

AN ABSTRACT OF A THESIS

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

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Department of Chemistry

#### ABSTRACT

### RATES AND MECHANISM OF DIPOSITIVE CARBONIUM ION HYDROLYSIS

by Norman Richard Roobol

The primary purpose of this thesis was to further investigate the scope of dipositive carbonium ion chemistry. The alkylation of polymethylbenzenes with anhydrous aluminum chloride and carbon tetrachloride, which was previously used to synthesize trichloromethyl compounds (1, 2, 3), was employed in the preparation of 3-fluoro-, chloro- and bromo-2,4,6-trimethylbenzotrichlorides, and 3-fluoro-2,4,5,6tetramethylbenzotrichloride. The yields were generally excellent and the reaction proceeded without rearrangement. By analogy with earlier work (1, 2, 3), these and other substituted benzotrichlorides were shown to form dipositive carbonium ions in 100% sulfuric acid.

The rates of hydrolysis of thirteen substituted phenylchlorodicarbonium ions were determined spectrophotometrically in various concentrations of 90-100% aqueous sulfuric acid. The hydrolyses were pseudo first-order with respect to dipositive ions. The kinetics revealed that the ability of substituents to stabilize dicarbonium ions was in the order methyl > hydrogen > halogen. There was evidence that destabilization of the transition state was caused by halogens in the meta position.

The mechanism of the hydrolysis was shown to proceed through the formation of an acylium ion intermediate. The acylium ion then reacted with water to form the carboxylic acid. The carboxylic acid was the only product of the hydrolysis and in all cases the yield was quantitative.

Dipositive carbonium ions were also formed in trifluoroacetic acid-boron trifluoride solutions. Mesitylchlorodicarbonium ion was treated with ethyl, isopropyl and tertiary butyl alcohols to yield the corresponding mesitoates. In an attempted reaction of this ion with a Grignard reagent it was found that the dipositive ion reacted with ether and tetrahydrofuran to give ethyl mesitoate and  $\delta$ -hydroxybutyl mesitoate. The reaction of the ion with n-butyllithium gave the butyl ester and suggested that the above reactions were due to the formation of unsymetrical mesitoic-trifluoroacetic anhydride.

 H. Hart and R. W. Fish, J. Am. Chem. Soc., <u>82</u>, 5419 (1960).
 H.Hart and R. W. Fish, J. Am. Chem Soc., <u>83</u>, 4460 (1961).
 R. R. Rafos, Ph.D. Thesis, Michigan State University, 1961, pp. 5-22.

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#### TABLE OF CONTENTS

			Page
INTRODUC	CTION .		1
RESULTS	AND DISC	CUSSION	6
I.	Prepara dica	tion of Substituted Phenylchloro- rbonium Ions	7
	A. B.	The Trichloromethylation Reaction Dication Formation in 100% Sulfuric	7
		Acid	15
II.	Kinetic: Carbo	<b>s</b> of Hydroly <b>sis</b> of Dipo <b>s</b> itive onium Ion <b>s</b>	17
	Α.	Rates and Half-Lives	17
	в.	The Hydrolysis Mechanism	32
III.	Reactio	ns of Mesitylchlorodicarbonium Ion	41
	А.	Reaction with Alcohols	44
	в.	Reaction with Ethers	45
	с.	Reaction with n-Butyllithium	45
EXPERIM	ENTAL .		52
I.	Preparat	tions of Substituted Benzotrichlorides	53
	Α.	Preparation of 3-Fluoro-2,4,6-	
		trimethylbenzotrichloride	53
		1. Preparation of 2-Nitromesitvlene	53
		2. Preparation of 2-Aminomesitylene	53
		3. Preparation of 2-Fluoromesitylene	54
		4. Preparation of 3-Fluoro-2.4.6-tri-	•••
		methylbenzotrichloride	55
		5. Hydrolysis of 3-Fluoro-2,4,6-tri-	
		methylbenzotrichloride	56
		6. Reaction of 3-Fluoro-2,4,6-tri-	
		methylbenzotrichloride in	
		100% Sulfuric Acid with water	56

в.	Preparation of 3-Chloro-2,4,6-	<b>6</b> 1
	trimetnyibenzötrichlöride	01
	1. Preparation of 2-Chloromesitylene	61
	2. Preparation of 3-Chloro-2,4,6-	
	trimethylbenzotrichloride	61
	3. Hydrolysis of 3-Chloro-2,4,6-	6.2
		63
	4. Reaction of 3-Chloro-2,4,6- trimethylbenzotrichloride	
	in 100% Sulfuric Acid with	
	water	63
c.	Preparation of 3-Bromo-2,4,6-tri-	
	methylbenzotrichloride	68
	1 Proparation of 2-Promomogitulana	68
	2. Preparation of 3-Bromo-2.4.6-	00
	trimethylbenzotrichloride	69
	-	
	a. Trichloromethylation of 2-	
	Bromomesitylene	69
	b. Bromination of 2,4,6-Trimethyl-	70
	benzoti ichi ol ide	10
	3. Hydrolysis of 3-Bromo-2,4,6-tri-	
	methylbenzotrichloride	74
	4. Reaction of 3-Bromo-2,4,6-tri-	
	methylbenzotrichloride in	
	Notor	76
	5. Preparation of 3-Bromomesitoic	70
	acid	76
n	Propagation of 2-Fluero 2 4 5 6-totra-	
ש.	methylbenzotrichloride	78
	1. Preparation of Dinitroisodurene	78
	2. Preparation of Aminonitroisodurene	78
	3. Preparation of Fluoronitroisodurene	79
	4. Preparation of Fluoroaminoisodurene	80
	5. Freparation of 3-Fluoro-2.4.5.6-	91
	tetramethylbenzotrichloride	81

# Page

		7. Hydrolysis of 3-Fluoro-2,4,5,6- tetramethylbenzotrichloride	82
		8. Reaction of 3-Fluoro-2,4,5,6-tetra- methylbenzotrichloride in 100% Sulfuric Acid with Water	86
II.	Att	empted Preparations of Substituted Benzo- trichlorides	90
	Α.	Attempted Preparation of 3-Nitro-2,4,6- trimethylbenzotrichloride	90
	в.	Attempted Preparation of 3-Hydroxy-2,4,6- trimethylbenzotrichloride	91
	c.	Attempted Preparation of 3-Iodo-2,4,6- trimethylbenzotrichloride	91
		1. Preparation of 2-Iodomesitylene	91
		<ol> <li>Attempted Preparation of 3-Iodo-2,4,</li> <li>6,trimethylbenzotrichloride</li> </ol>	92
	D.	Attempted Preparation of 4-Acetyl-2,3,5,6- tetramethylbenzotrichloride	93
		1. Preparation of Acetyldurene	93
		<ol> <li>Attempted Preparation of 4-Acetyl-</li> <li>2,3,5,6-tetramethylbenzotrichloride</li> </ol>	94
	E.	Attempted Preparation of 4-Vinyl-2,3,5,6- tetramethylbenzotrichloride	95
		1. Preparation of Methyldurylcarbinol	95
		<ol> <li>Preparation of VinyIdurene</li> <li>Attempted Preparation of 4-Vinyl-2,</li> </ol>	96
		3,5,6-tetramethylbenzotrichloride	96
	F.	Attempted Preparation of 4-Ethyl-2,3,5,6- tetramethylbenzotrichloride	97
		1. Preparation of Ethyldurene	97
		3,5,6-tetramethylbenzotrichloride	98

	G.	Attempted Preparation of 3,5-Dichloro- 2,4,6-trimethylbenzotrichloride	101
		1. Preparation of 2,4-Dichloromesi- tylene	101
		2. Attempted Preparation of 3,5- Dichloro-2,4,6-trimethylbenzotri- chloride	102
	н.	Attempted Preparation of 3,5-Dibromo-2, 4,6-trimethylbenzotrichloride	103
		<ol> <li>Preparation of 2,4-Dibromomesitylene</li> <li>Attempted Preparation of 3,5-</li> </ol>	103
		Dibromo-2,4,6-trimethylbenzotri- chloride	103
III.	Hyd	rolysis Rates of Substituted Phenylchlorodi- carbonium Ions	104
	A.	The Kinetic Method	104
	в.	Example of the Method	106
	c.	Determination of the Reaction Order	112
	D.	Wavelengths Used to Determine Dication Hydrolyses	114
IV.	Rea	ctions of Mesitylchlorodicarbonium Ion	115
	А. В.	Preparation of Silver Tetrafluoroborate Preparation of 2,4,6-Trimethylbenzotri-	115
		fluoride	115
		1. Reaction of 2,4,6-Trimethylbenzotri- chloride in Anhydrous Hydrogen	
		Fluoride	120
		2. Reaction of 2,4,6-Trimethylbenzotri-	
		fluoride in Annydrous Hydrogen Fluoride	120
	c.	Reactions with Alcohols	121
		L. Reaction with Ethyl Alcohol	121
		2. Reaction with Isopropyl Alcohol	122
		3. Reaction with t-Butvl Alcohol	124
		VI	

.

Page

D.	Reactions with Ethers	125
	<ol> <li>Reaction with Ether</li> <li>Reaction with Tetrahydrofuran</li> </ol>	125 127
E.	Attempted Cleavage of Ether with Tri- fluoroacetic Acid and Boron Tri- fluoride	128
F.	Reaction with Butan-1,4-diol	130
G.	Reaction with n-Butyllithium	130
н.	Preparation of 2,4,6-Trimethyl-n-valero- phenone	132
I.	Preparation of Pentamethylbenzoyl Chloride	134
SUMMARY		138
LITERATURE	CITED	141

Page

### LIST OF TABLES

TABLE		Page
1.	Half-lives of the hydrolysis of pentamethyl- phenylchlorodicarbonium ion in 97.6% sulfuric acid	18
2.	Rates and half-lives of the hydrolysis of pentamethylphenylchlorodicarbonium ion	20
3.	Rates and half-lives of the hydrolysis of 4- fluoro-2,3,5,6-tetramethylphenylchlorodi- carbonium ion	22
4.	Rates and half-lives of the hydrolysis of 4- chloro-2,3,5,6-tetramethylphenylchlorodi- carbonium ion	23
5.	Rates and half-lives of the hydrolysis of 4- bromo-2,3,5,6-tetramethylphenylchlorodi- carbonium ion	23
6.	Relative rates of the hydrolysis of 4-methyl-, fluoro-, chloro- and bromo-tetramethylphenyl- dicarbonium ions	24
7.	Rates and half-lives of the hydrolysis of 3- fluoro-, chloro- and bromo-2,4,5,6-tetra- methylphenylchlorodicarbonium ions in 97.6% sulfuric acid	26
8.	Rates and half-lives of the hydrolysis of 2- chloro-3,4,5,6-tetramethylphenylchloro- dicarbonium ion	27
9.	Rates and half-lives of the hydrolysis of 2,3,4,5-tetramethylphenylchlorodicarbonium ion	29
10.	Rates and half-lives of the hydrolysis of 2,4,6- trimethylphenylchlorodicarbonium ion	29

# TABLE

11.	Rates and half-lives of the hydrolysis of 3- fluoro-, chloro- and bromo-2,4,6-trimethyl- phenylchlorodicarbonium ion	30
12.	Rates and half-lives of the hydrolysis of penta- methylbenzoylium ion at 25.00	35
13.	A comparison of calculated and experimental values of t <sub>1/2 max</sub> and % reaction max	38
14.	Absorbance of 4-bromo-2,3,5,6-tetramethyl- phenylchlorodica <b>r</b> bonium ion in 99.5% sulfuric acid at 25.0° <u>+</u> 0.08°. Cell I	106
15.	Log <b>abs</b> orbance of 4-bromo-2,3,5,6-tetramethyl- phenylchlorodicarbonium ion. Cell I	106
16.	Absorbance of 4-bromo-2,3,5,6-tetramethylphenyl- chlorodicarbonium ion in 99.5% sulfuric acid at 25.0° <u>+</u> 0.08°. Cell II	109
17.	Log absorbance of 4-bromo-2,3,5,6-tetramethyl- phenylchlorodicarbonium ion. Cell II	109

# LIST OF FIGURES

FIGURE		Page
1.	Plot of $t_{1/2}$ versus % sulfuric acid for the	
	hydroly <b>sis</b> of pentamethylphenylchloro- dicarbonium ion	21
2.	<pre>Plot of relative rates of 4-substituted-2,3,5,6-     tetramethylphenylchlorodicarbonium ions vs.</pre>	25
3.	Plot of 294mµ absorbance vs. time for the hy- drolysis of pentamethylphenylchlorodicarbonium ion in 90% sulfuric acid	، 36
4.	Plot of 294mµ absorbance vs. time for the hy- drolysis of pentamethylphenylchlorodi- carbonium ion in 92% sulfuric acid	37
5.	Infrared spectrum of 3-fluoro-2,4,6-trimethyl- benzotrichloride	57
6.	Proton magnetic resonance spectra of 3-fluoro- 2,4,6-trimethylbenzotrichloride	58
7.	Infrared spectrum of 3-fluoromesitoic acid	60
8.	Infrared spectrum of 3-chloro-2,4,6-trimethyl- benzotrichloride	64
9.	Proton magnetic resonance spectra of 3-chloro- 2,4,6-trimethylbenzotrichloride	65
10.	Infrared spectrum of 3-chloromesitoic acid	67
11.	Infrared spectrum of 3-bromo-2,4,6-trimethyl- benzotrichloride	71
12.	Proton magnetic resonance spectra of 3-bromo- 2,4,6-trimethylbenzotrichloride	73

## FIGURE

13.	Infrared spectrum of 3-bromomesitoic acid	75
14.	Infrared spectrum of 3-fluoro-2,4,5,6-tetramethyl- benzotrichloride	83
15.	Proton magnetic resonance spectra of 3-fluoro- 2,4,5,6-tetramethylbenzotrichloride	85
16.	Infrared <b>s</b> pectrum of 3-fluoro-2,4,5,6-tetra- methylbenzoic acid	87
17.	Comparison of the visible spectra of some dications in 100% sulfuric acid	89
18.	Infrared spectrum of ethyldurene	99
19.	Proton magnetic resonance spectrum of ethyldurene	100
20.	Plot of absorbance of 4-bromo-tetramethylphenyl- chlorodicarbonium ion versus time. Cell I .	108
21.	Plot of log absorbance of 4-bromo-tetramethyl- phenylchlorodicarbonium ion versus time. Cell I	109
22.	Plot of absorbance of 4-bromo-tetramethylphenyl- chlorodicarbonium ion versus time. Cell II	110
23.	Plot of log absorbance of 4-bromo-tetramethyl- phenylchlorodicarbonium ion versus time. Cell II	111
24.	Infrared <b>s</b> pectrum of 2,4,6-trimethylbenzotri- fluoride	118
25.	Fluorine magnetic resonance spectrum of 2,4,6- trimethylbenzotrifluoride	119
26.	Infrared spectrum of ethyl mesitoate prepared from mesitylchlorodicarbonium ion and ethyl alcohol	123

# FIGURE

27.	Infrared spectrum of ethyl mesitoate prepared from mesitylchlorodicarbonium ion and ether	126
28.	Comparison of the infrared spectra of >-hydroxy-n- butyl mesitoate from mesitylchlorodicarbonium ion and (a.) tetrahydrofuran and (b.) butan- l,4-diol	129
29.	Infrared spectrum of n-butyl mesitoate	133
30.	Infrared spectrum of 2,4,6-trimethyl-n-valero- phenone	135
31.	Infrared <b>s</b> pectrum of pentamethylbenzoyl chloride	137

INTRODUCTION

The intense red color of pentamethylbenzotrichloride (I) dissolved in 100% sulfuric acid was shown (1) to be due to the formation of the "extraordinary" dipositive carbonium ion (II).



The term "extraordinary" is applied to dipositive carbonium ions which have been produced by two ionizations at a single carbon atom to distinguish them from "ordinary" dipositive carbonium ions formed by single ionizations at two separate sites in a molecule (1). All the dipositive carbonium ions in the present work are of the extraordinary type.

These ions are named "dicarbonium ion" or "methylene dication" as derivatives of  $CH_2^{++}$ , based on the formal structure  $Ar \stackrel{++}{-}C-Cl$  corresponding to the parent molecule which ionizes to form the dipositive ion. Ion II can be named pentamethyl-phenylchlorodicarbonium ion or pentamethylphenylchloromethylene dication.

The structure II was established by cryoscopic

measurements which showed that five particles were produced in solution by one mole of pentamethylbenzotrichloride. Two moles of hydrogen chloride could be rapidly swept from the solution which then gave a three-fold molal freezing point depression. Conductance measurements indicated that two bisulfate ions were produced. Structure II was supported by the visible, ultraviolet and nuclear magnetic resonance spectra of the solution.

The same means were used to show that 2,3,4,5tetramethylbenzotrichloride and 2,4,6-trimethylbenzotrichloride also form dications (2). Later the 4-halotetramethylbenzotrichlorides (III) were proved to react in an analogous manner in 100% sulfuric acid (3).



Another proof of the structure of these dipositive ions was their quantitative hydrolysis to the corresponding carboxylic acids. It was thought that the kinetics of the hydrolysis of a number of different dicarbonium ions might help to show what effect ring substituents have on the stability or reactivity of the ions. A major purpose of this thesis

was to determine the kinetics of the hydrolysis in aqueous sulfuric acid of a number of substituted dicarbonium ions. The synthesis of some new benzotrichlorides which form dipositive carbonium ions in 100% sulfuric acid is reported.

The difficulty with studying in detail the chemistry of dipositive ions in 100% sulfuric acid is obvious. A number of other systems have been used to produce these ions. They can be prepared by adding excess aluminum chloride to a solution of the benzotrichloride in nitromethane or nitrobenzene and by adding boron trifluoride or silver tetrafluoroborate to nitromethane solutions of the trichloromethyl compound. The rapid reaction of the dipositive ion with the solvent severely limits the utility of these systems.

Another system is trifluoroacetic acid saturated with boron trifluoride. The benzotrichlorides are not very soluble in trifluoroacetic acid, but when boron trifluoride is passed into the mixture the benzotrichloride dissolves rapidly giving a deep red solution of the dication.

The reaction of pentamethylbenzotrichloride with trifluoroacetic acid—boron trifluoride has been studied (2). The red crystalline material which remained after evaporation of the solvent had visible and nuclear magnetic resonance spectra similar to those of II, except for solvent effects.

However, attempts to convert the red crystalline residue to a salt of definite composition by recrystallization were not successful, and when heat was used to remove the solvent there was some indication that the mixed anhydride IV was formed (2).



Nevertheless, this system seemed to be the best known method for examining the chemistry of dicarbonium ions. To this end the chlorotrifluoroborate salt of mesitylchloromethylene dication (V) was prepared. Several reactions of



the salt will be given here.

# RESULTS AND DISCUSSION

I. Preparation of Substituted Phenylchlorodicarbonium Ions.

#### A. The Trichloromethylation Reaction

The condensation of carbon tetrachloride with benzene in the presence of anhydrous aluminum chloride was studied by many workers during the decades following the initial report of this reaction in 1877 (4, 5) by Friedel and Crafts. The products varied according to the conditions (6); however, benzophenone dichloride and triphenylchloromethane were the main substances obtained under the ordinary conditions of the reaction (7, 8). Similar reactions using chlorobenzene or bromobenzene gave 4,4'-dichloro-(or bromo-) benzophenone dichloride (VI) (9, 10).



In the reaction with o-, m-and p-dichlorobenzene and paradibromobenzene again only two chlorine atoms of the carbon tetrachloride were substituted (11, 12). That chlorine in the ring inhibits the Friedel-Crafts reaction can be seen from the respective yields with benzene and p-dichlorobenzene, which were 90% and 25%.

In an attempted condensation of carbon tetrachloride with anisole only traces of the dimethoxybenzophenone dichloride were isolated (8). The poor yield was presumably due to complex formation between anisole and aluminum chloride.

Benzene homologs reacted in a manner analogous to benzene itself. The products with toluene were mainly 4,4'-dimethylbenzophenone dichloride (VII) and tri-ptolylmethane (VIII) (7, 8).



VIII

In none of the above reactions was any substituted benzotrichloride isolated. Boeseken carefully examined the products of the reaction with benzene but was not able to find even a trace of benzotrichloride. He concluded that

further reaction of the trichloromethyl compound was too rapid to enable it to be isolated (11).



No one, however, reported using a large excess of carbon tetrachloride in an attempt to isolate benzotrichloride from the reaction. In one case a trichloromethyl group was introduced into a compound, but a benzotrichloride was not formed. Carbon tetrachloride, aluminum chloride and p-cresol gave 4-methyl-4-trichloromethylcyclohexa-2,5-dienone (IX) in good yield (13).



The use of the Friedel-Crafts reaction to add a trichloromethyl group to a polymethyl substituted benzene nucleus was reported by Hart and Fish (1) who used a method of synthesis communicated to them by Rolih and Peters (14) to make pentamethylbenzotrichloride (X) from pentamethylbenzene. The method employed a 7-fold molar excess of carbon tetrachloride, probably to prevent the possible formation of di-and triphenylmethane derivatives.



Later they extended the method to prepare 2,4,6trimethylbenzotrichloride from mesitylene and 2,3,4,5-tetramethylbenzotrichloride (XI) from durene (2). Isodurene and prehnitene were treated in a similar manner and also gave



(XI) (15). The methyl migration which occurred when the bulky trichloromethyl group was introduced into durene or isodurene

parallels the rearrangement which takes place during the Jacobsen reaction. The sulfonic acids of durene, isodurene and prehnitene all give prehnitene on hydrolysis (16). In both types of reaction a methyl group migrates so that only one methyl remains ortho to the bulky group, but methyl migration does not occur with the prehnitene derivative where this arrangement is already present in the molecule. Mesitylene reacted without rearrangement under Friedel-Crafts conditions. Likewise, mesitylene sulfonic acid does not rearrange (16).

It is not certain whether the methyl migration occurred before or after the introduction of a trichloromethyl group. No attempts were made to examine starting material for rearrangement. Low temperature (10-15<sup>°</sup>) reaction gave only rearranged product in poor yield. The steric strain in the trichloromethyl derivatives of durene and isodurene are not appreciably different from that in the corresponding mesitylene compound apart from buttressing effects of meta methyl groups which would cause an increase in steric interactions between the ortho methyl groups and the trichloromethyl groups. These effects would be especially noticeable in the durene derivative where both ortho methyls are buttressed closer to the bulky group. Other evidence (vide infra) indicates

that the reason(s) for methyl migration may not be exclusively stereochemical.

The 4-halo- (fluoro-, chloro- and bromo-) 2,3,5,6tetramethylbenzotrichlorides (III) were synthesized from the corresponding halodurenes without rearrangement (3). The halodurenes are penta-substituted and methyl migration is not possible.

In the present work, three halo-substituted mesitylenes were allowed to react with carbon tetrachloride and aluminum chloride by the method described for the preparation of X (1). 3-Bromo-, chloro- and fluoro-2,4,6-trimethylbenzotrichloride (XIIa, b and c) were formed without rearrangement. This is significant because 2-halomesitylenes might be expected to yield rearranged products since isodurene, which they resemble



structurally, formed a rearranged trichloromethyl compound. The buttressing effect by the bromine atom in XIIa should be very similar to that caused by the meta methyl group in

the isodurene derivative, but no migration occurred. The structure of XIIa was unequivocally established.

Bromination of 2,4,6-trimethylbenzotrichloride provided an independent synthesis of XIIa. This gave a compound which had a boiling point and an infrared spectrum identical to those of the material produced by the Friedel-Crafts reaction. Each of the two materials was hydrolyzed to 3-bromomesitoic acid by pouring their 100% sulfuric acid solution on ice. The acids obtained melted at the same temperature and a mixed melting point was not depressed.

3-Bromomesitoic acid, formed by the above reaction, was also prepared by (a) the hydrolysis of XIIa in aqueous acetone and (b) by bromination of mesitoic acid. The acids had identical melting points, infrared spectra and neutralization equivalents. A mixed melting point of the three acids showed no depression.

Since the bromine atom is larger than chlorine or fluorine, rearrangement would be most likely in the formation of XIIa. Since this was shown not to occur, by analogy XIIb and c were assumed to have the structures indicated.

XIIb and c were hydrolyzed by dissolving them in 100% sulfuric acid and pouring the solution on ice. Hydrolysis was also accomplished by refluxing aqueous acetone solutions.

Both methods gave 3-chloromesitoic acid from XIIb and 3fluoromesitoic acid from XIIc. In each instance the acids were shown to be identical by melting point, mixed melting point, neutralization equivalent, and infrared spectrum.

The Friedel-Crafts reaction of fluoroisodurene gave 3-fluoro-2,4,5,6-tetramethylbenzotrichloride (XIII). This was hydrolyzed to 3-fluoro-2,4,5,6-tetramethylbenzoic acid



by refluxing in aqueous acetone and by pouring a solution of XIII in 100% sulfuric acid on ice. The acids were shown by melting point, neutralization equivalent, infrared spectrum and mixed melting point to be identical.

Attempts to trichloromethylate 2-iodomesitylene, 2-nitromesitylene and mesitol were not successful. The reaction also failed with 2,4-dibromo- and 2,4-dichloromesitylene and with acetyldurene, ethyldurene and vinyldurene. There was partial recovery of starting material in the attempted reaction with mesitol and acetyldurene. With the other compounds tarry materials which were not identified were the main products.

#### B. Dication Formation in 100% Sulfuric Acid

All the dicarbonium ions were formed from substituted benzotrichlorides in 100% sulfuric acid. The previous work of Hart and Fish (1, 2) has firmly established the formation of dications in 100% sulfuric acid solutions of pentamethylbenzotrichloride, 2,3,4,5-tetramethylbenzotrichloride, 2,4,6trimethylbenzotrichloride. That polymethyl benzotrichlorides containing ring halogens produce dications when similarly treated has been shown by Rafos (3). It was felt that the rigorous proof of dicarbonium ion formation by these workers made it unnecessary to repeat those experiments on the new dicarbonium ions whose hydrolysis rates will be reported later in this work.

The steric requirements for dication formation are present in all of the previously unreported benzotrichlorides used here. The trichloromethyl group is nearly as large as a tertiary butyl group and rotation is restricted with respect to the ortho methyl groups. The steric repulsion between the trichloromethyl group and the ortho methyl groups provides a driving force for the loss of two chlorine atoms. The steric repulsion is not relieved by the loss of only one

chlorine atom because the resulting carbonium ion cannot be stabilized unless the two remaining chlorine atoms lie in the same plane as the ring. Once again steric interactions with



the ortho methyl groups are very unfavorable. The loss of the second chlorine atom eliminates any steric strain by forming a linear structure.



The other requirement for formation of dications is also fulfilled by these compounds. Alkyl groups or other electron releasing groups are apparently necessary to stabilize dicarbonium ions and other carbonium ions. Perchlorotoluene hydrolyzed to pentachlorobenzoic acid only after being heated to 100° in concentrated sulfuric acid for 48 hours (17). Another hindered compound, 2-dichloromethylbenzotrichloride was not even soluble in 100% sulfuric acid (17). Sterically hindered acids such as pentamethylbenzoic acid, mesitoic acid and 2,3,5,6-tetramethylbenzoic acids form acylium ions in 100% sulfuric acid but equally sterically hindred acids such as 2,4,6-tribromobenzoic acid and 3,5dibromomesitoic acid do not (18, 19).

All the trichloromethyl compounds described in this thesis dissolved rapidly in 100% sulfuric acid with the evolution of hydrogen chloride and gave brilliant red solutions which when poured over ice instantaneously precipitated the corresponding carboxylic acids in quantitative yields. By comparison of the structure and reaction of the new compounds with the reported benzotrichlorides all can be shown to form phenylchlorodicarbonium ions in 100% sulfuric acid.

II. Kinetics of Hydrolysis of Dications in Aqueous Sulfuric
Acids at 25.0<sup>o</sup>.

The apparatus and techniques used to determine the kinetics are described in the Experimental section of this work. The hydrolysis rate of pentamethylphenylchlorodicarbonium ion (II) was initially determined at two different concentrations



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II

of the dication in 97.6% sulfuric acid by making use of the two major absoprtions at  $545m\mu$  and  $393m\mu$ . The results are summarized in Table 1. The values of  $t_{1/2}$  agreed within 10% for a ten-fold change in concentration.

Table 1. Half-lives of the hydrolysis of Pentamethylphenylchlorodicarbonium Ion (II) in 97.6% sulfuric acid.

Concentration of II	Measured at $\lambda$	Averaged t <sub>1/2</sub> (min.)
9.94 x $10^{-5}$ M	393 mµ	95.5
$9.06 \times 10^{-4} M$	545 mµ	103.9

The straight lines obtained when the log of the concentration of dication (log absorbance) was plotted versus time indicated a first-order reaction. In addition, the values of k, the rate constant, were calculated from experimental values of concentration and time. The values showed no significant variation during a given run.

The amount of water in the aqueous sulfuric acid at the concentrations used for hydrolysis of dicarbonium ions was in great excess to that of the ions. Even at high acid strengths the water is not completely protonated. The concentration of unprotonated water in 99.75% acid has been calculated to be  $1.6 \times 10^{-2}$  molal (20). Since the dication concentrations were less than  $1 \times 10^{-4}$  molal it can be seen
that the water concentration was always much larger. Because the water concentration was essentially constant during a given run, the reactions are considered pseudo first-order.

The hydrolysis of II was run in eight concentrations of sulfuric acid (Table 2). A plot of  $t_{1/2}$  versus the sulfuric acid concentration (Figure 1) shows that near 99% there is an abrupt change in the values of  $t_{1/2}$ . From 99.0% to 99.75%, a change of less than 1%, the  $t_{1/2}$  increased approximately 2000 minutes; but decreasing the acid concentration by the same percent, to 98.25%, caused a decrease of about 200 minutes. This effect is not as startling as it may appear at first glance. It can be seen from the figure that any two-fold increase in the percentage of water in the sulfuric acid caused the value of  $t_{1/2}$  to be approximately halved. For example, from 99.5% acid (0.5% water) to 99.0% acid (1.0% water) the  $t_{1/2}$  went from about 900 minutes to 400 minutes; and from 98% (2% water) to 96% (4% water)  $t_{1/2}$  went from 150 to 70 minutes. This is what might be expected since water was one of the reactants.

The data for the hydrolysis of 4-fluoro-, chloro- and bromo-2,3,5,6-tetramethylphenychlorodicarbonium ions (XIV a, b and c) (Tables 3, 4, and 5) reveal that replacing the 4-methyl group with halogen increased the rate of hydrolysis. The reason for the rate increase is probably that a halogen

% н <sub>2</sub> so <sub>4</sub>	k (sec. <sup>-1</sup> )	t <sub>1/2</sub> (min.)
99.75	$5.13 \times 10^{-6}$ 5.49 x 10^{-6}	2250 2110
99.50	$1.25 \times 10^{-5}$ $1.25 \times 10^{-5}$	928 928
99.25	$2.02 \times 10^{-5}$ 2.05 x 10^{-5}	574 564
99.0	$3.08 \times 10^{-5}$ 2.96 x 10 <sup>-5</sup>	375 390
97.6	$1.03 \times 10^{-4}$ 1.01 x 10-4	112.3 114.7
96.0	$1.73 \times 10^{-4}$ 1.67 x 10^{-4}	67.0 69.2
94.0	$3.86 \times 10^{-4}$ $3.88 \times 10^{-4}$	29.9 29.8
92.0	6.11 x $10^{-4}$ 5.73 x $10^{-4}$	18.9 20.1
90.0	$1.22 \times 10^{-3}$ $1.22 \times 10^{-3}$	9.47 9.47

Table 2. Rates and half-lives of the hydrolysis of pentamethylphenylchlorodicarbonium ion.



Figure 1. Plot of t<sub>1/2</sub> versus % sulfuric acid for the hydrolysis of pentamethylphenylchlorodicarbonium ion.

% н <sub>2</sub> so <sub>4</sub>	k (sec. <sup>-1</sup> )	t <sub>1/2</sub> (min.)
99.5	$4.75 \times 10^{-4}$ $4.78 \times 10^{-4}$	24.3 24.2
99.0	$1.17 \times 10^{-3}$ $1.22 \times 10^{-3}$	9.86 9.50
97.6	$4.36 \times 10^{-3}$ $4.12 \times 10^{-3}$	2.65 2.79
94.0	$1.43 \times 10^{-2}$ 1.37 x 10^{-2}	0.81 0.84

Table 3. Rates and half-lives of the hydrolysis of 4-fluoro-2,3,5,6-tetramethylphenylchlorodicarbonium ion.

% н <sub>2</sub> so <sub>4</sub>	k (sec. <sup>-1</sup> )	t <sub>1/2</sub> (min.)
99.5	$1.65 \times 10^{-3}$ $1.69 \times 10^{-3}$	6.98 6.82
99.0	$3.68 \times 10^{-3}$ $3.62 \times 10^{-3}$	3.20 3.24
97.6	9.60 x $10^{-3}$ 9.80 x $10^{-3}$	1.20

Table 4.	Rates	and	half-liv	ve <b>s</b> o	E the	hydrolysis	of	4-chloro-
	2,3,5	,6-te	etramethy	lphe	nylch	lorodicarbo	niu	n ion.

Table 5.	Rates	and	half-liv	re <b>s</b> of	the	hydrolysis	of	4-bromo-
	2,3,5,	,6-te	etramethy	lphen	ylch.	lorodicarbo	niur	n ion.

99.5	$1.97 \times 10^{-3}$ 1.94 x 10^{-3}	5.85 5.95
99.0	$4.30 \times 10^{-3}$ $4.46 \times 10^{-3}$	2.69 2.59
97.6	$1.33 \times 10^{-2}$ 1.23 x 10 <sup>-2</sup>	0.87 0.94



X = Fluorine XIVaX = Chlorine XIVb X = Bromine XIVc

XIV

cannot stabilize the transition state as effectively as a methyl group. Table 6 shows the relative rates of the hydrolysis in three acid concentrations. The stabilizing ability of the 4- substituents was methyl  $\rangle$  fluorine  $\rangle$  chlorine  $\rangle$  bromine. On the basis of  $\sigma_{para}$  values for these substituents this would be the predicted order. A plot of  $\sigma_{para}$  versus log k does not give a straight line, but an approximate relationship between  $\sigma_{para}$  and reaction rates is shown by a plot of  $\sigma_{para}$ versus rate which gives a nearly straight line (Figure 2).

Table 6. Relative rates of hydrolysis of 4-methyl-, fluoro-, chloro- and bromo-2,3,5,6-tetramethylphenylchlorodicarbonium ions.

4-Substituent	99.5% н <sub>2</sub> so <sub>4</sub>	99.0% н <sub>2</sub> so <sub>4</sub>	97.6% н <sub>2</sub> so <sub>4</sub>	Average
Methyl	1	1	1	1
Fluorine	38.2	39.7	41.6	40
Chlorine	134	121	95.1	117
Bromine	157	145	126	143



Figure 2. Plot of relative rates of 4-substituted-2,3,5,6tetramethylphenylchlorodicarbonium ions vs. o values.

When the 3-methyl group of II was exchanged for halogen the rate increase (Table 7) was larger than when the 4-methyl group was similarly replaced. The average relative rate increase from 3-methyl to 3-halogen was 170, while in the 4position it was 100. There was no appreciable difference in the rates for the 3-halogen dications, but with each halogen the 3-derivative hydrolyzed more rapidly than the 4-isomer. The inductive effect of a given substituent is larger in the meta than in the para position because of the shorter distance

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involved (21), and resonance stabilization is not possible in the meta position.

Table 7. Rates and half-lives of the hydrolysis of 3-fluoro-, chloro- and bromo-2,4,5,6-tetramethylphenylchlorodicarbonium ion in 97.6% sulfuric acid.

3-Substituent	k (sec. <sup>-1</sup> )	t <sub>1/2</sub> (min.)
Fluorine	$1.95 \times 10^{-2}$ 1.70 x 10 <sup>-2</sup>	0.59 0.68
Chlorine	$1.91 \times 10^{-2}$ 1.83 x 10^{-2}	0.61 0.63
Bromine	$1.55 \times 10^{-2}$ 1.50 x 10^{-2}	0.75 0.77

If one compares the predicted order for the rates of the pentamethyl, 4-halotetramethyl, and 3-halotetramethyl dicarbonium ion derivatives based on  $(\sigma_{para} + \sigma_{meta})$  values (22), the order is the same as the experimental order for these seven dications except for 3-bromo-2,4,5,6-tetramethylphenylchlorodicarbonium ion. It would be expected to hydrolyze most rapidly, but it was found to react more slowly than the other 3-halogen dications. The reason for this is not apparent.

2-Chloro-3,4,5,6-tetramethylphenylchloromethylene dication (XV) was hydrolyzed in 97.6% sulfuric acid (Table 8).



If the 2-,3- and 4-chloro isomers are compared it can be shown that the relative rates for these dicarbonium ions were 1.35, 2.10, and 1.0 respectively. The fastest reaction occurred with the 3-chloro derivative which shows that the least amount of transition state stabilization occurred when halogen was in the meta position. Since the stereochemical difference of the 2-isomer could affect the rate of its hydrolysis, it may not be correct to assume that the above data reflect only stability differences among the three dications.

Table 8. Rates and half-lives of the hydrolysis of 2-chloro-3,4,5,6-tetramethylphenylchlorodicarbonium ion.

% н <sub>2</sub> so <sub>4</sub>	k (sec. <sup>-1</sup> )	t <sub>1/2</sub> (min.)
97.6	$1.19 \times 10^{-2}$	0.97
	$1.22 \times 10^{-2}$	0.95

Only a single hydro-tetramethylbenzotrichloride could be prepared because durene, isodurene and prehnitene gave

the same trichloromethylation product. The values for the hydrolysis of the corresponding dication, 2,3,4,5-tetramethyl-phenylchlorodicarbonium ion (XVI) are given in Table 9. Stereochemical differences should be very important when the



2-substituted tetramethylphenylchloromethylene dications (II, XV, XVI) are compared. The relative rates for methyl, hydrogen and chlorine in 97.6% acid are respectively, 1, 107 and 119, indicating thatortho methyl stabilizes much better than hydrogen or chlorine. Stereochemical differences are significant since the small size of hydrogen would tend to allow a less restricted approach of water molecules to the charged carbon atom in XVI than in II and XV.

The kinetics of 2,4,6-trimethylphenylchlorodicarbonium ion (XVII) were determined in two acid concentrations (Table 10). The substitution of halogen for hydrogen caused a rate increase. The data for the 3-halogen derivatives of

% н <sub>2</sub> so <sub>4</sub>	k (sec. <sup>-1</sup> )	t <sub>1/2</sub> (min.)
97.6	$1.08 \times 10^{-2}$ $1.10 \times 10^{-2}$	1.07 1.05

Table 9. Rates and half-lives of the hydrolysis of 2,3,4,5tetramethylphenylchlorodicarbonium ion.



Table 10. Rates and half-lives of the hydrolysis of 2,4,6trimethylphenylchlorodicarbonium ion.

% н <sub>2</sub> so <sub>4</sub>	k (sec. <sup>-1</sup> )	t <sub>1/2</sub> (min.)
97.6	5.49 x $10^{-3}$ 5.28 x $10^{-3}$	2.11 2.19
94.0	9.55 x $10^{-3}$ 10.6 x $10^{-3}$	1.21 1.09

XVII (XVIIIa, b and c) appear in Table 11. The chloro derivative



X = Fluorine XVIIIa
X = Chlorine XVIIIb
X = Bromine XVIIIc

reacted only slightly faster than XVII, but the bromo- and fluoro- dications were considerably accelerated. The rate of XVIIIa was too great to be measured accurately even in 99.5% sulfuric acid, although the ion was completely stable in 100% sulfuric acid. After several days in 100% acid no hydrolysis had occurred.

Table 11. Rates and half-lives of the hydrolysis of 3-fluoro-, chloro- and bromo-2,4,6-trimethylphenylchlorodicar-bonium ions.

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3-Substituent	% H <sub>2</sub> SO <sub>4</sub>	k (sec. <sup>-1</sup> )	t <sub>1/2</sub> (min.)
Fluorine	99.5	$7.7 \times 10^{-2*}$	0.15*
Chlorine	97.6	5.80 x $10^{-3}$ 5.63 x $10^{-3}$	2.00 2.05
Chlorine	94.0	1.06 x 10 <sup>-2</sup> 1.11 x 10 <sup>-2</sup>	1.09 1.04
Bromine	99.0	$3.63 \times 10^{-2}$ 3.85 x 10^{-2}	0.32 0.30

\*Approximate values.

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One conclusion that can be drawn from all the data presented is that dications are stabilized more effectively by electron releasing groups than by electron attracting groups. Dicarbonium ions were stabilized best by methyl groups, somewhat less stabilized by hydrogen, and very slightly (if at all) by halogen. Another conclusion is that halogens, and especially meta halogens, destabilize the transition state. These two conclusions are in agreement with the data on the ability of various hindered benzoic acid derivatives to form acylium ions in 100% sulfuric acid. Pentamethylbenzoic acid e.g. gives the acylium ion XIX in 100% acid (18). That halogens destabilize acylium ions is shown by the fact that mesitoic acid (XX) forms an acylium



ion, but 2,4,6-tribromobenzoic acid (XXI), which is equally sterically hindered, does not (23, 24). When the ring hydrogens of XX were substituted by bromine (XXII) the acid

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no longer formed an acylium ion (23) which shows destabilization by meta halogens.



Acylium ions are formed in the hydrolysis of extraordinary dicarbonium ions. Ion XIX has been examined by several workers (1, 25) who reported that this ion had a strong ultraviolet absorption band at 294mµ. When solutions of II were cursorily examined at this wavelength the absorbance at zero time was zero, but it increased rapidly with time, attained a maximum value, and then slowly decreased. This indicated that II hydrolyzed rapidly to XIX which then slowly reacted with water to form the carboxylic acid. If II hydrolyzed to XIX with a rate constant  $k_1$  and XIX hydrolyzed to carboxylic acid with a rate constant  $k_2$  these reactions could be treated as series first-order reactions.



Before proceeding further, it is worthwhile to consider the general case of series first-order reactions (26); A  $\xrightarrow{k_1}$  B  $\xrightarrow{k_2}$  C,  $\xrightarrow{dA}_{dt} = k_1 A$  (1) and  $\xrightarrow{dB}_{dt} = k_1 A - k_2 B$  (2). The equation for A integrates to A-A<sub>o</sub>e<sup>-k</sup>1<sup>t</sup> where A<sub>o</sub> = initial concentration of A. Substituting in (2) gives  $\xrightarrow{dB}_{dt} = k_1 A_o e^{-k_1 t} - k_2 B$  (3). If B<sub>o</sub> = 0 (as is true in dication hydrolyses) integrating yields B =  $\frac{A_o K_1}{K_2 K_1}$  X ( $e^{-k_1 t} - e^{-k_2 t}$ ) (4). This can be simplified by introducing dimensionless parameters and variables. Let  $\beta = \frac{B}{A_o}$ 

(which will vary only between 0 and 1); and let  $\tau = k_1 t$ and  $K = \frac{k_2}{k_1}$ . Thus  $\beta = \frac{1}{K-1} (e^{-\tau} - e^{-K\tau})$  (5).

The concentration of B as measured by  $\beta$  goes through a maximum if  $k_1 \ge k_2$ . Using (5) and setting  $\frac{d\beta}{dt} = 0$  it is found that  $\tau$  max =  $\frac{1 \cdot \ln K}{K-1}$  (6) and the value of  $\beta$  at the maximum is  $B_{max} = K \frac{K}{1-K}$ . If  $k_1$  and  $k_2$  (and thus K) are known, it is possible to calculate the theoretical time at which the maximum value for B occurs and the % reaction  $\max$  since this is equal to  $100\beta_{max}$ .

Returning to the hydrolysis study of dicarbonium ions, the rate of hydrolysis of XIX was determined in 92.0% and 90.0% sulfuric acids (Table 12). Pentamethylbenzoic acid was dissolved in 100% sulfuric acid and mixed with aqueous sulfuric acid to give solutions of the desired acid strength. The disappearance of the 294mµ band was followed spectrophotometrically at  $25.0^{\circ}$  and the rate constants were determined by the same graphic method used for dication hydrolysis rate constants. The reaction was found to be pseudo first-order with respect to acylium ion and considerably slower than the hydrolysis of II.

If the reaction proceeded as previously proposed, the concentration of XIX must reach a maximum value since  $k_1$  was found to be greater than  $k_2$ . To determine if this occurred, the hydrolysis of dication II was followed carefully at the 294mµ band in 92.0% and 90.0% sulfuric acid. A plot of

% н <sub>2</sub> so <sub>4</sub>		k (sec. <sup>-1</sup> )	t <sub>1/2</sub> (min.)
92.0		$4.20 \times 10^{-5}$ $4.06 \times 10^{-5}$	275 284
	Average	4.13 x $10^{-5}$	279
90.0		$1.12 \times 10^{-4}$ $1.14 \times 10^{-4}$	103 101
	Average	$1.13 \times 10^{-4}$	102

Table 12. Rates and half-lives of the hydrolysis of pentamethylbenzoylium ion (XIX) at 25.0°.

absorbance versus time (Figures 3, 4) revealed that a maximum value was indeed reached and that the general shape of the curve was that expected for the concentration of "B" in a series first-order reaction when  $k_1 > k_2$ . The experimental curves were examined to determine what calculated values for  $k_1$  and  $k_2$  would exactly describe the observed curve. For 90.0% acid  $k_1$  (sec.<sup>-1</sup>) observed was  $1.22 \times 10^{-4}$ and  $k_2$  observed was  $1.13 \times 10^{-5}$ ; and the values obtained by "fitting" the curve were  $1.1 \times 10^{-4}$  for  $k_1$  and  $1.0 \times 10^{-5}$ for  $k_2$ . For 92.0% acid  $k_1$  observed was  $5.92 \times 10^{-4}$  and  $k_2$ observed was  $4.13 \times 10^{-5}$ . Fitted values for  $k_1$  and  $k_2$ were, respectively,  $6.8 \times 10^{-4}$  and  $6.0 \times 10^{-5}$ . The fitted values probably reflect more accurate values for the individual rate constants, but the ratio of  $\frac{k_1}{k_2}$  is about the





Plot of 294mµ absorbance vs. time vs. time for the hydrolysis of pentamethylphenylchlorodicarbonium ion in 92% sulfuric acid.

same for observed and fitted k's. In 90.0%  $\frac{k_1}{k_2}$  observed is 1.08; fitted is 1.10. In 92.0%  $\frac{k_1}{k_2}$  observed is 1.43 and fitted is 1.14.

By using the experimentally (and separately) determined values of  $k_1$  and  $k_2$  and substituting various values of t in equation (4) it is possible to calculate the value of the concentration of XIX at any time t. This was done for a sufficient number of points so that a plot of the concentration of XIX versus time accurately described the curve. The calculated and experimental curves were very similar for both 92.0% and 90.0% sulfuric acids. The calculated and experimental values of  $t_{max}$  and % reaction compared very closely (Table 13).

Table 13. A comparison of calculated and experimental values for t and % reaction for the concentration of pentamethylbenzoylium ion in the hydrolysis of pentamethylphenylchlorodicarbonium ion.

% н <sub>2</sub> so <sub>4</sub>	t (min.) max		% reaction max	
	calc.	exp.	calc.	exp.
92.0	809	788 792	80.9	86.4 85.8
90.0	359	375 399	78.3	84.0 80.7

These results prove that acylium ion XIX was an intermediate in the hydrolysis of II. The following mechanism is postulated. The ultraviolet spectrum had no absorption



which could be attributed to structure XXIII. The loss of a proton and hydrogen chloride from II could occur simultaneously or in rapid succession, and could happen in the order reversed from that shown. No hydrogen chloride was evolved since it is soluble at the concentrations used (27). The acylium ion would react with water to form the carboxylic acid. The acid was found to be the only product of hydrolysis.

It can be shown that this mechanism is applicable for the hydrolysis of all the dications. The dications least likely to form acylium ions were 2, 3, 4, 5-tetramethylphenylchlorodicarbonium ion (XVI) and 3-bromo-2,4,6-trimethylphenylchlorodicarbonium ion (XVIIIc); the former because it had only a single ortho methyl and the latter because XXII did not form an acylium ion. The acylium ions formed in 100% sulfuric acid from pentamethylbenzoic and mesitoic acids have very strong ( $\epsilon = \sim 60,000$ ) absorption bands near 290mu (20). The acids derived from XVI and XVIIIc both had strong ( $\epsilon = -60,000$ ) absorption bands at 290mµ which indicated acylium ion formation. The dications gave rapidly increasing absorption at this wavelength until a maximum was attained which indicated that the acylium ions were being formed. The fast rate of reaction for these dicarbonium ions made it necessary to use 99.5% sulfuric acid to measure the increasing 290mµ absorption and at this acid strength the acylium ions did not hydrolyze; however, the carboxylic acids immediately precipitated when the solutions were poured onto ice. It is logical to assume that all the dications hydrolyzed by the proposed pathway.

III. Reactions of Mesitylchlorodicarbonium Ion.

To study a variety of reactions of dicarbonium ions it was necessary to prepare them in some solvent other than 100% sulfuric acid. The tetrafluoroborate anion was desirable for its non-nucleophilic character and for the stability it would give to the doubly charged carbonium ion (28, 29). Anhydrous silver tetrafluoroborate was prepared and attempts were made to form dications with this salt. A large number of solvents were tried but it was not possible to obtain one which would dissolve silver tetrafluoroborate but not react with the trichloromethyl compound, the dicarbonium ion, or the silver salt.

The feasibility of dication tetrafluoroborate formation in anhydrous fluoboric acid was investigated. Anhydrous hydrogen fluoride was condensed in a polyethylene vessel and saturated with dry boron trifluoride. Addition of 2,4,6trimethylbenzotrichloride (XXIV) to the acid caused the immediate evolution of hydrogen chloride and the solution became dark red. These conditions caused the replacement of the chlorine atoms by fluorine to form 2,4,6-trimethylbenzotrifluoride (XXV). This structure was established by infrared spectrum, fluorine magnetic resonance spectrum, and elemental analysis. XXV was not formed in hydrogen fluoride containing



no boron trifluoride. A solution of XXIV in liquid hydrogen fluoride gave a quantitative yield of mesitoic acid when carefully treated with water, but XXV was unchanged by this procedure.

To determine if trifluoromethyl compounds would form dications a sample of XXV was added to 100% sulfuric acid. It did not dissolve to a noticeable extent and the acid remained colorless. That dipositive ions were not produced is not unexpected when one considers the inertness of the trifluoromethyl group (30, 31).

Silver tetrafluoroborate in liquid anhydrous sulfur dioxide also gave trifluoromethylmesitylene (XXV) when allowed to react with XXIV.

Mesitylchlorodicarbonium chlorotrifluoroborate (XXVI) was prepared by bubbling boron trifluoride into a suspension of XXIV in trifluoroacetic acid containing a small amount of

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anhydride (2). The identity of the anion is not certain and it is possible that more than a single anion is present in the salt. There is evidence for both chlorotrifluoroborate and trifluoroacetate ions.

Dications were formed when boron trifluoride was passed into a nitromethane solution of XXIV, and also when this gas was passed into a neat sample of XXIV. In these cases the anion is undoubtedly chlorotrifluoroborate. When trifluoroacetic acid was used as the solvent there was no evolution of hydrogen chloride. This suggests that the two chlorine ions lost by the benzotrichloride to produce the dication, reacted with boron trifluoride to yield chlorotrifluoroborate anions.

Hart and Fish reported (2) some evidence for the presence of trifluoroacetate. Heating the salt of II under reduced pressure caused the formation of what appeared to be a mixed anhydride of trifluoroacetic and pentamethylbenzoic acids (IV). The reaction products of XXVI in several instances also supported the presence of trifluoroacetate in the salt.

A cold sample of XXVI was allowed to react with ethyl, isopropyl, and t-butyl alcohols. The reactions gave good yields of the corresponding mesitoates. The ethyl and isopropyl

XXVI + ROH 
$$\longrightarrow$$
 CH<sub>3</sub>  $\xrightarrow{CH_3}_{CH_3}$  R = Ethyl  
CH<sub>3</sub>  $\xrightarrow{CH_3}_{OR}$  R = Isopropyl  
= t-Butyl

esters formed very rapidly but t-butyl alcohol reacted very slowly in comparison. The esters were identified by a comparison of their physical properties with the reported values (24, 32) and by their infrared spectra which were consistent with their structures. In addition, all were rapidly converted to mesitoic acid when dissolved in 100% sulfuric acid and then hydrolyzed.

Newman attempted the preparation of these same esters by dissolving mesitoic acid in 100% sulfuric acid and pouring the solution into a large excess of the appropriate alcohol. He was able to make ethyl and isopropyl mesitoates but this method failed to give any t-butyl mesitoate (24). The reaction

fai in pro <u>me</u>t 19 ch et re 119 T: g ]( т. • • p ł ¥ ÷ failed presumably due to the rapid hydrolysis of this compound in acid by alkyl-oxygen fission (33,34). The present work provides an alternate route to the t-butyl esters of polymethylbenzoic acids.

It was hoped that the reaction of XXVI with methylmagnesium iodide would indicate the location of the positive charges in the ion. Methylmagnesium iodide was prepared in ether and XXVI was slowly added to this solution. A vigorous reaction occurred and a colorless liquid was isolated as the main product of the reaction. Its identity was surprising. The infrared spectrum of the material indicated that it was a carbonyl compound. Elemental analysis revealed it contained no halogen; bromine in carbon tetrachloride was not decolorized. The compound was dissolved in concentrated sulfuric acid and poured on ice. The white precipitate which formed immediately was shown by melting point and infrared spectrum to be mesitoic acid. This suggested that the material was a mesitoate. It was hydrolyzed and the alcohol portion was isolated. It gave a positive iodoform test and was identified by the 3,5dinitrobenzoate derivative as ethanol. The reaction product was ethyl mesitoate. Elemental analysis was consistent with this assignment.

The reaction was repeated with ether that had been

carefully dried over sodium and distilled to remove any ethoxide ion present. The ethyl ester was again formed. The reaction was run a third time without methylmagnesium iodide. The ester was produced in approximately the same yield (50%) as before. The presence of the Grignard reagent was obviously not essential to the reaction.

The formation of an ester when XXVI was treated with ether was totally unexpected. Expecially unusual was the fact that the product had two oxygen atoms per molecule. It was this aspect of the reaction with ether that was more closely examined. Water used in the workup of the product was the first suspected source of oxygen atoms. The reaction with ethyl ester was repeated and the untreated reaction mixture was distilled. The major fractions were trifluoroacetic acid and ethyl mesitoate. The yield of ester was unchanged. The presence of trifluoroacetic acid is in accord with the previous report (2) that heating the salt of II gave the anhydride IV.

If ether were being cleaved to ethyl alcohol, this would explain ester formation since this alcohol had been shown to yield the ethyl ester. A solution of trifluoroacetic acid saturated with boron trifluoride was added to ether and allowed to react. The mixture was distilled into fractions

and the infrared absorption spectra were examined for bands due to ethyl alcohol or ethyl trifluoroacetate. None was found in any of the fractions or the residue, showing that ether was not cleaved by these reagents.

The following is a possible mechanism for the formation of the ester from the dication and ether.





The reaction can also be explained by the formation of a mixed anhydride which could then react with ether or a trifluoroacetic acid-ether addition compound. Trifluoroacetic acid and ether form the addition compound 3  $CF_3COOH \cdot 2$  $(CH_3CH_2)_2O$  at room temperature (35) and this may be the the reactive species in forming the ester. The visible spectrum and deep red color of the material, however, indicated that the anhydride was not the only component because the anhydride would be colorless. A possible mechanism for anhydride formation and its reaction with ether is



The possible intermediacy of the acylium ion in these reactions could be tested experimentally.

Another common solvent for Grignard reagents is tetrahydrofuran. This cyclic ether also reacted with XXVI and gave a high boiling  $(210^{\circ} \text{ at } 0.08 \text{ mm.})$  mesitoate which was probably  $\delta$ -hydroxybutyl mesitoate (XXVII). The infrared



XXVII

spectrum of the ester was consistent with this structure. A sample of XXIV was dissolved in 100% sulfuric acid and poured into butan-1,4-diol. The ester produced had an infrared spectrum and refractive index identical to those of XXVII. Elemental analysis of XXVII gave an accurate value for percentage hydrogen but the carbon value was 1% lower than calculated. The ester was easily hydrolyzed in sulfuric acid to mesitoic acid.

It was decided to treat XXVI with an organometallic compound which could be prepared in an inert solvent. n-Butyllithium was prepared in n-pentane and allowed to react with XXVI. The product after hydrolytic workup was shown by its infrared spectrum to be a carbonyl compound which was first assumed to be 2,4,6-trimethyl-n-valerophenone
(XXVIII). This compound was synthesized by Friedel-Crafts



acylation of mesitylene, but it proved to be different (dissimilar boiling point, infrared spectrum and refractive index) from the reaction product. The product was hydrolyzed by pouring a concentrated sulfuric acid solution on ice. Mesitoic acid was formed immediately indicating that the product was the n-butyl ester of mesitoic acid. Its infrared spectrum supported this structure. Elemental analysis agreed with calculated values for n-butyl mesitoate. The literature value for the boiling point of this compound compared favorably with the value found experimentally. No other physical properties are reported (36).

In this reaction the only possible source of oxygen atoms was trifluoroacetic acid. Care was taken to exclude any trace of moisture from the reaction. The apparatus and reagents were carefully dried and the reaction was run under a stream of dry nitrogen. Water was used to destroy the excess butyllithium, but this aqueous workup would not explain butyl ester being formed. Once again the best explanation is that a mixed anhydride formed and reacted with the organometallic compound. EXPERIMENTAL

#### I. Preparations of Substituted Benzotrichlorides

A. Preparation of 3-Fluoro-2,4,6-trimethylbenzotrichloride

#### 1. Preparation of 2-Nitromesitylene (39)

A solution of 40 g. (0.33 mole) of mesitylene in 60 g. of acetic anhydride was cooled to  $10^{\circ}$  and a solution of 31.5 g. (0.5 mole) of fuming nitric acid, \* 20 g. of glacial acetic acid and 20 g. of acetic anhydride was added with stirring. The reaction was kept between  $15^{\circ}$  and  $20^{\circ}$  during the addition, then stirred for two hours at room temperature. The mixture was heated to  $50^{\circ}$  for 10 minutes, cooled and poured slowly into 800 ml. of a water-ice mixture with vigorous stirring. Forty grams of sodium chloride was added, and the cooled mixture was filtered. The solid was washed repeatedly with water, and recrystallized from 95% ethanol to yield 47 g. (85%) of pale yellow flakes of 2-nitromesitylene, m.p.  $41-42^{\circ}$ .

#### 2. Preparation of 2-Aminomesitylene (40)

A mixture of 20 g. (0.121 mole) of 2-nitromesitylene,

<sup>\*</sup>The fuming nitric acid was added to the cold acetic acid-acetic anhydride solution at such a rate that the temperature remained below 20°. An explosive reaction will take place if the fuming nitric acid is added too rapidly.

15 g. (0.30 mole) of 99% hydrazine hydrate and 200 ml. of absolute ethanol was heated on a steam bath to incipient reflux and a small amount (about 2 g.) of Raney nickel was added. The evolution of gas began immediately. The mixture was heated gently for 1 hour and about 4 g. of Raney nickel was added to decompose the excess hydrazine hydrate. The hot mixture was filtered, treated with Norite, filtered again, cooled and poured into 2 1. of water. The aqueous mixture was extracted with 150 ml. of ether. The ether layer was separated and dried over sodium sulfate. The solvent was evaporated and the residue was distilled to yield 14.3 g. (87.7%) of 2aminomesitylene, b.p. 230-232<sup>0</sup>.

#### 3. Preparation of 2-Fluoromesitylene

A mixture of 14.3 g. (0.106 mole) of 2-aminomesitylene and 100 ml. of 6M sulfuric acid was stirred magnetically and cooled to  $0^{\circ}$ . Solid sodium nitrite was added slowly to maintain the temperature at  $0-5^{\circ}$  until an excess of nitrous acid was indicated by starch-iodide test paper. Fluoboric acid (41) (50 ml.) was added and a pale yellow precipitate formed. The precipitate was filtered, washed with 30 ml. of ice-cold water, 50 ml. of cold absolute ethanol and 200 ml. of cold ether. The solid was dried and decomposed by gentle warming

in a flask fitted with a condenser. The residue was predominantly liquid. The liquid was dissolved in 100 ml. of ether, washed with 50 ml. of 5% sodium carbonate and 50 ml. of water and dried over Drierite. The ether was evaporated and the residue was distilled to yield 10.2 g. (70%) of 2-fluoromesitylene, b.p.  $67-68^{\circ}$  at 20 mm.;  $n_{\rm D}^{25}$  1.4804. McBee and Leech (38) reported the b.p.  $166.6^{\circ}$  at 744 mm. and  $n_{\rm D}^{25}$  1.4809 for this compound.

#### 4. Preparation of 3-Fluoro-2,4,6-trimethylbenzotrichloride

A slurry of 21 g. (0.158 mole) of powdered anhydrous aluminum chloride and 75 ml. of carbon tetrachloride was stirred and heated at 37-42<sup>°</sup> while a solution of 10 g. (0.0725 mole) of fluoromesitylene in 25 ml. of carbon tetrachloride was added slowly over a two hour period. After the addition of the fluoromesitylene solution, stirring and heating were continued for two hours.

The purple complex was slowly poured into a vigorously stirred mixture of 400 g. of ice, 400 ml. of water and 1 l. of carbon tetrachloride. The carbon tetrachloride was washed with warm water and dried with calcium chloride. The solvent was removed on a Rinco rotary evaporator and distilled to give 14.6 g. (79%) of 3-fluoro-2,4,6-trimethylbenzotri-

chloride, b.p. 85-88<sup>°</sup> at 0.5 mm. Its infrared spectrum is shown in Figure 5 and its proton magnetic resonance spectra in Figure 6.

<u>Anal</u>. Calcd. for C<sub>10</sub>H<sub>10</sub>Cl<sub>3</sub>F: C, 47.00; H, 3.94; Cl, 41.62. Found: C, 46.87; H, 4.11; Cl, 41.77.

#### 5. Hydrolysis of 3-Fluoro-2,4,6-trimethylbenzotrichloride

A sample of 3 g. (0.0117 mole) of 3-fluoro-2,4,6trimethylbenzotrichloride was dissolved in 50 ml. of 80% acetone and the solution was refluxed overnight. The solution was cooled to  $0^{\circ}$  and filtered. The solid was recrystallized from 80% acetone to yield 2.04 g. (95%) of white needles of fluoromesitoic acid, m.p. 132°. Its infrared spectrum is shown in Figure 7. (MM)

<u>Anal</u>. Calcd. for C<sub>10</sub>H<sub>10</sub>FO<sub>2</sub>: C, 65.92; H, 6.09. Neutralization Equivalent: 182.2. Found: C, 66.17; H, 6.07. Neturalization Equivalent: 181.3.

# <u>Reaction of 3-Fluoro-2,4,6-trimethylbenzotrichloride in 100%</u> <u>Sulfuric Acid with Water</u>

3-Fluoro-2,4,6-trimethylbenzotrichloride (1.6 g., 0.0063 mole) was dissolved in 10 ml. of 100% sulfuric acid









(1) H









with stirring. This intensely red solution was poured onto 100 g. of an ice-water mixture. The white precipitate was filtered, washed with 100 ml. of water and recrystallized from 80% acetone to yield 0.84 g. (73.6%) of fluoromesitoic acid, m.p. 168.5-169.5°. A mixed melting point with the acid obtained from the hydrolysis in 80% acetone was not  $\rangle$ depressed. Both acids gave identical infrared spectra.

B. Preparation of 3-Chloro-2,4,6-trimethylbenzotrichloride

#### 1. Preparation of 2-Chloromesitylene (38)

Mesitylene (97.2 g., 0.809 mole) and 1 g. of degreased iron filings were placed in a flask from which light was rigorously excluded. The mixture was magnetically stirred and cooled to ice temperature in a bath. Chlorine (33.7 g., 0.475 mole) was dried by bubbling the gas through a concentrated sulfuric acid scrubbing tower and passed into the mixture at such a rate that the temperature did not exceed  $10^{\circ}$ . The mixture was aerated for 30 minutes and distilled to yield 52.7 g. (82%) of 2-chloromesitylene, b.p. 67-68° at 1.8 mm.

# 2. <u>Preparation of 3-Chloro-2,4,6-trimethylbenzotrichloride</u>

A mechanically stirred slurry of anhydrous powdered

aluminum chloride and 100 ml. of carbon tetrachloride was maintained at  $37^{\circ}$  while a solution of 35.9 g. (0.223 mole) of 2-chloromesitylene in 60 ml. of carbon tetrachloride was added dropwise. The temperature was kept between  $37^{\circ}$  and  $42^{\circ}$  during the addition of the chloromesitylene solution. The addition required about 3 hours. The mixture was heated at  $37^{\circ}$  and stirred for 2 hours longer, then allowed to cool to room temperature.

Approximately one-quarter of the reaction mixture was slowly poured into a beaker containing 1 1. of carbon tetrachloride, 500 ml. of water and 500 g. of ice. The contents of the beaker were stirred mechanically to affect complete hydrolysis of the complex. This was repeated three times to hydrolyze the remaining three-quarters of the reaction mixture. The carbon tetrachloride layers were combined to give two 2-1. portions of solution and each portion was washed twice with 500 ml. of  $60^{\circ}$  water and dried over calcium chloride. The carbon tetrachloride was removed on a Rinco rotary evaporator and the residue was distilled twice to give 50.9 g. (80.3%) of 3-chloro-2,4,6-trimethylbenzotrichloride, b.p. 117-118<sup>°</sup> at 0.6 mm.

<u>Anal</u>. Calcd. for C<sub>10</sub>H<sub>10</sub>Cl<sub>4</sub>: C, 44.15; H, 3.70; Cl, 52.14. Found: C, 44.23; H, 3.75; Cl, 52.10.

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Its infrared spectrum is shown in Figure 8 and its proton magnetic resonance spectra in Figure 9.

#### 3. Hydrolysis of 3-Chloro-2,4,6-trimethylbenzotrichloride

3-Chloro-2,4,6-trimethylbenzotrichloride (6.6 g., 0.0242 mole) was dissolved in 75 ml. of 80% aqueous acetone. The solution was refluxed for 6 hours on a steam bath, reduced in volume to approximately 30 ml. and diluted with water to 100 ml. The mixture was cooled and filtered. The solid was washed with 150 ml. of water and recrystallized from 80% acetone to yield 4.51 g. (94%) of 3-chloromesitoic acid, m.p. 139-140°.

<u>Anal</u>. Calcd. for C<sub>10</sub>H<sub>11</sub>Cl0<sub>2</sub>: C, 60.46; H, 5.58; Cl, 17.85. Found: C, 60.25; H, 5.48; Cl, 17.88. Its infrared spectrum is shown in Figure 10.

# 4. <u>Reaction of 3-Chloro-2,4,6-trimethylbenzotrichloride in</u> <u>100% Sulfuric Acid with Water</u>

A sample of 4.97 g. (0.0183 mole) of 3-chloro-2,4,6trimethylbenzotrichloride was dissolved in 20 ml. of 100% sulfuric acid. The solution became dark red and liberated hydrogen chloride. The sulfuric acid solution was poured over 100 g. of ice with stirring. The solid which precipitated was filtered and washed with 100 ml. of water. The dried





(a) in carbon tetrachloride; reference tetramethylsilane.

(b) in 100% deuterosulfuric acid; reference methanesulfonic acid.



Figure 9. Proton magnetic resonance spectra of 3-chloro-2,4,6-trimethylbenzotrichloride.





solid was recrystallized twice from 80% aqueous acetone and finally fron n-pentane to yield 2.88 g. (79.4%) of 3-chloromesitoic acid. A mixed m.p. with the acid obtained from hydrolysis in aqueous acetone showed no depression. The infrared spectra of these two acids were identical.

Neutralization Equivalent. Calcd. for  $C_{10}H_{11}Cl_2$ : 198.7. Found: 200.3.

C. Preparation of 3-Bromo-2,4,6-trimethylbenzotrichloride

#### 1. Preparation of 2-Bromomesitylene (37)

A solution of 19.8 g. (0.169 mole) of mesitylene in 50 ml. of carbon tetrachloride was cooled to 5° in an icesalt bath and a solution of 27.2 g. (0.170 mole) of bromine in 50 ml. of carbon tetrachloride was added slowly with stirring. The addition required 0.5 hours, during which time the temperature was kept between 5° and 15°. The mixture was allowed to stand for 1 hour, washed with 100 ml. of water and two 50-ml. portions of 10% sodium hydroxide and dried over calcium chloride. The solvent was removed on a Rinco rotary evaporator. The residue was poured into a solution of 2 g. of sodium in 50 ml. of 95% ethanol and the solution was refluxed for 1 hour. It was then allowed to stand overnight and poured in 300 ml. of water. The layers were separated and the aqueous layer was extracted with three 50ml. portions of carbon tetrachloride. The extracts were added to the bromomesitylene. This solution was washed with 500 ml. of water and dried over calcium chloride. The solvent was removed on a Rinco rotary evaporator and the residue was distilled to yield 23.1 g. (73%) of 2-bromomesitylene, b.p. 104-105° at 16 mm.

#### 2. Preparation of 3-Bromo-2, 4, 6-trimethylbenzotrichloride

a. A mixture of 26.7 g. (0.20 mole) of powdered aluminum chloride and 75 ml. of carbon tetrachloride was mechanically stirred and heated to  $37^{\circ}$ . A solution of 19.9 g. (0.10 mole) of 2-bromomesitylene in 75 ml. of carbon tetrachloride was added dropwise over a period of approximately 2 hours, while the temperature was maintained at  $37-42^{\circ}$ . After the addition of the bromomesitylene solution the reaction was stirred and heated an additional 2 hours. Throughout the reaction atmospheric moisture was excluded with a Drierite drying tube.

One-half of the cooled mixture was poured into a mechanically stirred mixture of 1 1. of carbon tetrachloride, 500 ml. of water and 500 g. of ice. The mixture was stirred until all of the purple-black complex was hydrolyzed. The other half of the reaction mixture was treated similarly.

The carbon tetrachloride layers were separated, combined, washed with two 250-ml. portions of warm water and dried overnight with calcium chloride. The solution was filtered and the solvent was removed with a Rinco rotary evaporator. The residue was distilled to give 30.7 g. (97%) of 3-bromo-2,4,6-trimethylbenzotrichloride, b.p. 125° at 0.1 mm.

<u>Anal</u>. Calcd. for C<sub>10</sub>H<sub>10</sub>BrCl<sub>3</sub>: C, 37.95; H, 3.19; Br, 25.25; Cl, 33.61.

Found: C, 38.13; H, 3.28; Br, 25.30; Cl, 33.40. Its infrared spectrum is shown in Figure 11 and its proton magnetic resonance spectra in Figure 12.

b. A solution of 20 g. (0.084 mole) of 2,4,6-trimethylbenzotrichloride in 100 ml. of dry carbon tetrachloride was stirred magnetically in a flask protected from atmospheric moisture with a drying tube. Light was excluded from the reaction vessel, then a solution of 27 g. (0.168 mole) of bromine in 25 ml. of carbon tetrachloride was added dropwise during a twohour period. After the addition of the bromine solution the mixture was stirred for three hours.

Carbon tetrachloride (100 ml.) was added to the mixture which was then washed with 10% sodium thiosulfate to remove the unreacted bromine. (A large amount of bromine remained in the reaction mixture before the washing with sodium





(a) in carbon tetrachloride; reference tetramethylsilane.

(b) in 100% deuterosulfuric acid; reference methanesulfonic acid.



Figure 12. Proton magnetic resonance spectra of 3-bromo-2,4,6-trimethylbenzotrichloride.

thiosulfate.) The solution was washed with 250 ml. of water and dried over calcium chloride. The carbon tetrachloride was removed on a Rinco rotary evaporator and the residue was distilled to yield 23.7 g. (89%) of 3-bromo-2,4,6trimethylbenzotrichloride, b.p. 122-124<sup>o</sup> at 0.1 mm. This material had an infrared spectrum identical to that in part a.

## 3. Hydrolysis of 3-Bromo-2,4,6-trimethylbenzotrichloride

A solution of 5 g. (0.0126 mole) of 3-bromo-2,4,6trimethylbenzotrichloride in 75 ml. of 80% aqueous acetone was refluxed overnight. The solvent was removed on a Rinco rotary evaporator and the white solid residue was recrystallized several times from 80% acetone. There was obtained 3.3 g. (86%) of 3-bromomesitoic acid, m.p. 160-161°. Further recrystallization did not raise the melting point of this compound.

Anal. Calcd, for C<sub>10</sub>H<sub>11</sub>BrO<sub>2</sub>: C, 49.40; H, 4.56; Br, 13.12. Neutralization Equivalent: 243.1. Found: C, 49.64; H, 4.62; Br, 13.09. Neutralization Equivalent: 247.9.

Its infrared spectrum is shown in Figure 13.





# 4. <u>Reaction of 3-Bromo-2,4,6-trimethylbenzotrichloride in</u> 100% Sulfuric Acid with Water

A sample of 4 g. (0.0127 mole) of 3-bromo-2,4,6trimethylbenzotrichloride was dissolved in 50 ml. of sulfuric acid. It was necessary to shake the mixture to dissolve the trichloromethyl compound which evolved hydrogen chloride as it dissolved. The red-brown sulfuric acid solution was poured slowly onto ice with stirring. The white precipitate which formed immediately was filtered, washed with water and dissolved in 10% sodium hydroxide. The alkaline solution was cooled in an ice bath and 2M hydrochloric acid was added with stirring until the mixture was acidic. The precipitated solid was filtered and washed with water. After several recrystallizations from 80% aqueous acetone the 3-bromomesitoic acid (2.2 g., 72%) melted at 160-161°. The infrared spectrum of this acid was identical to that of the acid obtained from the hydrolysis of the corresponding trichloromethyl compound in aqueous acetone. A mixed melting point of the two acids was not depressed.

#### 5. Preparation of 3-Bromomesitoic Acid

Five grams (0.0206 mole) of mesitoic acid was dissolved in 75 ml. of carbon tetrachloride. The solution was magnetically

stirred and a solution of 3.5 g. (0.022 mole) of bromine in 25 ml. of carbon tetrachloride was added dropwise over a period of approximately 15 minutes. The reaction was stirred for one hour after the addition of the bromine solution. The carbon tetrachloride solution was washed free of bromine with two 100-ml. portions of 7% sodium thiosulfate solution, and washed with 100 ml. of water. The solution was dried overnight with calcium chloride and the solvent was removed on a Rinco rotary evaporator. The residue was recrystallized repeatedly from 80% aqueous acetone to yield 3.5 g. (47.3%) of 3-bromomesitoic acid, m.p. 159-160°. The infrared spectrum was identical to the spectrum of the acid formed by hydrolysis of 3-bromo-2,4,6-trimethylbenzotrichloride in 80% aqueous acetone. An intimate mixture of the acids formed by hydrolysis of 3-bromo-2,4,6-trimethylbenzotrichloride in 80% acetone, by pouring a sulfuric acid solution of 3-bromo-2,4,6-trimethylbenzotrichloride on ice and by bromination of mesitoic acid melted at 160-161°.

Neutralization Equivalent: Calcd. for C<sub>10</sub><sup>H</sup><sub>10</sub><sup>BrO</sup><sub>2</sub>: 243.1. Found: 245.8.

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

#### 1. Preparation of Dinitroisodurene (42)

A solution of 13.4 g. (0.10 mole) of isodurene in 100 ml. of chloroform was cooled to  $10^{\circ}$  and stirred rapidly while a solution of 16 ml. of fuming nitric acid in 75 ml. of concentrated sulfuric acid was added at such a rate that the temperature did not exceed 50°. The chloroform layer was immediately separated and poured into 500 ml. of 10% sodium carbonate. Twelve portions were dinitrated as above. The combined chloroform solutions were washed with two 1-1. portions of 2.5% sodium carbonate and dried over calcium chloride. The solution was filtered and the chloroform was distilled until crystals appeared. Four times the volume of 95% ethanol (approximately 2 1.) was added and the solution was cooled to 10°. The solid was filtered and washed with two 100-ml. portions of (10°) 95% ethanol. The yellow crystals of dinitroisodurene weighed 185.5 g. (54%), m.p. 179-181°.

# 2. Preparation of Aminonitroisodurene (42)

Dinitroisodurene (60 g., 0.268 mole) and 1500 ml. of 95% ethanol were heated to reflux and a solution of sodium disulfide (prepared by heating a solution of 210 g. [0.875 mole] of  $Na_2S \cdot 9H_2O$  in 600 ml. of water with 27 g. [0.845 mole]

of flowers of sulphur) was added slowly with mechanical stirring. After the addition the mixture was stirred and refluxed for 10 hours. The volume was reduced to approximately 200 ml. and the residue was poured into 2 1. of cold water. The precipitate was filtered, washed with 300 ml. of cold water, and dissolved in 4 1. of boiling 2N hydrochloric acid. The hot filtered solution was cooled and made basic with ammonium hydroxide. The solid was filtered, washed with water and dried. A total of 185 g. (0.827 mole) of dinitroisodurene was reduced in this manner. The total yield was 162.5 g. (100%) of aminonitroisodurene, m.p. 137-140<sup>°</sup>.

#### 3. Preparation of 3-Fluoronitroisodurene (43)

Aminonitroisodurene (162.5 g., 0.839 mole) was converted to nitroisodurene diazonium fluoroborate in 10 g. portions. Ten grams of aminonitroisodurene was added to 100 ml. of 6M sulfuric acid and the mixture was cooled to  $0^{\circ}$ . Solid sodium nitrite was added slowly to maintain a  $0-5^{\circ}$ temperature until an excess of nitrous acid was indicated by starch-iodide paper. Fifty-five ml. of 40% fluoboric acid was added and a white solid precipitated. The solid was filtered, washed with 30 ml. of ice cold water, 50 ml. of

cold 95% ethanol, and 200 ml. of cold ether. The total dried salt weighed 233 g. (91%).

The diazonium fluoroborate was decomposed by carefully heating 30 g. portions with a burner in a l l. flask fitted with a downward condenser. The total residue was dissolved in 2 l. of ether, washed twice with 500-ml. portions of 5% sodium hydroxide and twice with 500-ml. portions of water, then dried over Drierite. The solvent was evaporated and the residue was dissolved in 95% ethanol, treated with Norite and recrystallized. The yield of 3-fluoronitroisodurene after three recrystallizations was 84.6 g. (56.4%), m.p. 76-78<sup>0</sup>.

## 4. Preparation of 3-Fluoroaminoisodurene (43)

Fluoronitroisodurene (50 g., 0.254 mole) was dissolved in 500 ml. of glacial acetic acid. Tin (100 g., 0.84 mole) and 500 ml. of concentrated hydrochloric acid were added gradually with vigorous mechanical stirring. The solution was stirred and refluxed for 5 hours. After 1 hour the reaction became clear. The cooled mixture was made basic with concentrated potassium hydroxide and steam distilled for 4 hours. The solid in the cooled distillate was filtered, washed with water, and dried. The yield was 41.2 g. (97.1%) of aminofluoroisodurene, m.p. 60-63<sup>°</sup>.

#### 5. Preparation of Fluoroisodurene (43, 44)

To a boiling solution of 8 ml. of concentrated hydrochloric acid in 200 ml. of water was added 10 g. (0.060 mole) of aminofluoroisodurene which guickly dissolved on stirring. The solution was cooled to  $10^{\circ}$  and 10 ml. of conc. hydrochloric acid was added. The mixture was stirred magnetically and cooled to 0°. Solid sodium nitrite was added slowly to maintain the temperature at  $0-5^{\circ}$  until an excess of nitrous acid was indicated by starch-iodide test paper. Cold 50% hypophosphorous acid (95 ml.) was added and the loosly stoppered mixture was allowed to stand for 2 days at room temperature. The mixture was extracted with 200 ml. of ether, washed with two 50-ml. portions of 10% sodium hydroxide and 100 ml. of water and dried with magnesium sulfate. The solvent was evaporated and the residue was dissolved in 150 ml. of 30-60° petroleum ether and adsorbed on a 900 g. column of alumina. The column was eluted with 3 1. of petroleum ether and on evaporation of the solvent there remained 23.6 g. of fluoroisodurene, n<sub>p</sub><sup>25</sup> 1.4922; b.p. 87-88<sup>o</sup> at 17 mm.

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

A slurry of 26.6 g. (0.20 mole) of powdered anhydrous aluminum chloride and 150 ml. of carbon tetrachloride was

stirred and heated at  $37-42^{\circ}$  while a solution of 15.2 g. (0.10 mole) of fluoroisodurene in 100 ml. of carbon tetrachloride was added dropwise over a 1.5 hour period. After the addition heating and stirring were continued for 2.5 hours.

The black complex was slowly added with mechanical stirring to a mixture of 500 g. of ice, 500 ml. of water and 1500 ml. of carbon tetrachloride. The carbon tetrachloride layer was washed with two 100-ml. portions of warm (60°) water and dried with calcium chloride. The solvent was evaporated and the residual material was distilled, b.p. 117° at 0.6 mm. The distillate was redistilled, b.p. 109° at 0.5 mm., to give 19.9 g. (74%) of yellow oily liquid identified as 3-fluoro-2,4,5,6-tetramethylbenzotrichloride.

Anal. Calcd. for C<sub>11</sub>H<sub>12</sub>Cl<sub>3</sub>F: C, 49.01; H, 4.49; Cl, 39,46; F, 7.05.

Found: C, 49.27; H, 4.60; Cl, 39.52; F, 6.91. Its infrared spectrum is shown in Figure 14 and its proton magnetic resonance spectra in Figure 15.

### 7. Hydrolysis of 3-Fluoro-2,4,5,6-tetramethylbenzotrichloride

A sample of 2.00 g. (0.0075 mole) of 3-fluoro-2,4,5,6tetramethylbenzotrichloride was dissolved in 100 ml. of 80% ×

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(a) in carbon tetrachloride; reference tetramethylsilane.

(b) in 100% deuterosulfuric acid; reference methane sulfonic acid.



Figure 15. Proton magentic resonance spectra of 3-fluoro-2,4,5,6-tetramethylbenzotrichloride.

aqueous acetone. The solution was refluxed for 10 hours, cooled and filtered. The solid was recrystallized four times from 80% acetone to give 1.22 g. (84%) of 3-fluoro-2,4,5,6tetramethylbenzoic acid, m.p. 160-161<sup>°</sup>.

<u>Anal</u>. Calcd. for C<sub>11</sub>H<sub>13</sub>FO<sub>2</sub>: C, 67.33; H, 6.68; F, 9.68. Neutralization Equivalent: 196.2. Found: C, 67.43; H, 6.64; F, 9.55. Neutralization Equivalent: 195.4.

Its infrared spectrum is shown in Figure 16.

## 8. <u>Reaction of 3-Fluoro-2,4,5,6-tetramethylbenzotrichloride</u> in 100% Sulfuric Acid with Water

Three grams (0.0113 mole) of 3-fluoro-2,4,5,6tetramethylbenzotrichloride was dissolved in 20 ml. of 100% sulfuric acid. The solution was allowed to stand for 5 minutes and poured onto 100 g. of ice with stirring. The white precipitate was filtered, washed with 200 ml. of water and recrystallized from 80% acetone. The dried solid melted at 160-161<sup>°</sup> and a mixed melting point with the acid obtained by hydrolysis in 80% acetone showed no depression. The infrared spectra of both acids were identical.

Neutralization Equivalent calcd. for C<sub>11</sub>H<sub>13</sub>FO<sub>2</sub>: 196.2. Found: 194.4.





Figure 17. Comparison of the visible spectra of some dications in 100% sulfuric acid.

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### II. Attempted Preparation of Substituted Benzotrichlorides

## A. <u>Attempted Preparation of 3-Nitro-2,4,6-trimethylbenzotri-</u> <u>chloride</u>

A mechanically stirred slurry of 71 g. (0.532 mole) of powdered anhydrous aluminum chloride and 100 ml. of carbon tetrachloride was heated at  $37-42^{\circ}$ . A solution of 22 g. (0.133 mole) of 2-nitromesitylene in 50 ml. of carbon tetrachloride was added dropwise over a 2 hour period. The reaction mixture became very black. It was heated and stirred for 2 hours after the addition was completed. Heating was discontinued and the mixture was allowed to cool to room temperature. The reaction was poured slowly into a mechnically stirred mixture of 1500 ml. of carbon tetrachloride, 750 ml. of water and 750 g. of ice. It was necessary to stir this mixture for about 45 minutes to hydrolyze the complex. Some (1-2 g.) insoluble material which remained at this point was discarded. The separated carbon tetrachloride layer was washed with four 300-ml. portions of warm (60 $^{\circ}$ ) water and dried over calcium chloride. The carbon tetrachloride was removed with a Rinco rotary evaporator. There remained an oily black material which could not be recrystallized from n-pentane and could not be identified. Further attempts to purify this material were not successful.

## B. <u>Attempted Preparation of 3-Hydroxy-2,4,6-trimethylbenzotri-</u> <u>chloride</u>

A slurry of 38.2 g. (0.286 mole) of powdered anhydrous aluminum chloride and 100 ml. of carbon tetrachloride was heated to 37° and stirred mechanically. To the slurry was added a solution of 19.4 g. (0.143 mole) of mesitol in 250 ml. of carbon tetrachloride. The mesitol solution was added dropwise over a period of 3.25 hours. The reaction was heated and stirred for 3 additional hours. The mixture was allowed to cool at room temperature and was poured into a well-stirred mixture of 1500 ml. of carbon tetrachloride, 750 ml. of water and 750 g. of ice. When the complex was completely hydrolyzed the carbon tetrachloride layer was separated, washed with two 100-ml. portions of warm water and dried overnight with calcium chloride. The solvent was removed on a Rinco rotary evaporator. The tan solid residue was recrystallized from n-pentane to yield 11.2 g. (58%) of recovered mesitol, m.p. 69°.

## C. Attempted Preparation of 3-Iodo-2,4,6-trimethylbenzotrichloride

### 1. Preparation of 2-Iodomesitylene (47)

Mesitylene (36 g., 0.30 mole) and iodine (30 g., 0.236 mole) were placed in a flask which was fitted with a reflux

condenser. To this mixture 12 ml. of concentrated nitric acid was slowly added. The reaction started without warming. The mixture was heated for 30 minutes on a steam bath, then it was cooled and poured into 900 ml. of cold water. The aqueous mixture was extracted with 150 ml. of chloroform. The chloroform layer was washed with 50 ml. of .10% sodium hydroxide, 50 ml. of 7% sodium thiosulfate and 100 ml. of water and dried over anhydrous sodium carbonate. The chloroform was removed on a Rinco rotary evaporator. The residue was recrystallized twice from absolute ethanol to give 52 g. (89% based on iodine) of iodomesitylene, m.p. 29°.

## 2. <u>Attempted Preparation of 3-Iodo-2,4,6-trimethylbenzotri-</u> <u>chloride</u>

A slurry of 68 g. (0.42 mole) of powdered anhydrous aluminum chloride and 200 ml. of carbon tetrachloride was heated to 37-42<sup>°</sup> and stirred mechanically. Over a period of 2.5 hours a solution of 52 g. (0.211 mole) of 2-iodomesitylene in 100 ml. of carbon tetrachloride was added. The reaction was heated and stirred for 1.5 hours after the addition was completed. During the reaction a small amount of iodine vapor was liberated.

The reaction mixture was allowed to cool to room temperature and was poured into a mechanically stirred mixture

of 1500 ml. of carbon tetrachloride, 750 ml. of water and 750 g. of ice. The dark syrupy complex characteristic of the trichloromethylation reaction had not formed and it was not necessary to stir the mixture longer than two minutes. The carbon tetrachloride layer was separated, washed twice with 300 ml. of 60<sup>°</sup> water and dried over calcium chloride. The solvent was removed on a Rinco rotary evaporator.

The residue, a brown mobile liquid, was distilled to yield 28 g. of a red liquid, b.p. 78-85<sup>o</sup> at 0.6 mm. This liuqid was taken up in pentane, washed with 7% sodium thiosulfate and dried over Drierite. The pentane was evaporated to give a colorless liquid which was shown by its infrared spectrum and freezing point to be iodomesitylene (54%).

The residue from the distillation was dissolved in 25 ml. of dry pentane, filtered and cooled in dry ice. A black greasy precipitate formed. No product was isolable.

### D. Attempted Preparation of 4-Acety1-2,3,5,6-tetramethylbenzotrichloride

### 1. Preparation of Acetyldurene (48)

A solution of 200 g. (1.49 moles) of durene, 133.5 g. (1.70 moles) of acetyl chloride and 1 l. of carbon disulfide was stirred mechanically in a flask protected from atmospheric

moisture with a drying tube. Powdered anhydrous aluminum chloride (227 g., 1.70 moles) was placed in a flask connected to the reaction vessel by large bore (three guarter inch inside diameter) rubber tubing. The aluminum chloride was added gradually over a two-hour period. The addition caused the mixture to reflux and to become dark red. The reaction was stirred for 3 additional hours and poured into 2 1. of ice water with stirring. The carbon disulfide was washed with three 500-ml. portions of 10% sodium hydroxide and 500 ml. of water. The carbon disulfide was evaporated in a stream of air and the brown residue was recrystallized from ether to give 193 g. (73%) of impure acetyldurene, m.p. 71-73°. The pure material melted at 72-74° after two recrystallizations from 95% ethanol. Smith and Guss (49) reported a melting point of 73° for this compound.

## 2. <u>Attempted Preparation of 4-Acetyl-2,3,5,6-tetramethyl-benzotrichloride</u>

A slurry of 20 g. (0.15 mole) of powdered anhydrous aluminum chloride and 100 ml. of carbon tetrachloride was stirred mechanically and heated at 37-42<sup>°</sup>. A solution of 25 g. (0.142 mole) of acetyldurene in 75 ml. of carbon tetrachloride was added dropwise over a two-hour period. After the addition of the acetyldurene solution the reaction was heated and

stirred for two hours.

The black complex was added slowly with vigorous mechanical stirring to a mixture of 150 g. of ice, 150 ml. of water and 300 ml. of carbon tetrachloride. The carbon tetrachloride layer was separated, washed with two 75-ml. portions of  $60^{\circ}$  water and dried over calcium chloride. The solvent was removed on a Rinco rotary evaporator. The residue was recrystallized from pentane to yield 19.5 g. (78%) of a white solid which was shown by melting point and infrared analysis to be recovered acetyldurene.

E. Attempted Preparation of 4-Vinyl-2,3,5,6-tetramethylbenzotrichloride

### 1. Preparation of Methyldurylcarbinol (50)

A solution of 20 g. (0.114 mole) of acetyldurene in 120 ml. of dry ether was added dropwise to a stirred slurry of 4.32 g. (0.114 mole) of lithium aluminum hydride and 120 ml. of dry ether. The addition required 1.5 hours. The reaction was stirred for three hours, cooled in an ice bath and gradually treated with 40 ml. of water. The mixture was poured into 300 ml. of 10% sulfuric acid with stirring. The ether layer was separated, washed with 100 ml. of 5% sodium carbonate and 100 ml. of water and dried over Drierite. The solution was filtered and the ether was removed on a Rinco rotary evaporator to yield 19.5 g. (96%) of methyldurylcarbinol m.p. 49<sup>°</sup>. An infrared spectrum of this compound had no bands indicative of carbonyl absorption.

#### 2. Preparation of Vinyldurene (50)

A distillation apparatus containing a mixture of 18.5 g. (0.104 mole) of methyldurylcarbinol, 0.6 g. of potassium hydrogen sulfate and 0.5 g. of p-tertiary-butylcatechol at a pressure of 20 mm. was immersed for several minutes in an oil bath heated at 180°, but the mixture foamed so excessively that heating was stopped. Repeated attempts to distill the mixture were unsuccessful due to bumping and foaming.

The mixture was taken up in ether, washed with 10% sodium hydroxide and water, and dried over Drierite. The solvent was removed on a Rinco rotary evaporator and the residue was distilled to yield 4 g. (25%) of vinyldurene, b.p. 114-115<sup>°</sup> at 18 mm.

## 3. <u>Attempted Preparation of 4-Vinyl-2,3,5,6-tetramethyl-benzotrichloride</u>

A mechanically stirred slurry of 8 g. (0.055 mole) of powdered anhydrous aluminum chloride and 70 ml. of carbon tetrachloride was heated to  $37^{\circ}$ . A solution of 4 g. (0.025 mole) of vinyldurene in 30 ml. of carbon tetrachloride was added dropwise over a period of one hour. The reaction was heated and stirred for 3 additional hours and allowed to cool to room temperature. The cooled mixture was poured slowly into a mechanically stirred mixture of 750 ml. of carbon tetrachloride, 400 ml. of water and 400 g. of ice. When the black complex had completely hydrolyzed, the carbon tetrachloride layer was separated, washed with two 100-ml. portions of warm water and dried with calcium chloride. The solvent was removed on a Rinco rotary evaporator. The residue was a carbon-like solid which was not soluble in pentane. The black material was not identified.

F. Attempted Preparation of 4-Ethyl-2,3,5,6-tetramethylbenzotrichloride

### 1. Preparation of Ethyldurene (45)

Sodium (16 g.) was dissolved in 500 ml. of redistilled diethyleneglycol in a flask protected from atmospheric moisture with a drying tube. The solution was heated to 180° (all temperatures were measured with the thermometer in the liquid). Completely anhydrous hydrazine was prepared by refluxing 70 g. (1.40 moles) of 99% hydrazine hydrate over 70 g. of sodium hydroxide pellets for 3 hours, then poured slowly into the

hot solution. After refluxing for 30 minutes the mixture was allowed to cool to room temperature and 36 g. (0.222 mole) of acetyldurene was quickly added. The temperature was raised to 180° for 3 days, then the excess hydrazine was distilled out until the temperature rose to 220°. The reaction was refluxed for 4 days during which time the temperature gradually decreased to 194°. The cooled mixture was poured into 3.5 1. of cold water and the white solid precipitate was filtered and recrystallized from 95% ethanol to give 25.6 g. (77.2%) of ethyldurene, m.p. 50-51.5°. Crawford and Magill (46) report a melting point of 54° for this compound. Its infrared spectrum is shown in Figure 18 and its proton magnetic resonance spectrum in Figure 19.

# 2. <u>Attempted Preparation of 4-Ethyl-2,3,5,6-tetramethyl-benzotrichloride</u>

A mechanically stirred slurry of 10.7 g. (0.08 mole) of powdered anhydrous aluminum chloride and 70 ml. of carbon tetrachloride was heated at  $37^{\circ}$  and a solution of 5.5 g. (0.034 mole) of ethyldurene in 30 ml. of carbon tetrachloride was added dropwise during a 2 hour period. The reaction was stirred for 2 hours at  $37^{\circ}$  after the addition of the hydrocarbon. The mixture was allowed to cool to room temperature and poured into a mechanically stirred mixture of 500 ml. of









carbon tetrachloride, 250 ml. of water and 250 g. of ice. When the complex had completely hydrolyzed the carbon tetrachloride layer was washed with warm (60<sup>°</sup>) water and dried over calcium chloride. The solvent was removed on a Rinco rotary evaporator to give a brown oil which was not identified. Recrystallization was attempted but no solid could be isolated. The oil did not give a red color in 100% sulfuric acid and did not evolve hydrogen chloride.

## G. Attempted Preparation of 3,5-Dichloro-2,4,6-trimethyl benzotrichloride

#### 1. Preparation of 2,4-Dichloromesitylene (51)

A solution of 35 g. (0.227 mole) of 2-chloromesitylene in 35 ml. of carbon tetrachloride was cooled to  $0^{\circ}$  in a saltice bath. Degreased iron turnings (0.5 g.) were added and 17.7 g. (0.25 mole) of chlorine (dried by bubbling through a concentrated sulfuric acid scrubbing tower) was passed into the reaction at such a rate that the temperature did not exceed  $10^{\circ}$ . The addition of the chlorine required about 2 hours.

The solvent was evaporated and the white solid residue was dissolved in 500 ml. of ether, washed with 100 ml. of 10% sodium hydroxide and dried over Drierite. The ether was removed on a Rinco rotary evaporator and the residue was dissolved with heating in 700 ml. of absolute ethanol. The solution was cooled to room temperature and filtered to remove trichloromesitylene. The filtrate was reduced in volume to 100 ml. and poured into 500 ml. of cold water. The precipitate was filtered and dissolved in 300 ml. of absolute ethanol. The solution was cooled to room temperature, filtered to remove the last traces of trichloromesitylene, then cooled to  $-5^{\circ}$  for 4 hours. The white solid was filtered and dried to give 25 g. (64%) of white needles of 2,4-dichloromesitylene, m.p.  $56-59^{\circ}$ .

## 2. <u>Attempted Preparation of 3,5-Dichloro-2,4,6-trimethyl-benzotrichloride</u>

A slurry of 35.3 g. (0.264 mole) of powdered anhydrous aluminum chloride and 200 ml. of carbon tetrachloride was heated to 37-42° and stirred mechanically. During a 2 hour period a solution of 25 g. (0.132 mole) of 2,4-dichloromesitylene in 100 ml. of carbon tetrachloride was added dropwise. The mixture was heated and stirred for 2.5 hours after the addition was completed. The reaction mixture was allowed to cool to room temperature and was poured into a mechanically stirred mixture of 1200 ml. of carbon tetrachloride, 600 ml. of water and 600 g. of ice. After the complex was completely hydrolyzed the carbon tetrachloride layer was washed with 300 ml. of 60°

water and dried over calcium chloride. The solvent was removed on a Rinco rotary evaporator. The residue was an oily black material which could not be recrystallized and could not be identified.

This reaction was repeated at room temperature with a 10 g. sample of dichloride and the same results were obtained.

H. Attempted Preparation of 3,5-Dibromo-2,4,6-trimethylbenzotrichloride

#### 1. Preparation of 2, 4-Dibromomesitylene (52)

Mesitylene (30 g., 0.25 mole) was stirred magnetically and bromine (80 g., 0.5 mole) was added slowly through a dropping funnel over a 3 hour period. Light was excluded from the reaction during this time.

The reaction mixture was dissolved in 200 ml. of ether and washed with 7% sodium thiosulfate solution until the ether layer was colorless. The solvent was evaporated and the residue was recrystallized from absolute ethanol to give 52 g. (75%) of 2,4-dibromomesitylene, m.p. 63-65<sup>0</sup>.

### 2. <u>Attempted Preparation of 3,5-Dibromo-2,4,6-trimethylbenzotri-</u> <u>chloride</u>

A slurry of 18 g. (0.135 mole) of powdered anhydrous aluminum chloride and 60 ml. of carbon tetrachloride was stirred mechanically and heated to  $37-42^{\circ}$ . A solution of 18.7 g. (0.067 mole) of dibromomesitylene in 40 ml. of carbon tetrachloride was added dropwise over a period of 1.5 hours. After the addition the reaction was stirred and heated at  $37^{\circ}$ for 2 hours. The mixture became dark black. It was cooled to room temperature and poured slowly into a mechanically stirred mixture of 1 1. of carbon tetrachloride, 500 ml. of water and 500 g. of ice. The carbon tetrachloride layer was separated, washed with two 500-ml. portions of warm water and dried over calcium chloride. The solvent was removed on a Rinco rotary evaporator. The residue (15.7 g.) was a black tar which could not be identified or purified.

The above reaction was repeated at room temperature and identical results were obtained.

## III. Hydrolysis Rates of Substituted Phenylchlorodicarbonium Ions.

#### A. The Kinetic Method

In each case the dipositive ions were formed by dissolving the trichloromethyl compound in 100% sulfuric acid and this stock solution was diluted with aqueous sulfuric acid such that the resulting solution was of the desired acidwater composition. One hundred percent sulfuric acid was prepared by mixing 98% and fuming acids until a maximum freezing point was obtained using the freezing point appartaus of Hart and Fish (1).

The reaction rates were determined spectrophotometrically using a Beckman model DU spectrophotometer equipped with thermospacers. Reactions were carried out in ground glass-stoppered quartz absorption cells inside the cell housing of the spectrophotometer. The temperature of the cell housing was maintained at  $25.0^{\circ} \pm .08^{\circ}$  by circulating water from a constant-temperature bath through the thermospacers.

The hydrolysis reactions were pseudo first-order and the rates were determined by measuring the rate of the disappearance of one or more absorption bands due to the dicarbonium ion. This was readily accomplished since the dicarbonium ions absorb strongly in the visible region but the acids formed by their hydrolysis have no visible absorption. The rate constants were calculated from the slopes of the excellent straight lines obtained in plots of ln A (absorbance) versus time (in seconds) or from plots of ln ( $A_t - A_\infty$ ) versus time, where  $A_t$  is the value of absorbance at time t, and  $A_\infty$  is the final absorbance.

This method of calculation can be shown to be accurate within 3%. The rate constants are averages of at least two

runs. In general, agreement between runs was 2-4%.

### B. Example of Data and Calculations

Table 14. Absorbance of 4-bromo-2,3,5,6-tetramethylphenylchlorodicarbonium ion in 99.5% sulfuric acid at  $25.0^{\circ} \pm 0.08^{\circ}$ . Cell I.

Reading	Time (seconds)	Absorbance		
1	68	0.741		
2	129	0.650		
3	179	0.590		
4	241	0.520		
5	294	0.470		
6	367	0.410		
7	443	0.355		
8	519	0.310		
9	607	0.265		
10	701	0.225		
11	816	0.185		
12	8	0.000		

Table 15. Log absorbance of 4-bromo-2,3,5,6-tetramethylphenylchlorodicarbonium ion. Cell I.

Time (seconds)	Absorbance	Log Absorbance
50	0.769	0.886 - 1 = -0.114
150	0.625	0.796 - 1 = -0.204
250	0.511	0.708 - 1 = -0.292
350	0.422	0.625 - 1 = -0.375
450	0.350	0.544 - 1 = -0.456





Reading	Time (seconds)	Absorbance		
1	100	0.699		
2	150	0.630		
3	211	0.560		
4	268	0.500		
5	335	0.440		
6	405	0.385		
7	479	0.335		
8	561	0.290		
9	642	0.250		
10	757	0.205		
11	889	0.165		
12	00	0.000		

Table 16. Absorbance of 4-bromo-2,3,5,6-tetramethylphenylchlorodicarbonium ion in 99.5% sulfuric acid at  $25.0^{\circ} + 0.08^{\circ}$ . Cell II.

## Table 17. Log absorbance of 4-bromo-2,3,5,6-tetramethylphenylchlorodicarbonium ion. Cell II.

Time (seconds)	Absorbance	Log Absorbance
50	0.767	0.885 - 1 = -0.115
150	0.634	0.802 - 1 = -0.198
250	0.520	0.716 - 1 = -0.284
350	0.427	0.630 - 1 = -0.370
450	0.352	0.547 - 1 = -0.453









### C. The Determination of Reaction Order

Since the concentrations of the reacting species in the hydrolysis, i.e., dication and water, were present in widely different concentrations and the concentration of water was essentially constant during a given run, the reaction order will be expressed as pseudo n-th order. The rate expression is then

$$\frac{-dc}{dt} = kc^n \tag{1}$$

where c is dication concentration and n the reaction order. Separating the variables by multiplying by dt and dividing by  $c^n$ ,

$$\frac{-dc}{c^n} = kdt$$
(2)

and integrating between the limits  $c = c_0$  at t = 0 and  $c = c_0$ at t = t, gives

$$\ln \left(\frac{c}{c}\right) = kt \text{ or } \ln c = \ln c_0 - kt \qquad (3) \text{ and } (4)$$

A plot of log c versus time should be linear with a slope of

 $\frac{-k}{2,303}$ . This was found to be true for all the kinetic runs. Using equation (4) in the form  $k = \frac{1}{t} \ln \left(\frac{c_0}{c}\right)$  (5) and substituting successive experimental values of c and t

gives another check on reaction order. The k's calculated

by (5) showed no significant deviation throughout any given run and it may be concluded that the reaction is first-order in dication.

The half-life method of finding the order n with respect to dication was also used. For all values of n,

$$t_{1/2} = \int \frac{(n, k)}{c^{n-1}}$$
 (6)

where f is some function of n and k and therefore constant for a given reaction at constant temperature, and c is the dication concentration or a function thereof. In logarithmic form (6) becomes

$$\log t_{1/2} = \log f - (n-1) \log c$$
 (7)

By applying (7) to any two pair of data for  $t_{1/2}$  and c  $(t_{1/2}', c' \text{ and } t_{1/2}'', c'')$  and substracting to eliminate the log f term one obtains the Noyes equation.

$$n = \frac{\log t_{1/2}' - \log t_{1/2}'}{\log c'' - \log c'}$$
(8)

The half-lives  $t_{1/2}'$  and  $t_{1/2}''$  were equal within accepted experimental error (Table 1); the second term therefore was zero and n = 1.

D.	Wavelengths Used to Determine Dication Hydrolyse	s (Di	ications
	were formed in 100% sulfuric acid from the corre-	spond	ling
	benzotrichlorides).		
Com	bound		(mµ)
1.	Pentamethylbenzotrichloride	393,	545
2.	2,3,4,5-Tetramethylbenzotrichloride		545
3.	2,4,6 <sub>7</sub> Trimethylbenzotrichloride		485
4.	4-Chloro-2,3,5,6-Tetramethylbenzotrichloride		519
5.	4-Bromo-2,3,5,6-Tetramethylbenzotrichloride		519
6.	4-Fluoro-2,3,5,6-Tetramethylbenzotrichloride		500
7.	3-Bromo-2,4,5,6-Tetramethylbenzotrichloride		535
8.	3-Chloro-2,4,5,6-Tetramethylbenzotrichloride		530
9.	2-Chloro-3,4,5,6-Tetramethylbenzotrichloride		544
10.	3-Fluoro-2,4,5,6-Tetramethylbenzotrichloride		540
11.	3-Fluoro-2,4,6-Trimethylbenzotrichloride		480
12.	3-Chloro-2,4,6-Trimethylbenzotrichloride		483
13.	3-Bromo-2,4,6-Trimethylbenzotrichloride		500

- 1-3 synthesized by the author but previously reported by Hart and Fish (1, 2).
- 4-6 synthesized by Rafos (3), 6 with the author.
- 7-9 synthesized by C. Buehler (15).
- 10-13 synthesized by the author.

IV. Reactions of Mesitylchlorodicarbonium Ion

### A. Preparation of Anhydrous Silver Tetrafluoroborate (54)

A slurry of 34 g. (0.268 mole) of silver fluoride and 40 g. of nitromethane (dried over calcium chloride) was stirred magnetically in a vessel protected from atmospheric moisture. Dry boron trifluoride (bubbled through a concentrated sulfuric acid scrubbing tower) was passed into the solution for about 30 minutes. The addition of boron trifluoride caused a rapid rise in the temperature of the reaction. It was maintained at  $60^{\circ}$  by occasionally raising an ice bath around the reaction flask. When only a small amount of silver fluoride remained the addition of boron trifluoride was stopped and dry nitrogen was bubbled through the mixture for one hour to remove the excess boron trifluoride. The nitromethane solution was filtered through a sintered glass disk in an atmosphere of dry nitrogen. The solvent was evaporated under reduced pressure to yield 38.8 g. (74.6%) of silver tetrafluoroborate. This was stored under dry npentane in the dark.

### B. Preparation of 2,4,6-Trimethylbenzotrifluoride

1. Approximately 30 ml. of anhydrous hydrogen fluoride was distilled from a gas cylinder and condensed in a

polyethylene vessel protected from atmospheric moisture by a polyethylene tube containing Drierite. Dry boron trifluoride (bubbled through a concentrated sulfuric acid scrubbing tower) was slowly passed into the liquid hydrogen fluoride for 30 minutes. Thirteen grams (10 ml., 0.0517 mole) of 2,4,6-trimethylbenzotrichloride was added dropwise into the magnetically stirred liquid. The acid solution became dark red immediately and hydrogen chloride\* was evolved. The mixture was stirred for 3 hours, then a vacuum was applied to remove the hydrogen fluoride. The purple solid which remained was taken up in 50 ml. of dry ether and added slowly with stirring to 50 ml. of an ether solution of methyl magnesium iodide. The addition caused the ether to reflux mildly and a solid to precipitate. After the addition the mixture was refluxed on a steam bath for 30 minutes. To the cooled solution was added 30 ml. of water. A vigorous reaction ensued and a gelatinous solid formed.

The ether layer was separated, washed with 100 ml. of 10% sodium hydroxide and dried over Drierite. The alkaline wash was acidified with hydrochloric acid but no mesitoic acid precipitated. The ether was removed on a Rinco rotary

<sup>\*</sup>A loop of copper wire was dipped into silver nitrate solution and held in the stream of the exit gases. An immediate precipitate of silver chloride was formed.

evaporator to give 5.8 g. of a brown liquid which was distilled to give 2.8 g. (25.2%) of colorless 2,4,6-trimethylbenzotrifluoride, b.p.  $30-32^{\circ}$  at 0.5 mm.,  $n_D^{20}$  1.4563.

<u>Anal</u>. Calcd. for  $C_{10}H_{11}F_3$ : C, 63.82; H, 5.89.

Found: C, 63.70; H, 6.22.

Its infrared spectrum is shown in Figure 24 and its fluorine magnetic resonance spectrum in Figure 25.

2. Approximately 275 ml. of liquid sulfur dioxide was condensed in a flask cooled in a dry ice-acetone bath and silver tetrafluoroborate (25 g., 0.128 mole) was added with stirring. To the cold mixture 13 g. (10 ml., 0.0517 mole) of 2,4,6-trimethylbenzotrichloride was added dropwise. The addition caused the solution to become bright red and an immediate precipitate of silver chloride to form. The mixture was stirred for 30 minutes after which time the cooling bath was removed. When most of the sulfur dioxide had evaporated 150 ml. of dry ether was slowly added, causing the red color to blacken. The ether solution was washed with 100 ml. of water and dried over Drierite. The ether was evaporated and the residue was distilled to yield 1.4 g. (13%) of 2,4,6trimethylbenzotrifluoride, b.p. 33-40° at 0.6 mm. An infrared spectrum of this material was identical to the spectrum of the trifluoromethyl compound formed in liquid hydrogen fluoride.








# B-1. <u>Reaction of 2,4,6-Trimethylbenzotrichloride in Anhydrous</u> <u>Hydrogen Fluoride</u>

About 10 ml. of anhydrous hydrogen fluoride was condensed in a polyethylene test tube. Moisture was carefully excluded. A 1.3 g. (1 ml., 0.0042 mole) sample of 2,4,6trimethylbenzotrichloride was added. The solution became red immediately. The reaction was stirred magnetically at room temperature for 3 hours. At this point 50 ml. of water was carefully added over a two hour period. The mixture was poured into 200 ml. of ice water and filtered. The white material was recrystallized from 80% acetone to give 0.85 g. (94%) of mesitoic acid, m.p. 151-152<sup>0</sup>.

# B-2. <u>Reaction of 2,4,6-Trimethylbenzotrifluoride in Anhydrous</u> <u>Hydrogen Fluoride</u>.

About 10 ml. of anhydrous hydrogen fluroide was condensed in a polyethylene vessel and 1.0 g. of 2,4,6-trimethylbenzotrifluoride was added slowly. The colorless mixture was stirred magnetically for 3 hours at room temperature. Fifty ml. of water was added slowly over a two hour period. The mixture was poured into 200 ml. of water and the aqueous mixture was extracted with 50 ml. of ether. The ether layer was separated and dried over sodium sulfate. The ether was distilled at atmospheric pressure and the residue was distilled under vacuum to give 0.77 g. (77%) of recovered 2,4,6trimethylbenzotrifluoride, b.p. 93-96<sup>o</sup> at 15 mm. The recovered material had an infrared spectrum identical to that of the starting material.

C. Reactions with Alcohols

#### 1. Reaction with Ethyl Alcohol

Thirteen grams (10 ml., 0.055 mole) of 2,4,6-trimethylbenzotrichloride was added to a solution of 45 ml. of trifluoroacetic acid and 5 ml. of trifluoroacetic anhydride in a flask protected from atmospheric moisture with a drying tube. A stream of dry boron trifluoride (bubbled through a concentrated sulfuric acid scrubbing tower) was slowly passed into the solution for 30 minutes.

The reaction became dark purple as the boron trifluoride was added. The solvent was removed under reduced pressure without heating. The residue was cooled to  $-20^{\circ}$ and poured into 25 ml. of carefully dried absolute ethyl alcohol. After 2 or 3 minutes the alcohol began to boil. It was alternately swirled and cooled in an ice bath for 5 minutes. The excess alcohol was removed on a Rinco rotary evaporator. The liquid residue was washed with 50 ml. of 5% sodium hydroxide and 50 ml. of water. Acidification of the sodium hydroxide wash gave no precipitate of mesitoic acid.

The liquid was distilled to yield 6.6 g. (63%) of ethyl mesitoate, b.p.  $80-81^{\circ}$  at 0.6 mm.,  $n_{D}^{20}$  1.5007. Newman (24) reported the b.p. of ethyl mesitoate to be  $115^{\circ}$  at 6.0-6.5 mm. The infrared spectrum is shown in Figure 26.

# 2. <u>Reaction with Isopropyl Alcohol</u>

Thirteen grams (0.055 mole) of 2,4,6-trimethylbenzotrichloride was dissolved in 45 ml. of trifluoroacetic acid and 5 ml. of trifluoroacetic anhydride in a flask protected with a drying tube. Dry boron trifluoride (bubbled through a concentrated sulfuric acid scrubbing tower) was slowly passed into the solution for 30 minutes. The solvent was removed on a Rinco rotary evaporator without heating. The residue was cooled to  $-20^{\circ}$  and poured into 25 ml. of carefully dried isopropyl alcohol. No visible reaction occurred when the reaction was allowed to stand for 10 minutes. It was warmed slightly on a steam bath to start the reaction.

The excess isopropyl alcohol was evaporated and the residue was washed with 50 ml. of 5% sodium hydroxide and 50 ml. of water. The alkaline wash was acidified with hydrochloric acid; no mesitoic acid precipitated. The liquid was





distilled to give 6.7 g. (58%) of isopropyl mesitoate, b.p.  $83-86^{\circ}$  at 0.6 mm.,  $n_{D}^{20}$  1.4949. Newman (24) reported the boiling point to be  $120-121^{\circ}$  at 6.0-6.5 mm.

## 3. Reaction with t-Butyl Alcohol

To a solution of 45 ml. of trifluoroacetic acid and 5 ml. of trifluoroacetic anhydride in a flask protected from atmospheric moisture with a drying tube was added 6.5 g. (0.028 mole) of 2,4,6-trimethylbenzotrichloride. A stream of dry boron trifluoride (bubbled thorugh a concentrated sulfuric acid scrubbing tower) was slowly passed into the solution for 30 minutes. The solvent was removed under reduced pressure without heating. The residue was poured into 60 ml. of carefully dried t-butyl alcohol. It was necessary to cool the reaction on an ice bath.

The mixture was allowed to stand for 3 hours, then 100 ml. of ether was added and the ether solution was washed free of any remaining dication with 100 ml. of 5% sodium hydroxide and dried over Drierite. After the ether was evaporated the residue was distilled to give 3.8 g. (63%) of tertiary-butyl mesitoate, b.p. 99° at 0.7 mm.,  $n_D^{20}$  1.4922. Stimson and Watson (32) reported the boiling point of this compound to be 96-98° at 0.6 mm.

#### D. Reaction with Ethers

### 1. Reaction with Ether

A 6.5 g. (0.0274 mole) portion of 2,4,6-trimethylbenzotrichloride was mixed with a solution of 20 ml. of trifluoroacetic acid and 2 ml. of trifluoroacetic anhydride. A stream of dry boron trifluoride (bubbled through a concentrated sulfuric acid scrubbing tower) was slowly passed into the mixture for 30 minutes. The solvent was removed under reduced pressure without heating and 10 ml. of dry pentane was added and evaporated similarly. The purple residue was added dropwise over a 1.5 hour period with magnetic stirring to 50 ml. of ether which had been dried over sodium wire and distilled through a 40 cm. Vigreux column. The mixture was stirred for an additional 30 minutes and then refluxed gently for 1 hour. The excess ether was distilled at atmospheric pressure and the black residue was distilled at reduced pressure to yield 2 g. of trifluoroacetic acid, b.p. 33-43<sup>0</sup> at 0.3 mm. and 4 g. of a red liquid which was redistilled to give 2.6 g. (49%) of ethyl mesitoate, b.p. 77-80° at 0.8 mm.,  $n_{p}^{20}$  1.5016. The infrared spectrum in shown in Figure 27.

<u>Anal</u>. Calcd. for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>: C, 74.96; H, 8.39. Found: C, 75.06; H, 8.45.





# 2. Reaction with Tetrahydrofuran

To a solution of 45 ml. of trifluoroacetic acid and 5 ml. of trifluoroacetic anhydride was added 6.5 g. (5 ml., 0.028) of 2,4,6-trimethylbenzotrichloride. A stream of dry boron trifluoride (bubbled through a concentrated sulfuric acid scrubbing tower) was slowly passed into the solution for 30 minutes.

The reaction became dark purple as the boron trifluoride The solvent was removed under reduced pressure was added. without heating. The residue was added to 150 ml. of tetrahydrofuran which had been carefully dried over lithium aluminum hydride and distilled. The mixture was refluxed for one hour, then 100 ml. of water was added slowly with stirring. The reaction mixture was shaken with 125 ml. of ether. The ether layer was washed with 100 ml. of 5% sodium hydroxide and dried over magnesium sulfate. The aqueous alkaline layer was acidified with dilute hydrochloric acid to yield 0.3 g. (6.7%) of mesitoic acid. The ether was evaporated and the residue was distilled to give 5.52 g. (85%) of  $\delta$ -hydroxybutyl mesitoate, b.p.  $200-210^{\circ}$  at 0.08 mm.,  $n_{D}^{25}$  1.4638. When corrected for mesitoic acid the yield was 91.5%

<u>Anal</u>. Calcd. for C<sub>14</sub>H<sub>20</sub>O<sub>3</sub>: C, 71.20; H, 8.53. Found: C, 69.79, 69.78; H, 8.82, 8.78.

The ester gave mesitoic acid when hydrolyzed with concentrated sulfuric acid. Its infrared spectrum is shown in Figure 28.

# E. Attempted Clevage of Ether with Trifluoroacetic Acid and Boron Trifluoride

A solution of 6 g. of trifluoroacetic acid was 0.6 g. of trifluoroacetic anhydride was saturated with boron trifluoride by slowly passing the dry gas (bubbled through a concentrated sulfuric acid scrubbing tower) into the solution. The solution was then poured slowly into 50 ml. of dry ether with stirring. The mixture was stirred for 3 hours and then refluxed gently on a steam bath for 2 hours. The mixture was distilled and the following fractions, none of which were positively identified, were collected: (1) 47 ml. of ether, b.p.  $35-36^{\circ}$ ; (2) 1.1 g., b.p.  $36-40^{\circ}$ ; (3) 5.8 g., b.p.  $40-77^{\circ}$ ; and there remained (4) 1.8 g. of liquid residue.

None of the fractions had infrared absorption bands indicative of ethanol or ethyl trifluoroacetate being present in the fraction. A 0.6 g. portion of the residue was dissolved in 10 ml. of pentane and washed with dilute sodium bicarbonate to remove any trifluoroacetic acid. The pentane layer was separated, dried over sodium sulfate and reduced in volume to 1 ml. An infrared spectrum showed no ethanol and no ethyl





trifluoroacetate was present. When 10% ethanol was added to the pentane solution, the infrared spectrum had an absorption band at 2.77  $\mu$  which indicated that ethanol could be detected if it were formed.

# F. Reaction of 2,4,6-Trimethylbenzotrichloride in 100% Sulfuric Acid with Butan-1,4-diol.

A 6.5 g. (5 ml., 0.0274 mole) sample of 2,4,6-trimethylbenzotrichloride was dissolved in 100 ml. of 100% sulfuric acid and poured slowly into 100 ml. of cold butan-1,4-diol with stirring. The mixture was stirred for 4 hours at room temperature, then poured carefully into 1 l. of ice water. The aqueous mixture was extracted with 200 ml. of ether and the ether layer was washed with 10% sodium carbonate. The ether was dried over Drierite. After the ether was removed, the brown residue was distilled to give 4.33 g. (66.6%) of  $\delta$ -hydroxybutyl mesitoate, b.p. 206-207° at 0.07 mm.,  $n_D^{25}$ 1.4638. This material had an infrared spectrum identical to that of the ester formed from mesitylchlorodicarbonium ion and tetrahydrofuran. (Figure 28).

#### G. Reaction with n-Butyllithium

A mixture of 1.25 g. (0.143 g. atom) of finely cut lithium and 30 ml. of dry pentane was stirred magnetically

and cooled to  $-10^{\circ}$  in a dry ice-acetone bath. A solution of 10 g. (0.07 mole) of n-butyl bromide in 15 ml. of dry pentane was added slowly. The mixture was stirred and allowed to warm to  $0-10^{\circ}$  for 2 hours. It was decanted through a glass tube containing a loose glass wool plug.

The chlorotrifluoroborate salt of mesitylchlorodicarbonium ion was prepared by passing a stream of dry boron trifluoride (bubbled through a concentrated sulfuric acid scrubbing tower) into a solution of 6.5 g. (0.0274 mole) of 2,4,6-trimethylbenzotrichloride in 45 ml. of trifluoroacetic acid and 5 ml. of trifluoroacetic anhydride for 30 minutes. The solvent was removed under reduced pressure without heating. The salt was covered with 10 ml. of dry pentane.

The salt was added slowly to the magnetically stirred solution of n-butyllithium (53). The addition caused mild refluxing. The reaction was stirred for 1 hour. At this point the sweep of dry nitrogen under which all operations had been done was stopped and 100 ml. of water was added dropwise to the stirred solution. The pentane layer was separated and washed with 50 ml. of 5% sodium hydroxide. The alkaline wash was acidified with 2 M hydrochloric acid. The white solid which precipitated was filtered, washed with water and dried to give 1.5 g. (33.5%) of mesitoic acid, m.p. 149-150<sup>°</sup>.

The pentane layer was dried over sodium sulfate and filtered. The solvent was removed on a Rinco rotary evaporator and the residue was distilled to yield 3.9 g. (65%) of n-butyl mesitoate, b.p.  $163^{\circ}$  at 17 mm.;  $n_{D}^{25}$  1.4801. The reported b.p. is  $147.5-149^{\circ}$  at 12 mm. (36).

<u>Anal</u>. Calcd. for C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>: C, 76.32; H, 9.15.

Found: C, 76.04; H, 9.17.

A solution of this ester in concentrated sulfuric acid was poured on ice and mesitoic acid immediately precipitated. Its infrared spectrum is shown in Figure 29.

H. Preparation of 2,4,6-Trimethyl-n-valerophenone

A mixture of 16 g. (0.086 mole) of n-valeric anhydride, 12 g. (0.09 mole) of powdered anhydrous aluminum chloride and 50 g. of carbon disulfide was stirred mechanically in a flask protected from atmospheric moisture with a drying tube. A solution of 9 g. (0.083 mole) of mesitylene in 10 g. of carbon disulfide was added dropwise. This mixture was stirred for 1 hour, then heated to reflux and stirred for 1.5 hours. The cooled reaction was poured on 200 g. of ice to hydrolyze the aluminum chloride complex. The carbon disulfide layer was separated, washed with 50 ml. of water, 50 ml. of 5%



Figure 29. Infrared spectrum of n-butyl mesitoate.

sodium hydroxide and again with 50 ml. of water and dried over sodium sulfate. The carbon disulfide was removed on a Rinco rotary evaporator. The residue was distilled to give 1.5 g. of recovered mesitylene, b.p.  $31-35^{\circ}$  at 0.8 mm., and 12.2 g. (96% corrected for recovered mesitylene) of 2,4,6trimethyl-n-valerophenone, b.p.  $89-90^{\circ}$  at 0.07 mm.;  $n_{D}^{25}$  1.5038. Its infrared spectrum is given in Figure 30.

Anal. Calcd. for C<sub>14</sub>H<sub>20</sub>O: C, 82.30; H, 9.87. Found: C, 81.67, 81.96; H, 8.98, 9.19.

## I. Preparation of Pentamethylbenzoyl Chloride

Pentamethylbenzoic acid 0.98 g. (0.0051 mole) was gently refluxed in 8.2 g. (5 ml., 0.07 mole) of thionyl chloride which had been freshly distilled. The reflux condenser was fitted with a drying tube. After the solution had refluxed for 4 hours the excess thionyl chloride was distilled out of the mixture and 50 ml. of dry petroleum ether was added to the residue. A small amount of very high melting insoluble material was removed by filtration. The filtrate was evaporated to dryness. An infrared spectrum of the white solid showed a strong absorption at 5.59µ and a medium absorption at 5.90µ, due respectively to the carbonyl absorption of acid chloride and the carboxylic





acid. Recrystallization from petroleum ether enriched the solid in acid and the filtrate in acid chloride. To obtain pure acid chloride it was necessary to recrystallize by this reverse procedure 10 times and then additional recrystallizations did not change the melting point or the infrared spectrum of the acid chloride. The yield of pure pentamethylbenzoyl chloride, m.p. 75-78°, was 0.65 g. (60.5%). Its infrared spectrum is given in Figure 31.

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

The infrared spectra were determined in purified carbon tetrachloride on a Perkin-Elmer Model 21 Recording ( Infrared Spectrophotometer with 0.5 mm. solution cells.

Proton magnetic resonance spectra were determined with a Varian Associates Model A-60 Analytical NMR Spectrometer and the fluorine magnetic resonance spectrum with a high-resolution nuclear-induction type NMR spectrometer, Varian Associates (VA) Model V-4300-2.





#### SUMMARY

1. Four new trichloromethyl compounds, 3-fluoro-, chloro- and bromo-2,4,6-trimethylbenzotrichlorides, and 3fluoro-2,4,5,6-tetramethylbenzotrichloride were prepared by Friedel-Crafts alkylation with anhydrous aluminum chloride and carbon tetrachloride. No rearrangement occurred during the reactions.

2. Each of the benzotrichlorides was hydrolyzed by refluxing in aqueous acetone and by pouring a solution in 100% sulfuric acid on ice. Both methods of hydrolysis gave quantitative yields of the corresponding carboxylic acid.

3. The rates of hydrolysis of the following dipositive carbonium ions were determined in 90 to 100% aqueous sulfuric acid. All dications were prepared in 100% sulfuric acid from the substituted benzotrichlorides.

(a) pentamethylphenylchlorodicarbonium ion

(b) 2,3,4,5-tetramethylphenylchlorodicarbonium ion

(c) 2,4,6-trimethylphenylchlorodicarbonium ion

(d-f) 4-fluoro-, chloro- and bromo-2,3,5,6-tetramethylphenylchlorodicarbonium ion

(g-i) 3-fluoro-, chloro- and bromo-2,4,5,6-tetramethylphenylchlorodicarbonium ion

(j-1) 3-fluoro-, chloro- and bromo-2,4,6-trimethylphenylchlorodicarbonium ion

(m) 2-chloro-3,4,5,6-tetramethylphenylchlorodicarbonium ion.

The kinetics showed that methyl groups stabilized dicarbonium ions better than hydrogen, which in turn stabilized better than halogens. For the 4-substituted-2,3,5, 6-tetramethylphenylchloromethylene dications the average relative rates in three acid concentrations were

methyl = 1
fluorine = 40
chlorine = 117
bromine = 143.

Stabilization of the transition state by halogen was indicated to be least at the meta position.

4. The hydrolysis mechanism proceeded through an acylium ion intermediate which hydrolyzed to carboxylic acid at a rate slower than the hydrolysis of dication to acylium ion. The appearance and disappearance of the intermediate was determined experimentally, and also calculated from the experiment values for the two rate constants. The methods gave nearly identical plots of concentration versus time.

5. Mesitylchlorodicarbonium ion was prepared in

trifluoroacetic acid saturated with boron trifluoride. It gave mesitoates when treated with ethyl, isopropyl and tertiarybutyl alcohols. Reaction with ether and tetrahydrofuran gave ethyl mesitoate and  $\delta$ -hydroxybutyl mesitoate and with nbutyllithium yielded n-butyl mesitoate. These reactions indicated that trifluoroacetic acid and the dication reacted to form unsymetrical trifluoroacetic-mesitoic anhydride which then reacted to give mesitoates.

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